Table of Contents

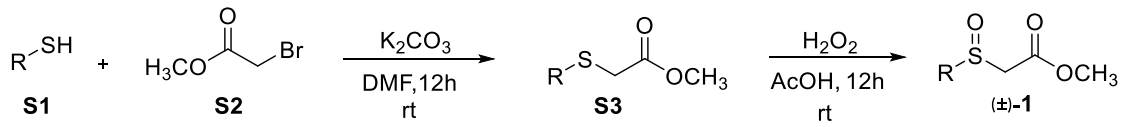
General Information

All NMR experiments were recorded on Bruker Ascend-600 spectrometer, Varian Inova-400 spectrometer and Bruker Ascend-400 spectrometer. Data for ^{1}H and ^{13}C-NMR spectra are reported as follows: chemical shift (δ, ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublets of doublets, dt = doublet of triplets and m = multiplet), and coupling constant (Hz). ISCO flash chromatography was used for purifications. Mass spectra were acquired on an Agilent Technologies 1200 series LC/MS using indicated ionization methods. Optical rotation was measured on a Rudolph Research Analytical Autopol® IV Polarimeter at λ = 589 nm, unless otherwise noted. Enantiomeric excess was measured on a Shimadzu Prominence HPLC with the column and solvent system indicated with each characterized compound.

Materials and Methods

All commercially available reagents were used as received unless otherwise stated. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and Sigma Aldrich. All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (DCM) and toluene were purified by passing the previously degassed solvents through two activated alumina columns and were stored under inert argon atmosphere prior to use.

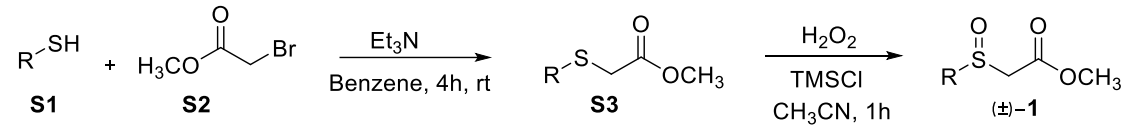
I General procedure A



To a stirred mixture of thiol **S1** (9.07 mmol, 1.0 equiv) and K_2CO_3 (2.50 g, 18.14 mmol, 2.0 equiv) in DMF (20 mL) was added methyl bromoacetate **S2** (1.65 g, 10.88 mmol, 1.2 equiv), and the resulting mixture was stirred at room temperature until the completion of reaction as indicated by LCMS analysis (typically within 12h). The reaction mixture was poured into ice-water (20 mL), and the mixture thus obtained was extracted with EtOAc (3 × 40 mL). The combined extracts were washed with brine (2 × 40 mL), dried over anhydrous Na_2SO_4 and evaporated on a rotary evaporator to afford a residue, which was purified by ISCO flash chromatography.

30% hydrogen peroxide (0.9 mL, 8.00 mmol, 1.0 equiv) was added dropwise at 25 ^{o}C to a solution of mercapto acetate **S3** (8.00 mmol, 1.0 equiv) in AcOH (3.6 mL). The resulting mixture was stirred for 2-12h. When the reaction was over (as monitored by LCMS), the mixture was diluted with H_2O and extracted with EtOAc (3 × 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated on a rotary evaporator to afford a residue, which was purified by ISCO flash chromatography to give desired product (±)-**1**.

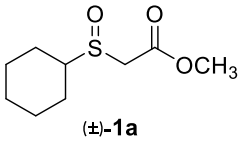
II General procedure B



A mixture of thiol **S1** (9.07 mmol, 1.0 equiv), Et_3N (1.3 mL, 9.07 mmol, 1.0 equiv) and methyl bromoacetate **S2** (1.38 g, 9.07 mmol, 1.0 equiv) in benzene (25 mL) was stirred at room temperature for 4h. The reaction mixture was diluted with H_2O and extracted with ethyl acetate. The combined organic layers were dried with anhydrous Na_2SO_4, filtered and the solvent was removed under vacuum. Purification of the crude product by ISCO flash chromatography gave the title compound **S3**.

In a round-bottomed flask equipped with a stir bar, a solution of sulfide **S3** (8.00 mmol, 1.0 equiv) in CH_3CN (25 mL) was prepared. Aqueous 30% hydrogen peroxide (1.3 mL, 12.0 mmol, 1.5 equiv) and TMSCl (864 mg, 8.00 mmol, 1.0 equiv) were added and the mixture was stirred at 25°C for 1h. The progress of the reaction was monitored by LCMS. After disappearance of the sulfide, the reaction mixture was quenched by adding H_2O (10 mL), extracted with EtOAc (3 × 30 mL), and the combined organic layers were dried with anhydrous Na_2SO_4. Then the crude product (±)-**1** was purified by ISCO flash chromatography.

Methyl 2-(cyclohexylsulfinyl)acetate (±)-**1a**



(±)-**1a**

Synthesized by General procedure A.

Methyl 2-(cyclohexylthio)acetate S3a

Yield: 92%. Purified by ISCO flash column chromatography (9:1 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.54 (s, 3H), 3.07 (s, 2H), 2.67 - 2.58 (m, 1H), 1.84 - 1.77 (m, 2H), 1.62 - 1.55 (m, 2H), 1.46 - 1.40 (m, 1H), 1.22 - 1.01 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 51.9, 43.5, 32.7, 31.4, 25.6, 25.4.

ESI MS. $C_9H_{17}O_2S$ m/z $[M+H]^+$ calc. 189.1, found 189.1.

Methyl 2-(cyclohexylsulfinyl)acetate (±)-**1a**

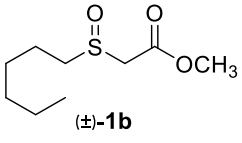
Yield: 88%. Purified by ISCO flash column chromatography (7:3 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, MeOD) δ 3.95 (d, J = 16.0 Hz, 1H), 3.79 (s, 3H), 3.73 (d, J = 16.0 Hz, 1H), 2.91 - 2.83 (m, 1H), 2.11 - 2.05 (m, 1H), 1.96 -1.84 (m, 3H), 1.77 - 1.70 (m, 1H), 1.54 - 1.27 (m, 5H).

^{13}C NMR (151 MHz, MeOD) δ 167.7, 59.9, 53.6, 53.2, 27.5, 26.5, 26.4, 26.1, 25.3.

ESI MS. $C_9H_{17}O_3S$ m/z $[M+H]^+$ calc. 205.1, found 205.1.

Methyl 2-(hexylsulfinyl)acetate (±)-**1b**



(±)-**1b**

Synthesized by General procedure A.

Methyl 2-(hexylthio)acetate S3b

Yield: 90%. Purified by ISCO flash column chromatography (9:1 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.71 (s, 3H), 3.19 (s, 2H), 2.63 - 2.55 (m, 2H), 1.60 - 1.53 (m, 2H), 1.31 - 1.21 (m, 6H), 0.86 (t, J = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 52.4, 33.5, 32.8, 31.4, 29.0, 28.5, 22.6, 14.1.

ESI MS. $C_9H_{19}O_2S$ m/z $[M+H]^+$ calc. 191.1, found 191.1.

Methyl 2-(hexylsulfinyl)acetate (±)-**1b**

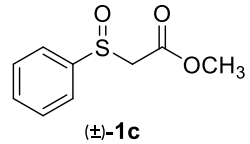
Yield: 86%. Purified by ISCO flash column chromatography (7:3 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.67 (d, J = 4.0 Hz, 2H), 2.93 - 2.72 (m, 2H), 1.82 - 1.71 (m, 2H), 1.51 - 1.41 (m, 2H), 1.34 - 1.29 (m, 4H), 0.88 (t, J = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 55.8, 53.1, 52.9, 31.4, 28.5, 22.5, 22.5, 14.1.

ESI MS. $C_9H_{19}O_3S$ m/z $[M+H]^+$ calc. 207.1, found 207.1.

Methyl 2-(phenylsulfinyl)acetate (±)-**1c**



(±)-**1c**

Synthesized by General procedure B.

Methyl 2-(phenylthio)acetate S3c

Yield: 91%. Purified by ISCO flash column chromatography (9:1 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.41 (m, 2H), 7.34 - 7.28 (m, 2H), 7.27 - 7.23 (m, 1H), 3.73 (s, 3H), 3.67 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 135.0, 129.9, 129.1, 127.1, 52.6, 36.6.

ESI MS. $C_9H_{11}O_2S$ m/z $[M+H]^+$ calc. 183.0, found 183.0.

Methyl 2-(phenylsulfinyl)acetate (±)-**1c**

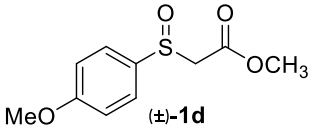
Yield: 87%. Purified by ISCO flash column chromatography (1:1 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 - 7.64 (m, 2H), 7.56 - 7.50 (m, 3H), 3.83 (d, J =16.0 Hz, 1H), 3.70 - 3.64 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 143.2, 131.9, 129.5, 124.2, 77.3, 61.7, 52.8.

ESI MS. $C_9H_{11}O_3S$ m/z $[M+H]^+$ calc. 199.0, found 199.0.

Methyl 2-((4-methoxyphenyl)sulfinyl)acetate (±)-**1d**



(±)-**1d**

Synthesized by General procedure B.

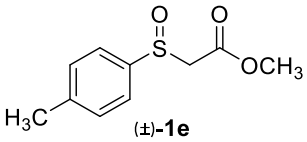
Methyl 2-((4-methoxyphenyl)thio)acetate S3d

Yield: 90%. Purified by ISCO flash column chromatography (4:1 hexane:EtOAc v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 - 7.31 (m, 2H), 6.89 - 6.74 (m, 2H), 3.76 (s, 3H), 3.66 (s, 3H), 3.50 (s, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 170.4, 159.7, 134.2, 124.8, 114.7, 55.3, 52.4, 38.4.
ESI MS. $C_{10}H_{13}O_3S$ m/z $[M+H]^+$ calc. 213.1, found 213.1.

Methyl 2-((4-methoxyphenyl)sulfinyl)acetate (±)-**1d**
Yield: 87%. Purified by ISCO flash column chromatography (2:3 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 - 7.53 (m, 2H), 7.00 - 6.95 (m, 2H), 3.83 - 3.78 (m, 4H), 3.72 - 3.48 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 162.6, 134.0, 126.2, 114.9, 61.6, 55.6, 52.6.
ESI MS. $C_{10}H_{13}O_4S$ m/z $[M+H]^+$ calc. 229.0, found 229.1.

Methyl 2-(*p*-tolylsulfinyl)acetate (±)-**1e**

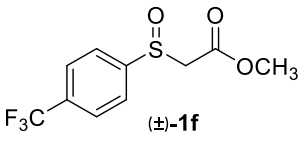


(±)-**1e**

Synthesized by General procedure B.
Methyl 2-(*p*-tolylthio)acetate S3e
Yield: 92%. Purified by ISCO flash column chromatography (9:1 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 - 7.26 (m, 2H), 7.11 - 7.06 (m, 2H), 3.67 (s, 3H), 3.57 (s, 2H), 2.29 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 137.2, 131.2, 130.8, 129.9, 52.4, 37.1, 20.9.
ESI MS. $C_{10}H_{13}O_2S$ m/z $[M+H]^+$ calc. 197.1, found 197.1.

Methyl 2-(*p*-tolylsulfinyl)acetate (±)-**1e**
Yield: 90%. Purified by ISCO flash column chromatography (3:2 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 - 7.55 (m, 2H), 7.35 - 7.33 (m, 2H), 3.84 (d, J = 16.0 Hz, 1H), 3.70 (s, 3H), 3.64 (d, J = 16.0 Hz, 1H), 2.42 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 142.6, 139.9, 130.2, 124.3, 61.8, 52.9, 21.6.
ESI MS. $C_{10}H_{13}O_3S$ m/z $[M+H]^+$ calc. 213.1, found 213.1.

Methyl 2-((4-(trifluoromethyl)phenyl)sulfinyl)acetate (±)-**1f**



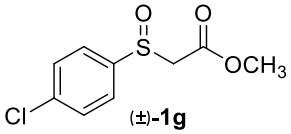
(±)-**1f**

Synthesized by General procedure B.
Methyl 2-((4-(trifluoromethyl)phenyl)thio)acetate S3f
Yield: 89%. Purified by ISCO flash column chromatography (9:1 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.9 Hz, 2H), 3.74 (s, 3H), 3.72 (s, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 169.7, 140.6, 128.6 (q), 128.1, 126.0 (q), 125.0 (q), 52.9, 35.2.

ESI MS. $C_{10}H_{10}F_3O_2S$ m/z $[M+H]^+$ calc. 251.0, found 251.0.

Methyl 2-((4-(trifluoromethyl)phenyl)sulfinyl)acetate(±)-**1f**
Yield: 86%. Purified by ISCO flash column chromatography (2:1 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 4H), 3.85 (d, J = 12.0 Hz, 1H), 3.75 - 3.71 (m, 4H).
^{13}C NMR (151MHz, $CDCl_3$) δ 164.9, 147.6, 133.8 (q), 126.6 (q), 124.8, 122.5(q), 61.4, 53.1.
ESI MS. $C_{10}H_{10}F_3O_3S$ m/z $[M+H]^+$ calc. 267.0, found 267.1.

Methyl 2-((4-chlorophenyl)sulfinyl)acetate (±)-**1g**

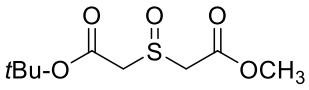


(±)-**1g**

Synthesized by General procedure B.
Methyl 2-((4-chlorophenyl)thio)acetate S3g
Yield: 91%. Purified by ISCO flash column chromatography (9:1 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 - 7.34 (m, 2H), 7.31 - 7.27 (m, 2H), 3.73 (s, 3H), 3.64 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 133.5, 133.3, 131.5, 129.3, 52.7, 36.7.
ESI MS. $C_9H_{10}ClO_2S$ m/z $[M+H]^+$ calc. 217.0, found 217.0.

Methyl 2-((4-chlorophenyl)sulfinyl)acetate (±)-**1g**
Yield: 88%. Purified by ISCO flash column chromatography (2:1 hexane:EtOAc v/v).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 - 7.61 (m, 2H), 7.52 - 7.50 (m, 2H), 3.83 (d, J = 12.0 Hz, 1H), 3.70 (s, 3H), 3.67 (d, J = 12.0 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.0, 141.6, 138.2, 129.8, 125.7, 61.5, 52.9.
ESI MS. $C_9H_{10}ClO_3S$ m/z $[M+H]^+$ calc. 233.0, found 233.0.

***tert*-Butyl 2-((2-methoxy-2-oxoethyl)sulfinyl)acetate** (±)-**1h**



(±)-**1h**

Synthesized by modified General procedure A.
***tert*-Butyl 2-((2-methoxy-2-oxoethyl)thio)acetate S3h**
Yield: 91%. Purified by ISCO flash column chromatography (4:1 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 (s, 3H), 3.34 (s, 2H), 3.24 (s, 2H), 1.42 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 168.9, 81.9, 52.4, 34.8, 33.3, 27.9.

***tert*-butyl 2-((2-methoxy-2-oxoethyl)sulfinyl)acetate** (±)-**1h**
To a solution of above thiol (1.0 g, 4.54 mmol, 1.0 equiv) in dichloromethane (25 mL) at 0°C was added 3-chloroperoxybenzoic acid (1.1 g, 4.95 mmol, 1.1 equiv). The resulting mixture was allowed to warm to room temperature after addition and was stirred at ambient temperature for 3h. The reaction was quenched with saturated solution of sodium sulfite (20 mL) and water layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried over

Na_2SO_4, filtered, and concentrated to give the crude product, which was purified using ISCO flash chromatography.

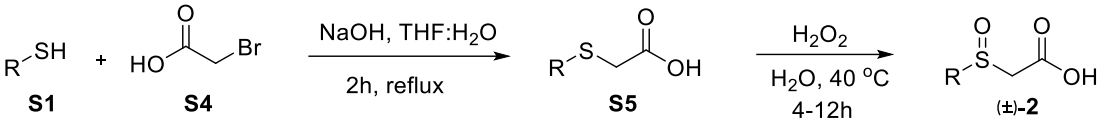
Yield: 76%. Purified by ISCO flash column chromatography (1:1 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.02 (d, J = 16.0 Hz, 1H), 3.94 (d, J = 12.0 Hz, 1H), 3.84 - 3.68 (m, 5H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 164.1, 84.0, 56.7, 55.4, 53.1, 28.1.

ESI MS. $C_9H_{15}O_5S$ m/z $[M-H]^+$ calc. 235.1, found 235.0.

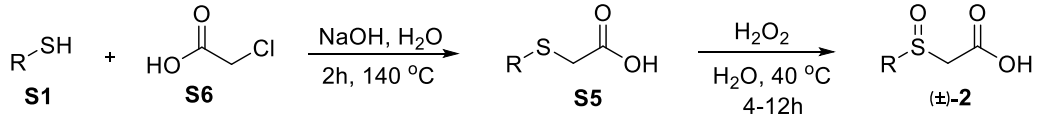
III General procedure C



To a solution of thiol **S1** (10.58 mmol, 1.0 equiv) in THF (10 mL) was added NaOH (846 mg, 21.16 mmol, 2.0 equiv) in water (15.6 mL). Bromoacetic acid **S4** (1.46 g, 10.58 mmol, 1.0 equiv) was dissolved in THF (10 mL) and added to the reaction mixture. After stirring at reflux for 2h, the reaction mixture was cooled and acidified with 6N HCl. The water layer was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude **S5** was used directly in the next step without purification.

30% hydrogen peroxide (0.9 mL, 8.00 mmol, 1.0 equiv) was added to a solution of mercaptoacetic acid **S5** (8.00 mmol, 1.0 equiv) in distilled water (10 mL). The rapidly stirred mixture was heated at 40°C for 4-12h. When the reaction was over as monitored by LCMS, the mixture was allowed to cool to room temperature. Then the reaction mixture was diluted with water and extracted with EtOAc (3 × 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude (±)-**2** was used directly for the next step without any further purification.

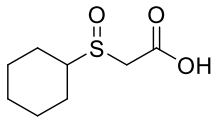
IV General procedure D



To a solution of thiol **S1** (10.58 mmol, 1.0 equiv) and chloroacetic acid **S6** (994 mg, 10.58 mmol, 1.0 equiv) in H_2O (15 mL) was slowly added NaOH (846 mg, 21.16 mmol, 2.0 equiv). The resulting mixture was refluxed for 2h, then cooled to room temperature, and acidified with 6N HCl to pH 2. Then filtration gave thiol derivative **S5** which was used directly in the next step.

30% hydrogen peroxide (0.9 mL, 8.00 mmol, 1.0 equiv) was added to a solution of mercaptoacetic acid **S5** (8.00 mmol, 1.0 equiv) in H_2O (10 mL). The rapidly stirred mixture was heated at 40°C for 4-12h. When the reaction was over, the mixture was allowed to cool to room temperature and water was removed under vacuum, washed with toluene (15 mL) and dried.

2-(Cyclohexylsulfinyl)acetic acid (±)-**2a**



(±)-**2a**

Synthesized by General procedure C.

2-(Cyclohexylthio)acetic acid S5a

Yield: 90%.

^{1}H NMR (400 MHz, MeOD) δ 3.24 (s, 2H), 2.84 - 2.77 (m, 1H), 2.05 - 1.97 (m, 2H), 1.80 - 1.72 (m, 2H), 1.66 - 1.59 (m, 1H), 1.39 - 1.22 (m, 5H).

^{13}C NMR (151 MHz, MeOD) δ 174.7, 44.9, 34.3, 32.8, 32.7, 27.0, 26.9.

ESI MS. $C_8H_{15}O_2S$ m/z $[M+H]^+$ calc. 175.1, found 175.1.

2-(Cyclohexylsulfinyl)acetic acid (±)-**2a**

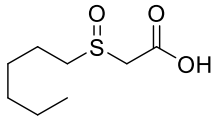
Yield: 91%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (d, J =12.0 Hz, 1H), 3.61 (d, J = 16.0 Hz, 1H), 2.98 - 2.90 (m, 1H), 2.19 - 2.12 (m, 1H), 1.97 - 1.85 (m, 3H), 1.75 - 1.69 (m, 1H), 1.55 - 1.20 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 58.5, 50.9, 26.4, 25.3 (d), 25.0, 24.6.

ESI MS. $C_8H_{15}O_3S$ m/z $[M+H]^+$ calc. 191.1, found 191.1.

2-(Hexylsulfinyl)acetic acid (±)-**2b**



(±)-**2b**

Synthesized by General procedure C.

2-(Hexylthio)acetic acid S5b

Yield: 89%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.24 (s, 2H), 2.67 - 2.63 (m, 2H), 1.64 -1.54 (m, 2H), 1.42 - 1.22 (m, 6H), 0.88 (t, J = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 33.6, 32.9, 31.5, 28.9, 28.5, 22.6, 14.1.

ESI MS. $C_8H_{15}O_2S$ m/z $[M-H]^+$ calc. 175.1, found 175.1.

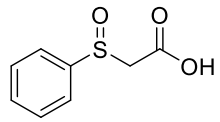
2-(Hexylsulfinyl)acetic acid (±)-**2b**

Yield: 87%.

^{1}H NMR (400 MHz, MeOD) δ 3.91 (d, J = 16.0 Hz, 1H), 3.72 (d, J = 16.0 Hz, 1H), 2.95 - 2.90 (m, 2H), 1.82 - 1.74 (m, 2H), 1.52 - 1.48 (m, 1H), 1.40 - 1.30 (m, 5H), 0.95 - 0.90 (m, 3H). **^{13}C NMR** (151 MHz, MeOD) δ 168.4, 56.6, 52.9, 39.8, 32.6, 29.4, 23.6, 23.5, 14.3.

ESI MS. $C_8H_{17}O_3S$ m/z $[M+H]^+$ calc. 193.1, found 193.1.

2-(Phenylsulfinyl)acetic acid (±)-**2c**



(±)-**2c**

Synthesized by General procedure D.

2-(Phenylthio)acetic acid S5c

Yield: 92%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.41 (m, 2H), 7.34 - 7.28 (m, 2H), 7.27 - 7.23 (m, 1H), 3.67 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 134.6, 130.2, 129.3, 127.4, 36.7.

ESI MS. $C_8H_7O_2S$ m/z $[M-H]^+$ calc. 167.0, found 167.0.

2-(Phenylsulfinyl)acetic acid (±)-**2c**

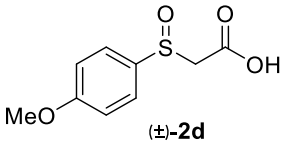
Yield: 90%.

^{1}H NMR (400 MHz, MeOD) δ 7.78 - 7.72 (m, 2H), 7.63 - 7.57 (m, 3H), 3.93 (d, J = 16.0 Hz, 1H), 3.87 (d, J = 16.0 Hz, 1H).

^{13}C NMR (151 MHz, MeOD) δ 167.9, 143.6, 133.0, 130.6, 125.5, 62.1.

ESI MS. $C_8H_9O_3S$ m/z $[M+H]^+$ calc. 185.0, found 185.0.

2-((4-Methoxyphenyl)sulfinyl)acetic acid (±)-**2d**



(±)-**2d**

Synthesized by General procedure D.

2-((4-Methoxyphenyl)thio)acetic acid S5d

Yield: 93%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 - 7.42 (m, 2H), 6.87 - 6.84 (m, 2H), 3.80 (s, 3H), 3.54 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1, 159.9, 134.4, 124.6, 114.9, 55.5, 38.7.

ESI MS. $C_9H_{11}O_3S$ m/z $[M+H]^+$ calc. 199.0, found 199.1.

2-((4-Methoxyphenyl)sulfinyl)acetic acid (±)-**2d**

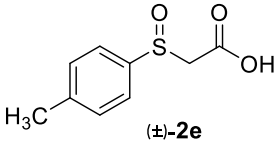
Yield: 89%.

^{1}H NMR (400 MHz, DMSO) δ 7.70 - 7.63 (m, 2H), 7.14 - 7.11 (m, 2H), 3.91 (d, J = 12.0 Hz, 1H), 3.82 - 3.78 (m, 4H).

^{13}C NMR (101 MHz, DMSO) δ 166.8, 161.7, 134.6, 126.4, 114.8, 61.4, 55.5.

ESI MS. $C_9H_{11}O_4S$ m/z $[M+H]^+$ calc. 215.0, found 215.1.

2-(*p*-Tolylsulfinyl)acetic acid (±)-**2e**



(±)-**2e**

Synthesized by General procedure D.

2-(*p*-Tolylthio)acetic acid S5e

Yield: 89%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 - 7.33 (m, 2H), 7.13 - 7.10 (m, 2H), 3.61 (s, 2H), 2.33 (s, 3H).

^{13}C NMR (151 MHz, CDCl3) δ 175.8, 137.8, 131.1, 130.8, 130.1, 37.4, 21.2.

ESI MS. $C_9H_{11}O_2S$ m/z $[M+H]^+$ calc. 183.0, found 183.1.

2-(*p*-Tolylsulfinyl)acetic acid (±)-**2e**

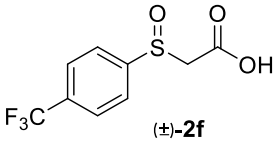
Yield: 90%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 3.81 (d, J = 16.0 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 143.1, 137.8, 130.6, 124.6, 59.1, 21.6.

ESI MS. $C_9H_{11}O_3S$ m/z $[M+H]^+$ calc. 199.0, found 199.1.

2-((4-(Trifluoromethyl)phenyl)sulfinyl)acetic acid (±)-**2f**



(±)-**2f**

Synthesized by General procedure D.

2-((4-(Trifluoromethyl)phenyl)thio)acetic acid S5f

Yield: 88%.

^{1}H NMR (600 MHz, DMSO) δ 12.95 (s, 1H), 7.66 - 7.63 (m, 2H), 7.50 - 7.48 (m, 2H), 3.96 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 170.2, 142.2, 126.7, 125.6 (q), 125.5 (q), 123.4, 33.8.

ESI MS. $C_9H_8F_3O_2S$ m/z $[M+H]^+$ calc. 237.0, found 237.0.

2-((4-(Trifluoromethyl)phenyl)sulfinyl)acetic acid (±)-**2f**

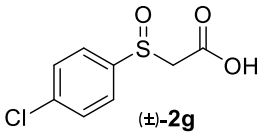
Yield: 85%.

^{1}H NMR (400 MHz, MeOD) δ 7.93 (q, J = 8.4 Hz, 4H), 4.04 (d, J = 16.0 Hz, 1H), 3.90 (d, J = 16.0 Hz, 1H).

^{13}C NMR (151 MHz, MeOD) δ 167.8, 148.7, 134.5 (q), 127.5 (q), 126.4, 126.0 (q), 61.9.

ESI MS. $C_9H_8F_3O_3S$ m/z $[M+H]^+$ calc. 253.0, found 253.0.

2-((4-Chlorophenyl)sulfinyl)acetic acid (±)-**2g**



(±)-**2g**

Synthesized by General procedure D.

2-((4-Chlorophenyl)thio)acetic acid S5g

Yield: 89%.

^{1}H NMR (400 MHz, MeOD) δ 7.38 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 3.70 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.9, 133.7, 132.9, 131.7, 129.5, 36.9.

ESI MS. $C_8H_8ClO_2S$ m/z $[M+H]^+$ calc. 203.0, found 203.0.

2-((4-Chlorophenyl)sulfinyl)acetic acid (±)-**2g**

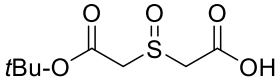
Yield: 87%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, J = 6.0 Hz, 2H), 7.56 (d, J = 12.0 Hz, 2H), 3.88 (d, J = 18.0 Hz, 1H), 3.70 (d, J = 12.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.6, 139.3, 138.9, 130.3, 125.8, 57.7.

ESI MS. $C_8H_8ClO_3S$ m/z $[M+H]^+$ calc. 219.0, found 219.1.

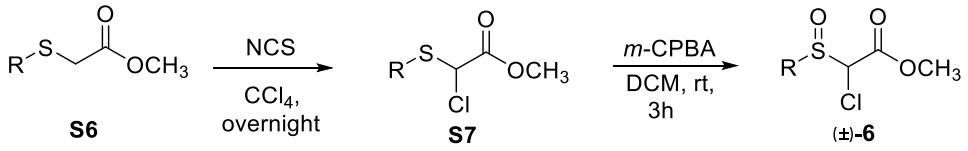
2-((2-(*tert*-Butoxy)-2-oxoethyl)sulfinyl)acetic acid (±)-**2h**



(±)-**2h**

Ester derivative (±)-**1h** (700 mg, 2.96 mmol, 1.0 equiv) in ethanol (2.36 mL) was treated with 2N NaOH (1.9 mL, 3.85 mmol, 1.3 equiv) and stirred at room temperature for 3h. Using 2N HCl the reaction mixture was neutralized to a pH of 5.0. Ethanol was removed under reduced pressure and the aqueous residue was diluted with water and EtOAc. At 0°C the pH was brought to 3 with 10% citric acid. The aqueous layer was extracted with EtOAc (3 × 30 mL) and combined organic layers were dried over Na_2SO_4, filtered, and concentrated to give the crude product, which was used directly for the next reaction without any purification.
ESI MS. $C_8H_{13}O_5S$ m/z $[M-H]^+$ calc. 221.1, found 221.0.

V General procedure E

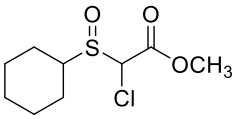


S6 **S7** (±)-**6**

To an ice cold solution of thio derivative **S6** (10.00 mmol, 1.0 equiv) in $CC1_4$ (30 mL) was added of N-chlorosuccinimide (1.34 g, 10.00 mmol, 1.0 equiv), and the resulting solution was stirred overnight at rt. Evaporation of the solvent and purification by ISCO flash chromatography gave desired product **S7** which was used for next step.

To a solution of the product of the previous step **S7** (8.00 mmol, 1.0 equiv) in DCM (10 mL) at 0°C was added 3-chloroperoxybenzoic acid (2.37 g, 9.6 mmol, 1.2 equiv). The resulting mixture was allowed to warm to room temperature and stirred at room temperature for 3h (monitored by LCMS). The reaction was quenched with saturated sodium sulfite (20 mL) and the mixture was stirred at room temperature for 5 min. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated to give the title compound (±)-**6** which was purified by ISCO flash chromatography.

Methyl 2-chloro-2-(cyclohexylsulfinyl)acetate (±)-**6a**

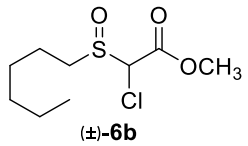


(±)-**6a**

Synthesized by General procedure E.
Yield: 82%. Purified by ISCO flash column chromatography (3:2 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12 (s, 0.6H), 5.04 (s, 0.4H) 3.85 (s, 3H), 3.00 - 2.88 (m, 1H), 2.13 - 1.21 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 164.5, 69.0, 65.6, 58.5, 56.9, 54.3, 54.1, 27.0, 26.3, 25.5, 25.2, 25.1, 25.0, 24.9, 23.1.
ESI MS. $C_9H_{16}ClO_3S$ m/z $[M+H]^+$ calc. 239.0, found 239.1.

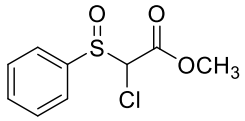
2-Chloro-2-(hexylsulfinyl)acetic acid (±)-**6b**



(±)-**6b**

Synthesized by General procedure E.
Yield: 81%. Purified by ISCO flash column chromatography (3:1 hexane:EtOAc v/v).
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.16 (s, 0.6H), 5.09 (s, 0.4H), 3.91 (s, 1.2H), 3.90 (s, 1.8H), 2.96 - 2.78 (m, 2H), 1.85 - 1.72 (m, 2H), 1.52 - 1.42 (m, 2H), 1.34 -1.29 (m, 4H), 0.90 - 0.87 (m, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 164.4, 164.3, 69.3, 68.9, 54.3, 54.2, 50.2, 49.7, 31.4, 28.5, 22.8, 22.5, 22.2, 14.1.
ESI MS. $C_9H_{18}ClO_3S$ m/z $[M+H]^+$ calc. 241.1, found 241.1.

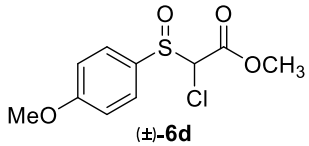
Methyl 2-chloro-2-(phenylsulfinyl)acetate (±)-**6c**



(±)-**6c**

Synthesized by General procedure E.
Yield: 87%. Purified by ISCO flash column chromatography (1:1 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 - 7.68 (m, 2H), 7.63 - 7.53 (m, 3H), 5.09 (s, 0.5H), 4.99 (s, 0.5H), 3.82 (s, 1.5H), 3.74 (s, 1.5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 139.8, 133.0, 132.8, 129.4, 129.2, 125.8, 125.2, 74.7, 72.8, 53.9.
ESI MS. $C_9H_{10}ClO_3S$ m/z $[M+H]^+$ calc. 233.0, found 233.0.

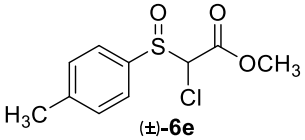
Methyl 2-chloro-2-((4-methoxyphenyl)sulfinyl)acetate (±)-**6d**



(±)-**6d**

Synthesized by General procedure E.
Yield: 89%. Purified by ISCO flash column chromatography (2:3 hexane:EtOAc v/v).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 - 7.61 (m, 2H), 7.04 - 7.02 (m, 2H), 5.08 (s, 0.5H), 4.97 (s, 0.5H), 3.86 (s, 3H), 3.81 (s, 1.5H), 3.72 (s, 1.5H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 164.2, 163.9, 163.5, 163.4, 130.1, 130.0, 127.8, 127.2, 114.9, 114.8, 74.4, 72.9, 55.7, 53.9.
ESI MS. $C_{10}H_{12}ClO_4S$ m/z $[M+H]^+$ calc. 263.0, found 263.0.

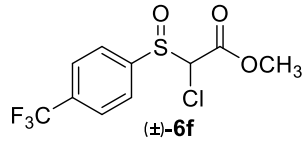
Methyl 2-chloro-2-(p-tolylsulfinyl)acetate (±)-**6e**



(±)-**6e**

Synthesized by General procedure E.
Yield: 83%. Purified by ISCO flash column chromatography (2:3 hexane:EtOAc v/v).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 - 7.55 (m, 2H), 7.35 - 7.33 (m, 2H), 5.09 (s, 0.5H), 4.98 (s, 0.5H), 3.80 (s, 1.5H), 3.72 (s, 1.5H), 2.42 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 163.8, 143.7, 143.6, 136.2, 135.9, 129.9, 129.8, 125.7, 125.1, 74.5, 72.8, 53.8, 21.5.
ESI MS. $C_{10}H_{12}ClO_3S$ m/z $[M+H]^+$ calc. 247.0, found 247.1.

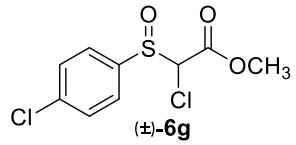
Methyl 2-chloro-2-((4-(trifluoromethyl)phenyl)sulfinyl)acetate (±)-**6f**



(±)-**6f**

Synthesized by General procedure E.
Yield: 78%. Purified by ISCO flash column chromatography (2:3 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 - 7.79 (m, 4H), 5.18 (s, 0.5H), 5.09 (s, 0.5H), 3.82 (s, 1.5H), 3.77 (s, 1.5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 163.5, 143.9, 143.7, 134.6 (q), 130.2 (q), 126.47, 126.3 (q), 125.9, 122.0 (q), 73.9, 72.8, 54.2.
ESI MS. $C_{10}H_9ClF_3O_3S$ m/z $[M+H]^+$ calc. 301.0, found 301.0.

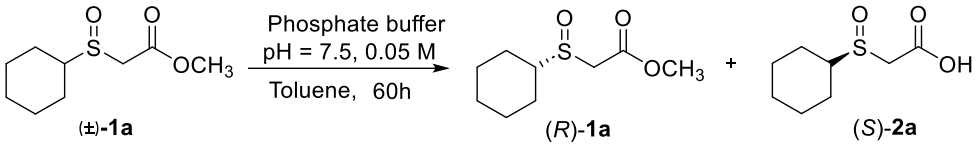
Methyl 2-chloro-2-((4-chlorophenyl)sulfinyl)acetate (±)-**6g**



(±)-**6g**

Synthesized by General procedure E.
Yield: 81%. Purified by ISCO flash column chromatography (1:1 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 - 7.57 (m, 2H), 7.49 - 7.46 (m, 2H), 5.15 (s, 0.5H), 5.05 (s, 0.5H), 3.75 (s, 1.5H), 3.71 (s, 1.5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 163.5, 139.2, 138.9, 137.9, 137.6, 129.5, 129.4, 127.1, 126.6, 74.0, 72.8, 53.9.
ESI MS. $C_9H_9Cl_2O_3S$ m/z $[M+H]^+$ calc. 267.0, found 266.9.

VI General Procedure for screening of enzymes for enzymatic resolution



To a solution of ester (±)-**1a** (50 mg, 0.24 mmol) in toluene (0.25 mL) were added phosphate buffer (2.0 mL of pH 7.5, 0.05 M) and enzyme (5 mg, 10 wt%) as indicated in Table S1. This heterogeneous mixture was stirred at 25 ^{o}C. The mixture was filtered through celite to remove the enzyme and extracted with EtOAc (3 × 10 mL). Evaporation of the solvent and ISCO flash chromatography gave enantioenriched ester derivative (*R*)-**1a**.

Acetic acid (0.5 mL) was added and aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over Na_2SO_4 and removal of the solvent gave acid (*S*)-**2a**.

Under a nitrogen atmosphere, a solution of (trimethylsilyl)diazomethane (2.0 M solution in diethyl ether, 0.7 mmol) was added to a solution of the acid derivative **2a** (0.07 mmol) in dry MeOH (0.3 mL) at 0 °C. The resulting mixture was warmed slowly to rt and stirred overnight. After completion of the reaction, the solvent was removed in vacuo. Purification by ISCO flash column chromatography afforded the ester derivative (*S*)-**1a**.

Table S1

Entry	Name of the Enzyme	% conversion by NMR[1]	% ee of **1a** (chiral HPLC)	Selectivity (E)
1	Lipase from Burkholderia sp.	2	0	0
2	Lipase from Pseudomonas sp	3	4	<5
3	Lipase from Candida sp.	15	16	24
4	Lipase from Rhizopus sp.	11	-3	<5
5	Lipase from Aspergillus sp.	44	14	1.6
6	Esterase from E. coli	26	-6	1.5
7	**Lipoprotein lipase from Burkholderia sp. (EC 3.1.1.3)**	**50**	**>99**	**>1000**
8	Lipase from Rhizopus oryzae	17	10	3.2

9	Lipase from Penicillium sp.	16	13	6.0
10	Lipase from Candida rugosa.	14	5	2.0
11	Lipase from Candida antarctica, type B	44	-7	1.3
12	Lipase from Candida antarctica, type A	33	30	5.5
13	Lipase from Thermomyces lanuginosas	20	19	8.8
14	Lipase from Mucor miehei	42	15	1.7
15	Lipase from Alcaligenes sp.	30	33	10
16	Esterase from pig liver	33	35	8.3

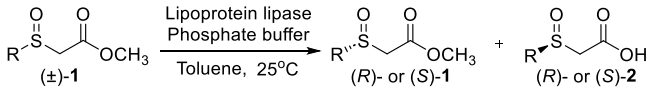
1: 1,3,5 trimethoxybenzene was uses an internal indicator for NMR

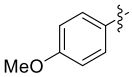
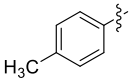
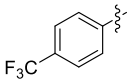
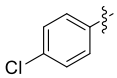
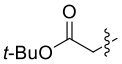
The configurations are assigned by comparing the optical rotations as shown in TableS2.

Table S2

Entry	Compound	Observed specific rotation $[\alpha]^{25}_D$	Known specific rotation[1] $[\alpha]_D$
1	(*R*)-**1g**	+216.25 (c 0.27, EtOH)	+201 (0.0138M, EtOH)
2	(*S*)-**1g**	-199.96 (c 0.26, EtOH)	-184 (0.0227M, EtOH)

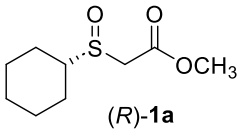
Table S3. Enzymatic resolution of a-sulfinyl carboxylates.[a]



Entry	Cmpd	R	Buffer pH	Time (h)	% Yield **1** (% ee)	% Yield **2** (% ee)	Selectivity (E)[d]
1[b]	**1a**/**2a**		7.5	16	46 (>98)	30 (99)	50
2[b]	**1b**/**2b**	*n*-Hex	9.0	12	46 (>98)	32 (>99)	50
3	**1c**/**2c**		7.5	16	48 (>99)	35 (>99)	120
4	**1d**/**2d**		7.5	15	47 (>99)	36 (96)	80
5	**1e**/**2e**		7.5	15	46 (>99)	35 (>99)	61
6	**1f**/**2f**		8.6	14	45 (>99)	33 (>99)	49
7	**1g**/**2g**		7.5	16	45 (>99)	33 (98)	49
8[b],[c]	**1h**/**2h**		9.5	60	44 (>99)	30 (89)	41

[a] Reactions on a 1 g scale with 10 wt% lipoprotein lipase from *Burkholderia sp*., 8:1 50 mM phosphate buffer:toluene unless otherwise noted. [b] 30 wt% lipase. [c] 100 mM phosphate buffer. [d] Lower limit to selectivity factor based on recovered starting material according to E = Ln[(1-c)(1-ee)]/Ln[(1-c)(1+ee), using 1-yield as conversion (c).

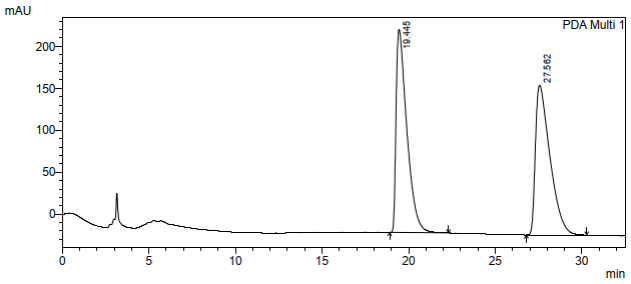
HPLC of Compound 1a



[α]^{25}D of (*R*)**-1a** +25.99 (c 0.5, EtOH).

Chiral HPLC Chiralcel OD-H, 10% IPA/hexanes, 1.0 mL/min, 210nm.

(±)-**1a**



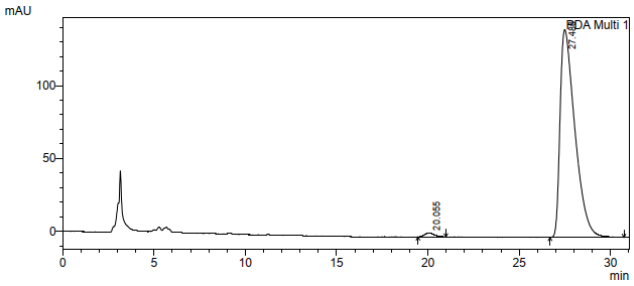
1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Area %
1	19.445	10460433	50.065
2	27.562	10433478	49.935
Total		20893911	100.000

(*R*)-**1a**



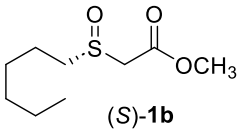
1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Area %
1	20.055	100217	1.231
2	27.486	8038443	98.769
Total		8138661	100.000

HPLC of Compound 1b



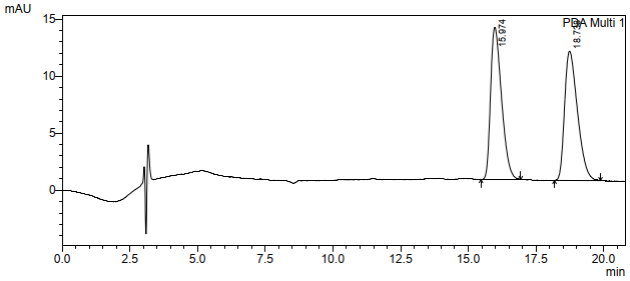
(*S*)-**1b**

[α]$^{25}_{D}$ of (*S*)-**1b** -23.19 (c 0.25, EtOH).

[α]$^{25}_{D}$ of (*R*)-**1b** +25.18 (c 0.135, EtOH)

Chiral HPLC Chiralcel OD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**1b**



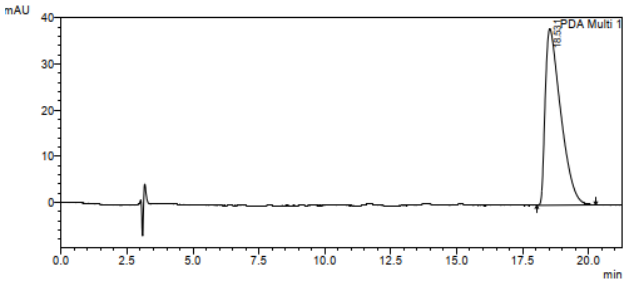
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	15.974	375177	49.935
2	18.738	376160	50.065
Total		751337	100.000

(*S*)-**1b**



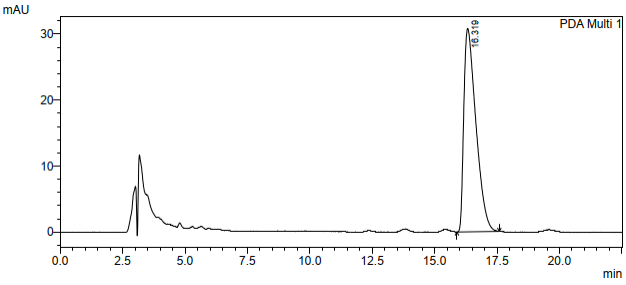
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	18.531	1561190	100.000
Total		1561190	100.000

(*R*)-**1b {from** (*R*)-**2b}**



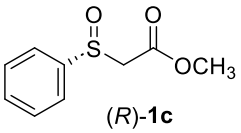
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	16.319	1039233	100.000
Total		1039233	100.000

HPLC of Compound 1c



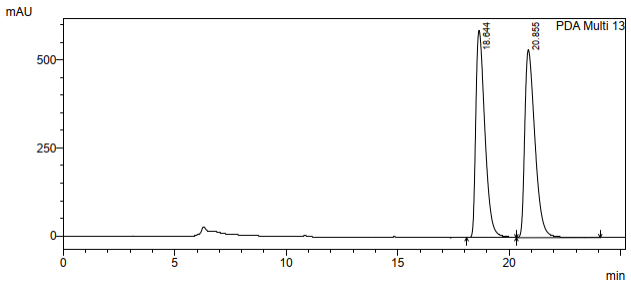
(*R*)-**1c**

[α]$^{25}_{D}$ of (*R*)-**1c** +234.34 (c 0.25, EtOH).

[α]$^{25}_{D}$ of (*S*)-**1c** -203.29 (c 0.18, EtOH).

Chiral HPLC Chiralcel OD-H, 30% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**1c**



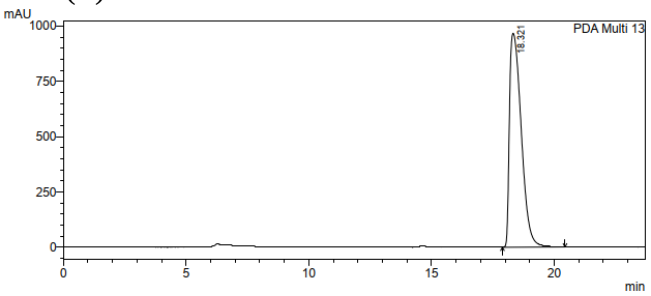
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	18.644	16706357	49.568
2	20.855	16997620	50.432
Total		33703977	100.000

(*R*)-**1c**



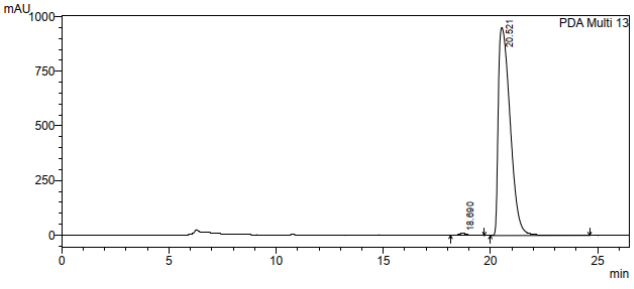
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	18.321	32231790	100.000
Total		32231790	100.000

(*S*)-**1c {from** (*S*)-**2c}**



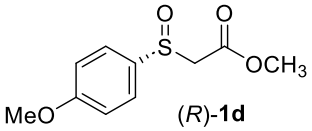
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

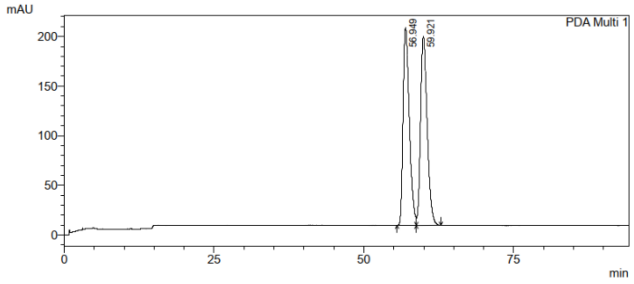
Peak#	Ret. Time	Area	Area %
1	18.690	253616	0.689
2	20.521	36573263	99.311
Total		36826879	100.000

HPLC of Compound 1d



(*R*)-**1d**

[α]$^{27}_{D}$ of (*R*)-**1d** +191.94 (c 0.25, EtOH).
[α]$^{27}_{D}$ of (*S*)-**1d** -151.16 (c 0.25, EtOH)
Chiral HPLC Chiralpak AD-H, 5% IPA/hexanes, 1.0 mL/min, 254nm.
(±)-**1d**



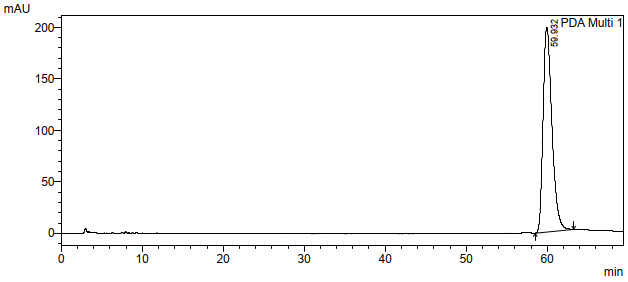
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	56.949	14536098	49.721
2	59.921	14699138	50.279
Total		29235236	100.000

(*R*)-**1d**



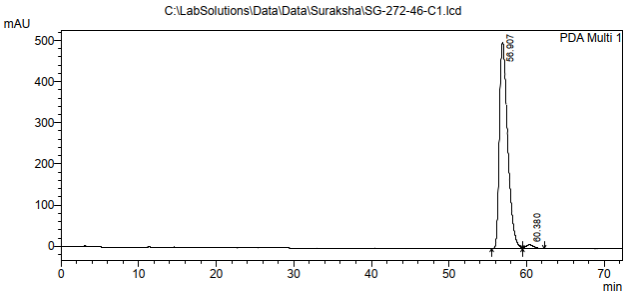
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	59.932	15153000	100.000
Total		15153000	100.000

(*S*)-**1d {from** (*S*)-**2d}**



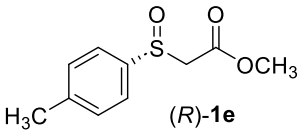
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	56.907	37303441	98.164
2	60.380	697872	1.836
Total		38001314	100.000

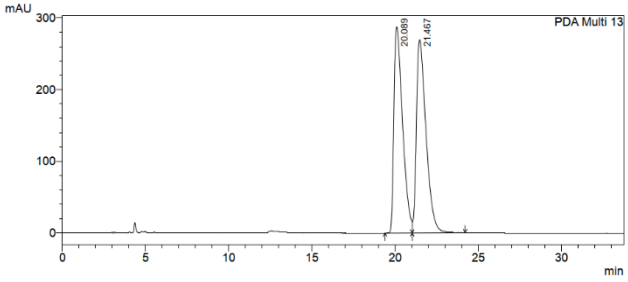
HPLC of Compound 1e



(*R*)-**1e**

[α]$^{25}_{D}$ of (*R*)-**1e** +217.29 (c 0.15, EtOH)
[α]$^{26}_{D}$ of (*S*)-**1e** -147.96 (c 0.25, EtOH)
Chiral HPLC Chiralcel OD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**1e**



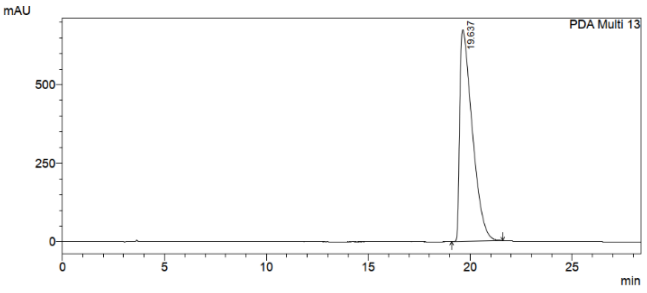
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	20.089	10422464	49.069
2	21.467	10817838	50.931
Total		21240302	100.000

(*R*)-**1e**



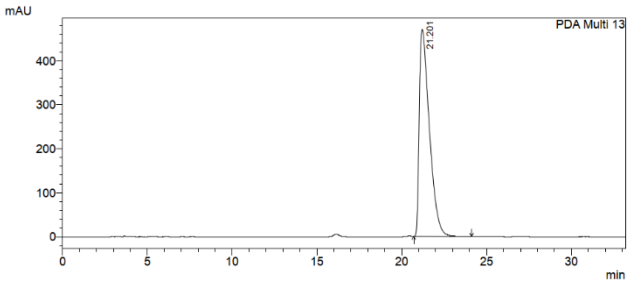
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	19.637	28895161	100.000
Total		28895161	100.000

(*S*)-**1e {from** (*S*)-**2e}**



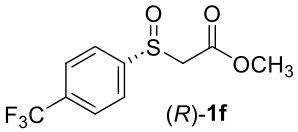
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	21.201	19537487	100.000
Total		19537487	100.000

HPLC of Compound 1f



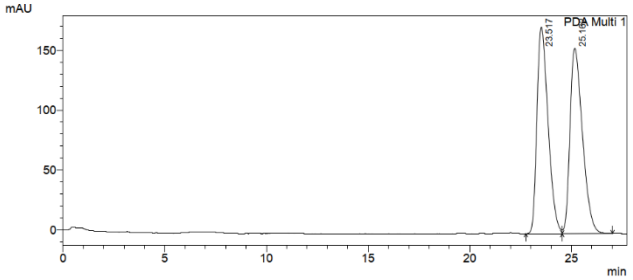
(*R*)-**1f**

[α]^{25}D of (*R*)-**1f** +211.80 (c 0.135, EtOH)

[α]^{25}D of (*S*)-**1f** -180.76 (c 0.125, EtOH)

Chiral HPLC Chiralcel OD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**1f**



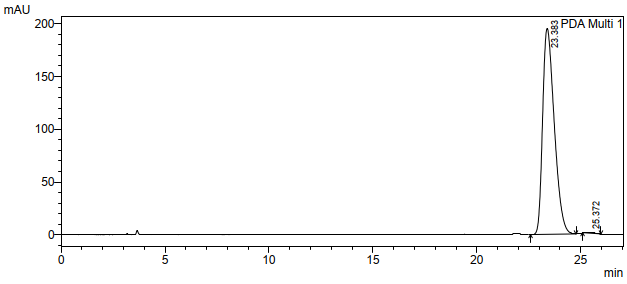
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	23.517	6573511	49.843
2	25.162	6615035	50.157
Total		13188547	100.000

(*R*)-**1f**



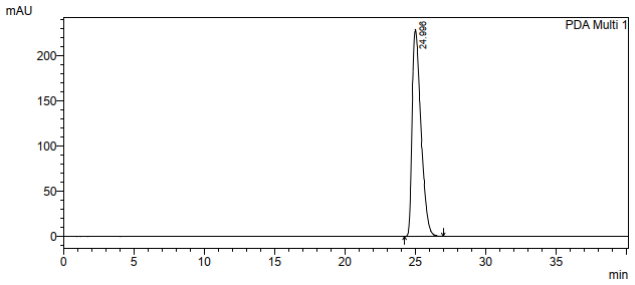
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	23.383	7565747	99.715
2	25.372	21615	0.285
Total		7587362	100.000

(*S*)-**1f {from** (*S*)-**2f}**



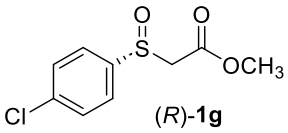
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	24.996	9944800	100.000
Total		9944800	100.000

HPLC of Compound 1g



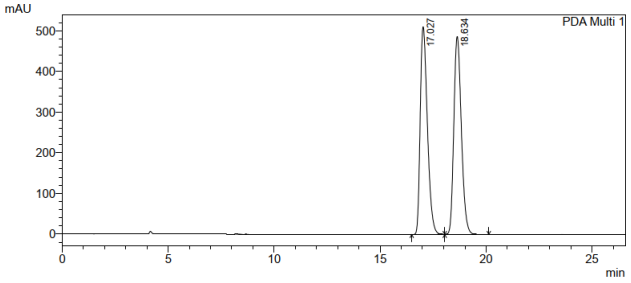
(*R*)-**1g**

[α]$^{25}_{D}$ of (*R*)-**1g** +216.25 (c 0.27, EtOH)

[α]$^{25}_{D}$ of (*S*)-**1g** -199.96 (c 0.26, EtOH)

Chiral HPLC Chiralpak AD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**1g**



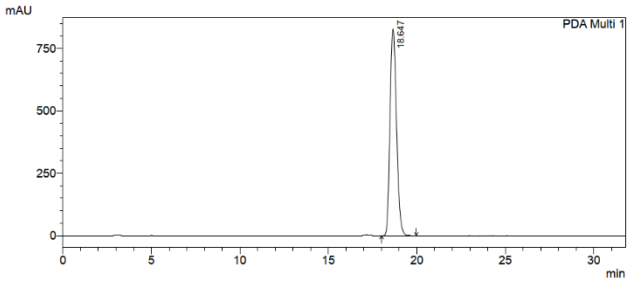
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	17.027	11992085	49.883
2	18.634	12048166	50.117
Total		24040251	100.000

(*R*)-**1g**



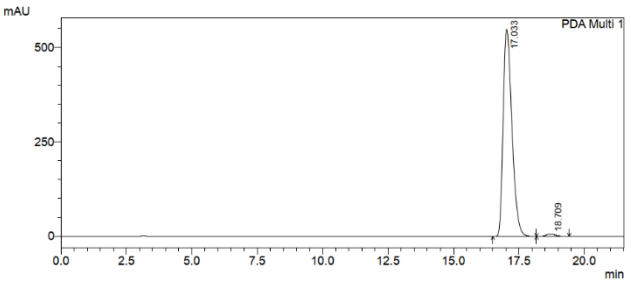
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	18.647	21302560	100.000
Total		21302560	100.000

(*S*)-**1g {from** (*S*)-**2g}**



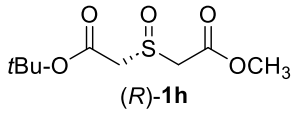
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	17.033	12843593	98.818
2	18.709	153647	1.182
Total		12997240	100.000

HPLC of Compound 1h



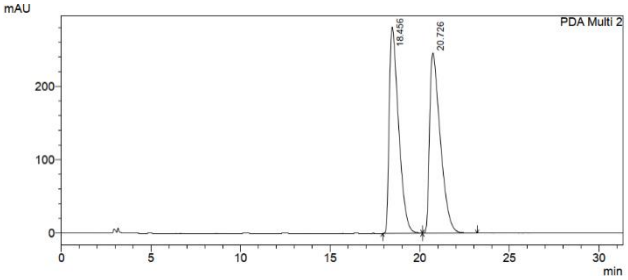
(*R*)-**1h**

[α]$^{25}_{D}$ of (*R*)-**1h** -15.99 (c 0.20, EtOH).

[α]$^{25}_{D}$ of (*S*)-**1h** +12.30 (c 0.13, EtOH).

Chiral HPLC Chiralcel OD-H, 10% IPA/hexanes, 1.0 mL/min, 229nm.

(±)-**1h**



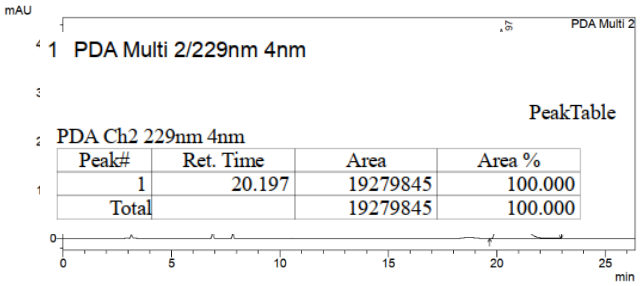
1 PDA Multi 2/229nm 4nm

PeakTable

PDA Ch2 229nm 4nm

Peak#	Ret. Time	Area	Area %
1	18.456	10213279	49.926
2	20.726	10243399	50.074
Total		20456678	100.000

(*R*)-**1h**



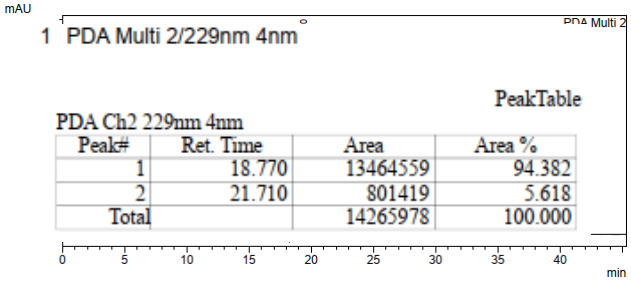
1 PDA Multi 2/229nm 4nm

PeakTable

PDA Ch2 229nm 4nm

Peak#	Ret. Time	Area	Area %
1	20.197	19279845	100.000
Total		19279845	100.000

(*S*)-**1h {from** (*S*)-**2h}**



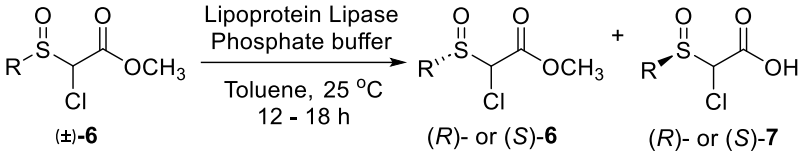
1 PDA Multi 2/229nm 4nm

PeakTable

PDA Ch2 229nm 4nm

Peak#	Ret. Time	Area	Area %
1	18.770	13464559	94.382
2	21.710	801419	5.618
Total		14265978	100.000

VII General procedure for enzymatic resolution of *α*-Chloro sulfinyl acetate.



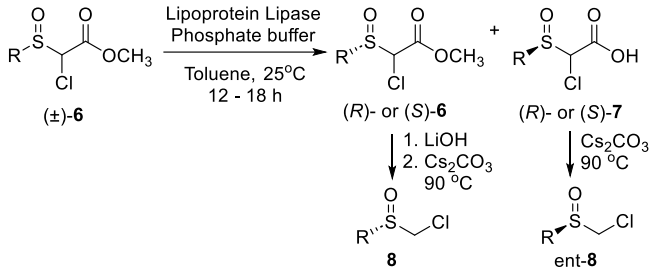
(±)-**6** (*R*)- or (*S*)-**6** (*R*)- or (*S*)-**7**

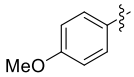
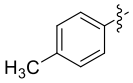
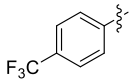
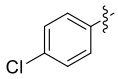
To a solution of the ester (±)-**6** (0.5 mmol) in toluene (0.5 mL) were added phosphate buffer (4.0 mL, see table 2 in manuscript) and Lipoprotein lipase (20 wt%). This heterogeneous mixture was stirred at 25 °C. The mixture was filtered through celite to remove the enzyme and extracted with EtOAc (3 × 15 mL). Evaporation of the solvent and ISCO flash chromatography gave enantiopure ester **6**.

1N HCl was added to the aqueous layer to bring pH 3.0 and aqueous layer was extracted first with EtOAc (3 × 15 mL) then with DCM (3 × 15 mL). The combined organic layers were dried over Na_2SO_4 and concentration in vacuo gave acid **7**.

Under a nitrogen atmosphere, a solution of (trimethylsilyl)diazomethane (0.5 mL, 2.0 M solution in diethyl ether, 1.0 mmol, 5.0 equiv) was added to a solution of the acid derivative **7** (0.2 mmol, 1.0 equiv) in dry MeOH (0.5 mL) at 0 °C. The resulting mixture was warmed slowly to rt and stirred overnight. After completion of the reaction, the solvent was removed in vacuo. Purification by ISCO flash column chromatography afforded the ester derivative.

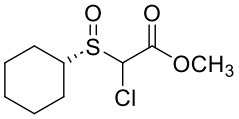
Table S4. Asymmetric synthesis of chloromethyl sulfoxides.[a]



Entry	R	pH	% Yield **6** (% ee)	% Yield **7** (% ee)	% Yield **8** (% ee)	Selectivity (E)[c]
1[b]		9.5	39 (>99)	unstable	--	22
2[b]	*n*-Hex	9.5	41 (>99)	28 (99)	(*S*)-**8b** 65 (99)	27
3		8.6	46 (>99)	35 (>99)	(*S*)-**8c**: 81 (98) (*R*)-**8c**: 78 (99)	41
4		8.6	42 (>99)	32 (90)	(*S*)-**8d** 80 (99)	31
5		8.6	41 (>99)	30 (93)	(*S*)-**8e** 73 (97)	27
6		8.6	40 (>99)	25 (95)	(*S*)-**8f** 66 (>99)	24
7		8.6	40 (>99)	31 (98)	(*S*)-**8g** 81 (>99)	24

[a] Reactions on a 0.1-0.2 g scale with 20 wt% enzyme, 8:1 50 mM phosphate buffer : toluene unless otherwise noted. [b] 100 mM phosphate buffer. [c] Lower limit to selectivity factor based on recovered starting material according to E = Ln[(1-c)(1-ee)]/Ln[(1-c)(1+ee), using 1-yield as conversion (c).

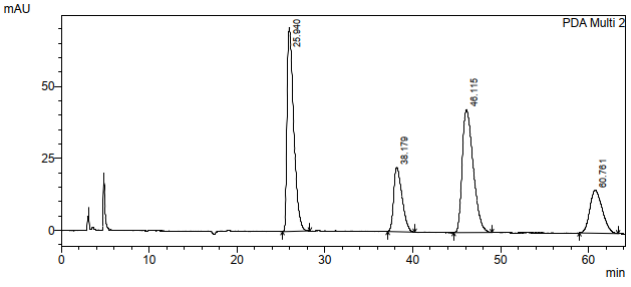
HPLC of Compound 6a



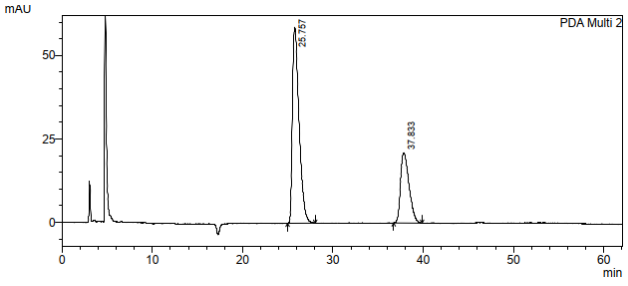
(*S*)-**6a**

[α]$^{25.8}_{D}$ of (*S*)-**6a** +27.19 (c 0.125, EtOH)
Chiral HPLC Chiralpak AS-H, 10% IPA/hexanes, 1.0 mL/min, 229nm.

(±)-**6a**



(*S*)-**6a**



1 PDA Multi 2/229nm 4nm

PeakTable

PDA Ch2 229nm 4nm

Peak#	Ret. Time	Area	Area %
1	25.940	3738557	35.877
2	38.179	1485675	14.257
3	46.115	3719914	35.698
4	60.761	1476221	14.167
Total		10420367	100.000

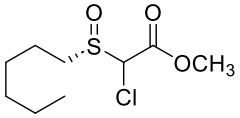
1 PDA Multi 2/229nm 4nm

PeakTable

PDA Ch2 229nm 4nm

Peak#	Ret. Time	Area	Area %
1	25.757	3025605	68.603
2	37.833	1384721	31.397
Total		4410326	100.000

HPLC of Compound 6b



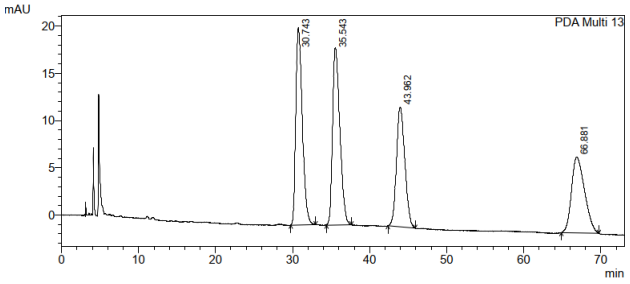
(*S*)-**6b**

[α]$^{25.8}_{D}$ of (*S*)-**6b** -39.99 (c 0.15, EtOH)

[α]$^{25}_{D}$ of (*R*)-**6b** +35.55 (c 0.135, EtOH)

Chiral HPLC Chiralpak AS-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**6b**



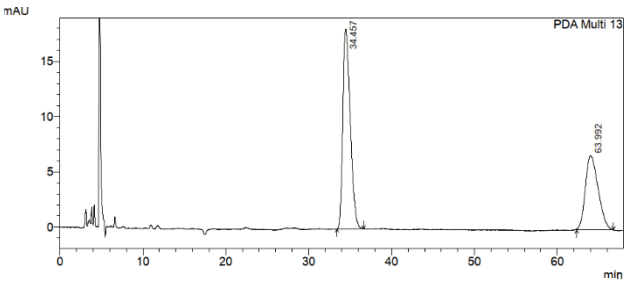
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	30.743	1232105	28.183
2	35.543	1233811	28.222
3	43.962	959235	21.942
4	66.881	946612	21.653
Total		4371763	100.000

(*S*)-**6b**



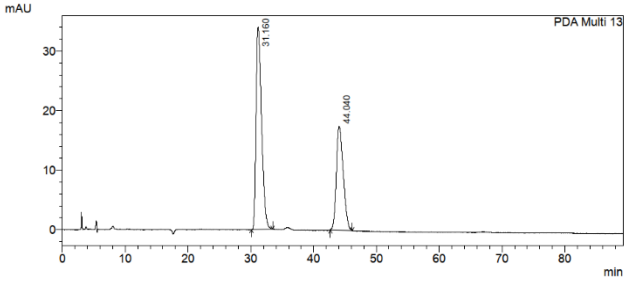
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	34.457	1130976	61.006
2	63.992	722904	38.994
Total		1853880	100.000

(*R*)-**6b {from** (*R*)-**7b}**



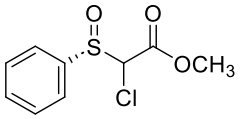
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	31.160	2099156	61.195
2	44.040	1331124	38.805
Total		3430280	100.000

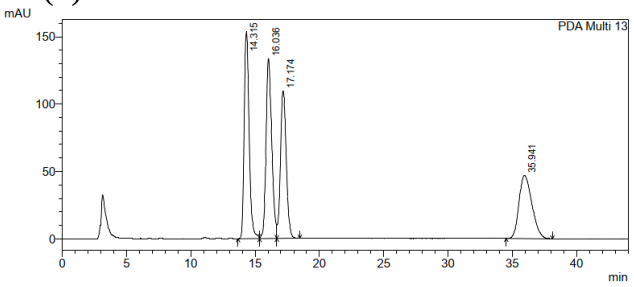
HPLC of Compound 6c



(*S*)-**6c**

[α]$^{25}_{D}$ of (*S*)-**6c** +173.68 (c 0.525, EtOH)
[α]$^{25}_{D}$ of (*R*)-**6c** -132.28 (c 0.130, EtOH)
Chiral HPLC Chiralpak AS-H, 30% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**6c**



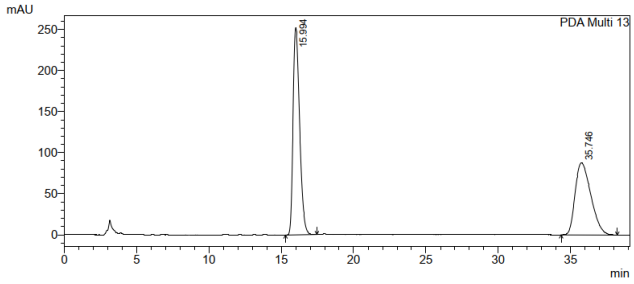
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	14.315	4090148	27.462
2	16.036	4121423	27.672
3	17.174	3403633	22.853
4	35.941	3278699	22.014
Total		14893903	100.000

(*S*)-**6c**



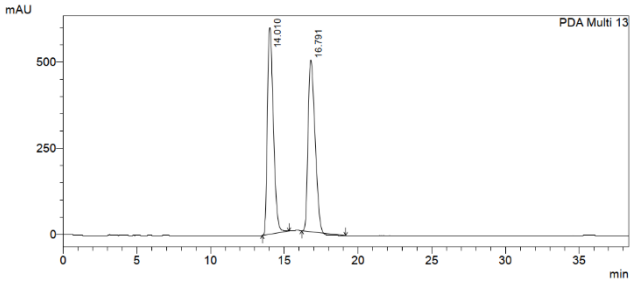
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	15.994	7949327	54.407
2	35.746	6661638	45.593
Total		14610965	100.000

(*R*)-**6c {from** (*R*)-**7c}**



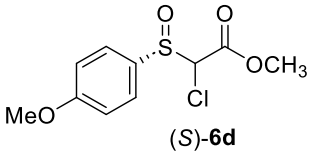
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	14.010	16877790	50.971
2	16.791	16234513	49.029
Total		33112302	100.000

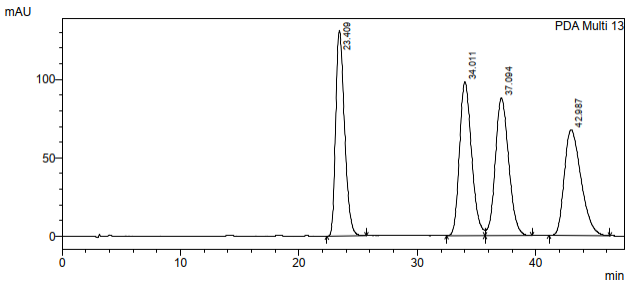
HPLC of Compound 6d



(*S*)-**6d**

[α]$^{25.5}_{D}$ of (*S*)-**6d** +158.63 (c 0.150, EtOH)
[α]$^{25}_{D}$ of (*R*)-**6d** -136.44 (c 0.085, EtOH)
Chiral HPLC Chiralpak AS-H, 30% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**6d**



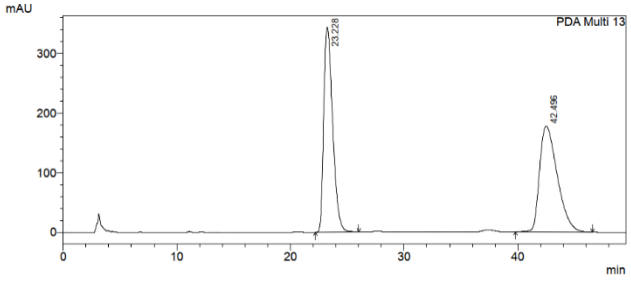
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	23.409	6787596	24.901
2	34.011	6958937	25.529
3	37.094	6882651	25.250
4	42.987	6629305	24.320
Total		27258490	100.000

(*S*)-**6d**



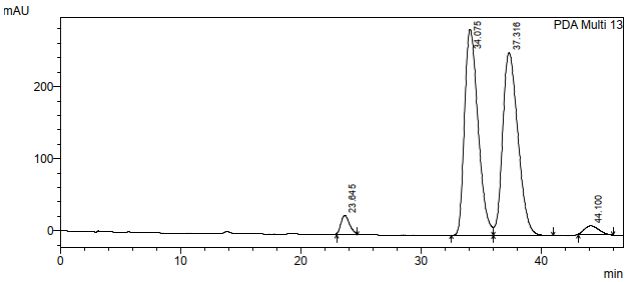
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	23.228	18743015	49.384
2	42.496	19210670	50.616
Total		37953685	100.000

(*R*)-**6d {from** (*R*)-**7d}**



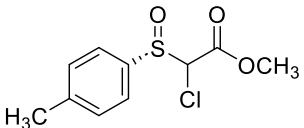
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	23.645	1377774	2.915
2	34.075	22406459	47.414
3	37.316	22400257	47.400
4	44.100	1072974	2.270
Total		47257463	100.000

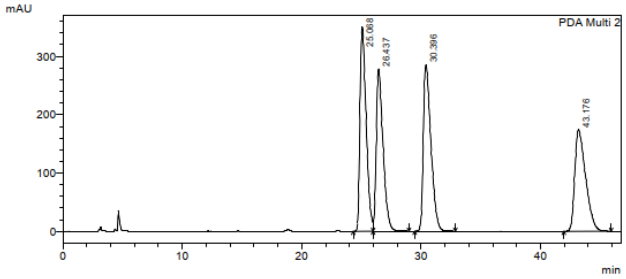
HPLC of Compound 6e



(*S*)-**6e**

[α]$^{25}_{D}$ of (*S*)-**6e** +173.68 (c 0.525, EtOH)
[α]$^{25}_{D}$ of (*R*)-**6e** -132.28 (c 0.130, EtOH)
Chiral HPLC Chiralcel OJ-H, 10% IPA/hexanes, 1.0 mL/min, 229nm.

(±)-**6e**



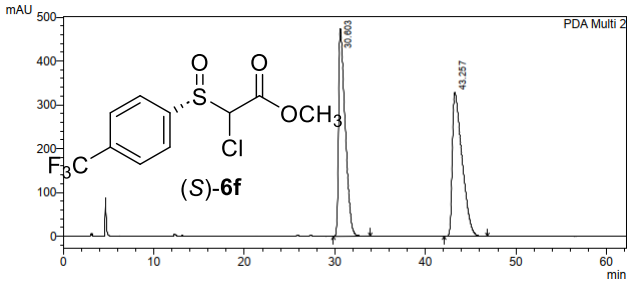
1 PDA Multi 2/229nm 4nm

PeakTable

PDA Ch2 229nm 4nm

Peak#	Ret. Time	Area	Area %
1	25.068	12541291	26.542
2	26.437	11105851	23.504
3	30.396	12642965	26.757
4	43.176	10960414	23.196
Total		47250521	100.000

(*S*)-**6e**



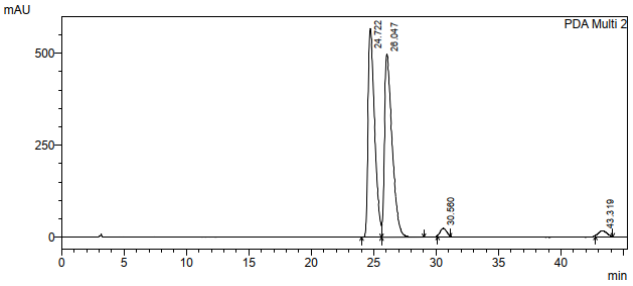
1 PDA Multi 2/229nm 4nm

PeakTable

PDA Ch2 229nm 4nm

Peak#	Ret. Time	Area	Area %
1	30.603	24166534	49.652
2	43.257	24504906	50.348
Total		48671440	100.000

(*R*)-**6e {from** (*R*)-**7e}**



1 PDA Multi 2/229nm 4nm

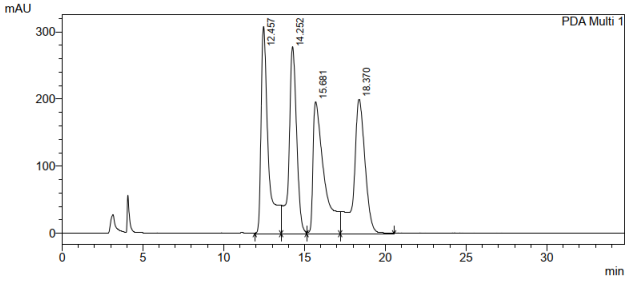
PeakTable

PDA Ch2 229nm 4nm

Peak#	Ret. Time	Area	Area %
1	24.722	20545189	47.494
2	26.047	21166112	48.929
3	30.560	796943	1.842
4	43.319	750518	1.735
Total		43258762	100.000

HPLC of Compound 6f

[α]^{25}D of (*S*)-**6f** +143.17 (c 0.250, EtOH)
[α]^{25}D of (*R*)-**6f** -31.99 (c 0.050, EtOH)
Chiral HPLC Chiralpak AS-H, 20% IPA/hexanes, 1.0 mL/min, 254nm.
(±)-**6f**



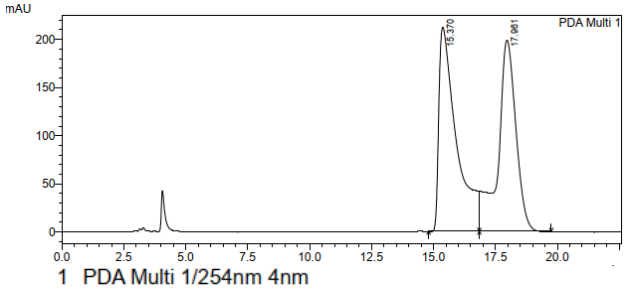
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.457	9660773	25.276
2	14.252	9283964	24.291
3	15.681	9408999	24.618
4	18.370	9866761	25.815
Total		38220497	100.000

(*S*)-**6f**



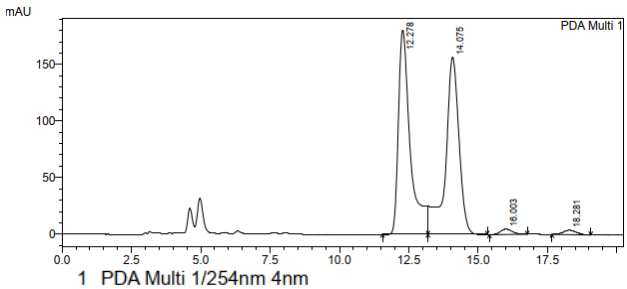
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	15.370	10386203	51.147
2	17.961	9920448	48.853
Total		20306650	100.000

(*R*)-**6f {from** (*R*)-**7f}**



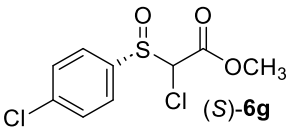
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

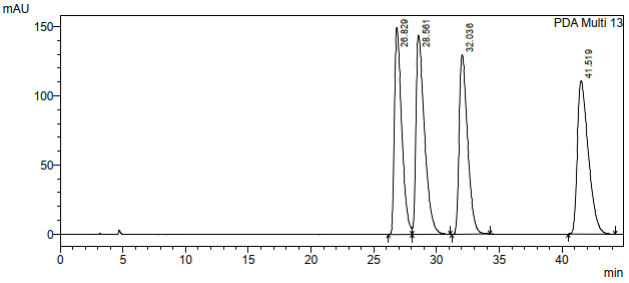
Peak#	Ret. Time	Area	Area %
1	12.278	5357937	49.006
2	14.075	5298470	48.462
3	16.003	143828	1.316
4	18.281	132930	1.216
Total		10933165	100.000

HPLC of Compound 6g



(*S*)-**6g**

[α]$^{25.7}_{D}$ of (*S*)-**6g** +147.16 (c 0.125, EtOH)
[α]$^{25}_{D}$ of (*R*)-**6g** -164.76 (c 0.125, EtOH)
Chiral HPLC Chiralcel OJ-H, 10% IPA/hexanes, 1.0 mL/min, 254nm
(±)-**6g**



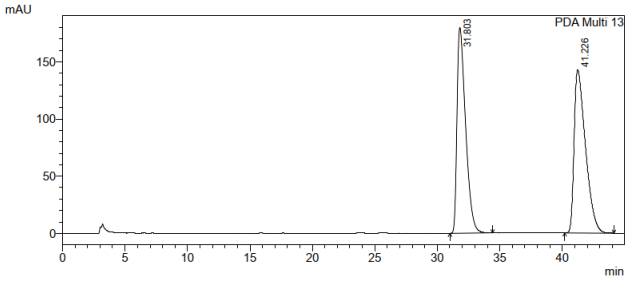
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	26.829	6084353	23.681
2	28.561	6840163	26.623
3	32.036	6032330	23.478
4	41.519	6736283	26.218
Total		25693128	100.000

(*S*)-**6g**



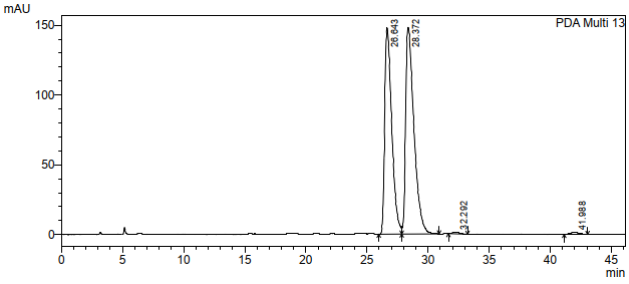
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	31.803	8610417	48.769
2	41.226	9045212	51.231
Total		17655630	100.000

(*R*)-**6g {from** (*R*)-**7g}**



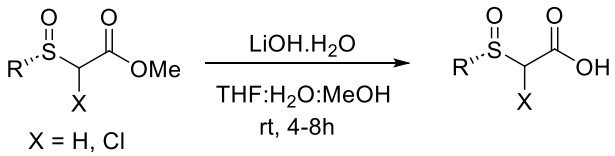
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	26.643	5909401	45.315
2	28.372	7010928	53.762
3	32.292	48458	0.372
4	41.988	71969	0.552
Total		13040756	100.000

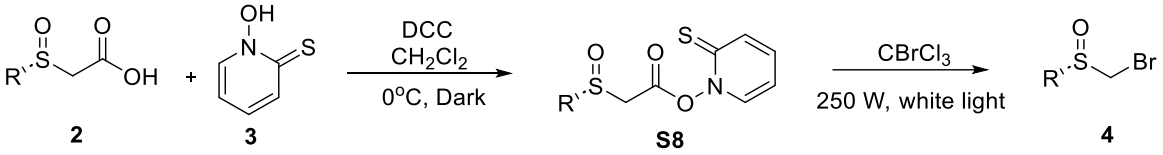
VII. General procedure for methyl ester hydrolysis



X = H, Cl

A mixture of methyl ester (1.0 mmol, 1.0 equiv), lithium hydroxide (63 mg, 1.5 mmol, 1.5 equiv), THF (2 mL), water (1 mL) and MeOH (0.5 mL) was stirred at room temperature for 4h. The organic solvent was removed under reduced pressure, and the residue obtained was then acidified to pH 5 with 1 N HCl, and the mixture was extracted with EtOAc (3 × 10 mL). The combined extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude acid which was used for the next step without further purification.

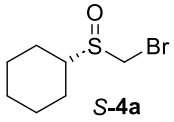
VIII. General procedure for Barton decarboxylative bromination



To an ice cold solution of sulfoxide acetic acid **2** (0.2 mmol, 1.0 equiv) in dry, degassed CH_2Cl_2 (2 mL) was added N-hydroxypyridine-2-thione **3** (30 mg, 0.24 mmol, 1.2 equiv). After stirring for 5 min. DCC (49 mg, 0.24 mmol, 1.2 equiv) in CH_2Cl_2 (1 mL) was added and stirred for 30 min. at rt. Then the mixture was filtered through a celite pad and concentrated under reduced pressure without heating gave crude product which was used for the next step without further purification.

Irradiation of Ester in the presence of $BrCCl_3$. An ice-cold solution of ester **S8** (0.2 mmol) in dry, degassed $BrCCl_3$ (2 mL) was irradiated with a 250 W tungsten lamp under an inert atmosphere until the disappearance of the starting material as monitored by LCMS. Concentration and ISCO flash chromatography gave the desired product **4**.

(*S*)- **((Bromomethyl)sulfinyl)cyclohexane 4a**



Yield: 68%. Purified by ISCO flash column chromatography (4:1 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.37 (d, J = 8.0 Hz, 1H), 4.23 (d, J = 12.0 Hz, 1H), 2.94 - 2.86 (m, 1H), 2.11 - 2.05 (m, 1H), 1.97 - 1.79 (m, 3H), 1.74 - 1.68 (m, 1H), 1.60 - 1.24 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 57.3, 41.6, 26.6, 25.4, 25.1, 23.9.

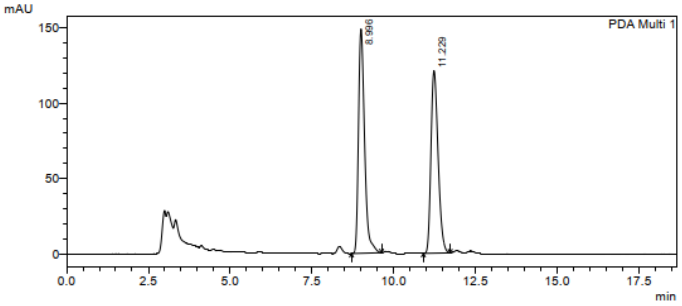
ESI MS. $C_7H_{14}BrOS$ m/z $[M+H]^+$ calc. 225.0, found 224.9.

$[\alpha]^{25}_D$ of (*S*)-**4a** -14.99 (c 0.120, EtOH).

$[\alpha]^{25}_D$ of (*R*)-**4a** +13.33 (c 0.090, EtOH).

Chiral HPLC Chiralpak AD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**4a**



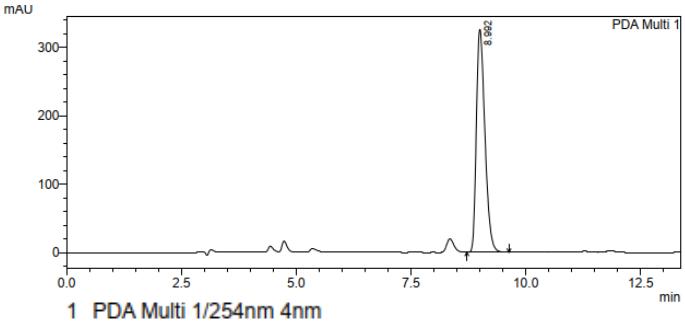
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.996	1945564	51.305
2	11.229	1846556	48.695
Total		3792120	100.000

(*S*)-**4a**

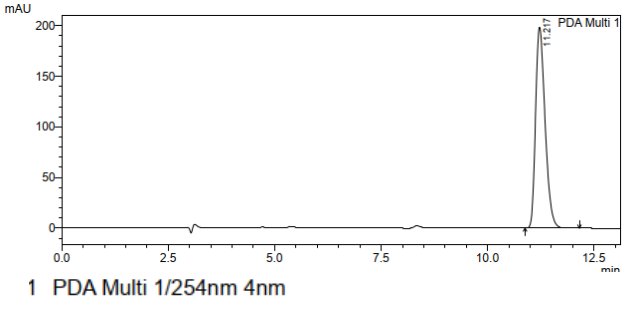


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.992	4235841	100.000
Total		4235841	100.000

(*R*)-**4a**

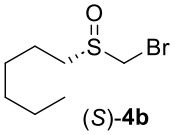


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	11.217	3088258	100.000
Total		3088258	100.000

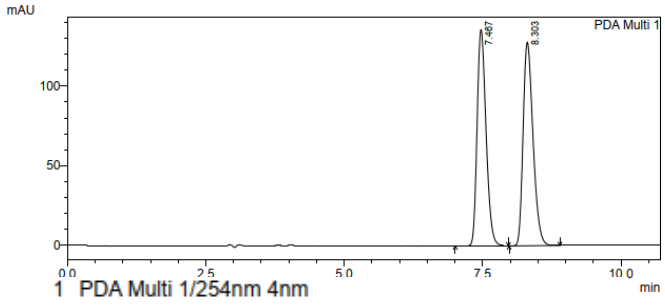
(*S*)-**1-((Bromomethyl)sulfinyl)hexane 4b**



(*S*)-**4b**

Yield: 70%. Purified by ISCO flash column chromatography (4:1 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.30 (d, J = 12.0 Hz, 1H), 4.22 (d, J = 12.0 Hz, 1H), 2.91 - 2.79 (m, 2H), 1.79 - 1.71 (m, 2H), 1.54 - 1.40 (m, 2H), 1.36 - 1.27 (m, 4H), 0.89 (t, J = 8.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 51.2, 43.6, 31.4, 28.5, 22.5, 22.1, 14.1.
ESI MS. $C_7H_{16}BrOS$ m/z $[M+H]^+$ calc. 227.0, found 227.0.
[α]$^{25}_D$ -49.13 (c 0.175, EtOH).
Chiral HPLC Chiralpak AD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**4b**

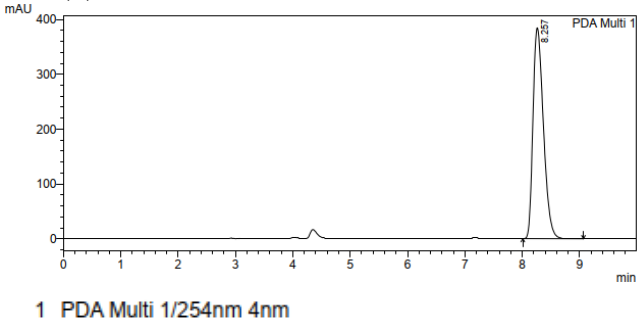


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	7.467	1527007	48.935
2	8.303	1593483	51.065
Total		3120490	100.000

(*S*)-**4b**

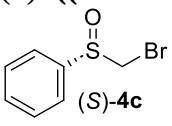


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.257	4865590	100.000
Total		4865590	100.000

(*S*)- **((Bromomethyl)sulfinyl)benzene 4c**



(*S*)-**4c**

Yield: 87%. Purified by ISCO flash column chromatography (6:1 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 - 7.68 (m, 2H), 7.58 - 7.54 (m, 3H), 4.35 (d, J = 12.0 Hz,

1H), 4.25 (d, *J* = 8.0 Hz, 1H).

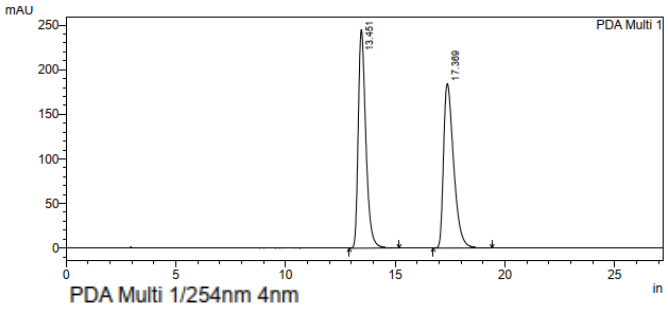
^{13}C NMR (151 MHz, $CDCl_3$) δ 141.7, 132.3, 129.4, 124.9, 124.7, 48.9.

ESI MS. C_7H_8BrOS m/z $[M+H]^+$ calc. 218.9, found 218.9.

$[\alpha]^{25}_D$ +205.33 (c 0.26, EtOH).

Chiral HPLC Chiralcel OD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**4c**

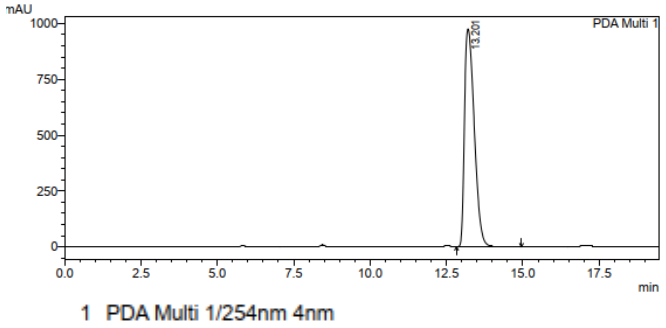


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	13.451	5879298	49.921
2	17.369	5897841	50.079
Total		11777139	100.000

(*S*)-**4c**

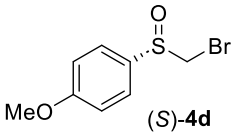


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	13.201	21744266	100.000
Total		21744266	100.000

(*S*)-**1-((Bromomethyl)sulfinyl)-4-methoxybenzene 4d**



(*S*)-**4d**

Yield: 89%. Purified by ISCO flash column chromatography (4:1 hexane:EtOAc v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 - 7.61 (m, 2H), 7.05 - 7.03 (m, 2H), 4.27 (d, *J* = 12.0 Hz, 1H), 4.23 (d, *J* = 12.0 Hz, 1H), 3.86 (s, 3H).

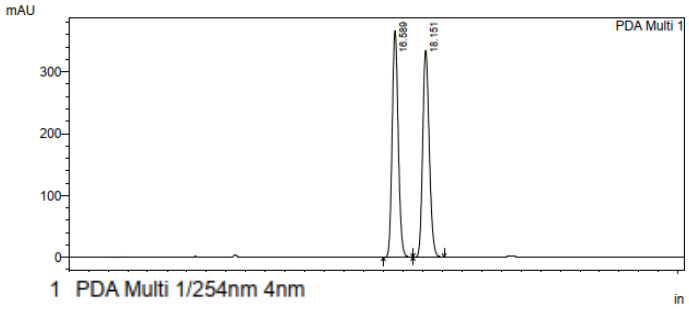
^{13}C NMR (151 MHz, $CDCl_3$) δ 162.9, 132.4, 126.9, 114.9, 55.7, 48.9.

ESI MS. $C_8H_{10}BrO_2S$ m/z $[M+H]^+$ calc. 248.9, found 249.0

$[\alpha]^{25}_D$ +173.67 (c 0.175, EtOH).

Chiral HPLC Chiralpak AD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**4d**

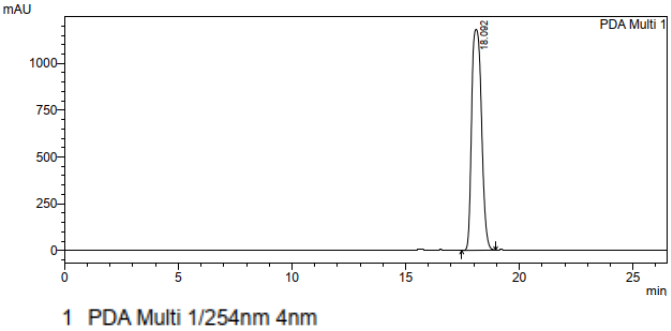


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	16.589	7837909	50.142
2	18.151	7793434	49.858
Total		15631343	100.000

(*S*)-**4d**

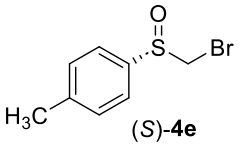


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	18.092	35637477	100.000
Total		35637477	100.000

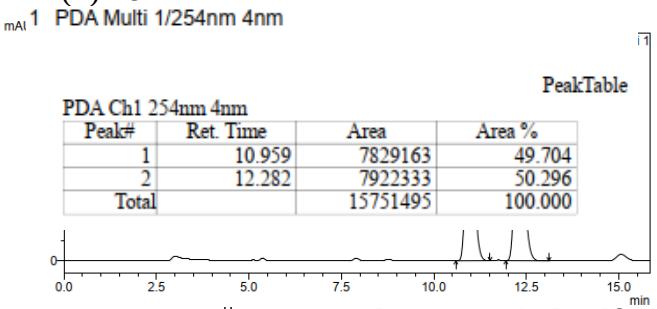
(*S*)-1-((Bromomethyl)sulfinyl)-4-methylbenzene 4e



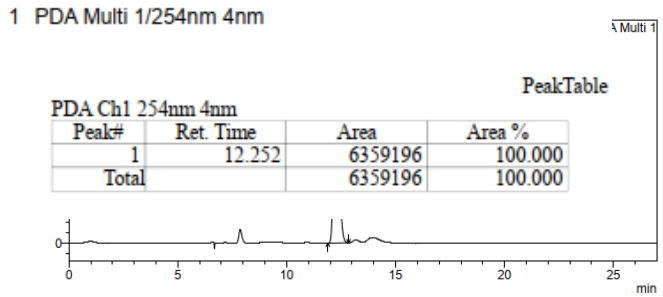
(*S*)-**4e**

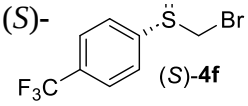
Yield: 83%. Purified by ISCO flash column chromatography (6:1 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 - 7.57 (m, 2H), 7.37 - 7.35 (m, 2H), 4.31 (d, J = 12.0 Hz, 1H), 4.23 (d, J = 12.0 Hz, 1H), 2.43 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 138.5, 130.1, 124.9, 48.9, 21.6.
ESI MS. $C_8H_{10}BrOS$ m/z $[M+H]^+$ calc. 232.9, found 233.0.
$[\alpha]^{26}_D$ +209.55 (c 0.125, EtOH).
Chiral HPLC Chiralpak AD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm

(±)-**4e**



(*S*)-**4e**

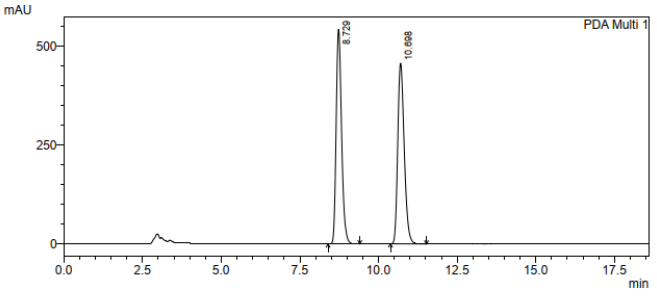


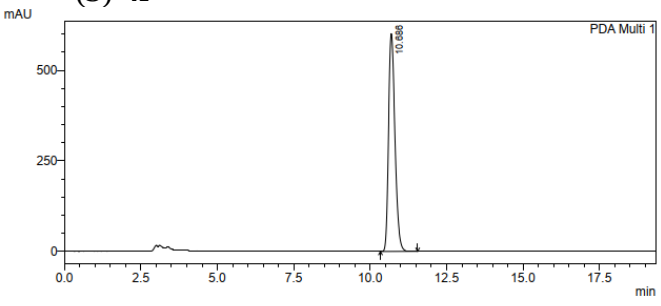
(*S*)-  **1-((bromomethyl)sulfinyl)-4-(trifluoromethyl)benzene 4f**

(*S*)-**4f**

Yield: 68%. Purified by ISCO flash column chromatography (6:1 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 4H), 4.39 (d, J = 8.0 Hz, 1H), 4.28 (d, J = 8.0 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 145.9, 134.0 (q), 126.4 (q), 125.6, 122.6 (q), 48.5.
ESI MS. $C_8H_7BrF_3OS$ m/z $[M+H]^+$ calc. 286.9, found 286.9.
$[\alpha]^{25}_D$ +162.36 (c 0.25, EtOH).
Chiral HPLC Chiralpak AD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm

(±)-**4f**





1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.729	6532604	49.771
2	10.698	6592766	50.229
Total		13125370	100.000

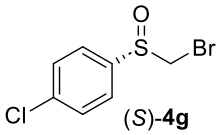
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.686	8751498	100.000
Total		8751498	100.000

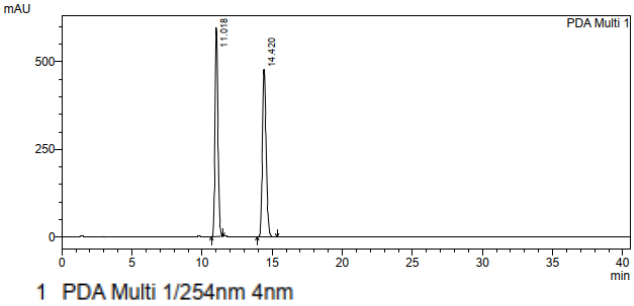
(*S*)-1-((bromomethyl)sulfinyl)-4-chlorobenzene 4g



(*S*)-**4g**

Yield: 71%. Purified by combi flash column chromatography (4:1 hexane:EtOAc v/v).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 - 7.64 (m, 2H), 7.55 - 7.53 (m, 2H), 4.33 (d, J = 12.0 Hz, 1H), 4.25 (d, J = 12.0 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 140.1, 138.7, 129.8, 126.5, 126.4, 48.7.
ESI MS. $C_7H_7BrClOS$ m/z $[M+H]^+$ calc. 252.9, found 252.9.
$[\alpha]^{25}_D$ +191.96 (c 0.25, EtOH).
Chiral HPLC Chiralpak AD-H, 5% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**4g**

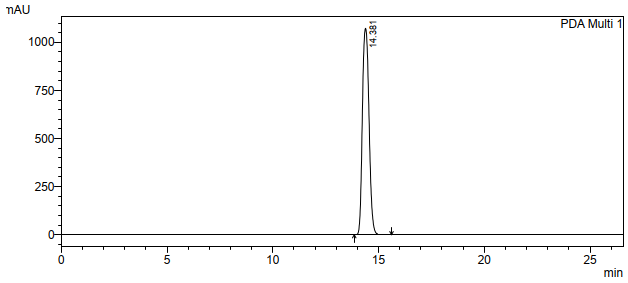


1 PDA Multi 1/254nm 4nm

PeakTable
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	11.018	8973331	49.463
2	14.420	9168173	50.537
Total		18141504	100.000

(*S*)-**4g**

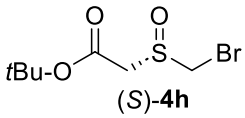


1 PDA Multi 1/254nm 4nm

PeakTable
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	14.381	23311559	100.000
Total		23311559	100.000

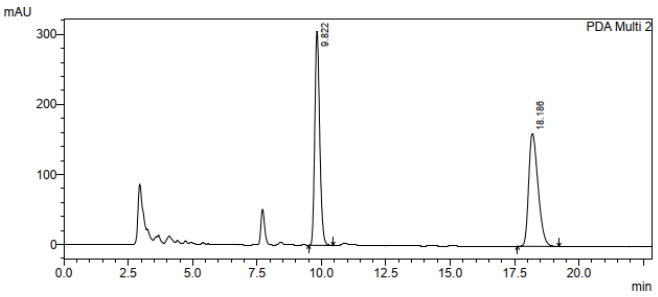
tert-Butyl (*S*)-2-((bromomethyl)sulfinyl)acetate 4h



(*S*)-**4h**

Yield: 48%. Purified by ISCO flash column chromatography (4:1 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.59 (d, J = 12.0 Hz, 1H), 4.45 (d, J = 12.0 Hz, 1H), 3.92 (d, J = 12.0 Hz, 1H), 3.67 (d, J = 16.0 Hz, 1H), 1.50 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 84.2, 55.2, 44.7, 28.1.
ESI MS. $C_7H_{13}BrO_3SNa$ m/z $[M+Na]^+$ calc. 278.9, found 279.0
$[\alpha]^{25}_D$ -17.59 (c 0.125, EtOH).
Chiral HPLC Chiralpak AD-H, 10% IPA/hexanes, 1.0 mL/min, 229nm.

(±)-**4h**



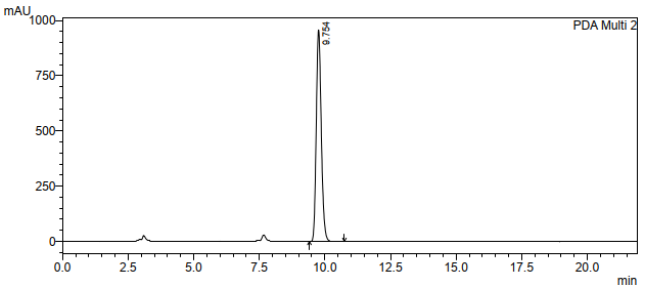
1 PDA Multi 2/229nm 4nm

PeakTable

PDA Ch2 229nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.822	4059460	49.932
2	18.186	4070525	50.068
Total		8129985	100.000

(*S*)-**4h**



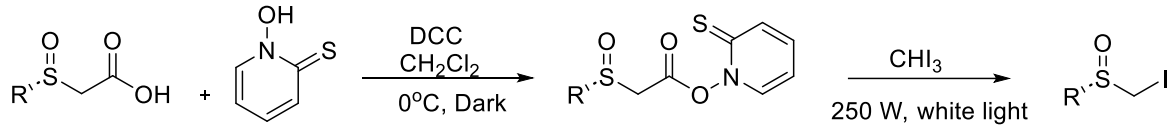
1 PDA Multi 2/229nm 4nm

PeakTable

PDA Ch2 229nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.754	12777560	100.000
Total		12777560	100.000

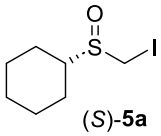
IX. General procedure for Barton decarboxylative iodination



2 **3** **S8** **5**

To an ice cold solution of sulfoxide acetic acid **2** (0.2 mmol, 1.0 equiv) in dry, degassed CH_2Cl_2 (3 mL) was added N-hydroxypyridine-2-thione **3** (30 mg, 0.24 mmol, 1.2 equiv). After stirring for 5 min. DCC (49 mg, 0.24 mmol, 1.2 equiv) in CH_2Cl_2 (1 mL) was added and stirred for 30 min. at rt. Then added CHI_3 (157 mg, 0.4 mmol, 2.0 equiv) and then ice cold solution was irradiated with a 250 W tungsten lamp under an inert atmosphere until the disappearance of the starting material as monitored by LCMS. Filtration of the solution through celite, concentration and ISCO flash chromatography gave the desired compound **5**.

(*S*)-((Iodomethyl)sulfinyl)cyclohexane 5a



(*S*)-**5a**

Yield: 51%. Purified by ISCO flash column chromatography (6:1 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 (d, J = 8.0 Hz, 1H), 4.16 (d, J = 8.0 Hz, 1H), 2.75 - 2.65 (m, 1H), 2.15 - 2.08 (m, 1H), 1.97 - 1.81 (m, 3H), 1.75 - 1.68 (m, 1H), 1.64 - 1.54 (m, 1H), 1.43 - 1.22 (m, 4H).

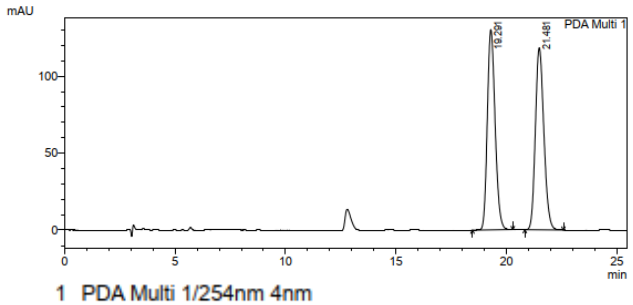
^{13}C NMR (101 MHz, $CDCl_3$) δ 60.0, 26.6, 25.4, 25.3, 25.1, 24.1, 18.0.

ESI MS. $C_7H_{14}IOS$ m/z $[M+H]^+$ calc. 273.0, found 273.0.

$[\alpha]^{25}_D$ -2.66 (c 0.075, EtOH).

Chiral HPLC Chiralpak AD-H, 5% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**5a**

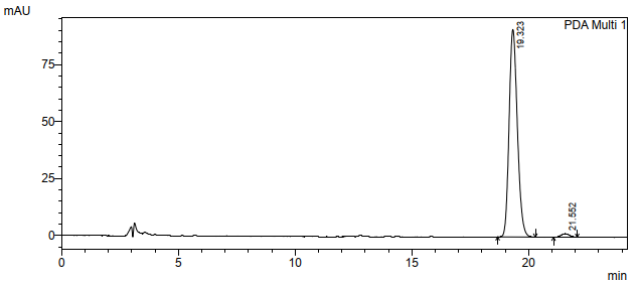


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	19.291	3183483	50.160
2	21.481	3163167	49.840
Total		6346650	100.000

(*S*)-**5a**

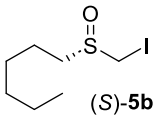


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	19.323	2234145	98.205
2	21.552	40844	1.795
Total		2274989	100.000

(*S*)-**1-((Iodomethyl)sulfinyl)hexane 5b**



(*S*)-**5b**

Yield: 58%. Purified by ISCO flash column chromatography (6:1 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25 (d, J = 12.0 Hz, 1H), 4.14 (d, J = 12.0 Hz, 1H), 2.84 - 2.71 (m, 2H), 1.77 - 1.69 (m, 2H), 1.53 - 1.28 (m, 6H), 0.90 (t, J = 8.0 Hz, 3H).

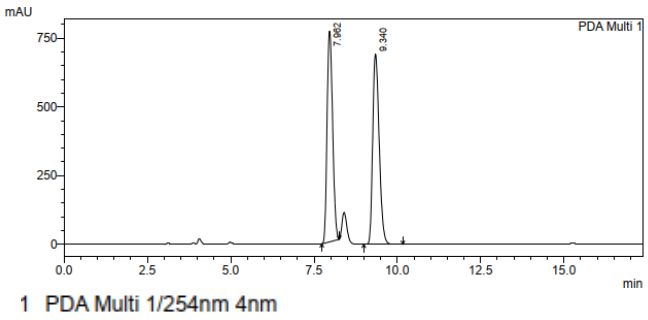
^{13}C NMR (101 MHz, $CDCl_3$) δ 53.6, 31.4, 28.6, 22.5, 22.3, 19.7, 14.1.

ESI MS. $C_7H_{16}IOS$ m/z $[M+H]^+$ calc. 275.0, found 275.0.

$[\alpha]^{25}_D$ -40.79 (c 0.25, EtOH).

Chiral HPLC Chiralpak AD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**5b**

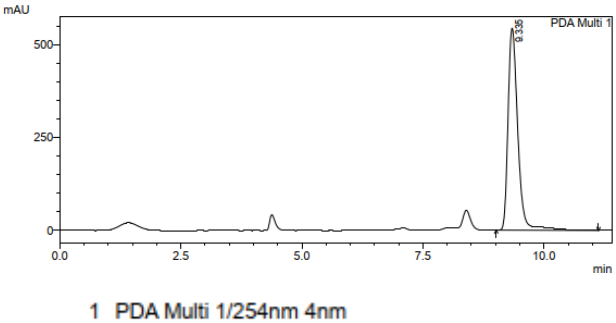


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	7.962	8851524	48.585
2	9.340	9367014	51.415
Total		18218537	100.000

(*S*)-**5b**

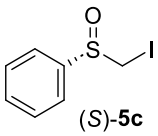


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.335	7645389	100.000
Total		7645389	100.000

(*S*)-**((Iodomethyl)sulfinyl)benzene 5c**

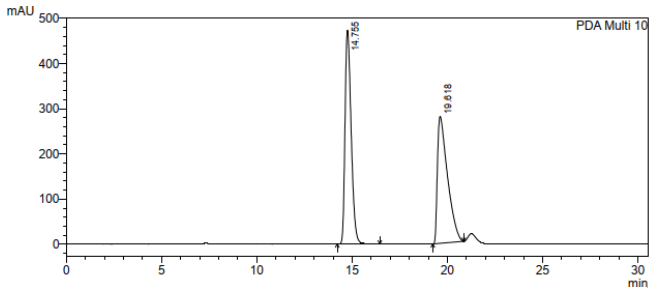


(*S*)-**5c**

Yield: 61%. Purified by ISCO flash column chromatography (6:1 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 - 7.64 (m, 2H), 7.58 - 7.52 (m, 3H), 4.40 (d, J = 12.0 Hz, 1H), 4.16 (d, J = 12.0 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 142.9, 132.1, 129.4, 124.8, 25.6.
ESI MS. C_7H_8IOS m/z $[M+H]^+$ calc. 266.9, found 266.9.
$[\alpha]^{25}_D$ +181.56 (c 0.25, EtOH).
Chiral HPLC Chiralcel OD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm

(±)-**5c**



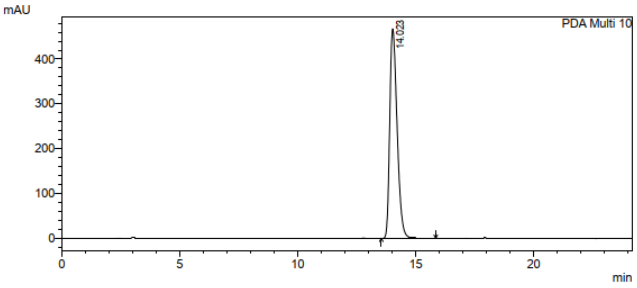
1 PDA Multi 10/254nm 4nm

PeakTable

PDA Ch10 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	14.755	10566037	50.520
2	19.618	10348517	49.480
Total		20914554	100.000

(*S*)-**5c**



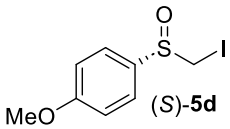
1 PDA Multi 10/254nm 4nm

PeakTable

PDA Ch10 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	14.023	10121318	100.000
Total		10121318	100.000

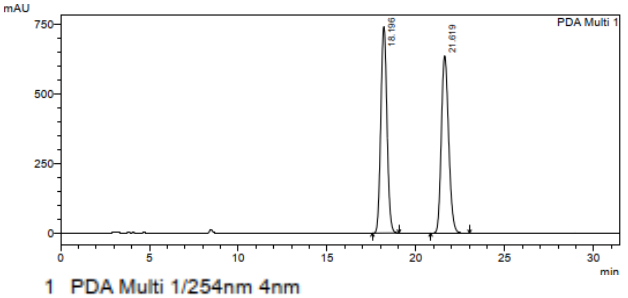
(*S*)-1-(Iodomethyl)sulfinyl)-4-methoxybenzene 5d



(*S*)-**5d**

Yield: 65%. Purified by ISCO flash column chromatography (4:1 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 - 7.56 (m, 2H), 7.03 - 7.00 (m, 2H), 4.33 (d, J = 8.0 Hz, 1H), 4.13 (d, J = 12.0 Hz, 1H), 3.85 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 133.6, 126.7, 114.8, 55.7, 25.7.
ESI MS. $C_8H_{10}IO_2S$ m/z $[M+H]^+$ calc. 280.9, found 281.0.
$[\alpha]^{25}_D$ +88.77 (c 0.25, EtOH).
Chiral HPLC Chiralpak AD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**5d**



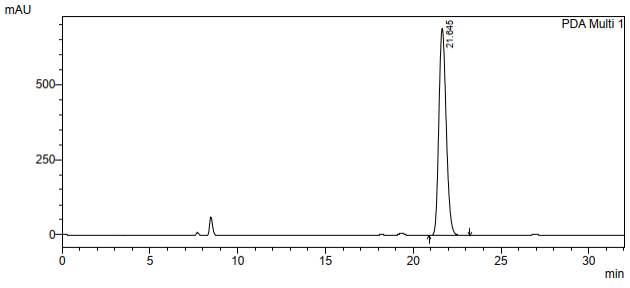
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	18.196	17936416	49.592
2	21.619	18231859	50.408
Total		36168276	100.000

(*S*)-**5d**



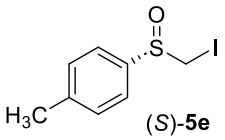
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	21.645	20060845	100.000
Total		20060845	100.000

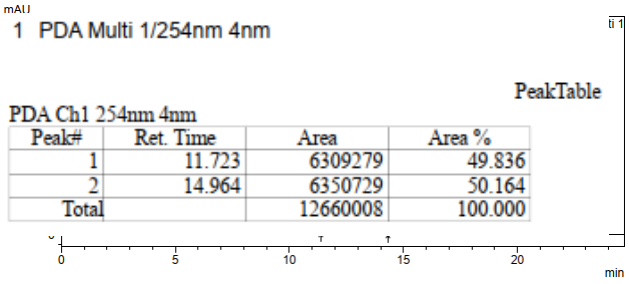
(*S*)-**1-((Iodomethyl)sulfinyl)-4-methylbenzene 5e**



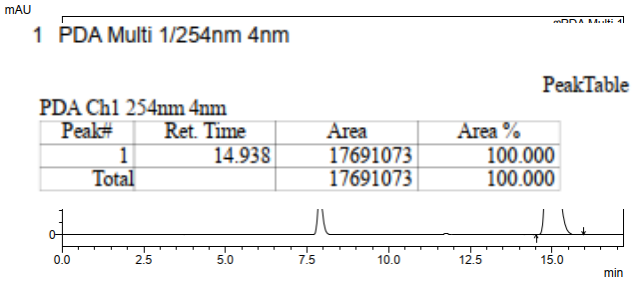
(*S*)-**5e**

Yield: 55%. Purified by ISCO flash column chromatography (6:1 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 - 7.52 (m, 2H), 7.35 - 7.32 (m, 2H), 4.37 (d, *J* = 12.0 Hz, 1H), 4.15 (d, *J* = 12.0 Hz, 1H), 2.43 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 139.6, 130.1, 124.8, 25.7, 21.7.
ESI MS. $C_8H_{10}IOS$ m/z $[M+H]^+$ calc. 232.9, found 233.0.
$[\alpha]^{26}_D$ +212.80 (c 0.140, EtOH).
Chiral HPLC Chiralpak AD-H, 5% IPA/hexanes, 1.0 mL/min, 254nm.

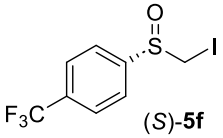
(±)-**5e**



(*S*)-**5e**



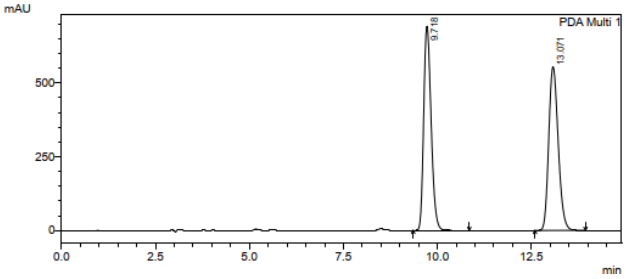
(*S*)-**1-((Iodomethyl)sulfinyl)-4-(trifluoromethyl)benzene 5f**



(*S*)-**5f**

Yield: 51%. Purified by ISCO flash column chromatography (6:1 hexane:EtOAc v/v).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 - 7.77 (m, 4H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.19 (d, *J* = 12.0 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 147.1, 134.1 (q), 126.3 (q), 125.4, 124.4 (q), 25.0.
ESI MS. $C_8H_7IF_3OS$ m/z $[M+H]^+$ calc. 334.9, found 334.9.
$[\alpha]^{25}_D$ +204.66 (c 0.85, EtOH).
Chiral HPLC Chiralpak AD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**5f**



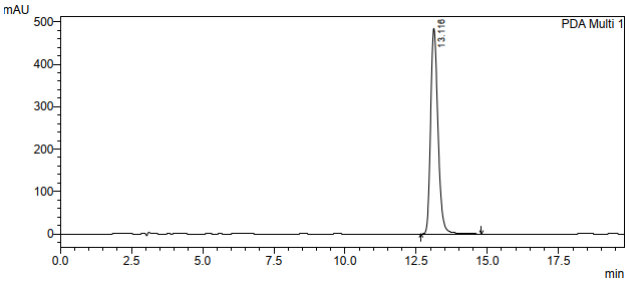
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.718	9491576	49.503
2	13.071	9682200	50.497
Total		19173776	100.000

(*S*)-**5f**



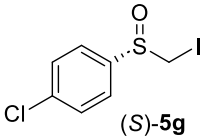
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	13.116	8722106	100.000
Total		8722106	100.000

(*S*)-**1-Chloro-4-((iodomethyl)sulfinyl)benzene 5g**



(*S*)-**5g**

Yield: 52%. Purified by ISCO flash column chromatography (4:2 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 - 7.57 (m, 2H), 7.54 - 7.50 (m, 2H), 4.39 (d, J = 8.0 Hz, 1H), 4.15 (d, J = 8.0 Hz, 1H).

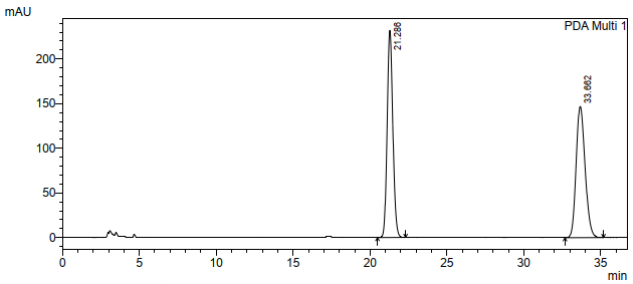
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 138.5, 129.7, 126.3, 25.3.

ESI MS. C_7H_7IClOS m/z $[M+H]^+$ calc. 300.9, found 300.9.

$[\alpha]^{25}_D$ +191.07 (c 0.18, EtOH).

Chiral HPLC Chiralpak AD-H, 5% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**5g**



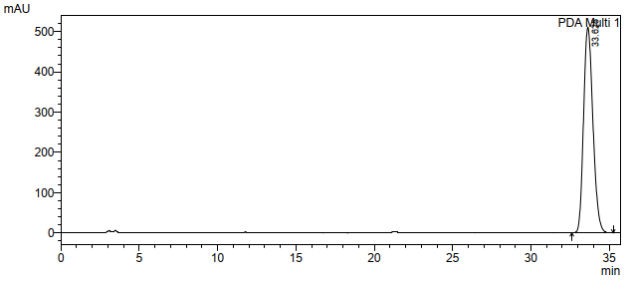
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	21.286	5964205	49.987
2	33.662	5967341	50.013
Total		11931546	100.000

(*S*)-**5g**



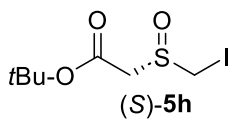
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	33.625	21229685	100.000
Total		21229685	100.000

(*S*)-***tert*-Butyl 2-((iodomethyl)sulfinyl)acetate 5h**

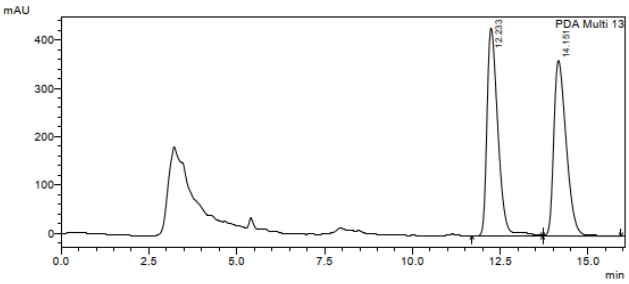


(*S*)-**5h**

Yield: 43%. Purified by ISCO flash column chromatography (4:1 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.52 (d, J = 8.0 Hz, 1H), 4.41 (d, J = 12.0 Hz, 1H), 3.76 (d, J = 16.0 Hz, 1H), 3.62 (d, J = 16.0 Hz, 1H), 1.49 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 84.2, 57.8, 28.1, 21.1.
ESI MS. $C_7H_{14}IO_3S$ m/z $[M+H]^+$ calc. 304.9, found 305.0.
$[\alpha]^{25}_D$ -27.99 (c 0.1, EtOH).
Chiral HPLC Chiralcel OD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**5h**



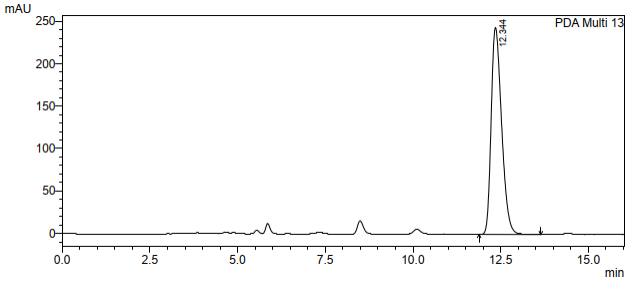
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.233	9312641	51.041
2	14.151	8932846	48.959
Total		18245487	100.000

(*S*)-**5h**



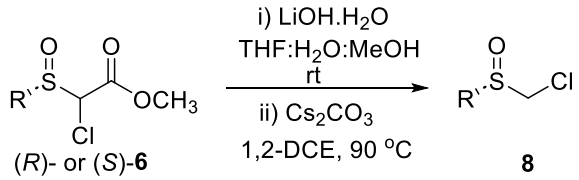
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.344	5052865	100.000
Total		5052865	100.000

X. General procedure for decarboxylation of α-Chloro sulfinyl acetate

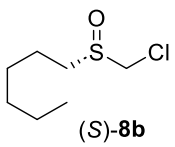


(*R*)- or (*S*)-**6** **8**

A mixture of methyl ester (0.1 mmol, 1.0 equiv), lithium hydroxide (8.0 mg, 0.2 mmol, 2.0 equiv), THF (0.5 mL), H_2O (0.25 mL) and CH_3OH (0.12 mL) was stirred at room temperature. The organic solvent was removed under reduced pressure, and the residue obtained was then acidified to pH 3 with 1 N HCl, and the mixture was extracted with EtOAc (3 × 10 mL). The combined extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude acid which was used for the next step without further purification.

To a stirred solution of the above acid in DCE (1 mL) was added solid Cs_2CO_3 (98 mg, 0.3 mmol, 3.0 equiv). The suspension was stirred for 4-12 h at 90 °C, and the reaction was quenched by addition of water. The aqueous layer was extracted with EtOAc (3 × 10 mL), and the combined organic layer was dried over anhydrous Na_2SO_4, evaporated under vacuum and purified by ISCO flash chromatography to give the desired product **8**.

(*S*)-1-((Chloromethyl)sulfinyl)hexane 8b

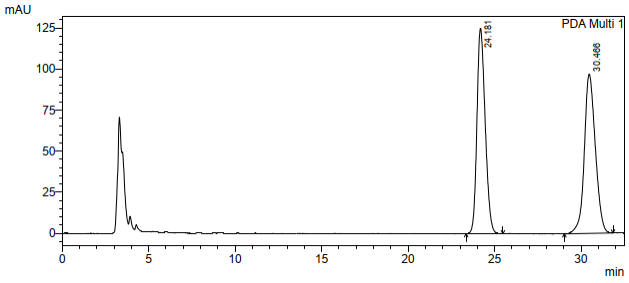


(*S*)-**8b**

Yield: 65%. Purified by ISCO flash column chromatography (3:2 hexane:EtOAc v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.41 (d, J = 12.0 Hz, 1H), 4.36 (d, J = 12.0 Hz, 1H), 2.90 - 2.82 (m, 2H), 1.83 - 1.74 (m, 2H), 1.53 - 1.43 (m, 2H), 1.36 - 1.29 (m, 4H), 0.90 (t, J = 6.0 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 55.9, 50.2, 31.4, 28.6, 22.5, 22.1, 14.1.
ESI MS. $C_7H_{16}ClOS$ m/z $[M+H]^+$ calc. 183.0, found 183.1.
$[\alpha]^{25}_D$ -59.18 (c 0.125, EtOH).
Chiral HPLC Chiralpak IC, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**8b**



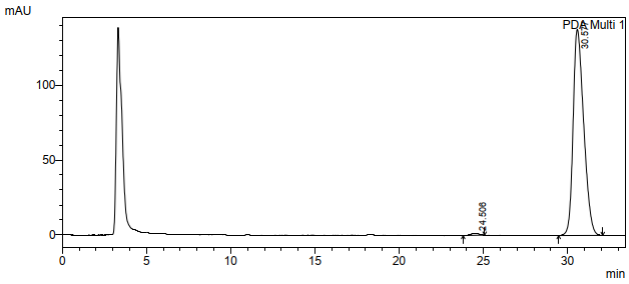
1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	24.181	4153011	49.104
2	30.466	4304580	50.896
Total		8457591	100.000

(*S*)-**8b**



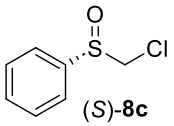
1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	24.506	44650	0.737
2	30.577	6009857	99.263
Total		6054507	100.000

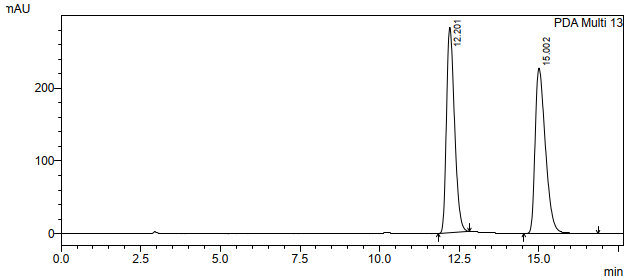
(*S*)-**((Chloromethyl)sulfinyl)benzene 8c**



(*S*)-**8c**

Yield: 81%. Purified by ISCO flash column chromatography (3:2 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 - 7.68 (m, 2H), 7.59 - 7.54 (m, 3H), 4.41 (d, J = 8.0 Hz, 1H), 4.37 (d, J = 12.0 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 132.3, 129.5, 124.9, 61.4.
ESI MS. C_7H_8ClOS m/z $[M+H]^+$ calc. 175.0, found 175.0.
$[\alpha]^{25}_D$ of (*S*)-**8c** +262.34 (c 0.125, EtOH).
$[\alpha]^{25}_D$ of (*R*)-**8c** -221.69 (c 0.230, EtOH).
Chiral HPLC Chiralcel OD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**8c**



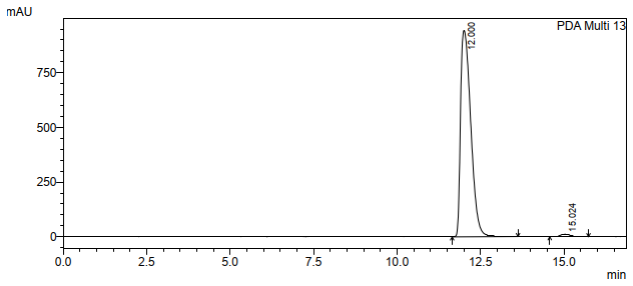
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.201	4976318	49.254
2	15.002	5127045	50.746
Total		10103362	100.000

(*S*)-**8c**



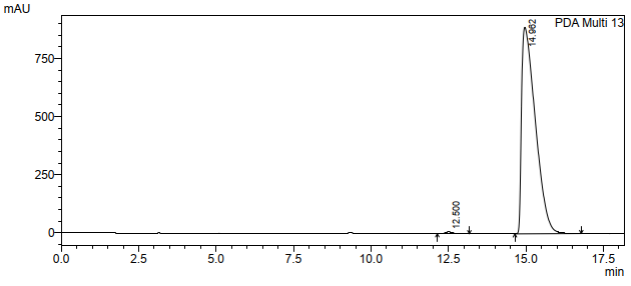
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.000	20087544	98.752
2	15.024	253938	1.248
Total		20341481	100.000

(*R*)-**8c**



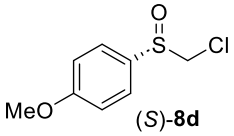
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.500	135060	0.488
2	14.962	27533844	99.512
Total		27668904	100.000

(*S*)-**1-((Chloromethyl)sulfinyl)-4-methoxybenzene 8d**



(*S*)-**8d**

Yield: 80%. Purified by ISCO flash column chromatography (1:1 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 - 7.61 (m, 2H), 7.07 - 7.02 (m, 2H), 4.37 (d, J = 8.0 Hz, 1H), 4.32 (d, J = 8.0 Hz, 1H), 3.86 (s, 3H).

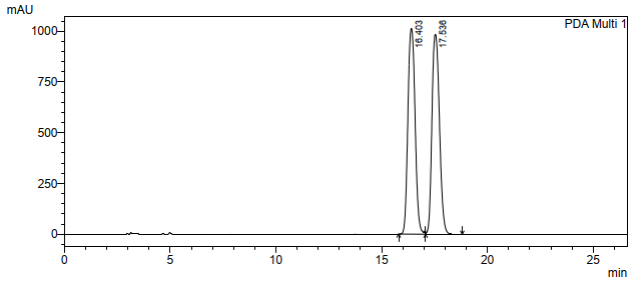
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 131.8, 126.9, 115.0, 61.2, 55.7.

ESI MS. $C_8H_{10}ClO_2S$ m/z $[M+H]^+$ calc. 205.0, found 205.1

$[\alpha]^{24.7}_D$ +217.73 (c 0.45, EtOH).

Chiral HPLC Chiralpak AD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**8d**



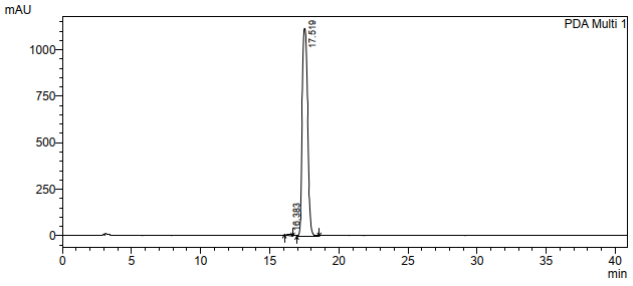
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	16.403	23973795	49.694
2	17.536	24268889	50.306
Total		48242684	100.000

(*S*)-**8d**



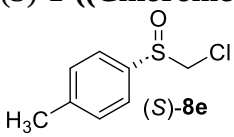
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	16.383	139501	0.453
2	17.519	30658816	99.547
Total		30798317	100.000

(*S*)-**1-((Chloromethyl)sulfinyl)-4-methylbenzene 8e**

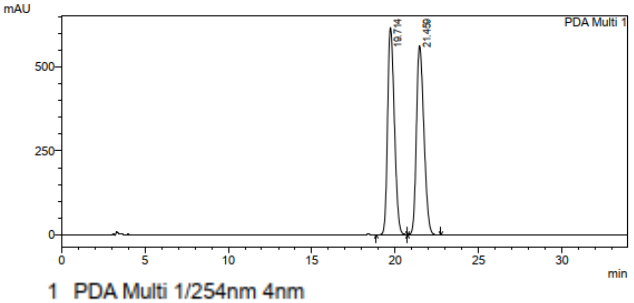


(*S*)-**8e**

Yield: 73%. Purified by ISCO flash column chromatography (3:2 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 - 7.56 (m, 2H), 7.41 - 7.32 (m, 2H), 4.36 (s, 2H), 2.43 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 137.8, 130.2, 124.9, 61.4, 21.6.
ESI MS. $C_8H_{10}ClOS$ m/z $[M+H]^+$ calc. 189.0, found 189.1.
$[\alpha]^{26}_D$ +238.34 (c 0.25, EtOH).
Chiral HPLC Chiralpak IC, 20% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**8e**



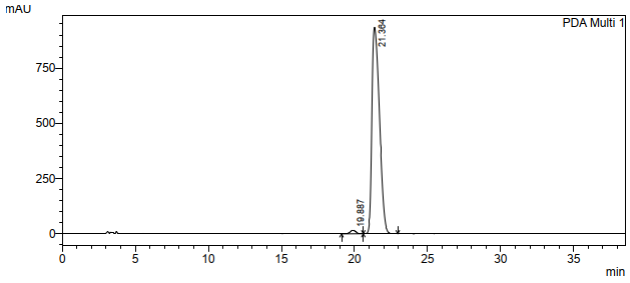
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	19.714	17464199	49.792
2	21.459	17609789	50.208
Total		35073989	100.000

(*S*)-**8e**



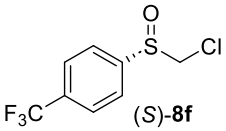
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	19.887	451068	1.324
2	21.364	33620973	98.676
Total		34072040	100.000

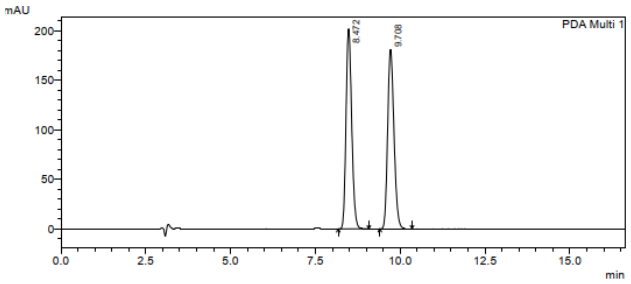
(*S*)-**1-((Chloromethyl)sulfinyl)-4-(trifluoromethyl)benzene 8f**



(*S*)-**8f**

Yield: 66%. Purified by ISCO flash column chromatography (7:3 hexane:EtOAc v/v).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (s, 4H), 4.46 (d, J = 12.0 Hz, 1H), 4.42 (d, J = 12.0 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 145.3, 126.5 (q), 125.6, 61.0.
ESI MS. $C_8H_7ClF_3OS$ m/z $[M+H]^+$ calc. 243.0, found 243.0.
$[\alpha]^{26}_D$ +135.97 (c 0.25, EtOH).
Chiral HPLC Chiralpak AD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**8f**



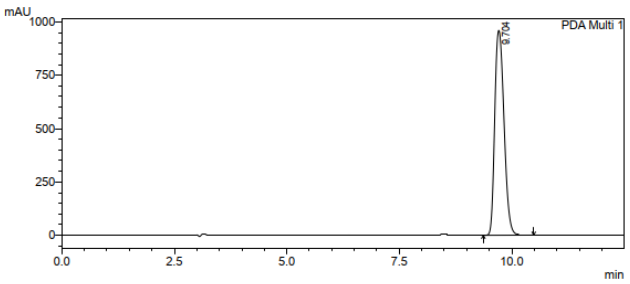
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.472	2351879	50.013
2	9.708	2350615	49.987
Total		4702494	100.000

(*S*)-**8f**



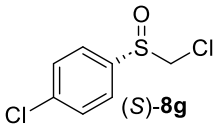
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

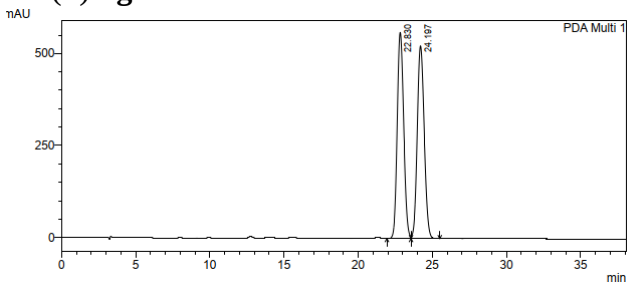
Peak#	Ret. Time	Area	Area %
1	9.704	13747110	100.000
Total		13747110	100.000

(*S*)-1-Chloro-4-((chloromethyl)sulfinyl)benzene 8g



Yield: 72%. Purified by ISCO flash column chromatography (3:2 hexane:EtOAc v/v).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 - 7.64 (m, 2H), 7.57 - 7.54 (m, 2H), 4.38 (s, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 139.4, 138.8, 129.8, 126.4, 61.1.
ESI MS. $C_7H_7Cl_2OS$ m/z $[M+H]^+$ calc. 208.9, found 209.0.
$[\alpha]^{25}_D$ +131.97 (c 0.1, EtOH).
Chiral HPLC Chiralpak IC, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-8g



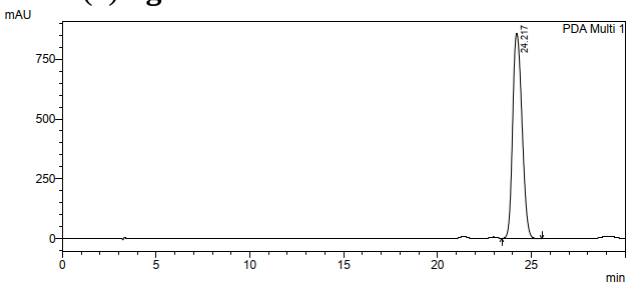
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	22.830	16932587	49.827
2	24.197	17050205	50.173
Total		33982792	100.000

(*S*)-8g



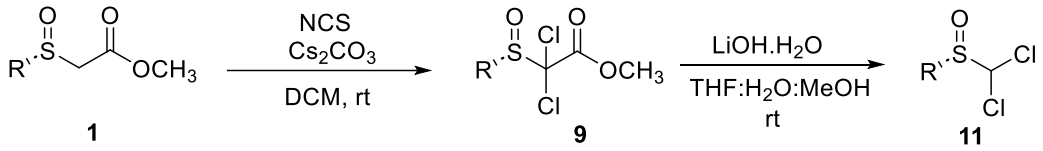
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	24.217	29690860	100.000
Total		29690860	100.000

XI. General procedure for the synthesis of (dichloromethyl)sulfinyl derivatives



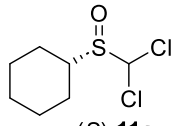
1 **9** **11**

To a solution of methyl ester **1** (0.2 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) was added Cs_2CO_3 (130 mg, 0.4 mmol, 2.0 equiv) at room temperature. Then N-chlorosuccinimide, (107 mg, 0.8 mmol, 4.0 equiv) was added and the resulting solution was stirred at room temperature for 4-12h. The reaction mixture was quenched by addition of water and the water layer was extracted with CH_2Cl_2 (3 × 10). The organic layers were combined and dried over Na_2SO_4. Filtration, followed by concentration *in vacuo* gave the crude product, which was then purified by ISCO flash column chromatography.

A mixture of above dichloro derivative **9** (0.1 mmol, 1.0 equiv), lithium hydroxide (8.0 mg, 0.2 mmol, 2.0 equiv), THF (0.5 mL), water (0.25 mL) and MeOH (0.12 mL), was stirred at room temperature for 4-6 h. The organic solvent was removed under reduced pressure, and the residue obtained was then acidified to pH 3 with 1 N HCl, and the mixture was extracted with

EtOAc (3 × 10 mL). The combined extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product which was purified by ISCO flash column chromatography.

(*S*)-((dichloromethyl)sulfinyl)cyclohexane 11a



(*S*)-**11a**

Methyl (*S*)-2,2-dichloro-2-(cyclohexylsulfinyl)acetate 9a

Yield: 81%, purified by ISCO flash column chromatography (7:3 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (s, 3H), 3.21 - 3.13 (m, 1H), 2.03 - 1.80 (m, 4H), 1.73 - 1.51 (m, 3H), 1.44 - 1.25 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 92.8, 59.2, 55.5, 29.4, 25.6, 25.3, 25.1, 25.1.

ESI MS $C_9H_{15}Cl_2O_3S$ m/z $[M+H]^+$ calc. 273.0, found 273.0.

(*S*)-((Dichloromethyl)sulfinyl)cyclohexane 11a

Yield: 72%, purified by ISCO flash column chromatography (4:1 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (s, 1H), 3.06 - 2.98 (m, 1H), 2.00 - 1.86 (m, 4H), 1.72 - 1.53 (m, 3H), 1.44 - 1.21 (m, 3H).

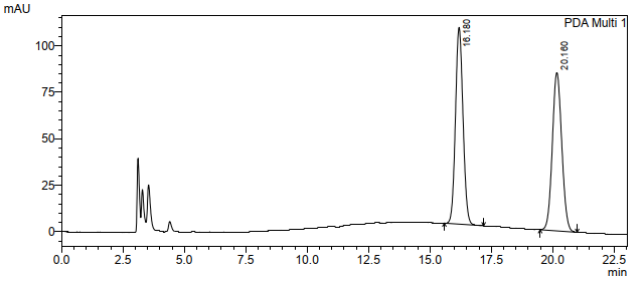
^{13}C NMR (101 MHz, $CDCl_3$) δ 79.8, 57.8, 27.6, 25.5, 25.3, 25.1, 23.8.

ESI MS. $C_7H_{13}Cl_2OS$ m/z $[M+H]^+$ calc. 215.0, found 215.0.

$[\alpha]^{25}_D$ -16.51 (c 0.230, EtOH).

Chiral HPLC Chiralpak IC, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**11a**



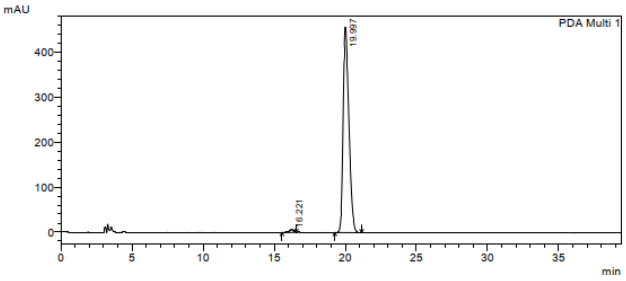
1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	16.180	2263609	49.819
2	20.160	2280061	50.181
Total		4543670	100.000

(*S*)-**11a**



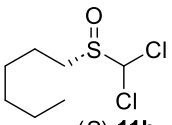
1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	16.221	147646	1.128
2	19.997	12942132	98.872
Total		13089778	100.000

(*S*)-1-((dichloromethyl)sulfinyl)hexane 11b



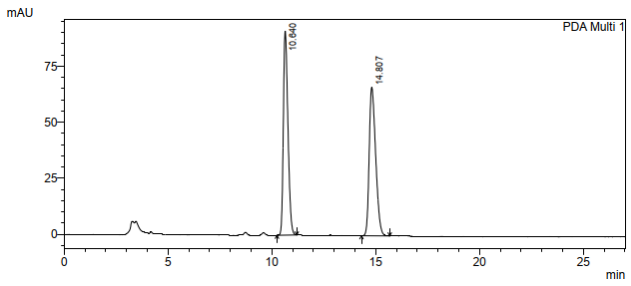
(*S*)-**11b**

Methyl (*S*)-2,2-dichloro-2-(hexylsulfinyl)acetate 9b

Yield: 75%, purified by ISCO flash column chromatography (7:3 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 3H), 2.97 - 2.90 (m, 1H), 2.84 - 2.77 (m, 1H), 1.88 - 1.77 (m, 2H), 1.55 - 1.38 (m, 2H), 1.34 - 1.25 (m, 4H), 0.86 (t, J = 8.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 92.3, 55.5, 50.0, 31.3, 28.5, 22.9, 22.4, 13.9.
ESI MS $C_9H_{17}Cl_2O_3S$ m/z $[M+H]^+$ calc. 275.0, found 275.1.

(*S*)-**1-((Dichloromethyl)sulfinyl)hexane 11b**
Yield: 70%, purified by ISCO flash column chromatography (3:1 hexane:EtOAc v/v).
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.29 (s, 1H), 2.96 - 2.87 (m, 2H), 1.90 - 1.80 (m, 2H), 1.55 - 1.44 (m, 2H), 1.36 - 1.31 (m, 4H), 0.90 (t, J = 6.0 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 80.5, 48.1, 31.4, 28.6, 22.5, 22.4, 14.1.
ESI MS. $C_7H_{15}Cl_2OS$ m/z $[M+H]^+$ calc. 217.0, found 217.0.
$[\alpha]^{25}_D$ -95.21 (c 0.21, EtOH).
Chiral HPLC Chiralpak IC, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**11b**



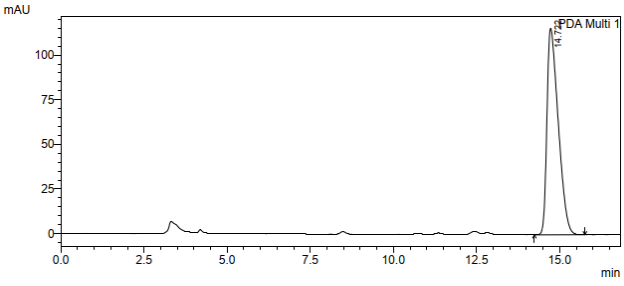
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.640	1395290	49.288
2	14.807	1435603	50.712
Total		2830893	100.000

(*S*)-**11b**



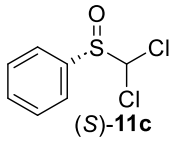
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	14.722	2739895	100.000
Total		2739895	100.000

(*S*)-**((Dichloromethyl)sulfinyl)benzene 11c**



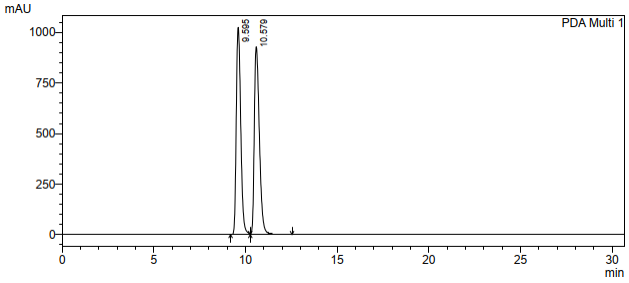
(*S*)-**11c**

Methyl (*S*)-**2,2-dichloro-2-(phenylsulfinyl)acetate 9c**
Yield: 93%, purified by ISCO flash column chromatography (7:3 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 - 7.77 (m, 2H), 7.64 - 7.59 (m, 1H), 7.55 - 7.51 (m, 2H), 3.85 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 138.1, 133.6, 128.8, 127.3, 55.2.
ESI MS $C_9H_9Cl_2O_3S$ m/z $[M+H]^+$ calc. 266.9, found 266.9.

(*S*)-**((Dichloromethyl)sulfinyl)benzene 11c**
Yield: 85%, purified by ISCO flash column chromatography (4:1 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 - 7.78 (m, 2H), 7.66 - 7.55 (m, 3H), 6.18 (s, 1H).
^{13}C NMR (101 MHz, CDCl3) δ 138.2, 133.2, 129.1, 126.8, 83.2.

ESI MS. $C_7H_7Cl_2OS$ m/z $[M+H]^+$ calc. 208.9, found 208.9.
$[\alpha]^{25}_D$ +147.16 (c 0.5, EtOH).
Chiral HPLC Chiralcel OD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**11c**



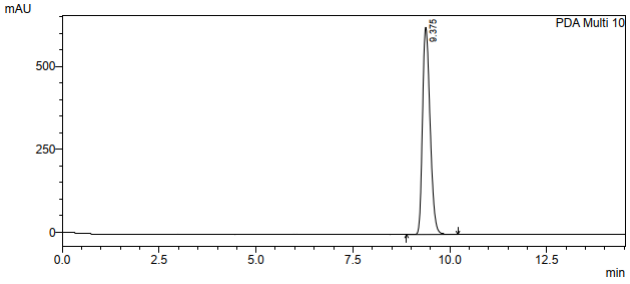
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.595	17371723	49.212
2	10.579	17928053	50.788
Total		35299775	100.000

(*S*)-**11c**



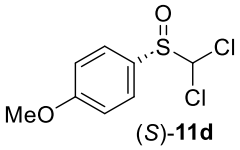
1 PDA Multi 10/254nm 4nm

PeakTable

PDA Ch10 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.375	8494603	100.000
Total		8494603	100.000

(*S*)-**1-((Dichloromethyl)sulfinyl)-4-methoxybenzene 11d**

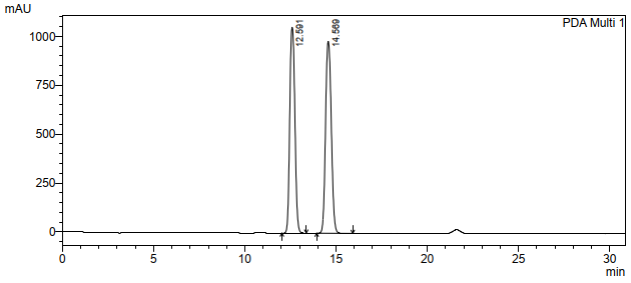


(*S*)-**11d**

Methyl (*S*)**-2,2-dichloro-2-((4-methoxyphenyl)sulfinyl)acetate 9d**
Yield: 92%, purified by ISCO flash column chromatography (3:2 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 - 7.68 (m, 2H), 7.03 - 6.99 (m, 2H), 3.86 (s, 3H), 3.84 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 163.1, 129.3, 128.6, 114.3, 94.5, 55.7, 55.2.
ESI MS $C_{10}H_{11}Cl_2O_4S$ m/z $[M+H]^+$ calc. 297.0, found 297.1.

(*S*)-**1-((Dichloromethyl)sulfinyl)-4-methoxybenzene 11d**
Yield: 86%, purified by ISCO flash column chromatography (7:3 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 - 7.70 (m, 2H), 7.07 - 7.03 (m, 2H), 6.14 (s, 1H), 3.87 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 128.8, 128.7, 114.6, 83.3, 55.7.
ESI MS. $C_8H_9Cl_2O_2S$ m/z $[M+H]^+$ calc. 238.9, found 239.1.
$[\alpha]^{25}_D$ +106.38 (c 0.125, EtOH).
Chiral HPLC Chiralpak IC, 20% IPA/hexanes, 1.0 mL/min, 254nm

(±)-**11d**



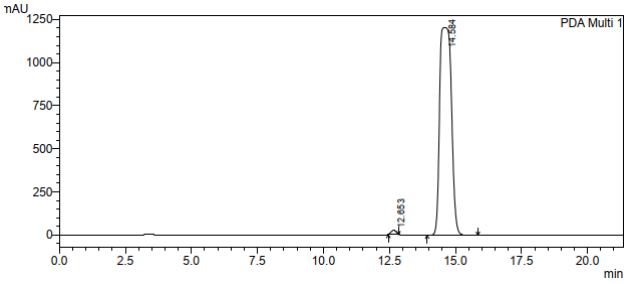
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.591	20549967	48.843
2	14.569	21523753	51.157
Total		42073720	100.000

(*S*)-**11d**



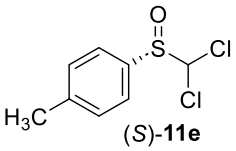
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.653	344303	0.915
2	14.584	37295341	99.085
Total		37639644	100.000

(*S*)-**1-((Dichloromethyl)sulfinyl)-4-methylbenzene 11e**



(*S*)-**11e**

Methyl (*S*)**-2,2-dichloro-2-(p-tolylsulfinyl)acetate 9e**

Yield: 91%, purified by ISCO flash column chromatography (3:2 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 - 7.67 (m, 2H), 7.36 - 7.34 (m, 2H), 3.89 (s, 3H), 2.45 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.2, 144.7, 134.8, 129.6, 127.4, 94.3, 55.3, 21.8.

ESI MS $C_{10}H_{11}Cl_2O_3S$ m/z $[M+H]^+$ calc. 281.0, found 281.1.

(*S*)-**1-((dichloromethyl)sulfinyl)-4-methylbenzene 11e**

Yield: 82%, purified by ISCO flash column chromatography (3:1 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 - 7.66 (m, 2H), 7.39 - 7.36 (m, 2H), 6.14 (s, 1H), 2.45 (s, 3H).

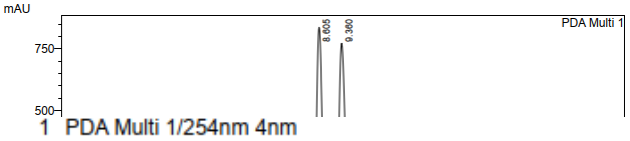
^{13}C NMR (151 MHz, $CDCl_3$) δ 144.1, 134.8, 129.9, 126.8, 83.2, 21.8.

ESI MS. $C_8H_9Cl_2OS$ m/z $[M+H]^+$ calc. 222.9, found 223.0.

$[\alpha]^{26}_D$ +175.95 (c 0.125, EtOH).

Chiral HPLC Chiralcel OD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**11e**



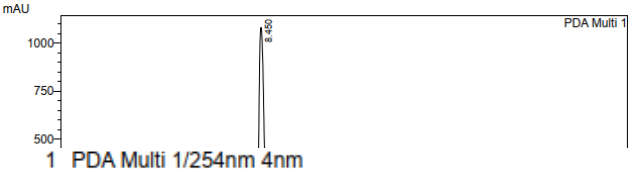
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.605	10518240	49.883
2	9.360	10567385	50.117
Total		21085624	100.000

(*S*)-**11e**



1 PDA Multi 1/254nm 4nm

PeakTable

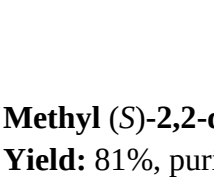
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.450	15466607	100.000
Total		15466607	100.000

(*S*)-**1-((Dichloromethyl)sulfinyl)-4-(trifluoromethyl)benzene 11f**

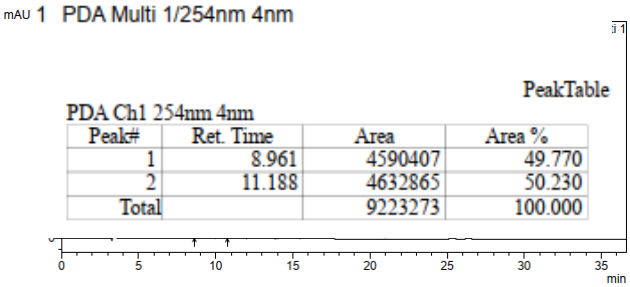
Methyl (*S*)-**2,2-dichloro-2-((4-(trifluoromethyl)phenyl)sulfinyl)acetate 9f**
Yield: 81%, purified by ISCO flash column chromatography (7:3 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 3.93 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 142.3, 135.5 (q), 128.2, 125.8 (q), 124.8 (q), 93.7, 55.6.
ESI MS. $C_{10}H_8Cl_2F_3OS$ m/z $[M+H]^+$ calc. 334.9, found 334.9.

(*S*)-**1-((dichloromethyl)sulfinyl)-4-(trifluoromethyl)benzene 11f**
Yield: 48%, purified by ISCO flash column chromatography (4:1 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.0 Hz, 2H), 7.85 (d, J = 8.0 Hz, 2H), 6.23 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 127.5, 126.1 (q), 82.6.
ESI MS. $C_8H_6F_3Cl_2OS$ m/z $[M+H]^+$ calc. 276.9, found 276.9.
[α]$^{25}_D$ +21.39 (c 0.215, CH_2Cl_2).
Chiral HPLC Chiralpak IC, 10% IPA/hexanes, 1.0 mL/min, 254nm.

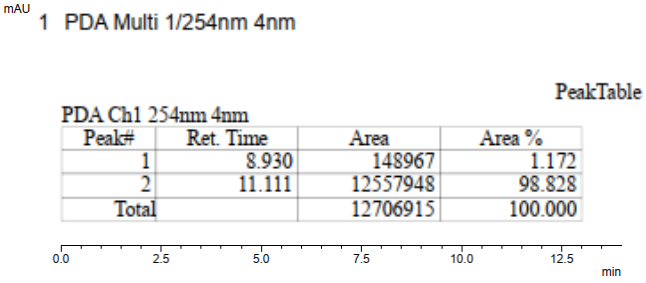


(*S*)-**11f**

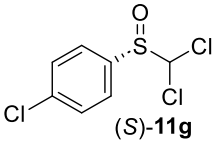
(±)-**11f**



(*S*)-**11f**



(*S*)-**1-Chloro-4-((dichloromethyl)sulfinyl)benzene 11g**

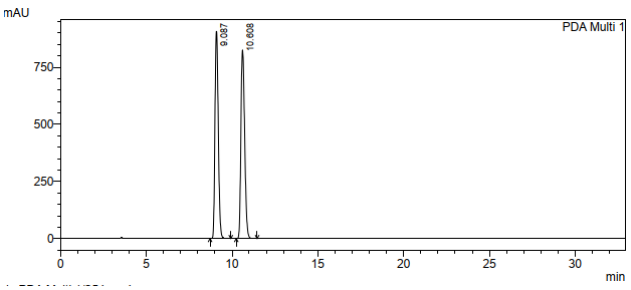


(*S*)-**11g**

Methyl (*S*)-**2,2-dichloro-2-((4-chlorophenyl)sulfinyl)acetate 9g**
Yield: 83%, purified by ISCO flash column chromatography (7:3 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 - 7.73 (m, 2H), 7.59 - 7.53 (m, 2H), 3.92 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 140.2, 136.5, 129.2, 128.8, 93.9, 55.4.
ESI MS. $C_9H_8Cl_3OS$ m/z $[M+H]^+$ calc. 300.9, found 301.0.

(*S*)-**1-Chloro-4-((dichloromethyl)sulfinyl)benzene 11g**
Yield: 56%, purified by ISCO flash column chromatography (3:1 hexane:EtOAc v/v).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 - 7.72 (m, 2H), 7.57 - 7.55 (m, 2H), 6.19 (s, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 139.9, 136.2, 129.5, 128.3, 82.8, 29.8.
ESI MS. $C_7H_6Cl_3OS$ m/z $[M+H]^+$ calc. 242.9, found 242.9.
[α]$^{25}_D$ +131.97 (c 0.25, EtOH).
Chiral HPLC Chiralpak AD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**11g**



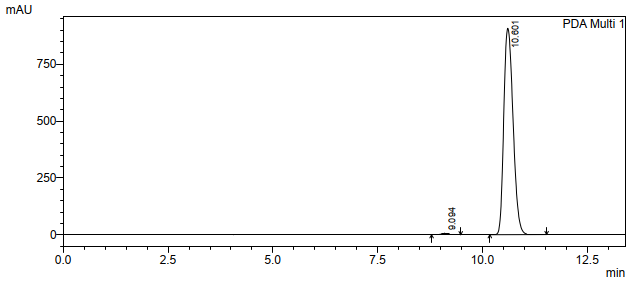
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.087	12223220	49.362
2	10.608	12539273	50.638
Total		24762493	100.000

(*S*)-**11g**



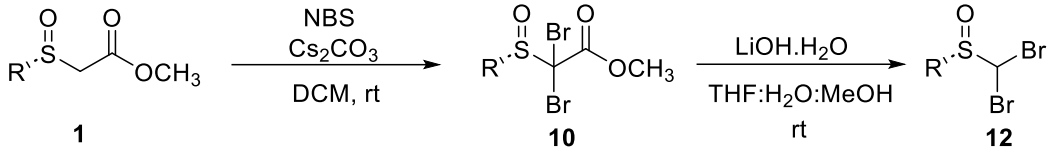
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.094	79222	0.562
2	10.601	14011985	99.438
Total		14091207	100.000

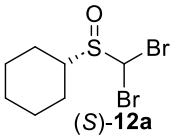
XII General procedure for the synthesis of (dibromomethyl)sulfinyl derivatives



To a solution of methyl ester **1** (0.2 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) were added Cs_2CO_3 (130 mg, 0.4 mmol, 2.0 equiv) and N-bromosuccinimide, (142 mg, 0.8 mmol, 4.0 equiv) at room temperature. The resulting solution was stirred at room temperature for 4-12h. The reaction mixture was quenched by addition of water, and the water layer was extracted with CH_2Cl_2 (3 × 10). The organic layers were combined and dried over Na_2SO_4. Filtration, followed by evaporation of the solvent gave the crude product, which was then purified by ISCO flash column chromatography.

A mixture of above dibromo derivative **10** (0.1 mmol, 1.0 equiv), lithium hydroxide (8.0 mg, 0.2 mmol), THF (0.5 mL), water (0.25 mL) and MeOH (0.12 mL), were stirred at room temperature for 4-6 h. The organic solvent was removed under reduced pressure, and the residue obtained was then acidified to pH 3 with 1 N HCl, and the mixture was extracted with EtOAc (3 × 10 mL). The combined extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product which was purified by ISCO flash column chromatography.

(*S*)-**((Dibromomethyl)sulfinyl)cyclohexane 12a**



(*S*)-**12a**

Methyl (*S*)**-2,2-dibromo-2-(cyclohexylsulfinyl)acetate 10a**

Yield: 81%, purified by ISCO flash column chromatography (3:1 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 3H), 3.14 - 3.07 (m, 1H), 2.09 - 1.81 (m, 4H), 1.67 - 1.26 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 71.8, 61.1, 55.5, 29.9, 25.7, 25.4, 25.3, 25.2.

ESI MS $C_9H_{15}Br_2O_3S$ m/z $[M+H]^+$ calc. 362.9, found 362.9.

(*S*)-**((Dibromomethyl)sulfinyl)cyclohexane 12a**

Yield: 65%, purified by ISCO flash column chromatography (4:1 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (s, 1H), 3.05 - 2.98 (m, 1H), 2.06 - 1.86 (m, 4H), 1.74 - 1.55 (m, 3H), 1.45 - 1.25 (m, 3H).

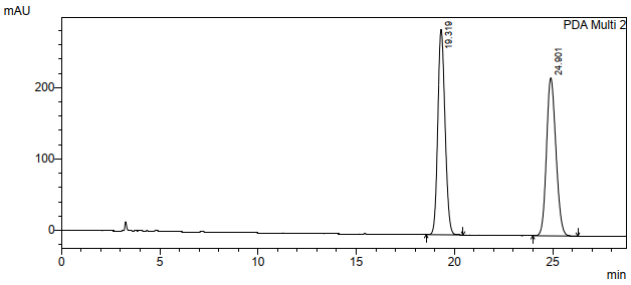
^{13}C NMR (101 MHz, $CDCl_3$) δ 59.5, 53.3, 28.0, 25.6, 25.3, 25.1, 24.1.

ESI MS. $C_7H_{13}Br_2OS$ m/z $[M+H]^+$ calc. 304.9, found 304.9

$[\alpha]^{25}_D$ -8.51 (c 0.235, EtOH).

Chiral HPLC Chiralpak IC, 10% IPA/hexanes, 1.0 mL/min, 220nm.

(±)-**12a**



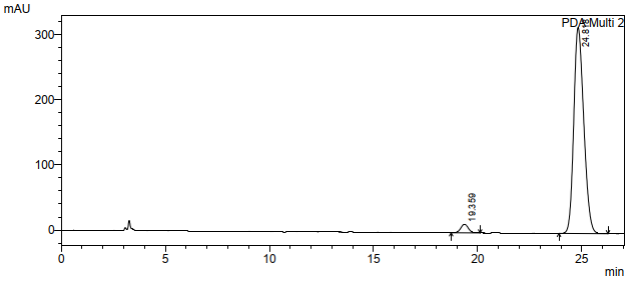
1 PDA Multi 2/220nm 4nm

PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	19.319	7386472	49.989
2	24.901	7389674	50.011
Total		14776146	100.000

(*S*)-**12a**



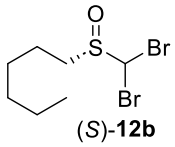
1 PDA Multi 2/220nm 4nm

PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	19.359	334481	3.074
2	24.818	10544856	96.926
Total		10879337	100.000

(*S*)-**1-((Dibromomethyl)sulfinyl)hexane 12b**



(*S*)-**12b**

Methyl (*S*)**-2,2-dibromo-2-(hexylsulfinyl)acetate 10b**

Yield: 79%, purified by ISCO flash column chromatography (7:3 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (s, 3H), 3.12 - 3.05 (m, 1H), 2.82 - 2.75 (m, 1H), 1.94 - 1.78 (m, 2H), 1.57 - 1.41 (m, 2H), 1.37 - 1.28 (m, 4H), 0.88 (t, J = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 71.5, 55.6, 52.2, 31.4, 28.6, 23.1, 22.4, 14.0.

ESI MS $C_9H_{17}Br_2O_3S$ m/z $[M+H]^+$ calc. 364.9, found 365.0

(*S*)-**1-((dibromomethyl)sulfinyl)hexane 12b**

Yield: 68%, purified by ISCO flash column chromatography (4:1 hexane:EtOAc v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.29 (s, 1H), 2.96 - 2.87 (m, 2H), 1.91 - 1.79 (m, 2H), 1.55 - 1.45 (m, 2H), 1.36 - 1.30 (m, 4H), 0.95 - 0.85 (m, 3H).

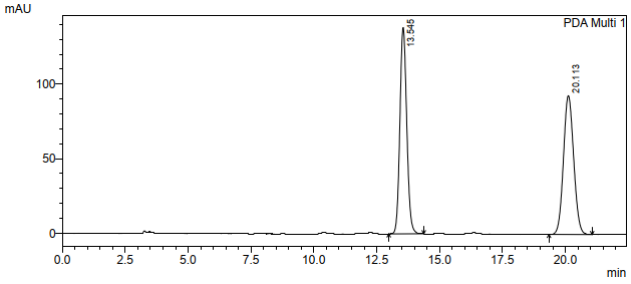
^{13}C NMR (151 MHz, $CDCl_3$) δ 80.5, 48.1, 31.4, 28.6, 22.5, 22.4, 14.1.

ESI MS. $C_7H_{15}Br_2OS$ m/z $[M+H]^+$ calc. 306.9, found 306.9.

$[\alpha]^{25}_D$ -97.75 (c 0.09, EtOH).

Chiral HPLC Chiralpak IC, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**12b**



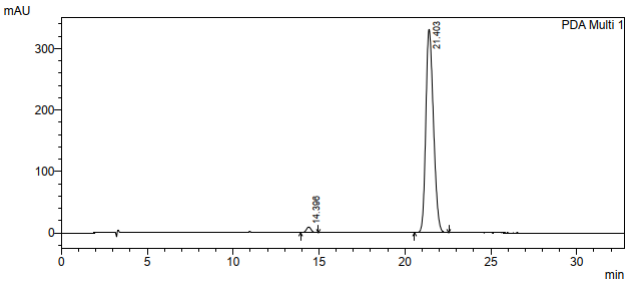
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	13.545	2624530	50.019
2	20.113	2622514	49.981
Total		5247043	100.000

(*S*)-**12b**



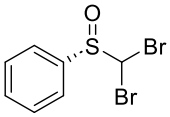
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	14.396	182100	1.752
2	21.403	10211980	98.248
Total		10394079	100.000

(*S*)-**((Dibromomethyl)sulfinyl)benzene 12c**



(*S*)-**12c**

Methyl (*S*)**-2,2-dibromo-2-(phenylsulfinyl)acetate 10c**

Yield: 92%, purified by ISCO flash column chromatography (7:3 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 - 7.82 (m, 2H), 7.63 - 7.59 (m, 1H), 7.54 - 7.49 (m, 2H), 3.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 138.9, 133.5, 128.6, 127.8, 74.2, 55.4.

ESI MS $C_9H_9Br_2O_3S$ m/z $[M+H]^+$ calc. 356.8, found 356.8

(*S*)-**((Dibromomethyl)sulfinyl)benzene 12c**

Yield: 79%, purified by ISCO flash column chromatography (4:1 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 - 7.80 (m, 2H), 7.66 - 7.62 (m, 1H), 7.59 - 7.54 (m, 2H), 6.15 (s, 1H).

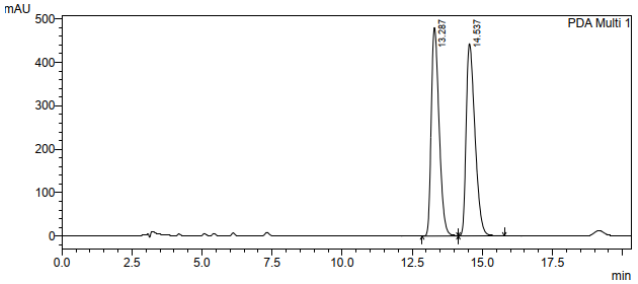
^{13}C NMR (101 MHz, $CDCl_3$) δ 133.2, 129.0, 126.9, 57.8.

ESI MS. $C_7H_7Br_2OS$ m/z $[M+H]^+$ calc. 298.8, found 298.8

$[\alpha]^{25}_D$ +135.97 (c 0.05, EtOH).

Chiral HPLC Chiralcel OD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**12c**



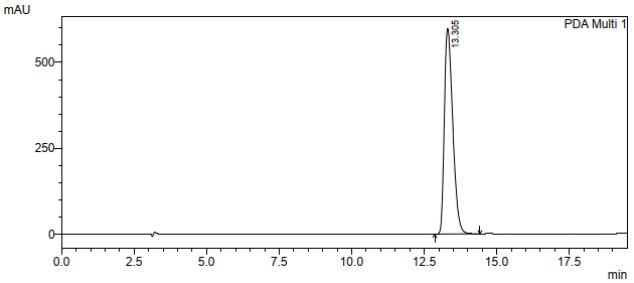
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	13.287	9325394	49.071
2	14.537	9678514	50.929
Total		19003908	100.000

(*S*)-**12c**



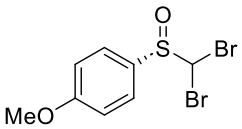
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	13.305	12060169	100.000
Total		12060169	100.000

(*S*)-**1-((Dibromomethyl)sulfinyl)-4-methoxybenzene 12d**



(*S*)-**12d**

Methyl (*S*)**-2,2-dibromo-2-((4-methoxyphenyl)sulfinyl)acetate 10d**

Yield: 87%, purified by ISCO flash column chromatography (1:1 hexane:EtOAc v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 - 7.76 (m, 2H), 7.03 – 7.00 (m, 2H), 3.89 (s, 3H), 3.87 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.9, 163.6, 129.8, 129.7, 114.1, 75.2, 55.7, 55.4.

ESI MS $C_{10}H_{11}Br_2O_4S$ m/z $[M+H]^+$ calc. 386.9, found 387.0.

(*S*)-**1-((Dibromomethyl)sulfinyl)-4-methoxybenzene 12d**

Yield: 82%, purified by ISCO flash column chromatography (3:2 hexane:EtOAc v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 - 7.73 (m, 2H), 7.06 - 7.04 (m, 2H), 6.13 (s, 1H), 3.88 (s, 3H).

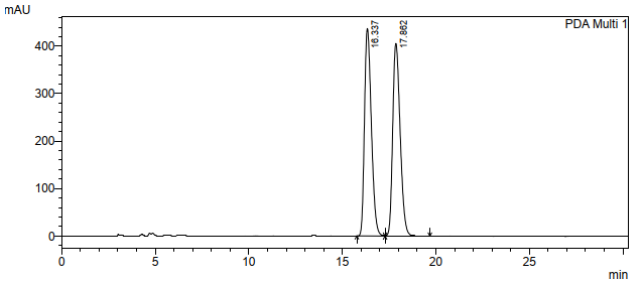
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.7, 129.6, 128.9, 114.4, 58.6, 55.8.

ESI MS. $C_8H_9Br_2O_2S$ m/z $[M+H]^+$ calc. 328.9, found 329.0

$[\alpha]^{25}_D$ +116.77 (c 0.25, EtOH).

Chiral HPLC Chiralcel OD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**12d**



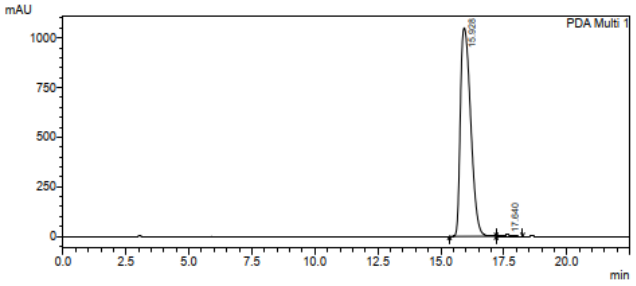
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	16.337	11156642	49.848
2	17.862	11224566	50.152
Total		22381208	100.000

(*S*)-**12d**



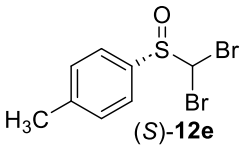
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	15.928	29952336	99.323
2	17.640	204257	0.677
Total		30156593	100.000

(*S*)-**1-((Dibromomethyl)sulfinyl)-4-methylbenzene 12e**



(*S*)-**12e**

Methyl (*S*)**-2,2-dibromo-2-(*p*-tolylsulfinyl)acetate 10e**

Yield: 87%, purified by ISCO flash column chromatography (3:2 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 - 7.72 (m, 2H), 7.35 - 7.32 (m, 2H), 3.90 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.6, 144.6, 135.9, 129.4, 127.8, 74.7, 55.5, 21.9.

ESI MS $C_{10}H_{11}Br_2O_3S$ m/z $[M+H]^+$ calc. 370.9, found 371.0.

(*S*)-**1-((dibromomethyl)sulfinyl)-4-methylbenzene 12e**

Yield: 75%, purified by ISCO flash column chromatography (4:1 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 - 7.68 (m, 2H), 7.38 - 7.34 (m, 2H), 6.13 (s, 1H), 2.45 (s, 3H).

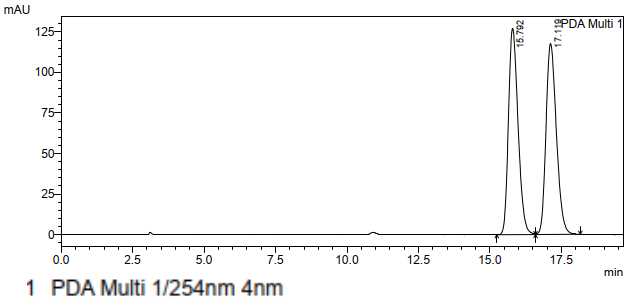
^{13}C NMR (151 MHz, $CDCl_3$) δ 144.1, 135.8, 129.7, 126.9, 58.2, 21.8.

ESI MS. $C_8H_9Br_2OS$ m/z $[M+H]^+$ calc. 312.9, found 313.0

$[\alpha]^{26}_D$ +114.14 (c 0.24, EtOH).

Chiral HPLC Chiralcel OD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**12e** (*S*)-**12e**

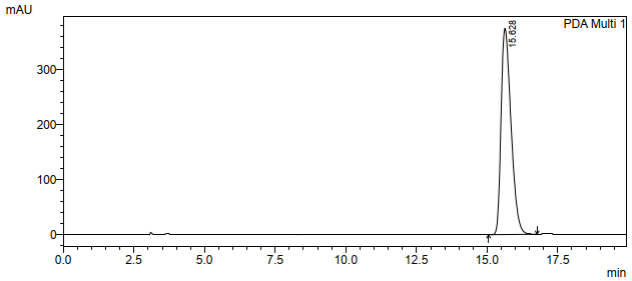


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	15.792	2969385	49.924
2	17.119	2978480	50.076
Total		5947865	100.000



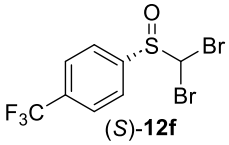
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	15.628	9209776	100.000
Total		9209776	100.000

(*S*)-1-((Dibromomethyl)sulfinyl)-4-(trifluoromethyl)benzene 12f



(*S*)-**12f**

Methyl (*S*)-2,2-dibromo-2-((4-(trifluoromethyl)phenyl)sulfinyl)acetate 10f

Yield: 76%, purified by ISCO flash column chromatography (7:3 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 - 7.99 (m, 2H), 7.81 - 7.78 (m, 2H), 3.93 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 143.4, 135.3 (q), 128.6, 125.6 (q), 124.8 (q), 73.2, 55.7.

ESI MS. $C_{10}H_8Br_2F_3OS$ m/z $[M+H]^+$ calc. 424.8, found 424.8.

(*S*)-1-((dibromomethyl)sulfinyl)-4-(trifluoromethyl)benzene 12f

Yield: 30%, purified by ISCO flash column chromatography (4:1 hexane:EtOAc v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, J = 6.0 Hz, 2H), 7.84 (d, J = 6.0 Hz, 2H), 6.21 (s, 1H).

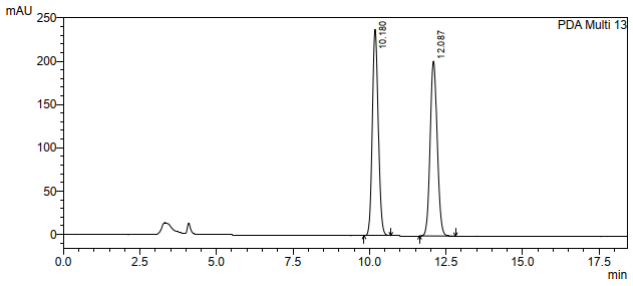
^{13}C NMR (151 MHz, $CDCl_3$) δ 143.1, 134.8 (q), 128.2, 127.6, 125.9 (q), 122.5(q), 56.8.

ESI MS. $C_8H_6F_3Br_2OS$ m/z $[M+H]^+$ calc. 366.8, found 366.8.

$[\alpha]^{25}_D$ +29.33 (c 0.075, CH_2Cl_2).

Chiral HPLC Chiralpak IC, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-12f



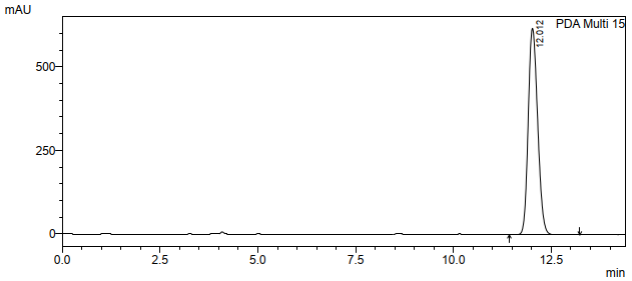
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.180	3228021	49.853
2	12.087	3247045	50.147
Total		6475066	100.000

(*S*)-12f



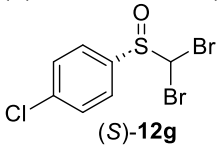
1 PDA Multi 15/254nm 4nm

PeakTable

PDA Ch15 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.012	10384974	100.000
Total		10384974	100.000

(*S*)-1-Chloro-4-((dibromomethyl)sulfinyl)benzene 12g



(*S*)-**12g**

Methyl (*S*)-2,2-dibromo-2-((4-chlorophenyl)sulfinyl)acetate 10g

Yield: 79%, purified by ISCO flash column chromatography (7:3 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 - 7.78 (m, 2H), 7.53 - 7.49 (m, 2H), 3.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 140.1, 137.6, 129.3, 128.9, 73.9, 55.6.

ESI MS. $C_9H_8Br_2ClOS$ m/z $[M+H]^+$ calc. 390.8, found 390.9.

(*S*)-1-Chloro-4-((dibromomethyl)sulfinyl)benzene 12g

Yield: 35%, purified by ISCO flash column chromatography (4:1 hexane:EtOAc v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 - 7.75 (m, 2H), 7.56 - 7.54 (m, 2H), 6.17 (s, 1H).

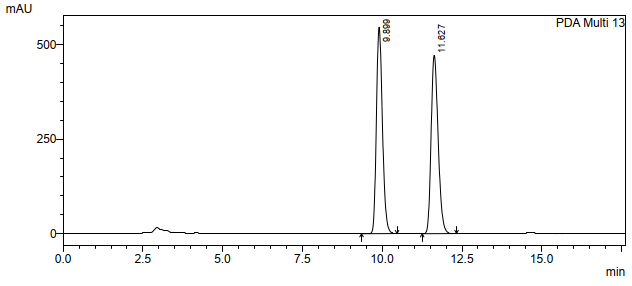
^{13}C NMR (151 MHz, $CDCl_3$) δ 139.8, 137.2, 129.3, 128.4, 57.4.

ESI MS. $C_7H_6Br_2ClOS$ m/z $[M+H]^+$ calc. 332.8, found 332.8.

$[\alpha]^{25}_D$ +30.46 (c 0.24, CH_2Cl_2).

Chiral HPLC Chiralpak AD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**12g**



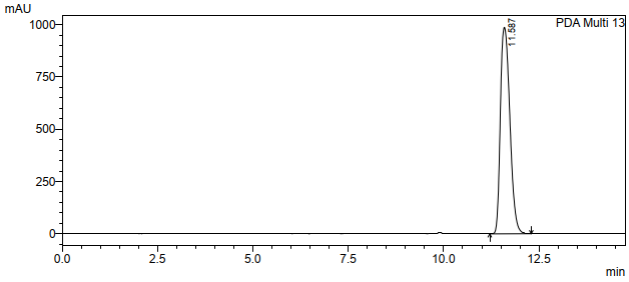
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.899	7181659	49.907
2	11.627	7208512	50.093
Total		14390172	100.000

(*S*)-**12g**



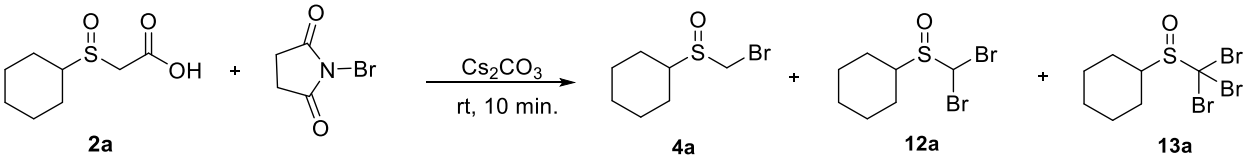
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	11.587	17088552	100.000
Total		17088552	100.000

XIII. General procedure for decarboxylative tribromination



2a **4a** **12a** **13a**

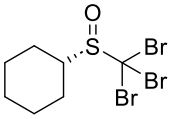
To a solution of the acid **2a** (0.1 mmol, 1.0 equiv) in solvent (Table **S2**, 2.0 mL) was added solid Cs_2CO_3 (65 mg, 0.2 mmol, 2.0 equiv). N-bromosuccinimide (178 mg, 1.0 mmol, 10 equiv) was added portion wise in the reaction mixture, stirred for 10 min at room temperature and checked LCMS. After the completion of the reaction, the reaction mixture was diluted by addition of EtOAc and water. The aqueous layer was extracted with EtOAc (3 × 10) and the combined organic layer was washed with water and dried over anhydrous Na_2SO_4, evaporated under vacuum and purified by ISCO flash chromatography.

Table S5

Entry	Solvent	**4a**[1]	**12a**[1]	**13a**[1]
1	DMF[a]	21	3	1
2	1,4-Dioxane	5	3	1
3	THF	1	2	-
4	**DMSO**	**1**	**-**	**12**
5	CH_3CN	1	1	1
6	MeOH[b]	1	-	-
7	EtOH[b]	7	1	-
8	IPA	6	1	3
9	n-Butanol[c]	13	1	-
10	t-Butanol	2	1	-
11	Acetone	-	-	-
12	CCl_4	2	1	1
13	HMPA	1	1	1
14	Diethyl ether	2	2	1
15	Diethylene glycol	1	2.5	1.5
16	TFE	1	1	-

1: Uncorrected peak areas by LCMS.
a: Ratio of 1a:1b:1c was not consistent
b: Not a clean reaction
c: Racemisation observed

(*S*)-((Tribromomethyl)sulfinyl)cyclohexane 13a

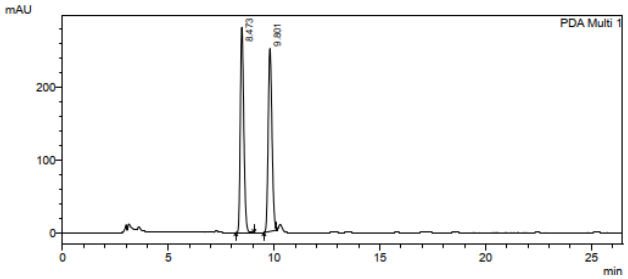


(*S*)-**13a**

Yield: 63%, purified by ISCO flash column chromatography (4:1 hexane:EtOAc v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.08 - 3.00 (m, 1H), 2.23 - 2.11 (m, 2H), 1.96 - 1.74 (m, 3H), 1.73 - 1.59 (m, 2H), 1.52 - 1.27 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 62.6, 58.5, 30.7, 25.9, 25.4, 25.3, 25.2.
ESI MS $C_7H_{12}Br_3OS$ m/z $[M+H]^+$ calc. 382.8, found 382.8.
$[\alpha]^{25}_D$ -25.99 (c 0.10, EtOH).
Chiral HPLC Chiralpak AD-H, 5% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**13a**



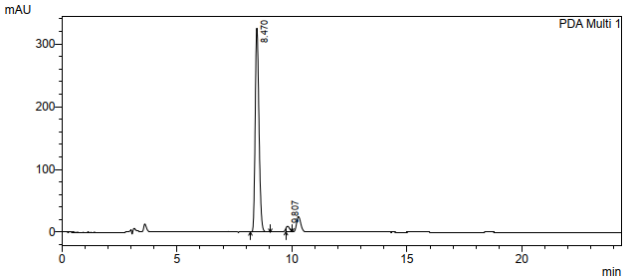
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.473	3193922	50.491
2	9.801	3131751	49.509
Total		6325673	100.000

(*S*)-**13a**



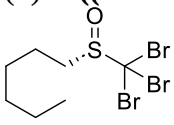
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.470	3723885	97.750
2	9.807	85718	2.250
Total		3809603	100.000

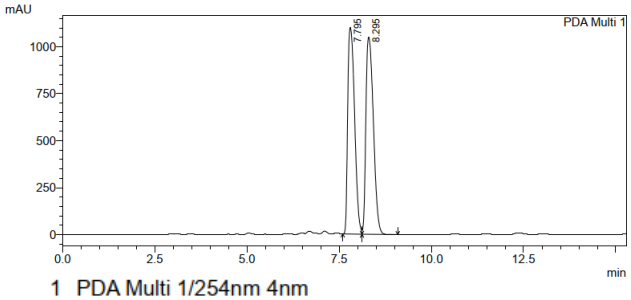
(*S*)-**1-((Tribromomethyl)sulfinyl)hexane 13b**



(*S*)-**13b**

Yield: 67%, purified by ISCO flash column chromatography (4:1 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.35 - 3.28 (m, 1H), 2.74 - 2.67 (m, 1H), 2.00 - 1.88 (m, 2H), 1.60 - 1.47 (m, 2H), 1.38 - 1.32 (m, 4H), 0.91 (t, J = 4.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 57.8, 54.2, 31.4, 28.8, 23.3, 22.5, 14.1.
ESI MS $C_7H_{14}Br_3OS$ m/z $[M+H]^+$ calc. 384.8, found 384.8.
$[\alpha]^{25}_D$ -19.99 (c 0.25, EtOH).
Chiral HPLC Chiralpak AD-H, 5% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**13b**



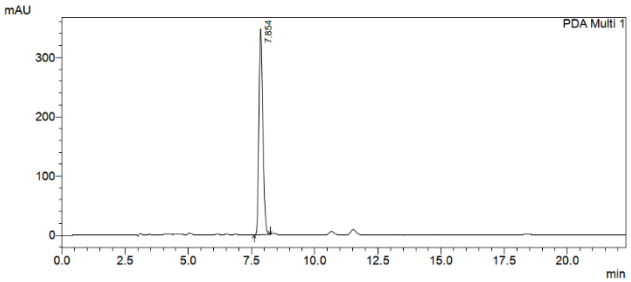
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	7.795	14231983	48.941
2	8.295	14847811	51.059
Total		29079794	100.000

(*S*)-**13b**



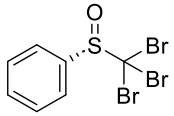
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	7.854	3778755	100.000
Total		3778755	100.000

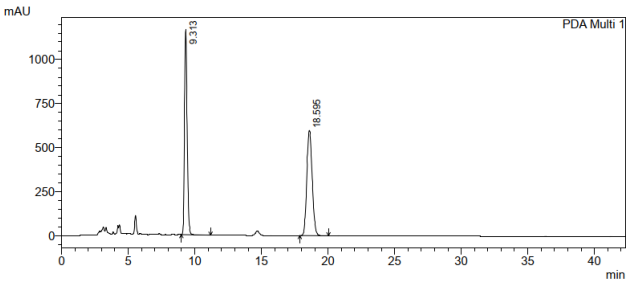
(*S*)-((Tribromomethyl)sulfinyl)benzene 13c



(*S*)-**13c**

Yield: 85%, purified by ISCO flash column chromatography (4:1 hexane:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 - 7.99 (m, 2H), 7.70 - 7.65 (m, 1H), 7.57 - 7.53 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 133.8, 128.6, 61.4.
ESI MS $C_7H_6Br_3OS$ m/z $[M+H]^+$ calc. 376.7, found 376.7.
$[\alpha]^{25}_D$ +17.59 (c 0.25, EtOH).
Chiral HPLC Chiralcel OD-H, 20% IPA/hexanes, 1.0 mL/min, 220nm.

(±)-**13c**



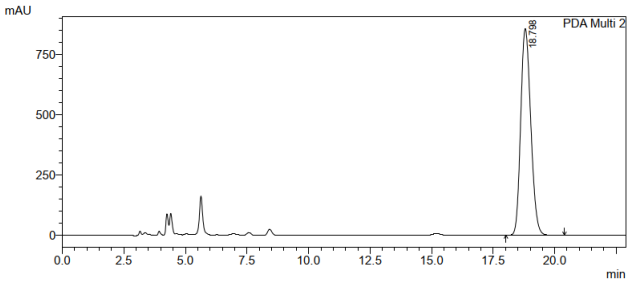
1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.313	16179822	49.259
2	18.595	16666343	50.741
Total		32846165	100.000

(*S*)-**13c**



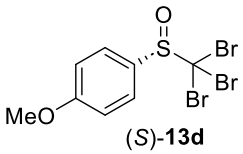
1 PDA Multi 2/220nm 4nm

PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	18.798	24307529	100.000
Total		24307529	100.000

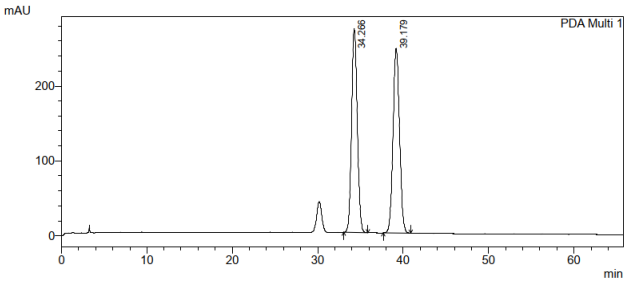
(*S*)-1-Methoxy-4-((tribromomethyl)sulfinyl)benzene 13d



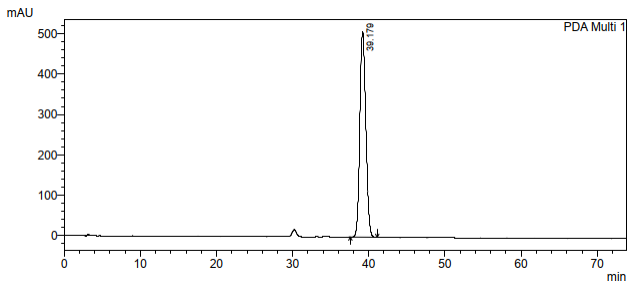
(*S*)-**13d**

Yield: 90%, purified by ISCO flash column chromatography (7:3 hexane:EtOAc v/v).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 - 7.93 (m, 2H), 7.05 - 7.02 (m, 2H), 3.89 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 164.2, 136.1, 130.8, 114.1, 63.4, 55.8.
ESI MS $C_8H_8Br_3O_2S$ m/z $[M+H]^+$ calc. 406.8, found 407.0.
$[\alpha]^{25}_D$ +106.38 (c 0.25, EtOH).
Chiral HPLC Chiralpak IC, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**13d**



(*S*)-**13d**



1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	34.266	12696477	49.249
2	39.179	13083902	50.751
Total		25780379	100.000

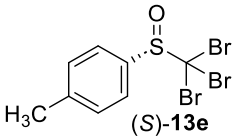
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	39.179	27752985	100.000
Total		27752985	100.000

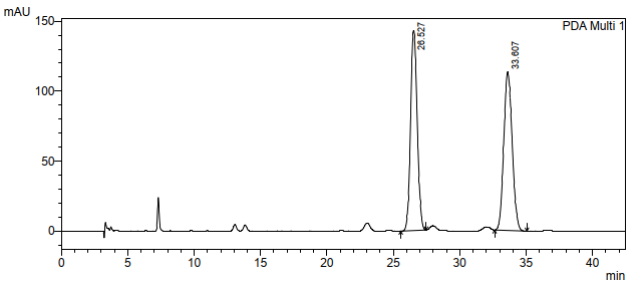
(*S*)-1-Methyl-4-((tribromomethyl)sulfinyl)benzene 13e

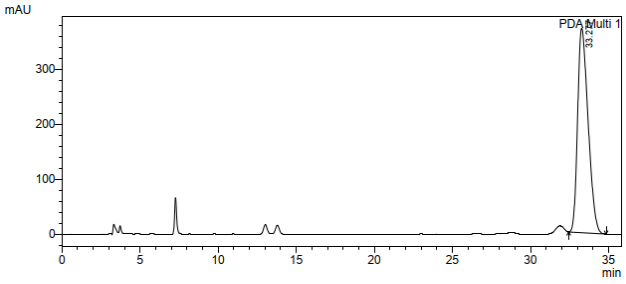


(*S*)-**13e**

Yield: 81%, purified by ISCO flash column chromatography (4:1 hexanes:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 - 7.87 (m, 2H), 7.42 - 7.33 (m, 2H), 2.44 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 136.8, 129.3, 128.5, 62.3, 21.9.
ESI MS $C_8H_8Br_3OS$ m/z $[M+H]^+$ calc. 390.8, found 390.8.
$[\alpha]^{26}_D$ +19.99 (c 0.25, EtOH).
Chiral HPLC Chiralpak IC, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**13e** (*S*)-**13e**





1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	26.527	4980111	49.946
2	33.607	4990819	50.054
Total		9970930	100.000

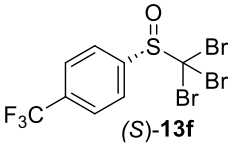
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	33.277	17380630	100.000
Total		17380630	100.000

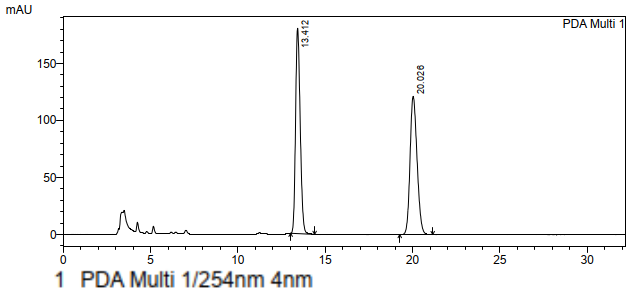
(*S*)-1-((Tribromomethyl)sulfinyl)-4-(trifluoromethyl)benzene 13f



(*S*)-**13f**

Yield: 60%, purified by combi flash column chromatography (7:3 hexanes:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 - 8.15 (m, 2H), 7.88 - 7.81 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 135.2 (q), 129.1, 125.6 (q), 124.8 (q), 59.4.
ESI MS $C_8H_5Br_3F_3OS$ m/z $[M+H]^+$ calc. 444.7, found 444.7.
$[\alpha]^{25}_D$ +19.19 (c 0.125, EtOH).
Chiral HPLC Chiralpak IC, 10% IPA/hexanes, 1.0 mL/min, 254nm.

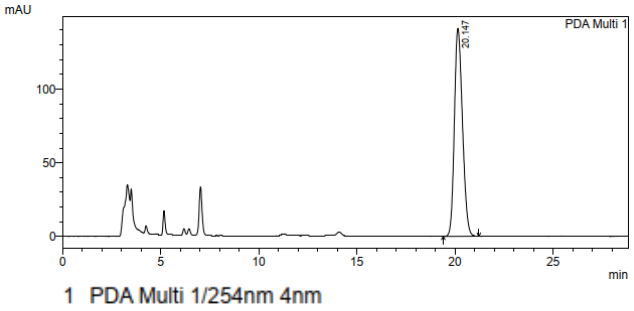
(±)-**13f** (*S*)-**13f**



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	13.412	3323936	49.589
2	20.026	3378995	50.411
Total		6702930	100.000

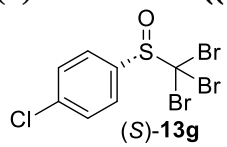


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	20.147	4040017	100.000
Total		4040017	100.000

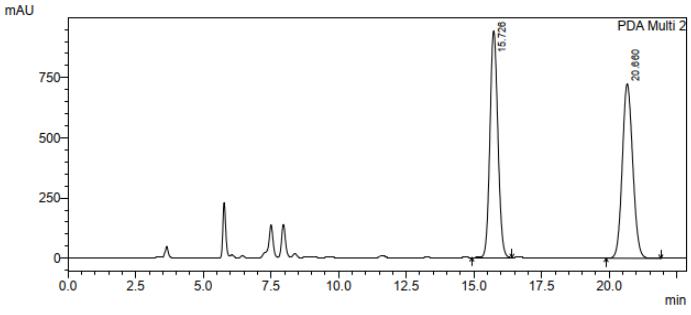
(*S*)-1-Chloro-4-((tribromomethyl)sulfinyl)benzene 13g



(*S*)-**13g**

Yield: 65%, purified by ISCO flash column chromatography (7:3 hexanes:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 138.4, 129.8, 128.9, 60.9.
ESI MS C_6H_5ClOS m/z $[M+H]^+$ calc. 410.7, found 410.7.
$[\alpha]^{25}_D$ +19.63 (c 0.275, EtOH).
Chiral HPLC Chiralpak IC, 10% IPA/hexanes, 1.0 mL/min, 229nm.

(±)-**13g**

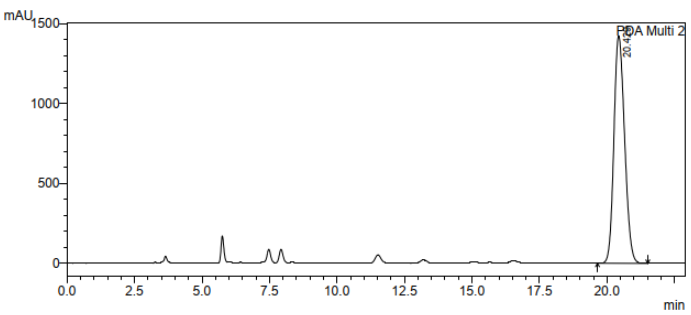


PeakTable

PDA Ch2 229nm 4nm

Peak#	Ret. Time	Area	Area %
1	15.726	19271228	49.738
2	20.660	19474457	50.262
Total		38745685	100.000

(*S*)-**13g**

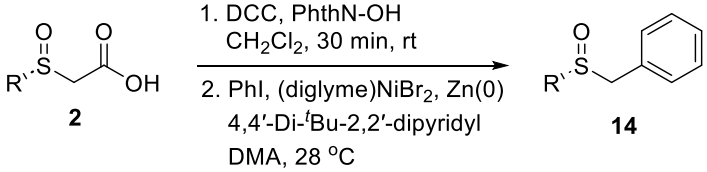


PeakTable

PDA Ch2 229nm 4nm

Peak#	Ret. Time	Area	Area %
1	20.429	39261407	100.000
Total		39261407	100.000

XIV. General procedure for the Coupling of N-(acyloxy)Phthalimides and Aryl Iodides

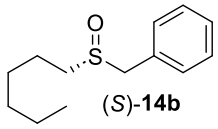


To a solution of carboxylic acid **2** (0.15 mmol, 1.0 equiv) and NHPI (26 mg, 0.16 mmol, 1.2 equiv) in anhydrous CH_2Cl_2 (1.0 mL) was added DCC (33mg, 0.16 mmol, 1.2 equiv). The reaction was monitored by LCMS (typical time was 30 min). After consumption of all starting material, the solvent was removed on a rotary evaporator at 35 °C under reduced pressure and dried on a high-vacuum line for at least 5 minutes to remove residue of CH_2Cl_2. The resulting crude was used for the next reaction.

The catalyst (dtbbpy)$NiBr_2$ was generated by pre-stirring of $NiBr_2$(diglyme) (5.0 mg, 0.014 mmol) and 4-4′-di-tert-butyl-2,2′-bipyridine (4.0 mg, 0.014 mmol) in DMA (0.2 mL) for ~10 min.

Reactions were set up in a nitrogen filled glove box. To an oven-dried 1-dram vial fitted with a Teflon-coated stir-bar was added above prestirred (dtbbpy)$NiBr_2$ (14 mol%, 0.2 mL), N-(acyloxy)phthalimide (0.15 mmol, 1.5 equiv), aryl iodide (11μL, 0.1 mmol, 1.0 equiv), zinc powder (13mg, 0.2 mmol, 2.0 equiv), and DMA (0.4 mL). The vial was capped and removed from the glove box, and heated in a reaction block set to 28 °C on the benchtop with stirring until the reaction was complete as monitored by LCMS. Upon reaction completion the reaction mixture was filtered through a short plug of silica gel to remove metal salts and eluted with diethyl ether. DMA was removed by adding water to the organic layer and extracting the aqueous layer with diethyl ether (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by ISCO flash chromatography to afford the pure product **14**.

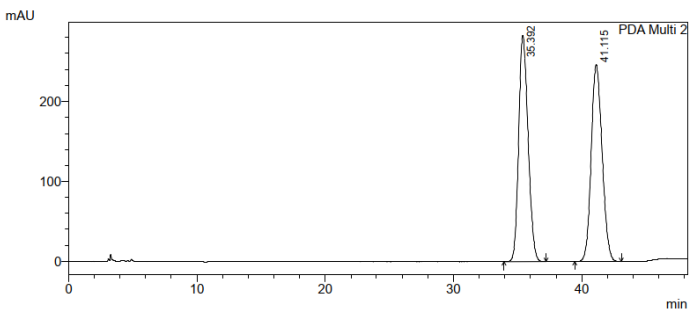
(*S*)-**((Hexylsulfinyl)methyl)benzene 14b**



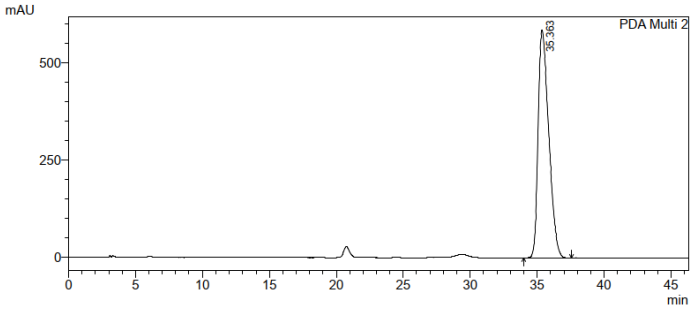
(*S*)-**14b**

Yield: 68%, purified by ISCO flash column chromatography (4:1 hexanes:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.28 (m, 5H), 4.02 (d, J = 12.0 Hz, 1H), 3.93 (d, J = 16.0 Hz, 1H), 2.58 - 2.54 (m, 2H), 1.79 - 1.68 (m, 2H), 1.49 - 1.23 (m, 6H), 0.87 (t, J = 8.0 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 130.2, 129.2, 128.5, 58.3, 50.9, 31.5, 28.6, 22.6, 22.5, 14.1.
ESI MS $C_{13}H_{21}OS$ m/z $[M+H]^+$ calc. 225.1, found 225.2.
$[\alpha]^{25}_D$ +7.99 (c 0.125, EtOH)
Chiral HPLC Chiralpak IC, 10% IPA/hexanes, 1.0 mL/min, 229nm.

(±)-**14b**



(*S*)-**14b**



1 PDA Multi 2/229nm 4nm

PeakTable

PDA Ch2 229nm 4nm

Peak#	Ret. Time	Area	Area %
1	35.392	14469245	49.817
2	41.115	14575806	50.183
Total		29045051	100.000

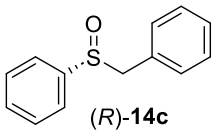
1 PDA Multi 2/229nm 4nm

PeakTable

PDA Ch2 229nm 4nm

Peak#	Ret. Time	Area	Area %
1	35.363	32337106	100.000
Total		32337106	100.000

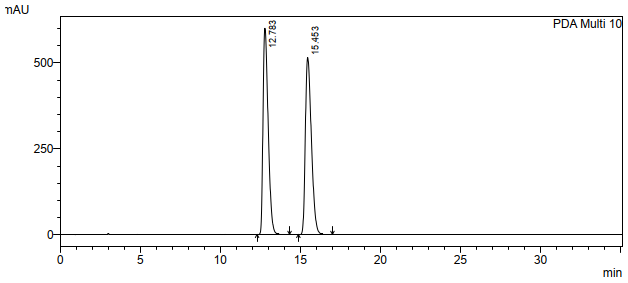
(*R*)-(Benzylsulfinyl)benzene 14c



(*R*)-**14c**

Yield: 70%, purified by ISCO flash column chromatography (4:1 hexanes:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 - 7.36 (m, 4H), 7.29 - 7.22 (m, 3H), 7.00 - 6.96 (m, 2H), 4.09 (d, J = 12.0 Hz, 1H), 3.99 (d, J = 12.0 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 131.3, 130.5, 129.3, 128.9, 128.6, 128.4, 124.6, 63.8.
ESI MS $C_{13}H_{13}OS$ m/z $[M+H]^+$ calc. 217.0, found 217.0.
$[\alpha]^{25}_D$ +199.95 (c 0.135, EtOH)
Chiral HPLC Chiralcel OD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**14c**



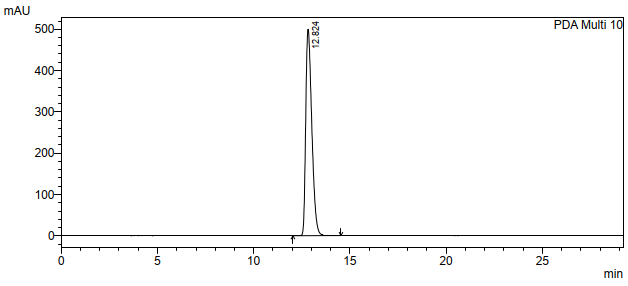
1 PDA Multi 10/254nm 4nm

PeakTable

PDA Ch10 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.783	13396725	49.819
2	15.453	13493806	50.181
Total		26890531	100.000

(*R*)-**14c**



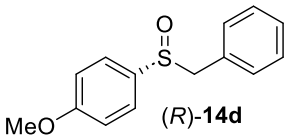
1 PDA Multi 10/254nm 4nm

PeakTable

PDA Ch10 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.824	10936443	100.000
Total		10936443	100.000

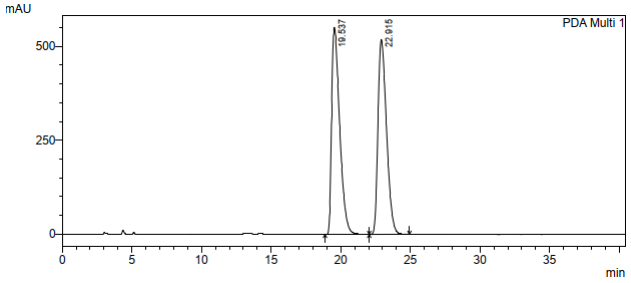
(*R*)-1-(Benzylsulfinyl)-4-methoxybenzene 14d



(*R*)-**14d**

Yield: 71%, purified by ISCO flash column chromatography (3:2 hexanes:EtOAc v/v)..
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 - 7.26 (m, 5H), 7.01 - 6.99 (m, 2H), 6.96 - 6.93 (m, 2H), 4.14 (d, J = 12.0 Hz, 1H), 3.98 (d, J = 12.0 Hz, 1H), 3.86 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 162.2, 133.6, 130.5, 129.4, 128.6, 128.3, 126.5, 114.5, 63.8, 55.6.
ESI MS $C_{14}H_{15}O_2S$ m/z $[M+H]^+$ calc. 247.1, found 247.1
$[\alpha]^{25}_D$ +155.96 (c 0.25, EtOH)
Chiral HPLC Chiralcel OD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**14d**



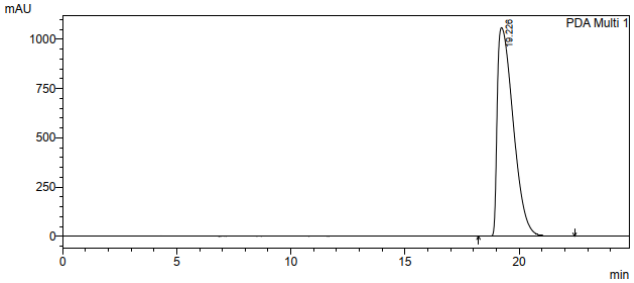
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	19.537	22207029	49.989
2	22.915	22217029	50.011
Total		44424058	100.000

(*R*)-**14d**



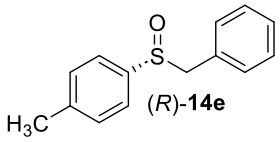
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

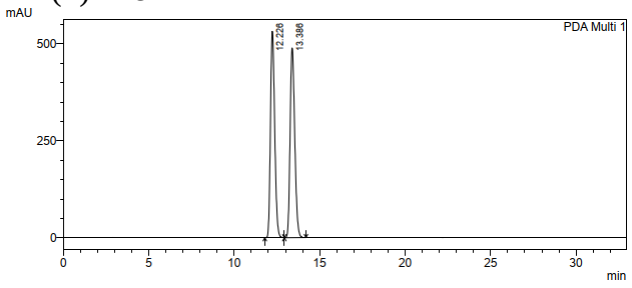
Peak#	Ret. Time	Area	Area %
1	19.226	51518941	100.000
Total		51518941	100.000

(*R*)-**1-(Benzylsulfinyl)-4-methylbenzene 14e**



Yield: 67%, purified by ISCO flash column chromatography (4:1 hexanes:EtOAc v/v).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 - 7.24 (m, 7H), 7.03 - 7.01 (m, 2H), 4.12 (d, J = 18.0 Hz, 1H), 3.99 (d, J = 12.0 Hz, 1H), 2.42 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 141.8, 139.7, 130.5, 129.7, 129.5, 128.6, 128.3, 124.6, 63.8, 21.6.
ESI MS $C_{14}H_{15}OS$ m/z $[M+H]^+$ calc. 231.1, found 231.0
$[\alpha]^{25}_D$ +193.55 (c 0.25, EtOH)
Chiral HPLC Chiralpak AD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**14e**



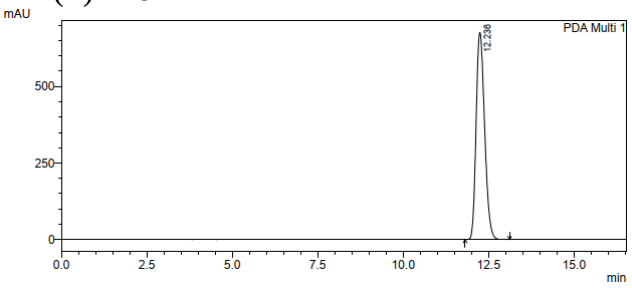
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.226	9156602	49.857
2	13.386	9209275	50.143
Total		18365877	100.000

(*R*)-**14e**



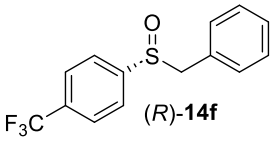
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

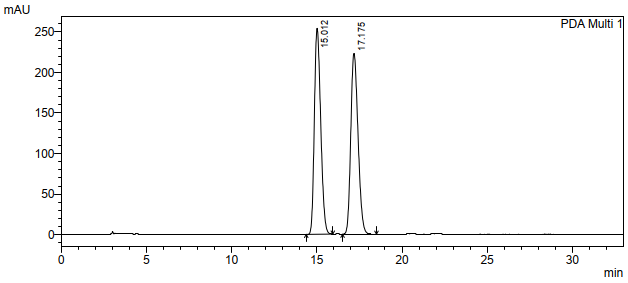
Peak#	Ret. Time	Area	Area %
1	12.236	11713550	100.000
Total		11713550	100.000

(*R*)-**1-(Benzylsulfinyl)-4-(trifluoromethyl)benzene 14f**



Yield: 65%, purified by ISCO flash column chromatography (3:1 hexanes:EtOAc v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.36 - 7.27 (m, 3H), 7.01 - 6.98 (m, 2H), 4.14 (d, J = 12.0 Hz, 1H), 4.06 (d, J = 12.0 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 147.3, 133.2 (q), 130.5, 128.8, 128.7, 128.5, 125.9 (q), 125.1, 124.5 (q), 63.5.
ESI MS $C_{14}H_{12}F_3OS$ m/z $[M+H]^+$ calc. 285.0, found 285.0.
$[\alpha]^{25}_D$ +208.84 (c 0.09, EtOH)
Chiral HPLC Chiralpak IC, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**14f**

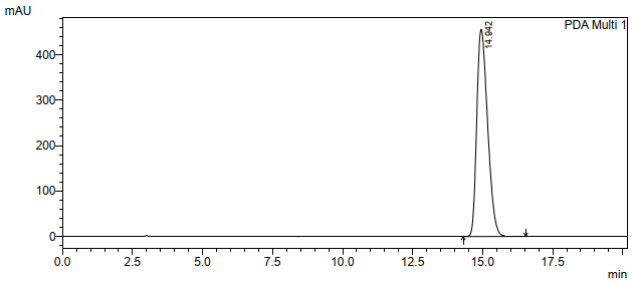


1 PDA Multi 1/254nm 4nm

PeakTable
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	15.012	6566897	49.914
2	17.175	6589572	50.086
Total		13156469	100.000

(*R*)-**14f**

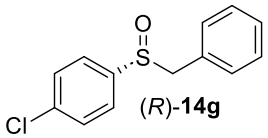


1 PDA Multi 1/254nm 4nm

PeakTable
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	14.942	12294310	100.000
Total		12294310	100.000

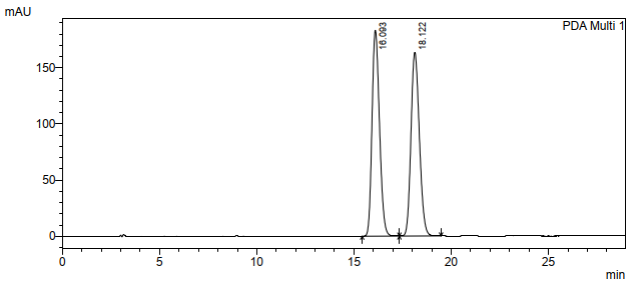
(*R*)-**1-(Benzylsulfinyl)-4-chlorobenzene 14g**



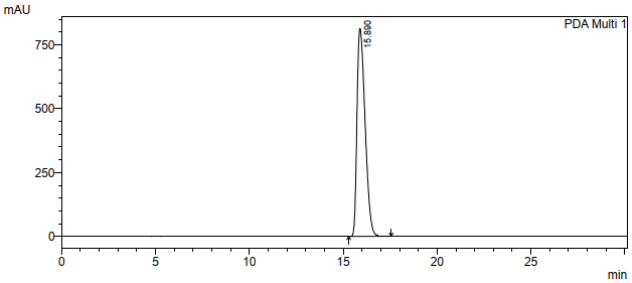
(*R*)-**14g**

Yield: 67%, purified by ISCO flash column chromatography (7:3 hexanes:EtOAc v/v).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 - 7.40 (m, 2H), 7.34 - 7.28 (m, 5H), 7.01 - 6.99 (m, 2H), 4.13 (d, J = 12.0 Hz, 1H), 4.01 (d, J = 12.0 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 141.3, 137.5, 130.5, 129.3, 128.7, 128.6, 126.0, 63.6.
ESI MS $C_{13}H_{12}ClOS$ m/z $[M+H]^+$ calc. 251.0, found 251.0.
$[\alpha]^{25}_D$ +193.29 (c 0.09, EtOH)
Chiral HPLC Chiralcel OD-H, 10% IPA/hexanes, 1.0 mL/min, 254nm.

(±)-**14g**



(*R*)-**14g**



1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	16.093	4903027	49.986
2	18.122	4905850	50.014
Total		9808877	100.000

1 PDA Multi 1/254nm 4nm

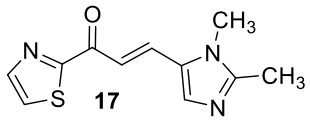
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	15.890	24413170	100.000
Total		24413170	100.000

XV Synthesis of sulfoxide inhibitors of 15-prostaglandin dehydrogenase (15-PGDH).

(*E*)-3-(1,2-dimethyl-1H-imidazol-5-yl)-1-(thiazol-2-yl)prop-2-en-1-one 17



17

To a solution of 1,2-dimethyl-1H-imidazole-5-carbaldehyde **15** (100 mg, 0.80 mmol, 1.0 equiv) and 1-(thiazol-2-yl)ethan-1-one **16** (102 mg, 0.80 mmol, 1.0 equiv) in EtOH (3 mL) was added piperidine (0.16 mL, 1.61 mmol, 2.0 equiv) at 25°C. The resulting solution was stirred at 90°C for 2 h. After that the solution was concentrated in vacuum to give a residue which was suspended in MTBE, and filtered. The filter cake was washed with MTBE and dried in vacuum to give the crude product. The crude product was again triturated with EtOAc, filtered and the filter cake was dried in vacuum to give the desired product **17** as a yellow solid which was used without additional purification.

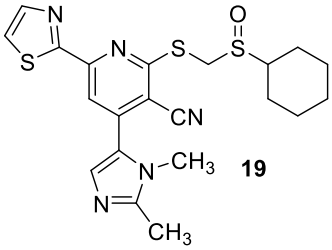
Yield: 62%.

^{1}H NMR (400 MHz, DMSO) δ 8.22 (d, J = 4.0 Hz, 1H), 8.18 (d, J = 4.0 Hz, 1H), 7.83 - 7.65 (m, 3H), 3.67 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 180.5, 168.1, 150.2, 145.1, 133.5, 131.4, 129.3, 127.9, 115.4, 30.8, 13.4.

ESI MS. $C_{11}H_{12}N_3OS$ m/z $[M+H]^+$ calc. 234.0, found 234.1.

2-(((Cyclohexylsulfinyl)methyl)thio)-4-(1,2-dimethyl-1H-imidazol-5-yl)-6-(thiazol-2-yl)nicotinonitrile 19



19

To a solution of compound **17** (25 mg, 0.11 mmol, 1.0 equiv) and 2-cyanoethanethioamide (17 mg, 0.17 mmol, 1.6 equiv) in CH_3CN (2 mL) was added TEA (29 μL, 0.21 mmol, 2.0 equiv) at 25°C and stirred at 80°C for 2 h (the progress of the reaction was monitored by LCMS). The reaction mixture was cooled and TEA (29 μL, 0.21 mmol, 2.0 equiv) and ((bromomethyl)sulfinyl)cyclohexane **4a** (26 mg, 0.12 mmol, 1.1 equiv, racemic, (*R*) or (*S*) separately) were added. The resulting mixture was stirred at 80°C for 12 h, then cooled, poured into water and extracted with EtOAc (3 × 10 mL). The combined extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product

which was purified by ISCO flash column chromatography to give the desired product **19** as a brown solid.

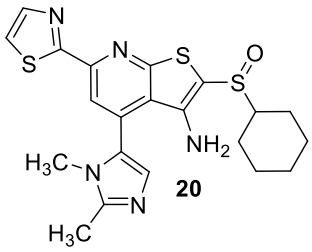
Yield: 46-51%, purified by ISCO flash column chromatography (49:1 DCM:MeOH v/v).

^{1}H NMR (400 MHz, MeOD) δ 8.04 (d, J = 4.0 Hz, 1H), 8.00 (s, 1H), 7.89 (d, J = 4.0 Hz, 1H), 7.41 (s, 1H), 4.95 (d, J = 16.0 Hz, 1H), 4.62 (d, J = 12.0 Hz, 1H), 3.69 (s, 3H), 2.97 (tt, J = 12.0, 4.0 Hz, 1H), 2.50 (s, 3H), 2.18 - 2.10 (m, 1H), 2.10 - 2.01 (m, 1H), 1.99 - 1.85 (m, 2H), 1.77 - 1.72 (m, 1H), 1.66 - 1.53 (m, 2H), 1.52 - 1.39 (m, 2H), 1.36 - 1.22 (m, 1H).

^{13}C NMR (101 MHz, MeOD) δ 167.7, 162.4, 153.5, 151.3, 146.2, 144.7, 131.2, 128.5, 125.7, 116.2, 115.7, 106.8, 59.7, 54.8, 47.8, 32.7, 28.3, 26.6, 26.1, 24.9, 13.2.

ESI MS: $C_{21}H_{24}N_5OS_3$ m/z $[M+H]^+$ calc. 458.1, found 458.2.

2-(Cyclohexyl sulfinyl)-4-(1,2-dimethyl-1H-imidazol-5-yl)-6-(thiazol-2-yl) thieno[2,3-b]pyridin-3-amine 20



20

To a solution of sulfoxide derivative **19** (26 mg, 0.05 mmol) in DMF (1 mL) and MeOH (0.5 ml) was added KOH (4 mg, 0.68 mmol, in 20 μL water) at 25°C, the resulting solution was stirred at 25°C for 20 min (the progress of the reaction was monitored by TLC). Then the reaction mixture was poured into water, and extracted with EtOAc (3 × 10 mL). The combined extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product which was purified by ISCO flash column chromatography to give the product **20** as a yellow solid.

Yield: 58-63%, purified by ISCO flash column chromatography (19:1 DCM:MeOH v/v).

^{1}H NMR (400 MHz, MeOD) δ 8.03 (s, 1H), 7.96 (d, J = 4.0 Hz, 1H), 7.77 (d, J = 4.0 Hz, 1H), 7.15 (s, 1H), 3.45 (s, 3H), 3.17 (tt, J = 12.0, 4.0 Hz, 1H), 2.49 (s, 3H), 2.27 - 2.25 (m, 1H), 1.97 - 1.90 (m, 1H), 1.83 - 1.79 (m, 1H), 1.77 - 1.67 (m, 2H), 1.65 - 1.55 (m, 1H), 1.48 - 1.35 (m, 2H), 1.37 - 1.26 (m, 2H).

^{13}C NMR (151 MHz, MeOD) δ 169.1, 163.3, 151.4, 149.5, 145.5, 128.4, 128.2, 125.4, 124.3, 119.8, 64.7, 31.8, 27.8, 26.9, 26.6, 26.2, 26.1, 13.1.

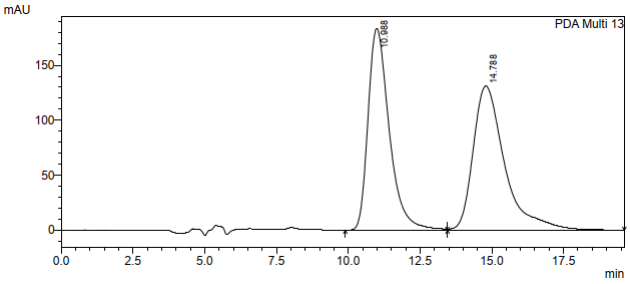
ESI MS: $C_{21}H_{24}N_5OS_3$ m/z $[M+H]^+$ calc. 458.1, found 458.2

$[\alpha]^{24}_D$ of (*S*)-**20** -92.36 (c 0.21, EtOH).

$[\alpha]^{24}_D$ of (*R*)-**20** +93.50 (c 0.216, EtOH).

Chiral HPLC Chiralcel OD-H, 60% IPA/hexanes, 0.7 mL/min, 254nm.

(±)-**20**



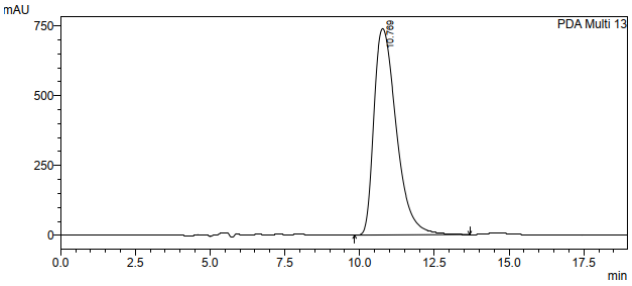
1 PDA Multi 13/254nm 4nm

PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.988	9439844	48.458
2	14.788	10040564	51.542
Total		19480408	100.000

(*S*)-**20**



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PeakTable

PDA Ch13 254nm 4nm

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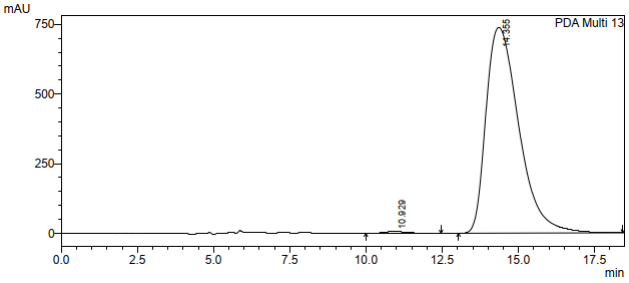
Total		38617955	100.000

(*R*)-**20**



1 PDA Multi 13/254nm 4nm

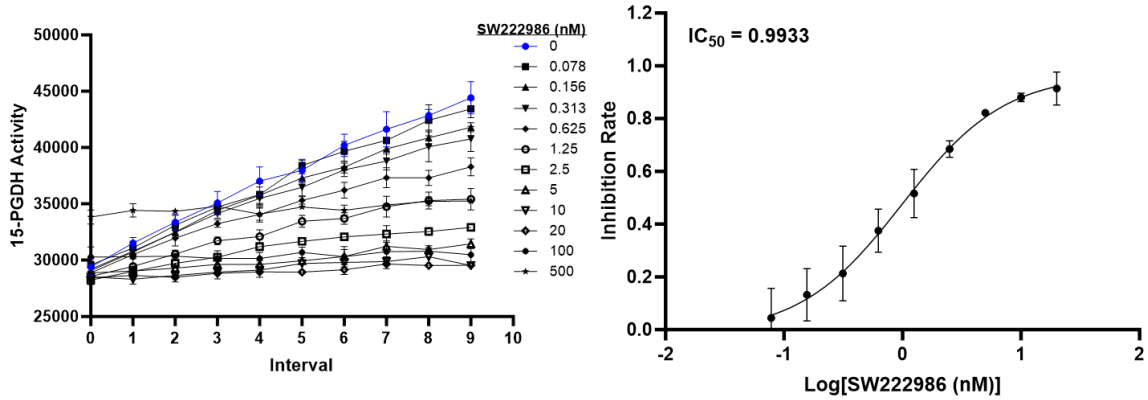
PeakTable

PDA Ch13 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.929	355596	0.637
2	14.355	55453810	99.363
Total		55809405	100.000

IC_{50} determination for inhibitors of 15-PGDH. Assays of 15-PGDH enzyme activity were carried out at 2 nM 15-PGDH, 300 μM NAD^+, 50 mM Tris-HCl, pH 7.5, 0.01% Tween 20, 0.1 mM DTT and 40 μM PGE2 (Sigma, cat. #P5640). Activity was determined as the rate of NADH generation as determined by fluorescence (Ex/Em=340 nM/485 nM) measured every 15 s for 3.5 min as described previously.[2] The IC_{50} values were calculated with GraphPad Prism 7 software (http://www.graphpad.com/scientific-software/prism/).

A.



B.

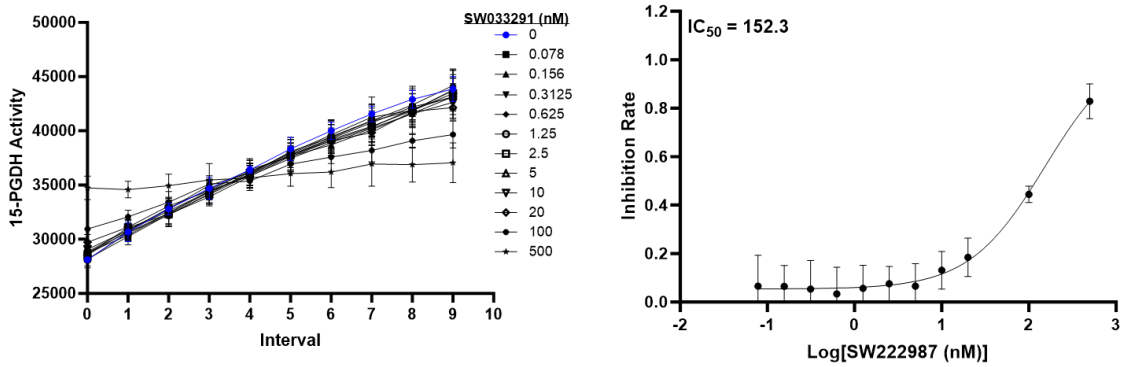
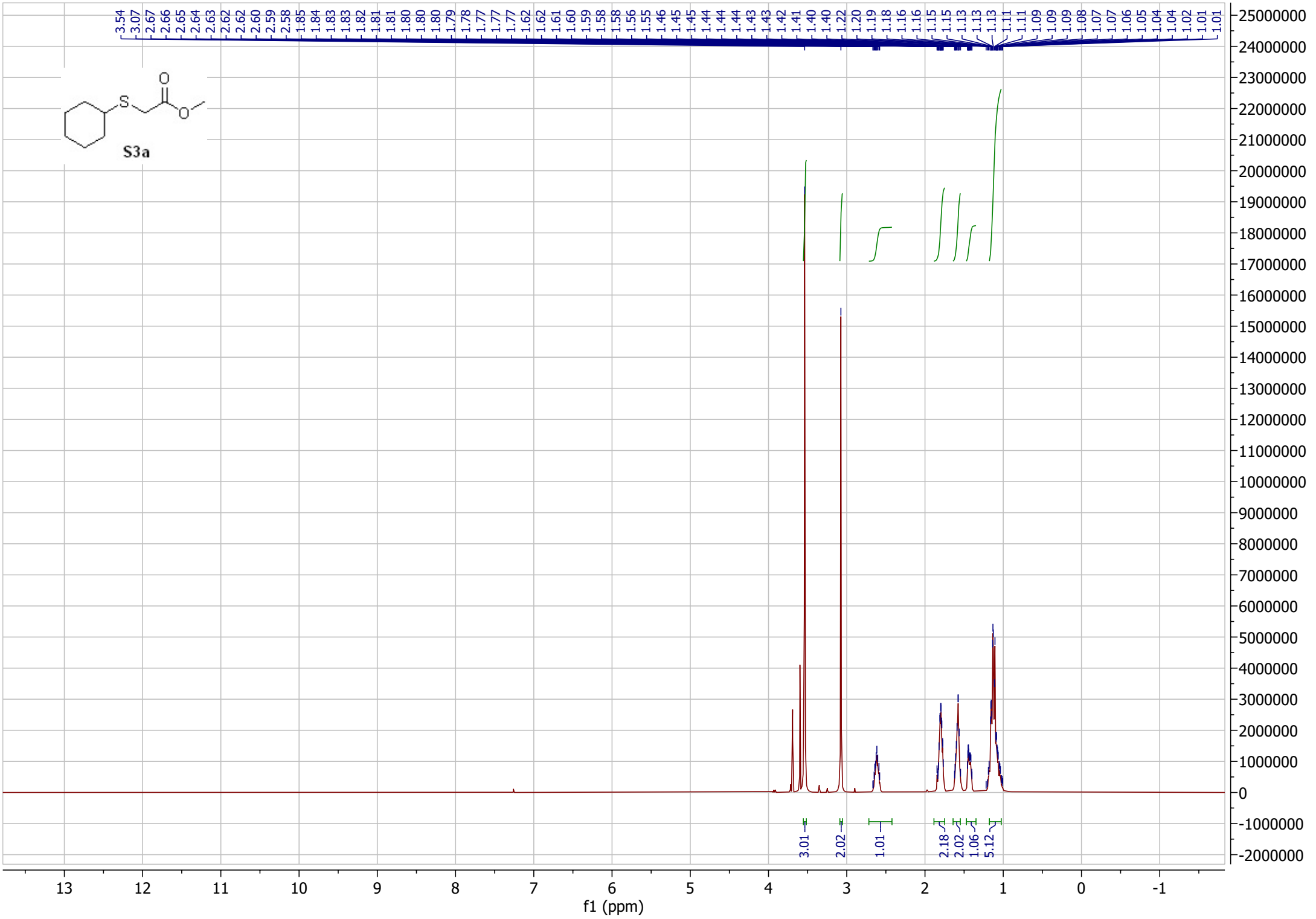


Figure S1. Enzyme activity and processed data for inhibition of 15-PGDH by A) (*R*)-**20** (aka SW222986) and B) (*S*)-**20** (aka SW222987).

1. K. Burgess, I. Henderson, *Tetrahedron Lett*. **1989**, *30*, 3633-3636.
2. M. I. Antczak, Y. Zhang, C. Wang, J. Doran, J. Naidoo, S. Voruganti, N. S. Williams, S. D. Markowitz, J. M. Ready, *J. Med. Chem.* **2017**, *60*, 3979-4001


S3a
3.54 3.07 2.67 2.66 2.65 2.64 2.63 2.62 2.62 2.60 2.59 2.58 1.85 1.84 1.83 1.83 1.82 1.81 1.81 1.80 1.80 1.80 1.79 1.78 1.77 1.77 1.77 1.62 1.61 1.60 1.59 1.58 1.58 1.56 1.55 1.46 1.45 1.44 1.44 1.44 1.43 1.43 1.42 1.41 1.40 1.40 1.22 1.20 1.19 1.18 1.16 1.16 1.15 1.15 1.13 1.13 1.13 1.11 1.11 1.09 1.09 1.09 1.08 1.07 1.07 1.06 1.05 1.04 1.04 1.02 1.01 1.01
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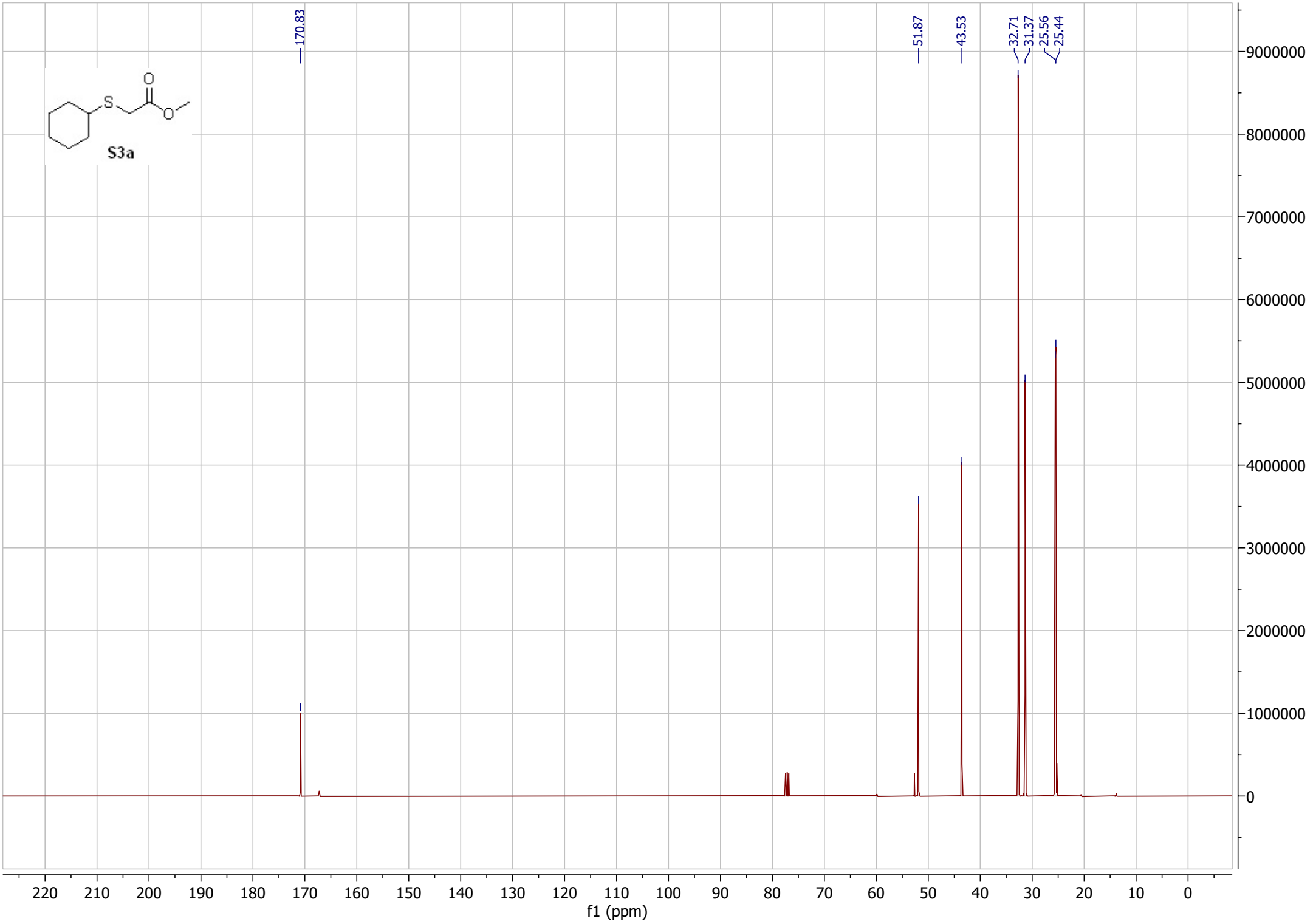
1.01
2.18
2.02
1.06
5.12
f1 (ppm)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51.87
43.53
32.71
31.37
25.56
25.44
S3a
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8000000
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6000000
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4000000
3000000
2000000
1000000
0
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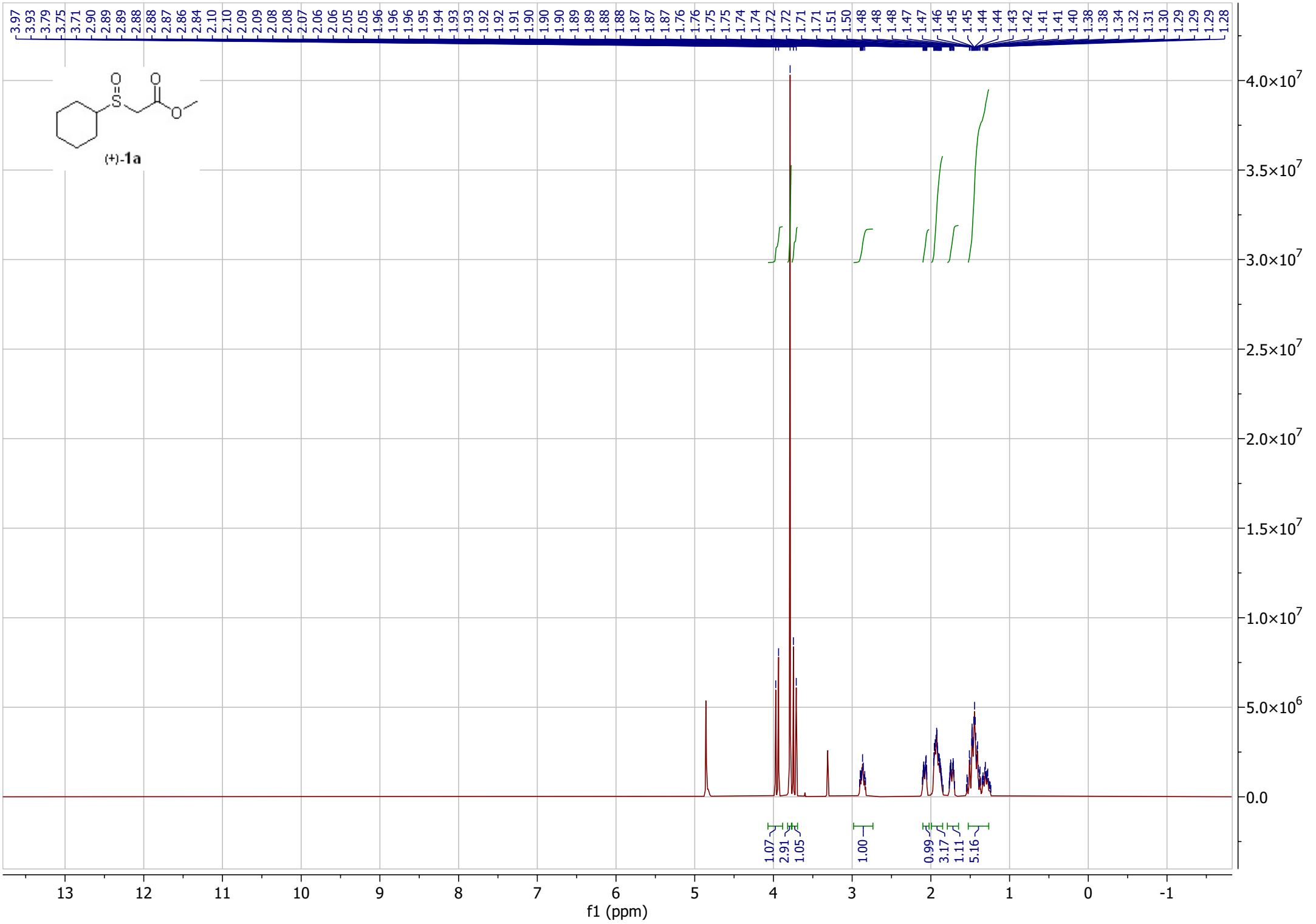
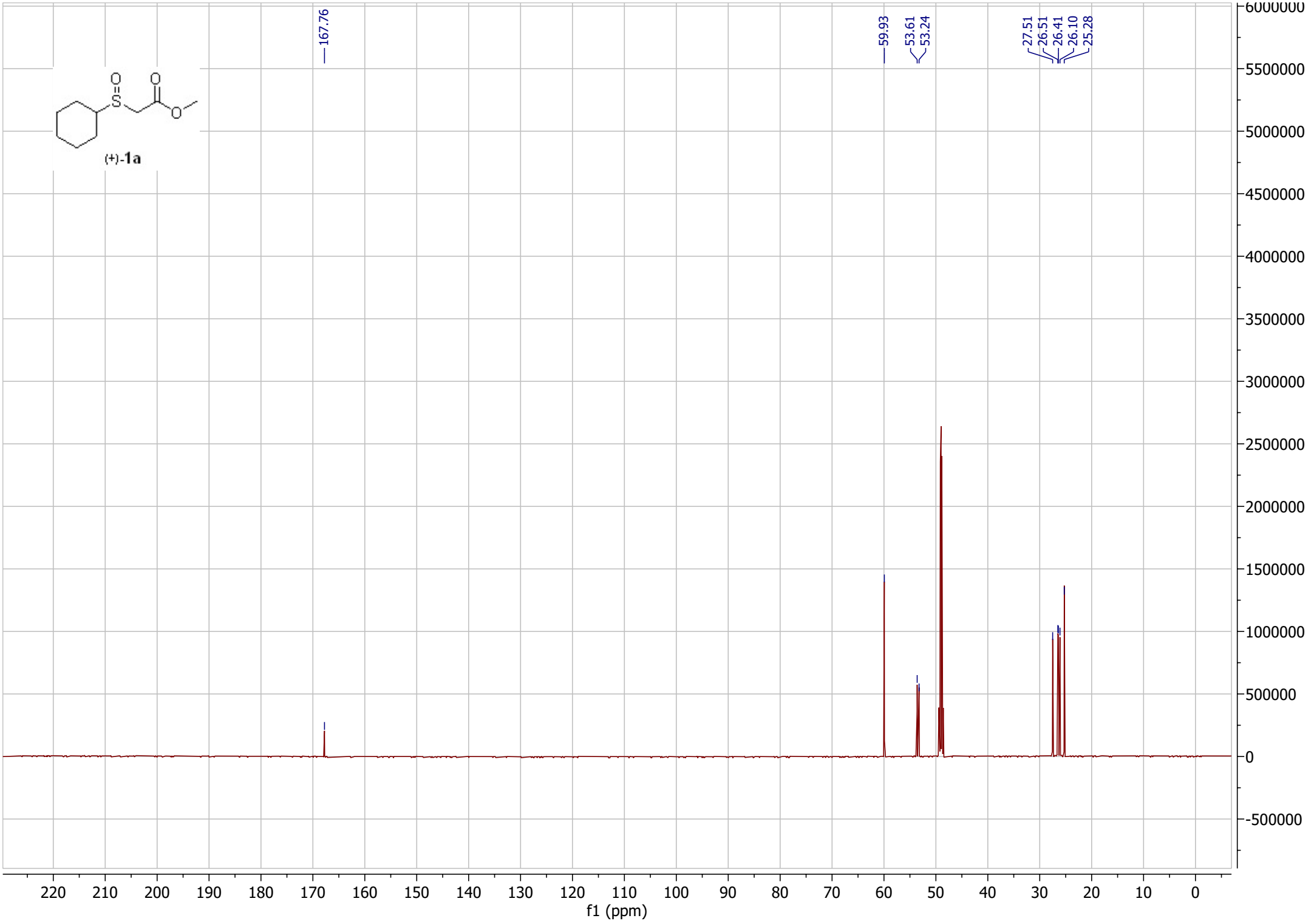
f1 (ppm)


(+)-1a
f1 (ppm)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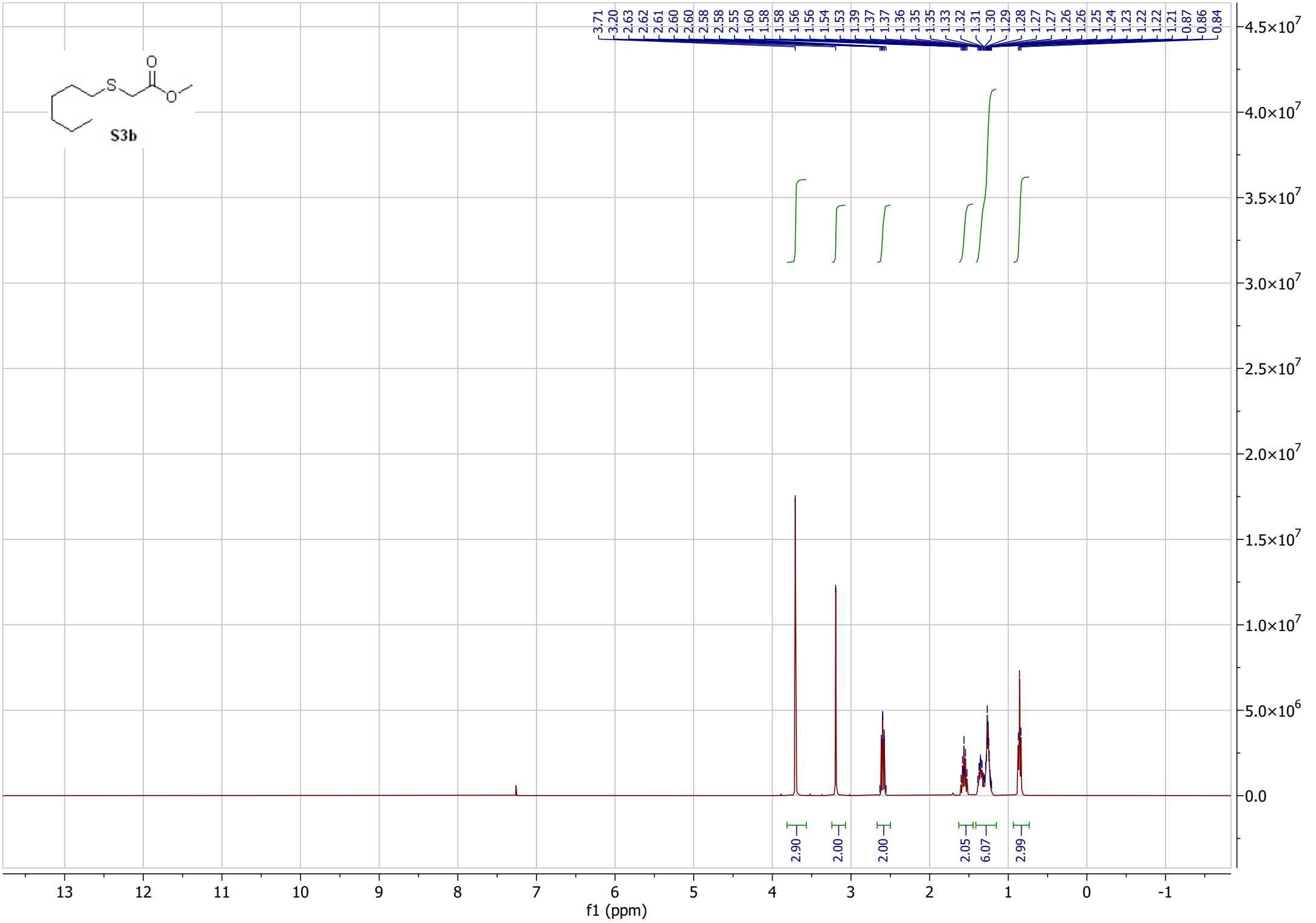
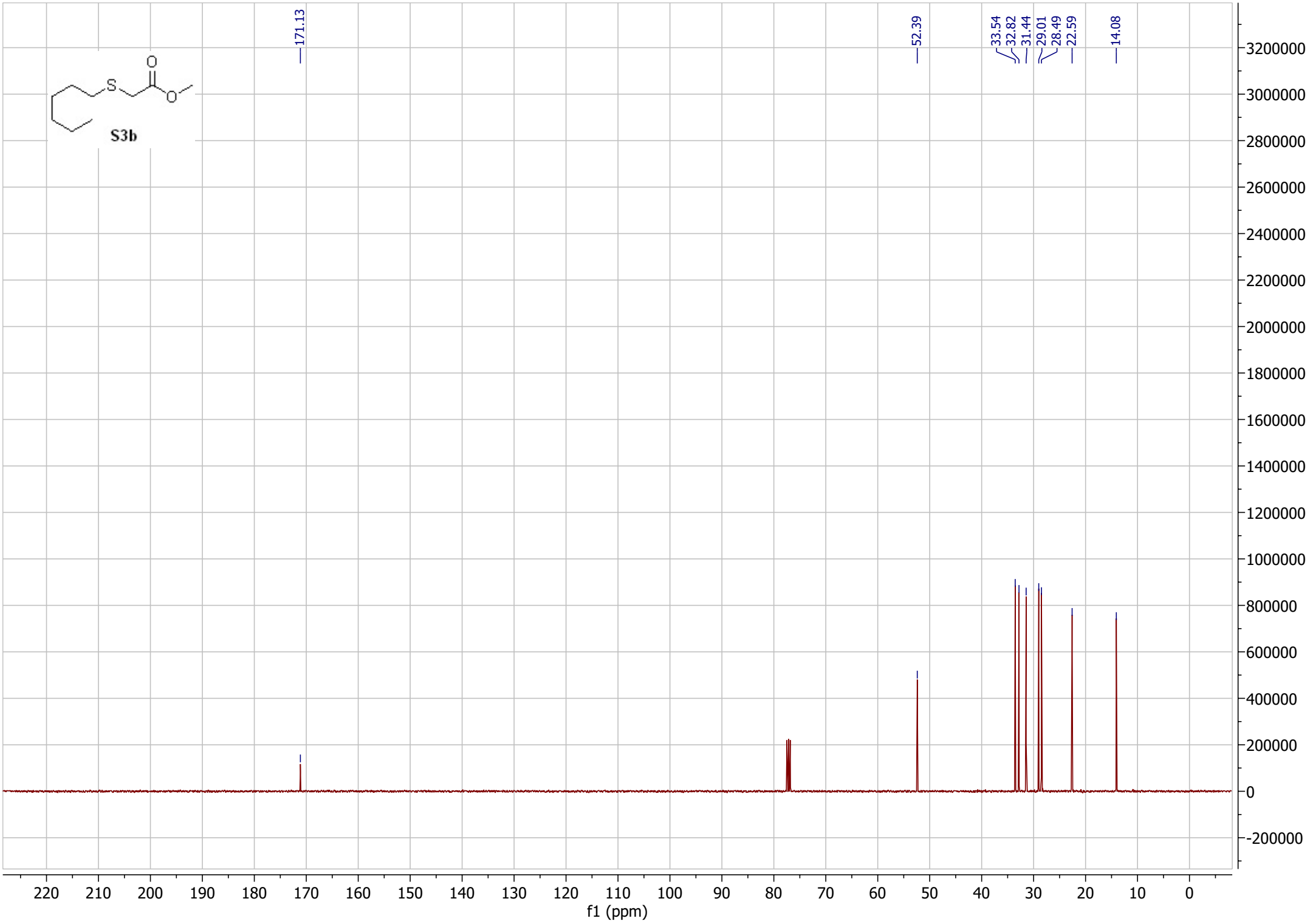
53.24
27.51
26.51
26.41
26.10
25.28
(+)-1a
f1 (ppm)


S3b
3.71 3.20 2.63 2.62 2.61 2.60 2.60 2.58 2.58 2.55 1.60 1.58 1.58 1.56 1.56 1.54 1.53 1.39 1.37 1.37 1.36 1.35 1.35 1.33 1.32 1.31 1.30 1.29 1.28 1.27 1.27 1.26 1.26 1.25 1.24 1.23 1.22 1.22 1.21 0.87 0.86 0.84
2.90
2.00
2.00
2.05
6.07
2.99
f1 (ppm)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32.82
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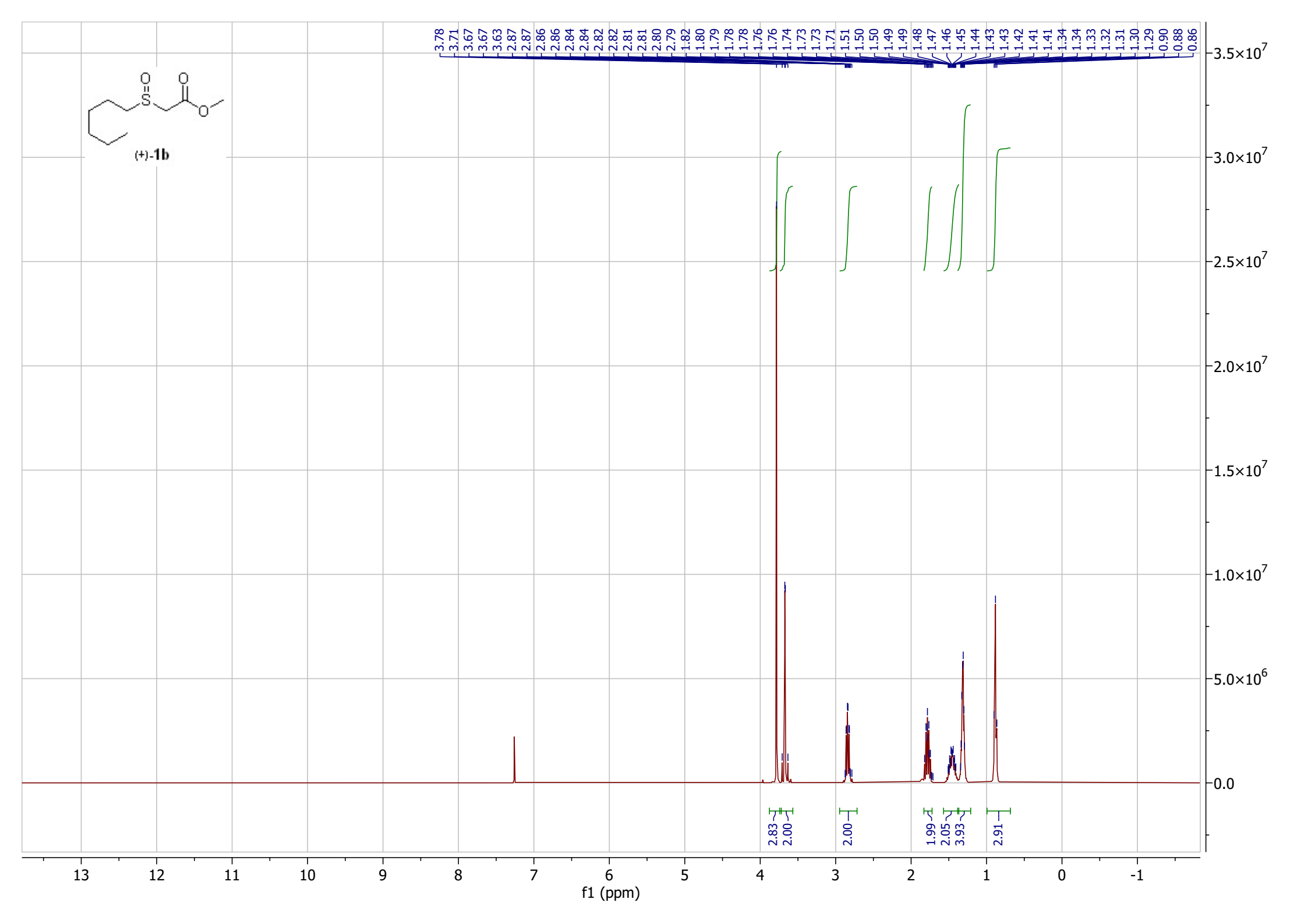
29.01
28.49
22.59
14.08
S3b
f1 (ppm)


(+)-1b
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3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
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2.83 2.00 2.00 1.99 2.05 3.93 2.91
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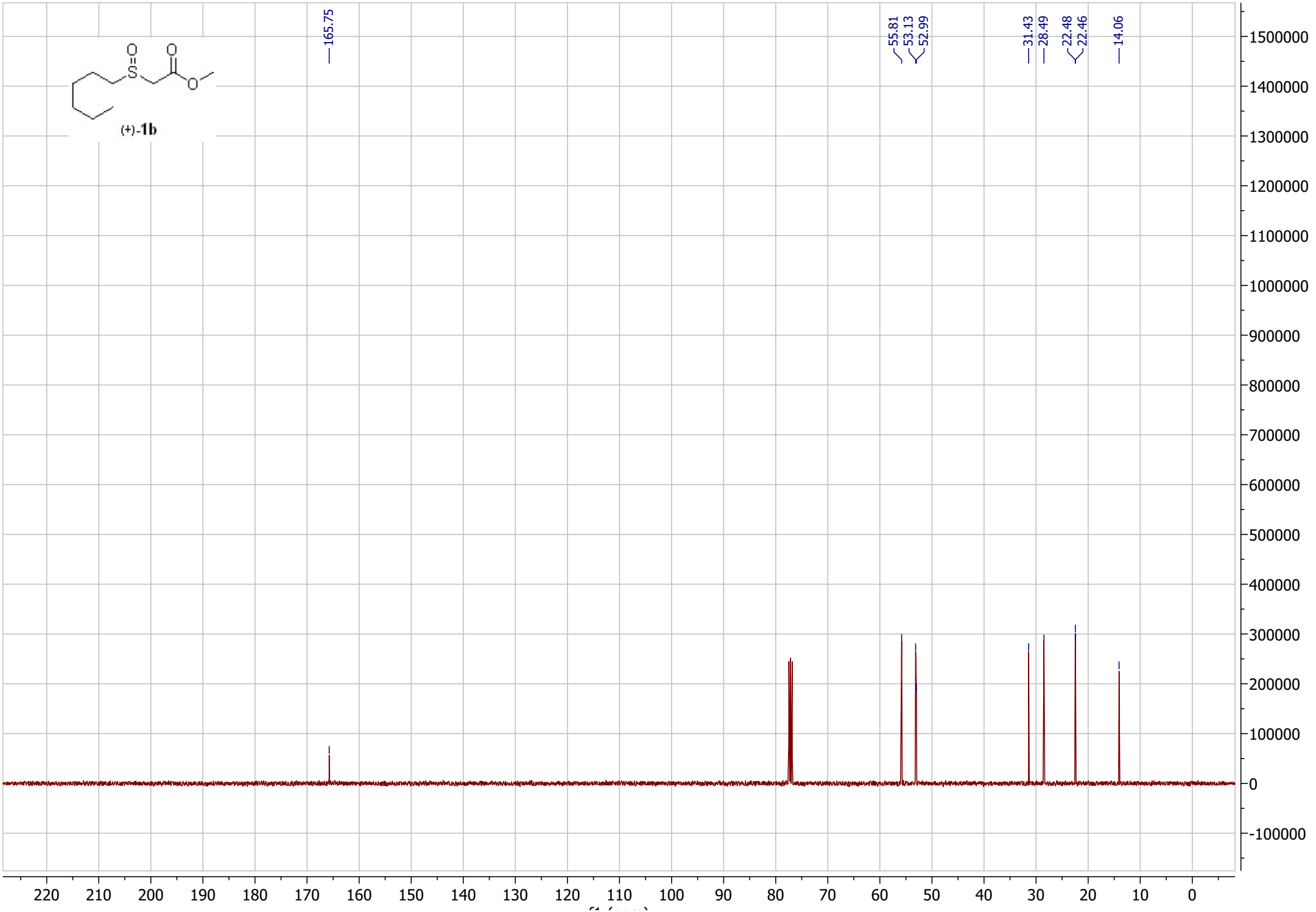
f1 (ppm)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22.48
22.46
14.06
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1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
220
210
200
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150
140
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70
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30
20
10
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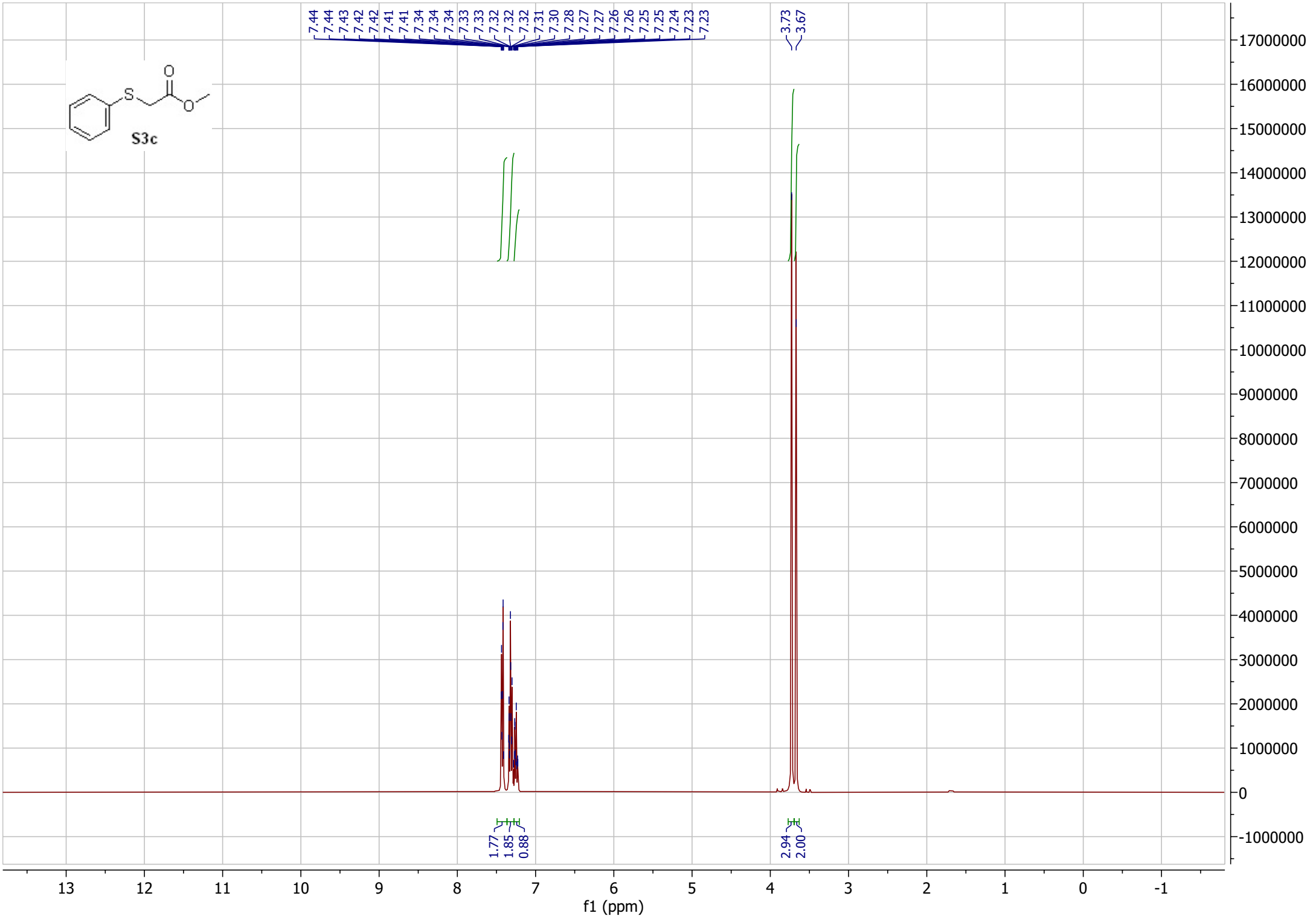
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7.41
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7.32
7.32
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7.27
7.26
7.26
7.25
7.25
7.24
7.23
7.23
3.73
3.67
1.77
1.85
0.88
2.94
2.00
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16000000
15000000
14000000
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11000000
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9000000
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7000000
6000000
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2000000
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10
9
8
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4
3
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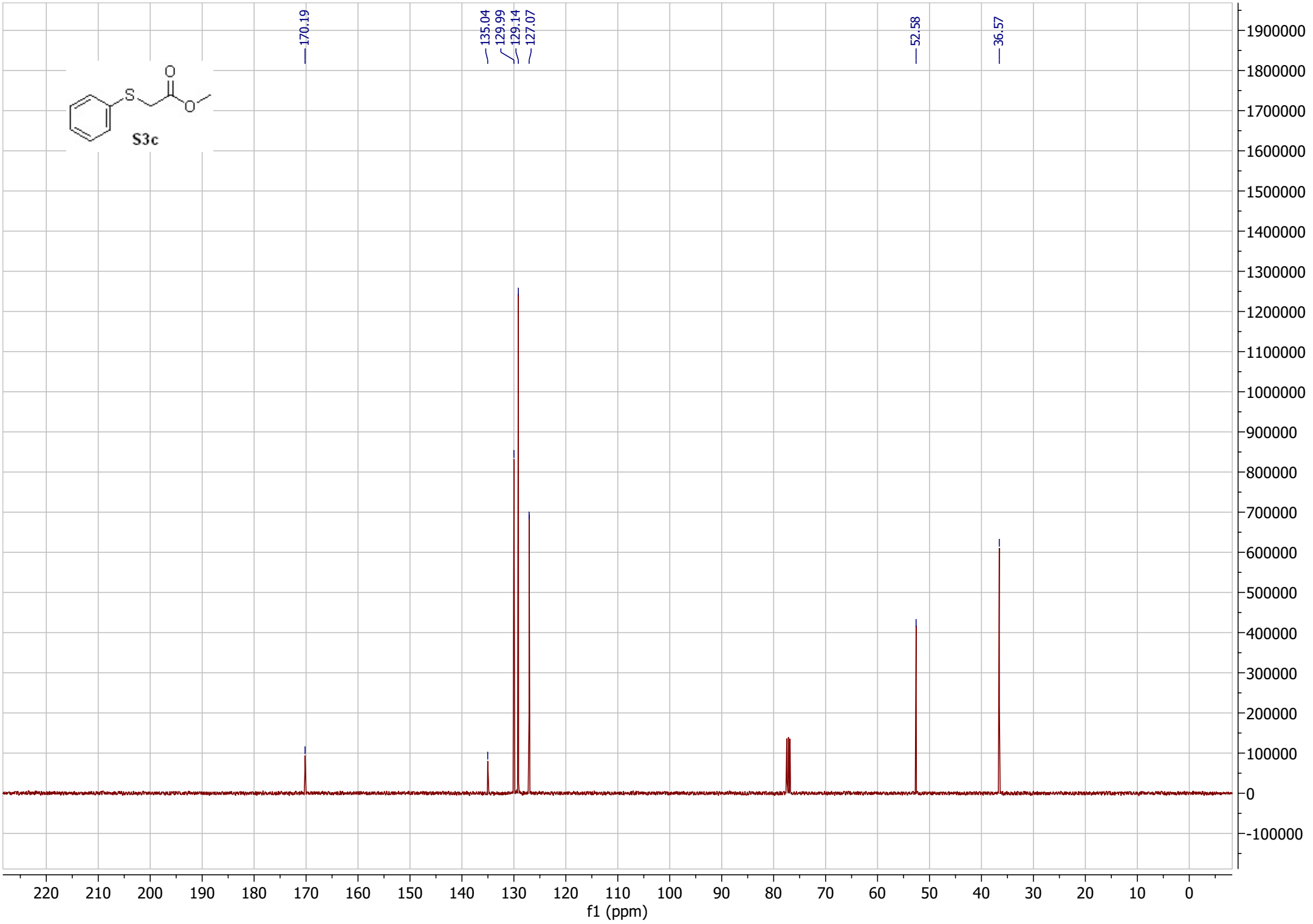
f1 (ppm)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127.07
52.58
36.57
S3c
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1600000
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1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
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210
200
190
180
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50
40
30
20
10
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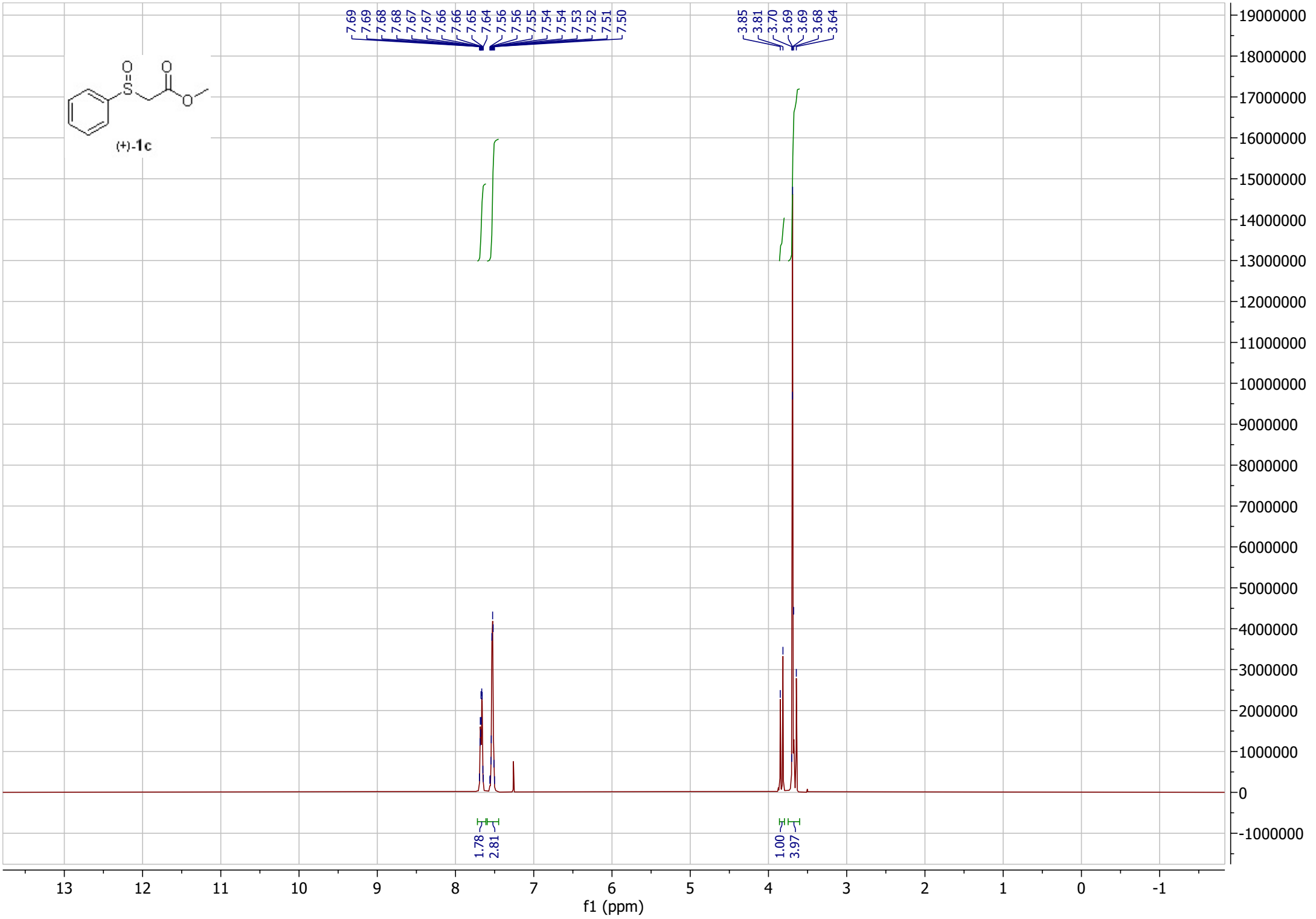
f1 (ppm)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7.68
7.67
7.67
7.66
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7.65
7.64
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7.54
7.54
7.53
7.52
7.51
7.50
3.85
3.81
3.70
3.69
3.69
3.68
3.64
(+)-1c
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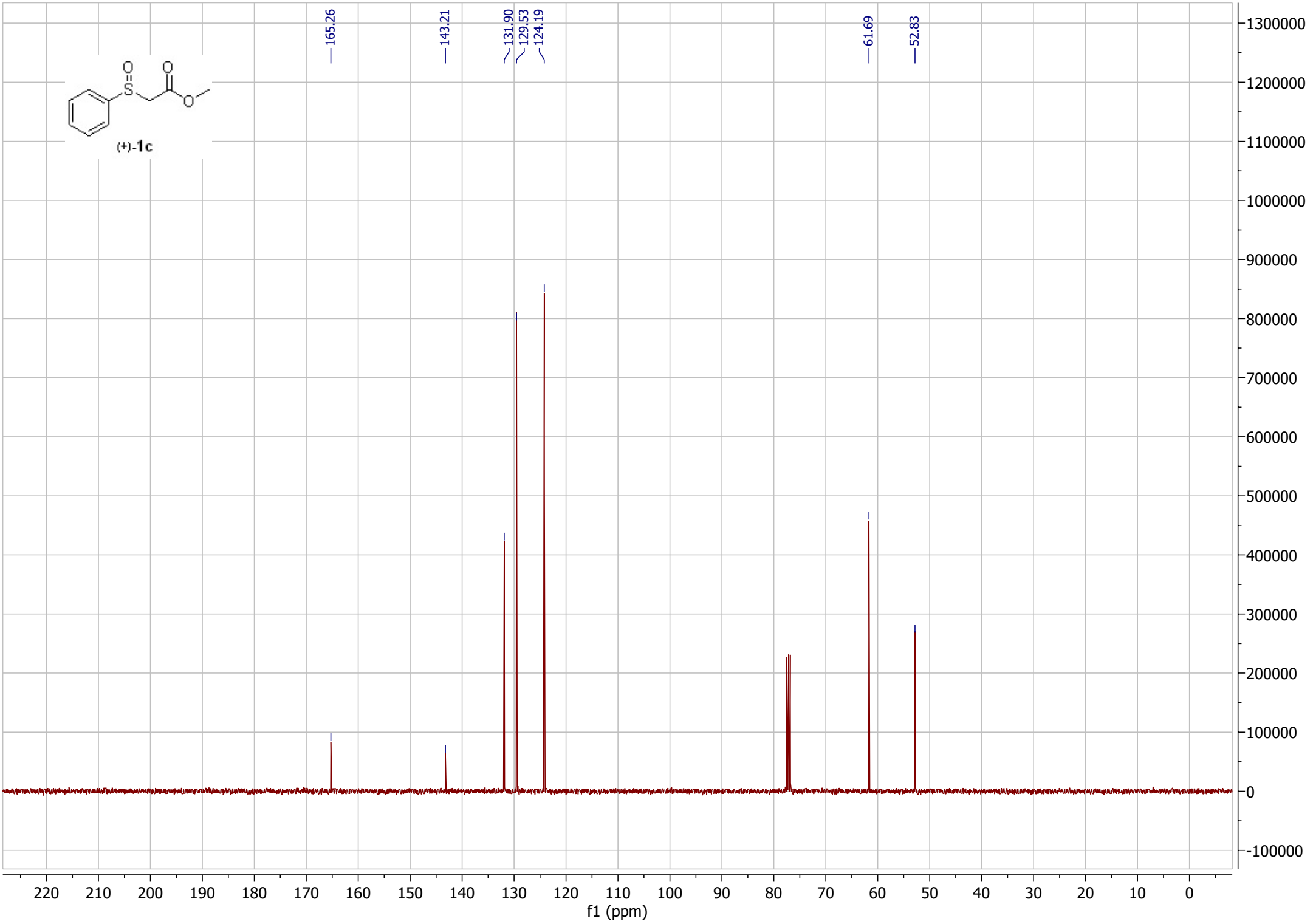
2.81
1.00
3.97
f1 (ppm)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52.83
(+)-1c
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1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
220
210
200
190
180
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130
120
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90
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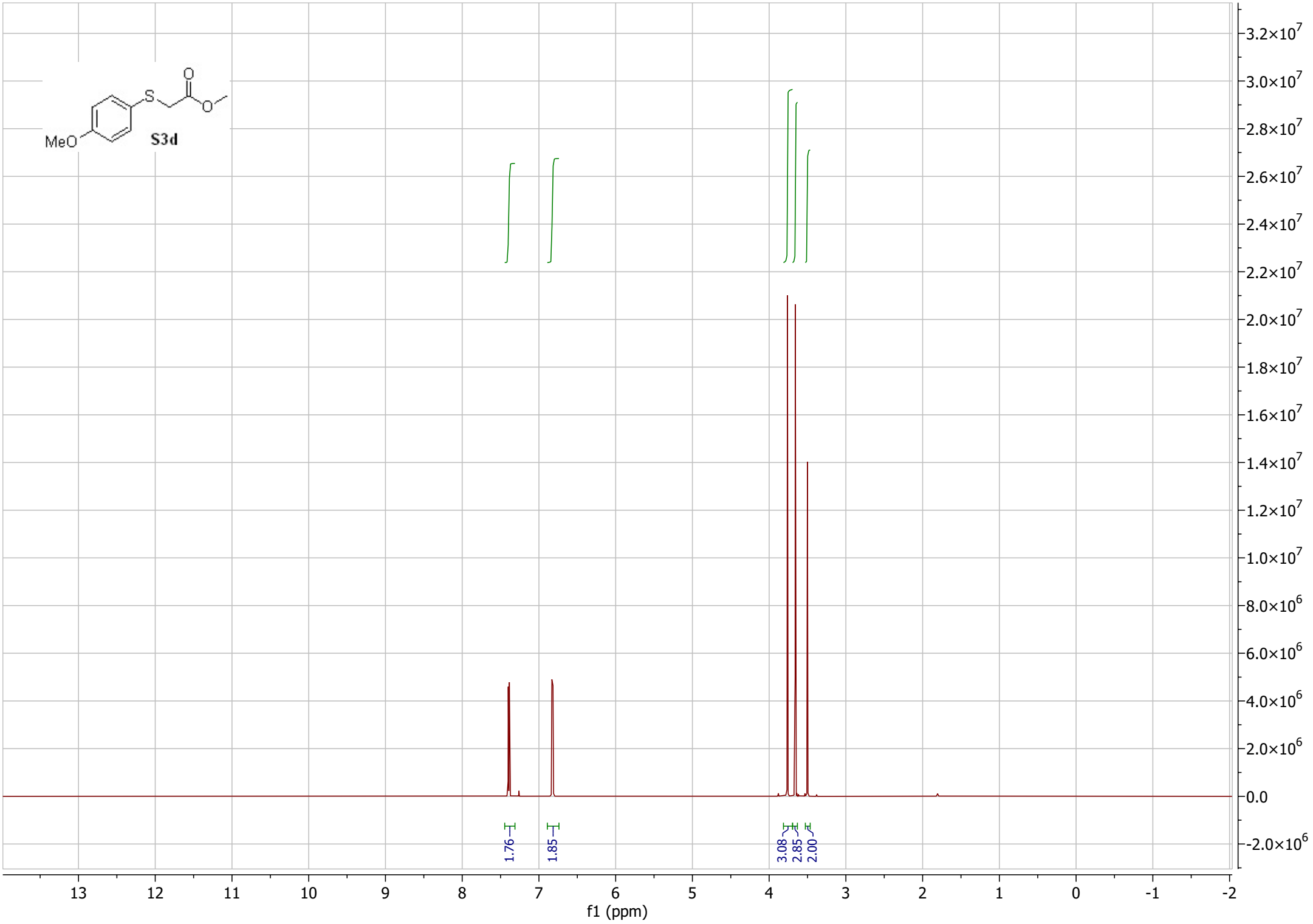
70
60
50
40
30
20
10
0
f1 (ppm)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O
O
S3d
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1.85
3.08
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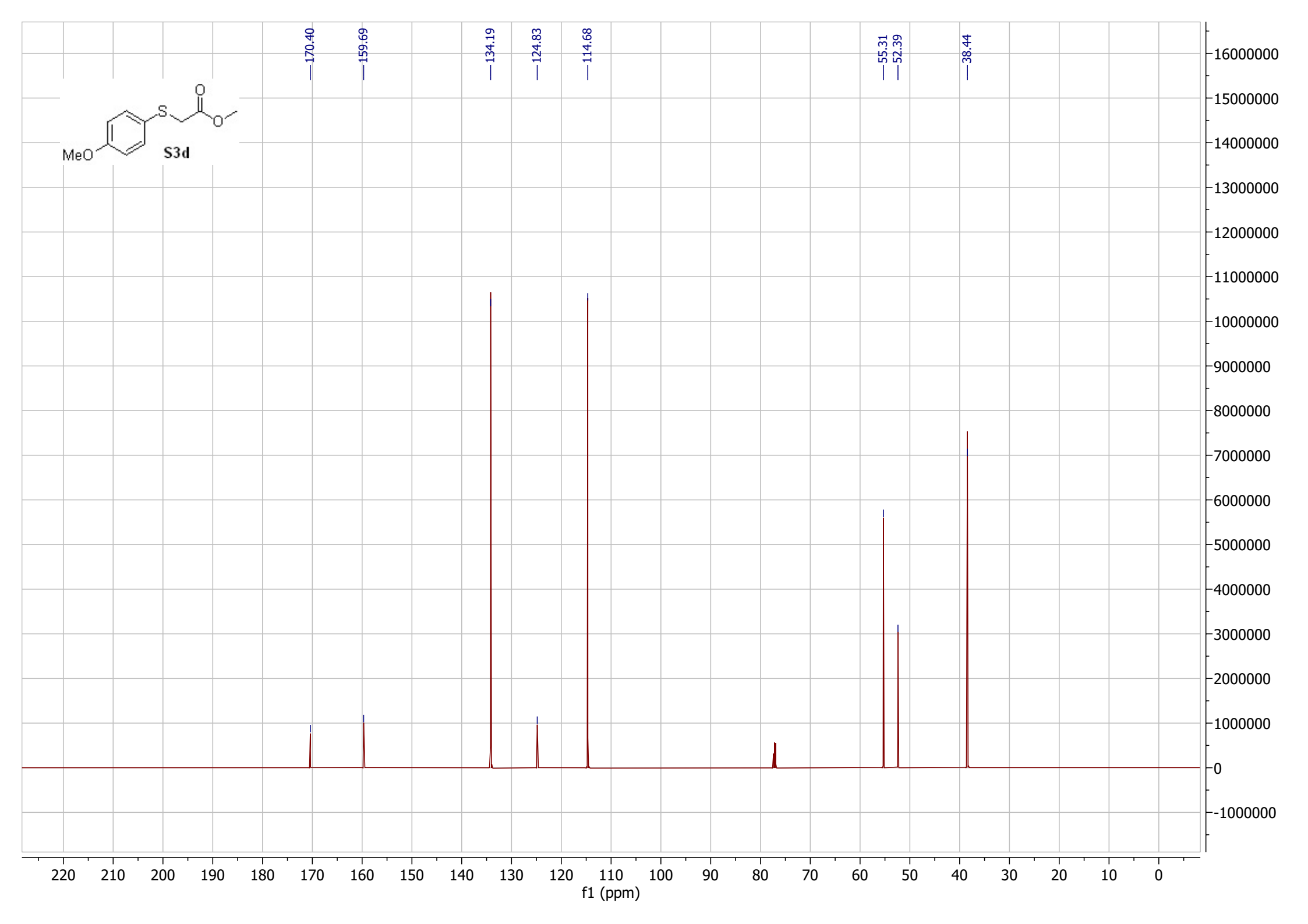
2.00
f1 (ppm)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114.68
55.31
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38.44
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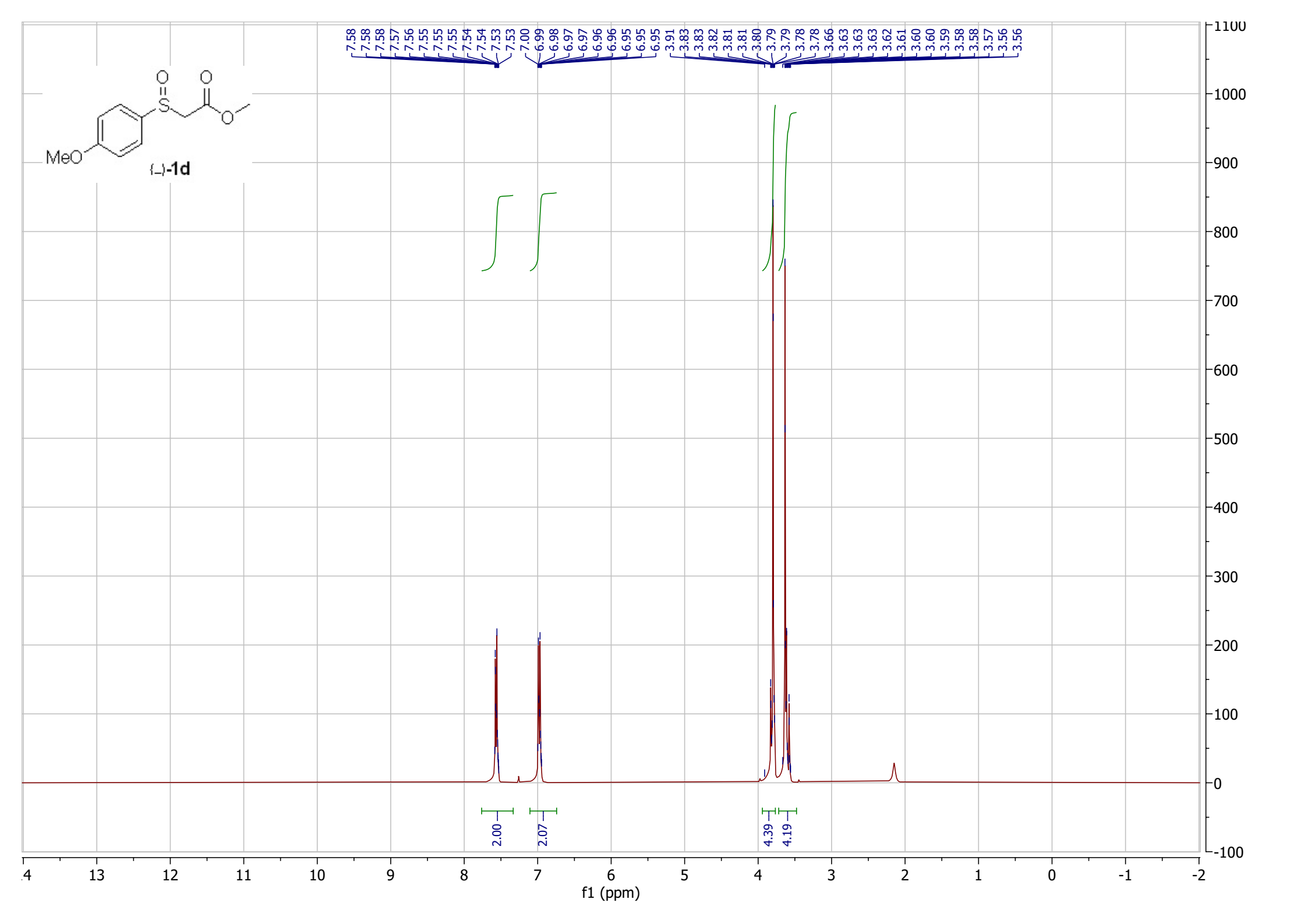
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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(–)-1d
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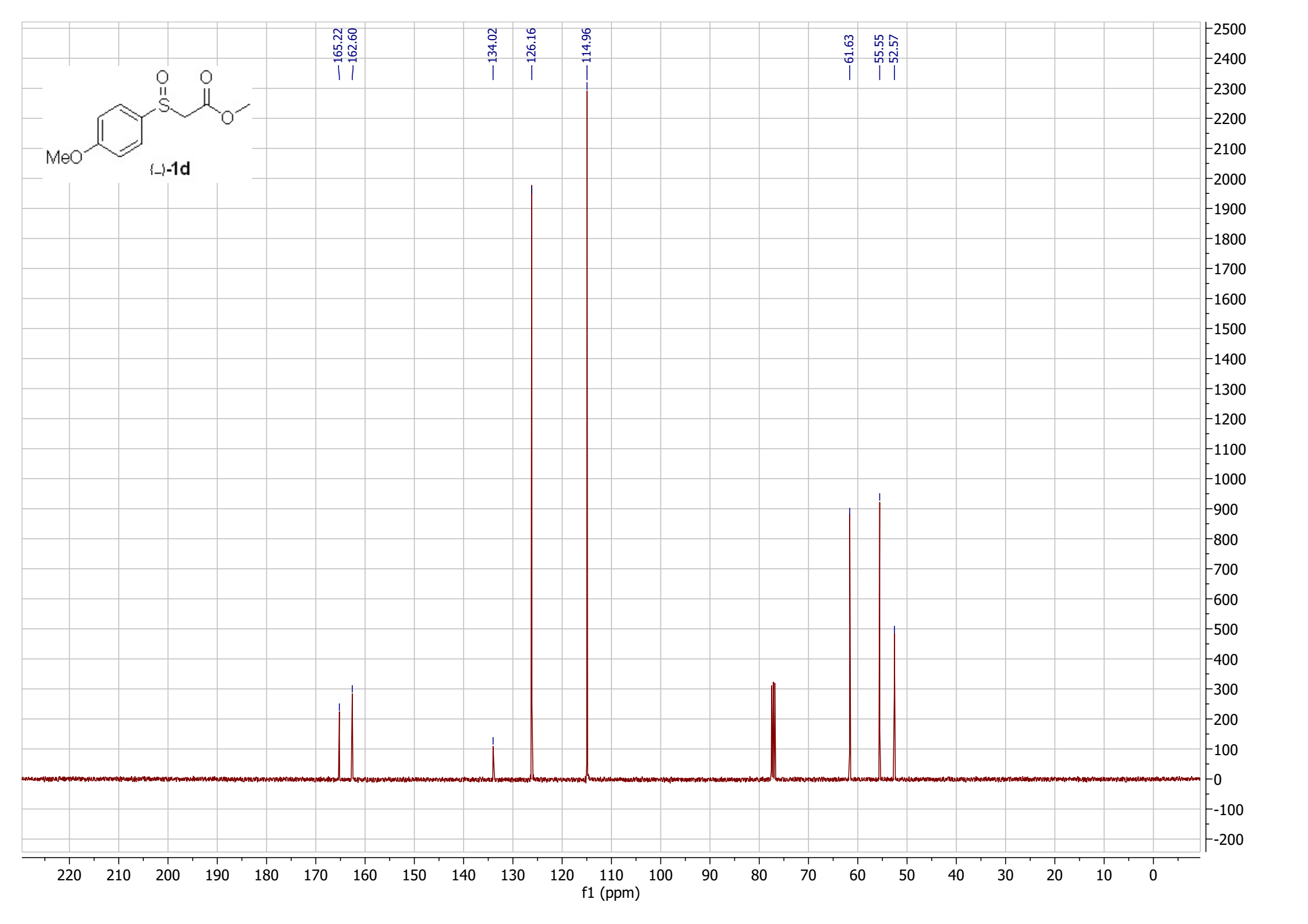
2.00
2.07
4.39
4.19
f1 (ppm)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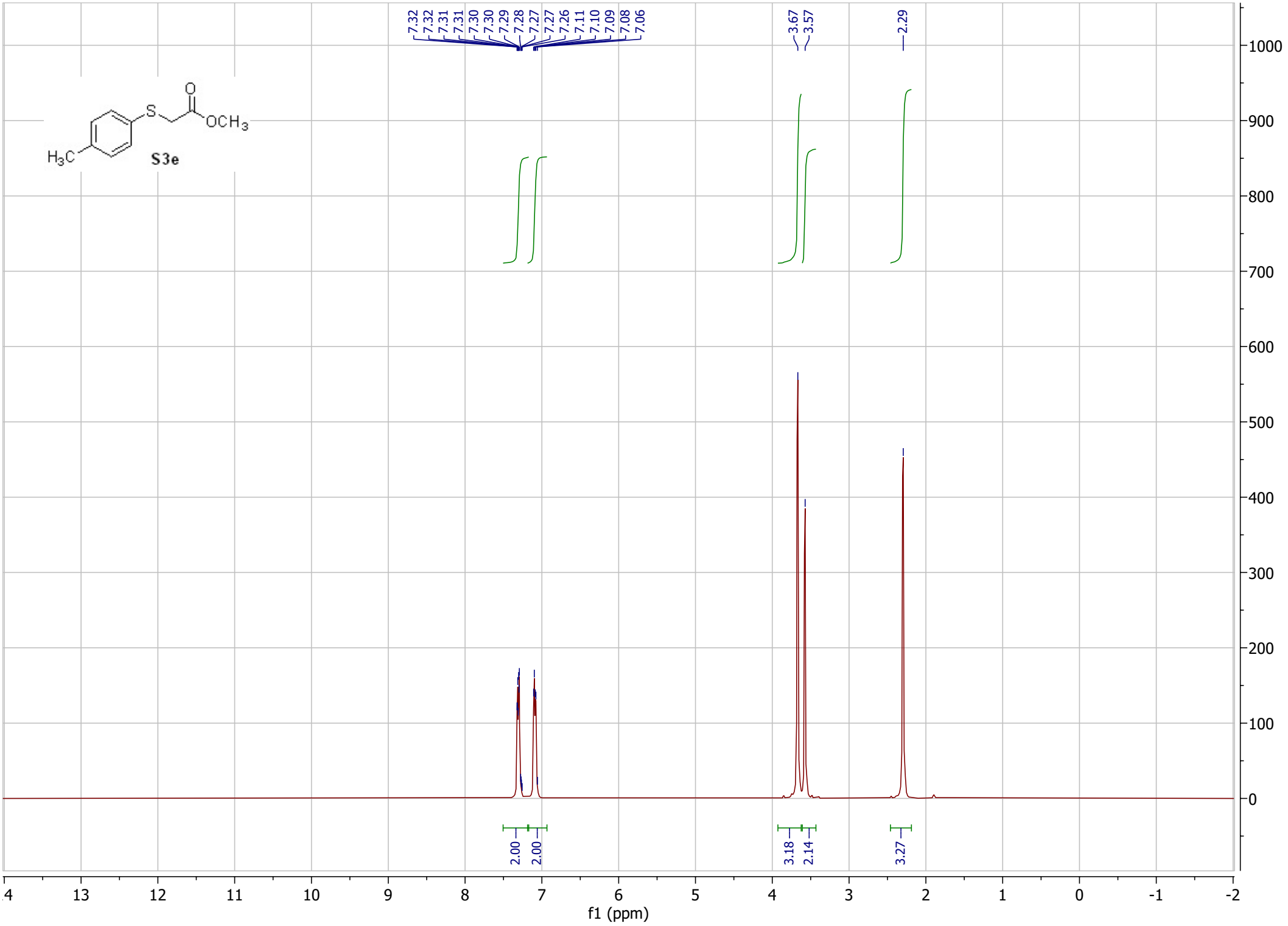
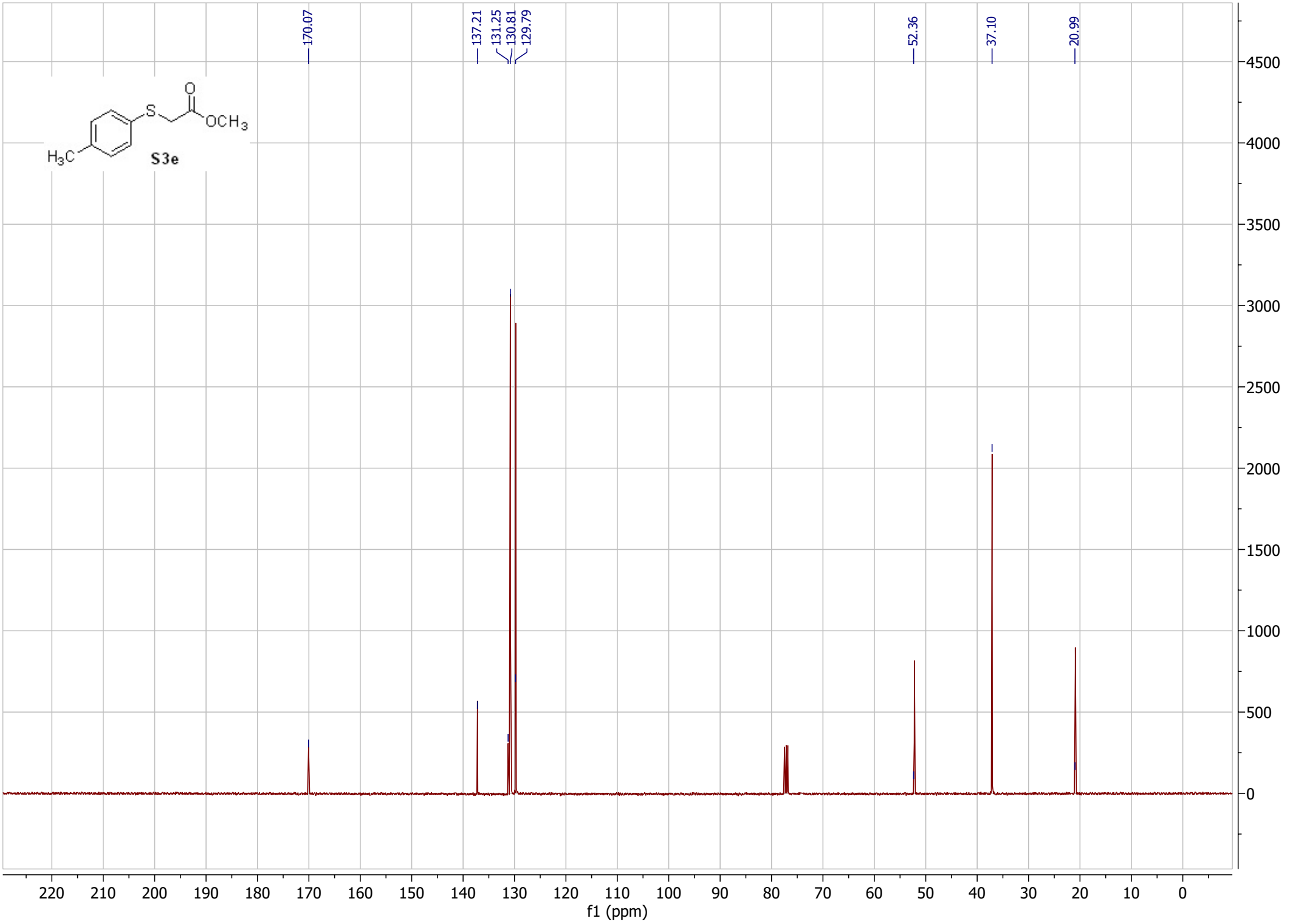
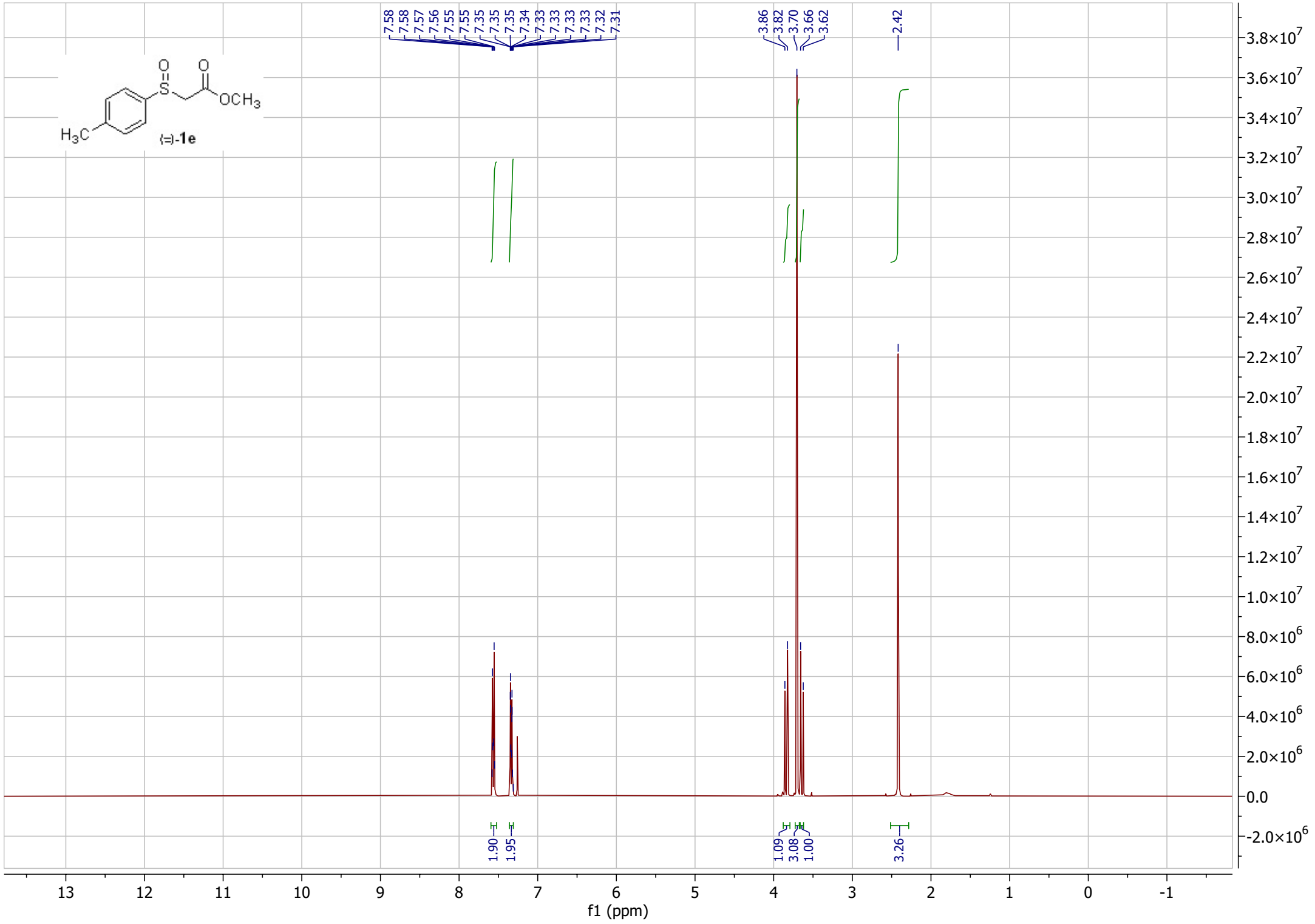
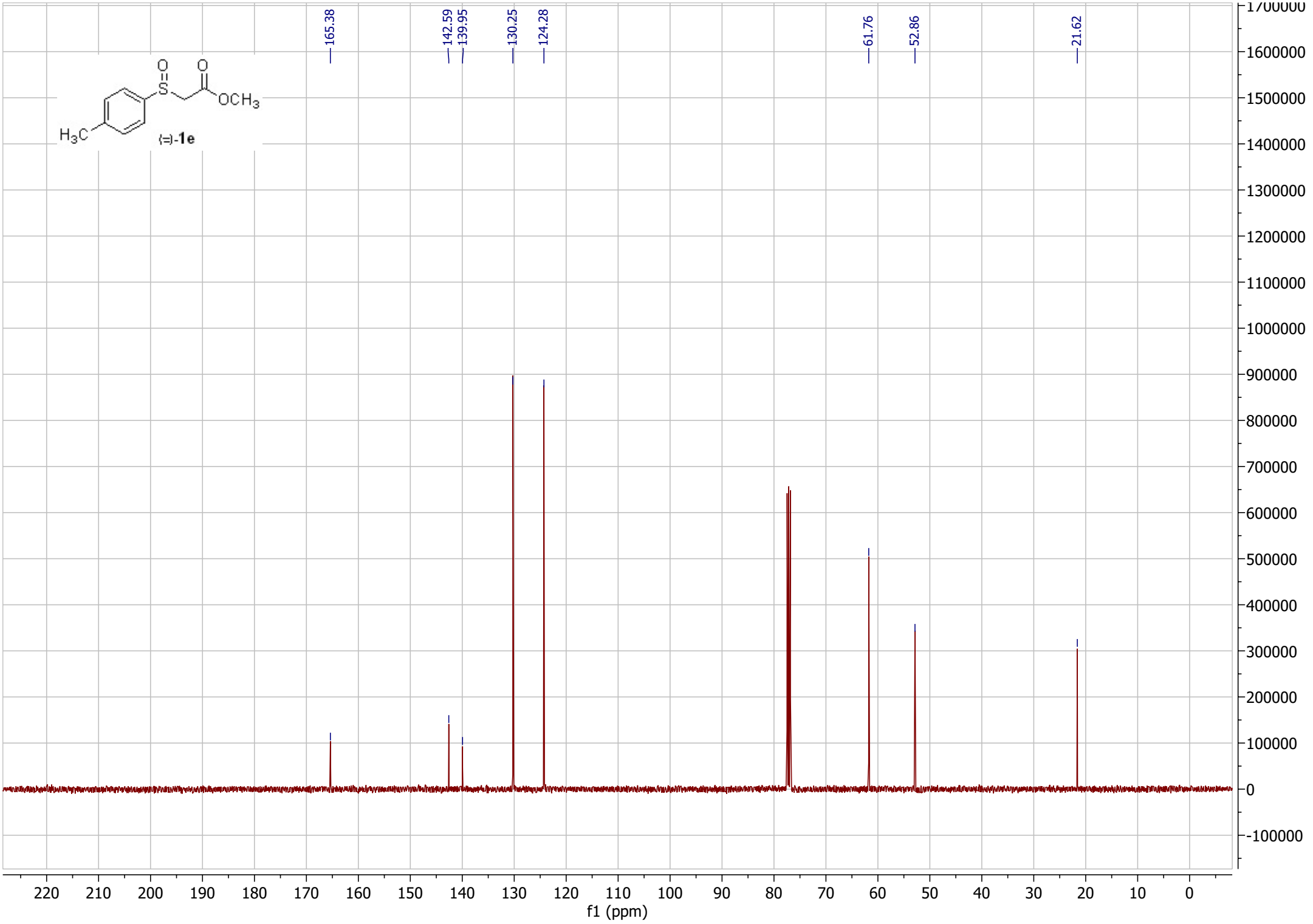
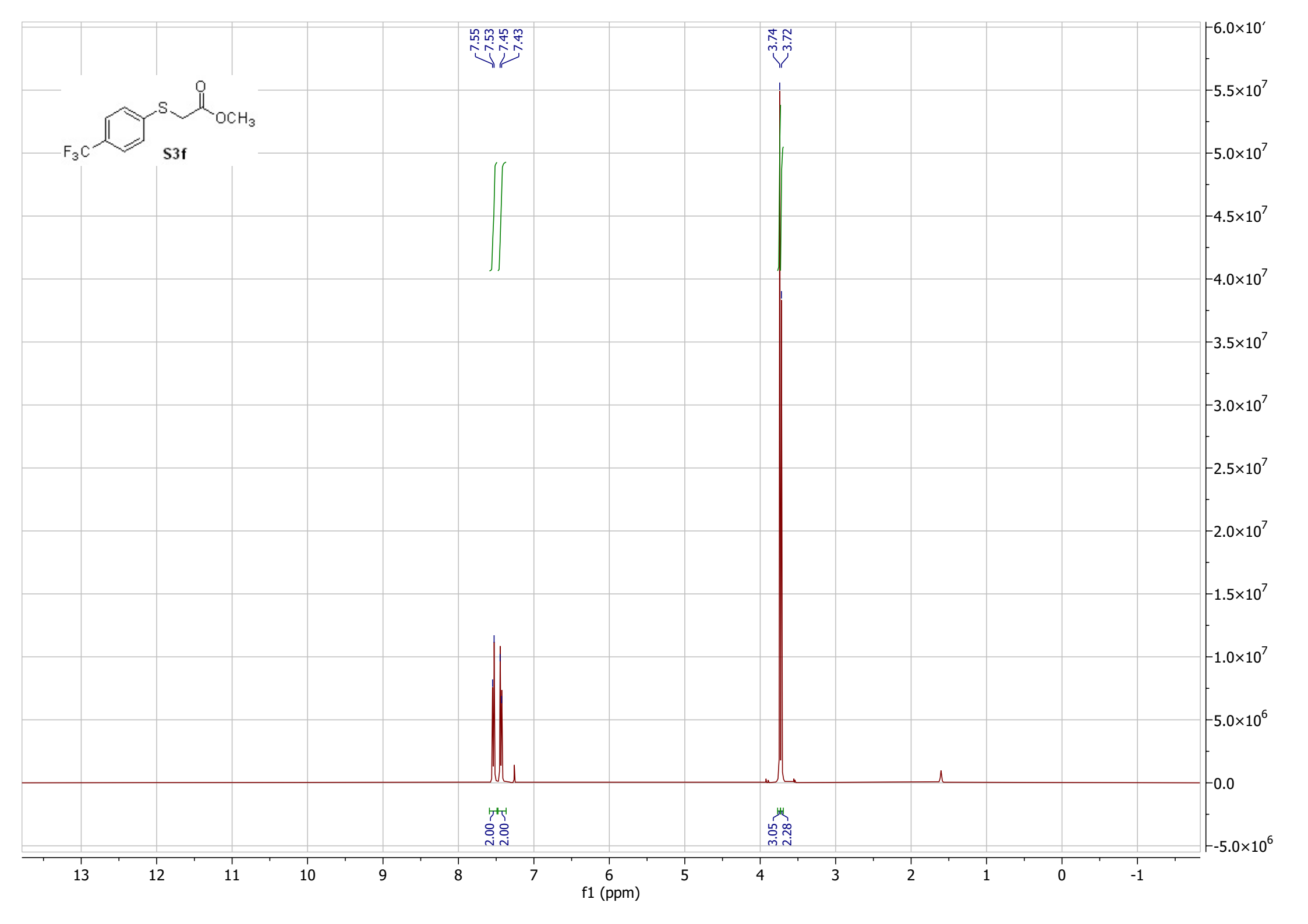
114.96
61.63
55.55
52.57
MeO
(–)-1d
f1 (ppm)

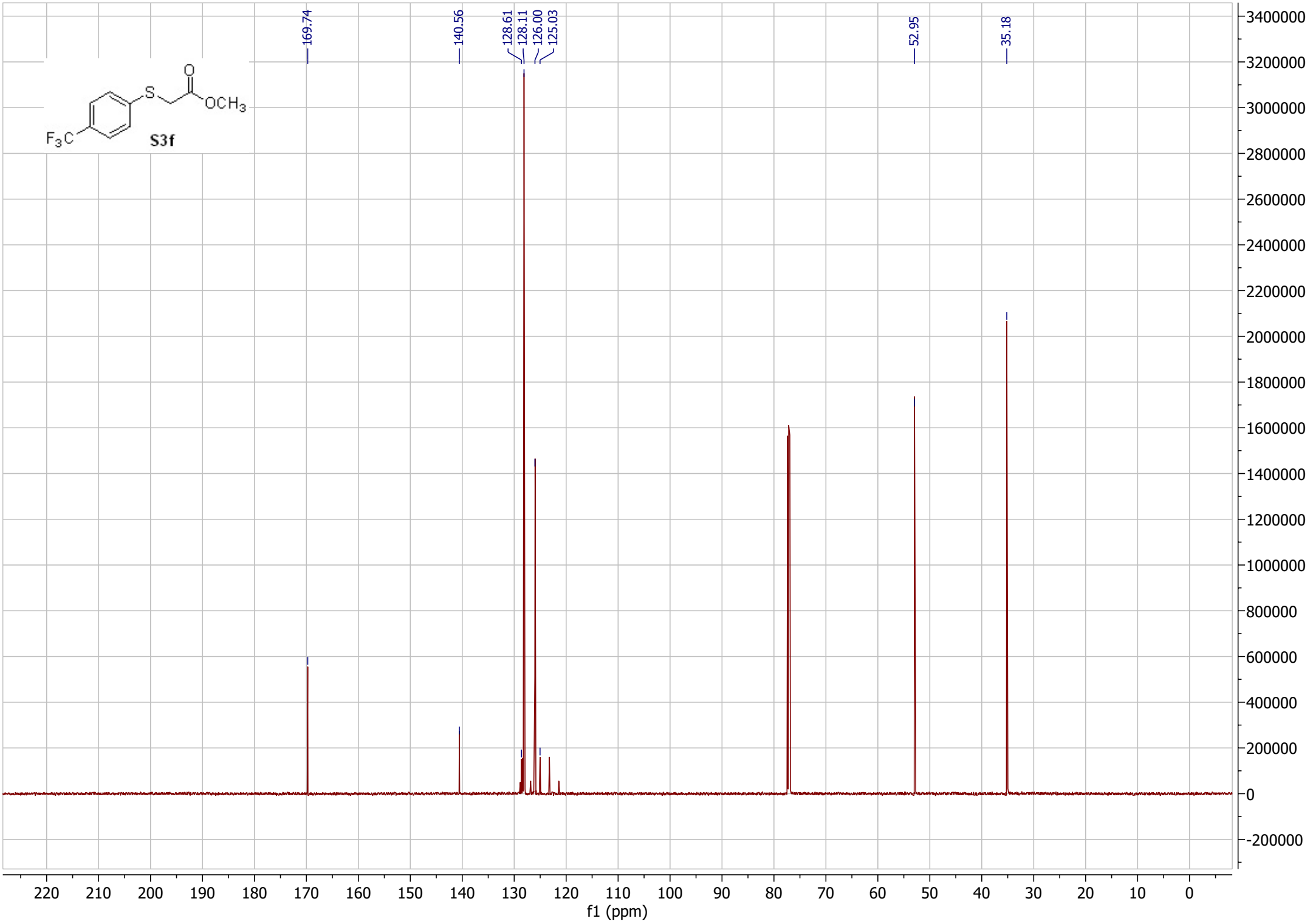

7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.27
7.27
7.26
7.11
7.10
7.09
7.08
7.06
3.67
3.57
2.29
S3e
2.00
2.00
3.18
2.14
3.27
f1 (ppm)

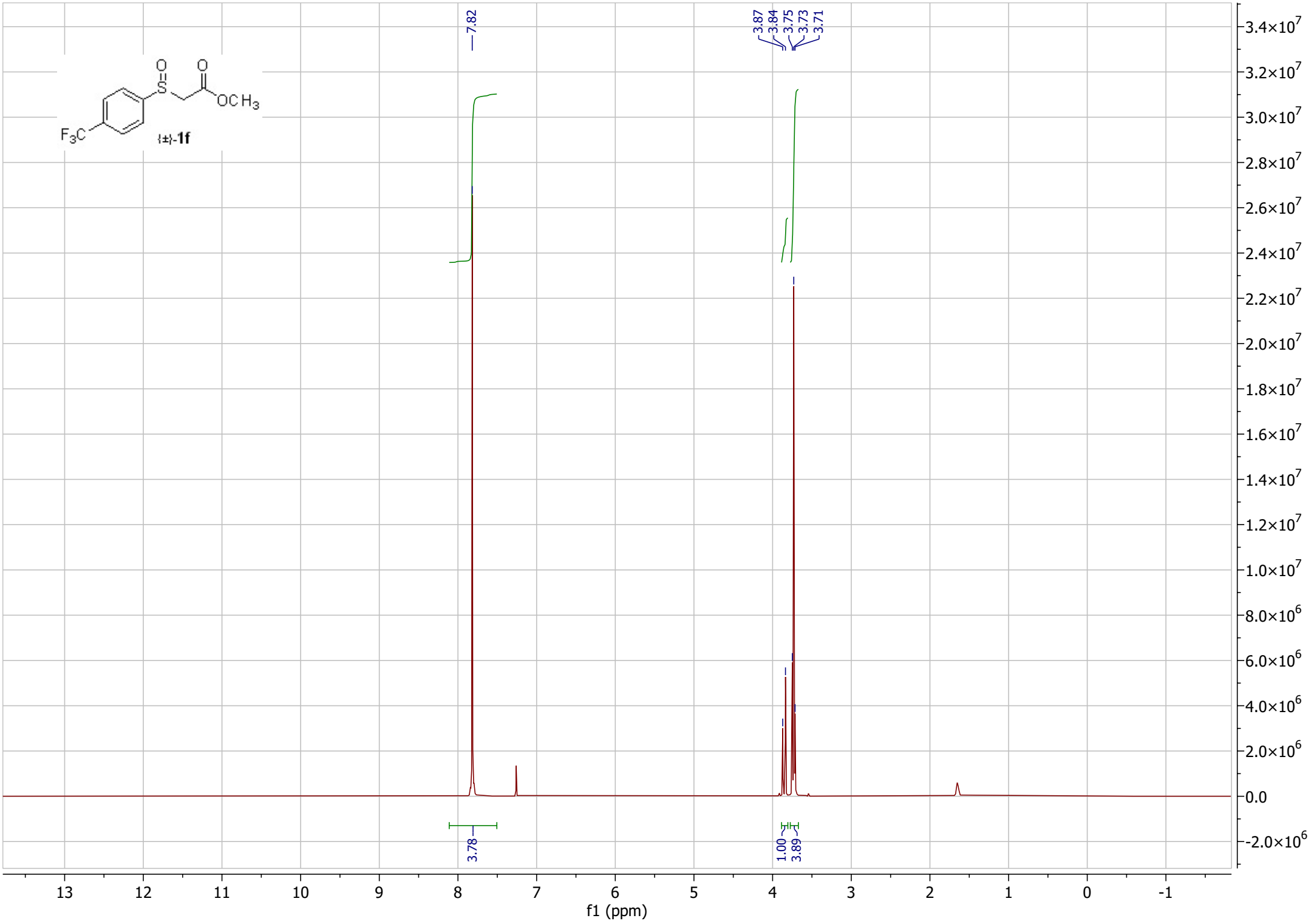

170.07
137.21
131.25
130.81
129.79
52.36
37.10
20.99
S3e
4500
4000
3500
3000
2500
2000
1500
1000
500
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

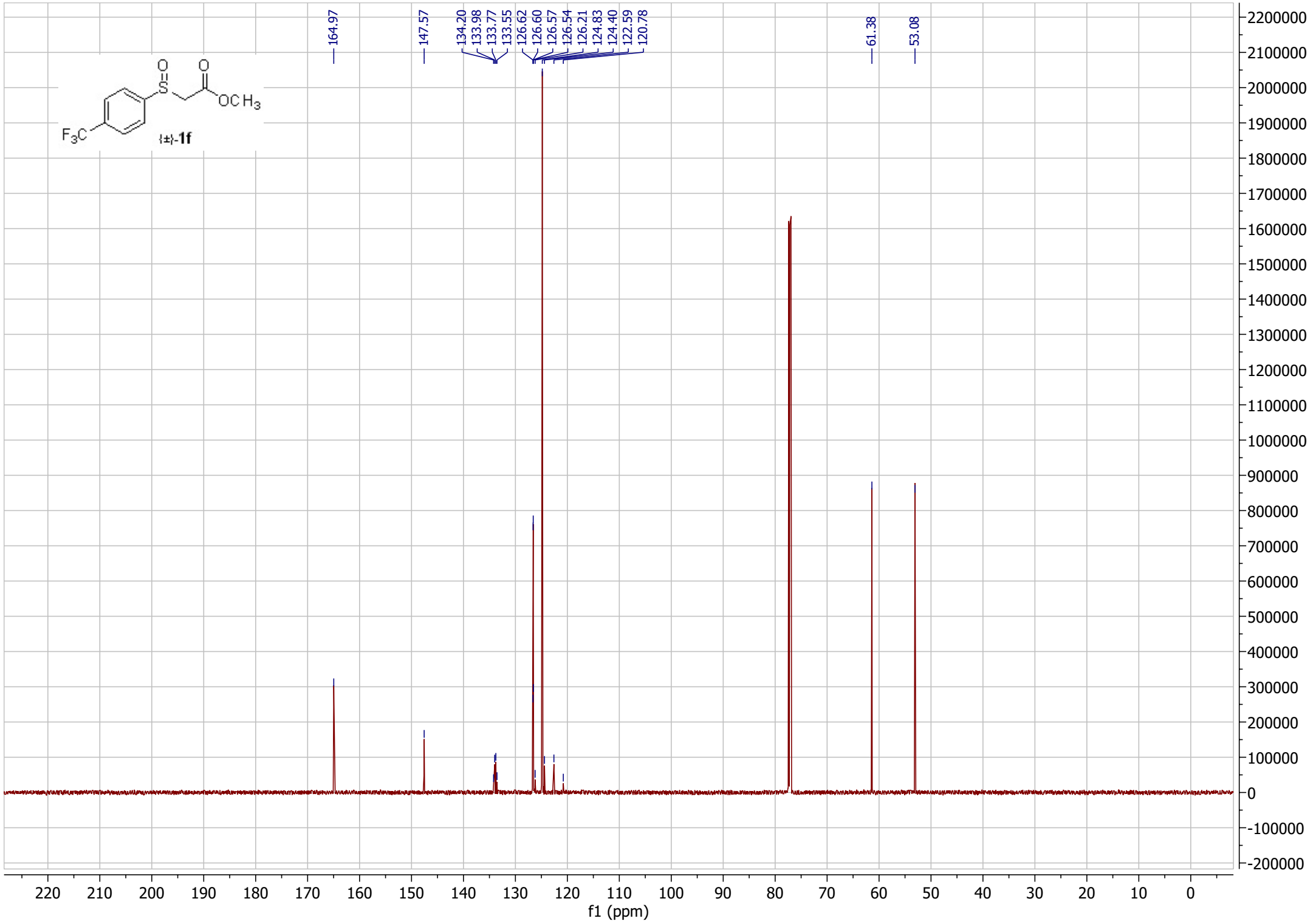

7.58
7.58
7.57
7.56
7.55
7.55
7.35
7.35
7.35
7.34
7.33
7.33
7.33
7.33
7.32
7.31
3.86
3.82
3.70
3.66
3.62
2.42
(±)-1e
1.90
1.95
1.09
3.08
1.00
3.26
f1 (ppm)

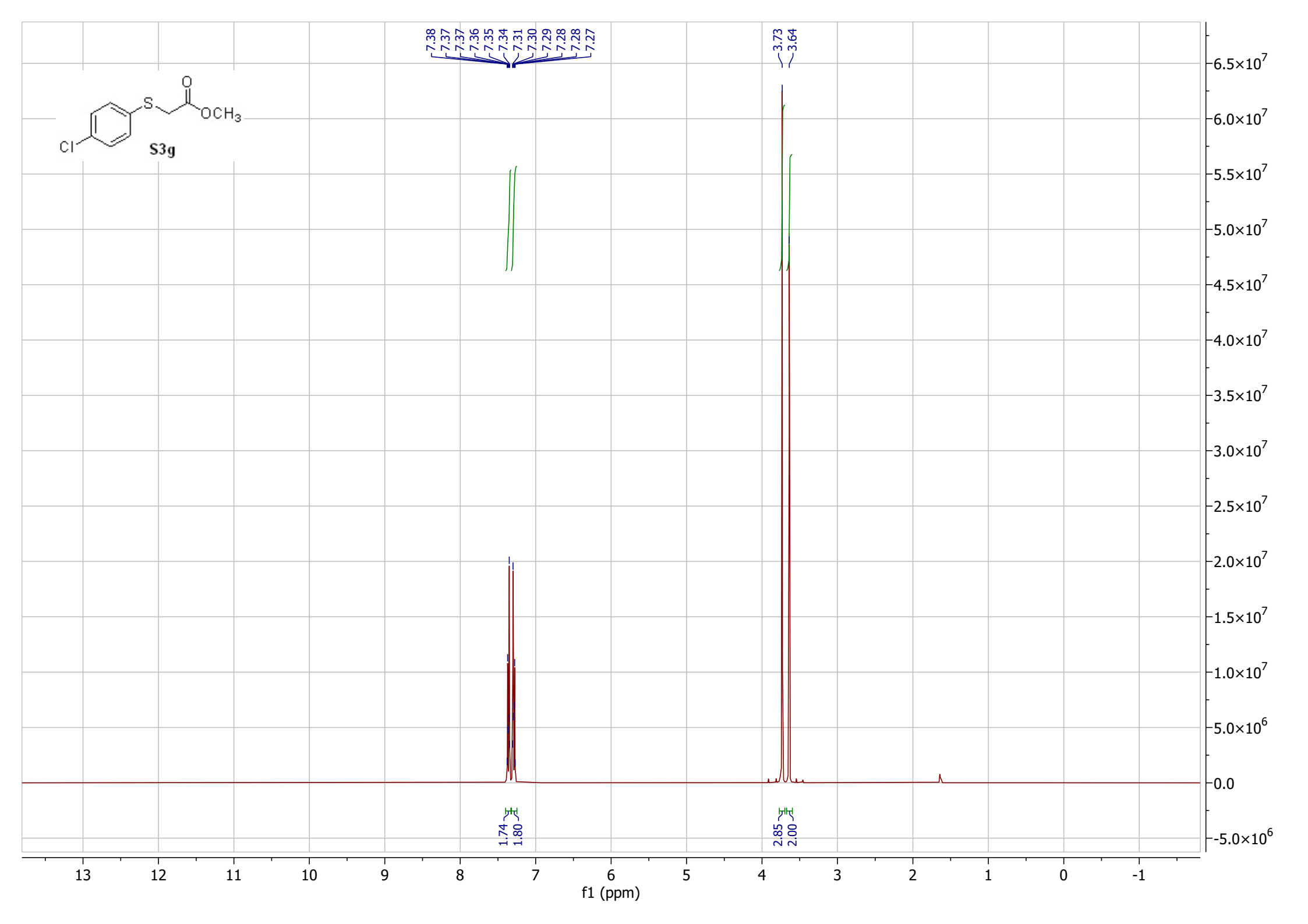

165.38
142.59
139.95
130.25
124.28
61.76
52.86
21.62
(±)-1e
f1 (ppm)

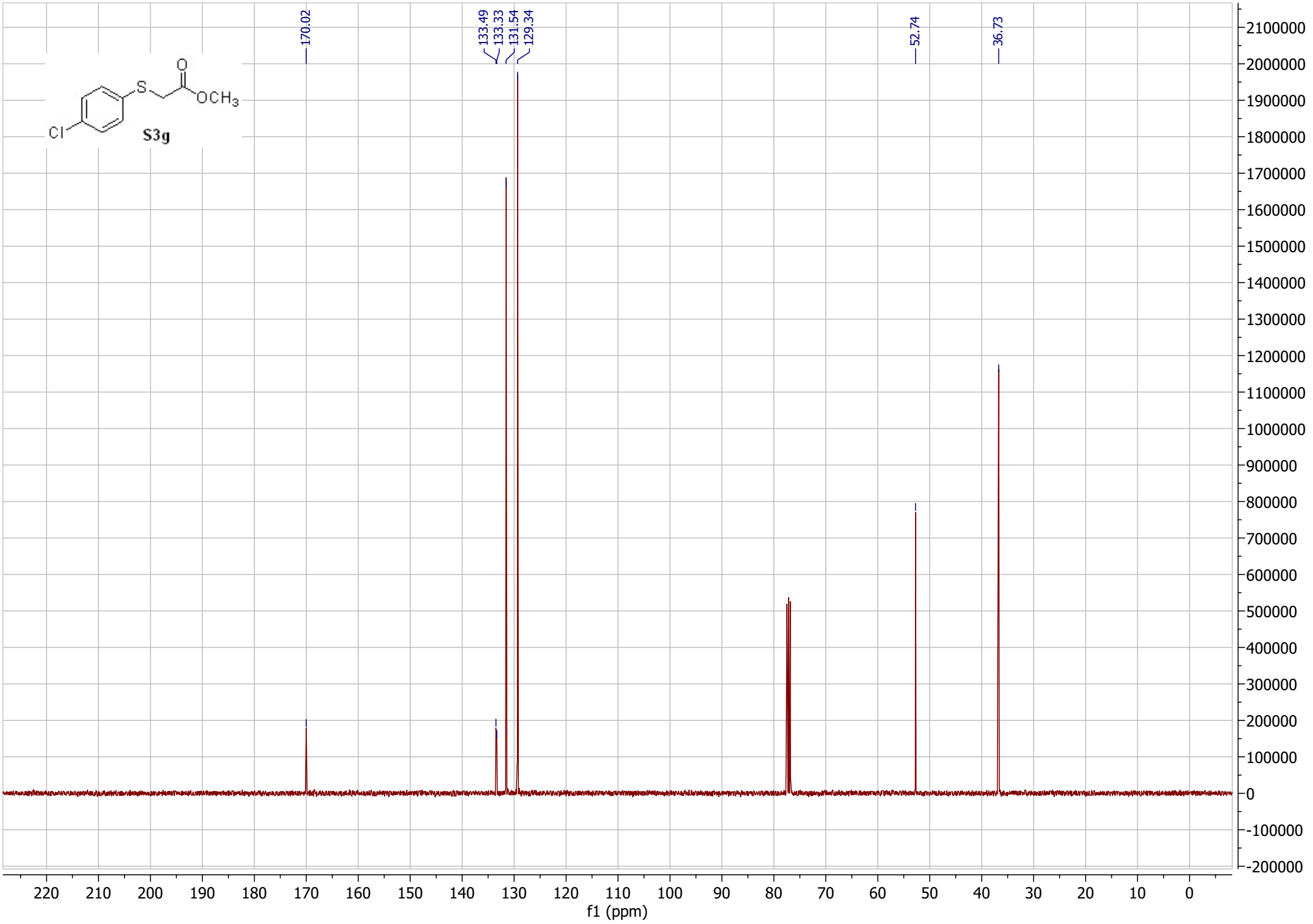

S3f
7.55
7.53
7.45
7.43
3.74
3.72
2.00
2.00
3.05
2.28
f1 (ppm)

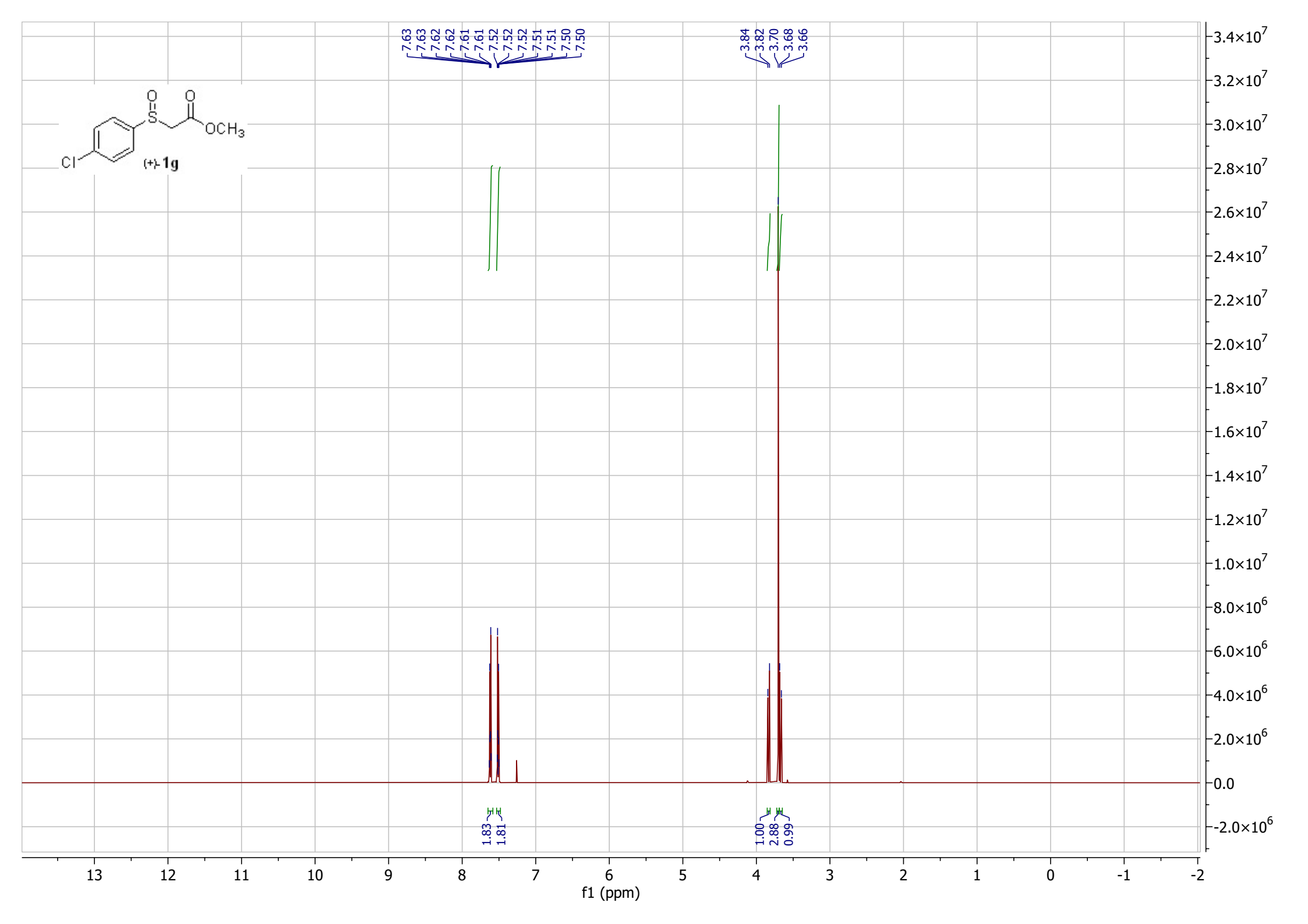

169.74
140.56
128.61
128.11
126.00
125.03
52.95
35.18
S
O
OCH3
F3C
S3f
3400000
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

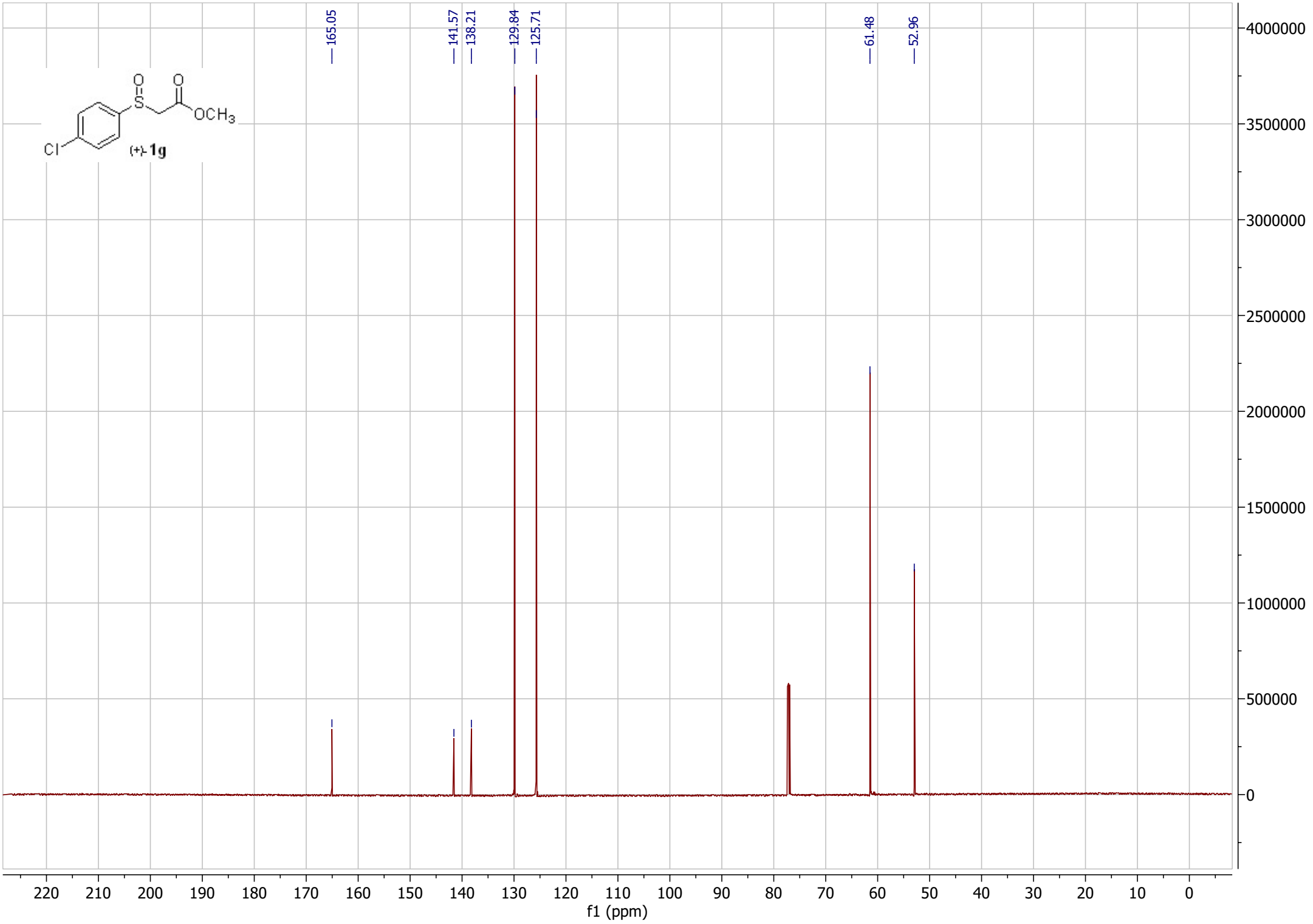

7.82
3.87
3.84
3.75
3.73
3.71
3.78
1.00
3.89
(±)-1f
f1 (ppm)

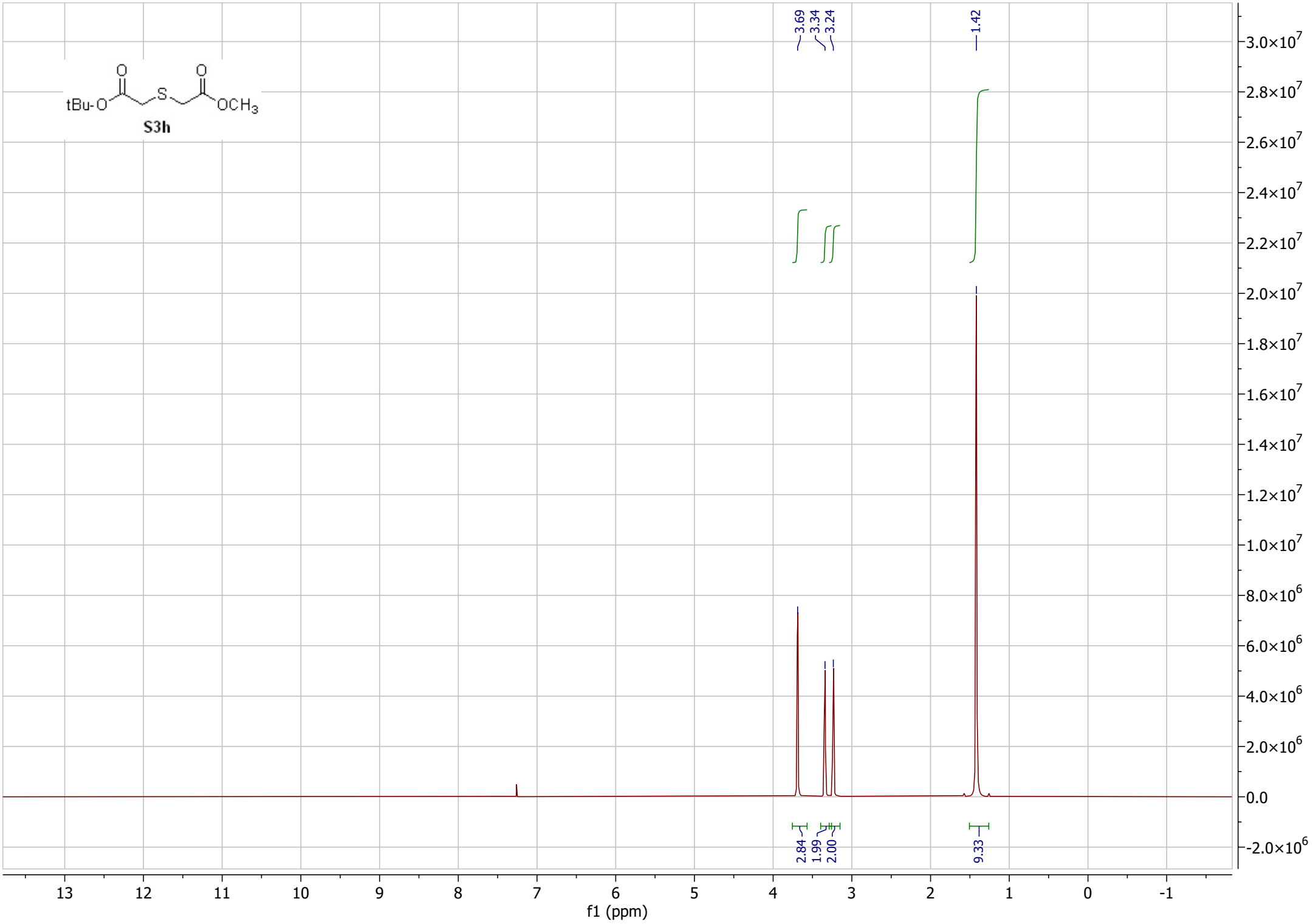

164.97
147.57
134.20
133.98
133.77
133.55
126.62
126.60
126.57
126.54
126.21
124.83
124.40
122.59
120.78
61.38
53.08
(±)-1f
f1 (ppm)

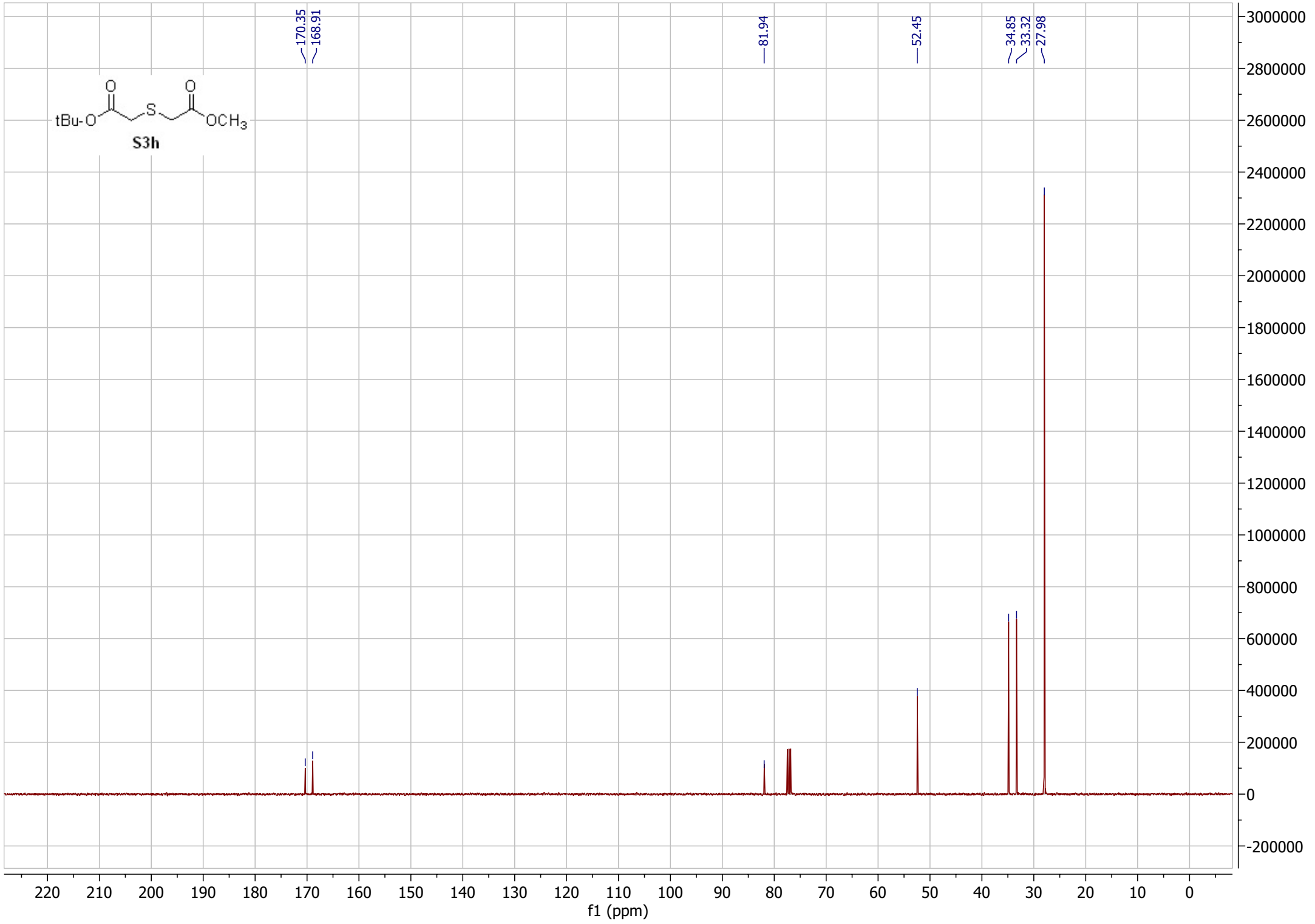

7.38
7.37
7.37
7.36
7.35
7.34
7.31
7.30
7.29
7.28
7.28
7.27
3.73
3.64
O
S
OCH3
Cl
S3g
1.74
1.80
2.85
2.00
6.5×10^7
6.0×10^7
5.5×10^7
5.0×10^7
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
-5.0×10^6
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

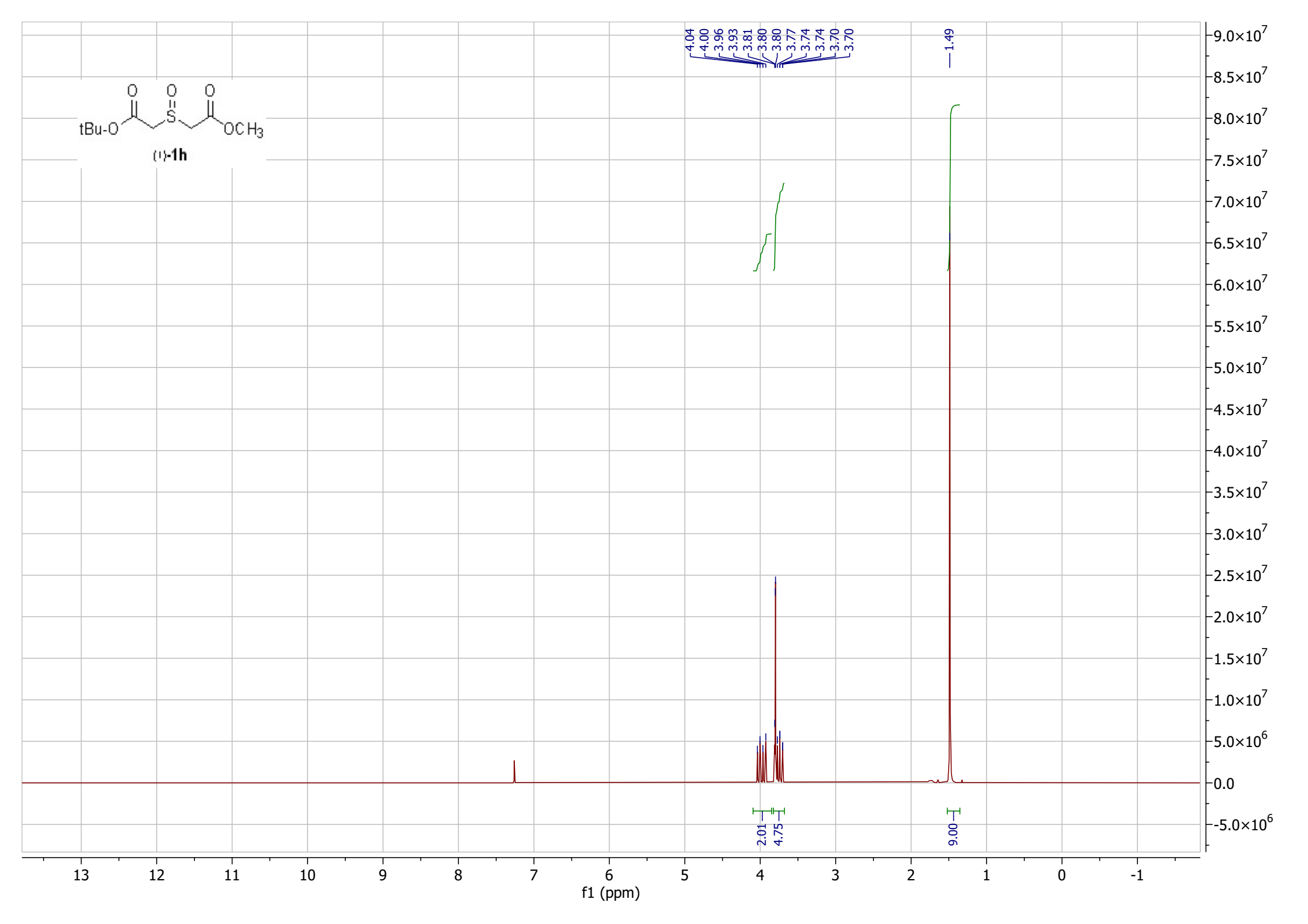

170.02
133.49
133.33
131.54
129.34
52.74
36.73
S3g
f1 (ppm)

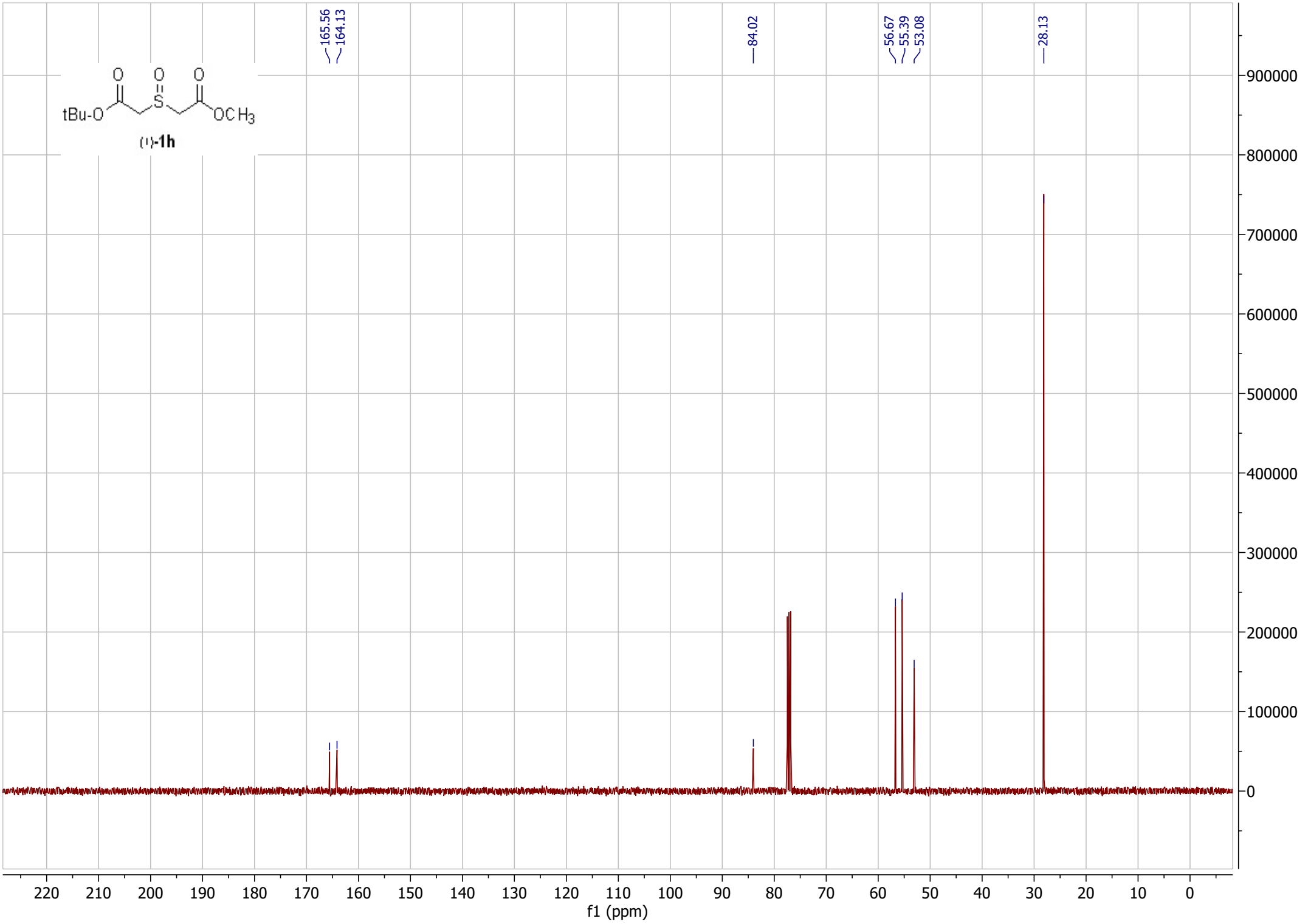

7.63
7.63
7.62
7.62
7.61
7.61
7.52
7.52
7.51
7.51
7.50
7.50
3.84
3.82
3.70
3.68
3.66
O
O
S
OCH3
Cl
(+)-1g
1.83
1.81
1.00
2.88
0.99
3.4×10^7
3.2×10^7
3.0×10^7
2.8×10^7
2.6×10^7
2.4×10^7
2.2×10^7
2.0×10^7
1.8×10^7
1.6×10^7
1.4×10^7
1.2×10^7
1.0×10^7
8.0×10^6
6.0×10^6
4.0×10^6
2.0×10^6
0.0
-2.0×10^6
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

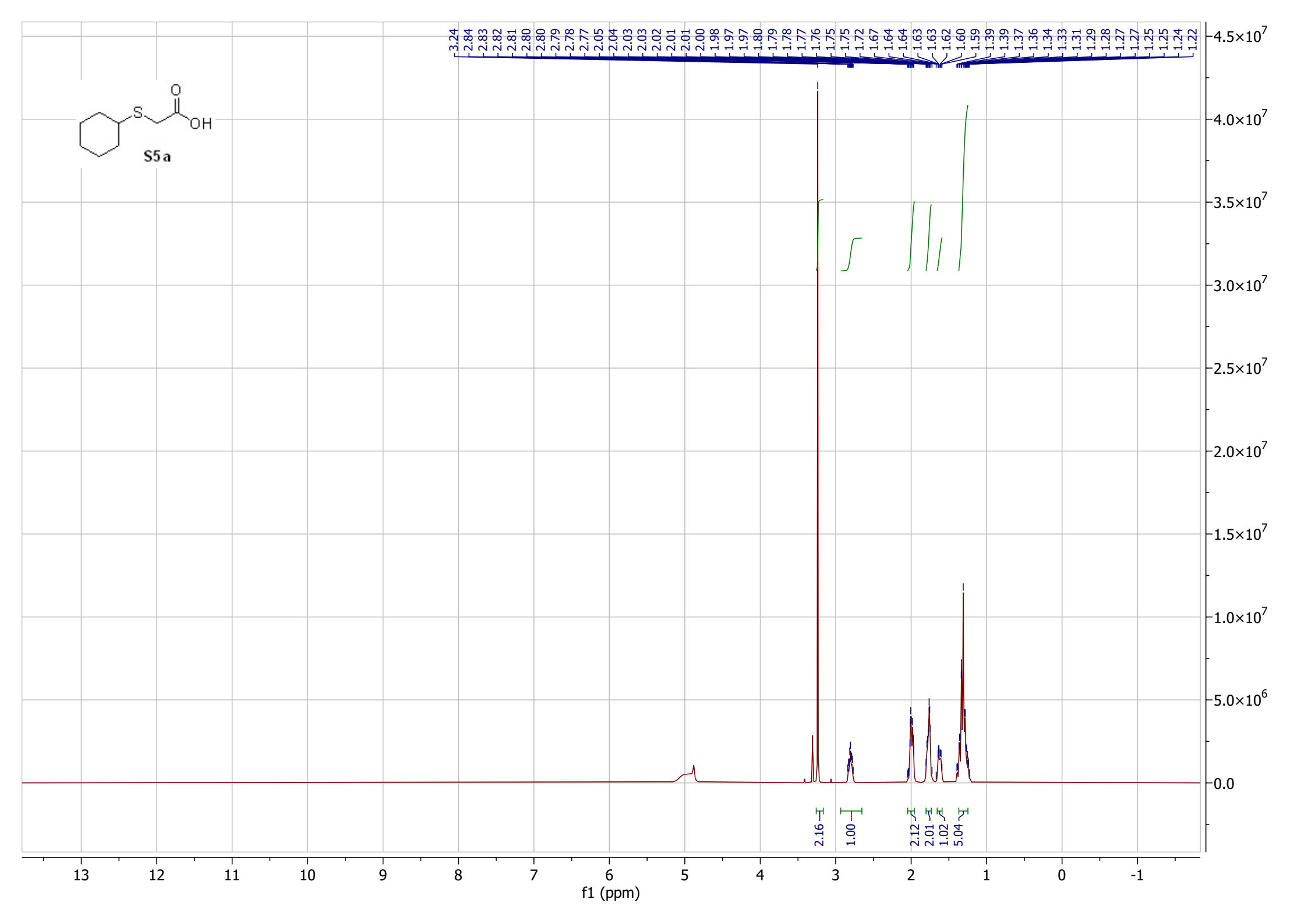

165.05
141.57
138.21
129.84
125.71
61.48
52.96
(+)-1g
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

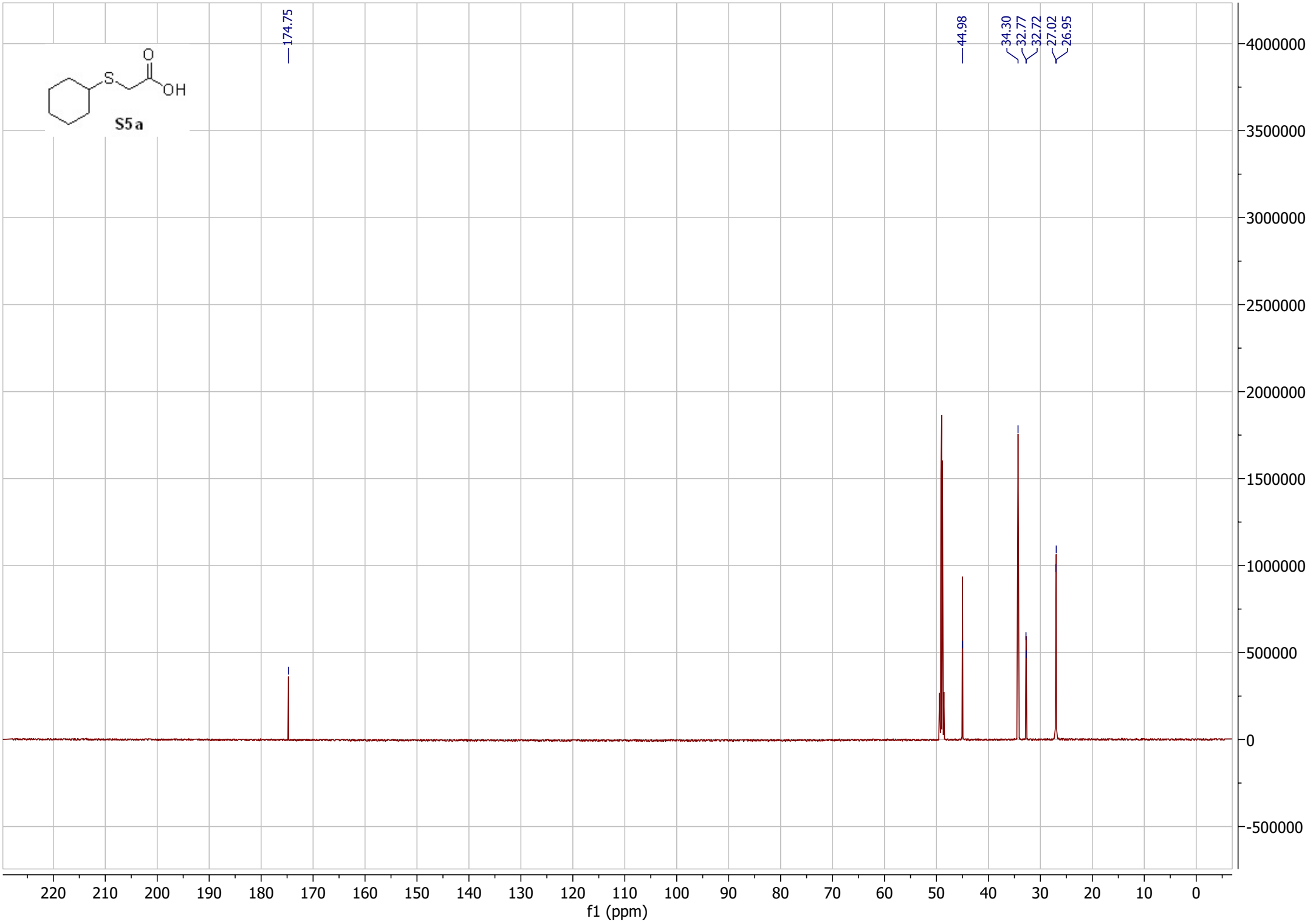

3.69
3.34
3.24
1.42
2.84
1.99
2.00
9.33
S3h
f1 (ppm)

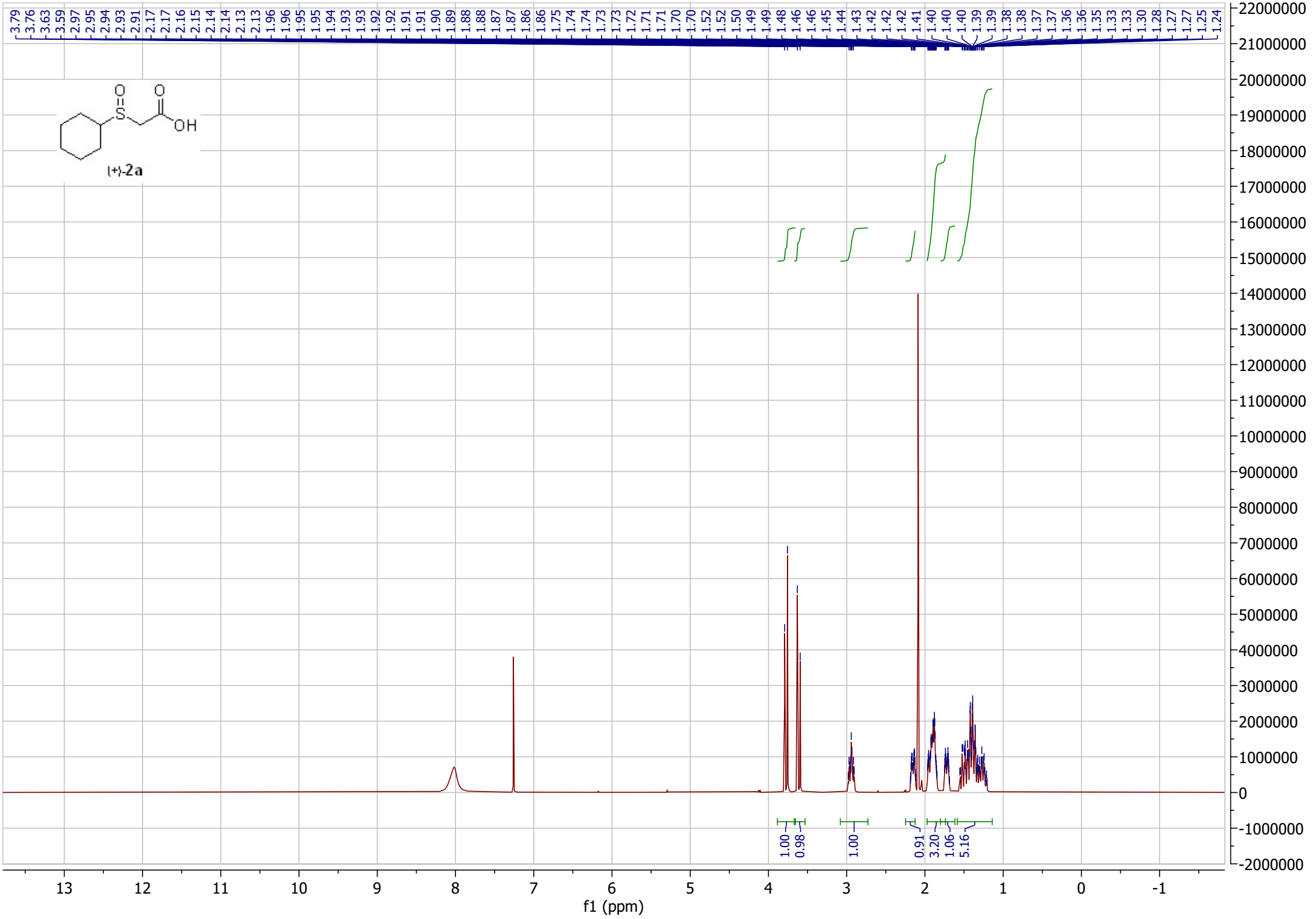

170.35
168.91
81.94
52.45
34.85
33.32
27.98
tBu-O
S
OCH3
S3h
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

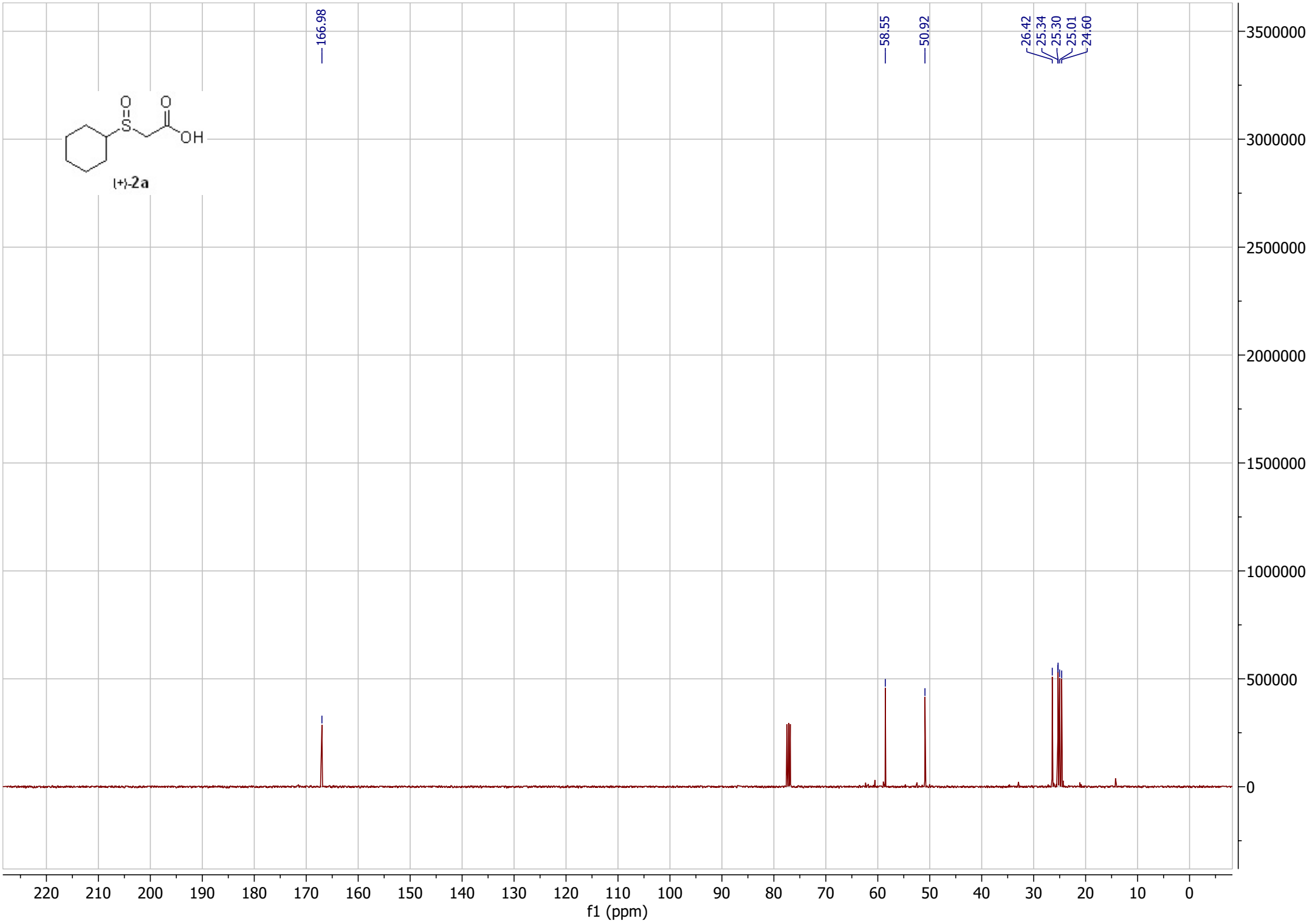

4.04
4.00
3.96
3.93
3.81
3.80
3.80
3.77
3.74
3.74
3.70
3.70
1.49
2.01
4.75
9.00
f1 (ppm)

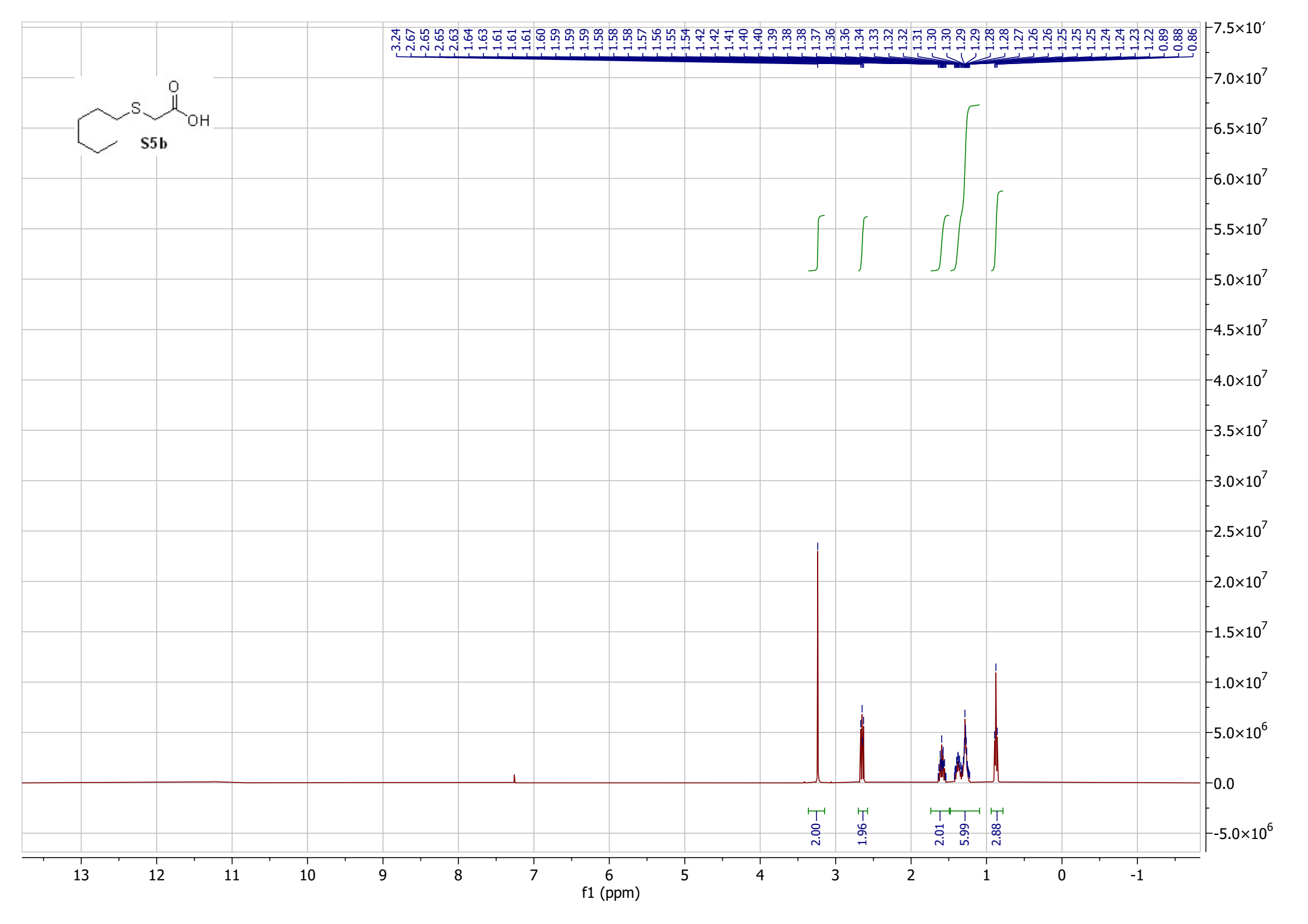

165.56
164.13
84.02
56.67
55.39
53.08
28.13
tBu-O
OCH3
(±)-1h
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

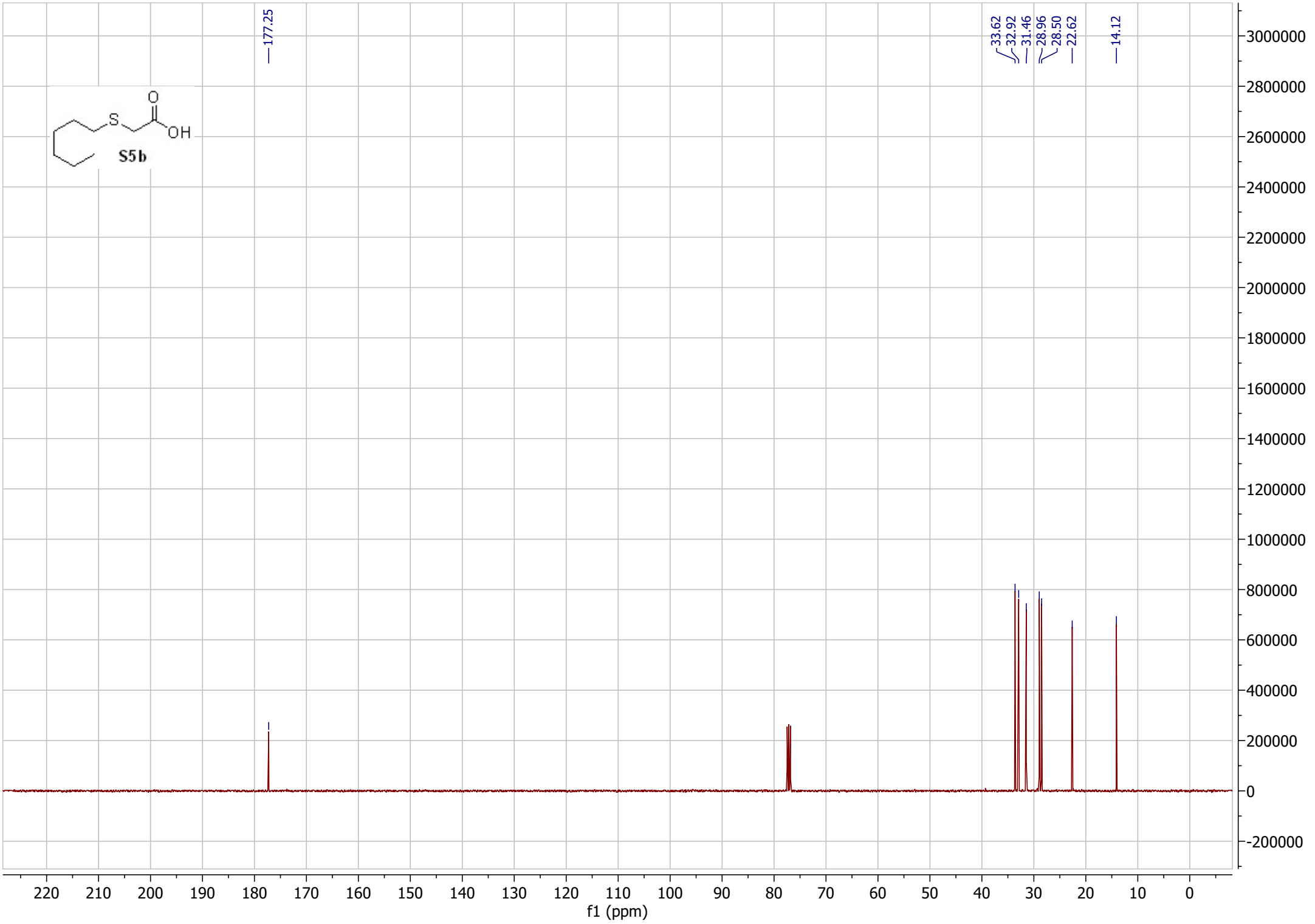

S5a
f1 (ppm)

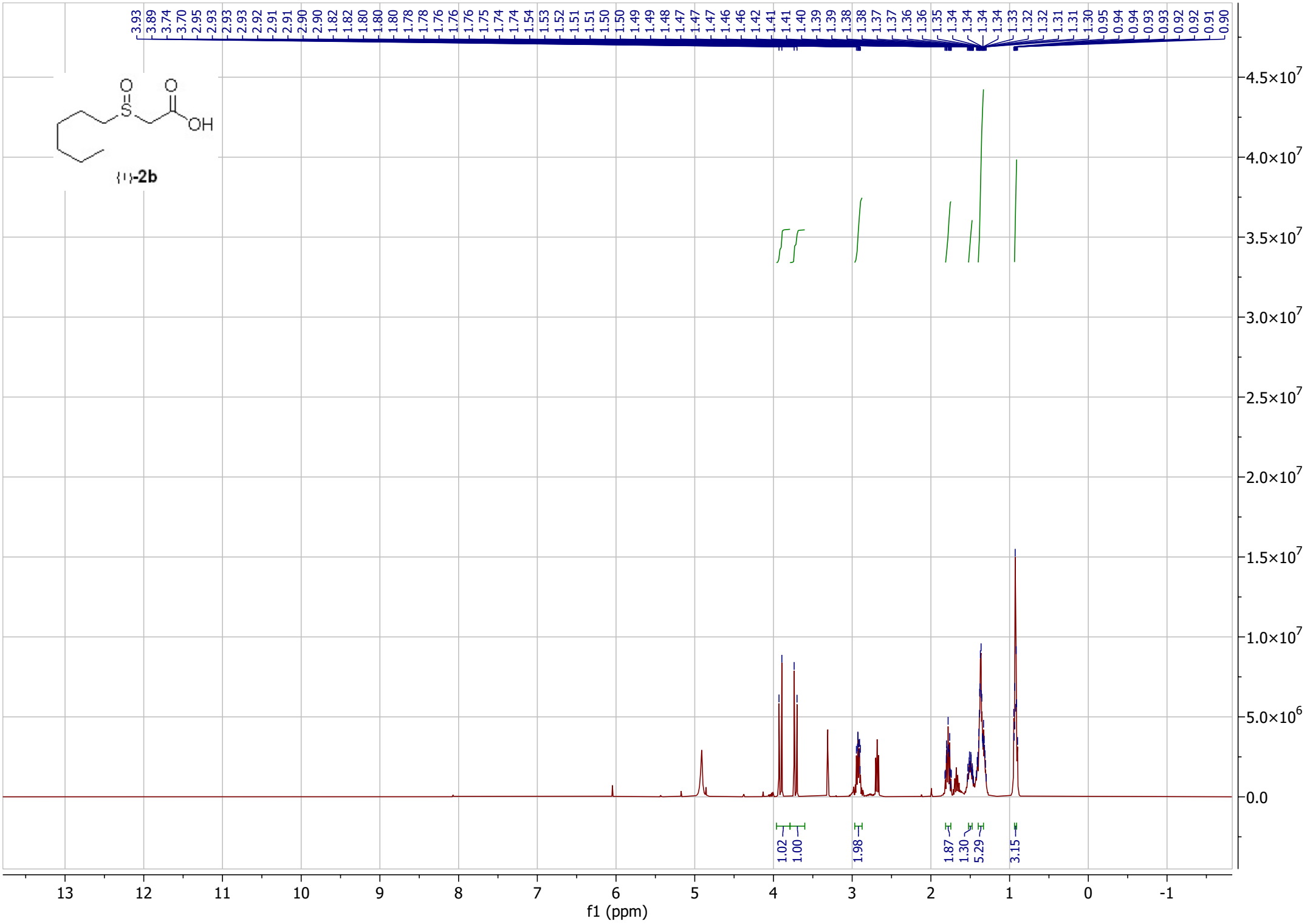

174.75
44.98
34.30
32.77
32.72
27.02
26.95
S5a
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

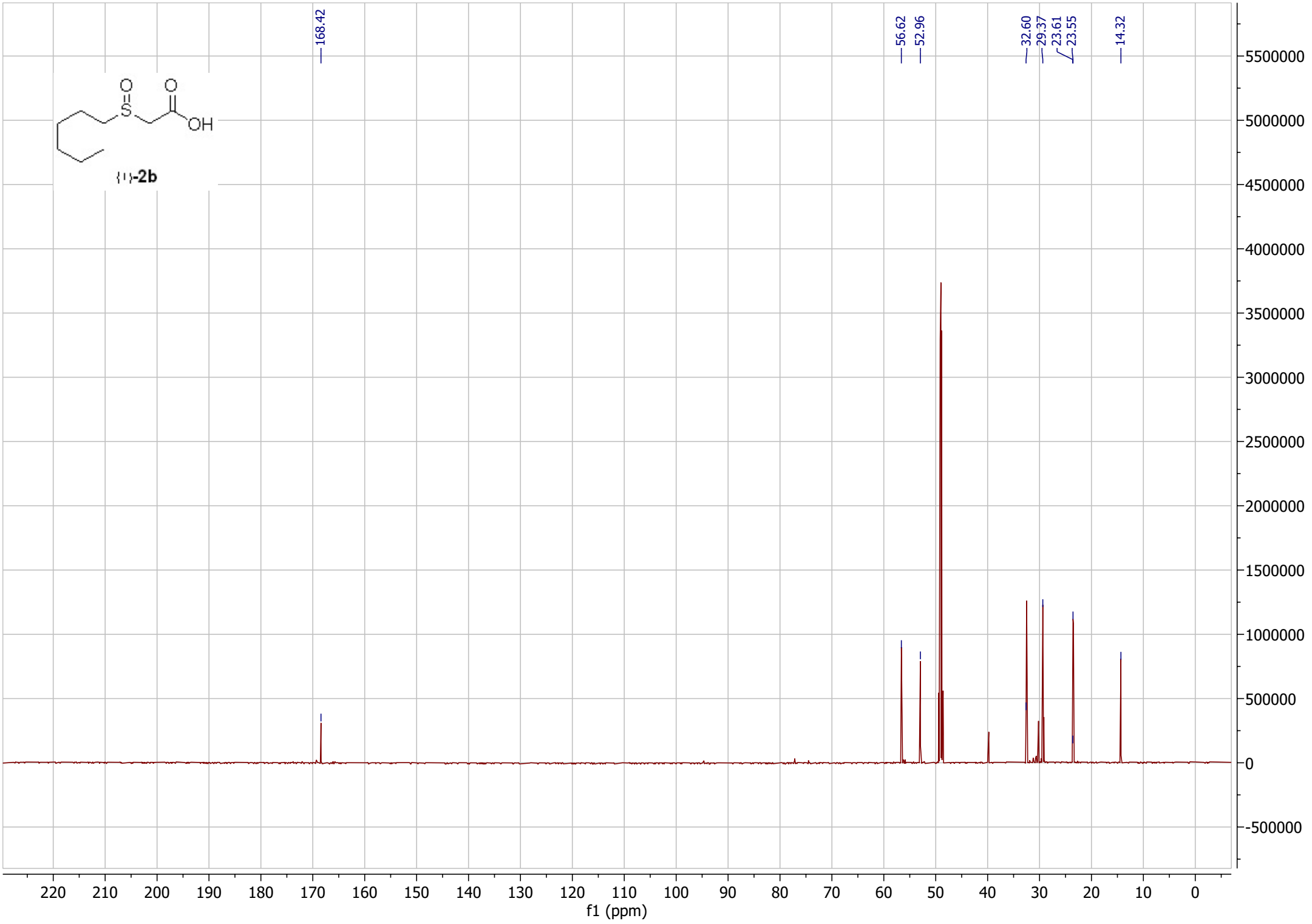

(+/-)-2a
f1 (ppm)
1.00
0.98
1.00
0.91
3.20
1.06
5.16

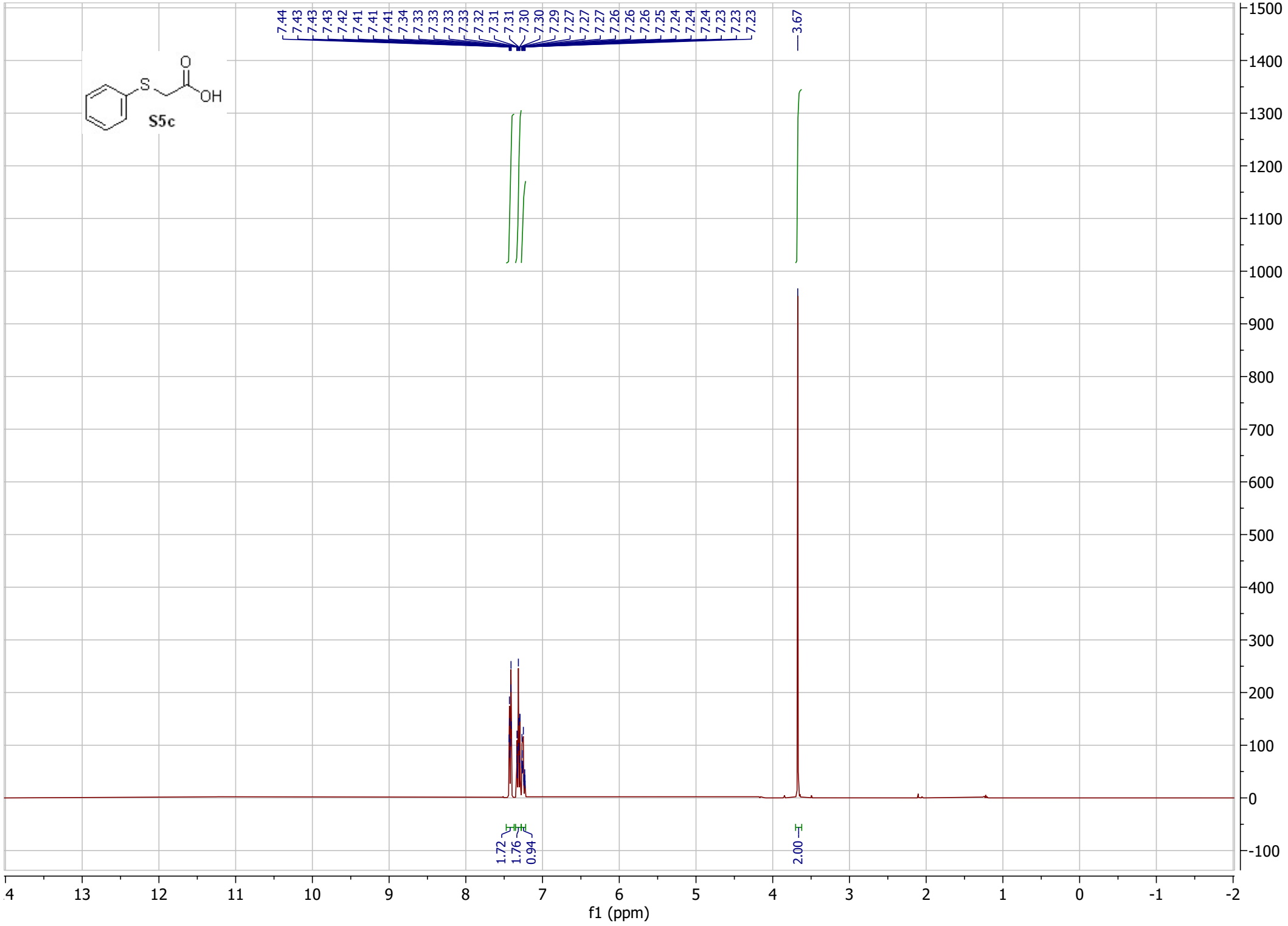

166.98
58.55
50.92
26.42
25.34
25.30
25.01
24.60
O
O
S
OH
(+)-2a
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

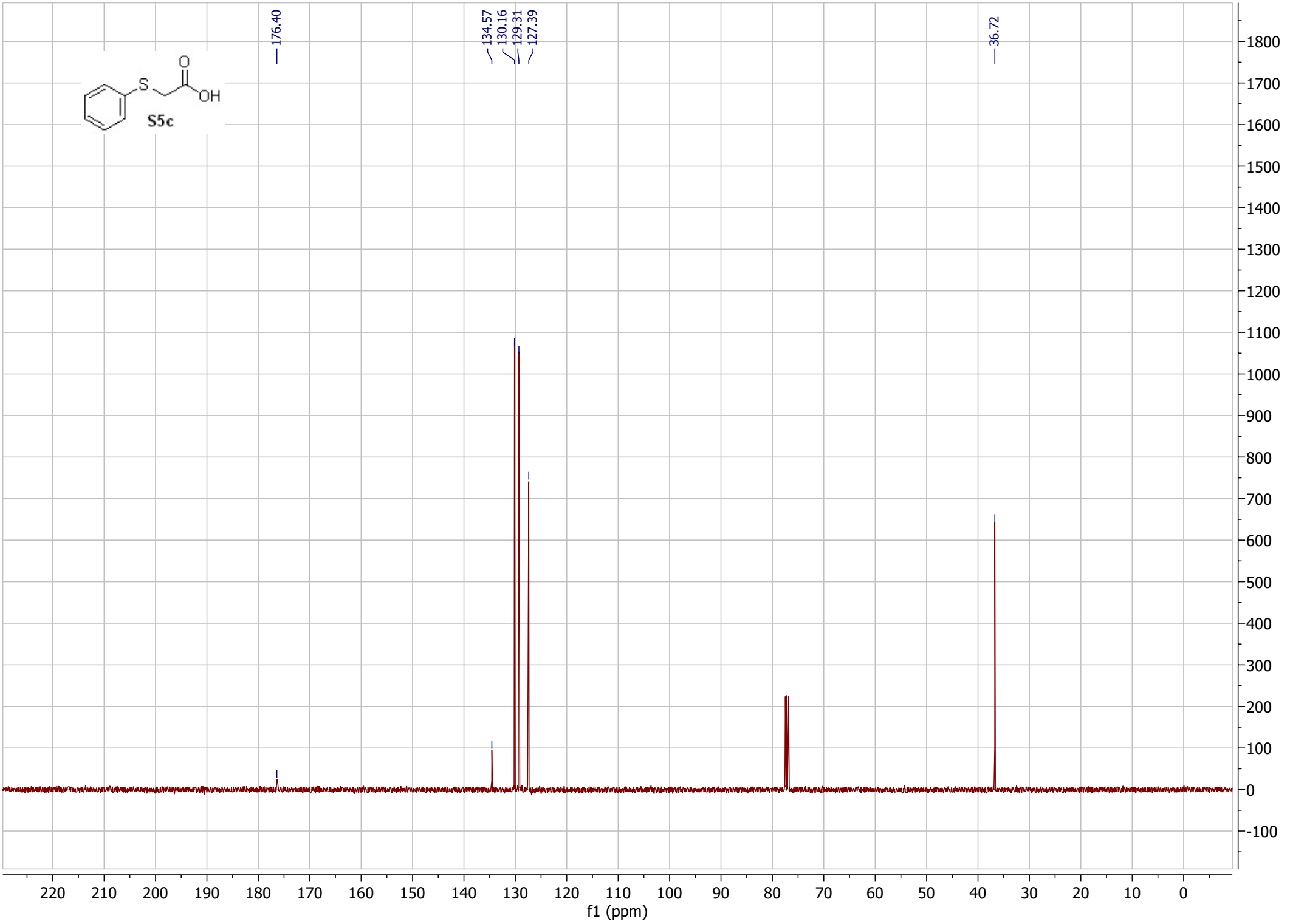

S5b
3.24 2.67 2.65 2.65 2.63 1.64 1.63 1.61 1.61 1.61 1.60 1.59 1.59 1.59 1.58 1.58 1.58 1.57 1.56 1.55 1.54 1.42 1.42 1.41 1.40 1.40 1.39 1.38 1.38 1.37 1.36 1.36 1.34 1.33 1.32 1.32 1.31 1.30 1.30 1.29 1.29 1.28 1.28 1.27 1.26 1.26 1.25 1.25 1.25 1.24 1.24 1.23 1.22 0.89 0.88 0.86
2.00
1.96
2.01
5.99
2.88
f1 (ppm)

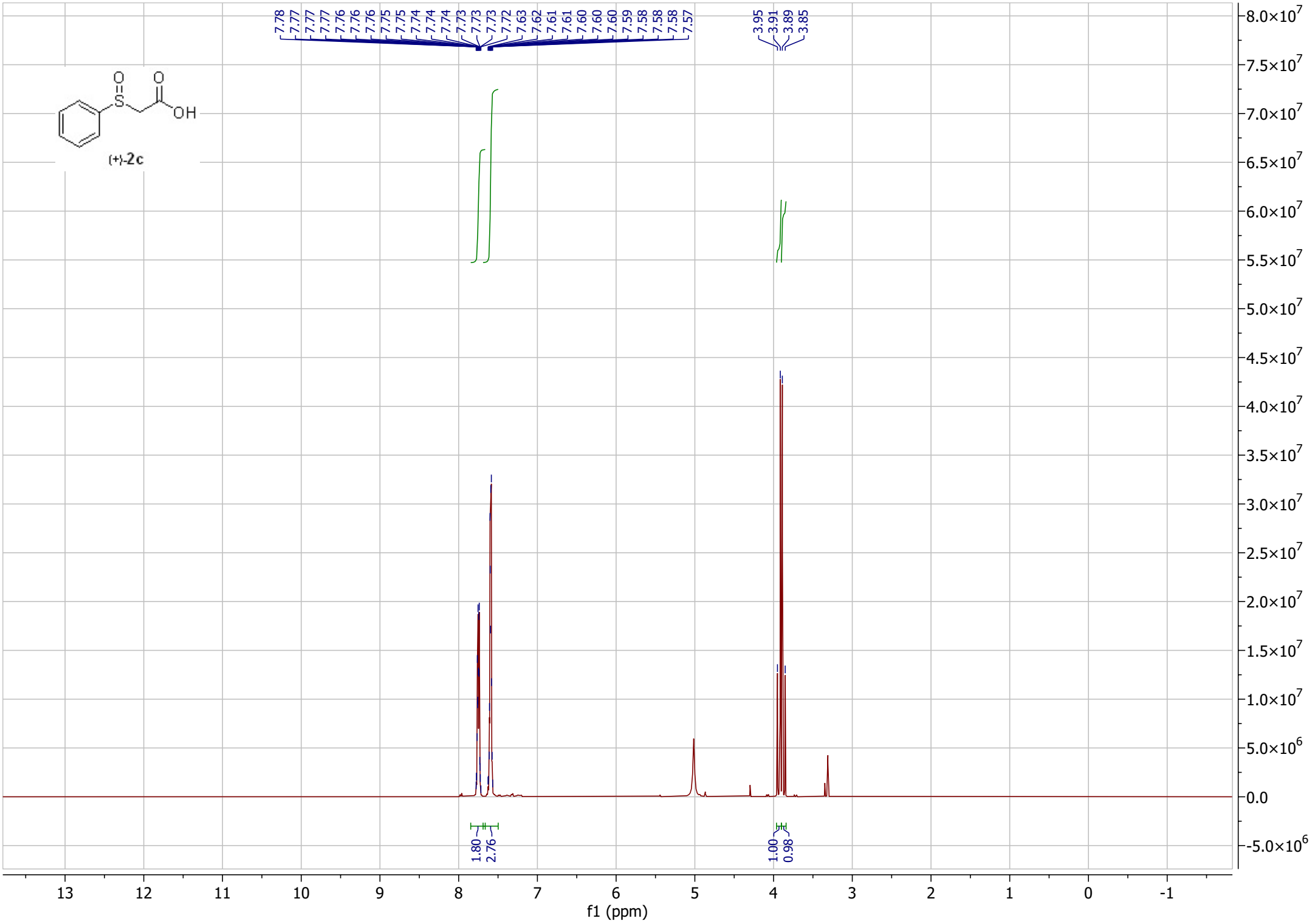

177.25
33.62
32.92
31.46
28.96
28.50
22.62
14.12
S5b
f1 (ppm)

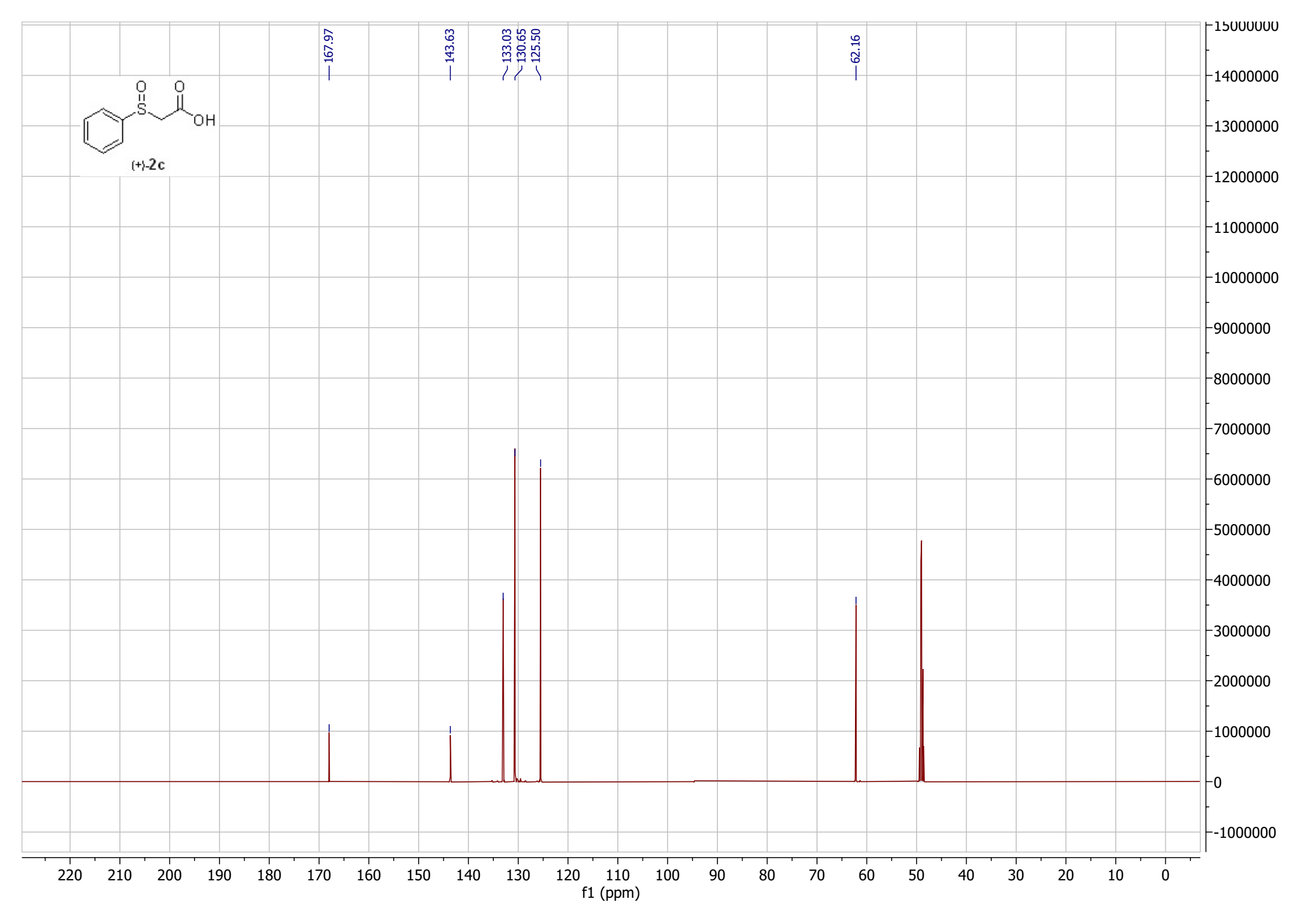

(±)-2b
f1 (ppm)
1.02
1.00
1.98
1.87
1.30
5.29
3.15

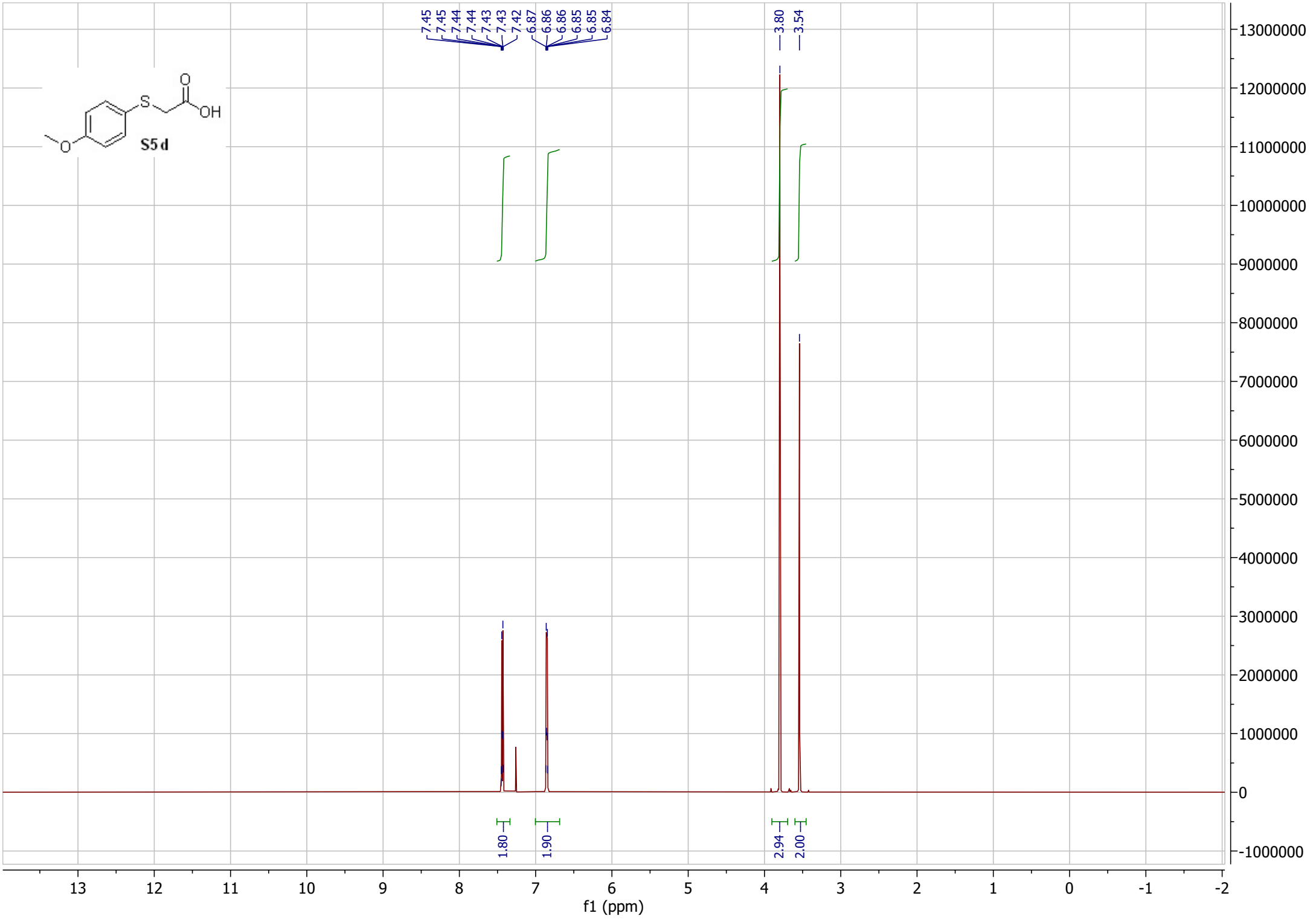

168.42
56.62
52.96
32.60
29.37
23.61
23.55
14.32
(±)-2b
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

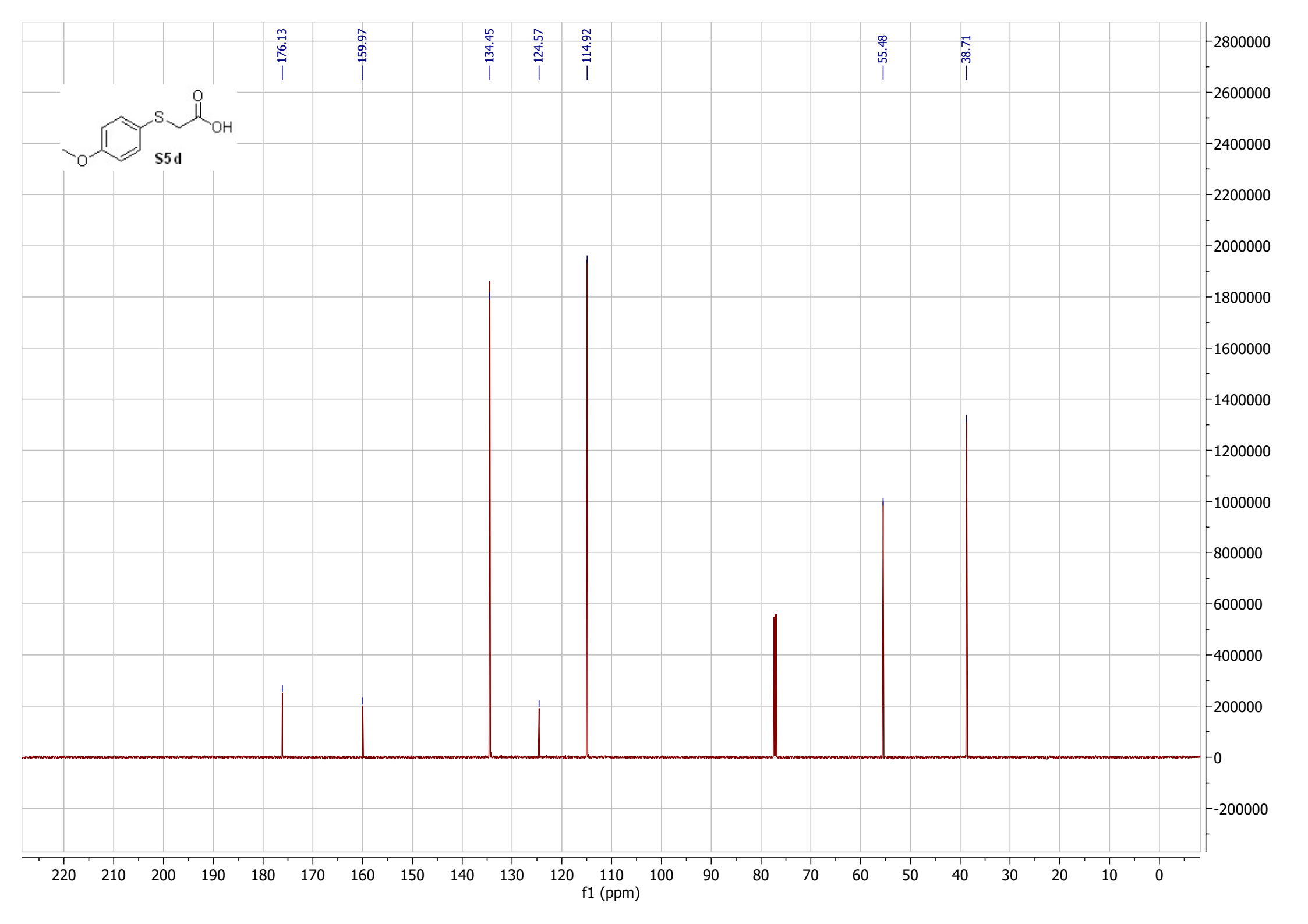

S5c
7.44 7.43 7.43 7.43 7.42 7.41 7.41 7.41 7.34 7.33 7.33 7.33 7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.27 7.27 7.27 7.26 7.26 7.26 7.25 7.24 7.24 7.24 7.23 7.23 7.23
3.67
1.72
1.76
0.94
2.00
f1 (ppm)

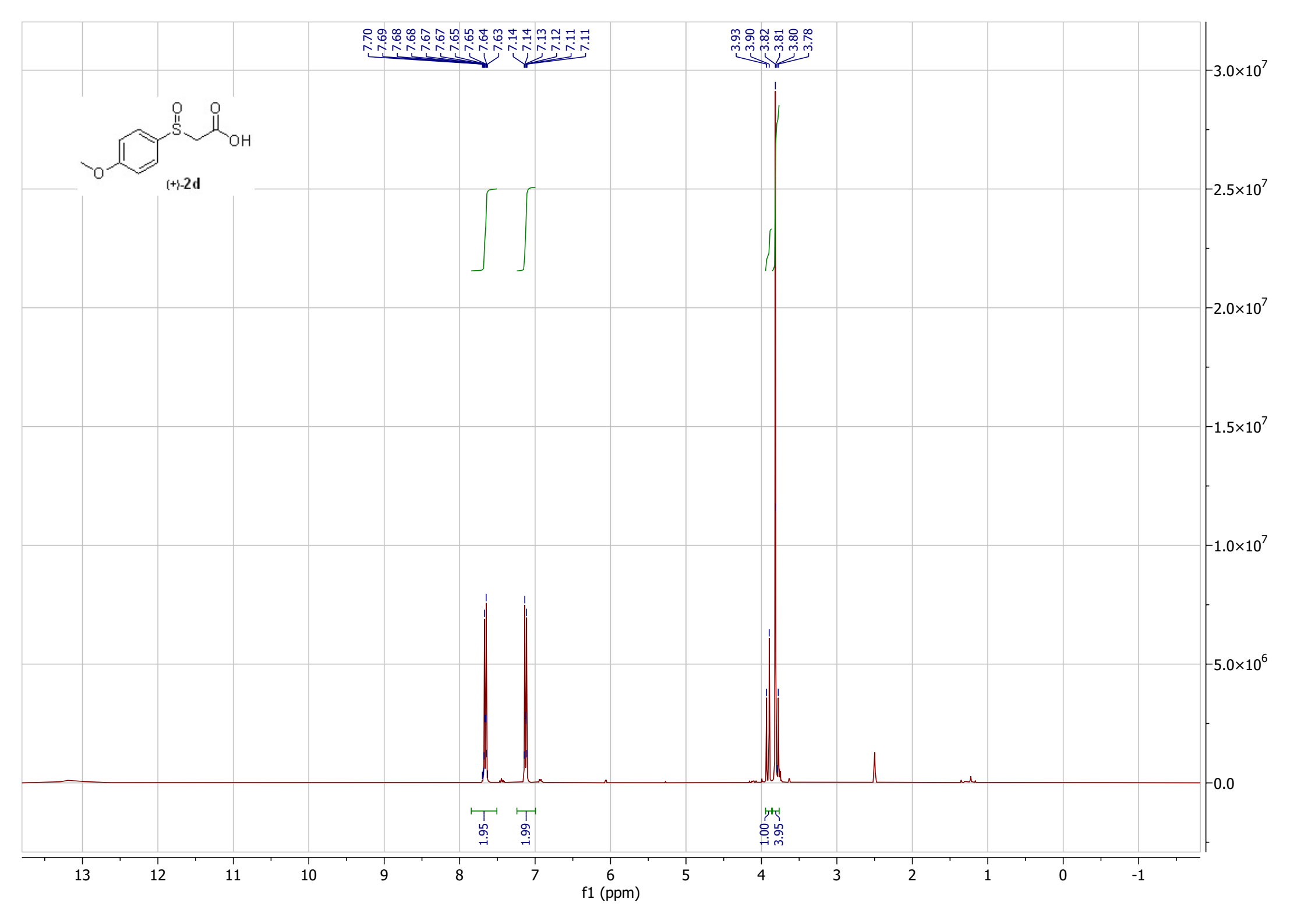

176.40
134.57
130.16
129.31
127.39
36.72
S
O
OH
S5c
f1 (ppm)

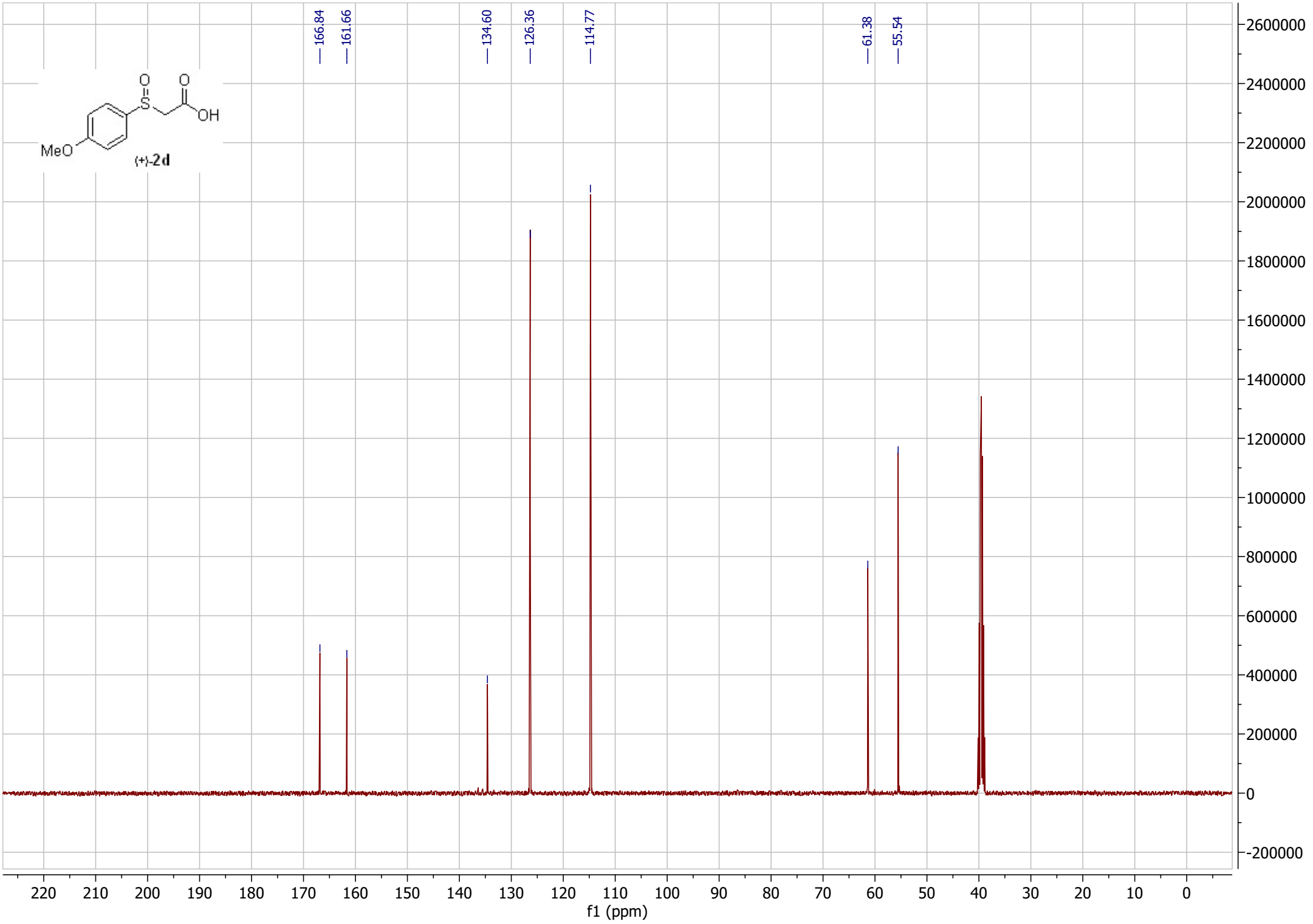

7.78 7.77 7.77 7.77 7.76 7.76 7.76 7.75 7.75 7.74 7.74 7.74 7.73 7.73 7.73 7.72 7.63 7.62 7.61 7.61 7.60 7.60 7.60 7.59 7.58 7.58 7.58 7.57
3.95 3.91 3.89 3.85
O
O
S
OH
(+)-2c
1.80
2.76
1.00
0.98
8.0×10^7
7.5×10^7
7.0×10^7
6.5×10^7
6.0×10^7
5.5×10^7
5.0×10^7
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
-5.0×10^6
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

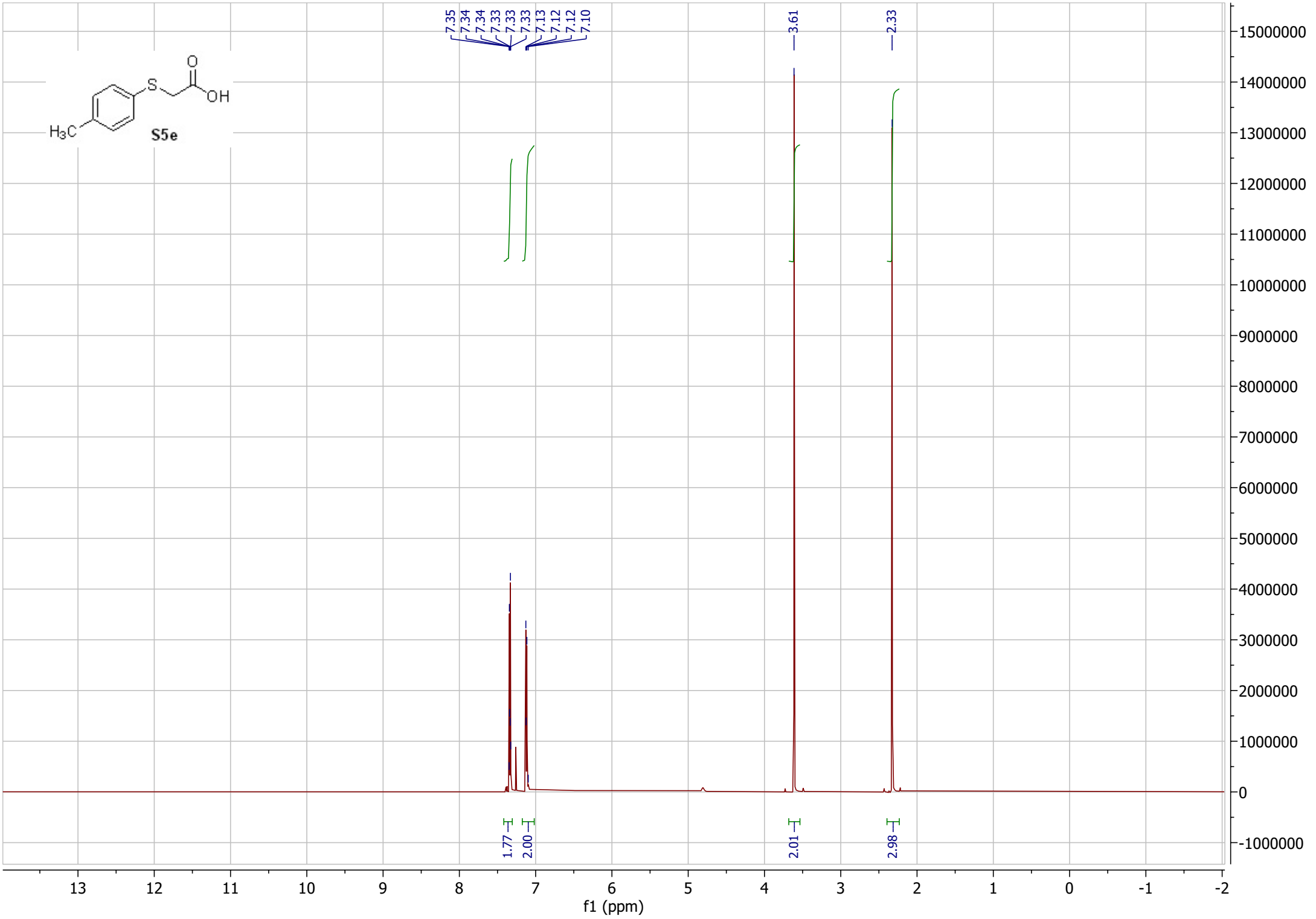

167.97
143.63
133.03
130.65
125.50
62.16
(+)-2c
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

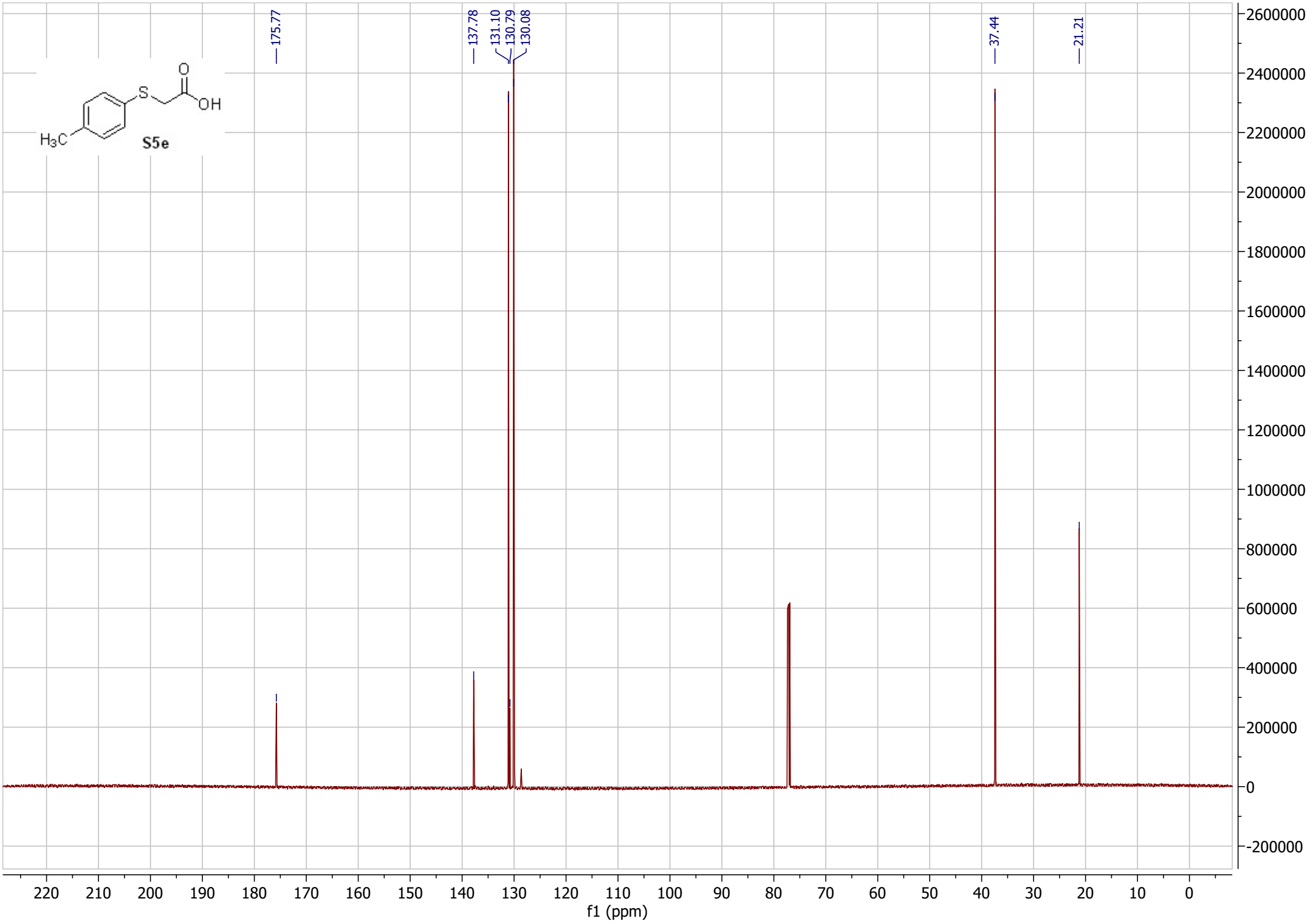

S5 d
7.45
7.45
7.44
7.44
7.43
7.43
7.42
6.87
6.86
6.86
6.85
6.85
6.84
3.80
3.54
1.80
1.90
2.94
2.00
f1 (ppm)

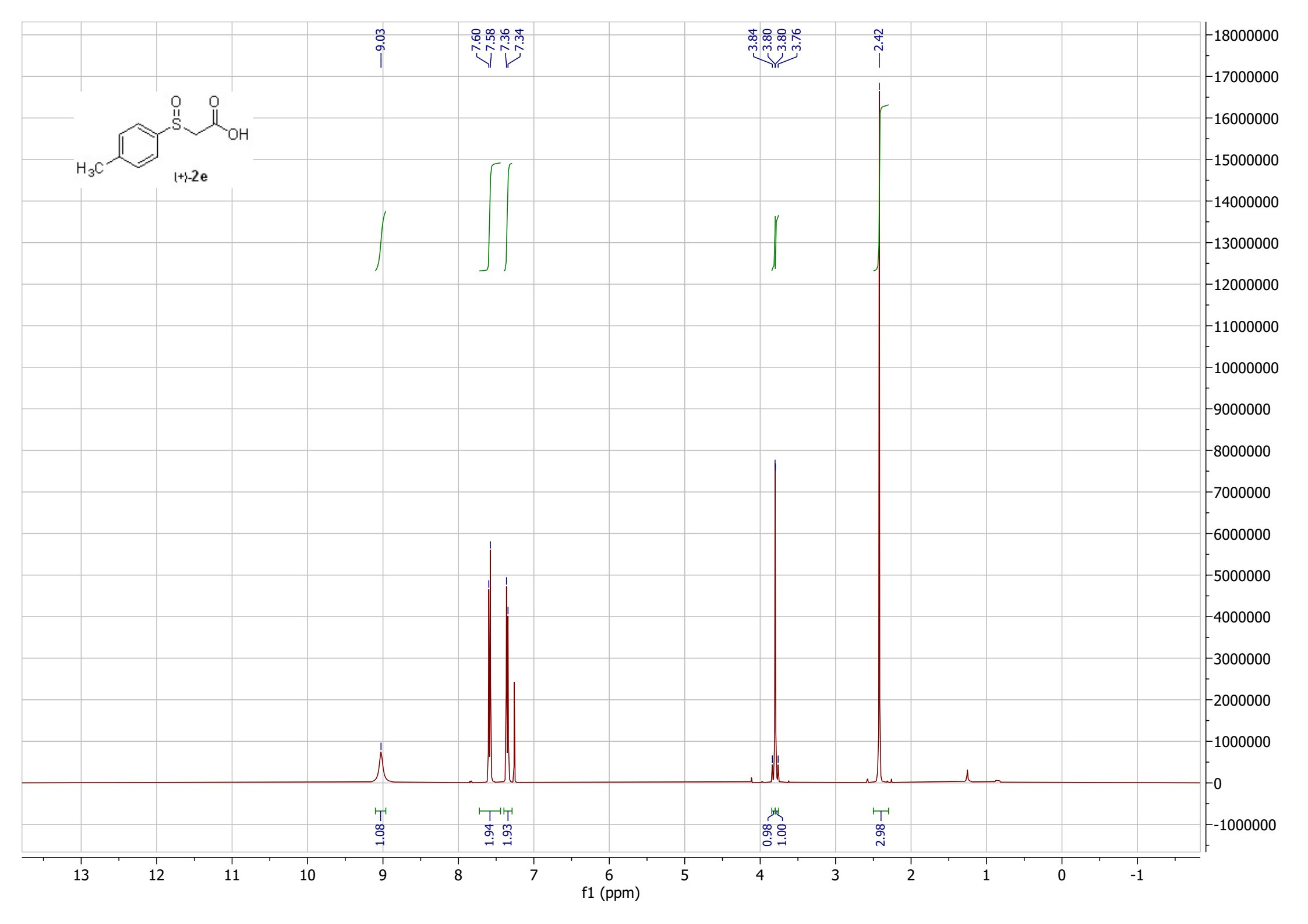

176.13
159.97
134.45
124.57
114.92
55.48
38.71
S
O
OH
O
S5 d
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

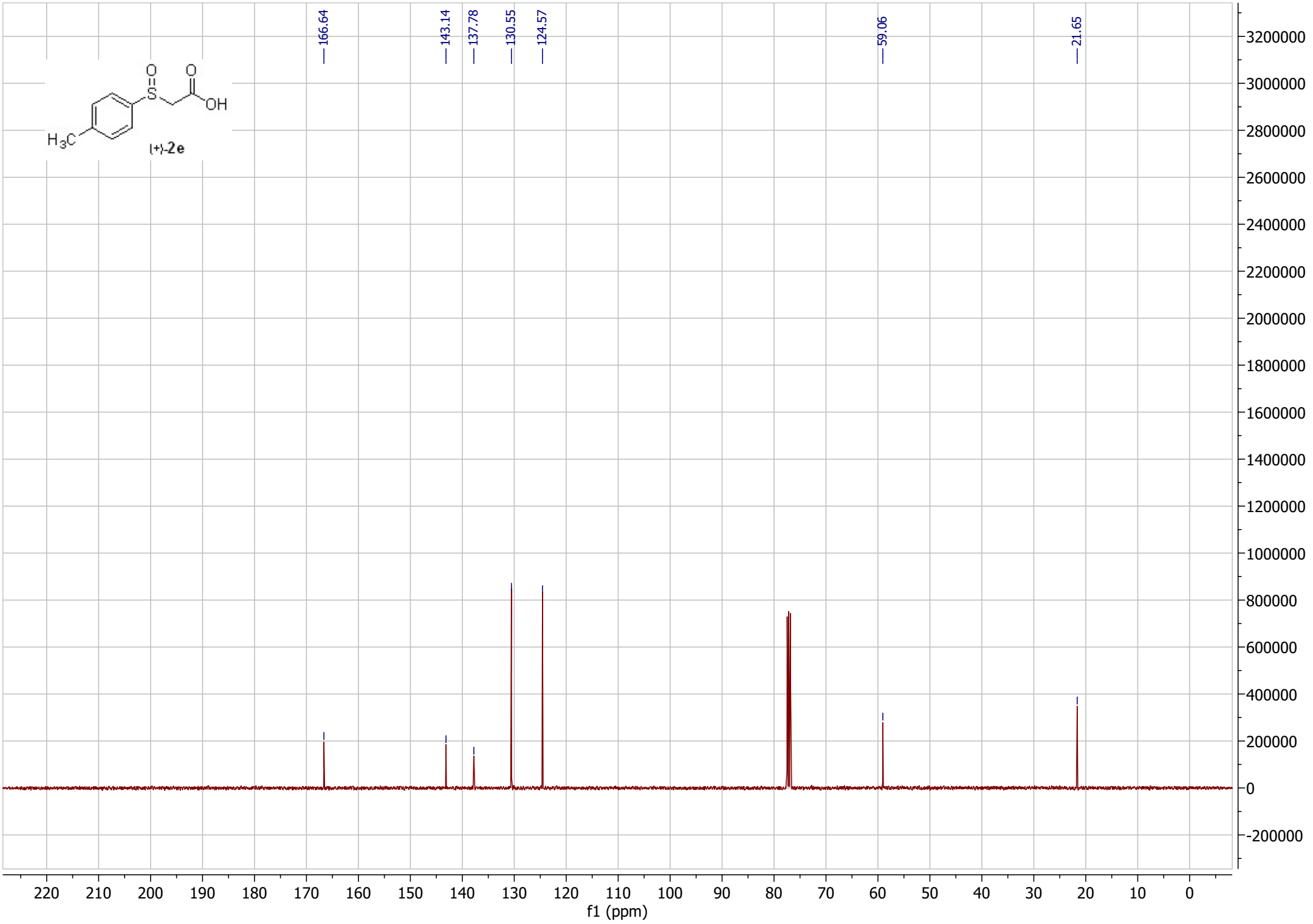

7.70
7.69
7.68
7.68
7.67
7.67
7.65
7.65
7.64
7.63
7.14
7.14
7.13
7.12
7.11
7.11
3.93
3.90
3.82
3.81
3.80
3.78
O
O
S=O
OH
O
(+)-2d
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
1.95
1.99
1.00
3.95
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

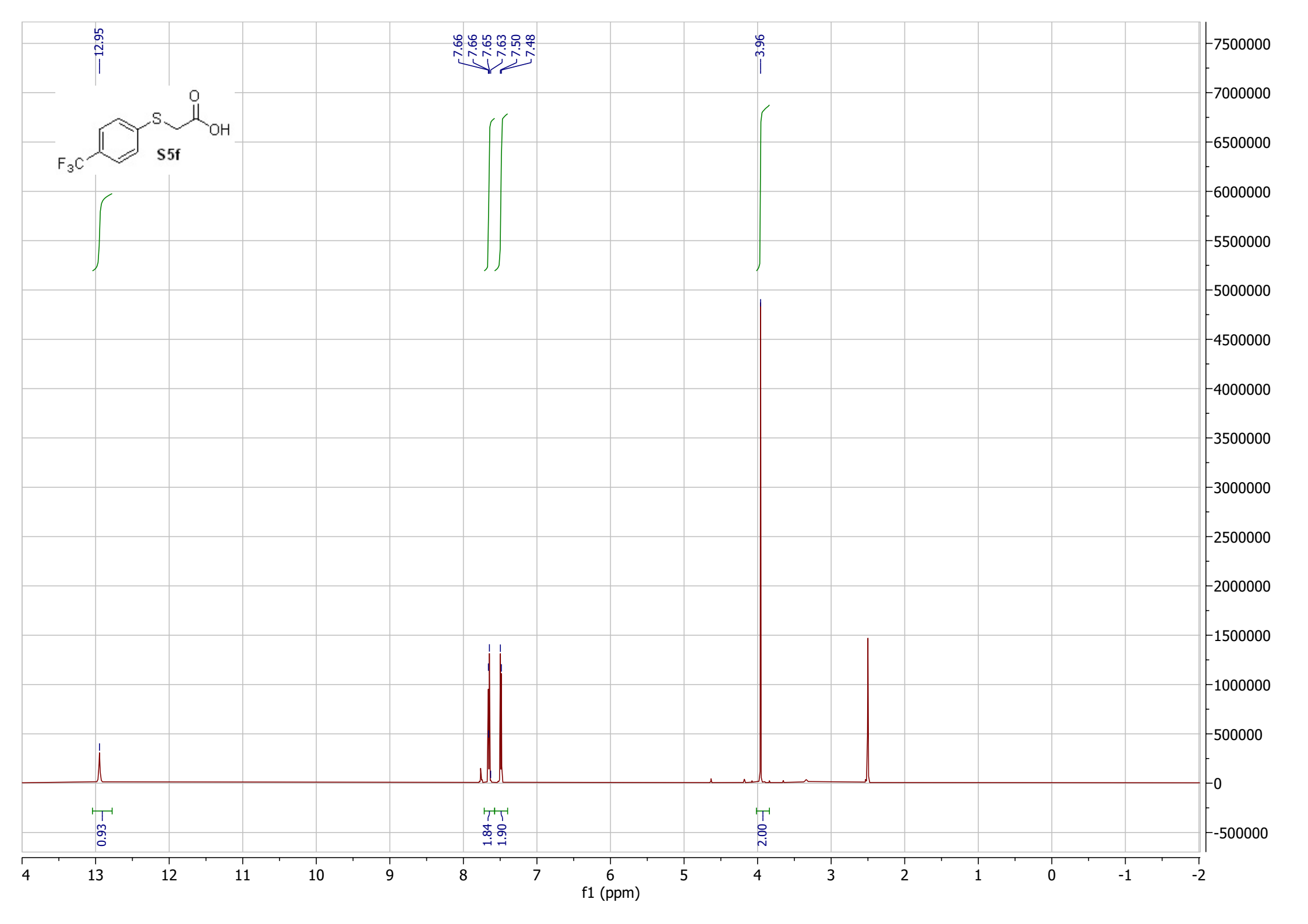

166.84
161.66
134.60
126.36
114.77
61.38
55.54
MeO
OH
(+)-2d
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

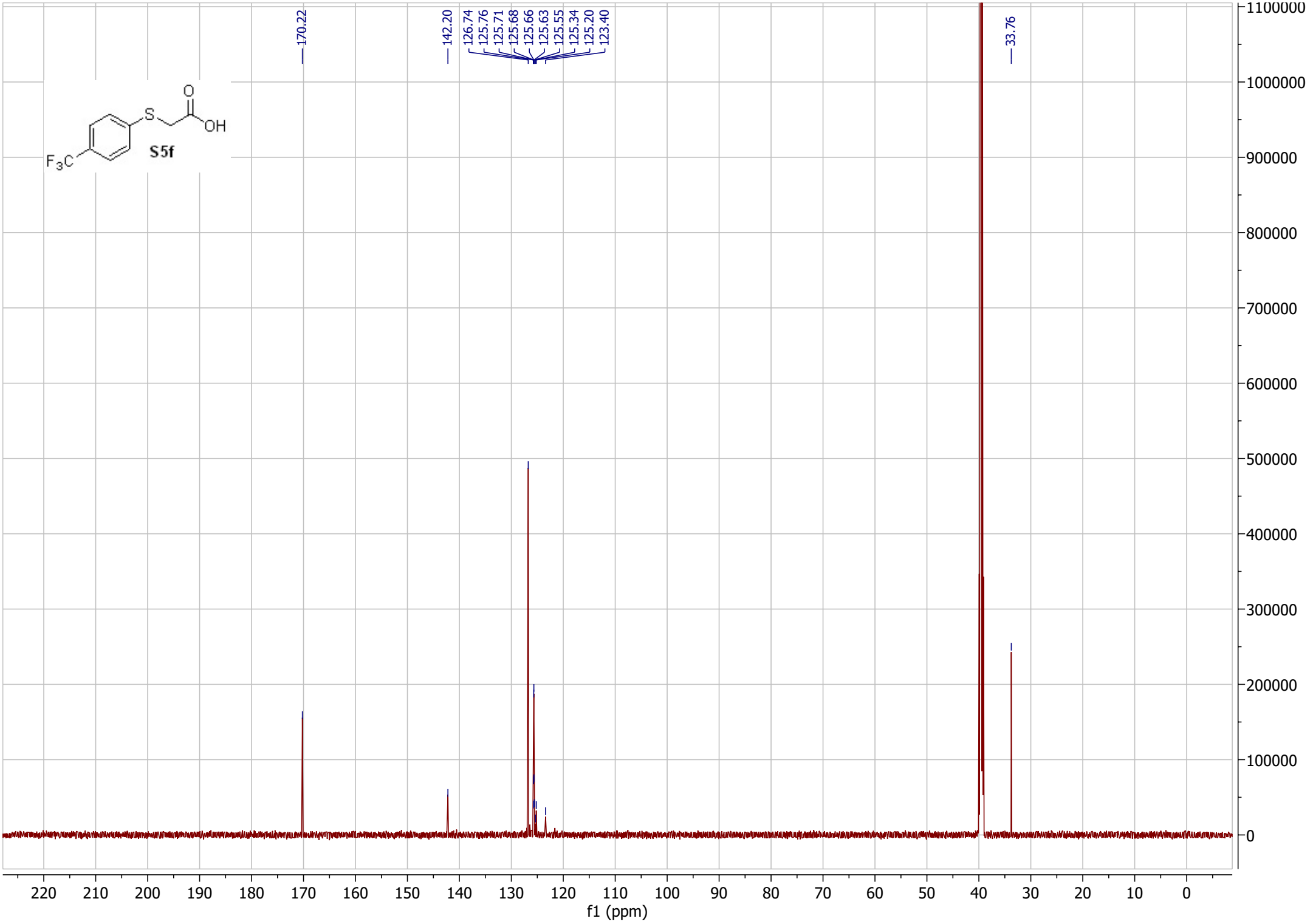

7.35
7.34
7.34
7.33
7.33
7.33
7.13
7.12
7.12
7.10
3.61
2.33
S5e
1.77
2.00
2.01
2.98
f1 (ppm)

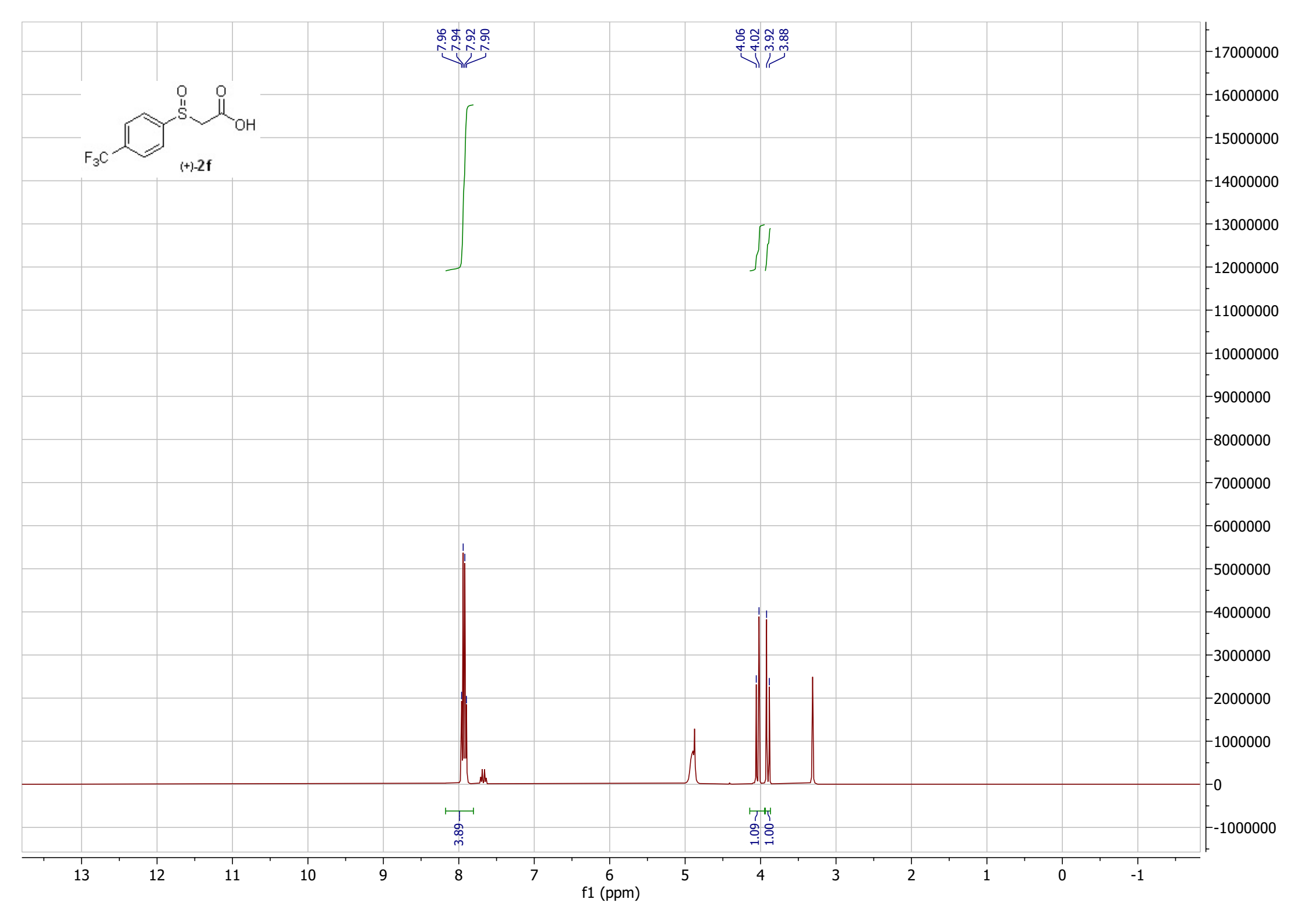

175.77
137.78
131.10
130.79
130.08
37.44
21.21
O
S
OH
H3C
S5e
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

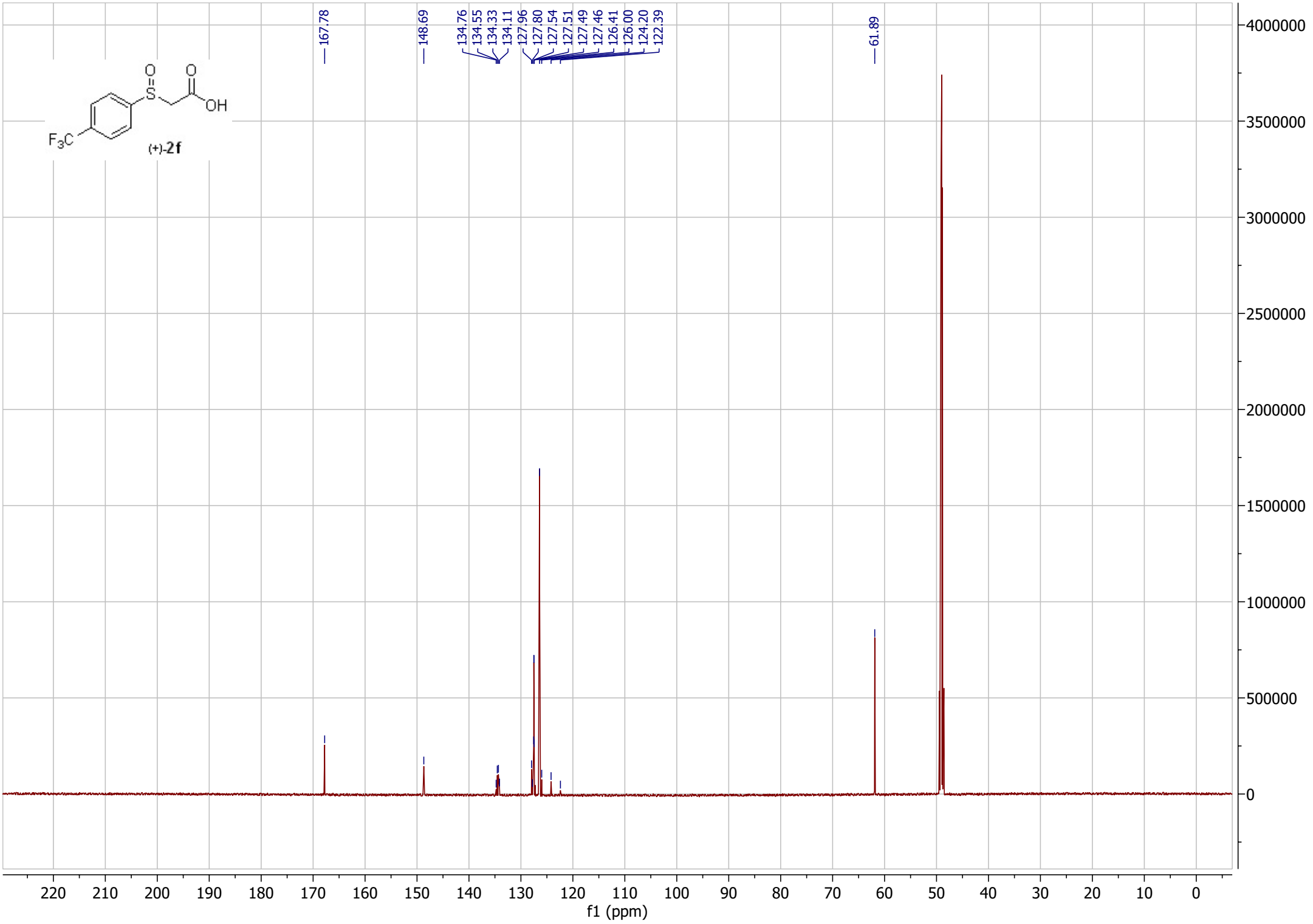

9.03
7.60
7.58
7.36
7.34
3.84
3.80
3.80
3.76
2.42
(+)-2e
1.08
1.94
1.93
0.98
1.00
2.98
f1 (ppm)

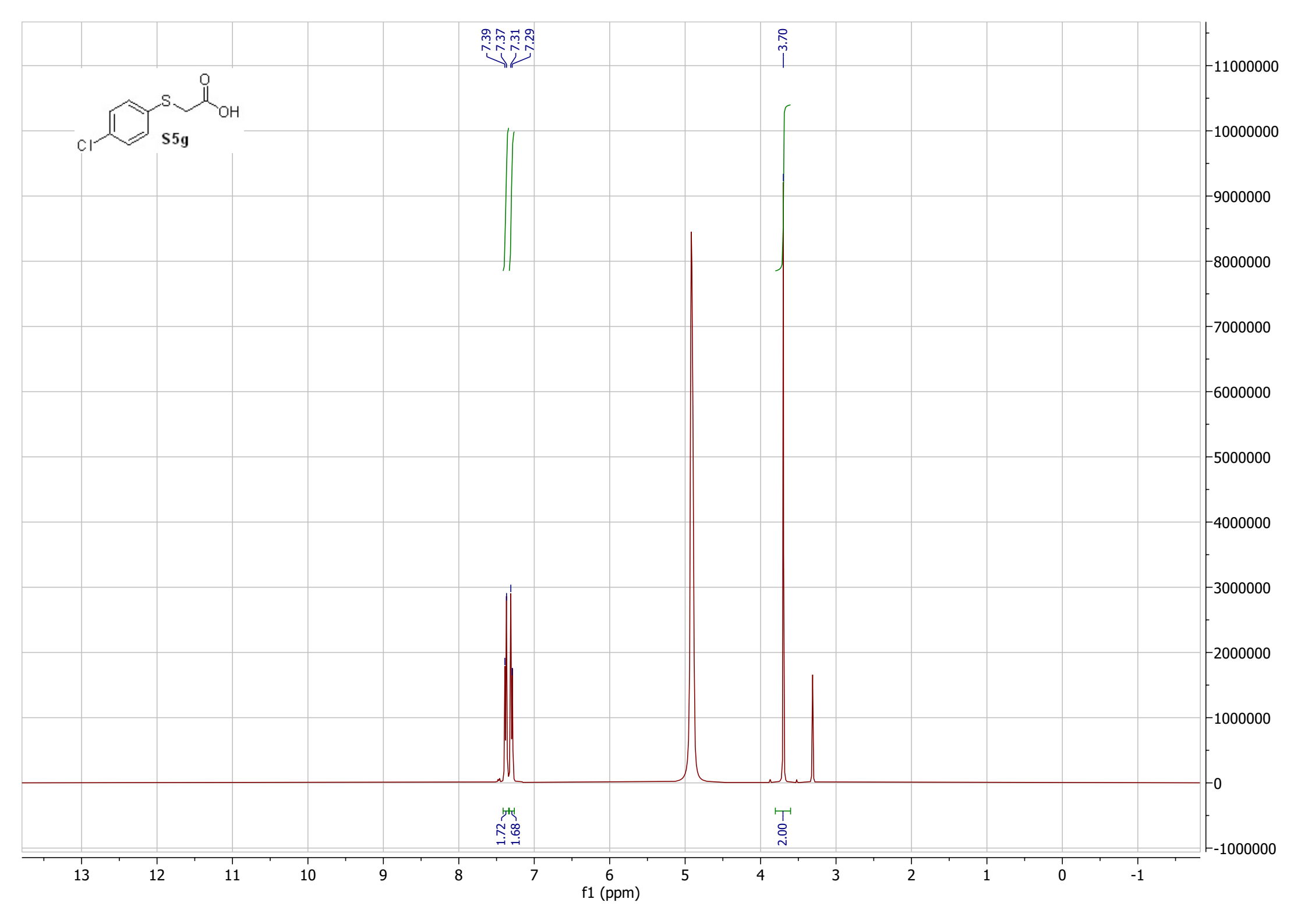

166.64
143.14
137.78
130.55
124.57
59.06
21.65
O
O
S
OH
H3C
(+)-2e
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

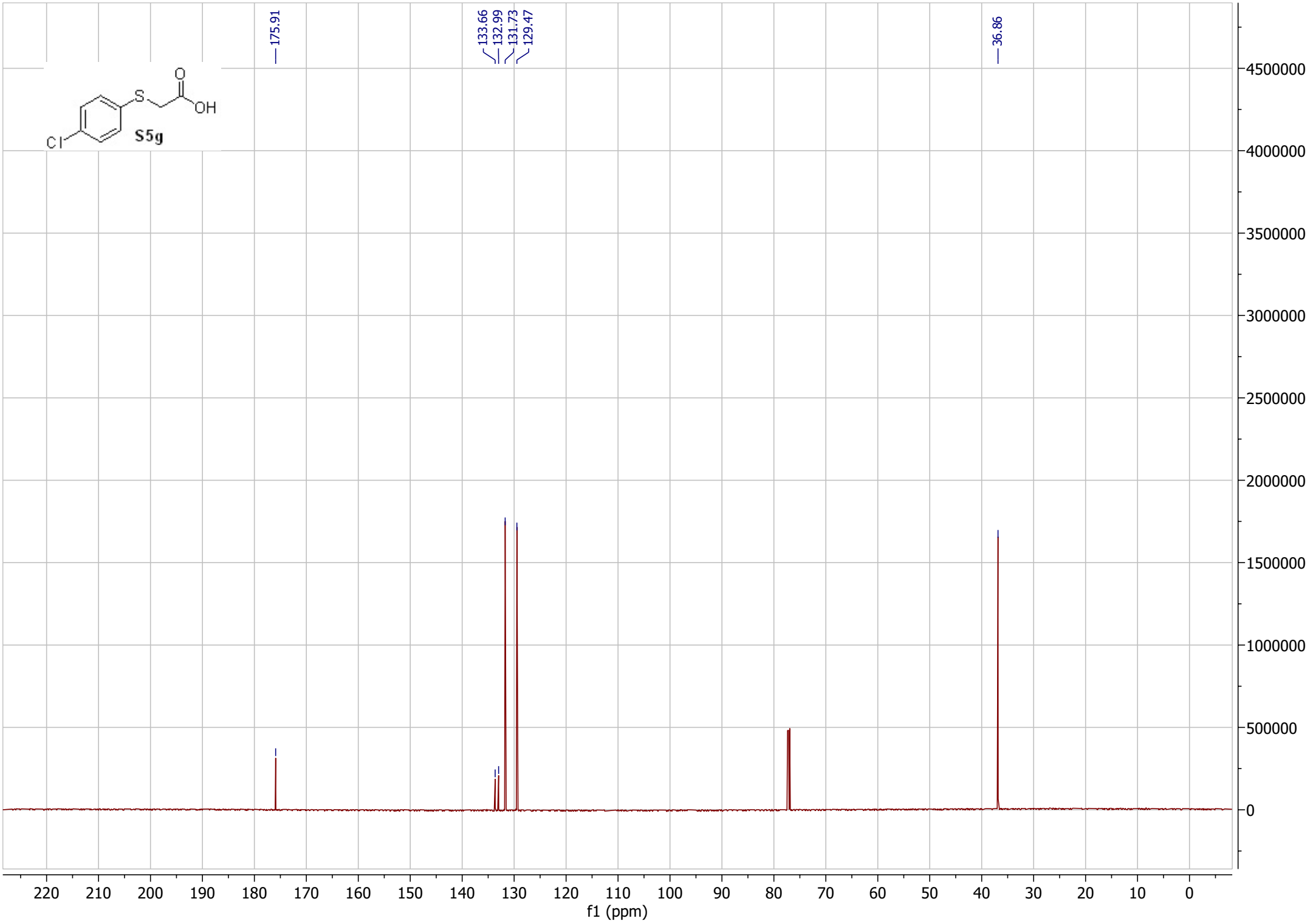

12.95
7.66
7.66
7.65
7.63
7.50
7.48
3.96
S5f
0.93
1.84
1.90
2.00
f1 (ppm)

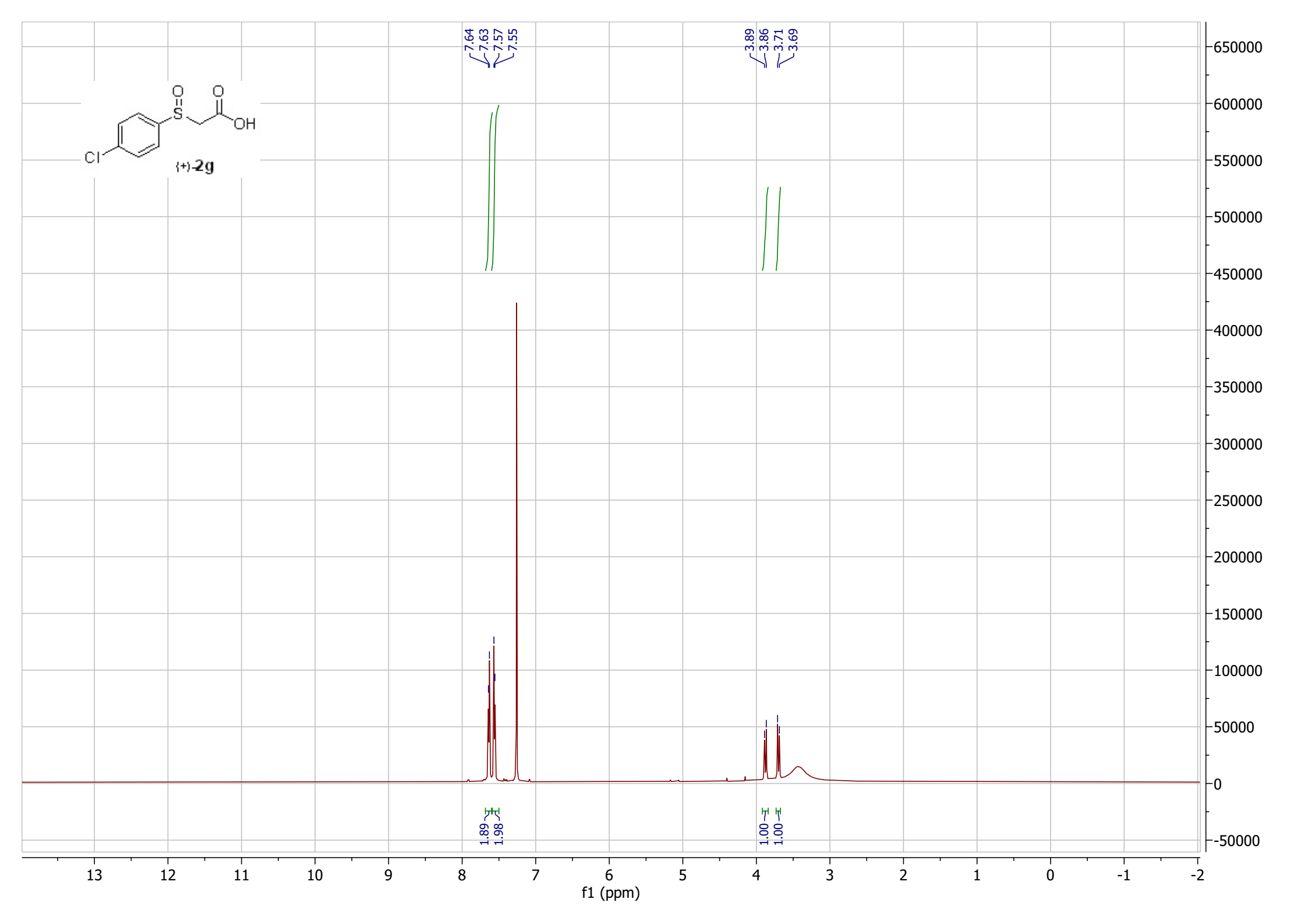

170.22
142.20
126.74
125.76
125.71
125.68
125.66
125.63
125.55
125.34
125.20
123.40
33.76
S5f
f1 (ppm)

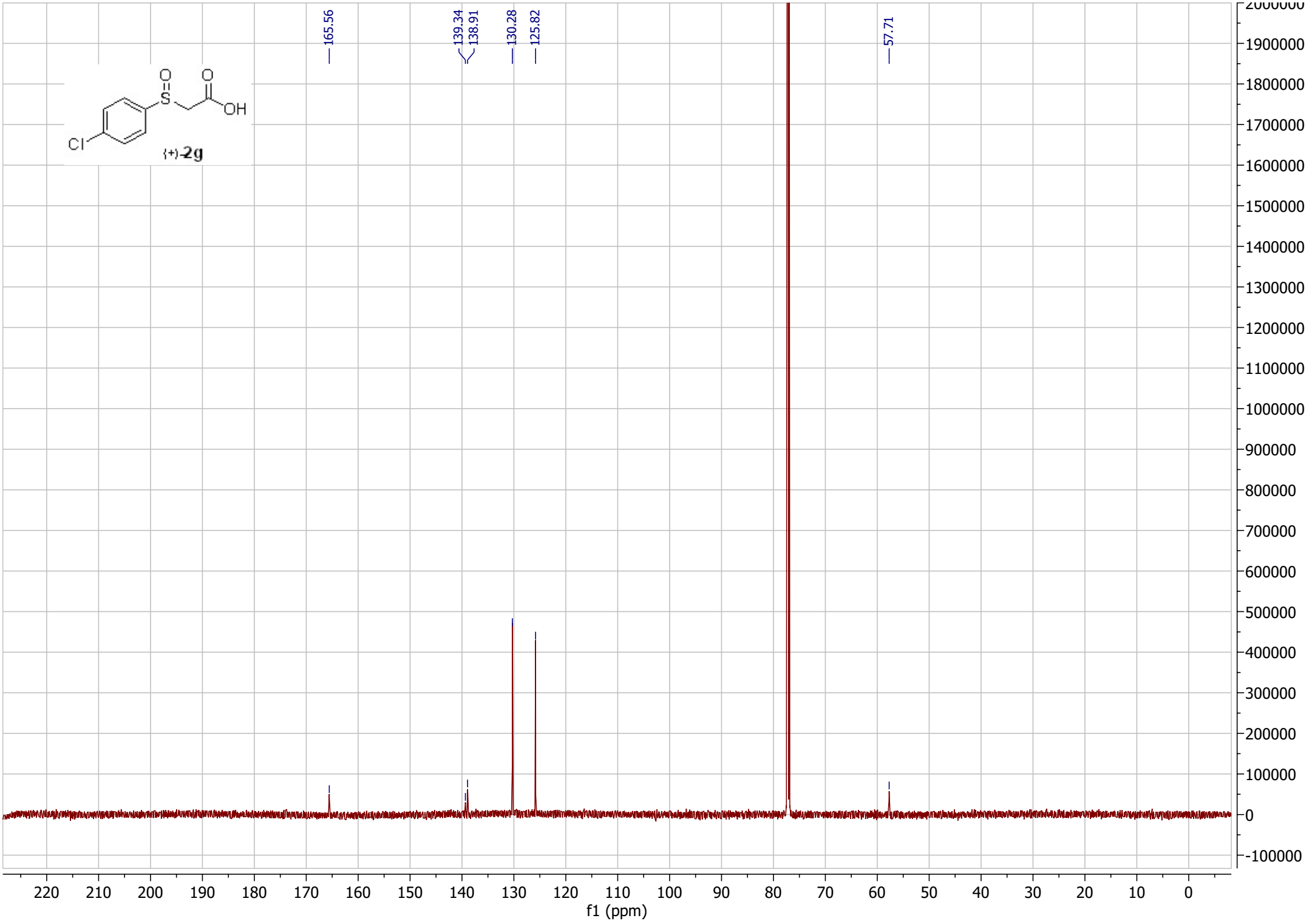

7.96
7.94
7.92
7.90
4.06
4.02
3.92
3.88
O
O
S
OH
F3C
(+)-2f
3.89
1.09
1.00
17000000
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

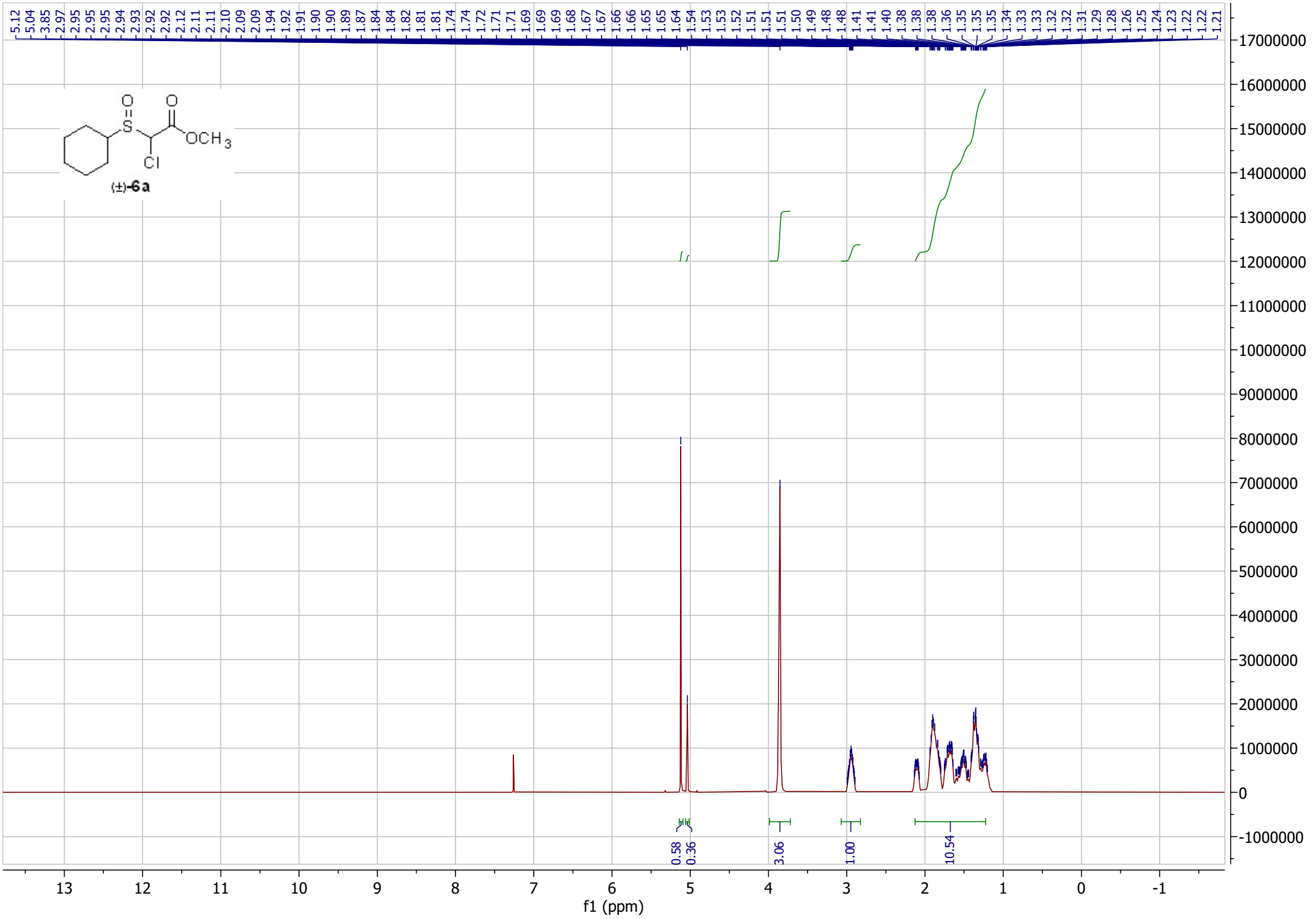

167.78
148.69
134.76
134.55
134.33
134.11
127.96
127.80
127.54
127.51
127.49
127.46
126.41
126.00
124.20
122.39
61.89
O
O
S
OH
F3C
(+)-2f
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

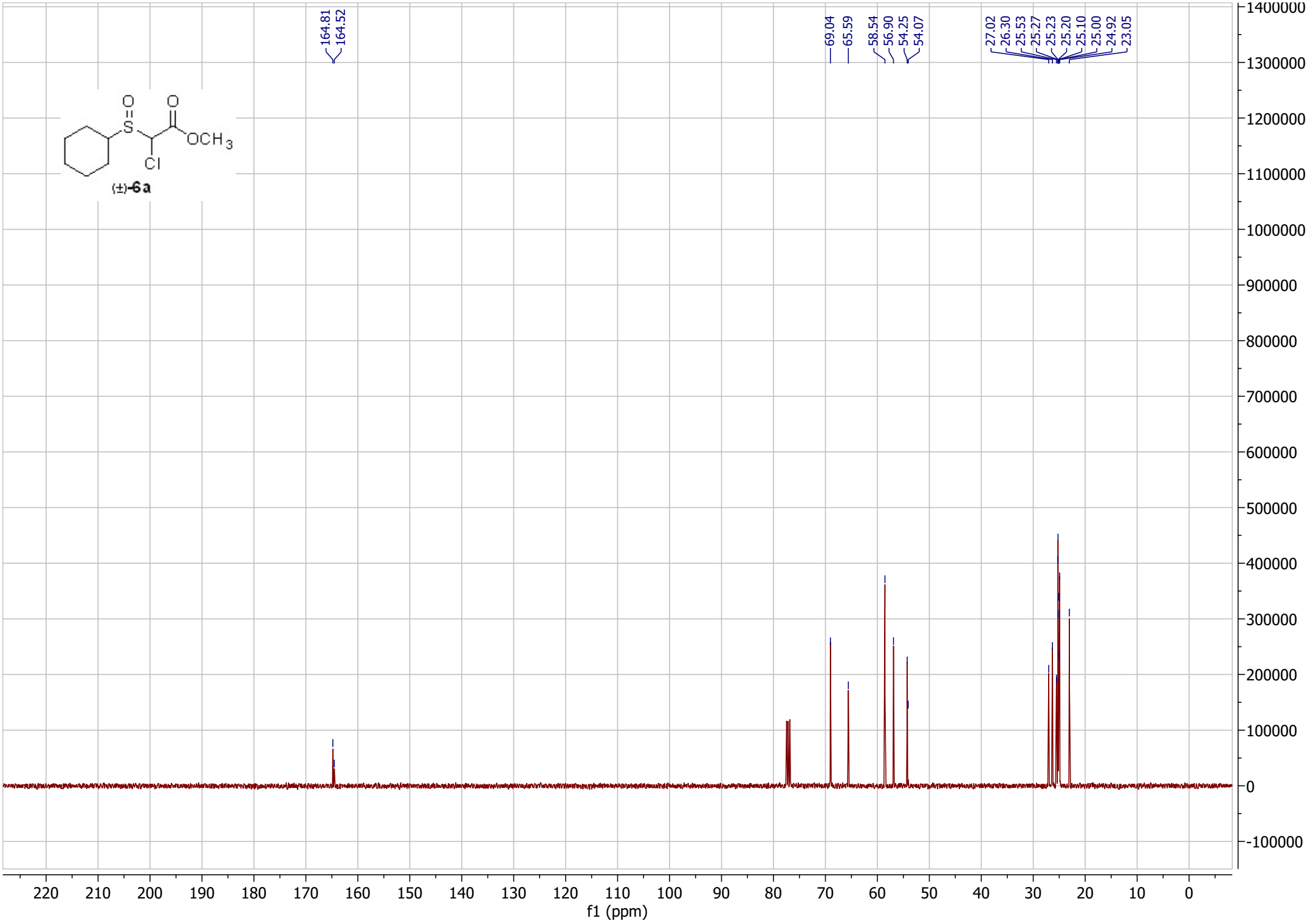

7.39
7.37
7.31
7.29
3.70
S5g
1.72
1.68
2.00
f1 (ppm)

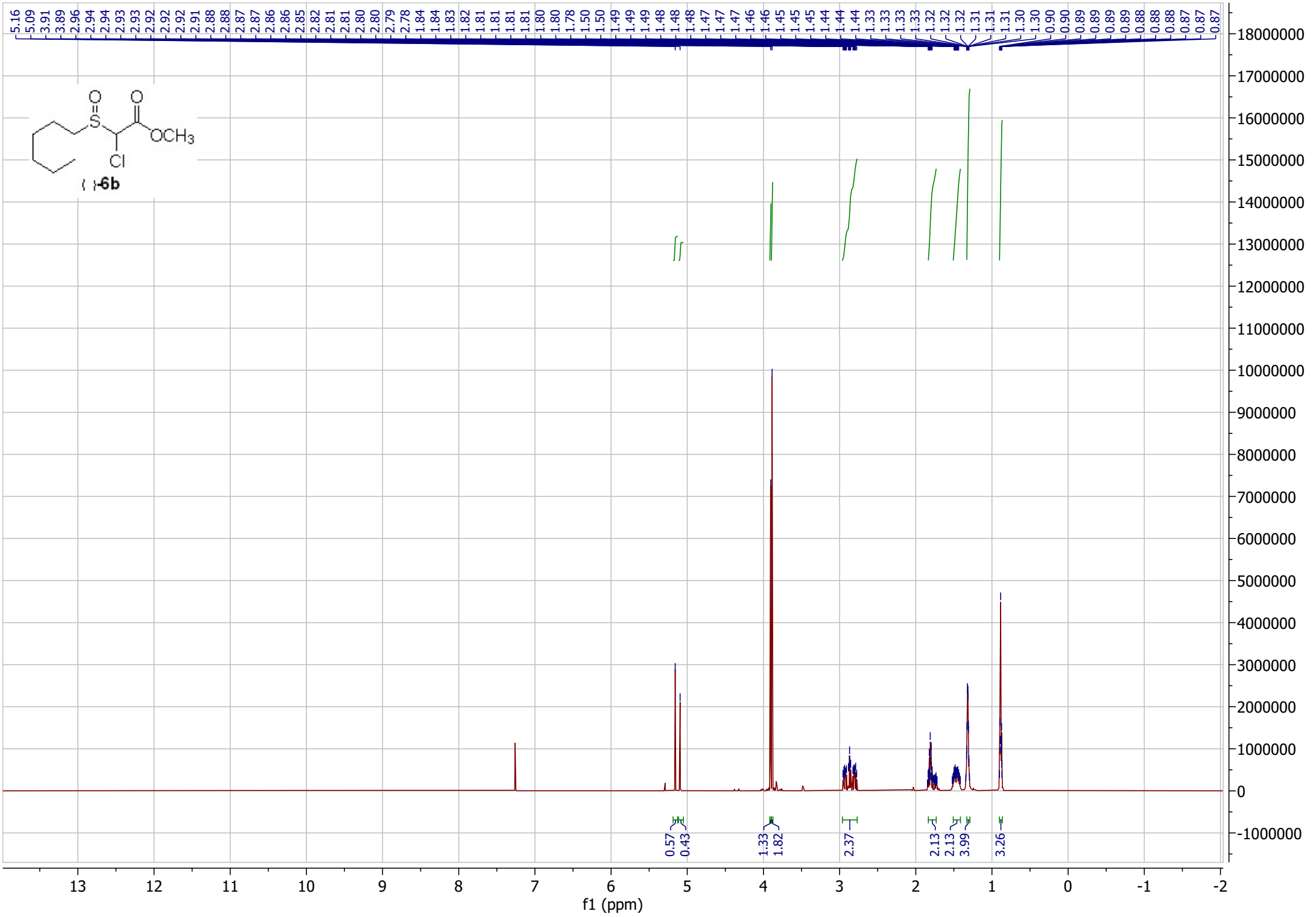

175.91
133.66
132.99
131.73
129.47
36.86
S5g
Cl
S
O
OH
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

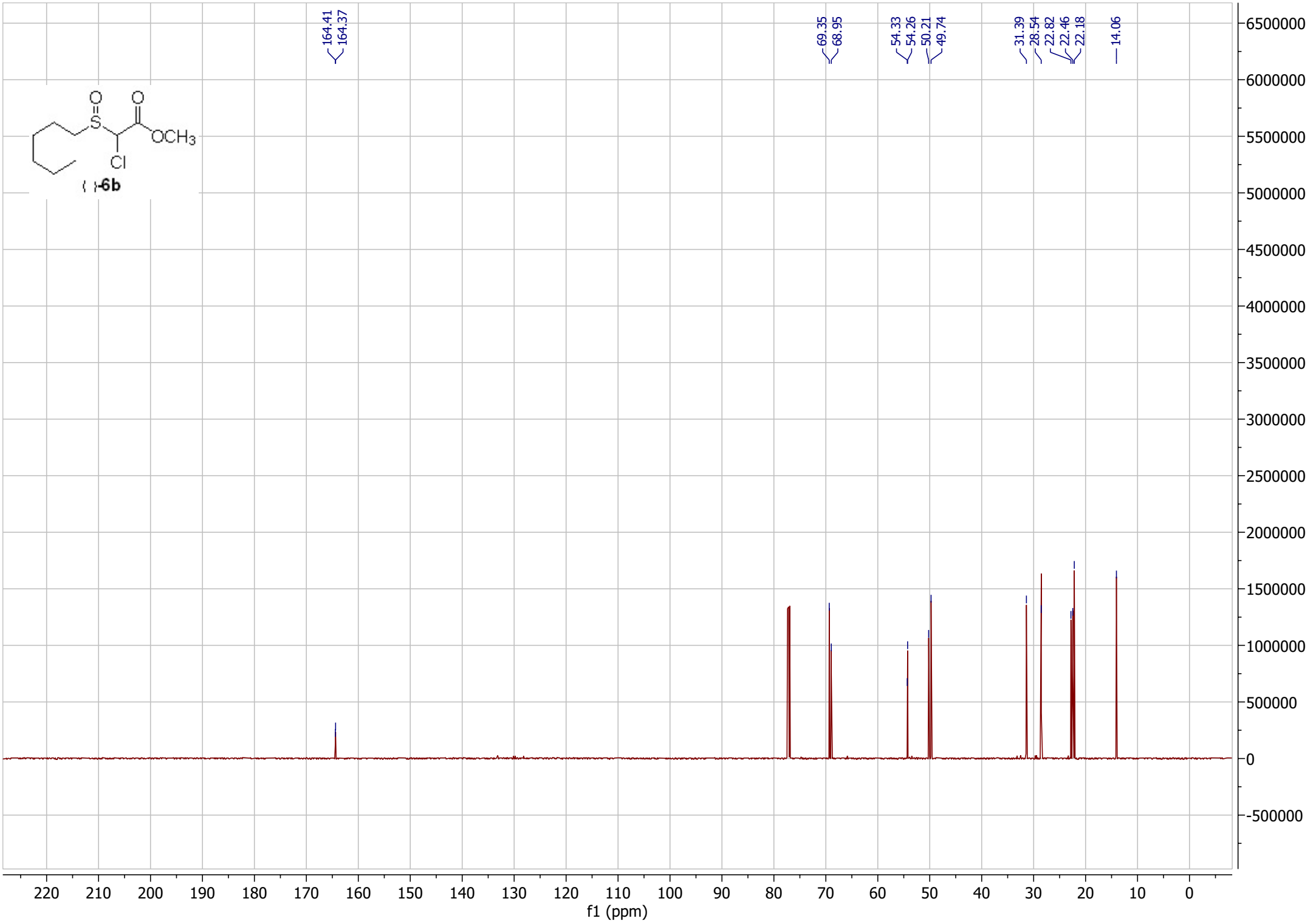

7.64
7.63
7.57
7.55
3.89
3.86
3.71
3.69
1.89
1.98
1.00
1.00
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)
O
O
S
OH
Cl
(+)-2g

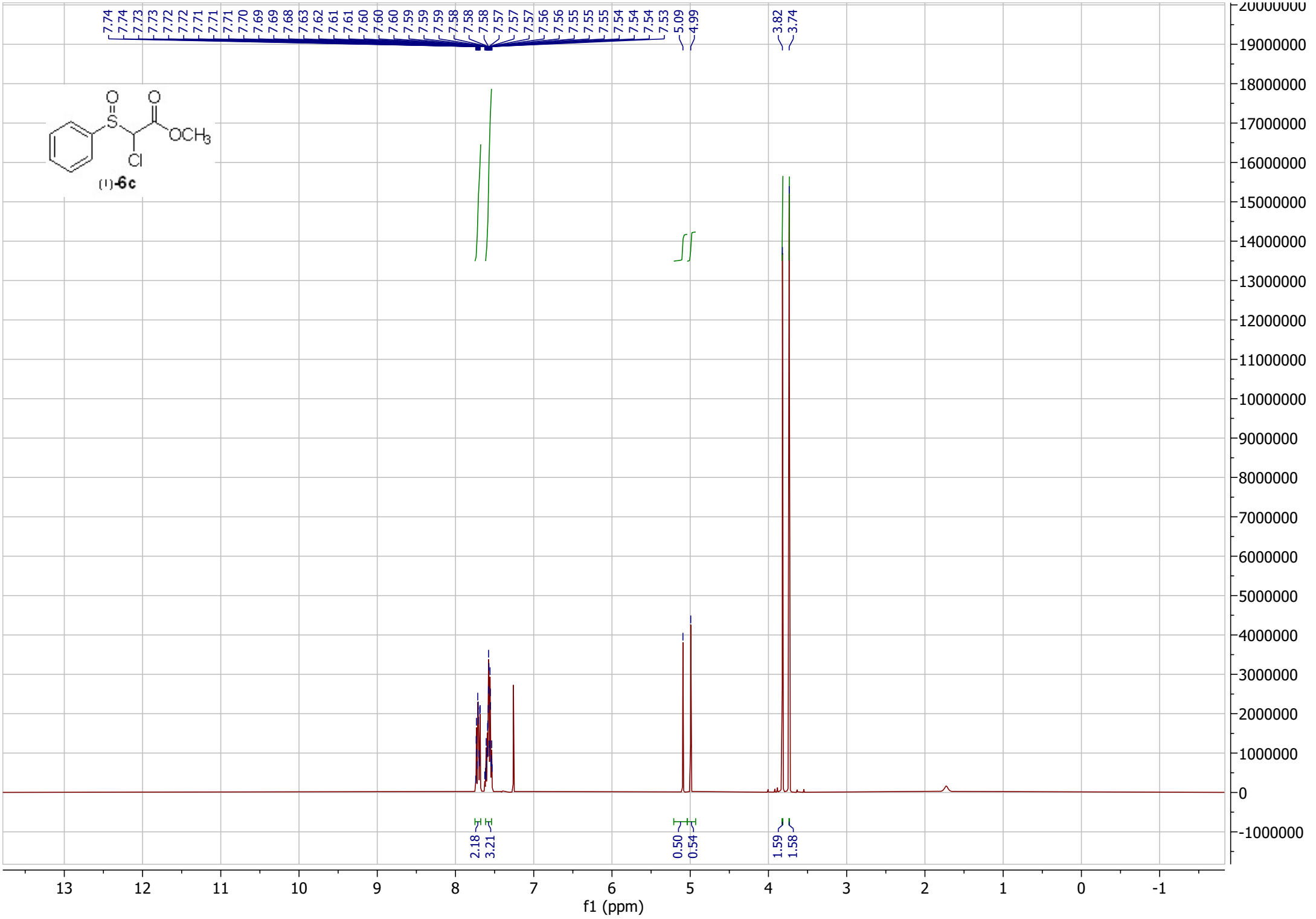

165.56
139.34
138.91
130.28
125.82
57.71
(+)-2g
f1 (ppm)

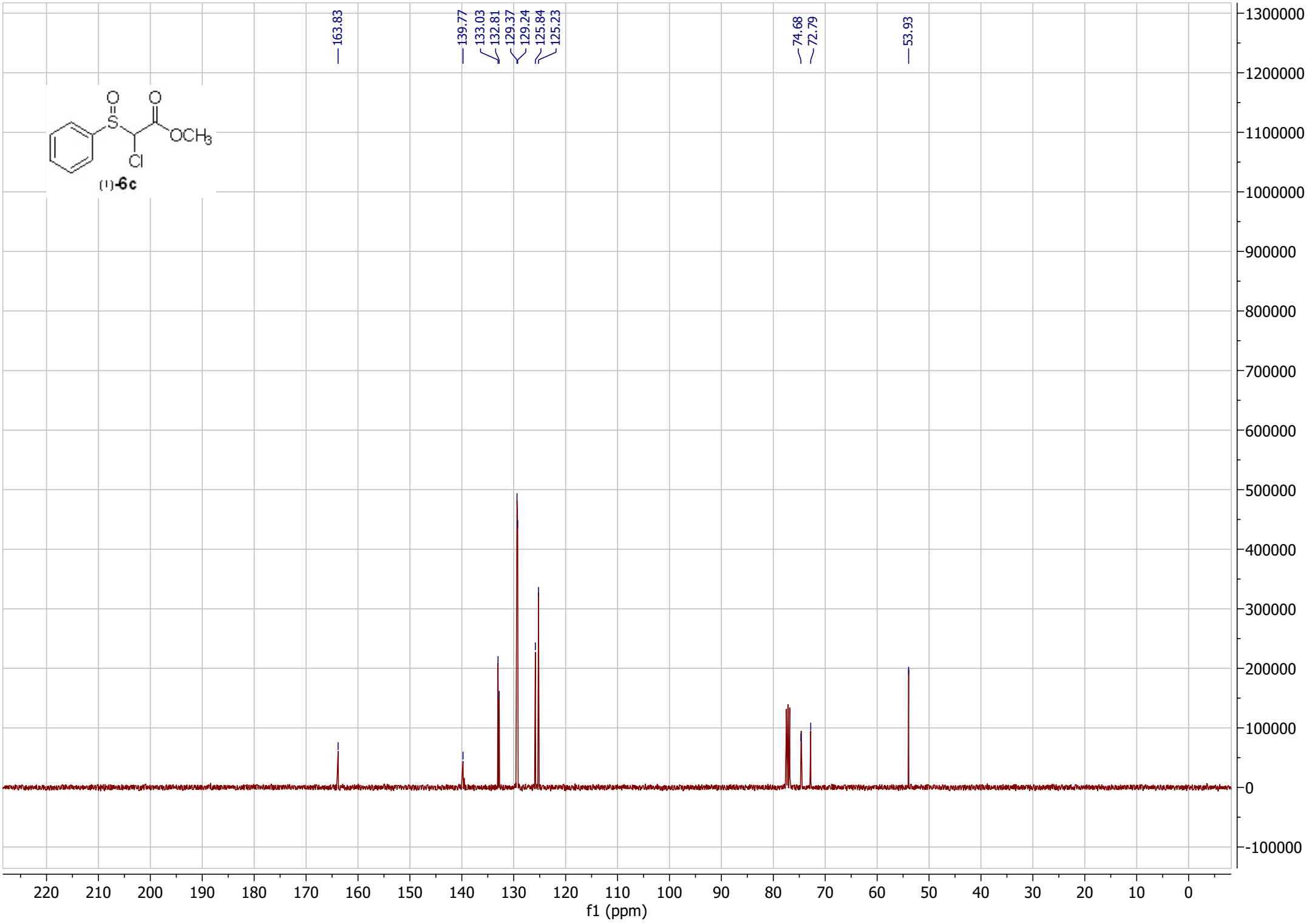

(±)-6a
0.58
0.36
3.06
1.00
10.54
f1 (ppm)

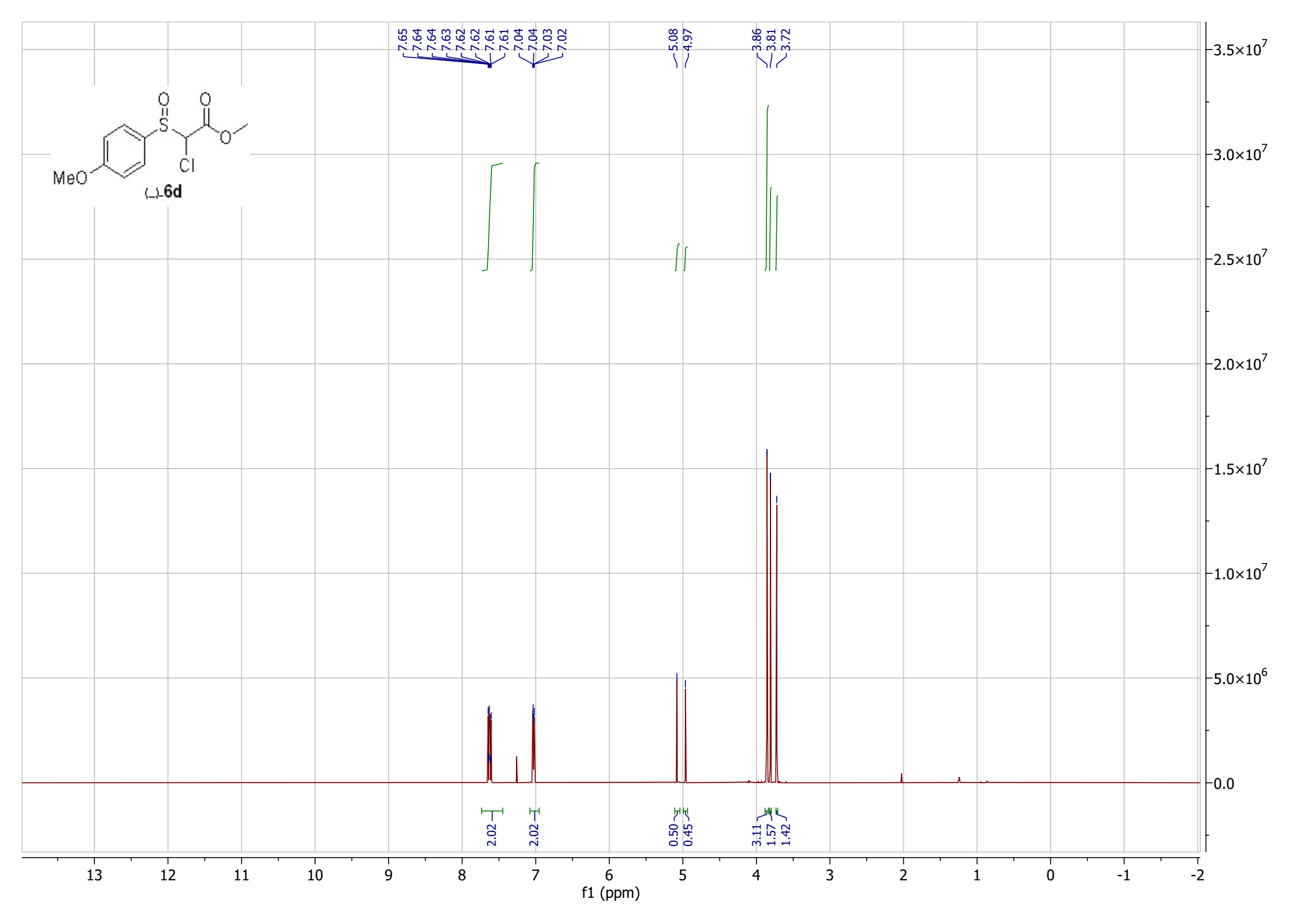

164.81
164.52
69.04
65.59
58.54
56.90
54.25
54.07
27.02
26.30
25.53
25.27
25.23
25.20
25.10
25.00
24.92
23.05
O
O
S
OCH3
Cl
(±)-6a
f1 (ppm)

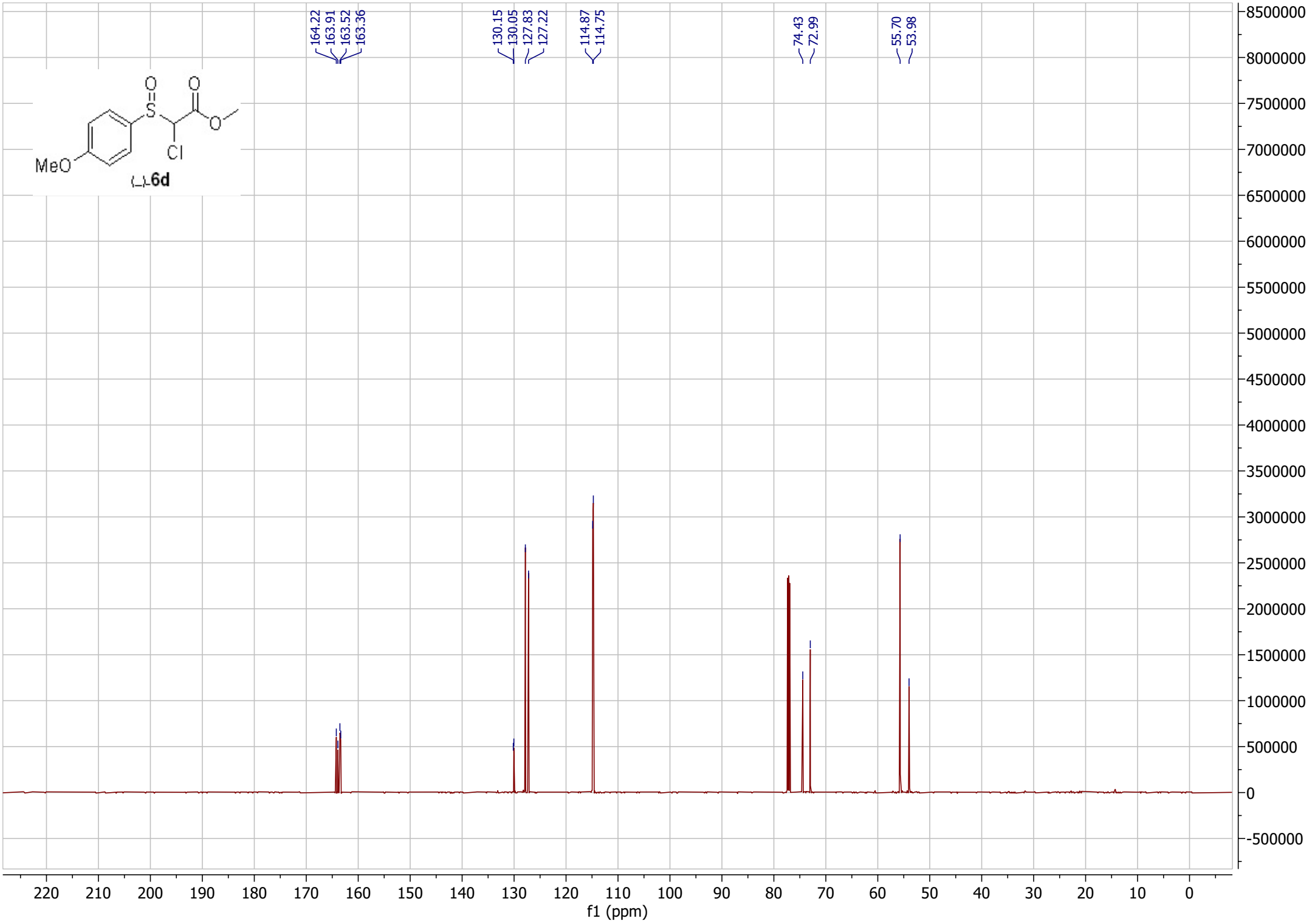

5.16 5.09 3.91 3.89 2.96 2.94 2.94 2.93 2.93 2.92 2.92 2.92 2.91 2.88 2.88 2.87 2.87 2.86 2.86 2.85 2.82 2.81 2.81 2.80 2.80 2.79 2.78 1.84 1.84 1.83 1.82 1.81 1.81 1.81 1.81 1.80 1.80 1.78 1.50 1.50 1.49 1.49 1.49 1.48 1.48 1.47 1.47 1.47 1.46 1.46 1.45 1.45 1.44 1.44 1.44 1.33 1.33 1.33 1.33 1.32 1.32 1.32 1.31 1.31 1.31 1.30 1.30 0.90 0.90 0.89 0.89 0.89 0.89 0.88 0.88 0.88 0.87 0.87 0.87
O
O
S
OCH3
Cl
(±)-6b
18000000
17000000
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
0.57
0.43
1.33
1.82
2.37
2.13
2.13
3.99
3.26
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

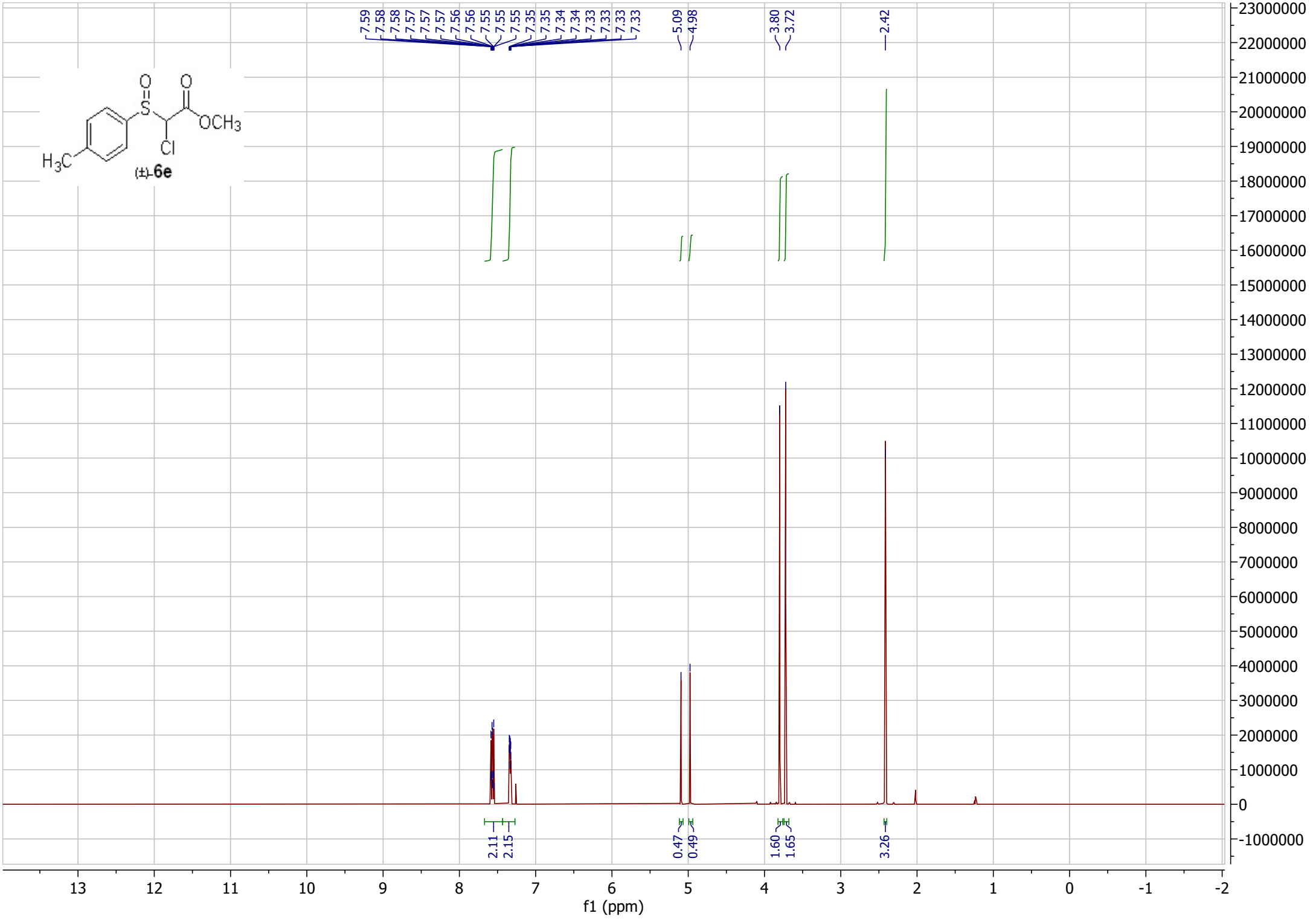

164.41
164.37
69.35
68.95
54.33
54.26
50.21
49.74
31.39
28.54
22.82
22.46
22.18
14.06
O
O
S
OCH3
Cl
(±)-6b
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

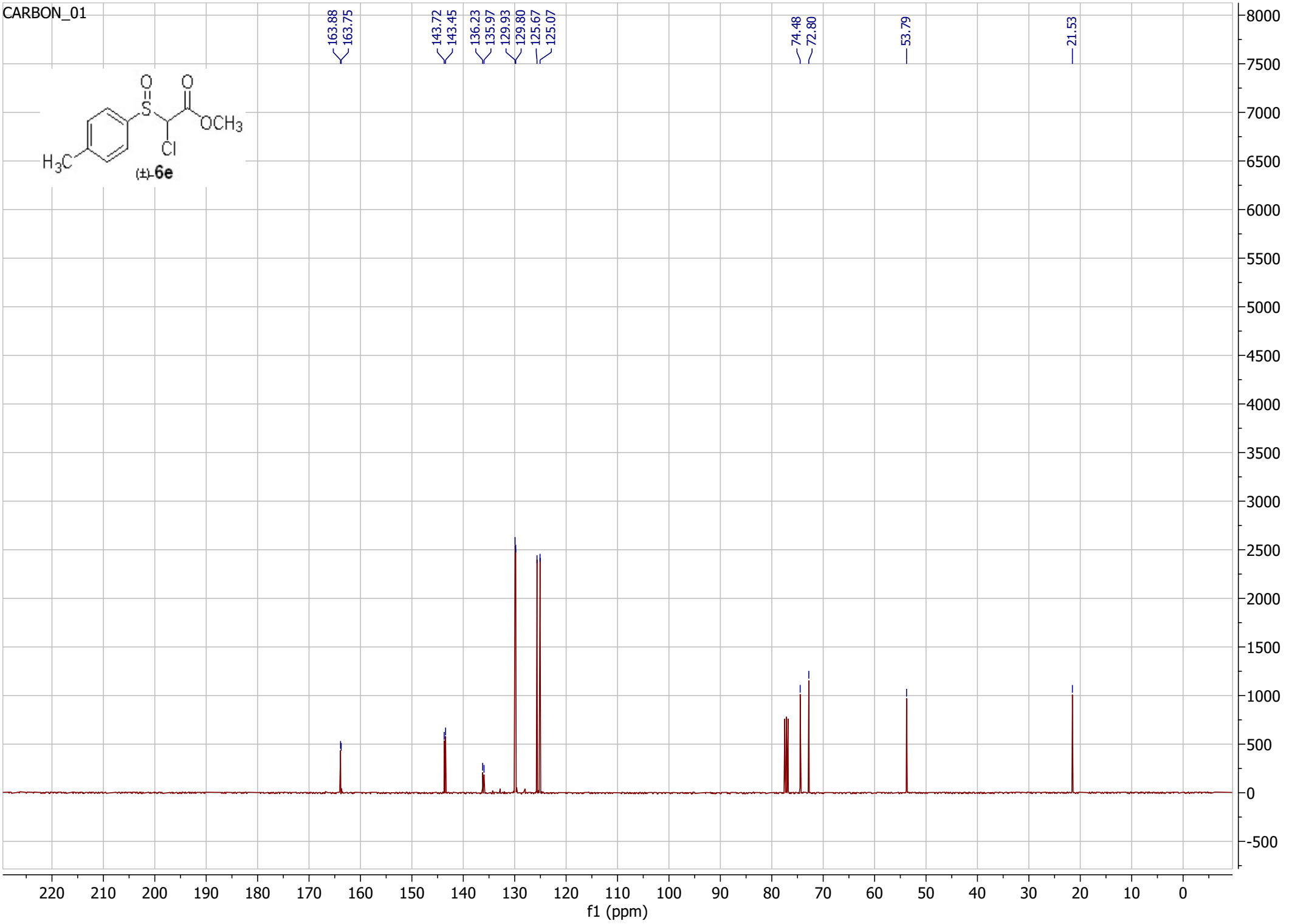

7.74 7.74 7.73 7.73 7.72 7.72 7.71 7.71 7.71 7.70 7.69 7.69 7.68 7.63 7.62 7.61 7.61 7.60 7.60 7.60 7.59 7.59 7.59 7.58 7.58 7.58 7.57 7.57 7.57 7.56 7.56 7.55 7.55 7.55 7.54 7.54 7.54 7.53 5.09 4.99 3.82 3.74
O
O
S
OCH3
Cl
(±)-6c
2.18 3.21 0.50 0.54 1.59 1.58
20000000 19000000 18000000 17000000 16000000 15000000 14000000 13000000 12000000 11000000 10000000 9000000 8000000 7000000 6000000 5000000 4000000 3000000 2000000 1000000 0 -1000000
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

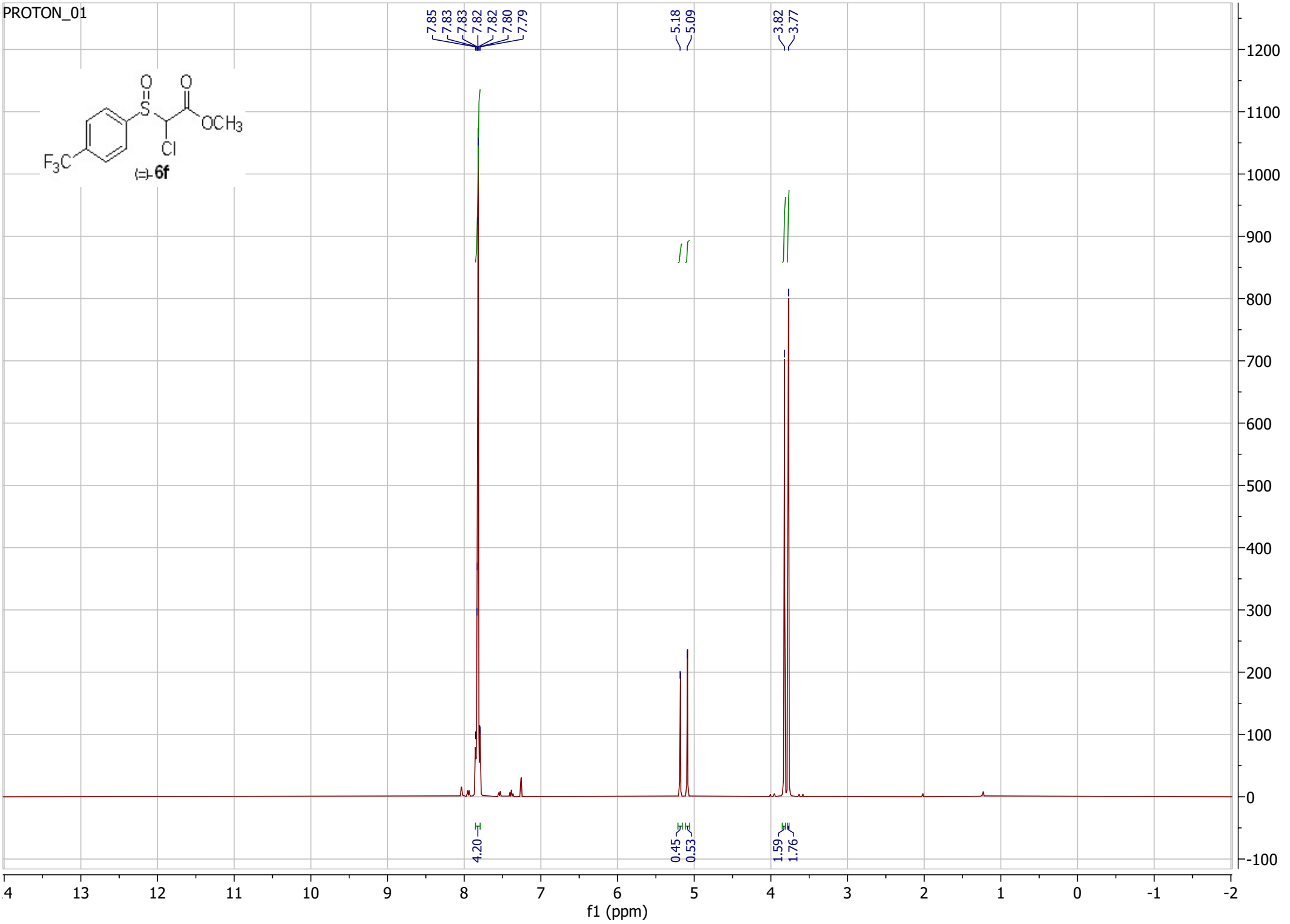

163.83
139.77
133.03
132.81
129.37
129.24
125.84
125.23
74.68
72.79
53.93
O
O
S
OCH3
Cl
(I)-6c
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

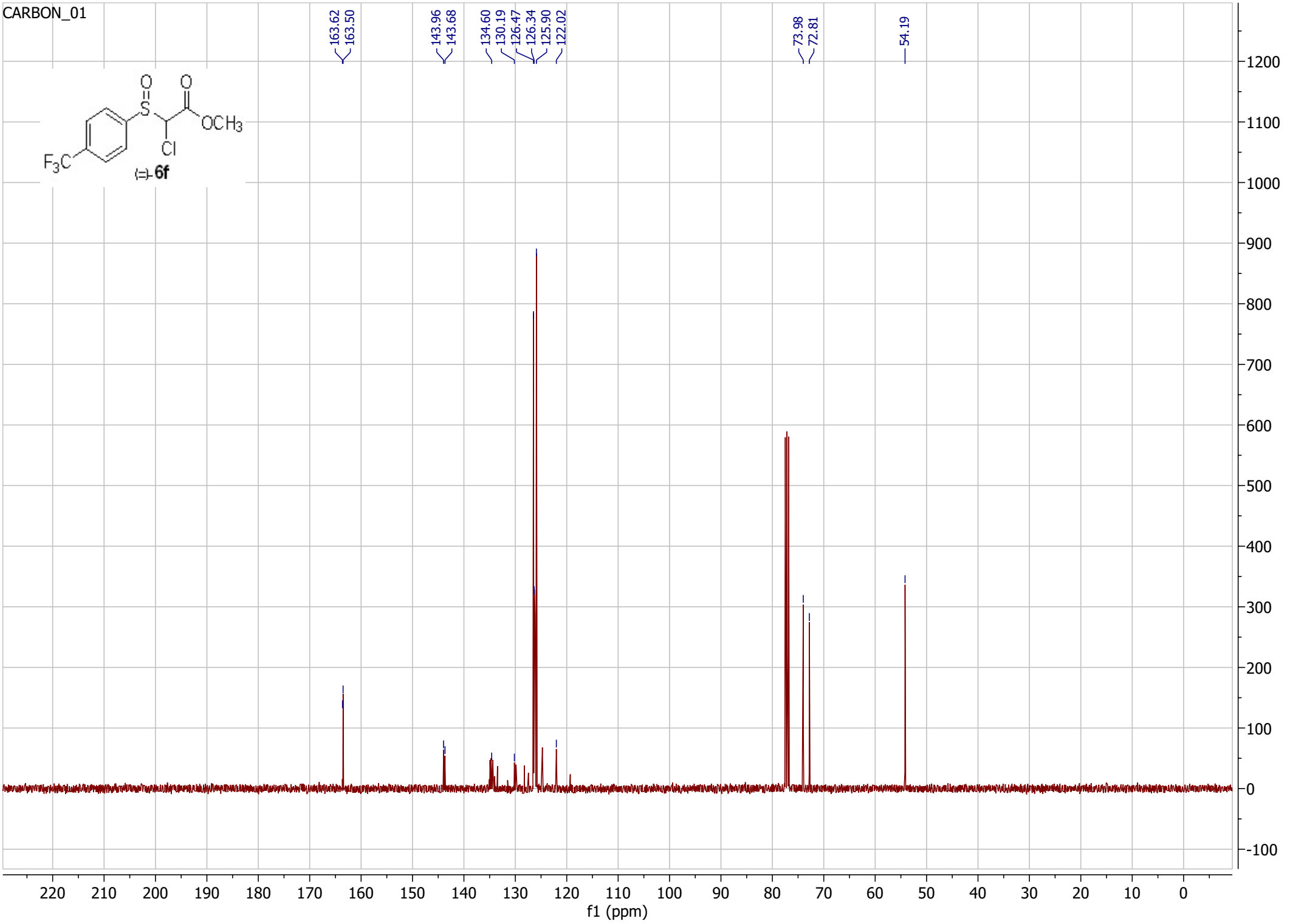

7.65
7.64
7.64
7.63
7.62
7.62
7.61
7.61
7.04
7.04
7.03
7.02
5.08
4.97
3.86
3.81
3.72
MeO
Cl
(±)6d
2.02
2.02
0.50
0.45
3.11
1.57
1.42
f1 (ppm)

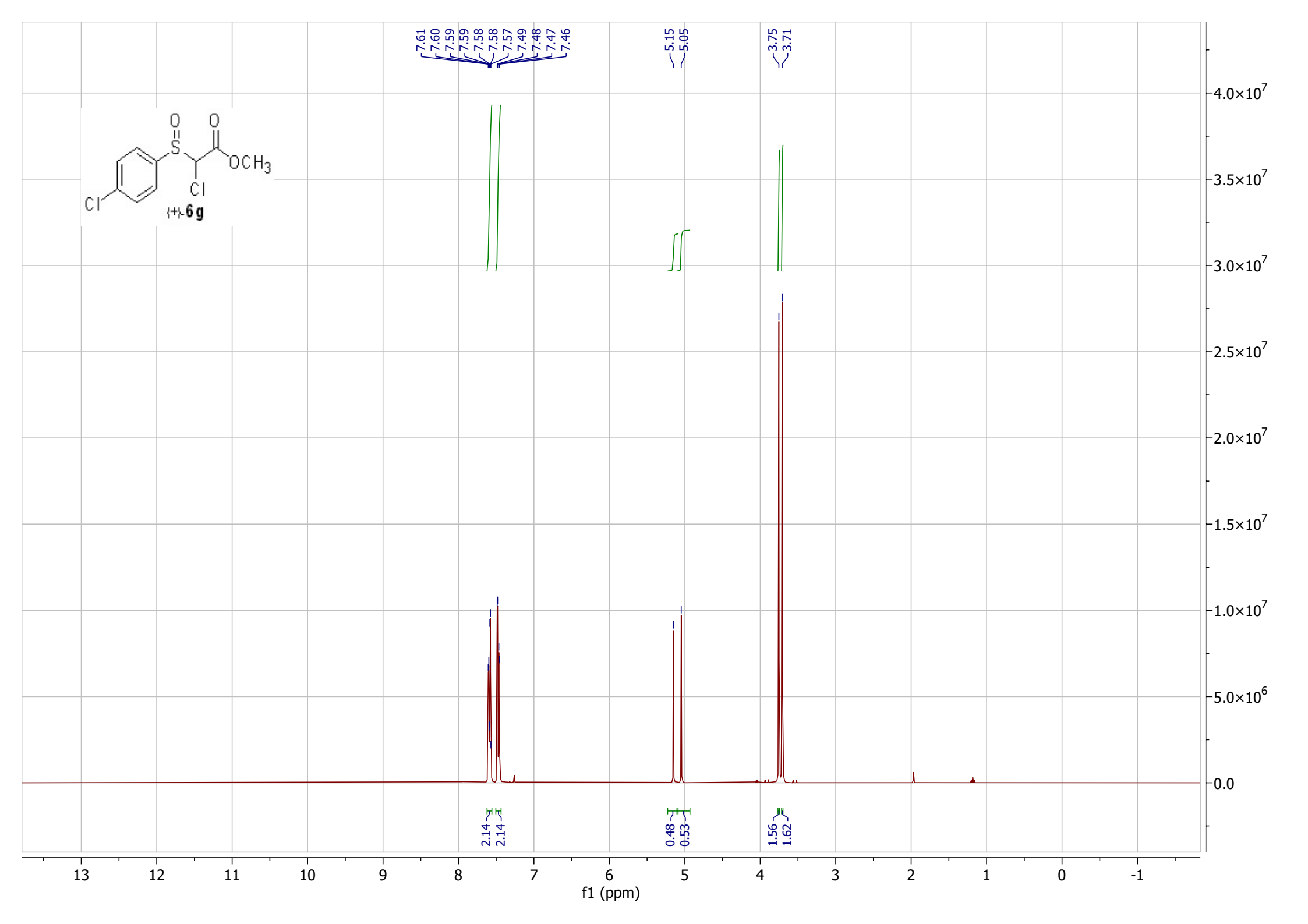

164.22
163.91
163.52
163.36
130.15
130.05
127.83
127.22
114.87
114.75
74.43
72.99
55.70
53.98
MeO
Cl
(±)6d
f1 (ppm)

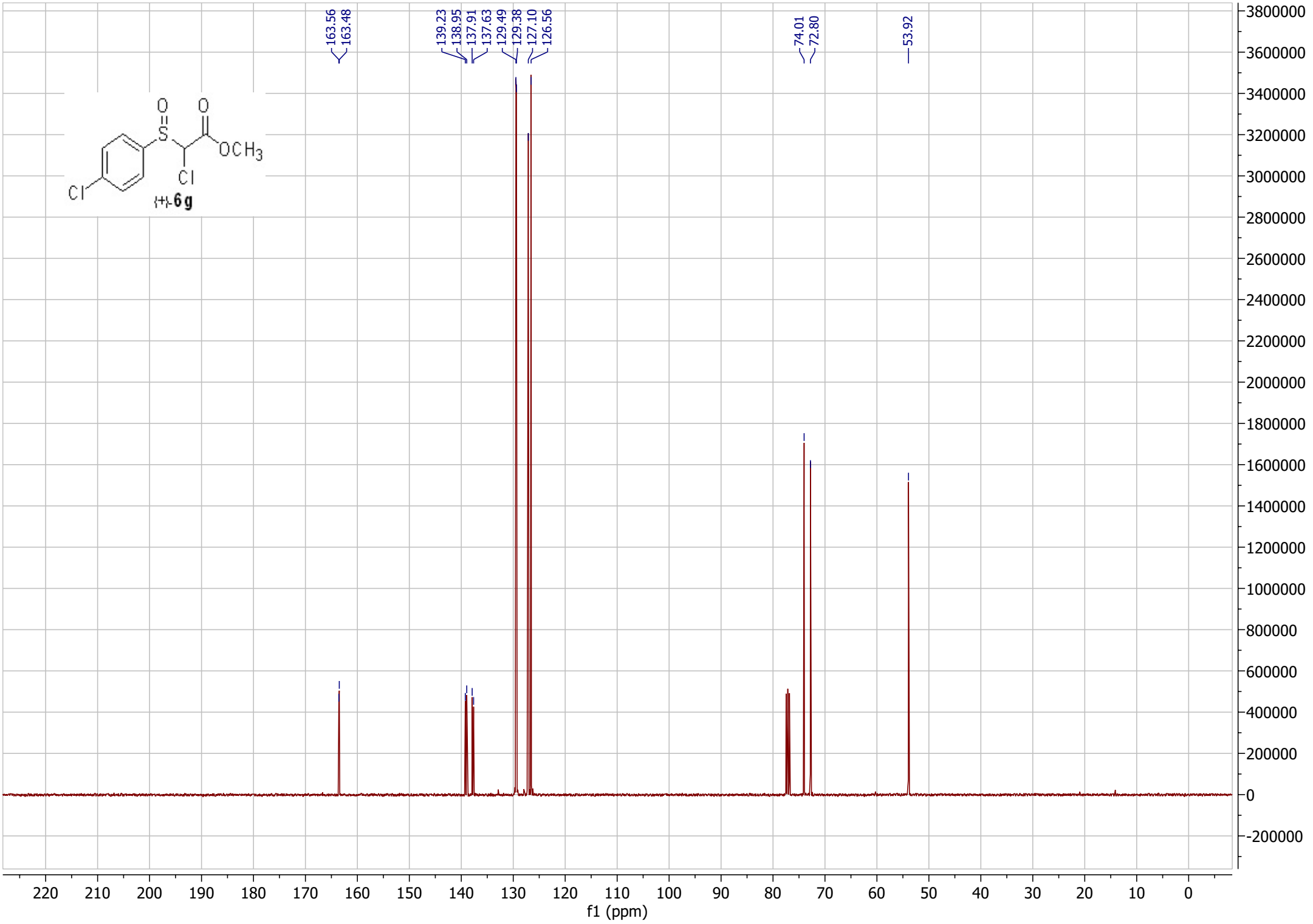

7.59
7.58
7.58
7.57
7.57
7.57
7.56
7.56
7.55
7.55
7.55
7.35
7.35
7.34
7.34
7.33
7.33
7.33
7.33
5.09
4.98
3.80
3.72
2.42
O
O
S
OCH3
Cl
H3C
(±)-6e
2.11
2.15
0.47
0.49
1.60
1.65
3.26
23000000
22000000
21000000
20000000
19000000
18000000
17000000
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

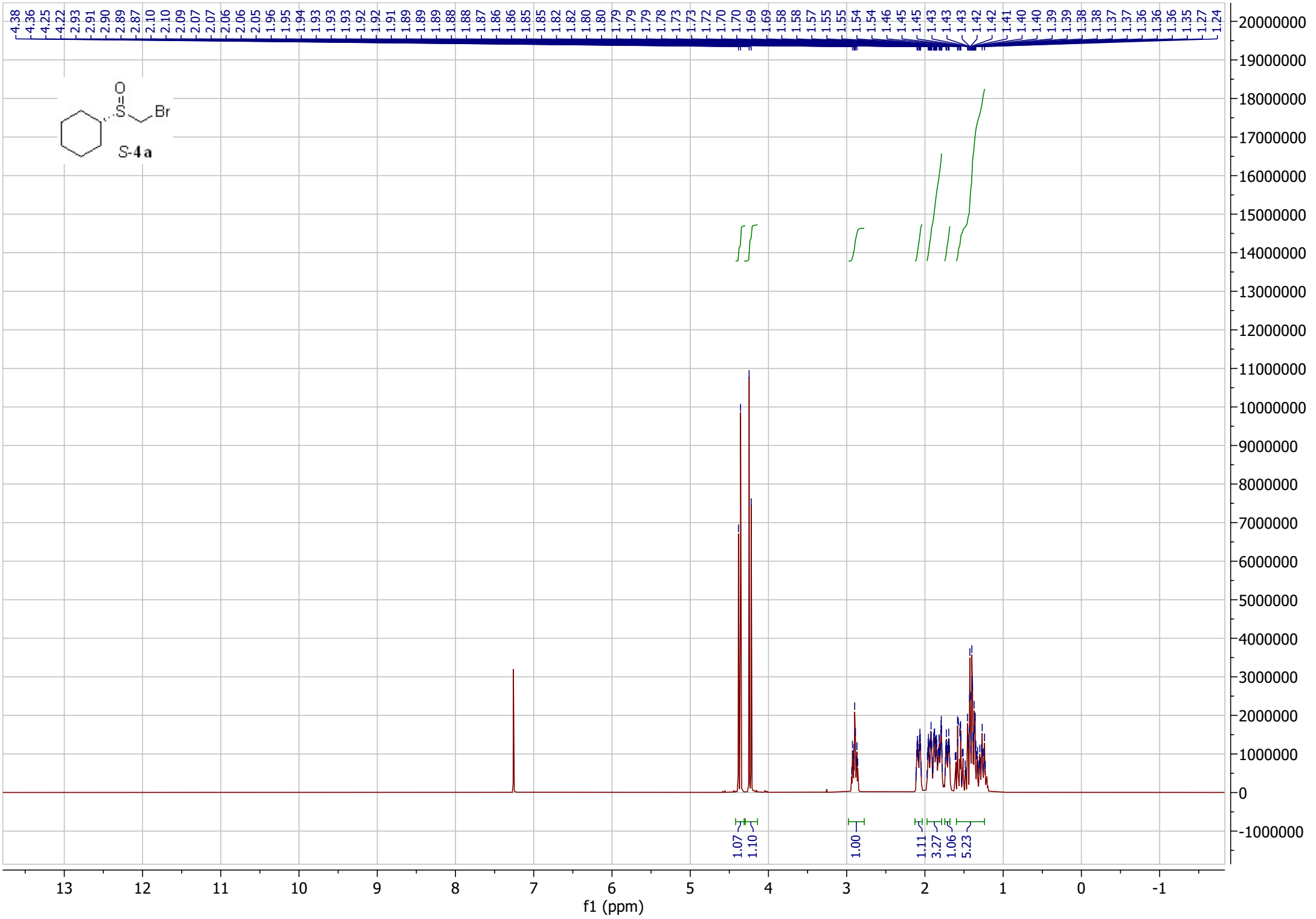

CARBON_01
163.88
163.75
143.72
143.45
136.23
135.97
129.93
129.80
125.67
125.07
74.48
72.80
53.79
21.53
O
O
S
OCH3
Cl
H3C
(±)-6e
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

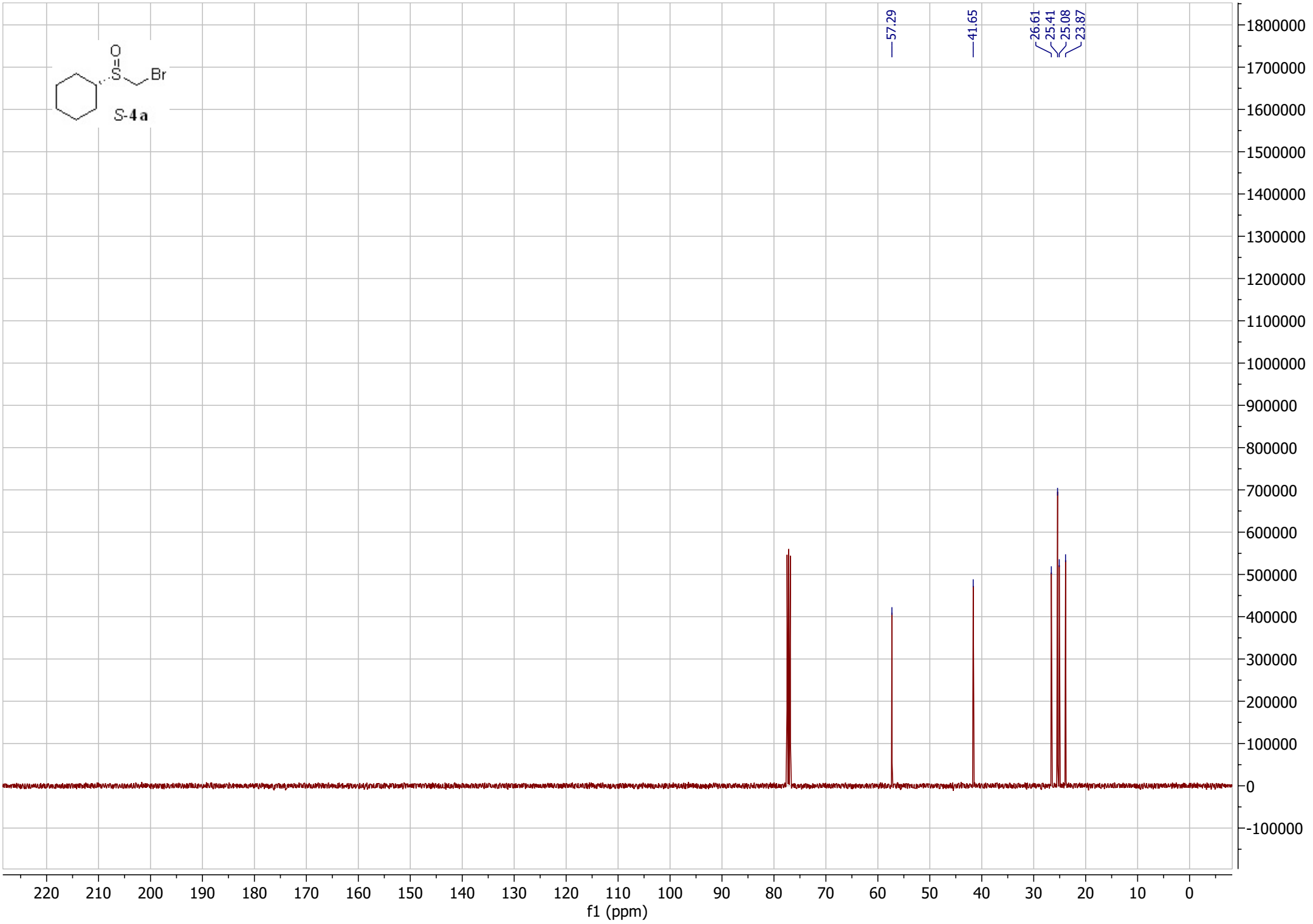

PROTON_01
7.85
7.83
7.83
7.82
7.82
7.80
7.79
5.18
5.09
3.82
3.77
O
O
S
OCH3
Cl
F3C
(±)-6f
4.20
0.45
0.53
1.59
1.76
f1 (ppm)

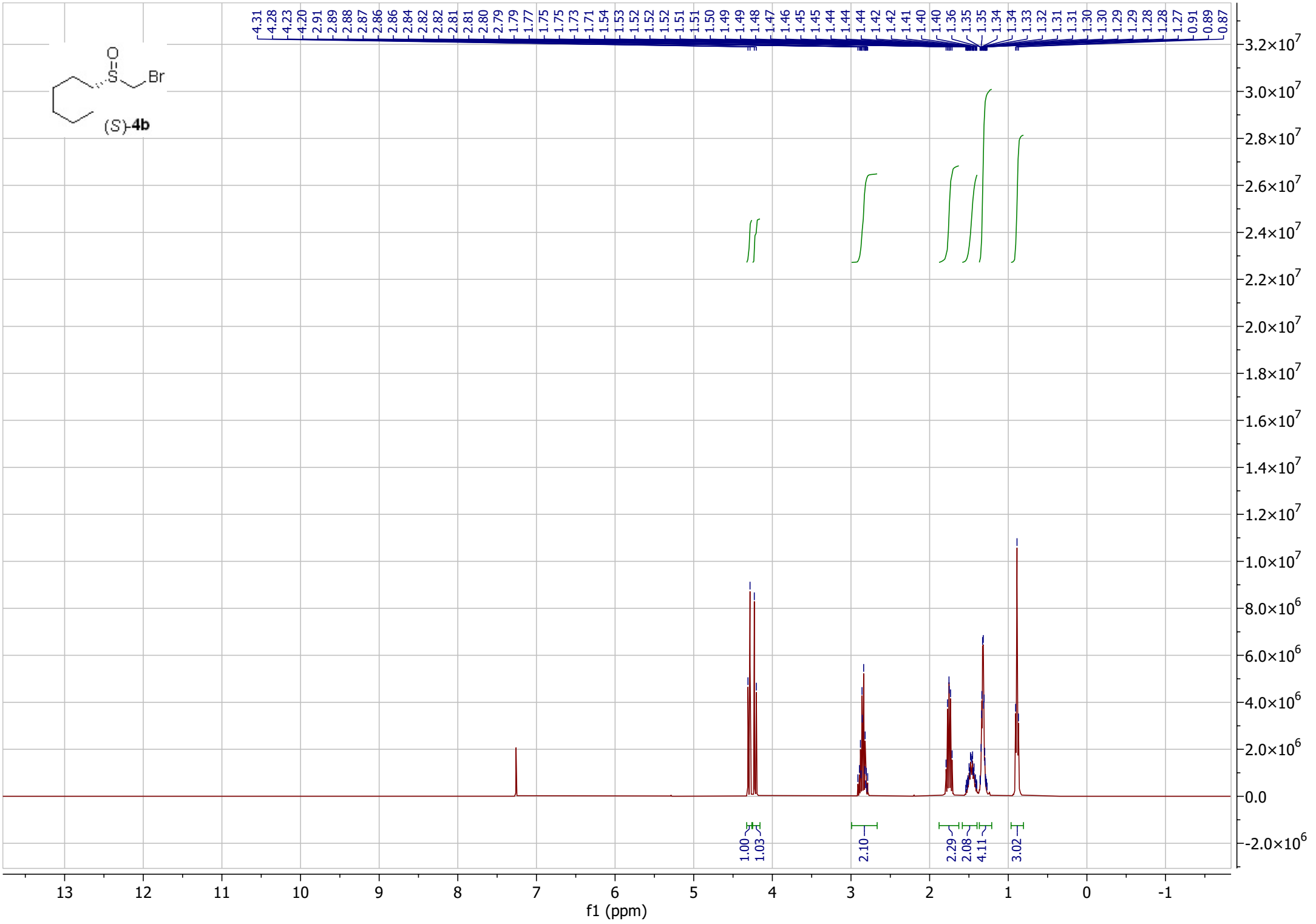

CARBON_01
163.62
163.50
143.96
143.68
134.60
130.19
126.47
126.34
125.90
122.02
73.98
72.81
54.19
O
O
S
OCH3
Cl
F3C
(±)-6f
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

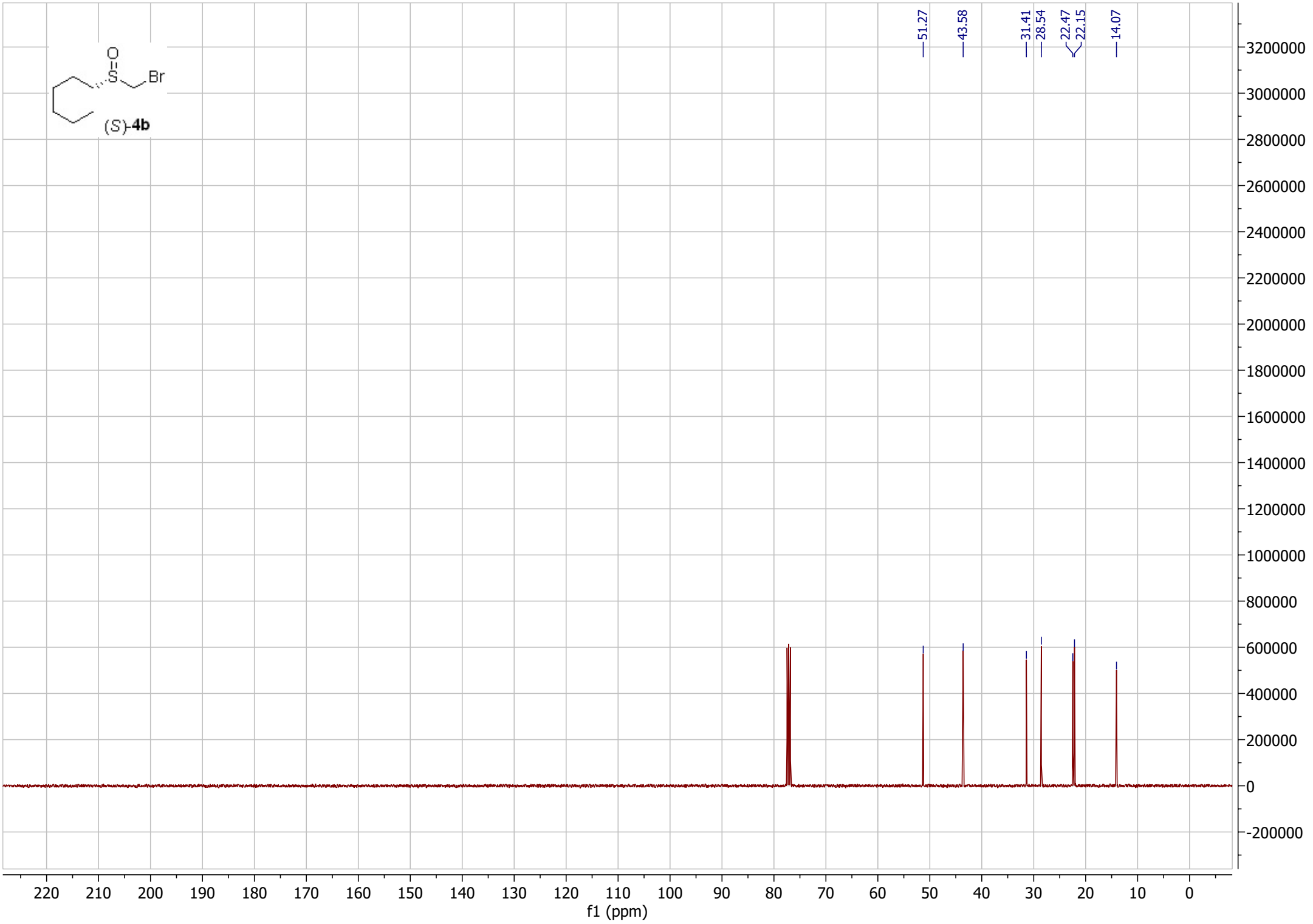

7.61
7.60
7.59
7.59
7.58
7.58
7.57
7.49
7.48
7.47
7.46
5.15
5.05
3.75
3.71
(±)-6g
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
2.14
2.14
0.48
0.53
1.56
1.62
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

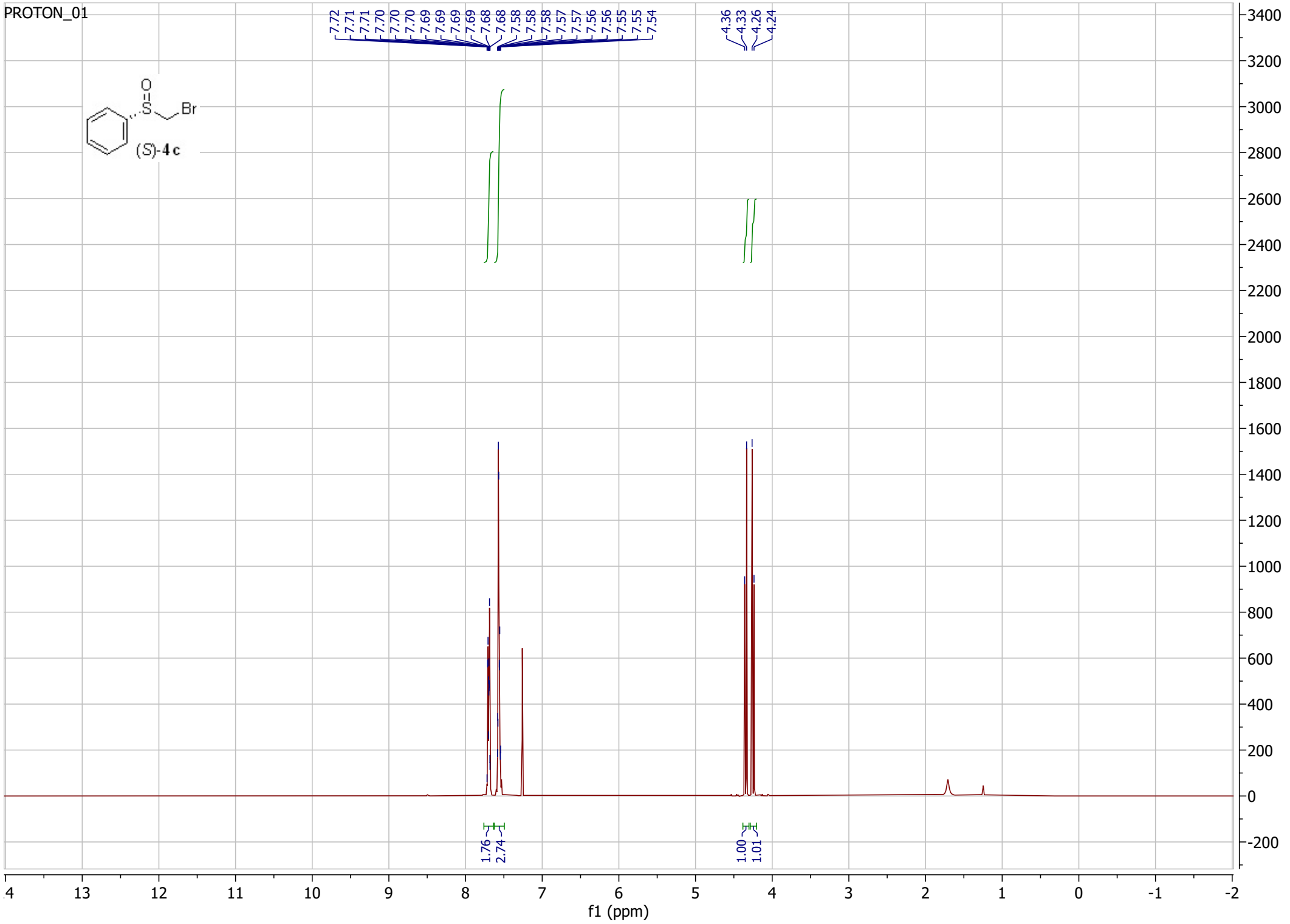

163.56
163.48
139.23
138.95
137.91
137.63
129.49
129.38
127.10
126.56
74.01
72.80
53.92
(±)-6g
f1 (ppm)

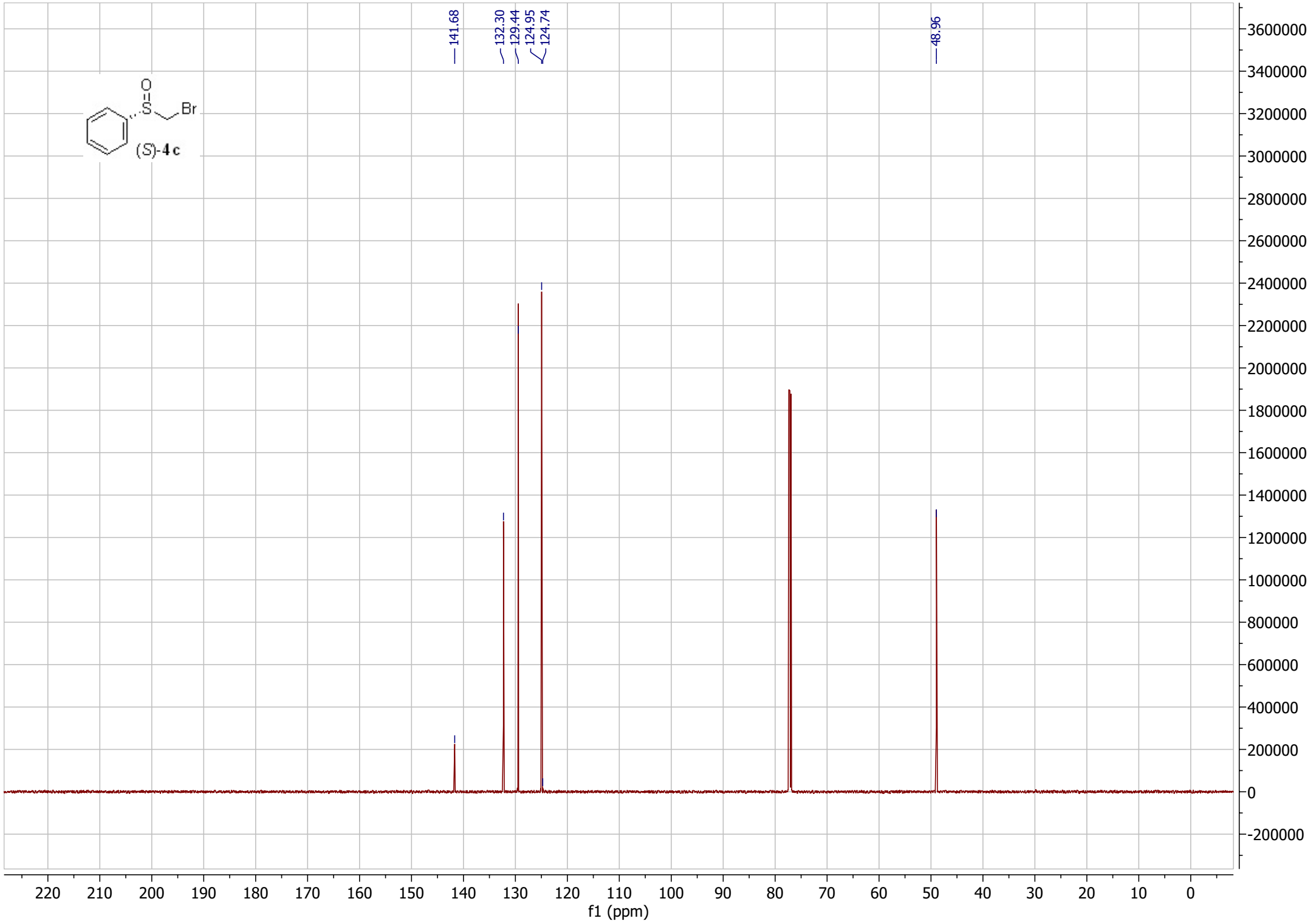

O
S
Br
S-4a
f1 (ppm)
1.07
1.10
1.00
1.11
3.27
1.06
5.23

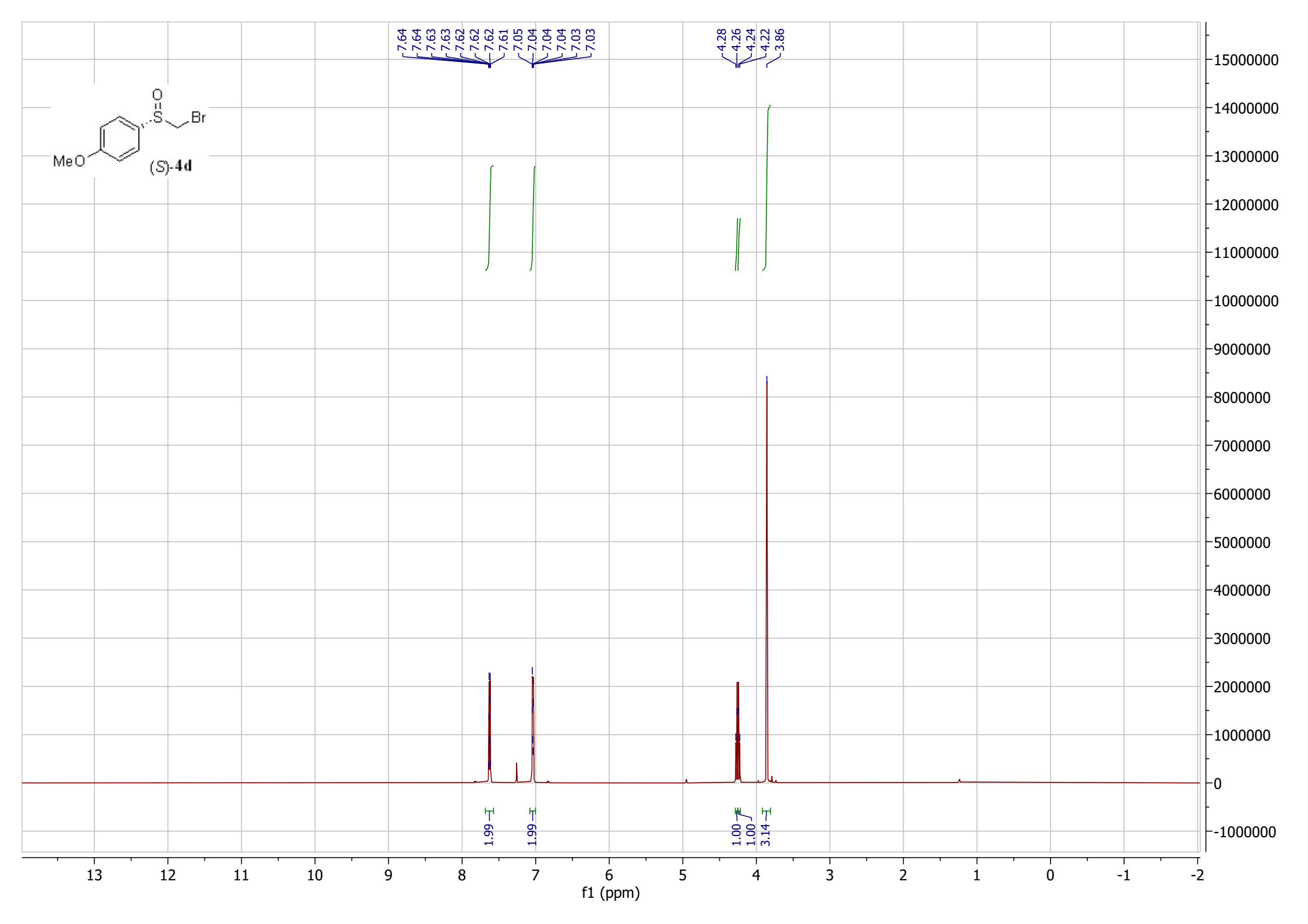

O
S
Br
S-4a
57.29
41.65
26.61
25.41
25.08
23.87
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

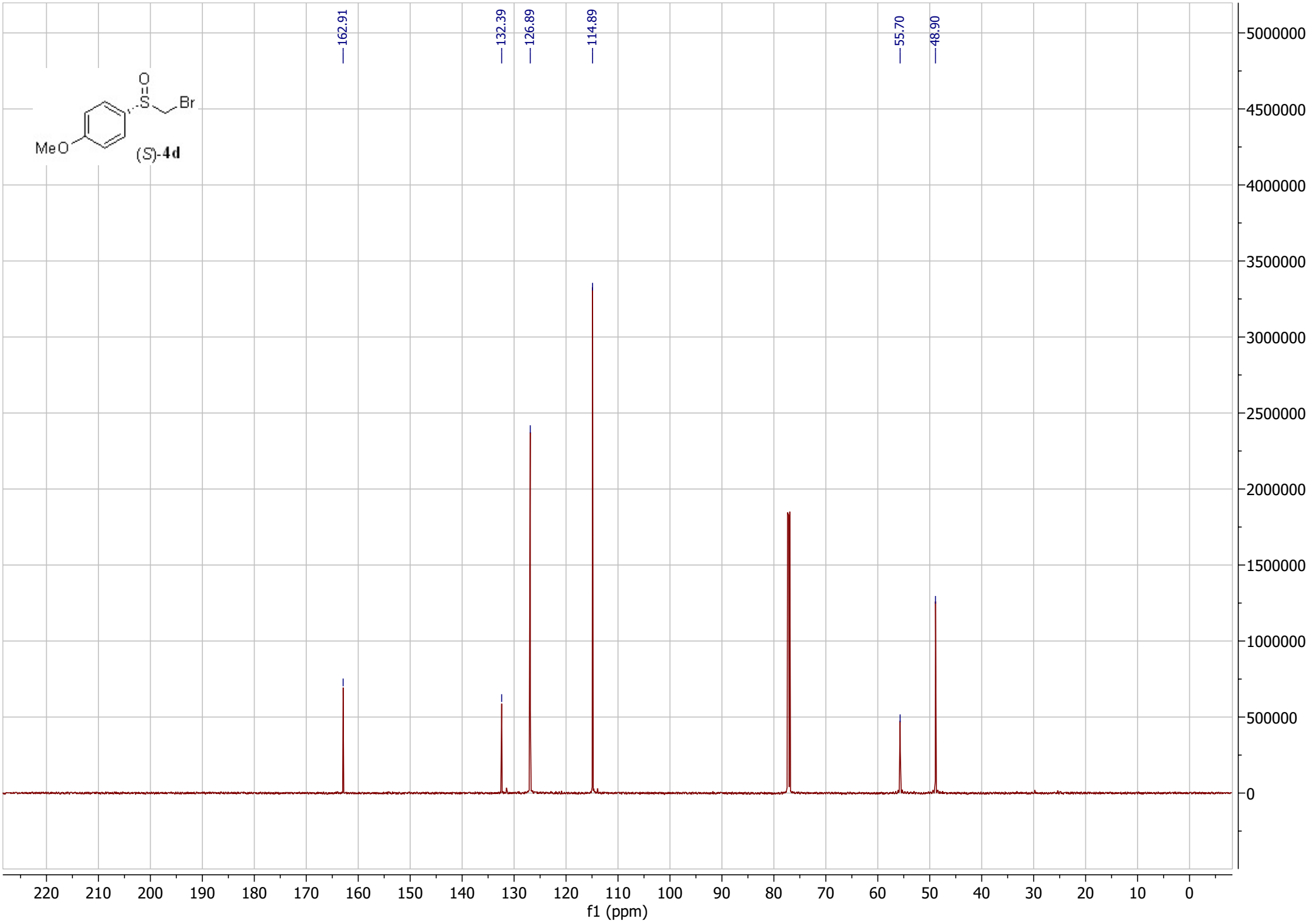

O
S
Br
(S)-4b
4.31 4.28 4.23 4.20 2.91 2.89 2.88 2.87 2.86 2.86 2.84 2.82 2.82 2.81 2.81 2.80 2.79 1.79 1.77 1.75 1.75 1.73 1.71 1.54 1.53 1.52 1.52 1.52 1.51 1.51 1.50 1.49 1.49 1.48 1.47 1.46 1.45 1.44 1.44 1.44 1.42 1.42 1.41 1.40 1.40 1.36 1.35 1.35 1.34 1.34 1.33 1.32 1.31 1.31 1.30 1.30 1.29 1.29 1.28 1.28 1.27 0.91 0.89 0.87
3.2×10^7
3.0×10^7
2.8×10^7
2.6×10^7
2.4×10^7
2.2×10^7
2.0×10^7
1.8×10^7
1.6×10^7
1.4×10^7
1.2×10^7
1.0×10^7
8.0×10^6
6.0×10^6
4.0×10^6
2.0×10^6
0.0
-2.0×10^6
1.00
1.03
2.10
2.29
2.08
4.11
3.02
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

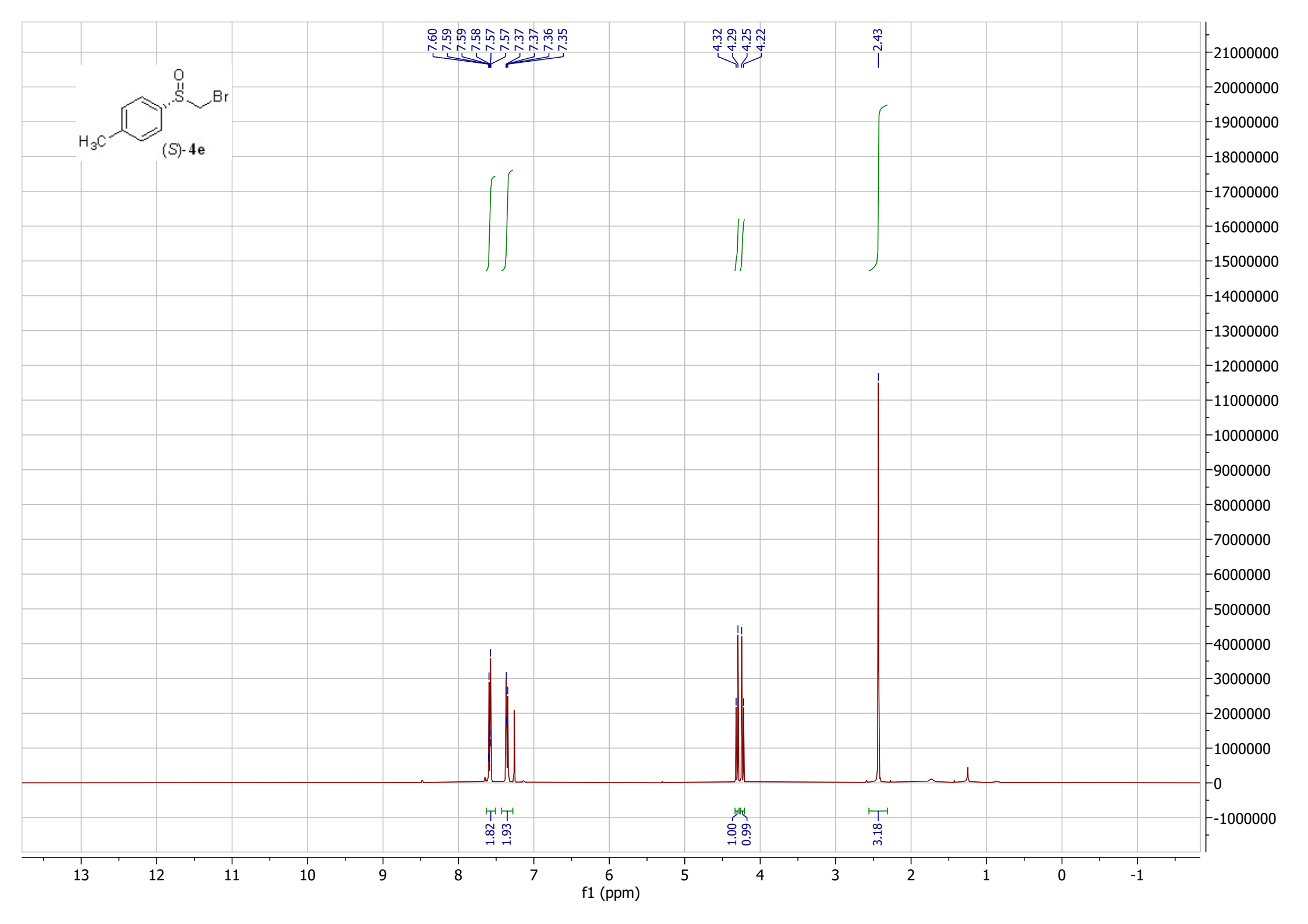

O
S
Br
(S)-4b
51.27
43.58
31.41
28.54
22.47
22.15
14.07
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

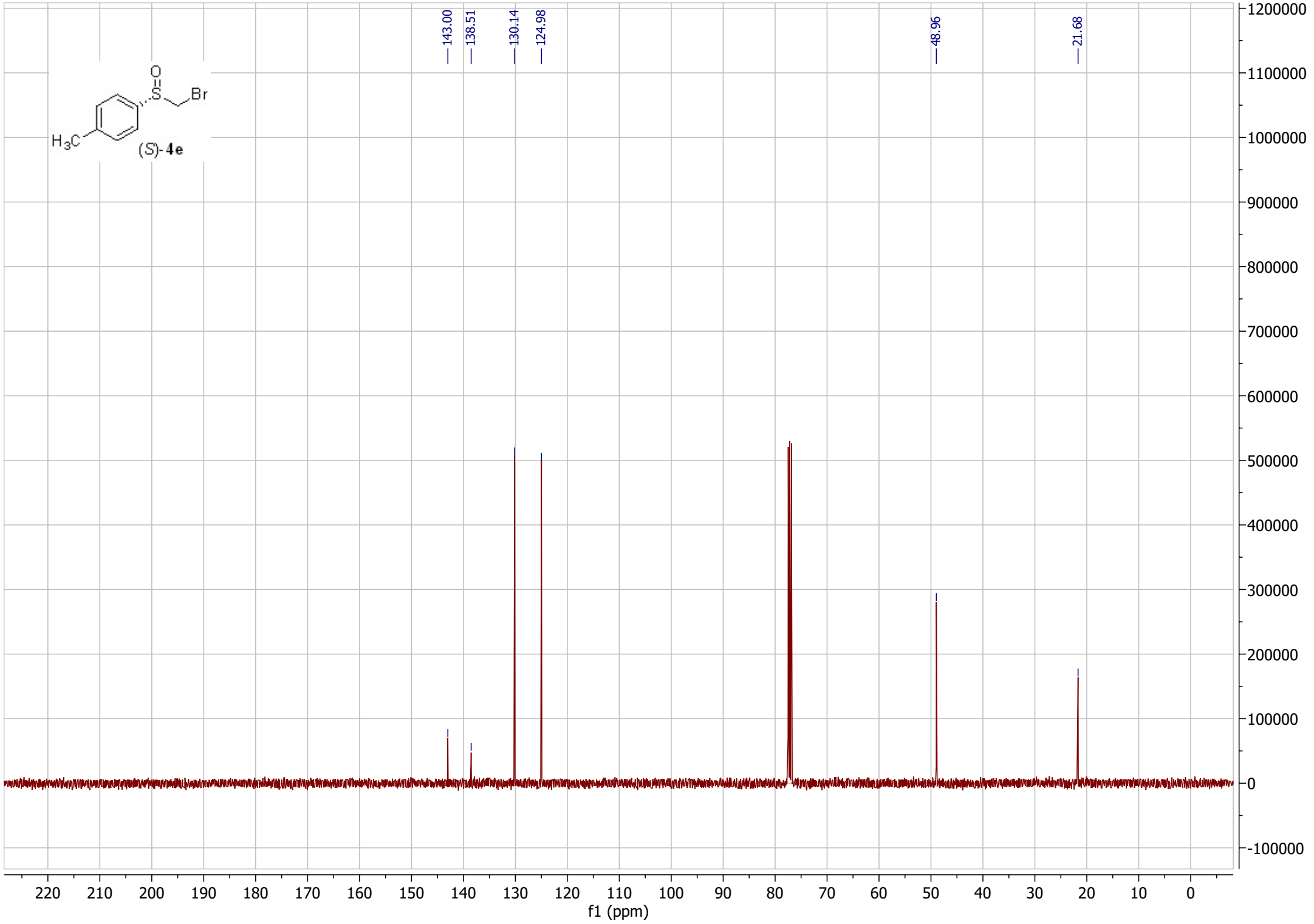

PROTON_01
7.72
7.71
7.71
7.70
7.70
7.70
7.69
7.69
7.69
7.69
7.68
7.68
7.58
7.58
7.58
7.57
7.57
7.56
7.56
7.55
7.55
7.54
4.36
4.33
4.26
4.24
O
S
Br
(S)-4c
1.76
2.74
1.00
1.01
f1 (ppm)

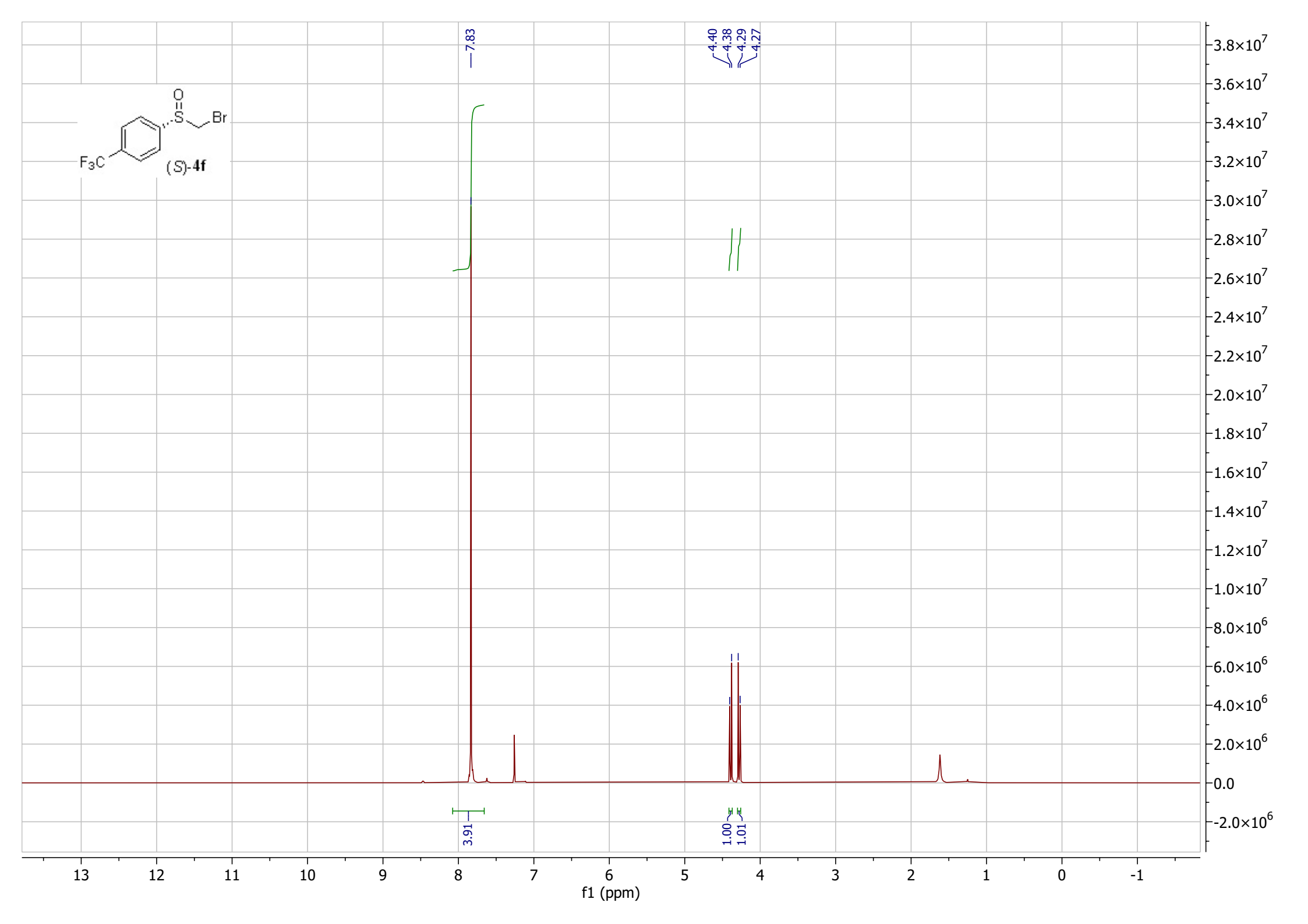

141.68
132.30
129.44
124.95
124.74
48.96
O
S
Br
(S)-4c
3600000
3400000
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

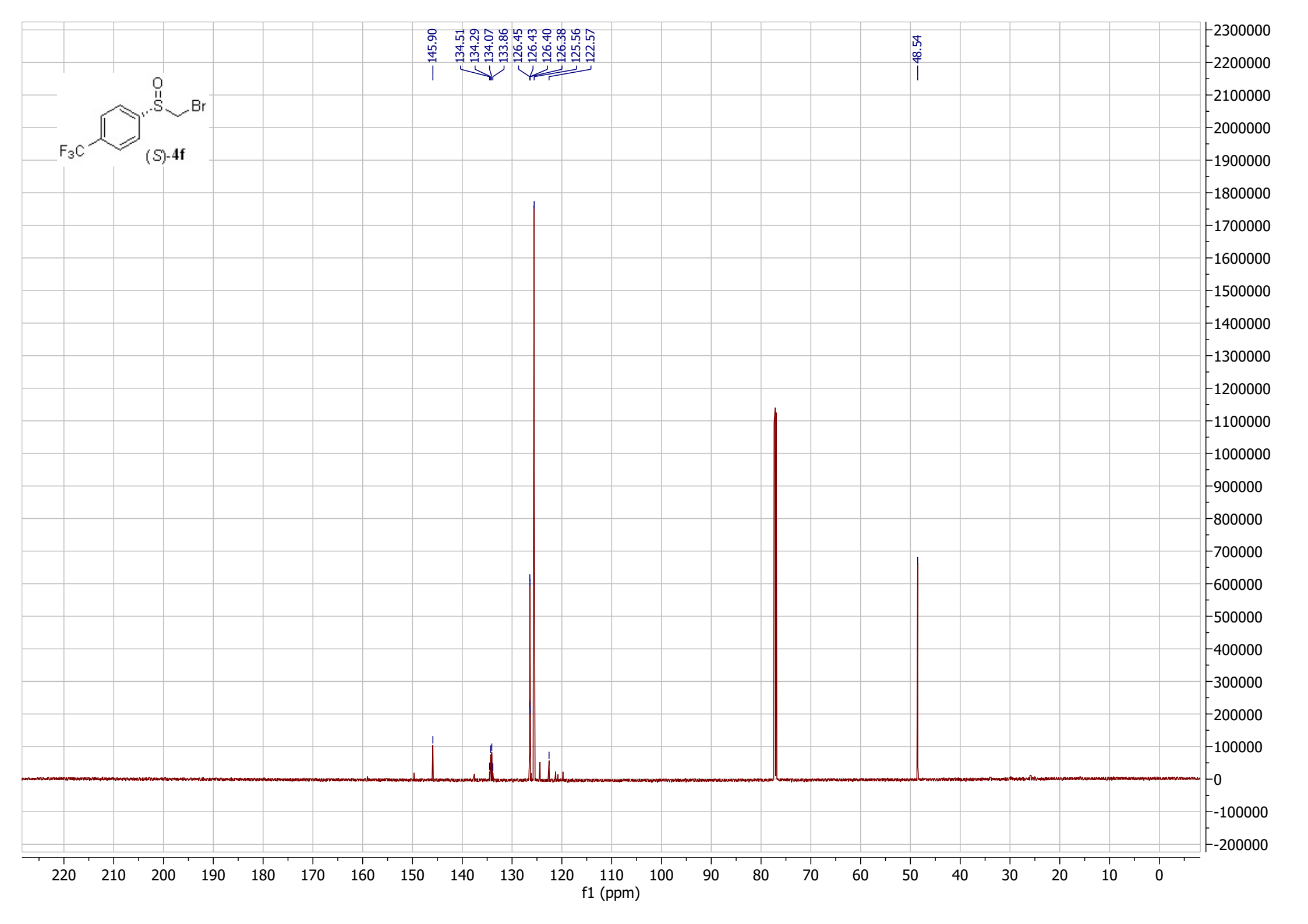

7.64
7.64
7.63
7.63
7.62
7.62
7.62
7.61
7.05
7.04
7.04
7.04
7.03
7.03
4.28
4.26
4.24
4.22
3.86
O
S
Br
MeO
(S)-4d
1.99
1.99
1.00
1.00
3.14
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

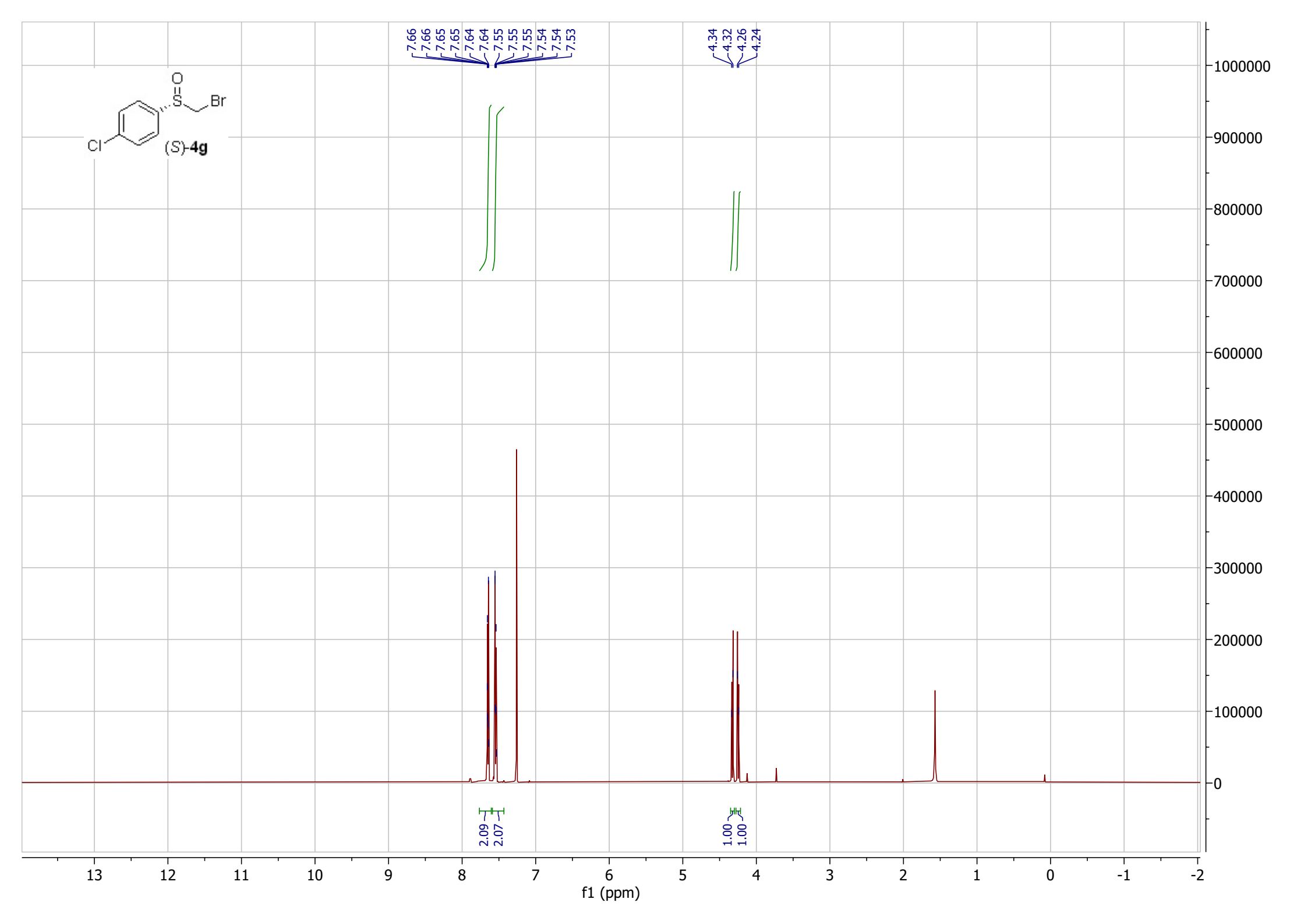

162.91
132.39
126.89
114.89
55.70
48.90
O
S
Br
MeO
(S)-4d
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

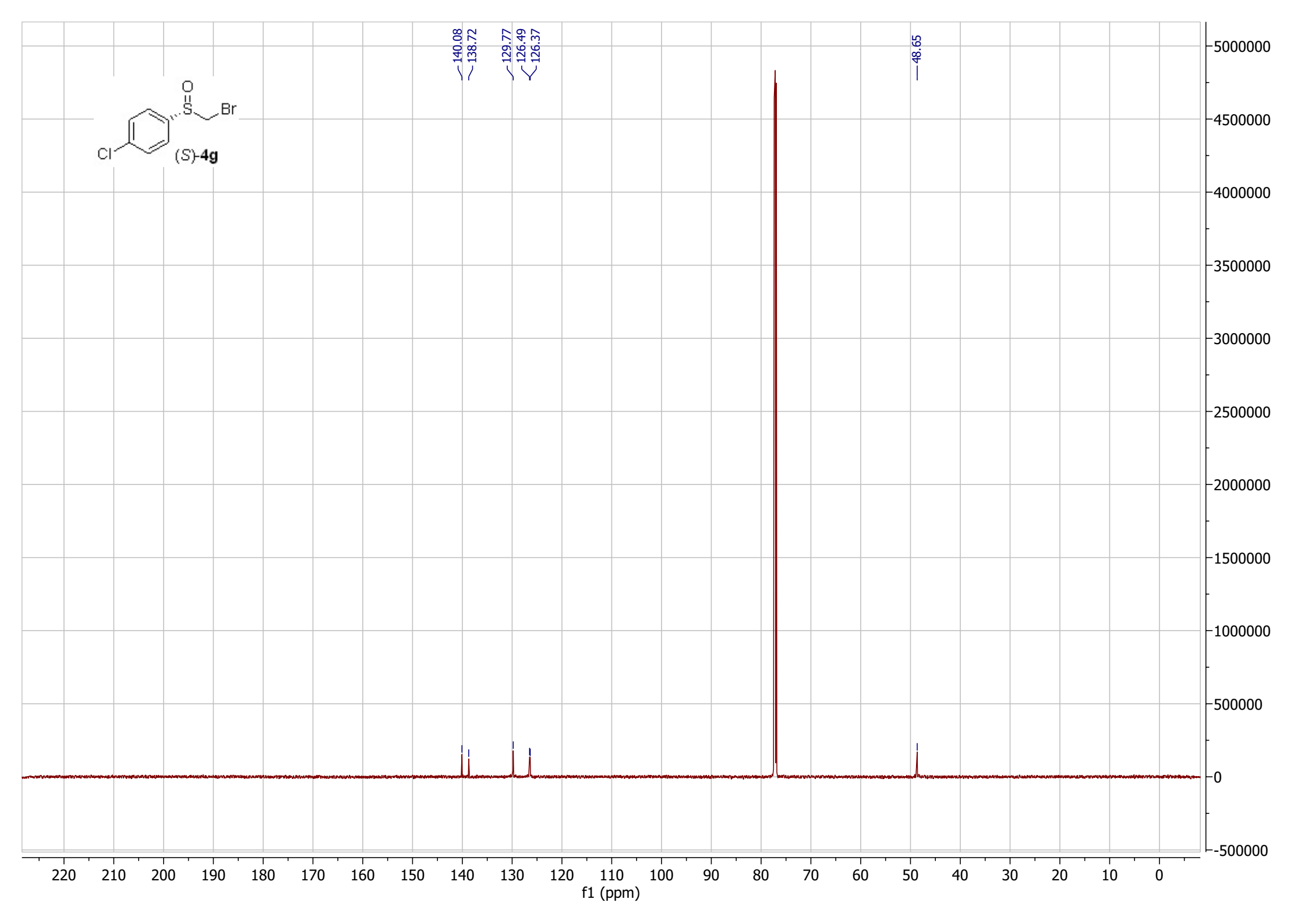

7.60
7.59
7.59
7.58
7.57
7.57
7.37
7.37
7.36
7.35
4.32
4.29
4.25
4.22
2.43
O
S
Br
H3C
(S)-4e
1.82
1.93
1.00
0.99
3.18
f1 (ppm)

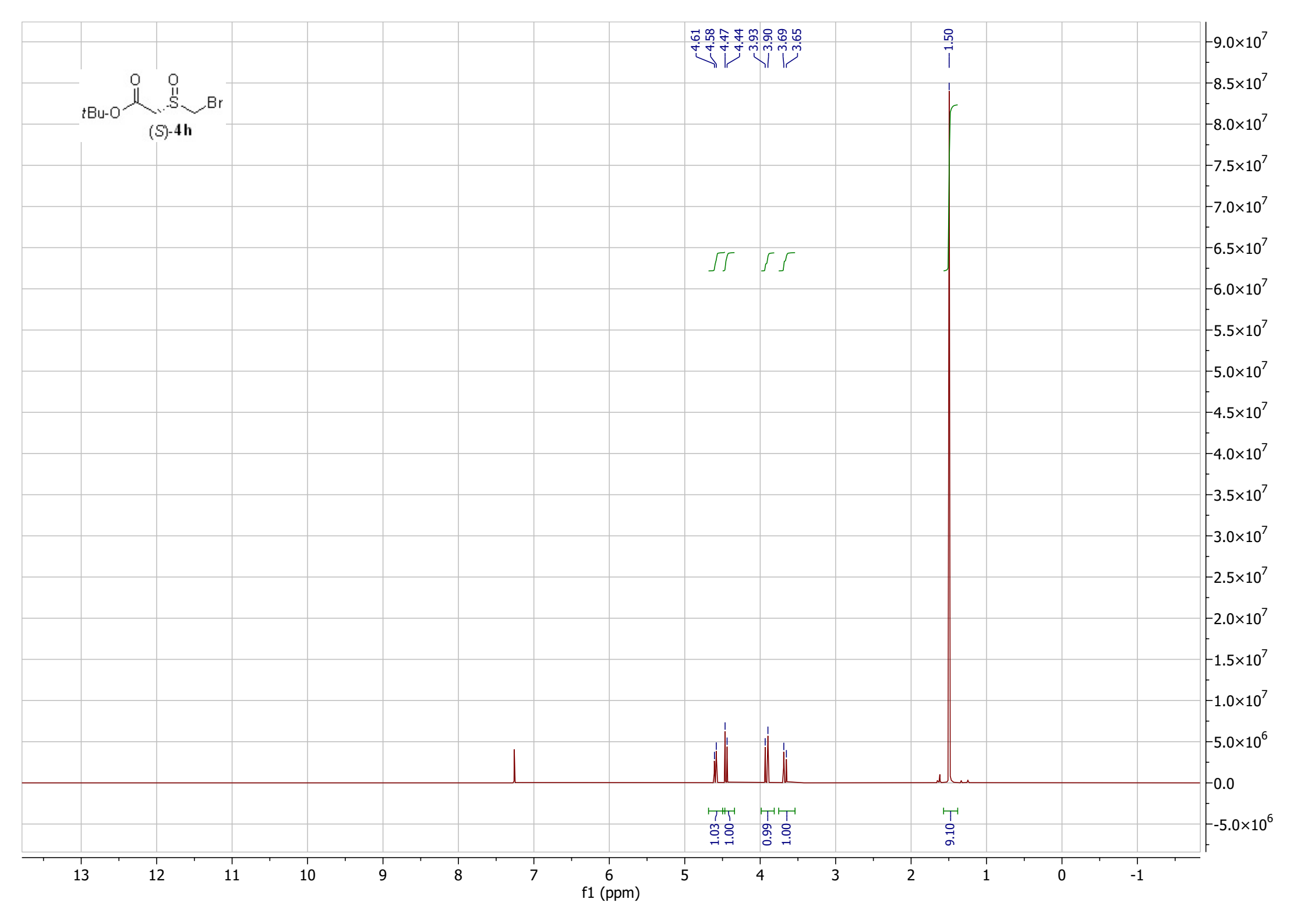

143.00
138.51
130.14
124.98
48.96
21.68
O
S
Br
H3C
(S)-4e
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

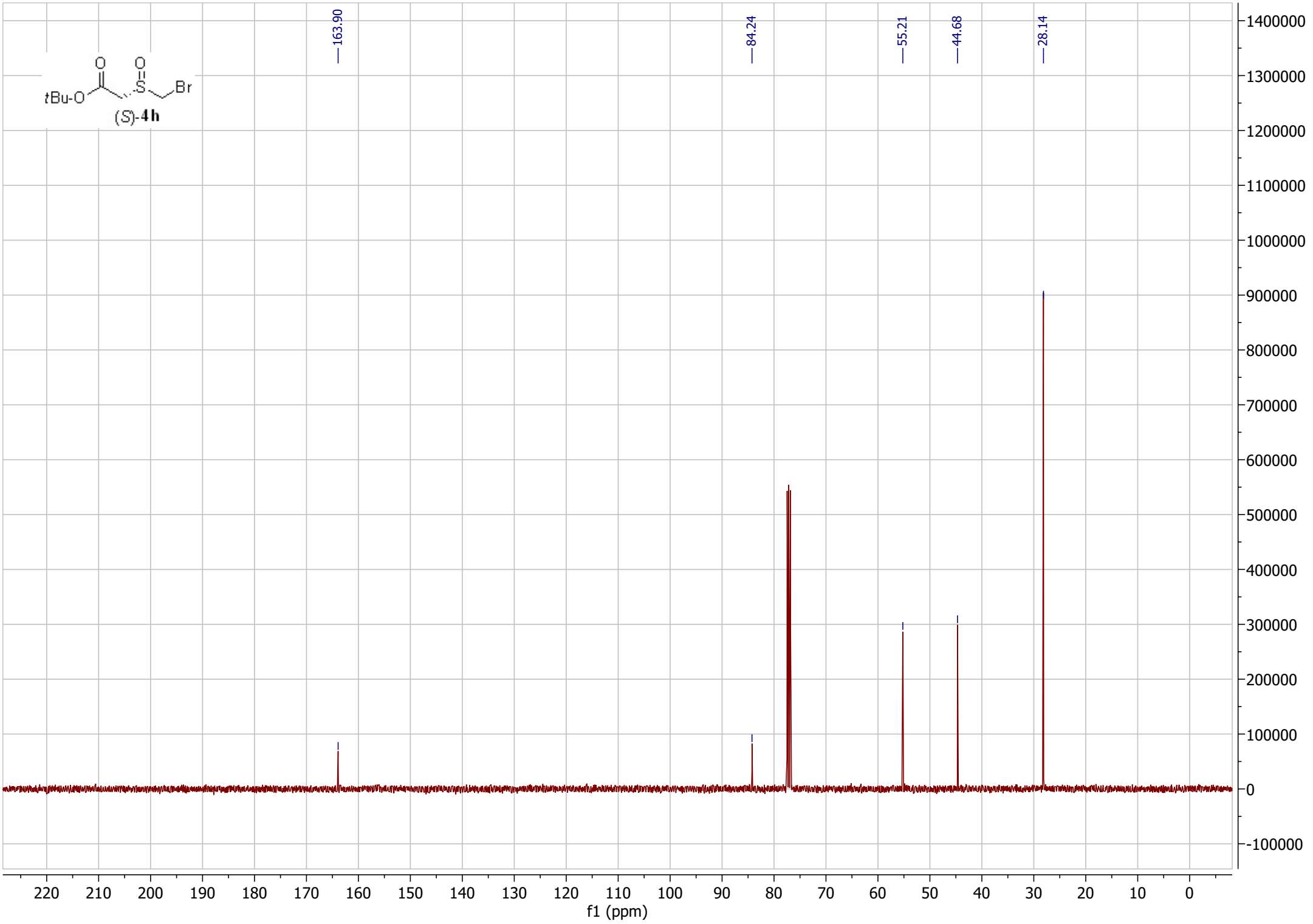

7.83
4.40
4.38
4.29
4.27
O
S
Br
F3C
(S)-4f
3.91
1.00
1.01
3.8×10^7
3.6×10^7
3.4×10^7
3.2×10^7
3.0×10^7
2.8×10^7
2.6×10^7
2.4×10^7
2.2×10^7
2.0×10^7
1.8×10^7
1.6×10^7
1.4×10^7
1.2×10^7
1.0×10^7
8.0×10^6
6.0×10^6
4.0×10^6
2.0×10^6
0.0
-2.0×10^6
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

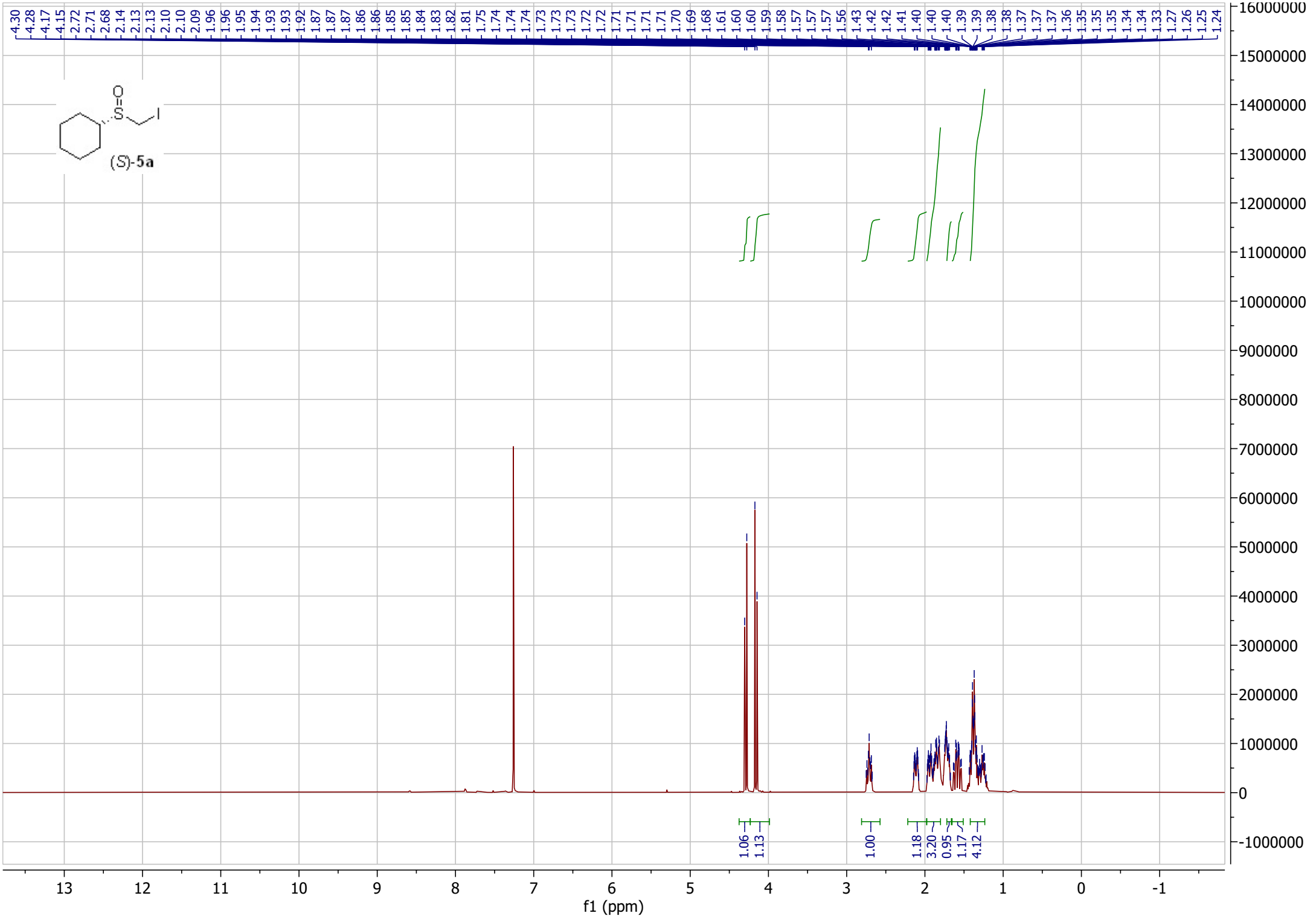

145.90
134.51
134.29
134.07
133.86
126.45
126.43
126.40
126.38
125.56
122.57
48.54
O
S
Br
F3C
(S)-4f
2300000
2200000
2100000
2000000
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
-200000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

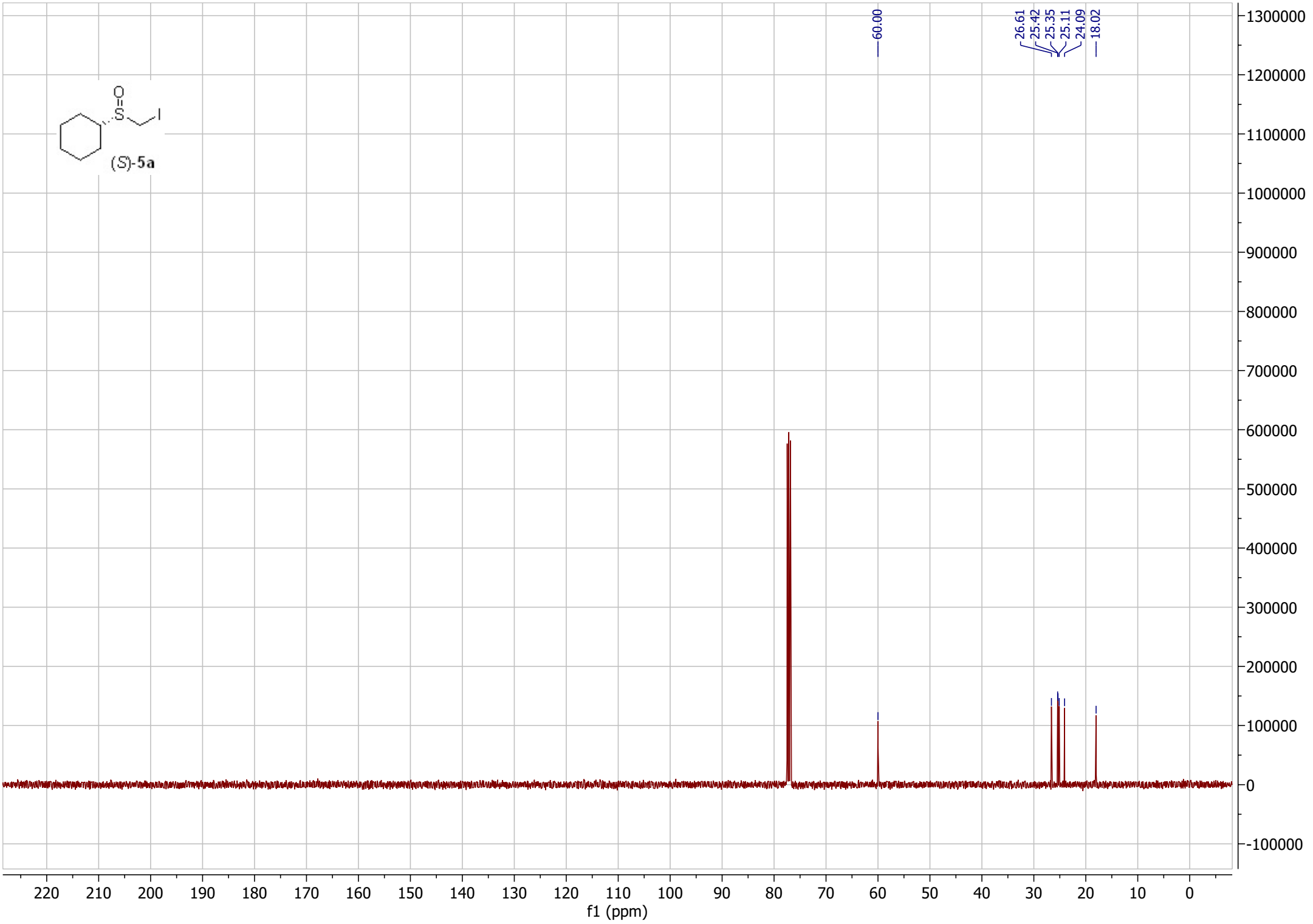

7.66
7.66
7.65
7.65
7.64
7.64
7.55
7.55
7.55
7.54
7.54
7.53
4.34
4.32
4.26
4.24
O
S
Br
Cl
(S)-4g
2.09
2.07
1.00
1.00
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

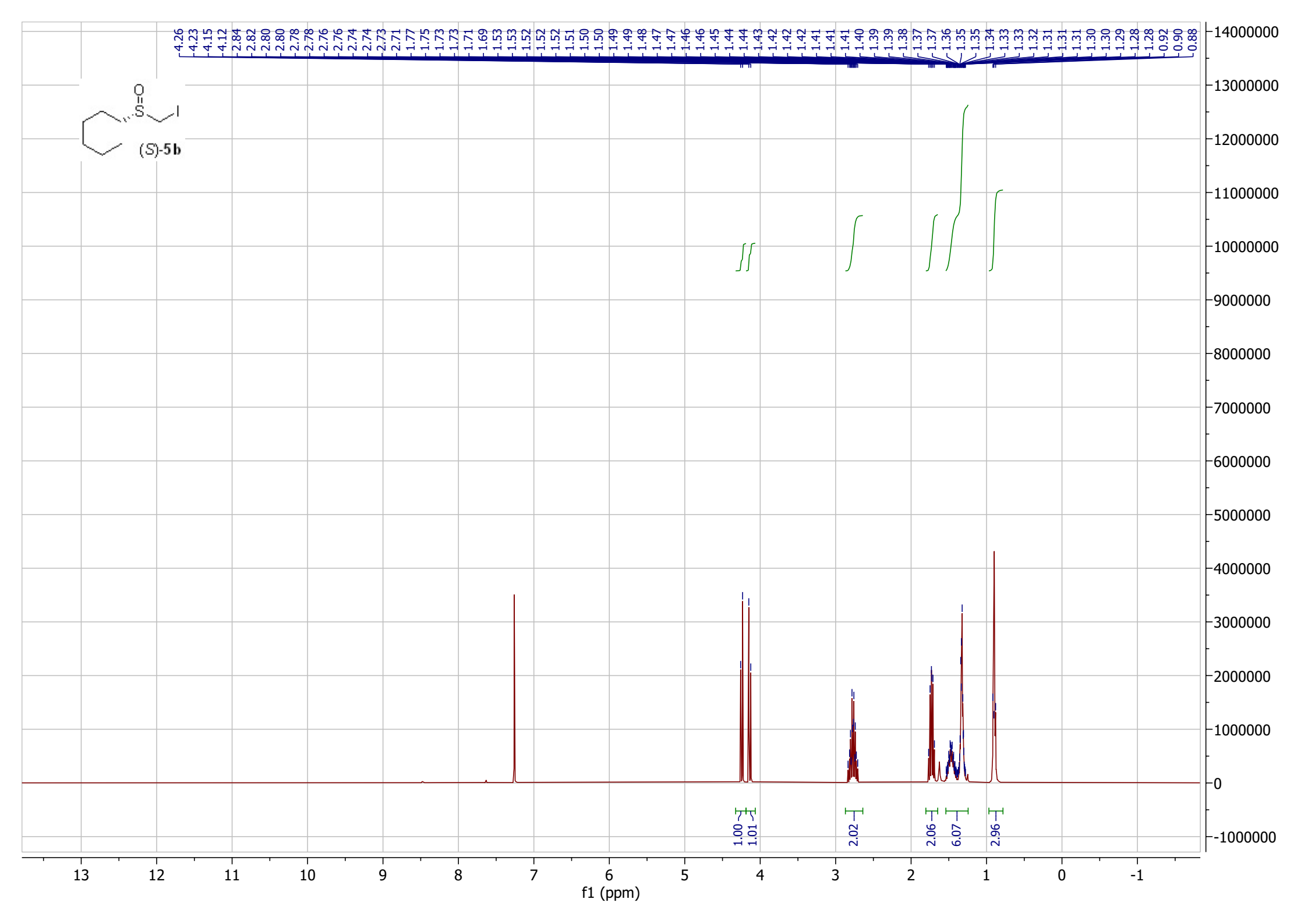

140.08
138.72
129.77
126.49
126.37
48.65
O
S
Br
Cl
(S)-4g
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

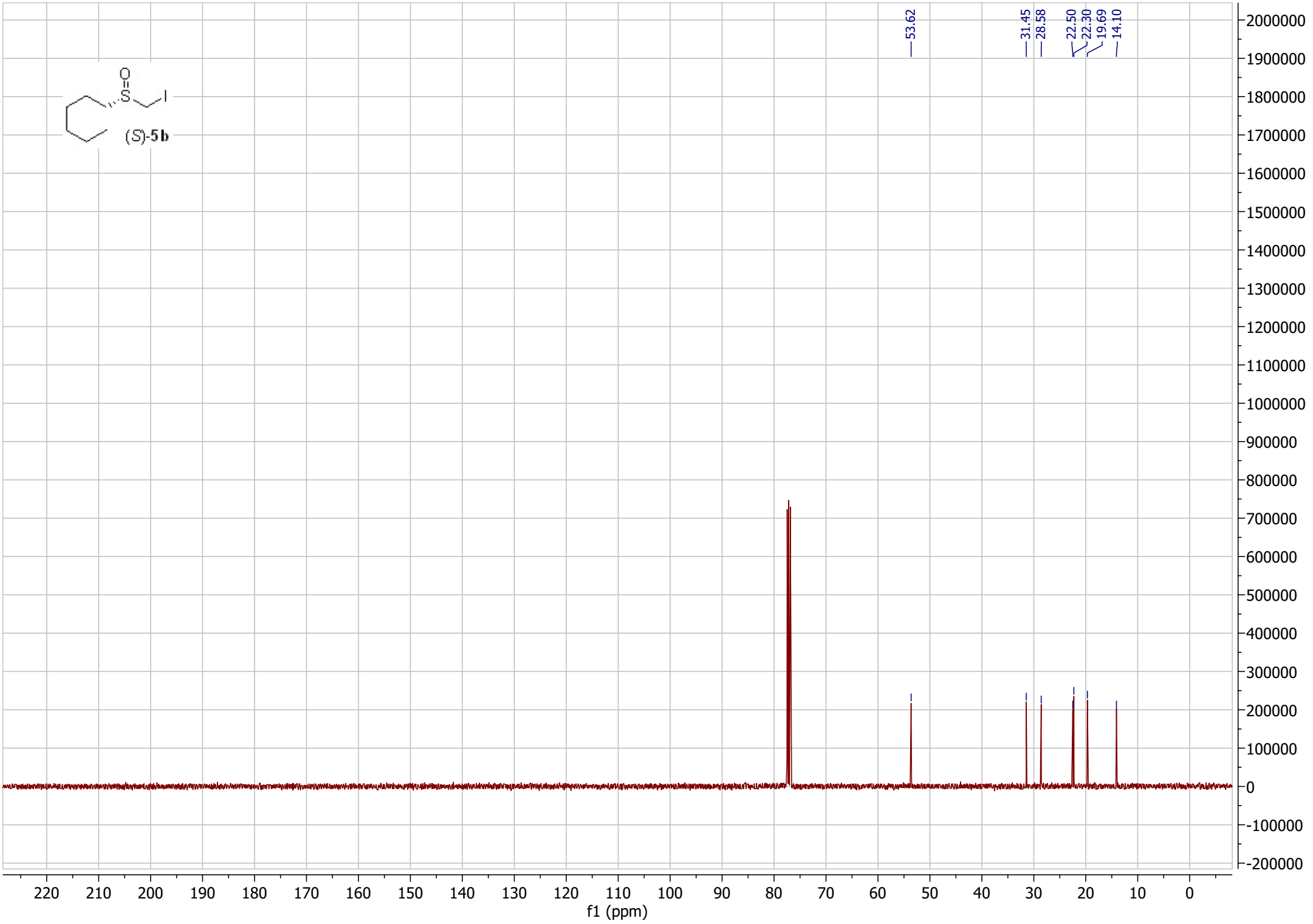

tBu-O
O
O
S
Br
(S)-4h
4.61
4.58
4.47
4.44
3.93
3.90
3.69
3.65
1.50
1.03
1.00
0.99
1.00
9.10
9.0×10^7
8.5×10^7
8.0×10^7
7.5×10^7
7.0×10^7
6.5×10^7
6.0×10^7
5.5×10^7
5.0×10^7
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
-5.0×10^6
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

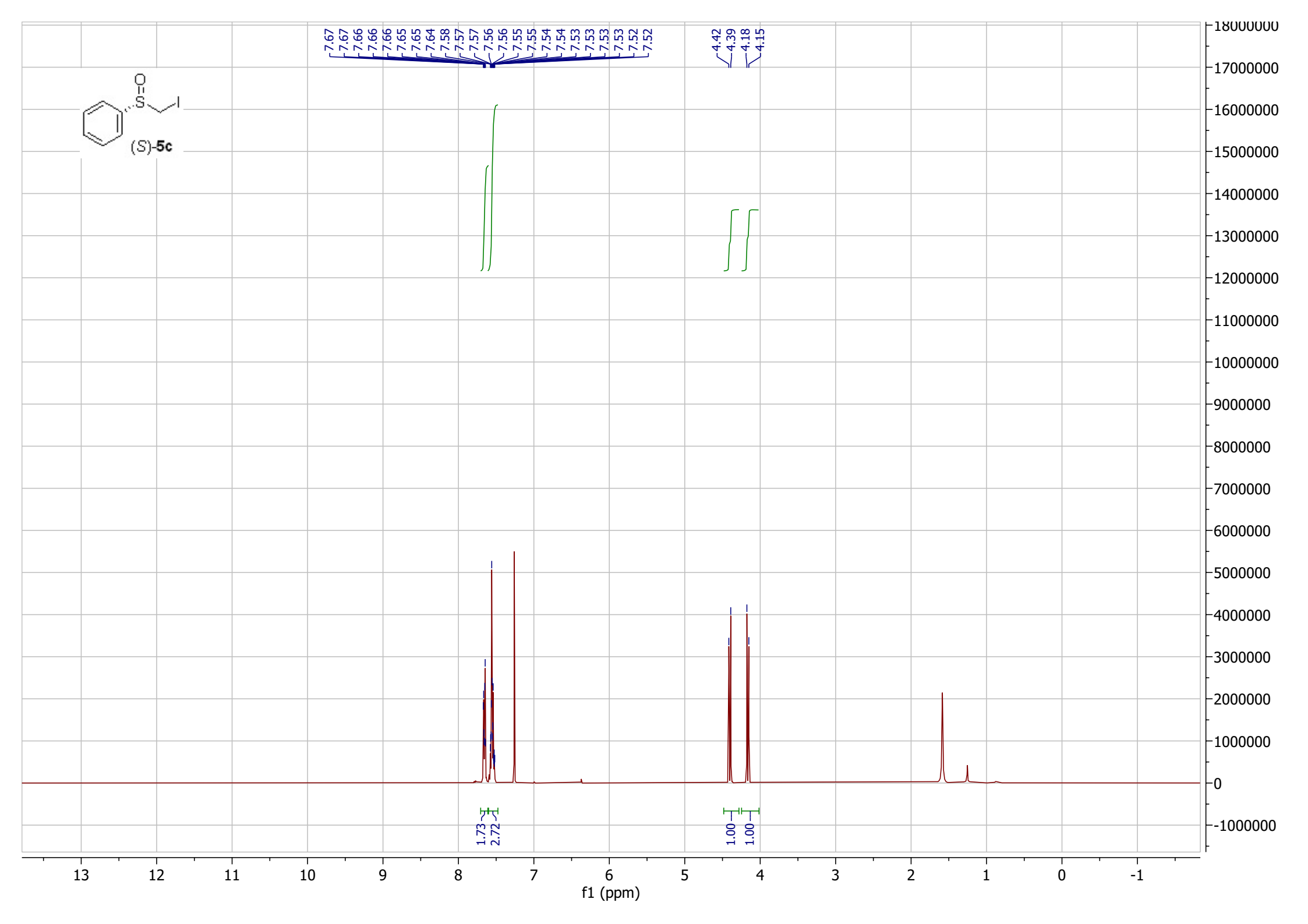

163.90
84.24
55.21
44.68
28.14
tBu-O
Br
(S)-4h
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

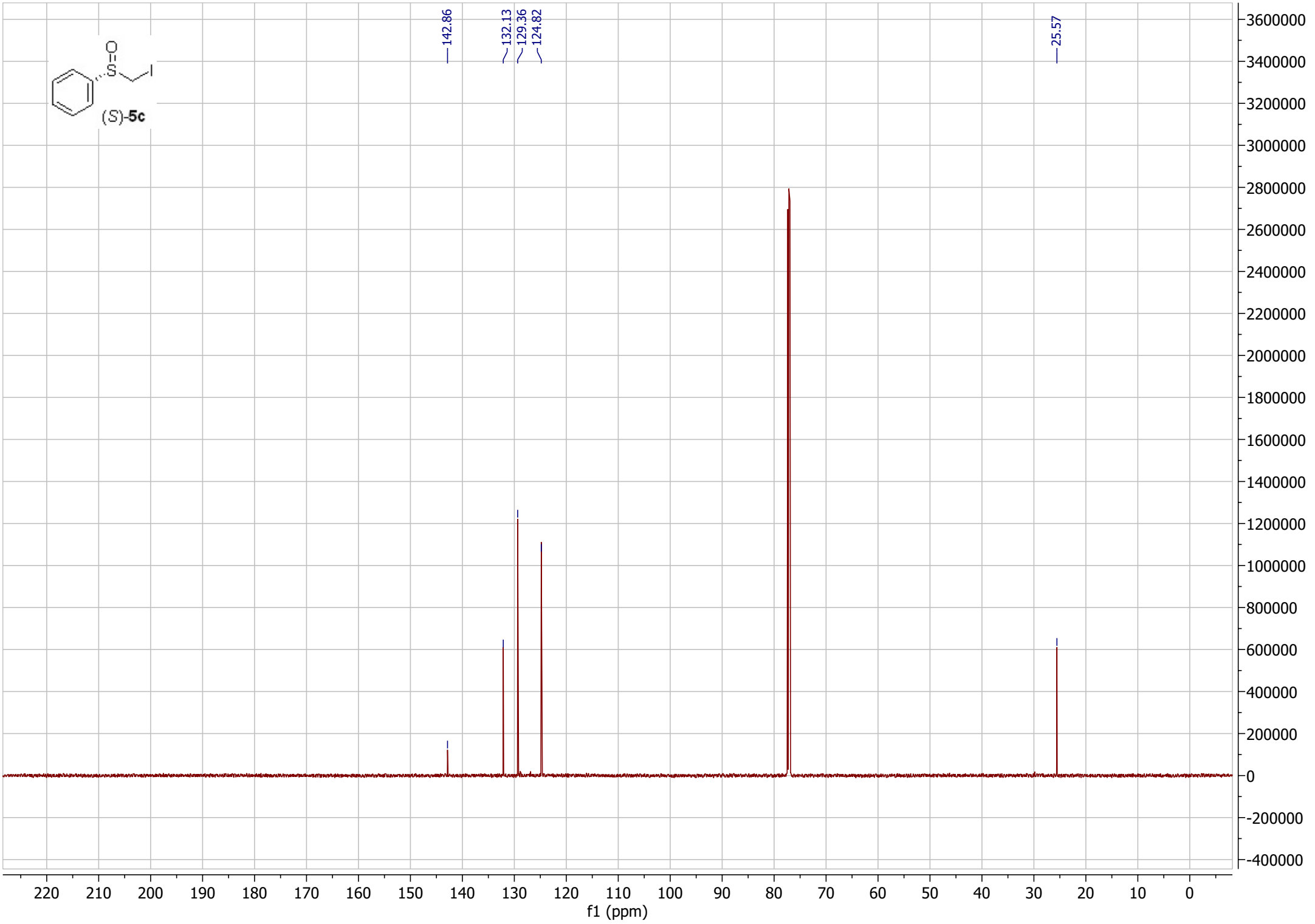

(S)-5a
f1 (ppm)
1.06
1.13
1.00
1.18
3.20
0.95
1.17
4.12

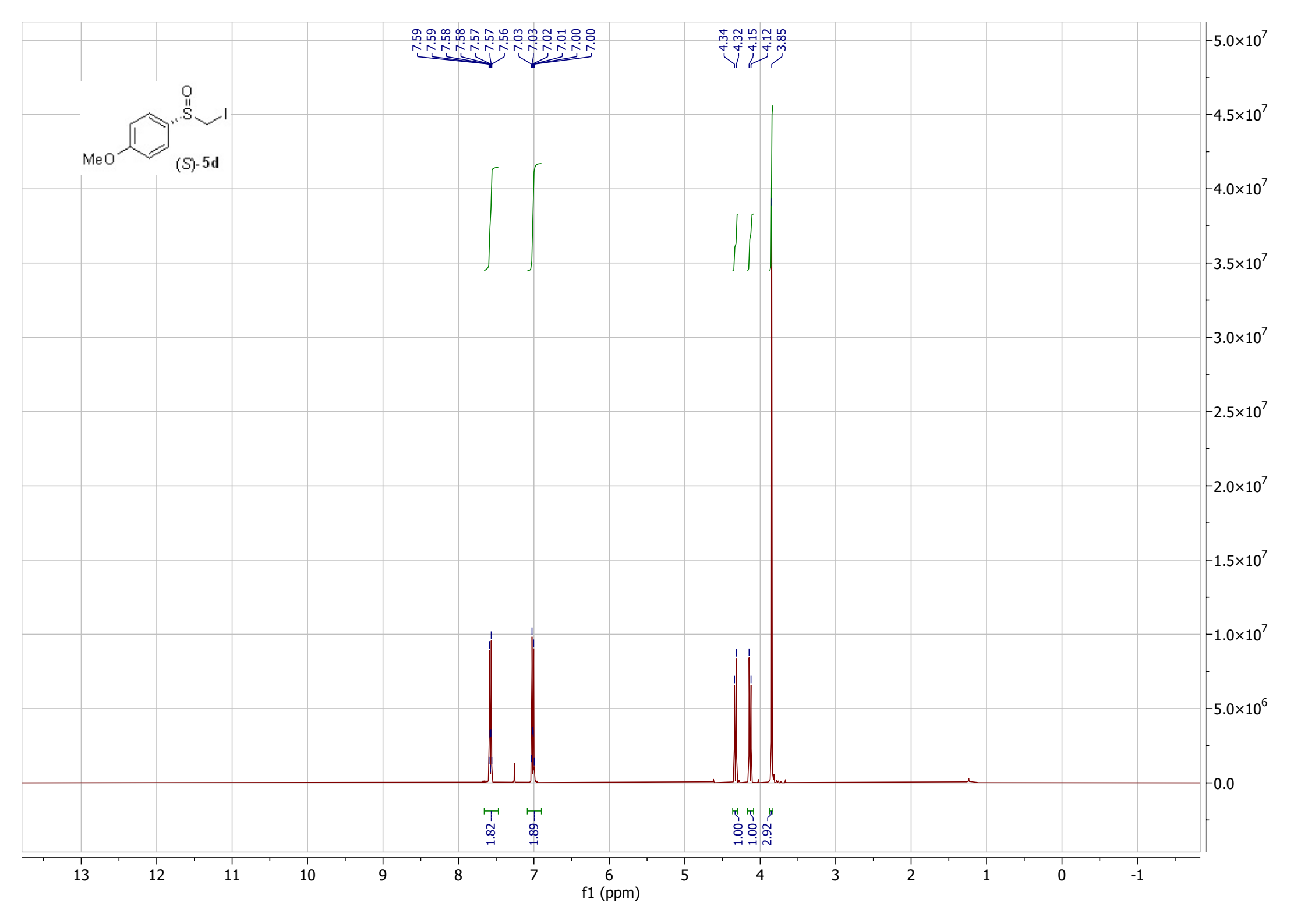

60.00
26.61
25.42
25.35
25.11
24.09
18.02
(S)-5a
f1 (ppm)

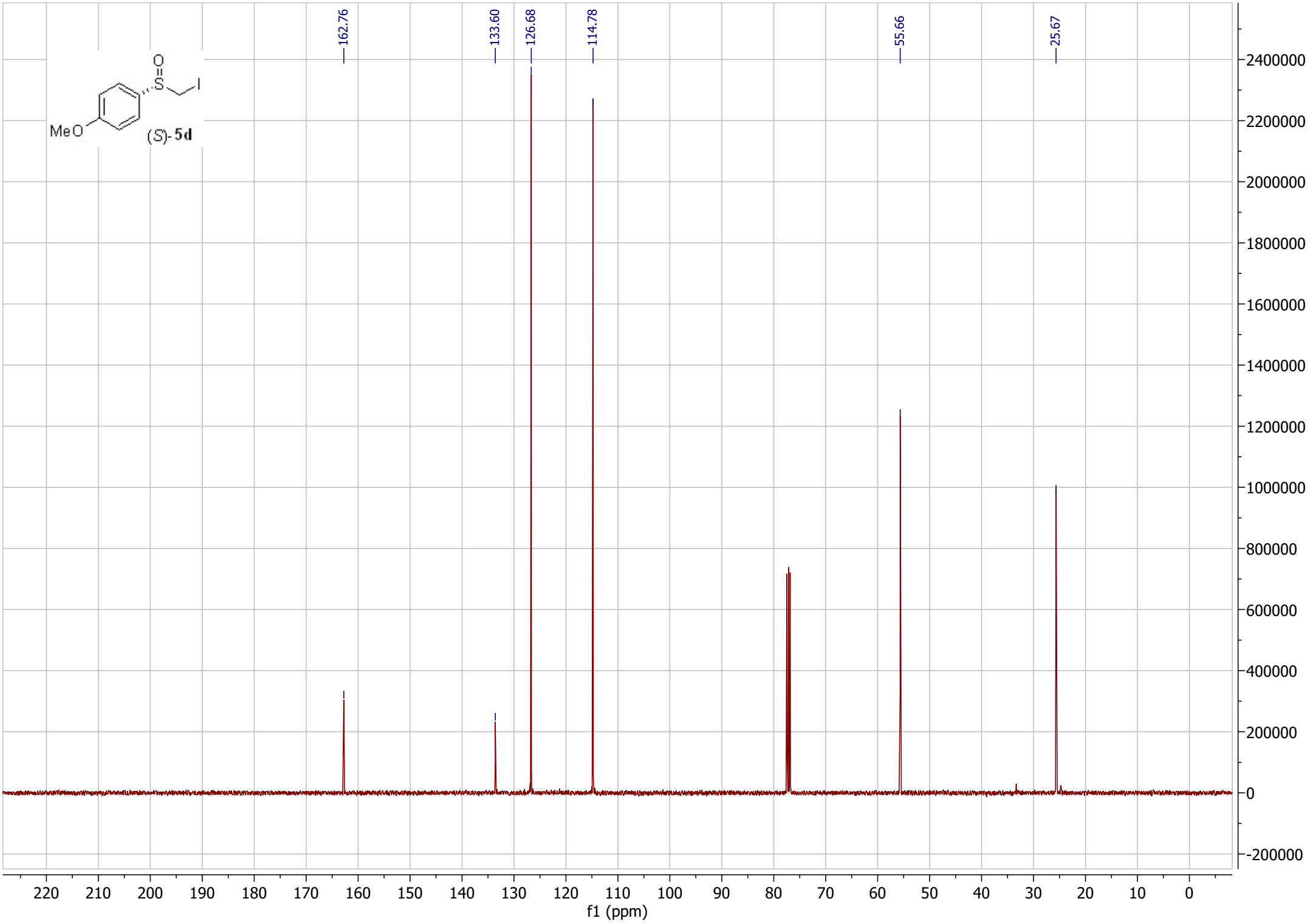

(S)-5b
f1 (ppm)
1.00
1.01
2.02
2.06
6.07
2.96

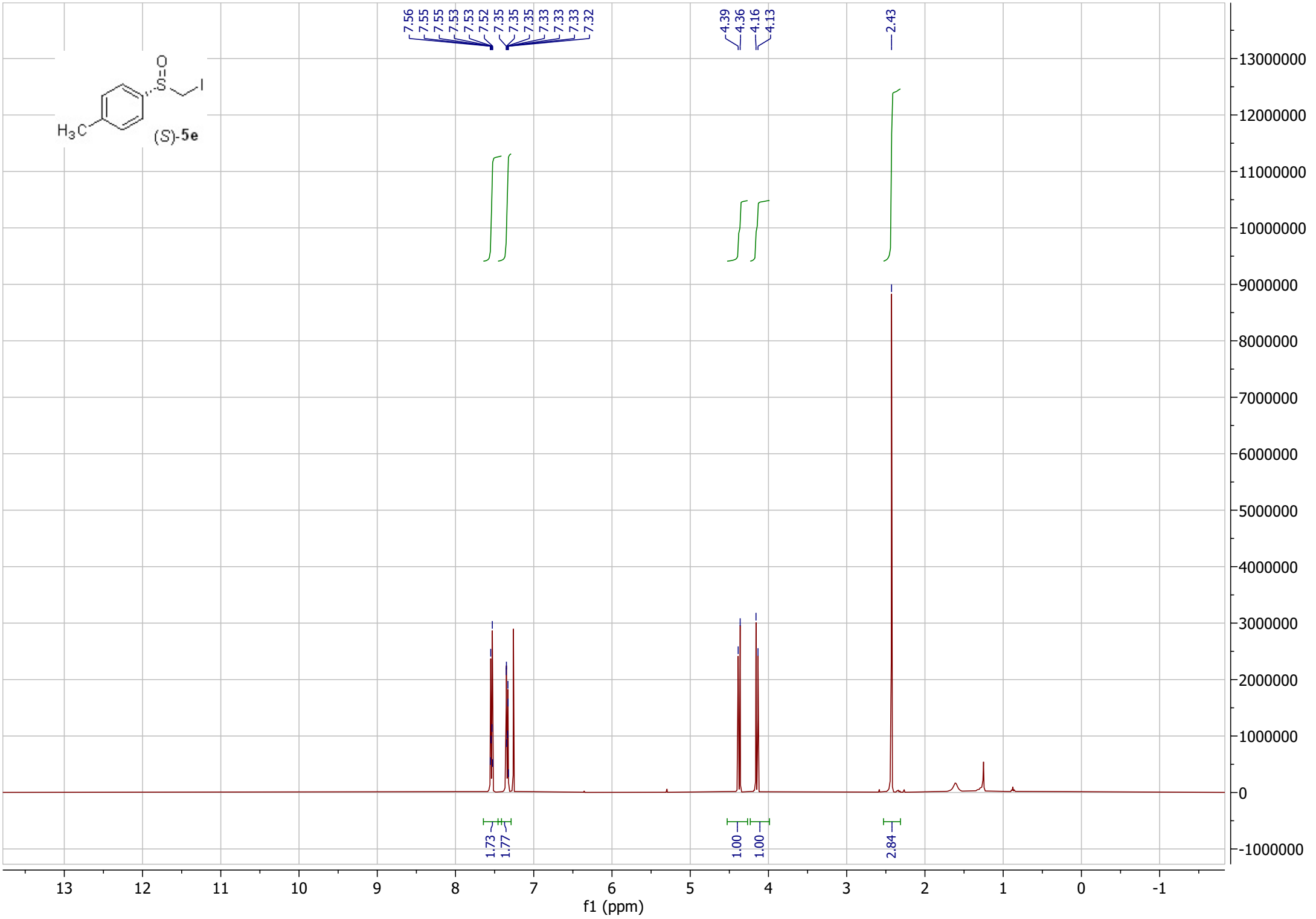

(S)-5b
53.62
31.45
28.58
22.50
22.30
19.69
14.10
f1 (ppm)

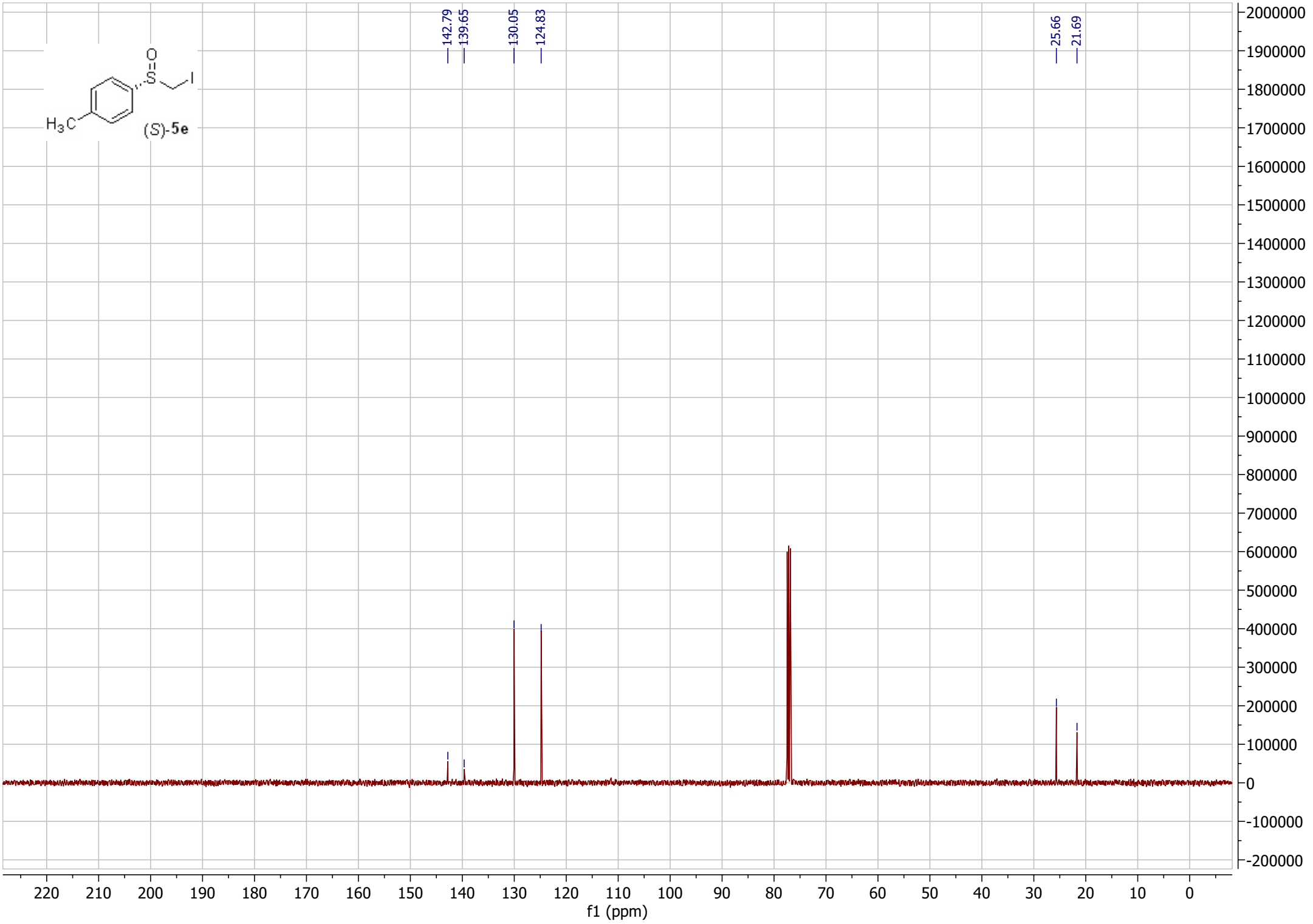

7.67
7.67
7.66
7.66
7.66
7.65
7.65
7.64
7.58
7.57
7.57
7.56
7.56
7.55
7.55
7.54
7.54
7.53
7.53
7.53
7.52
7.52
4.42
4.39
4.18
4.15
O
S
I
(S)-5c
1.73
2.72
1.00
1.00
f1 (ppm)

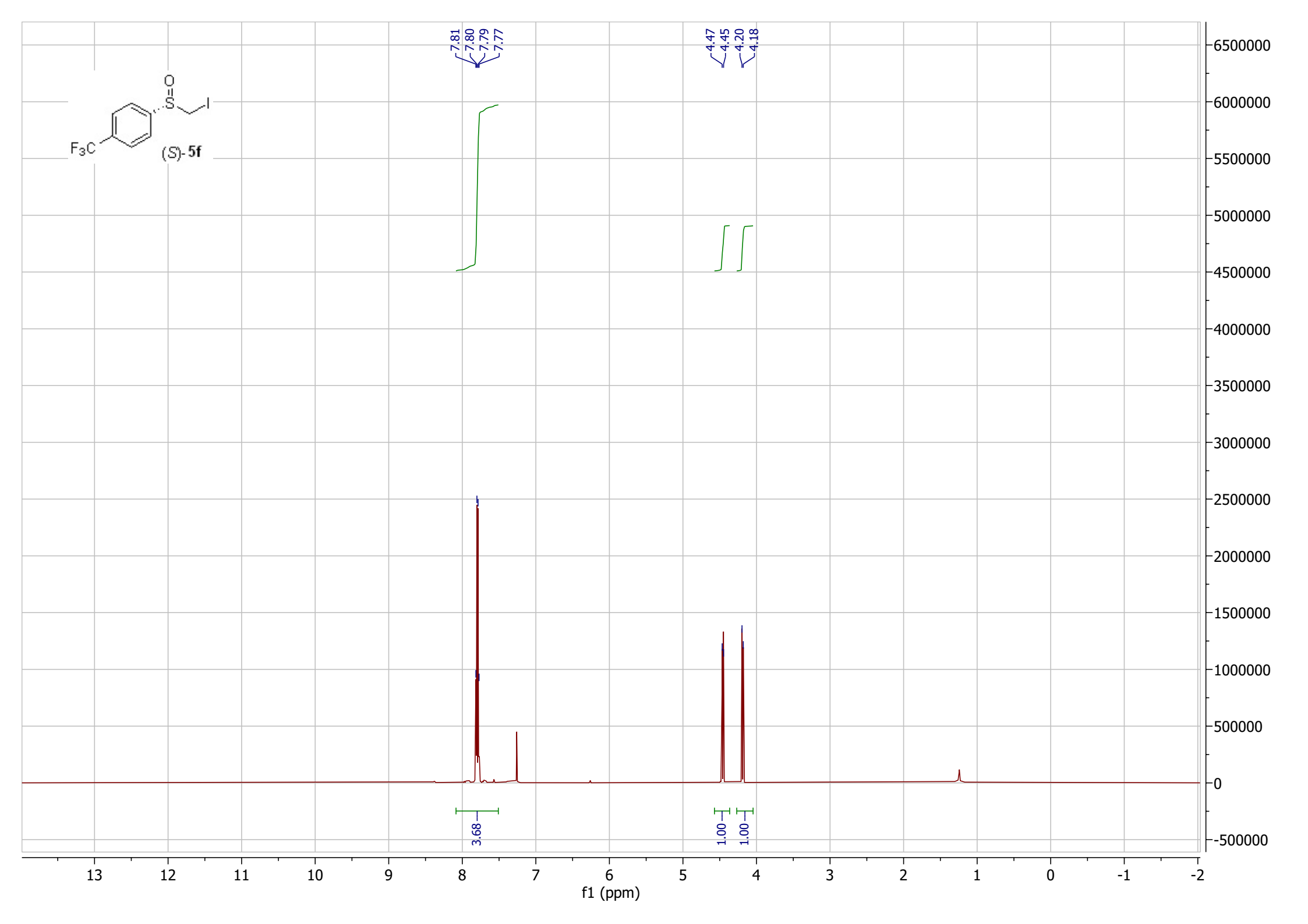

142.86
132.13
129.36
124.82
25.57
(S)-5c
f1 (ppm)

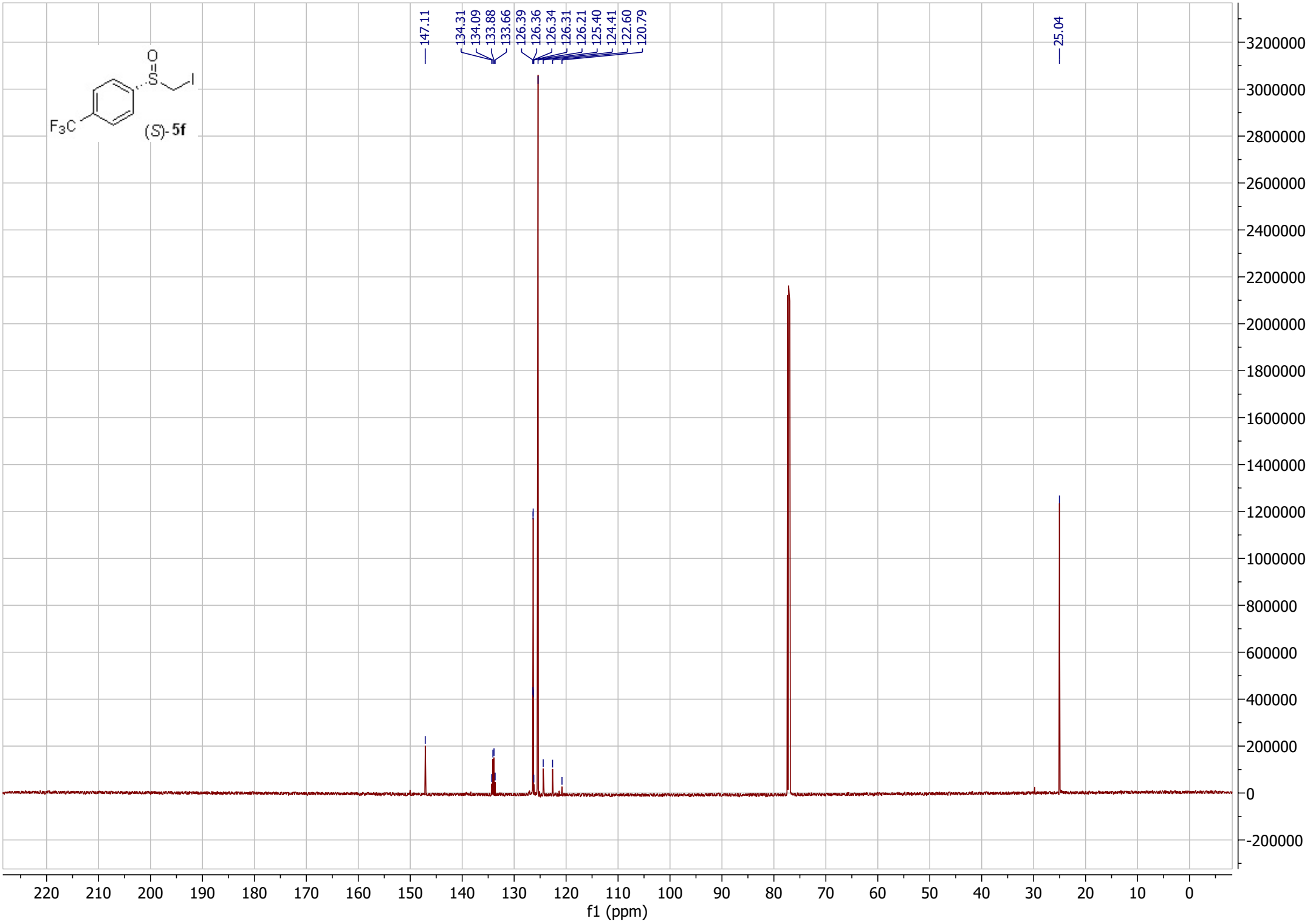

7.59
7.59
7.58
7.58
7.57
7.57
7.56
7.03
7.03
7.02
7.01
7.00
7.00
4.34
4.32
4.15
4.12
3.85
MeO
O
S
I
(S)-5d
1.82
1.89
1.00
1.00
2.92
5.0×10^7
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

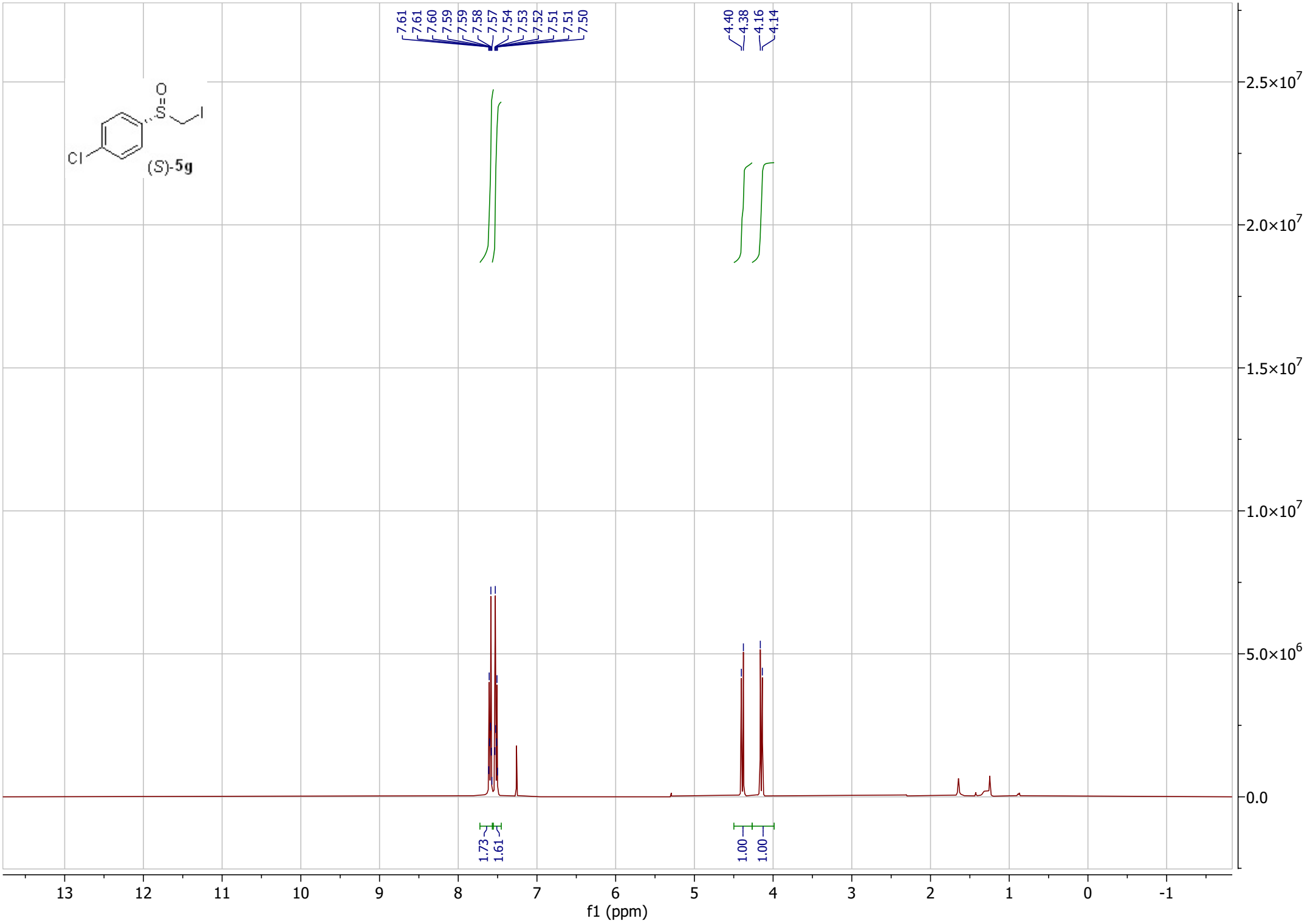

162.76
133.60
126.68
114.78
55.66
25.67
MeO
O
S
I
(S)-5d
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

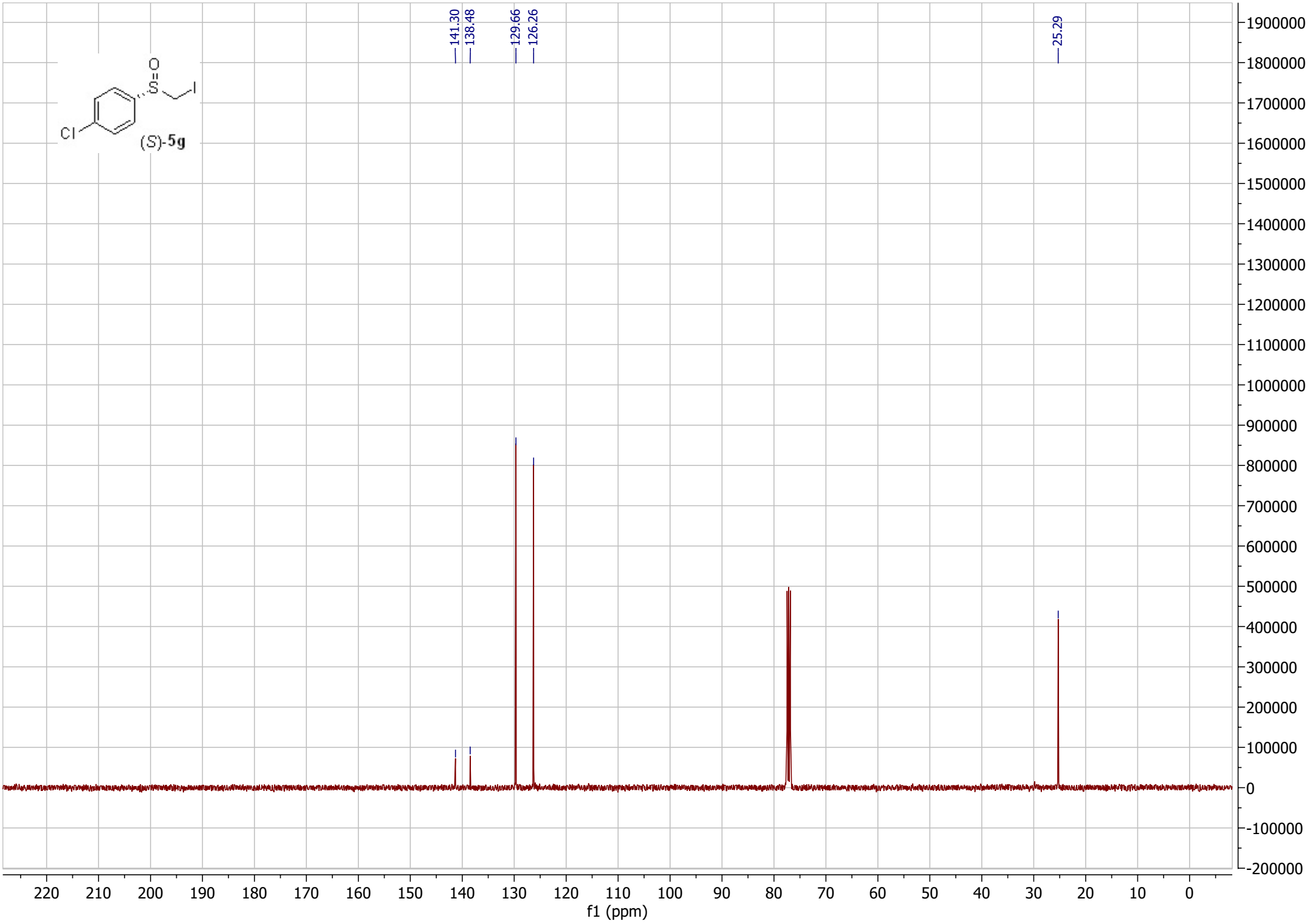

7.56
7.55
7.55
7.53
7.53
7.52
7.35
7.35
7.35
7.33
7.33
7.33
7.32
4.39
4.36
4.16
4.13
2.43
O
S
I
H3C
(S)-5e
1.73
1.77
1.00
1.00
2.84
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

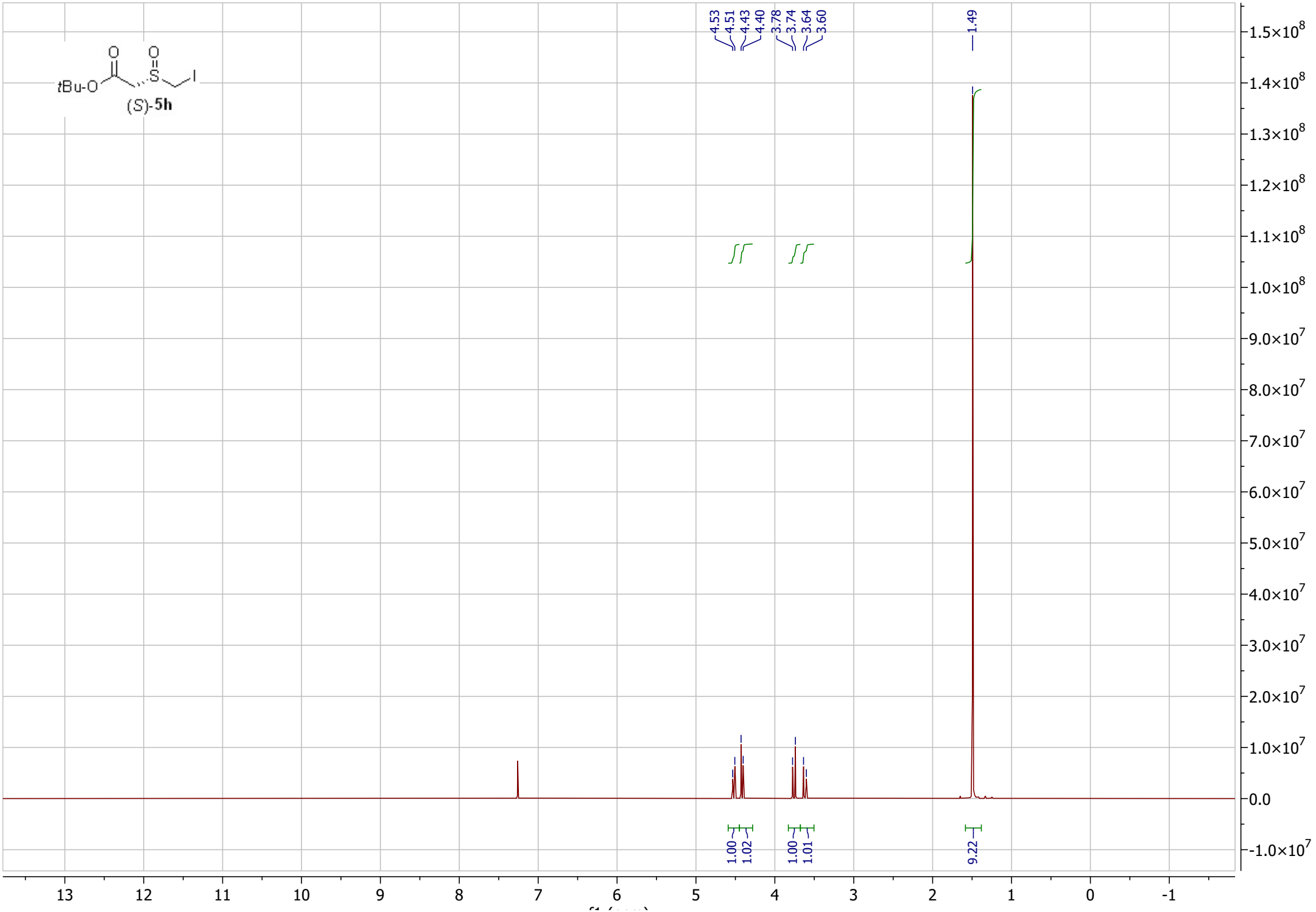

142.79
139.65
130.05
124.83
25.66
21.69
O
S
I
H3C
(S)-5e
2000000
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
-200000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

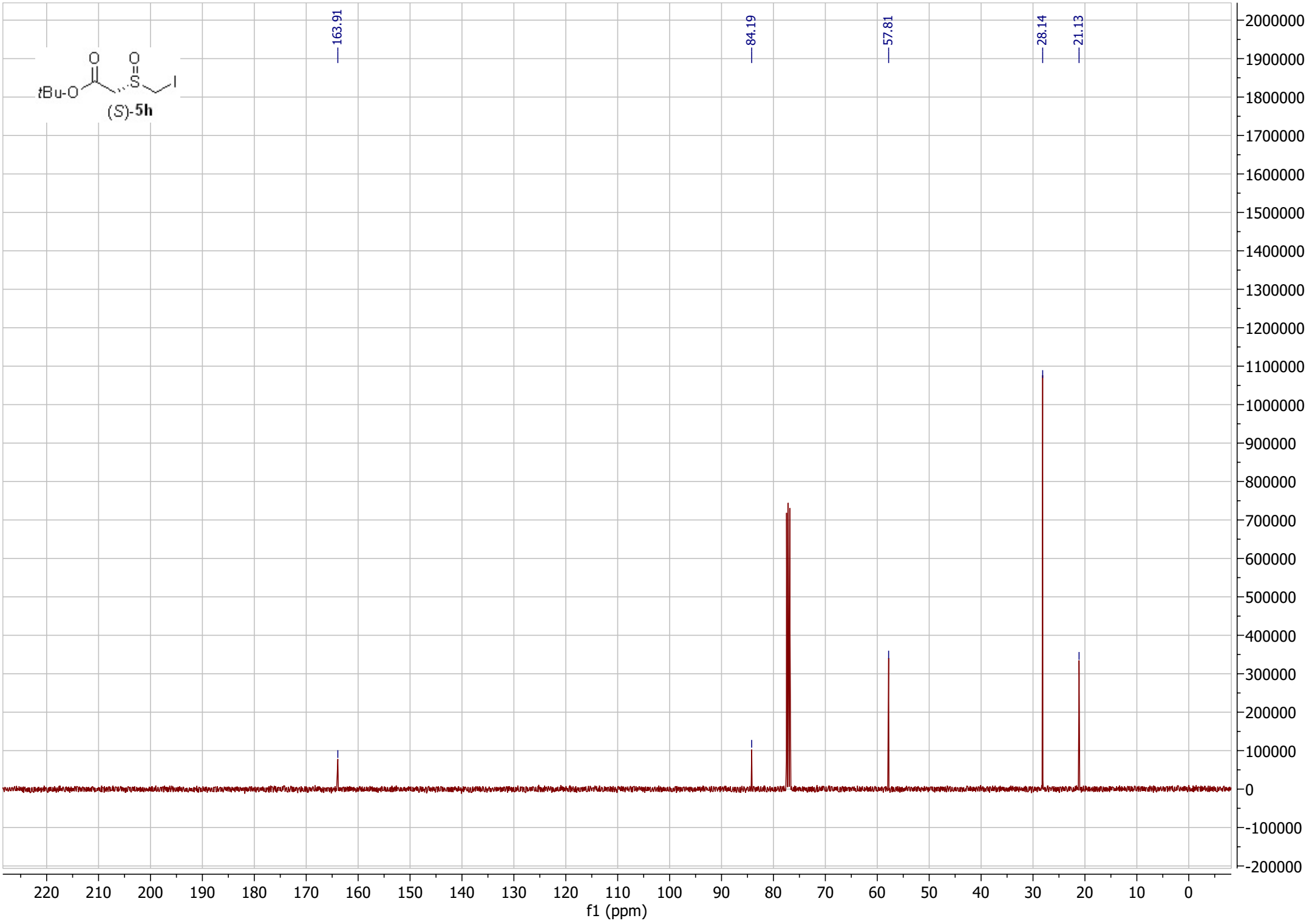

7.81
7.80
7.79
7.77
4.47
4.45
4.20
4.18
O
S
I
F3C
(S)-5f
3.68
1.00
1.00
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

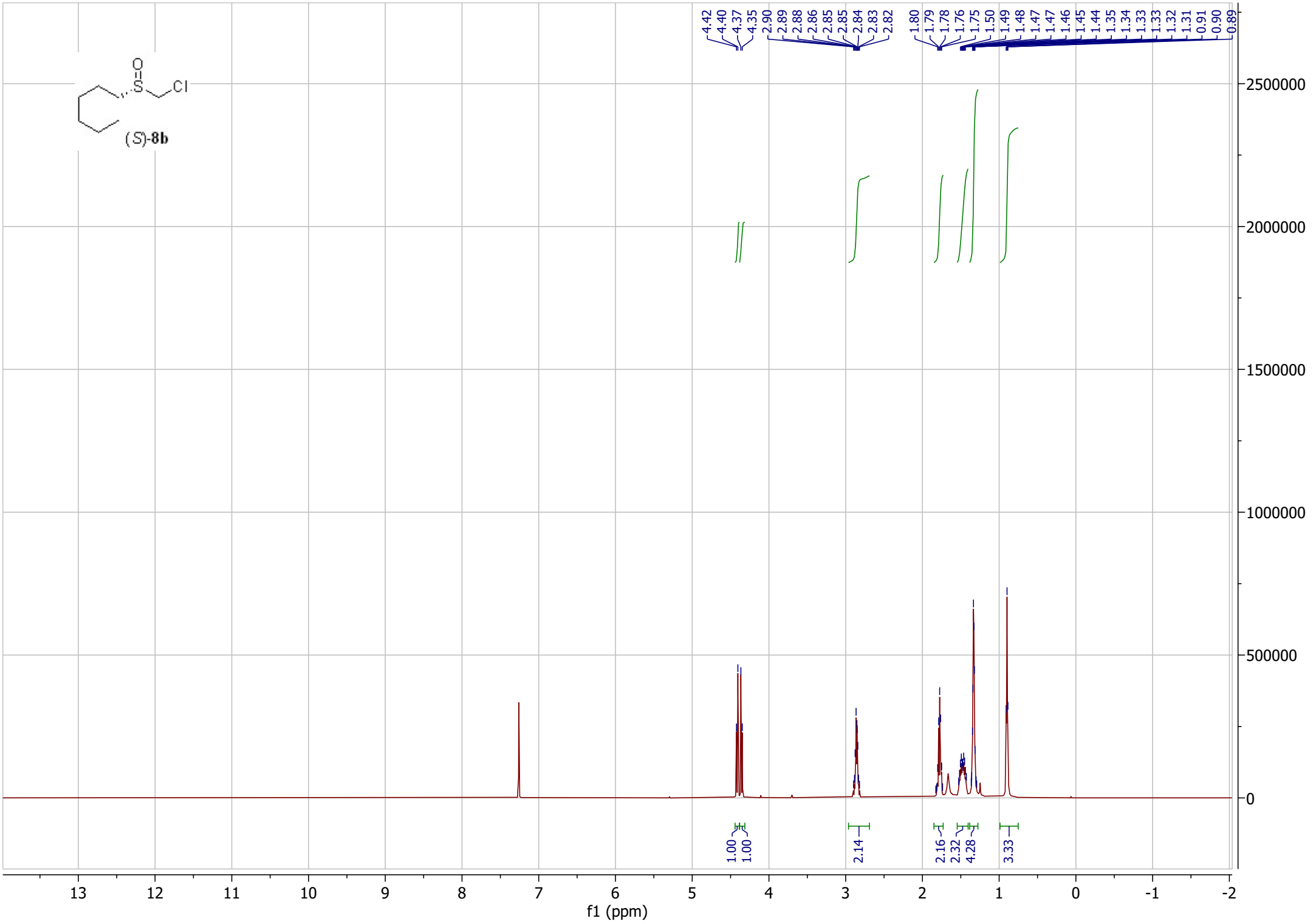

147.11
134.31
134.09
133.88
133.66
126.39
126.36
126.34
126.31
126.21
125.40
124.41
122.60
120.79
25.04
O
S
I
F3C
(S)-5f
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

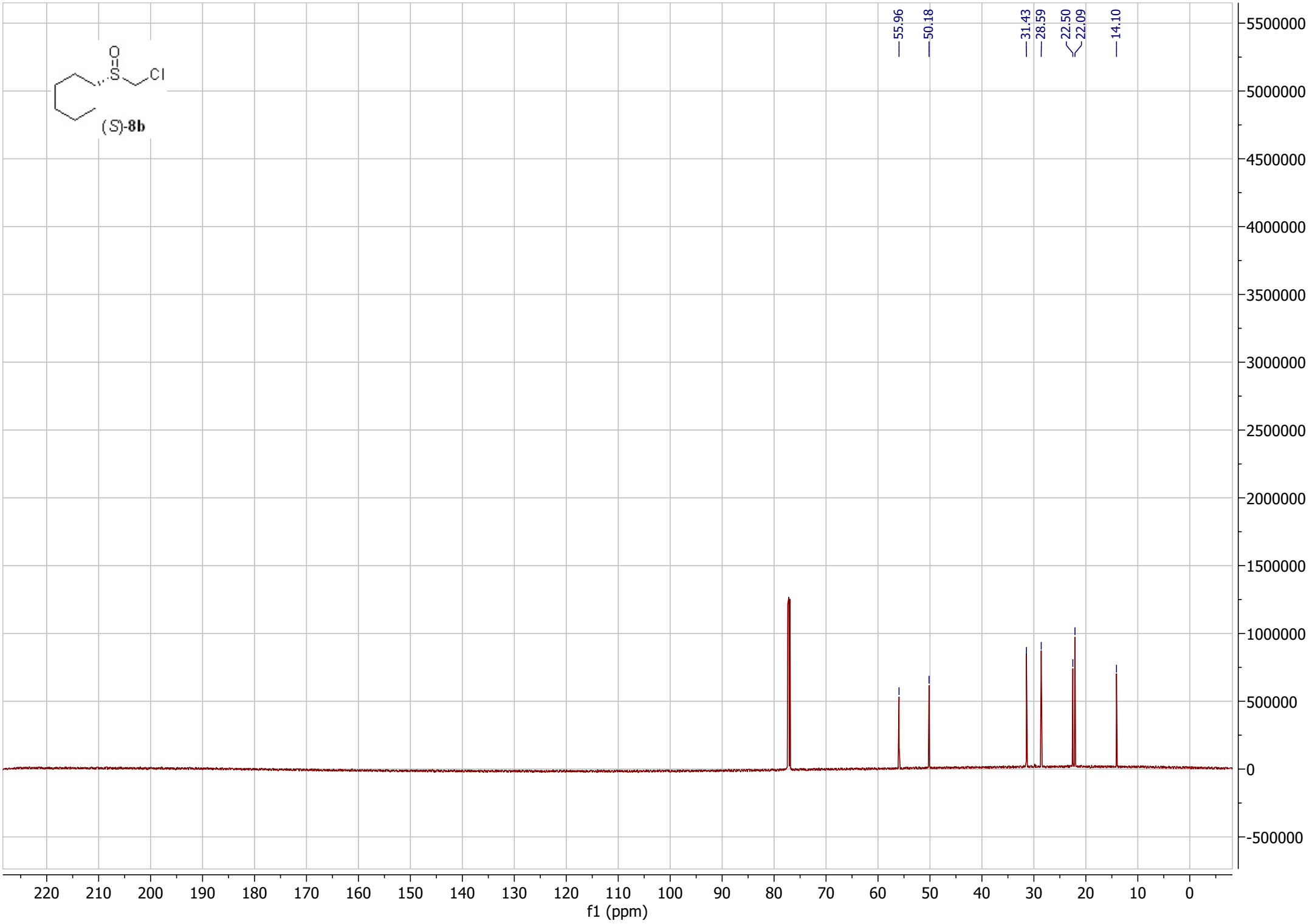

7.61
7.61
7.60
7.59
7.59
7.58
7.57
7.54
7.53
7.52
7.51
7.51
7.50
4.40
4.38
4.16
4.14
O
S
I
Cl
(S)-5g
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
1.73
1.61
1.00
1.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

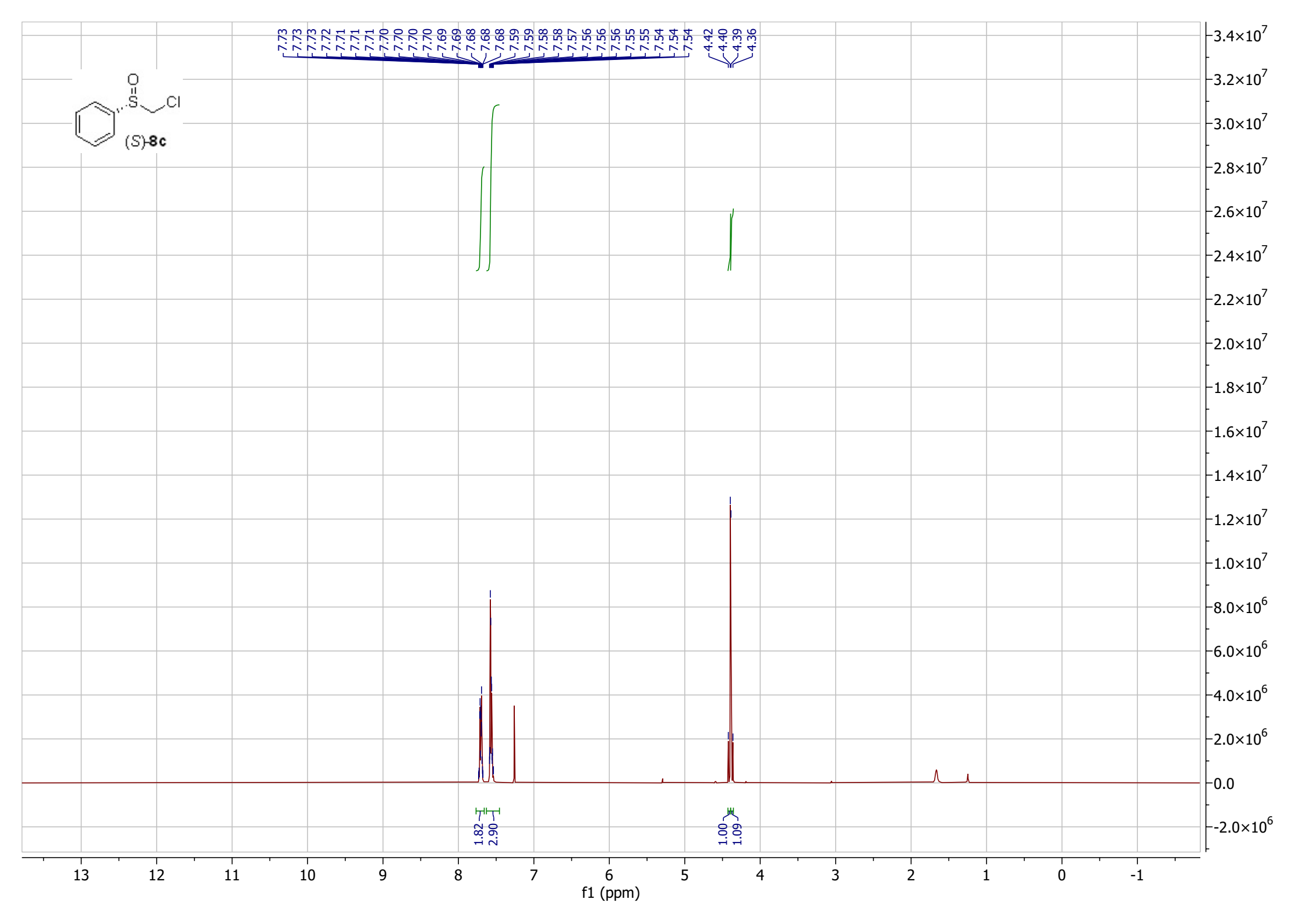

141.30
138.48
129.66
126.26
25.29
O
S
I
Cl
(S)-5g
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
-200000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

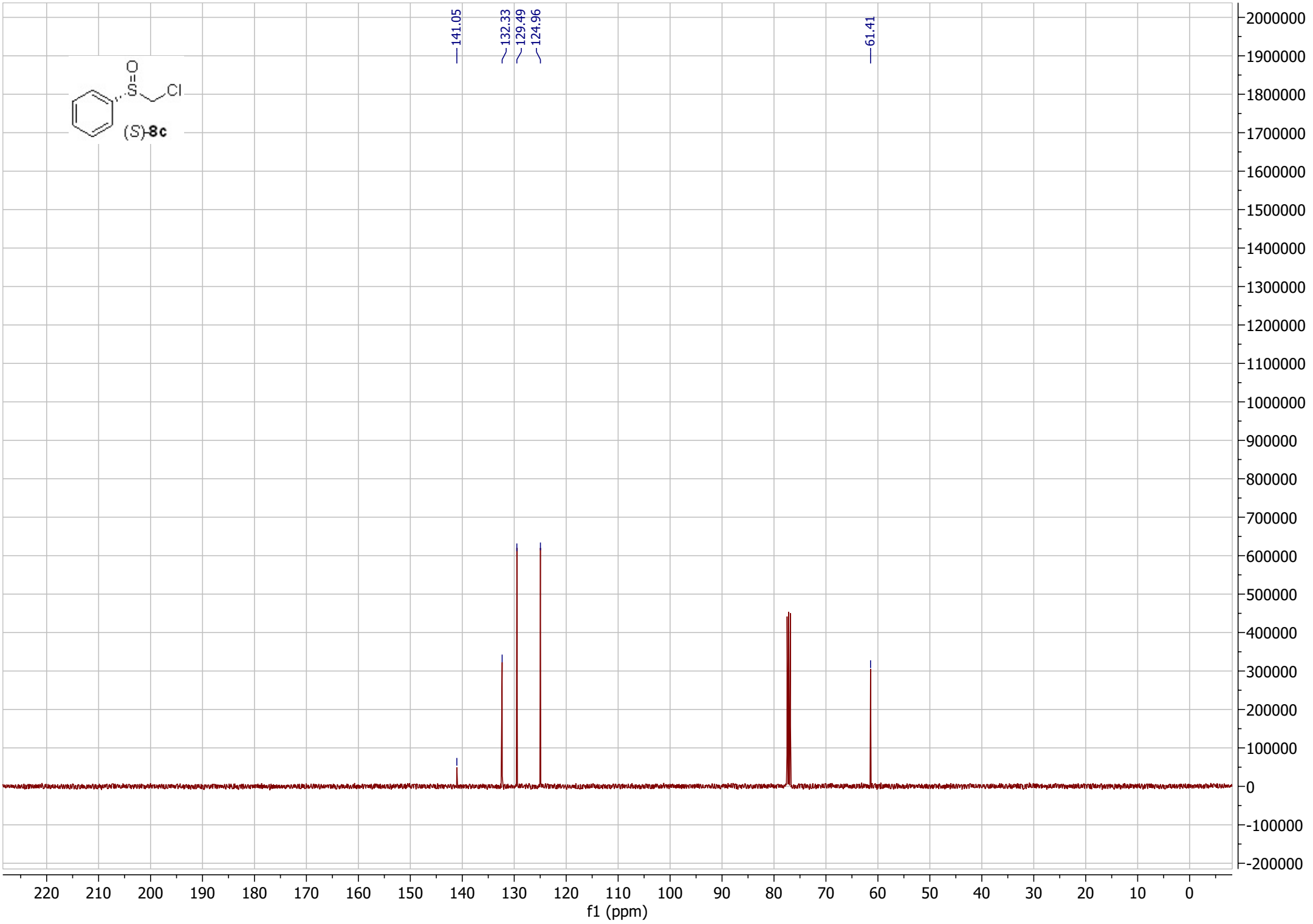

tBu-O
O
O
S
I
(S)-5h
4.53
4.51
4.43
4.40
3.78
3.74
3.64
3.60
1.49
1.00
1.02
1.00
1.01
9.22
1.5×10^8
1.4×10^8
1.3×10^8
1.2×10^8
1.1×10^8
1.0×10^8
9.0×10^7
8.0×10^7
7.0×10^7
6.0×10^7
5.0×10^7
4.0×10^7
3.0×10^7
2.0×10^7
1.0×10^7
0.0
-1.0×10^7
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1

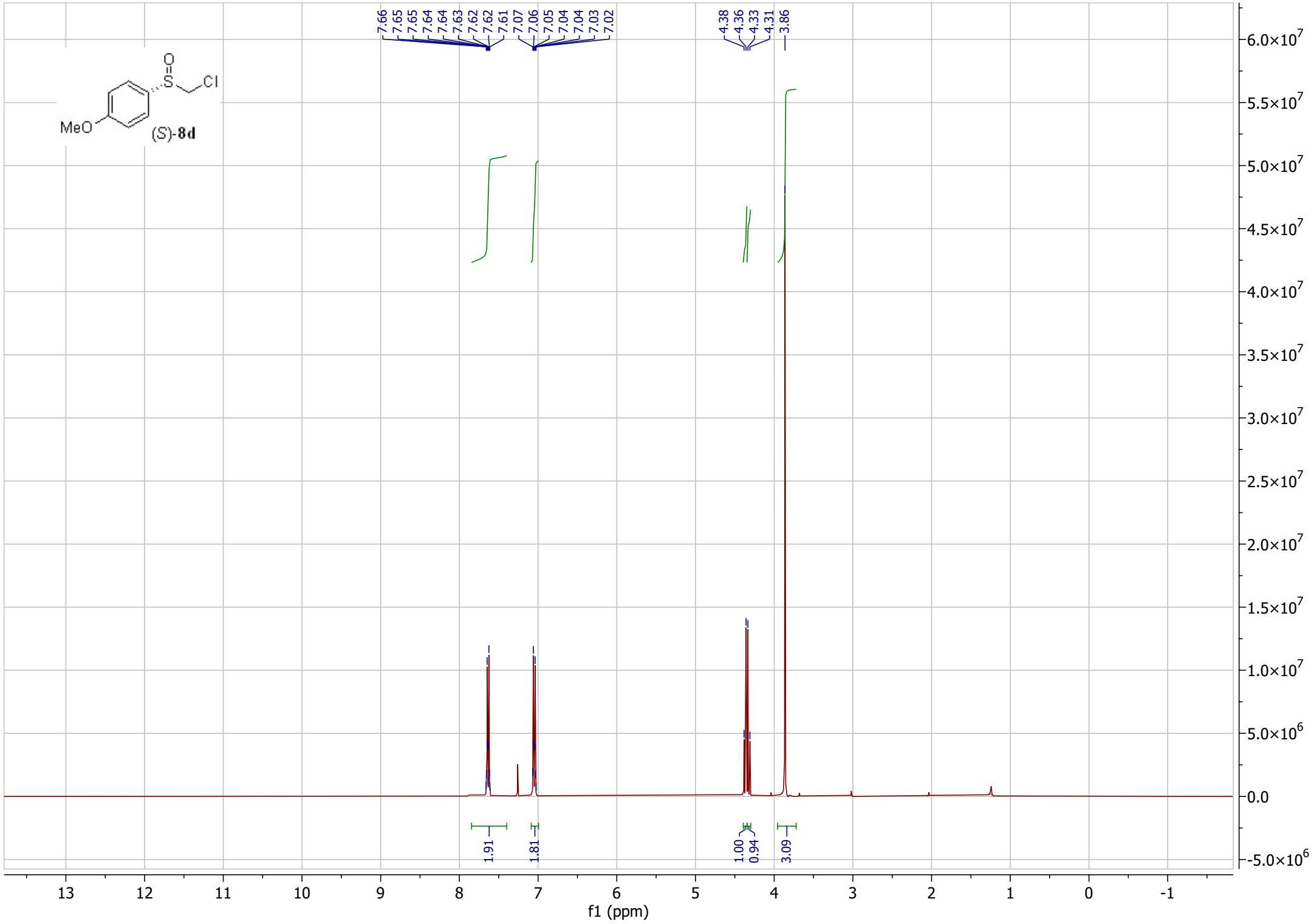

163.91
84.19
57.81
28.14
21.13
tBu-O
(S)-5h
f1 (ppm)

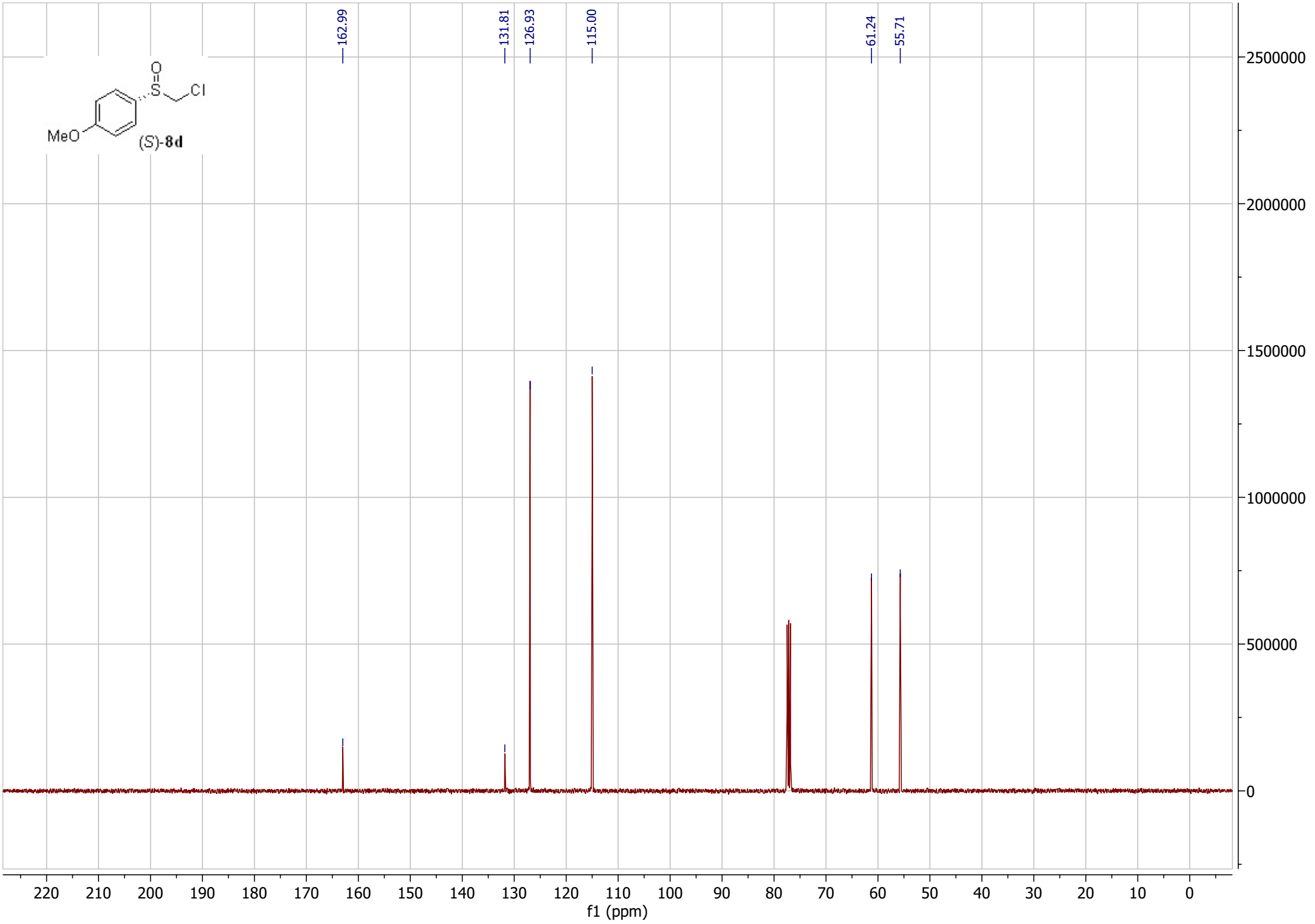

(S)-8b
4.42
4.40
4.37
4.35
2.90
2.89
2.88
2.86
2.85
2.85
2.84
2.83
2.82
1.80
1.79
1.78
1.76
1.75
1.50
1.49
1.48
1.47
1.47
1.46
1.45
1.44
1.35
1.34
1.33
1.33
1.32
1.31
0.91
0.90
0.89
2500000
2000000
1500000
1000000
500000
0
1.00
1.00
2.14
2.16
2.32
4.28
3.33
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

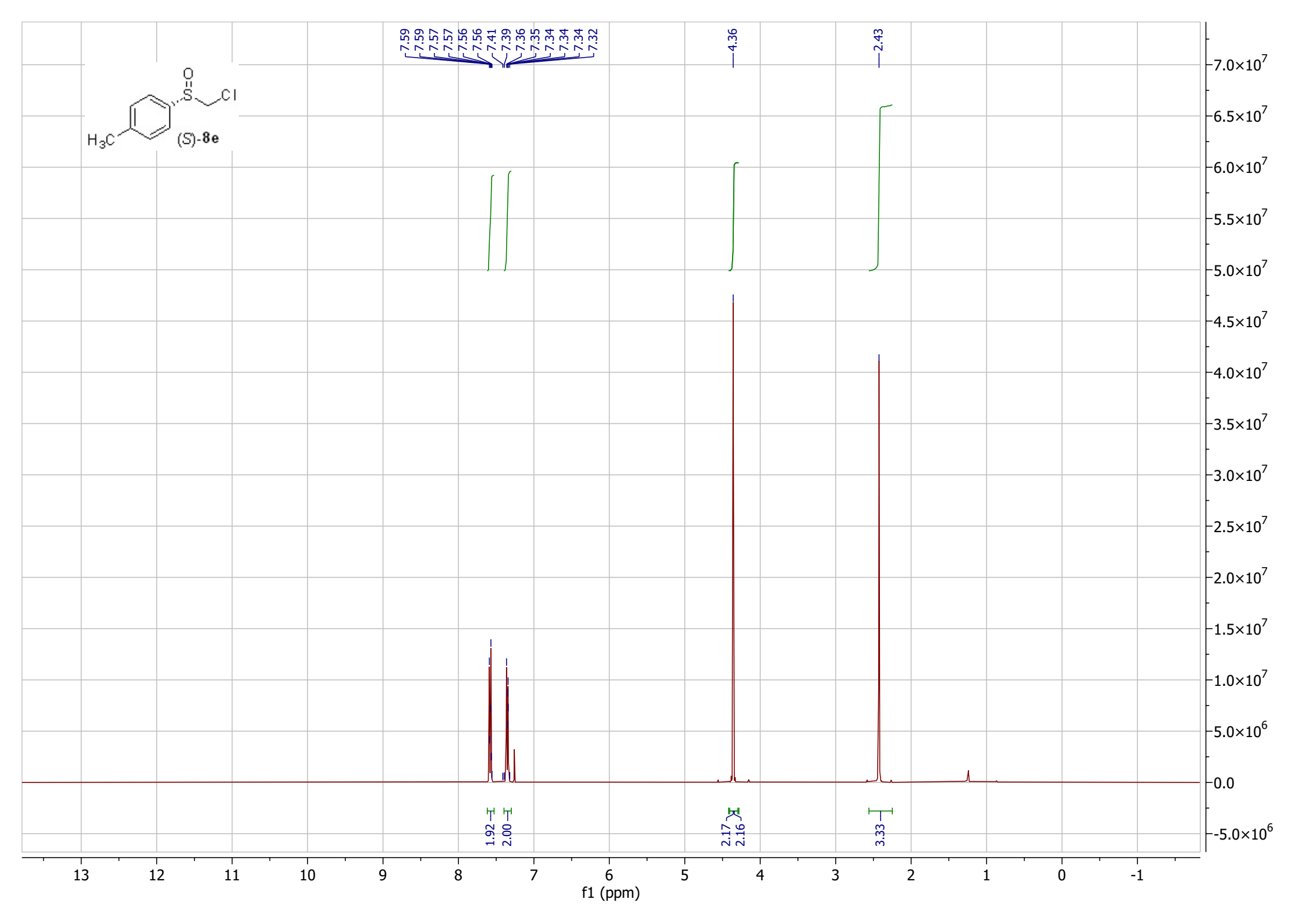

(S)-8b
55.96
50.18
31.43
28.59
22.50
22.09
14.10
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

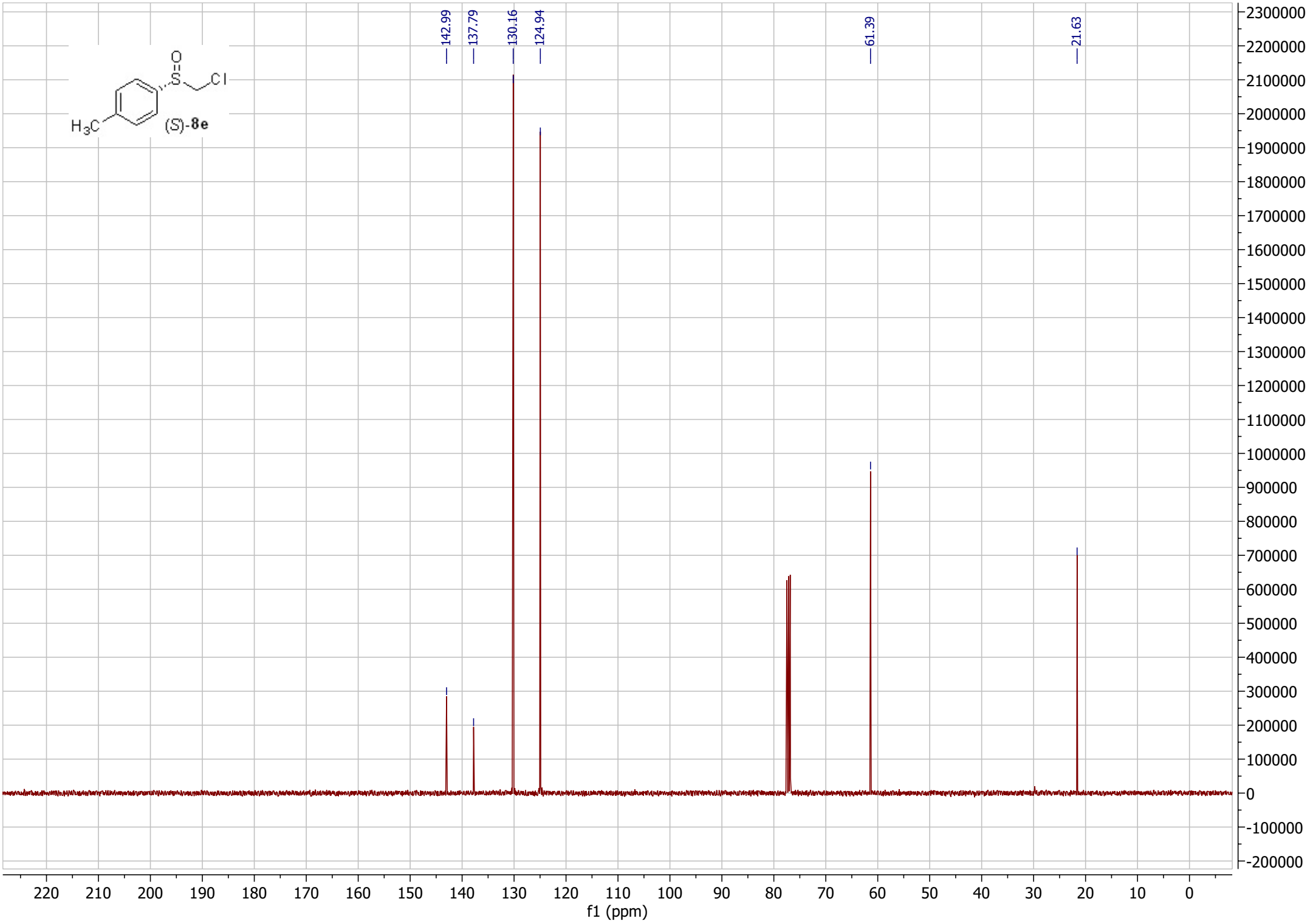

(S)-8c
7.73 7.73 7.73 7.72 7.71 7.71 7.71 7.70 7.70 7.70 7.70 7.69 7.69 7.68 7.68 7.68 7.59 7.59 7.58 7.58 7.57 7.56 7.56 7.56 7.55 7.55 7.54 7.54 7.54
4.42 4.40 4.39 4.36
1.82 2.90
1.00 1.09
f1 (ppm)

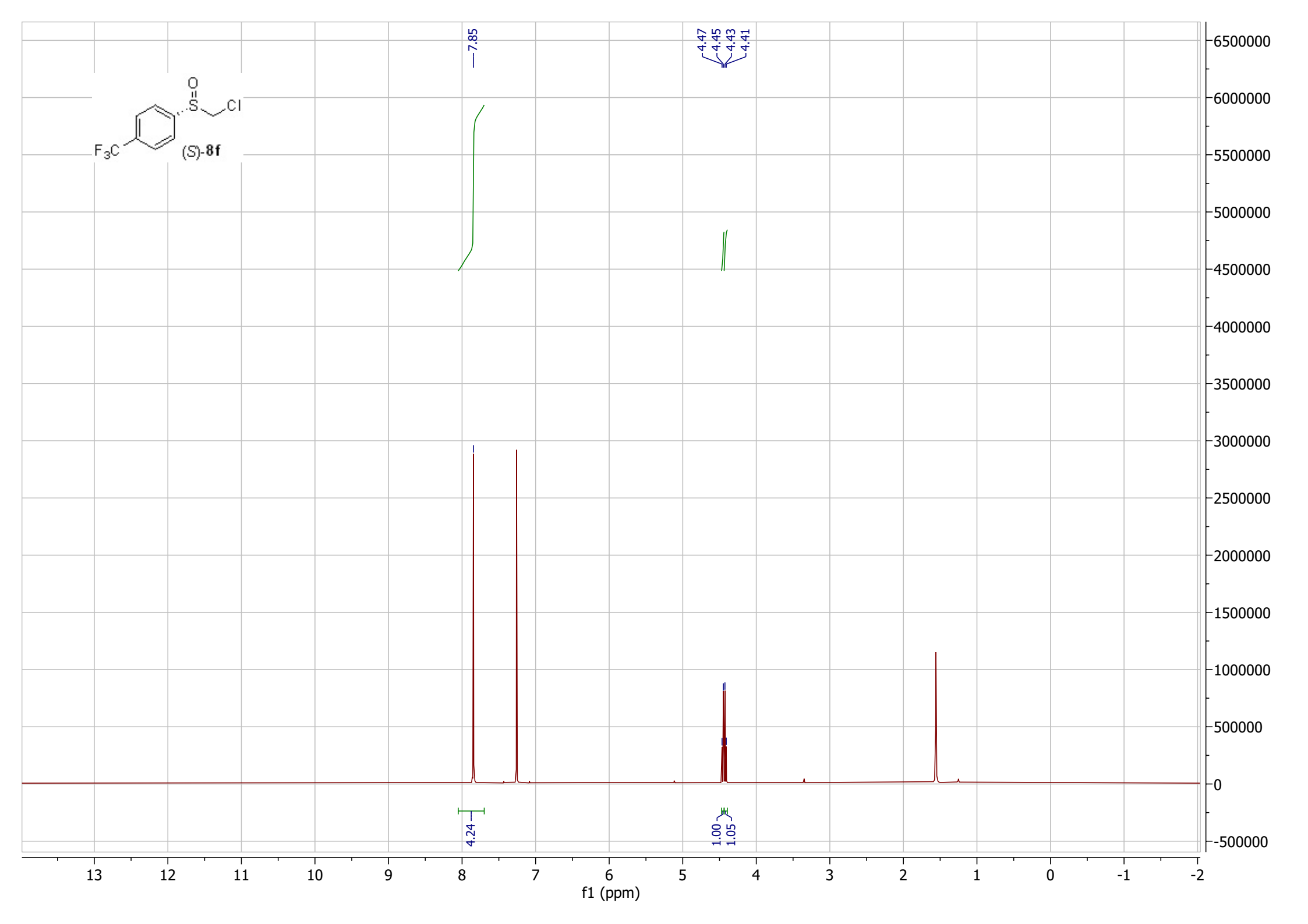

141.05
132.33
129.49
124.96
61.41
O
S
Cl
(S)-8c
2000000
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
-200000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

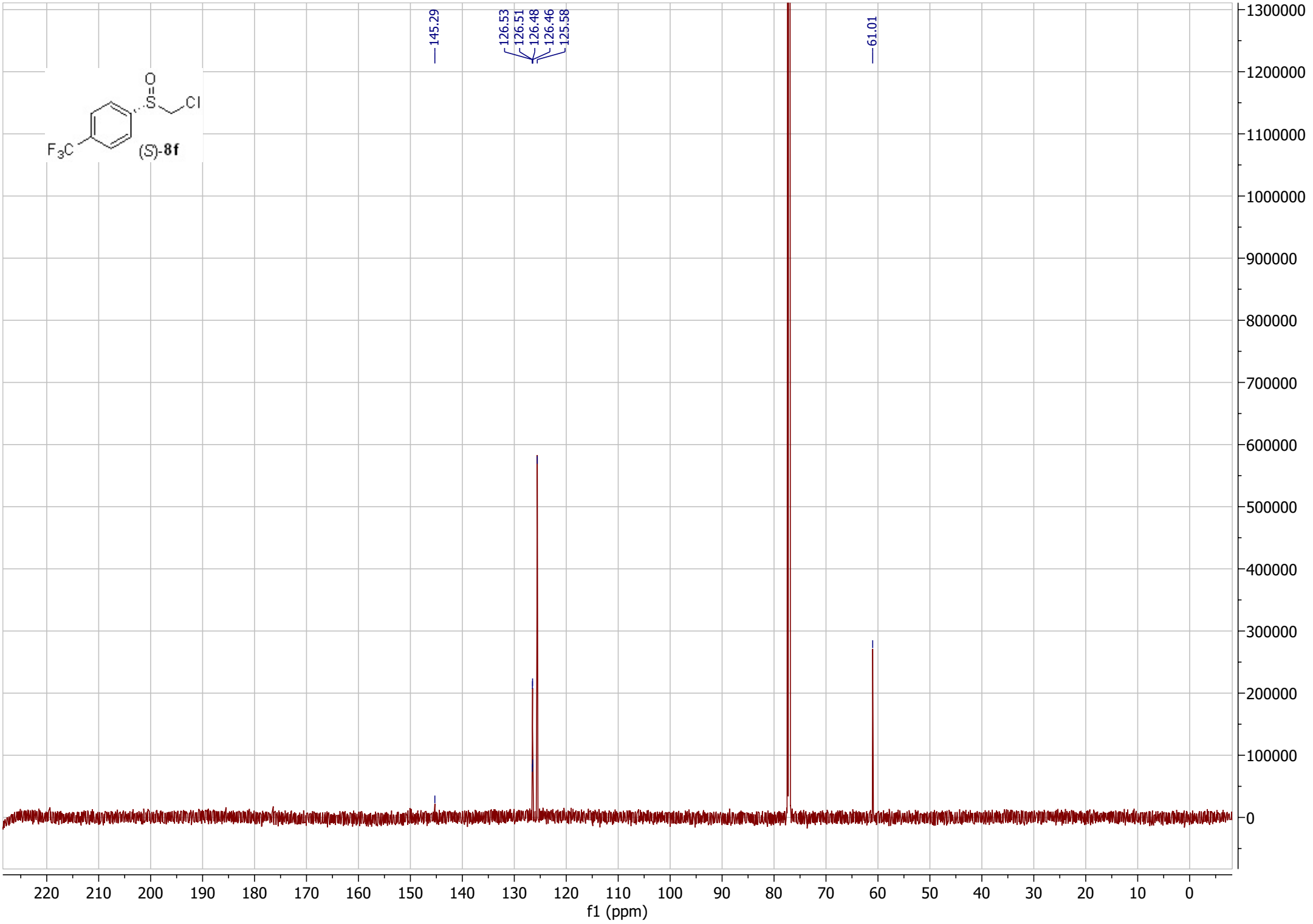

7.66
7.65
7.65
7.64
7.64
7.63
7.62
7.62
7.61
7.07
7.06
7.05
7.04
7.04
7.03
7.02
4.38
4.36
4.33
4.31
3.86
O
S
Cl
MeO
(S)-8d
1.91
1.81
1.00
0.94
3.09
6.0×10^7
5.5×10^7
5.0×10^7
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
-5.0×10^6
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

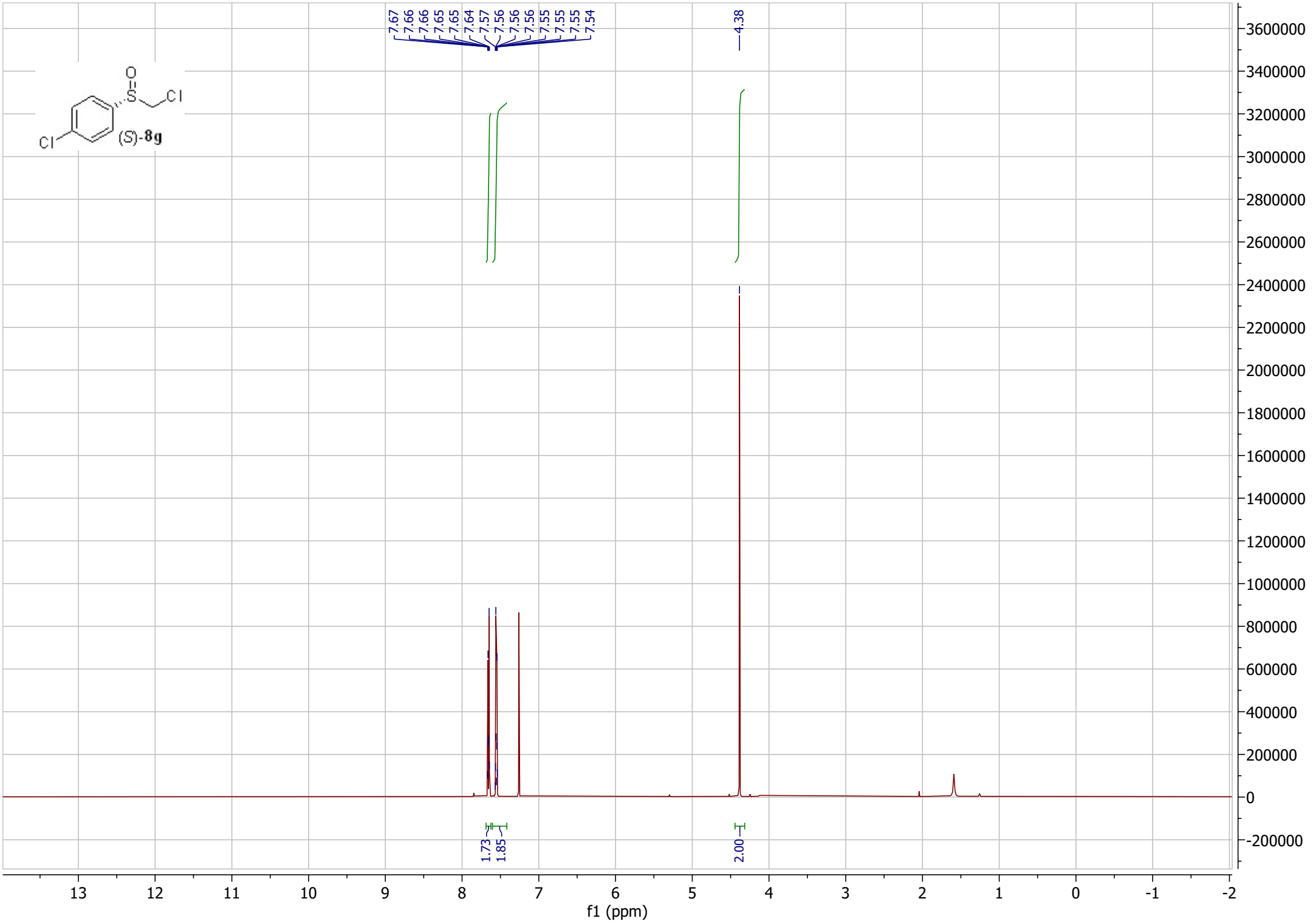

162.99
131.81
126.93
115.00
61.24
55.71
MeO
S
O
Cl
(S)-8d
2500000
2000000
1500000
1000000
500000
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

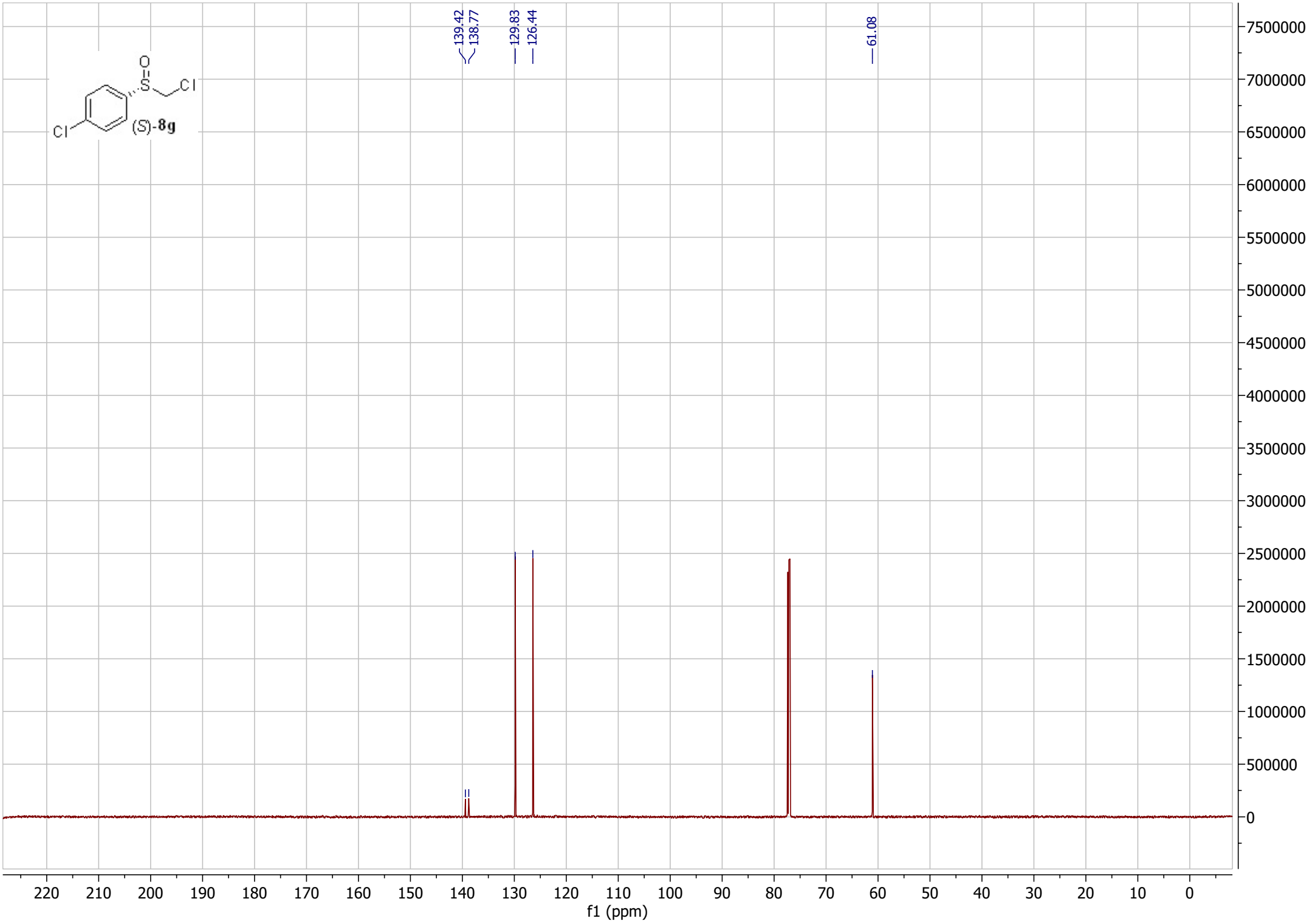

7.59
7.59
7.57
7.57
7.56
7.56
7.41
7.39
7.36
7.35
7.34
7.34
7.34
7.32
4.36
2.43
O
S
Cl
H3C
(S)-8e
1.92
2.00
2.17
2.16
3.33
7.0×10^7
6.5×10^7
6.0×10^7
5.5×10^7
5.0×10^7
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
-5.0×10^6
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

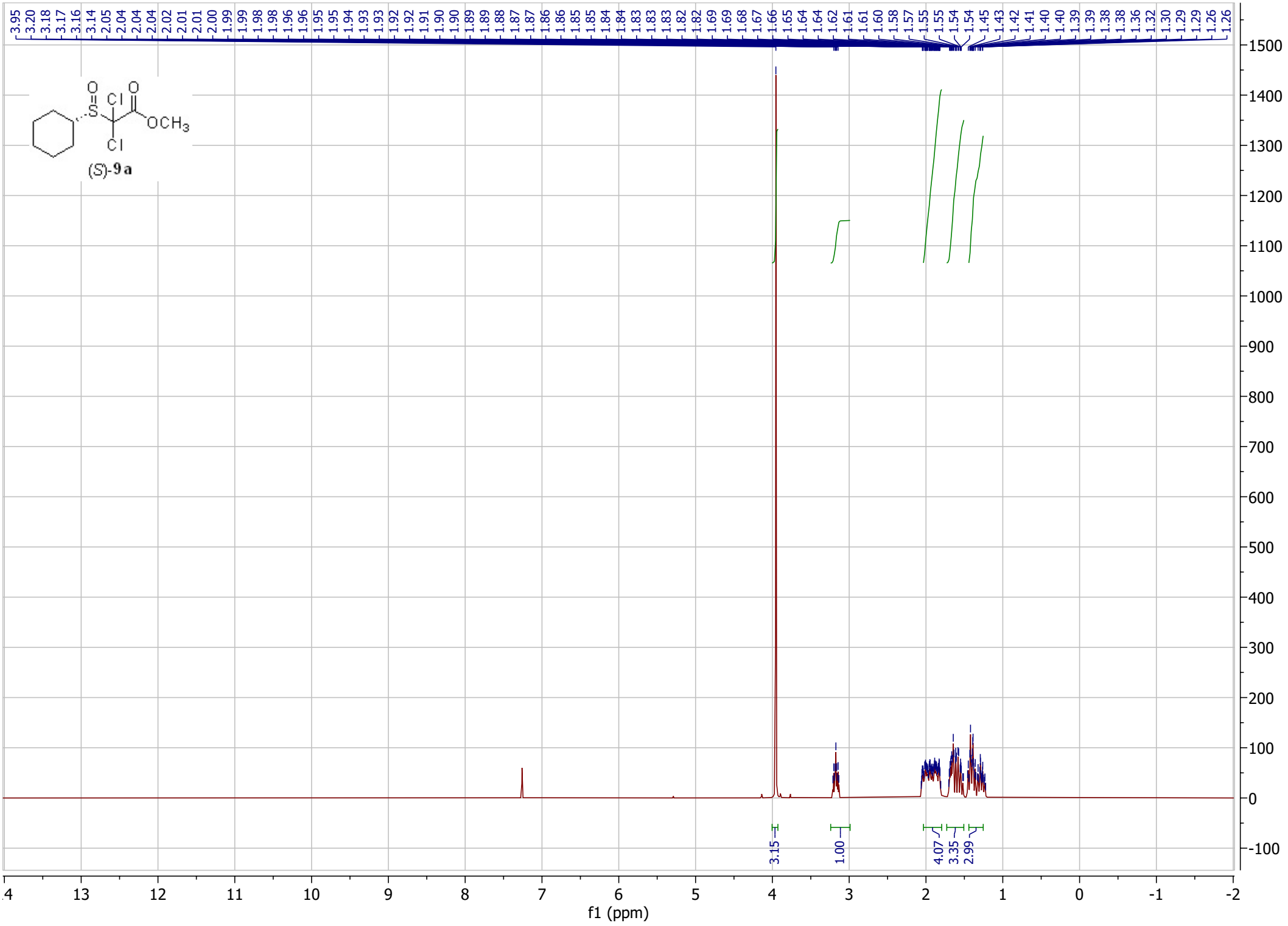

142.99
137.79
130.16
124.94
61.39
21.63
O
S
Cl
H3C
(S)-8e
2300000
2200000
2100000
2000000
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
-200000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

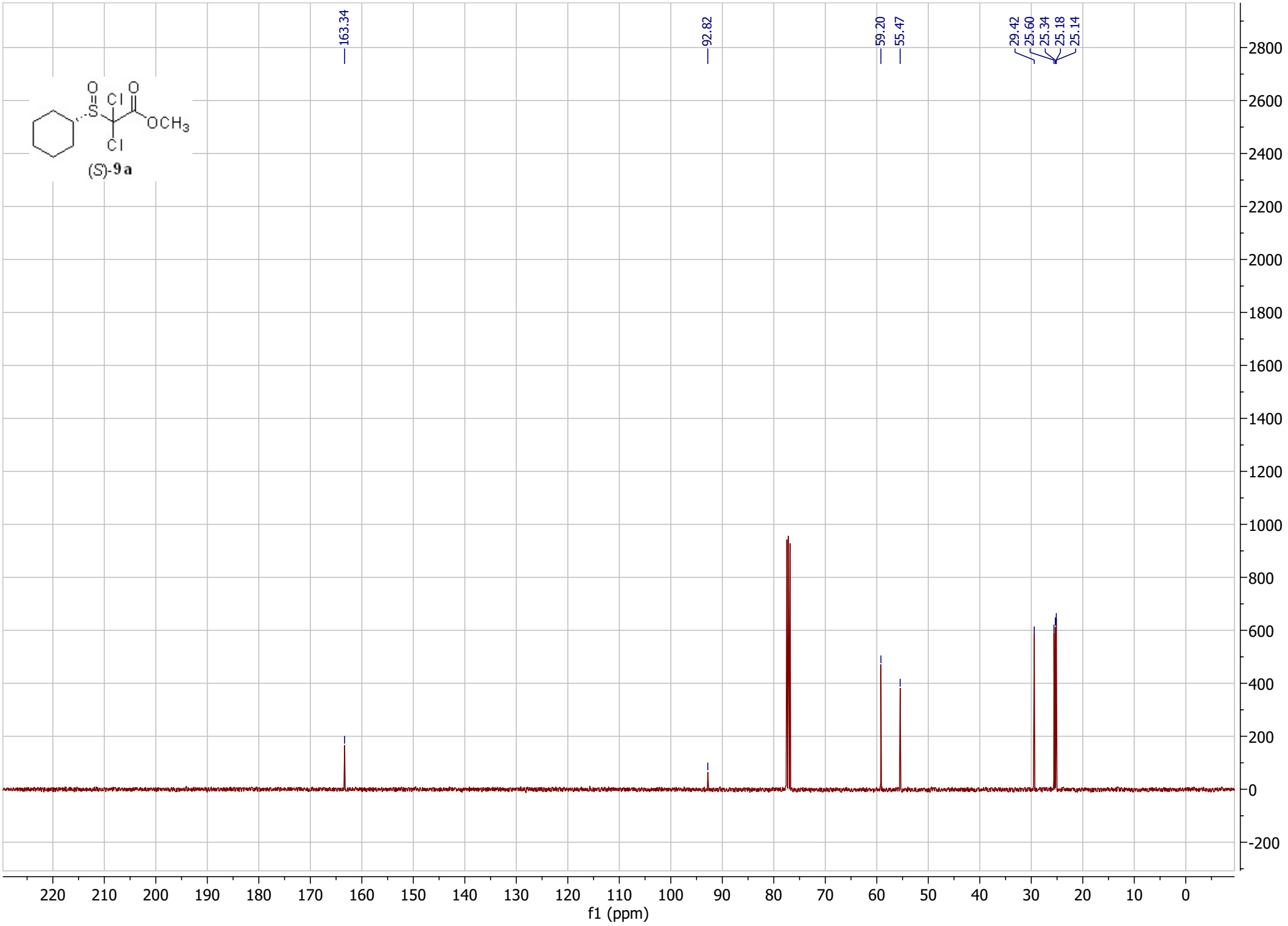

7.85
4.47
4.45
4.43
4.41
(S)-8f
4.24
1.00
1.05
f1 (ppm)

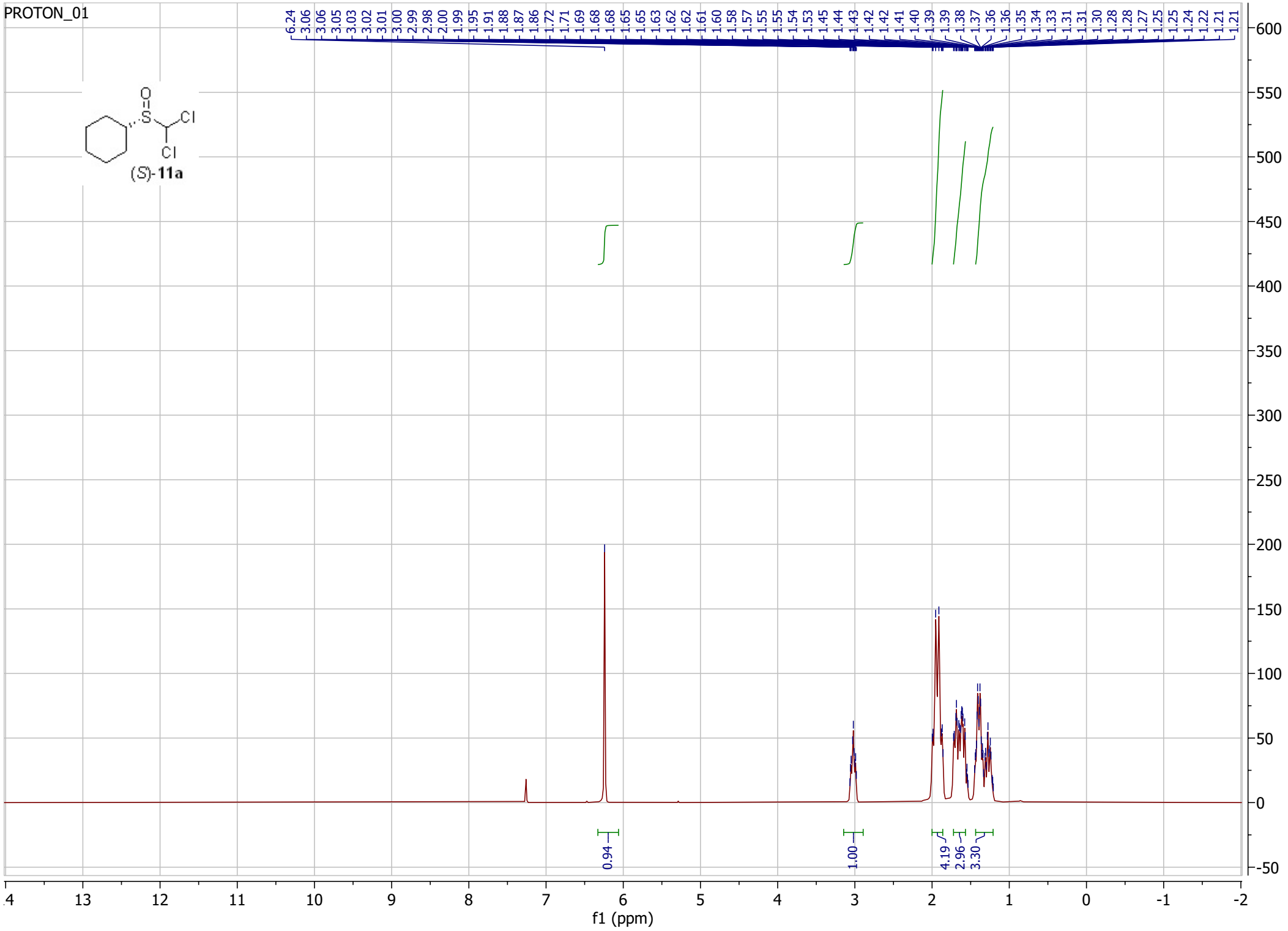

145.29
126.53
126.51
126.48
126.46
125.58
61.01
O
S
Cl
F3C
(S)-8f
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

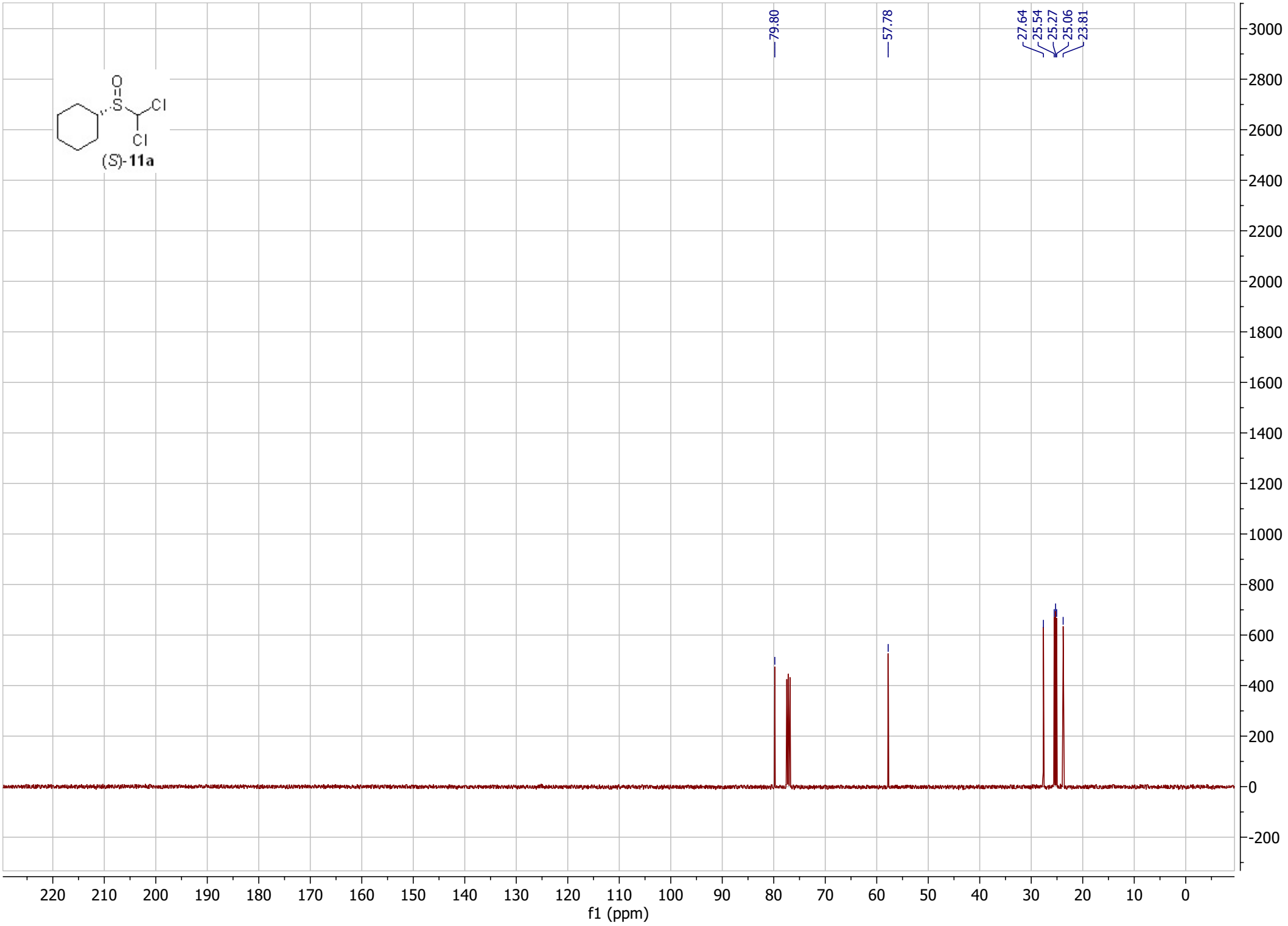

7.67
7.66
7.66
7.65
7.65
7.64
7.57
7.56
7.56
7.56
7.55
7.55
7.55
7.54
4.38
O
S
Cl
Cl
(S)-8g
1.73
1.85
2.00
3600000
3400000
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

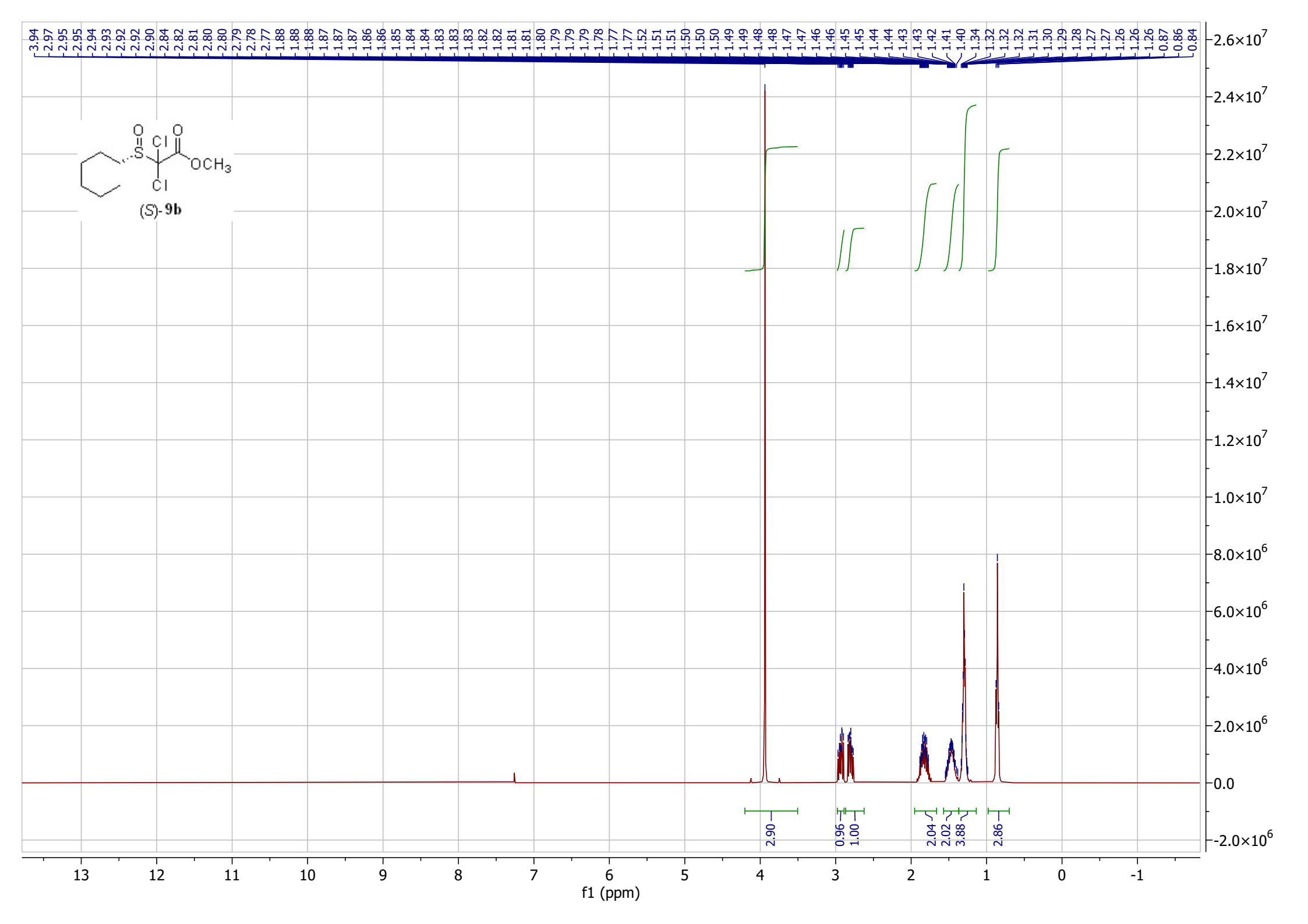

139.42
138.77
129.83
126.44
61.08
O
S
Cl
Cl
(S)-8g
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

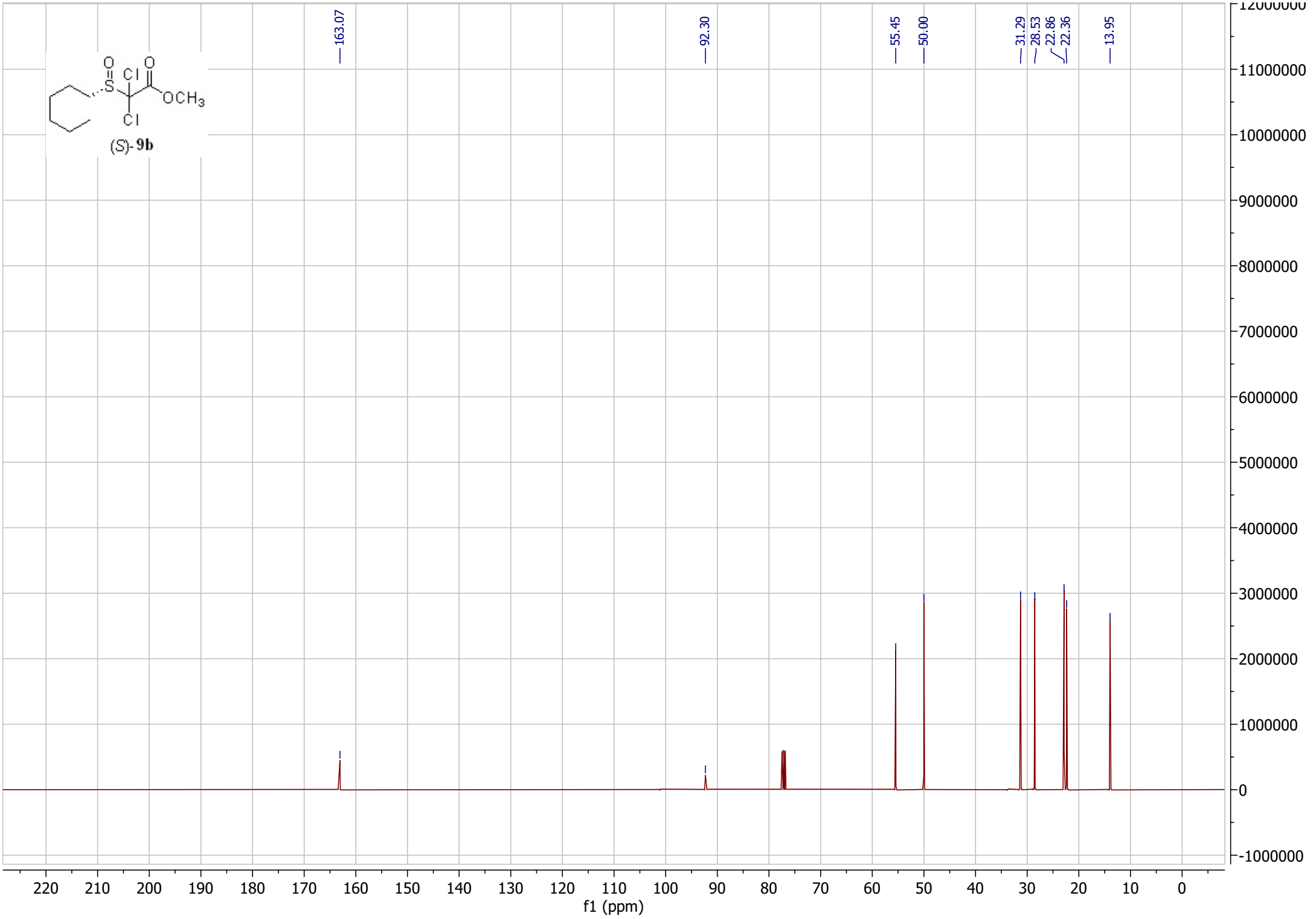

(S)-9a
f1 (ppm)
3.15
1.00
4.07
3.35
2.99

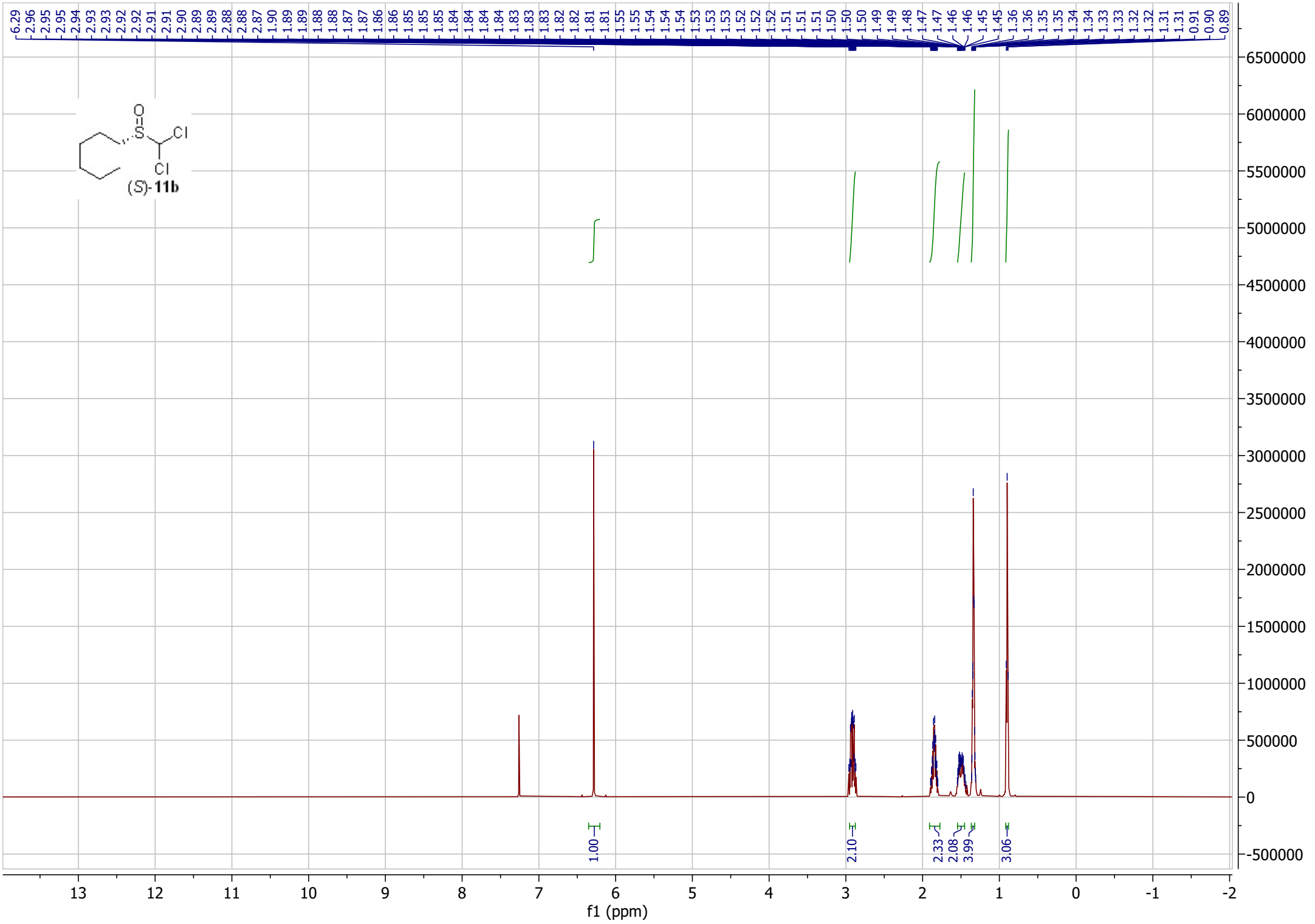

163.34
92.82
59.20
55.47
29.42
25.60
25.34
25.18
25.14
(S)-9a
f1 (ppm)

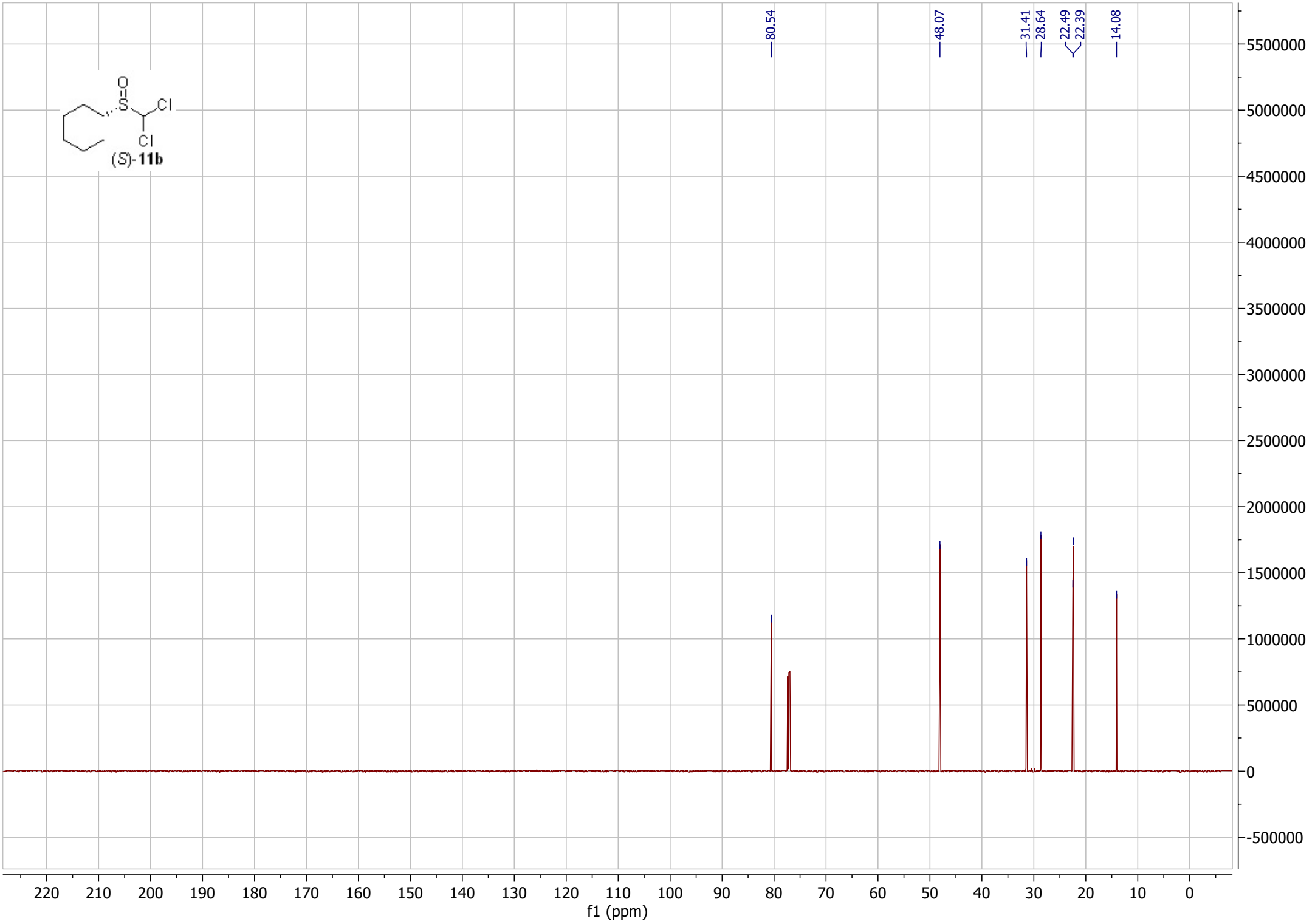

PROTON_01
(S)-11a
f1 (ppm)

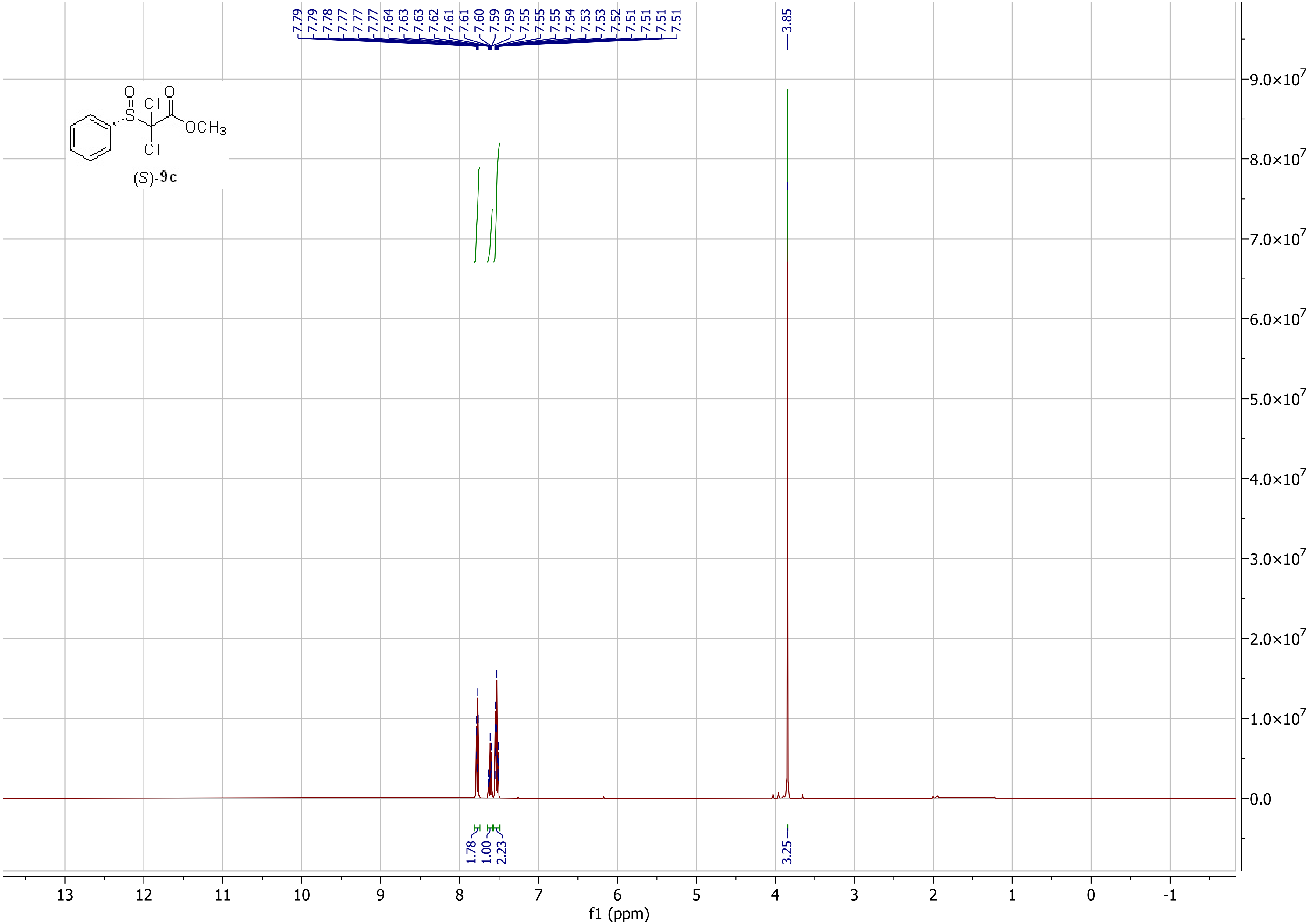

79.80
57.78
27.64
25.54
25.27
25.06
23.81
(S)-11a
f1 (ppm)


(S)-9b
f1 (ppm)
2.90
0.96
1.00
2.04
2.02
3.88
2.86

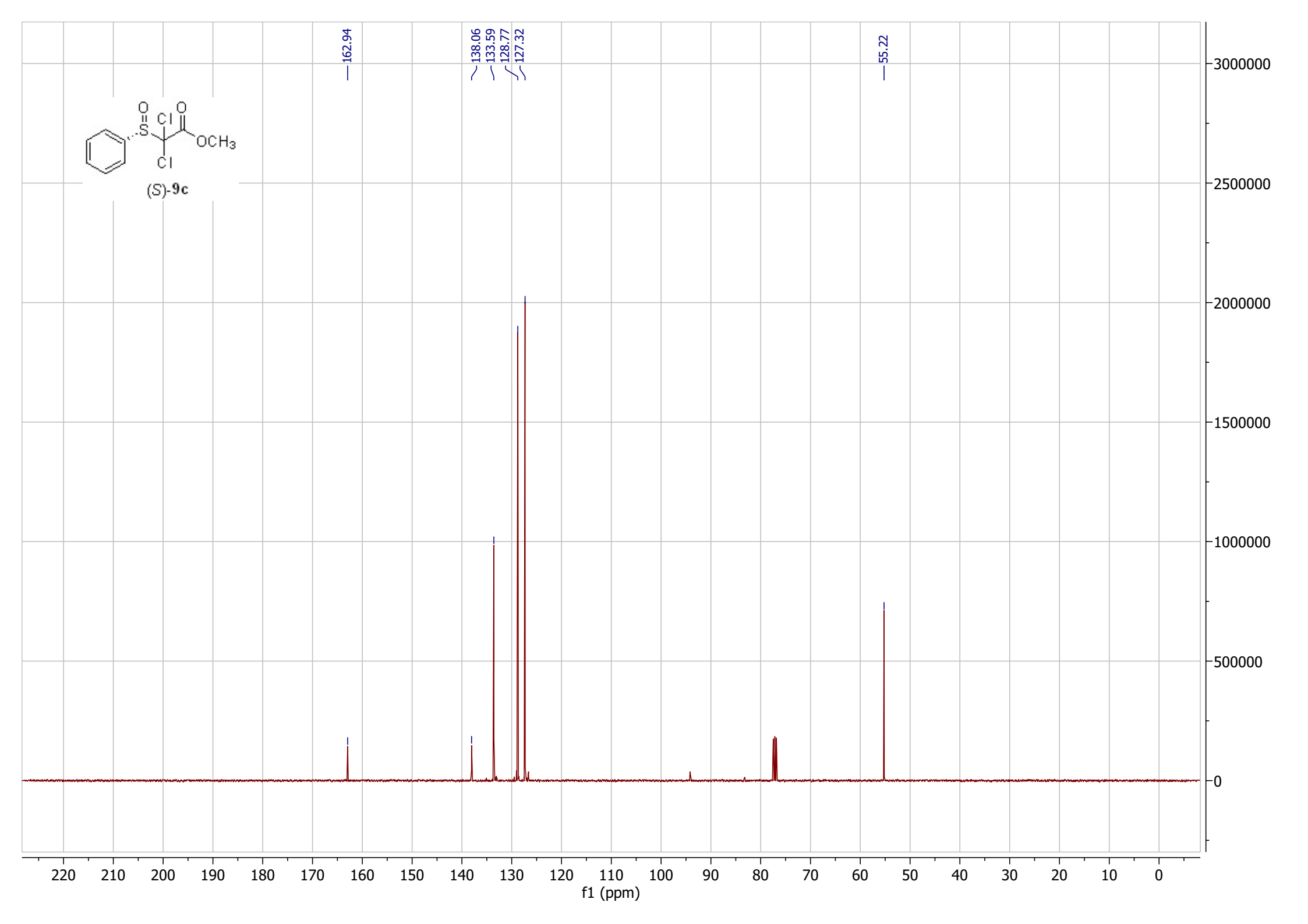

(S)-9b
163.07
92.30
55.45
50.00
31.29
28.53
22.86
22.36
13.95
f1 (ppm)

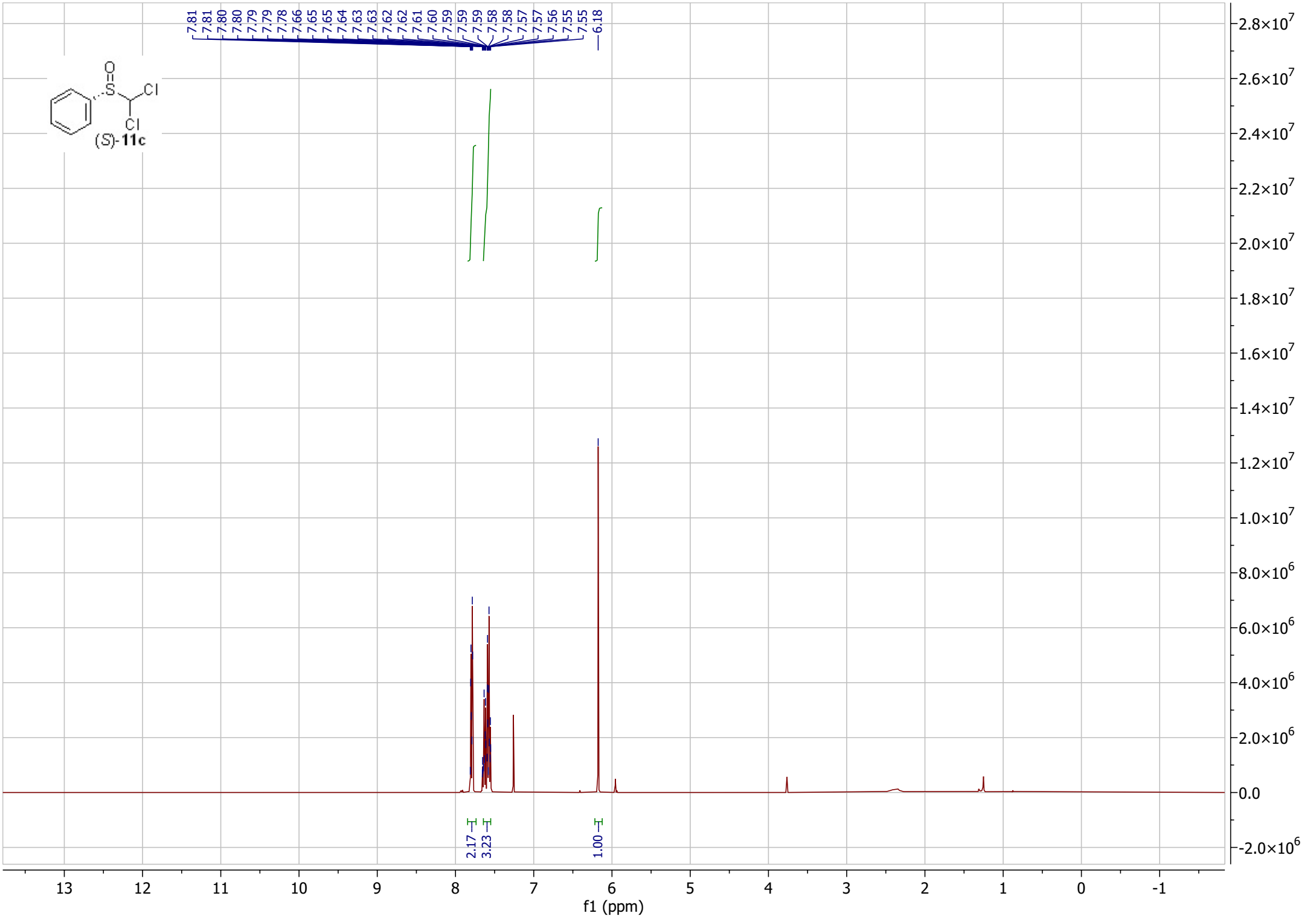

O
S
Cl
Cl
(S)-11b
f1 (ppm)
1.00
2.10
2.33
2.08
3.99
3.06

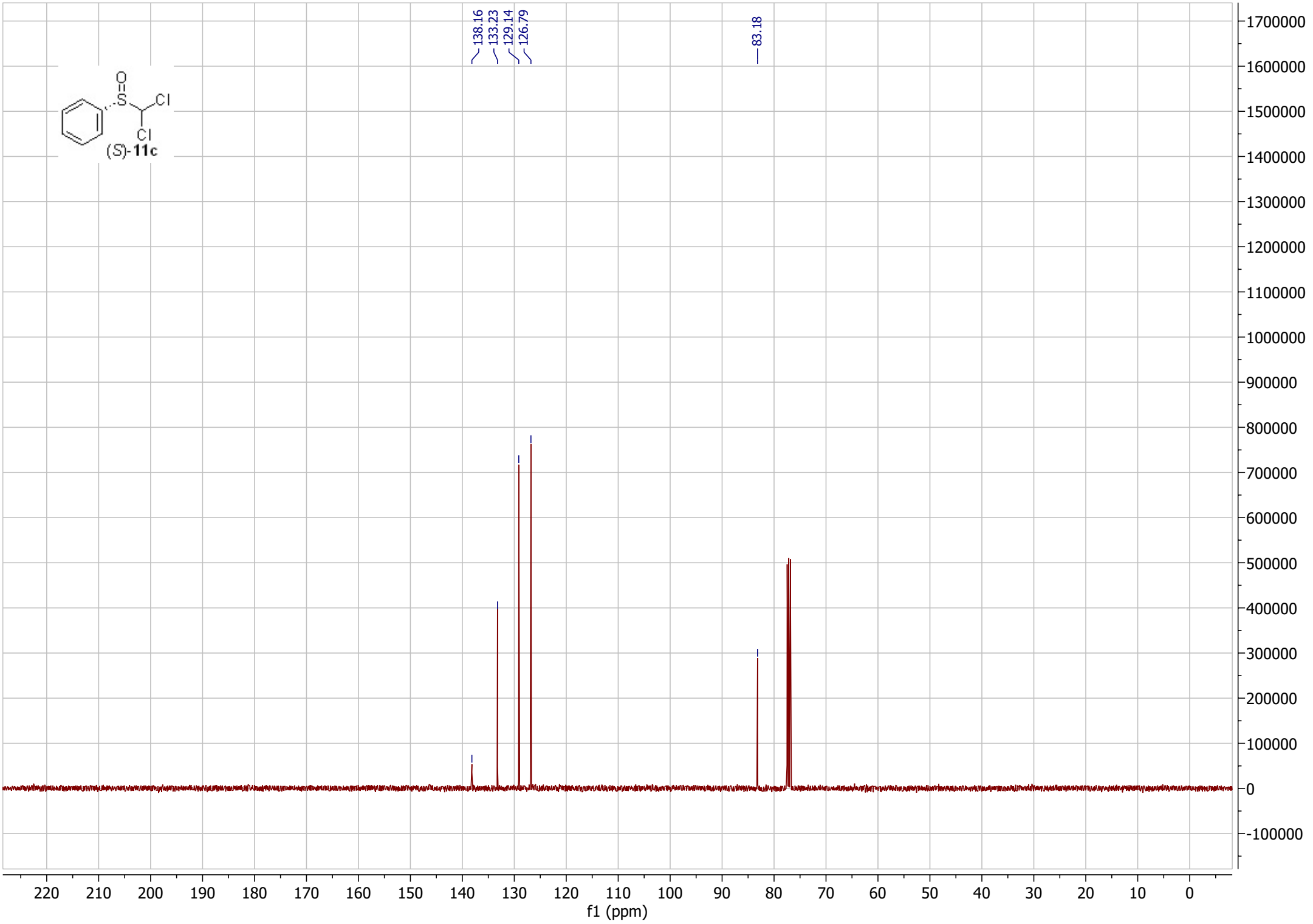

80.54
48.07
31.41
28.64
22.49
22.39
14.08
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
S
Cl
Cl
(S)-11b

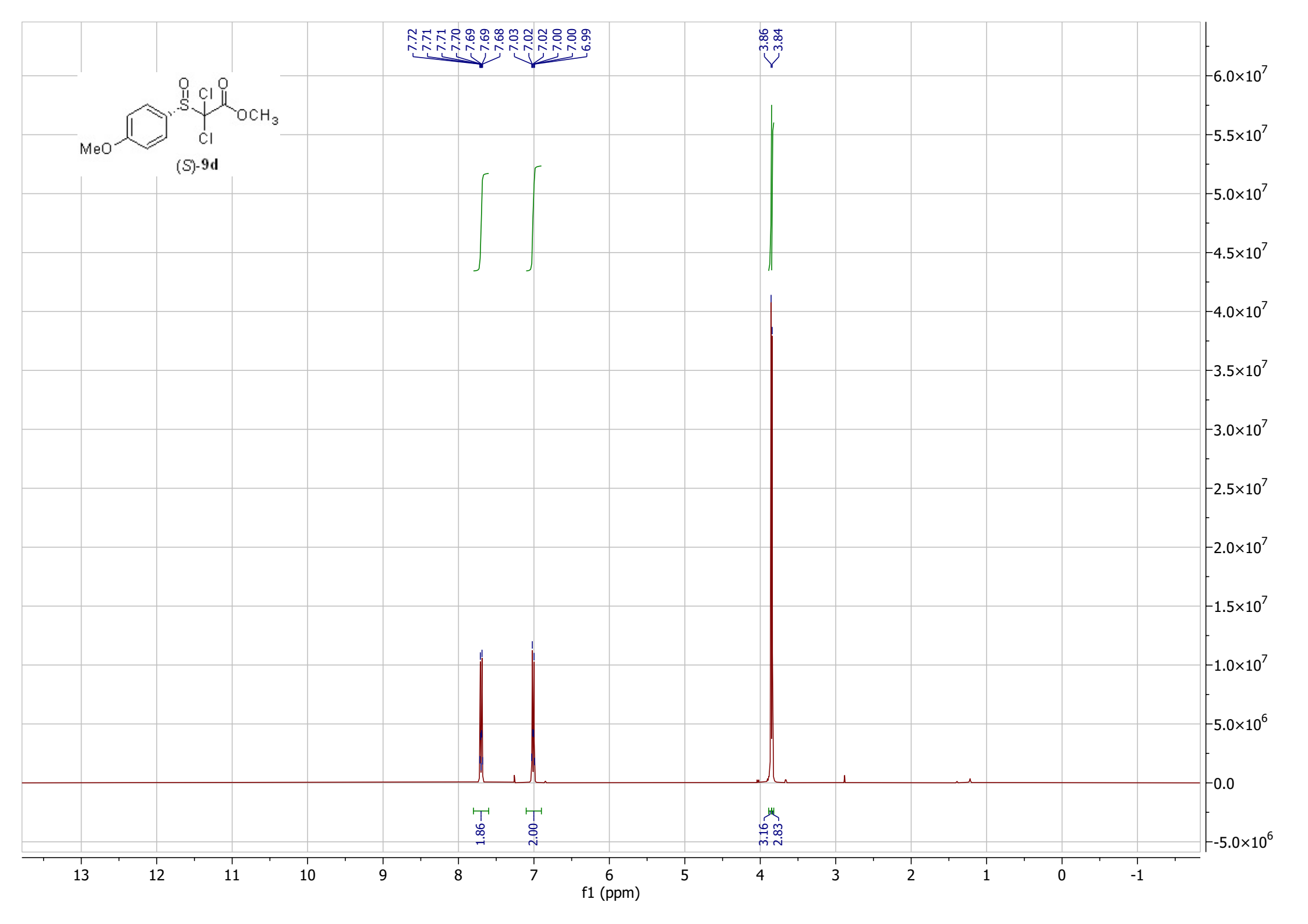


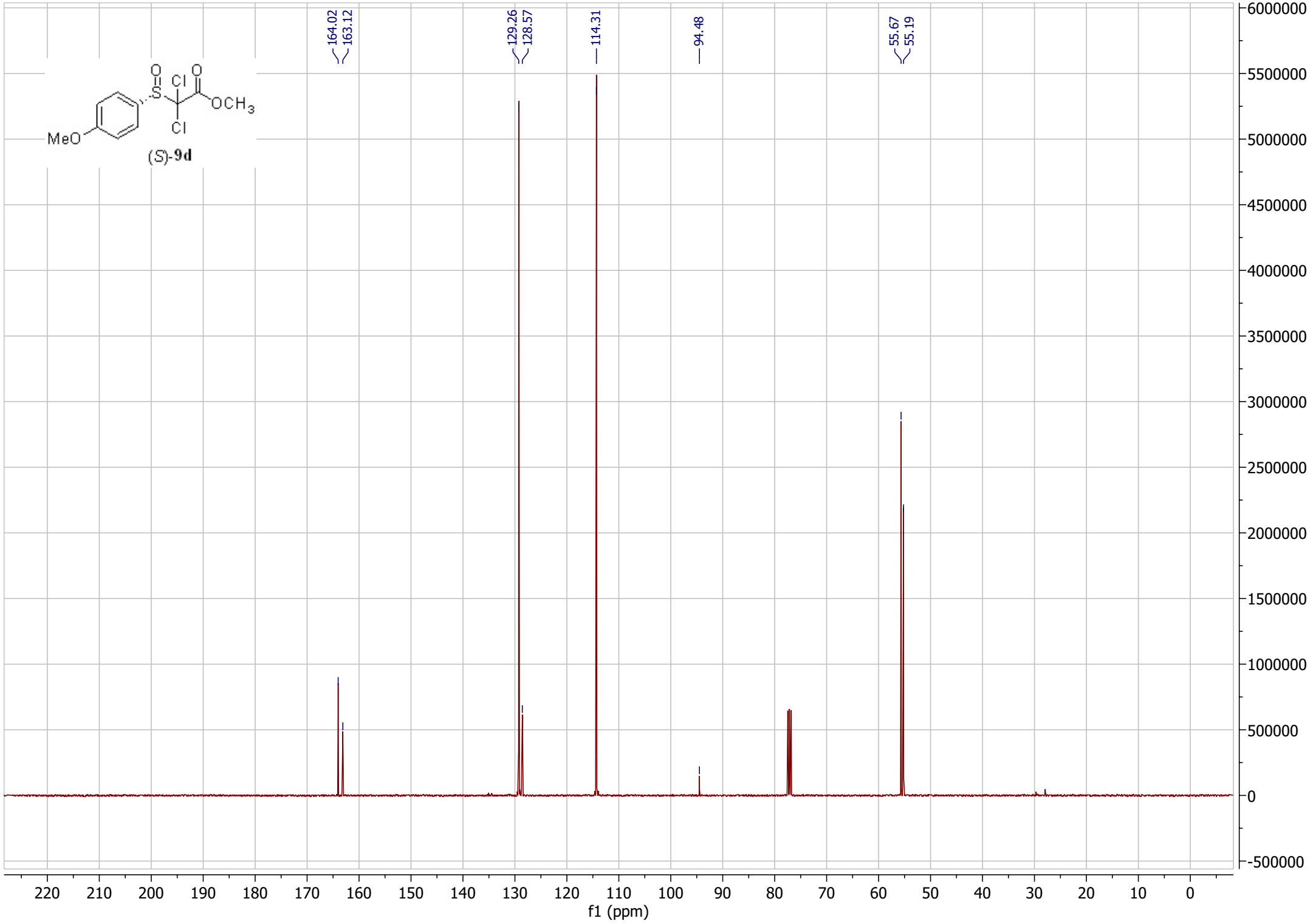
(S)-9c
7.79
7.79
7.78
7.77
7.77
7.77
7.64
7.63
7.63
7.62
7.61
7.61
7.60
7.59
7.59
7.55
7.55
7.55
7.54
7.53
7.53
7.52
7.51
7.51
7.51
7.51
3.85
9.0×10^7
8.0×10^7
7.0×10^7
6.0×10^7
5.0×10^7
4.0×10^7
3.0×10^7
2.0×10^7
1.0×10^7
0.0
1.78
1.00
2.23
3.25
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

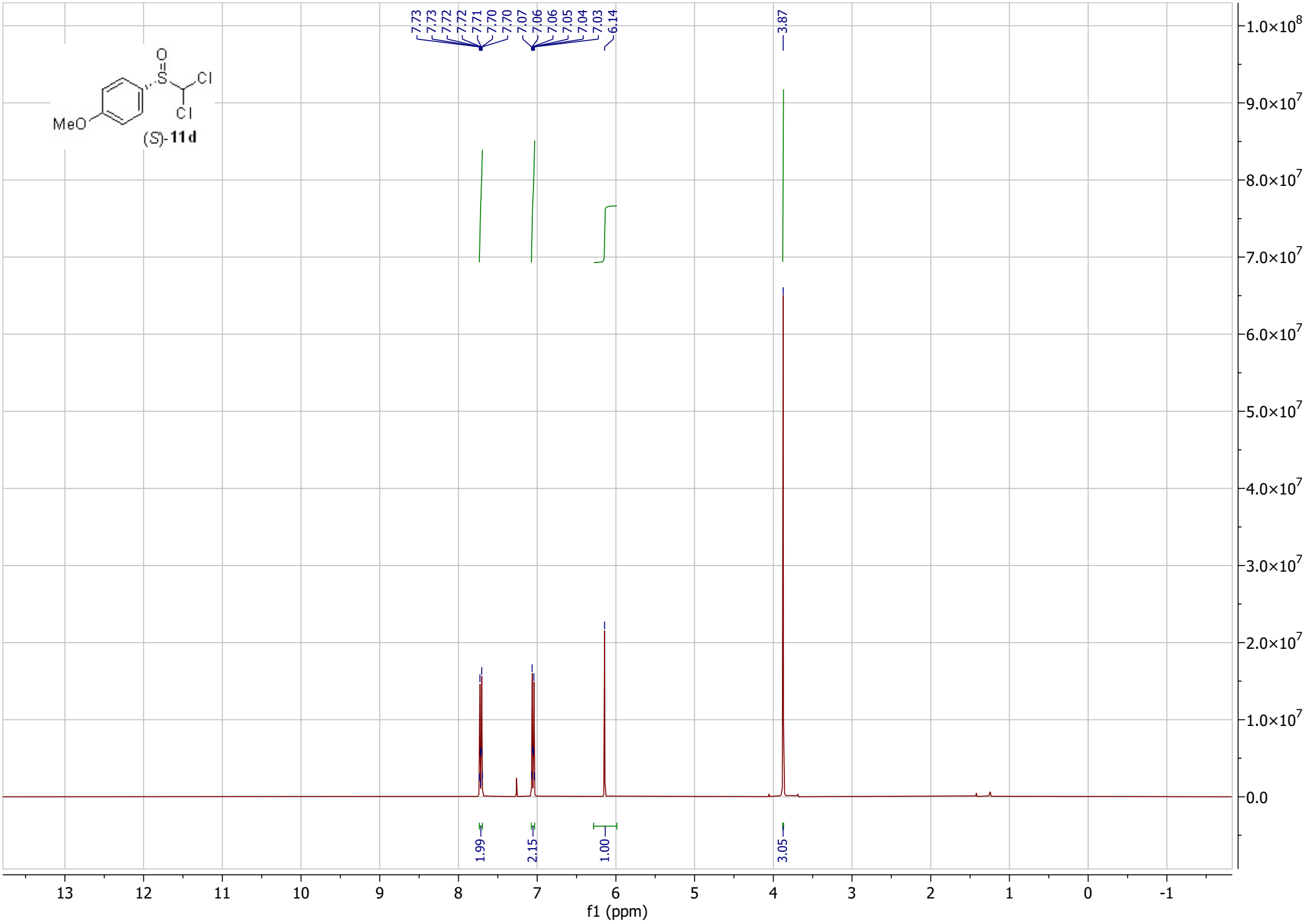

162.94
138.06
133.59
128.77
127.32
55.22
(S)-9c
3000000
2500000
2000000
1500000
1000000
500000
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

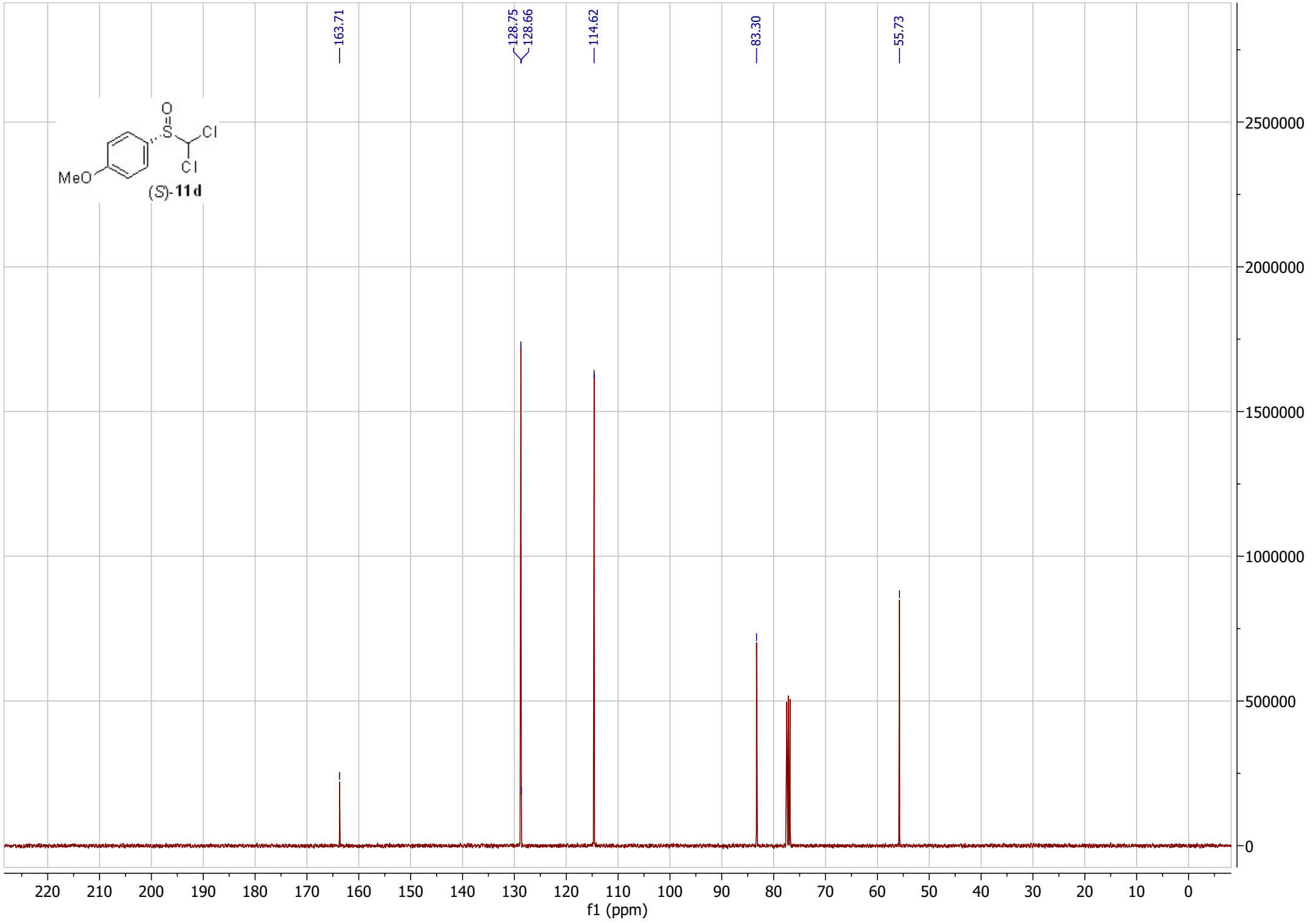

7.81
7.81
7.80
7.80
7.79
7.79
7.78
7.66
7.65
7.65
7.64
7.63
7.63
7.62
7.62
7.61
7.60
7.59
7.59
7.59
7.58
7.58
7.57
7.57
7.56
7.55
7.55
6.18
O
S
Cl
Cl
(S)-11c
2.8×10^7
2.6×10^7
2.4×10^7
2.2×10^7
2.0×10^7
1.8×10^7
1.6×10^7
1.4×10^7
1.2×10^7
1.0×10^7
8.0×10^6
6.0×10^6
4.0×10^6
2.0×10^6
0.0
-2.0×10^6
2.17
3.23
1.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

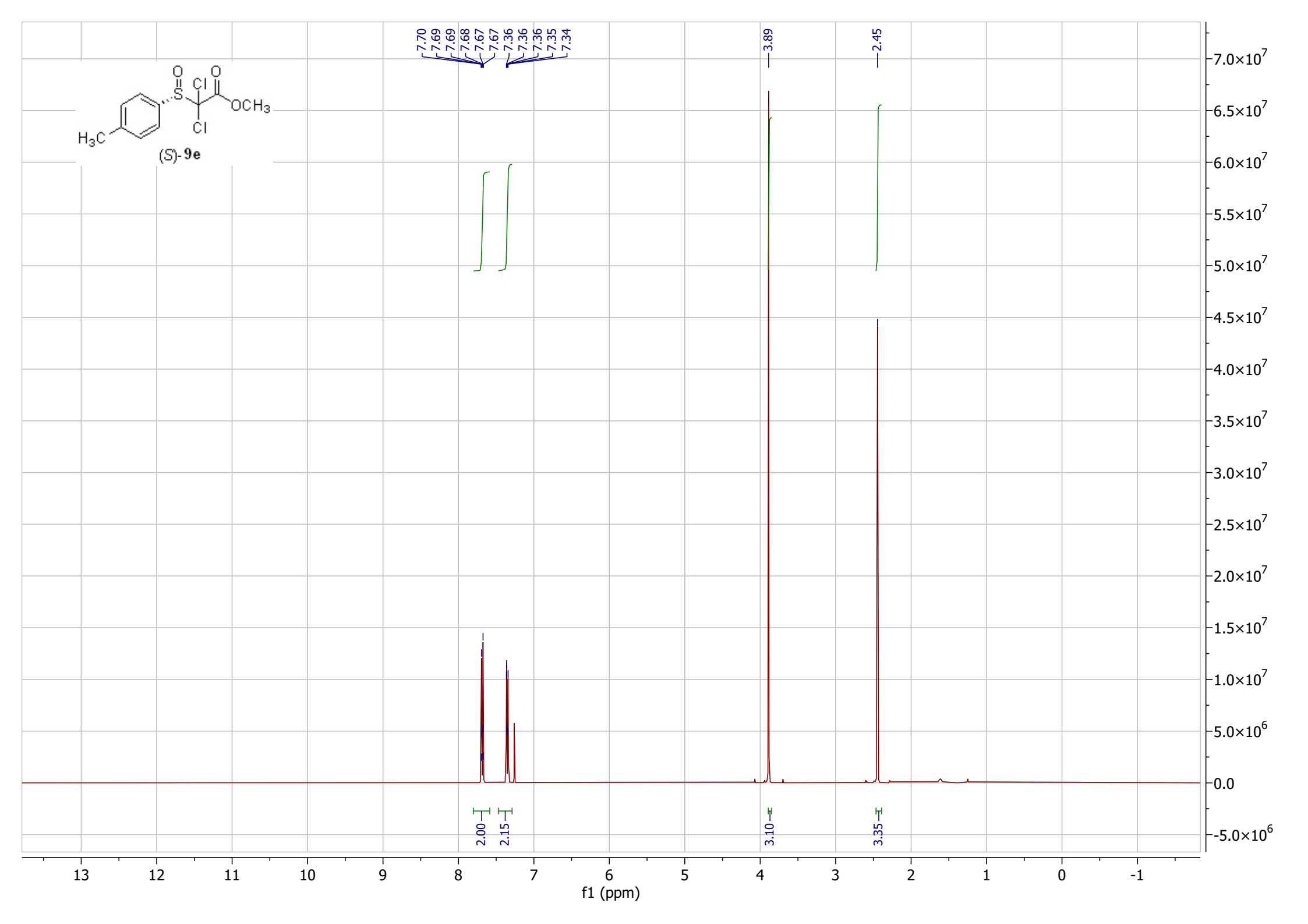

138.16
133.23
129.14
126.79
83.18
(S)-11c
f1 (ppm)

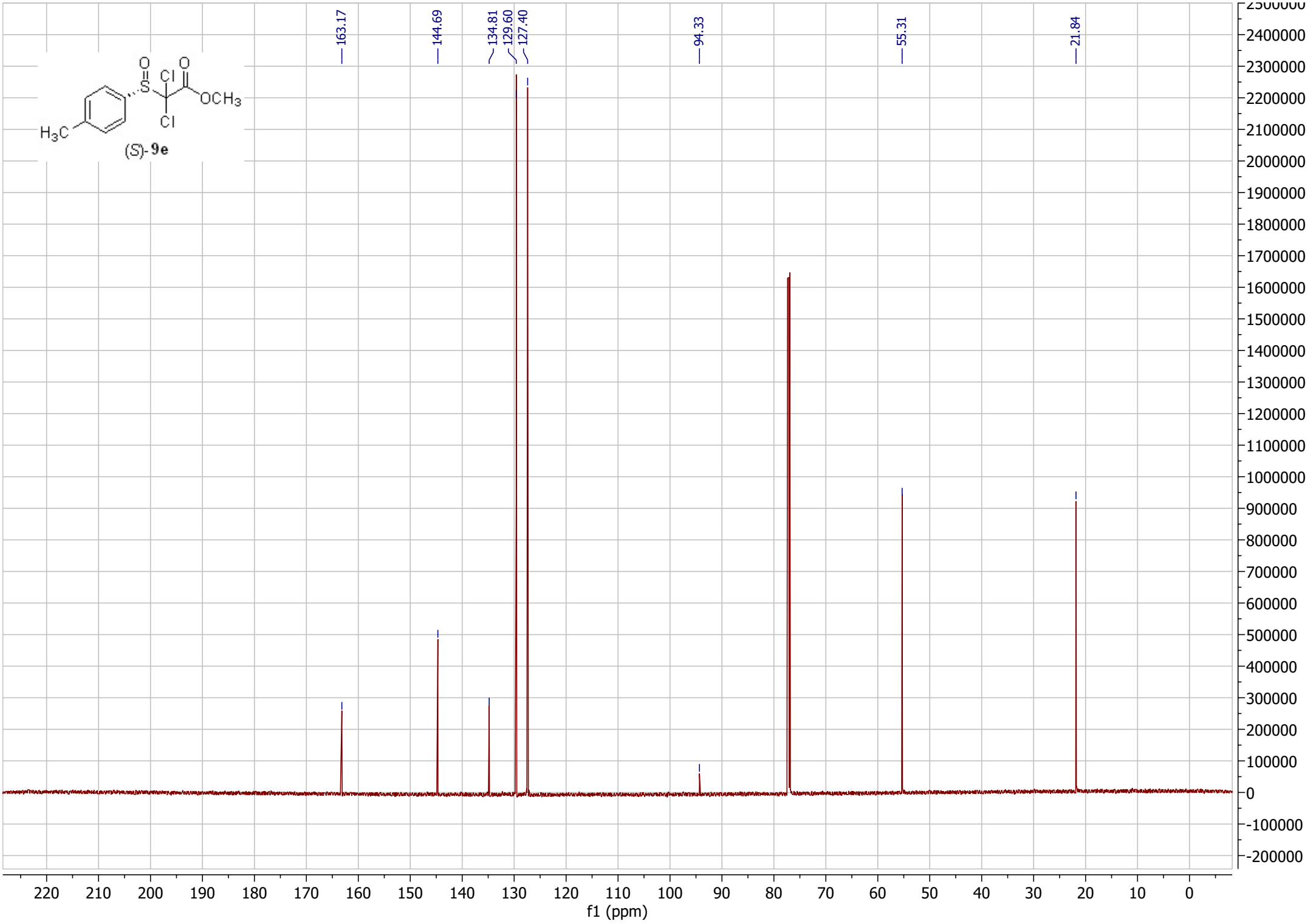

7.72
7.71
7.71
7.70
7.69
7.69
7.68
7.03
7.02
7.02
7.00
7.00
6.99
3.86
3.84
MeO
(S)-9d
1.86
2.00
3.16
2.83
f1 (ppm)

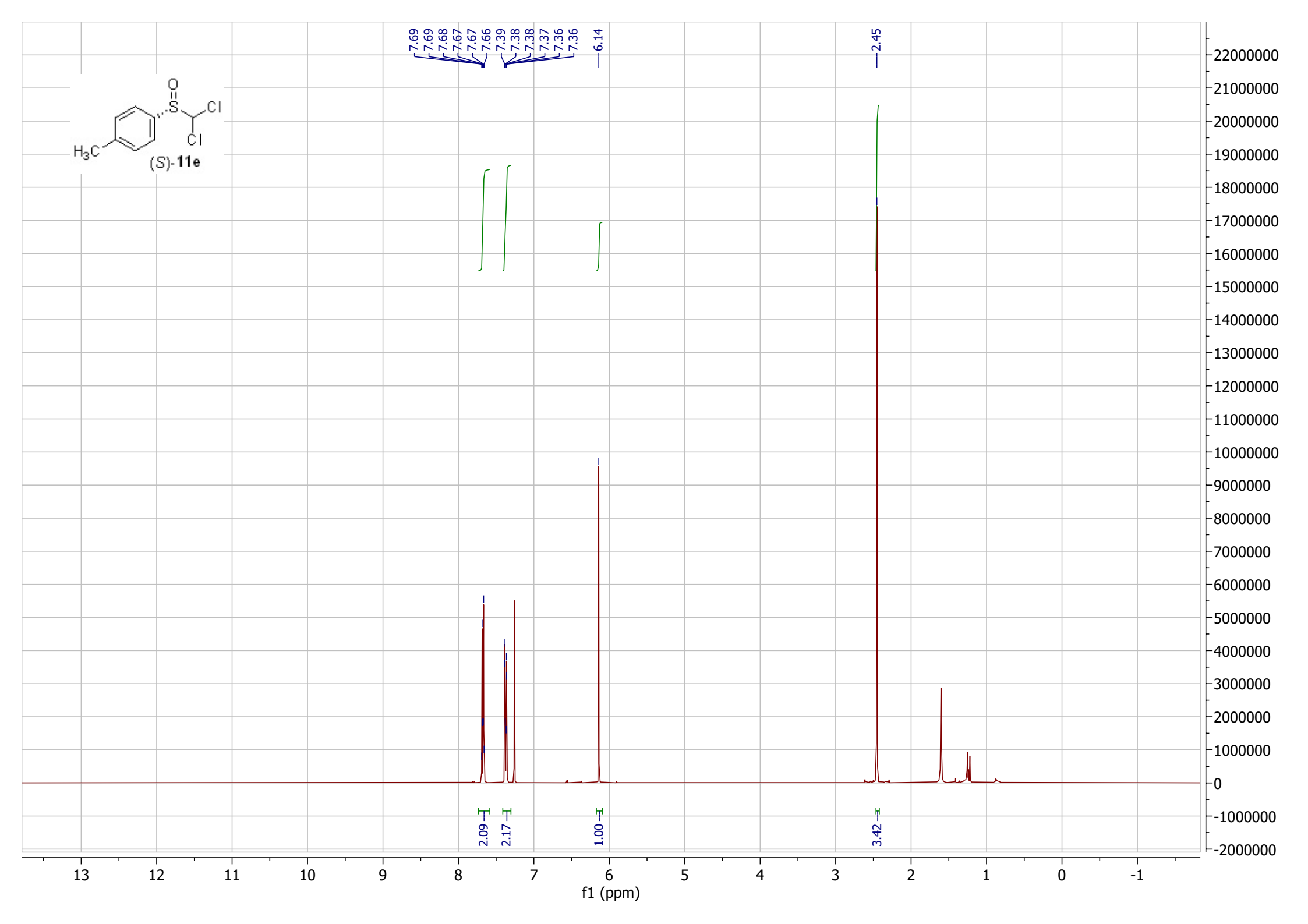

164.02
163.12
129.26
128.57
114.31
94.48
55.67
55.19
MeO
Cl
Cl
O
S
O
OCH3
(S)-9d
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

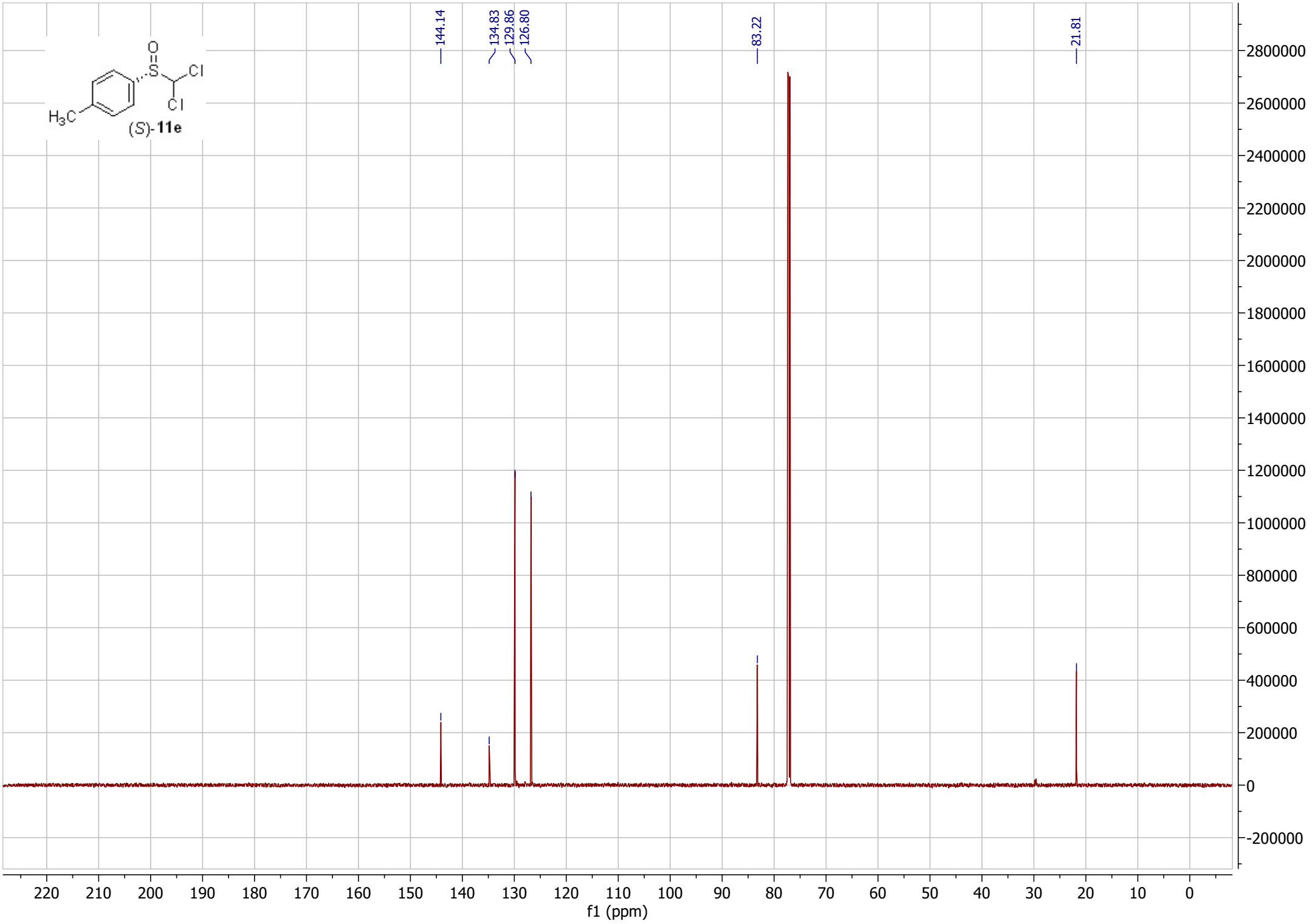

7.73
7.73
7.72
7.72
7.71
7.70
7.70
7.07
7.06
7.06
7.05
7.04
7.03
6.14
3.87
MeO
O
S
Cl
Cl
(S)-11d
1.99
2.15
1.00
3.05
1.0×10^8
9.0×10^7
8.0×10^7
7.0×10^7
6.0×10^7
5.0×10^7
4.0×10^7
3.0×10^7
2.0×10^7
1.0×10^7
0.0
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

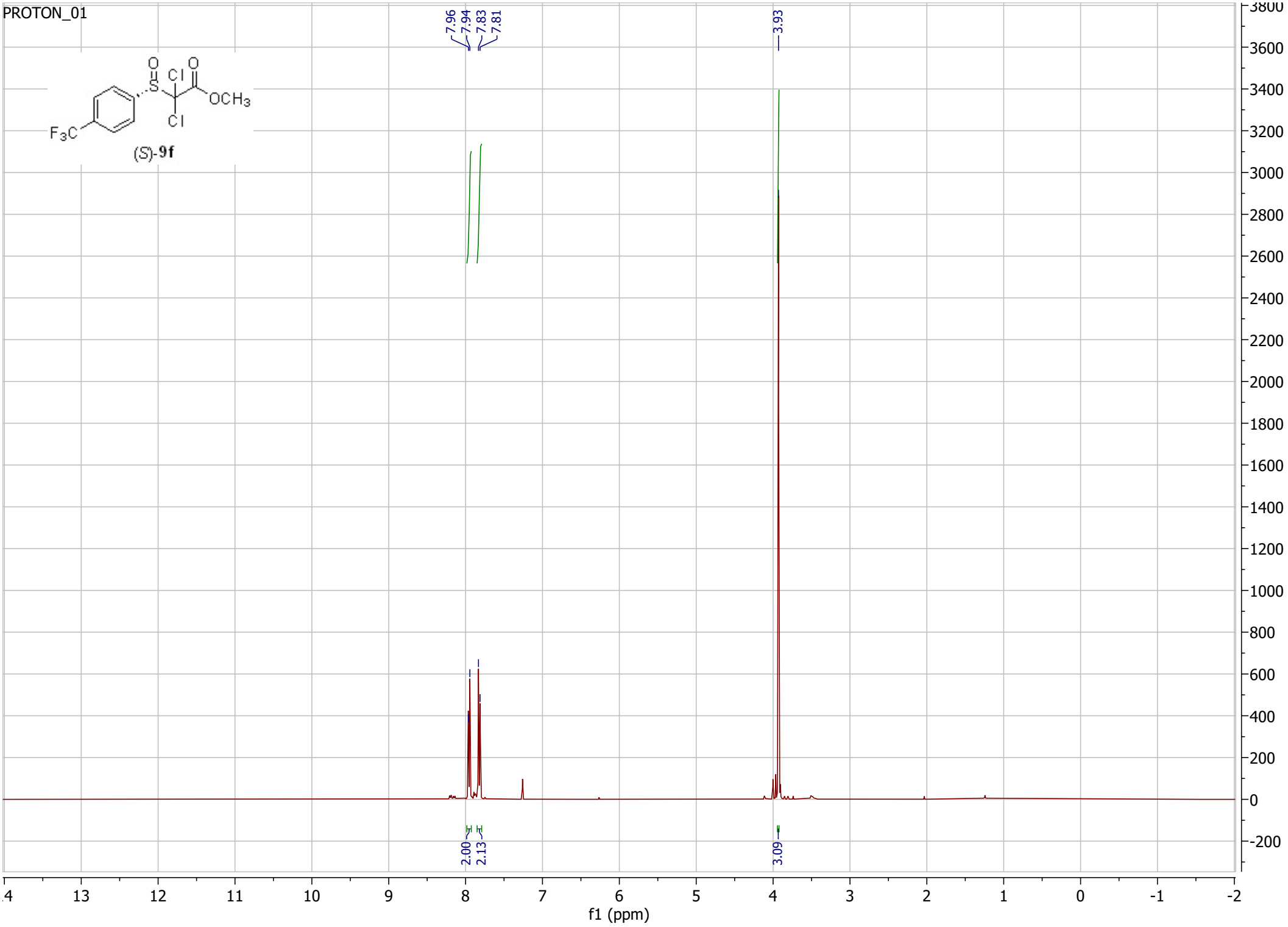

163.71
128.75
128.66
114.62
83.30
55.73
MeO
O
S
Cl
Cl
(S)-11d
2500000
2000000
1500000
1000000
500000
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

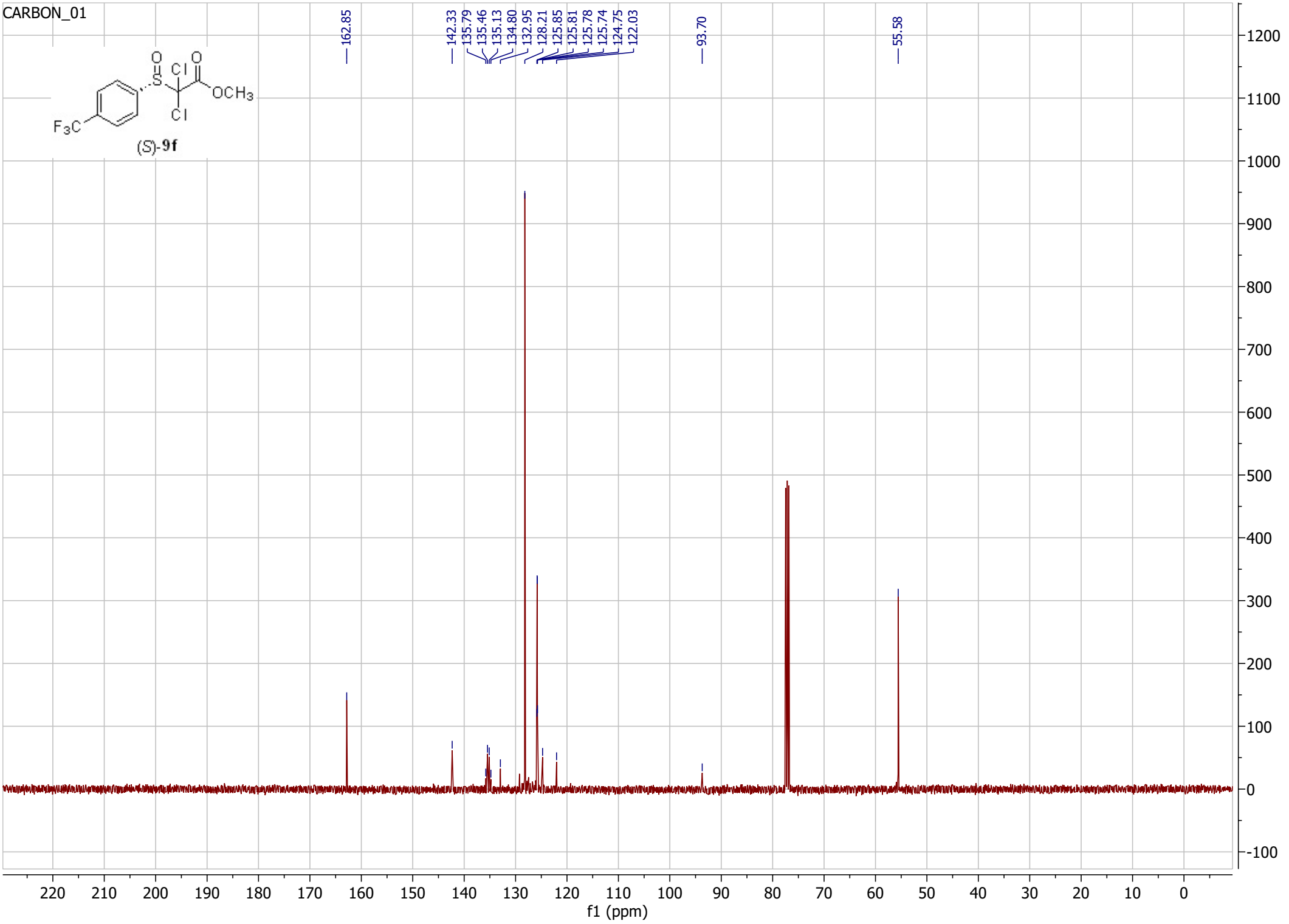

7.70
7.69
7.69
7.68
7.67
7.67
7.36
7.36
7.36
7.35
7.34
3.89
2.45
(S)-9e
2.00
2.15
3.10
3.35
f1 (ppm)

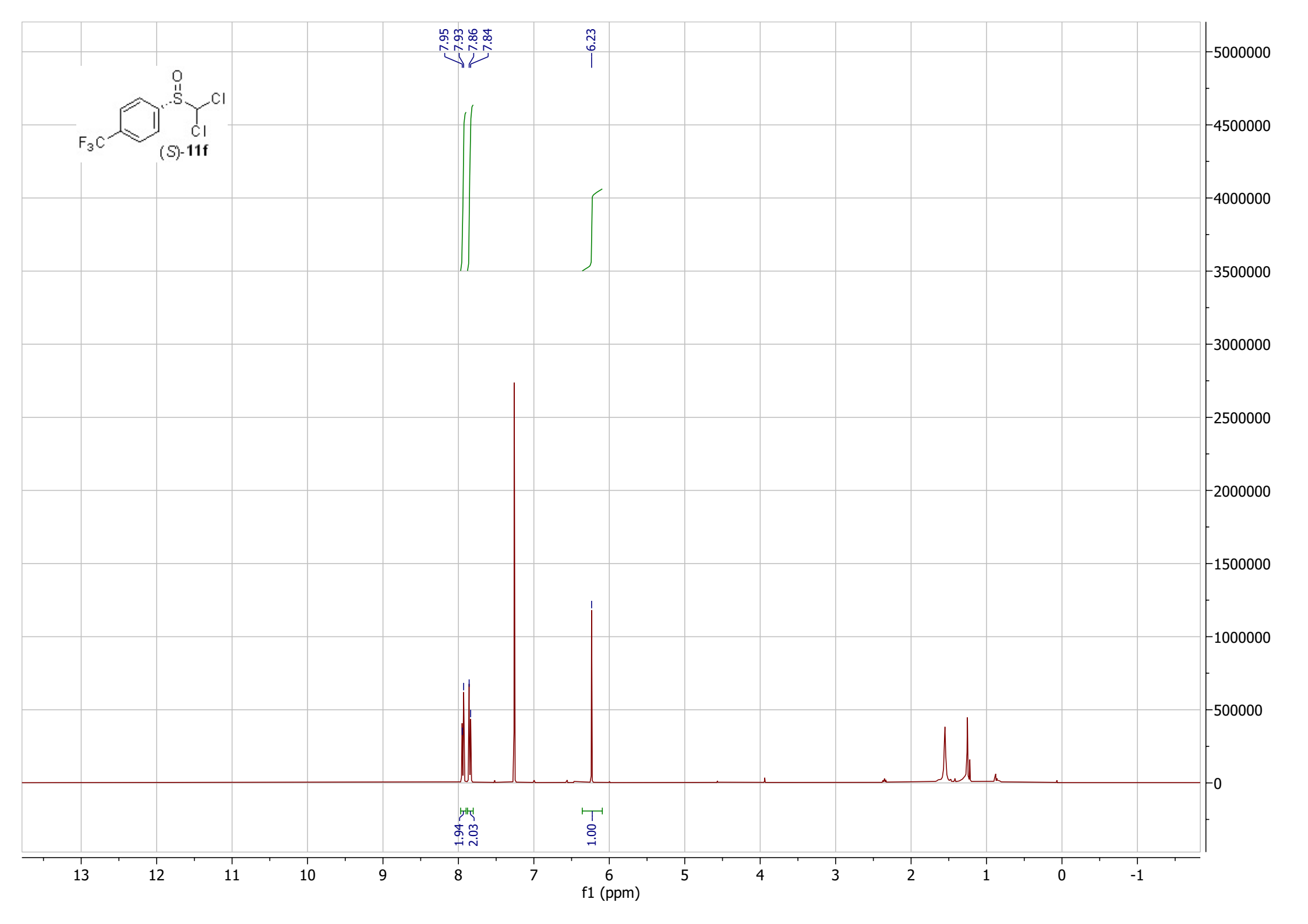

163.17
144.69
134.81
129.60
127.40
94.33
55.31
21.84
(S)-9e
f1 (ppm)

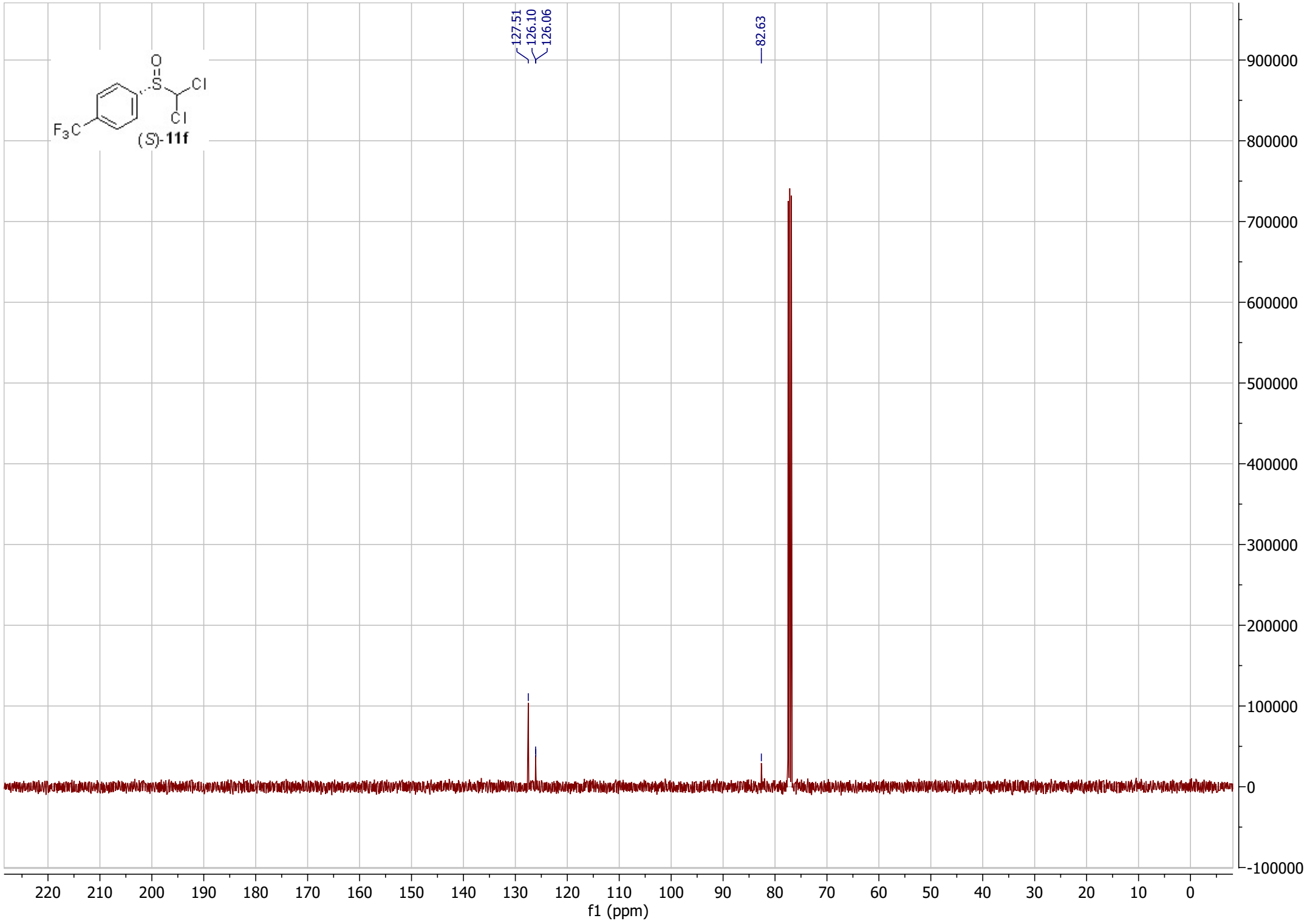

7.69
7.69
7.68
7.67
7.67
7.66
7.39
7.38
7.38
7.37
7.36
7.36
6.14
2.45
O
S
Cl
Cl
H3C
(S)-11e
2.09
2.17
1.00
3.42
f1 (ppm)

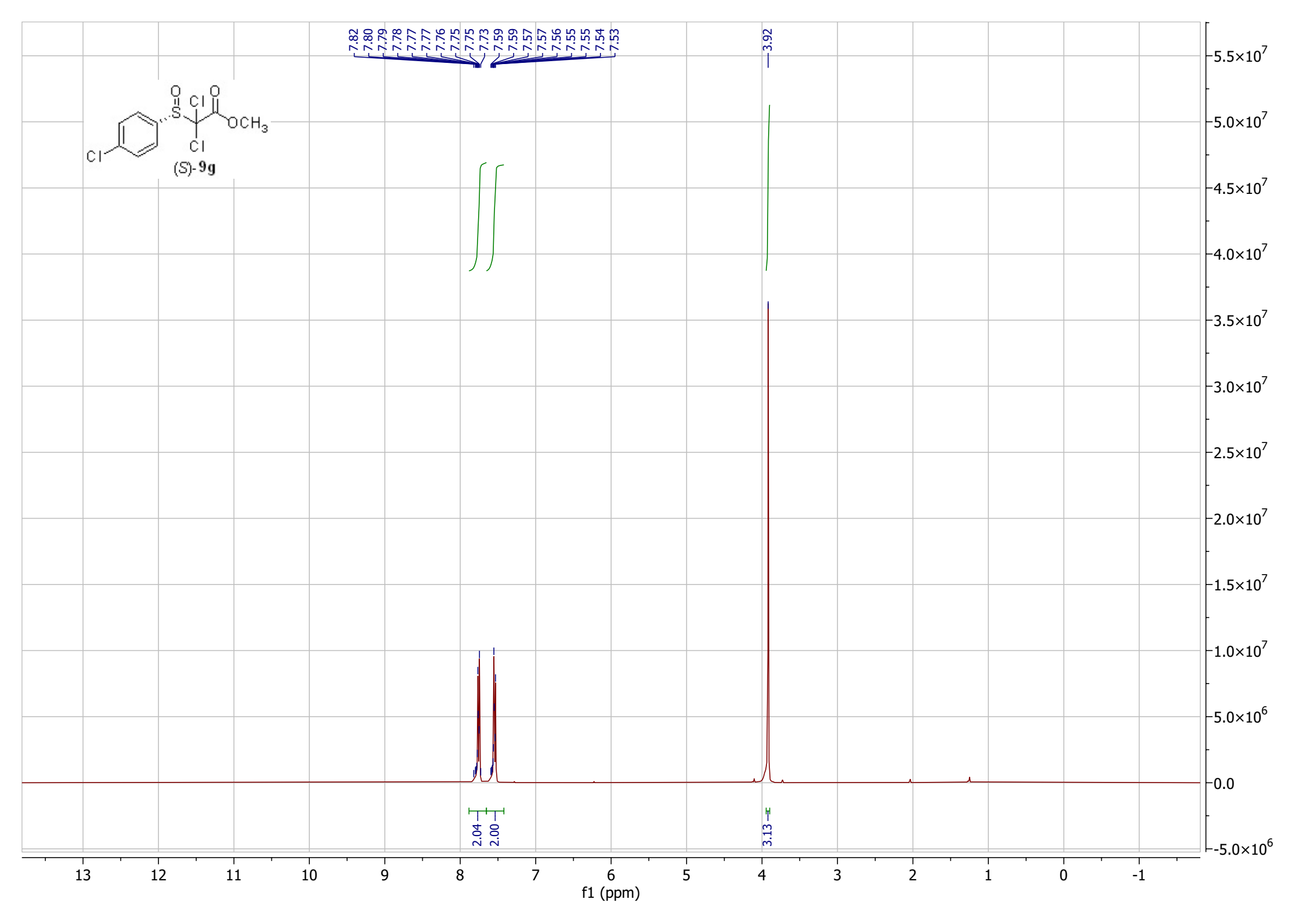

144.14
134.83
129.86
126.80
83.22
21.81
O
S
Cl
Cl
H3C
(S)-11e
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

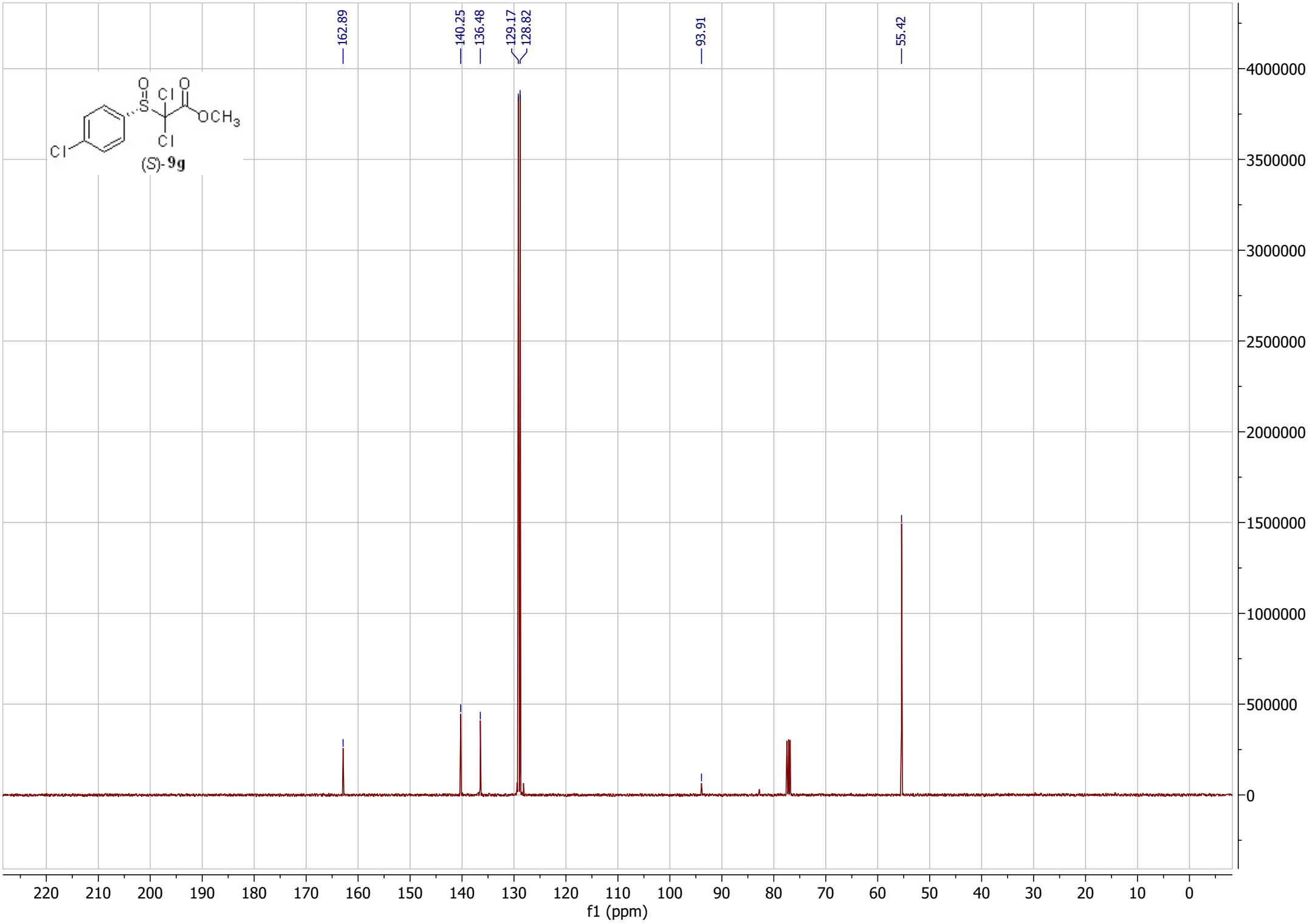

PROTON_01
7.96
7.94
7.83
7.81
3.93
(S)-9f
2.00
2.13
3.09
f1 (ppm)

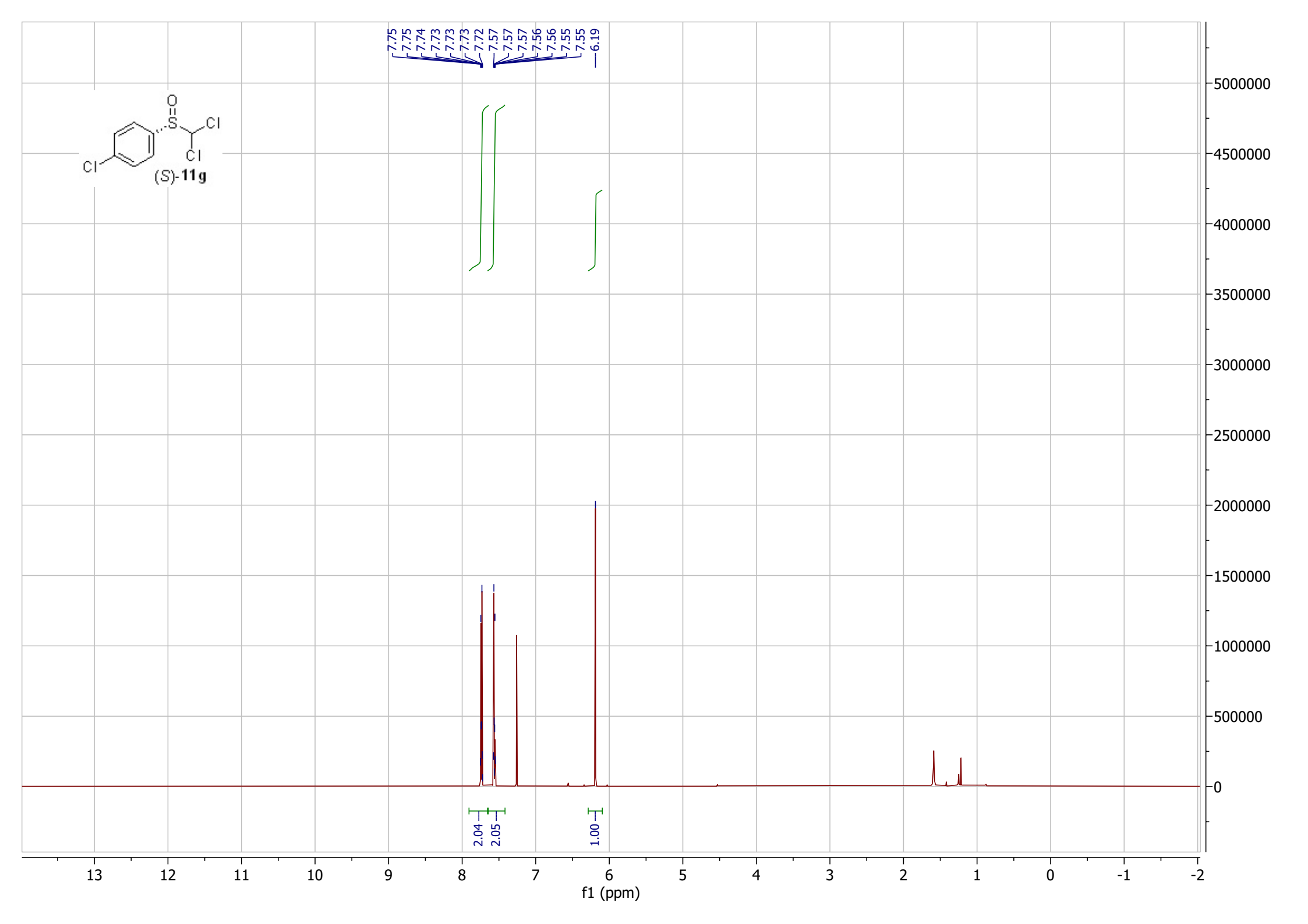

CARBON_01
162.85
142.33
135.79
135.46
135.13
134.80
132.95
128.21
125.85
125.81
125.78
125.74
124.75
122.03
93.70
55.58
(S)-9f
f1 (ppm)

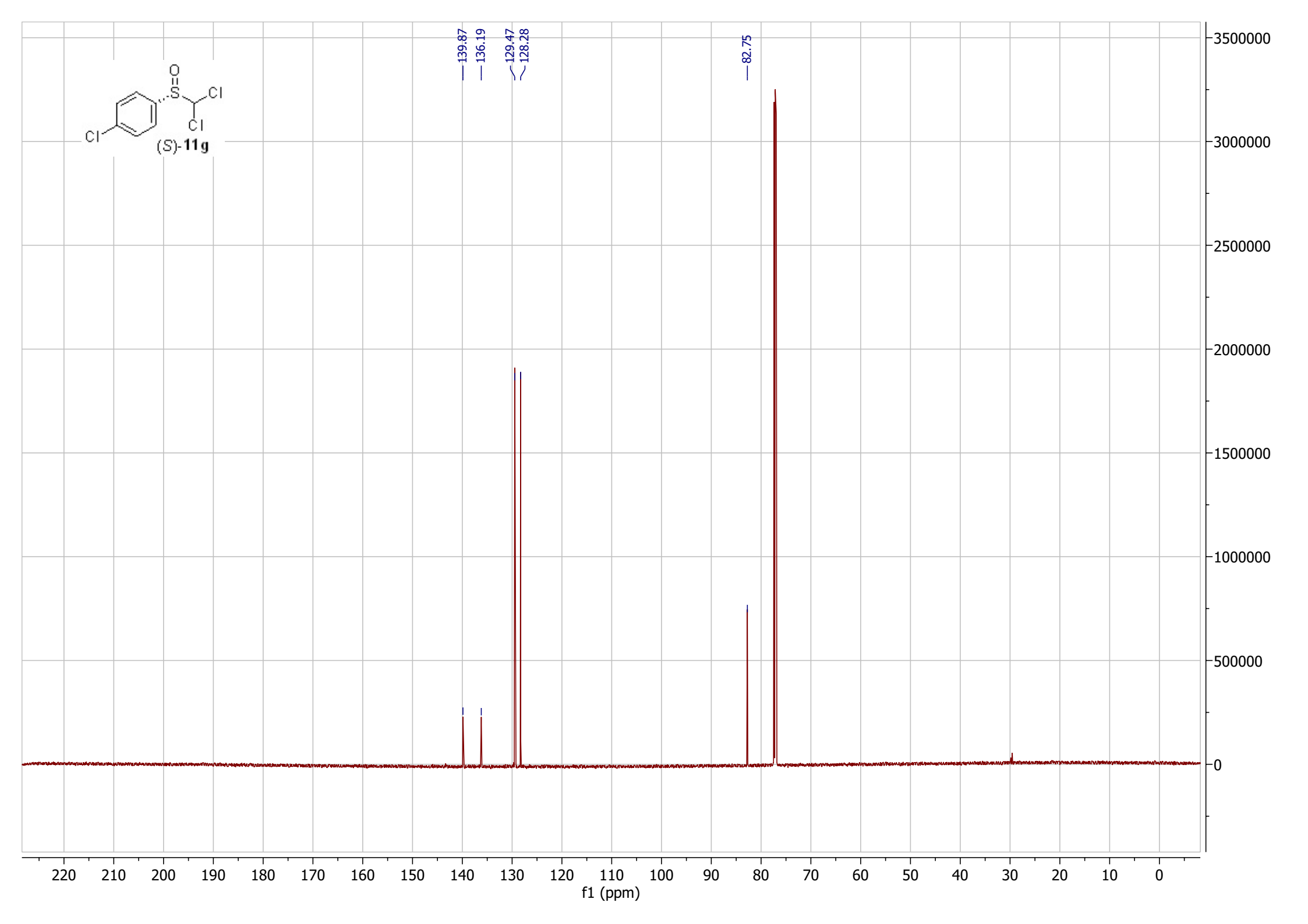

7.95
7.93
7.86
7.84
6.23
O
S
Cl
Cl
F3C
(S)-11f
1.94
2.03
1.00
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

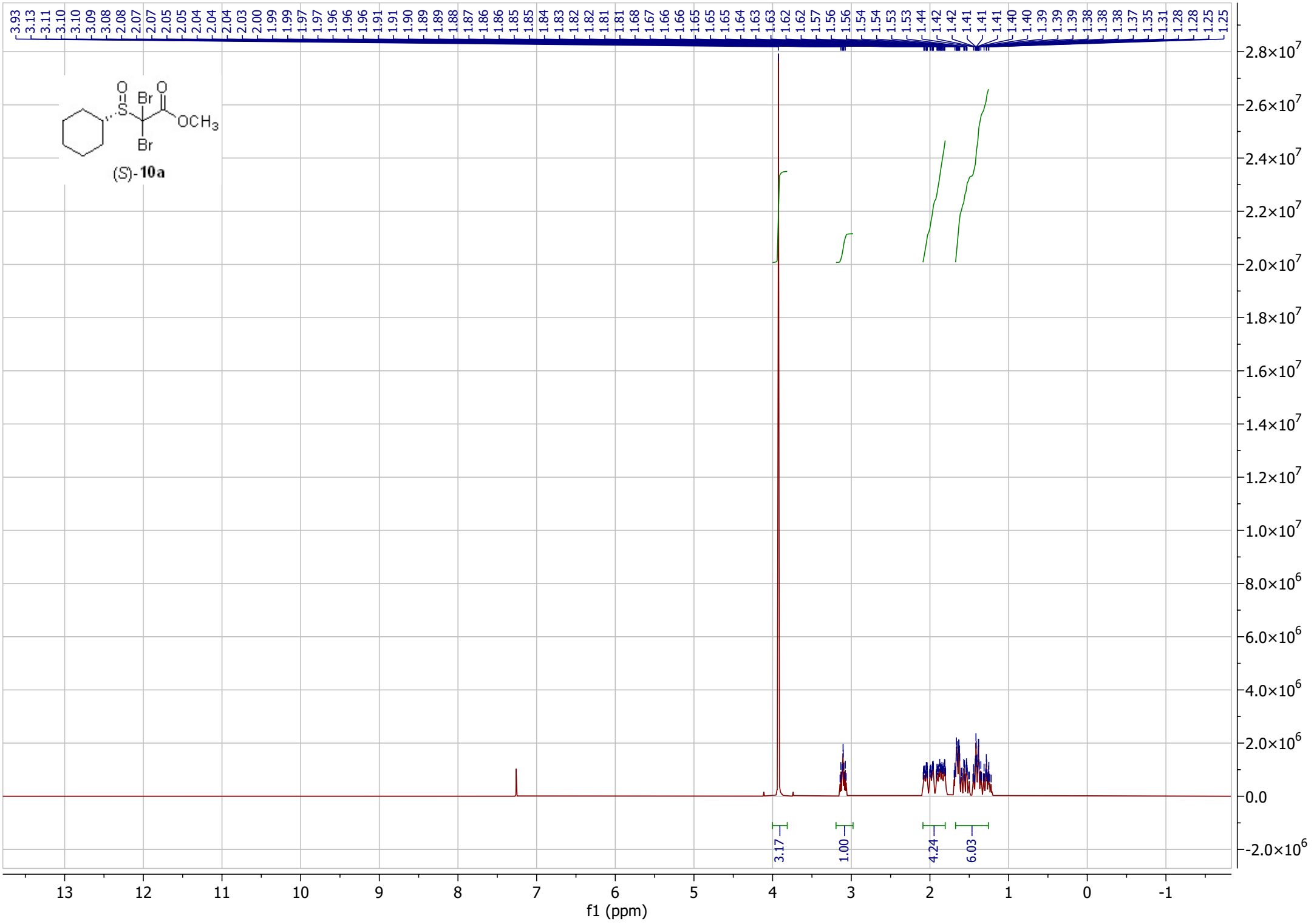

127.51
126.10
126.06
82.63
O
S
Cl
Cl
F3C
(S)-11f
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

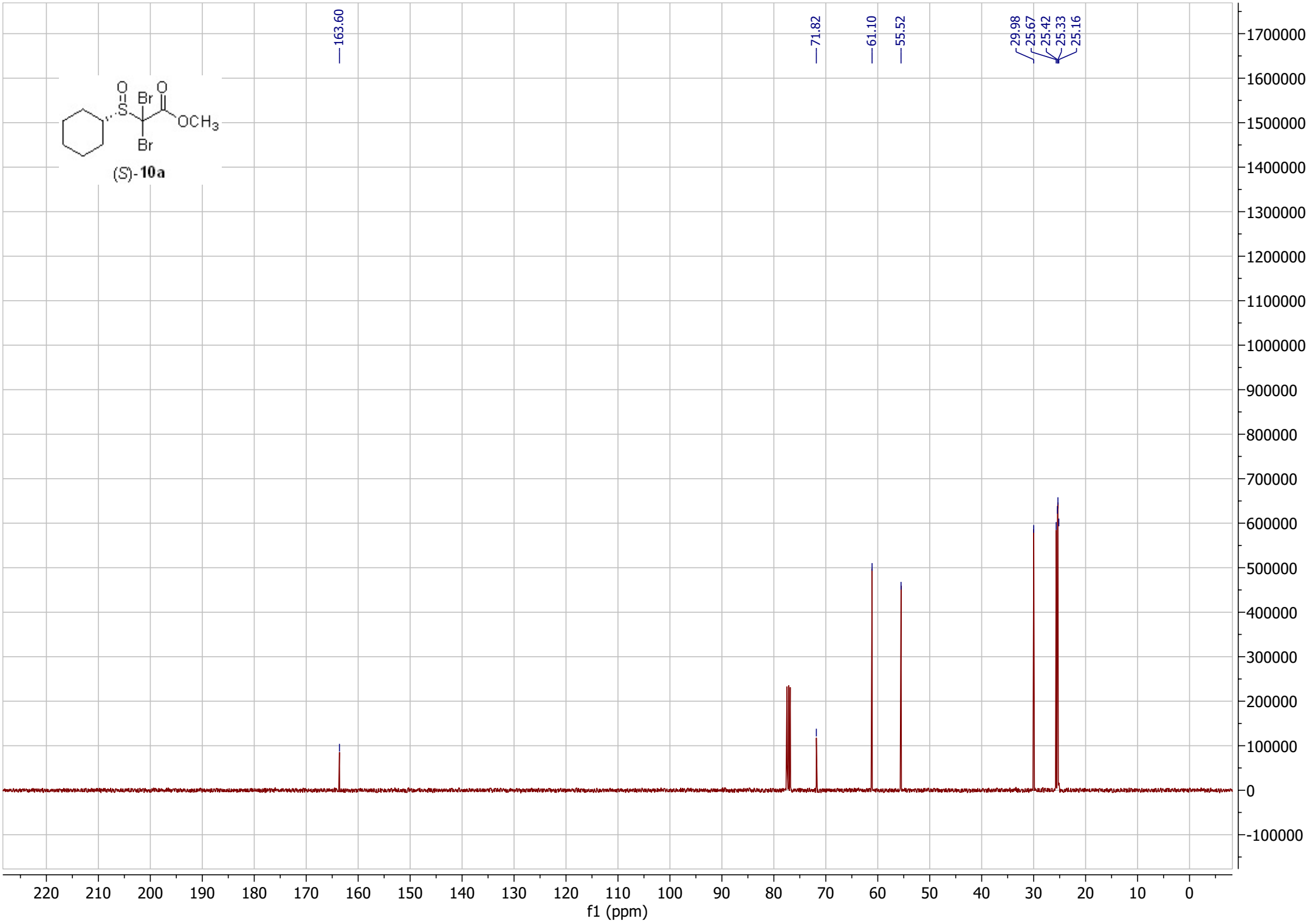

7.82
7.80
7.79
7.78
7.77
7.77
7.76
7.75
7.75
7.73
7.59
7.59
7.57
7.57
7.56
7.55
7.55
7.54
7.53
3.92
(S)-9g
2.04
2.00
3.13
f1 (ppm)

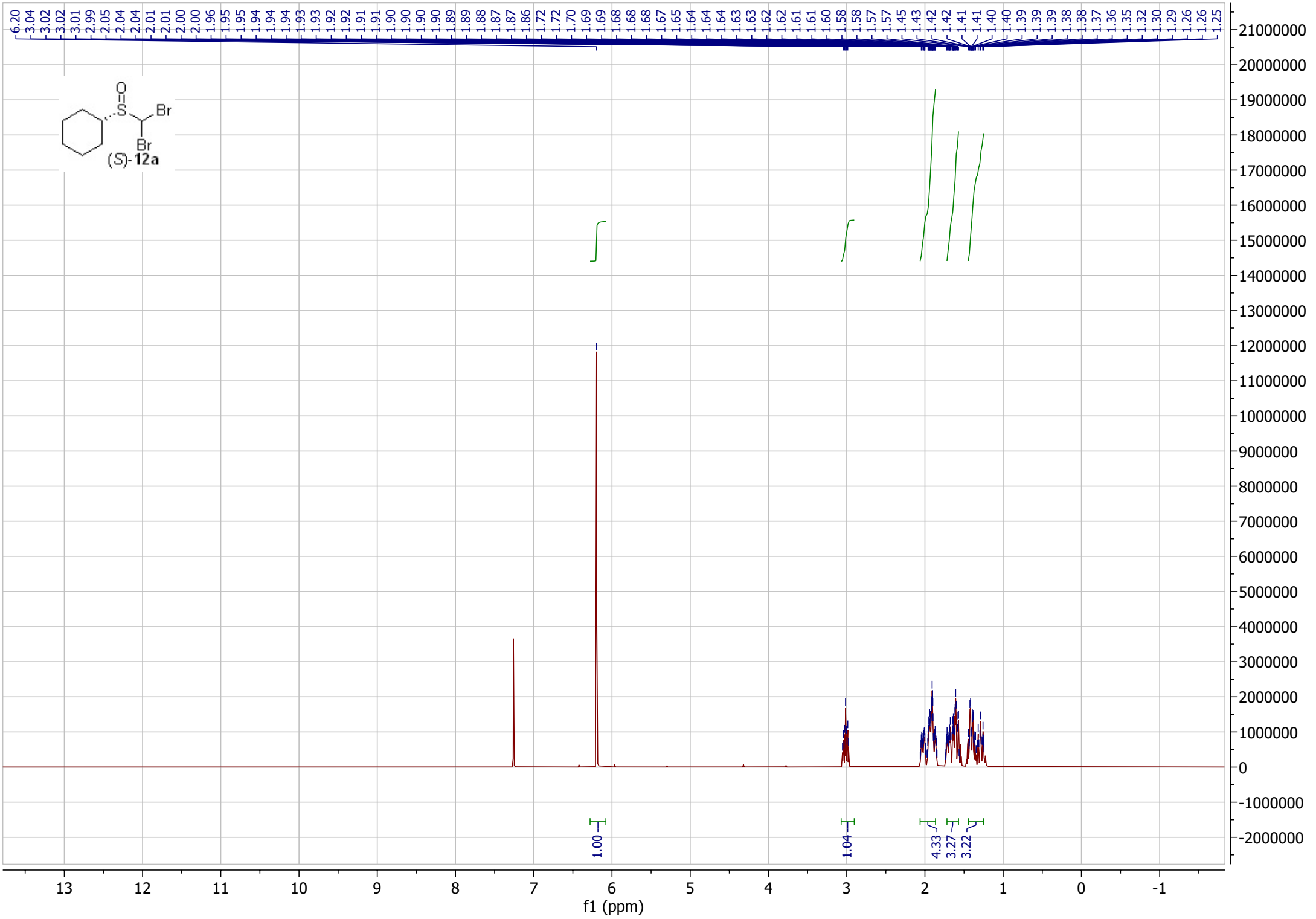

162.89
140.25
136.48
129.17
128.82
93.91
55.42
Cl
O
S
O
Cl
O
OCH3
Cl
(S)-9g
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

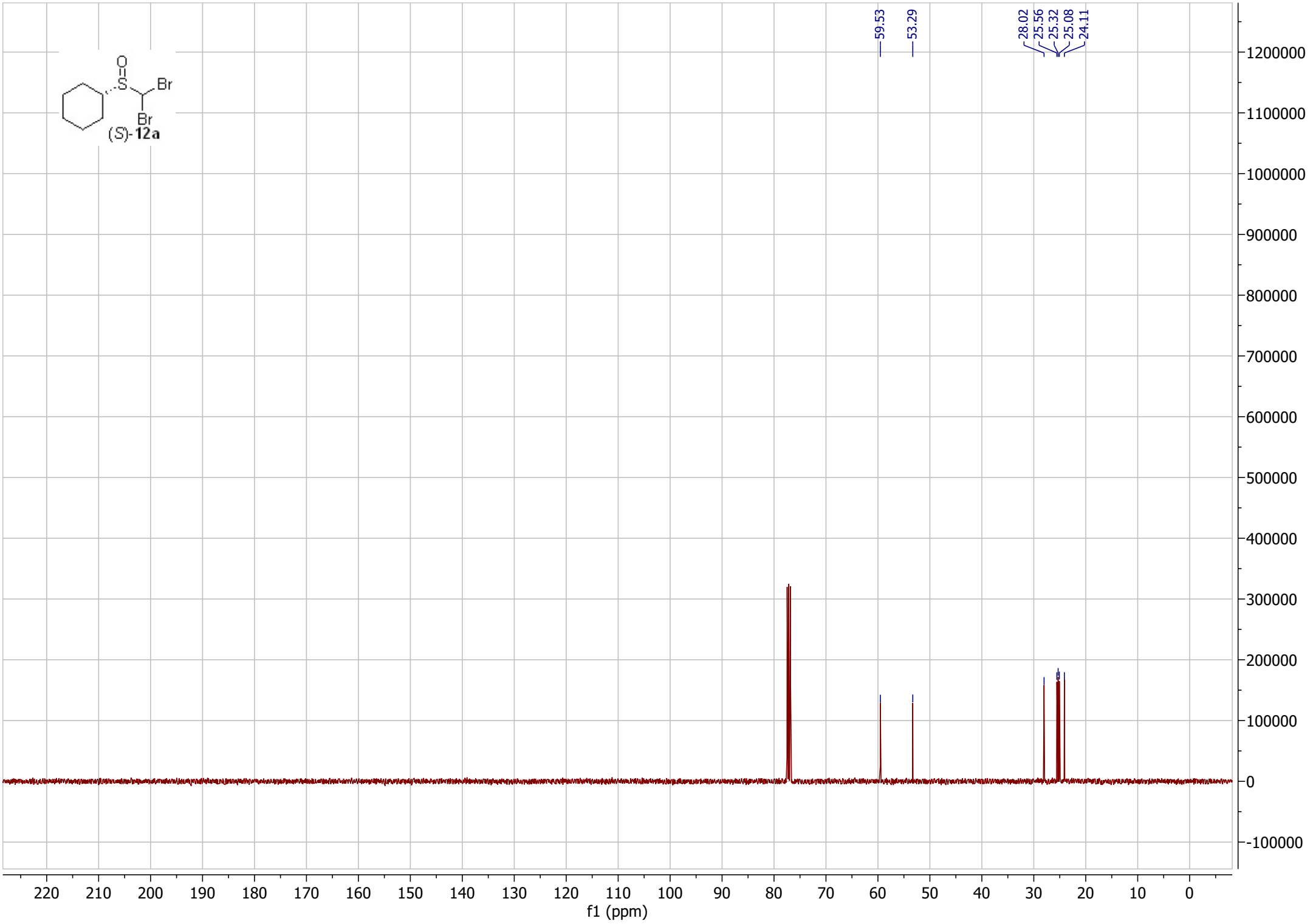

7.75
7.75
7.74
7.73
7.73
7.73
7.72
7.57
7.57
7.57
7.56
7.56
7.55
7.55
6.19
O
S
Cl
Cl
Cl
(S)-11g
2.04
2.05
1.00
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

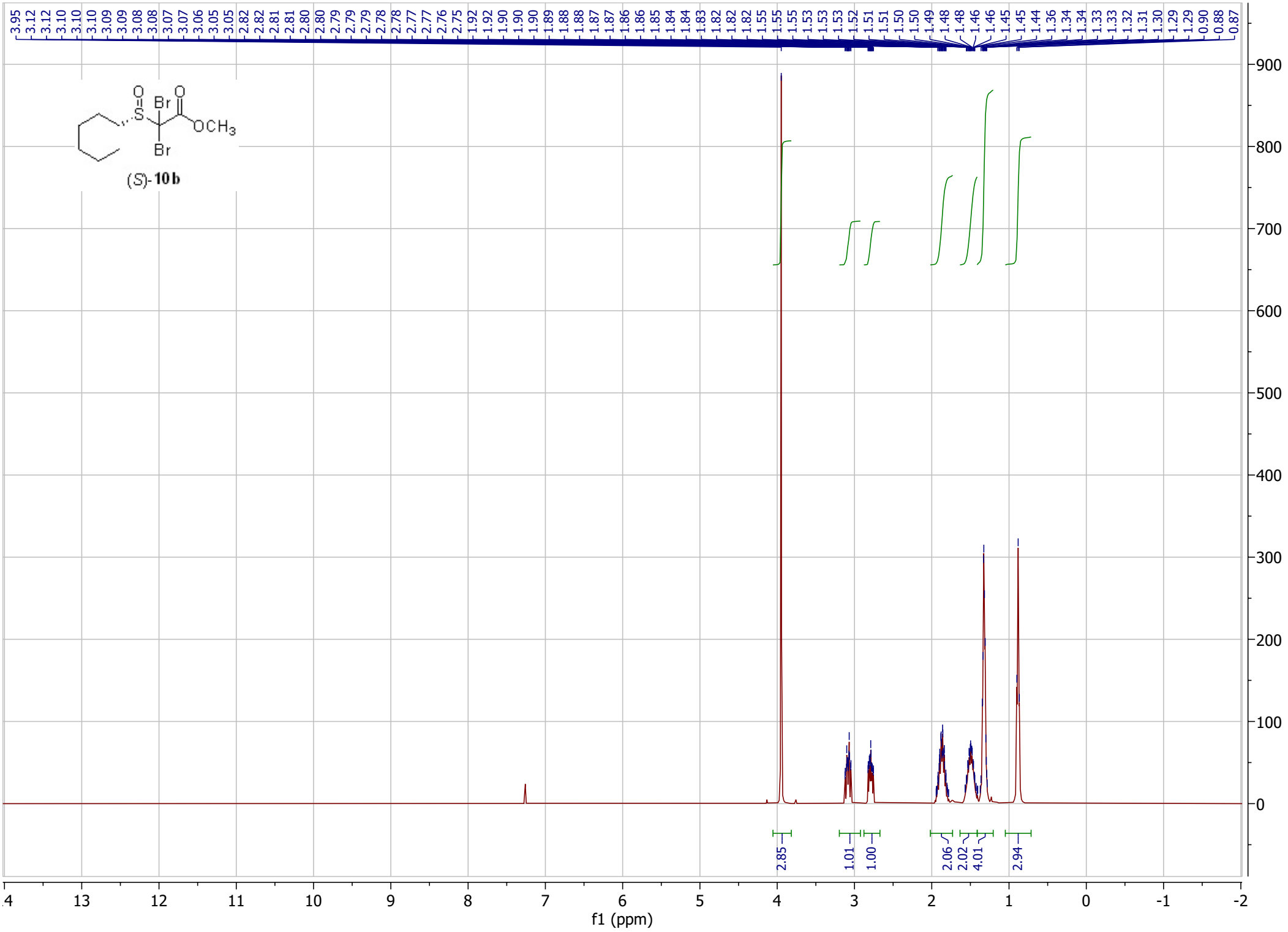

139.87
136.19
129.47
128.28
82.75
(S)-11g
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

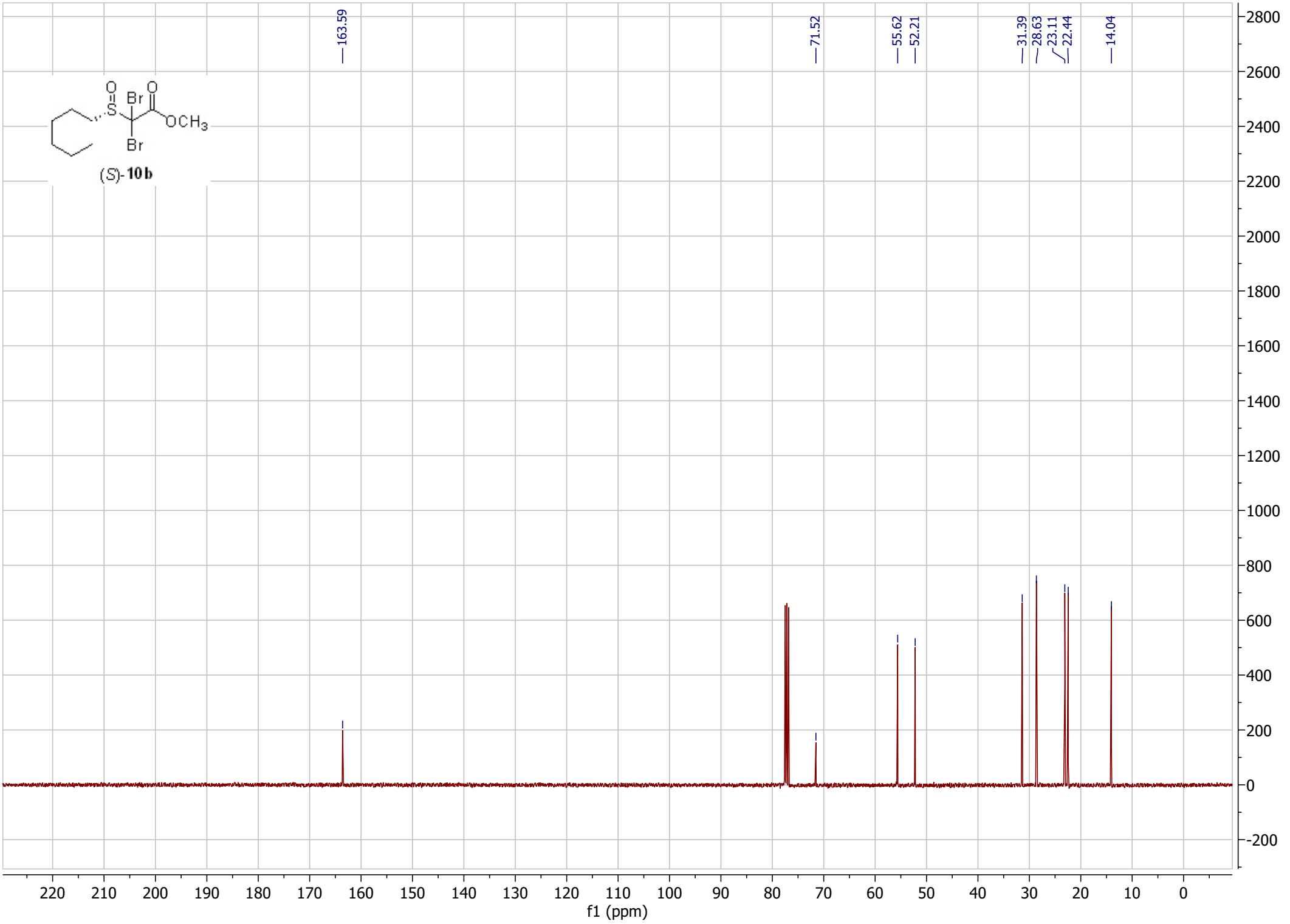

(S)-10a
f1 (ppm)
3.17
1.00
4.24
6.03

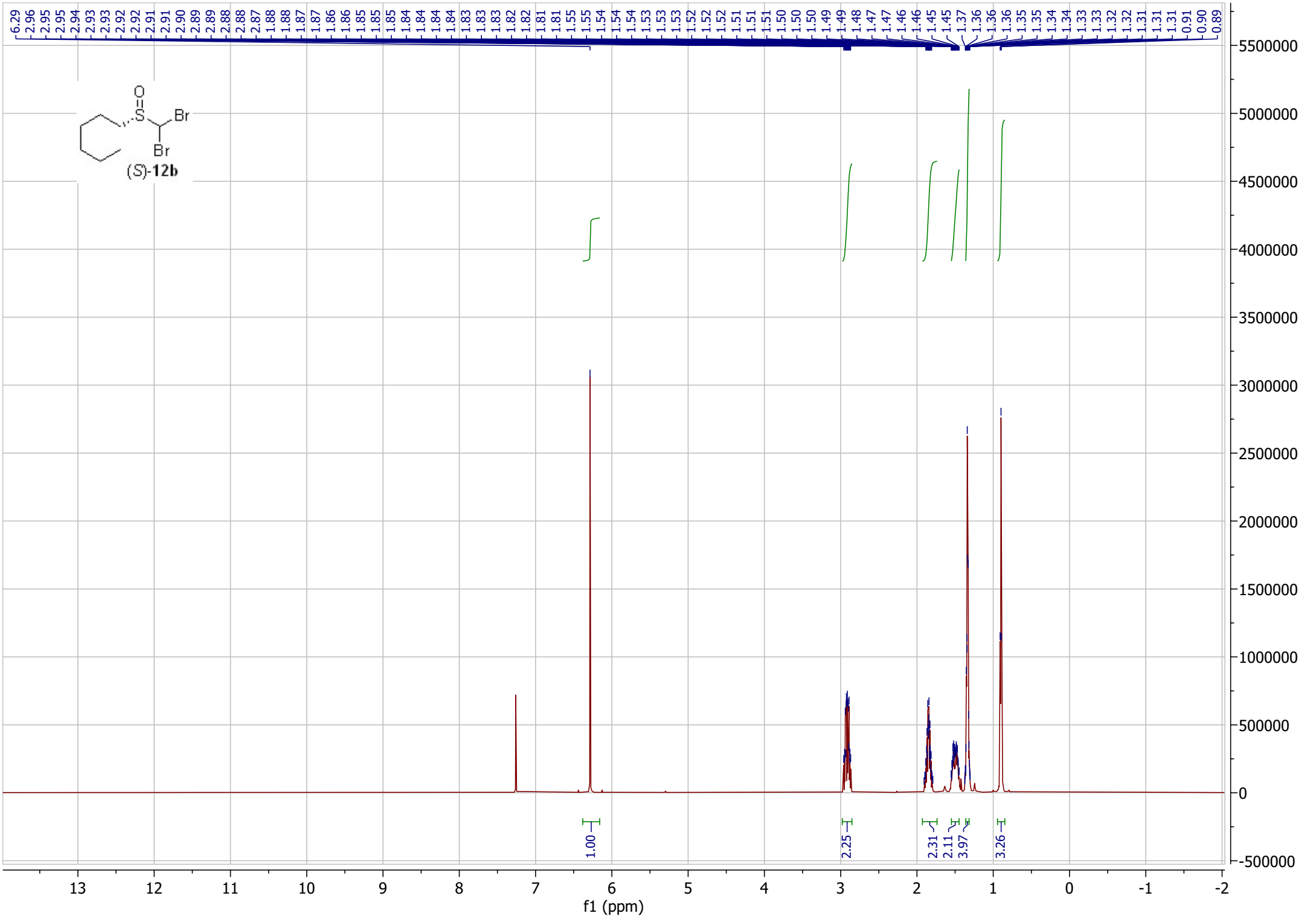

163.60
71.82
61.10
55.52
29.98
25.67
25.42
25.33
25.16
(S)-10a
f1 (ppm)

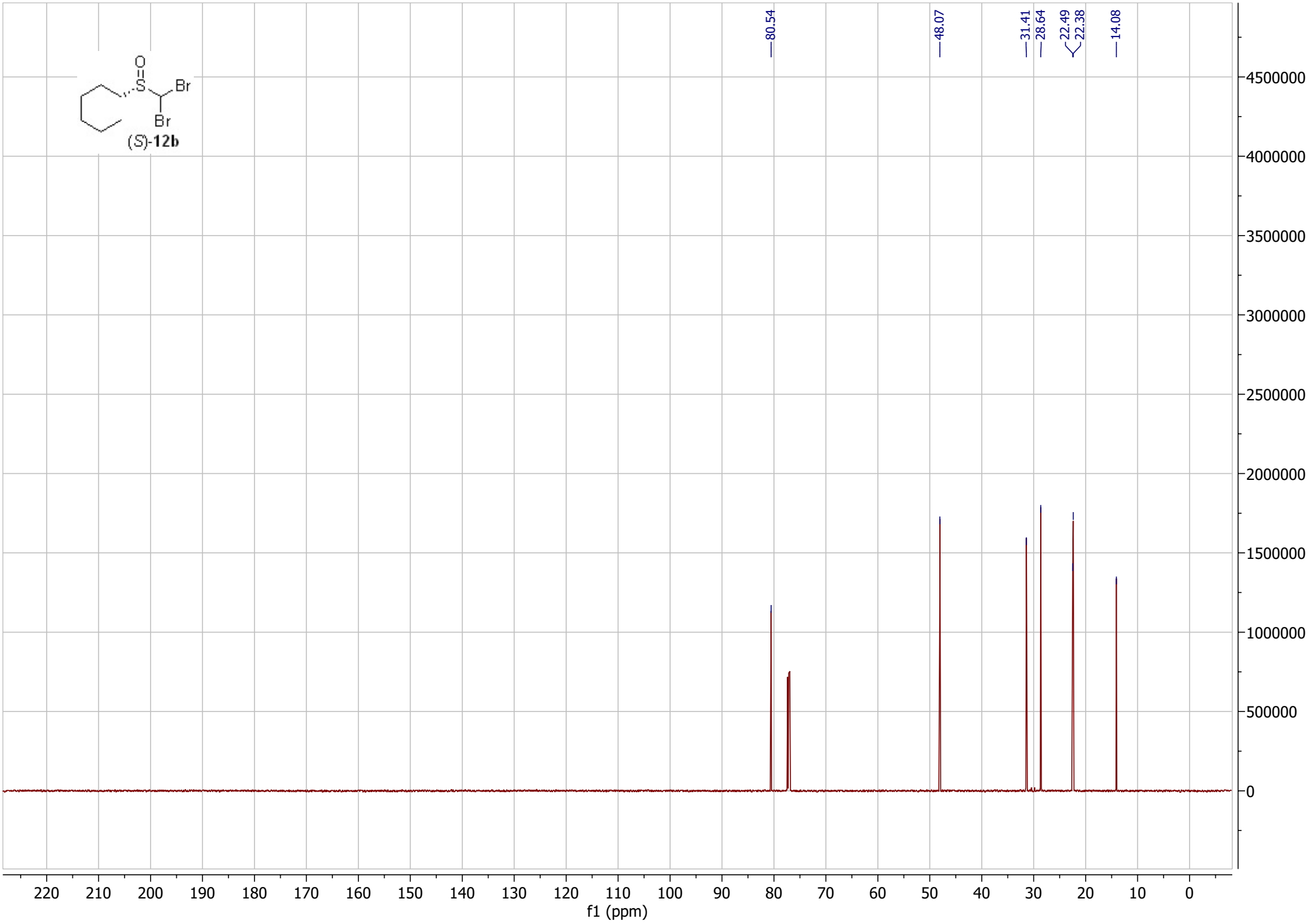

O
S
Br
Br
(S)-12a
6.20 3.04 3.02 3.02 3.01 2.99 2.05 2.04 2.04 2.01 2.01 2.00 2.00 1.96 1.95 1.95 1.94 1.94 1.94 1.93 1.93 1.92 1.92 1.91 1.91 1.90 1.90 1.90 1.90 1.89 1.89 1.88 1.87 1.87 1.86 1.72 1.72 1.70 1.69 1.69 1.68 1.68 1.68 1.67 1.65 1.64 1.64 1.64 1.63 1.63 1.62 1.62 1.61 1.61 1.60 1.58 1.58 1.57 1.57 1.45 1.43 1.42 1.42 1.41 1.41 1.40 1.40 1.39 1.39 1.39 1.38 1.38 1.37 1.36 1.35 1.32 1.30 1.29 1.26 1.26 1.25
21000000
20000000
19000000
18000000
17000000
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
-2000000
1.00
1.04
4.33
3.27
3.22
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

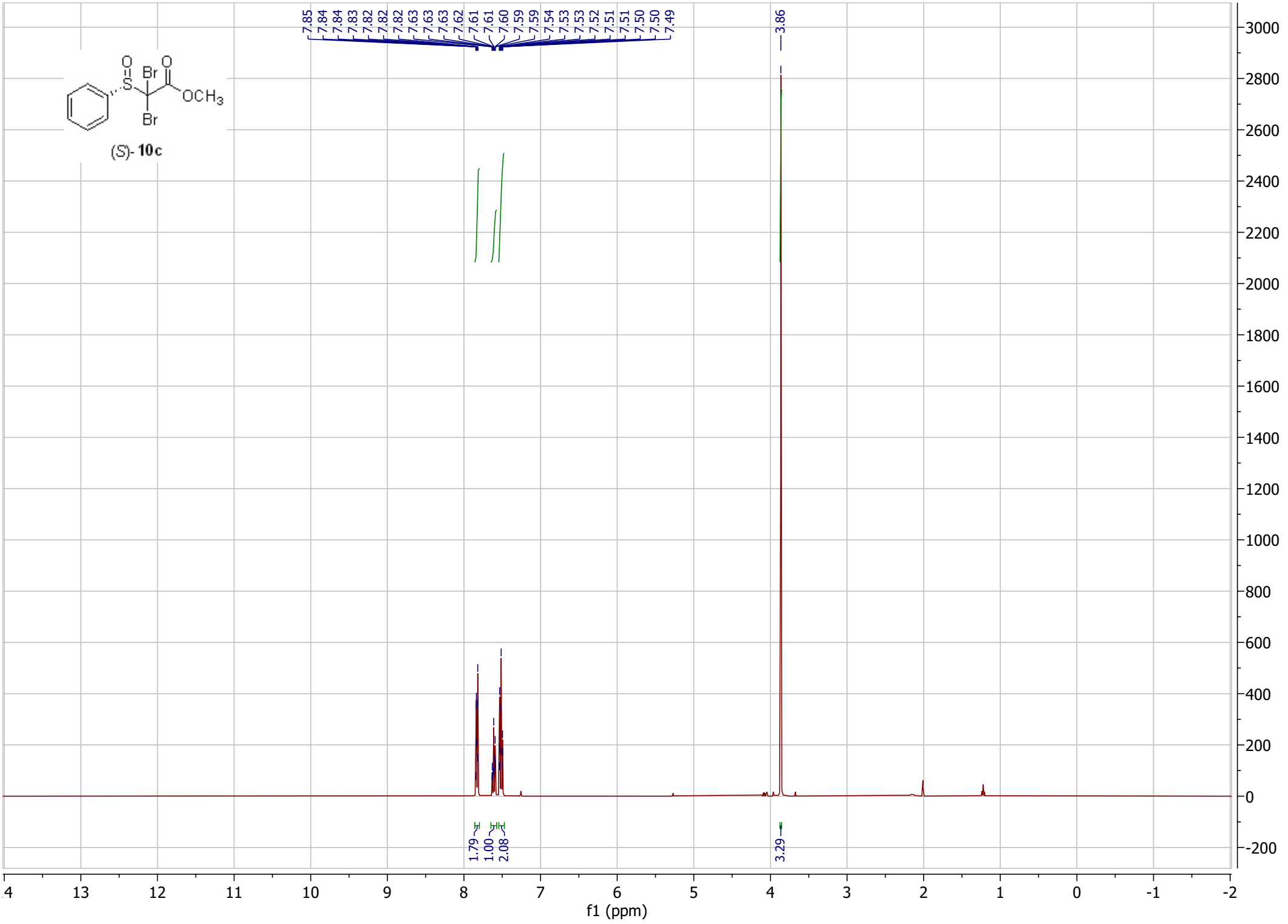

59.53
53.29
28.02
25.56
25.32
25.08
24.11
O
S
Br
Br
(S)-12a
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

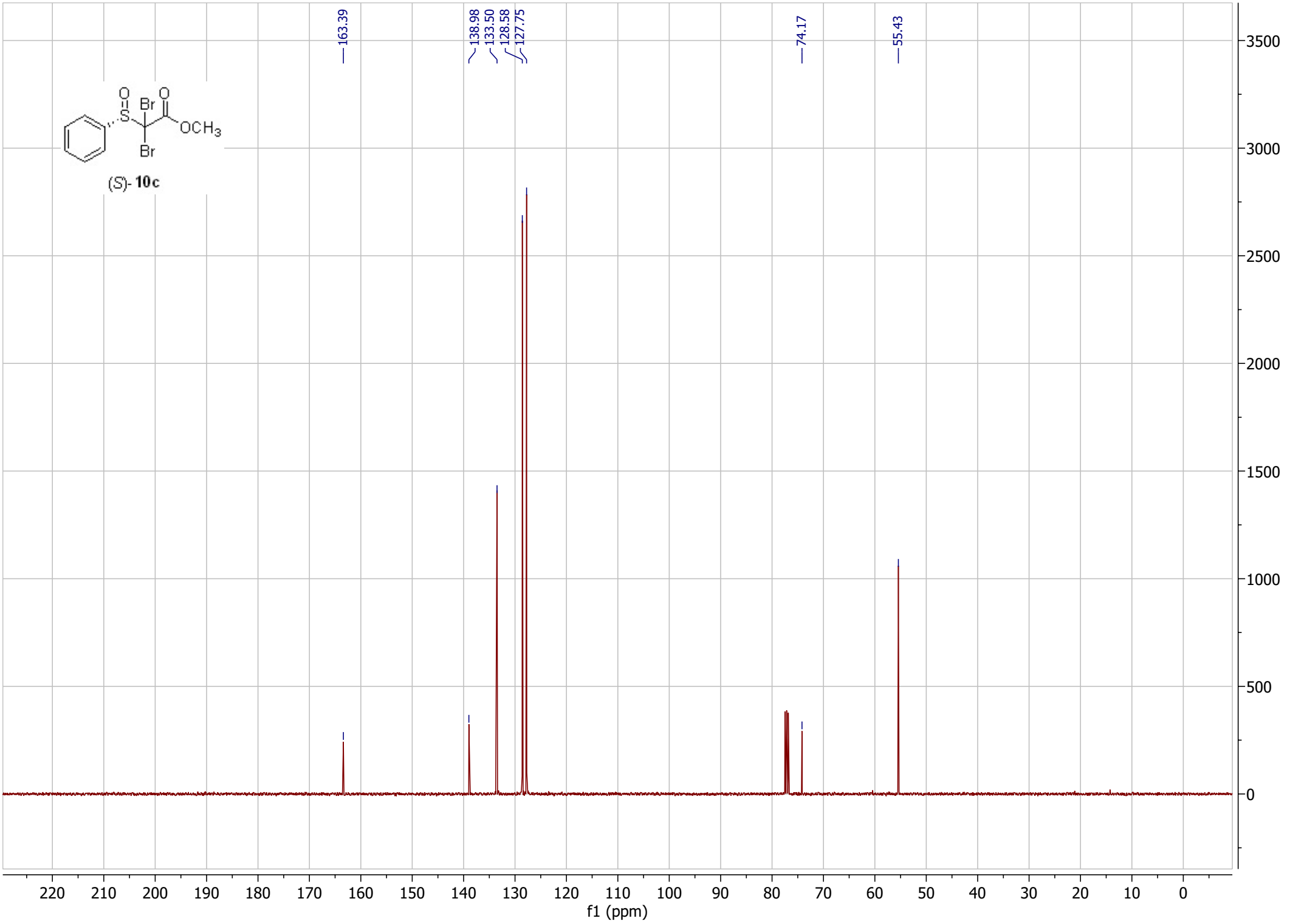

(S)-10b
f1 (ppm)
2.85
1.01
1.00
2.06
2.02
4.01
2.94

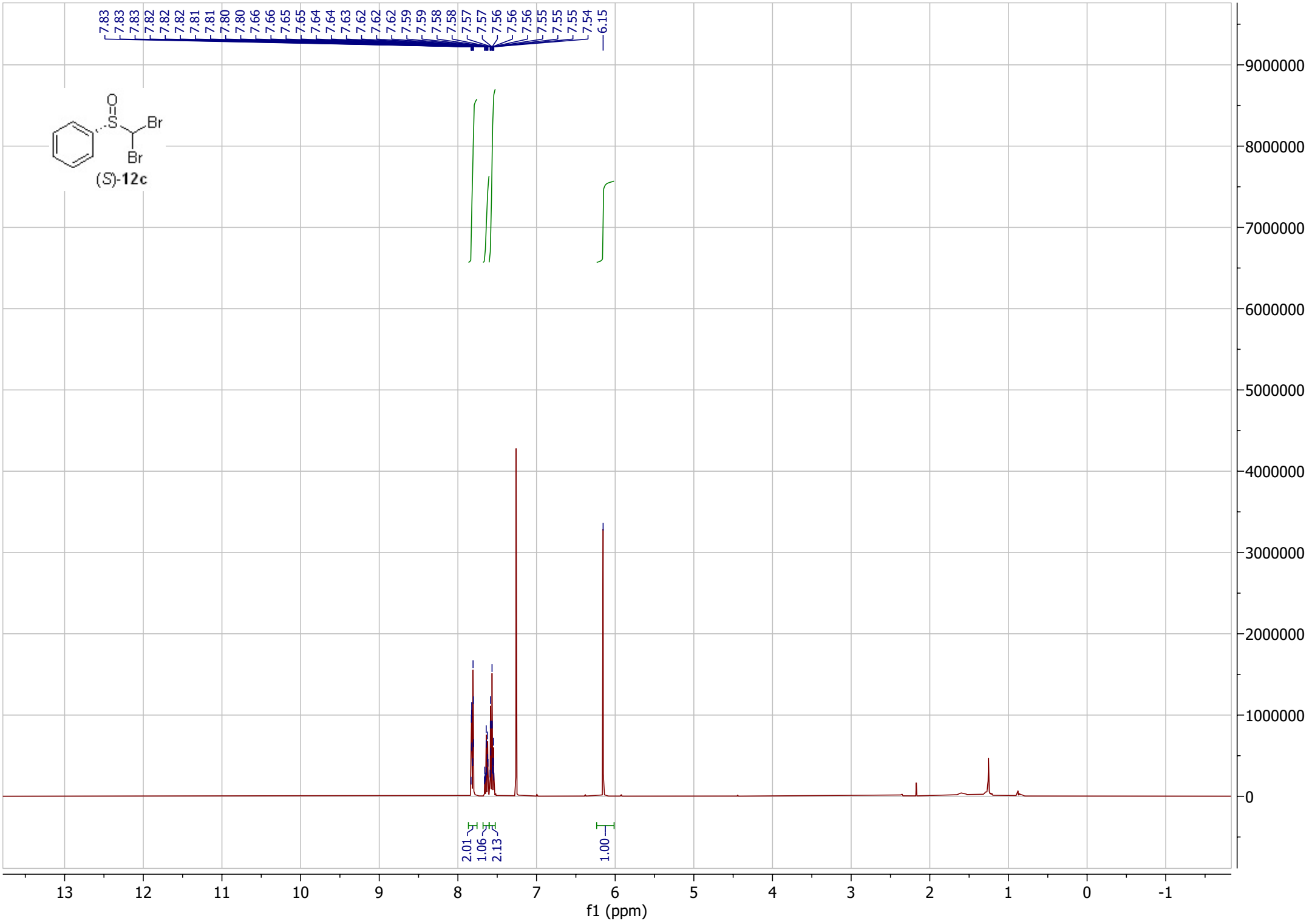

163.59
71.52
55.62
52.21
31.39
28.63
23.11
22.44
14.04
(S)-10b
f1 (ppm)

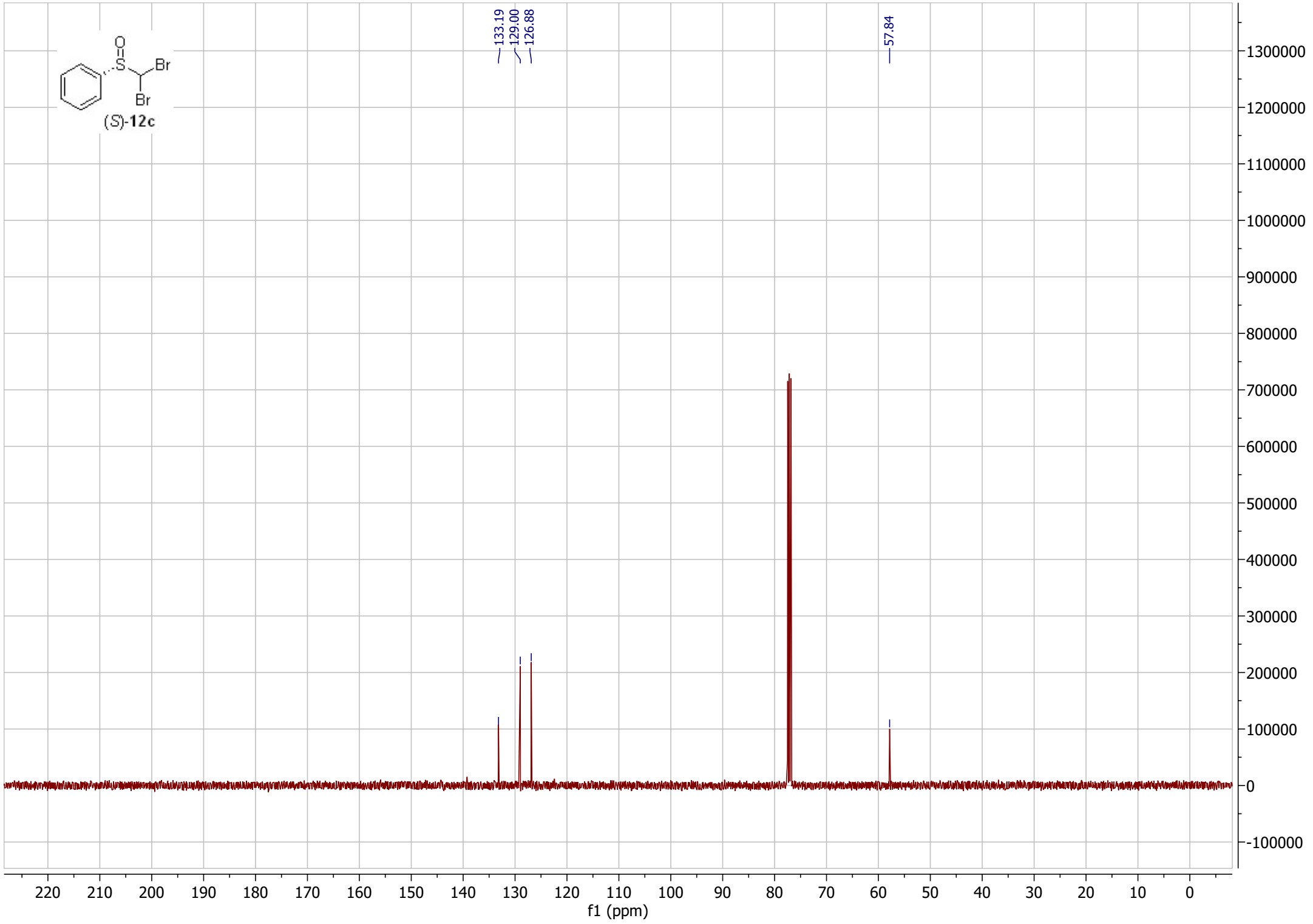

(S)-12b
f1 (ppm)
1.00
2.25
2.31
2.11
3.97
3.26

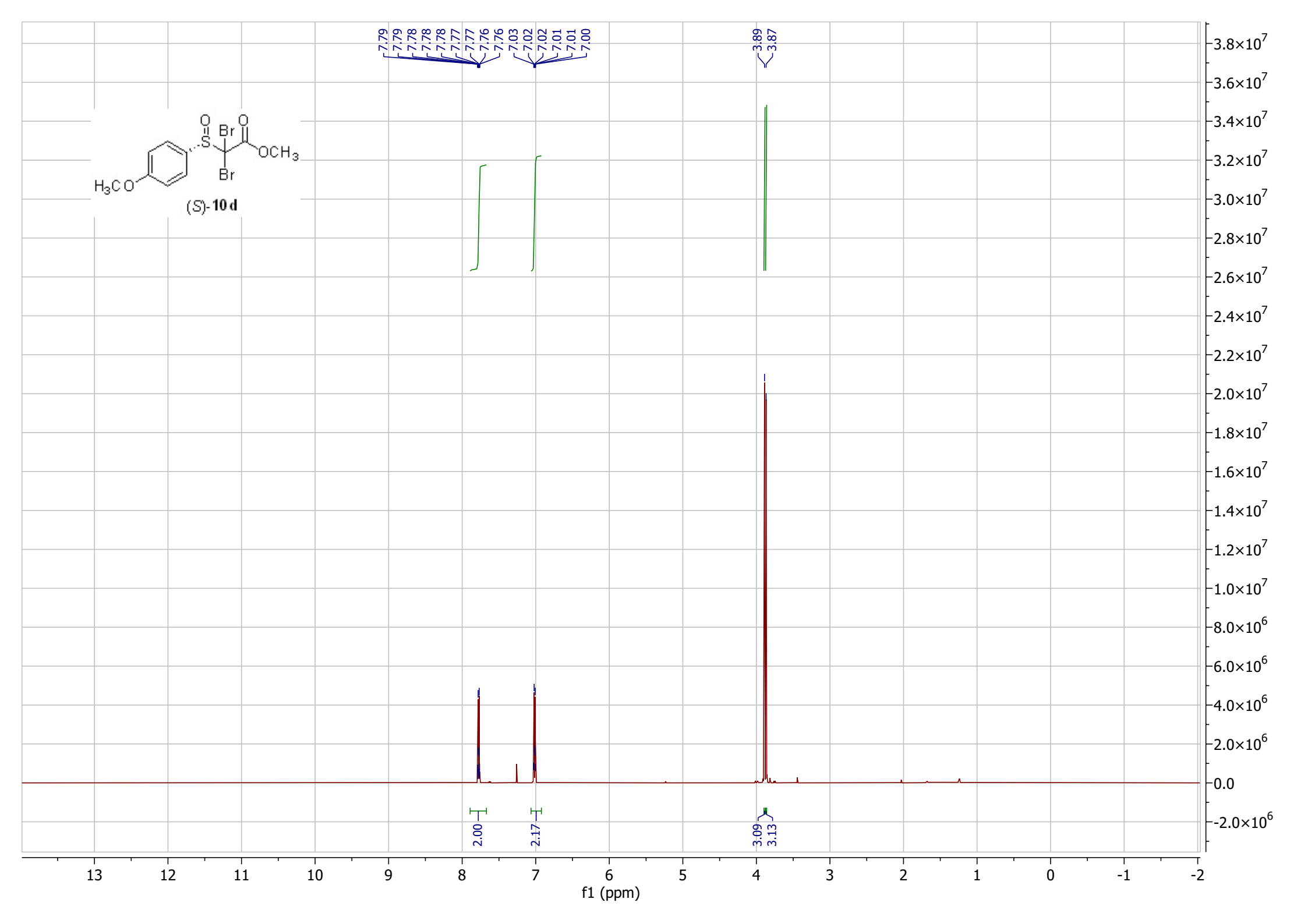

80.54
48.07
31.41
28.64
22.49
22.38
14.08
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
S
Br
Br
(S)-12b

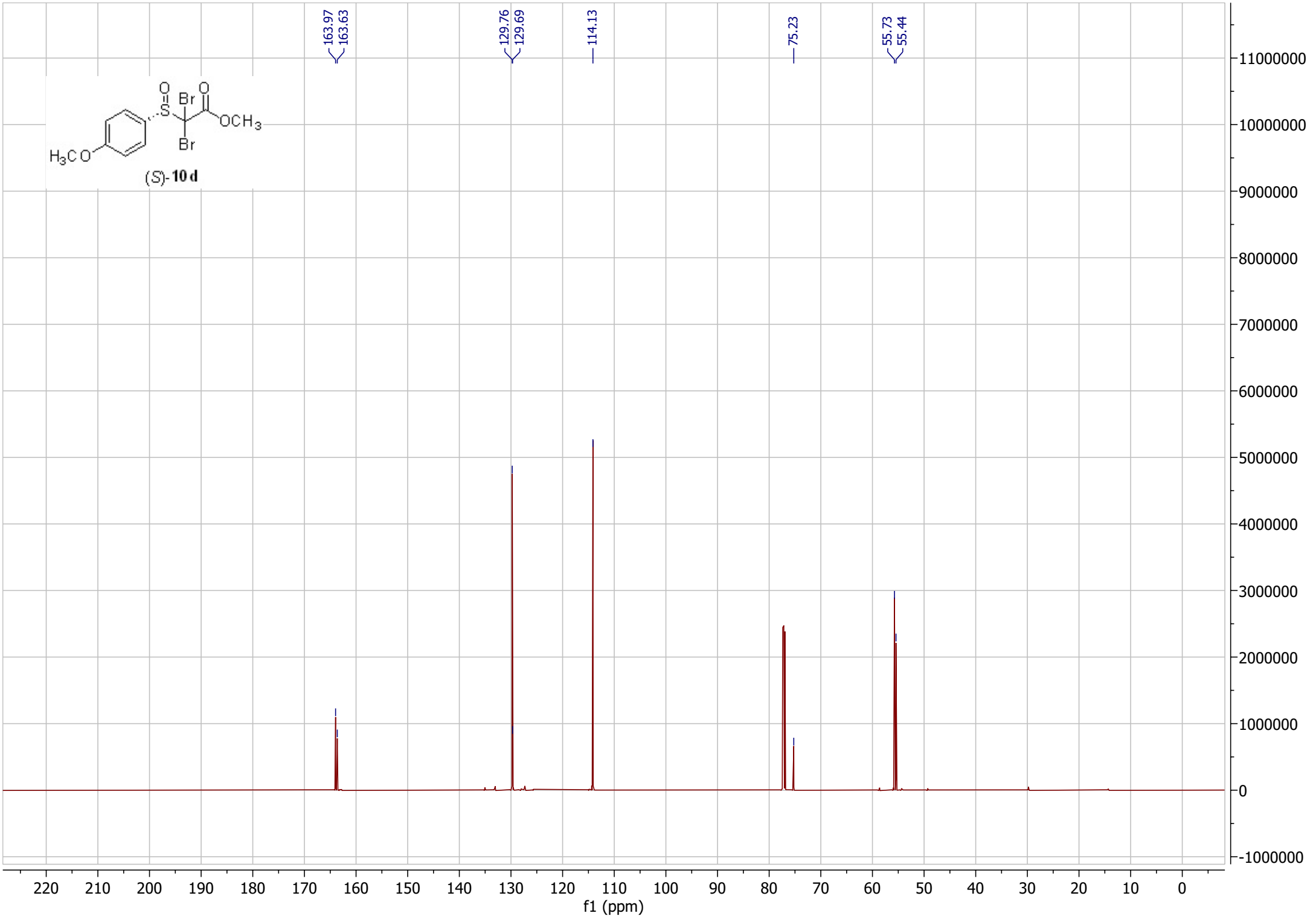

7.85
7.84
7.84
7.83
7.82
7.82
7.82
7.63
7.63
7.63
7.62
7.61
7.61
7.60
7.59
7.59
7.54
7.53
7.53
7.52
7.51
7.51
7.50
7.50
7.49
3.86
O
Br
O
S
OCH3
Br
(S)-10c
1.79
1.00
2.08
3.29
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

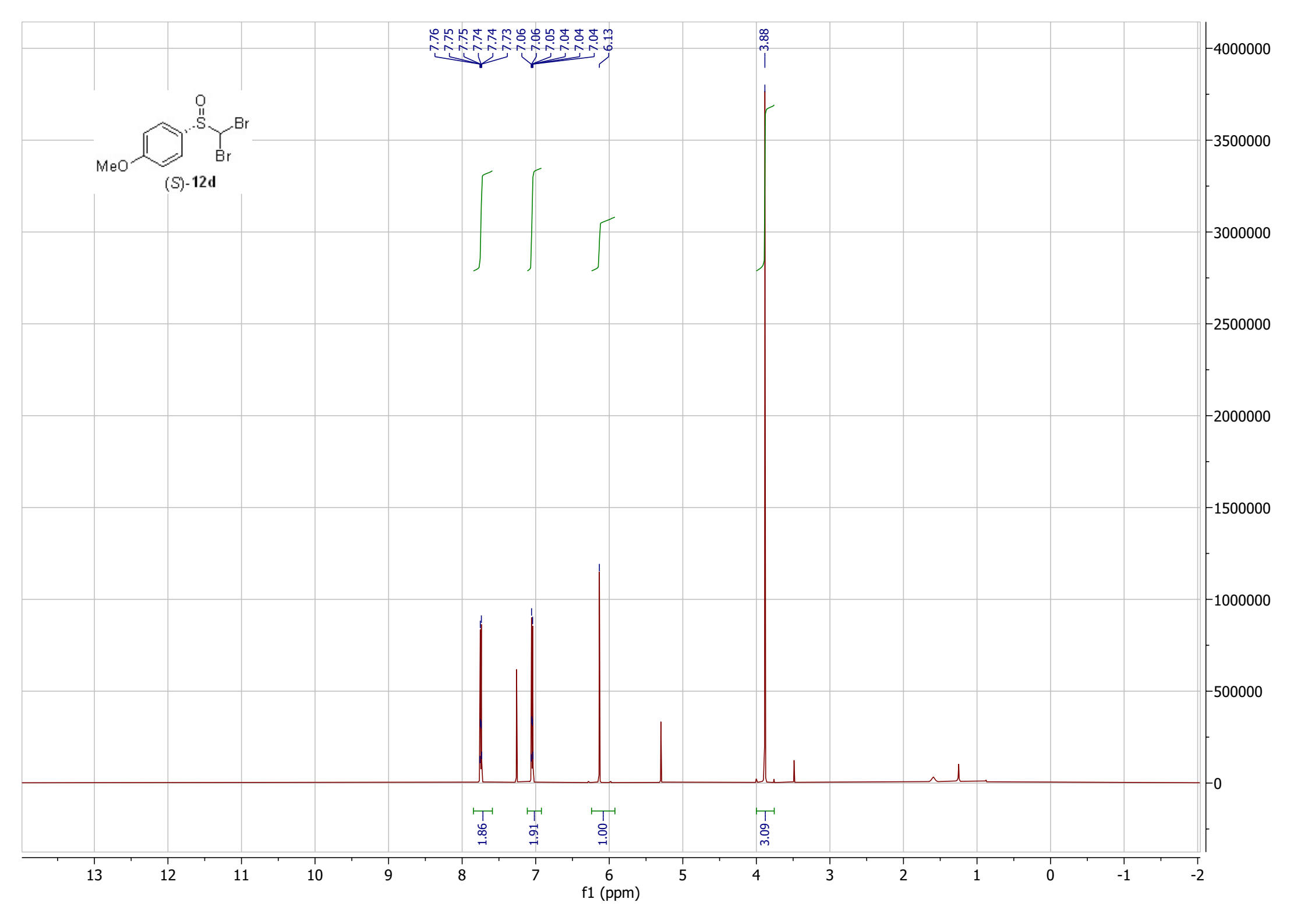

163.39
138.98
133.50
128.58
127.75
74.17
55.43
Br
O
O
S
OCH3
Br
(S)-10c
3500
3000
2500
2000
1500
1000
500
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

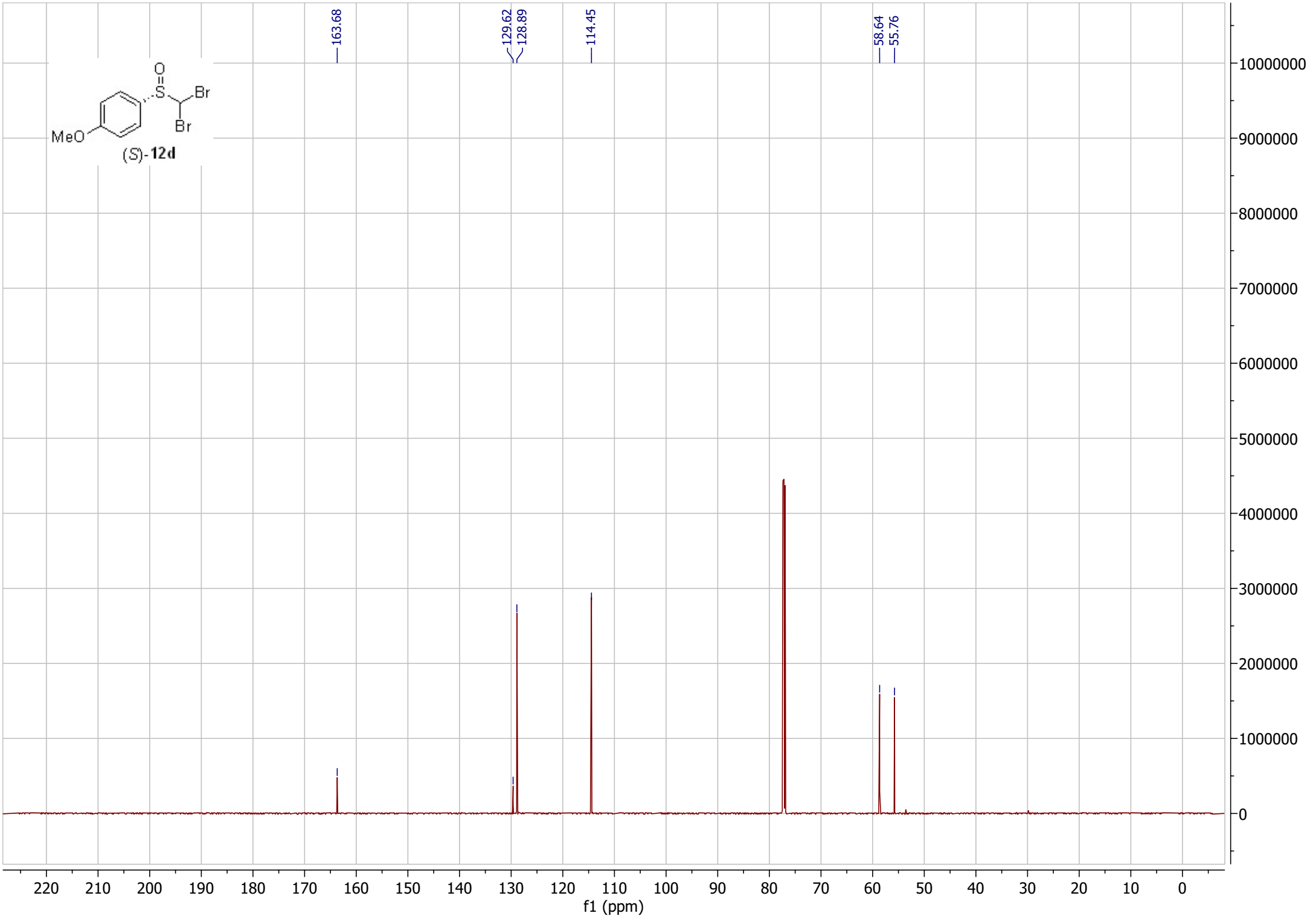

7.83 7.83 7.83 7.82 7.82 7.82 7.81 7.81 7.80 7.80 7.66 7.65 7.65 7.64 7.64 7.63 7.62 7.62 7.62 7.59 7.59 7.58 7.58 7.57 7.57 7.56 7.56 7.56 7.55 7.55 7.55 7.54 6.15
O
S
Br
Br
(S)-12c
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
2.01
1.06
2.13
1.00
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

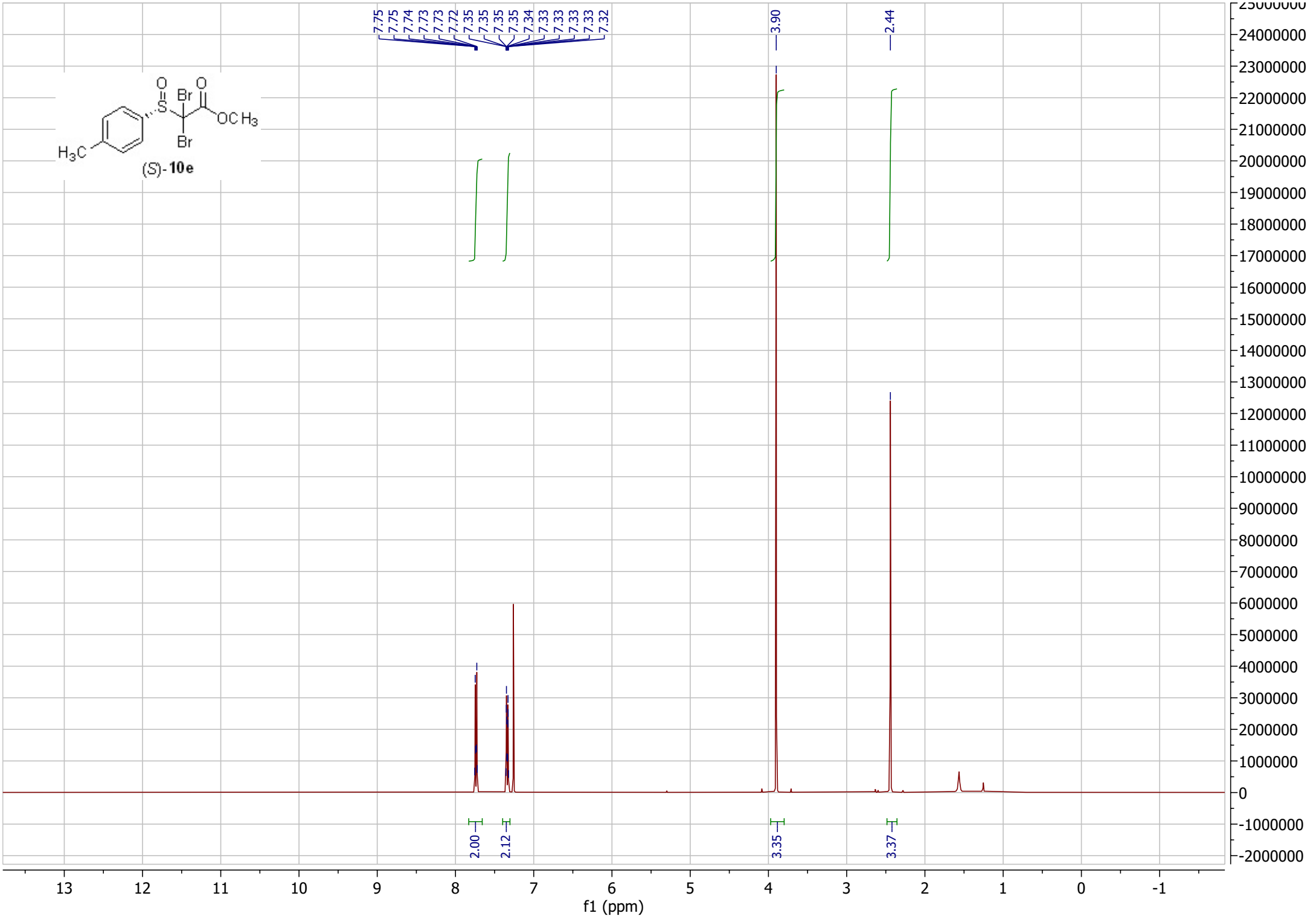

O
S
Br
Br
(S)-12c
133.19
129.00
126.88
57.84
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.79
7.79
7.78
7.78
7.78
7.77
7.77
7.76
7.76
7.03
7.02
7.02
7.01
7.01
7.00
3.89
3.87
O
S
Br
O
OCH3
Br
H3CO
(S)-10 d
2.00
2.17
3.09
3.13
3.8×10^7
3.6×10^7
3.4×10^7
3.2×10^7
3.0×10^7
2.8×10^7
2.6×10^7
2.4×10^7
2.2×10^7
2.0×10^7
1.8×10^7
1.6×10^7
1.4×10^7
1.2×10^7
1.0×10^7
8.0×10^6
6.0×10^6
4.0×10^6
2.0×10^6
0.0
-2.0×10^6
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

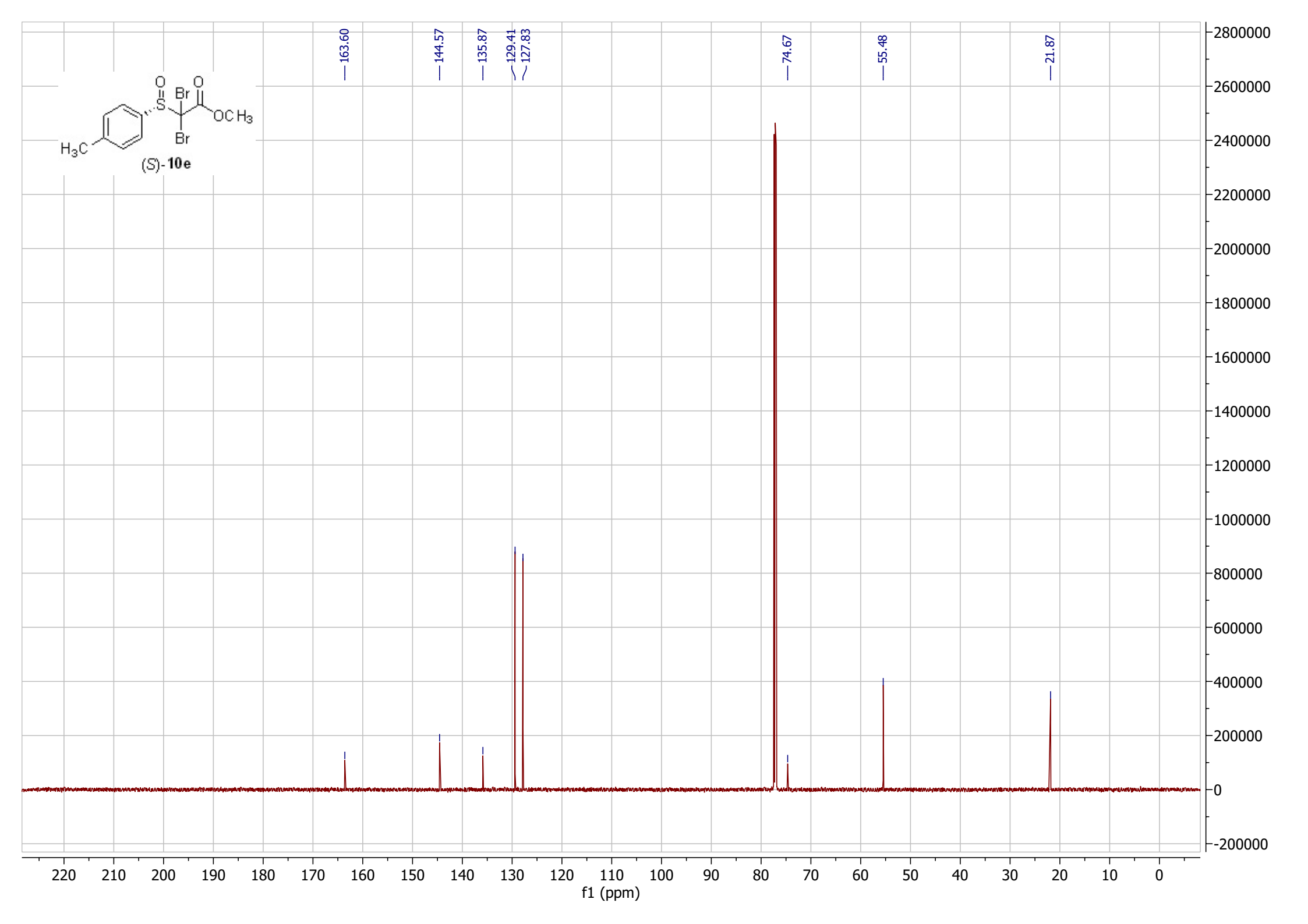

163.97
163.63
129.76
129.69
114.13
75.23
55.73
55.44
(S)-10 d
f1 (ppm)

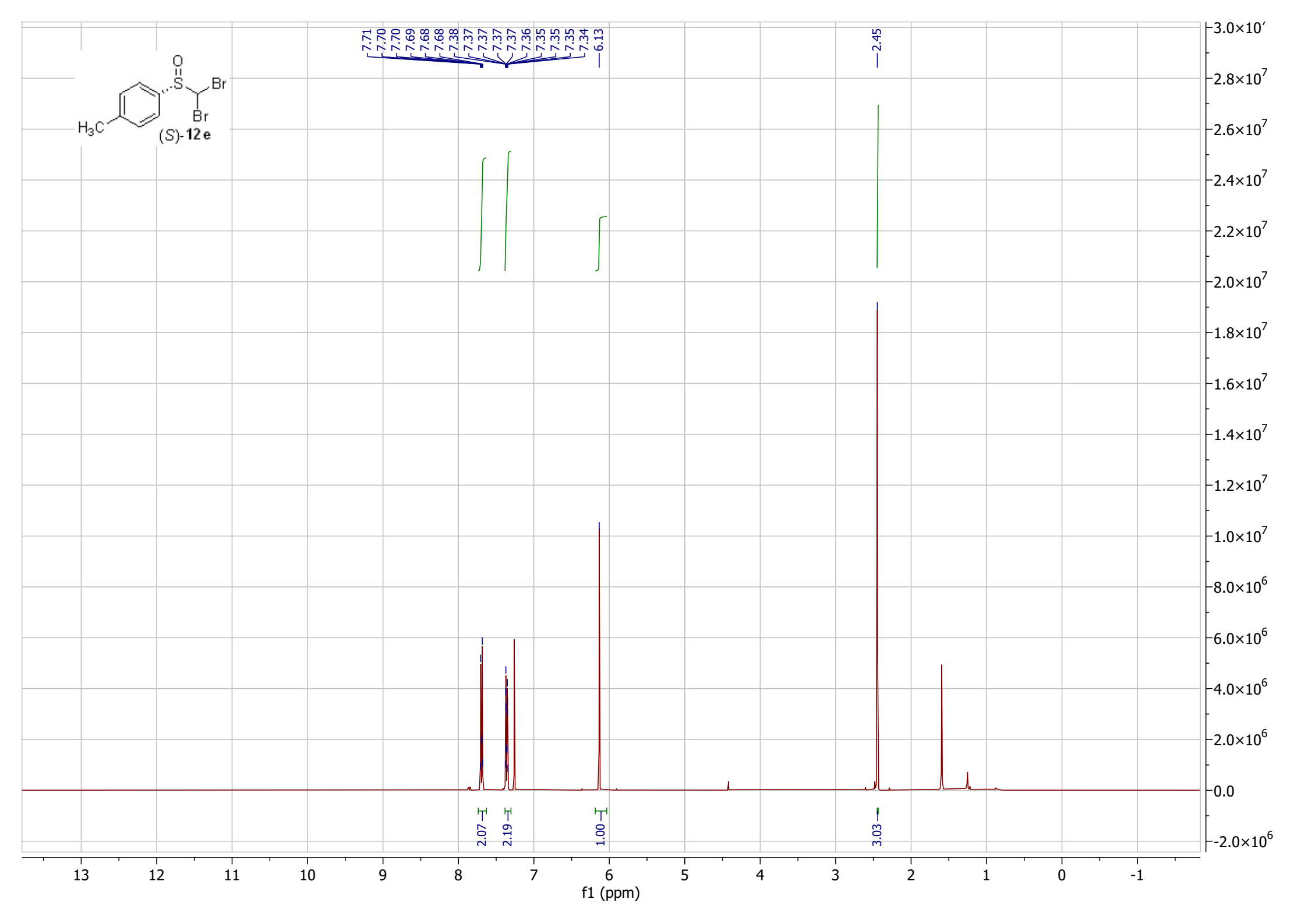

7.76
7.75
7.75
7.74
7.74
7.73
7.06
7.06
7.05
7.04
7.04
7.04
6.13
3.88
MeO
O
S
Br
Br
(S)-12d
1.86
1.91
1.00
3.09
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

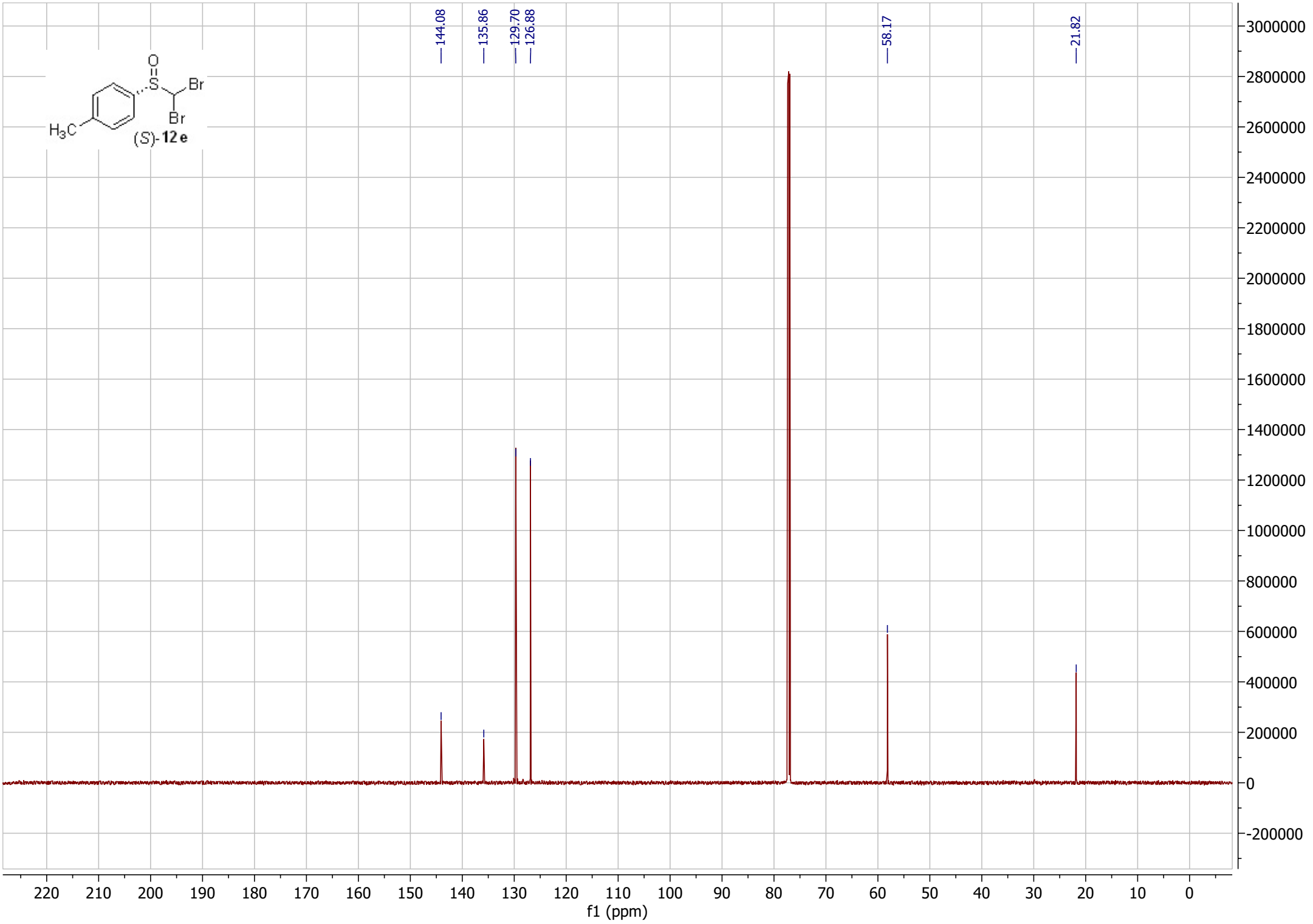

163.68
129.62
128.89
114.45
58.64
55.76
MeO
O
S
Br
Br
(S)-12d
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

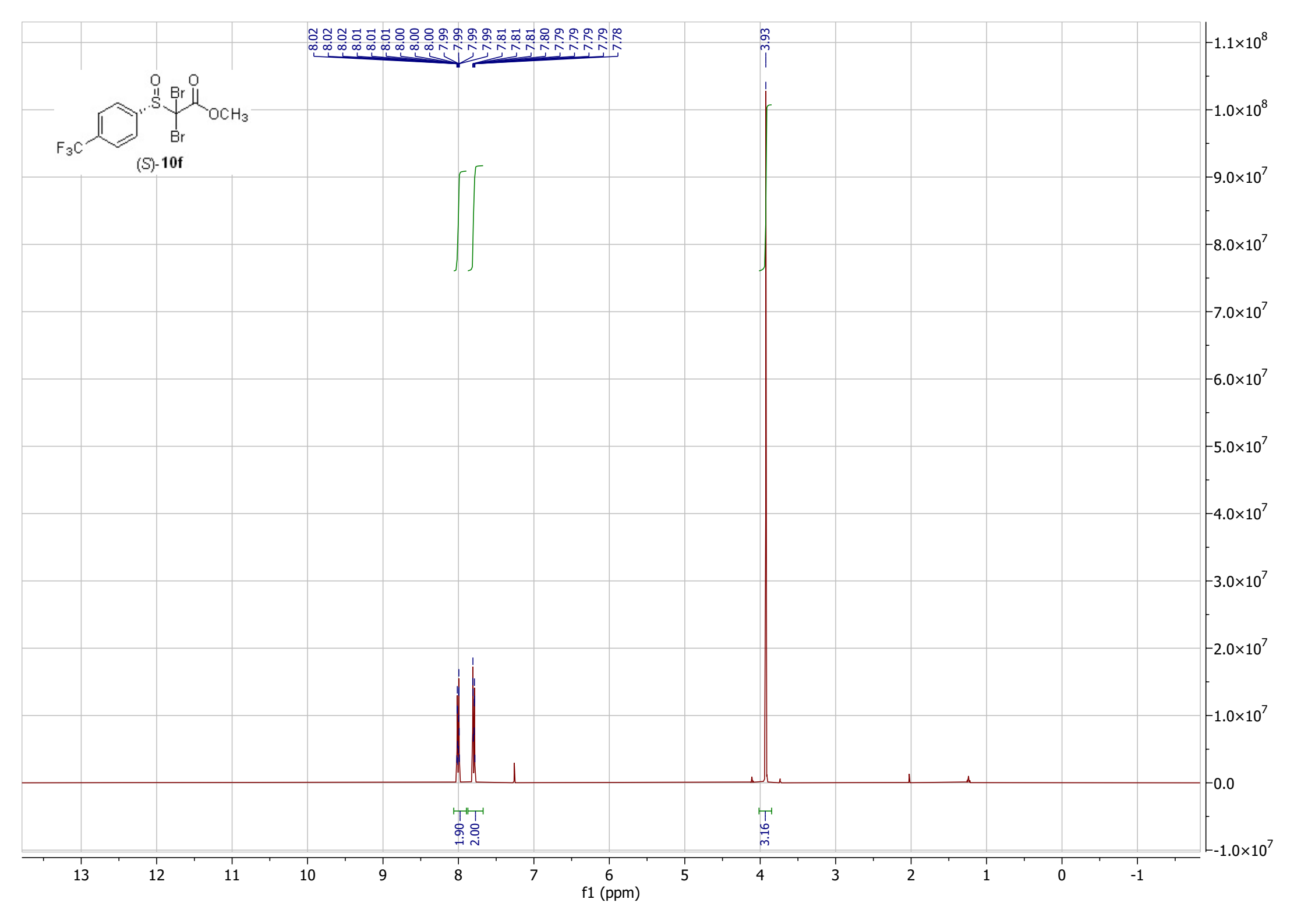

7.75
7.75
7.74
7.73
7.73
7.72
7.35
7.35
7.35
7.35
7.34
7.33
7.33
7.33
7.33
7.32
3.90
2.44
2.00
2.12
3.35
3.37
f1 (ppm)

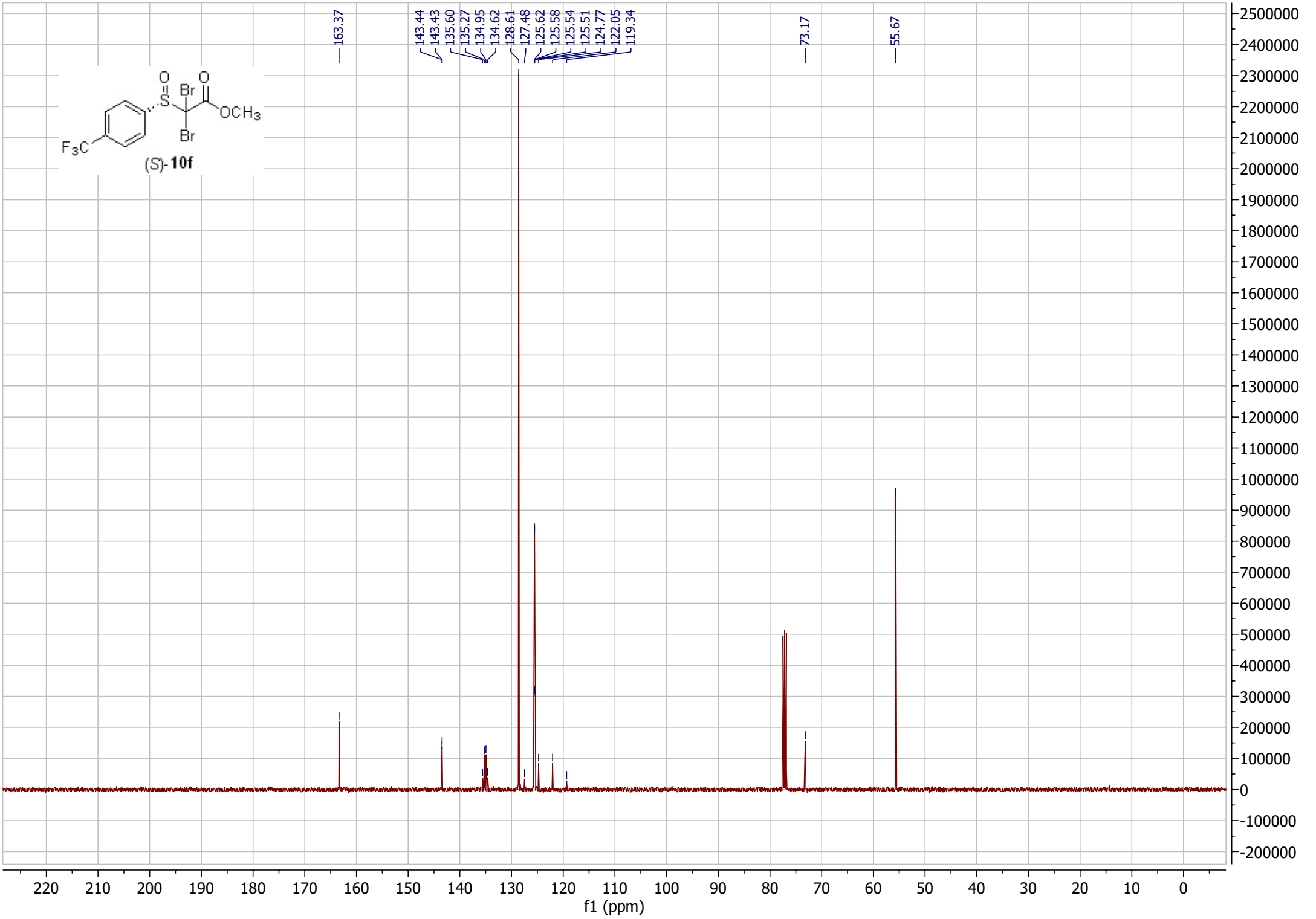
(*S*)-**10e**

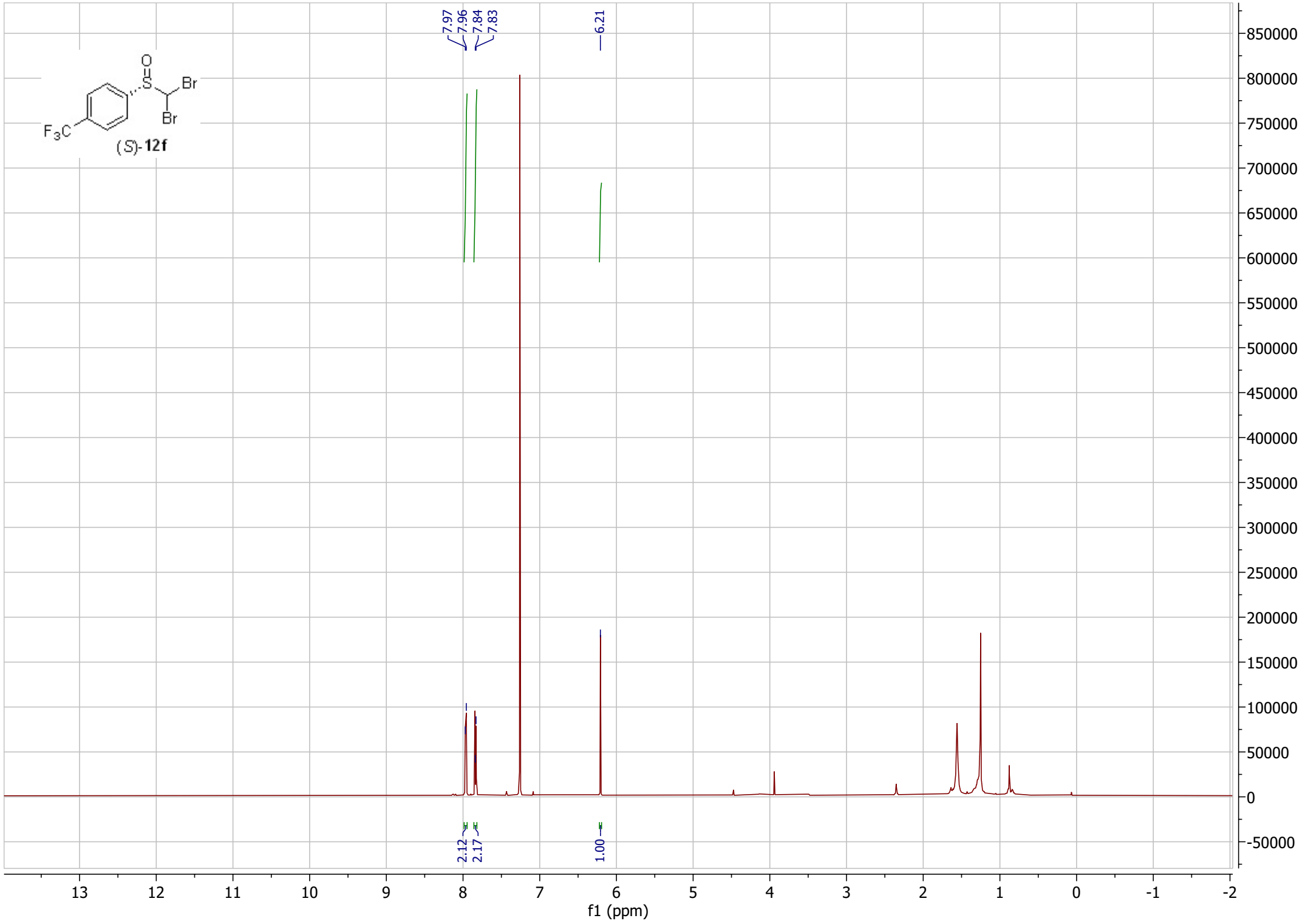

163.60
144.57
135.87
129.41
127.83
74.67
55.48
21.87
(S)-10e
f1 (ppm)

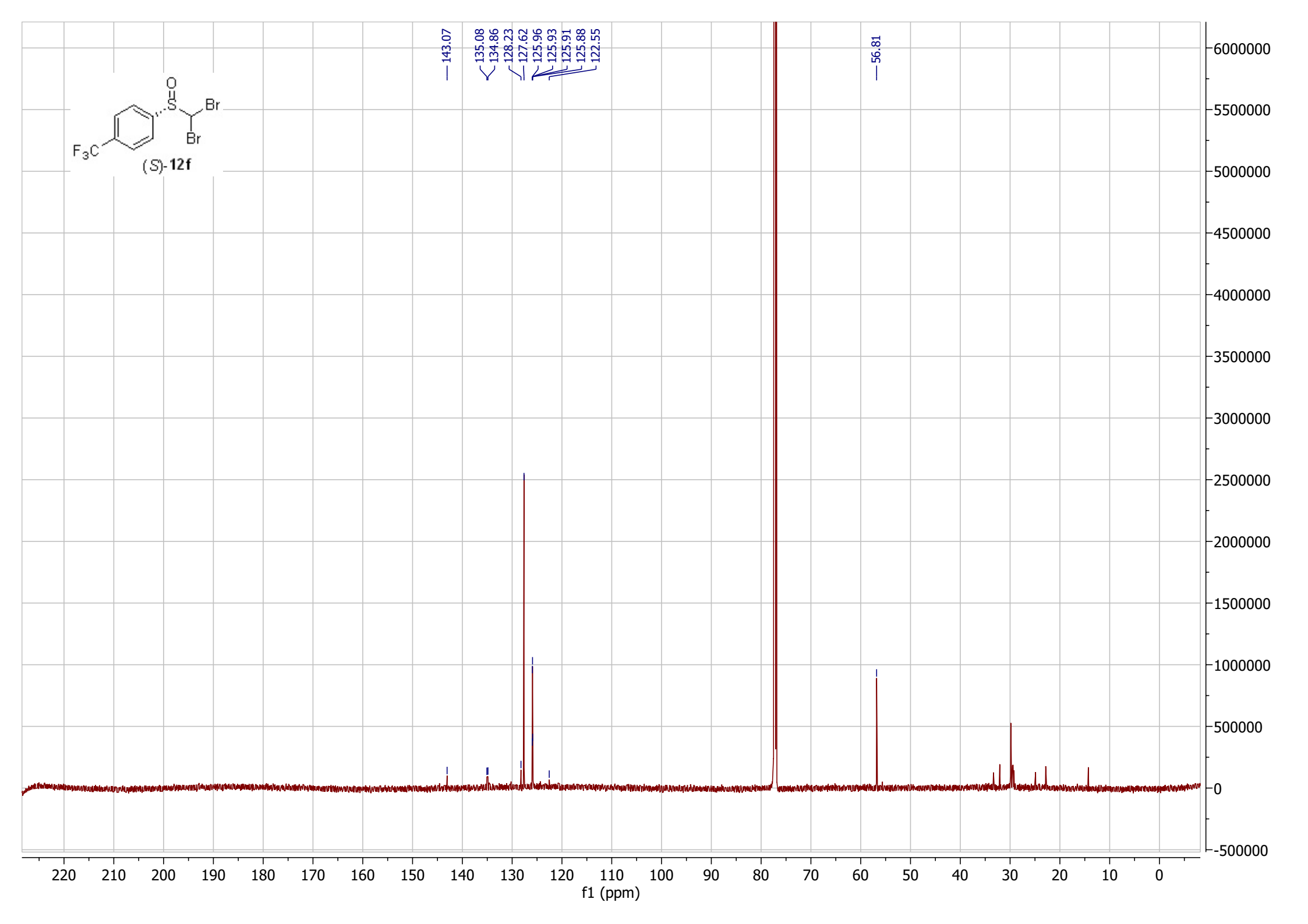

7.71
7.70
7.70
7.69
7.68
7.68
7.38
7.37
7.37
7.37
7.37
7.36
7.35
7.35
7.35
7.34
6.13
2.45
O
S
Br
Br
H3C
(S)-12e
2.07
2.19
1.00
3.03
3.0×10^7
2.8×10^7
2.6×10^7
2.4×10^7
2.2×10^7
2.0×10^7
1.8×10^7
1.6×10^7
1.4×10^7
1.2×10^7
1.0×10^7
8.0×10^6
6.0×10^6
4.0×10^6
2.0×10^6
0.0
-2.0×10^6
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

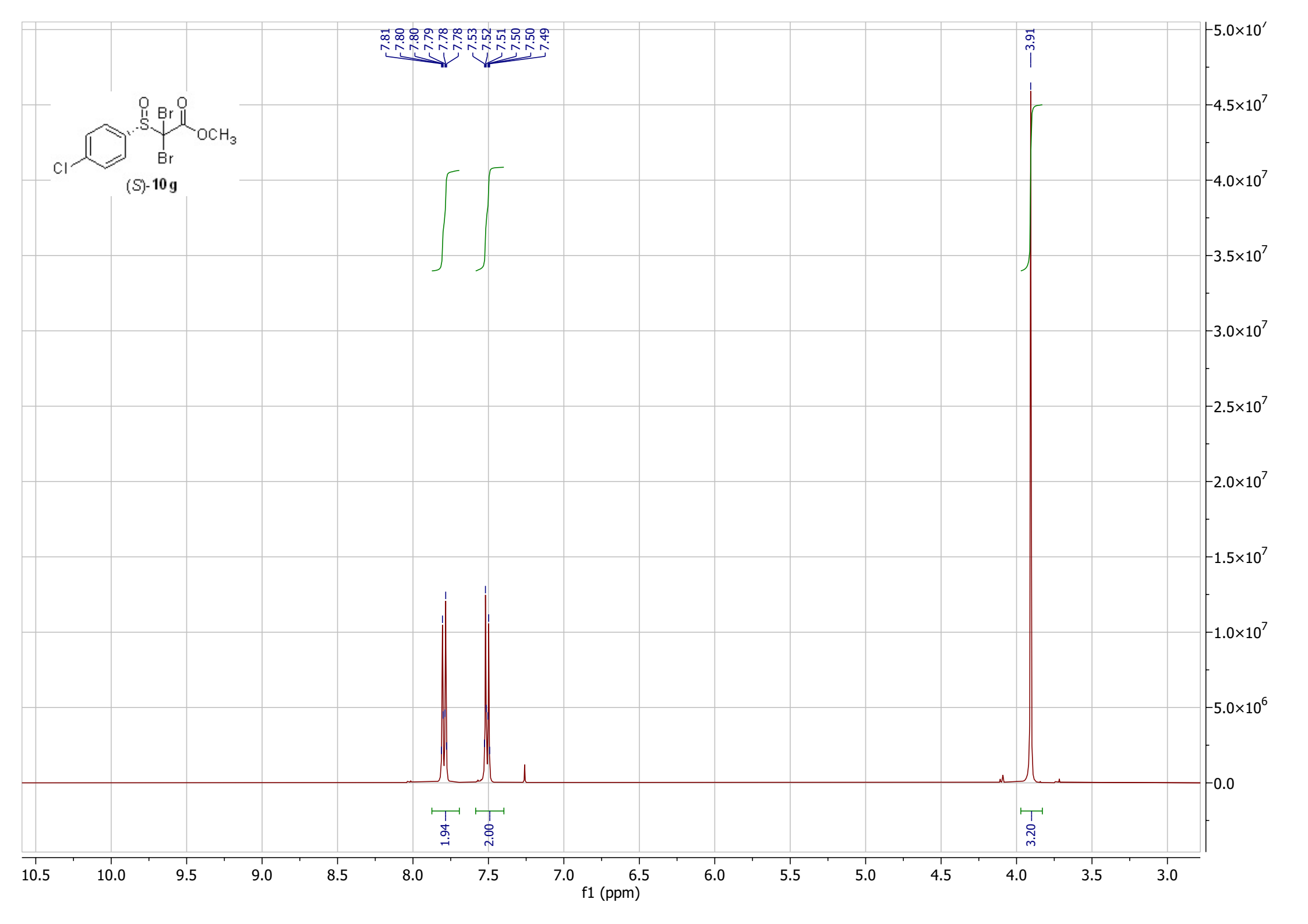

144.08
135.86
129.70
126.88
58.17
21.82
O
S
Br
Br
H3C
(S)-12e
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

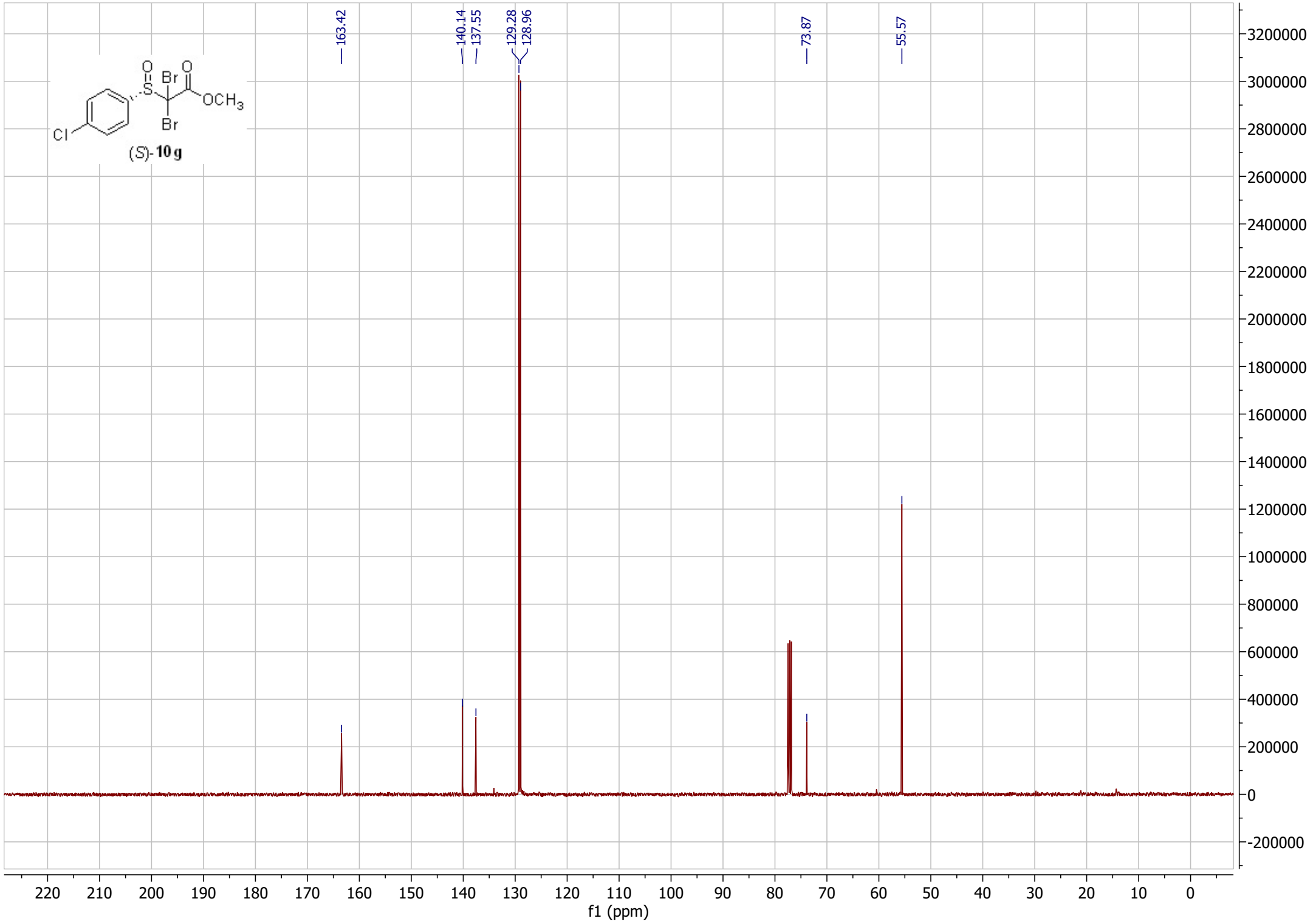

8.02
8.02
8.02
8.01
8.01
8.01
8.00
8.00
8.00
7.99
7.99
7.99
7.81
7.81
7.81
7.80
7.79
7.79
7.79
7.78
3.93
O
O
S
Br
OCH3
Br
F3C
(S)-10f
1.90
2.00
3.16
1.1×10^8
1.0×10^8
9.0×10^7
8.0×10^7
7.0×10^7
6.0×10^7
5.0×10^7
4.0×10^7
3.0×10^7
2.0×10^7
1.0×10^7
0.0
-1.0×10^7
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

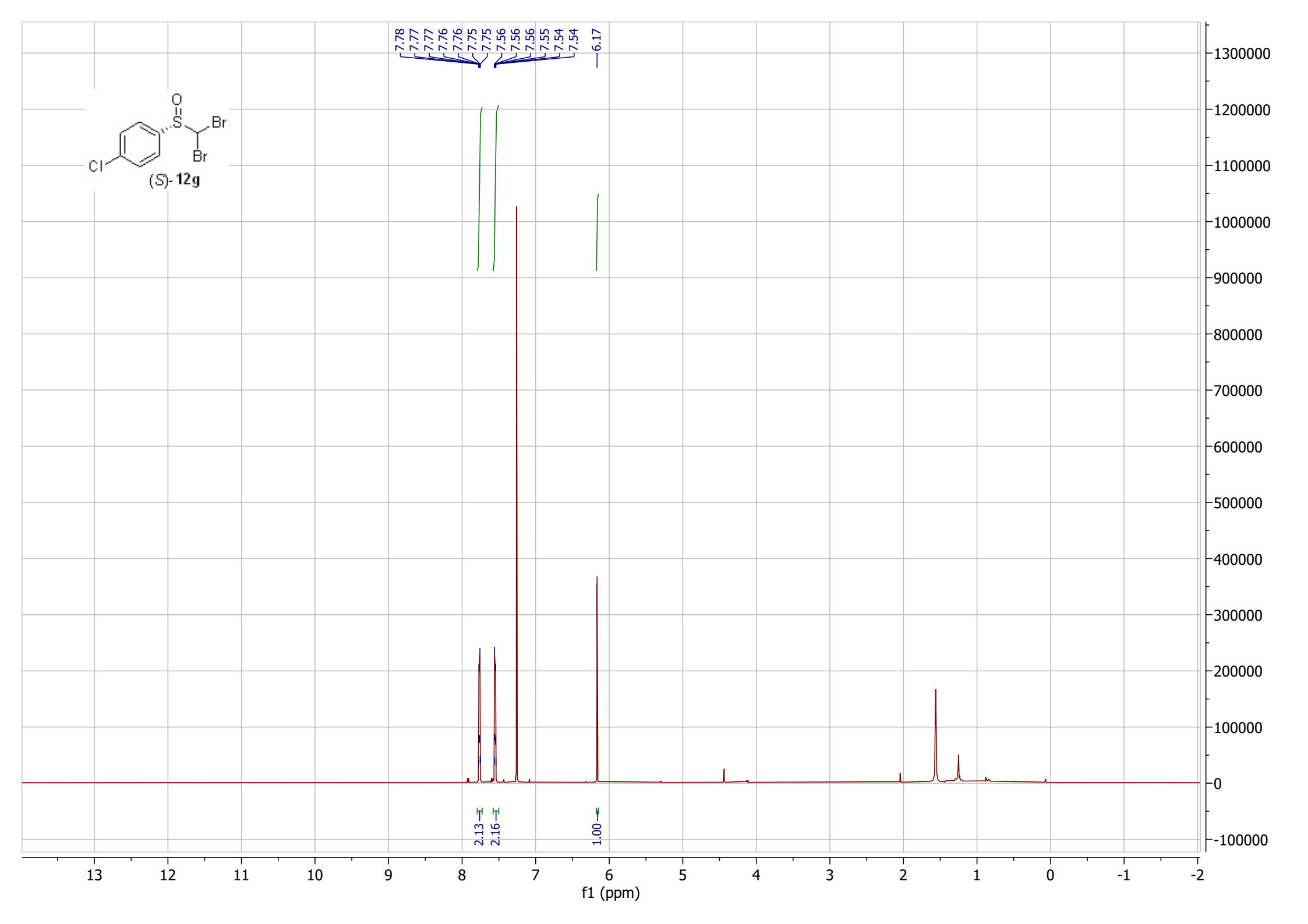

163.37
143.44
143.43
135.60
135.27
134.95
134.62
128.61
127.48
125.62
125.58
125.54
125.51
124.77
122.05
119.34
73.17
55.67
(S)-10f
f1 (ppm)

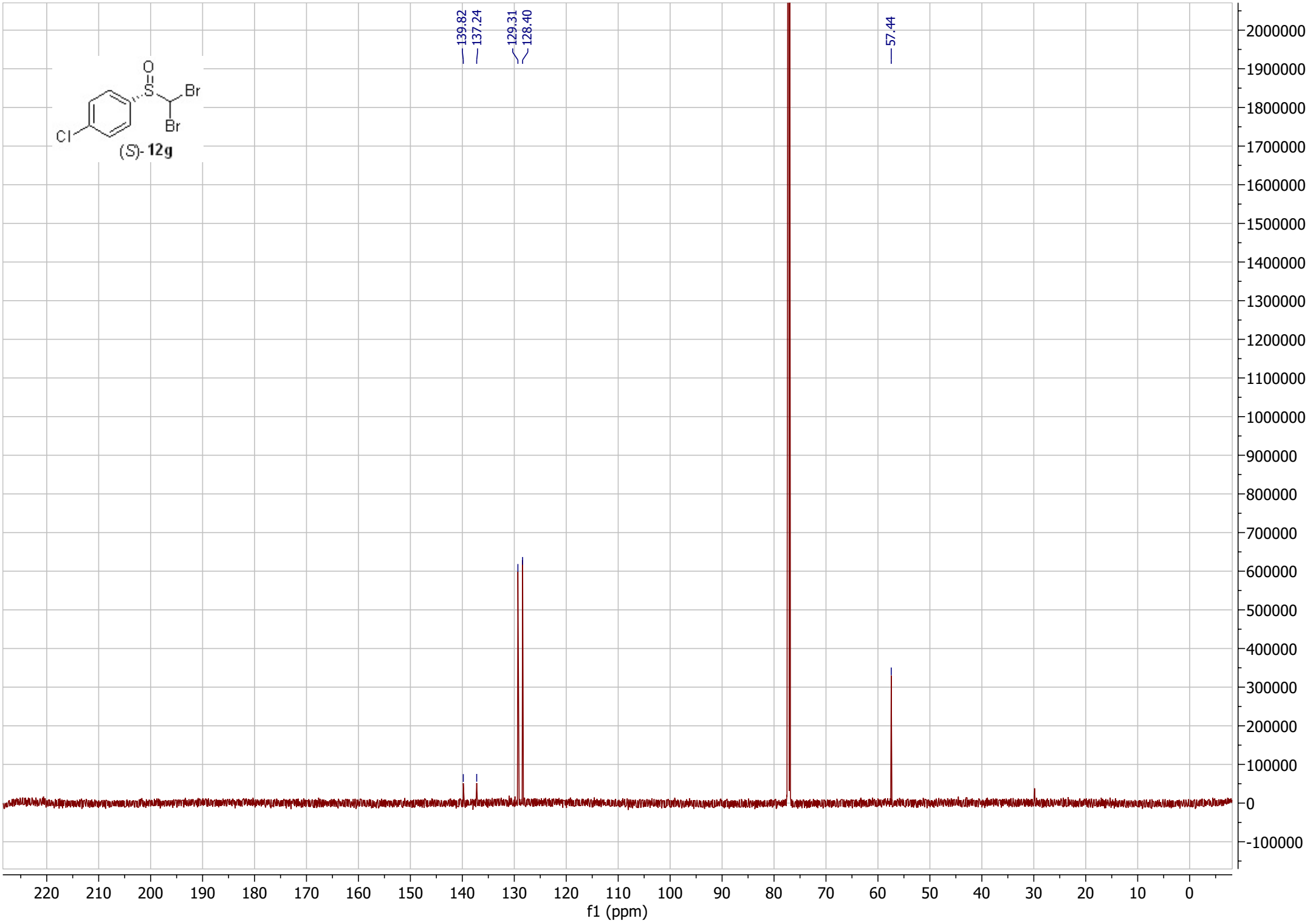

7.97
7.96
7.84
7.83
6.21
O
S
Br
Br
F3C
(S)-12f
2.12
2.17
1.00
850000
800000
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

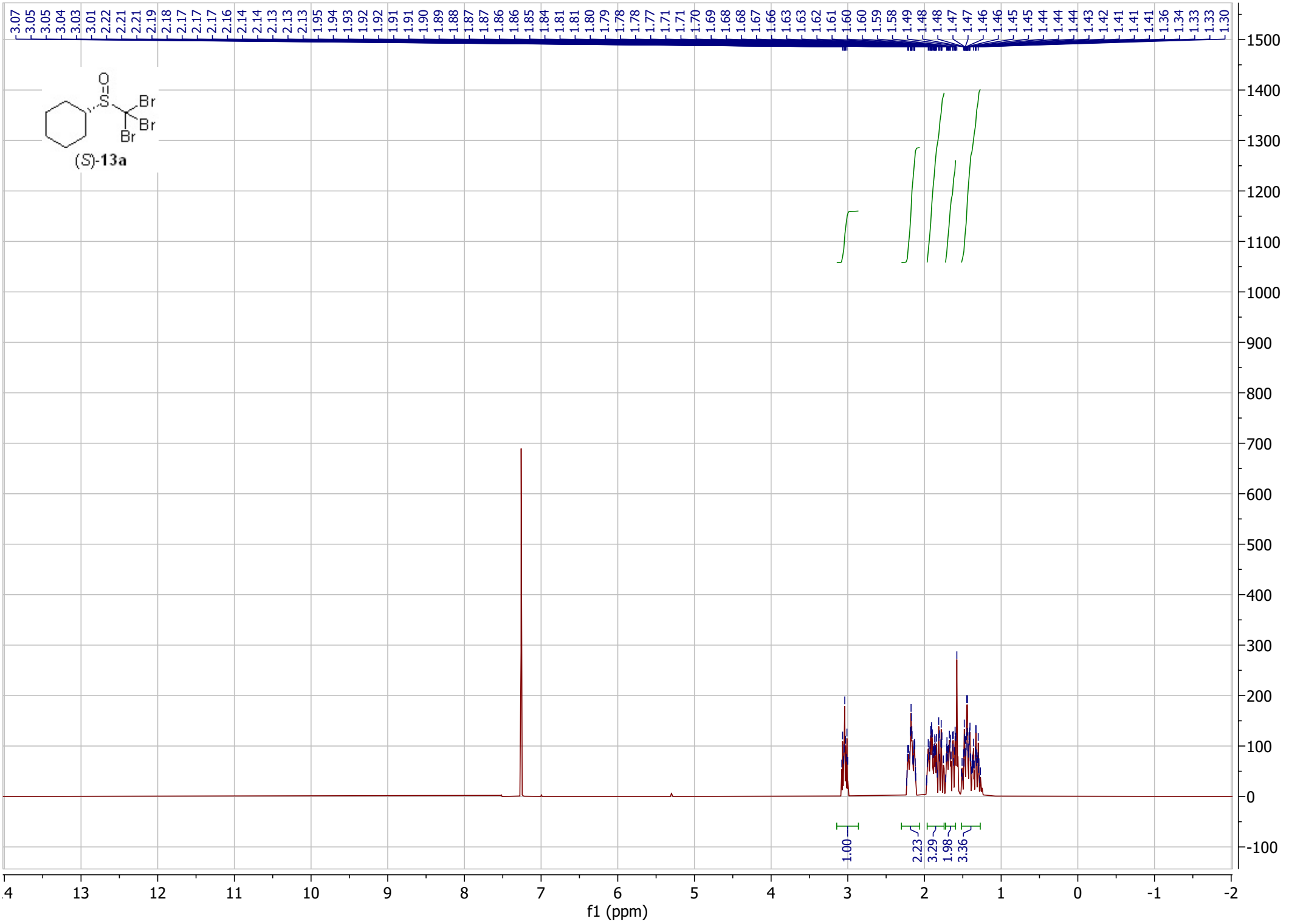

143.07
135.08
134.86
128.23
127.62
125.96
125.93
125.91
125.88
122.55
56.81
O
S
Br
Br
F3C
(S)-12f
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

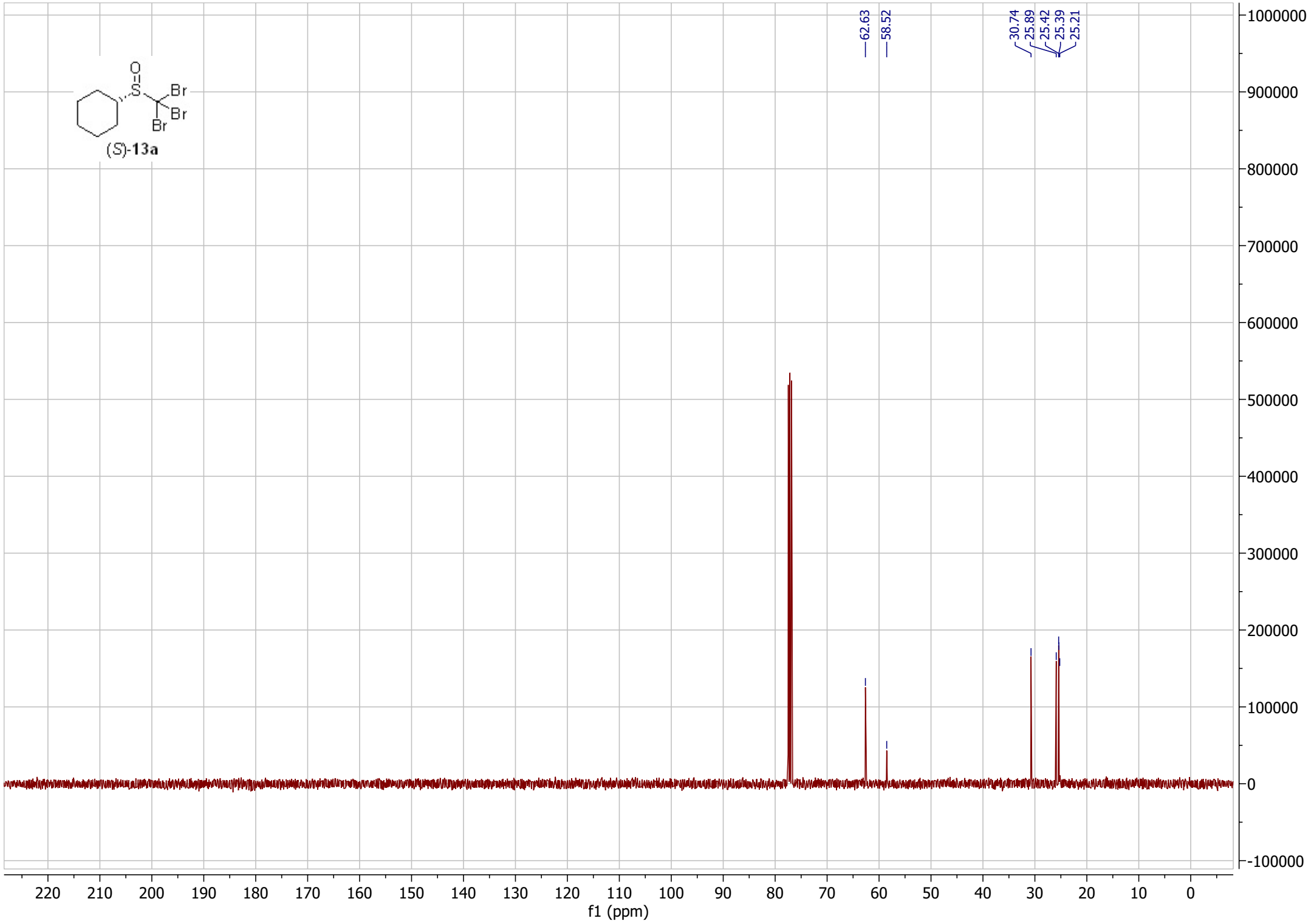

7.81
7.80
7.80
7.79
7.78
7.78
7.53
7.52
7.51
7.50
7.50
7.49
3.91
(S)-10g
1.94
2.00
3.20
f1 (ppm)

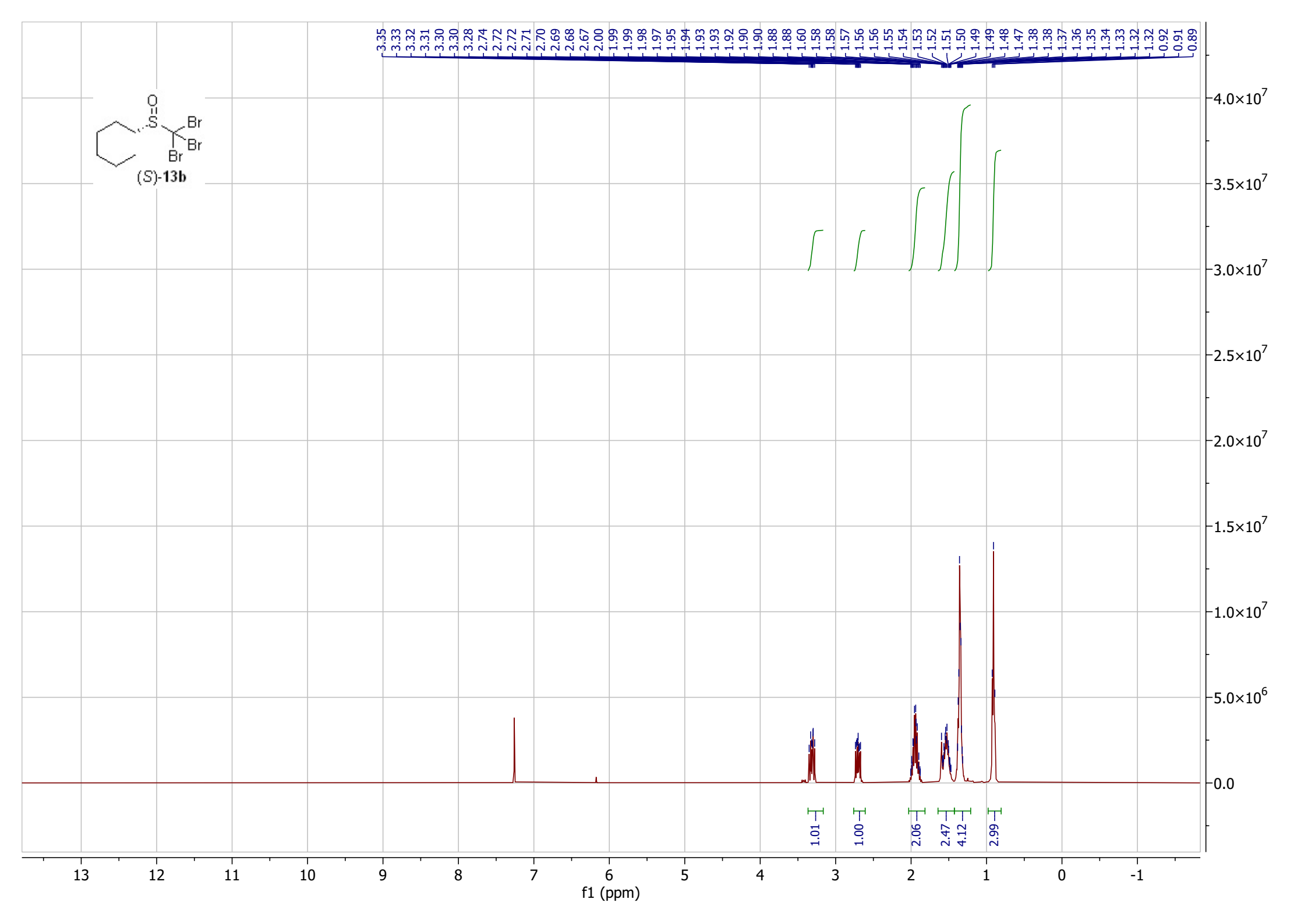

163.42
140.14
137.55
129.28
128.96
73.87
55.57
Cl
Br
Br
OCH3
(S)-10g
f1 (ppm)

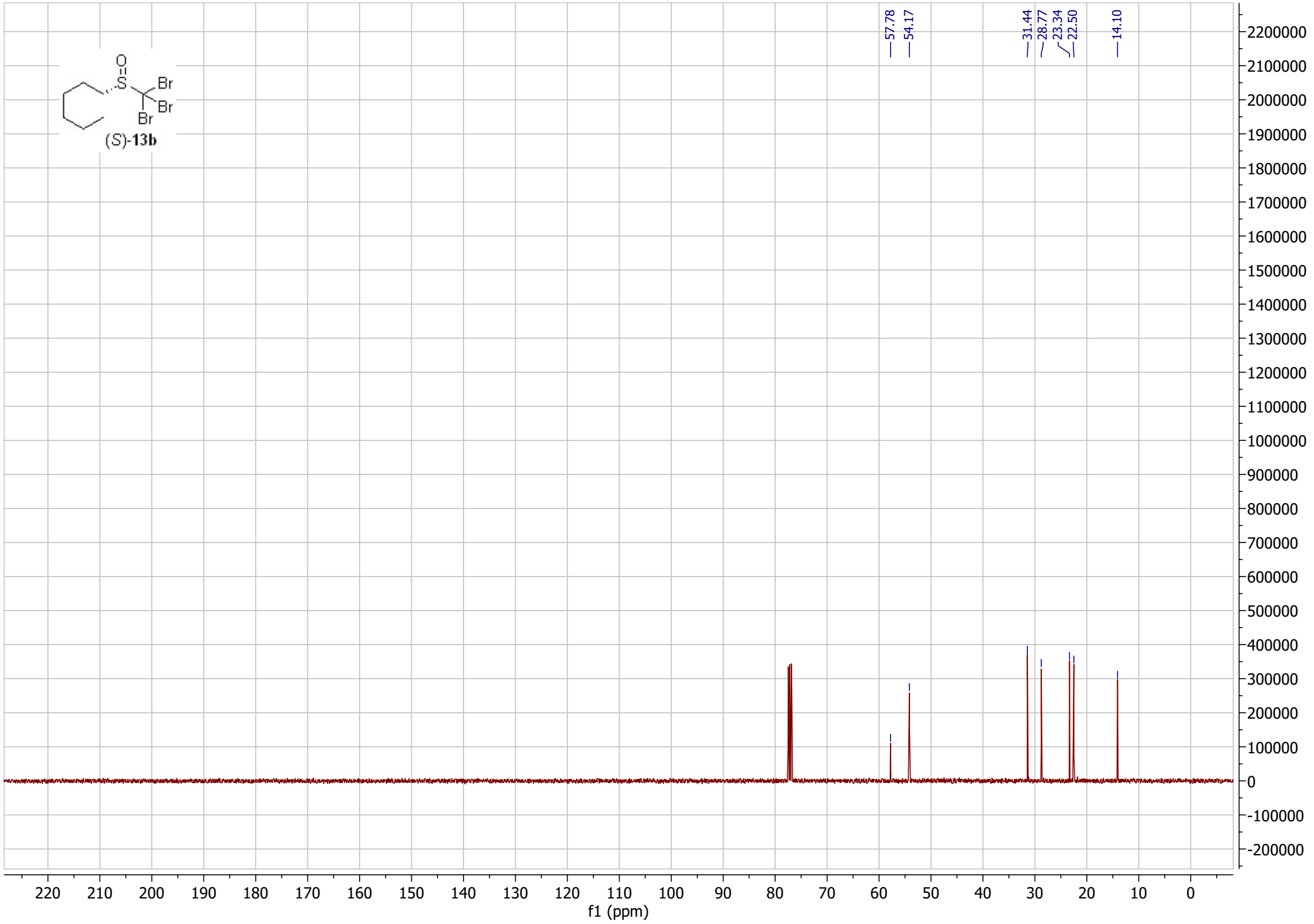

7.78
7.77
7.77
7.76
7.76
7.75
7.75
7.56
7.56
7.56
7.55
7.54
7.54
6.17
O
S
Br
Br
Cl
(S)-12g
2.13
2.16
1.00
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

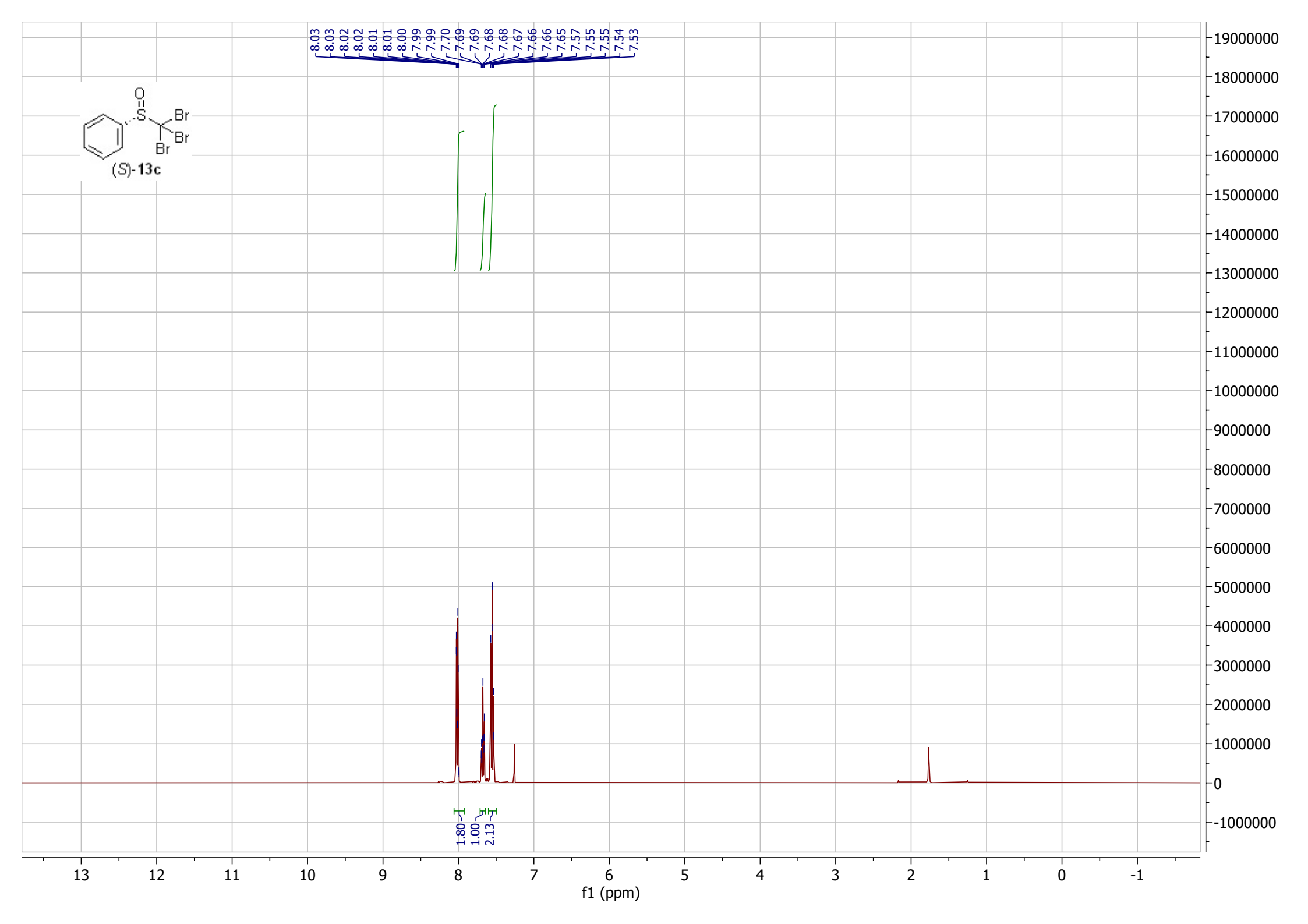

139.82
137.24
129.31
128.40
57.44
O
S
Br
Br
Cl
(S)-12g
2000000
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

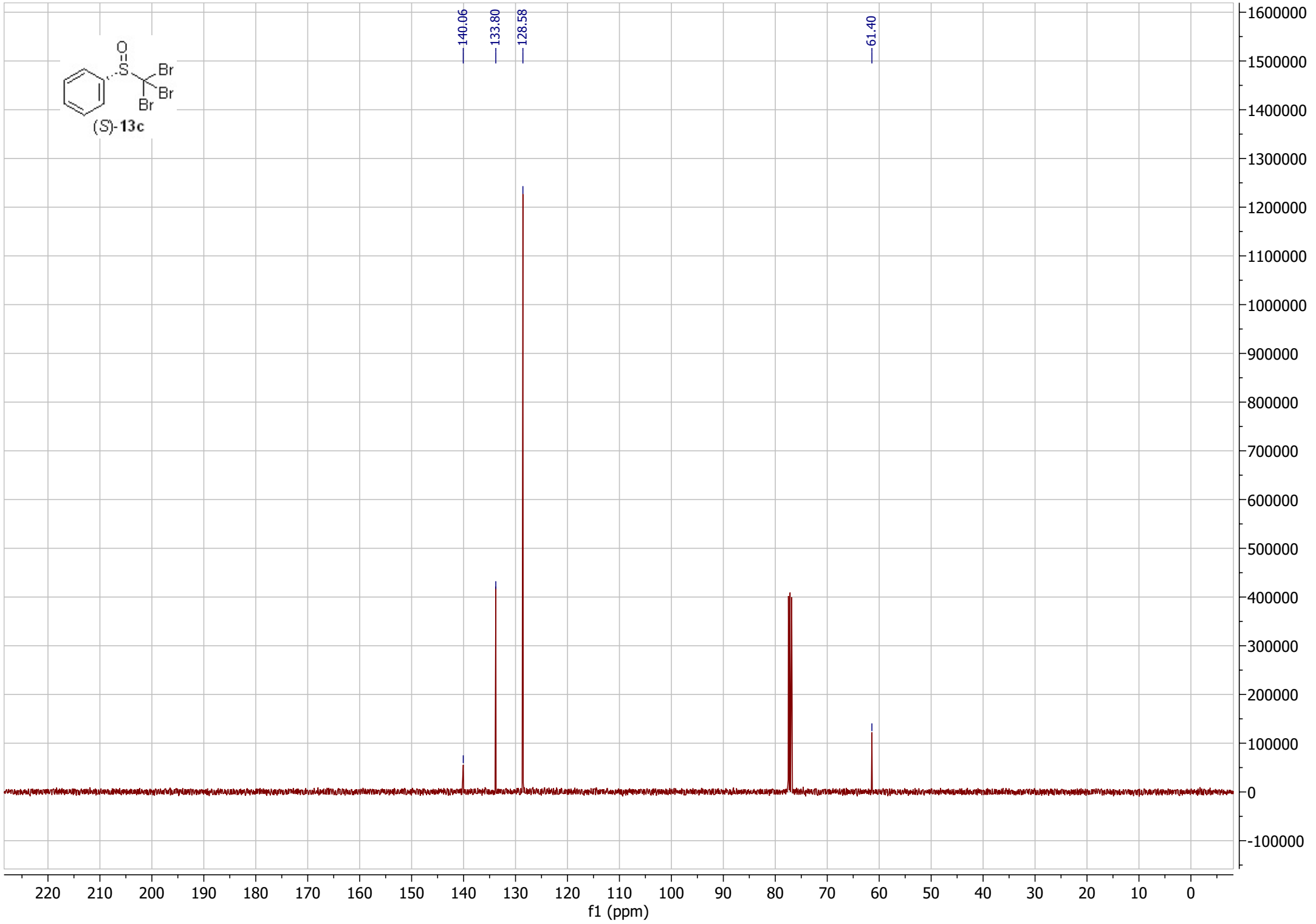

(S)-13a
f1 (ppm)
1.00
2.23
3.29
1.98
3.36

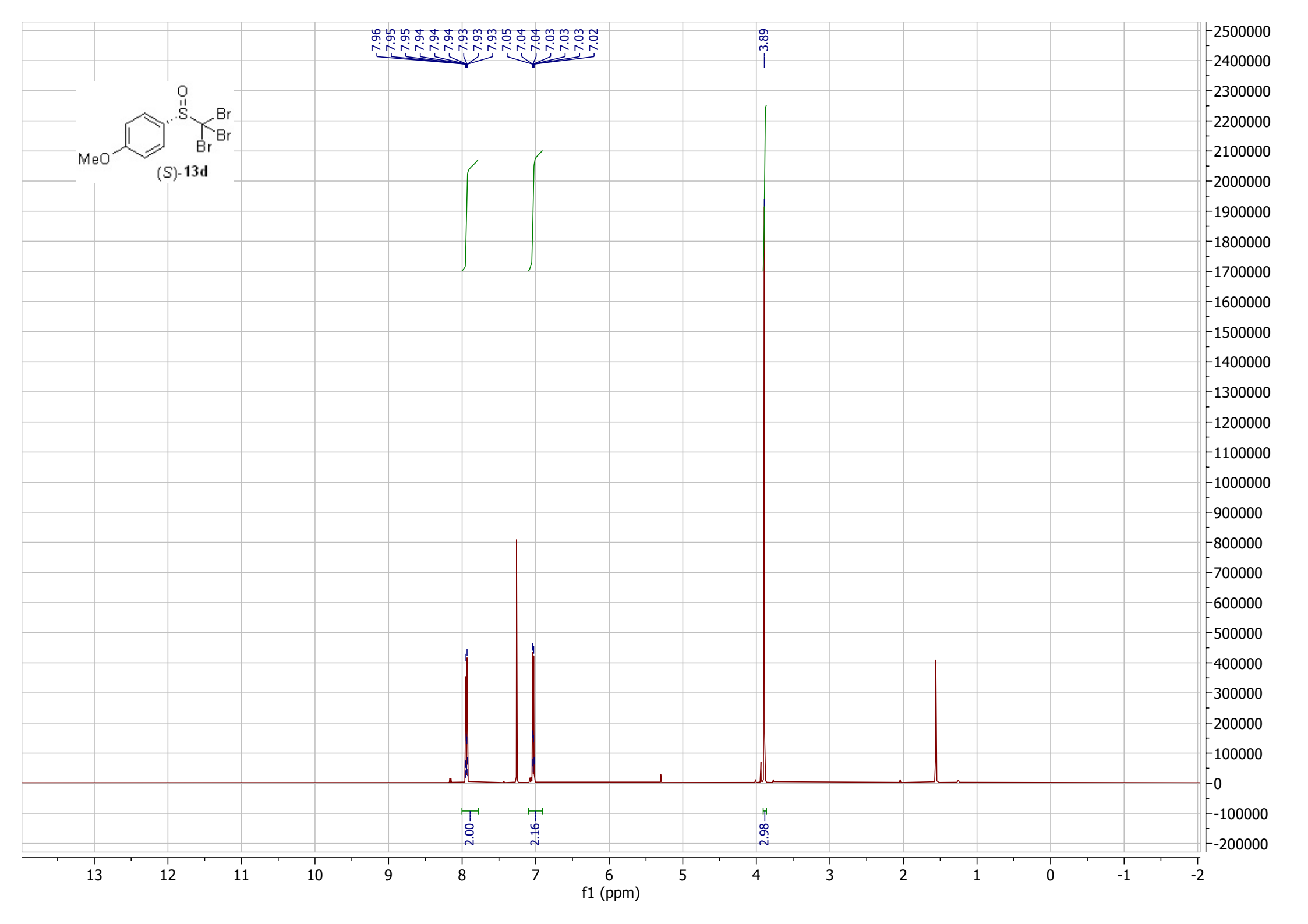

62.63
58.52
30.74
25.89
25.42
25.39
25.21
(S)-13a
f1 (ppm)

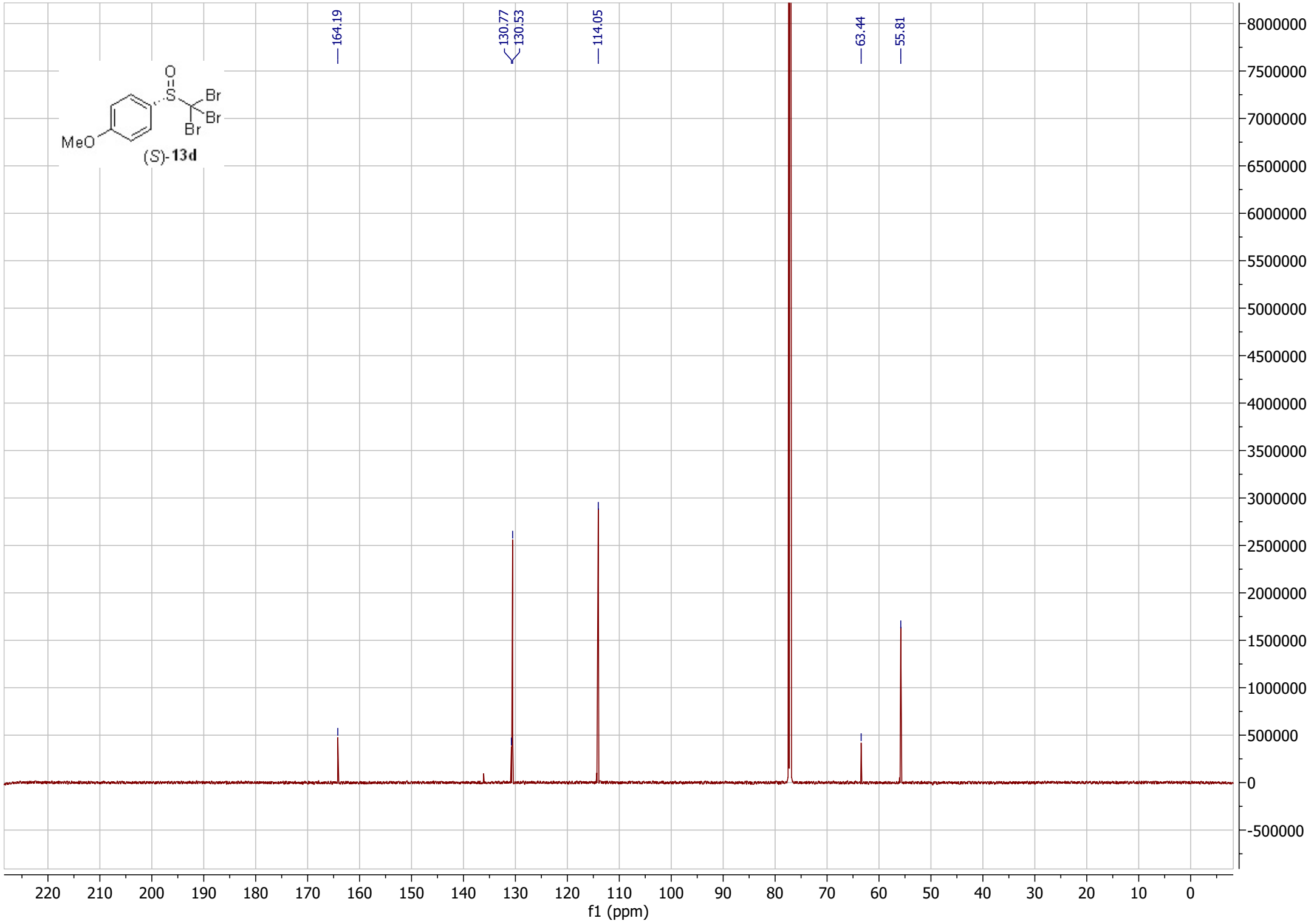

(S)-13b
f1 (ppm)
1.01
1.00
2.06
2.47
4.12
2.99

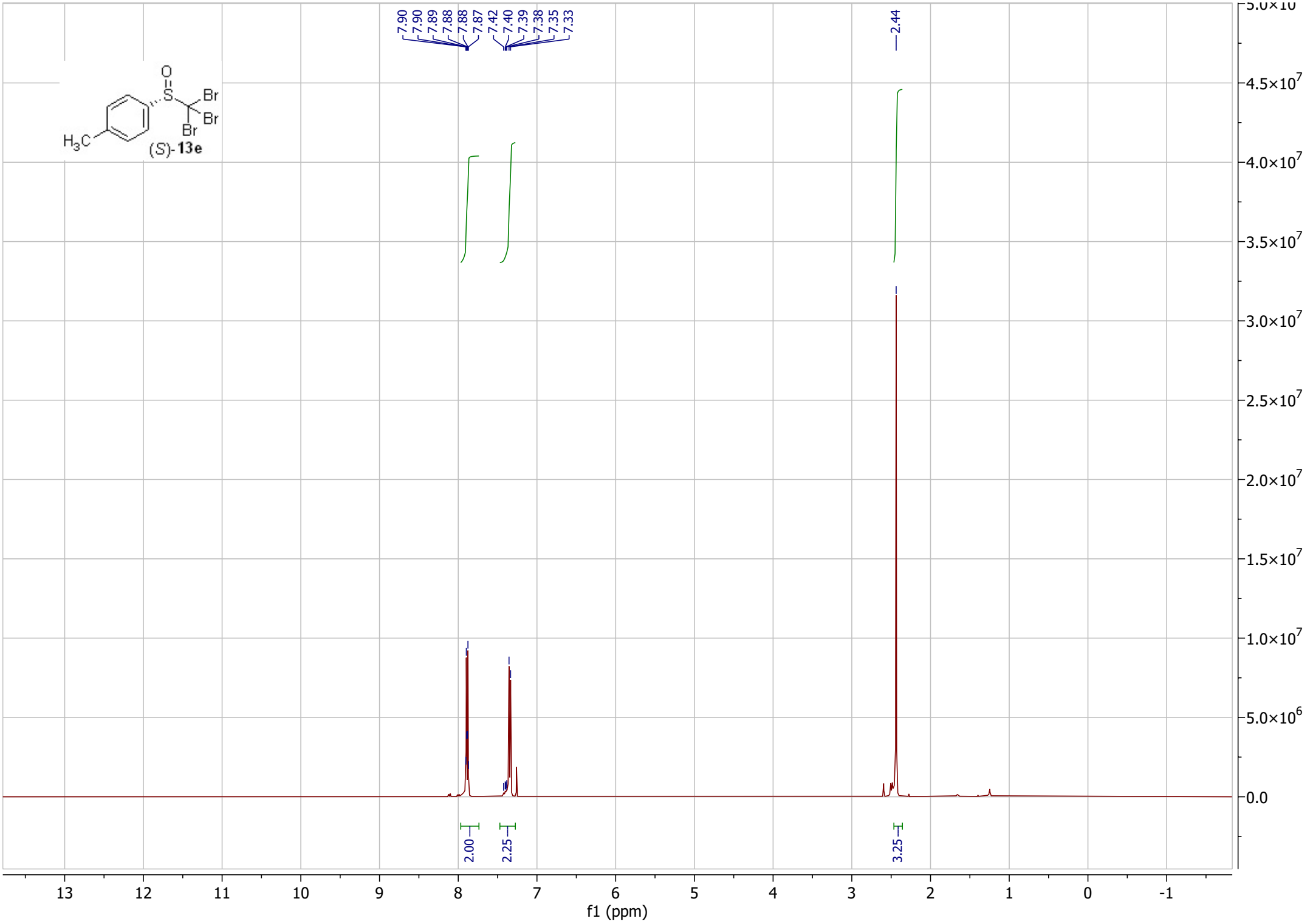

O
S
Br
Br
Br
(S)-13b
57.78
54.17
31.44
28.77
23.34
22.50
14.10
2200000
2100000
2000000
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
-200000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

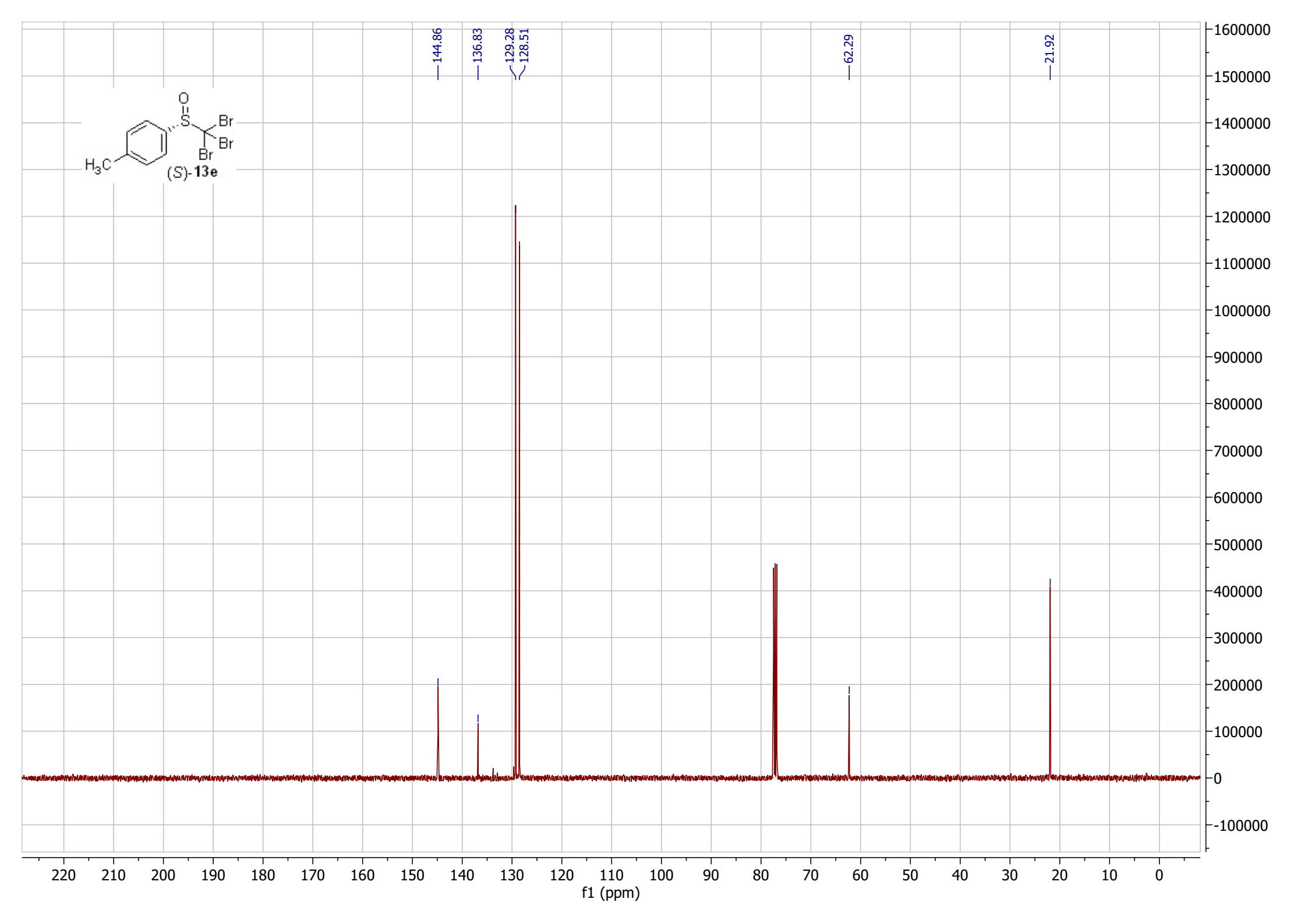

8.03
8.03
8.02
8.02
8.01
8.01
8.00
7.99
7.99
7.70
7.69
7.69
7.68
7.68
7.67
7.66
7.66
7.65
7.57
7.55
7.55
7.54
7.53
O
S
Br
Br
Br
(S)-13c
1.80
1.00
2.13
19000000
18000000
17000000
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

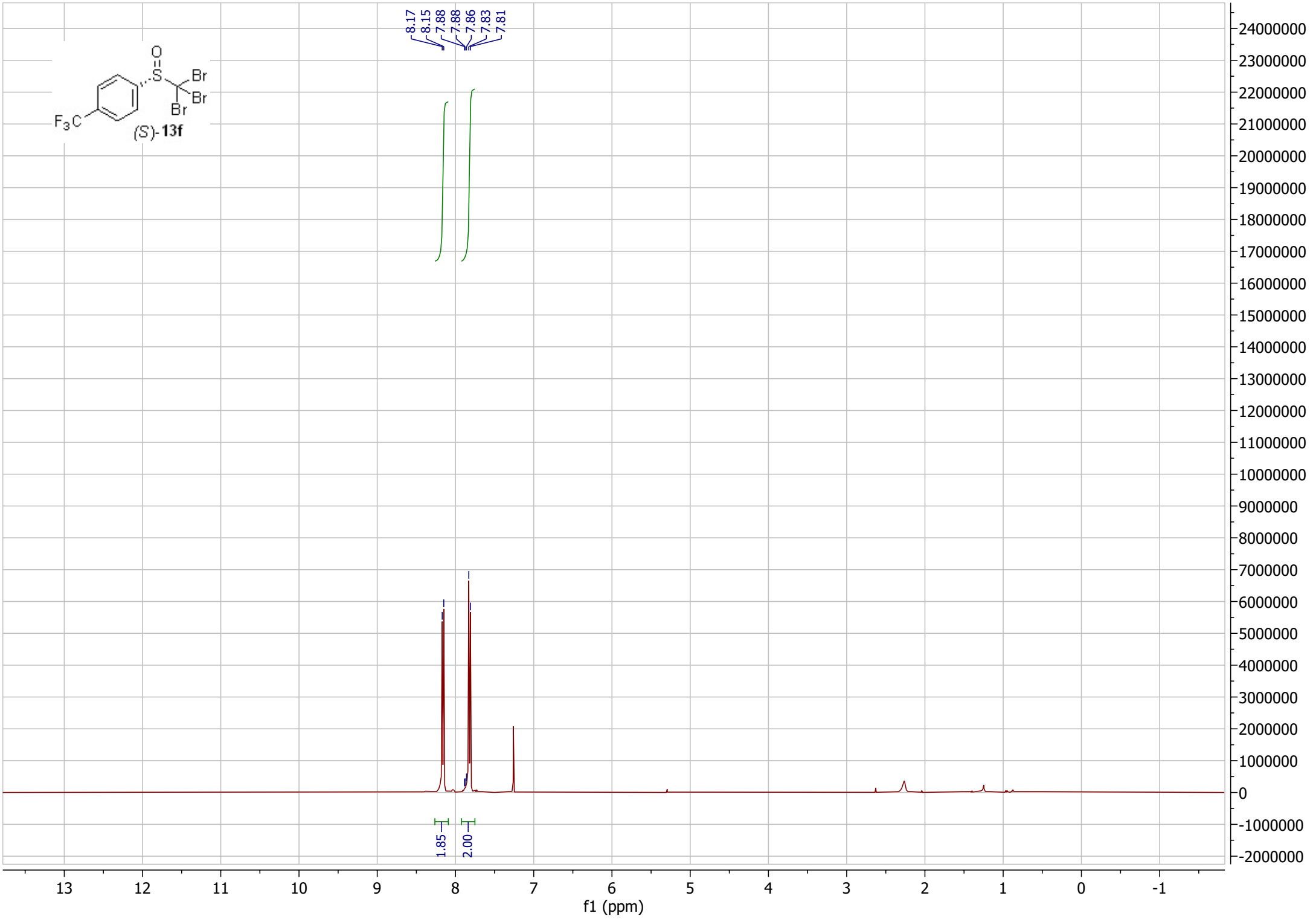

140.06
133.80
128.58
61.40
O
S
Br
Br
Br
(S)-13c
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

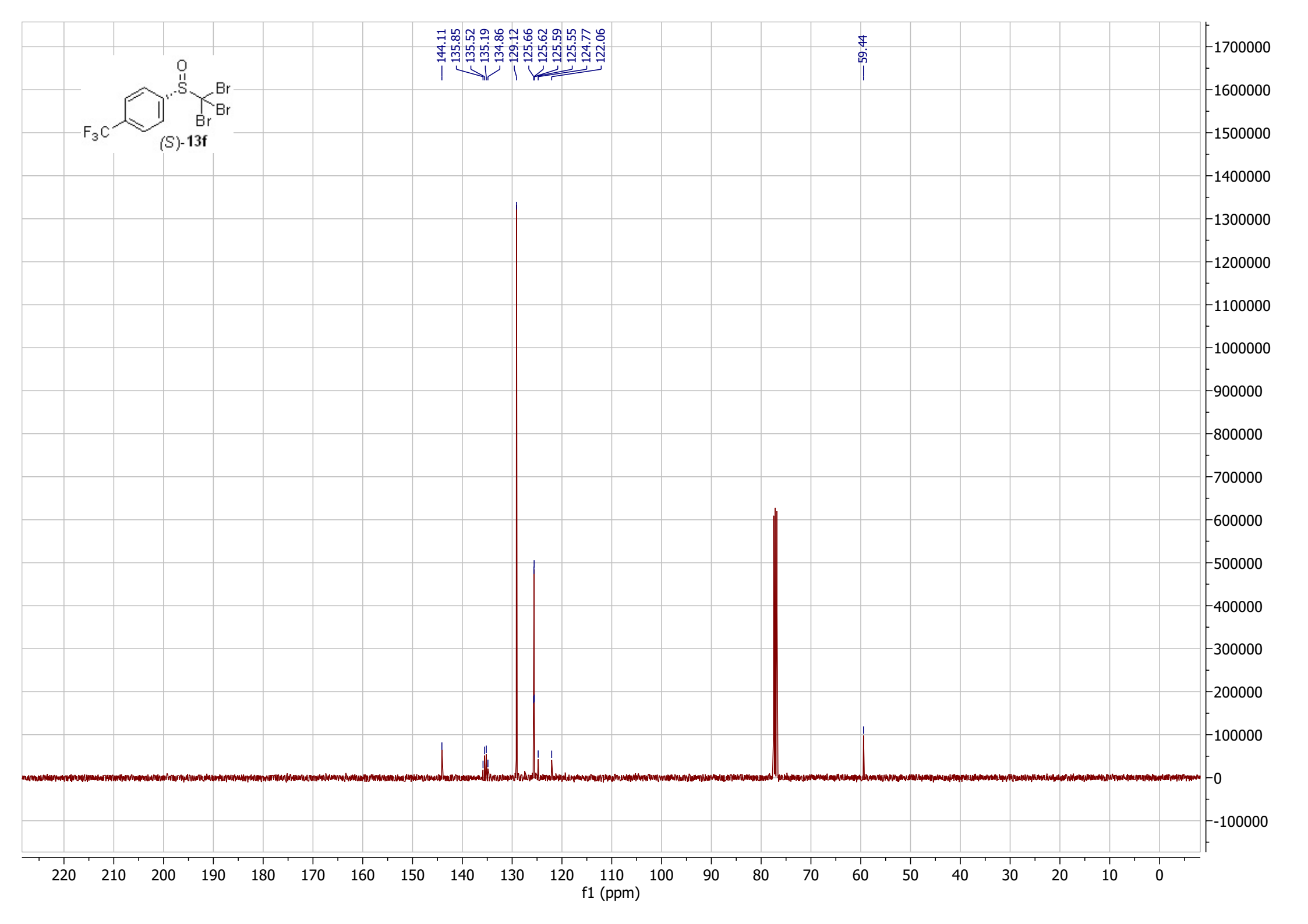

7.96
7.95
7.95
7.94
7.94
7.94
7.93
7.93
7.93
7.05
7.04
7.04
7.03
7.03
7.03
7.02
3.89
O
S
Br
Br
Br
MeO
(S)-13d
2.00
2.16
2.98
2500000
2400000
2300000
2200000
2100000
2000000
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
-200000
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

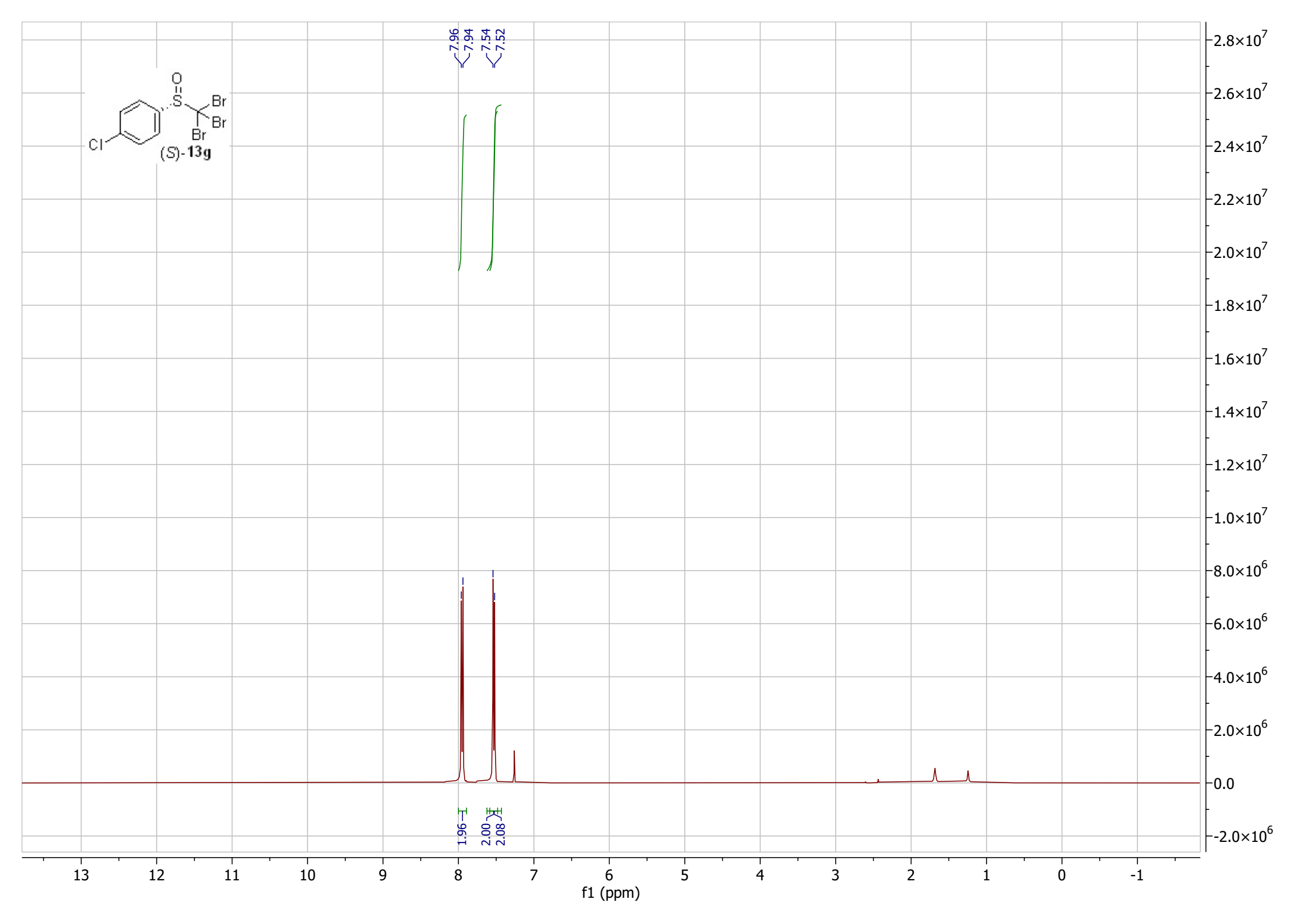

164.19
130.77
130.53
114.05
63.44
55.81
O
S
Br
Br
Br
MeO
(S)-13d
8000000
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

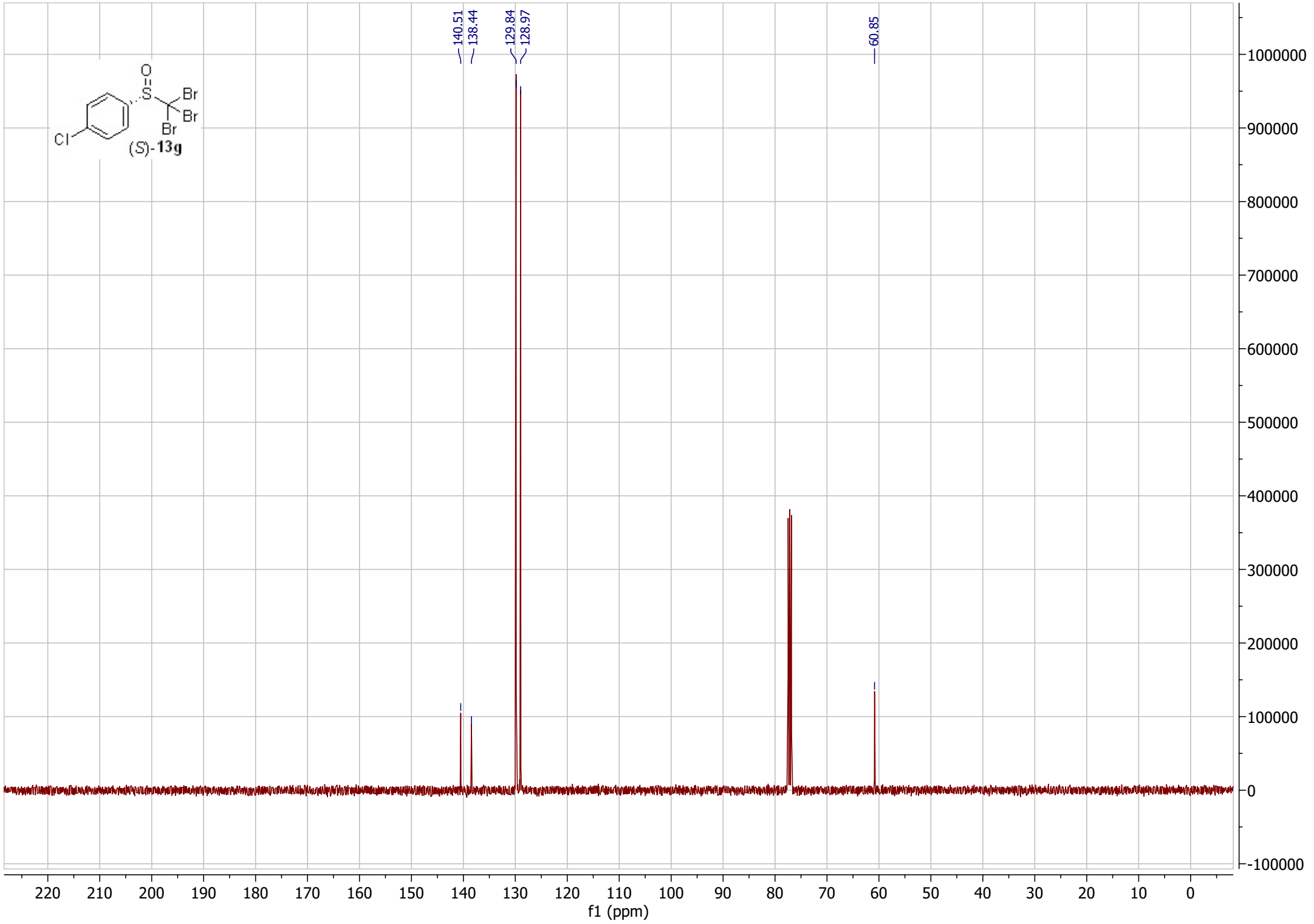

7.90
7.90
7.89
7.88
7.88
7.87
7.42
7.40
7.39
7.38
7.35
7.33
2.44
O
S
Br
Br
Br
H3C
(S)-13e
2.00
2.25
3.25
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

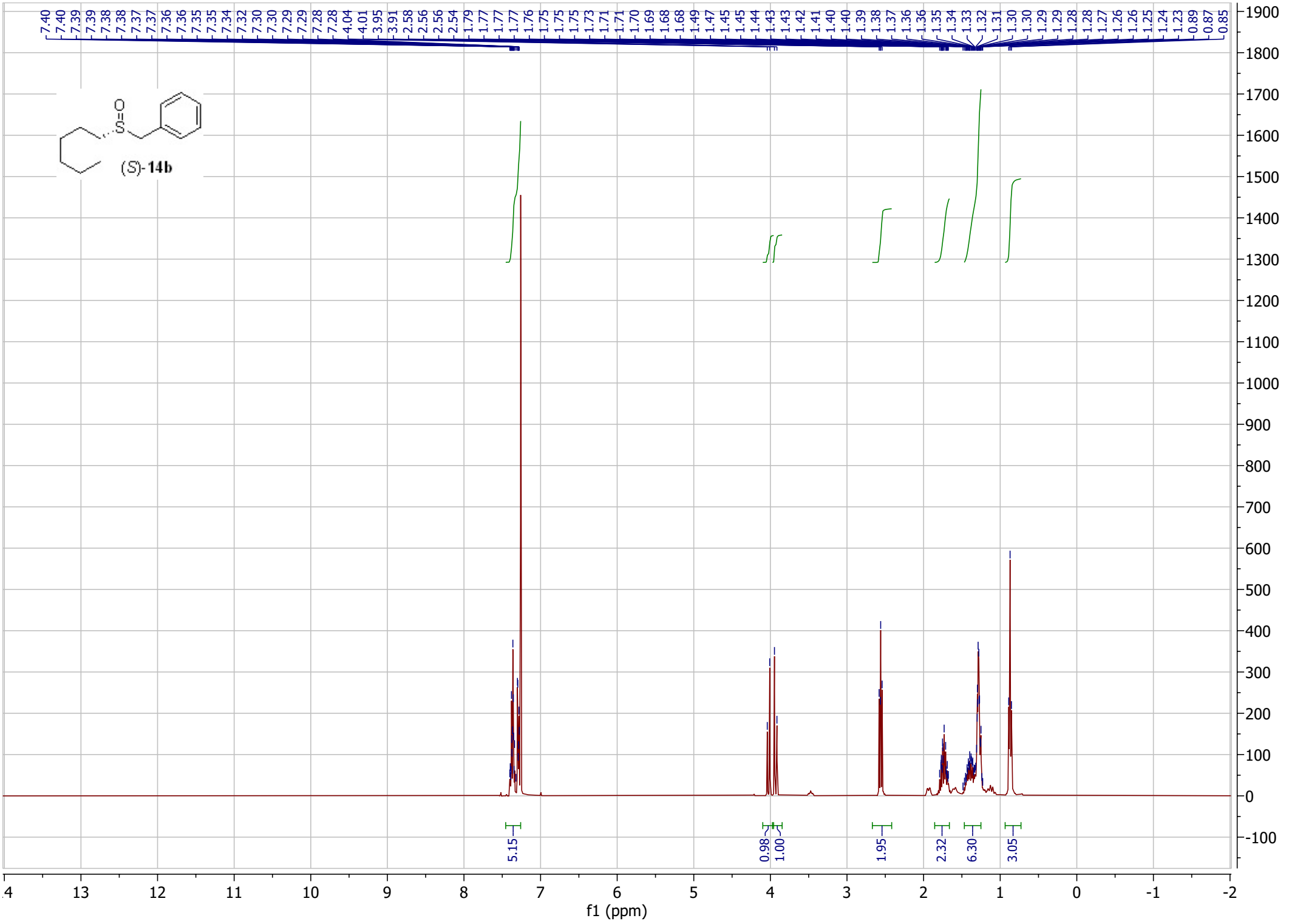

144.86
136.83
129.28
128.51
62.29
21.92
O
S
Br
Br
Br
H3C
(S)-13e
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

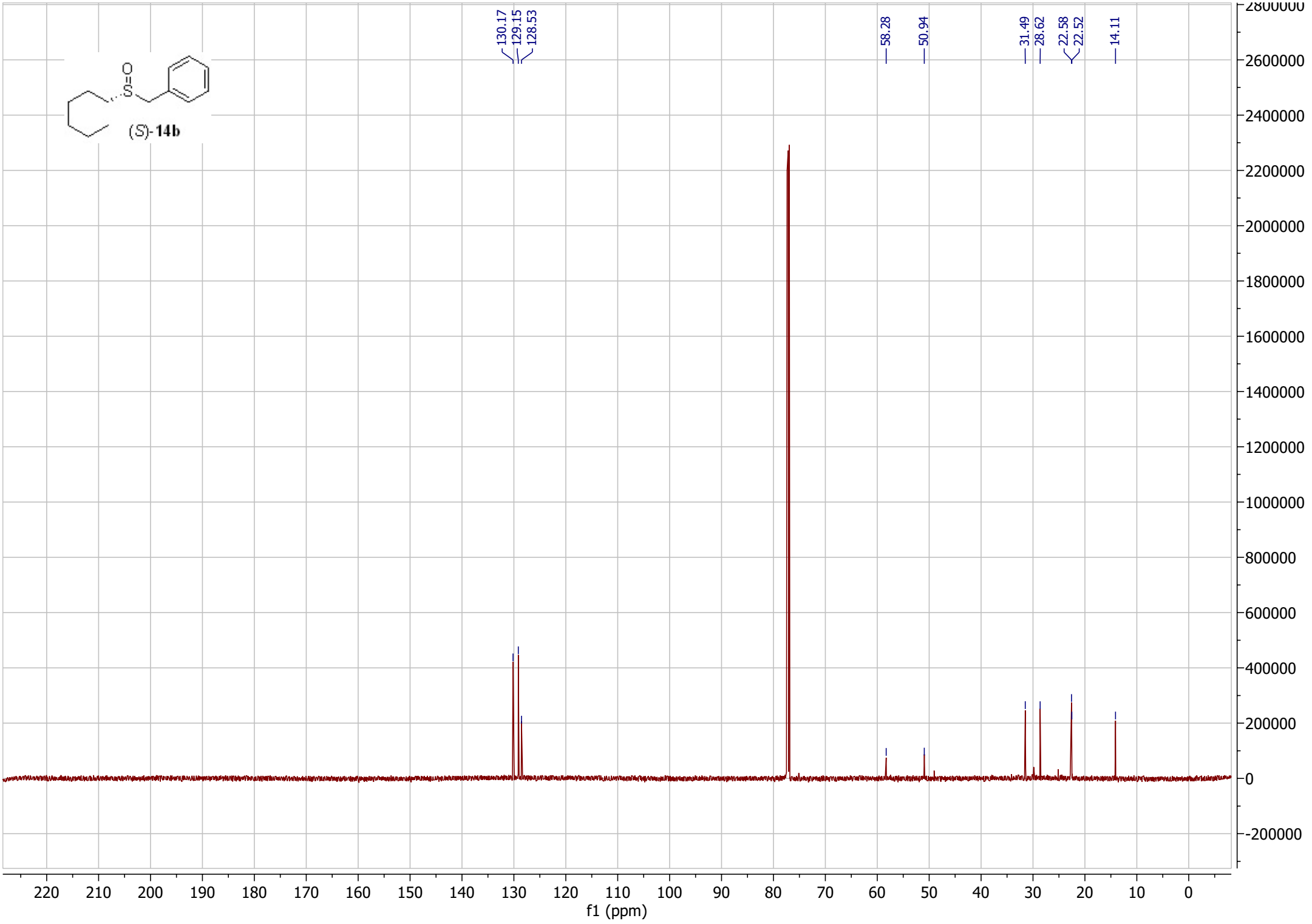

8.17
8.15
7.88
7.88
7.86
7.83
7.81
O
S
Br
Br
Br
F3C
(S)-13f
1.85
2.00
f1 (ppm)

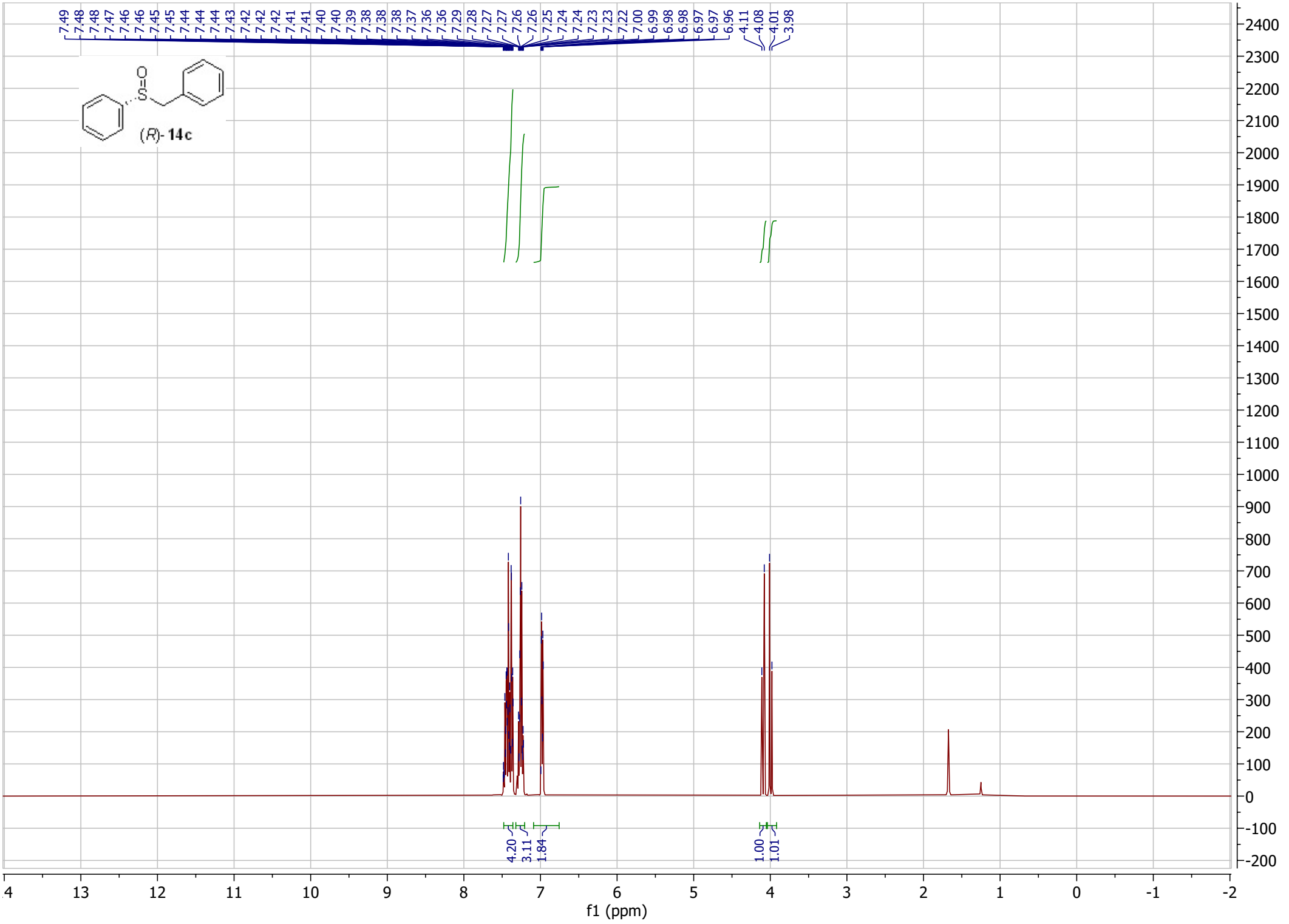

144.11
135.85
135.52
135.19
134.86
129.12
125.66
125.62
125.59
125.55
124.77
122.06
59.44
O
S
Br
Br
Br
F3C
(S)-13f
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

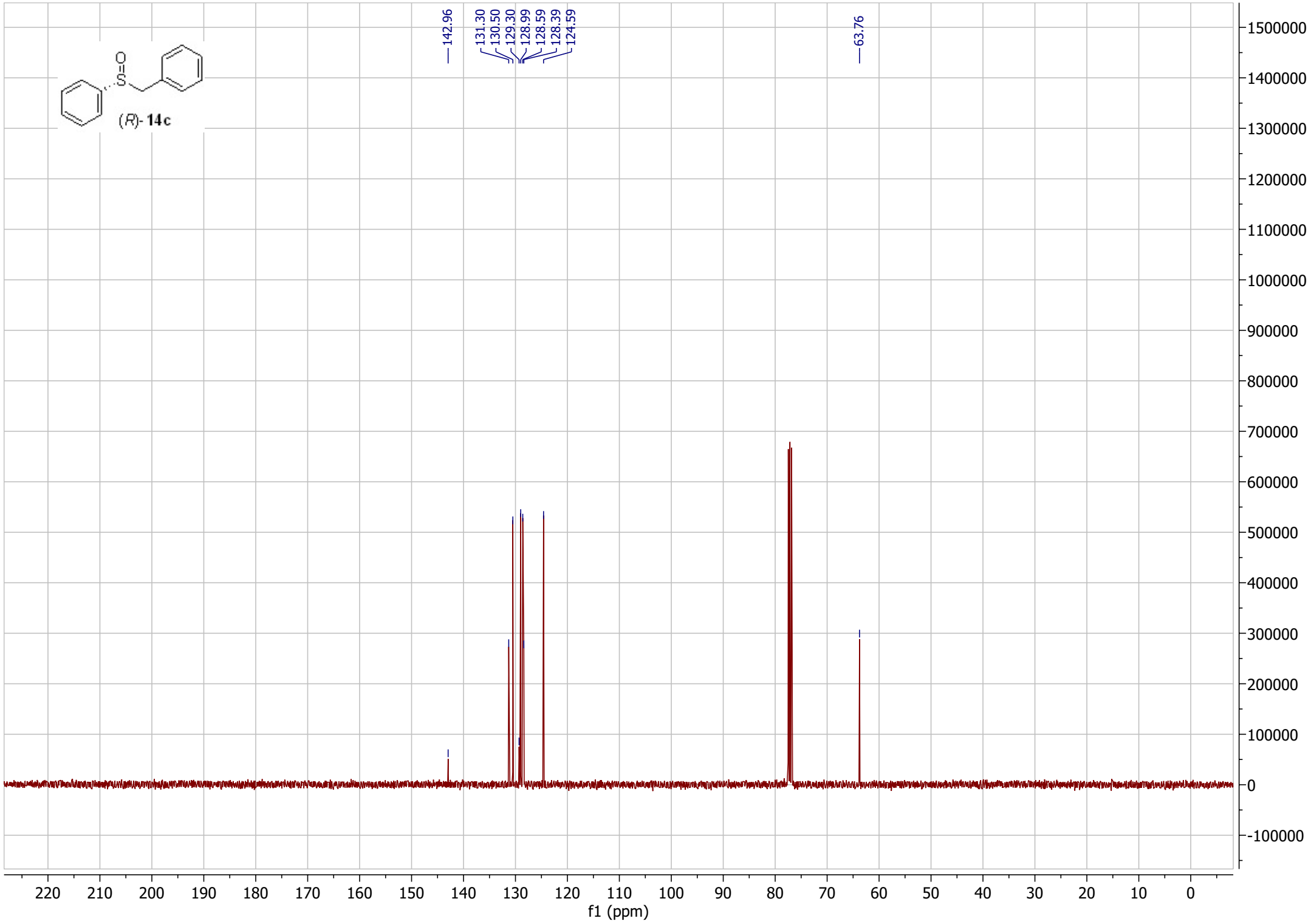

7.96
7.94
7.54
7.52
O
S
Br
Br
Br
Cl
(S)-13g
1.96
2.00
2.08
2.8×10^7
2.6×10^7
2.4×10^7
2.2×10^7
2.0×10^7
1.8×10^7
1.6×10^7
1.4×10^7
1.2×10^7
1.0×10^7
8.0×10^6
6.0×10^6
4.0×10^6
2.0×10^6
0.0
-2.0×10^6
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

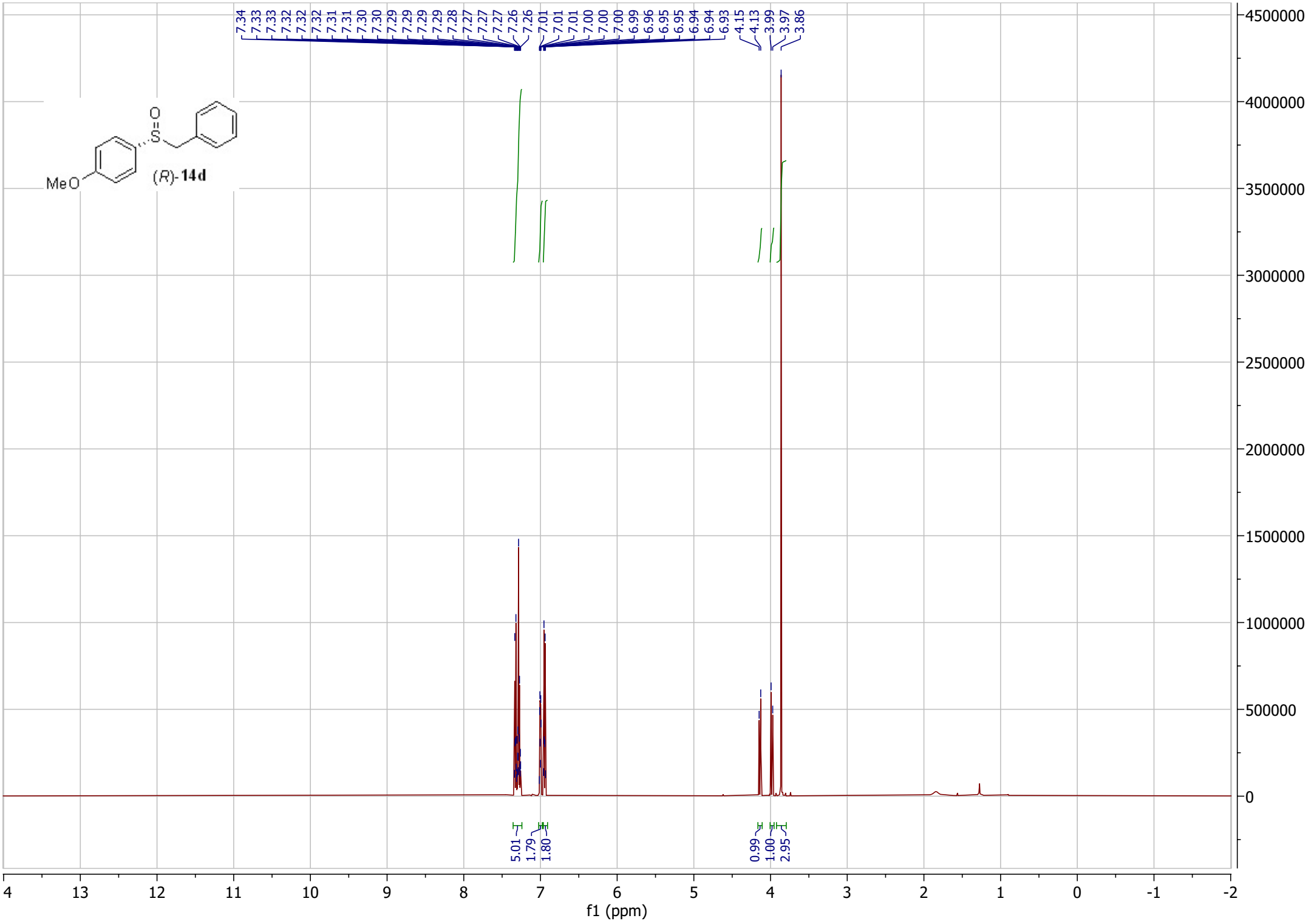

140.51
138.44
129.84
128.97
60.85
O
S
Br
Br
Br
Cl
(S)-13g
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

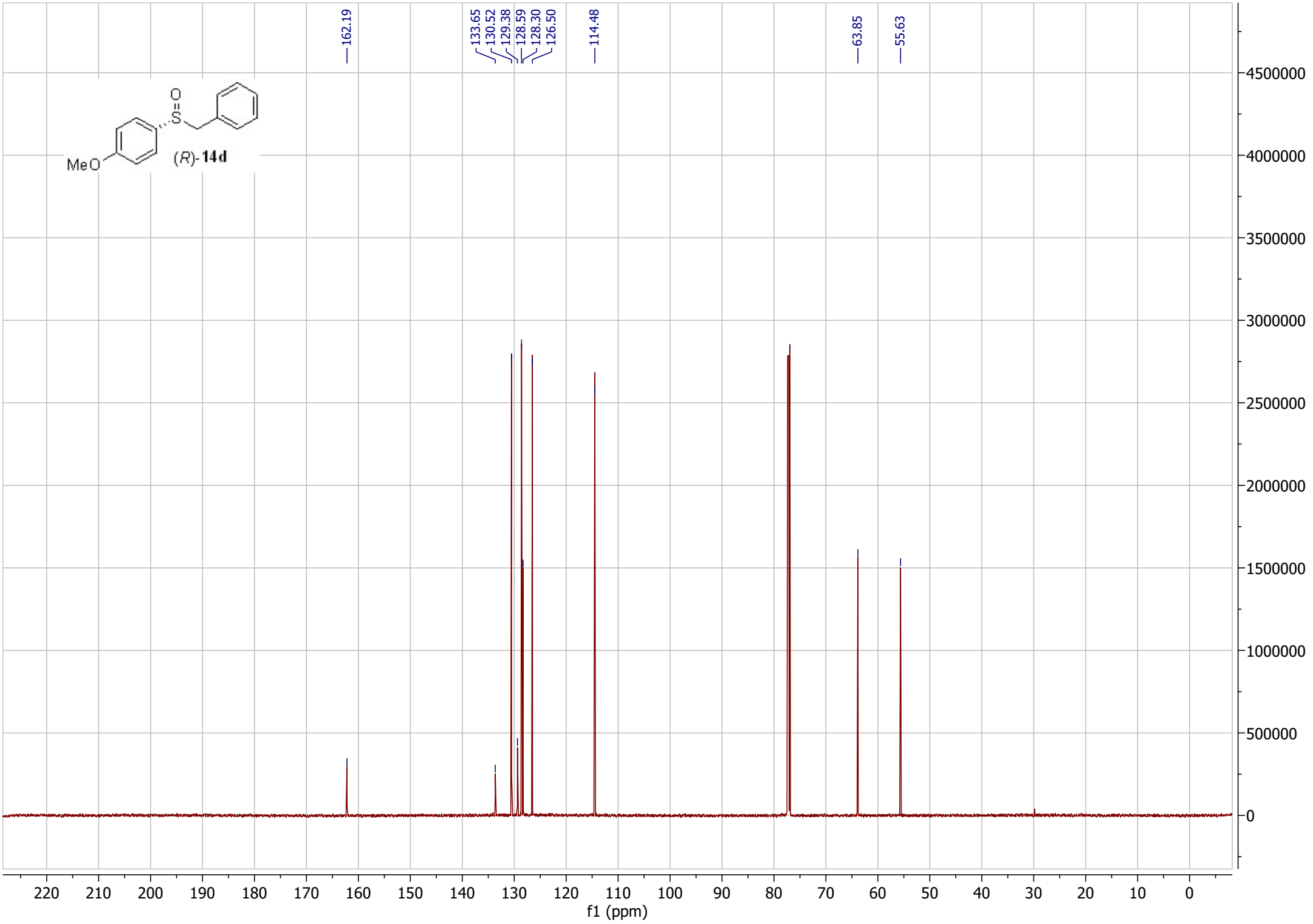

(S)-14b
f1 (ppm)

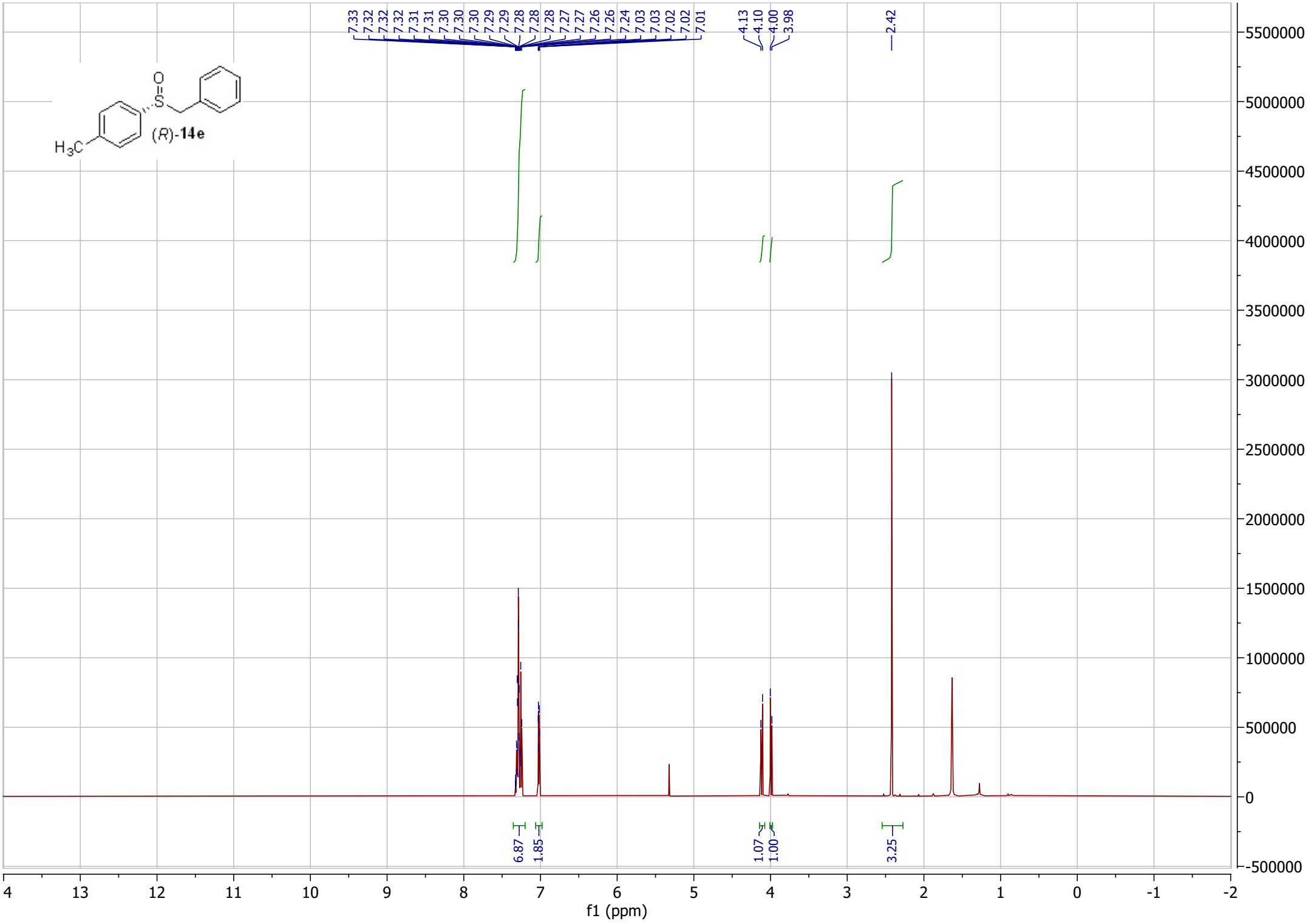

(S)-14b
130.17
129.15
128.53
58.28
50.94
31.49
28.62
22.58
22.52
14.11
f1 (ppm)

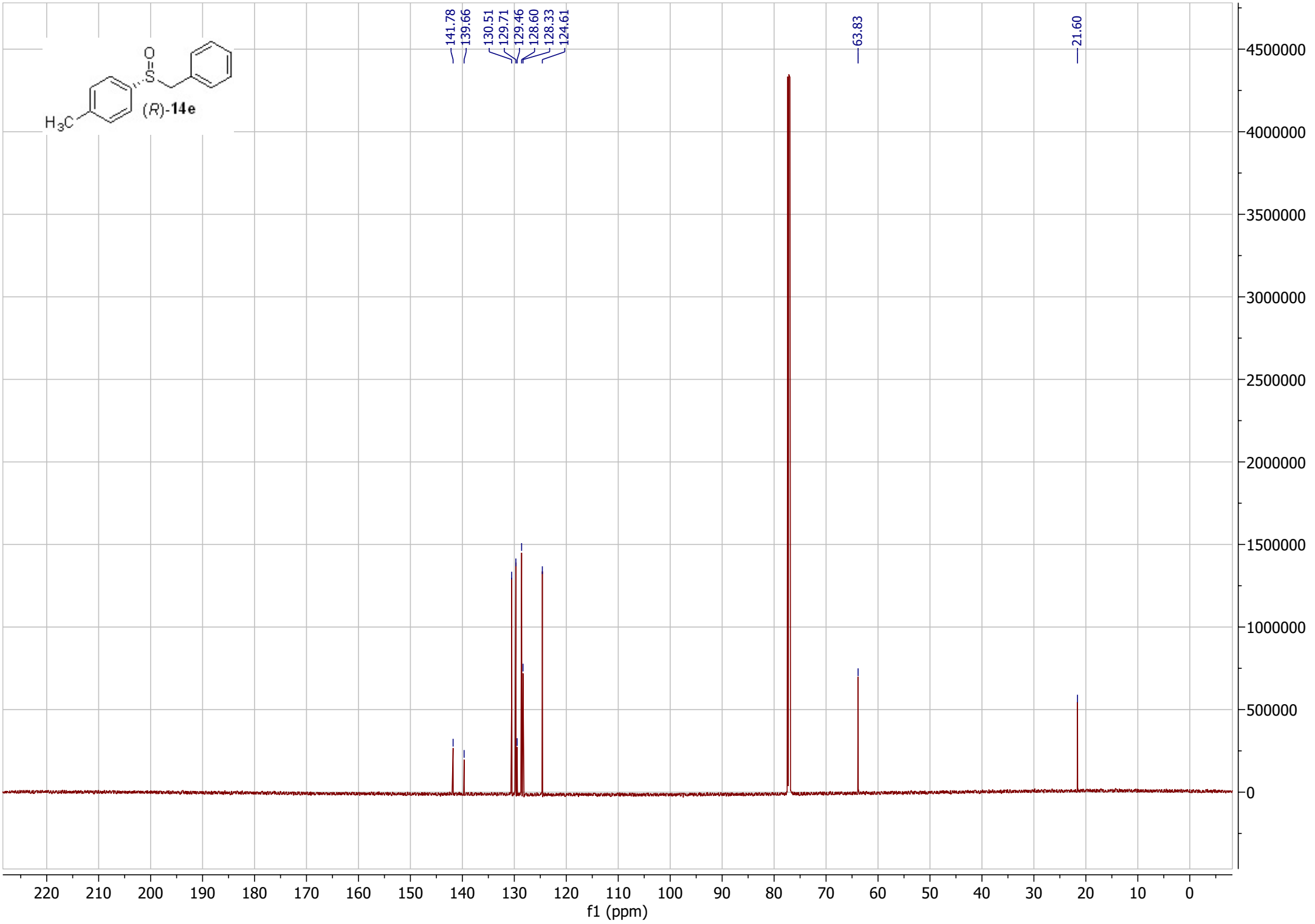

7.49 7.48 7.48 7.47 7.46 7.46 7.45 7.45 7.44 7.44 7.44 7.43 7.42 7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.38 7.38 7.38 7.37 7.36 7.36 7.29 7.28 7.27 7.27 7.26 7.26 7.25 7.24 7.24 7.23 7.23 7.22 7.00 6.99 6.98 6.98 6.97 6.97 6.96 4.11 4.08 4.01 3.98
O
S
(R)-14c
4.20
3.11
1.84
1.00
1.01
2400 2300 2200 2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100 -200
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

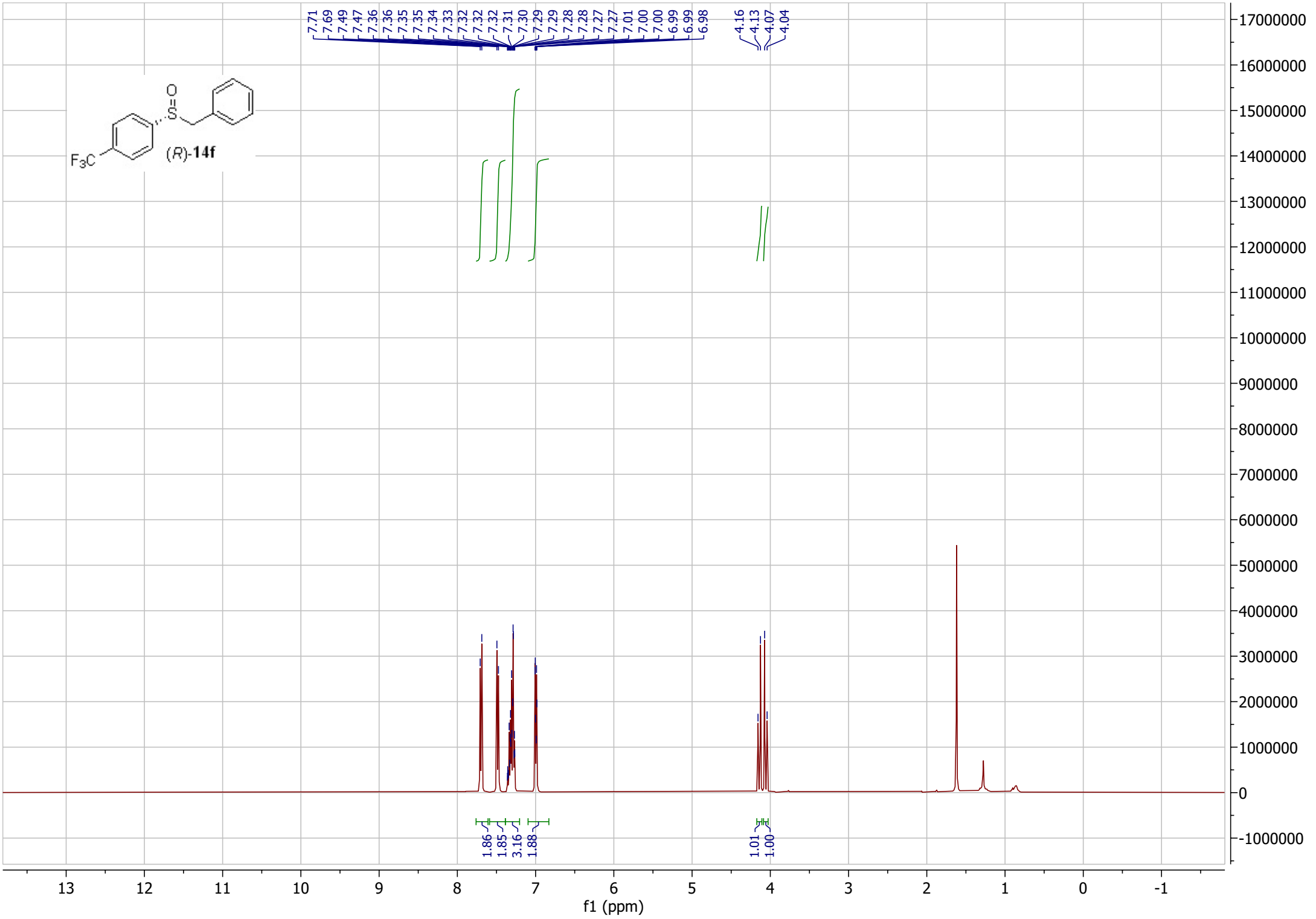

142.96
131.30
130.50
129.30
128.99
128.59
128.39
124.59
63.76
(R)-14c
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

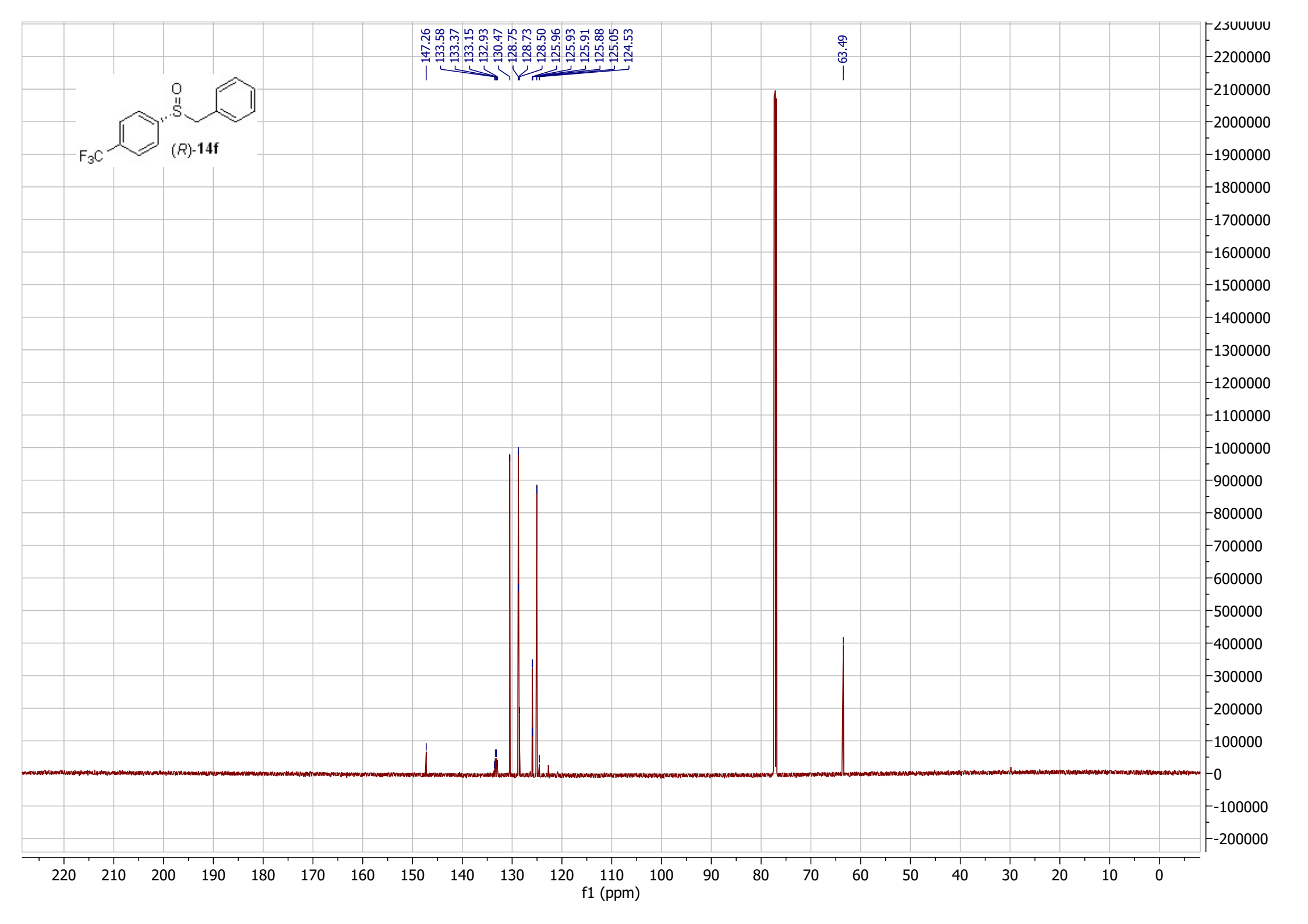

7.34 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.29 7.29 7.28 7.27 7.27 7.27 7.26 7.26 7.01 7.01 7.01 7.00 7.00 7.00 6.99 6.96 6.95 6.95 6.94 6.94 6.93 4.15 4.13 3.99 3.97 3.86
O
S=O
MeO
(R)-14d
5.01 1.79 1.80 0.99 1.00 2.95
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

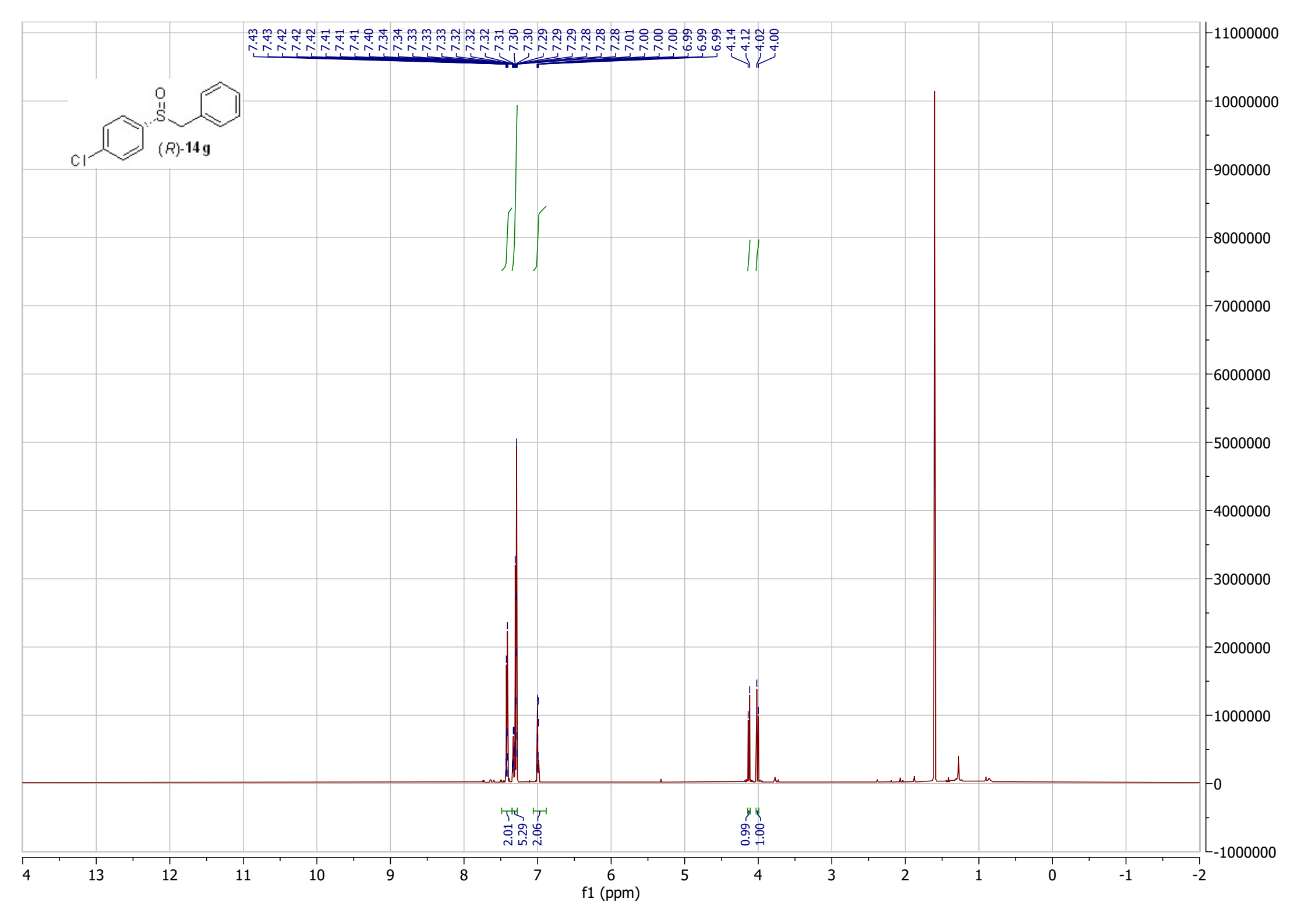

162.19
133.65
130.52
129.38
128.59
128.30
126.50
114.48
63.85
55.63
MeO
O
S
(R)-14d
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

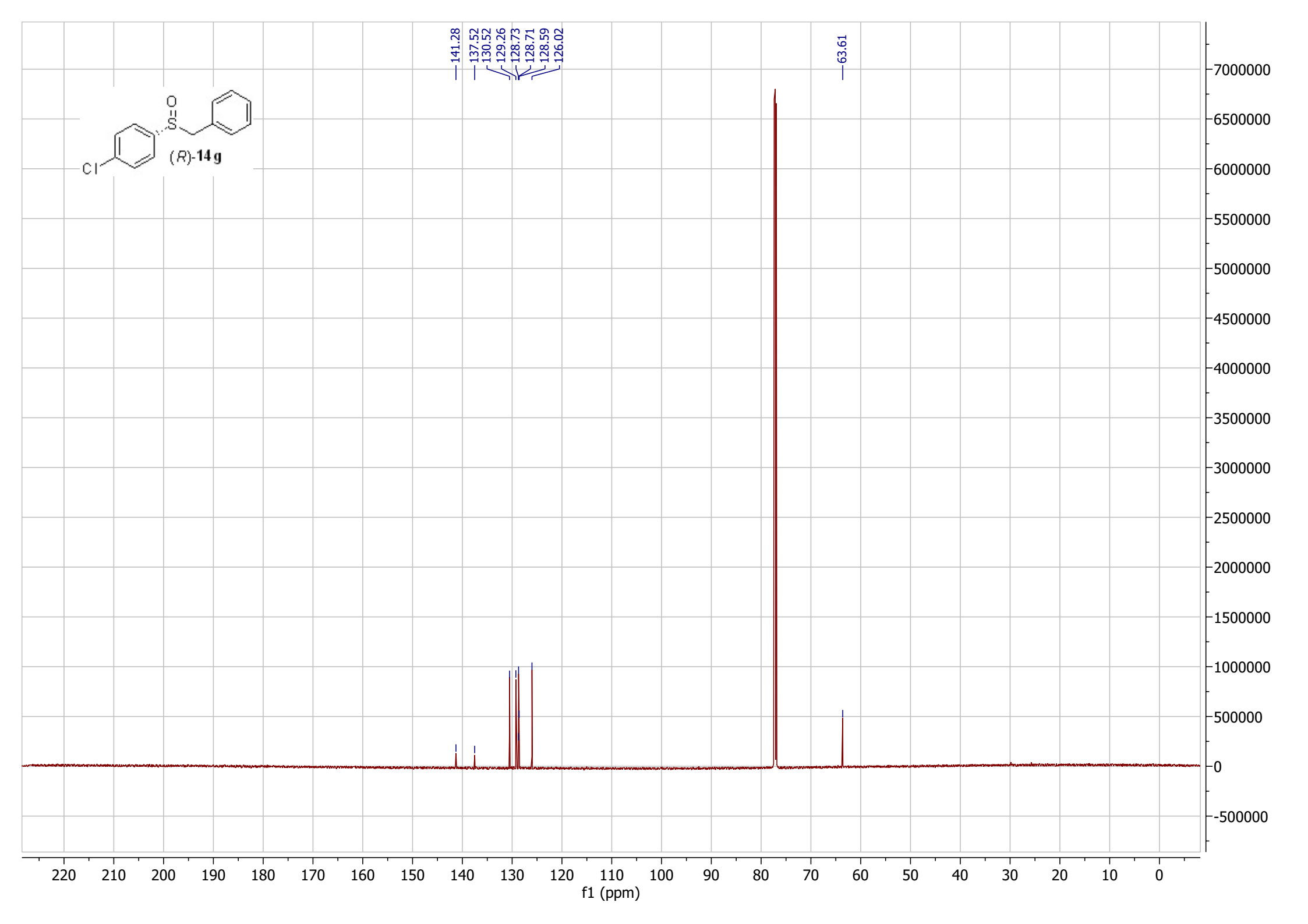

7.33
7.32
7.32
7.32
7.31
7.31
7.30
7.30
7.30
7.29
7.29
7.28
7.28
7.28
7.27
7.27
7.26
7.26
7.24
7.03
7.03
7.02
7.02
7.01
4.13
4.10
4.00
3.98
2.42
(R)-14e
6.87
1.85
1.07
1.00
3.25
f1 (ppm)

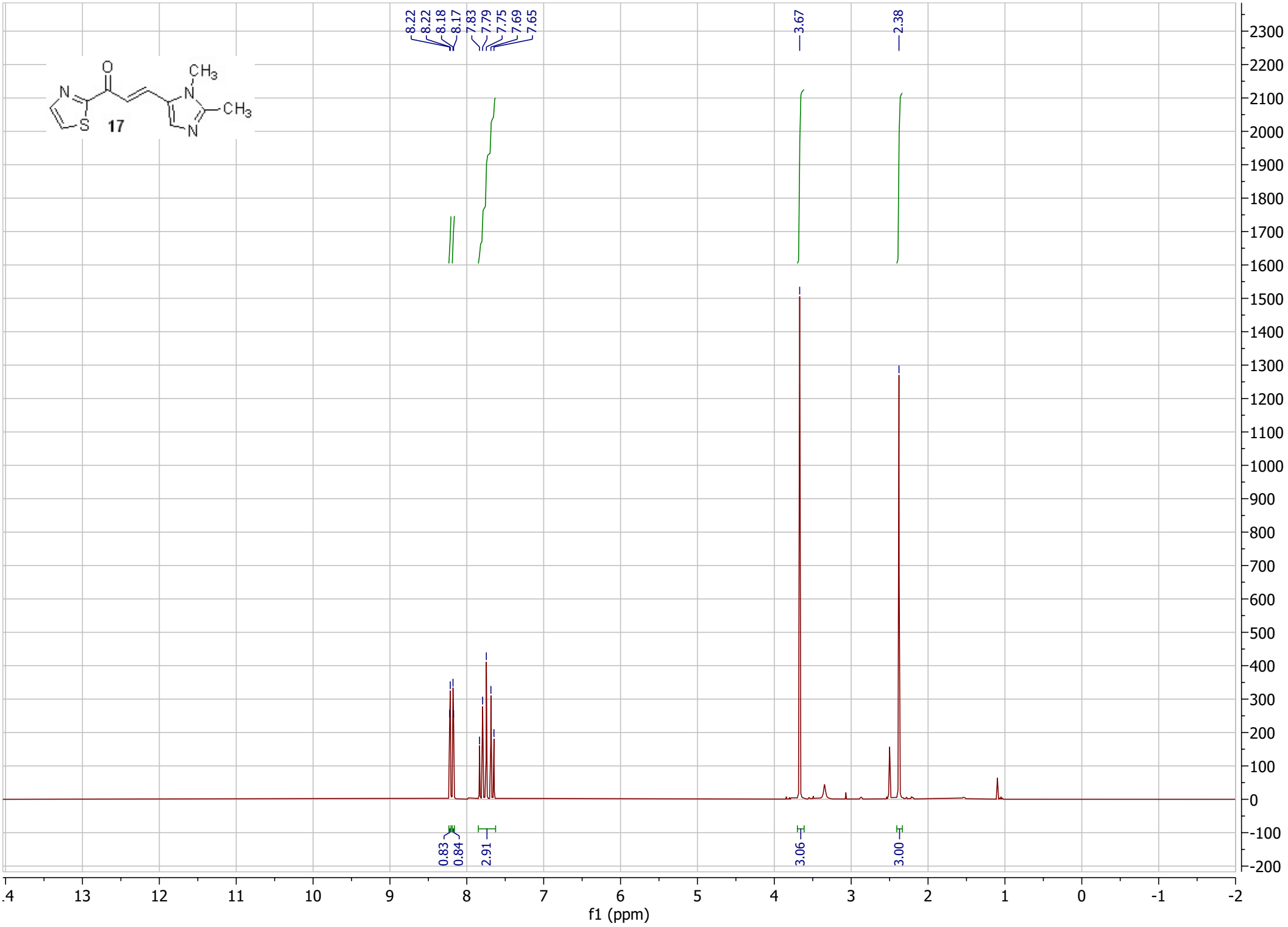

141.78
139.66
130.51
129.71
129.46
128.60
128.33
124.61
63.83
21.60
(R)-14e
H3C
O
S
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

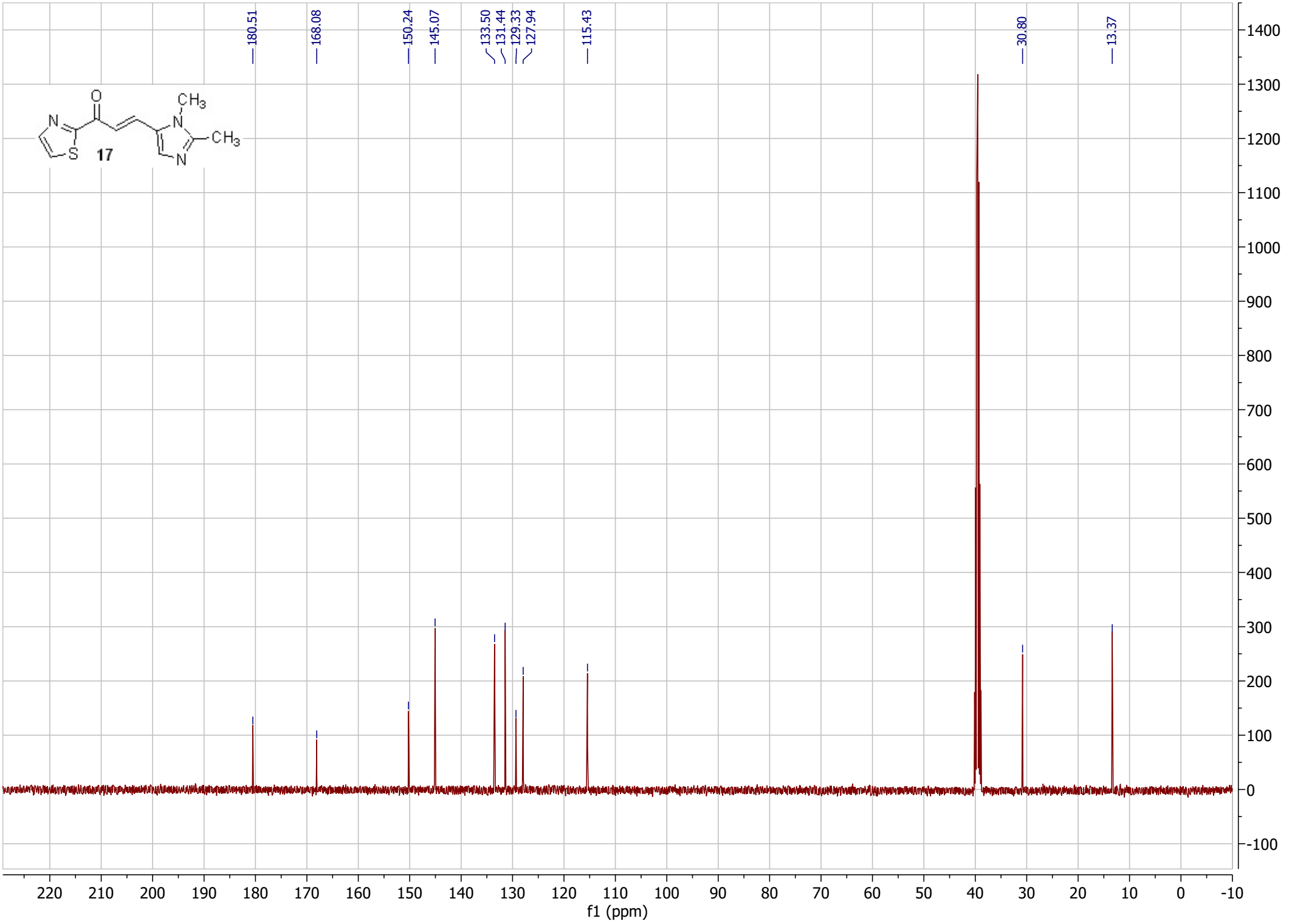

7.71
7.69
7.49
7.47
7.36
7.36
7.35
7.35
7.34
7.33
7.32
7.32
7.32
7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.01
7.00
7.00
6.99
6.99
6.98
4.16
4.13
4.07
4.04
O
S
F3C
(R)-14f
1.86
1.85
3.16
1.88
1.01
1.00
17000000
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

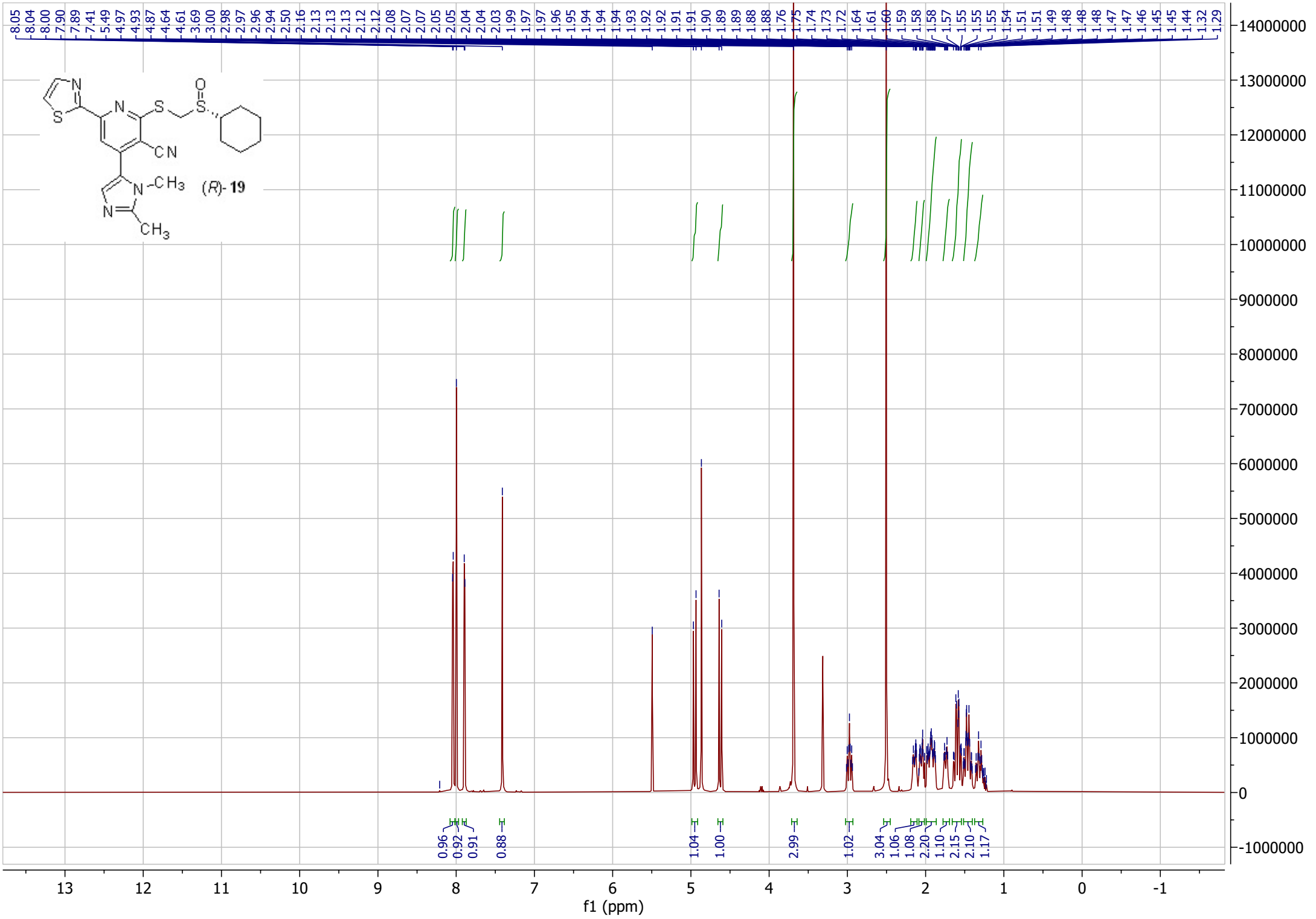

147.26
133.58
133.37
133.15
132.93
130.47
128.75
128.73
128.50
125.96
125.93
125.91
125.88
125.05
124.53
63.49
O
S
F3C
(R)-14f
f1 (ppm)

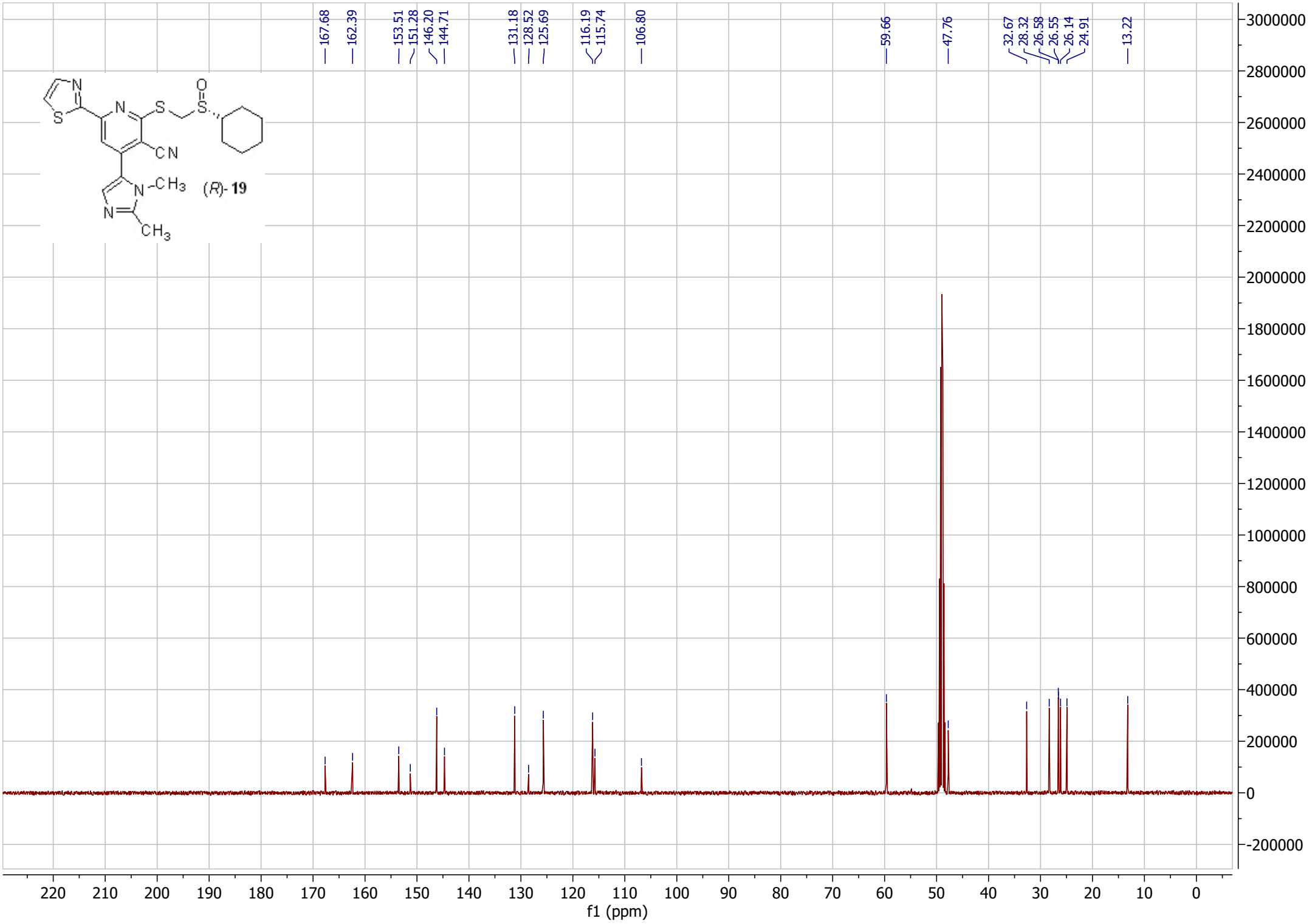

7.43 7.43 7.42 7.42 7.42 7.41 7.41 7.41 7.40 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.32 7.31 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.28 7.01 7.00 7.00 7.00 6.99 6.99 6.99 4.14 4.12 4.02 4.00
O
S
Cl
(R)-14g
2.01
5.29
2.06
0.99
1.00
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

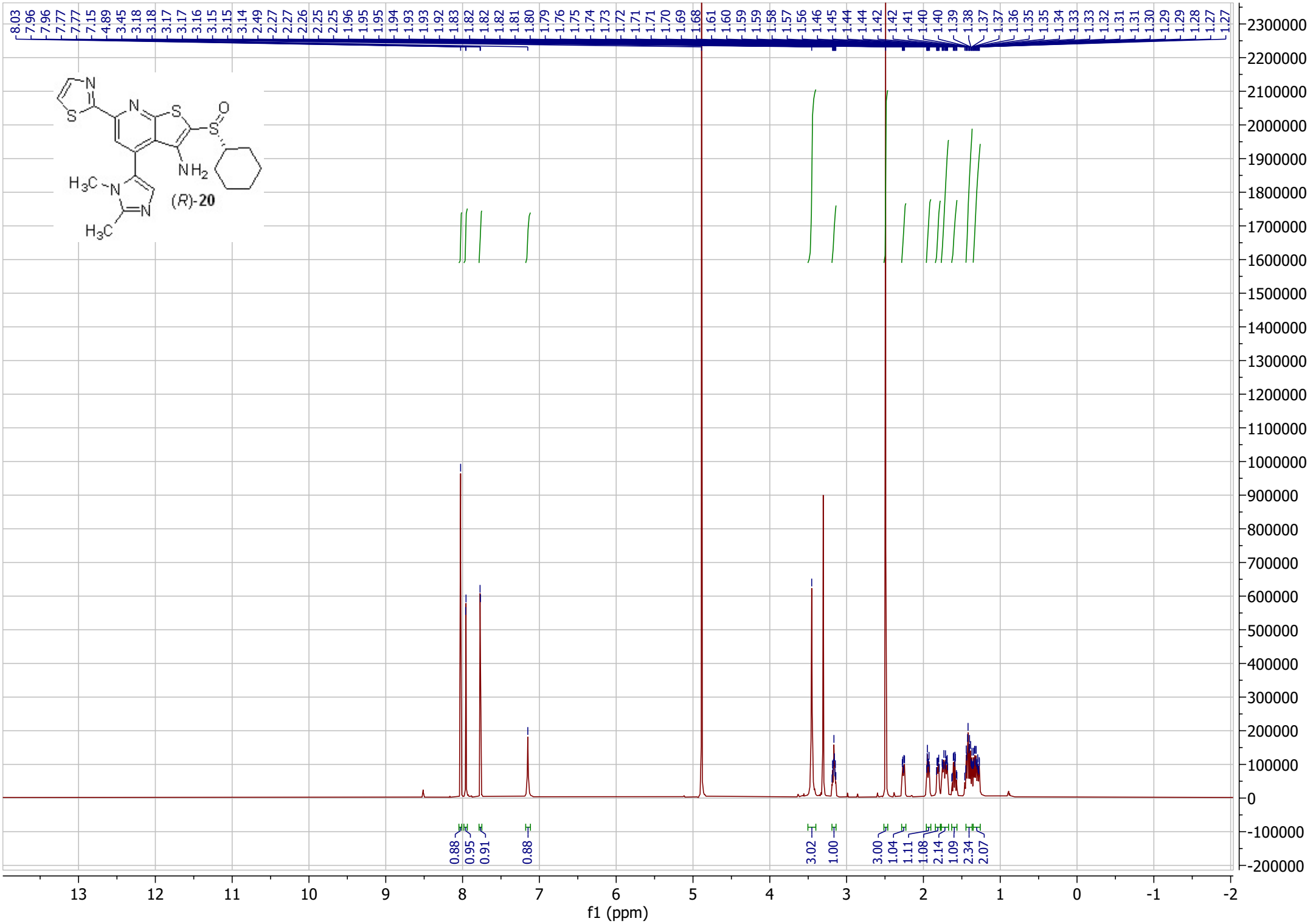

141.28
137.52
130.52
129.26
128.73
128.71
128.59
126.02
63.61
(R)-14g
Cl
O
S
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

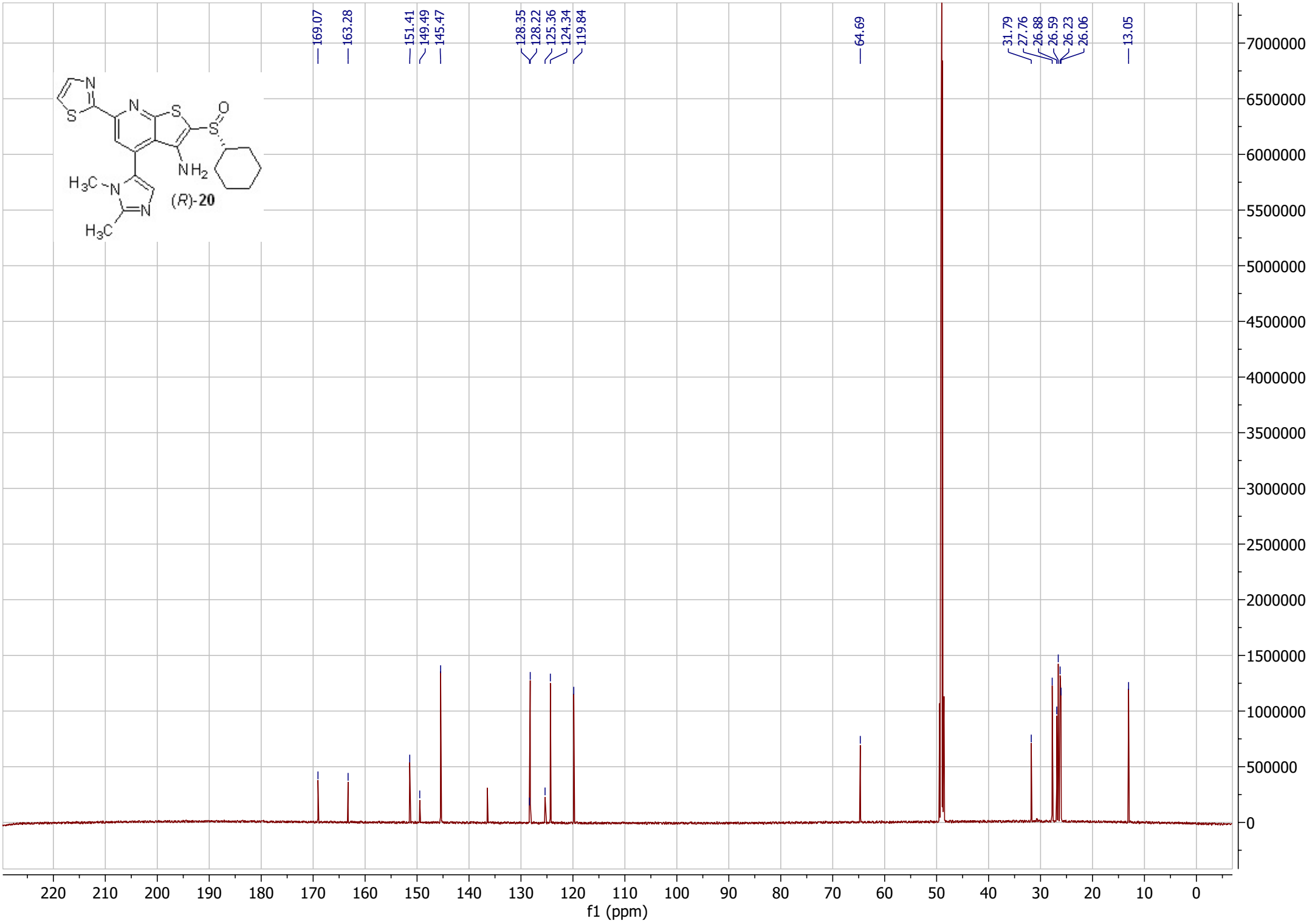

8.22
8.22
8.18
8.17
7.83
7.79
7.75
7.69
7.65
3.67
2.38
17
0.83
0.84
2.91
3.06
3.00
f1 (ppm)


180.51
168.08
150.24
145.07
133.50
131.44
129.33
127.94
115.43
30.80
13.37
O
N
S
17
CH3
N
CH3
N
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


(R)-19
f1 (ppm)


167.68
162.39
153.51
151.28
146.20
144.71
131.18
128.52
125.69
116.19
115.74
106.80
59.66
47.76
32.67
28.32
26.58
26.55
26.14
24.91
13.22
(R)-19
f1 (ppm)


(R)-20
f1 (ppm)


169.07
163.28
151.41
149.49
145.47
128.35
128.22
125.36
124.34
119.84
64.69
31.79
27.76
26.88
26.59
26.23
26.06
13.05
(R)-20
f1 (ppm)