Supporting Information

Emodin as a Novel Organic Photocatalyst for Selective Oxidation of Sulfides under Mild Conditions

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1. Materials and Methods

All commercially available reagents and solvents were used without further purification. Thin-layer chromatography was performed using silica gel plates F254. Visualization was accomplished with short wavelength UV light (254 nm) and UVA light (366 nm) sources. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV400 (400 MHz) spectrometer in $CDCl_3$ solutions with internal solvent signals (for ^{1}H and ^{13}C) as reference (7.26 and 77.2, 2.50 and 39.5 for $CDCl_3$ and DMSO-d_6, respectively). ^{1}H NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, br. s. = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, hept = heptet, dd = doublet of doublets, ddd = doublet of doublets of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet), coupling constants (Hz), and numbers of protons. Data for ^{13}C NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. High resolution mass spectra (HRMS) were recorded on Waters Xevo G2 Q-TOF instrument. HPLC measurements were performed with Waters 2695. UV–Vis measurements were performed with Shimadzu UV-3600plus spectrophotometer. Fluorescence measurements were performed with F-2700 spectrofluorometer. Photochemical reaction was carried out in the borosilicate glass bottle under visible light by a PHILIPS 5W blue LED at room temperature. The sample was placed at an approximate distance of 5 cm to the lamp. The light intensity was measured to be 6.51 mW/cm^2. The emission spectrum of each light source was measured with Hitachi F-2700 spectrofluorometer. The intensity of irradiation was measured by a FZ-A radiometer (Photoelectric Instrument Factory of Beijing Normal University) equipped with a 400−1000 nm sensor.

2. UV-Vis Absorption Spectra for Emodin in Solution and Solid State

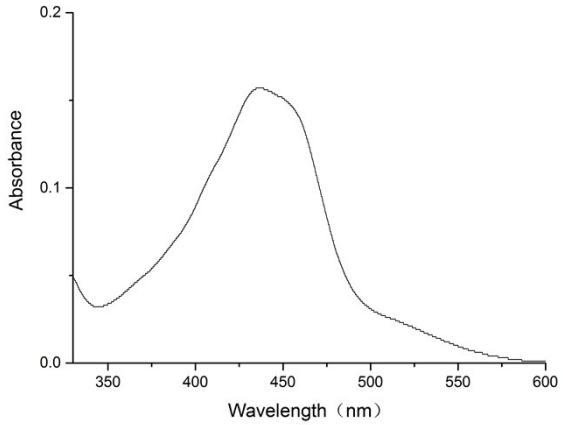


Fig. S1 UV-Vis Spectra for Emodin in CH_3OH ($1*10^{-5}$mol/L)

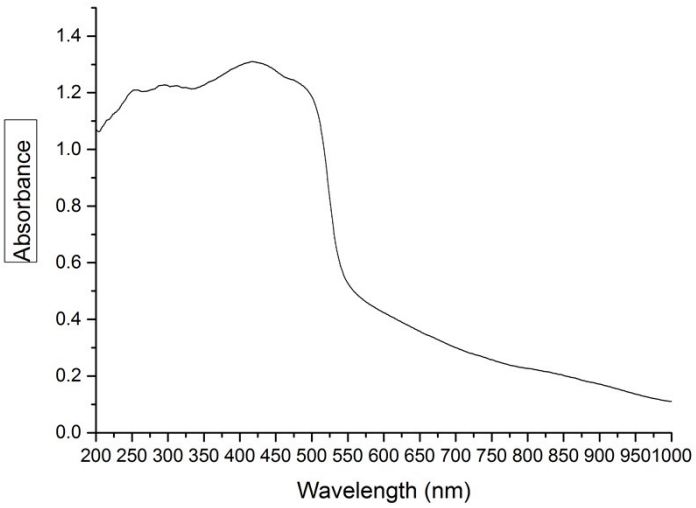


Fig. S2 UV-Vis Spectra for Emodin in solid state

3. Spectra of the Light Sources

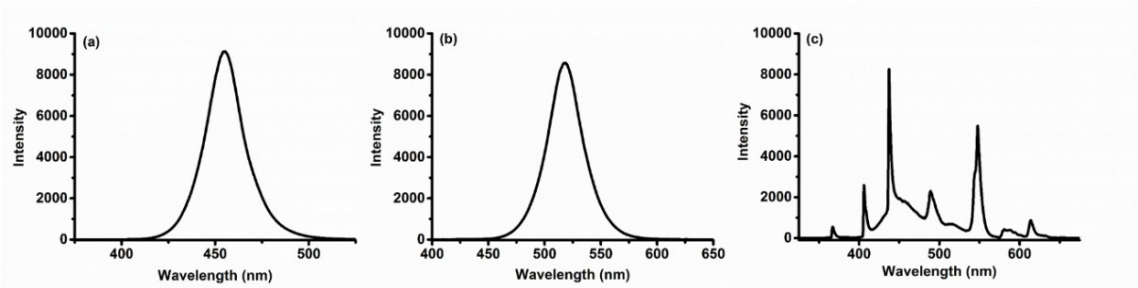


Fig. S3 Spectra of light sources. (a) blue LED, (b) green LED, (c) CFL.

4. Photostability Experiments of Emodin

(1) Confirm the retention of Emodin in the reaction with HPLC

In a dried schlenk tube, sulfides **1a** (0.25 mmol) and Emodin (1.5 mol%) was added in 2.0 mL methanol. Next, a balloon was purged with oxygen and fixed on the top of the schlenk tube. The reaction mixture was stirred and irradiated by 5 W blue LED at room temperature under an atmospheric pressure oxygen atmosphere for 14h. Take out 300 uL of reaction solution for monitoring with HPLC.

Table S1 Method for HPLC

Time	Methanol	0.2% Phosphoric acid solution
0-9min	15%	85%
9-10min	15%-85%	85%-15%
10-25min	85%	15%

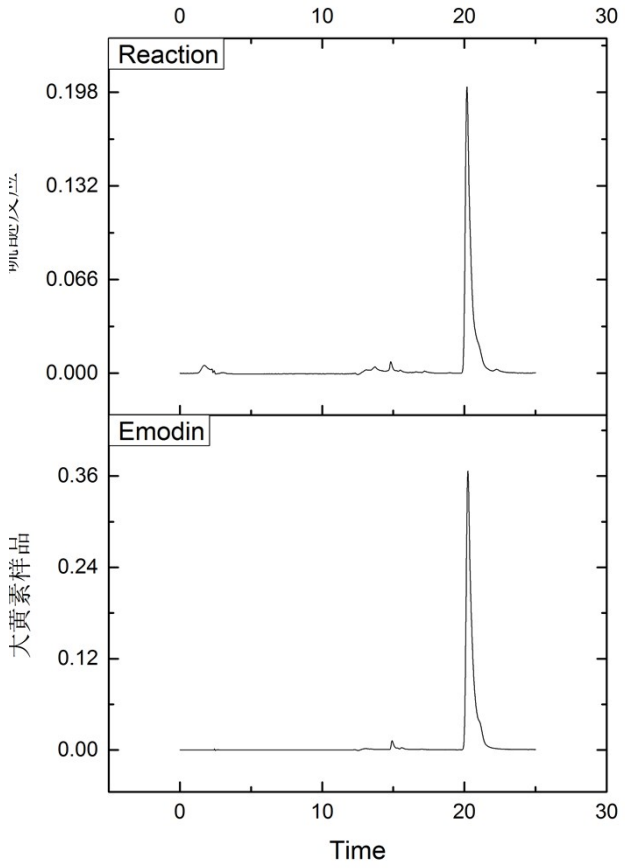


Fig. S4 HPLC of Emodin and the reaction solution

(2) Recovery of Emodin by column chromatography

In a dried schlenk tube, sulfides **1a** (0.25 mmol) and Emodin (1.5 mol%) was added in 2.0 mL methanol. Next, a balloon was purged with oxygen and fixed on the top of the schlenk tube. The reaction mixture was stirred and irradiated by 5 W blue LED at room temperature under an atmospheric pressure oxygen atmosphere for 14h. The reaction solution was concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography to afford Emodin (PE: EA = 30:1 to PE: EA = 3:1) with 62% recovery rate.

(3) Monitor the photostability of Emodin Using ^{1}H NMR

In a reaction tube, Emodin (0.1 mmol) was added in 1.0 mL methanol. The reaction mixture was stirred and irradiated by 5 W blue LED at room temperature for 14h. After concentrated in vacuum, 0.05mmol of *p*-methoxyacetophenone was added as internal standard, and the ^{1}H NMR recovery rate was 70%.

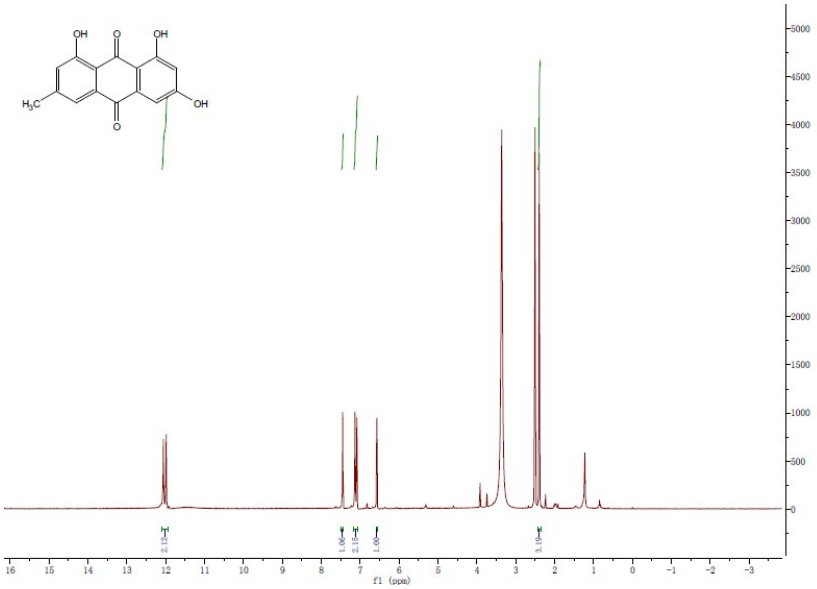


Fig. S5 ^{1}H NMR of Emodin

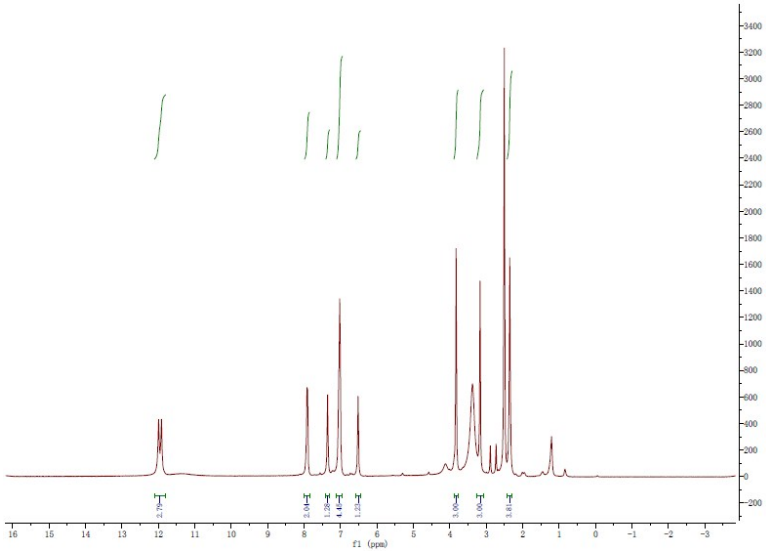


Fig. S6 ^{1}H NMR of emodin after irradiation with *p*-methoxyacetophenone as internal standard

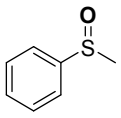
Table S2 ^{1}H NMR result for Emodin recovery after irradiation

chemical shift	Peak area	recovery rate
2.43	3.81	70%
6.58	1.23	68%
7.11	4.45	70%
7.40	1.28	71%
12.11	2.79	77%

5. General Procedures for the Selective Oxidation of Sulfides with Emodin

In a dried schlenk tube, sulfides **1** (0.5 mmol) and Emodin (1.5 mol%) was added in 2.0 mL methanol. Next, a balloon was purged with oxygen and fixed on the top of the schlenk tube. The reaction mixture was stirred and irradiated by 5 W blue LED at room temperature under an atmospheric pressure oxygen atmosphere. When the reaction was finished, the reaction mixture was diluted with brine. The aqueous phase was extracted with ethyl acetate for three times. The combined organic extracts were dried over Na_2SO_4, concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography to afford the desired product **2**.

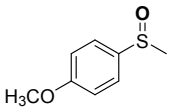
(Methylsulfinyl)benzene (**2a**)[1]



2a

The representative procedure was followed using methyl (phenyl)sulfane (**1a**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2a** (54 mg, 99%) as a white oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.67-7.64 (m, 2H, ArH), 7.56-7.48 (m, 3H, ArH), 2.73 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 145.7, 131.0, 129.3, 123.5, 43.9.

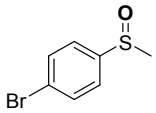
1-methoxy-4-(methylsulfinyl)benzene (**2b**)[2]



2b

The representative procedure was followed using (4-methoxyphenyl)(methyl)sulfane (**1b**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2b** (40 mg, 95%) as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.60 (d, 2H, J = 8 Hz, ArH), 7.04 (d, 2H, J = 8 Hz, ArH), 3.86 (s, 3H, OCH_3), 2.71 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 162.0, 136.7, 125.5, 114.9, 55.5, 44.0.

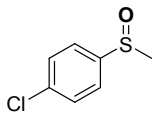
1-Bromo-4-(methylsulfinyl)benzene (**2c**)[3]



2c

The representative procedure was followed using (4-bromophenyl) (methyl)sulfane (**1c**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2c** (54 mg, 97%) as a white solid (m.p. = 76.2-78.1 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.67 (d, 2H, *J* = 8 Ha, ArH), 7.53 (d, 2H, *J* = 8 Hz, ArH), 2.72 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 144.9, 132.6, 125.4, 125.1, 44.0.

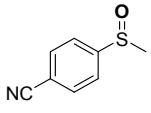
1-Chloro-4-(methylsulfinyl)benzene (**2d**)[4]



2d

The representative procedure was followed using (4-chlorophenyl)(methyl)sulfane (**1d**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2d** (40 mg, 93%) as a white oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.60 (d, 2H, *J* = 8 Hz, ArH), 7.51 (d, 2H, *J* = 8 Hz, ArH), 2.73 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 144.3, 137.2, 129.6, 125.0, 44.0.

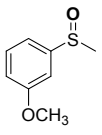
4-(Methylsulfinyl)benzonitrile (**2e**)[2]



2e

The representative procedure was followed using 4-(methylthio)benzonitrile (**1e**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2e** (21 mg, 52%) as a yellow solid (m.p. = 83.5-87.6 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.86-7.83 (m, 2H, ArH), 7.79-7.77 (m, 2H, ArH), 2.78 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 151.5, 133.0, 124.3, 117.7, 114.9, 43.8.

1-methoxy-3-(methylsulfinyl)benzene (**2f**)[5]

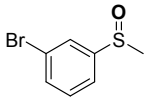


2f

The representative procedure was followed using (3-methoxyphenyl)(methyl)sulfane (**1f**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2f** (42 mg, 99%) as a light

yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.44-7.40 (m, 1H, ArH), 7.26-7.25 (m, 1H, ArH), 7.15-7.13 (m, 1H, ArH), 7.03-7.01 (m, 1H, ArH), 3.87 (s, 3H, OCH_3), 2.73 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 160.5, 147.2, 130.3, 117.4, 115.5, 107.9, 55.6, 44.0.

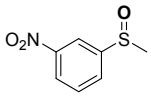
1-bromo-3-(methylsulfinyl)benzene (**2g**)[6]



2g

The representative procedure was followed using (3-bromophenyl) (methyl)sulfane (**1g**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2g** (55 mg, 98%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.82-7.81 (m, 1H, ArH), 7.64-7.62 (m, 1H, ArH), 7.56-7.54 (m, 1H, ArH), 7.43-7.39 (m, 1H, ArH), 2.75 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 148.1, 134.1, 130.8, 126.5, 122.6, 122.1, 44.1.

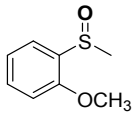
1-(Methylsulfinyl)-3-nitrobenzene (**2h**)[5]



2h

The representative procedure was followed using methyl(3-nitrophenyl)sulfane (**1h**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2h** (30 mg, 65%) as a yellow solid (m.p. = 112.6-115.3 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.53-8.52 (m, 1H, ArH), 8.39-8.36 (m, 1H, ArH), 8.04-8.01 (m, 1H, ArH), 7.81-7.77 (m, 1H, ArH), 2.83 (s, 3H, CH3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 148.7, 130.6, 129.3, 125.7, 119.0, 44.0.

1-methoxy-2-(methylsulfinyl)benzene (**2j**)[7]



2j

The representative procedure was followed using (2-methoxyphenyl)(methyl)sulfane (**1j**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2j** (42 mg, 98%) as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.82 (d, 1H, J = 8 Hz, ArH), 7.48-7.44 (m, 1H, ArH), 7.21-7.17 (m, 1H, ArH), 6.93 (d, 1H, J = 8 Hz, ArH), 3.89 (s, 3H, OCH_3), 2.78 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 154.8, 133.1, 132.0, 124.6, 121.7, 110.6, 55.7, 41.2.

1-bromo-2-(methylsulfinyl)benzene (**2k**)[2]

2k

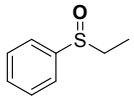
The representative procedure was followed using (2-bromophenyl) (methyl)sulfane (**1k**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2k** (27 mg, 51%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.97-7.94 (m, 1H, ArH), 7.61-7.56 (m, 2H, ArH), 7.40-7.36 (m, 1H, ArH), 2.83 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 145.5, 132.9, 132.3, 128.8, 125.7, 118.4, 41.9.

1-chloro-2-(methylsulfinyl)benzene (**2l**)[8]

2l

The representative procedure was followed using (2-chlorophenyl) (methyl)sulfane (**1l**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2l** (27 mg, 63%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.97-7.95 (m, 1H, ArH), 7.57-7.53 (m, 1H, ArH), 7.48-7.39 (m, 2H, ArH), 2.83 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 143.7, 132.0, 129.8, 128.2, 125.3, 41.7.

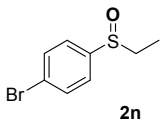
(Ethylsulfinyl)benzene (**2m**)[9]



2m

The representative procedure was followed using ethyl(phenyl)sulfane (**1m**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2m** (31 mg, 81%) as a light yellow solid (m.p. 139.2-141.1 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.63-7.61 (m, 2H, ArH), 7.55-7.48 (m, 3H, ArH), 2.96-2.87 (m, 1H, CH), 2.82-2.75 (m, 1H, CH), 1.20 (t, 3H, J = 8 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 143.3, 130.9, 129.1, 124.2, 50.3, 5.9.

1-Bromo-4-(ethylsulfinyl)benzene (**2n**)[10]

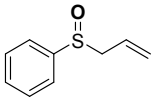


2n

The representative procedure was followed using (4-bromophenyl)(ethyl)sulfane (**1n**) (0.25 mmol) as

substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2n** (54 mg, 93%) as a light yellow solid (m.p. 139.2-141.1 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.67 (d, 2H, *J* = 8 Hz, ArH), 7.49 (d, 2H, *J* = 8 Hz, ArH), 2.96-2.71 (m, 2H, CH_2), 1.20 (t, 3H, *J* = 8 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 142.5, 132.4, 125.8, 125.4, 50.3, 5.8.

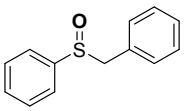
(Allylsulfinyl)benzene (**2o**)[11]



2o

The representative procedure was followed using allyl(phenyl)sulfane (**1o**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 2/1) yielded **2o** (19 mg, 45%) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.62-7.60 (m, 2H, ArH), 7.54-7.51 (m, 3H, ArH), 5.70-5.60 (m, 1H, CH), 5.34 (d, 1H, *J* = 8 Hz, CH), 5.20 (d, 1H, *J* = 16 Hz, CH), 3.61-3.48 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 142.0, 130.1, 128.0, 124.3, 123.3, 122.8, 59.9.

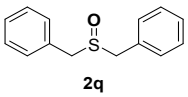
(Benzylsulfinyl)benzene (**2p**)[12]



2p

The representative procedure was followed using benzyl(phenyl)sulfane (**1p**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2p** (52 mg, 97%) as a white solid (m.p. = 123.0-124.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.47-7.36 (m, 5H, ArH), 7.29-7.21 (m, 3H, ArH), 6.98-6.96 (m, 2H, ArH), 4.00-3.97 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 142.8, 131.2, 130.4, 128.9, 128.5, 128.3, 124.5, 63.6.

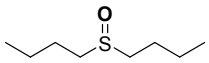
(Sulfinylbis(methylene))dibenzene (**2q**)[13]



2q

The representative procedure was followed using dibenzylsulfane (**1q**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2q** (44 mg, 77%) as a white solid (m.p. = 130.8-133.2 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.40-7.34 (m, 3H, ArH), 7.30-7.28 (m, 2H, ArH), 3.94-3.86 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 130.2, 130.1, 129.0, 128.4, 57.4.

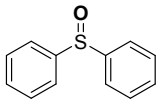
1-(Butylsulfinyl)butane (**2r**)[9]



2r

The representative procedure was followed using dibutylsulfane (**1r**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 3/1) yielded **2r** (39 mg, 97%) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.70-2.58 (m, 4H, $2CH_2$), 1.77-1.68 (m, 4H, $2CH_2$), 1.51-1.41 (m, 4H, $2CH_2$), 0.97-0.91 (m, 6H, $2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 52.1, 24.5, 22.3, 13.7.

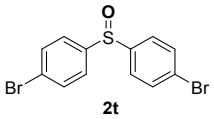
Sulfinyldibenzene (**2s**)[14]



2s

The representative procedure was followed using diphenylsulfane (**1s**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2s** (23 mg, 45%) as a white solid (m.p. = 70.5-72.1 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.66-7.64 (m, 4H, ArH), 7.49-7.42 (m, 6H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 145.6, 131.1, 129.4, 124.8.

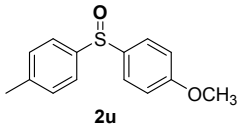
4,4'-Sulfinylbis(bromobenzene) (**2t**)[15]



2t

The representative procedure was followed using bis(4-bromophenyl) sulfane (**1t**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2t** (23 mg, 26%) as a white oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.61 (d, 2H, J = 8 Hz, ArH), 7.50 (d, 2H, J = 8 Hz, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 143.4, 131.7, 125.2, 124.9.

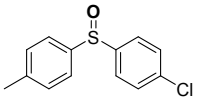
1-Methoxy-4-(p-tolylsulfinyl)benzene (**2u**)[16]



2u

The representative procedure was followed using (4-methoxyphenyl) (*p*-tolyl)sulfane (**1u**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2u** (49 mg, 79%) as a white oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.55 (d, 2H, J = 8 Hz, ArH), 7.49 (d, 2H, J = 8 Hz, ArH), 7.25 (d, 2H, J = 8 Hz, ArH), 6.95 (d, 2H, J = 8 Hz, ArH), 3.81 (s, 3H, OCH_3), 2.36 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 161.9, 142.8, 141.2, 137.1, 129.9, 127.1, 124.8, 114.8, 55.5, 21.4.

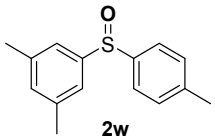
1-Chloro-4-(*p*-tolylsulfinyl)benzene (**2v**)[17]



2v

The representative procedure was followed using (4-chlorophenyl) (*p*-tolyl)sulfane (**1v**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2v** (13 mg, 21%) as a white oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.56 (d, 2H, *J* = 8 Hz, ArH), 7.51 (d, 2H, *J* = 8 Hz, ArH), 7.42 (d, 2H, *J* = 8 Hz, ArH), 7.27 (d, 2H, *J* = 8 Hz, ArH), 2.37 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 143.4, 141.0, 136.1, 129.2, 128.5, 125.0, 123.9, 20.4.

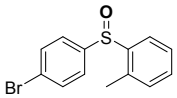
1,3-Dimethyl-5-(*p*-tolylsulfinyl)benzene (**2w**)[18]



2w

The representative procedure was followed using (3,5-dimethyl phenyl) (*p*-tolyl)sulfane (**1w**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2w** (12 mg, 20%) as a white oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.52 (d, 2H, *J* = 8 Hz, ArH), 7.26-7.23 (m, 4H, ArH), 7.03 (s, 1H, ArH), 2.36 (s, 3H, CH_3), 2.32 (s, 6H, $2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 145.4, 142.7, 141.4, 139.2, 132.7, 130.0, 125.0, 122.2, 21.4, 21.3.

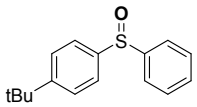
1-((4-bromophenyl)sulfinyl)-2-methylbenzene (**2x**)



2x

The representative procedure was followed using (4-bromophenyl)(o-tolyl)sulfane (**1x**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2x** (21 mg, 29%) as a white oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.91-7.88 (m, 1H, ArH), 7.58 (d, 2H, *J* = 8 Hz, ArH), 7.47 (d, 2H, *J* = 8 Hz, ArH), 7.43-7.36 (m, 2H, ArH), 7.20-7.18 (m, 1H, ArH), 2.37 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 143.9, 142.6, 135.8, 132.5, 131.3, 127.3, 125.6, 124.8, 18.6. HRMS (ESI-Q-TOF) exact mass calcd for $C_{13}H_{12}BrOS$ $[M + H]^+$ 294.9792, found 294.9798.

1-(tert-Butyl)-4-(phenylsulfinyl)benzene (**2y**)[19]



2y

The representative procedure was followed using (4-(*tert*-butyl) phenyl) (phenyl)sulfane (**1y**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2y** (13 mg, 20%) as a white oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.66-7.64 (m, 2H, ArH), 7.56 (d, 2H, J = 8 Hz, ArH), 7.48-7.41 (m, 5H, ArH), 1.30 (s, 9H, $3CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 153.7, 144.6, 141.3, 129.9, 128.2, 125.4, 123.8, 40.0, 30.1.

6. References

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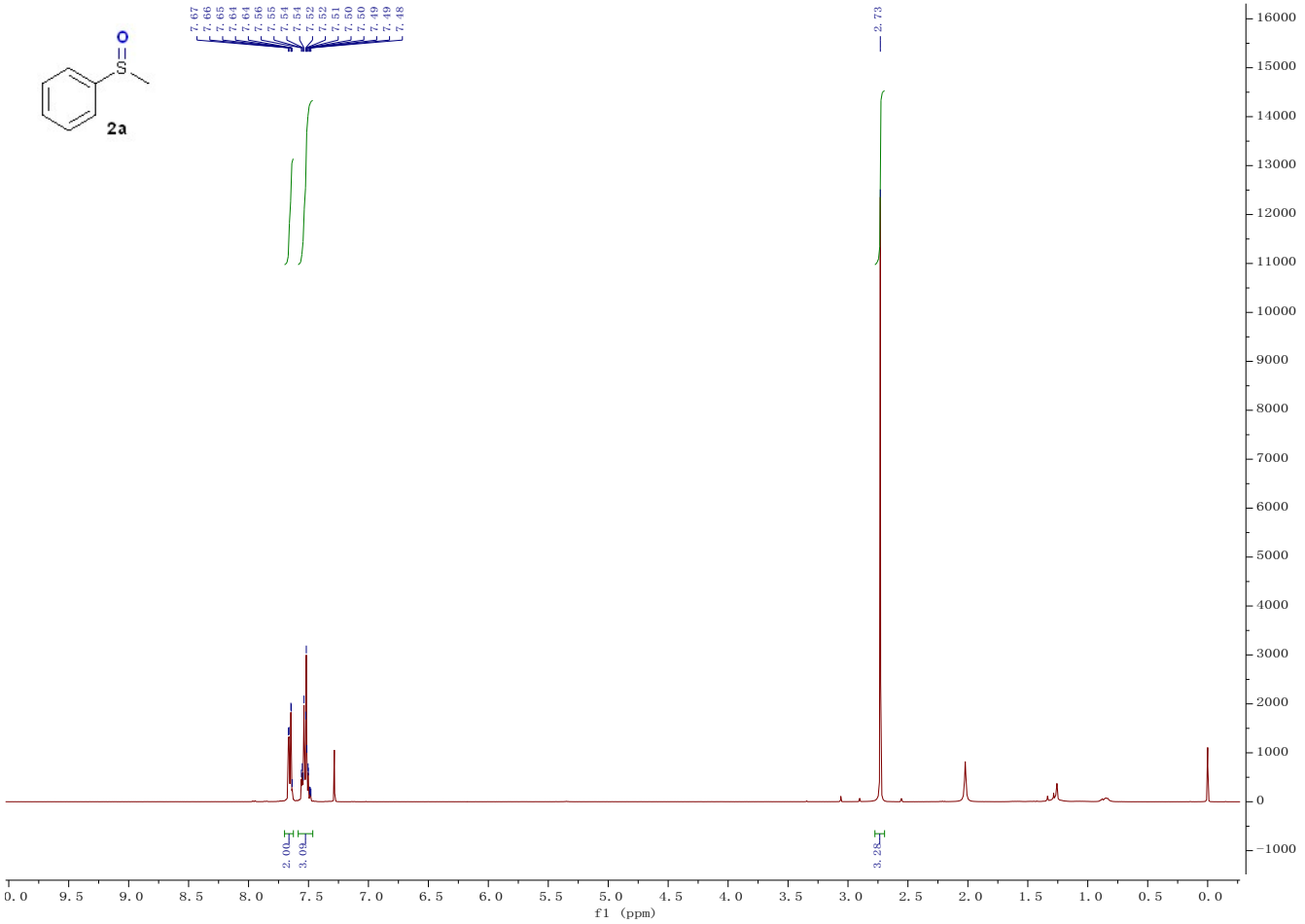
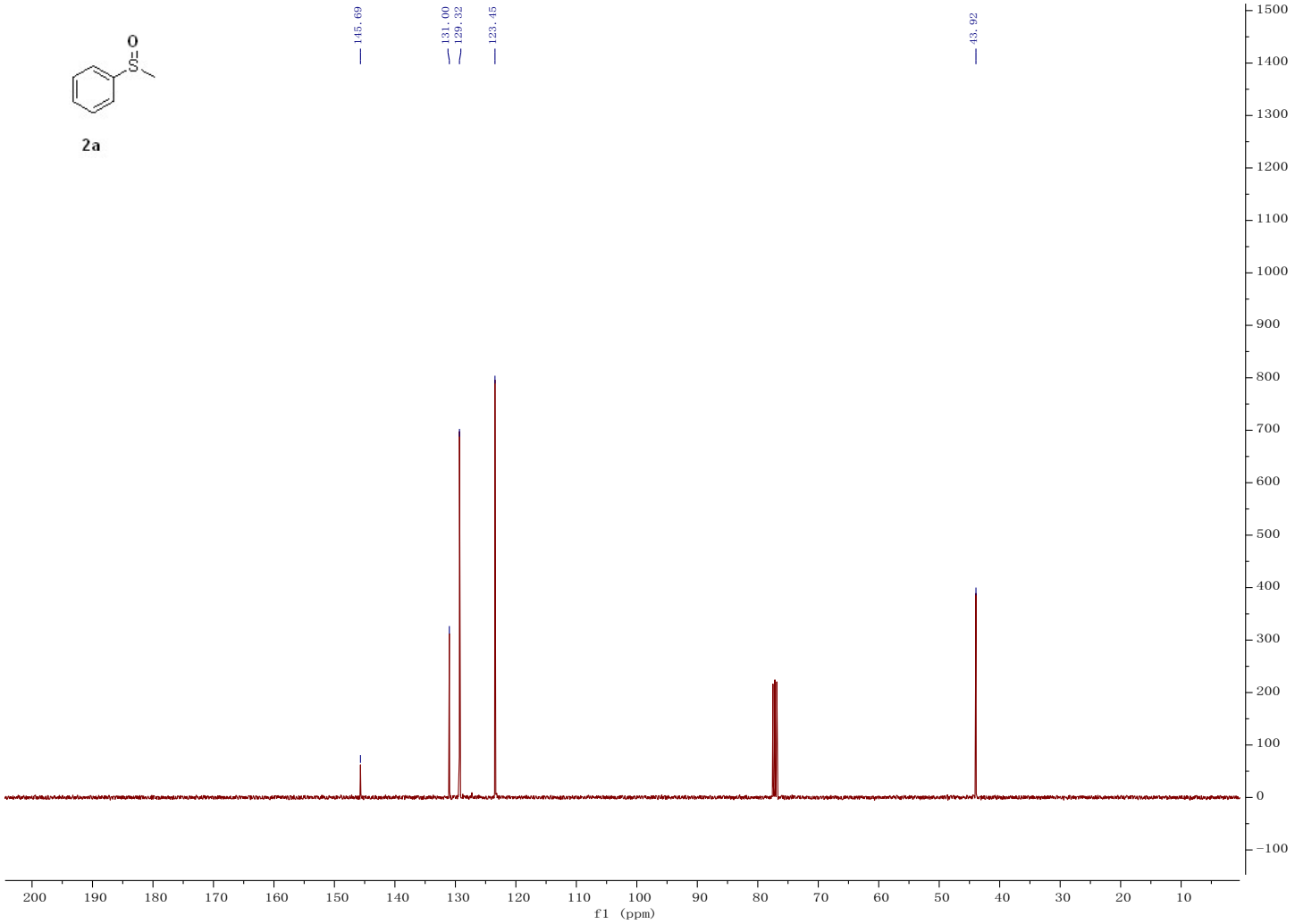
7. ^{1}H and ^{13}C spectra

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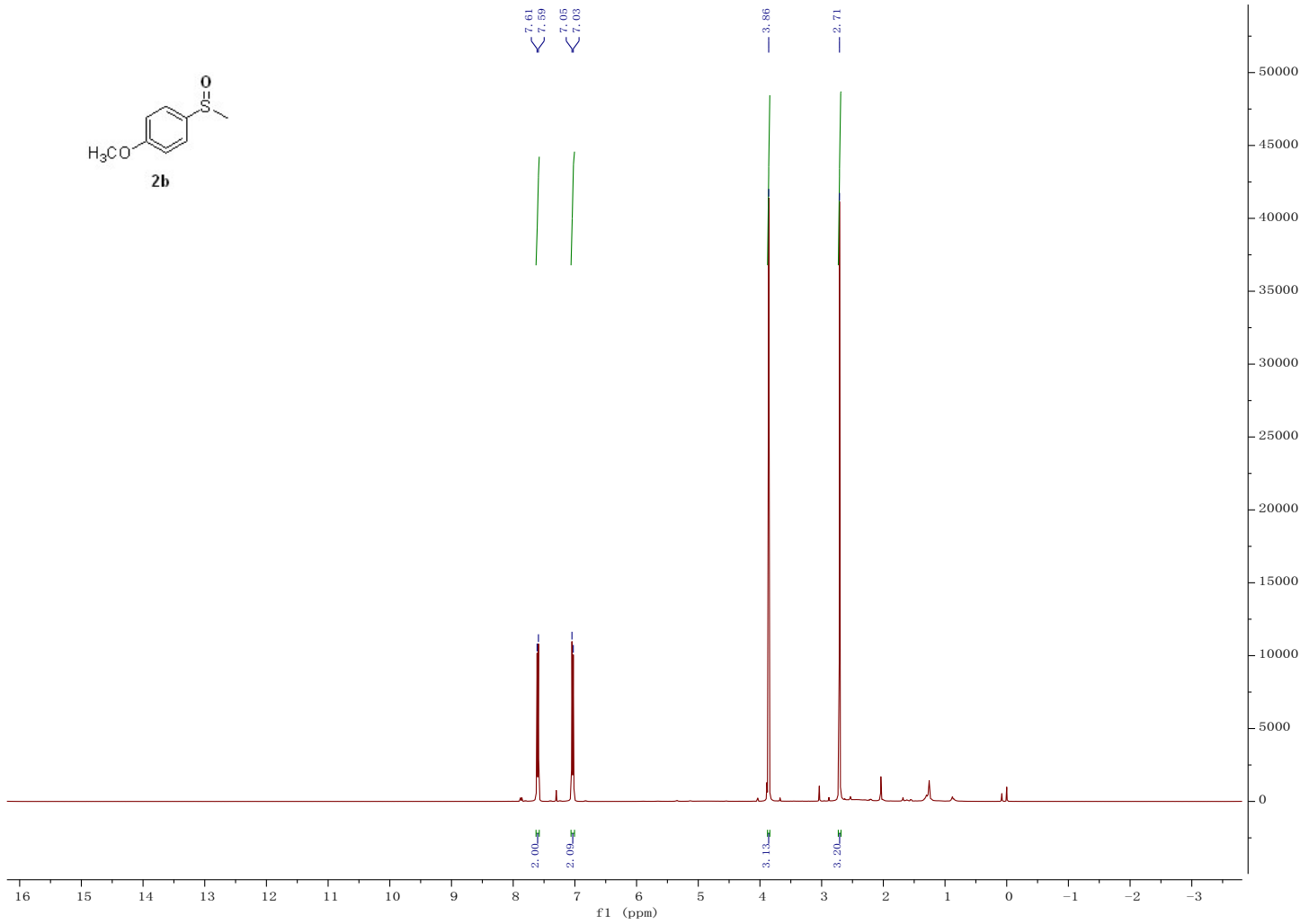
129.32
123.45
43.92
f1 (ppm)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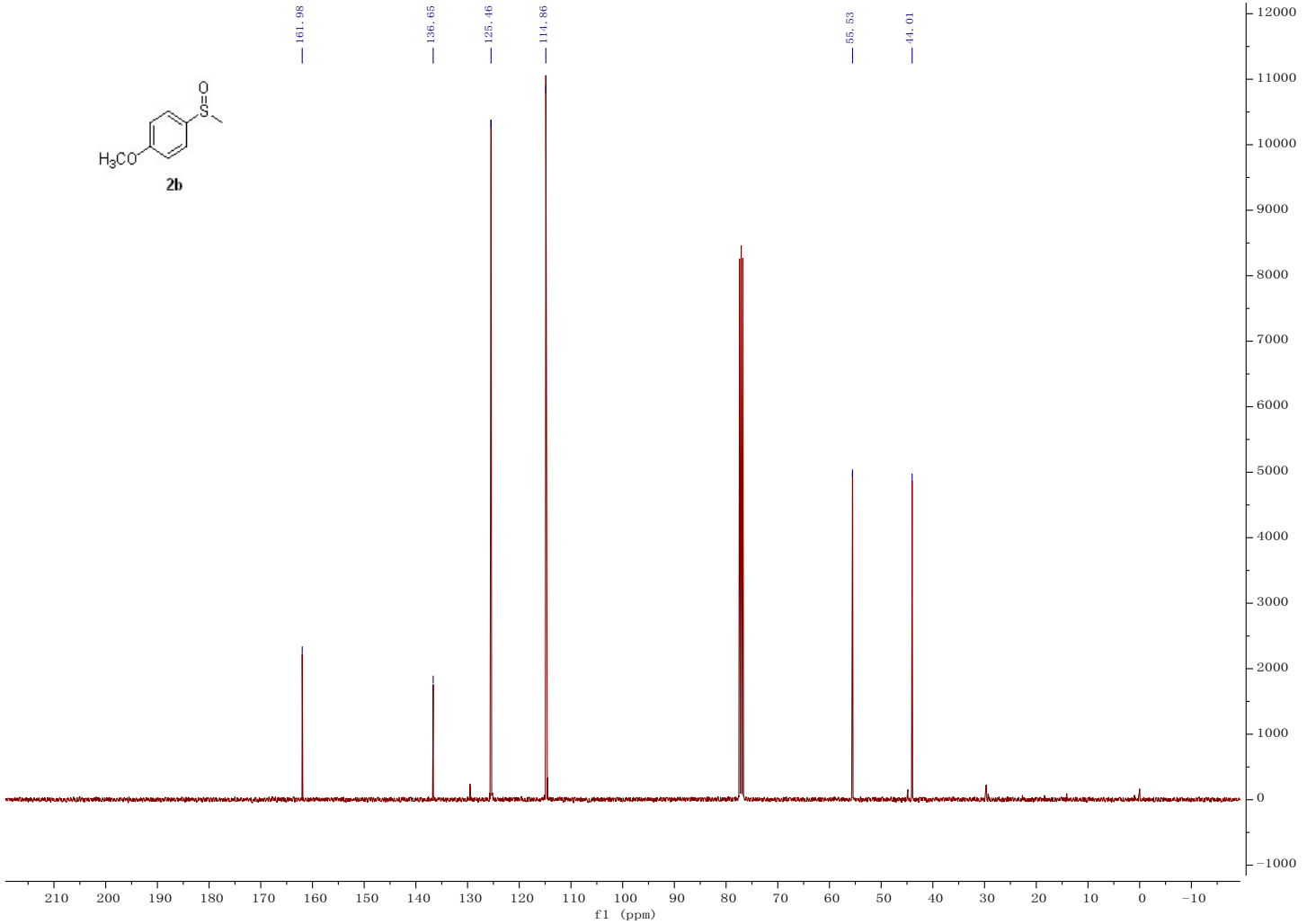
7.59
7.05
7.03
3.86
2.71
2b
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
2.00
2.09
3.13
3.20
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)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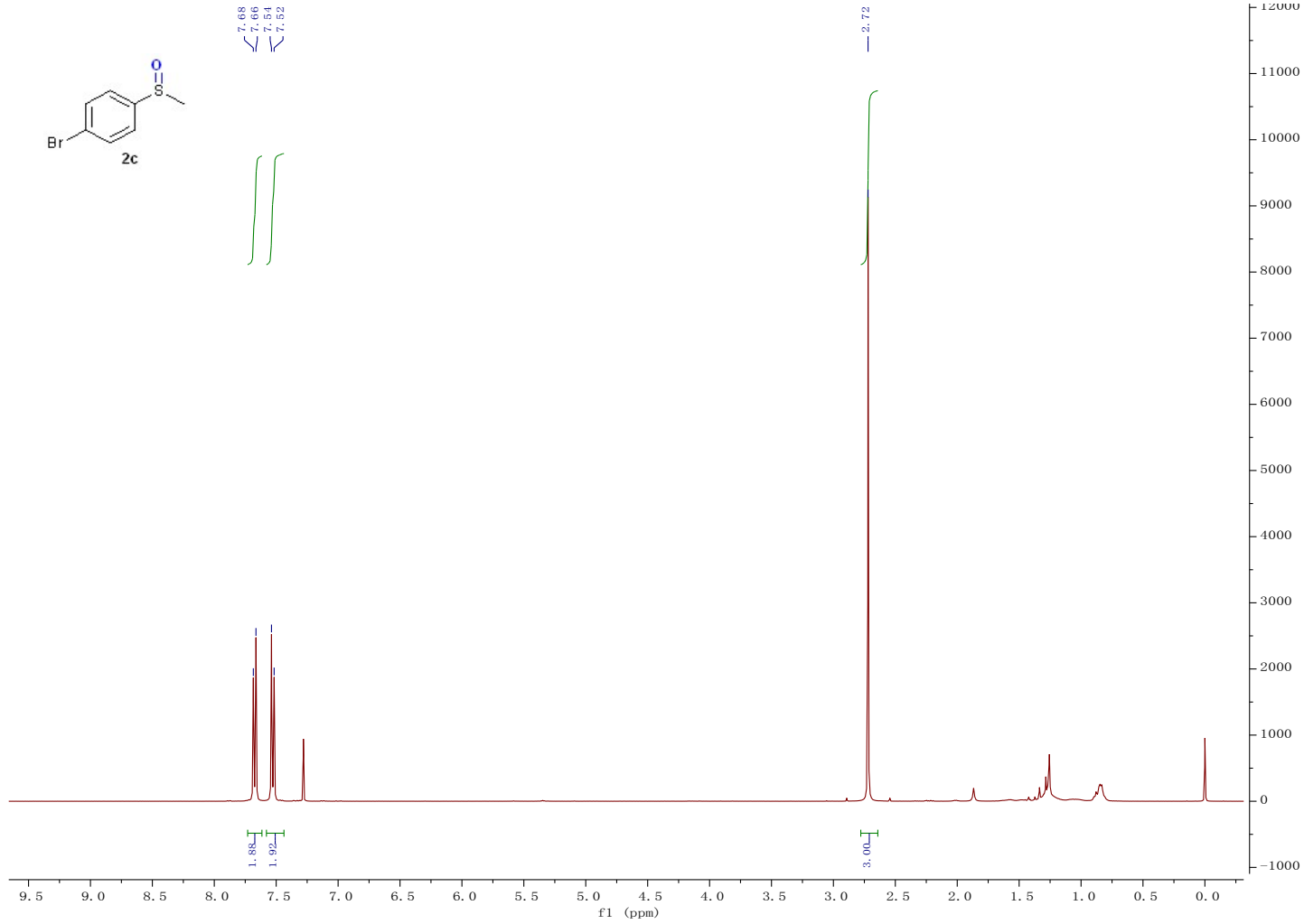
136.65
125.46
114.86
55.53
44.01
O
S
H3CO
2b
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.68
7.66
7.54
7.52
2.72
O
S
Br
2c
1.88
1.92
3.00
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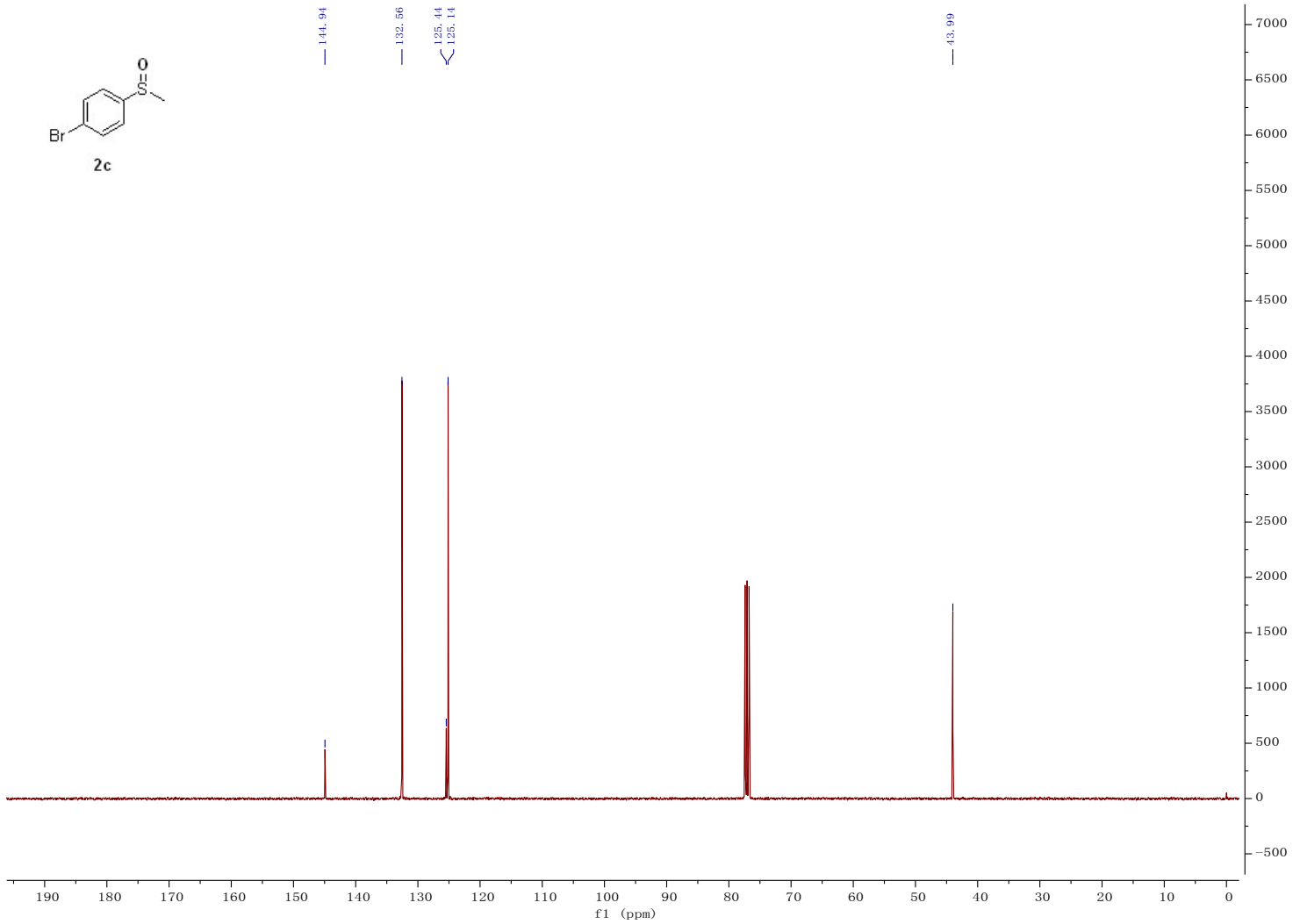
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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125.44
125.14
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Br
O
S
2c
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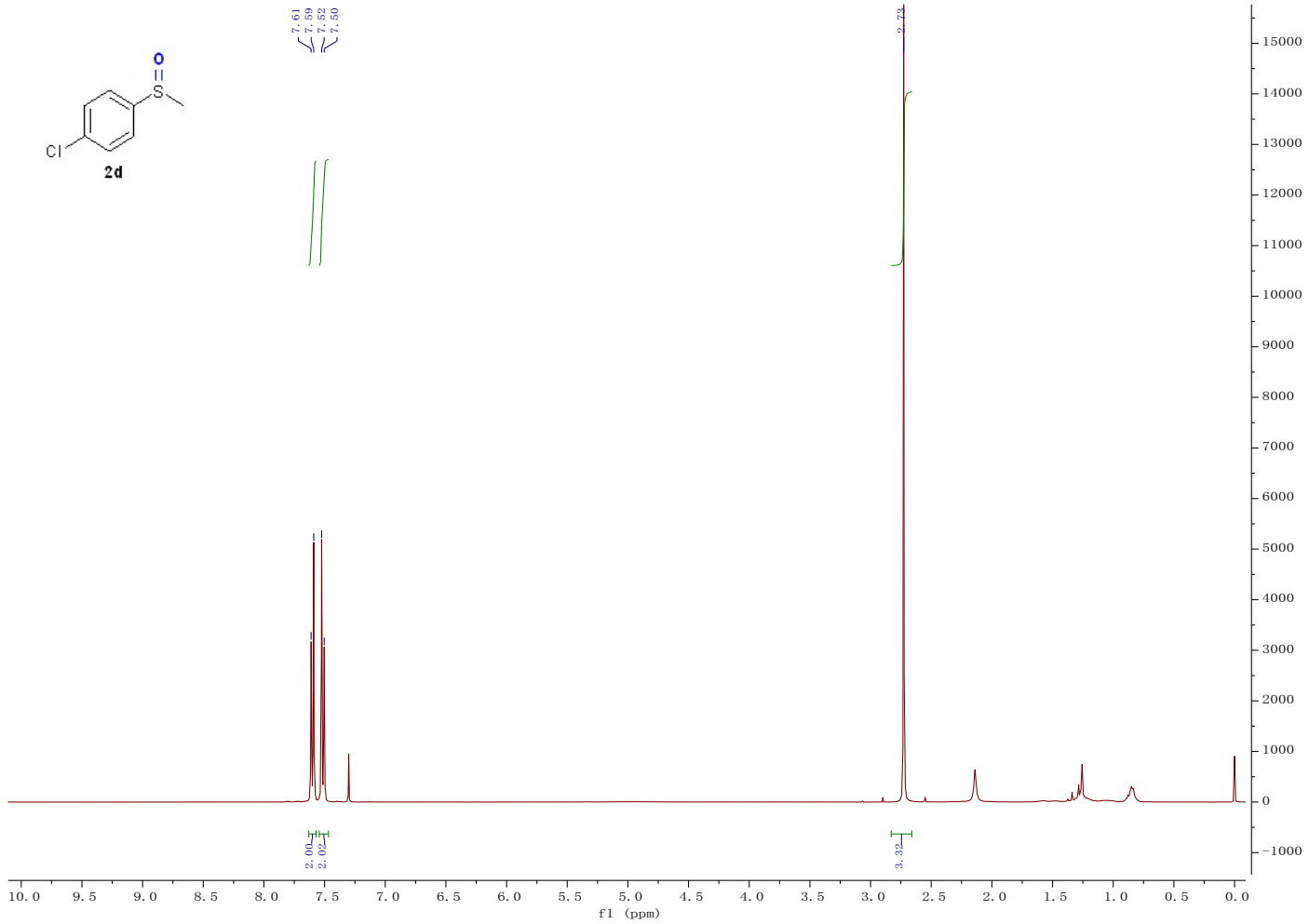
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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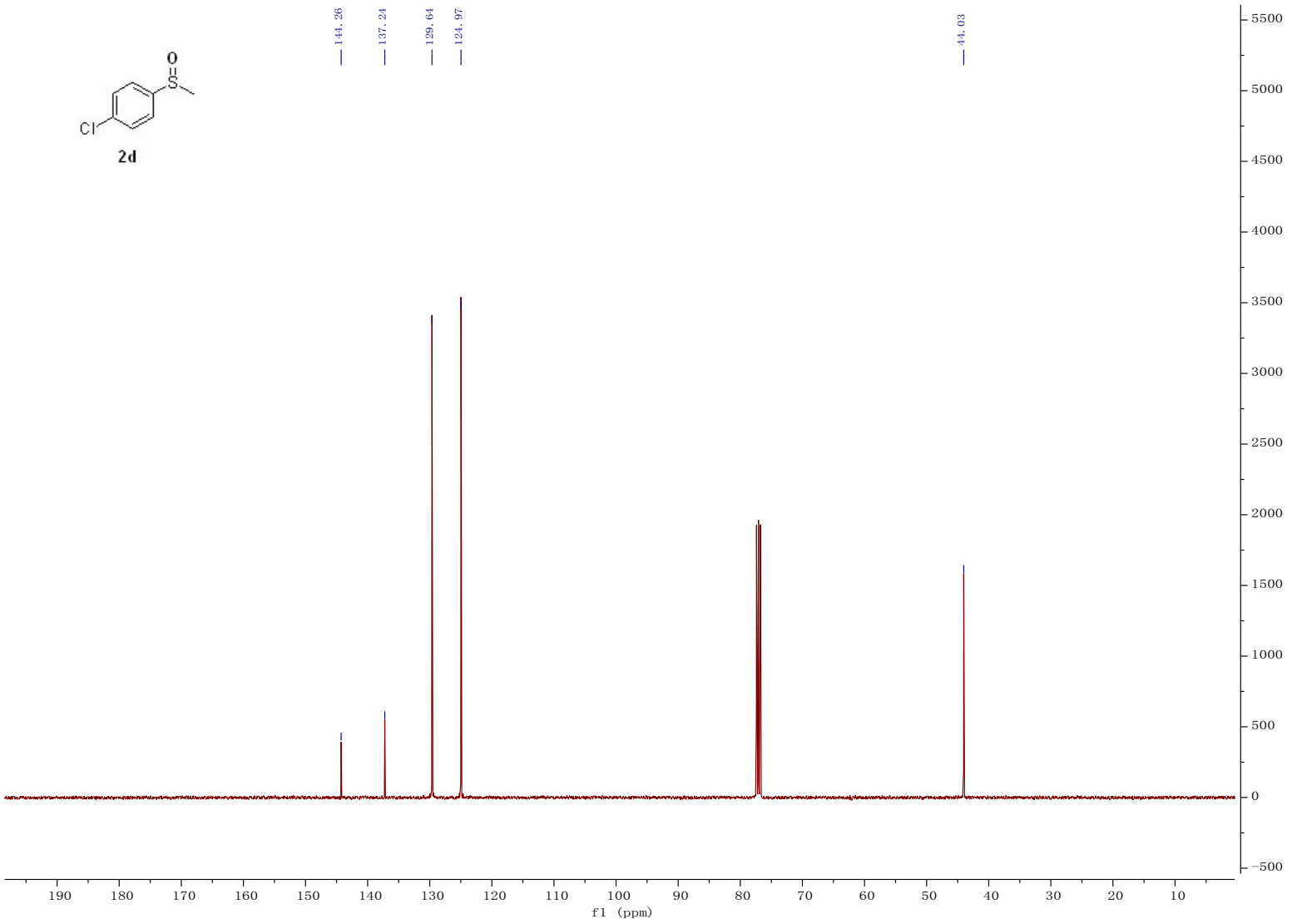
7.59
7.52
7.50
2.73
O
S
Cl
2d
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
2.00
2.02
3.32
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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Cl
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4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
190
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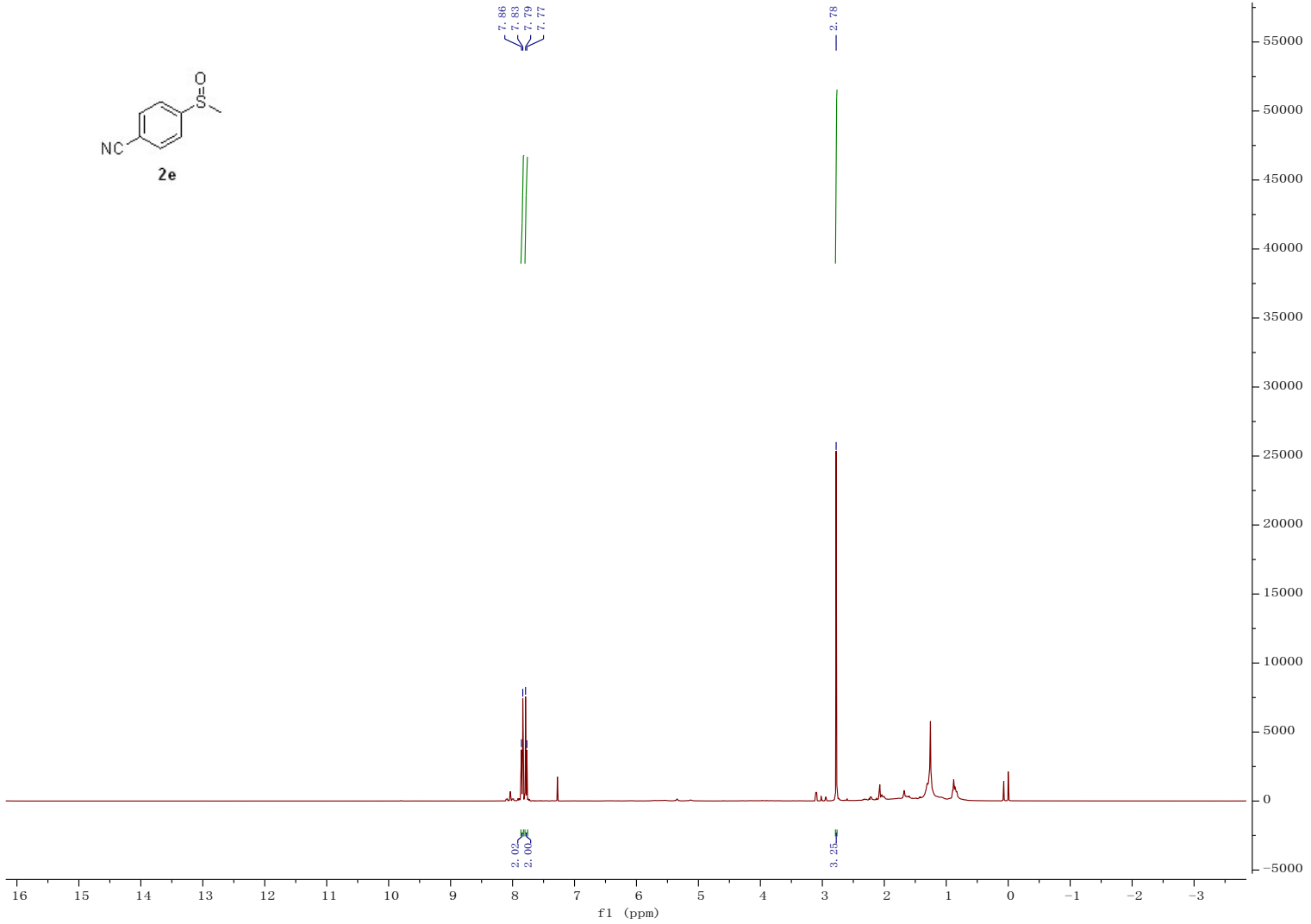
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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S
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2.02
2.00
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20000
15000
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5000
0
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16
15
14
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9
8
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5
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1
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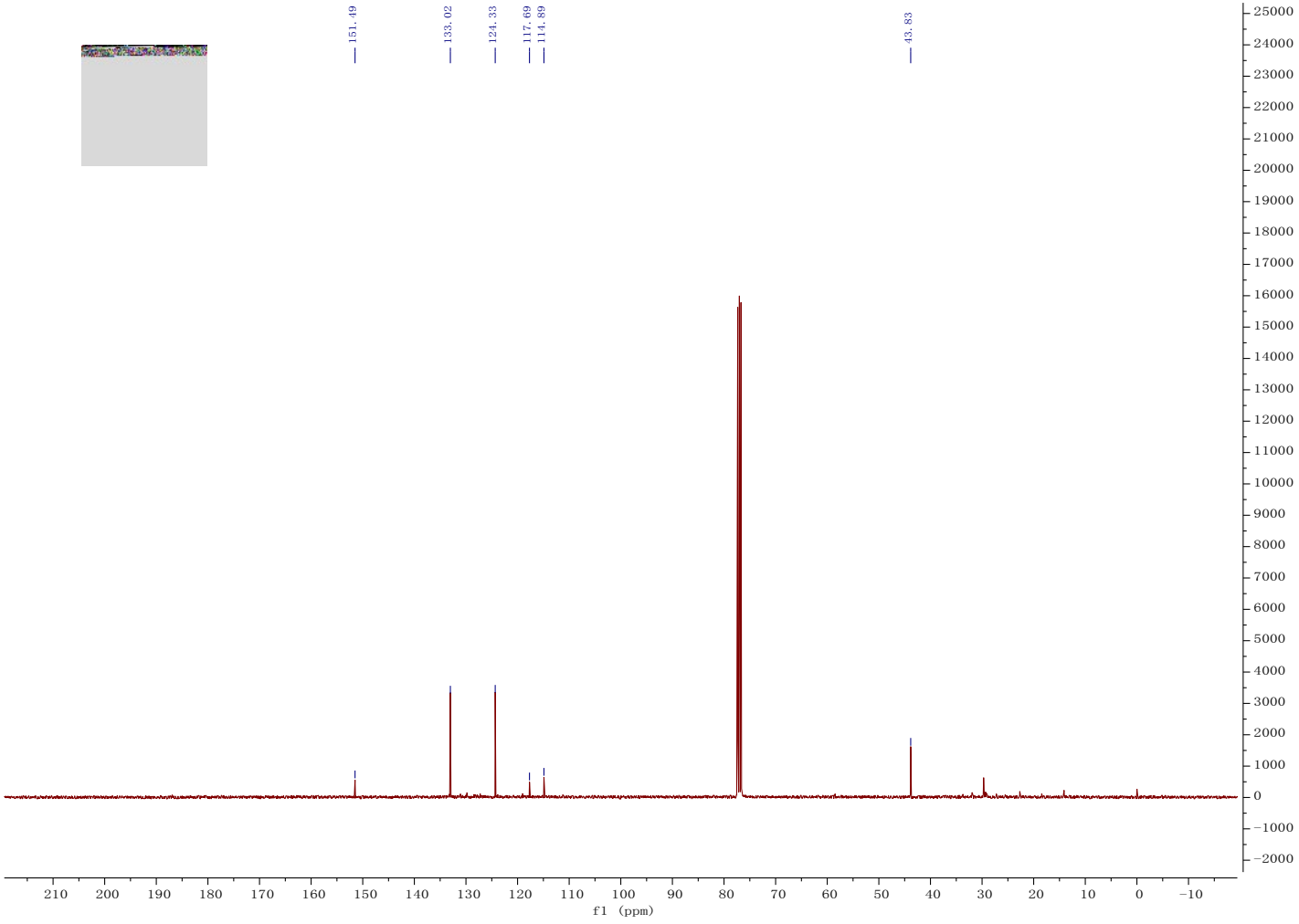
−2
−3
f1 (ppm)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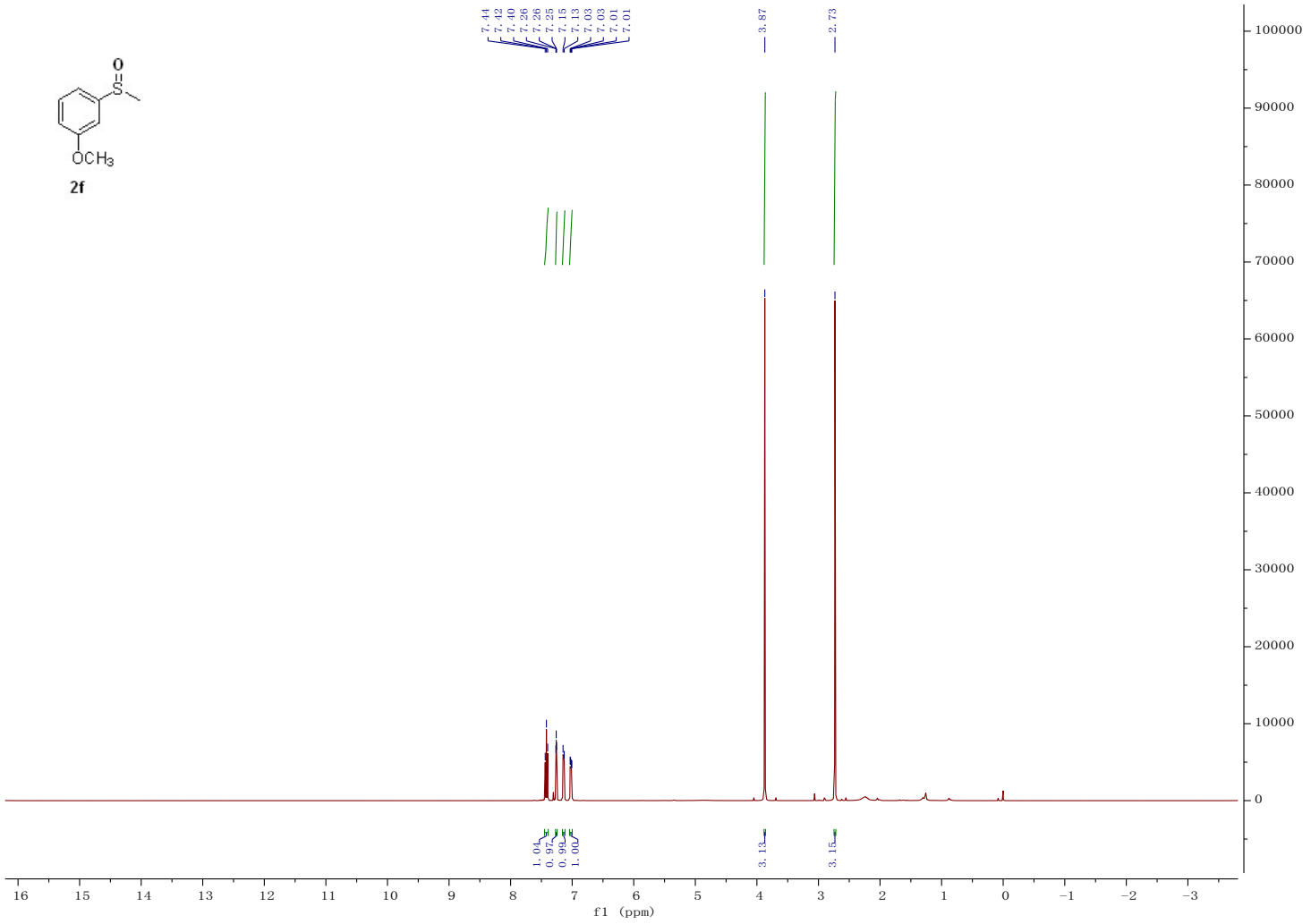
114.89
43.83
f1 (ppm)


O
S
OCH3
2f
7.44
7.42
7.40
7.26
7.26
7.25
7.15
7.13
7.03
7.03
7.01
7.01
3.87
2.73
1.04
0.97
0.96
1.00
3.13
3.15
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
16
15
14
13
12
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9
8
7
6
5
4
3
2
1
0
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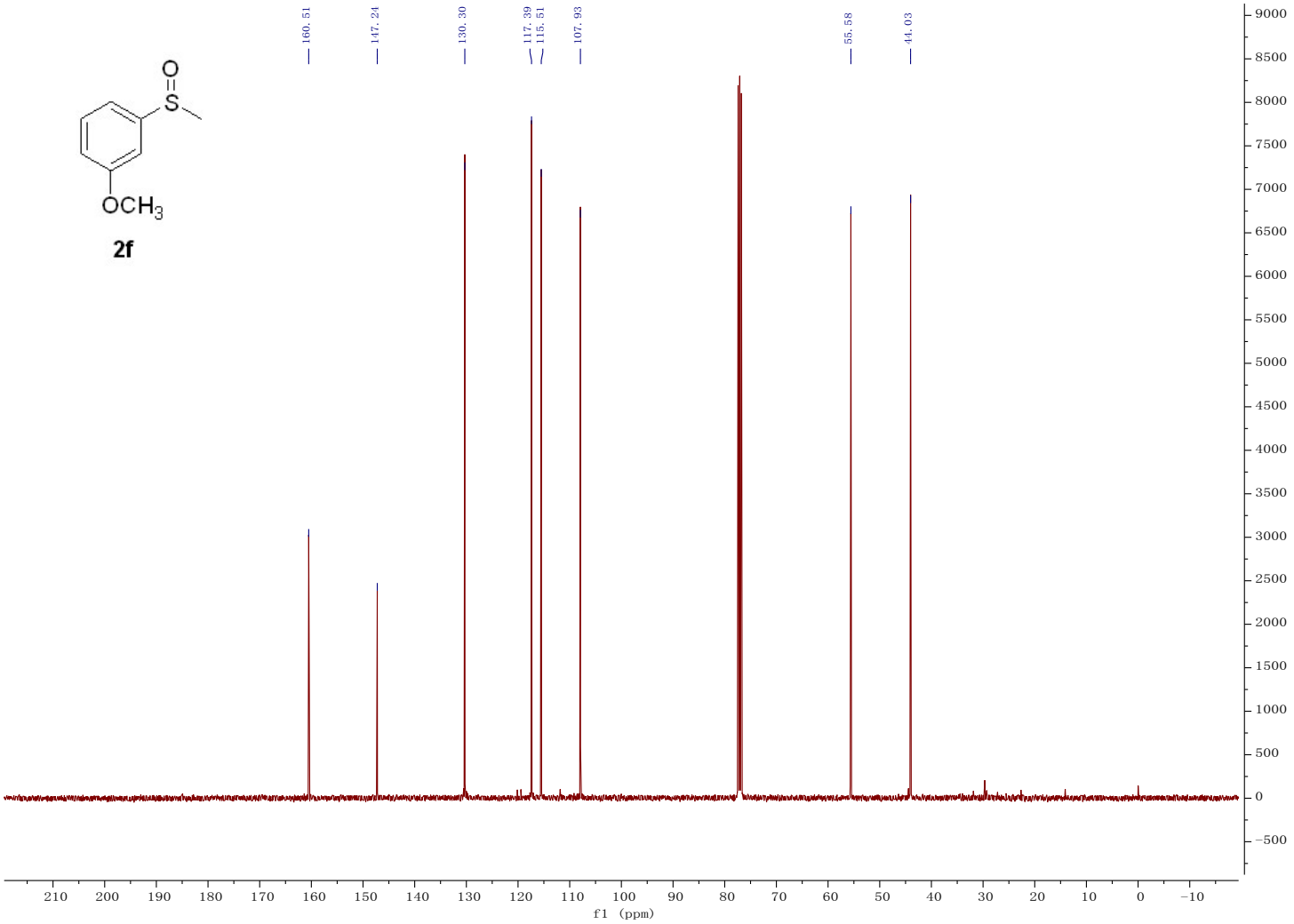
−2
−3
f1 (ppm)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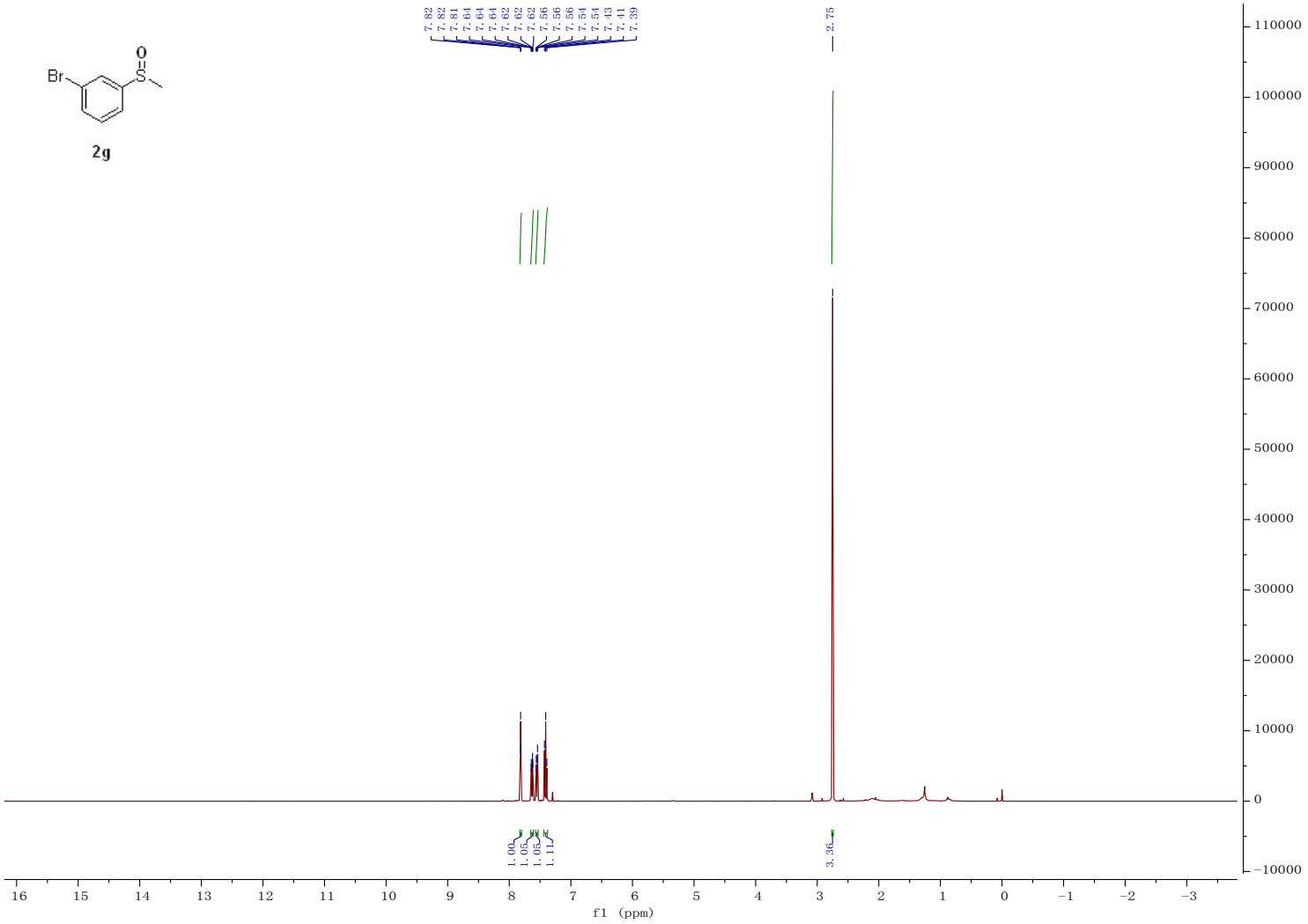
44.03
OCH3
2f
f1 (ppm)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S
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7.64
7.64
7.62
7.62
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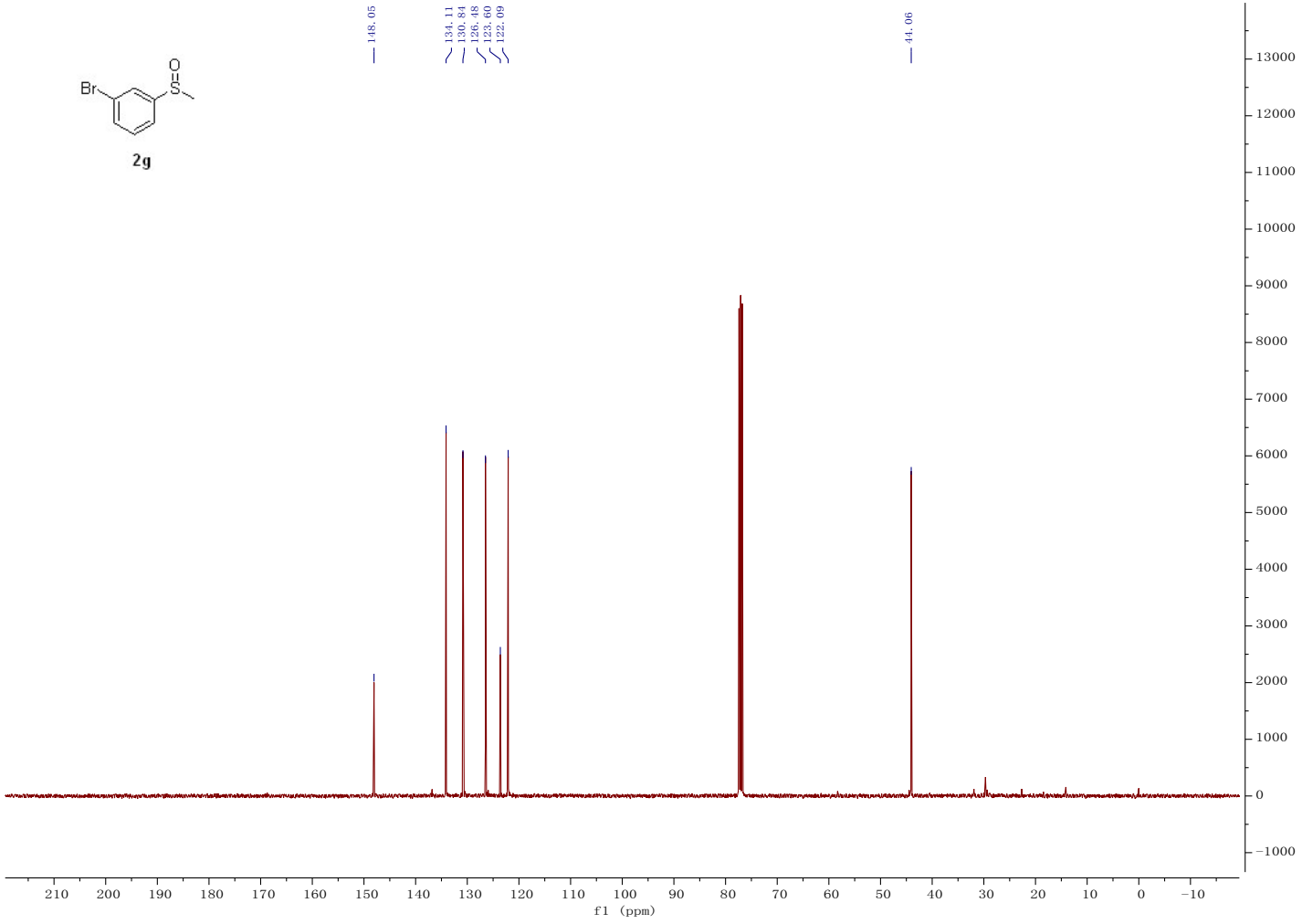
1.05
1.11
3.36
f1 (ppm)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134.11
130.84
126.48
123.60
122.09
44.06
Br
O
S
2g
13000
12000
11000
10000
9000
8000
7000
6000
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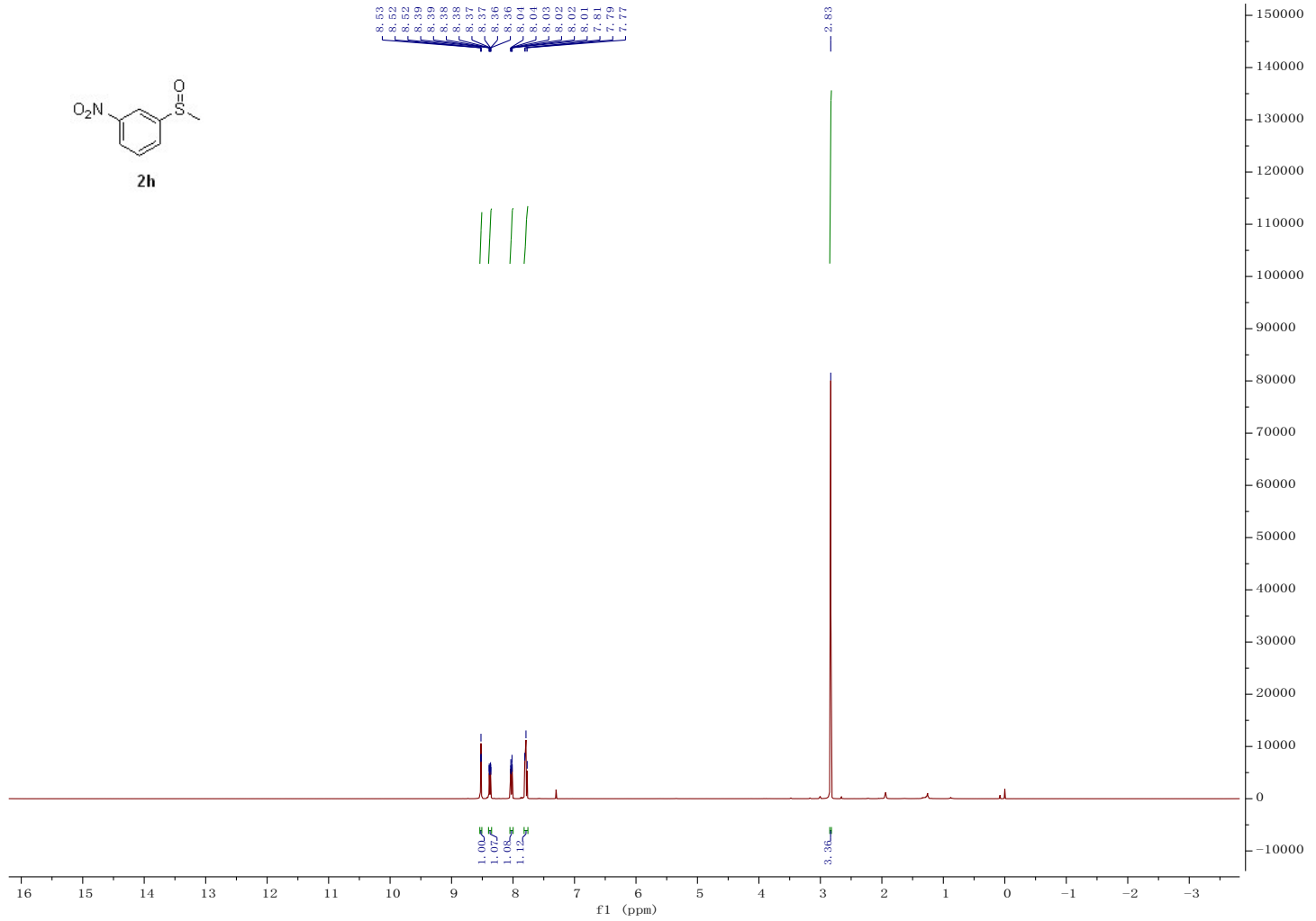
3000
2000
1000
0
−1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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8.37
8.37
8.36
8.36
8.04
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8.02
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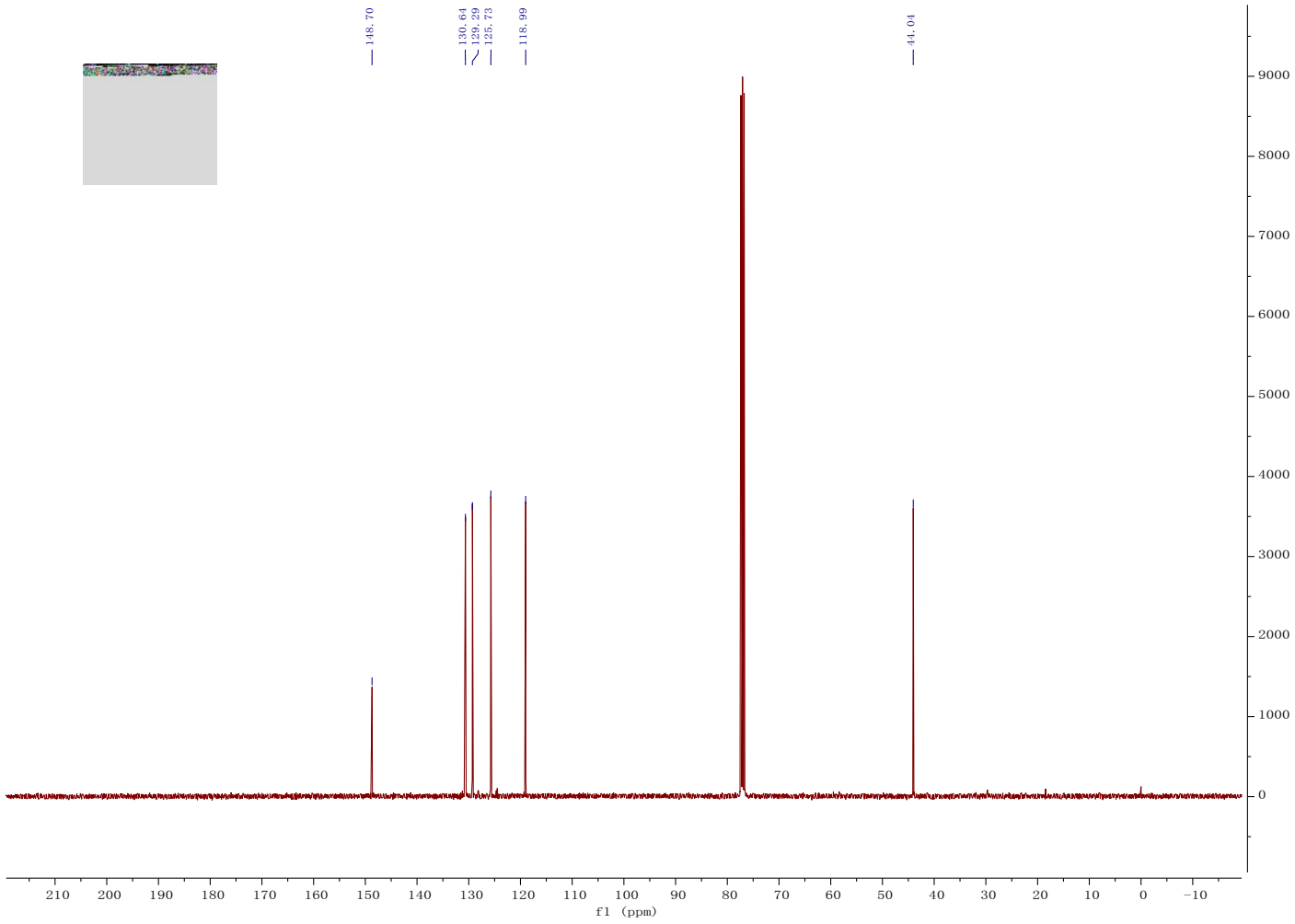
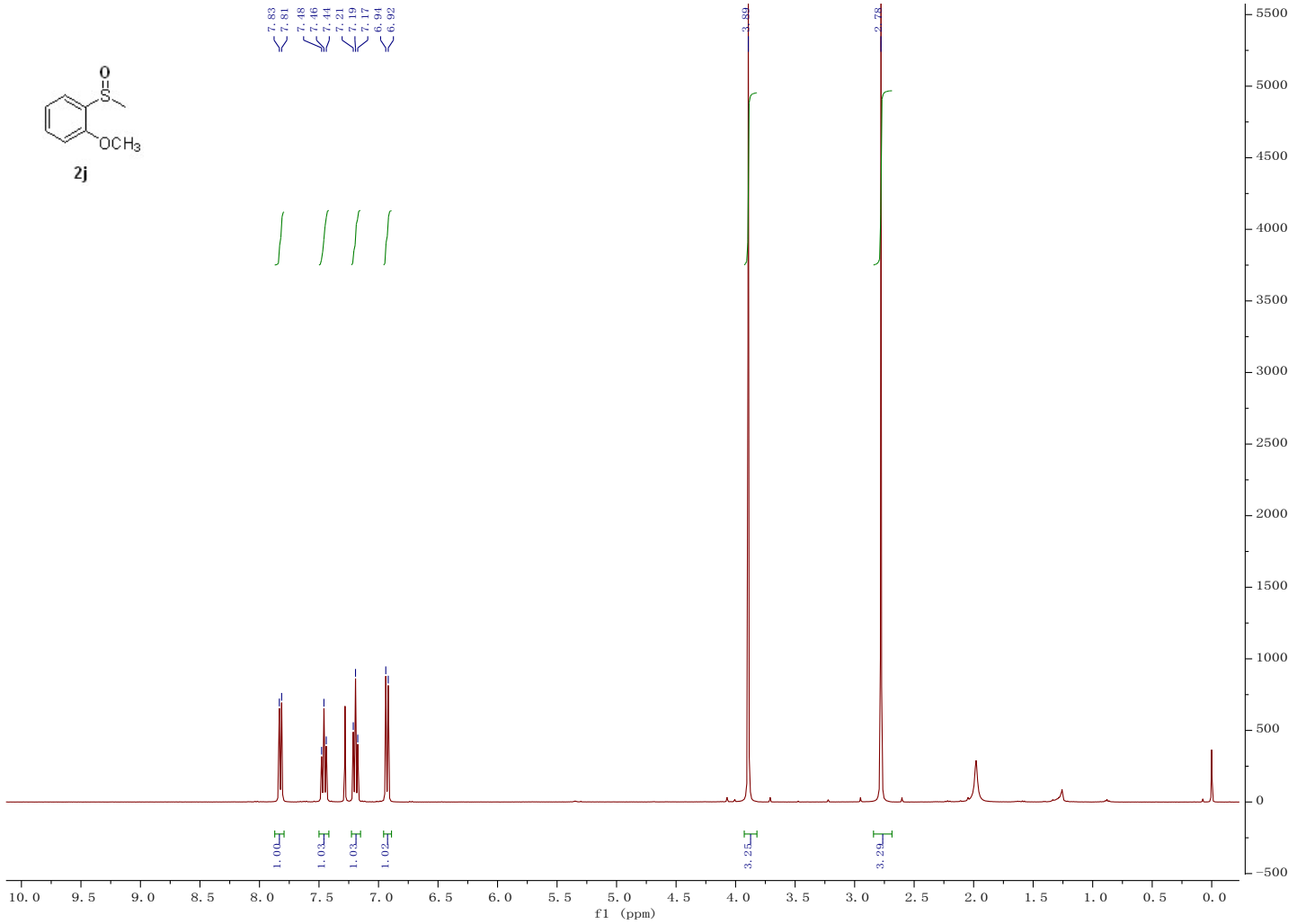
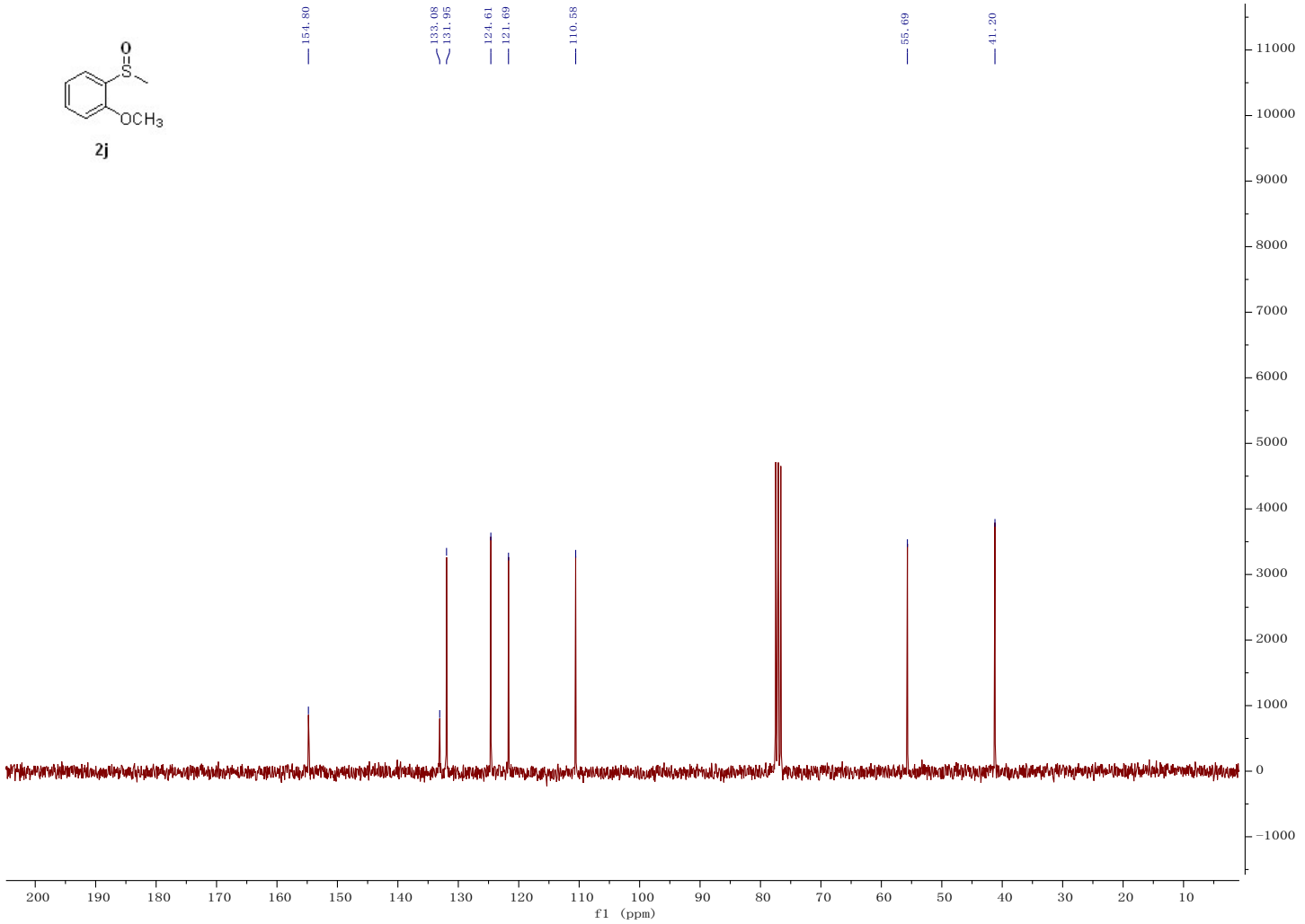
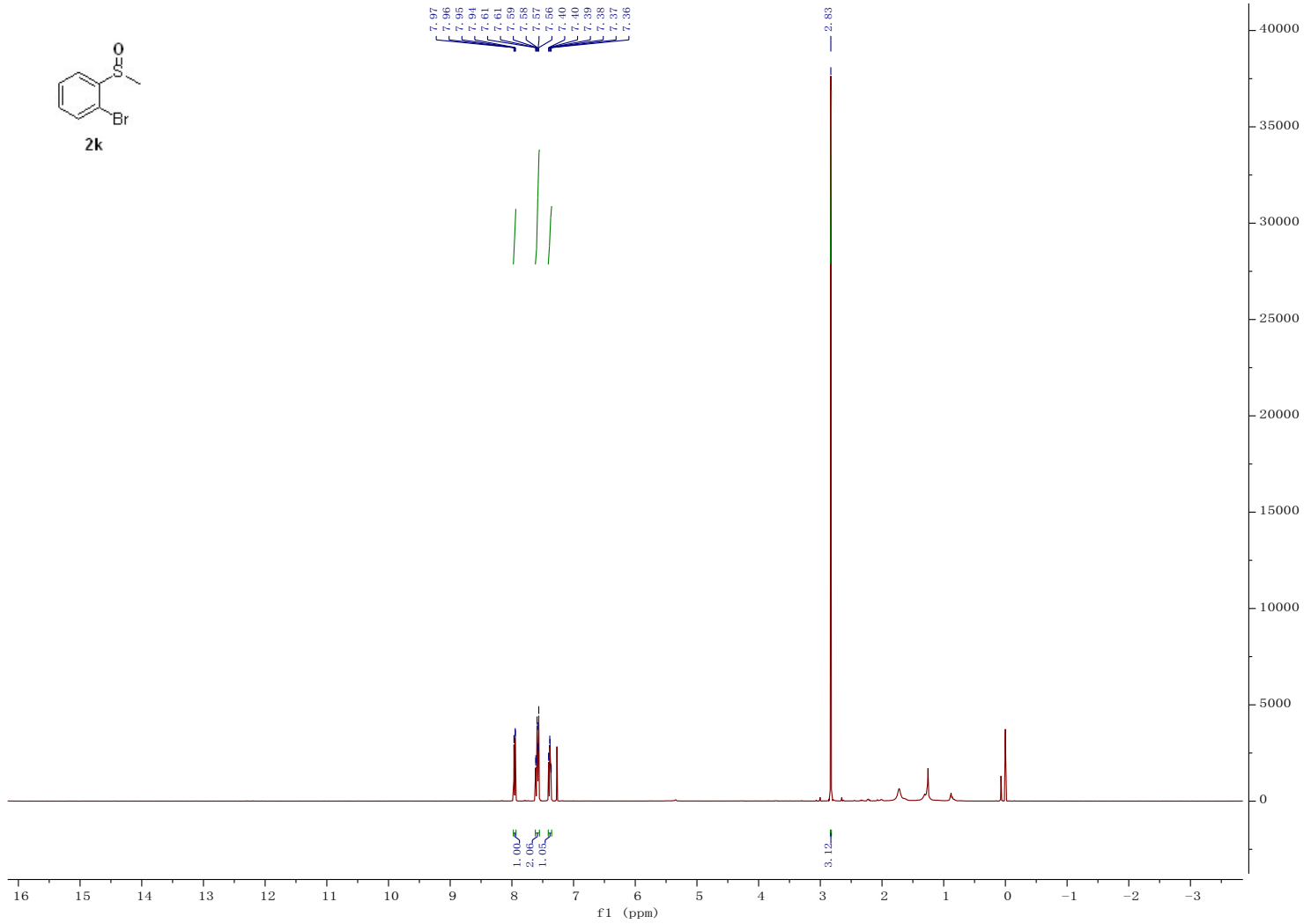
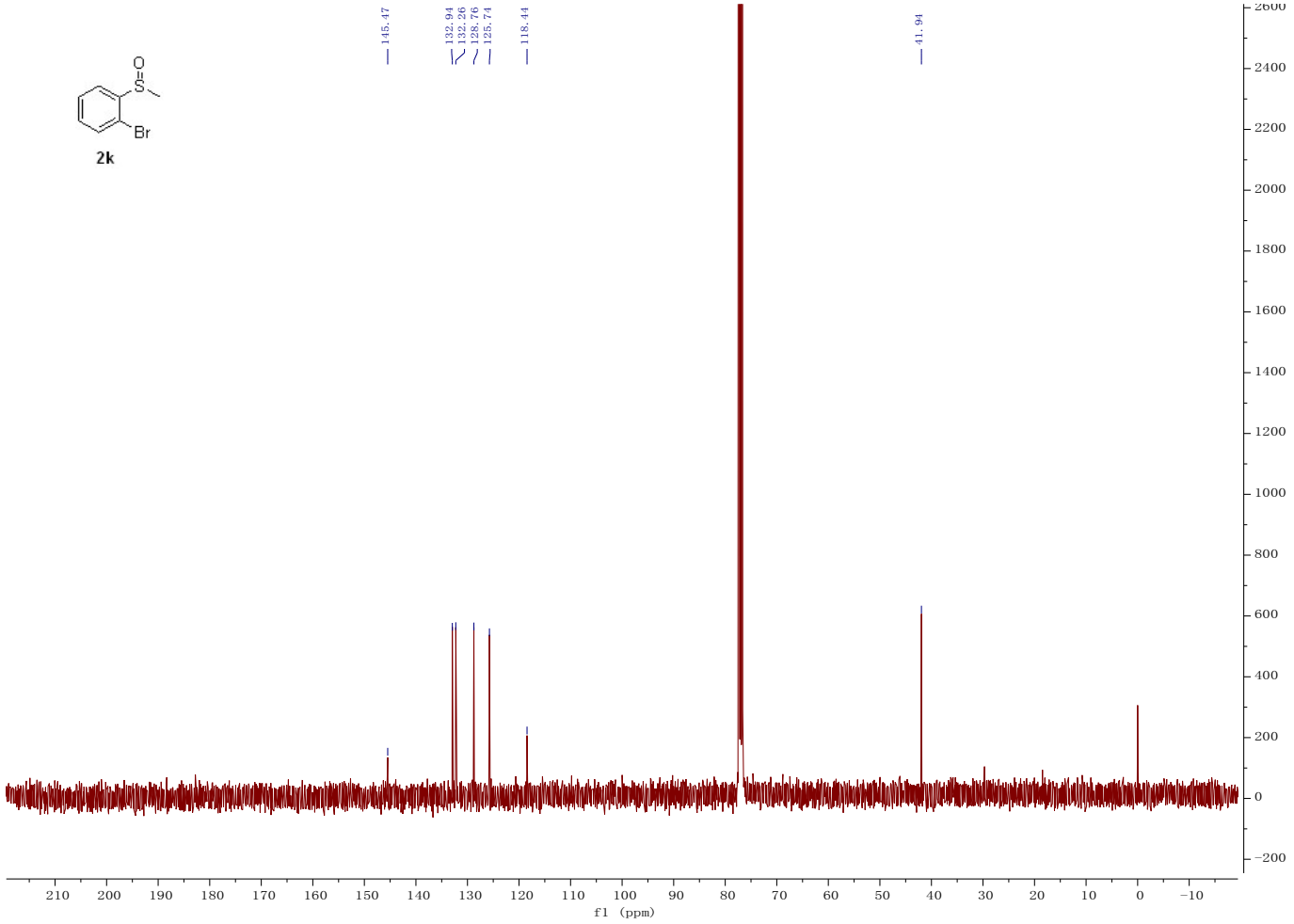
7.79
7.77
2.83
O2N
O
S
2h
1.00
1.07
1.08
1.12
3.36
f1 (ppm)

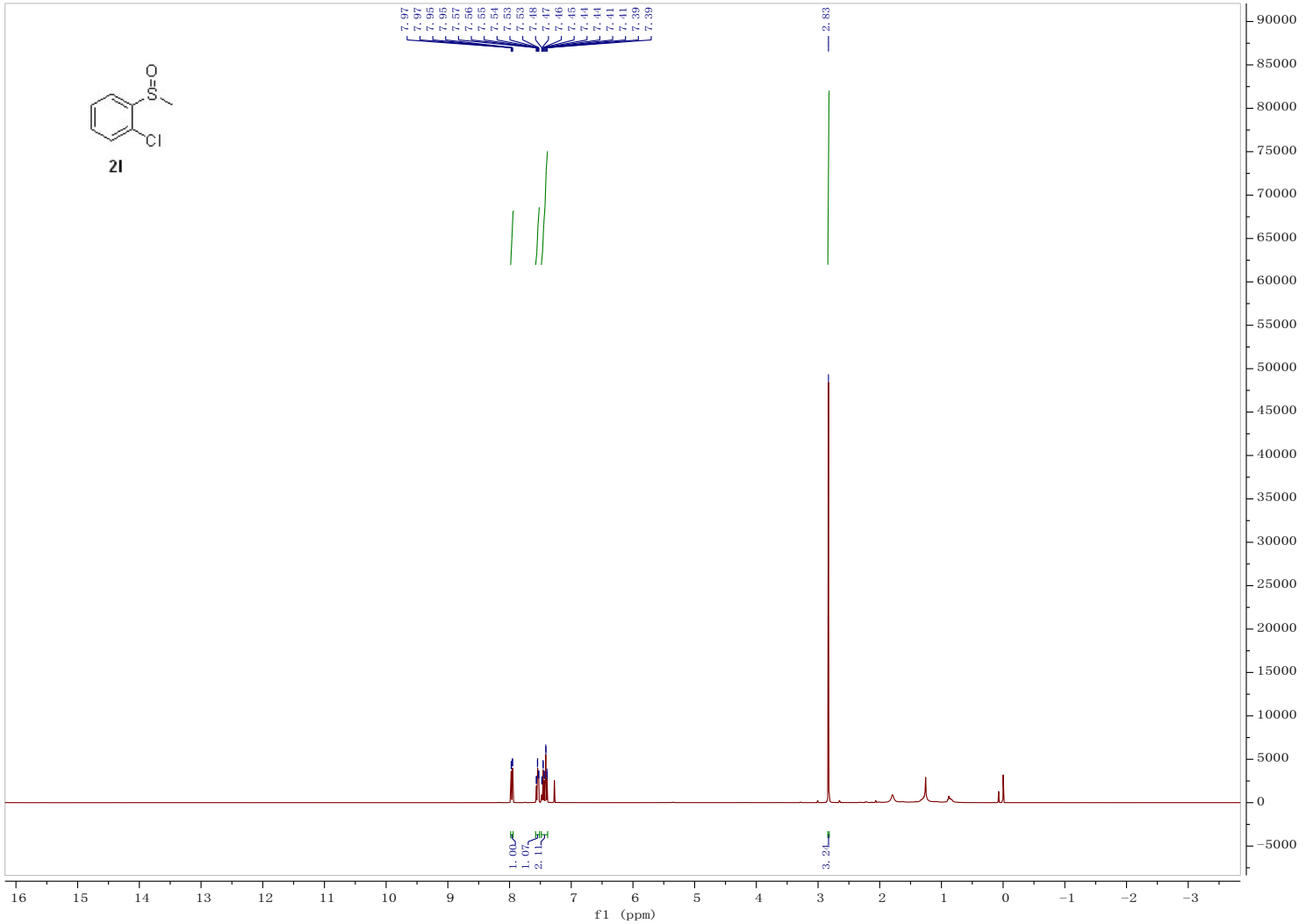

148.70
130.64
129.29
125.73
118.99
44.04
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

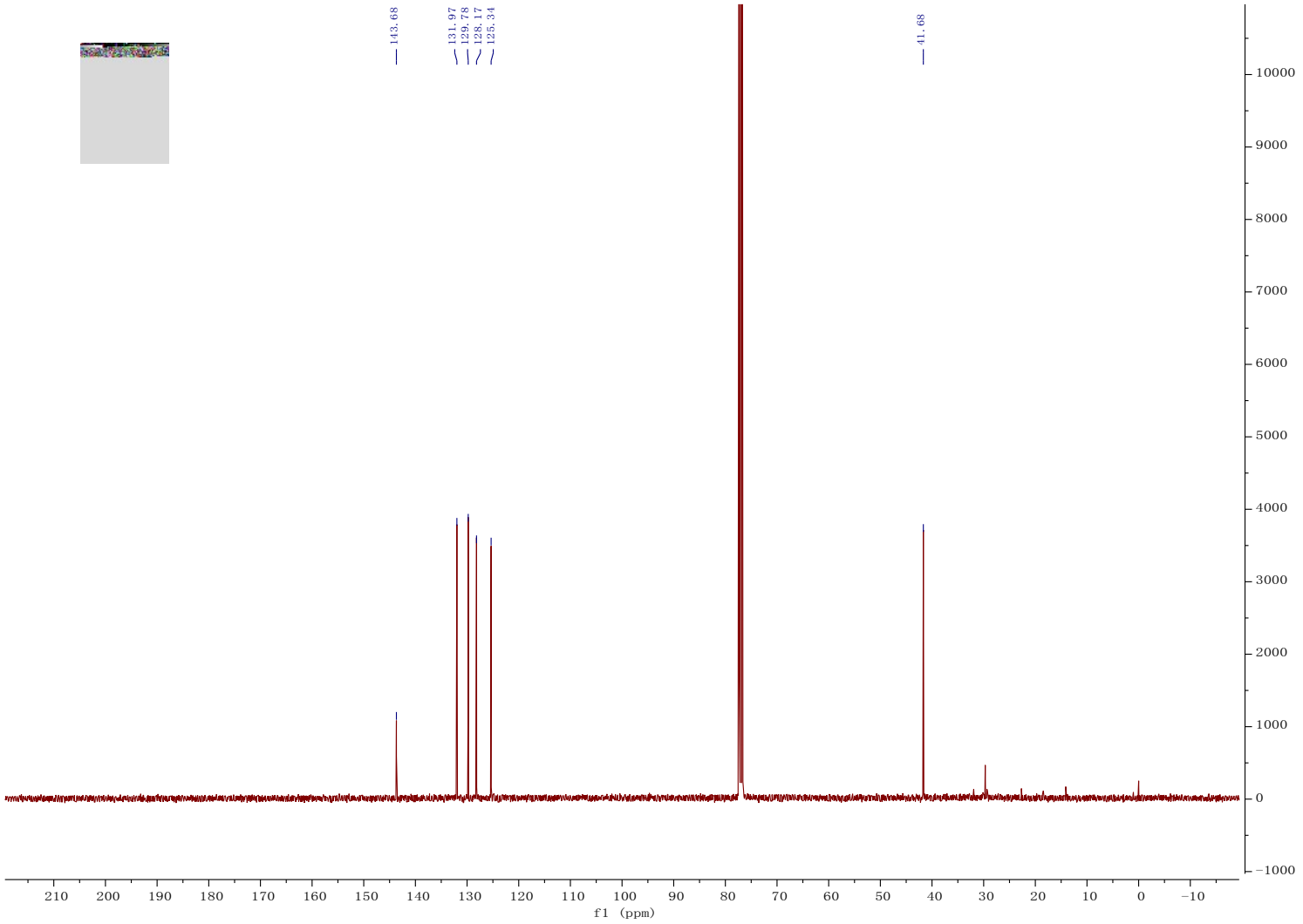

7.83
7.81
7.48
7.46
7.44
7.21
7.19
7.17
6.94
6.92
3.89
2.78
OCH3
2j
1.00
1.03
1.03
1.02
3.25
3.29
f1 (ppm)

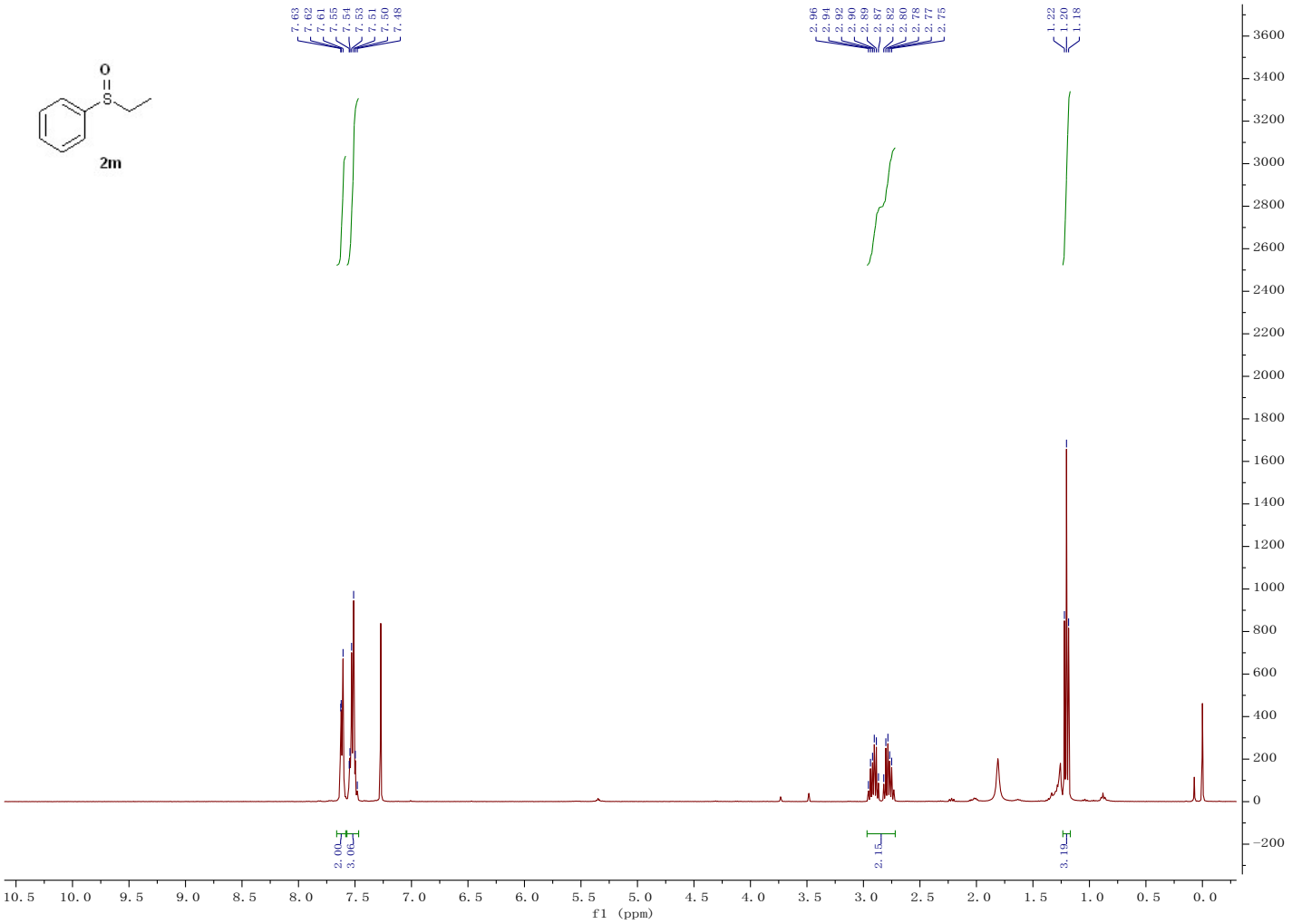

154.80
133.08
131.95
124.61
121.69
110.58
55.69
41.20
OCH3
2j
f1 (ppm)

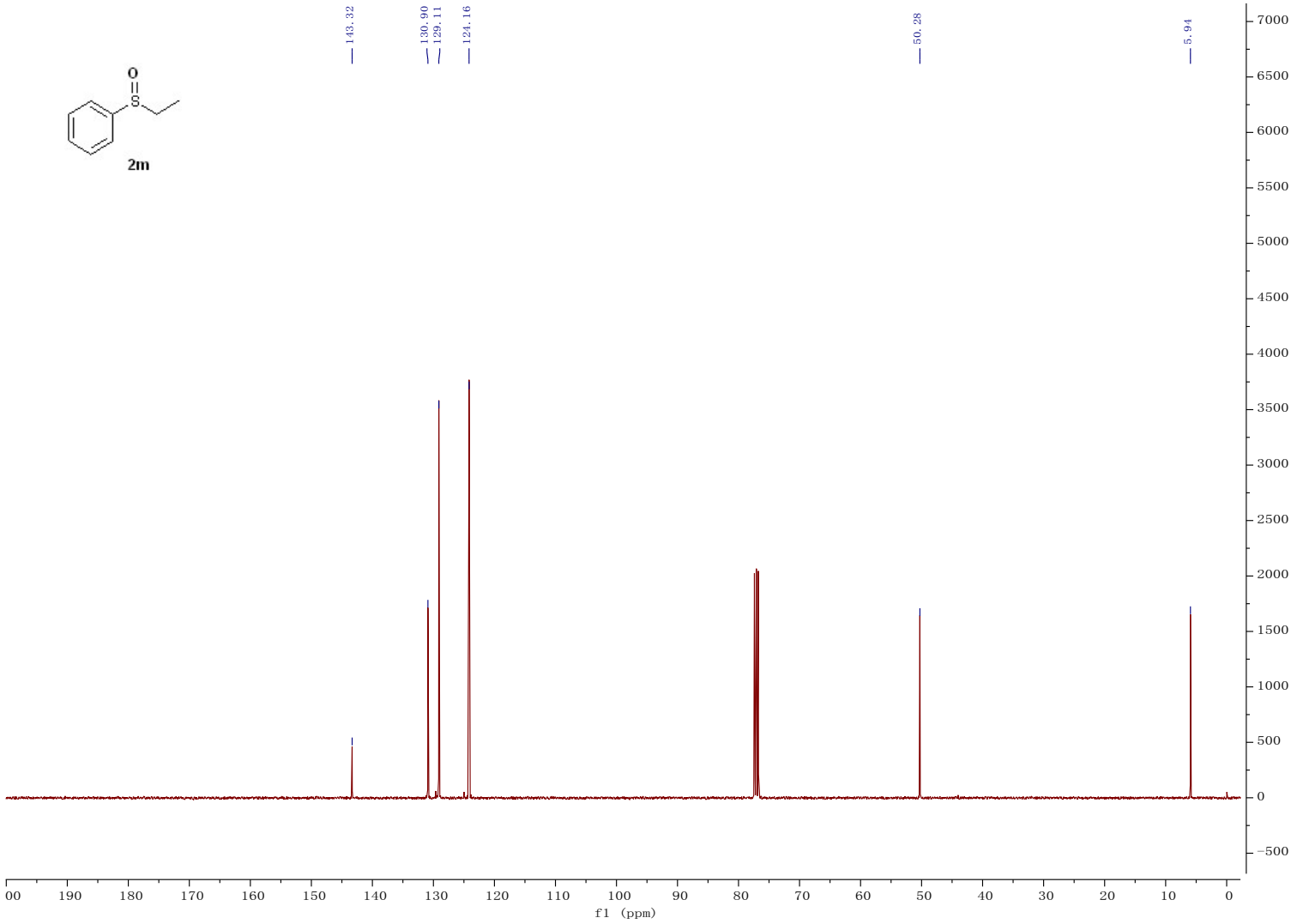

O
S
Br
2k
7.97
7.96
7.95
7.94
7.61
7.61
7.59
7.58
7.57
7.56
7.40
7.39
7.38
7.37
7.36
2.83
1.00
2.06
1.05
3.12
f1 (ppm)

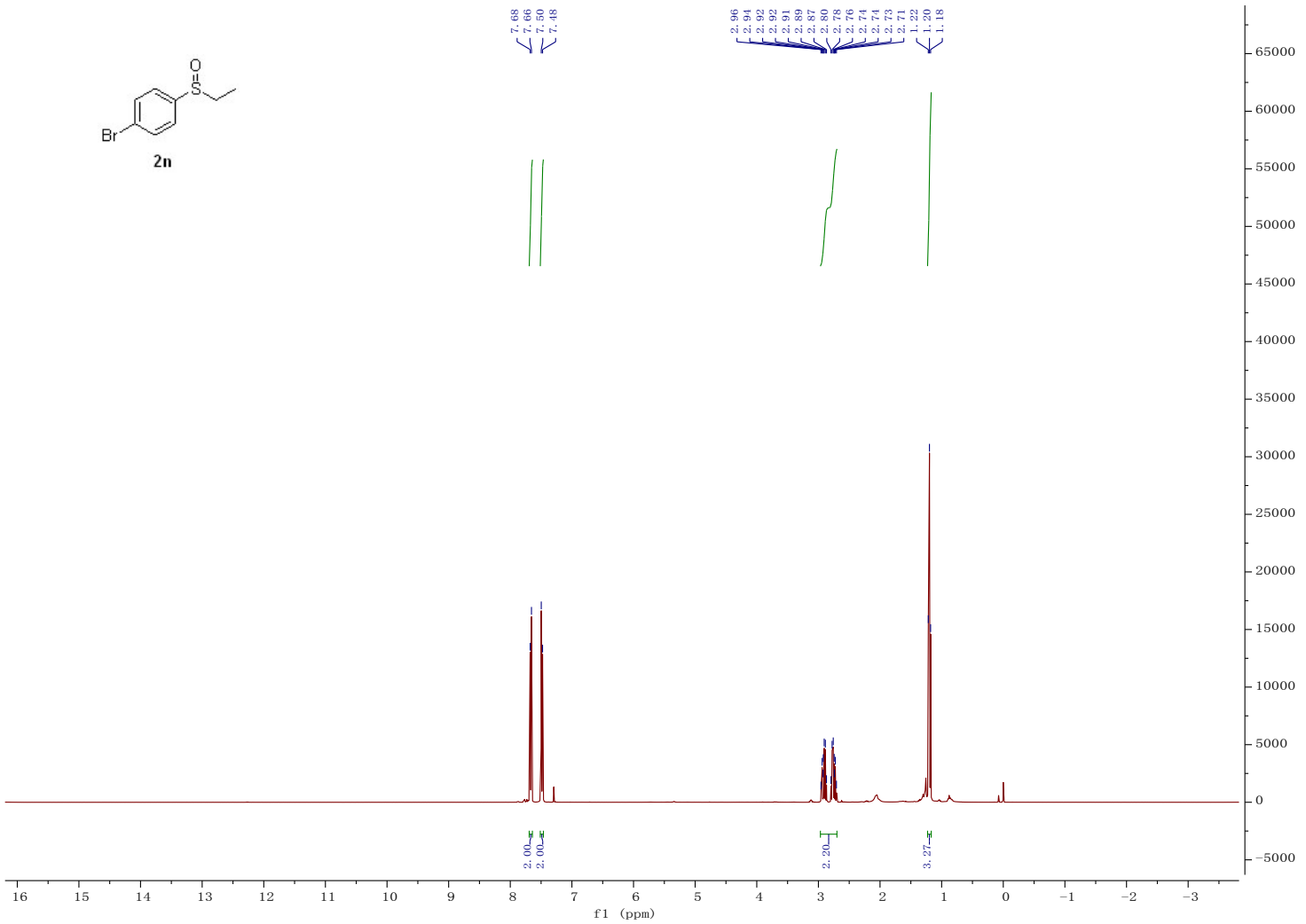

145.47
132.94
132.26
128.76
125.74
118.44
41.94
O
S
Br
2k
f1 (ppm)

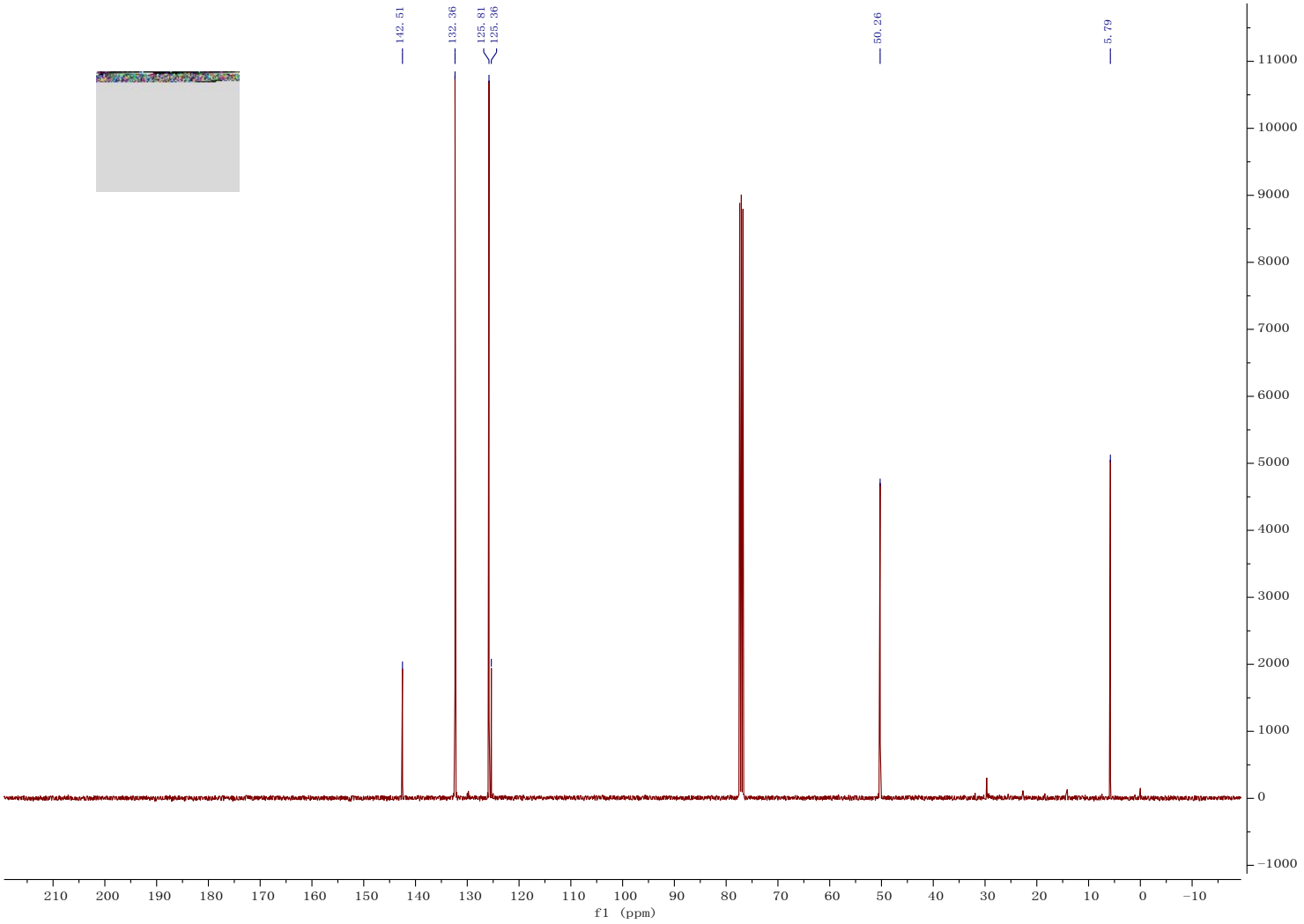

7.97
7.97
7.95
7.95
7.57
7.56
7.55
7.54
7.53
7.53
7.48
7.47
7.46
7.45
7.44
7.44
7.41
7.41
7.39
7.39
2.83
O
S
Cl
2l
1.00
1.07
2.11
3.24
f1 (ppm)

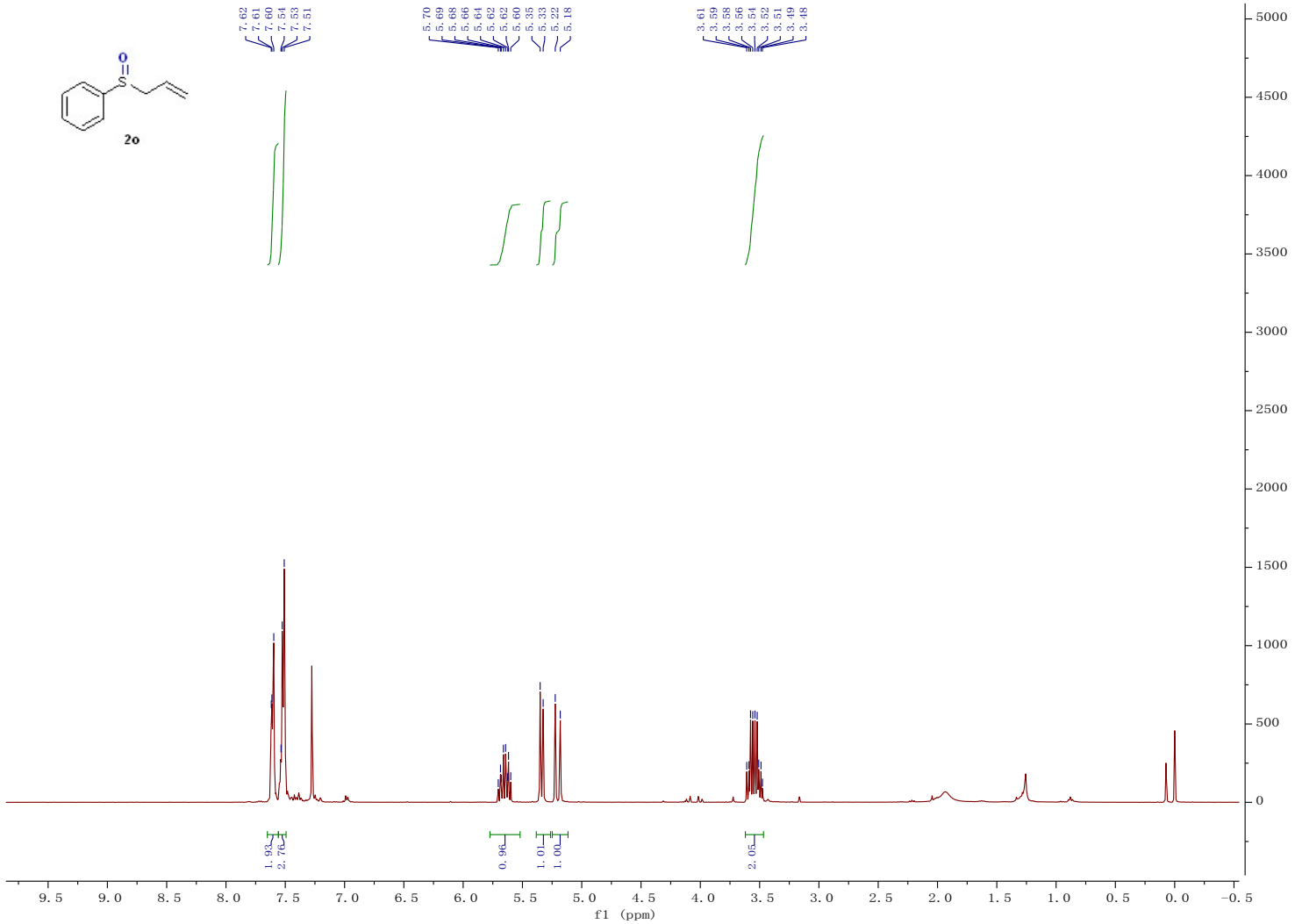

143.68
131.97
129.78
128.17
125.34
41.68
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

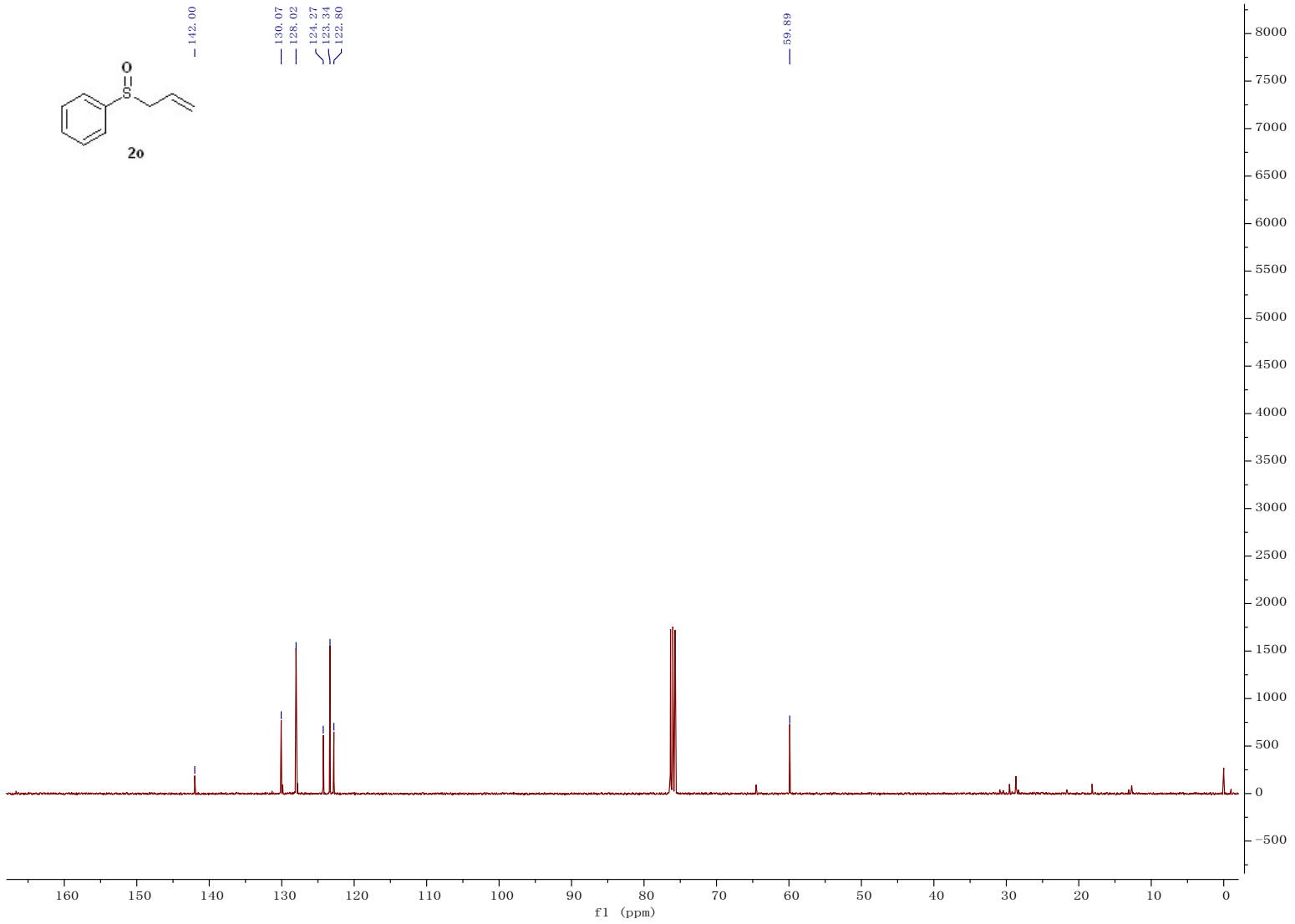

7.63
7.62
7.61
7.55
7.54
7.53
7.51
7.50
7.48
2.96
2.94
2.92
2.90
2.89
2.87
2.82
2.80
2.78
2.77
2.75
1.22
1.20
1.18
O
S
2m
2.00
3.06
2.15
3.19
f1 (ppm)

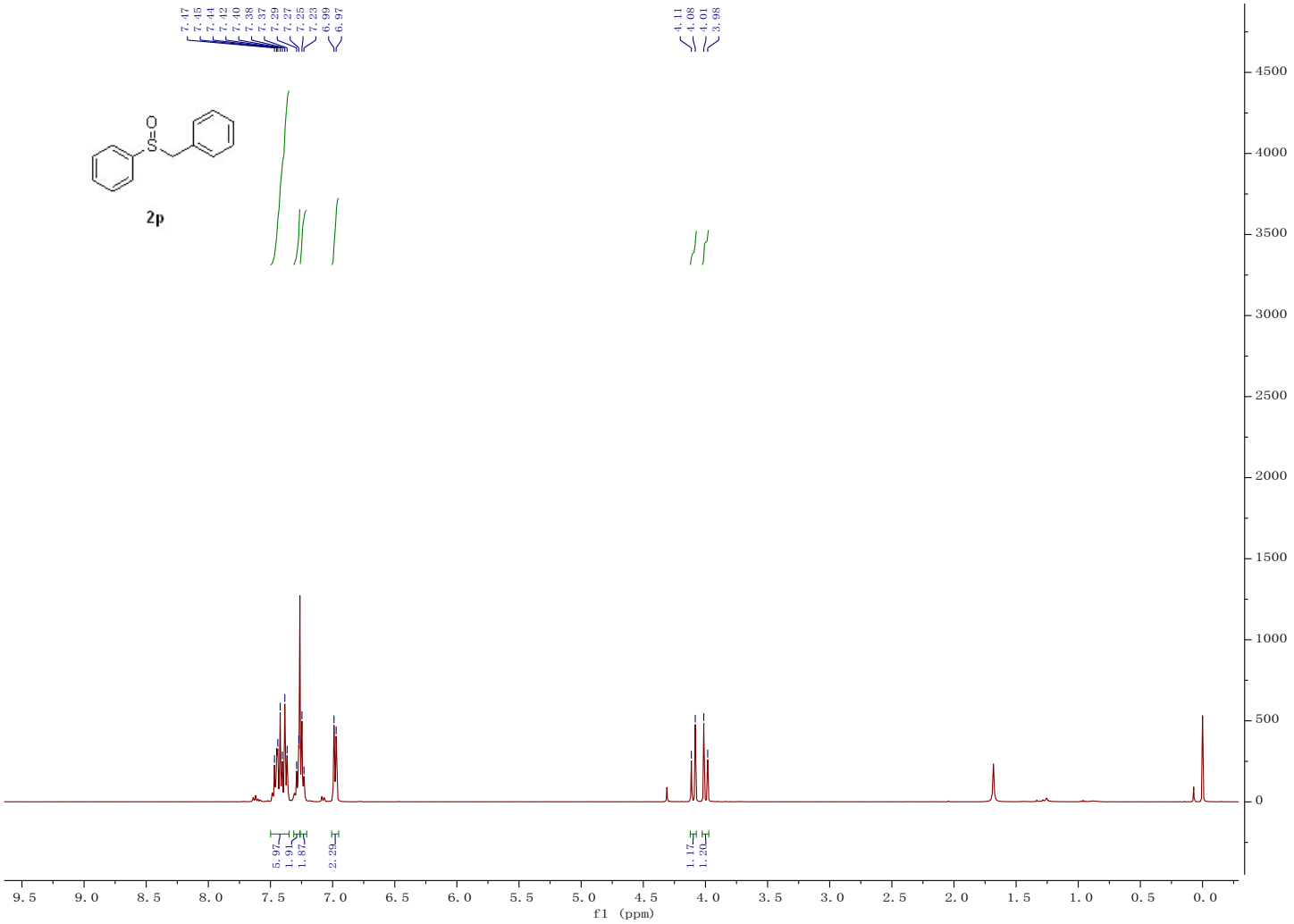

143.32
130.90
129.11
124.16
50.28
5.94
2m
f1 (ppm)

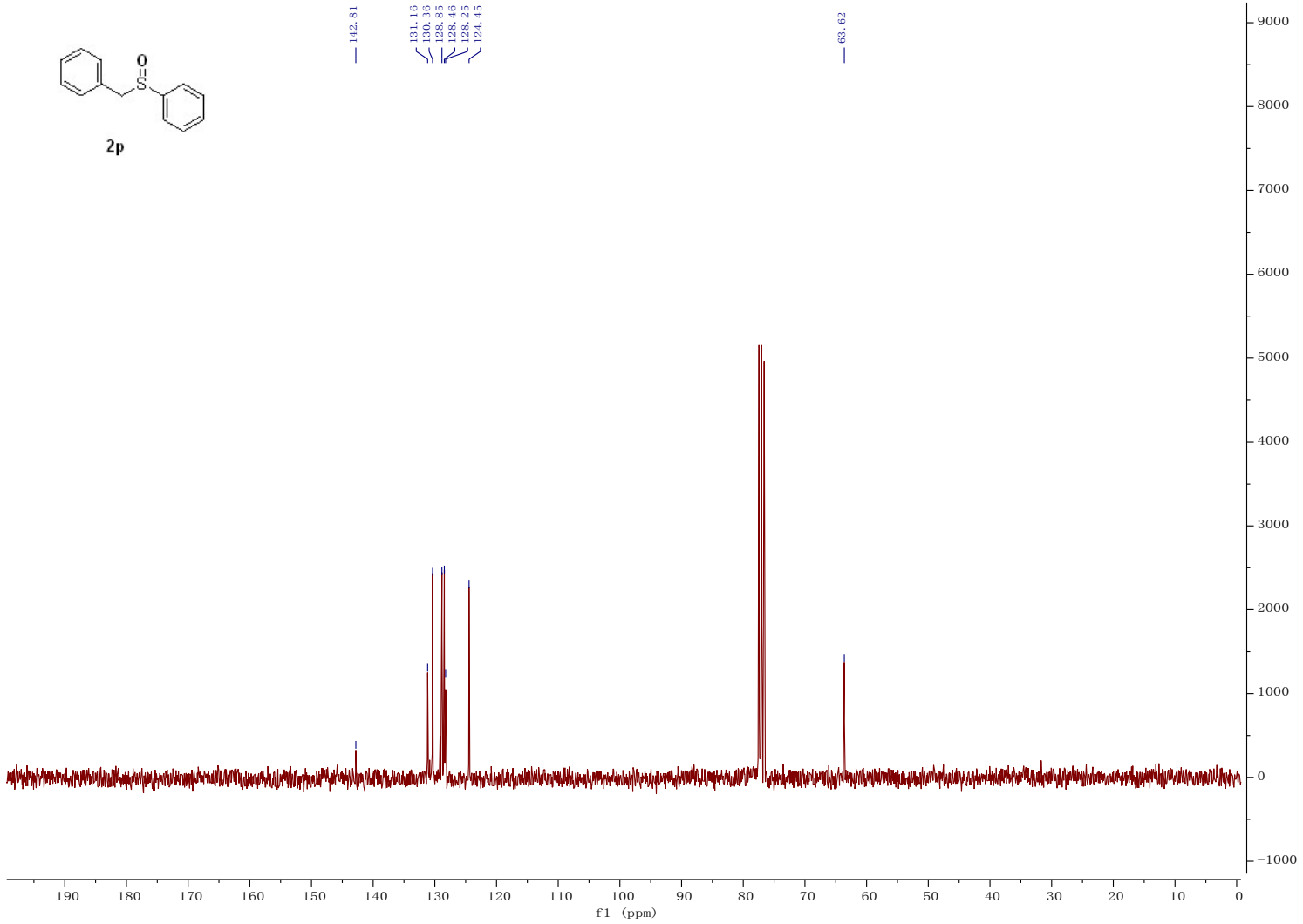

Br
O
S
2n
7.68
7.66
7.50
7.48
2.96
2.94
2.92
2.92
2.91
2.89
2.87
2.80
2.78
2.76
2.74
2.74
2.73
2.71
1.22
1.20
1.18
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
−5000
2.00
2.00
2.20
3.27
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)

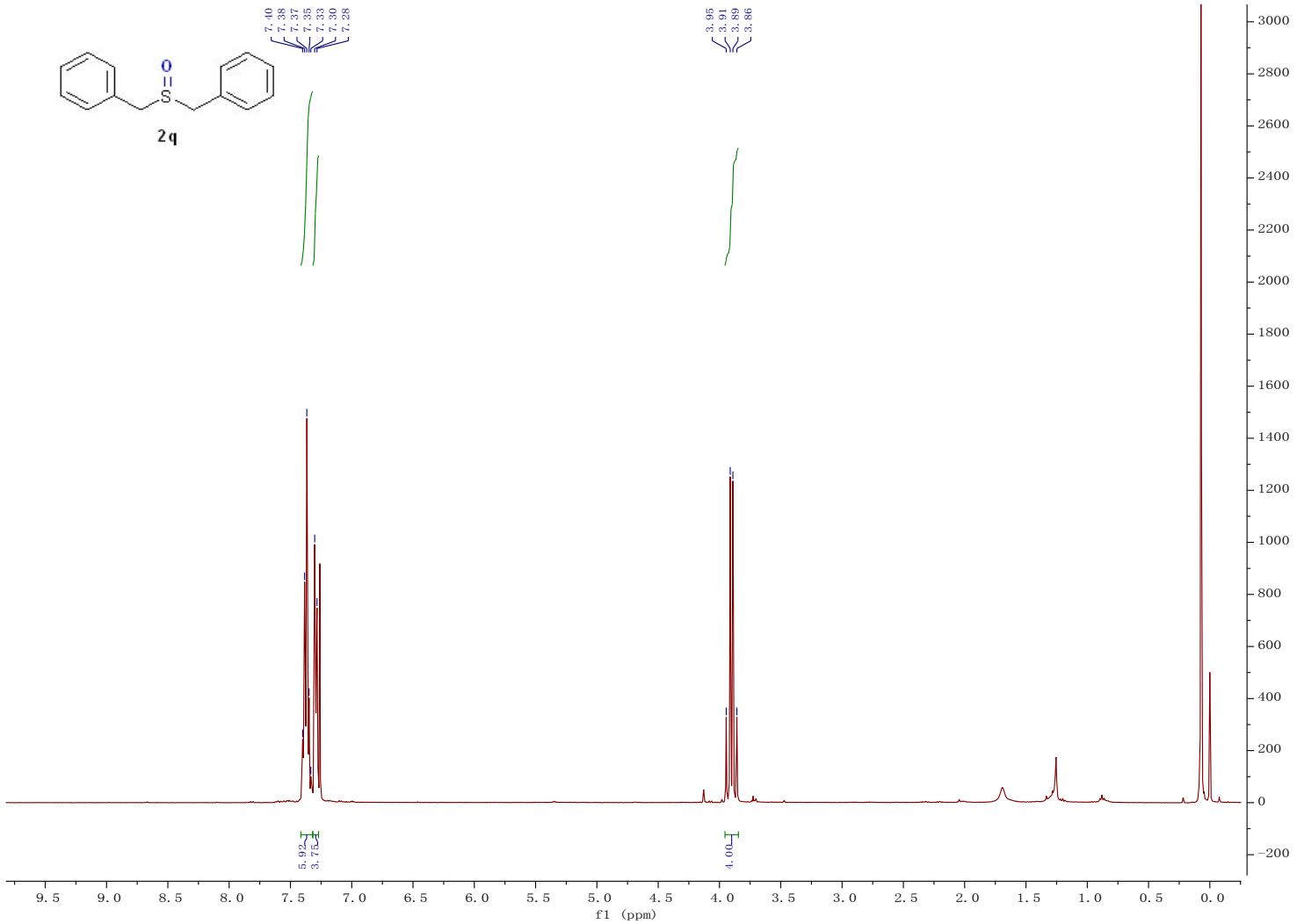

142.51
132.36
125.81
125.36
50.26
5.79
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

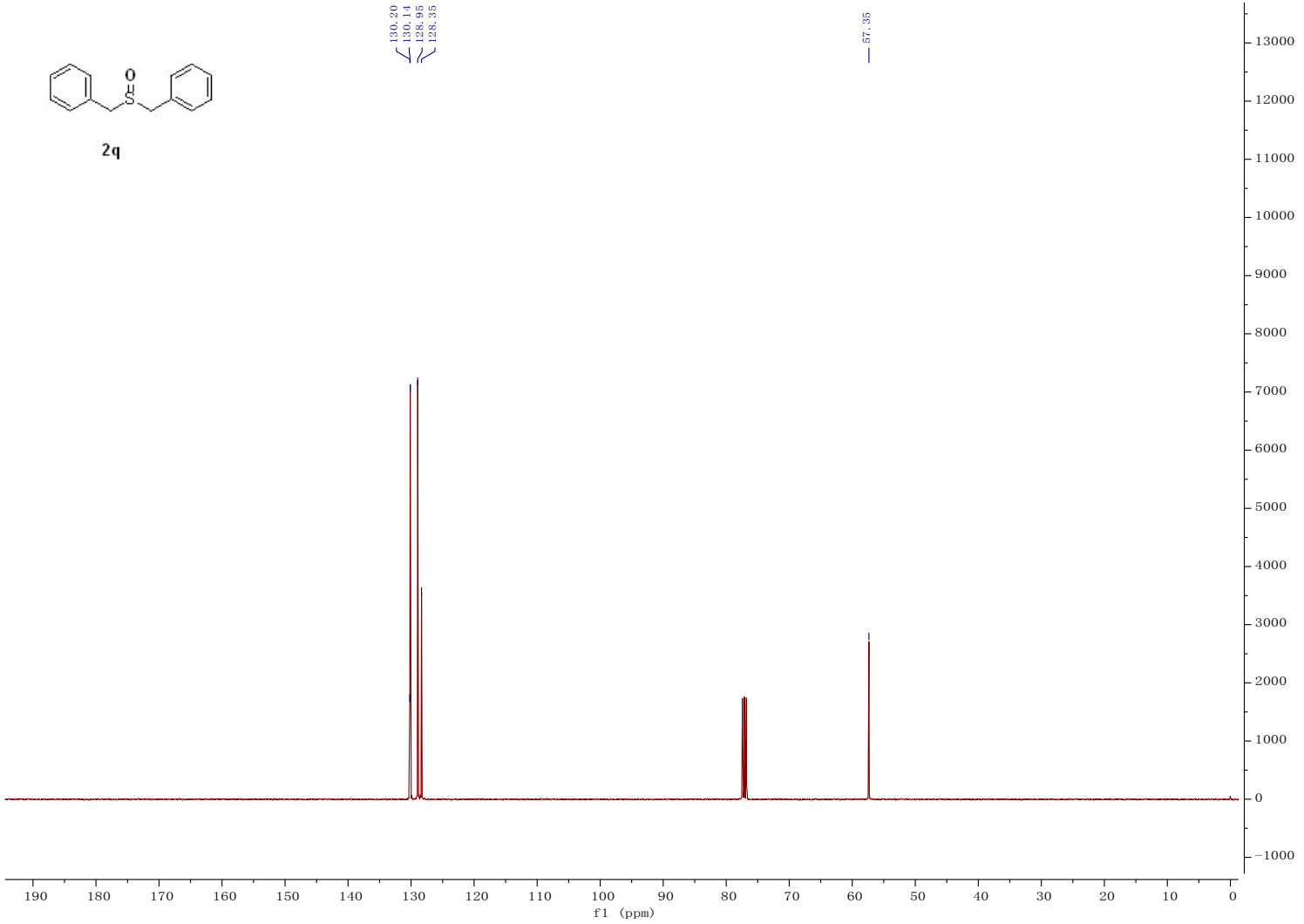

2o
7.62
7.61
7.60
7.54
7.53
7.51
5.70
5.69
5.68
5.66
5.64
5.62
5.62
5.60
5.35
5.33
5.22
5.18
3.61
3.59
3.58
3.56
3.54
3.52
3.51
3.49
3.48
1.93
2.76
0.96
1.01
1.00
2.05
f1 (ppm)

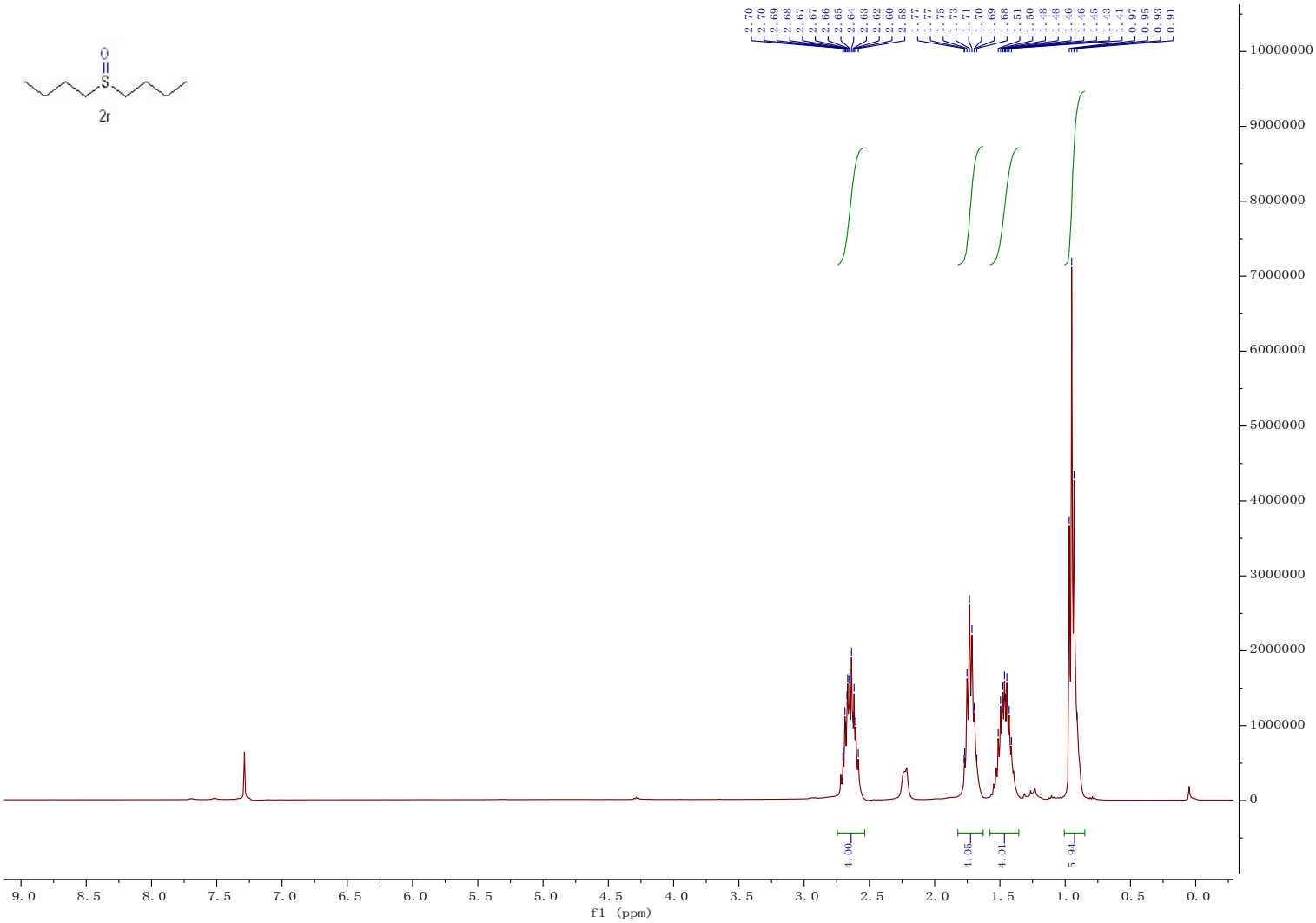

142.00
130.07
128.02
124.27
123.34
122.80
59.89
O
S
2o
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

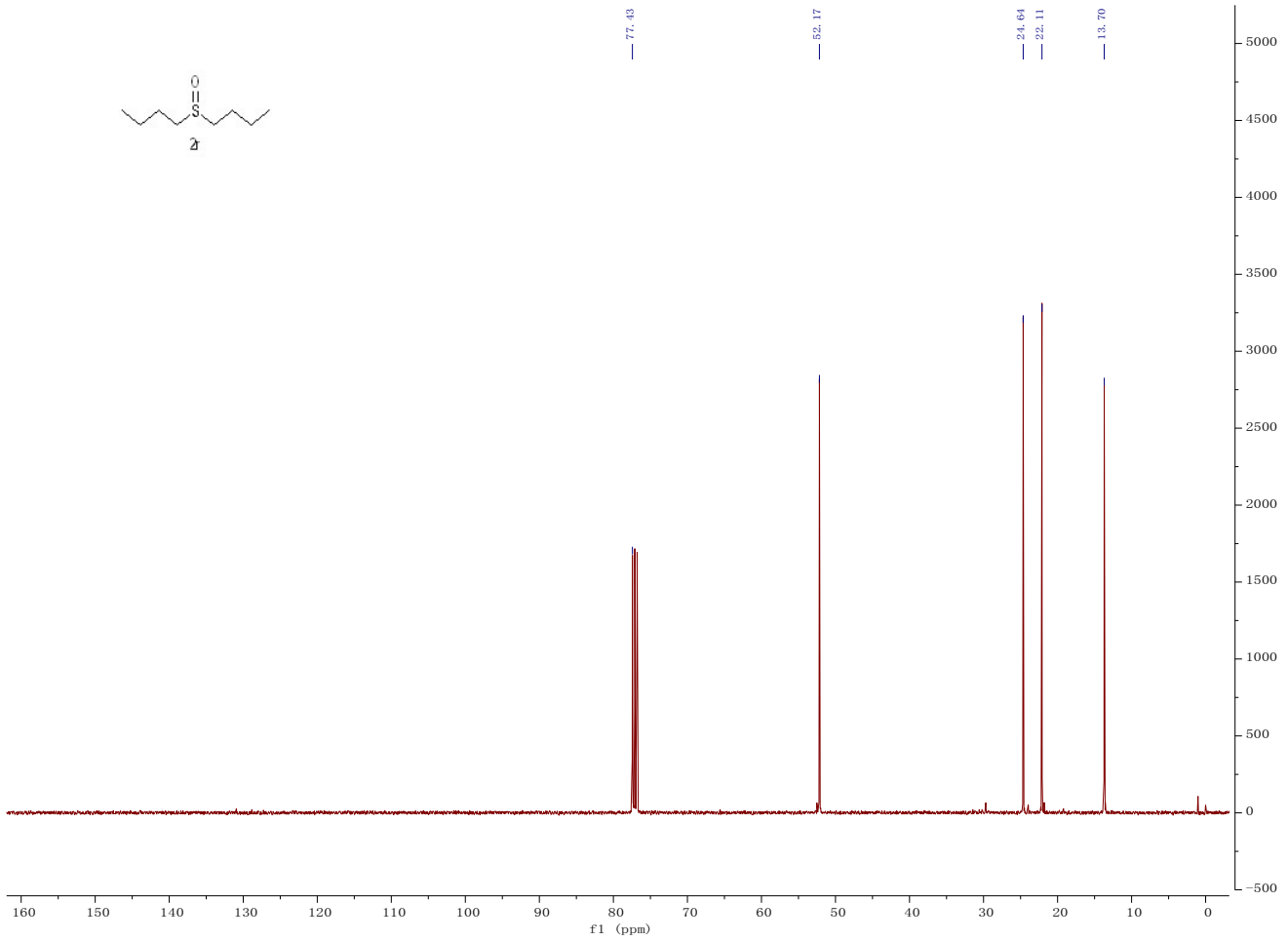

7.47
7.45
7.44
7.42
7.40
7.38
7.37
7.29
7.27
7.25
7.23
6.99
6.97
4.11
4.08
4.01
3.98
O
S
2p
4500
4000
3500
3000
2500
2000
1500
1000
500
0
5.97
1.91
1.87
2.29
1.17
1.20
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

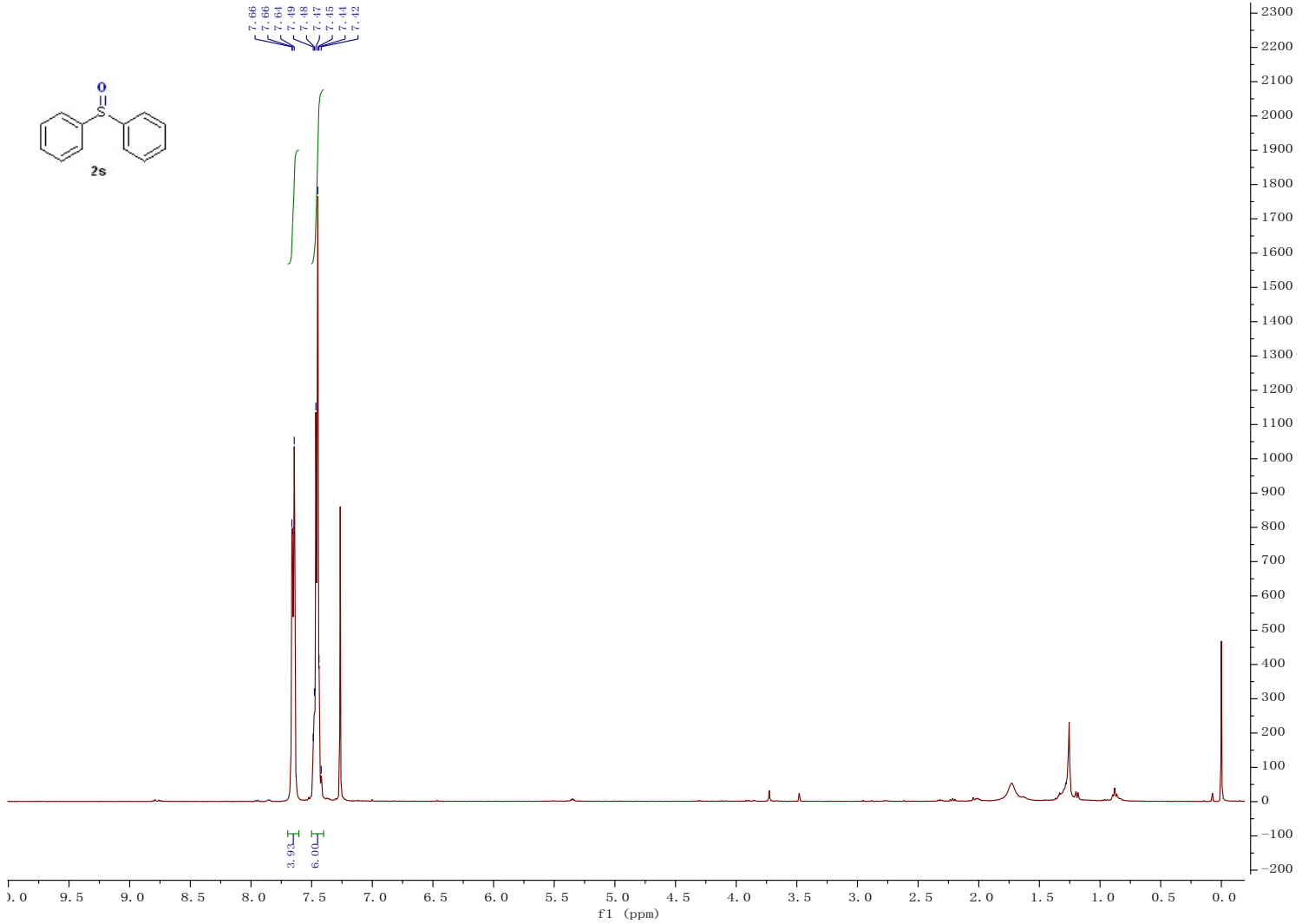

142.81
131.16
130.36
128.85
128.46
128.25
124.45
63.62
2p
f1 (ppm)

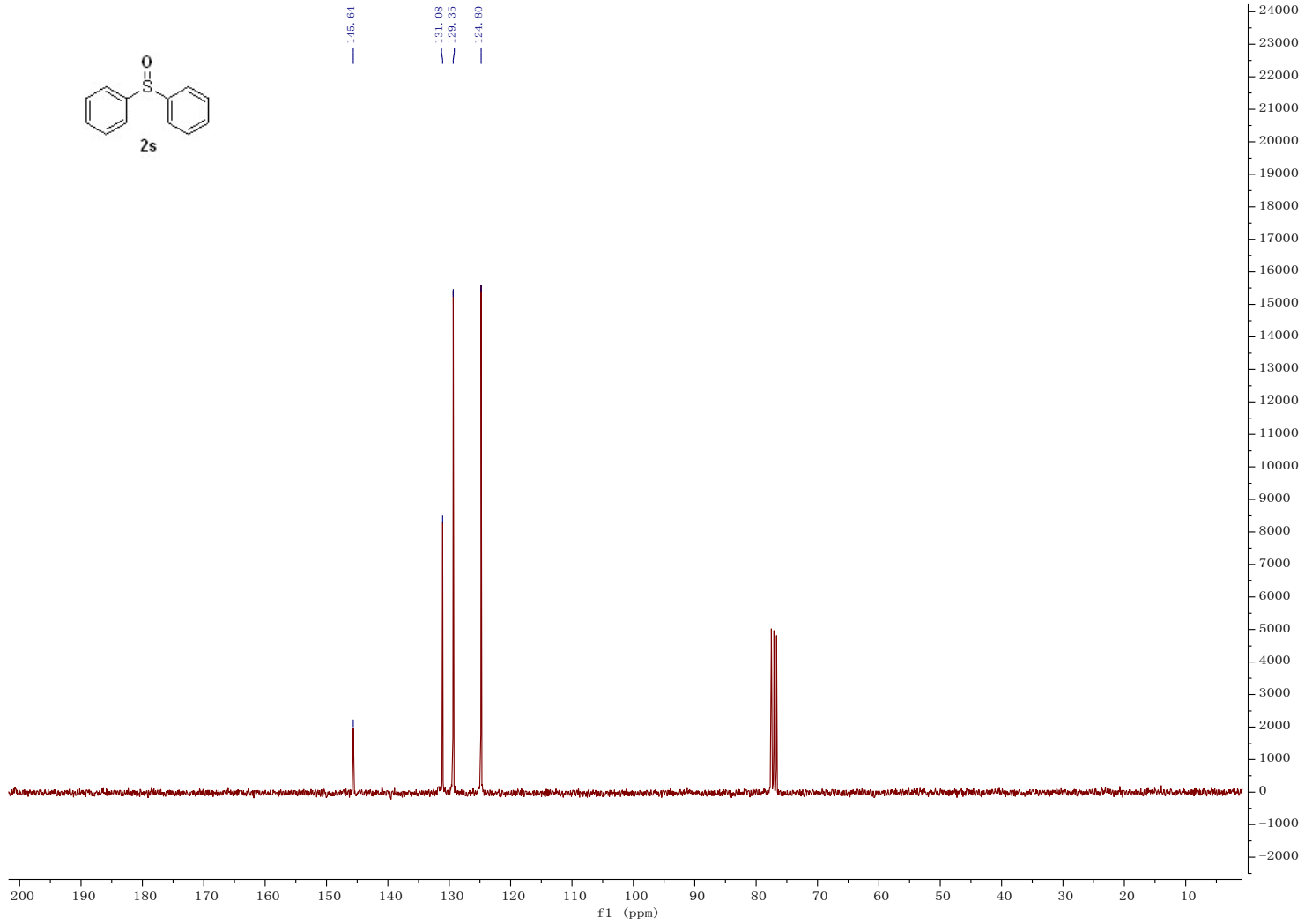

7.40
7.38
7.37
7.35
7.33
7.30
7.28
3.95
3.91
3.89
3.86
O
S
2q
5.92
3.75
4.00
f1 (ppm)

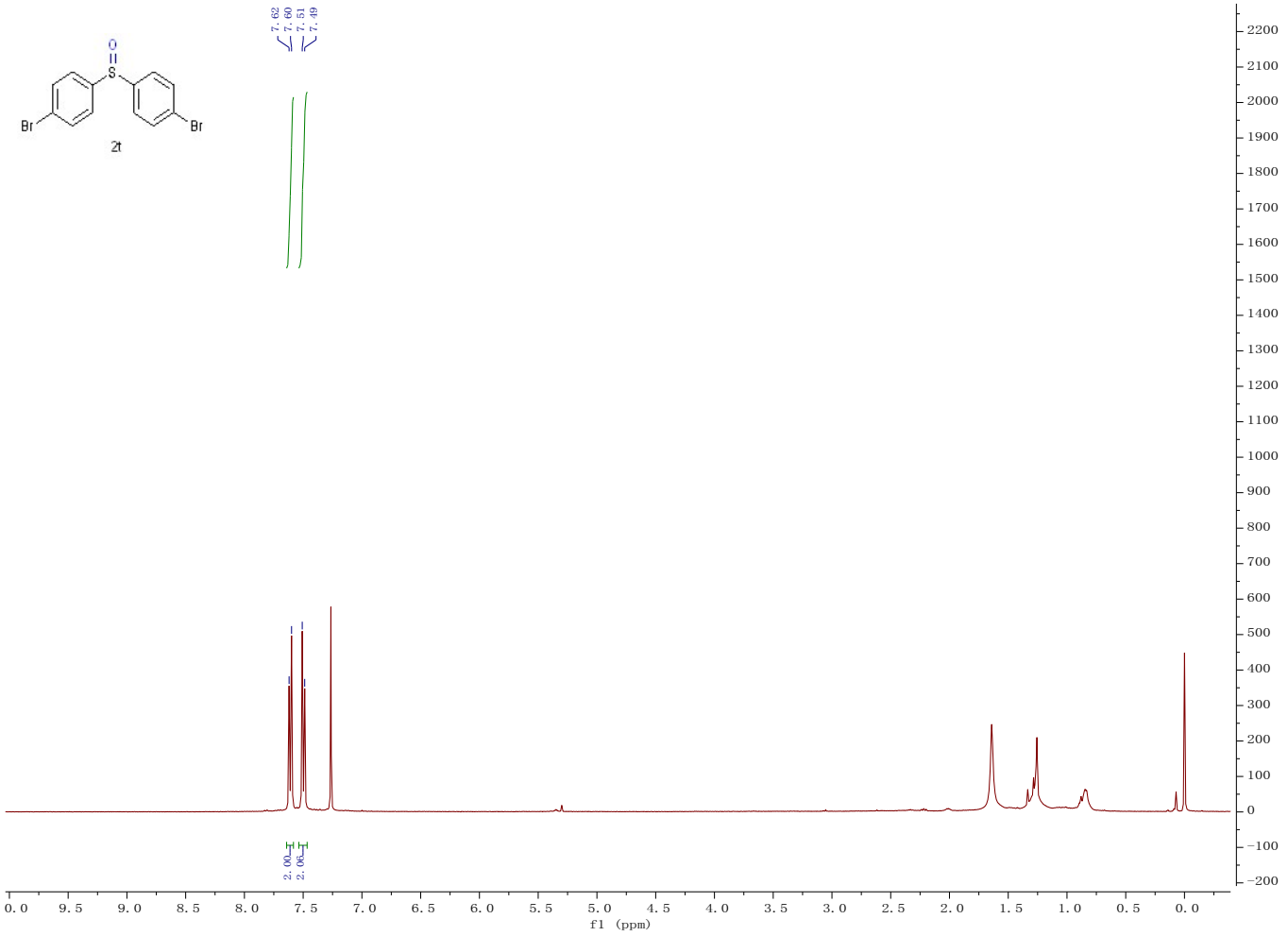

130.20
130.14
128.95
128.35
57.35
2q
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

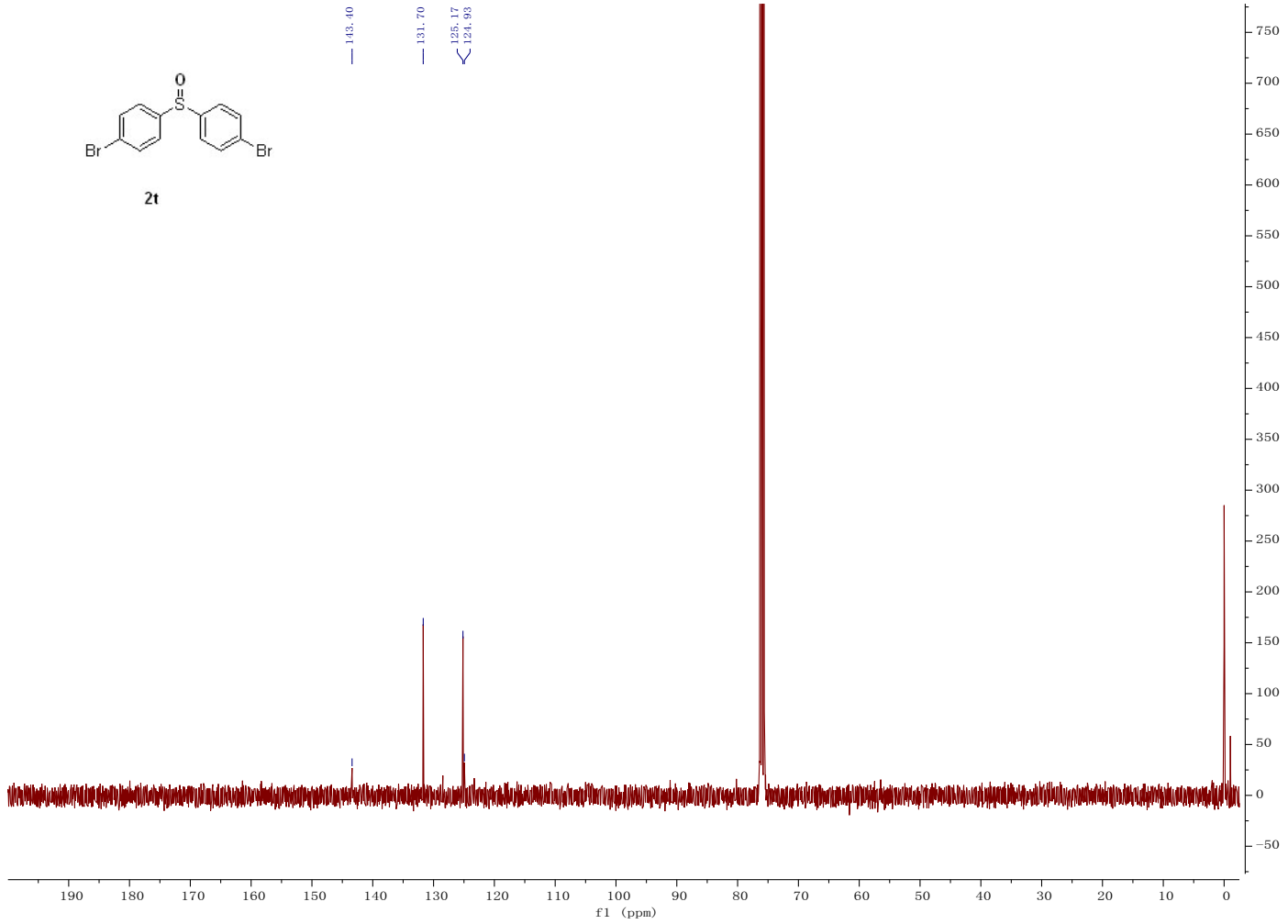

O
S
2r
2.70 2.70 2.69 2.68 2.67 2.67 2.66 2.65 2.64 2.63 2.62 2.60 2.58
1.77 1.77 1.75 1.73 1.71 1.70 1.69 1.68 1.51 1.50 1.48 1.48 1.46 1.46 1.45 1.43 1.41
0.97 0.95 0.93 0.91
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
4.00
4.05
4.01
5.94
9.0 8.5 8.0 7.5 7.0 6.5 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
f1 (ppm)

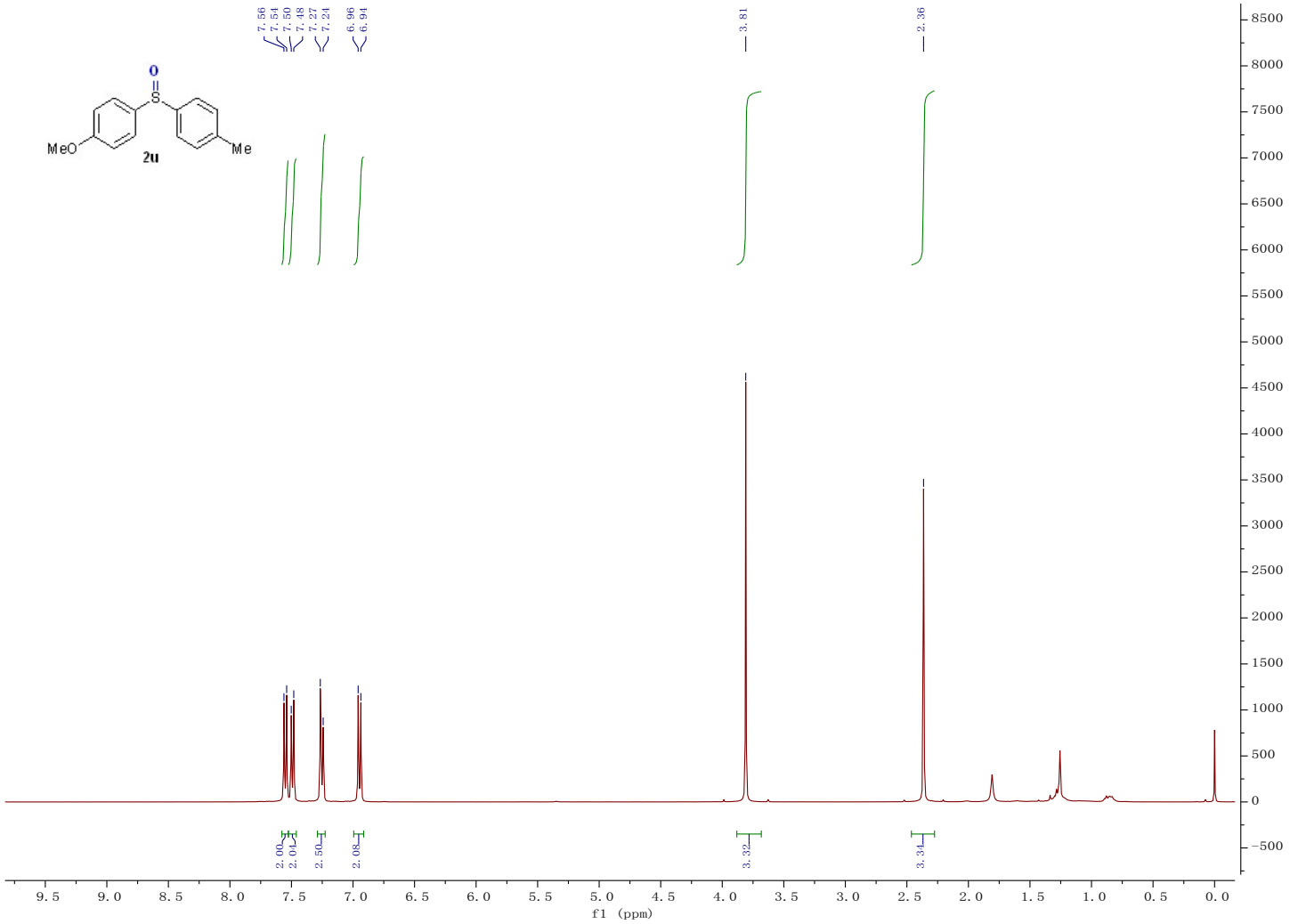

77.43
52.17
24.64
22.11
13.70
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

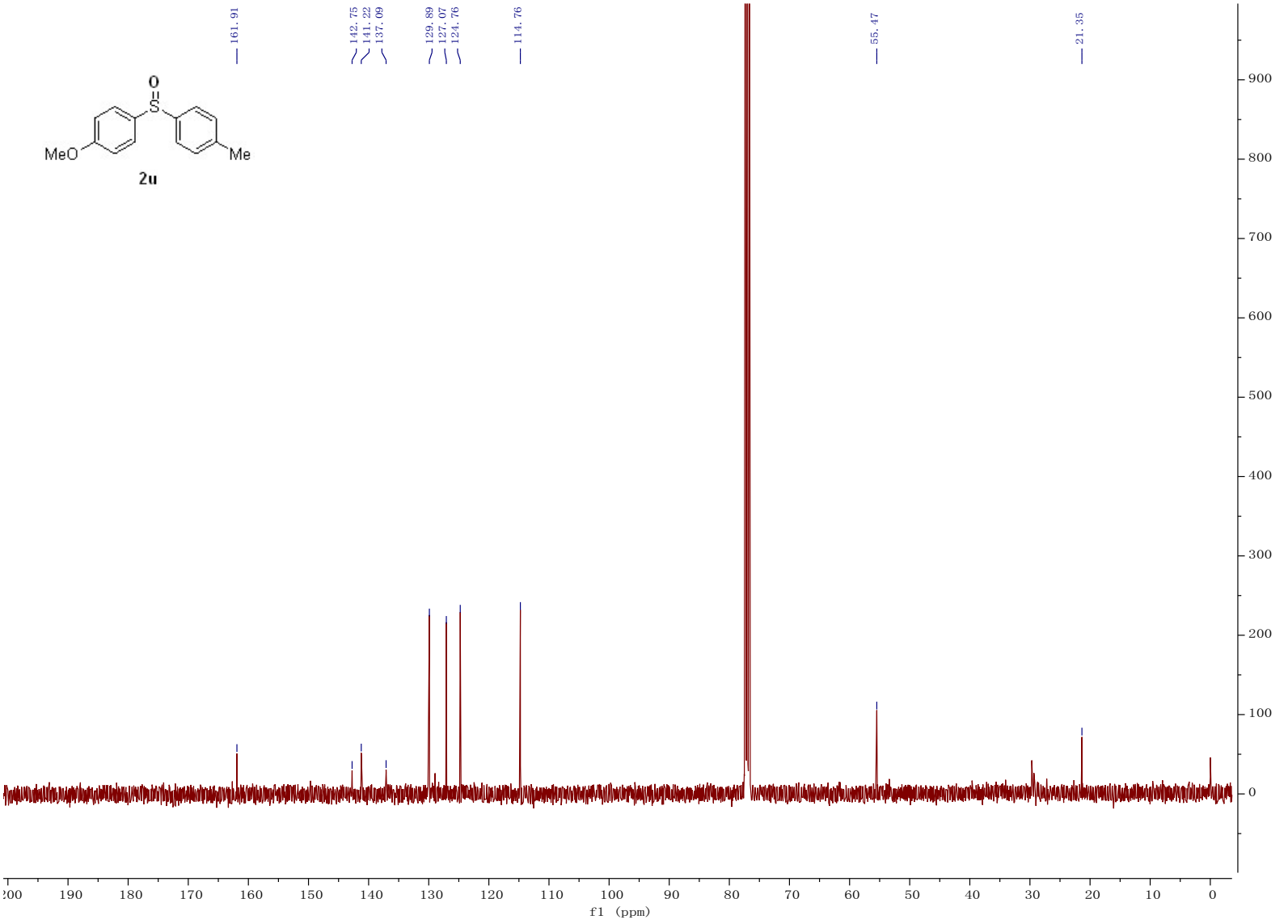

7.66
7.66
7.64
7.49
7.48
7.47
7.45
7.44
7.42
2s
3.93
6.00
f1 (ppm)


145.64
131.08
129.35
124.80
2s
f1 (ppm)

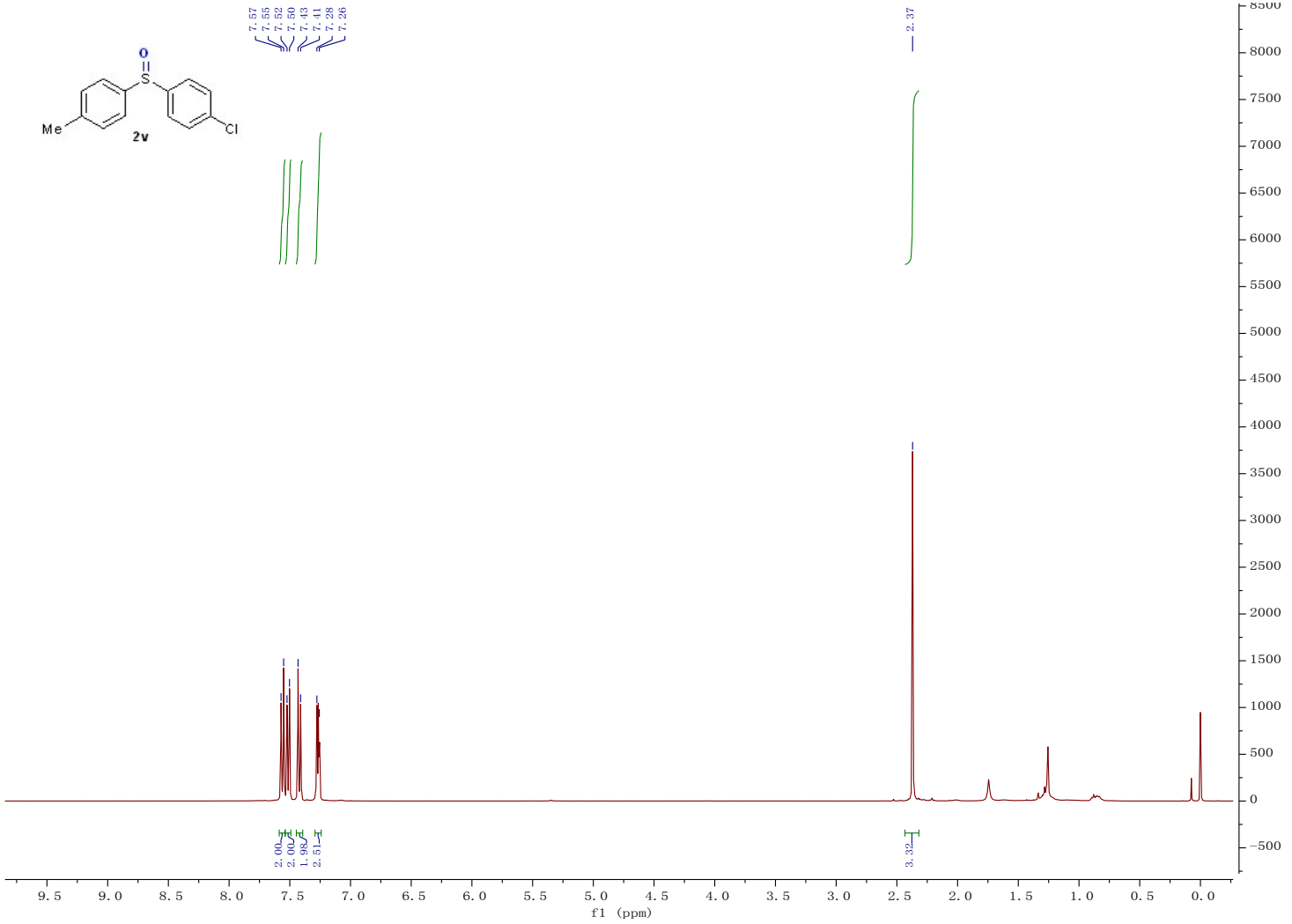

7.62
7.60
7.51
7.49
Br
Br
2t
2.00
2.06
f1 (ppm)

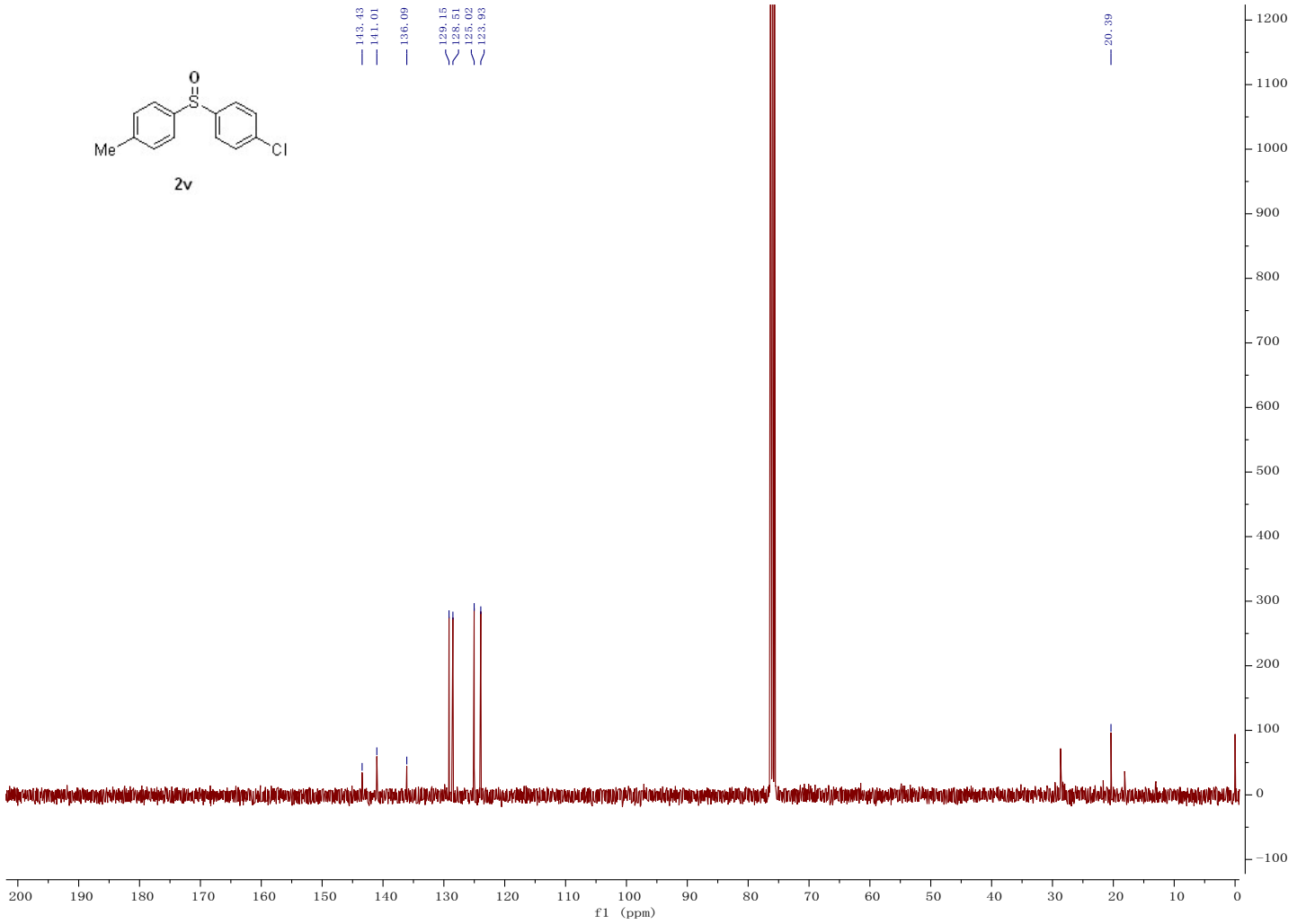

143.40
131.70
125.17
124.93
O
S
Br
Br
2t
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
−50
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

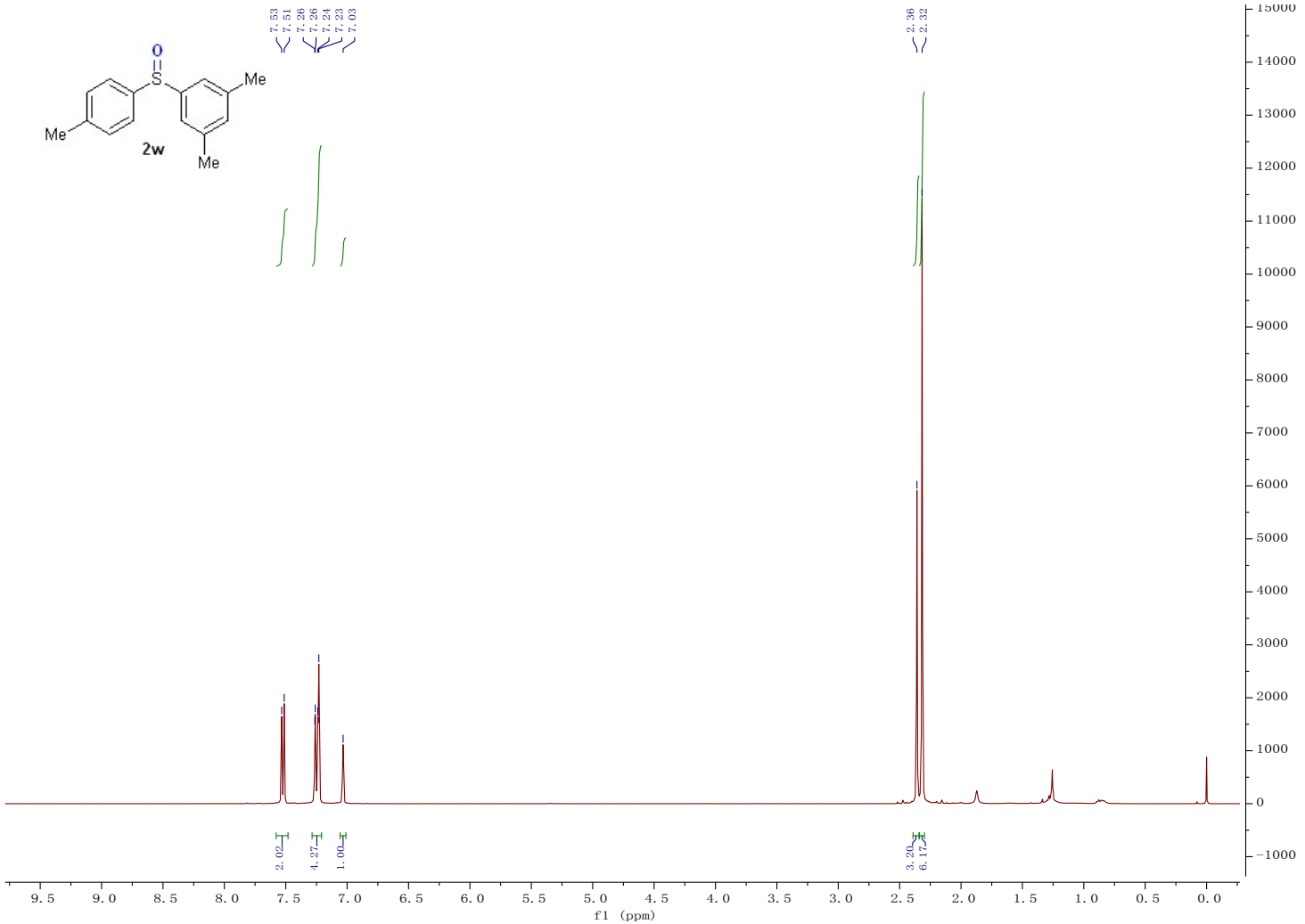

7.56
7.54
7.50
7.48
7.27
7.24
6.96
6.94
3.81
2.36
O
S
MeO
Me
2u
2.00
2.04
2.50
2.08
3.32
3.34
f1 (ppm)

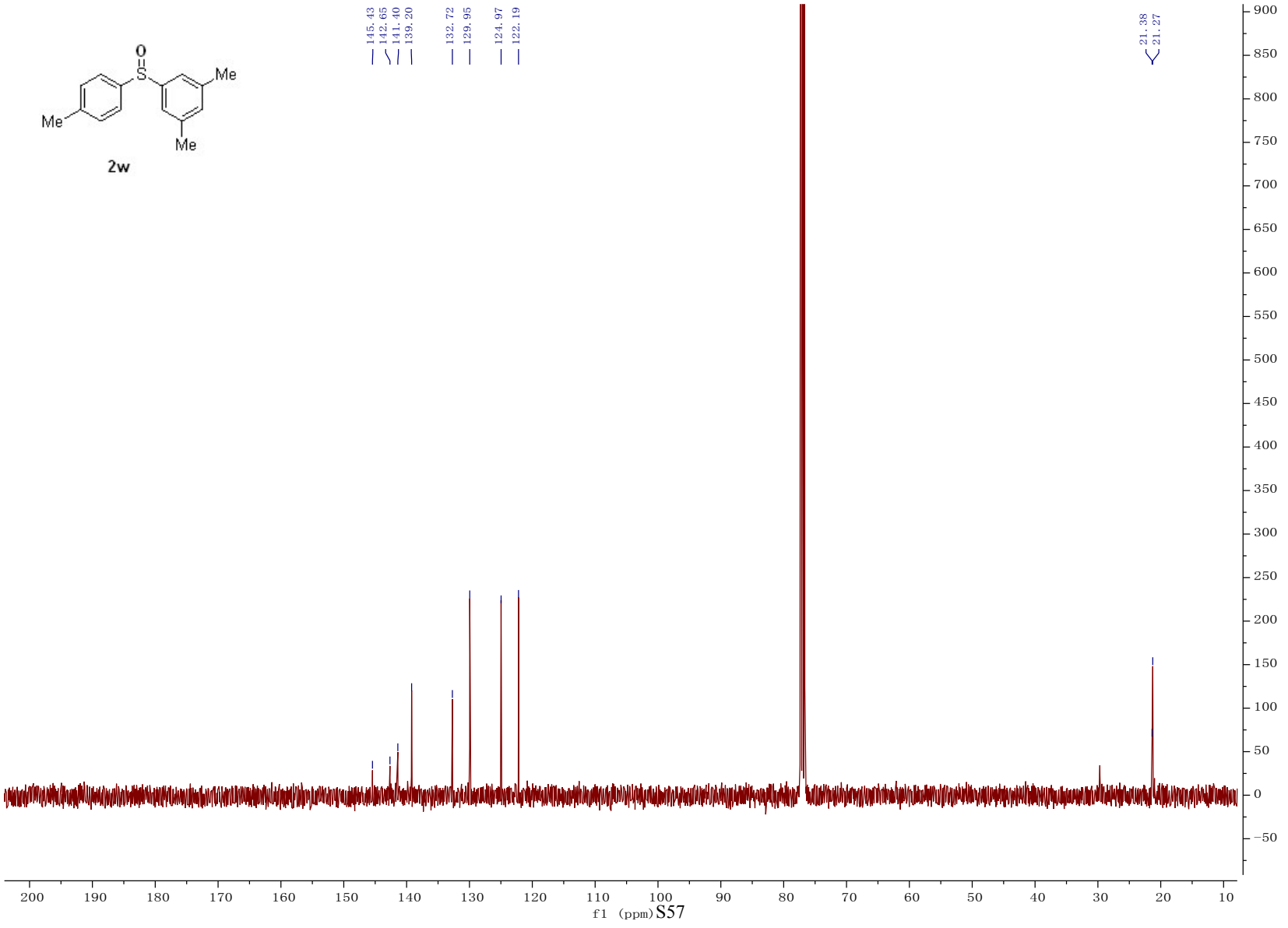

161.91
142.75
141.22
137.09
129.89
127.07
124.76
114.76
55.47
21.35
MeO
Me
2u
f1 (ppm)

2v

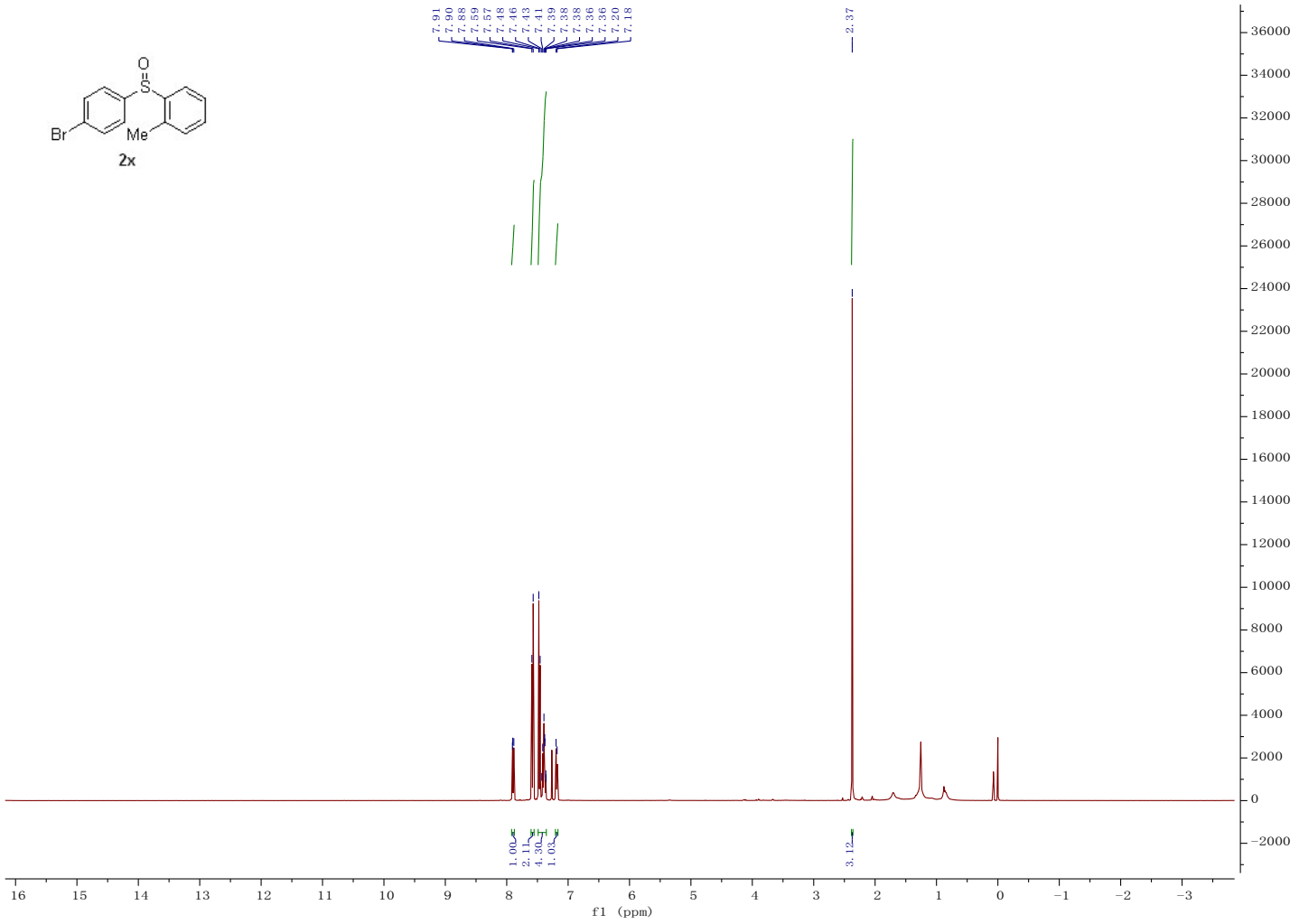

7.57
7.55
7.52
7.50
7.43
7.41
7.28
7.26
2.37
O
S
Me
Cl
2v
2.00
2.00
1.96
2.51
3.32
f1 (ppm)

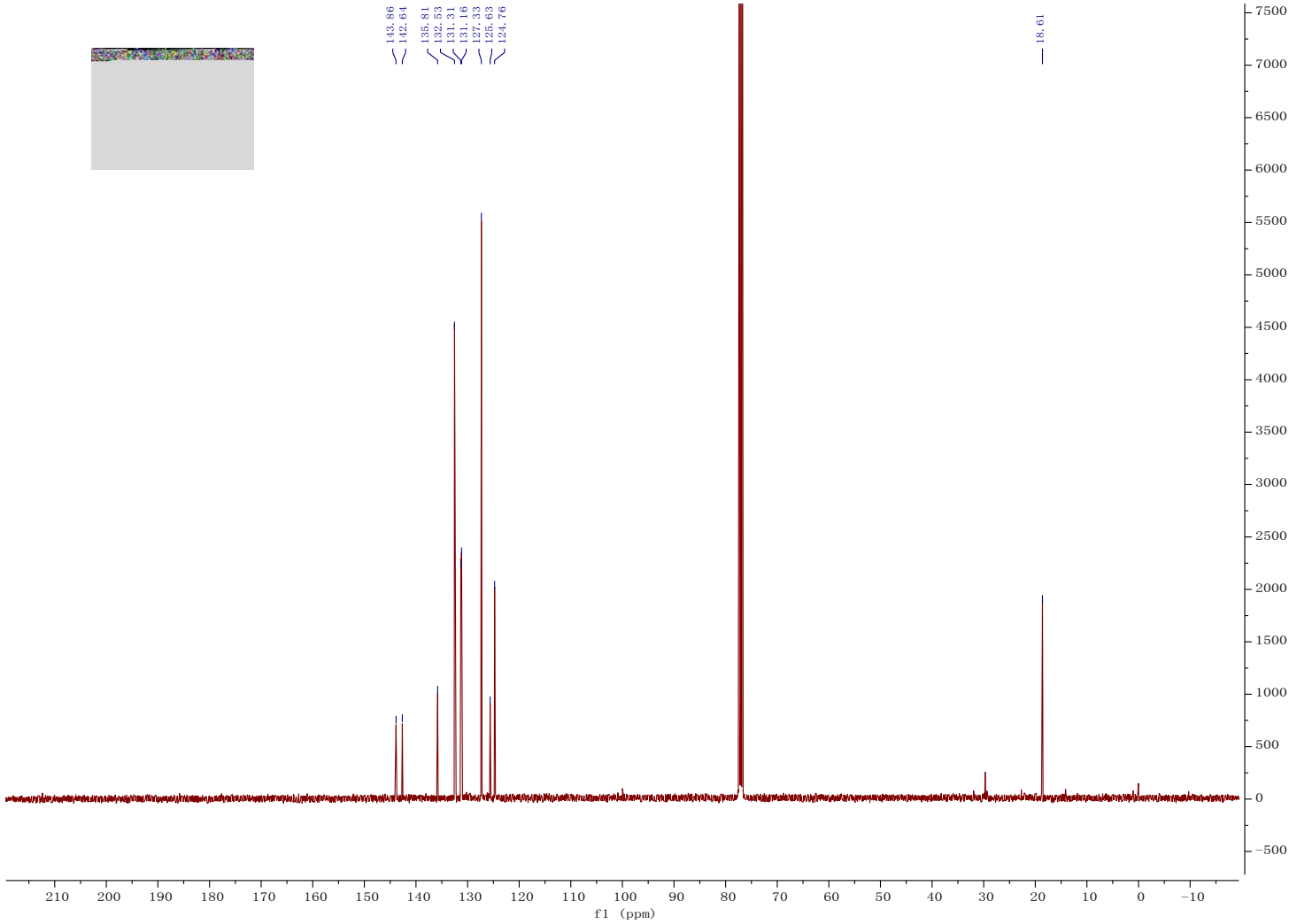

143.43
141.01
136.09
129.15
128.51
125.02
123.93
20.39
Me
Cl
O
S
2v
f1 (ppm)

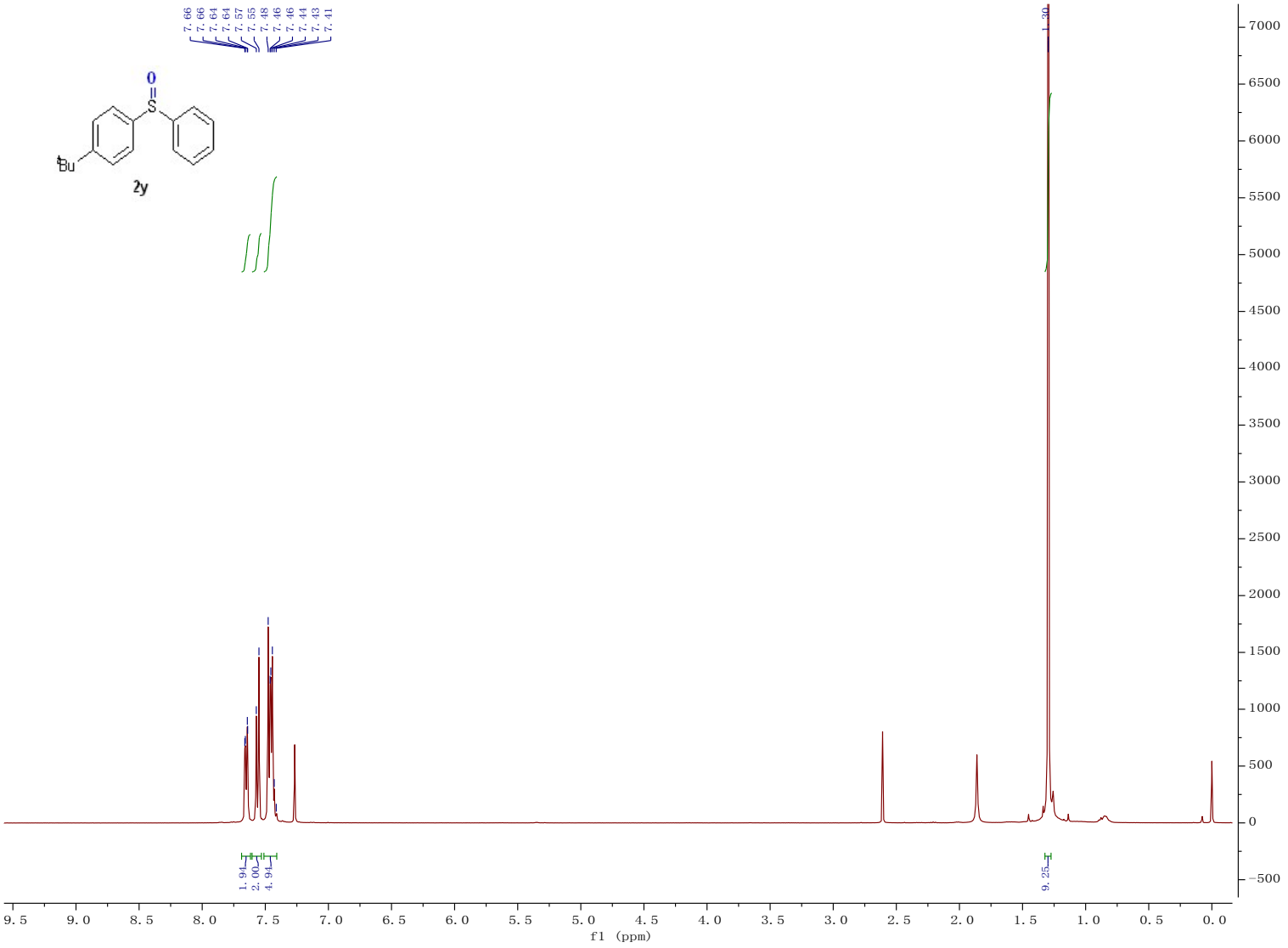

7.53
7.51
7.26
7.24
7.23
7.03
2.36
2.32
O
S
Me
Me
Me
2w
2.02
4.27
1.00
3.20
6.17
f1 (ppm)

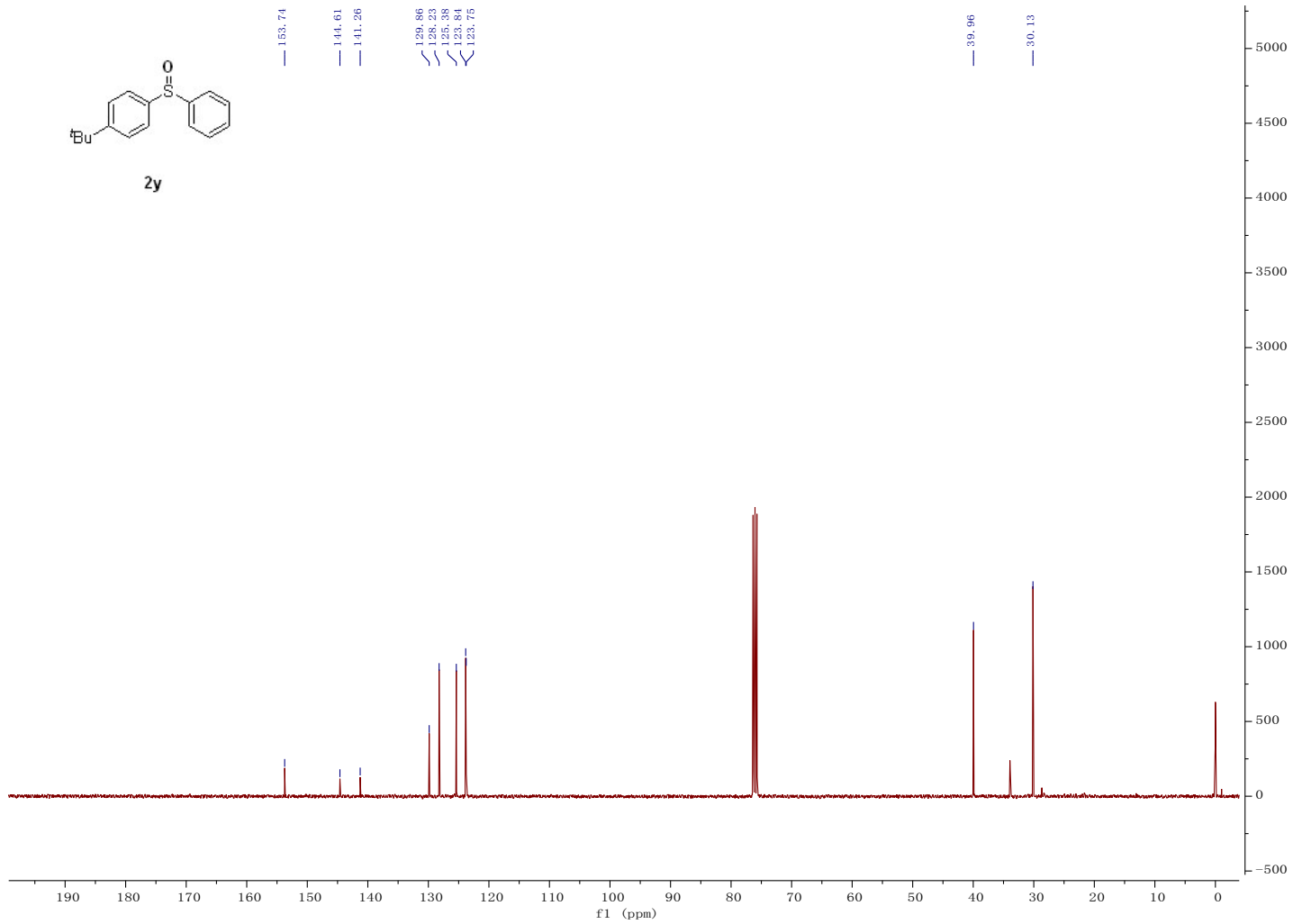

O
S
Me
Me
Me
2w
145.43
142.65
141.40
139.20
132.72
129.95
124.97
122.19
21.38
21.27
900
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
−50
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

X


O
S
Br
Me
2x
7.91
7.90
7.88
7.59
7.57
7.48
7.46
7.43
7.41
7.39
7.38
7.38
7.36
7.36
7.20
7.18
2.37
1.00
2.11
4.30
1.03
3.12
f1 (ppm)


143.86
142.64
135.81
132.53
131.31
131.16
127.33
125.63
124.76
18.61
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
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)


7.66
7.66
7.64
7.64
7.57
7.55
7.48
7.46
7.46
7.44
7.43
7.41
1.30
O
S
tBu
2y
1.94
2.00
4.94
9.25
f1 (ppm)


153.74
144.61
141.26
129.86
128.23
125.38
123.84
123.75
39.96
30.13
tBu
O
S
2y
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)