Arylation of Lithium Sulfinates with Diaryliodonium Salts: A Direct and Versatile Access to Arylsulfones

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Supporting Information

Content

1 General

Solvents All anhydrous solvents were purchased from commercial suppliers and stored over MS4A under an atmosphere of Argon. Solvents for column chromatography were technical standard.

Regents All starting materials, which were purchased from commercial sources, were used without further purification.
SO_2 (sulfur dioxide 3.8 from *Gerling, Holz & Co*) was used directly without further purification.
Commercially available diphenyliodonium salts were purchased. Following diaryliodonium salts were synthesized according to literature: Bis(4-methylphenyl)iodonium triflate (**3f**),[1] bis(2,4,6-trimethyl-phenyl)iodonium triflate (**3g**),[1] bis(2,4-dimethylphenyl)iodonium triflate (**3h**),[1] bis(4-methoxyphenyl)iodonium tosylate (**3i**),[2] bis(4-chlorophenyl)iodonium triflate (**3j**),[1] (2,4,6-trimethyl- phenyl)(phenyl)iodonium triflate (**3k**),[1] (2,4,6-triisopropylphenyl)(phenyl) iodonium triflate (**3l**),[3] (3-trifluoromethylphenyl)(4-methoxyphenyl) iodonium tosylate (**3m**)[4].

Chromatography Column chromatography was performed with Silica 0.04-0.063 mm/ 230-400 mesh. Thin layer chromatography was performed using aluminium plates coated with SiO_2. The spots were visualized by ultraviolet light.

NMR spectroscopy ^1H and ^{13}C NMR spectra were recorded at 400 or 500 MHz and 101 or 126 MHz, respectively. Chemical shifts are reported as δ-values relative to the residual $CDCl_3$-peak (δ = 7.26 ppm for ^1H and δ = 77.16 ppm for ^{13}C). Coupling constants (*J*) are given in Hz and multiplicities of the signals are abbreviated as follows: s = singlet; d = doublet; t = triplet; q = quartet; sp = septet; m = multiplet; dd = doublet of doublets and dt = doublet of triplets.

Mass Spectrometry Mass spectra (MS) were measured on a VG Plattform II - spectrometer using ESI (electrospray ionisation) techniques at the Department of Chemistry.

High resolution mass spectra (MALDI-HRMS) were measured on a MALDI LTQ Orbitrap XL using MALDI (Matrix-assisted Laser Desorption/Ionization) techniques at the Department of Chemistry.

Melting points are uncorrected.

Reactions All reactions were carried out under an inert atmosphere in dried glassware unless otherwise noted. All yields refer to isolated yields of compounds estimated to be > 95% pure as determined by ^1H-NMR.

SO_2 is a toxic and corrosive gas! It should be handled with care only in a well-ventilated fume-hood with the necessary precaution! It is possible to obtain the crude lithium sulfinates by passing a stream of sulfur dioxide through the solution of the organolithium reagent. However, with this technique a great excess of SO_2 is introduced into the reaction and has to be removed afterwards. In general better and more reproducible yields were obtained by using a defined amount of liquid SO_2. Therefore SO_2 was condensed into a dry and Ar-filled Schlenk-flask, cooled to -78 °C. Because of its high heat of evaporation, liquid and cooled SO_2 can be easily handled, measured and transferred with syringes. For small scale reactions, we recommend this procedure.

For the removal of excess SO_2 we employed the two following procedures. (For the removal of excess SO_2 (gaseous or liquid) appropriate measures to trap and destroy SO_2 should be taken, e.g. passing the SO_2 stream through an aq. NaOH solution.)

Procedure A: After warming the reaction mixture to 25 °C within 90 min the solvents and excess SO_2 were removed under reduced pressure. The residue was coevaporated with CH_2CL_2 (1.5 mL).

Procedure B: Excess SO_2 was removed by passing Ar through the solution for 30 min. Diaryliodonium salt **3** (0.50 mmol, 1.0 equiv) and DMF (1.0 mL) were added directly to the remaining solution/suspension. The flask was charged with a small distillation head and heated to 90 °C. After the lower boiling solvents (hexanes, pentane, cyclohexane and/or THF, Et_2O) were distilled off (typically within 1 h), the flask was capped with a rubber septum and heated for the remaining time. (As alternative the flask can be capped directly with a rubber septum pierced with a 20G needle and heated to 90 °C for 24 h. Low boiling solvents are evaporated directly into the atmosphere! This should be only done in a closed, well-ventilated fume-hood!)

Preparation of Benzenesulfinic Lithium Salt 2a

A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with Phenyllithium (**1a**) (32.2 mL, 50 mmol, 1.55 M solution in Et_2O, 1.0 equiv) and cooled to -40 °C. At this temperature, liquid SO_2 (1.1 mL, 55 mmol, 1.1 equiv) was added and the reaction mixture was allowed to warm to 25 °C within 90 min. It was then concentrated under reduced pressure and excess Et_2O was coevaporated two times with CH_2Cl_2 (150 mL) to get the solid benzenesulfinic lithium salt (**2a**) (11.32 g).*

* Note: The theoretical amount of lithium salt **2a** (formula weight: 148.11 g/mol) from 32.3 mL Phenyllithium (**1a**) is 7.41 g. The material obtained (11.32 g) should therefore contain 65% of **2a** (assuming 100% conversion). A purity of 65% of this material was thus assumed in later calculations.

TP 1: Typical Procedure for the Preparation of Sulfones from Benzenesulfinic Lithium Salt

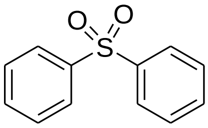
A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with benzenesulfinic acid lithium salt **2a** (1.5 equiv), aryliodonium salt **3** (1.0 equiv) and DMF (2.0 mL/mmol iodonium salt, 0.5 M). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL), dried over Na_2SO_4 and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc) afforded the analytically pure product.

TP 2: Typical Procedure for the Preparation of Sulfones from Alkyllithium Reagents

A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with Alkyllithium **7** (1.5 equiv) cooled to -78 °C and then liquid SO_2 (10 equiv) was added and the mixture was warmed to 25 °C within 90 min. After removal of SO_2 and solvents according to procedure A, diphenyliodonium triflate **3a** and (1.0 equiv) and DMF (2.0 mL/mmol iodonium salt, 0.5 M) were added. The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL), dried over Na_2SO_4 and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc) afforded the analytically pure product.

2 Experimental Procedures

1-(Phenylsulfonyl)benzene (4a)



1-(Phenylsulfonyl)benzene (**4a**) was synthesized starting from crude benzenesulfinic lithium salt (**2a**), from commercial phenyllithium (**1a**) or from phenyllithium prepared by lithiation of benzene (**5a**) with *n*BuLi.(5)

From benzenesulfinic lithium salt (2a): According to TP 1 **4a** was prepared from benzenesulfinic acid lithium salt (**2a**) (65w-%, 170.9 mg, 0.75 mmol) and diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (Cyclohexane:EtOAc 9:1 → 4:1) yielded the product as colorless solid (91.3 mg, 84%).

From phenyllithium (1a): A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with phenyllithium (**1a**) (0.65 mL, 1.55 M solution in Et_2O, 0.75 mmol, 1.5 equiv) and cooled to -78 °C and then liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. After warming to 25 °C the excess SO_2 and solvents were removed according to procedure A. Then diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL) were added and the mixture was stirred at 90 °C for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL), dried over Na_2SO_4 and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc 4:1) yielded the product as colorless solid (56.6 mg, 52%).

From benzene (5a) and *n*BuLi: To a solution of *n*BuLi (0.34 mL, 2.45 M in hexane, 0.80 mmol, 1.6 equiv) and TMEDA (0.11 mL, 0.75 mmol, 1.5 equiv) in a dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was added benzene (**5a**) (67 µL, 0.75 mmol, 1.5 equiv). The mixture was allowed to stir at 25 °C for 3 h. After removal of excess SO_2 and solvents by procedure A, diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL) were added and the mixture was stirred at 90 °C for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL), dried over Na_2SO_4 and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc 9:1 → 4:1) afforded the analytically pure product as colorless solid (90.0 mg, 83%).

m.p.: 122 - 125 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.98 - 7.92 (m, 4H), 7.59 - 7.54 (m, 2H), 7.54 - 7.48 (m, 4H).

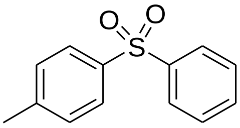
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 141.78, 133.31, 129.41, 127.81.

MS: m/z: calc. for $C_{12}H_{10}O_2S+Na^+$ 241.03, found 241.50.

R_f (Cyclohexane:EtOAc 9:1): 0.19.

Analytical data are consistent with literature.(6)

1-Methyl-4-(phenylsulfonyl)benzene (4b)



1-Methyl-4-(phenylsulfonyl)benzene (**4b**) was prepared according to TP 1 from benzenesulfinic acid lithium salt (**2a**) (65w-%, 170.9 mg, 0.75 mmol) and bis(4-methylphenyl)iodonium triflate (**3f**) (229.1 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (Cyclohexane:EtOAc 20:1 → 9:1) yielded the product as colorless solid (93.3 mg, 80%).

m.p.: 125 - 128 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.95 - 7.91 (m, 2H), 7.85 - 7.81 (m, 2H), 7.57 - 7.52 (m, 1H), 7.51 - 7.46 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 2.40 (s, 3H).

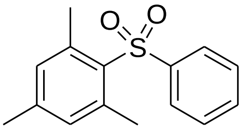
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 144.28, 142.16, 138.82, 133.11, 130.04, 129.34, 127.86, 127.64, 21.69.

MS: m/z: calc. for $C_{13}H_{12}O_2S+Na^+$ 255.05, found 255.50.

R_f (Cyclohexane:EtOAc 9:1): 0.22.

Analytical data are consistent with literature.(6)

1,3,5-Trimethyl-2-(phenylsulfonyl)benzene (4c)



1,3,5-Trimethyl-2-(phenylsulfonyl)benzene (**4c**) was prepared according to TP 1 from benzenesulfinic acid lithium salt (**2a**) (65w-%, 170.9 mg, 0.75 mmol) and bis(2,4,6-trimethylphenyl)iodonium triflate (**3g**) (257.2 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (Cyclohexane:EtOAc 20:1 → 9:1) yielded the product as colorless solid (87.3 mg, 67%).

1,3,5-Trimethyl-2-(phenylsulfonyl)benzene (**4c**) was also synthesized according to TP 1 from benzenesulfinic acid lithium salt (**2a**) (65w-%, 170.9 mg, 0.75 mmol) and (2,4,6-trimethylphenyl)(phenyl)iodonium triflate (**3k**) (236.1 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (Cyclohexane:EtOAc 20:1 →9:1) yielded the product as colorless solid (94.5 mg, 73%).

m.p.: 79 – 80 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.82 - 7.75 (m, 2H), 7.56 - 7.52 (m, 1H), 7.49 - 7.44 (m, 2H), 6.94 (s, 2H), 2.59 (s, 6H), 2.30 (s, 3H).

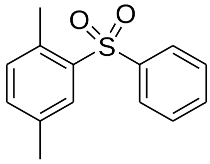
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 143.69, 143.50, 140.22, 133.93, 132.68, 132.32, 129.00, 126.32, 22.91, 21.13.

MS: m/z: calc. for $C_{15}H_{16}O_2S+Na^+$ 283.08, found 283.40.

R_f (Cyclohexane:EtOAc 9:1): 0.32.

Analytical data are consistent with literature.(6)

1,4-Dimethyl-2-(phenylsulfonyl)benzene (4d)



1,4-Dimethyl-2-(phenylsulfonyl)benzene (**4d**) was prepared according to TP 1 from benzenesulfinic acid lithium salt (**2a**) (65w-%, 170.9 mg, 0.75 mmol) and bis(2,4-dimethylphenyl)iodonium triflate (**3h**) (243.1 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (Cyclohexane:EtOAc 20:1 → 9:1) yielded the product as colorless solid (94.2 mg, 76%).

m.p.: 109 – 111 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.05 (br s, 1H), 7.88 - 7.84 (m, 2H), 7.59 - 7.54 (m, 1H), 7.52 - 7.47 (m, 2H), 7.28 (d, *J* = 5.2 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 2.42 (s, 3H), 2.37 (s, 3H).

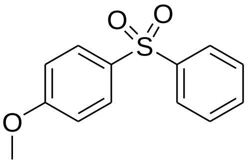
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 141.63, 138.52, 136.59, 134.94, 134.47, 133.04, 132.73, 129.88, 129.11, 127.70, 21.02, 19.82.

MS: m/z: calc. for $C_{14}H_{14}O_2S+Na^+$ 269.06, found 269.30.

R_f (Cyclohexane:EtOAc 9:1): 0.27.

Analytical data are consistent with literature.(6)

1-(4-Methoxyphenylsulfonyl)benzene (4e)



1-(4-Methoxyphenylsulfonyl)benzene (**4e**) was synthesized from crude benzenesulfinic acid lithium salt (**2a**), and from 4-methoxyphenyllithium (**1k**) prepared by halogen-lithium-exchange of 4-bromoanisole (**6c**) with *n*BuLi, and 4-iodoanisole (**6d**) with *t*BuLi, respectively.(7,8)

From benzenesulfinic acid lithium salt (2a): According to TP 1 **4e** was synthesized from benzenesulfinic acid lithium salt (**2a**) (65w-%, 170.9 mg, 0.75 mmol) and bis(4-methoxyphenyl)iodonium tosylate (**3i**) (256.2 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (Cyclohexane:EtOAc 9:1 → 1:1) yielded the product as colorless solid (91.5 mg, 74%).

From 4-bromoanisole (6c) and *n*BuLi: A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with 4-bromoanisole (**6c**) (0.1 mL, 1.5 equiv, 0.75 mmol) in dry THF (1.0 mL) and cooled to -78 °C and then *n*BuLi (0.38 mL, 2.13 M in hexane, 0.80 mmol, 1.6 equiv) was added dropwise. The mixture was allowed to stir at this temperature for 2 h, before liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. After warming to 25 °C within 90 min, excess SO_2 and solvents were removed according to procedure A. To the crude sulfinic acid lithium salt **2k** was added diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL), dried over

Na_2SO_4 and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc 9:1 → 4:1) yielded the product as a colorless solid (120.2 mg, 97%).

From 4-iodoanisole (6d) and *t*BuLi: A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with 4-iodoanisole (**6d**) (175.5 mg, 1.5 equiv, 0.75 mmol) in dry THF (1.0 mL) and cooled to -78 °C and then *t*BuLi (0.48 mL, 1.64 M in pentane, 0.80 mmol, 1.6 equiv) was added dropwise. The mixture was allowed to warm to -50 °C within 2 h, before liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. After warming to 25 °C within 90 min, excess SO_2 and solvents were removed according to procedure A. To the crude sulfinic acid lithium salt **2k** was added diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL), dried over Na_2SO_4 and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc 9:1 → 4:1) yielded the product as a colorless solid (65.2 mg, 53%).

m.p.: 86 - 88 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.93 - 7.90 (m, 2H), 7.90 - 7.86 (m, 2H), 7.56 - 7.51 (m, 1H), 7.51 - 7.46 (m, 2H), 6.99 - 6.94 (m, 2H), 3.84 (s, 3H).

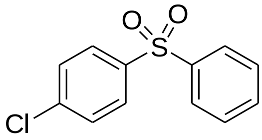
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 163.52, 142.53, 133.28, 132.95, 130.02, 129.32, 127.44, 114.64, 55.77.

MS: m/z: calc. for $C_{13}H_{12}O_3S+Na^+$ 271.04, found 271.40.

R_f (Cyclohexane:EtOAc 9:1): 0.10.

Analytical data are consistent with literature.(6)

1-(4-Chlorophenylsulfonyl)benzene (4f)



1-(4-Chlorophenylsulfonyl)benzene (**4f**) was prepared according to TP 1 from benzenesulfinic acid lithium salt (**2a**) (65w-%, 170.9 mg, 0.75 mmol) and bis(4-chlorophenyl)iodonium triflate (**3j**) (249.5 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (Cyclohexane:EtOAc 20:1 → 9:1) yielded the product as colorless solid (98.2 mg, 78%).

m.p.: 93 - 95 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.96 - 7.90 (m,2H), 7.90 - 7.86 (m, 2H), 7.61 - 7.56 (m, 1H), 7.55 - 7.49 (m, 2H), 7.49 - 7.45 (m, 2H).

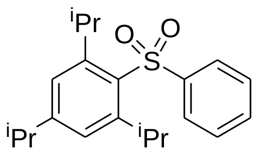
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 141.32, 140.26, 140.03, 133.58, 129.75, 129.55, 129.26, 127.77.

MS: m/z: calc. for $C_{12}H_9ClO_2S+Na^+$ 274.99, found 275.10.

R_f (Cyclohexane:EtOAc 9:1): 0.24.

Analytical data are consistent with literature.(6)

1,3,5-Triisopropyl-2-(phenylsulfonyl)benzene (4g)



1,3,5-Triisopropyl-2-(phenylsulfonyl)benzene (**4g**) was prepared according to TP 1 from benzenesulfinic acid lithium salt (**2a**) (65w-%, 170.9 mg, 0.75 mmol) and (2,4,6-triisopropylphenyl)(phenyl) iodonium triflate (**3l**) (278.2 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (Cyclohexane:EtOAc 20:1 → 9:1) yielded the product as colorless solid (139.9 mg, 81%).

m.p.: 120 - 123 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.79 - 7.73 (m, 2H), 7.55 - 7.50 (m, 1H), 7.50 - 7.45 (m, 2H), 7.16 (s, 2H), 4.17 (hept, *J* = 6.7 Hz, 2H), 2.90 (hept, *J* = 6.9 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 6H), 1.13 (d, *J* = 6.8 Hz, 12H).

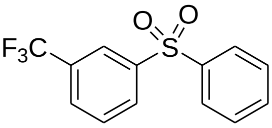
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 153.99, 151.45, 145.49, 132.38, 132.33, 129.06, 125.76, 124.15, 34.36, 29.54, 24.72, 23.69.

MS: m/z: calc. for $C_{21}H_{28}O_2S+Na^+$ 367.17, found 367.40.

R_f (Cyclohexane:EtOAc 9:1): 0.49.

Analytical data are consistent with literature.(9)

1-(Trifluoromethyl)-3-(phenylsulfonyl)benzene (4h)



1-(Trifluoromethyl)-3-(phenylsulfonyl)benzene (**4h**) was prepared starting from crude benzenesulfinic acid lithium salt (**2a**), and from [3-(trifluoromethyl)phenyl]-lithium (**1l**) synthesized by halogen-lithium-exchange of 3-bromobenzotrifluoride (**6e**) and 3-iodobenzotrifluoride (**6f**) with *n*BuLi.(10,11)

From benzenesulfinic acid lithium salt (2a): 4h was prepared according to TP 1 from benzenesulfinic acid lithium salt (**2a**) (65w-%, 170.9 mg, 0.75 mmol) and (4-methoxyphenyl)(3-trifluoromethylphenyl)iodonium tosylate (**3m**) (275.2 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (Cyclohexane:EtOAc 9:1 → 4:1) yielded the product as colorless solid (108.8 mg, 76%) and **4e** (7.4 mg, 6%) as by-product.

From 3-bromobenzotrifluoride (6e): A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with *n*BuLi (0.38 mL, 2.13 M in hexane, 0.80 mmol, 1.6 equiv) in dry Et_2O (1.0 mL) and cooled to 0°C. At this temperature 3-bromobenzotrifluoride (**6e**) (0.1 mL, 0.75 mmol, 1.5 equiv) was added dropwise and the mixture stirred for 1 h at 0 °C. Then it was cooled to -78 °C and liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. After warming to 25 °C within 90 min, excess SO_2 and solvents were removed according to procedure A. To the crude sulfinic acid lithium salt **2l** was added diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O

(15 mL), dried over Na_2SO_4 and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc 20:1 → 9:1) yielded the product as a colorless solid (106.3 mg, 74%).

From 3-iodobenzotrifluoride (6f): A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with *n*BuLi (0.38 mL, 2.13 M in hexane, 0.80 mmol, 1.6 equiv) in dry Et_2O (1.0 mL) and cooled to -78 °C. At this temperature 3-iodobenzotrifluoride (**6f**) (0.1 mL, 0.75 mmol, 1.5 equiv) was added dropwise and the mixture stirred for 1 h at -78 °C. Then liquid SO_2 (0.1 mL, 5.0 mmol, 10 equiv) was added. After warming to 25 °C within 90 min, excess SO_2 and solvents were removed according to procedure A. To the crude sulfinic acid lithium salt **2l** was added diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL), dried over Na_2SO_4 and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc 20:1 → 9:1) yielded the product as a colorless solid (118.9 mg, 83%).

m.p.: 78 - 80 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.22 (br s, 1H), 8.13 (d, *J* = 7.9 Hz, 1H), 8.00 - 7.95 (m, 2H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 7.9 Hz, 1H), 7.64 - 7.59 (m, 1H), 7.57 - 7.52 (m, 2H).

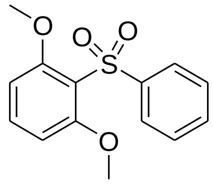
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 141.94 (d, *J* = 292.8 Hz), 133.91, 132.16 (q, *J* = 33.6 Hz), 131.10, 130.27, 130.04 (d, *J* = 3.3 Hz), 129.72, 128.01, 126.47, 124.82 (q, *J* = 3.7 Hz), 123.22 (d, *J* = 273.0 Hz).

MS: m/z: calc. for $C_{13}H_9F_3O_2S+H^+$ 287.04, found 287.30.

R_f (Cyclohexane:EtOAc 9:1): 0.16.

Analytical data are consistent with literature.(12)

1,3-Dimethoxy-2-(phenylsulfonyl)benzene (4i)



1,3-Dimethoxy-2-(phenylsulfonyl)benzene (**4i**) was synthesized from (2,6-dimethoxyphenyl)-lithium (**1b**) which was prepared by lithiation of 1,3-dimethoxybenzene (**5b**) with *n*BuLi and halogen-lithium-exchange of 2-iodo-1,3-dimethoxybenzene (**6h**) with *n*BuLi.(13,14)

From 1,3-dimethoxybenzene (5b): A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with 1,3-dimethoxybenzene (**5b**) (0.1 mL, 0.75 mmol, 1.5 equiv) in dry THF (1.0 mL) and cooled to 0 °C with an ice-bath. At this temperature *n*BuLi (0.34 mL, 2.45 M solution in hexane, 0.83 mmol, 1.65 eqiuv) was added dropwise and the mixture was stirred at 25 °C for 3.5 h. Then it was recooled to -30 °C and liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added at once. The mixture was allowed to warm to 25 °C within 60 min and then excess SO_2 was removes according to procedure A. To the crude sulfinic acid lithium salt **2b** was added diphenyliodonium triflate (**3a**) (215.1 mg, 0.5 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL), dried over Na_2SO_4 and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc 1:1) yielded the product as a colorless solid (110.3 mg, 79%).

From 2-iodo-1,3-dimethoxybenzene (6h): To a solution of 2-iodo-1,3-dimethoxybenzene (**6h**) (198.1 mg, 0.75 mmol, 1.5 equiv) in dry hexanes (3.5 mL) in a dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was added *n*BuLi (0.40 mL, 2.13 M in hexane, 0.85 mmol, 1.65 equiv) and the mixture stirred at 25 °C for 16 h. After cooling to -78 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added and the mixture was allowed to warm to 25 °C within 90 min. After removal of excess SO_2 and solvents according to Procedure A, to the crude sulfinic acid lithium salt **2b** was added diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL), dried over Na_2SO_4 and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc 4:1 → 1:1) yielded the product as a colorless solid (103.0 mg, 74%).

m.p.: 110 - 112 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.5 Hz, 2H), 7.55 - 7.42 (m, 3H), 7.39 (t, *J* = 8.4 Hz, 1H), 6.55 (d, *J* = 8.5 Hz, 2H), 3.75 (s, 6H).

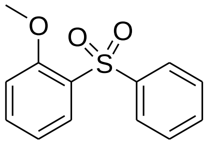
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 159.64, 144.64, 135.06, 132.43, 128.32, 127.35, 118.11, 105.44, 56.58.

MS: m/z: calc. for $C_{14}H_{14}O_4S+Na^+$ 301.05, found 301.30.

R_f (Cyclohexane:EtOAc 9:1): 0.05.

Analytical data are consistent with literature.(15)

1-(2-Methoxyphenylsulfonyl)benzene (4j)



1-(2-methoxyphenylsulfonyl)benzene (4j) was synthesized from 2-methoxyphenyllithium (**1c**) which was prepared by lithiation of anisole (**5c**) with *n*BuLi(16) and halogen-lithium-exchange of 2-bromoanisole (**6a**) with *n*BuLi.(7)

From anisole (5c): To a solution of anisole (**5c**) (0.82 mL, 0.75 mmol, 1.5 equiv) and TMEDA (0.22 mL, 1.5 mmol, 3.0 equiv) in dry Et_2O (1.0 mL) in a dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was added *n*BuLi (0.61 mL, 2.45 M in hexanes, 1.5 mmol, 3.0 equiv) dropwise. The mixture was allowed to stir at 25 °C for 30 min and then cooled to -78 °C and liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. After warming to 25 °C within 90 min, excess SO_2 and solvents were removed by procedure A. To the crude sulfinic acid lithium salt **2c** was added diphenyliodonium triflate (**3a**) (215.1 mg, 0.5 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL), dried over Na_2SO_4 and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc 20:1 → 4:1) yielded the product as a colorless solid (75.7 mg, 61%).

From 2-bromoanisole (6a): A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with *n*BuLi (0.33 mL, 2.45 M in hexanes, 0.80 mmol, 1.6 equiv) and cooled to -78 °C. Then 2-bromoanisole (**6a**) (0.1 mL, 0.75 mmol, 1.5 equiv) was added dropwise and the reaction mixture stirred at this temperature for 1 h, before liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. The mixture was allowed to warm to 25 °C within 90 min and then excess SO_2 and solvents were removed according to procedure A. To the crude sulfinic acid lithium salt **2c** was added diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL), dried over Na_2SO_4 and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc 9:1 → 4:1) yielded the product as a colorless solid (96.9 mg, 78%).

m.p.: 142 - 145 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.16 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.00 - 7.94 (m, 2H), 7.58 - 7.52 (m, 2H), 7.51 - 7.45 (m, 2H), 7.13 - 7.08 (m, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 3.75 (s, 3H).

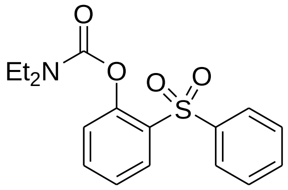
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 157.23, 141.68, 135.64, 133.01, 130.02, 129.16, 128.60, 125.41, 120.67, 112.61, 55.97.

MS: m/z: calc. for $C_{13}H_{12}O_3S+Na^+$ 271.04, found 271.40.

R_f (Cyclohexane:EtOAc 9:1): 0.09.

Analytical data are consistent with literature.(17)

2-(Phenylsulfonyl)phenyl diethylcarbamate (4k)



[2-[[(Diethylamino)carbonyl]oxy]phenyl]-lithium (**1d**) was synthesized according to literature by lithiation of phenyl diethylcarbamate (**5d**) with *s*BuLi.(18)

To a solution of *s*BuLi (0.70 mL, 1.2 M in cyclohexane, 0.83 mmol, 1.65 equiv) and TMEDA (0.12 mL, 0.83 mmol, 1.65 equiv) in a dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was added diethylcarbamate (**5d**) (154.0 mg, 0.75 mmol, 1.5 equiv) at -78 °C. The mixture stirred for 1 h at this temperature and then liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. The reaction was allowed to warm to 25 °C within 90 min. After removing excess SO_2 by procedure A, to the crude sulfinic acid lithium salt **2d** was added diphenyliodonium triflate (**3a**) (215.1 mg, 0.5 mmol, 1.0 equiv) and DMF (1.0 mL) and the reaction was stirred at 90 °C for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL), dried over Na_2SO_4 and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc 50:1 → 9:1) yielded the product as a colorless solid (77.8 mg, 47%).

m.p.: 92 - 93 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.15 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.88 – 7.80 (m, 2H), 7.65 – 7.52 (m, 2H), 7.52 – 7.42 (m, 2H), 7.37 (td, *J* = 7.8, 1.1 Hz, 1H), 7.21 (dd, *J* = 8.2, 0.9 Hz, 1H), 3.43 (q, *J* = 7.1 Hz, 2H), 3.23 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 152.37, 149.43, 141.47, 134.94, 133.29, 132.70, 130.05, 129.04, 127.37, 125.45, 125.11, 42.18, 41.91, 14.27, 13.28.

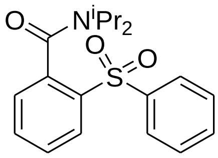
MS: m/z: calc. for $C_{17}H_{19}NO_4S+H^+$ 334.10, found 334.45.

HRMS: m/z: calc. for $C_{17}H_{19}NO_4S+K^+$ 372.06664, found 372.06664.

R$_f$ (Cyclohexane:EtOAc 4:1): 0.17.

IR (cm^{-1}): 2983 (w), 1723 (s), 1382 (w), 1365 (s), 1321 (m), 1155 (s), 1143 (s), 950 (m,), 750 (s), 731 (m), 586 (s).

2-(Phenylsulfonyl) diisopropylbenzamide (4l)



[2-[[Bis(1-methylethyl)amino]carbonyl]phenyl]-lithium (**1e**) was synthesized according to literature by lithiation of *N*,*N*-diisopropylbenzamide (**5e**) by *s*BuLi.$^{(19)}$

To a solution of *s*BuLi (0.70 mL, 1.2 M in cyclohexane, 0.83 mmol, 1.65 equiv) and TMEDA (0.12 mL, 0.83 mmol, 1.65 equiv) in a dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was added *N*,*N*-diisopropylbenzamide (154.0 mg, 0.75 mmol, 1.5 equiv) in dry THF (1.0 mL) at -78 °C. The mixture stirred for 1 h at this temperature and then liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. The reaction was allowed to warm to 25 °C within 90 min. After removing excess SO_2 by procedure B, diphenyliodonium triflate (**3a**) (215.1 mg, 0.5 mmol, 1.0 equiv) and DMF (1.0 mL) were added and the reaction was stirred at 90 °C for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL), dried over Na_2SO_4 and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc 4:1) yielded the product as a colorless solid (117.5 mg, 68%).

m.p.: 198 - 200 **°**C.

^{1}H-NMR (400 MHz, CDCl3): δ = 8.11 - 8.07 (m, 2H), 8.05 (d, *J* = 7.4 Hz, 1H), 7.58 - 7.44 (m, 5H), 7.22 (d, *J* = 6.8 Hz, 1H), 3.68 - 3.50 (m, 2H), 1.69 (d, *J* = 6.8 Hz, 3H), 1.55 (d, *J* = 6.8 Hz, 3H), 1.30 (d, *J* = 6.6 Hz, 3H), 1.09 (d, *J* = 6.6 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 167.91, 141.66, 138.52, 137.69, 133.56, 133.31, 130.36, 129.06, 129.01, 128.54, 127.03, 51.49, 46.00, 20.63, 20.52, 19.91, 19.56.

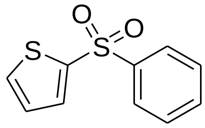
MS: m/z: calc. for $C_{19}H_{23}NO_3S+Na^+$ 368.13, found 368.30.

HRMS: m/z: calc. for $C_{19}H_{23}NO_3S+H^+$ 346.14714, found 346.14703.

R$_f$ (Cyclohexane:EtOAc 9:1): 0.07.

IR (cm^{-1}): 2362 (m), 1628 (m), 1340 (w), 1317 (m), 1153 (s), 782 (m), 759 (m), 730 (m), 688 (m), 625 (s).

2-(Phenylsulfonyl)thiophene (4m)



The organolithium compound 2-thienyl-lithium (**1f**) was synthesized according to literature by lithiation of thiophene (**5f**) with *n*BuLi.(5)

A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with *n*BuLi (0.34 mL, 2.45 M in hexanes, 0.83 mmol, 1.5 equiv) and cooled to -78 °C. Then thiophene (**5f**) (0.06 mL, 0.75 mmol, 1.5 equiv) was added dropwise and the mixture was allowed to warm to 0 °C and stirred at this temperature for 2 h. Then it was recooled to -78 °C and liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. After warming to 25 °C within 90 min, excess SO_2 and solvents were removed by procedure A. To the crude sulfinic acid lithium salt **2f** was added diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL), dried over Na_2SO_4 and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc 9:1 → 4:1) yielded the product as a colorless solid (95.6 mg, 85%).

m.p.: 120 - 122 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.02 - 7.97 (m, 2H), 7.70 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.64 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.60 - 7.56 (m, 1H), 7.54 - 7.50 (m, 2H), 7.09 - 7.07 (m, 1H).

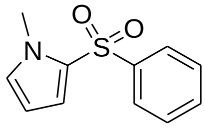
^{13}C-NMR (126 MHz, $CDCl_3$) δ = 143.18, 142.20, 134.02, 133.53, 133.45, 129.46, 127.99, 127.46.

MS: m/z: calc. for $C_{10}H_8O_2S_2+Na^+$ 246.99, found 247.40.

R_f (Cyclohexane:EtOAc 9:1): 0.19.

Analytical data are consistent with literature.(20)

1-Methyl-2-(phenylsulfonyl)-1*H*-pyrrole (4n)



(1-Methyl-1H-pyrrol-2-yl)-lithium (**1g**) was prepared by lithiation of *N*-methylpyrrol (**5g**) with *n*BuLi.(21)

A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with *N*-methylpyrrol (**5g**) (66 µL, 0.75 mmol, 1.5 equiv) and TMEDA (0.12 mL, 0.83 mmol, 1.65 equiv) and then *n*BuLi (0.34 mL, 2.45 M in hexanes, 0.83 mmol, 1.5 equiv) was added dropwise and the mixture was heated to 55 °C for 15 min. The mixture was then cooled to -78 °C and liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. After warming to 25 °C within 90 min, excess SO_2 and solvents were removed according to procedure A. To the crude sulfinic acid lithium salt **2g** was added diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL), dried over Na_2SO_4 and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc 9:1 → 4:1) yielded the product as a pale pink solid (55.9 mg, 51%).

m.p.: 79 - 81 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.91 - 7.86 (m, 2H), 7.58 - 7.54 (m, 1H), 7.53 - 7.48 (m, 2H), 7.04 (dd, *J* = 4.0, 1.9 Hz, 1H), 6.76 (t, *J* = 2.2 Hz, 1H), 6.17 (dd, *J* = 4.0, 2.6 Hz, 1H), 3.70 (s, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 142.30, 133.00, 129.80, 129.34, 128.00, 127.30, 119.01, 108.48, 35.76.

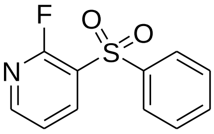
MS: m/z: calc. for $C_{11}H_{11}NO_2S+H^+$ 222.06, found 222.80.

HRMS: m/z: calc. for $C_{11}H_{11}NO_2S+H^+$ 222.05833, found 222.05796.

R$_f$ (Cyclohexane:EtOAc 9:1): 0.18.

IR (cm^{-1}): 1362 (w), 1295 (w), 1155 (s), 1128 (s), 752 (m), 725 (m), 688(s).

2-Fluoro-3-(phenylsulfonyl)pyridine (4o)



(2-Fluoro-3-pyridinyl)-lithium (**1h**) was prepared by lithiation of 2-fluoropyridine (**5h**) by LDA.$^{(22)}$
A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum, charged with diisopropylamin (0.12 mL, 0.85 mmol, 1.65 equiv) in dry THF (1.0 mL) was cooled to -78 °C and then *n*BuLi (0.35 mL, 2.45 M in hexane, 0.85 mmol, 1.65 equiv) was added dropwise. After stirring for 15 min at this temperature, the mixture was stirred for another 15 min at 0 °C. After recooling the *in situ* prepared LDA to -70 °C, 2-fluoropyridine (**5h**) (65 µL, 0.75 mmol, 1.5 equiv) was added dropwise and stirred at this temperature for 4 h. Then and liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. After warming to 25 °C within 90 min, excess SO_2 and solvents were removed according to procedure A. To the crude sulfinic acid lithium salt **2h** was added diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL), dried over Na_2SO_4 and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc 4:1 → 1:1) yielded the product as a colorless solid (55.9 mg, 51%).

m.p.: 90 - 92 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.56 - 8.51 (m, 1H), 8.43 - 8.38 (m, 1H), 8.05 - 8.00 (m, 2H), 7.68 - 7.64 (m, 1H), 7.59 - 7.54 (m, 2H), 7.43 - 7.39 (m, 1H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 158.87 (d, *J* = 245.4 Hz), 152.90 (d, *J* = 15.1 Hz), 140.96, 139.74, 134.42, 129.52, 128.63, 125.41 (d, *J* = 30.3 Hz), 122.23 (d, *J* = 4.7 Hz).

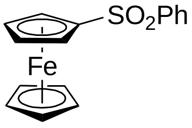
MS: m/z: calc. for $C_{11}H_8FNO_2S+Na^+$ 260.02, found 260.50.

HRMS: m/z: calc. for $C_{11}H_8FNO_2S+H^+$ 238.03325, found 238.03340.

R$_f$ (Cyclohexane:EtOAc 9:1): 0.15.

IR (cm^{-1}): 1448 (w), 14225m (w), 1326 (w), 1300 (w), 1156 (s), 1134 (s), 1091 (m), 1067 (m), 852 (m), 812 (m), 750 (m), 725 (s), 685 (s).

(Phenylsulfonyl)-ferrocene (4p)



Ferrocenyllithium (**1i**) was prepared according to literature by lithiation of ferrocene (**5i**) with *t*BuLi.[(23)]
A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with ferrocene (153.2 mg, 0.83 mmol, 1.65 equiv) in dry THF (1.0 mL) and cooled to 0 °C. At this temperature *t*BuLi (0.46 mL, 1.64 M in pentane, 0.75 mmol, 1.5 equiv) was added dropwise and the mixture was stirred for 15 min. After warming to 25 °C, the mixture was recooled to -78 °C and and liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. The reaction mixture was allowed to warm to 25 °C within 90 min. After removing excess SO_2 by procedure B, diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL) were added. The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL), dried over Na_2SO_4 and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc 9:1 → 4:1) yielded the product as an orange solid (68.8 mg, 42%).

m.p.: 140 - 145 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 7.5 Hz, 2H), 7.54 – 7.47 (m, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 4.69 (s, 2H), 4.51 (s, 5H), 4.41 (s, 2H).

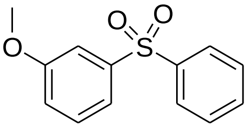
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 143.25, 132.68, 129.14, 126.83, 90.40, 71.28, 70.91, 69.41.

MS: m/z: calc. for $C_{16}H_{14}FeO_2S+Na^+$ 349.00, found 349.20.

R_f (Cyclohexane:EtOAc 9:1): 0.26.

Analytical data are consistent with literature.[(17)]

1-Methoxy-3-(phenylsulfonyl)benzene (4q)



(3-Methoxyphenyl)lithium (**1j**) was prepared by halogen-lithium-exchange from 3-bromoanisole (**6b**) and *n*BuLi.[(7)]
A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with *n*BuLi (0.33 mL, 2.45 M in hexanes, 0.80 mmol, 1.6 equiv) and cooled to -70 °C. Then 3-bromoanisole (**6b**) (0.1 mL, 0.75 mmol, 1.5 equiv) was added dropwise and the reaction mixture stirred at this temperature for 1 h, before liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. The mixture was allowed to warm to 25 °C within 90 min and then excess SO_2 and solvents were removed according to procedure A. To the crude sulfinic acid lithium salt **2j** was added diphenyliodonium triflate (**3a**) (215.1 mg, 0.5 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL), dried over Na_2SO_4 and the solvents

were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc 9:1 → 4:1) yielded the product as a colorless solid (114.7 mg, 92%).

m.p.: 89 - 91 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.98 - 7.91 (m, 2H), 7.59 - 7.54 (m, 1H), 7.53 - 7.48 (m, 3H), 7.46 - 7.43 (m, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.07 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1H), 3.84 (s, 3H).

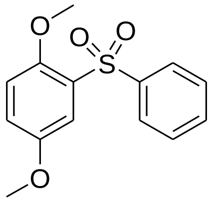
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 160.15, 142.83, 141.68, 133.33, 130.52, 129.40, 127.78, 120.06, 119.68, 112.37, 55.82.

MS: m/z: calc. for $C_{13}H_{12}O_3S+Na^+$ 271.04, found 271.13.

R_f (Cyclohexane:EtOAc 9:1): 0.15.

Analytical data are consistent with literature.(24)

1-(2,5-Dimethoxyphenylsulfonyl)benzene (4r)



(2,5-dimethoxyphenyl)-lithium (**1m**) was prepared according to literature by halogen-lithium-exchange of 1-bromo-2,4-dimethoxybenzene (**6g**) and *n*BuLi.(24)

To a solution of 1-bromo-2,4-dimethoxybenzene (**6g**) (0.11 mL, 0.75 mmol, 1.5 equiv) in dry THF (1.0 mL) in a dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was added *n*BuLi (0.56 mL, 1.2 mmol, 2.4 equiv) dropwise at 25 °C and then stirred for 2 h. After cooling to -78 °C, liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. After warming to 25 °C within 90 min, excess SO_2 and solvents were removed according to procedure A. To the crude sulfinic acid lithium salt **2m** was added diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL), dried over Na_2SO_4 and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc 9:1 → 1:1) yielded the product as a colorless solid (58.4 mg, 42%).

m.p.: 107 - 109 **°**C.

^{1}H-NMR: (500 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 8.8 Hz, 1H), 7.96 – 7.92 (m, 2H), 7.56 – 7.51 (m, 1H), 7.49 – 7.44 (m, 2H), 6.58 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.38 (d, *J* = 2.3 Hz, 1H), 3.84 (s, 3H), 3.72 (s, 3H).

^{13}C-NMR: (101 MHz, $CDCl_3$): δ = 165.77, 158.77, 142.25, 132.73, 131.87, 128.56, 128.19, 121.49, 104.76, 99.59, 55.97, 55.86.

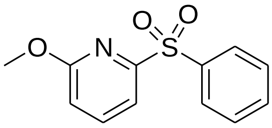
MS: m/z: calc. for $C_{14}H_{14}O_4S+Na^+$ 301.05, found 302.30.

HRMS: m/z: calc. for $C_{14}H_{14}O_4S+H^+$ 279.06856, found 279.06858.

R_f (Cyclohexane:EtOAc 9:1): 0.08.

IR (cm^{-1}): 1578 (m), 1299 (m), 1210 (m), 1144 (s), 1091 (s), 1020 (s), 829 (w), 733 (m), 691 (m), 610 (m).

2-Methoxy-6-(phenylsulfonyl)pyridine (4s)



(6-Methoxy-2-pyridinyl)-lithium (**1n**) was prepared via a halogen-lithium-exchange of 2-bromo-6-methoxypyridine (**6i**) and *t*BuLi according to literature.$^{(26)}$

A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with 2-bromo-6-methoxypyridine (**6i**) (141.0 mg, 0.75 mmol, 1.5 equiv) in dry THF (2.0 mL) and cooled to -78 °C. At this temperature *t*BuLi (0.91 mL, 1.64 M in pentane, 1.5 mmol, 3.0 equiv) was added dropwise and the mixture stirred for 15 min. Then liquid SO_2 (0.1 mL, 5.0 mmol, 10.0 equiv) was added. After warming to 25 °C within 90 min, excess SO_2 and solvents were removed according to procedure A. To the crude sulfinic acid lithium salt **2n** was added diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to 25 °C, sat. aqueous NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (15 mL). The combined organic layers were washed with dist. H_2O (15 mL), dried over Na_2SO_4 and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc 9:1 → 4:1) yielded the product as a colorless solid (44.3 mg, 36%).

m.p.: 57 - 59 **°**C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.12 – 8.06 (m, 2H), 7.79 – 7.76 (m, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.65 – 7.58 (m, 1H), 7.57 – 7.50 (m, 2H), 6.86 (dd, *J* = 7.8, 1.0 Hz, 1H), 3.86 (s, 3H).

^{13}C-NMR: (101 MHz, $CDCl_3$): δ = 164.17, 155.83, 139.84, 139.11, 133.74, 129.22, 129.00, 115.63, 115.04, 54.11.

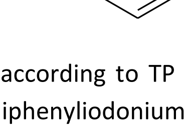
MS: m/z: calc. for $C_{12}H_{11}NO_3S+Na^+$ 272.04, found 272.20.

HRMS: m/z: calc. for $C_{12}H_{11}NO_3S+H^+$ 250.05324, found 250.05344

R_f (Cyclohexane:EtOAc 9:1): 0.21.

IR (cm^{-1}): 1601 (w), 1586 (w), 1469 (m), 1413 (m), 1315 (m), 1165 (s), 1147 (s), 1129 (s), 1016 (s), 984 (w), 805 (m), 727 (s), 687 (m).

1-(Methylsulfonyl)benzene (8a)



1-(Methylsulfonyl)benzene (**8a**) was prepared according to TP 2 from methyllithium (**7a**) (0.63 mL, 1.2 M in Et_2O, 0.75 mmol), SO_2 (0.1 mL, 5.0 mmol), diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (Cyclohexane:EtOAc 20:1 → 4:1) yielded the product as colorless solid (65.5 mg, 84%).

m.p.: 88 - 90 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.97 - 7.93 (m, 2H), 7.69 - 7.64 (m, 1H), 7.61 - 7.55 (m, 2H), 3.05 (s, 3H).

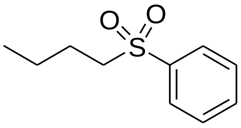
^{13}C-NMR (126 MHz, CDCl3): δ = 140.70, 133.84, 129.50, 127.48, 44.62.

MS: m/z: calc. for $C_7H_8O_2S$+Na^+ 179.01, found 179.70.

R$_f$ (Cyclohexane:EtOAc 9:1): 0.18.

Analytical data are consistent with literature.(27)

1-(Butylsulfonyl)benzene (8b)



1-(Butylsulfonyl)benzene (**8b**) was prepared according to TP 2 from *n*butyllithium (**7b**) (0.31 mL, 2.45 M in hexane, 0.75 mmol), SO_2 (0.1 mL, 5.0 mmol), diphenyliodonium triflate **3a** (215.1 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (Cyclohexane:EtOAc 20:1 → 4:1) yielded the product as colorless oil (88.4 mg, 89%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.97 - 7.87 (m, 2H), 7.69 - 7.63 (m, 1H), 7.60 - 7.54 (m, 2H), 3.13 - 3.04 (m, 2H), 1.75 - 1.64 (m, 2H), 1.39 (sext, *J* = 5.7 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).

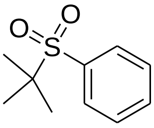
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 139.40, 133.72, 129.37, 128.18, 56.22, 24.75, 21.67, 13.61.

MS: m/z: calc. for $C_{10}H_{14}O_2S$+H^+ 199.06, found 199.60.

R$_f$ (Cyclohexane:EtOAc 9:1): 0.19.

Analytical data are consistent with literature.(28)

1-(*tert*-Butylsulfonyl)benzene (8c)



1-(*tert*-Butylsulfonyl)benzene (**8c**) was prepared according to TP 2 from *t*butyllithium (**7c**) (0.46 mL, 1.64 M in pentane, 0.75 mmol), SO_2 (0.1 mL, 5.0 mmol), diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (Cyclohexane:EtOAc 20:1 → 4:1) yielded the product as colorless solid (75.5 mg, 76%).

m.p.: 93 - 95 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.98 - 7.84 (m, 2H), 7.71 - 7.60 (m, 1H), 7.59 - 7.47 (m, 2H), 1.34 (s, 9H).

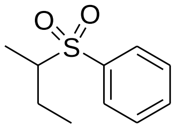
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 135.48, 133.67, 130.61, 128.84, 59.93, 23.76.

MS: m/z: calc. for $C_{10}H_{14}O_2S$+Na^+ 221.06, found 221.14.

R$_f$ (Cyclohexane:EtOAc 9:1): 0.19.

Analytical data are consistent with literature.(29)

1-(*sec*-Butylsulfonyl)benzene (8d)



1-(*sec*-Butylsulfonyl)benzene (**8d**) was prepared according to TP 2 from *s*butyllithium (**7d**) (0.63 mL, 1.2 M in cyclohexane, 0.75 mmol), SO_2 (0.1 mL, 5.0 mmol), diphenyliodonium triflate (**3a**) (215.1 mg, 0.50 mmol) in DMF (1.0 mL). Purification by chromatography (Cyclohexane:EtOAc 9:1 → 4:1) yielded the product as colorless oil (75.3 mg, 76%).

^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 7.91 - 7.85 (m, 2H), 7.68 - 7.62 (m, 1H), 7.60 - 7.53 (m, 2H), 3.02 - 2.89 (m, 1H), 2.07 - 1.95 (m, 1H), 1.50 - 1.36 (m, 1H), 1.27 (d, *J* = 6.9 Hz, 3H), 0.98 (t, *J* = 7.5 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 137.58, 133.66, 129.18, 129.15, 61.68, 22.64, 12.72, 11.29.

MS: m/z: calc. for $C_{10}H_{14}O_2S+Na^+$ 221.06, found 221.50.

R$_f$ (Cyclohexane:EtOAc 9:1): 0.21.

Analytical data are consistent with literature.(6)

3 Literature

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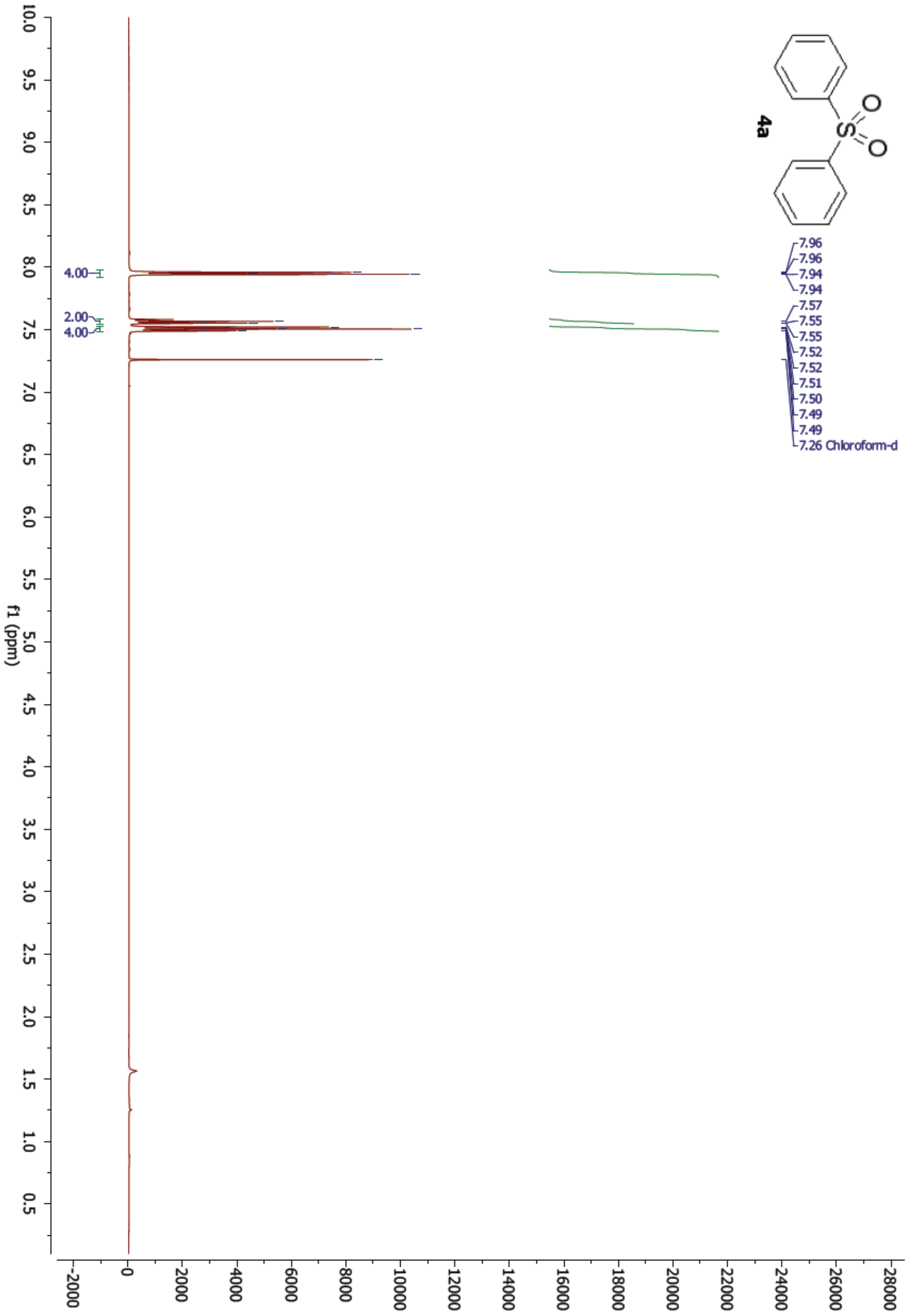
4 Spectra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O
S
O
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7.96
7.94
7.94
7.57
7.55
7.55
7.52
7.52
7.51
7.50
7.49
7.49
7.26 Chloroform-d
4.00
2.00
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
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4000
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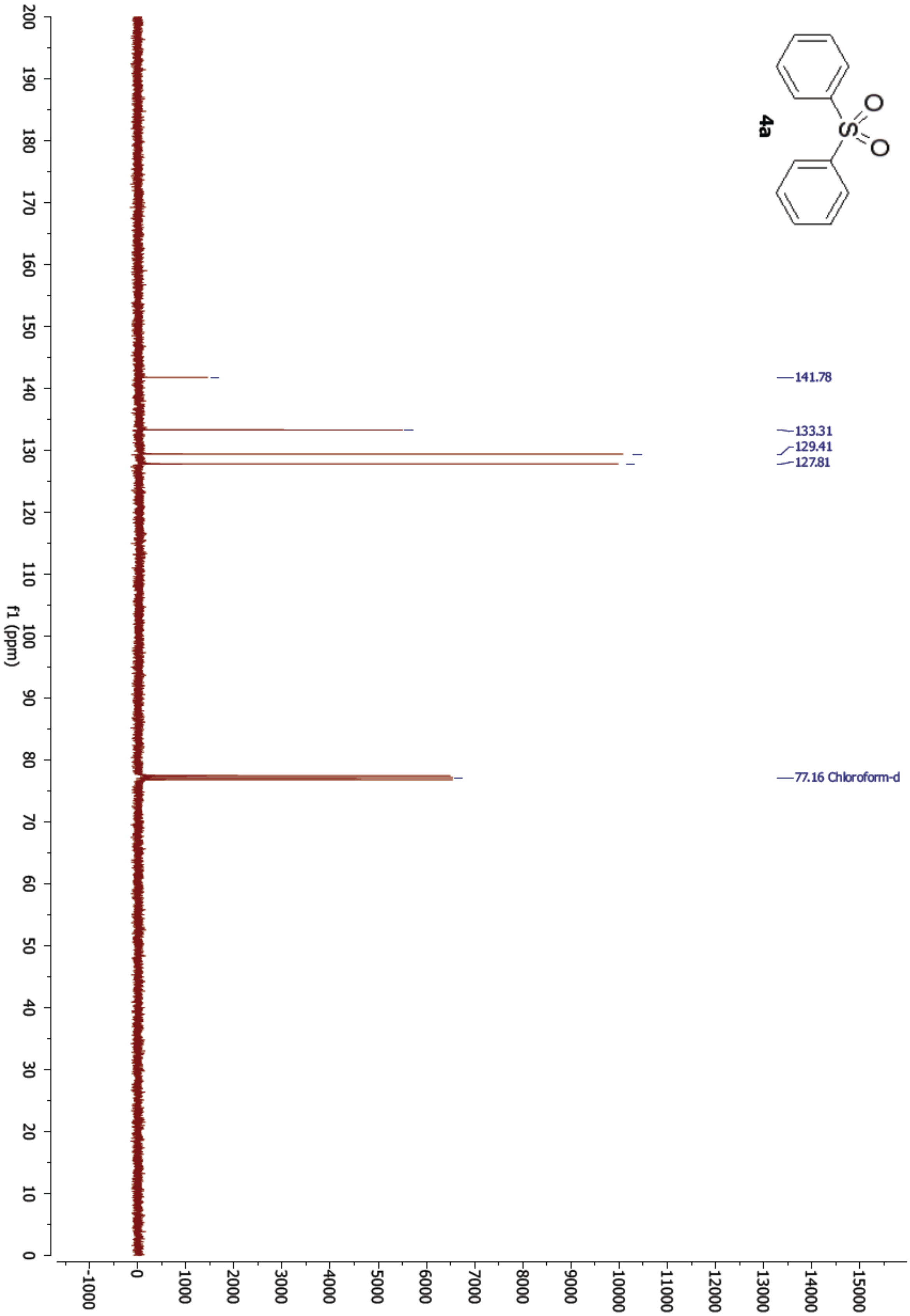
4a
141.78
133.31
129.41
127.81
77.16 Chloroform-d
f1 (ppm)
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190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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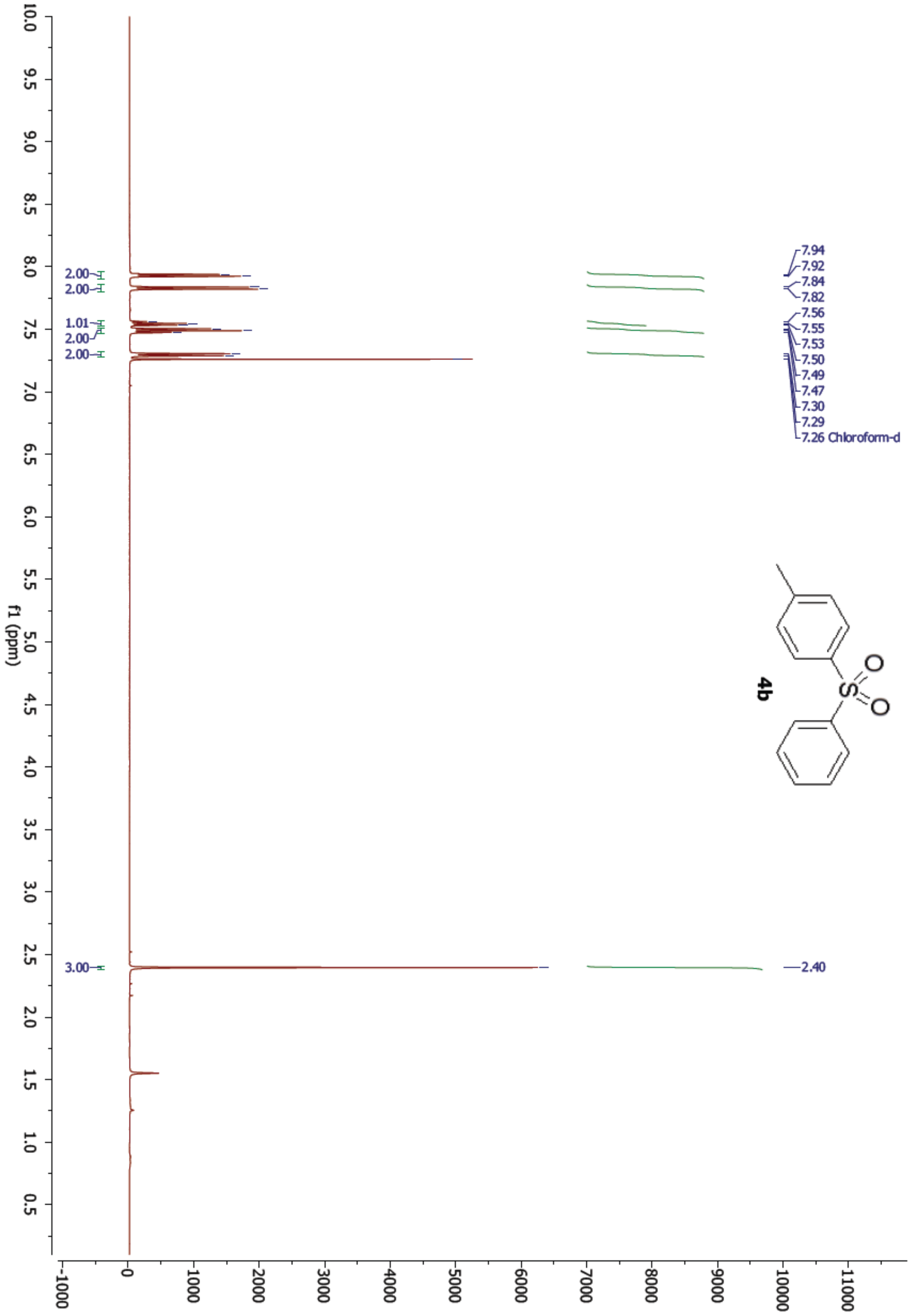

4b
7.94
7.92
7.84
7.82
7.56
7.55
7.53
7.50
7.49
7.47
7.30
7.29
7.26 Chloroform-d
2.40
2.00
2.00
1.01
2.00
2.00
3.00
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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5000
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10000
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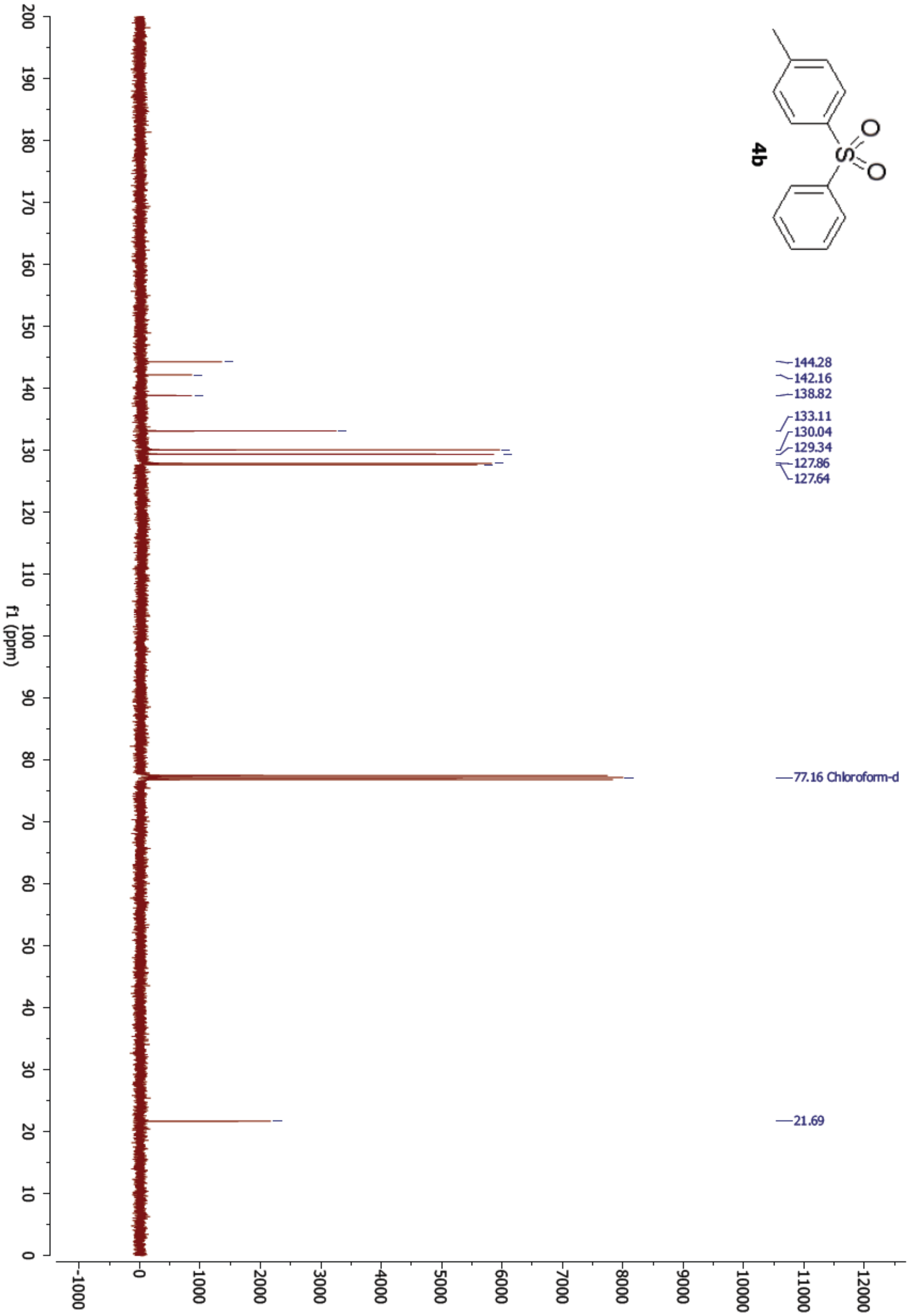

4b

144.28
142.16
138.82
133.11
130.04
129.34
127.86
127.64
77.16 Chloroform-d
21.69
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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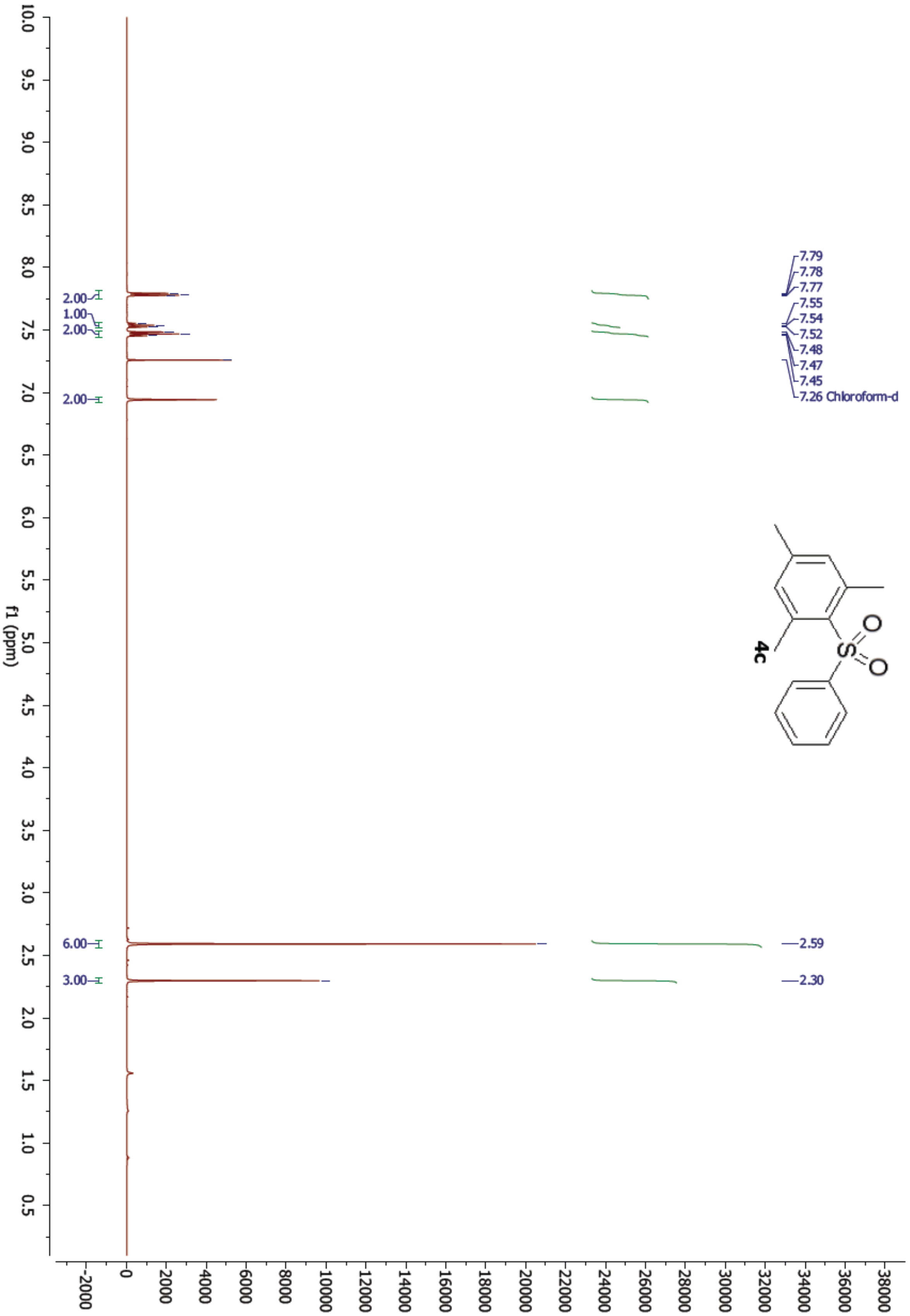
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1.00
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2.00
6.00
3.00
f1 (ppm)
10.0
9.5
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4000
6000
8000
10000
12000
14000
16000
18000
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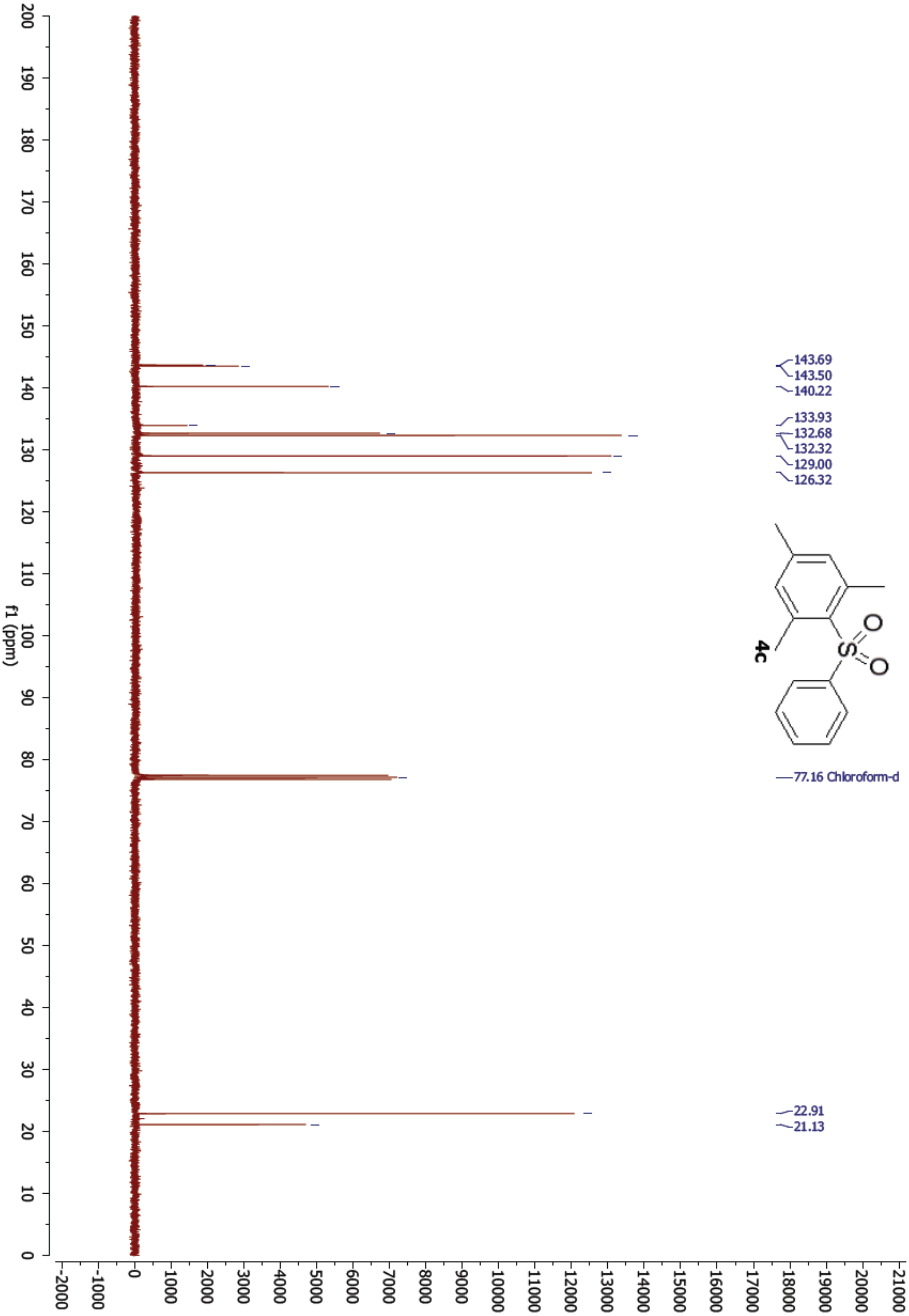
22000
24000
26000
28000
30000
32000
34000
36000
38000
S
O
O

4c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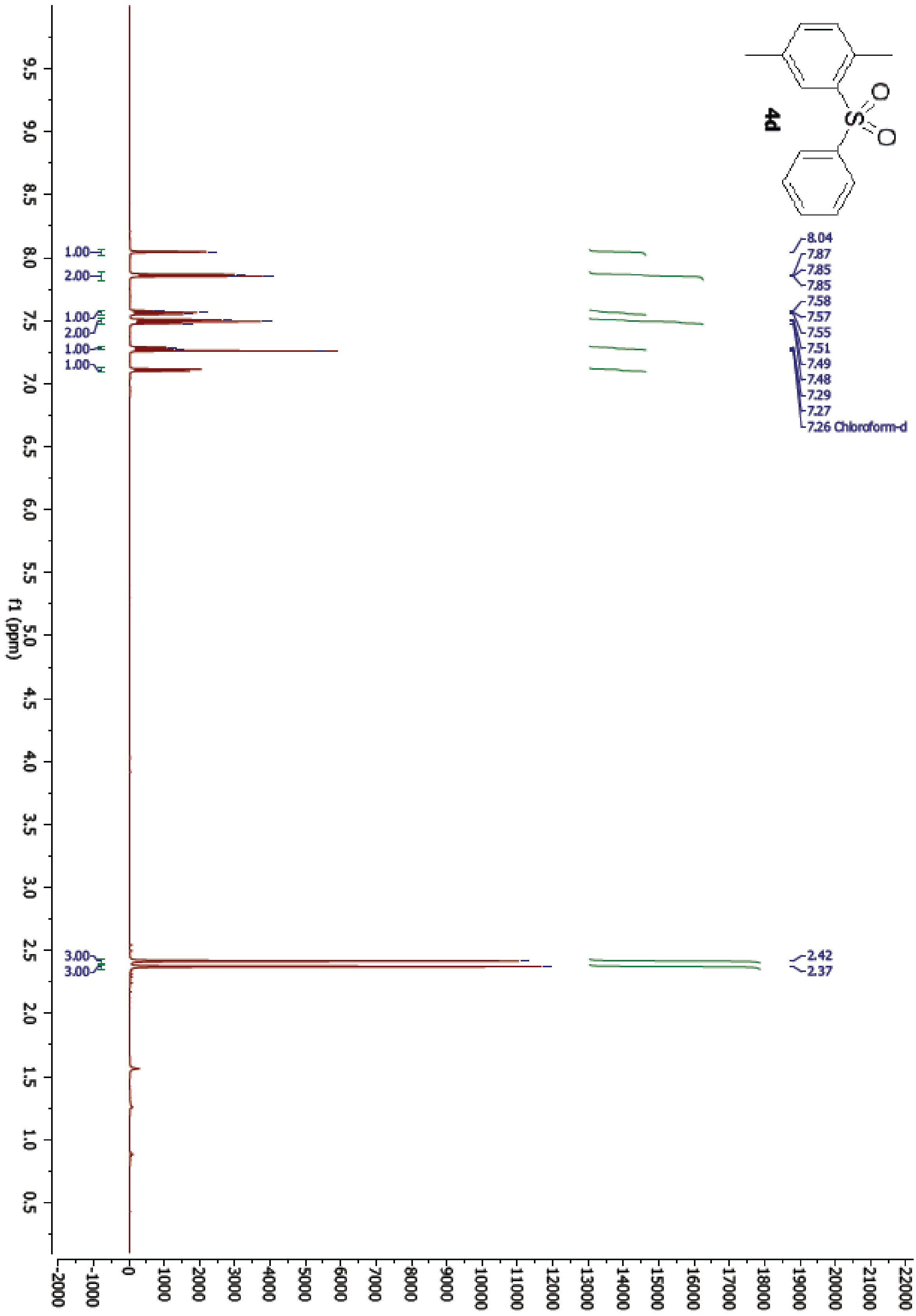
143.50
140.22
133.93
132.68
132.32
129.00
126.32
4c
77.16 Chloroform-d
22.91
21.13
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-2000
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000
15000
16000
17000
18000
19000
20000
21000


4d
8.04
7.87
7.85
7.85
7.58
7.57
7.55
7.51
7.49
7.48
7.29
7.27
7.26 Chloroform-d
2.42
2.37
1.00
2.00
1.00
2.00
1.00
1.00
3.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
-2000
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
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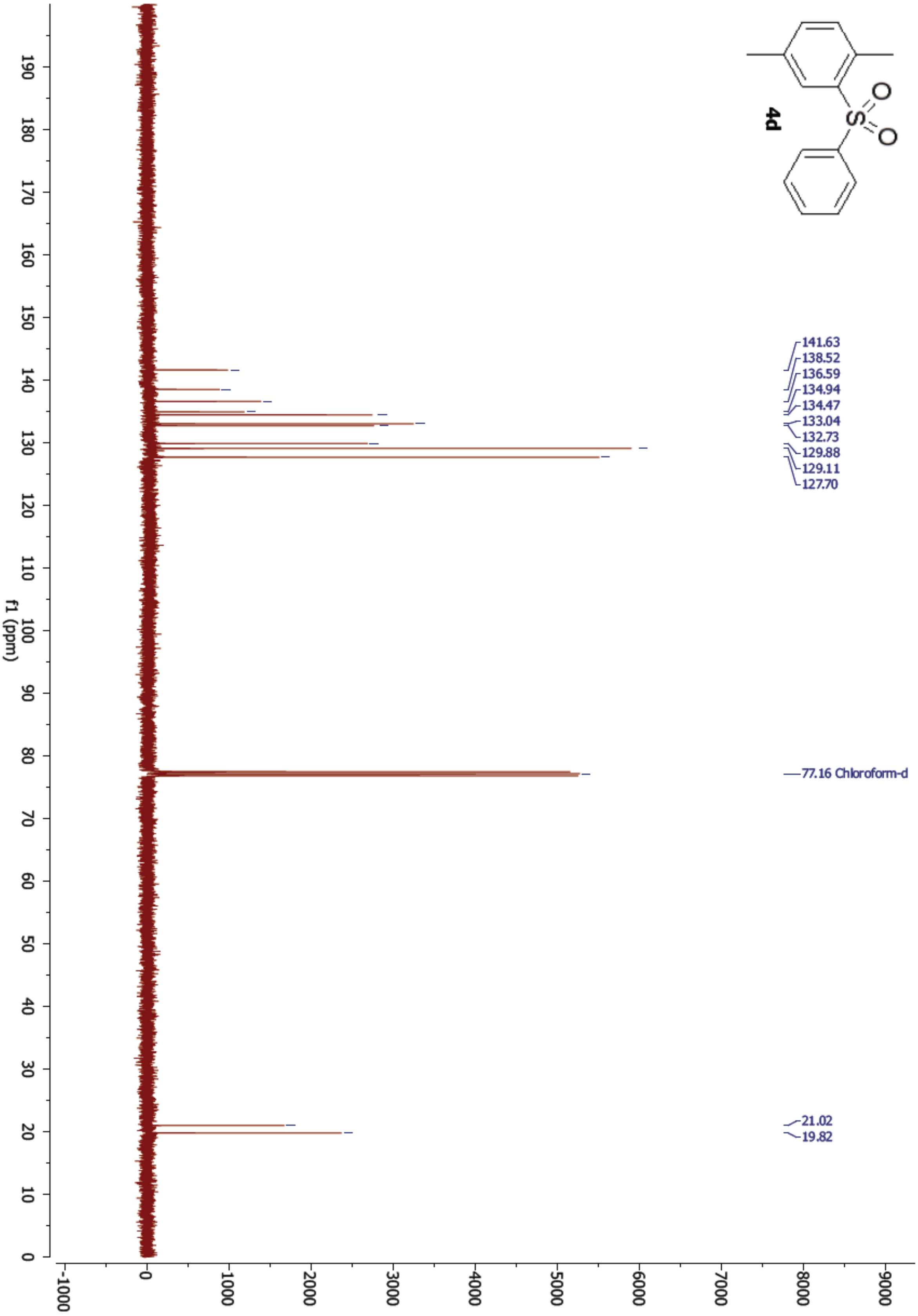
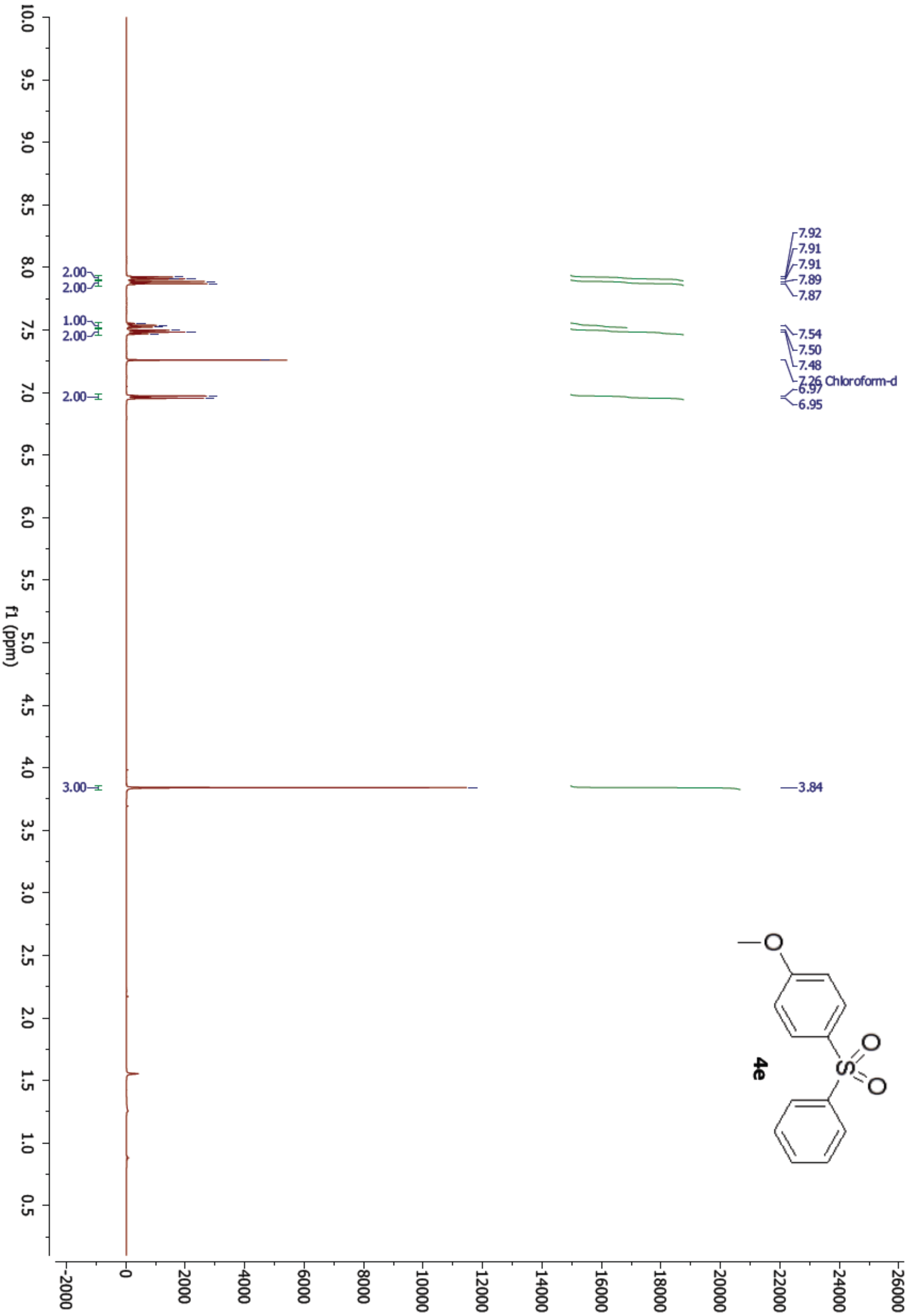
18000
19000
20000
21000
22000


4d

141.63
138.52
136.59
134.94
134.47
133.04
132.73
129.88
129.11
127.70
77.16 Chloroform-d
21.02
19.82
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000


4e
7.92
7.91
7.91
7.89
7.87
7.54
7.50
7.48
7.26 Chloroform-d
6.97
6.95
3.84
2.00
2.00
1.00
2.00
2.00
3.00
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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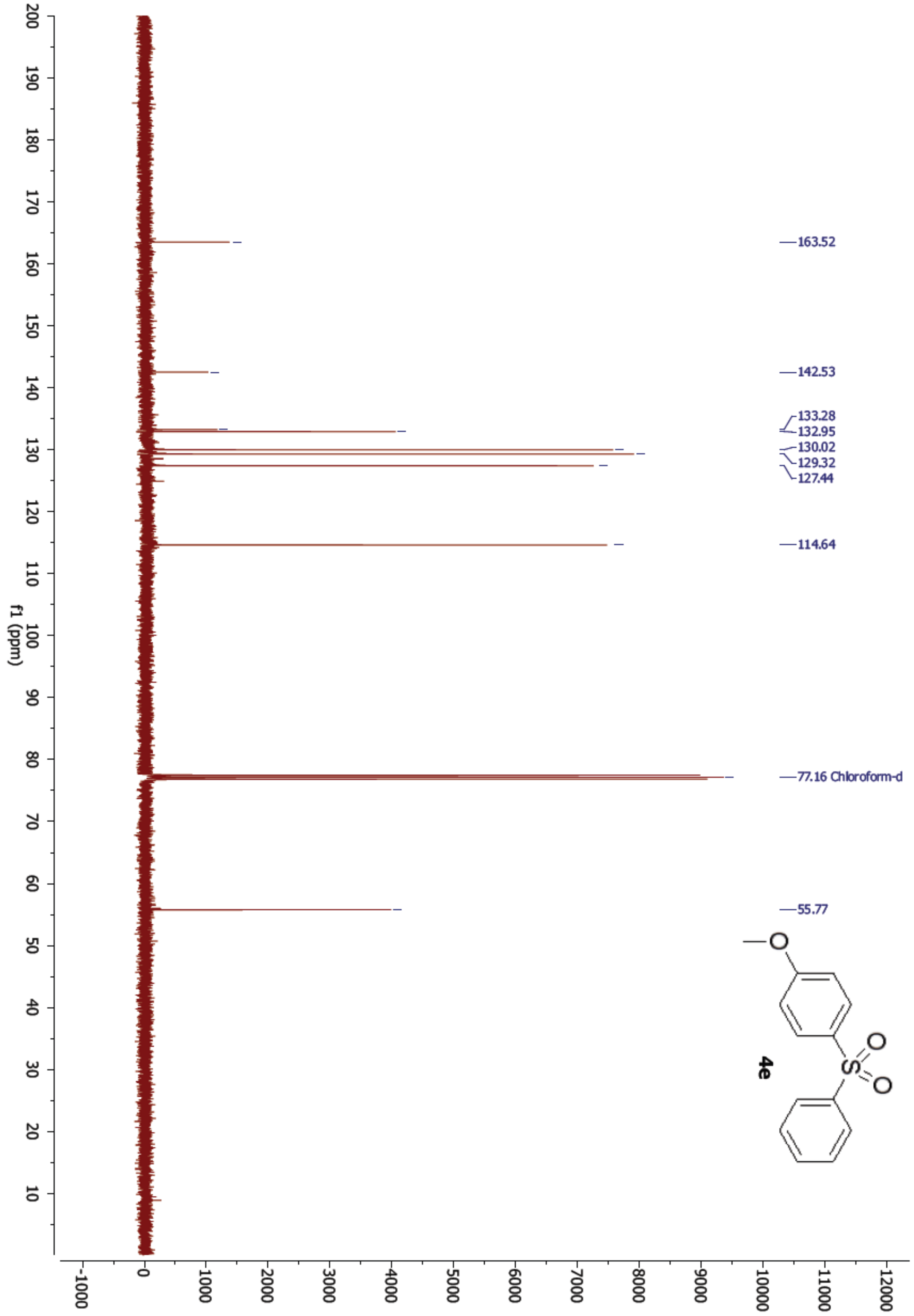
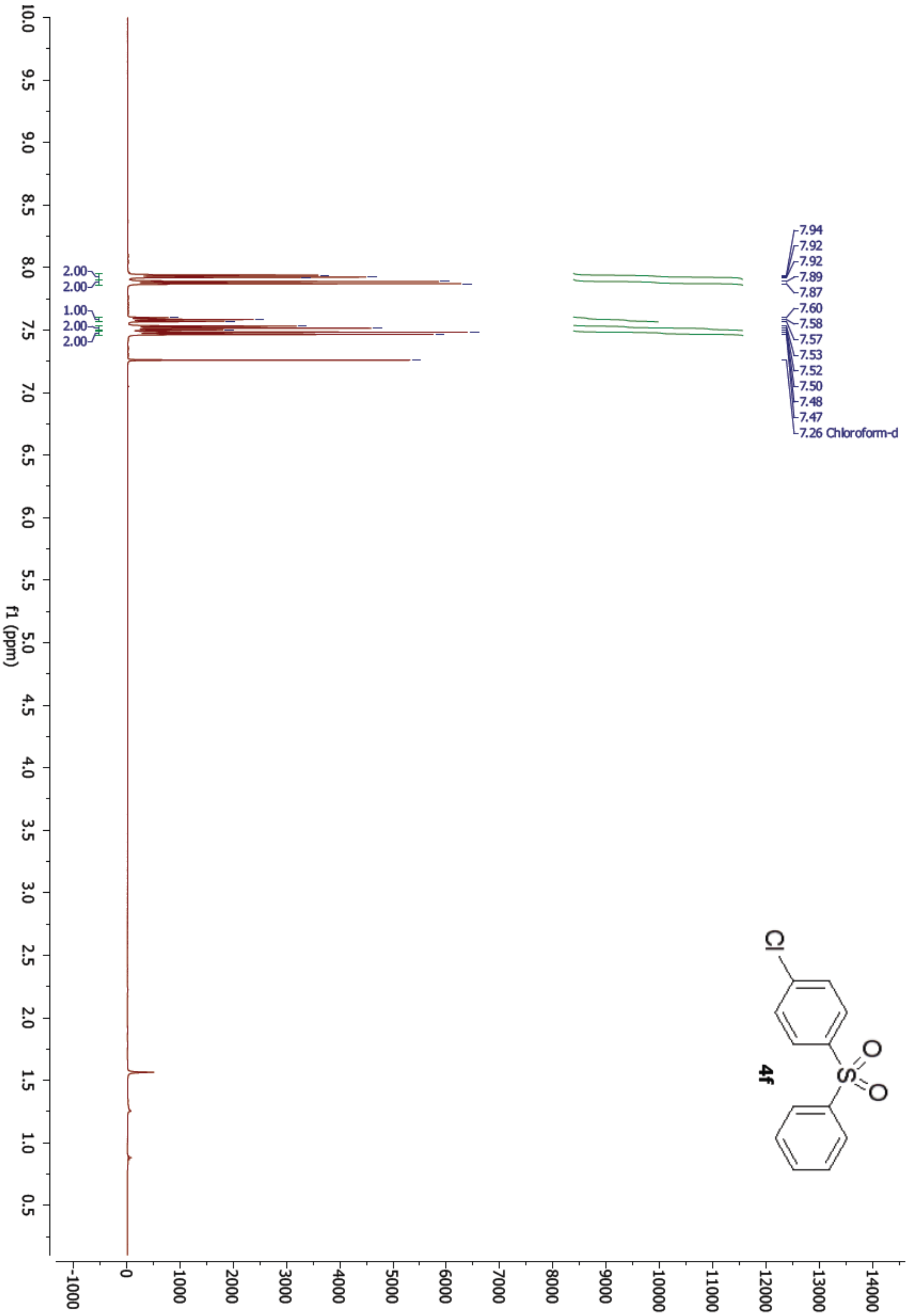
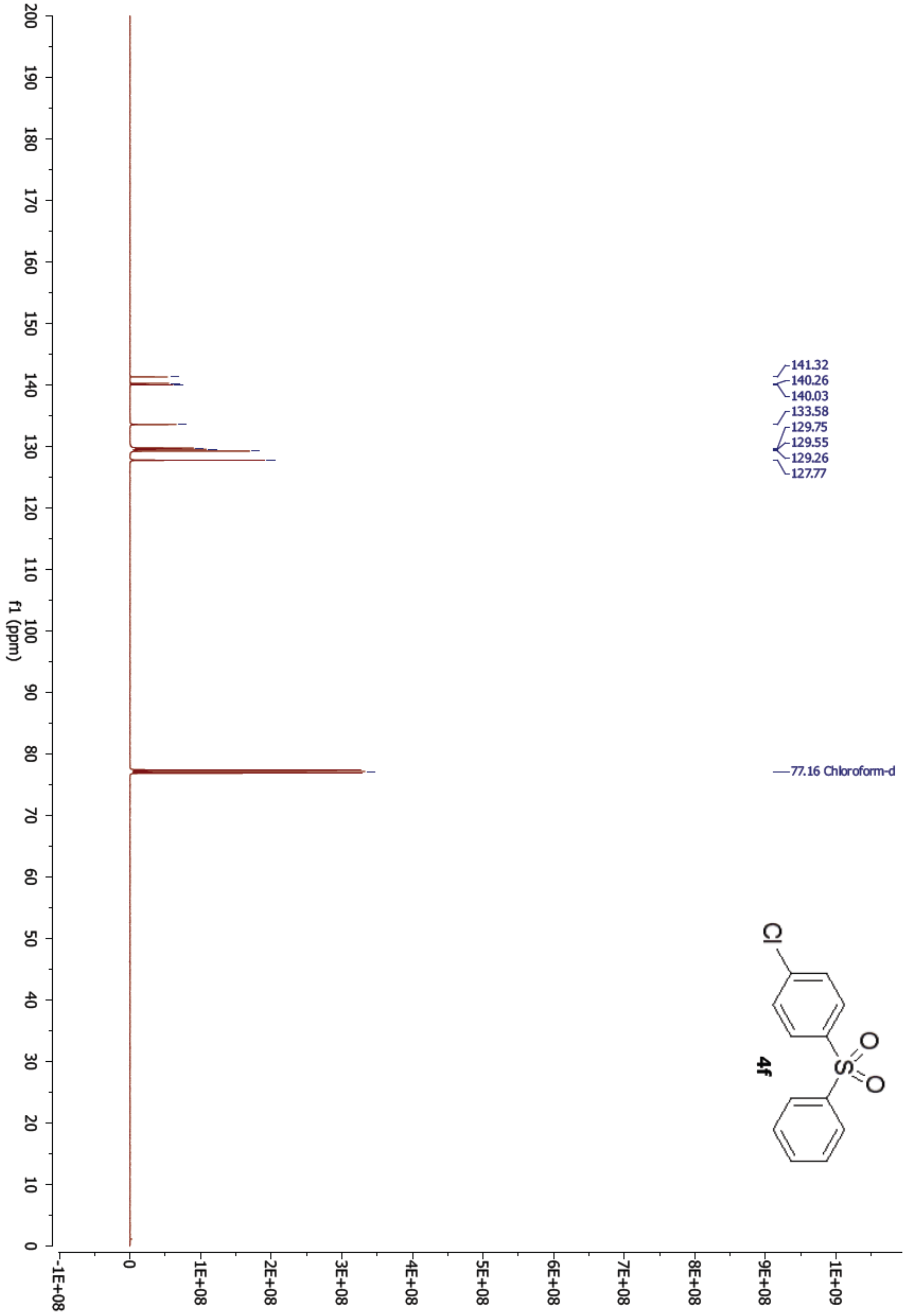
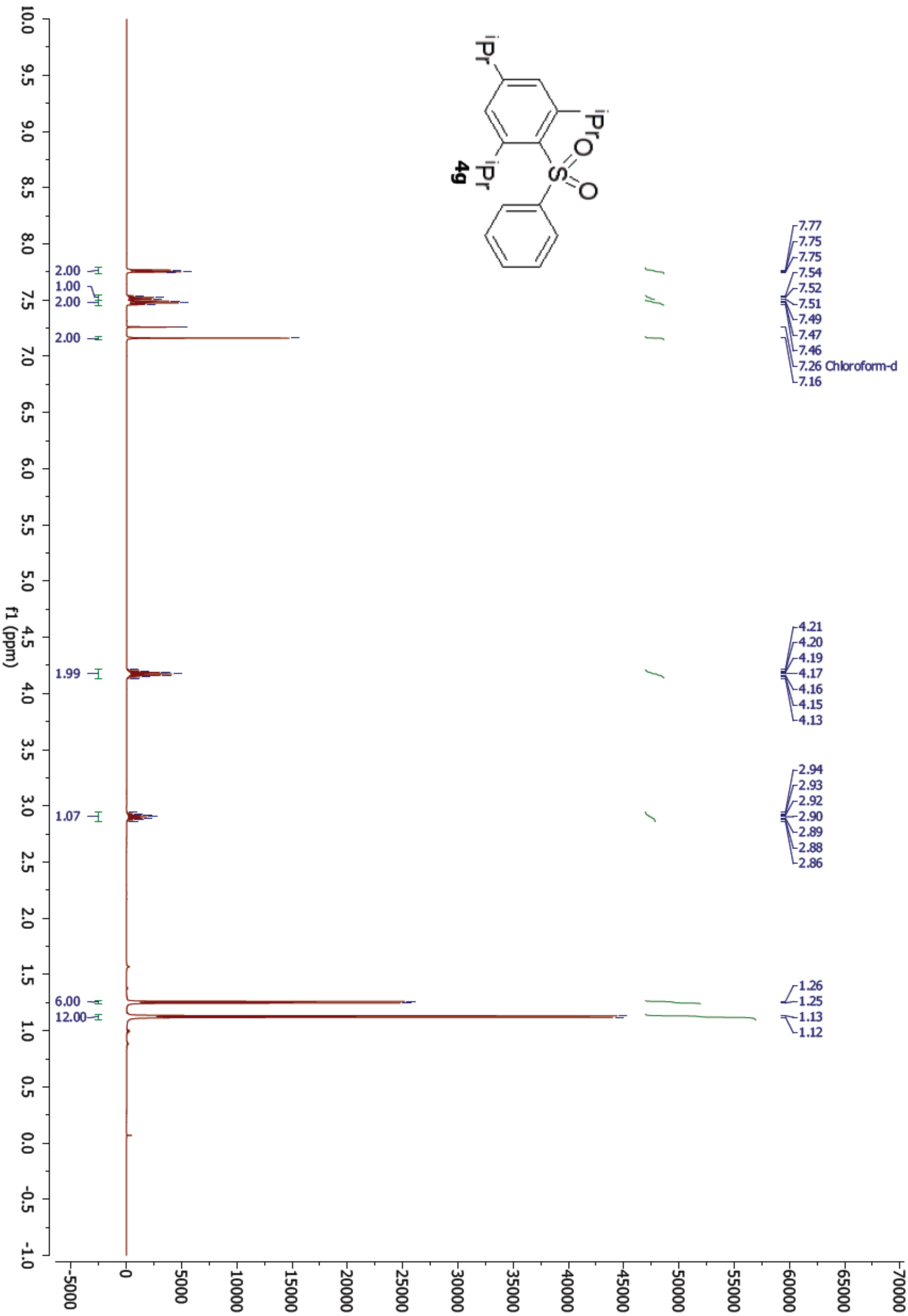
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
20000
22000
24000
26000

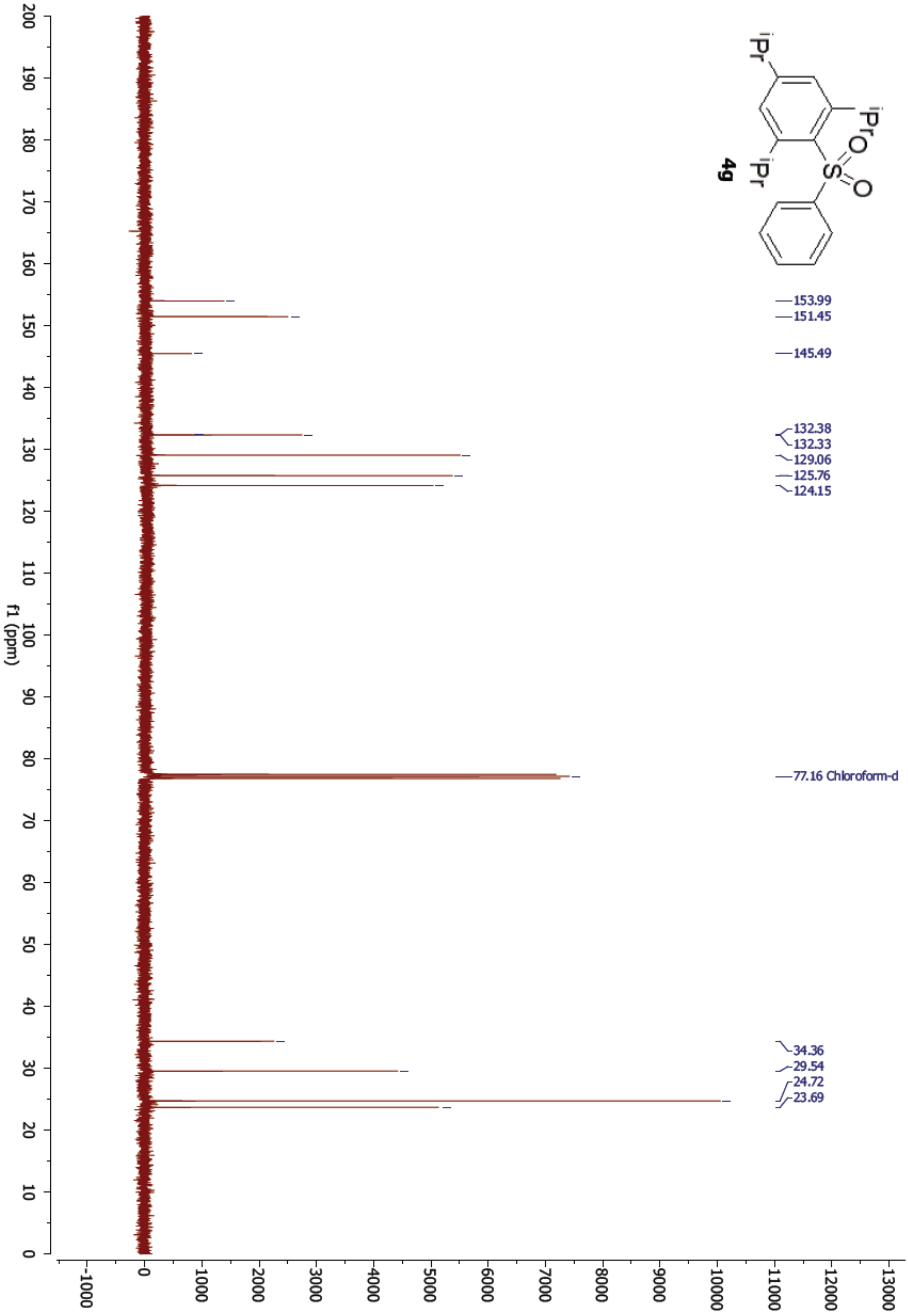

163.52
142.53
133.28
132.95
130.02
129.32
127.44
114.64
77.16 Chloroform-d
55.77
4e
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000


2.00
2.00
1.00
2.00
2.00
7.94
7.92
7.92
7.89
7.87
7.60
7.58
7.57
7.53
7.52
7.50
7.48
7.47
7.26 Chloroform-d
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
-1000 0 1000 2000 3000 4000 5000 6000 7000 8000 9000 10000 11000 12000 13000 14000
Cl
S
O
O
4f

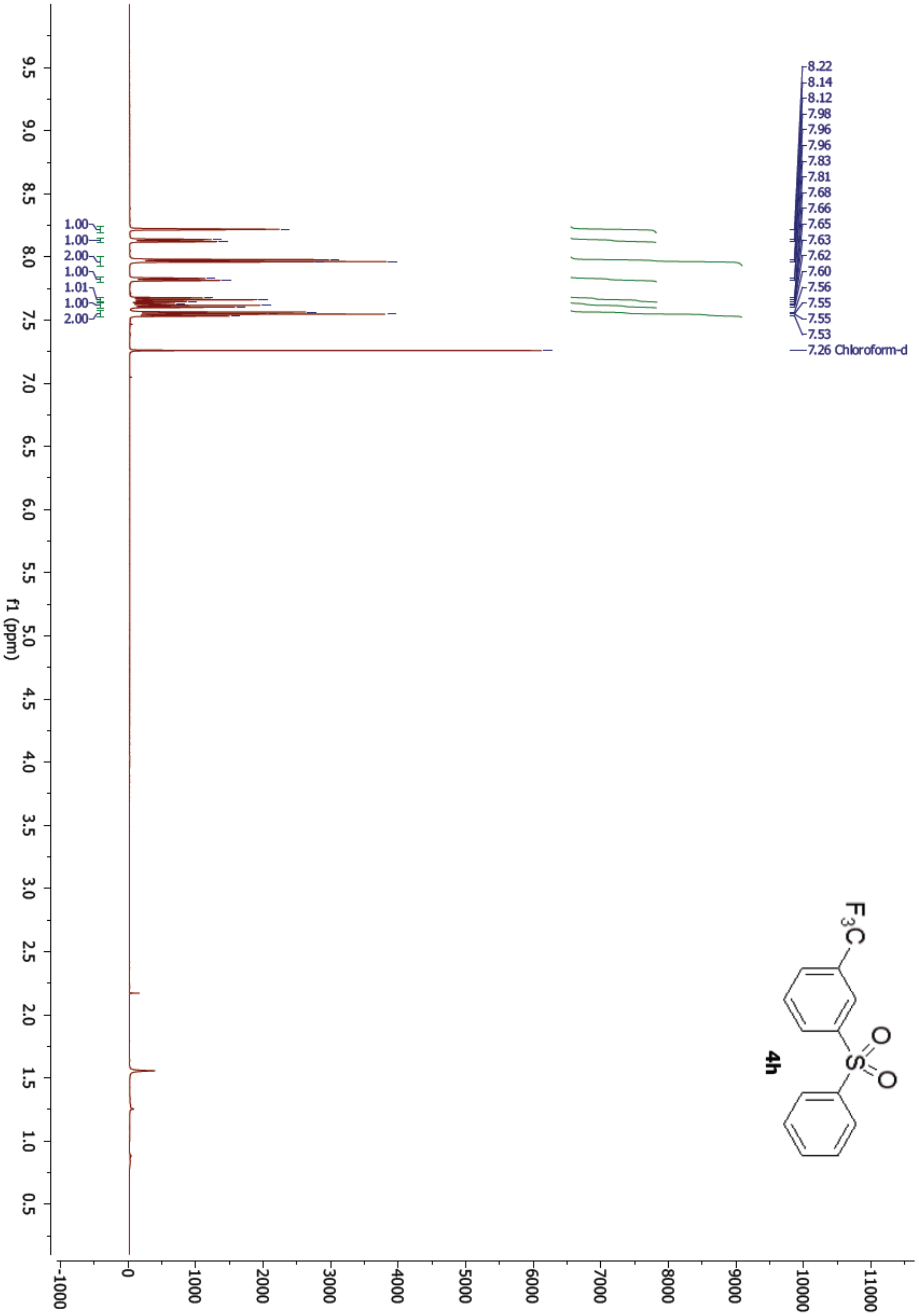

141.32
140.26
140.03
133.58
129.75
129.55
129.26
127.77
77.16 Chloroform-d
Cl
O
S
O
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1E+08
0
1E+08
2E+08
3E+08
4E+08
5E+08
6E+08
7E+08
8E+08
9E+08
1E+09

4f

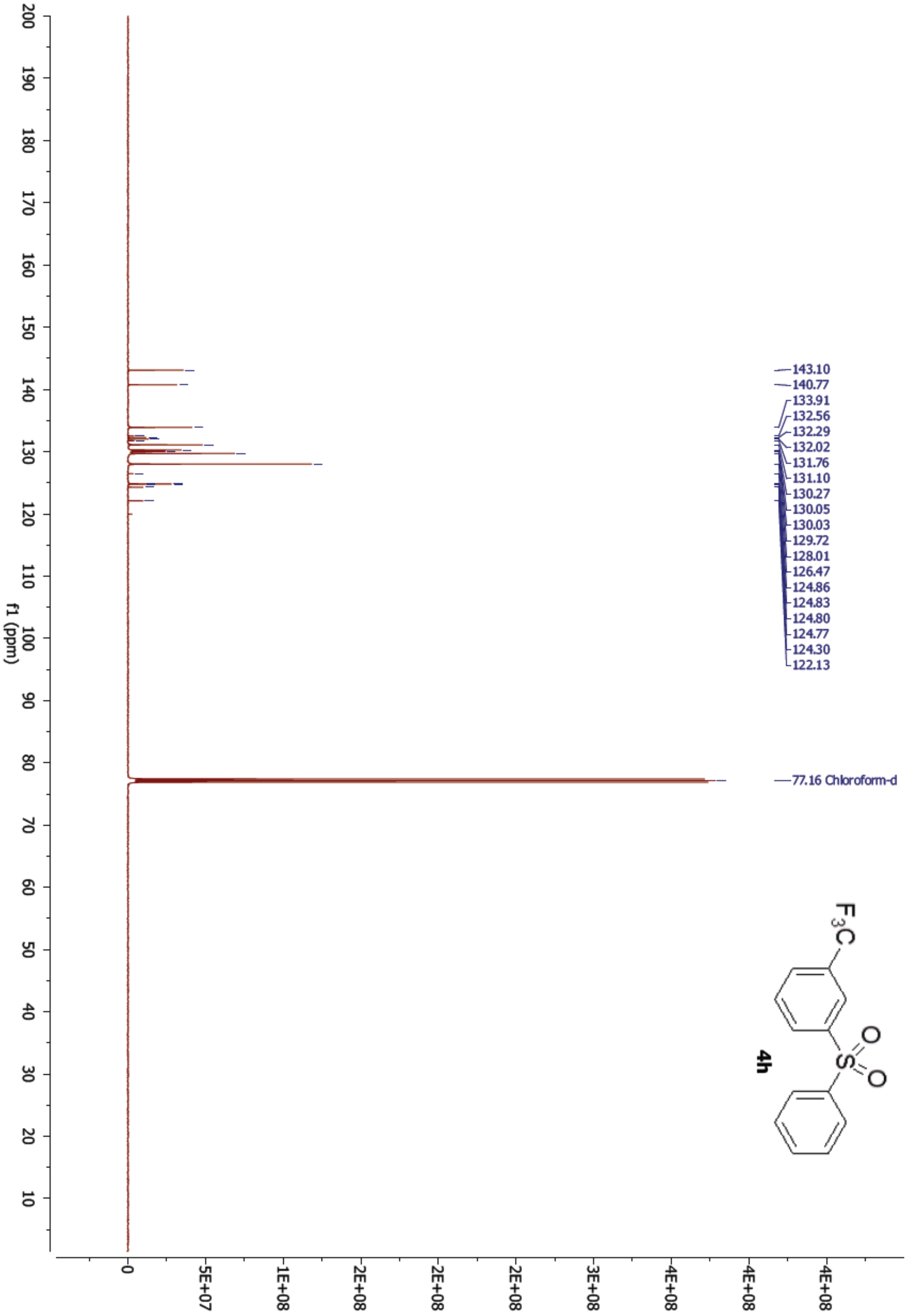

4g
iPr
iPr
iPr
S
O
O
7.77
7.75
7.75
7.54
7.52
7.51
7.49
7.47
7.46
7.26 Chloroform-d
7.16
4.21
4.20
4.19
4.17
4.16
4.15
4.13
2.94
2.93
2.92
2.90
2.89
2.88
2.86
1.26
1.25
1.13
1.12
2.00
1.00
2.00
2.00
1.99
1.07
6.00
12.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
-5000
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
50000
55000
60000
65000
70000

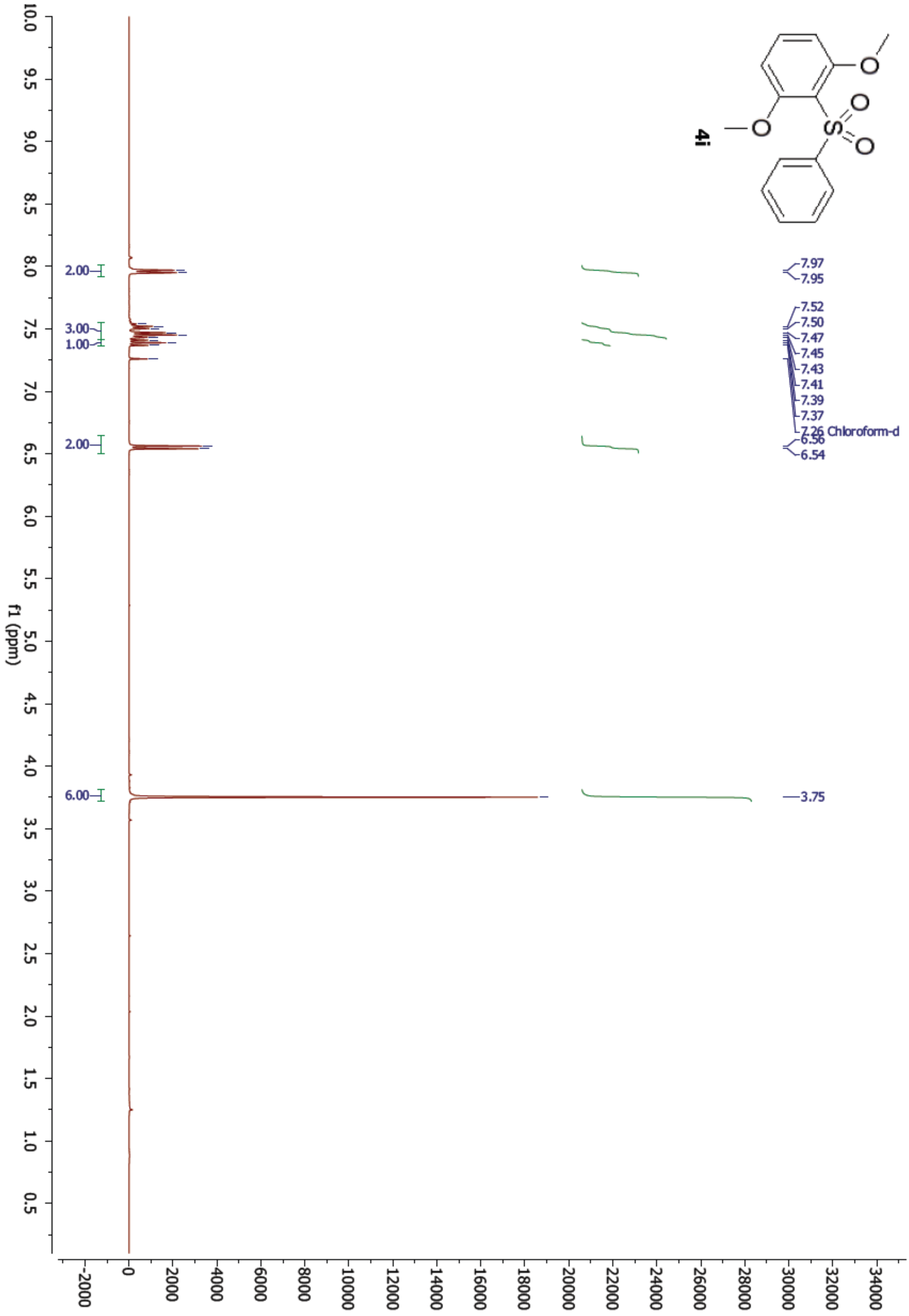


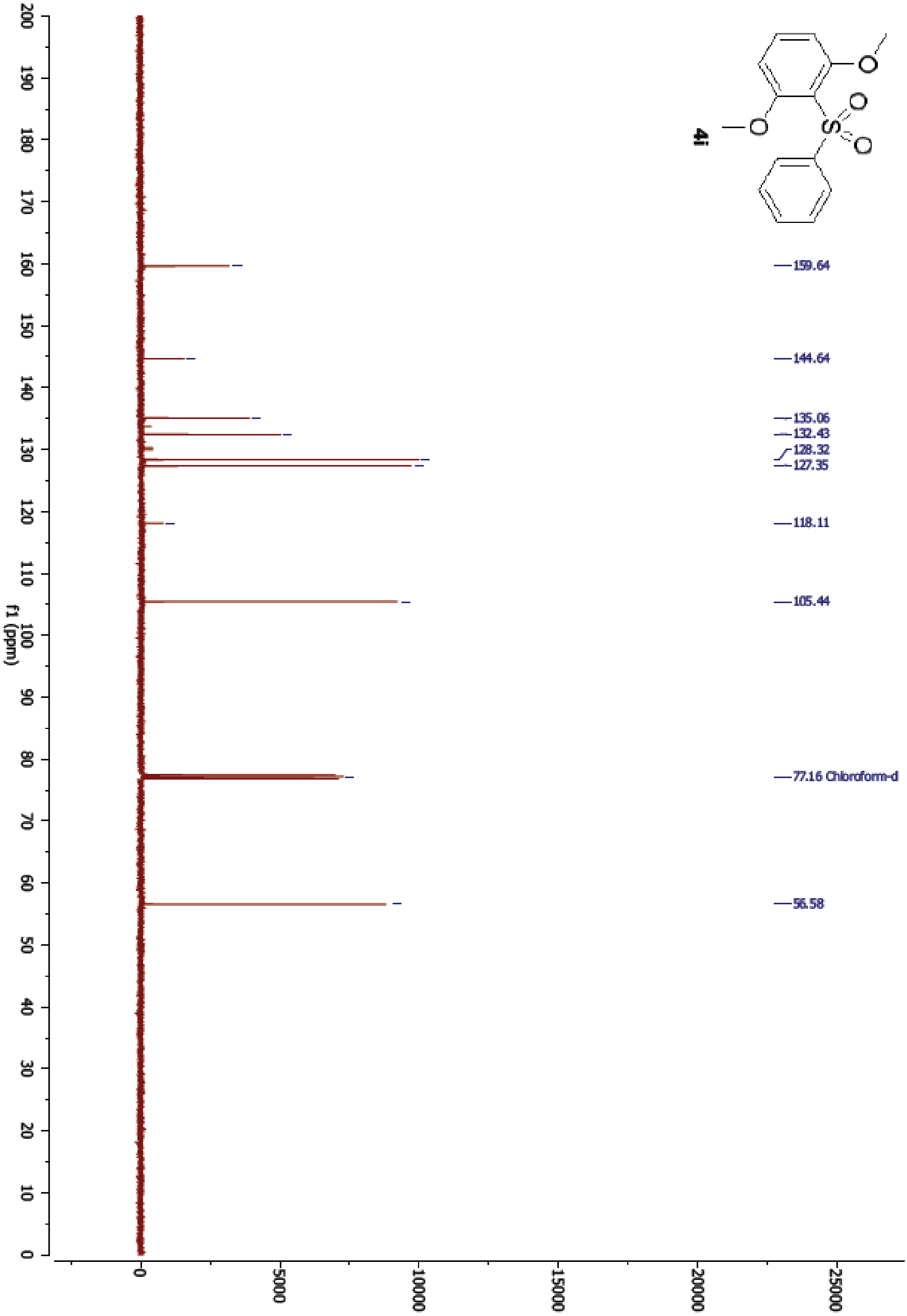
iPr
iPr
iPr
S
O
O
4g
153.99
151.45
145.49
132.38
132.33
129.06
125.76
124.15
77.16 Chloroform-d
34.36
29.54
24.72
23.69
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000

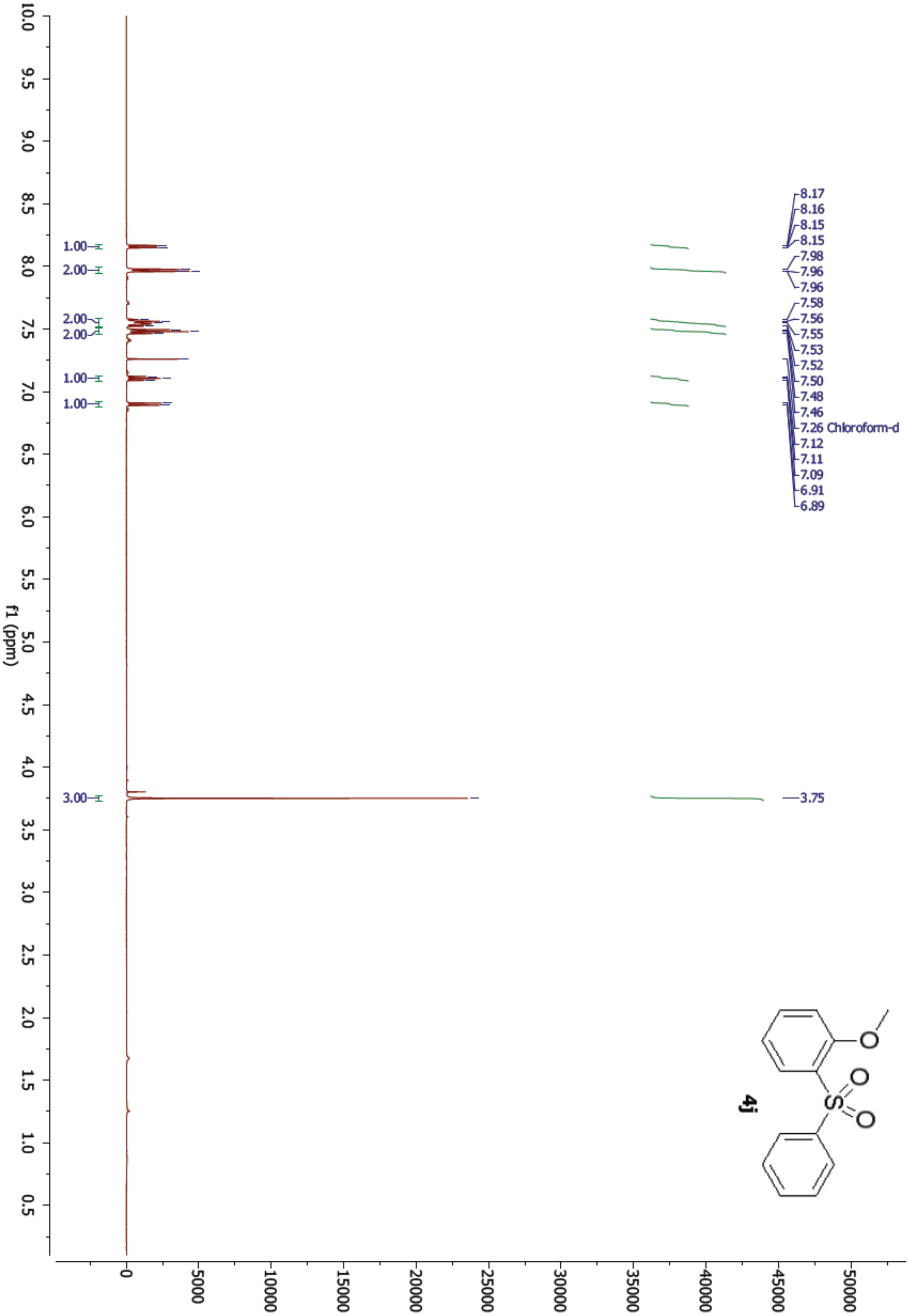


8.22
8.14
8.12
7.98
7.96
7.96
7.83
7.81
7.68
7.66
7.65
7.63
7.62
7.60
7.56
7.55
7.55
7.53
7.26 Chloroform-d
1.00
1.00
2.00
1.00
1.01
1.00
2.00
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
F3C
S
O
O
4h


143.10
140.77
133.91
132.56
132.29
132.02
131.76
131.10
130.27
130.05
130.03
129.72
128.01
126.47
124.86
124.83
124.80
124.77
124.30
122.13
77.16 Chloroform-d
F_3C
O
S
O
4h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
0
5E+07
1E+08
2E+08
2E+08
2E+08
3E+08
4E+08
4E+08
4E+08


4i
7.97
7.95
7.52
7.50
7.47
7.45
7.43
7.41
7.39
7.37
7.26 Chloroform-d
6.56
6.54
3.75
2.00
3.00
1.00
2.00
6.00
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-2000
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
20000
22000
24000
26000
28000
30000
32000
34000


4i
159.64
144.64
135.06
132.43
128.32
127.35
118.11
105.44
77.16 Chloroform-d
56.58
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0
5000
10000
15000
20000
25000


8.17
8.16
8.15
8.15
7.98
7.96
7.96
7.58
7.56
7.55
7.53
7.52
7.50
7.48
7.46
7.26 Chloroform-d
7.12
7.11
7.09
6.91
6.89
3.75
1.00
2.00
2.00
2.00
1.00
1.00
3.00
4j
O
S
O
O
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
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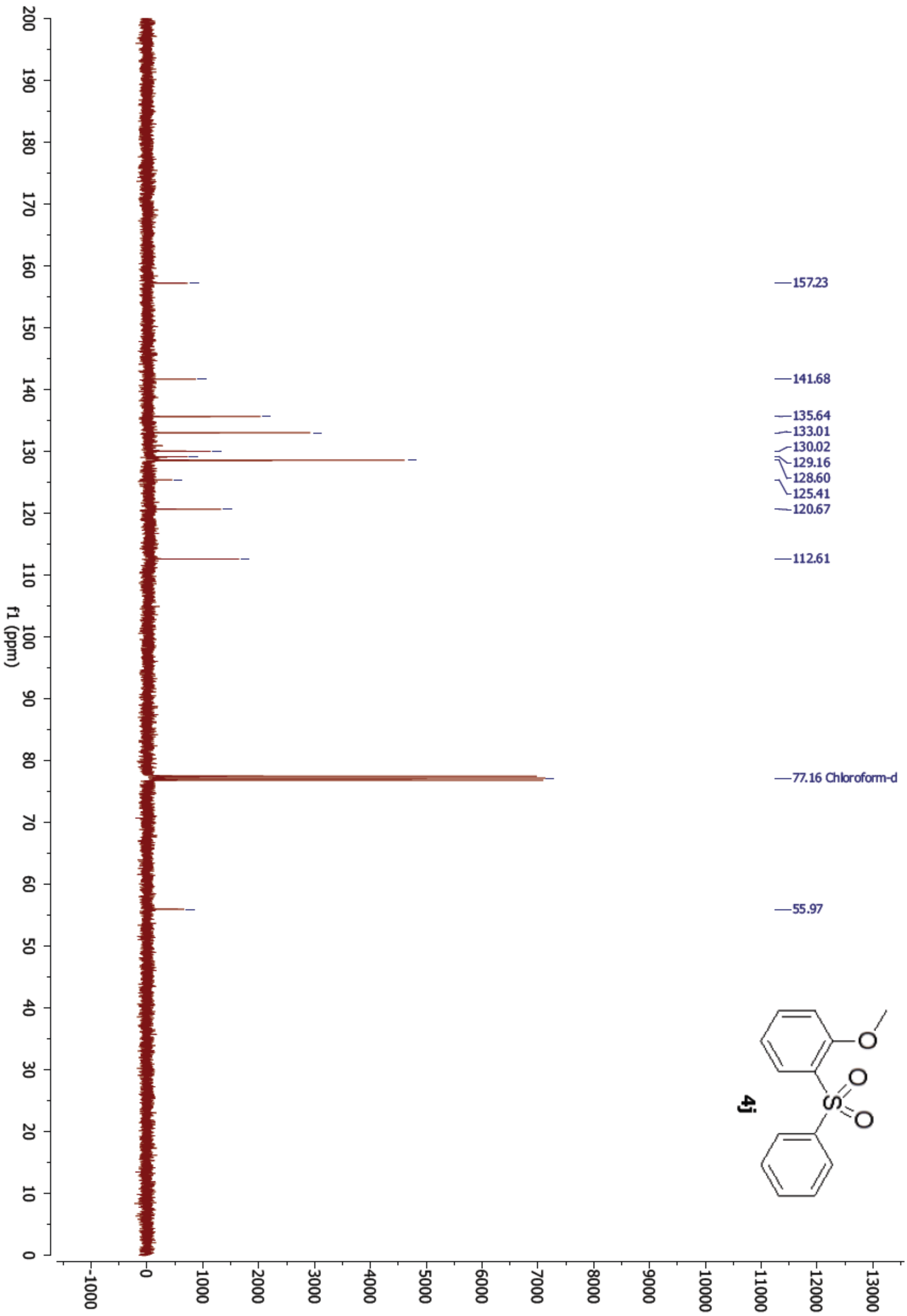
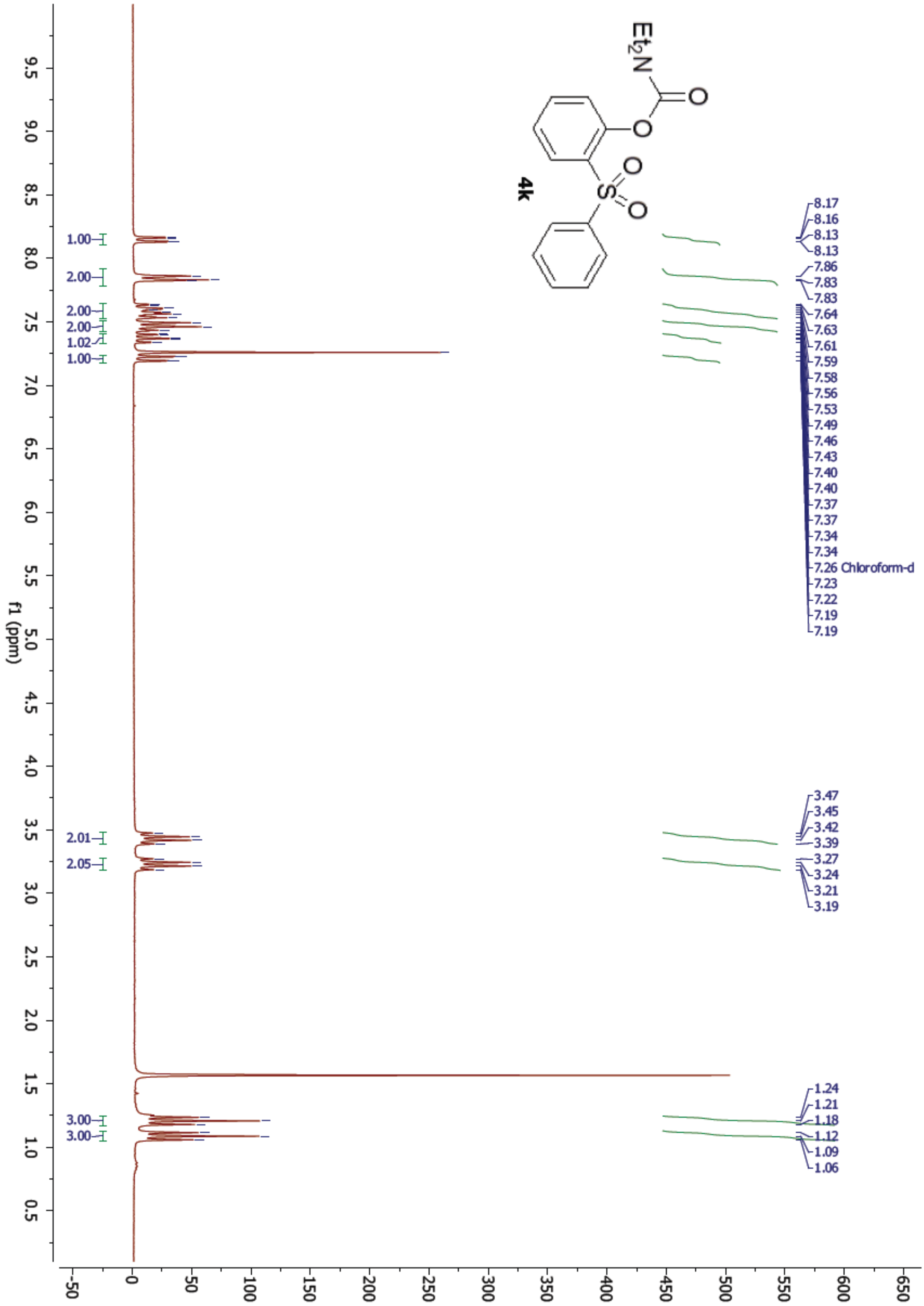
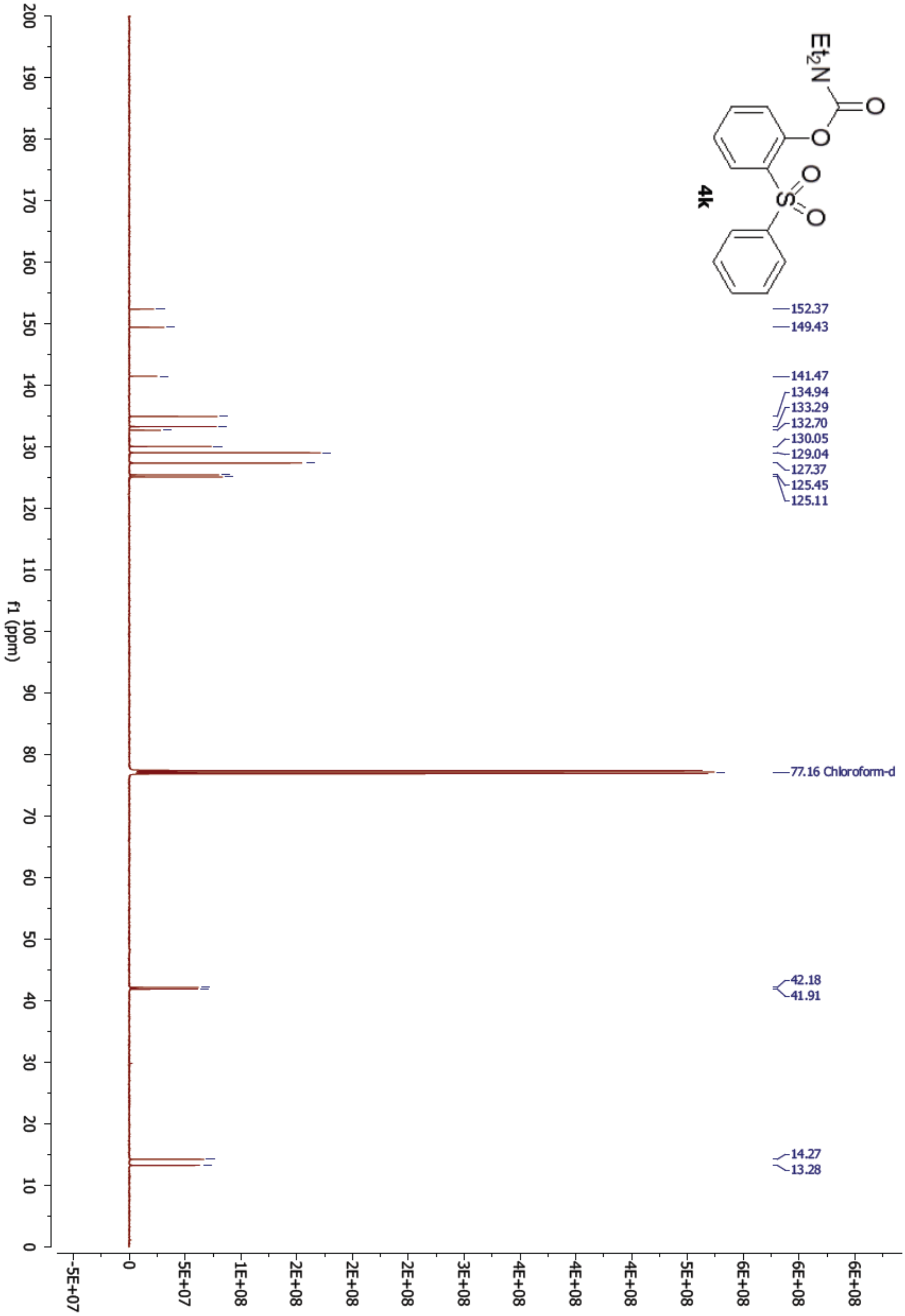
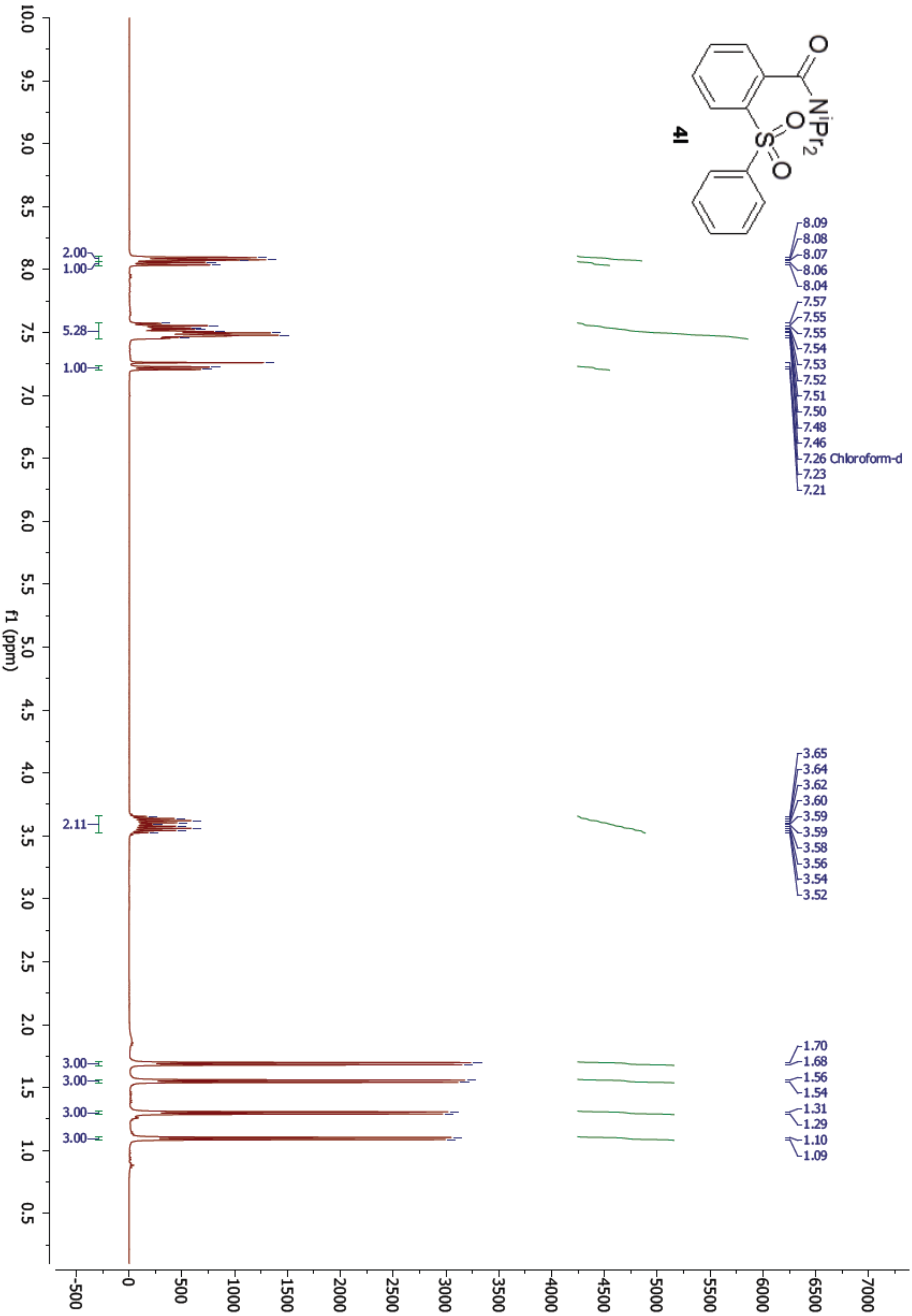
10000
15000
20000
25000
30000
35000
40000
45000
50000

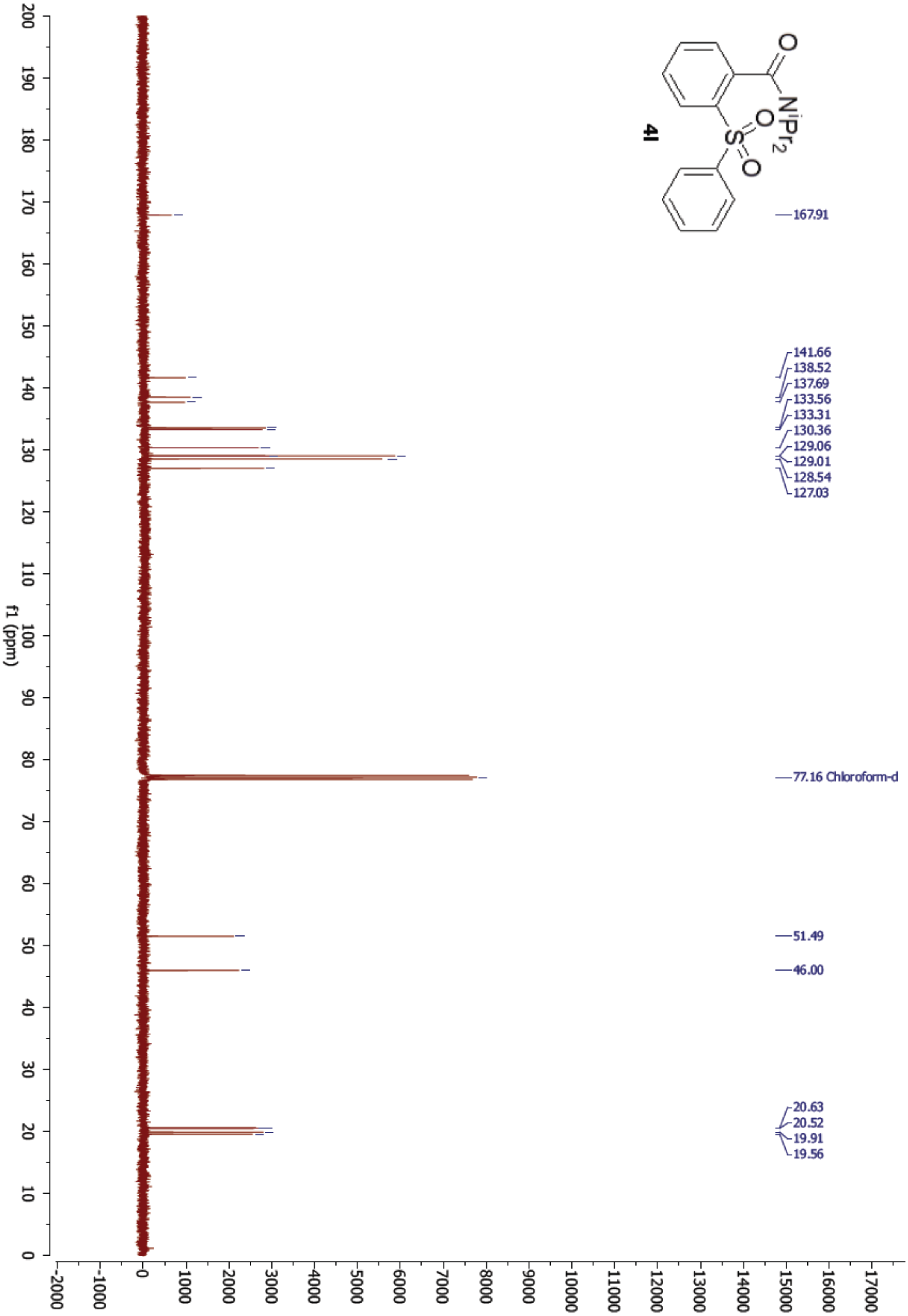

157.23
141.68
135.64
133.01
130.02
129.16
128.60
125.41
120.67
112.61
77.16 Chloroform-d
55.97
4j
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000


4k
Et2N
O
O
S
O
O
8.17
8.16
8.13
8.13
7.86
7.83
7.83
7.64
7.63
7.61
7.59
7.58
7.56
7.53
7.49
7.46
7.43
7.40
7.40
7.37
7.37
7.34
7.34
7.26 Chloroform-d
7.23
7.22
7.19
7.19
3.47
3.45
3.42
3.39
3.27
3.24
3.21
3.19
1.24
1.21
1.18
1.12
1.09
1.06
1.00
2.00
2.00
2.00
1.02
1.00
2.01
2.05
3.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
f1 (ppm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-50
0
50
100
150
200
250
300
350
400
450
500
550
600
650

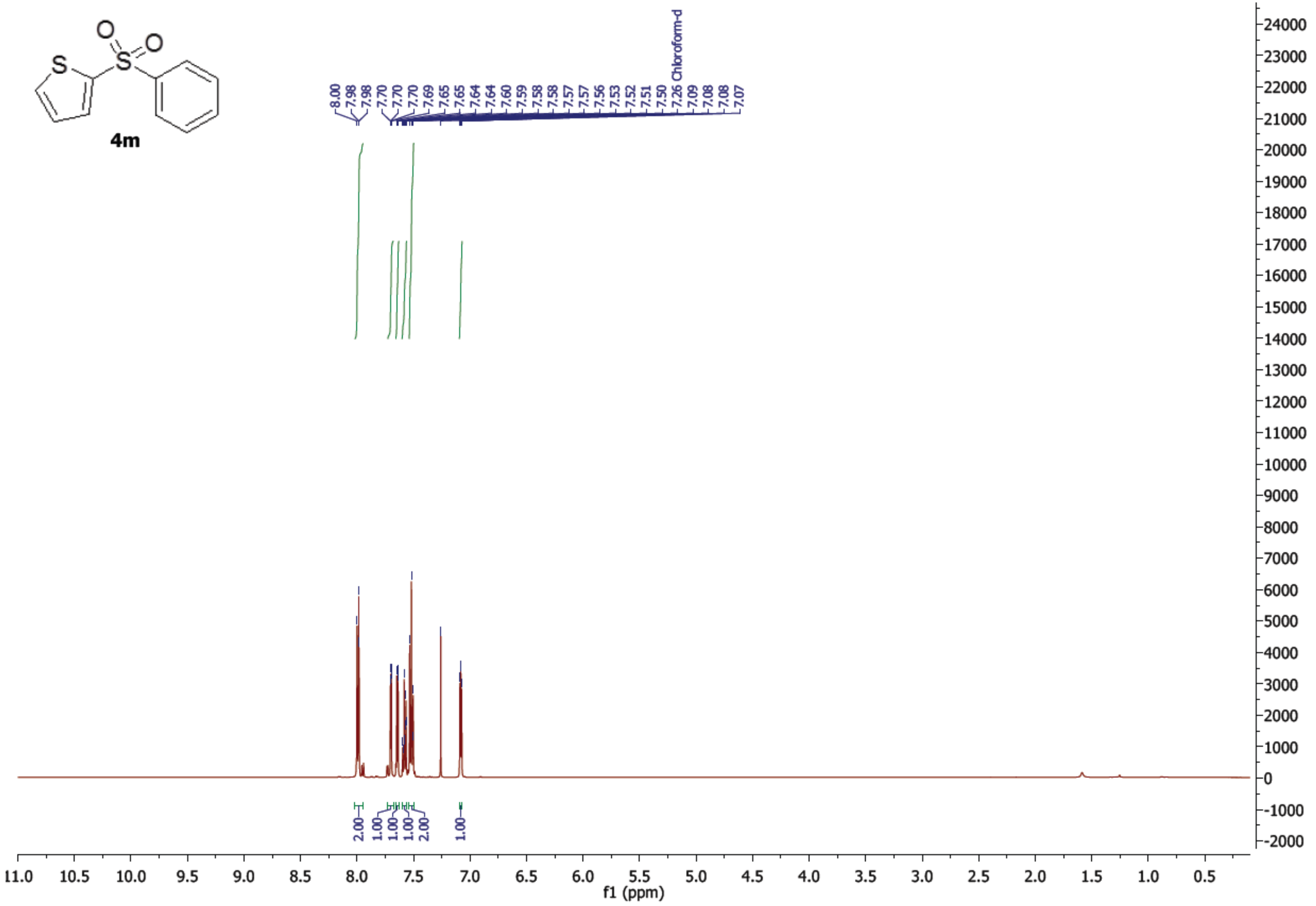

4k
Et2N
O
O
S
O
O
152.37
149.43
141.47
134.94
133.29
132.70
130.05
129.04
127.37
125.45
125.11
77.16 Chloroform-d
42.18
41.91
14.27
13.28
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-5E+07
0
5E+07
1E+08
2E+08
2E+08
2E+08
3E+08
4E+08
4E+08
4E+08
5E+08
6E+08
6E+08
6E+08


4l

NiPr2
O
S
O
O
8.09
8.08
8.07
8.06
8.04
7.57
7.55
7.55
7.54
7.53
7.52
7.51
7.50
7.48
7.46
7.26 Chloroform-d
7.23
7.21
3.65
3.64
3.62
3.60
3.59
3.59
3.58
3.56
3.54
3.52
1.70
1.68
1.56
1.54
1.31
1.29
1.10
1.09
2.00
1.00
5.28
1.00
2.11
3.00
3.00
3.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
-500
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000

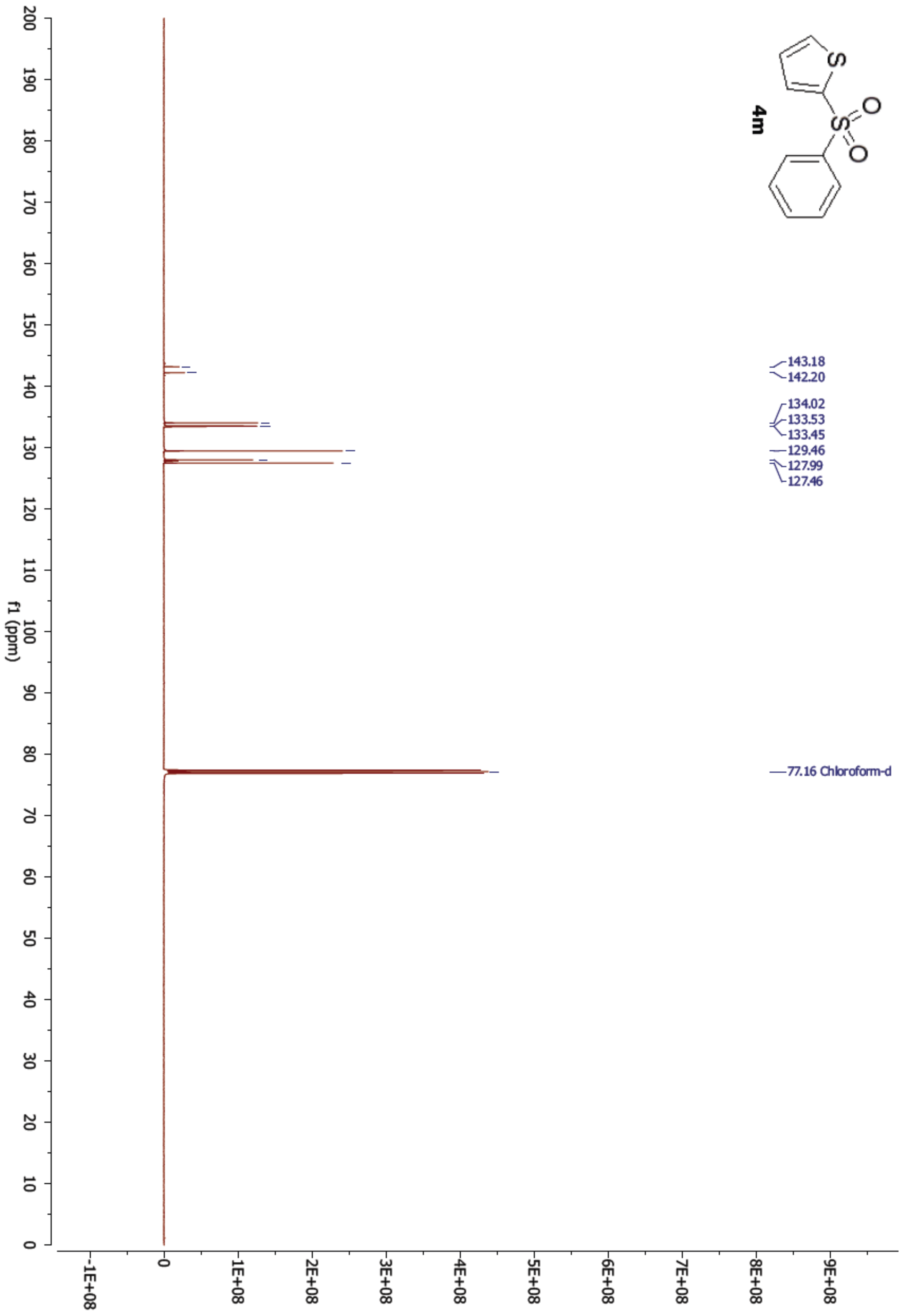

O
NiPr2
O
S
O
—167.91
141.66
138.52
137.69
133.56
133.31
130.36
129.06
129.01
128.54
127.03
—77.16 Chloroform-d
—51.49
—46.00
20.63
20.52
19.91
19.56
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
-2000
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000
15000
16000
17000

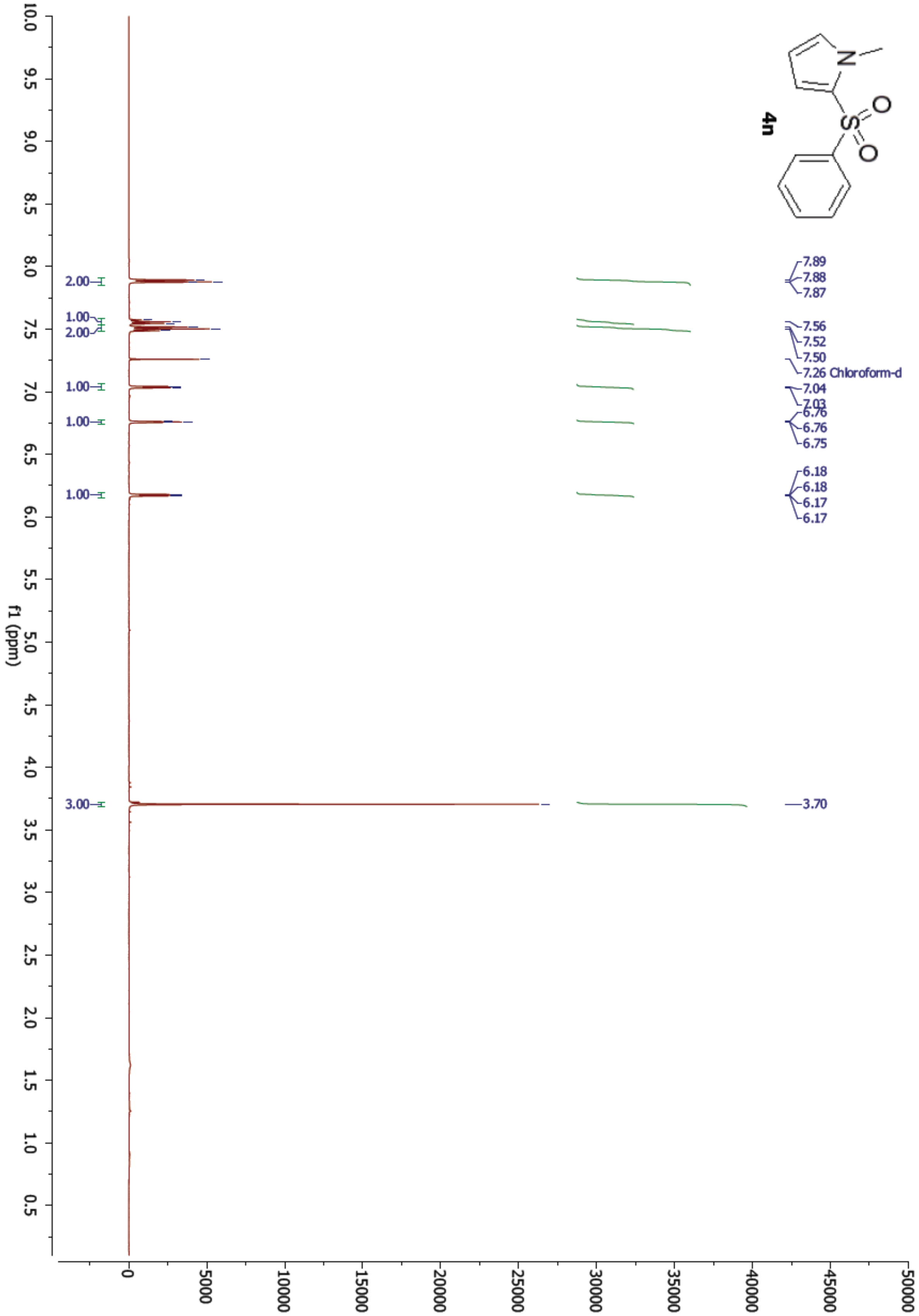
4l

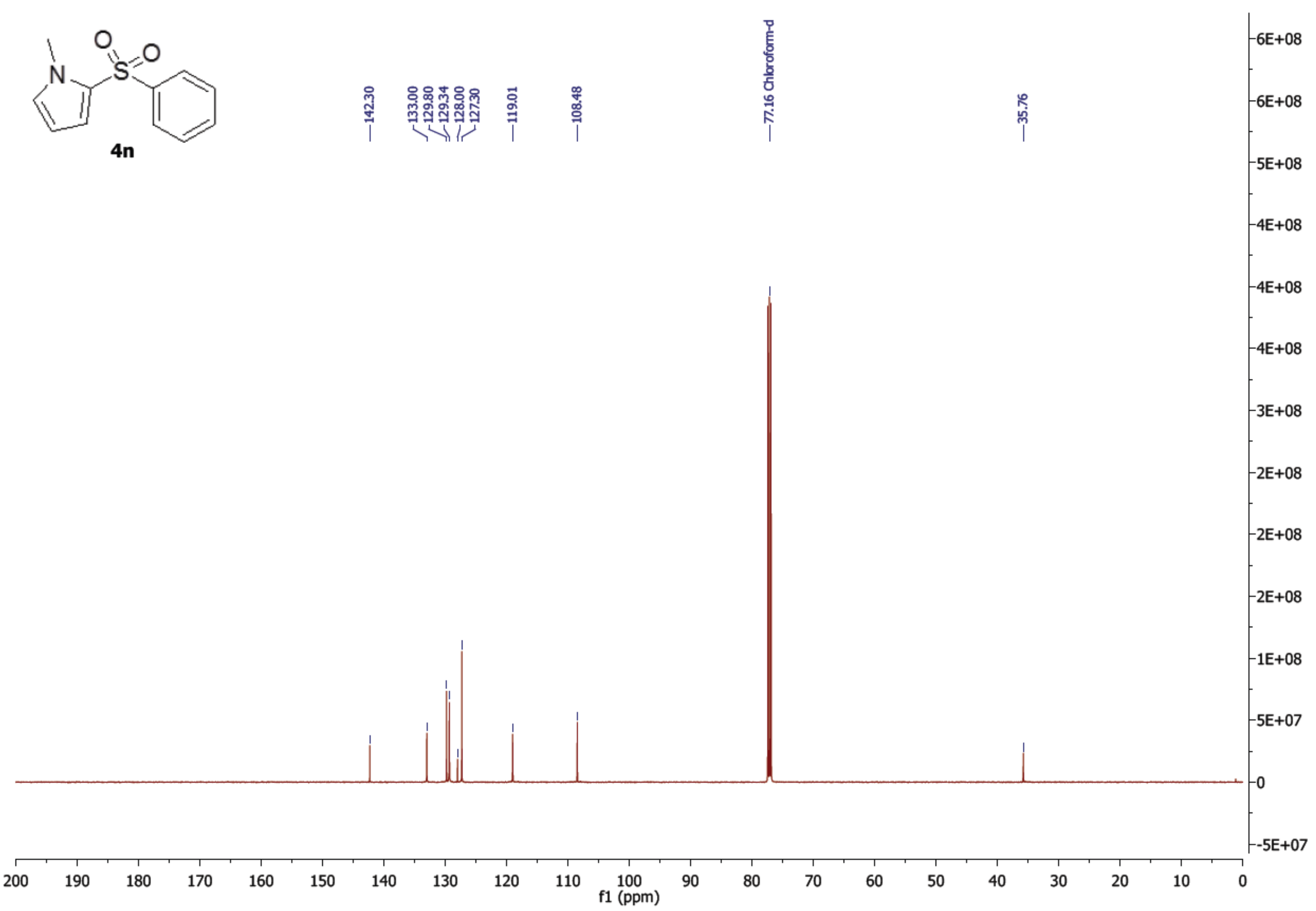


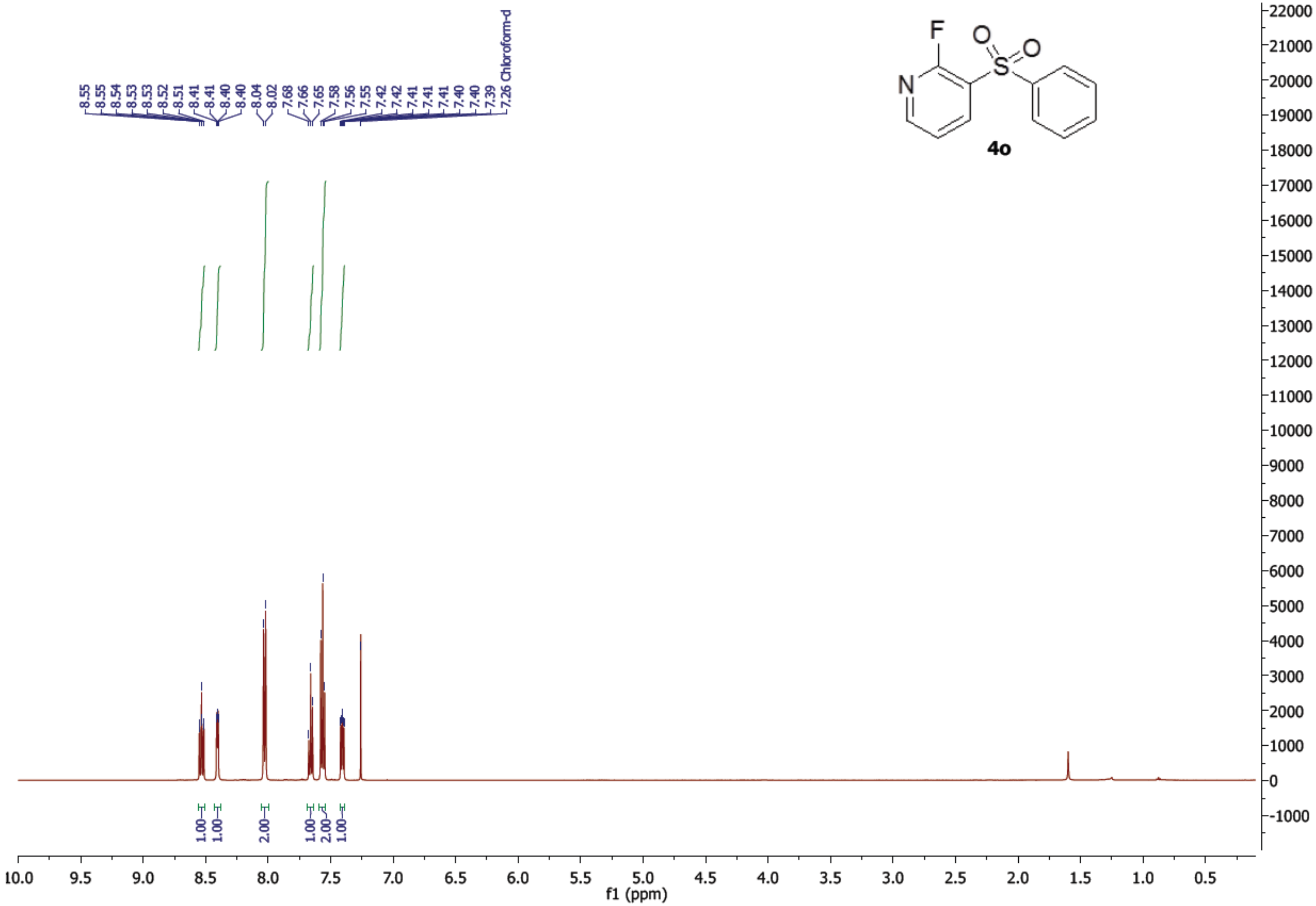
4m

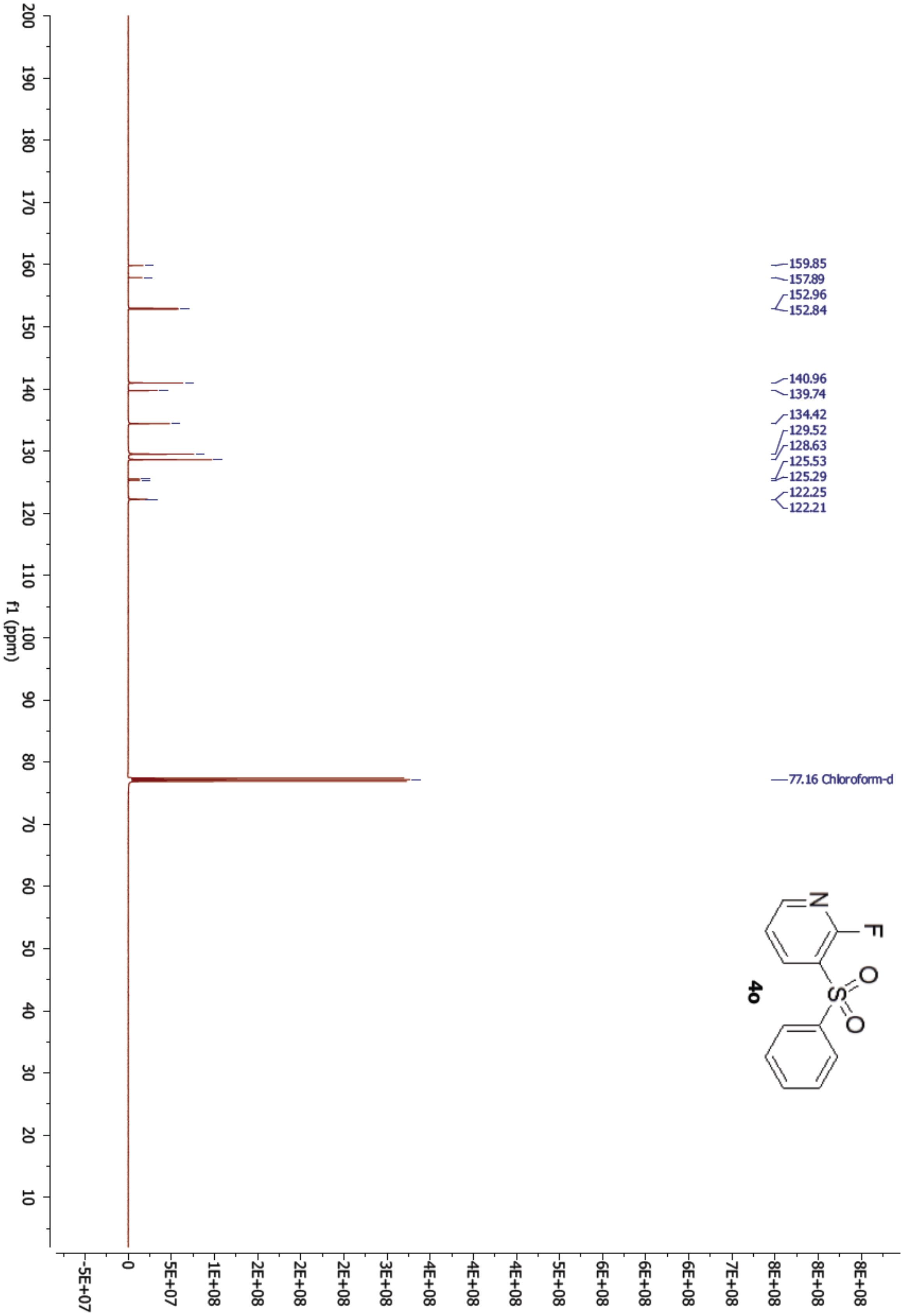
8.00
7.98
7.98
7.70
7.70
7.70
7.69
7.65
7.65
7.64
7.64
7.60
7.59
7.58
7.58
7.57
7.57
7.56
7.53
7.52
7.51
7.50
7.26 Chloroform-d
7.09
7.08
7.08
7.07
2.00
1.00
1.00
1.00
2.00
1.00
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


4m
143.18
142.20
134.02
133.53
133.45
129.46
127.99
127.46
77.16 Chloroform-d
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1E+08
0
1E+08
2E+08
3E+08
4E+08
5E+08
6E+08
7E+08
8E+08
9E+08

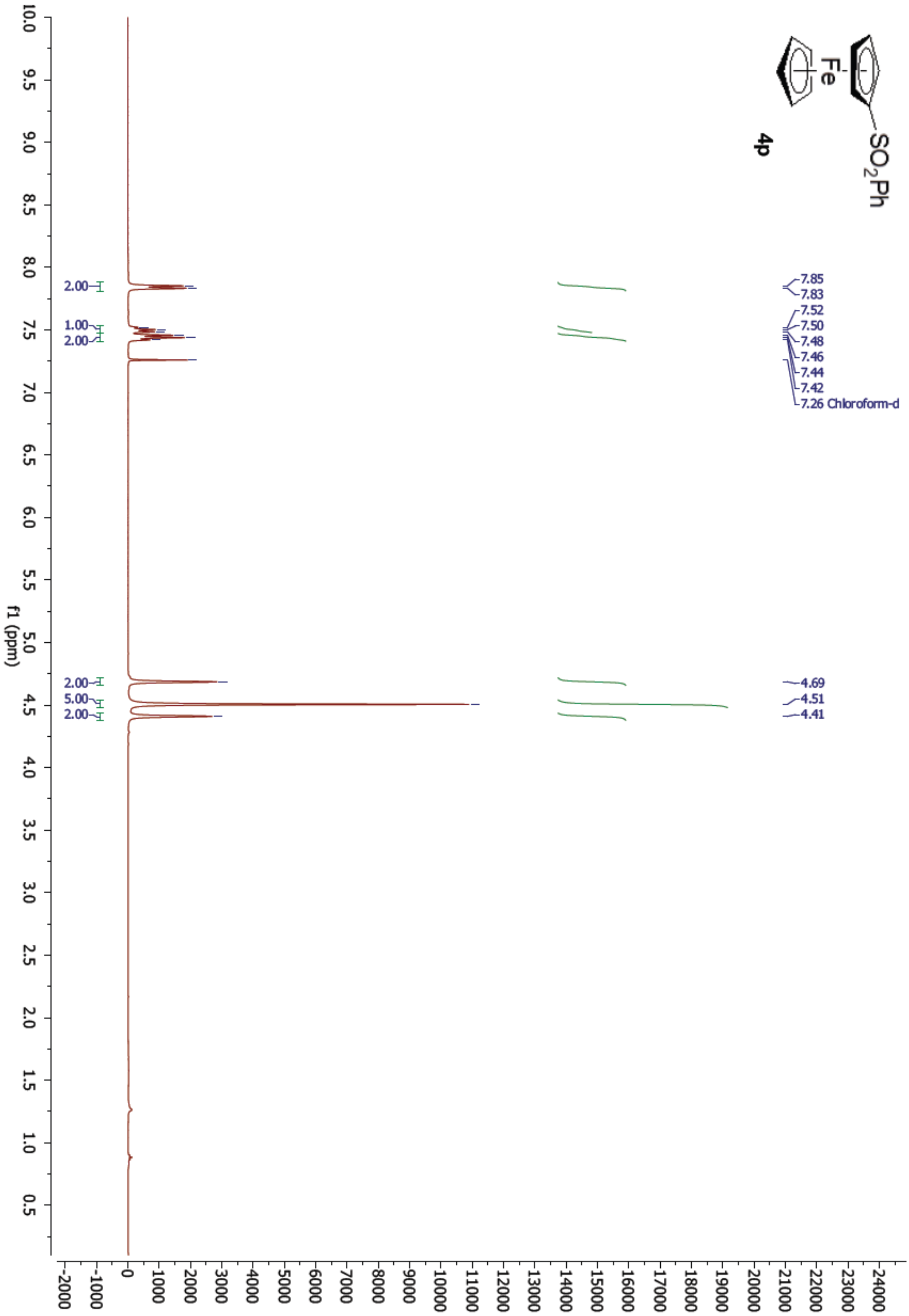

4n
N
S
O
O
7.89
7.88
7.87
7.56
7.52
7.50
7.26 Chloroform-d
7.04
7.03
6.76
6.76
6.75
6.18
6.18
6.17
6.17
3.70
2.00
1.00
2.00
1.00
1.00
1.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
50000


4n
142.30
133.00
129.80
129.34
128.00
127.30
119.01
108.48
77.16 Chloroform-d
35.76
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.55
8.55
8.54
8.53
8.53
8.52
8.51
8.41
8.41
8.40
8.40
8.04
8.02
7.68
7.66
7.65
7.58
7.56
7.55
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.39
7.26 Chloroform-d
1.00
1.00
2.00
1.00
2.00
1.00
4o
F
N
S
O
O
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000


4o

159.85
157.89
152.96
152.84
140.96
139.74
134.42
129.52
128.63
125.53
125.29
122.25
122.21
77.16 Chloroform-d
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
-5E+07
0
5E+07
1E+08
2E+08
2E+08
2E+08
3E+08
4E+08
4E+08
4E+08
5E+08
6E+08
6E+08
6E+08
7E+08
8E+08
8E+08
8E+08
N
F
O
S
O


SO2Ph
Fe
4p
7.85
7.83
7.52
7.50
7.48
7.46
7.44
7.42
7.26 Chloroform-d
4.69
4.51
4.41
2.00
1.00
2.00
2.00
5.00
2.00
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-2000
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000
15000
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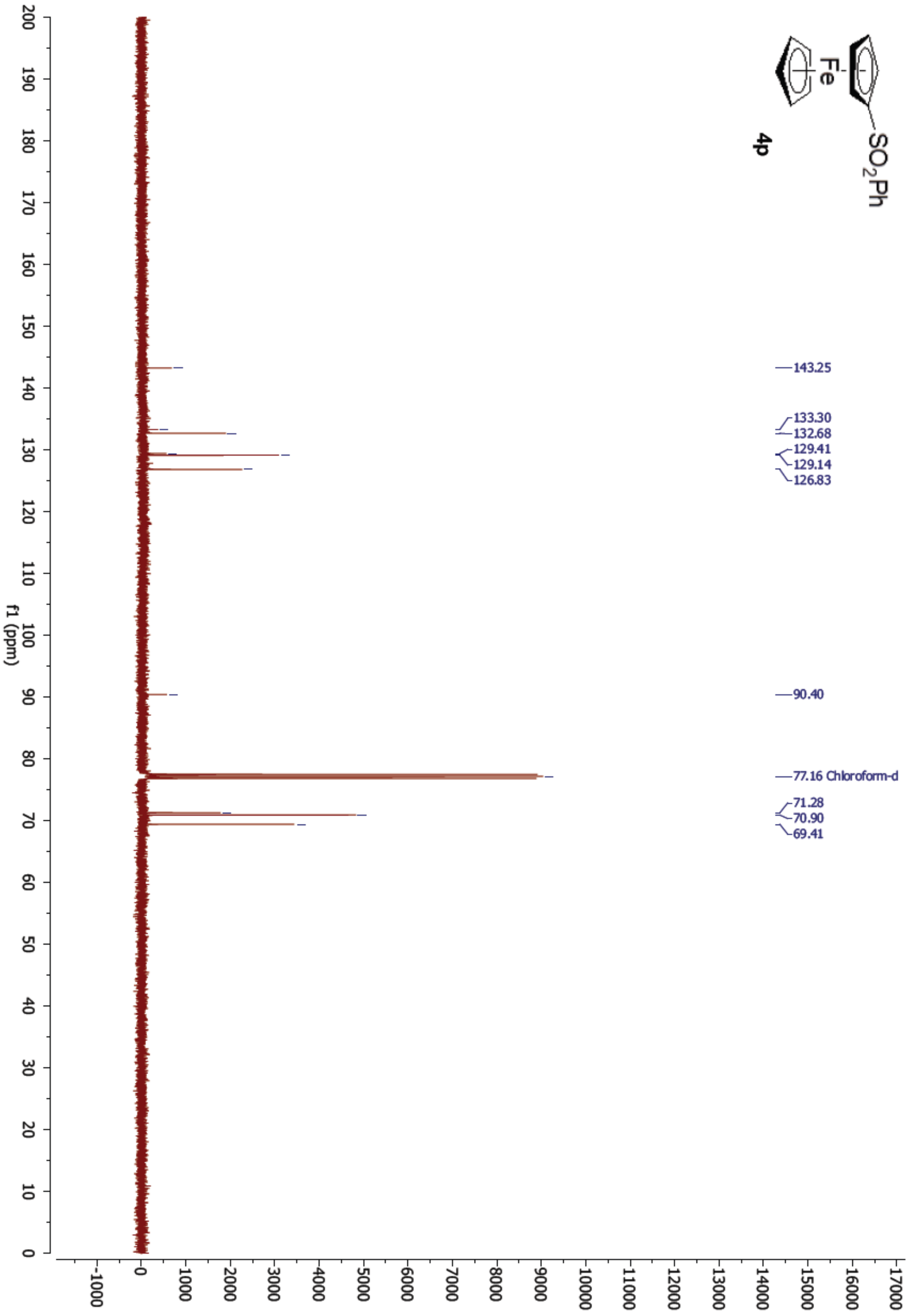
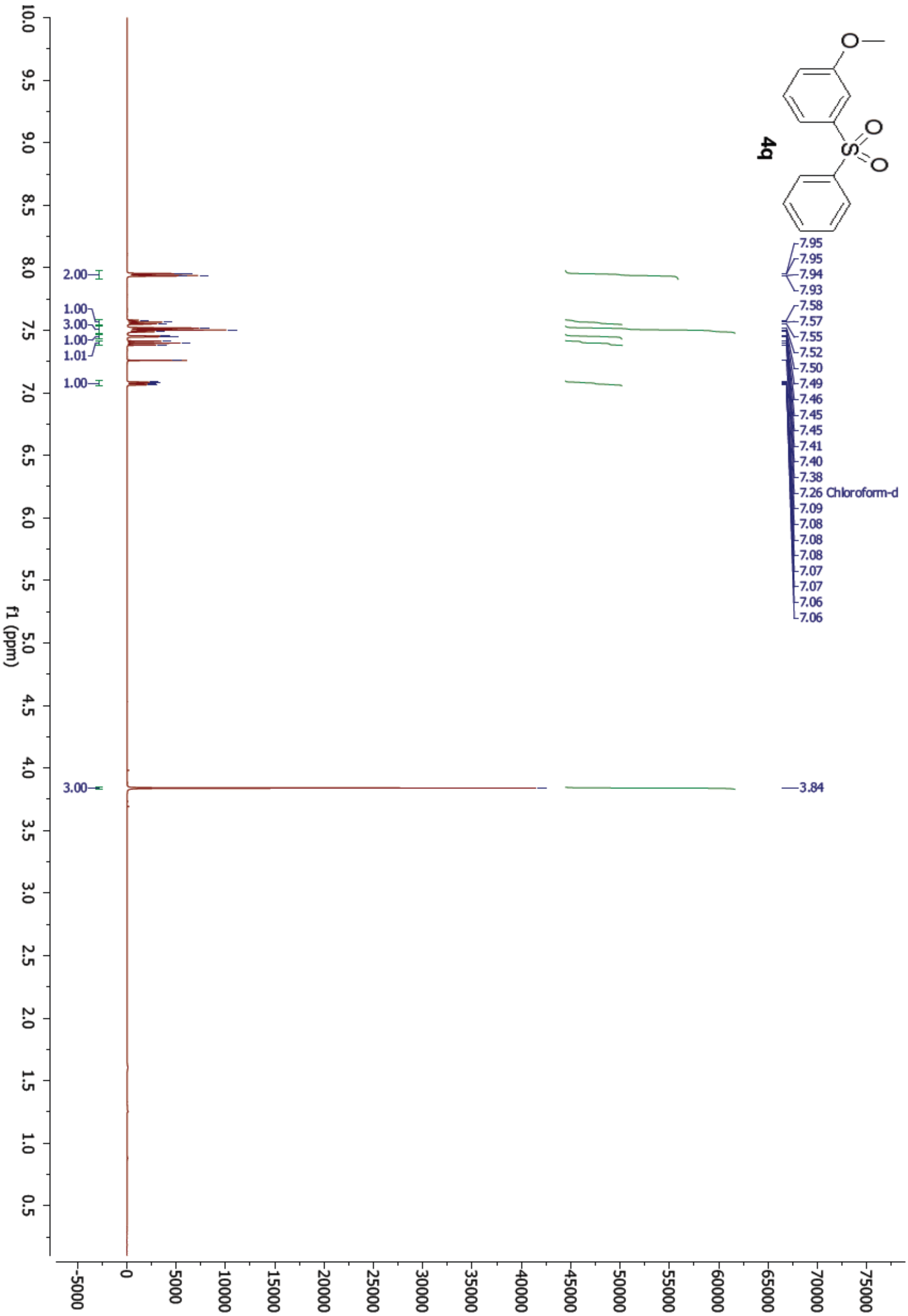
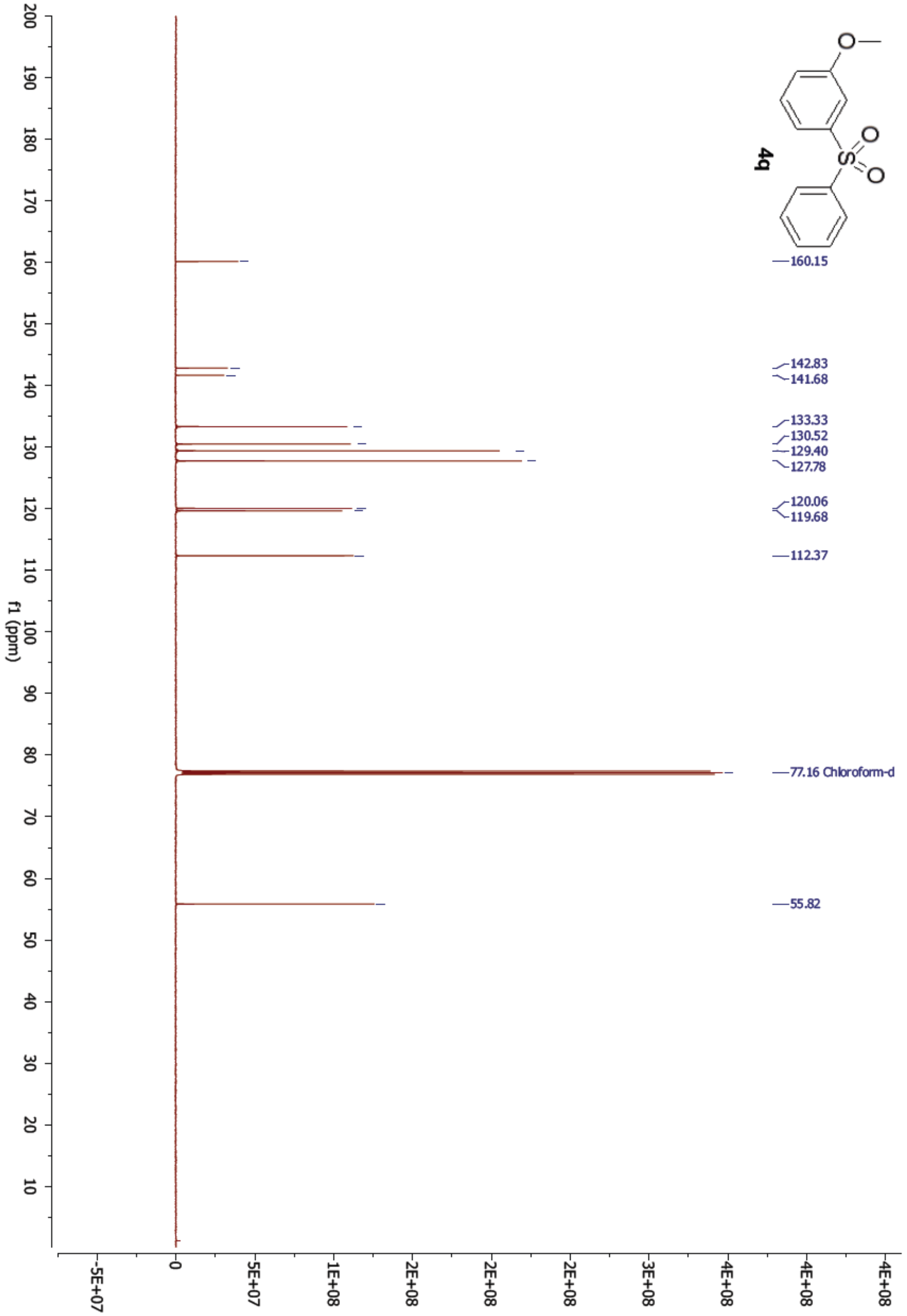
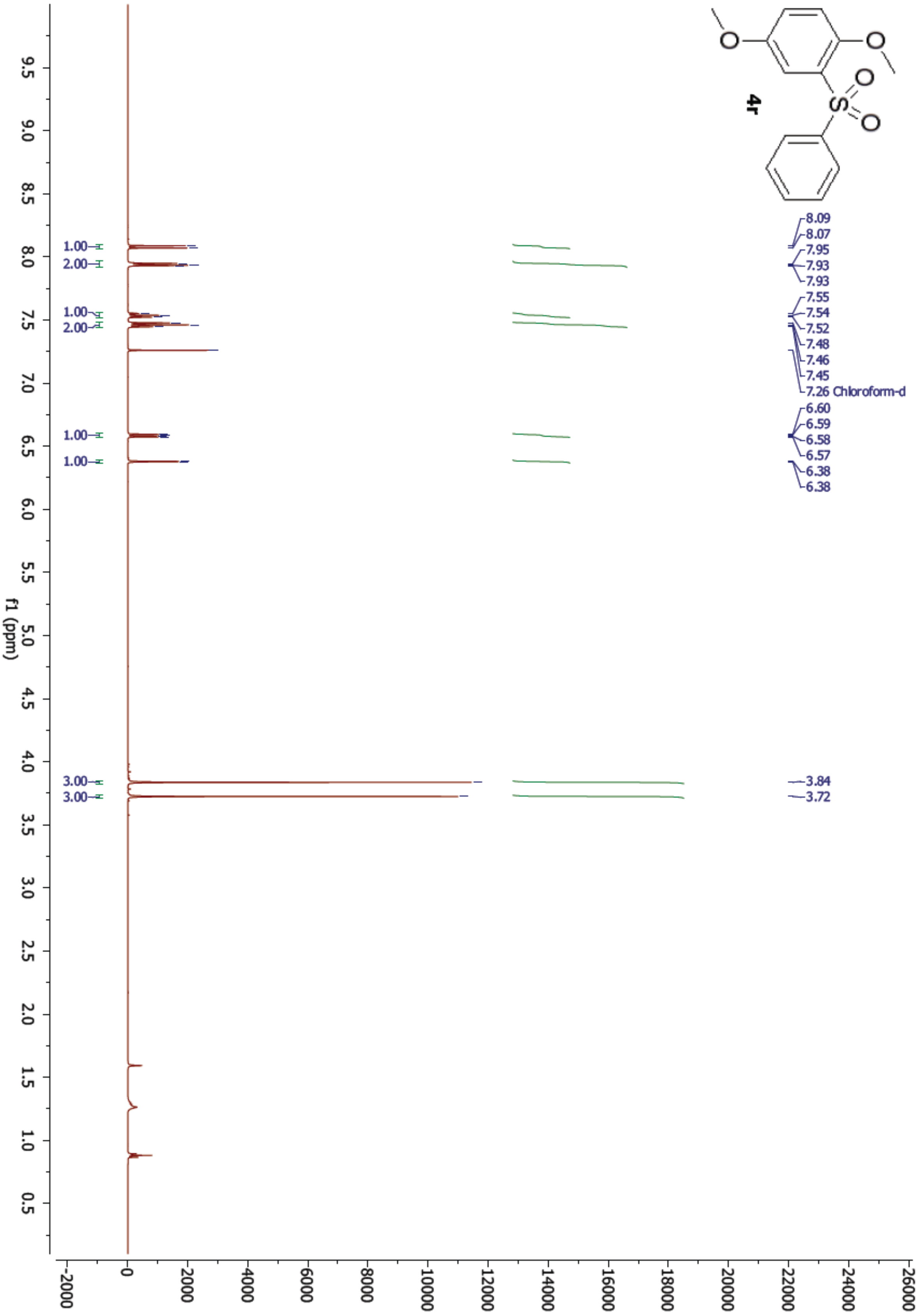
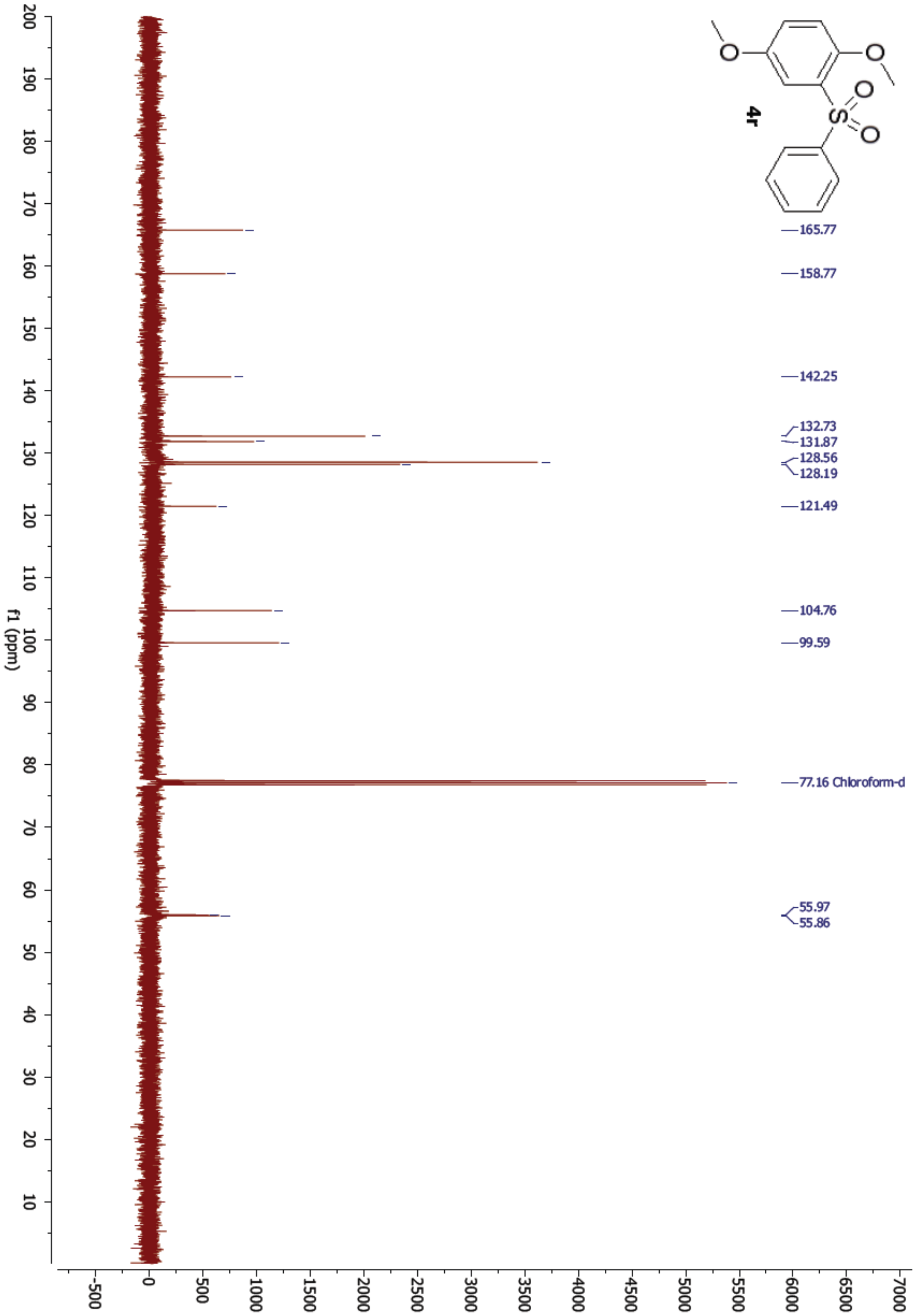
20000
21000
22000
23000
24000

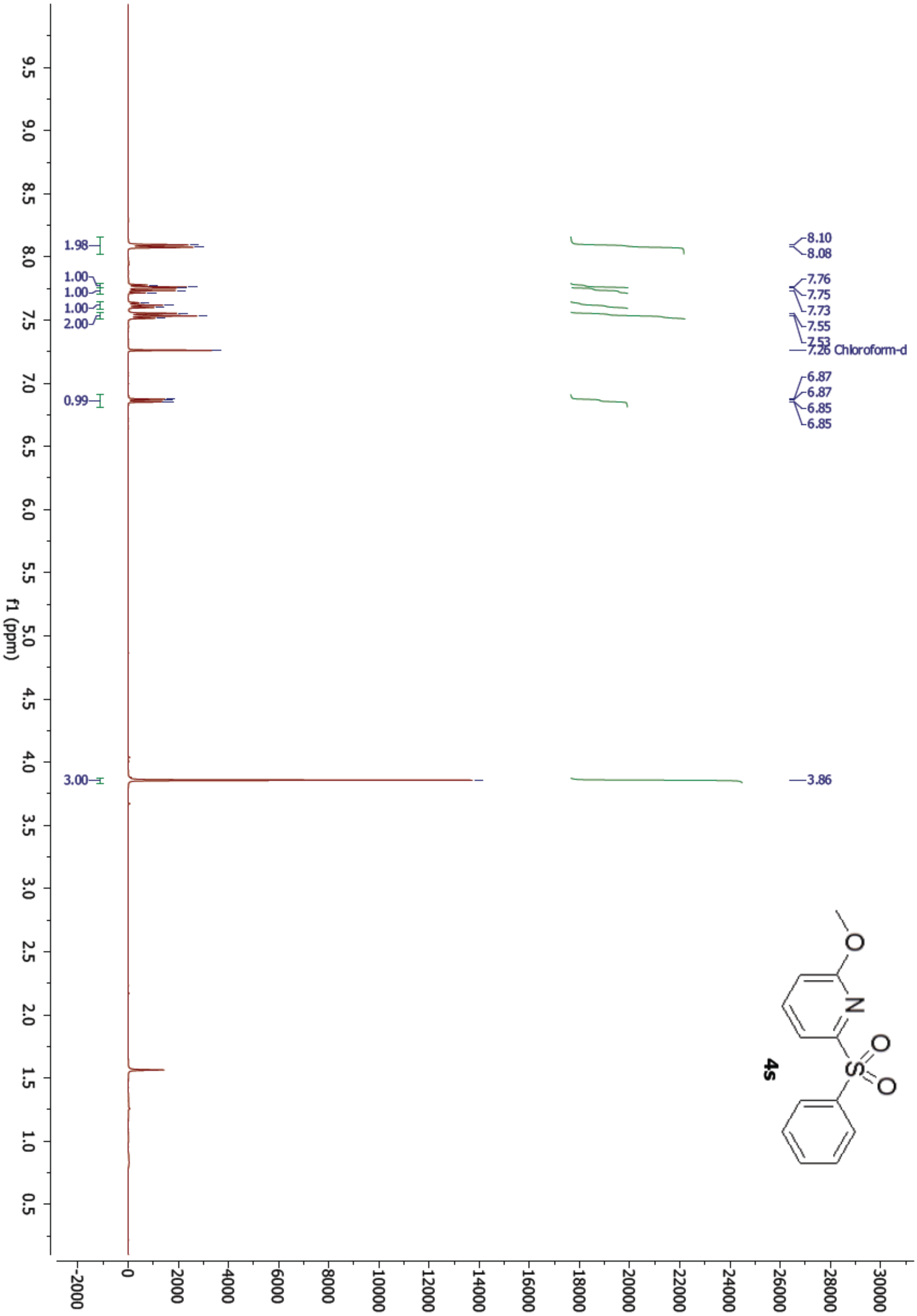

SO$_2$Ph
Fe
4p
143.25
133.30
132.68
129.41
129.14
126.83
90.40
77.16 Chloroform-d
71.28
70.90
69.41
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000
15000
16000
17000

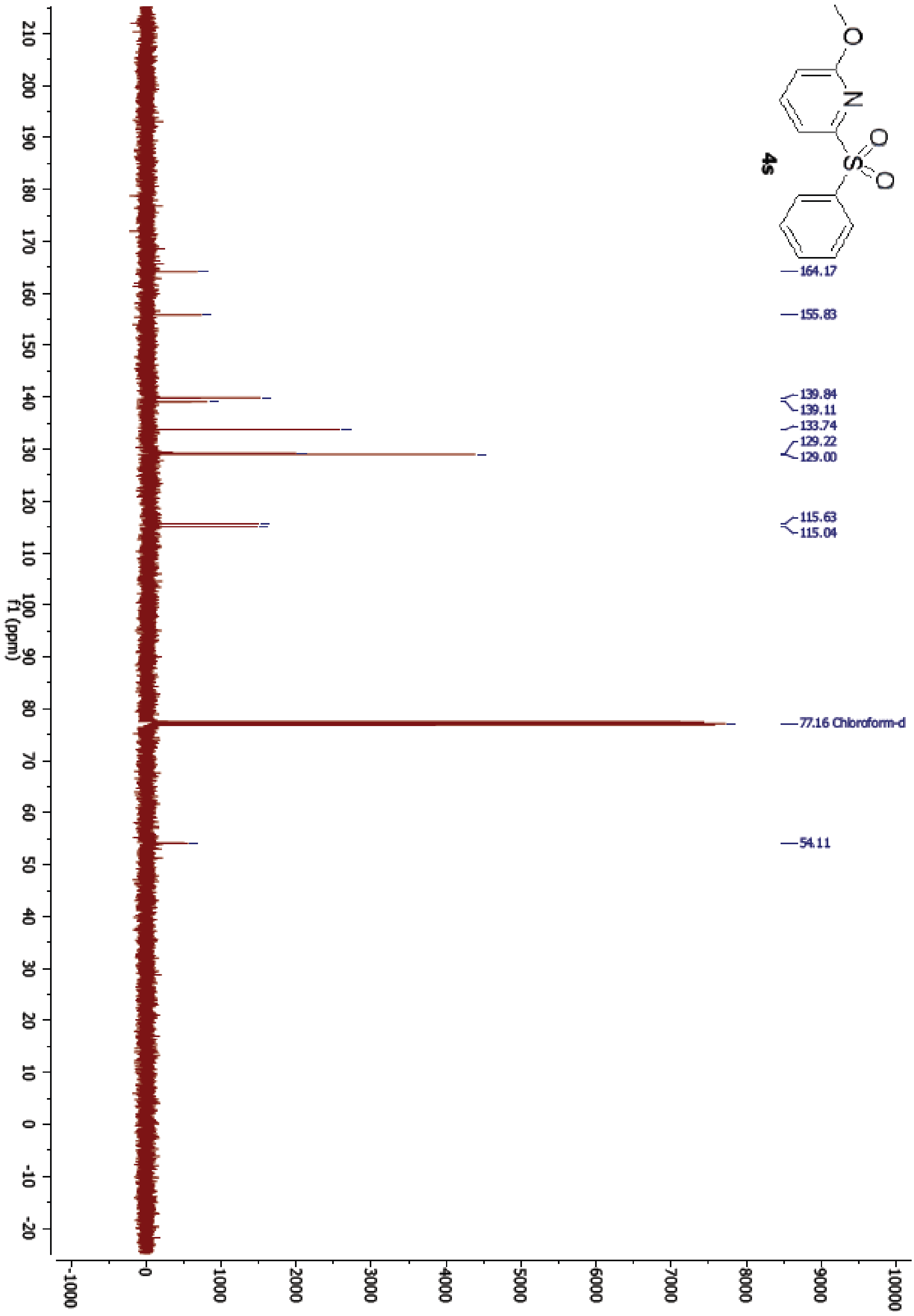

4q
7.95
7.95
7.94
7.93
7.58
7.57
7.55
7.52
7.50
7.49
7.46
7.45
7.45
7.41
7.40
7.38
7.26 Chloroform-d
7.09
7.08
7.08
7.08
7.07
7.07
7.06
7.06
3.84
2.00
1.00
3.00
1.00
1.01
1.00
3.00
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-5000
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
50000
55000
60000
65000
70000
75000

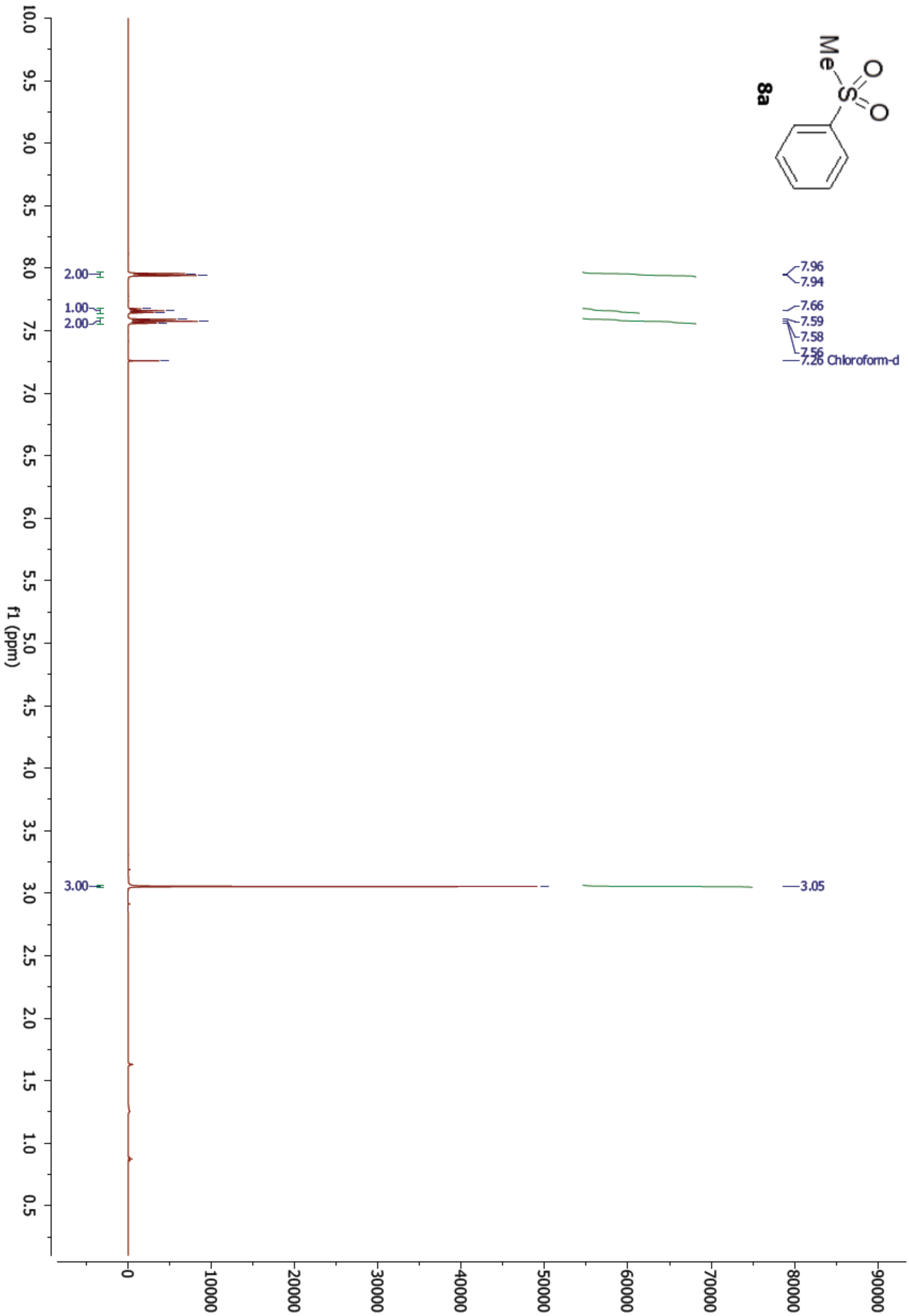

4q
160.15
142.83
141.68
133.33
130.52
129.40
127.78
120.06
119.68
112.37
77.16 Chloroform-d
55.82
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
-5E+07
0
5E+07
1E+08
2E+08
2E+08
2E+08
3E+08
4E+08
4E+08
4E+08

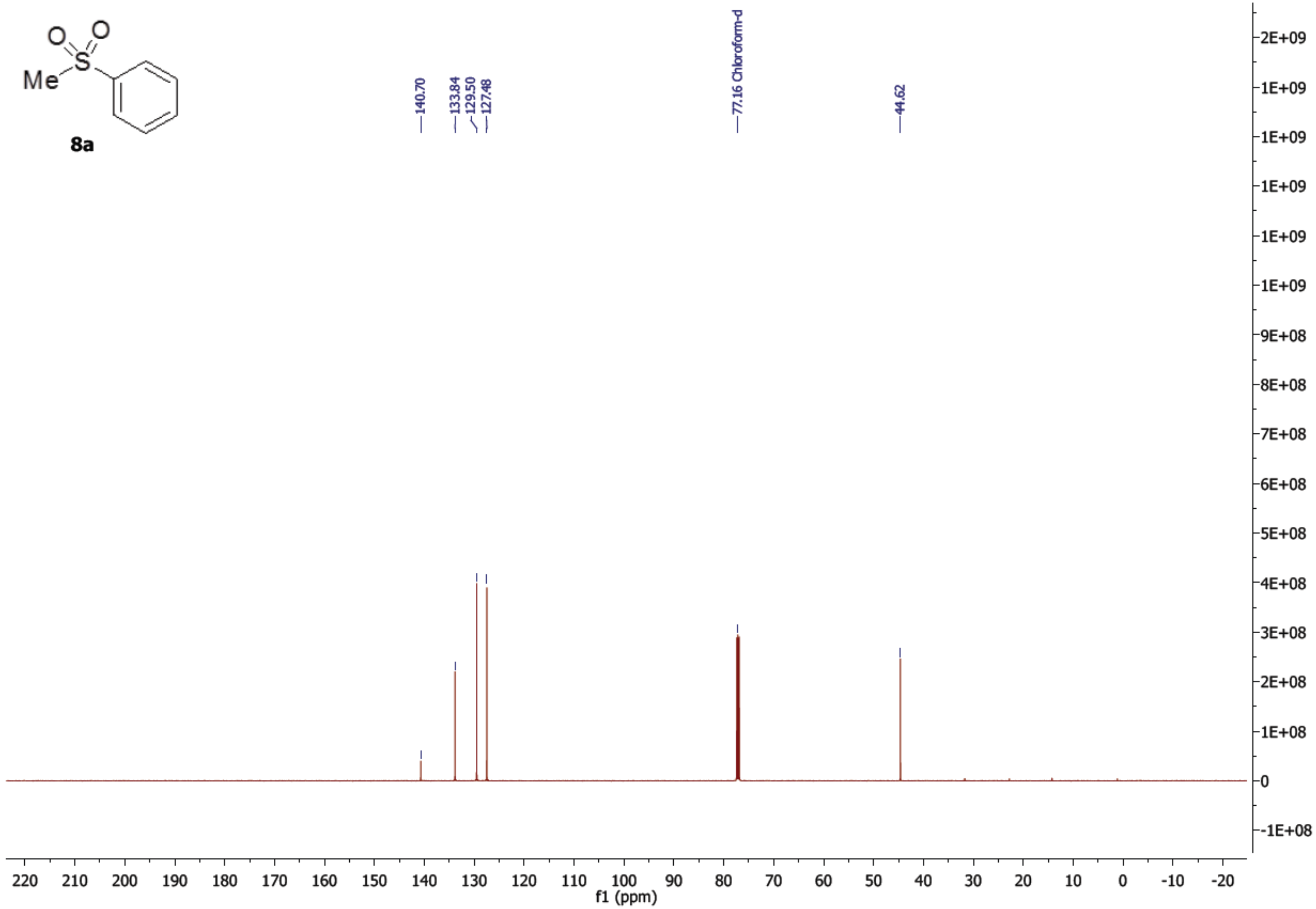

4r
8.09
8.07
7.95
7.93
7.93
7.55
7.54
7.52
7.48
7.46
7.45
7.26 Chloroform-d
6.60
6.59
6.58
6.57
6.38
6.38
3.84
3.72
1.00
2.00
1.00
2.00
1.00
1.00
3.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
-2000
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
20000
22000
24000
26000

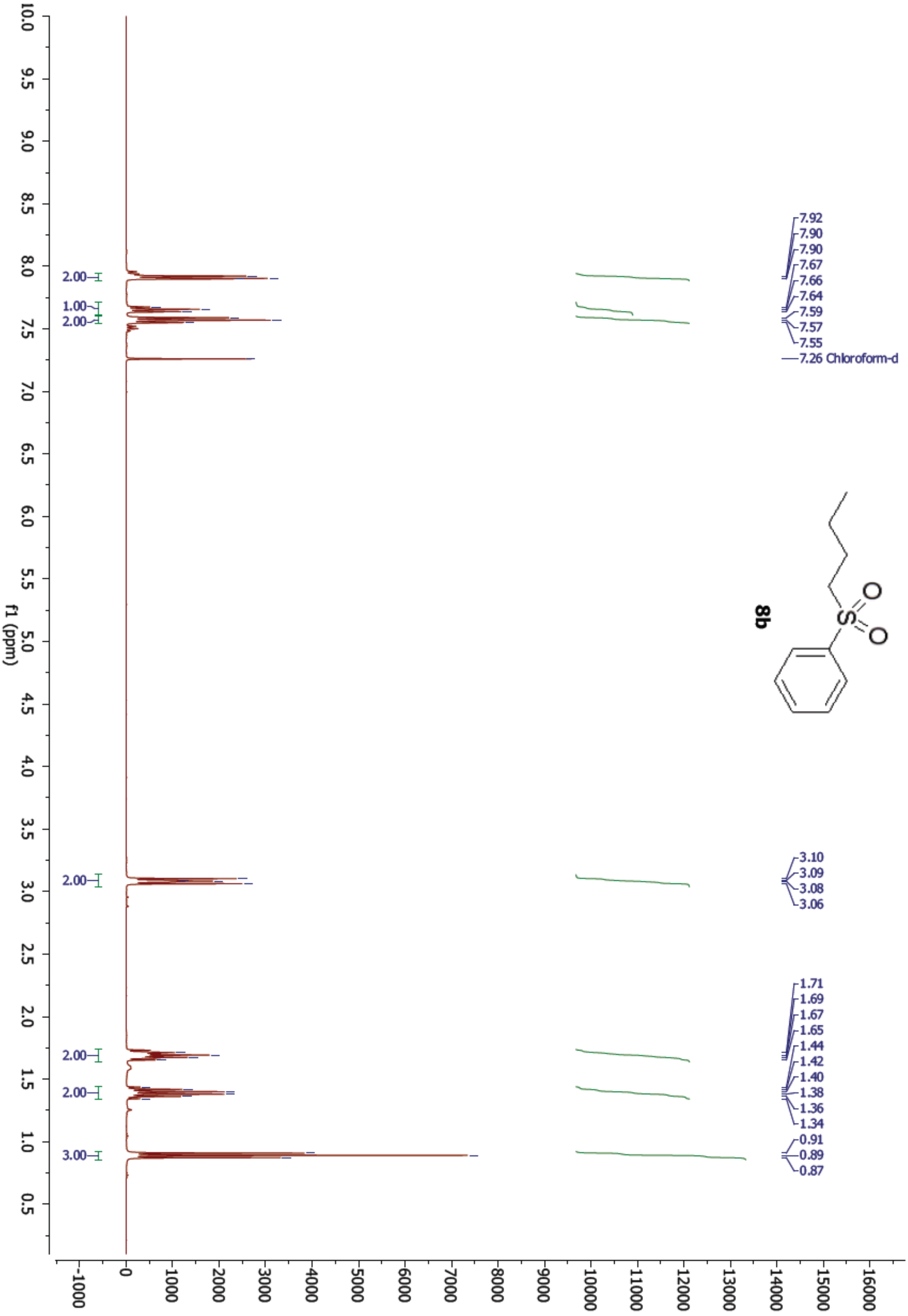

4r
165.77
158.77
142.25
132.73
131.87
128.56
128.19
121.49
104.76
99.59
77.16 Chloroform-d
55.97
55.86
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
-500
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000


1.98
1.00
1.00
1.00
2.00
0.99
3.00
8.10
8.08
7.76
7.75
7.73
7.55
7.53
7.26 Chloroform-d
6.87
6.87
6.85
6.85
3.86
4s
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-2000
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
20000
22000
24000
26000
28000
30000

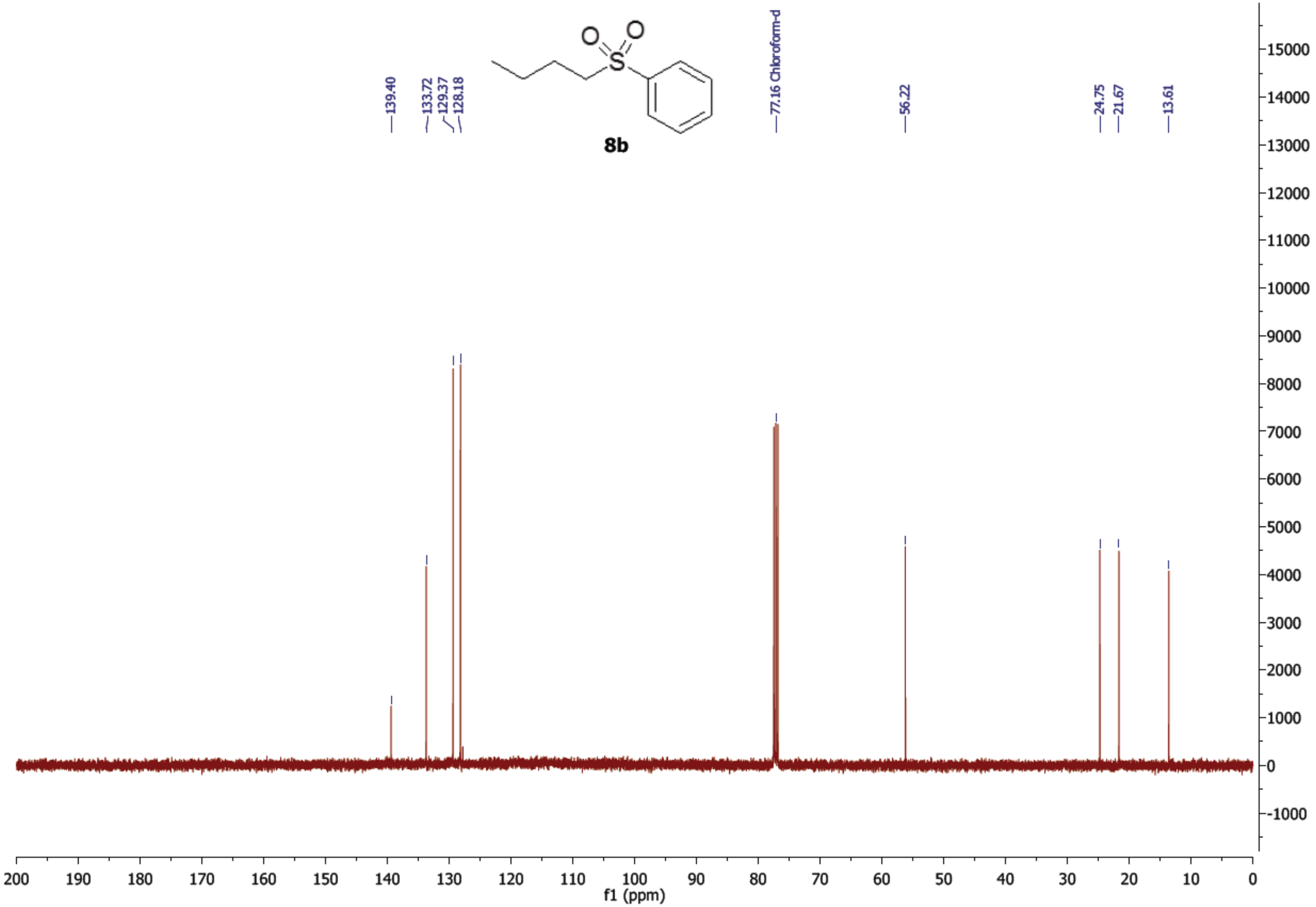

4s
164.17
155.83
139.84
139.11
133.74
129.22
129.00
115.63
115.04
77.16 Chloroform-d
54.11
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000


8a
Me
S
O
O
7.96
7.94
7.66
7.59
7.58
7.56
7.26 Chloroform-d
3.05
2.00
1.00
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
0
10000
20000
30000
40000
50000
60000
70000
80000
90000

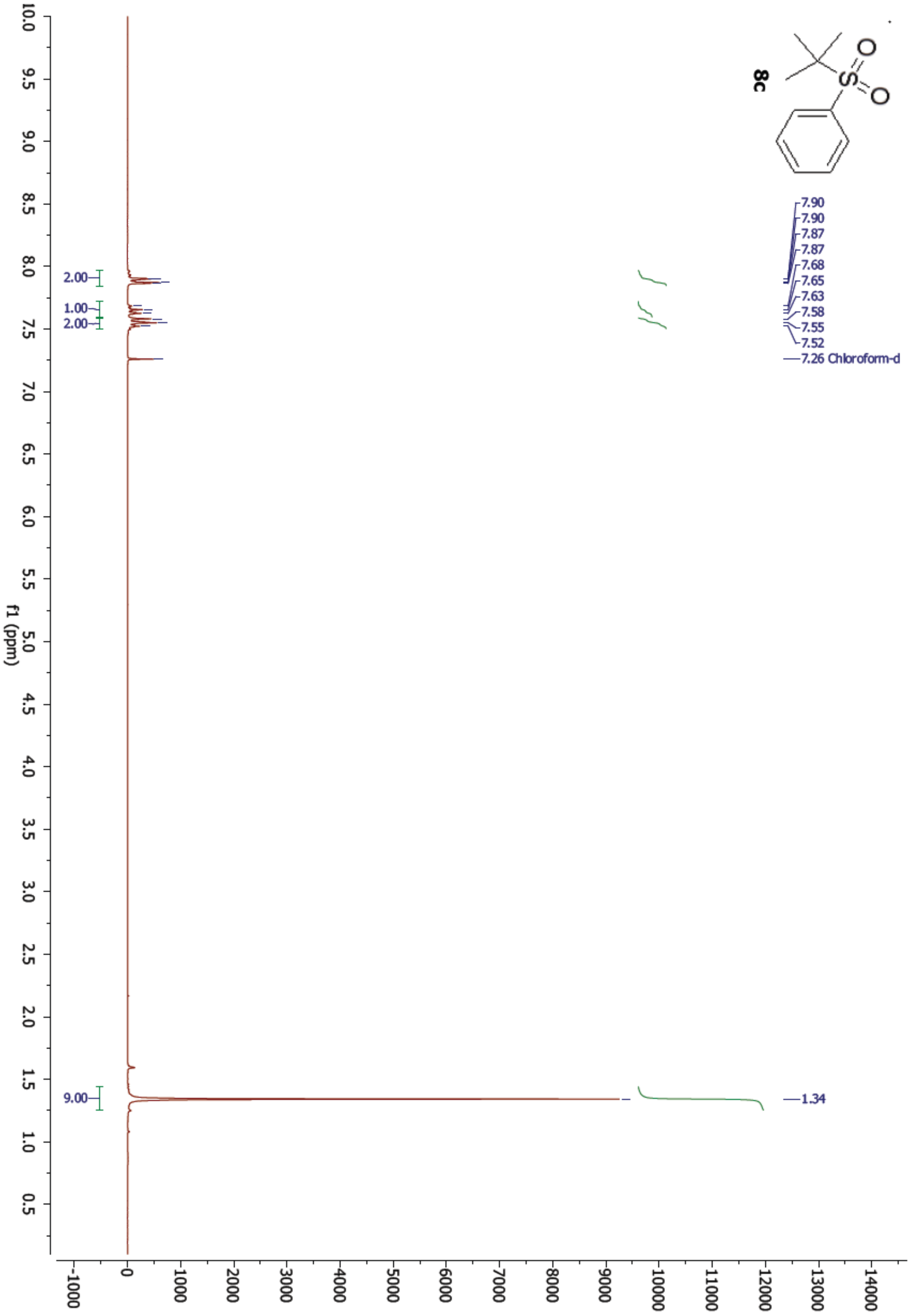

8a
Me
S
O
O
140.70
133.84
129.50
127.48
77.16 Chloroform-d
44.62
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)
2E+09
1E+09
1E+09
1E+09
1E+09
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08

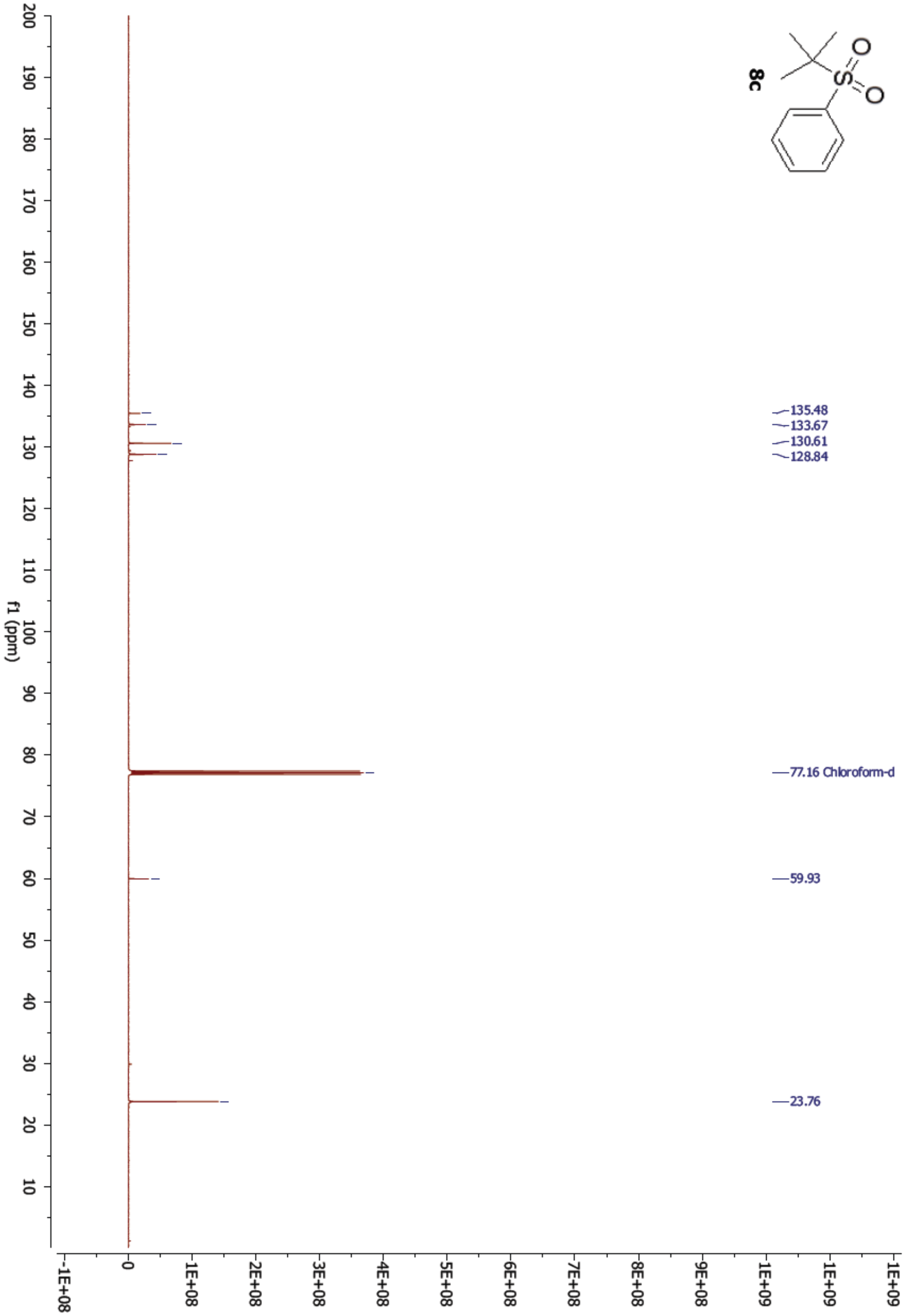


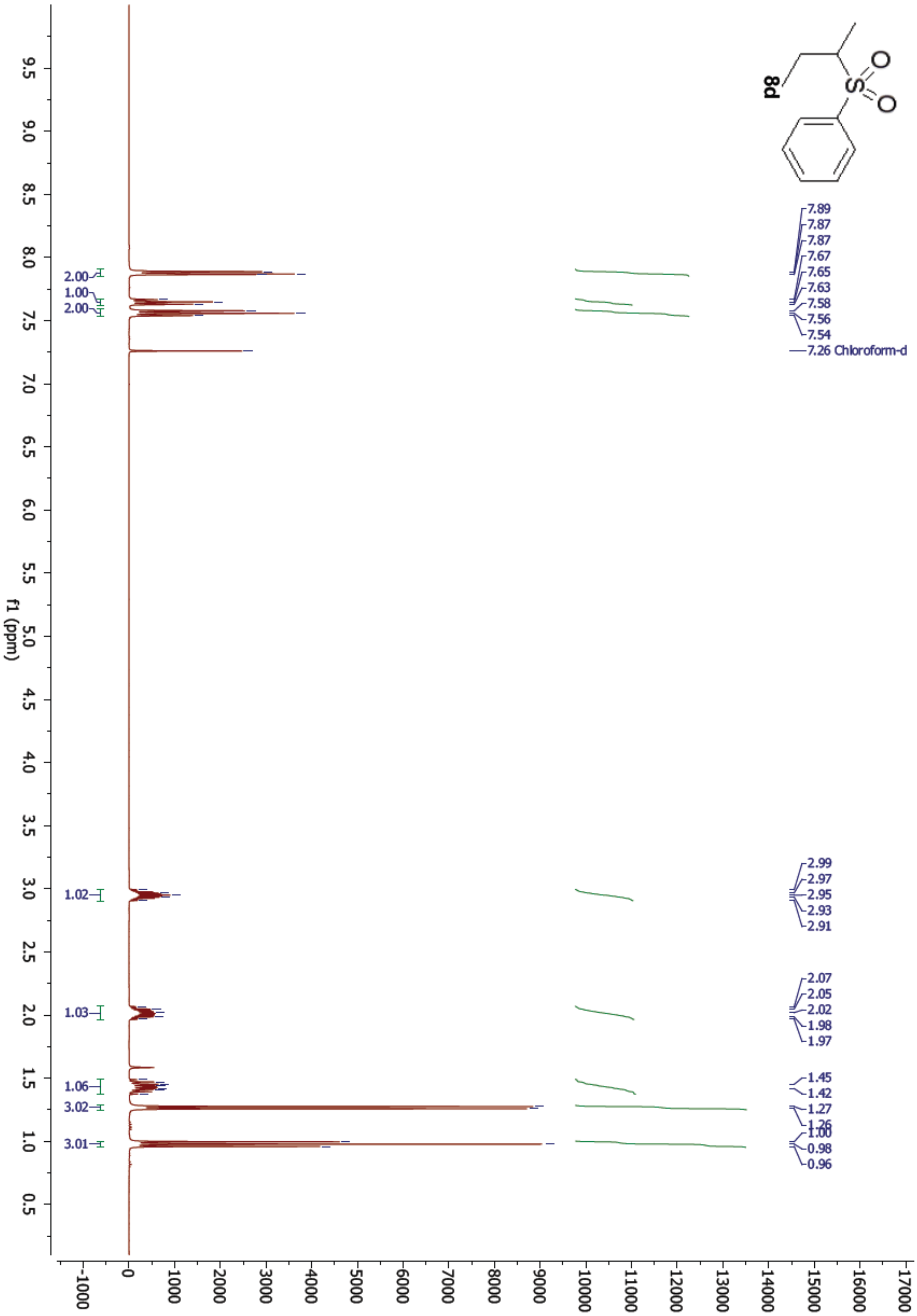
8b
O
S
O
7.92
7.90
7.90
7.67
7.66
7.64
7.59
7.57
7.55
7.26 Chloroform-d
3.10
3.09
3.08
3.06
1.71
1.69
1.67
1.65
1.44
1.42
1.40
1.38
1.36
1.34
0.91
0.89
0.87
2.00
1.00
2.00
2.00
2.00
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000
15000
16000

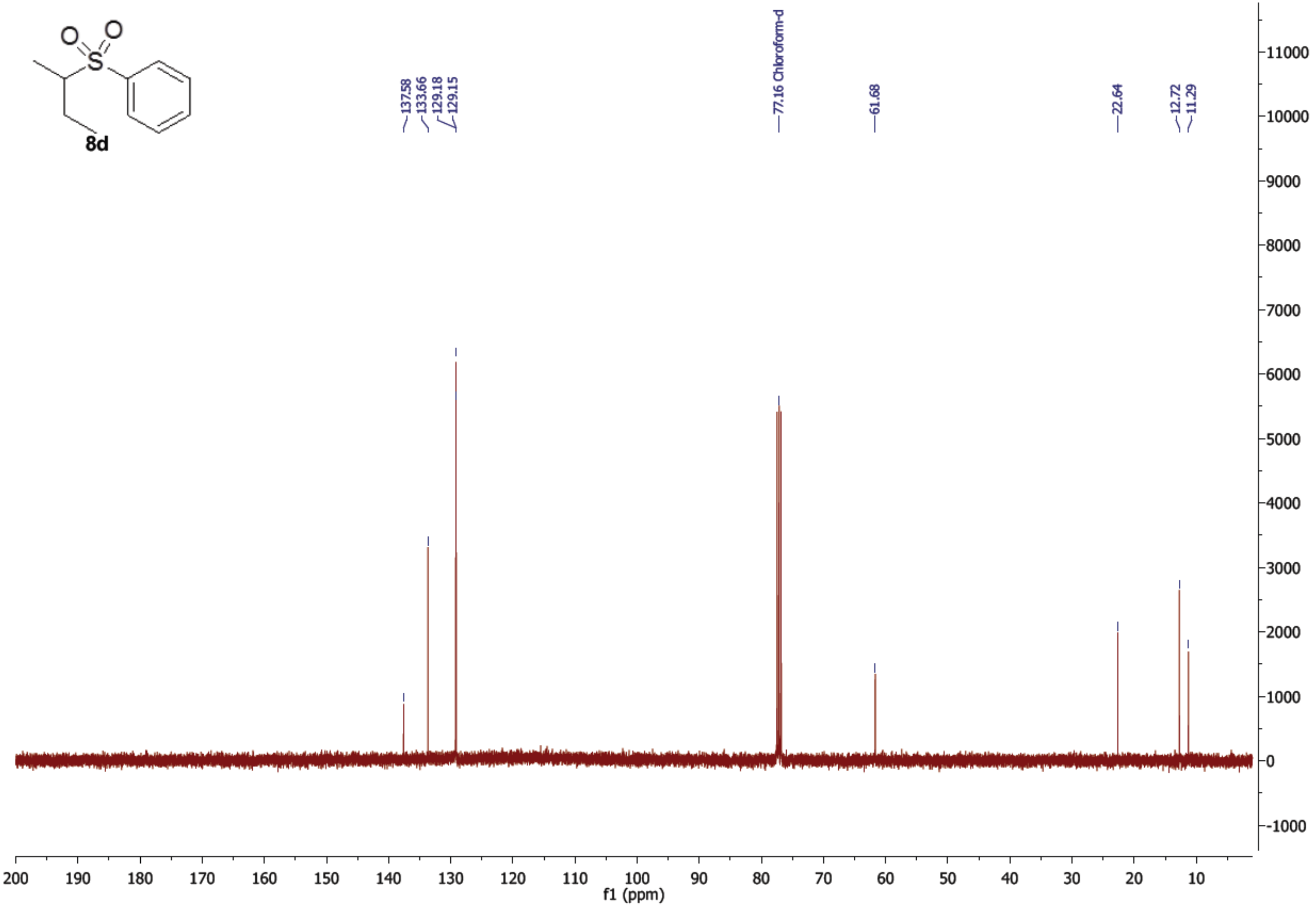

139.40
133.72
129.37
128.18
77.16 Chloroform-d
56.22
24.75
21.67
13.61
O
O
S
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

8b


8c
7.90
7.90
7.87
7.87
7.68
7.65
7.63
7.58
7.55
7.52
7.26 Chloroform-d
1.34
2.00
1.00
2.00
9.00
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000


8c
135.48
133.67
130.61
128.84
77.16 Chloroform-d
59.93
23.76
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
-1E+08
0
1E+08
2E+08
3E+08
4E+08
5E+08
6E+08
7E+08
8E+08
9E+08
1E+09
1E+09
1E+09


8d
O
S
O
7.89
7.87
7.87
7.67
7.65
7.63
7.58
7.56
7.54
7.26 Chloroform-d
2.99
2.97
2.95
2.93
2.91
2.07
2.05
2.02
1.98
1.97
1.45
1.42
1.27
1.26
1.00
0.98
0.96
2.00
1.00
2.00
1.02
1.03
1.06
3.02
3.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000
15000
16000
17000


8d
137.58
133.66
129.18
129.15
77.16 Chloroform-d
61.68
22.64
12.72
11.29
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)