Supporting Information

Visible-Light Photocatalysis of Aerobic Oxidation of Sulfides to Sulfoxides with Perylene Diimide Photocatalyst

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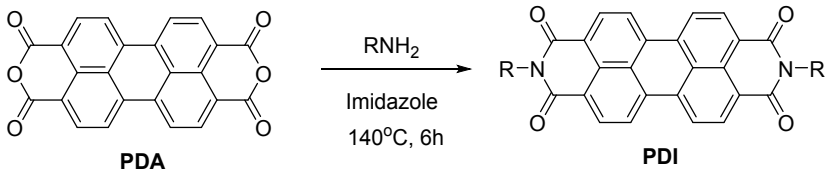
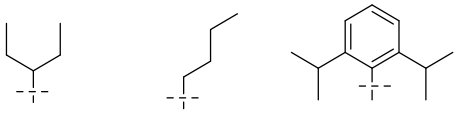
1. Materials and Methods

All commercially available reagents and solvents were used without further purification. PDIs were synthesized according to the literatures.[1] 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 $CDCl_3$ and DMSO-d_6 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. 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. ESR was recorded on Electron spin resonance spectrometer EMXplus-10/12.

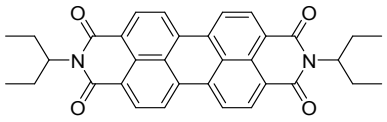
2. General Procedures for the Synthesis of PDIs

PDI was synthesized according to the literature procedure.[1] To a dry Schlenk flask, equipped with a stirring bar, 2.55 mmol of 3,4,9,10-perylenetetracarboxydianhydride, 10.6 mmol of aniline and 7.5 g of imidazole were added. The reaction mixture was heated to 190 ºC under N_2 and after 24h the reaction mixture was cooled to room temperature and diluted with 50 mL of EtOH and 60 mL of 2 M HCl. This mixture was stirred for 3 h, filtered and washed with EtOH/HCl and EtOH/water mixtures. The solid was purified by silica column chromatography yielding PDI as a red solid.





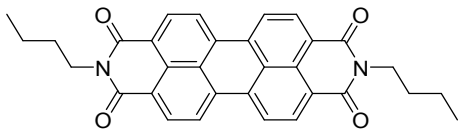
2,9-di(pentan-3-yl)anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (**PDI-1**)[2]



PDI-1

The representative procedure was followed using 3,4,9,10-perylenetetracarboxydianhydride and pentan-3-amine as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **PDI-1** (0.81 g, 60%) as a purple black solid (m.p. >300 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.80 (s, 8H, ArH), 5.13-5.06 (m, 2H, CH), 2.30-2.17 (m, 4H, $2CH_2$), 2.05-1.97 (m, 4H, $2CH_2$), 0.94 (t, 12H, J = 8 Hz, $4CH_3$).

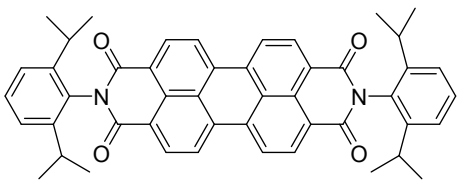
2,9-dibutylanthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (**PDI-2**)[3]



PDI-2

The representative procedure was followed using 3,4,9,10-perylenetetracarboxydianhydride and butan-1-amine as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **PDI-2** (0.74 g, 58%) as a brownish black solid (m.p. >300 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.78 (d, 4H, J = 8 Hz, ArH), 8.72 (d, 4H, J = 8 Hz, ArH), 4.25 (t, 4H, J = 8 Hz, $2CH_2$), 1.79-1.72 (m, 4H, $2CH_2$), 1.53-1.43 (m, 4H, $2CH_2$), 1.01 (t, 6H, J = 8 Hz, $2CH_3$).

2,9-bis(2,6-diisopropylphenyl)anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (**PDI-3**)[4]



PDI-3

The representative procedure was followed using 3,4,9,10-perylenetetracarboxydianhydride and 2,6-diisopropylaniline as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **PDI-3** (1.2 g, 66%) as a dark red solid (m.p. >300 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.84-8.77 (m, 8H, ArH), 7.56-7.52 (m, 2H, ArH), 7.40-7.38 (m, 4H, ArH), 2.82-2.76 (m, 4H, ArH), 1.22 (d, 24H, J = 8 Hz, $8CH_3$).

3. Solubility and UV-Vis Spectra for PDIs

Table S1 Solubility of PDI in different solvents

Solvent	**PDI-1**	**PDI-2**	**PDI-3**
MeOH	H	L	H
DMSO	H	L	H
DMF	H	H	H
CH_3CN	L	L	H
EtOH	L	L	H

H: high solubility;

L: low solubility

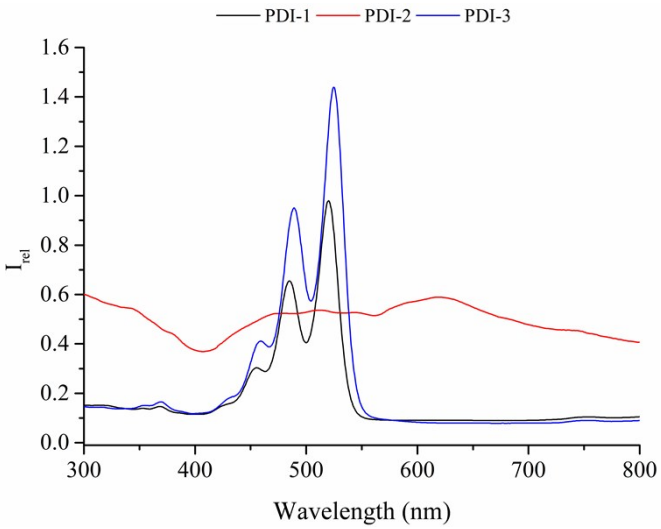


Figure S1. UV-Vis absorption spectra of PDIs ($2.8*10^{-5}$ mol/L in MeOH).

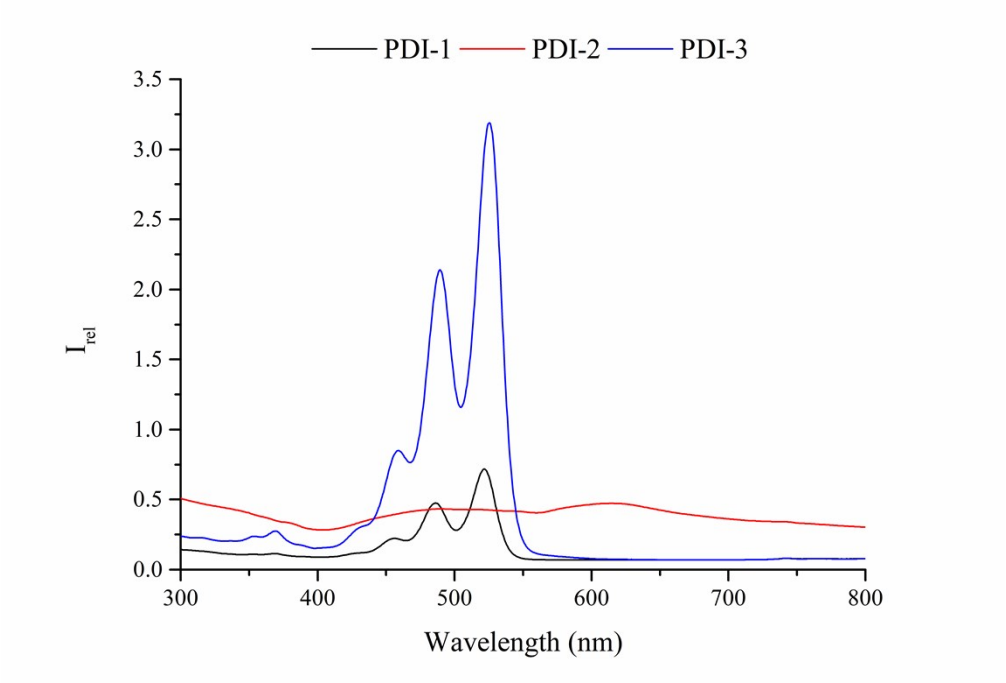


Figure S2. UV-Vis absorption spectra of PDIs ($2.8*10^{-5}$ mol/L in EtOH).

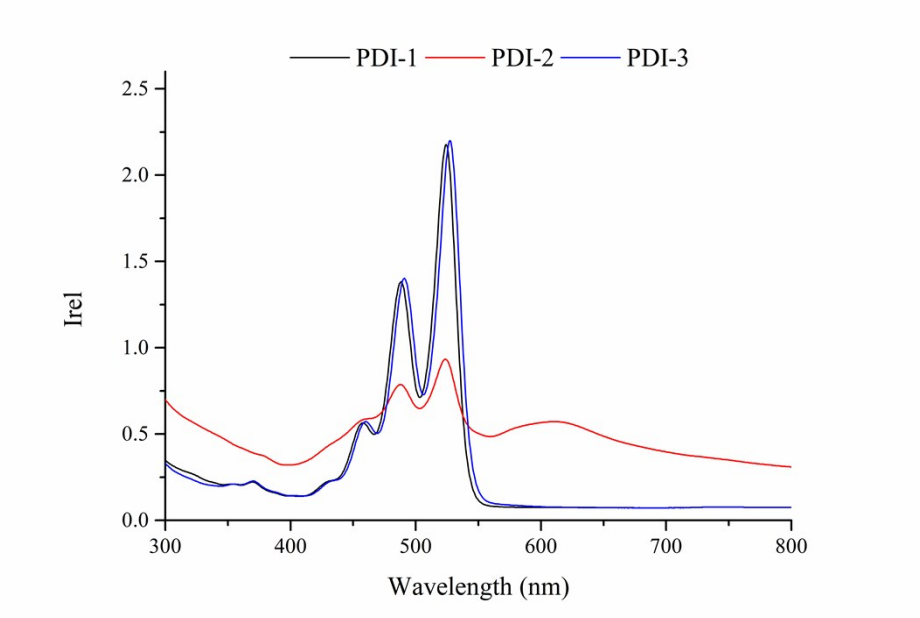


Figure S3. UV-Vis absorption spectra of PDIs ($2.8*10^{-5}$ mol/L in DMF).

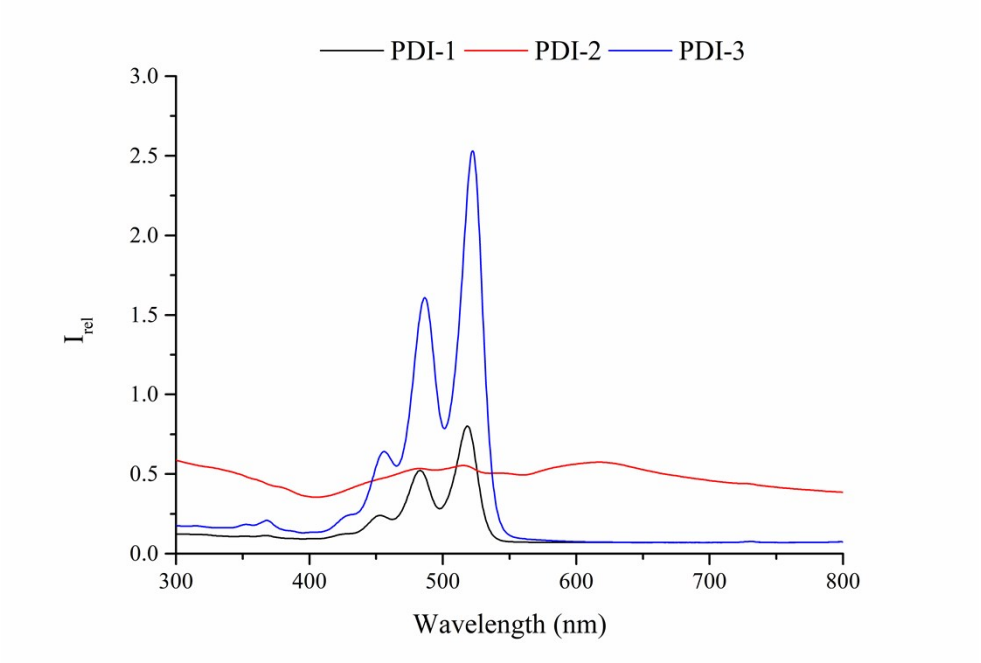


Figure S4. UV-Vis absorption spectra of PDIs ($2.8*10^{-5}$ mol/L in CH_3CN).

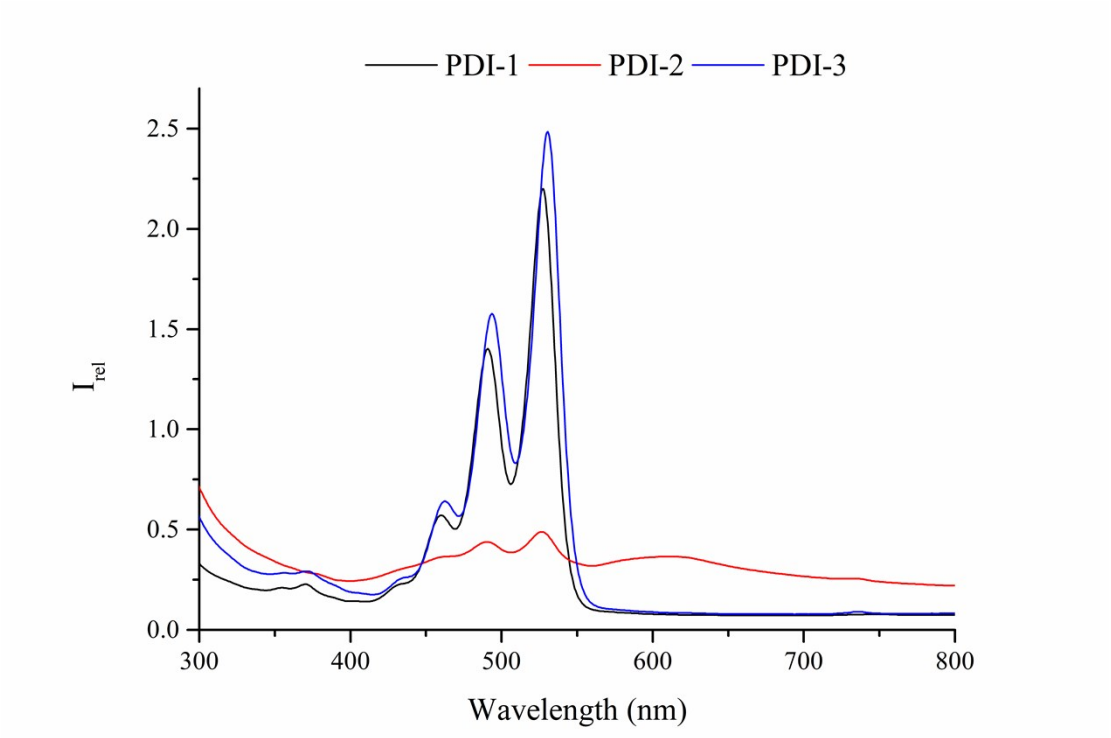


Figure S5. UV-Vis absorption spectra of PDIs ($2.8*10^{-5}$ mol/L in DMSO).

4. Spectra of the Light Source

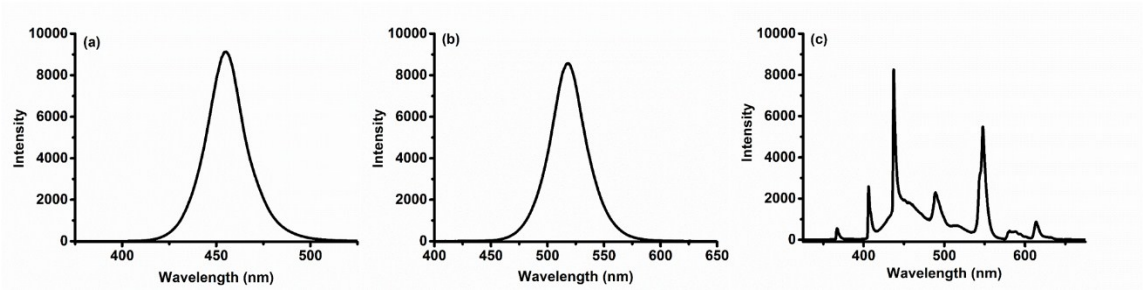
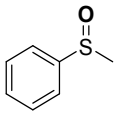


Figure S6. Spectra of light source. (a) blue LED, (b) green LED, (c) CFL.

5. General Procedures for the Selective Oxidation of Sulfides with PDI-3

In a dried schlenk tube, sulfides **1** (0.5 mmol) and **PDI-3** (2 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 washed with brine. The aqueous phase was re-extracted with ethyl acetate. 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**.

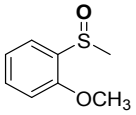
(Methylsulfinyl)benzene (**2a**)[5]



2a

The representative procedure was followed using methyl(phenyl)sulfane (**1a**) (0.50 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2a** (64 mg, 91%) 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-2-(methylsulfinyl)benzene (**2b**)[6]

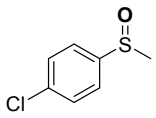


2b

The representative procedure was followed using (2-methoxyphenyl)(methyl)sulfane (**1b**) (0.50 mmol)

as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2b** (57 mg, 68%) 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.

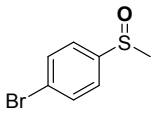
1-Chloro-4-(methylsulfinyl)benzene (**2c**)[7]



2c

The representative procedure was followed using (4-chlorophenyl)(methyl)sulfane (**1c**) (0.50 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2c** (70 mg, 82%) 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.

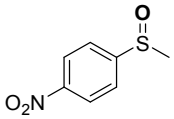
1-Bromo-4-(methylsulfinyl)benzene (**2d**)[8]



2d

The representative procedure was followed using (4-bromophenyl) (methyl)sulfane (**1d**) (0.50 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2d** (92 mg, 85%) 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.

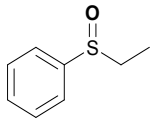
1-(Methylsulfinyl)-4-nitrobenzene (**2e**)[9]



2e

The representative procedure was followed using methyl (4-nitrophenyl) sulfane (**1e**) (0.50 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2e** (73 mg, 79%) as a white solid (m.p. = 145.0-147.2 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.40 (d, 2H, *J* = 8 Hz, ArH), 7.85 (d, 2H, *J* = 8 Hz, ArH), 2.80 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 153.3, 124.7, 124.5, 43.9.

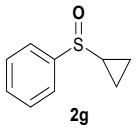
(Ethylsulfinyl)benzene (**2f**)[10]



2f

The representative procedure was followed using methyl ethyl(phenyl)sulfane (**1f**) (0.50 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2f** (68 mg, 89%) 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.

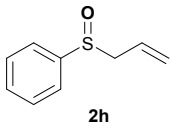
(Cyclopropylsulfinyl)benzene (**2g**)[11]



2g

The representative procedure was followed using methyl cyclopropyl(phenyl)sulfane (**1g**) (0.50 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 2/1) yielded **2g** (62 mg, 75%) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.68-7.66 (m, 2H, ArH), 7.55-7.50 (m, 3H, ArH), 2.30-2.24 (m, 1H, CH), 1.27-1.25 (m, 1H, CH), 1.07-1.01 (m, 1H, CH), 0.99-0.93 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 130.9, 129.2, 124.0, 33.8, 3.4, 2.8.

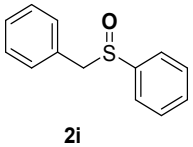
(Allylsulfinyl)benzene (**2h**)[12]



2h

The representative procedure was followed using methyl allyl(phenyl)sulfane (**1h**) (0.50 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 2/1) yielded **2h** (65 mg, 79%) 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 (**2i**)[13]

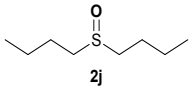


2i

The representative procedure was followed using benzyl(phenyl)sulfane (**1i**) (0.50 mmol) as substrate.

Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2i** (99 mg, 92%) 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.

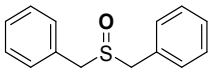
1-(Butylsulfinyl)butane (**2j**)[10]



2j

The representative procedure was followed using dibutylsulfane (**1j**) (0.50 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 3/1) yielded **2j** (76 mg, 95%) 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.

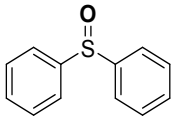
(Sulfinylbis(methylene))dibenzene (**2k**)[14]



2k

The representative procedure was followed using dibenzylsulfane (**1k**) (0.50 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2k** (103 mg, 90%) 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.

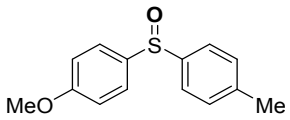
Sulfinyldibenzene (**2l**)[15]



2l

The representative procedure was followed using diphenylsulfane (**1l**) (0.50 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2l** (78 mg, 78%) as a white solid (m.p. = 70.5-72.1 °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.

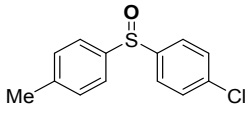
1-Methoxy-4-(*p*-tolylsulfinyl)benzene (**2m**)[16]



2m

The representative procedure was followed using (4-methoxyphenyl) (*p*-tolyl)sulfane (**1m**) (0.50 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2m** (99 mg, 81%) 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.

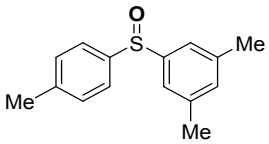
1-Chloro-4-(*p*-tolylsulfinyl)benzene (**2n**)[17]



2n

The representative procedure was followed using (4-chlorophenyl) (*p*-tolyl)sulfane (**1n**) (0.50 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2n** (96 mg, 77%) 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.

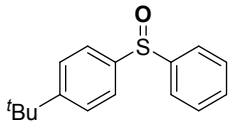
1,3-Dimethyl-5-(*p*-tolylsulfinyl)benzene (**2o**)[18]



2o

The representative procedure was followed using (3,5-dimethyl phenyl) (*p*-tolyl)sulfane (**1o**) (0.50 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2o** (106 mg, 87%) 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.

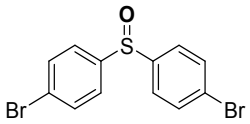
1-(tert-Butyl)-4-(phenylsulfinyl)benzene (**2p**)[19]



2p

The representative procedure was followed using (4-(*tert*-butyl) phenyl) (phenyl)sulfane (**1p**) (0.50 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2p** (107 mg, 83%) 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.

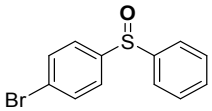
4,4'-Sulfinylbis(bromobenzene) (**2q**)[20]



2q

The representative procedure was followed using bis(4-bromophenyl) sulfane (**1q**) (0.50 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2q** (128 mg, 72%) 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-Bromo-4-(phenylsulfinyl)benzene (**2r**)[19]



2r

The representative procedure was followed using (4-bromophenyl) (phenyl) sulfane (**1r**) (0.50 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **2r** (87mg, 70%) as a white oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.64-7.62 (m, 2H, ArH), 7.59 (d, 2H, *J* = 8 Hz, ArH), 7.51 (d, 2H, *J* = 8 Hz, ArH), 7.48-7.46 (m, 3H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 145.3, 144.9, 132.5, 131.4, 129.5, 126.3, 125.6, 124.8.

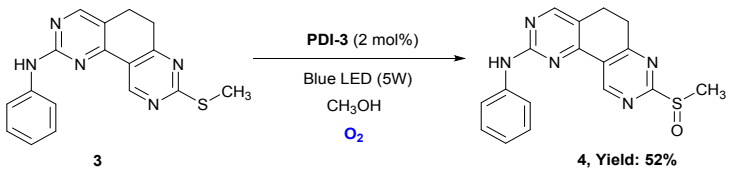
6. Gram-scale Reaction for the PDI-catalyzed Selective Oxidation.

In a 50 mL schlenk bottle with magnetic stirring bar, sulfide **1a** (20 mmol) and **PDI-3** (2 mol%) was added in 20 mL methanol. Next, a balloon was purged with oxygen and fixed on the top of the

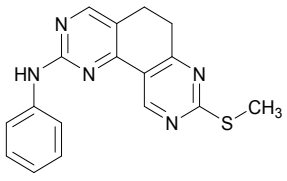
schlenk bottle. The reaction mixture was stirred and irradiated by 5 W blue LED at room temperature under an atmospheric pressure oxygen atmosphere. When the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with ethyl acetate. The combined organic 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 **2a** (2.24g, 80%).

7. Late-stage Functionalization of Sulfide for the Synthesis of Bioactive Sulfoxide 4

In a dried schlenk tube, sulfides **3** (0.2 mmol) and PDI-3 (2 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 washed with brine. The aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4, concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH: 20/1) to afford the desired product **4** (35 mg, 52%) as a light yellow solid (m.p. 196.8-199.4).

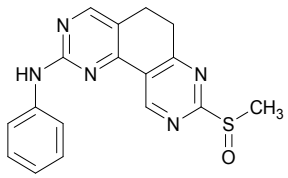


8-(methylthio)-*N*-phenyl-5,6-dihydropyrimido[4,5-*f*]quinazolin-2-amine (**3**)[21]



Sulfide **3** was prepared according to the literature.[22] ^{1}H NMR (400 MHz, DMSO-d_6): δ ppm 9.64 (s, 1H, NH), 9.15 (s, 1H, ArH), 8.43 (s, 1H, ArH), 7.81 (d, 2H, J = 8 Hz, ArH), 7.34-7.30 (m, 2H, ArH), 6.97-6.93 (m, 1H, ArH), 3.05-3.01 (m, 2H, CH_2), 2.95-2.92 (m, 2H, CH_2), 2.59 (s, 3H, CH_3).

8-(methylsulfinyl)-*N*-phenyl-5,6-dihydropyrimido[4,5-*f*]quinazolin-2-amine (**4**)



4

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 9.58 (s, 1H, ArH), 8.42 (s, 1H, ArH), 7.66 (d, 2H, J = 8 Hz, ArH), 7.40-7.36 (m, 2H, ArH), 7.12-7.08 (m, 1H, ArH), 3.41 (s, 3H, CH_3), 3.31-3.28 (m, 2H, CH_2), 3.07-3.03 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 174.9, 170.5, 159.7, 158.7, 155.1, 153.7, 140.9, 129.1, 126.8, 121.7, 119.2, 29.9, 21.8. HRMS (ESI–Q–TOF) exact mass calcd for $C_{17}H_{16}N_5OS$ $[M + H]^+$ 338.1076, found 338.1054.

8. Photostability Experiment of PDI-3

The stability experiment of **PDI-3** under this reaction condition was performed. UV-Visible spectra of the reaction mixture at the beginning and during the course of the reaction were collected to confirm the stability of the photocatalytic system. There was no new signal was detected and indicated the excellent stability of **PDI-3** as the photocatalyst under this reaction condition.

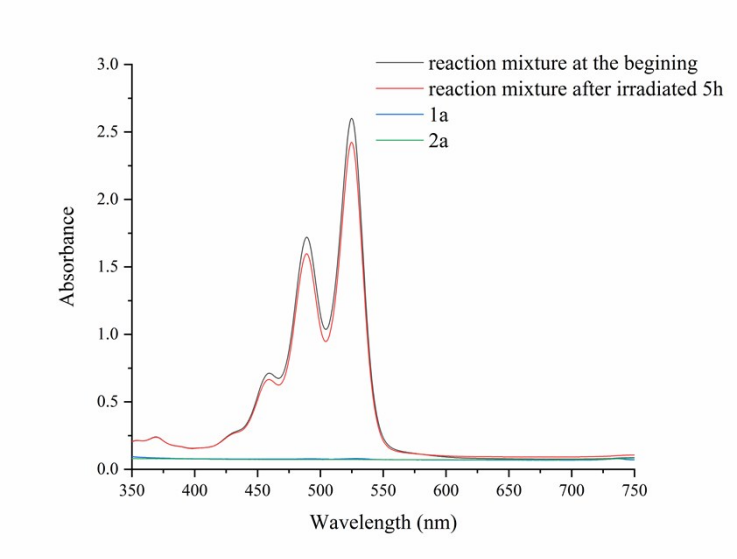
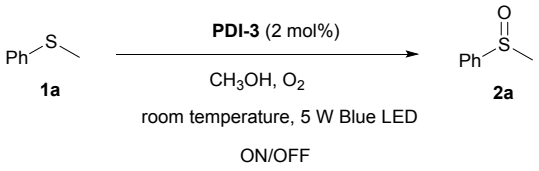


Figure S7. UV-Visible spectra of the reaction mixture at the beginning and during the course of the reaction at 5h.

9. Time Profile of the Photoxidation of Sulfide with and without Visible Light



In a dried schlenk tube, methyl phenyl sulfane (**1a**) (0.25 mmol) and **PDI-3** (2 mol%) was added in 2.0 mL CH_3OH. Next, a balloon was purged with oxygen and fixed on the top of the schlenk tube. Then, the reaction mixtures were placed under 5 W blue LED at given time intervals. The yield was detected by GC using diphenyl as internal standard.

Light ON/OFF	Time (h)	Yield of **2a**
0	0	0
2 hour on	2	28
1 hour off	3	30
2 hour on	5	53
1 hour off	6	55
2 hour on	8	73
1 hour off	9	75
2 hour on	11	91

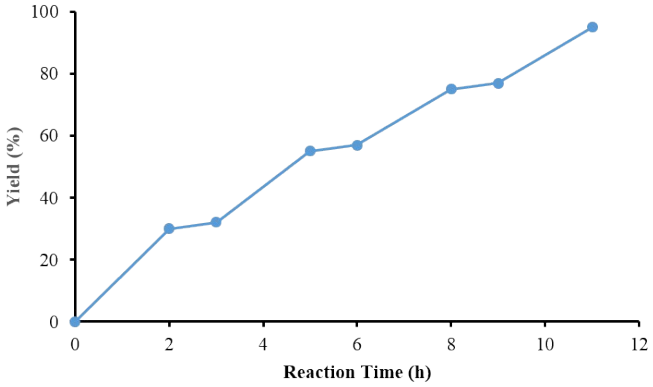


Figure S8. Time profile of the photoxidation of sulfide with and without visible light.

10. References

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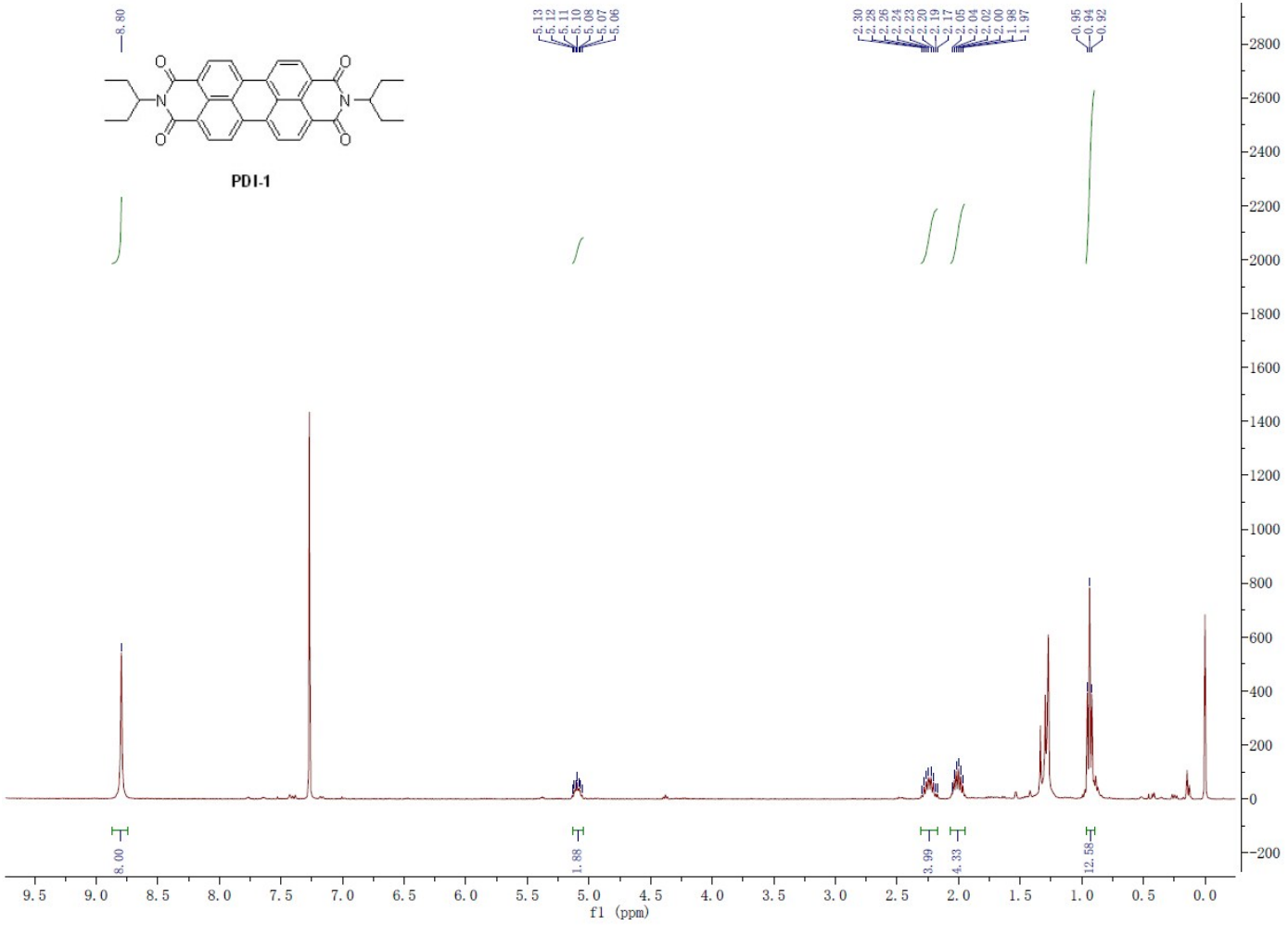
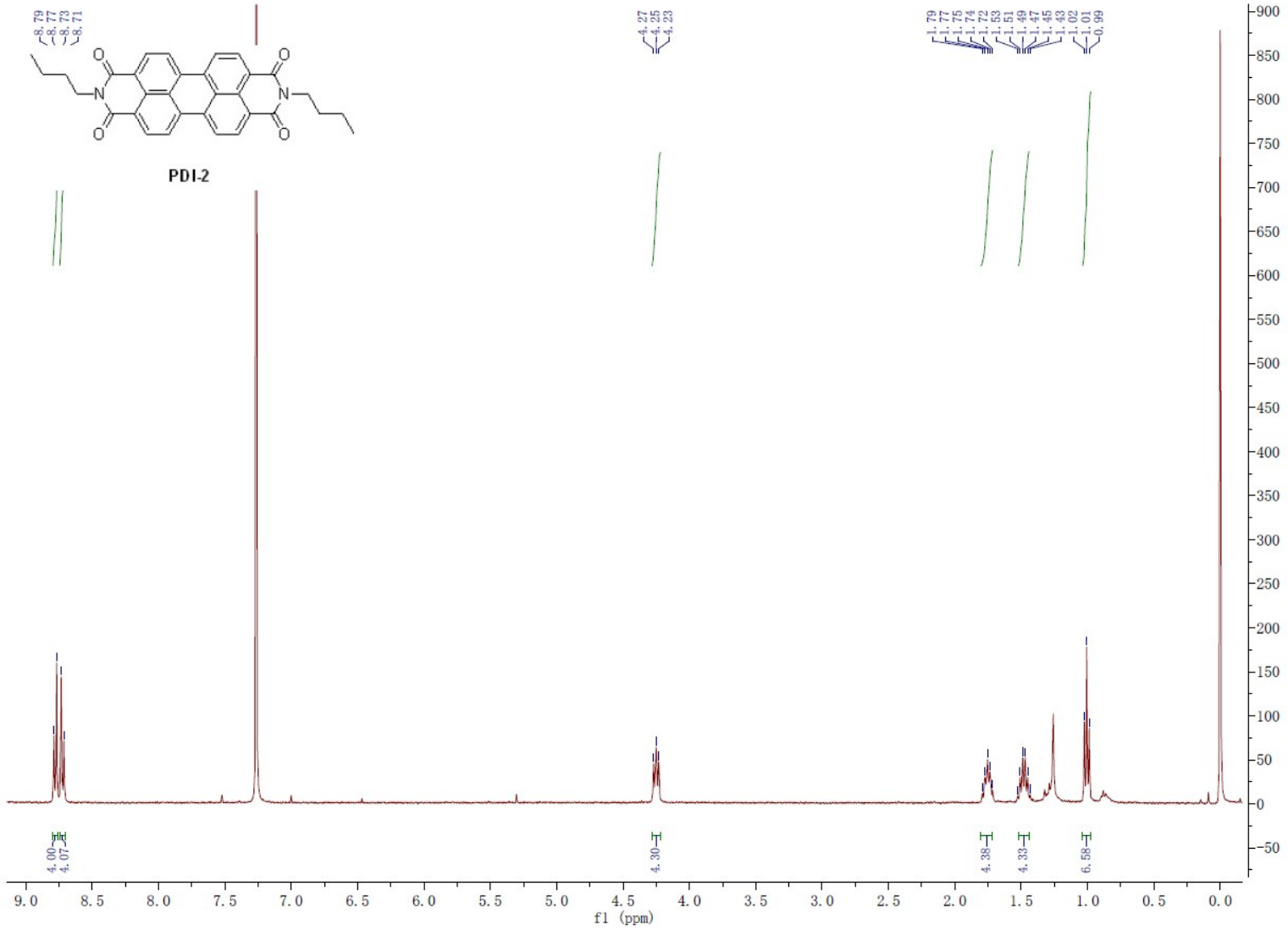
11. ^{1}H and ^{13}C spectra

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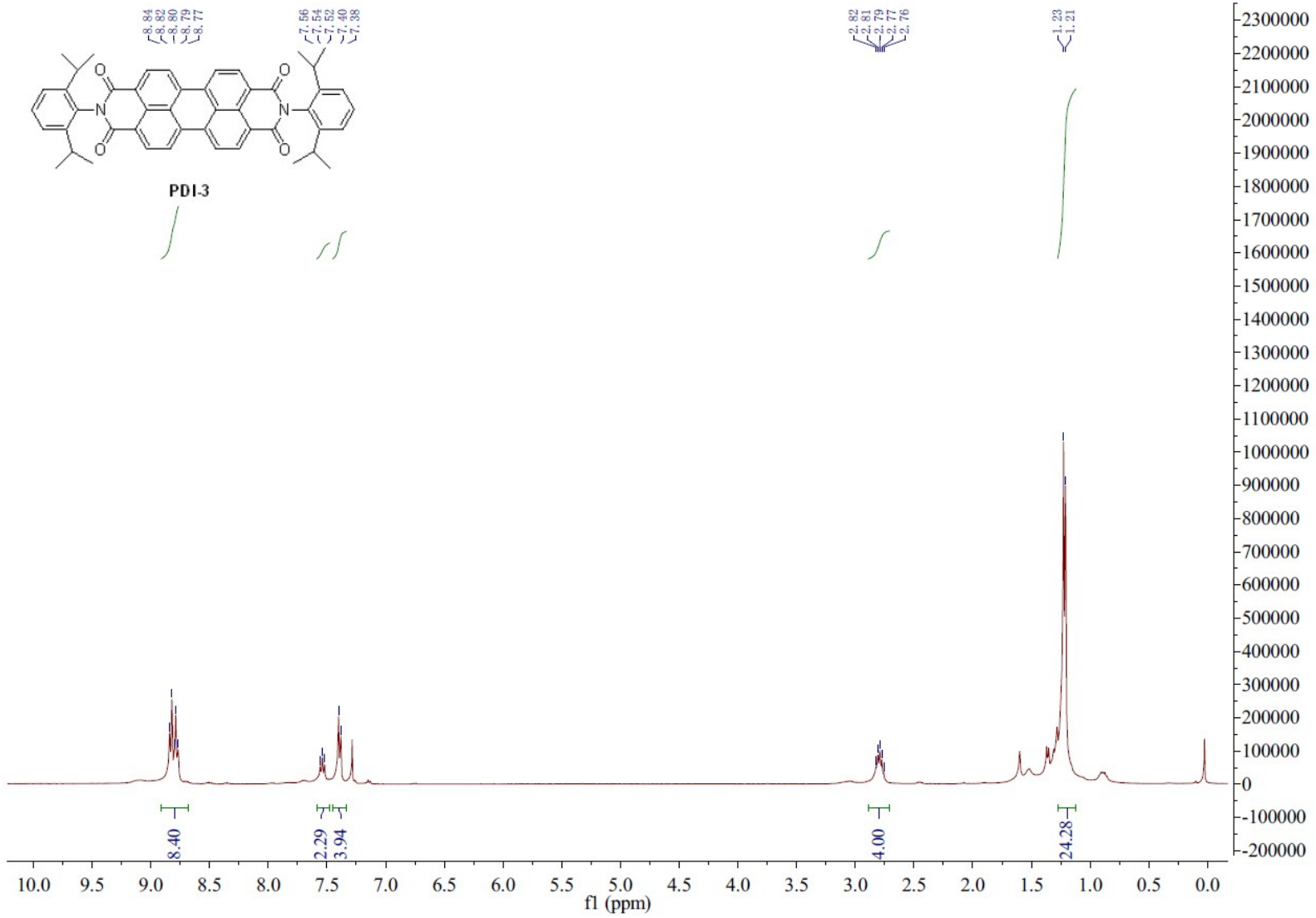
8.77
8.73
8.71
4.27
4.25
4.23
1.79
1.77
1.75
1.74
1.72
1.53
1.51
1.49
1.47
1.45
1.43
1.02
1.01
0.99
PDI-2
4.00
4.07
4.30
4.38
4.33
6.58
f1 (ppm)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8.82
8.80
8.79
8.77
7.56
7.54
7.52
7.40
7.38
2.82
2.81
2.79
2.77
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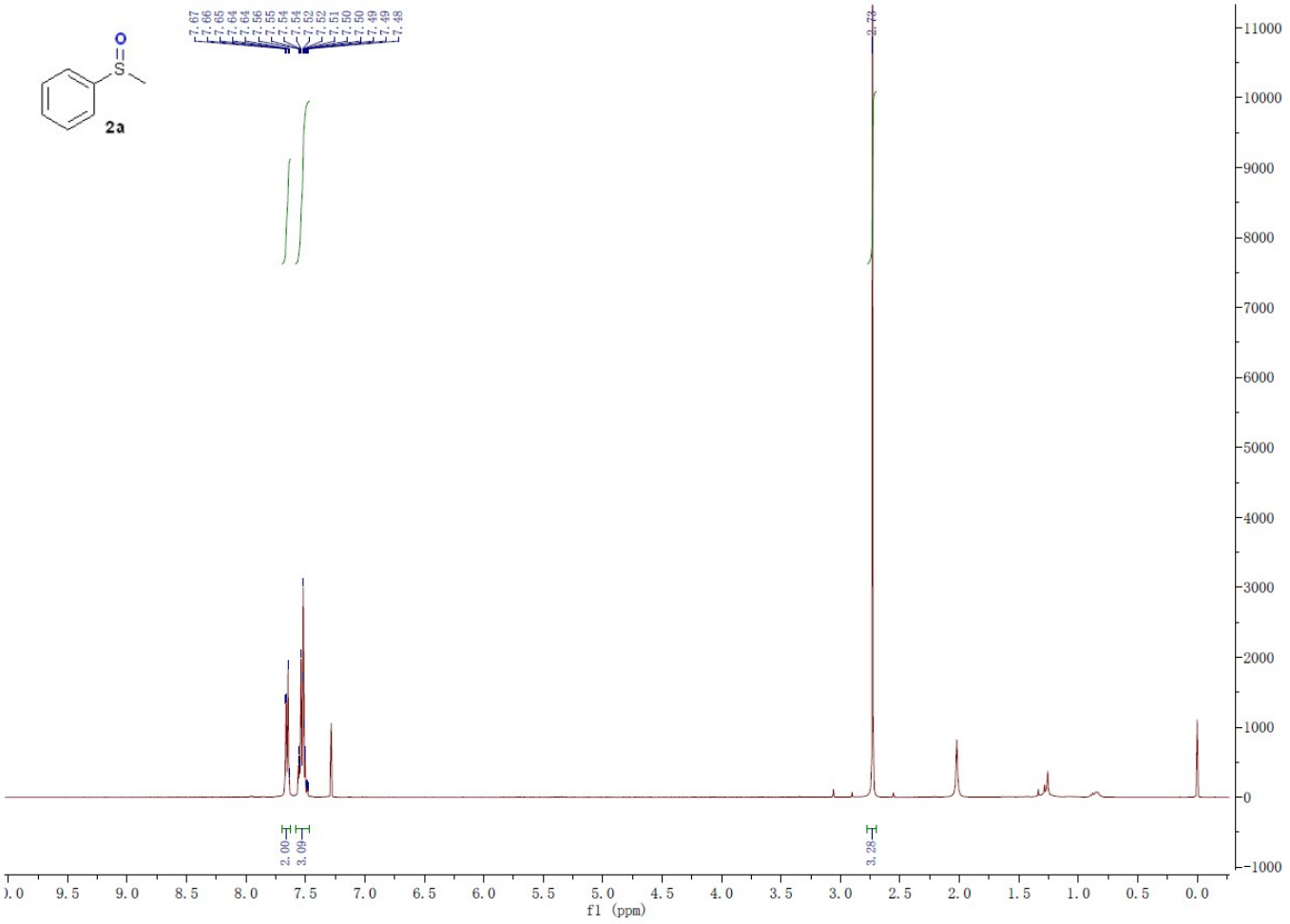
1.23
1.21
PDI-3
8.40
2.29
3.94
4.00
24.28
fl (ppm)


2a
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7.65
7.64
7.64
7.56
7.55
7.54
7.54
7.52
7.52
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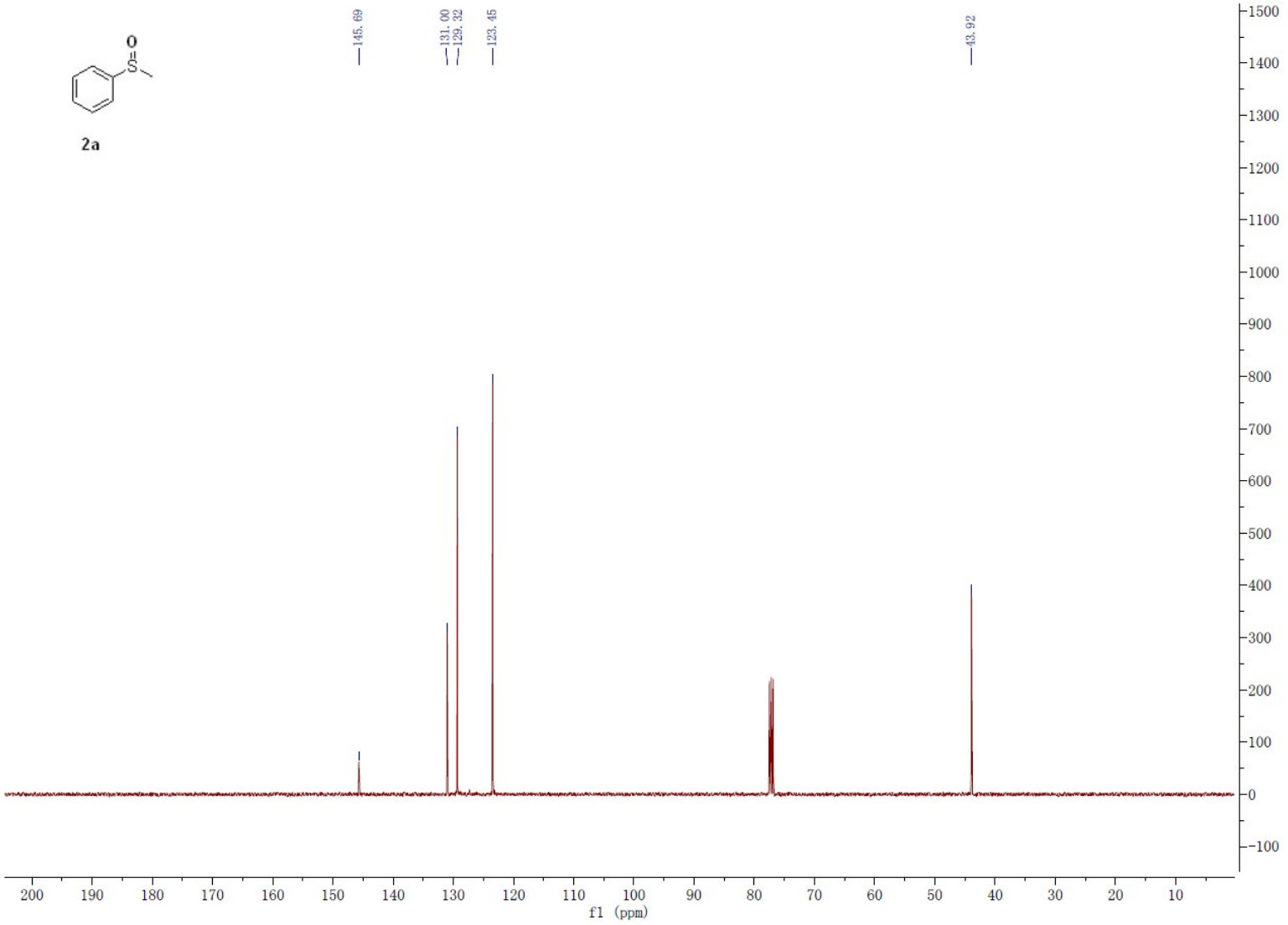
2.73
2.00
3.09
3.28
f1 (ppm)


2a
145.69
131.00
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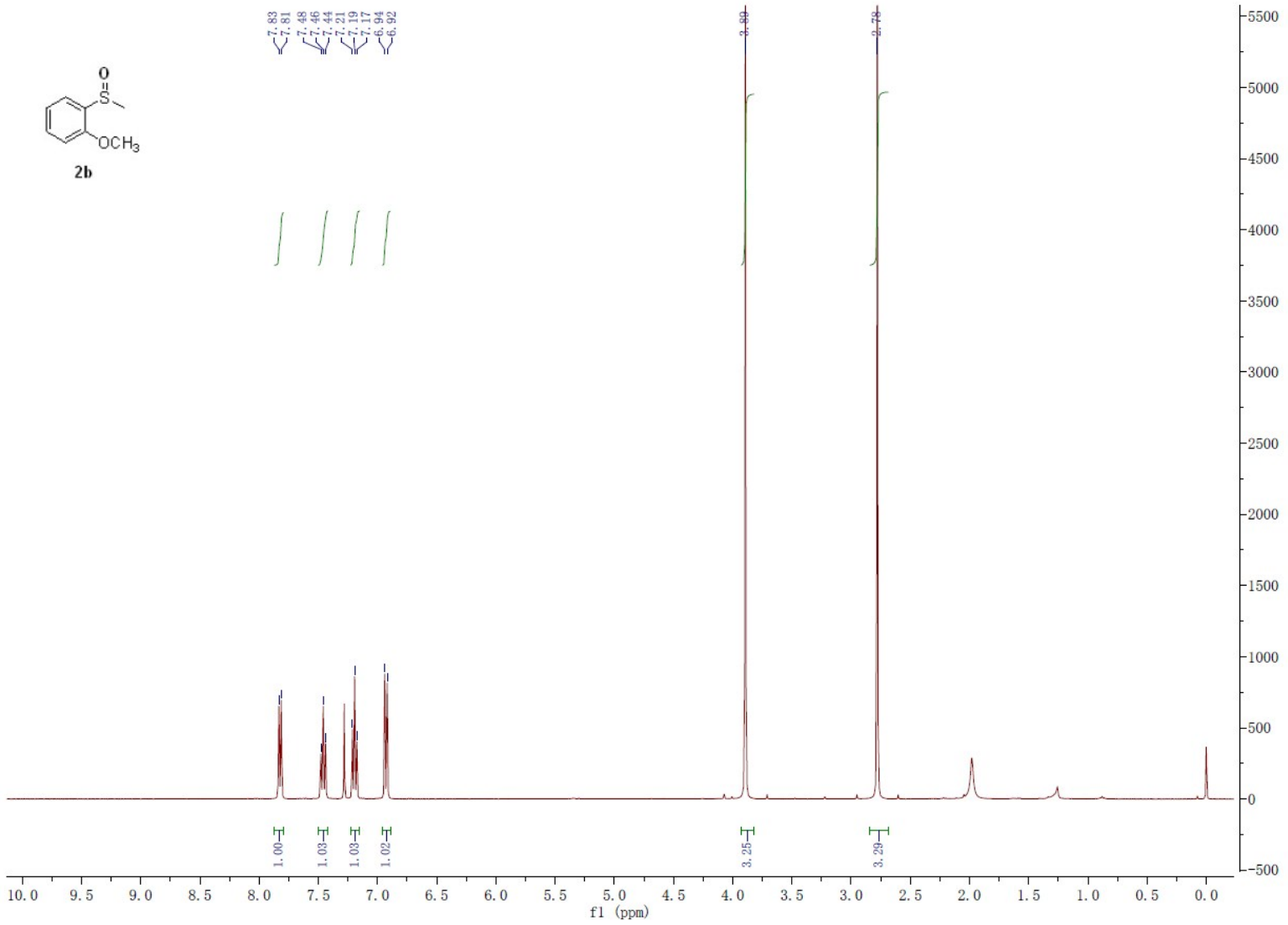
43.92
f1 (ppm)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7.44
7.21
7.19
7.17
6.94
6.92
3.89
2.78
O
S
OCH3
2b
1.00
1.03
1.03
1.02
3.25
3.29
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
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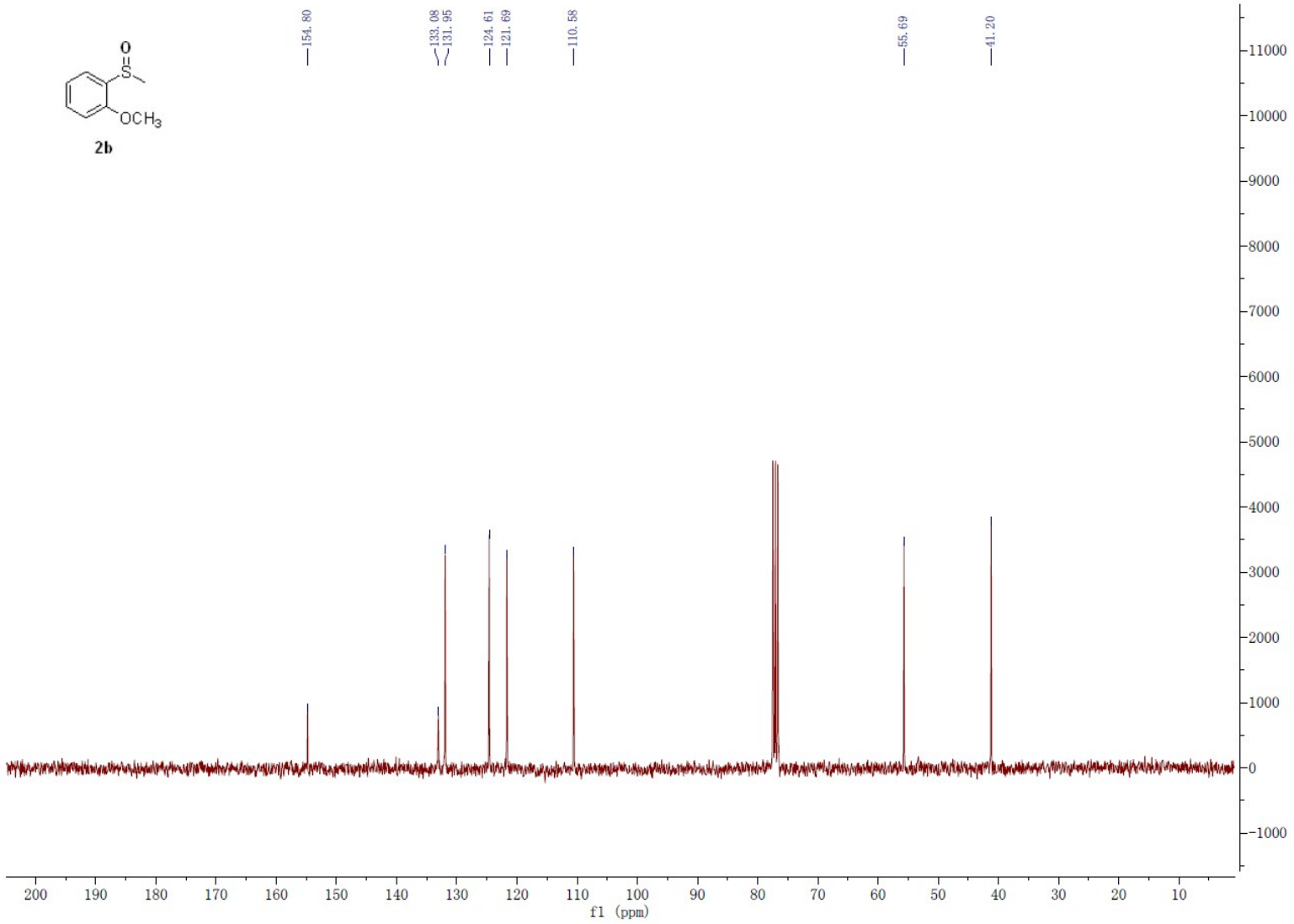
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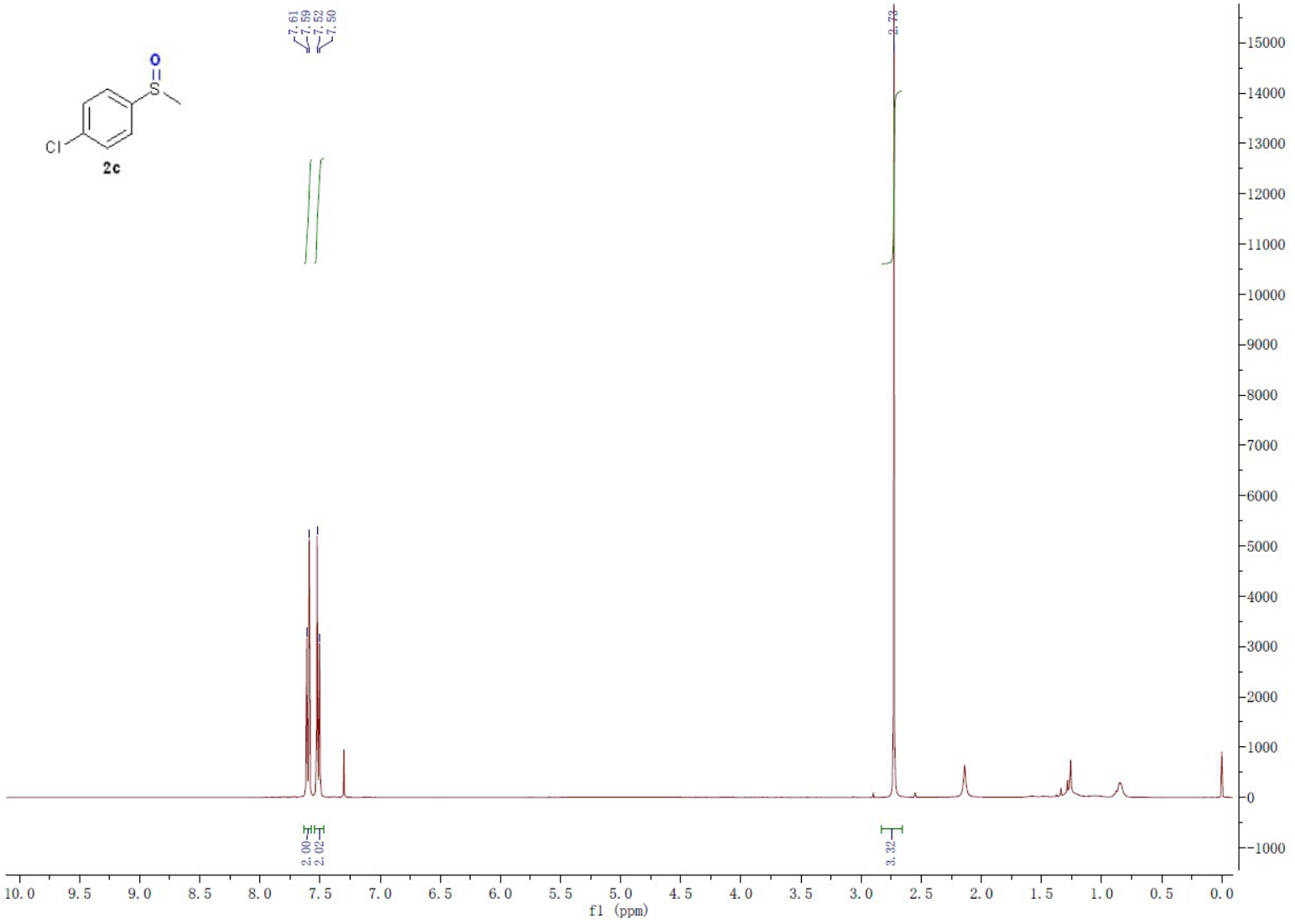
121.69
110.58
55.69
41.20
OCH3
2b
f1 (ppm)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7.59
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7.50
2.73
O
S
Cl
2c
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14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
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
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3.5
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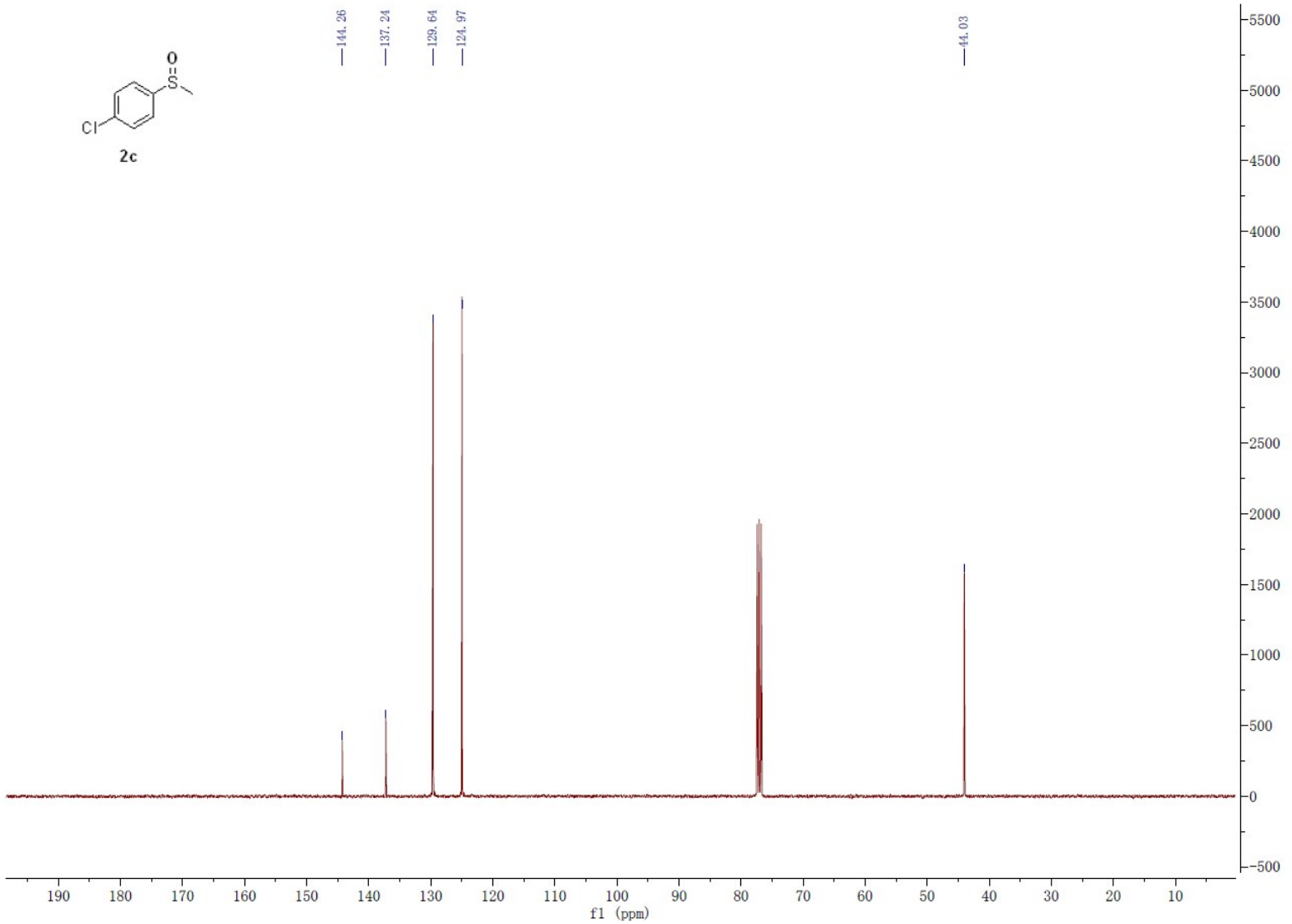
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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44.03
O
S
Cl
2c
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
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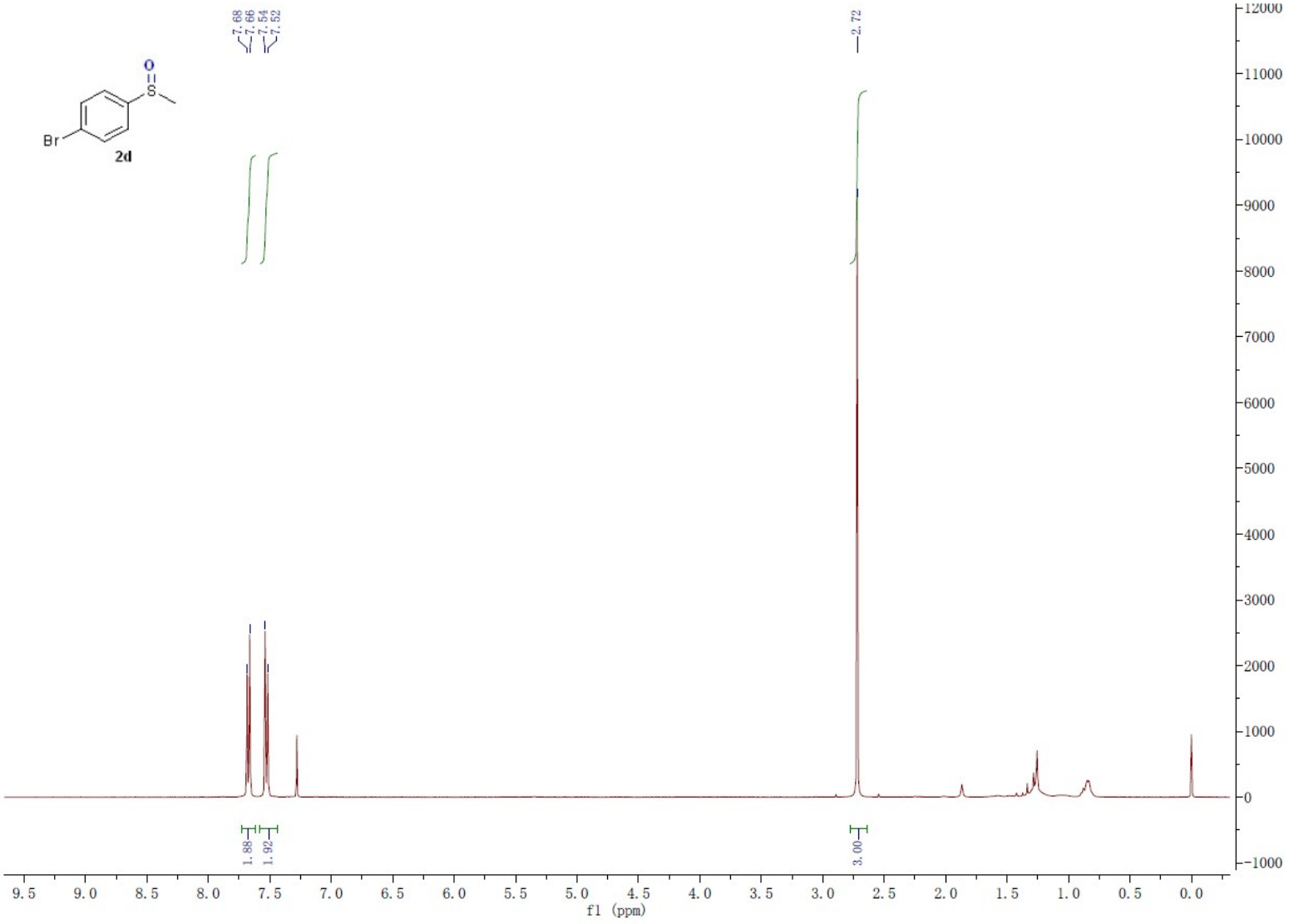
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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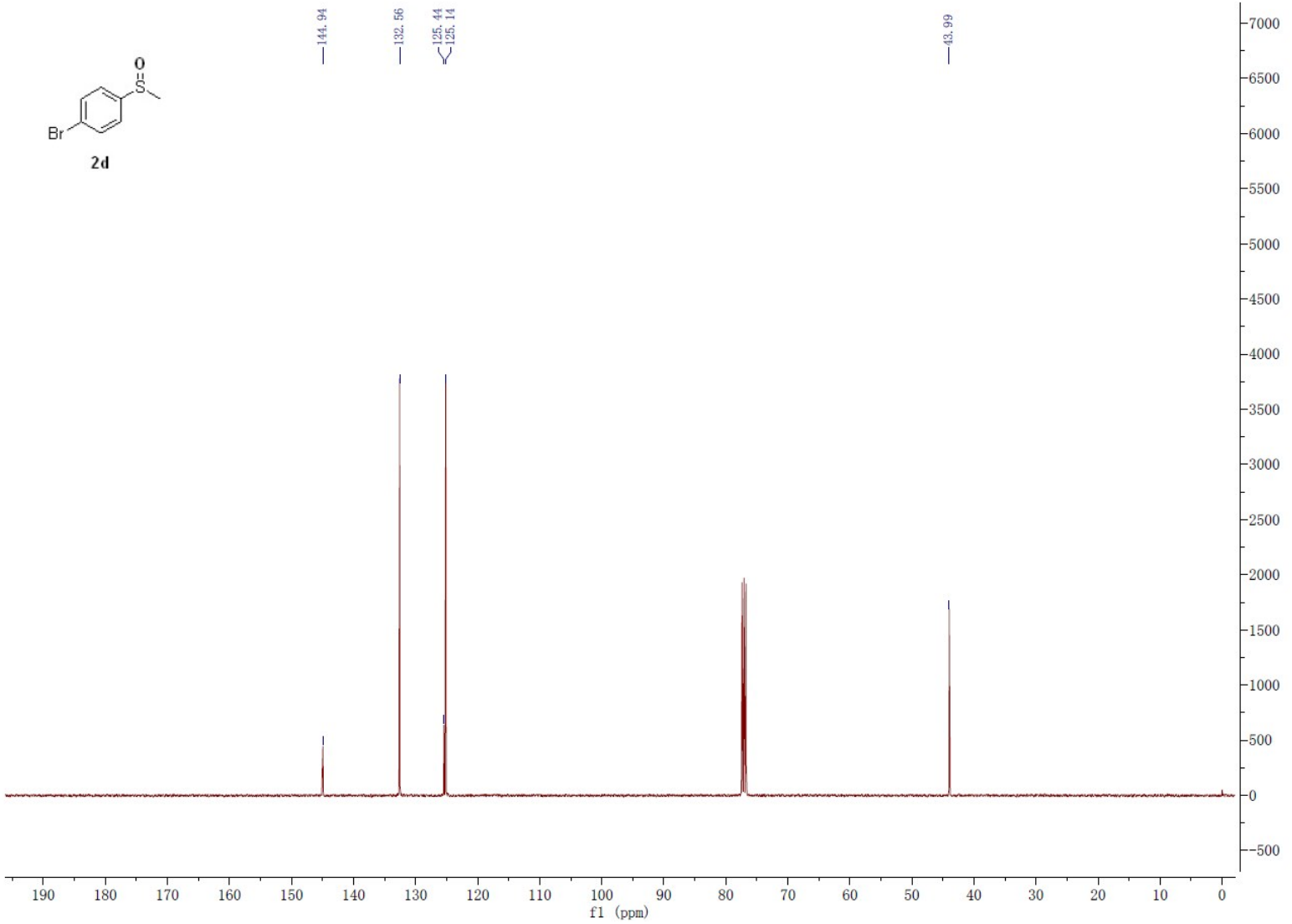
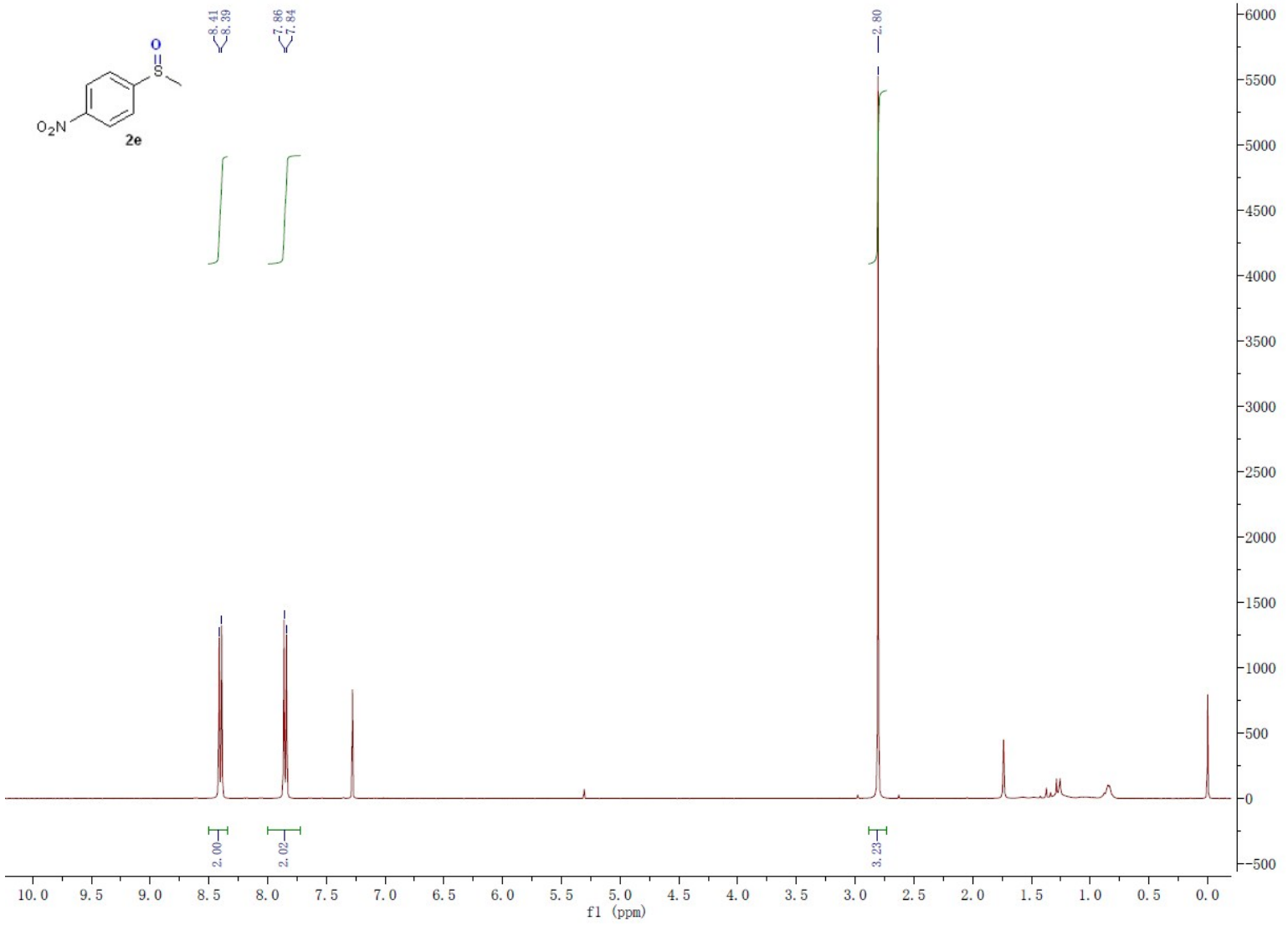
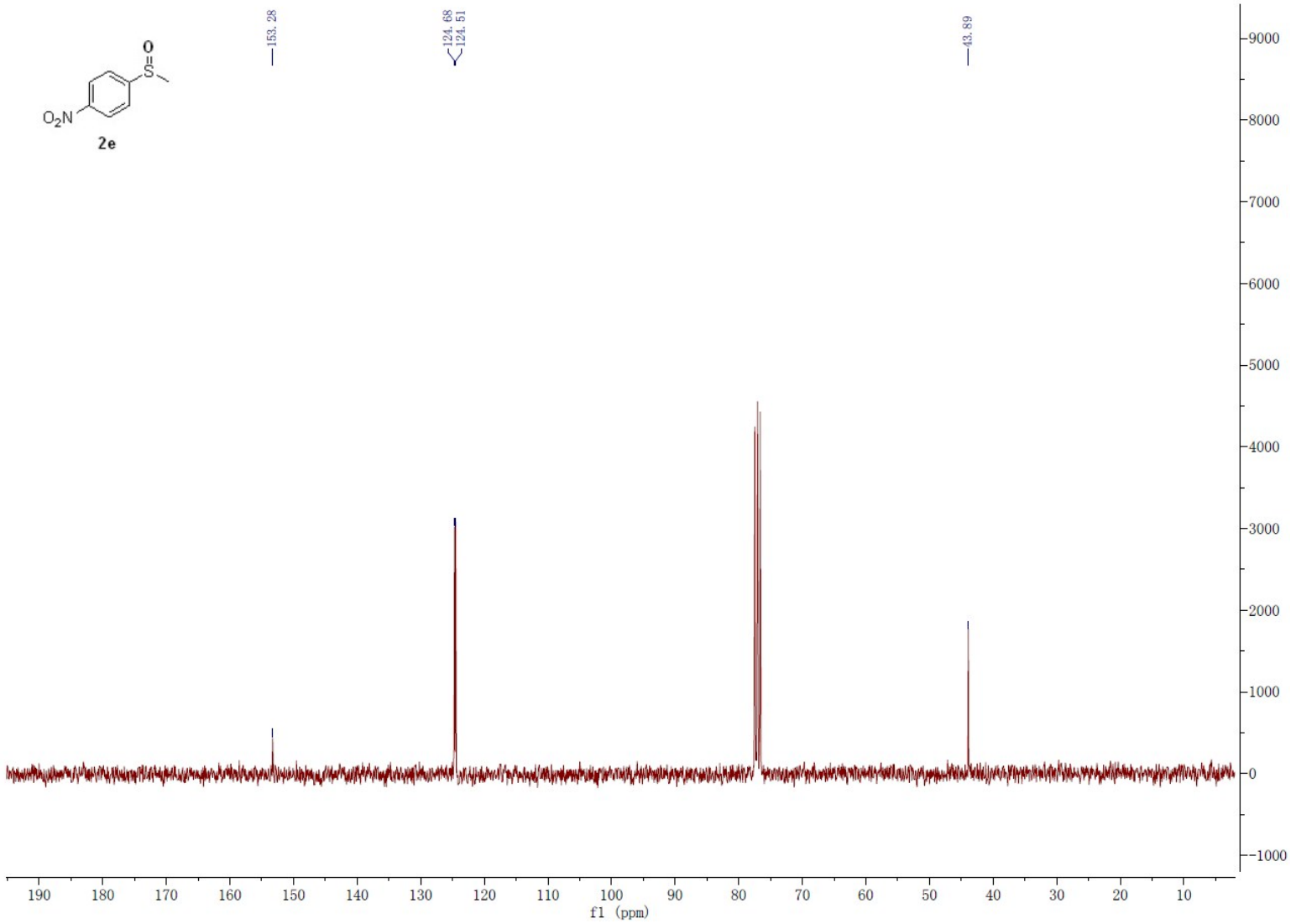
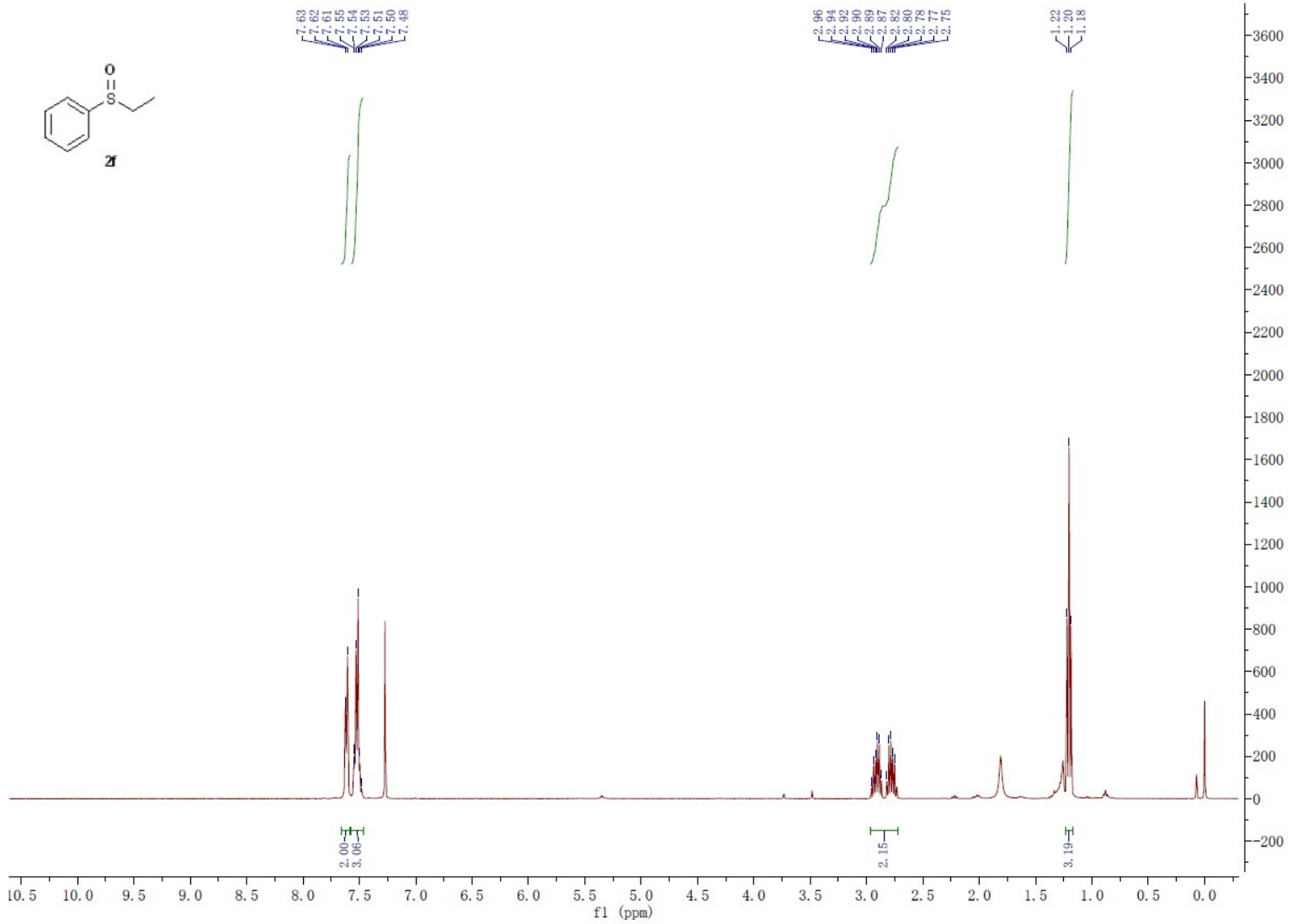
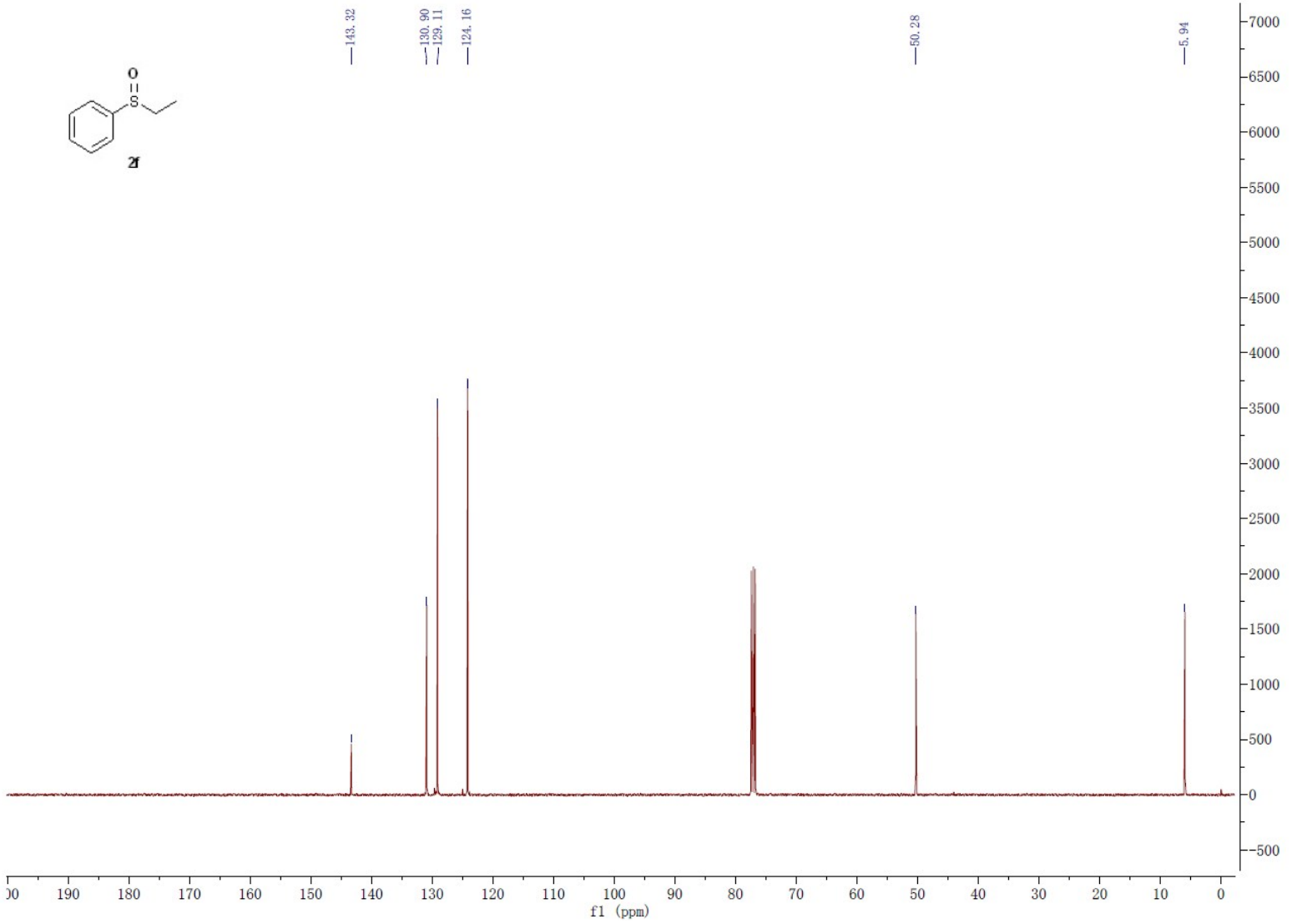
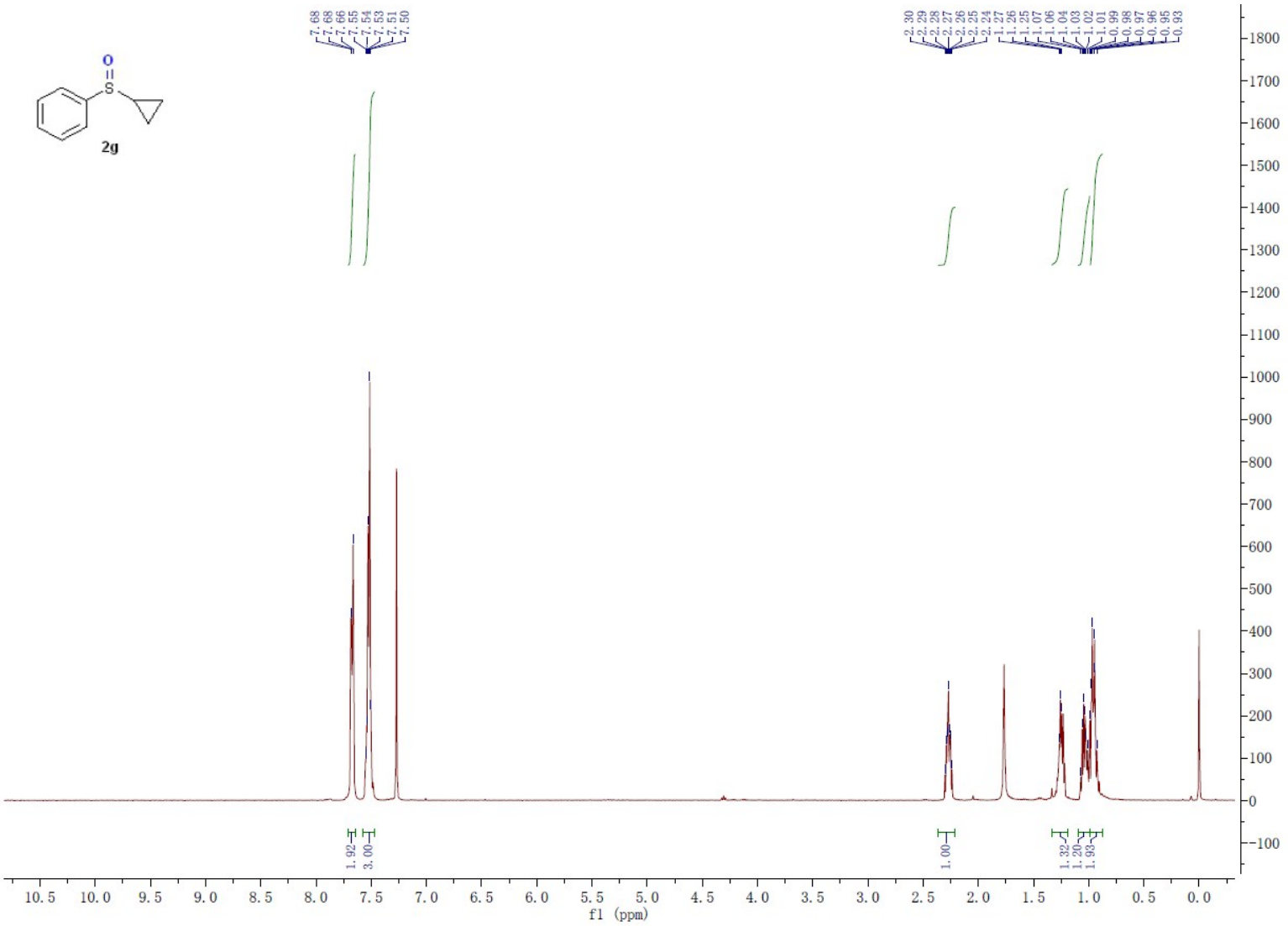

144.94
132.56
125.44
125.14
43.99
Br
O
S
2d
f1 (ppm)

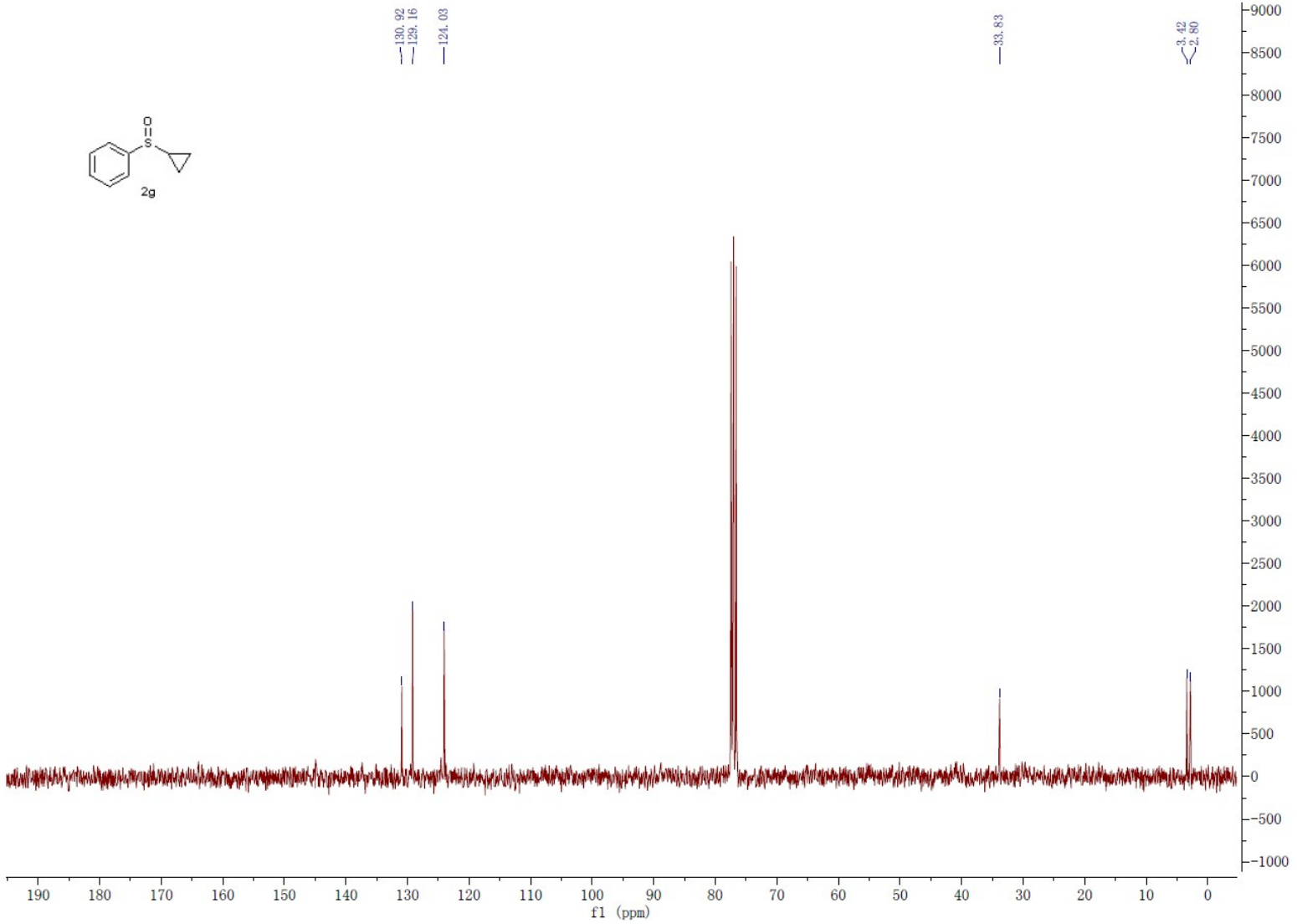

8.41
8.39
7.86
7.84
2.80
O
S
O2N
2e
2.00
2.02
3.23
f1 (ppm)

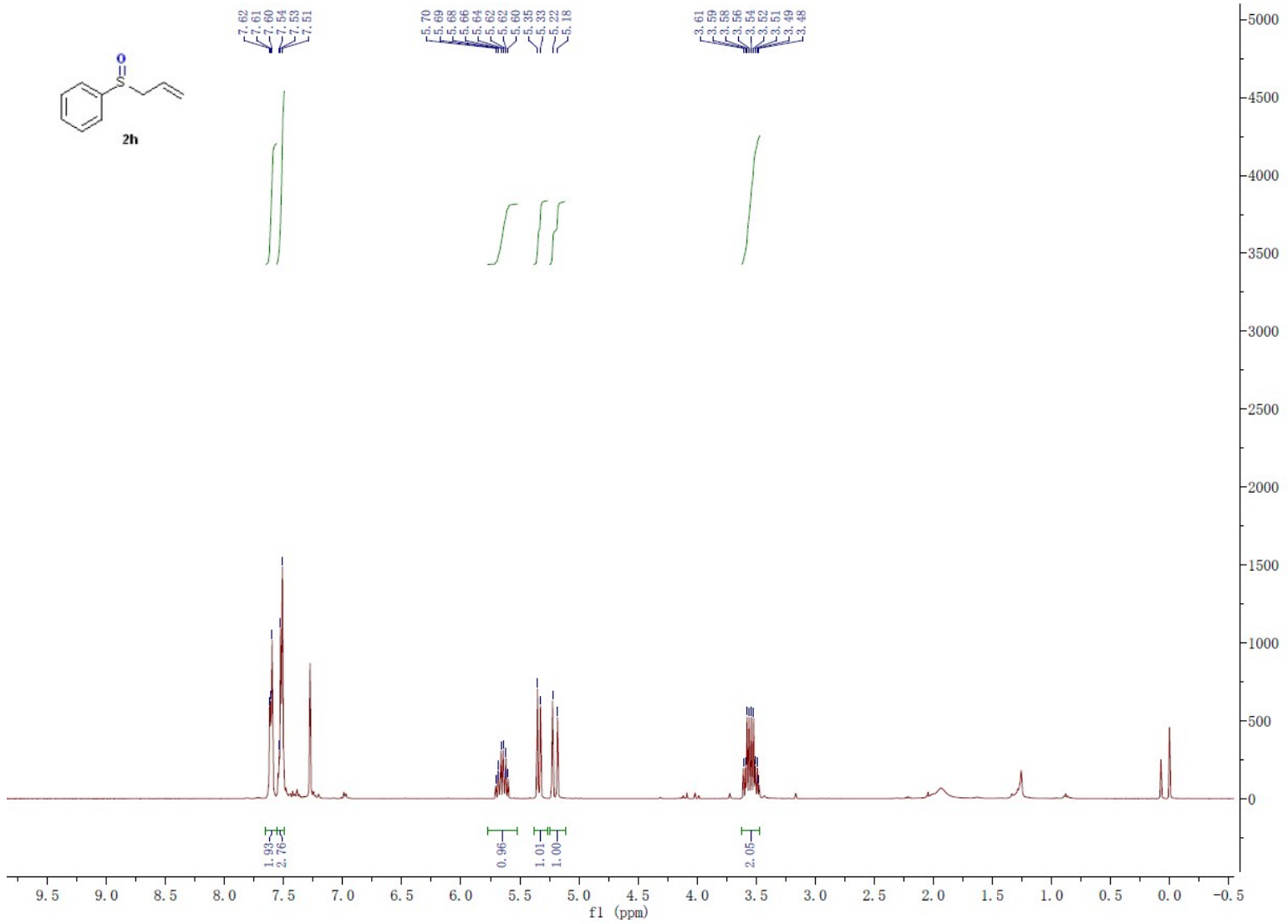

153.28
124.68
124.51
43.89
O
S
O2N
2e
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

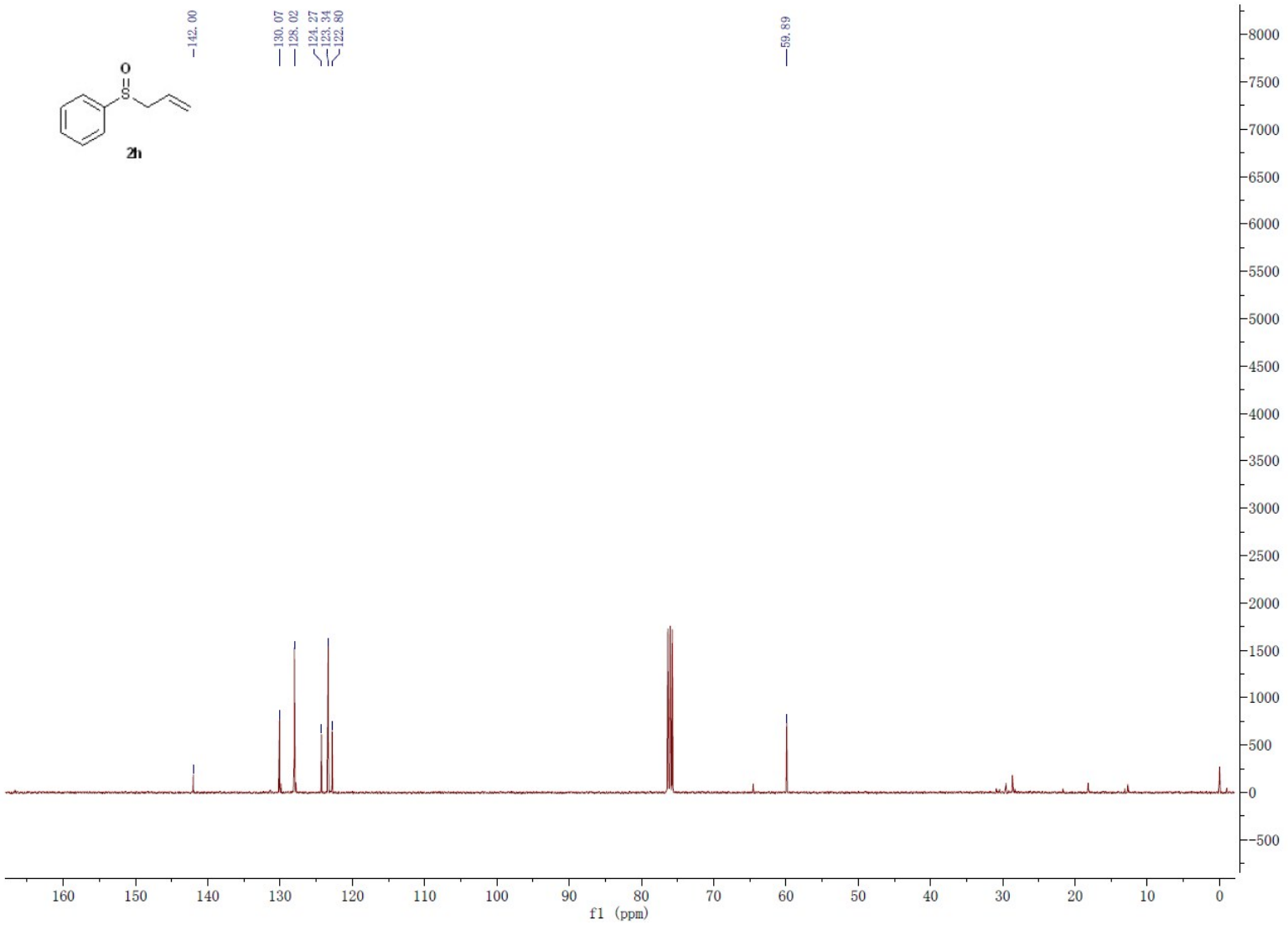

7.63
7.62
7.61
7.55
7.54
7.53
7.51
7.50
7.48
2.96
2.94
2.92
2.90
2.89
2.87
2.82
2.80
2.78
2.77
2.75
1.22
1.20
1.18
2f
2.00
3.06
2.15
3.19
f1 (ppm)

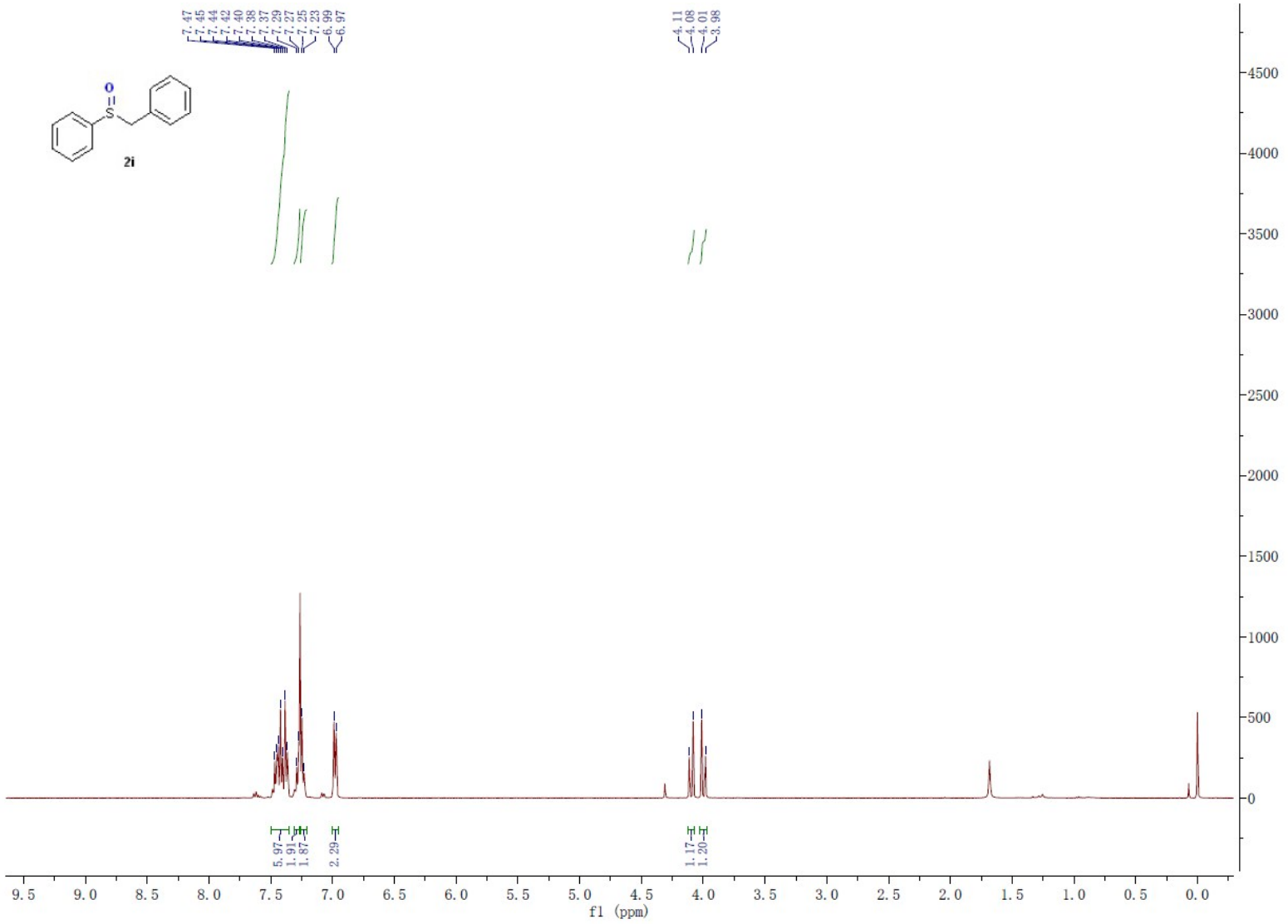

143.32
130.90
129.11
124.16
50.28
5.94
O
S
2f
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

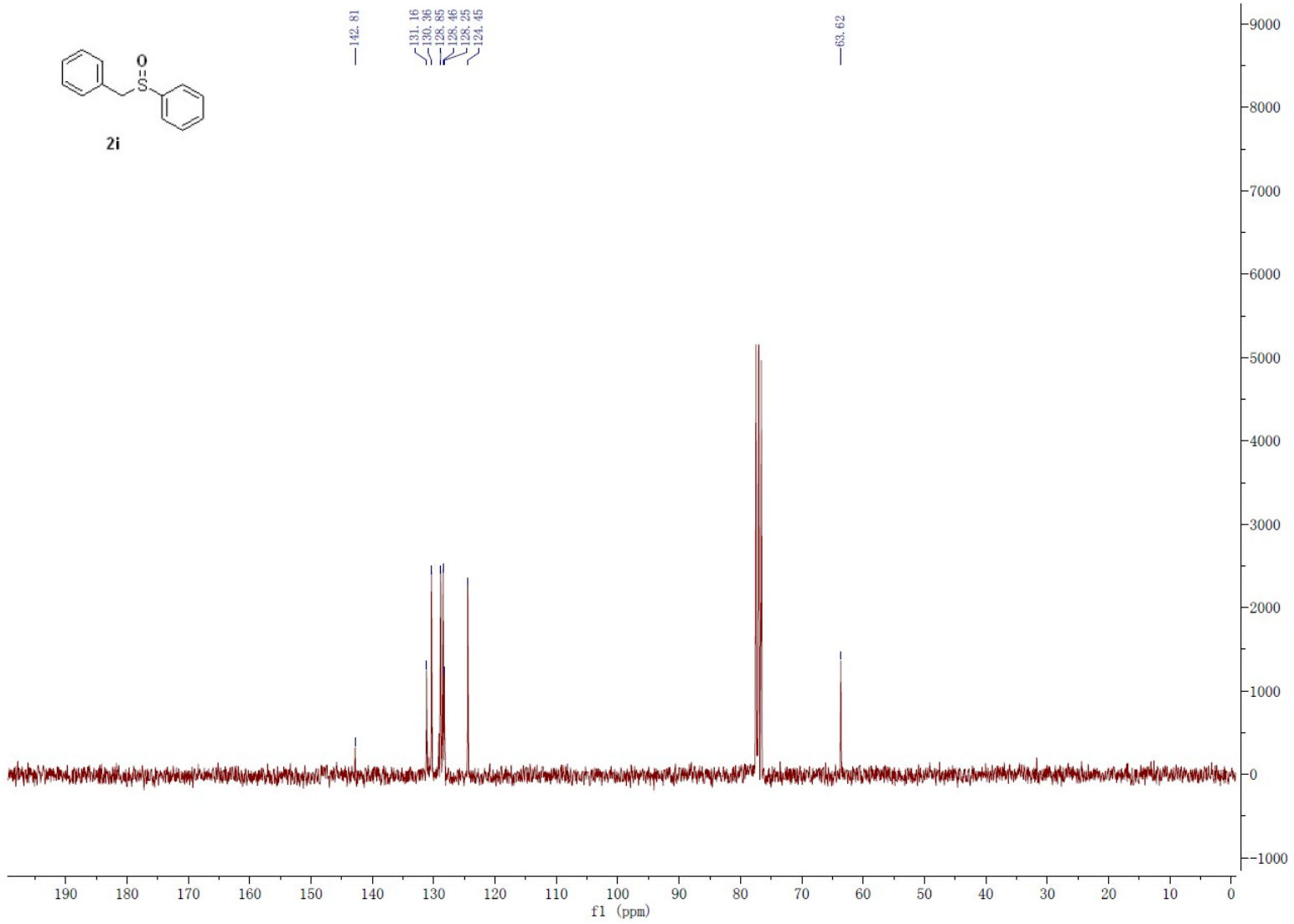

2g
7.68
7.68
7.66
7.55
7.54
7.53
7.51
7.50
2.30
2.29
2.28
2.27
2.26
2.25
2.24
1.27
1.26
1.25
1.07
1.06
1.04
1.03
1.02
1.01
0.99
0.98
0.97
0.96
0.95
0.93
1.92
3.00
1.00
1.32
1.20
1.93
f1 (ppm)

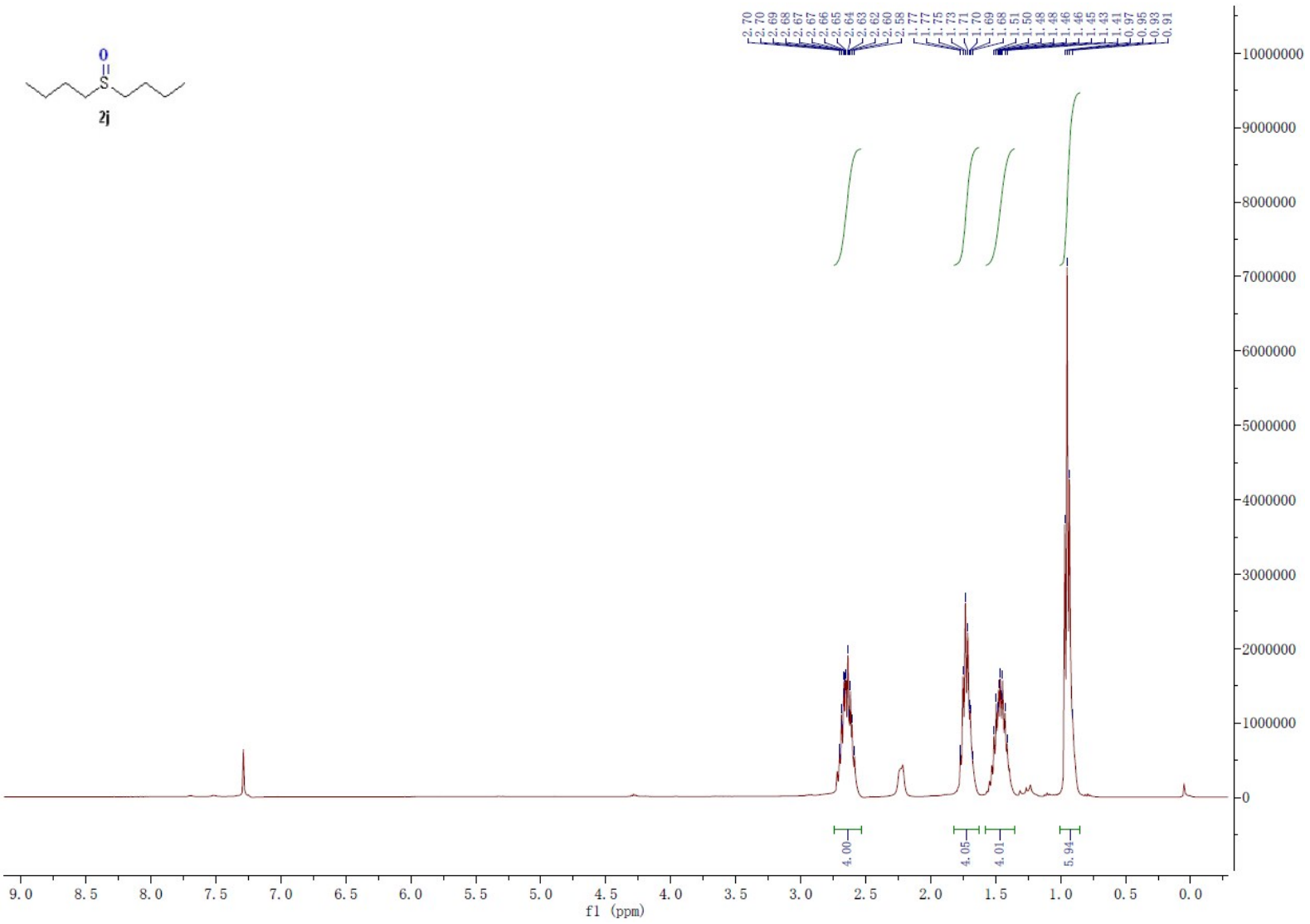

130.92
129.16
124.03
33.83
3.42
2.80
2g
f1 (ppm)

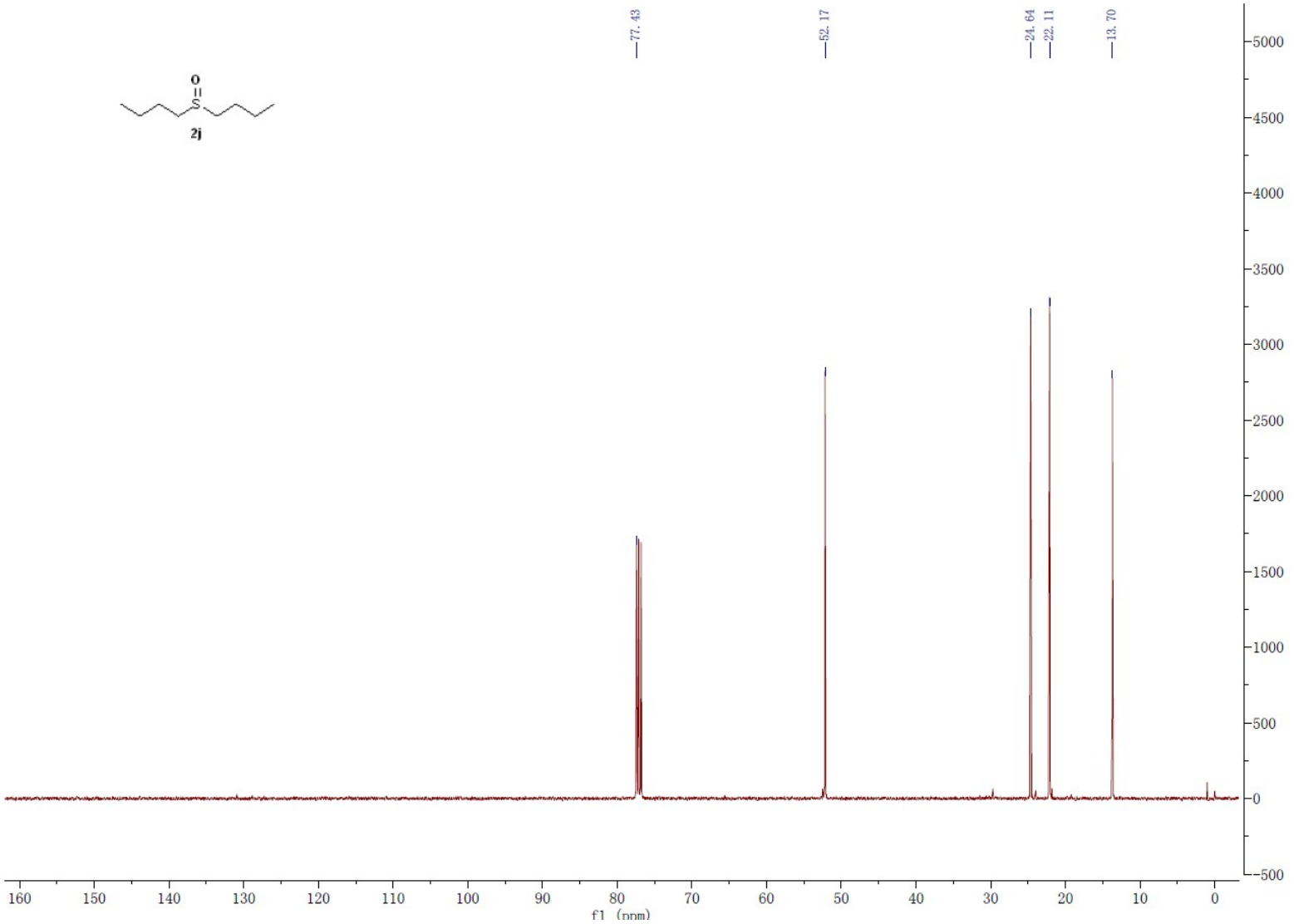

2h
7.62
7.61
7.60
7.54
7.53
7.51
5.70
5.69
5.68
5.66
5.64
5.62
5.62
5.60
5.35
5.33
5.22
5.18
3.61
3.59
3.58
3.56
3.54
3.52
3.51
3.49
3.48
1.93
2.76
0.96
1.01
1.00
2.05
f1 (ppm)

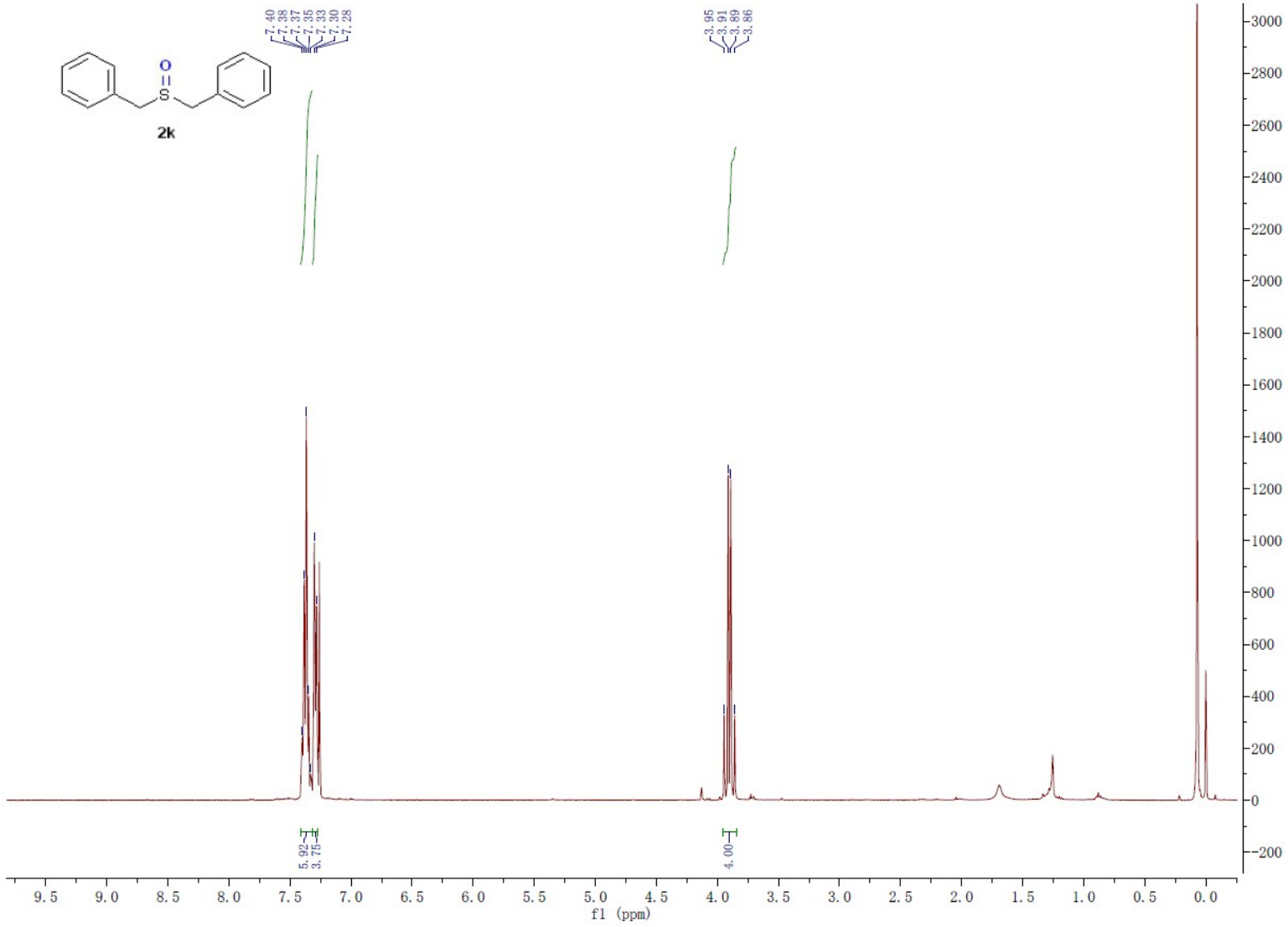

142.00
130.07
128.02
124.27
123.34
122.80
59.89
O
S
2h
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

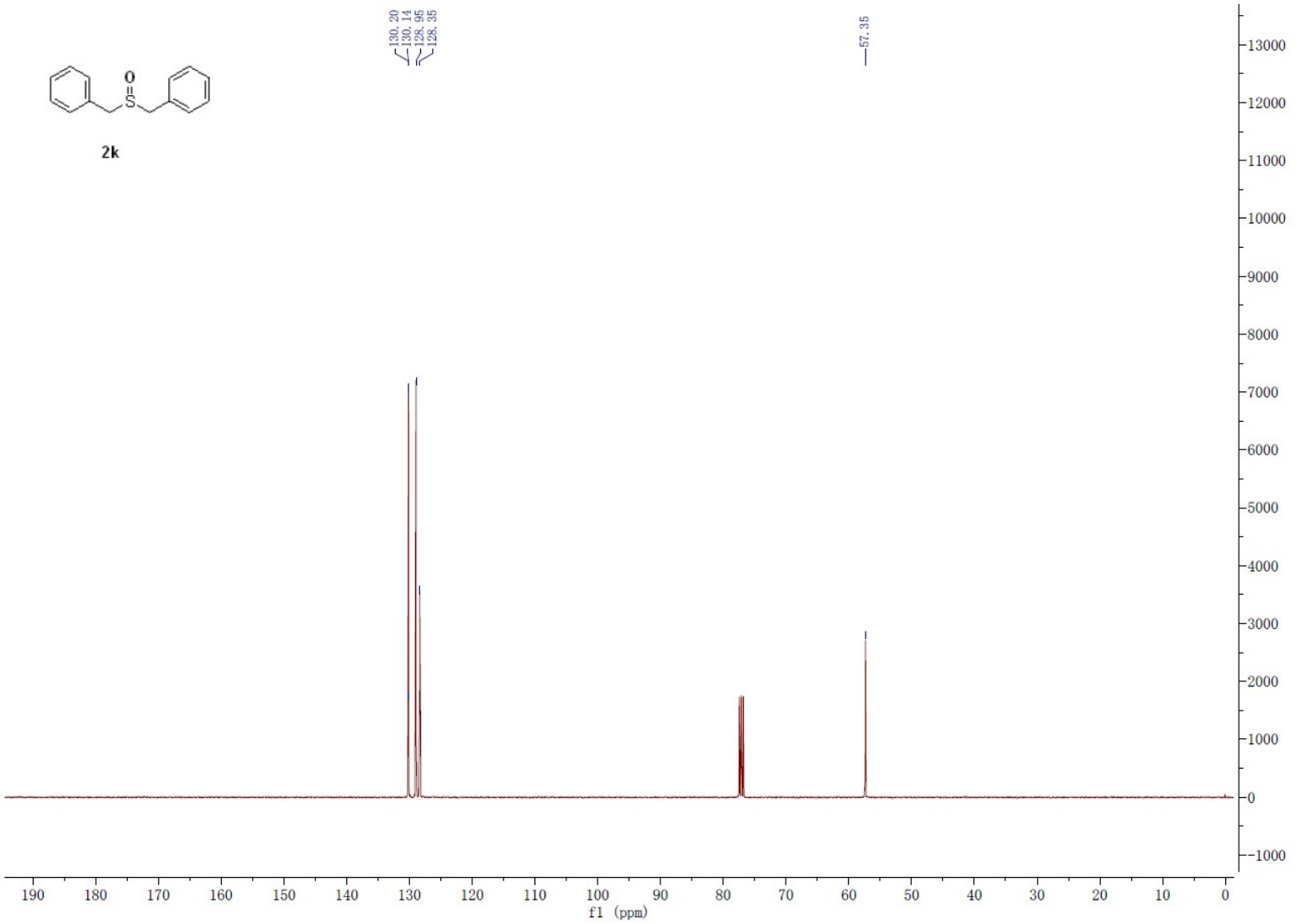

7.47
7.45
7.44
7.42
7.40
7.38
7.37
7.29
7.27
7.25
7.23
6.99
6.97
4.11
4.08
4.01
3.98
O
S
2i
4500
4000
3500
3000
2500
2000
1500
1000
500
0
5.97
1.91
1.87
2.29
1.17
1.20
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

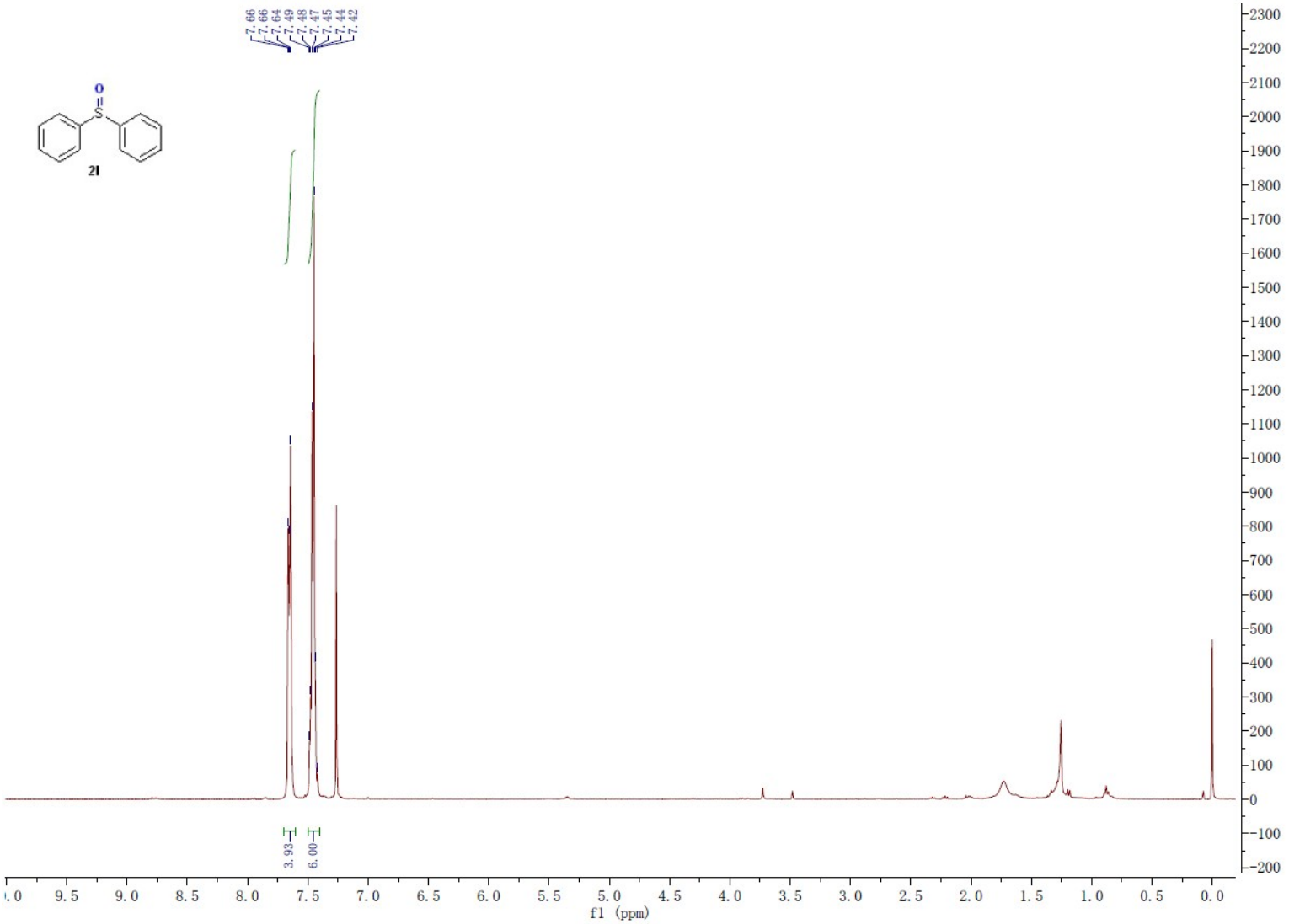

142.81
131.16
130.36
128.85
128.46
128.25
124.45
63.62
2i
f1 (ppm)

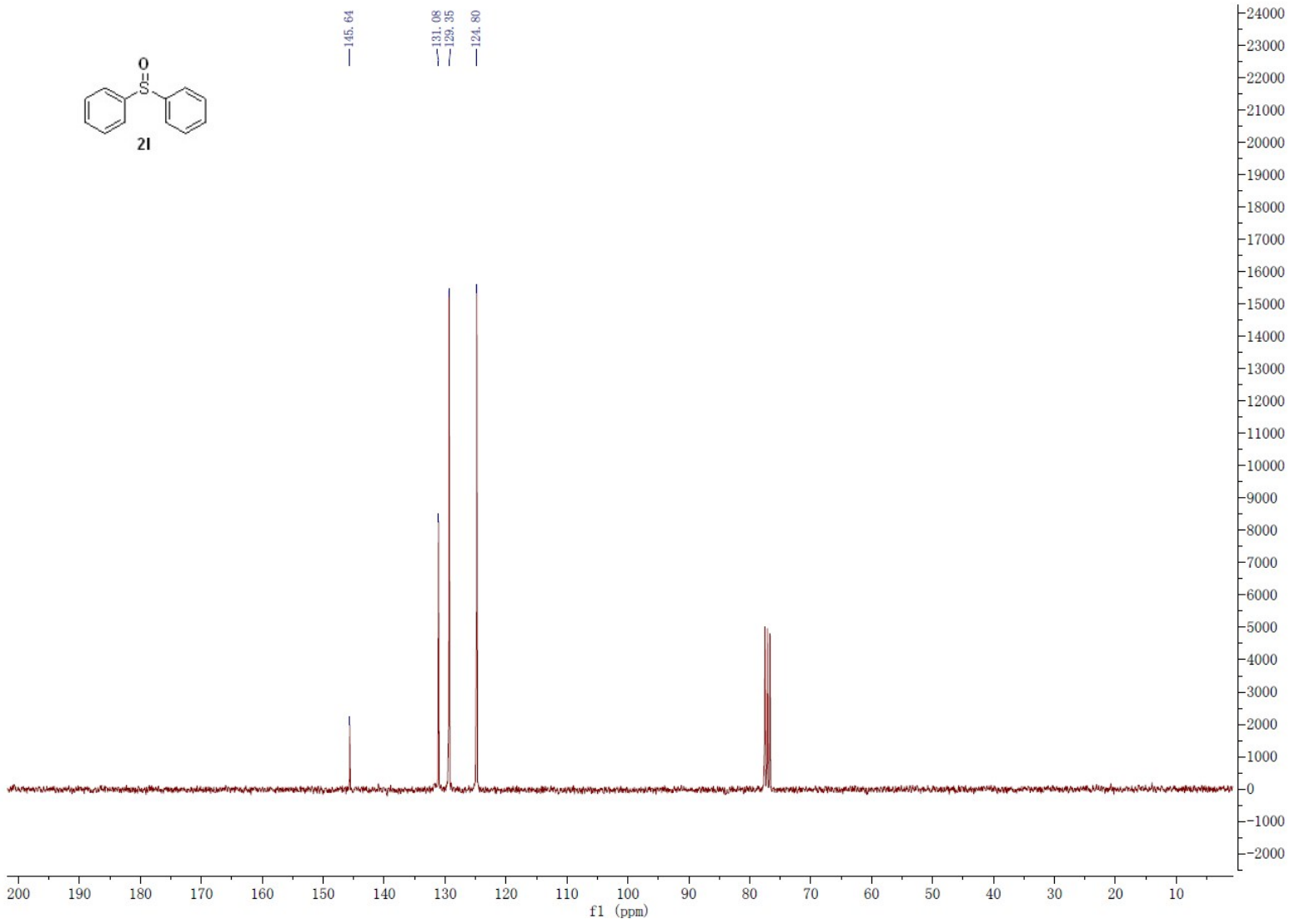

O
S
2j
2.70
2.70
2.69
2.68
2.67
2.67
2.66
2.65
2.64
2.63
2.62
2.60
2.58
1.77
1.77
1.75
1.73
1.71
1.70
1.69
1.68
1.51
1.50
1.48
1.48
1.46
1.46
1.45
1.43
1.41
0.97
0.95
0.93
0.91
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
4.00
4.05
4.01
5.94
9.0
8.5
8.0
7.5
7.0
6.5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

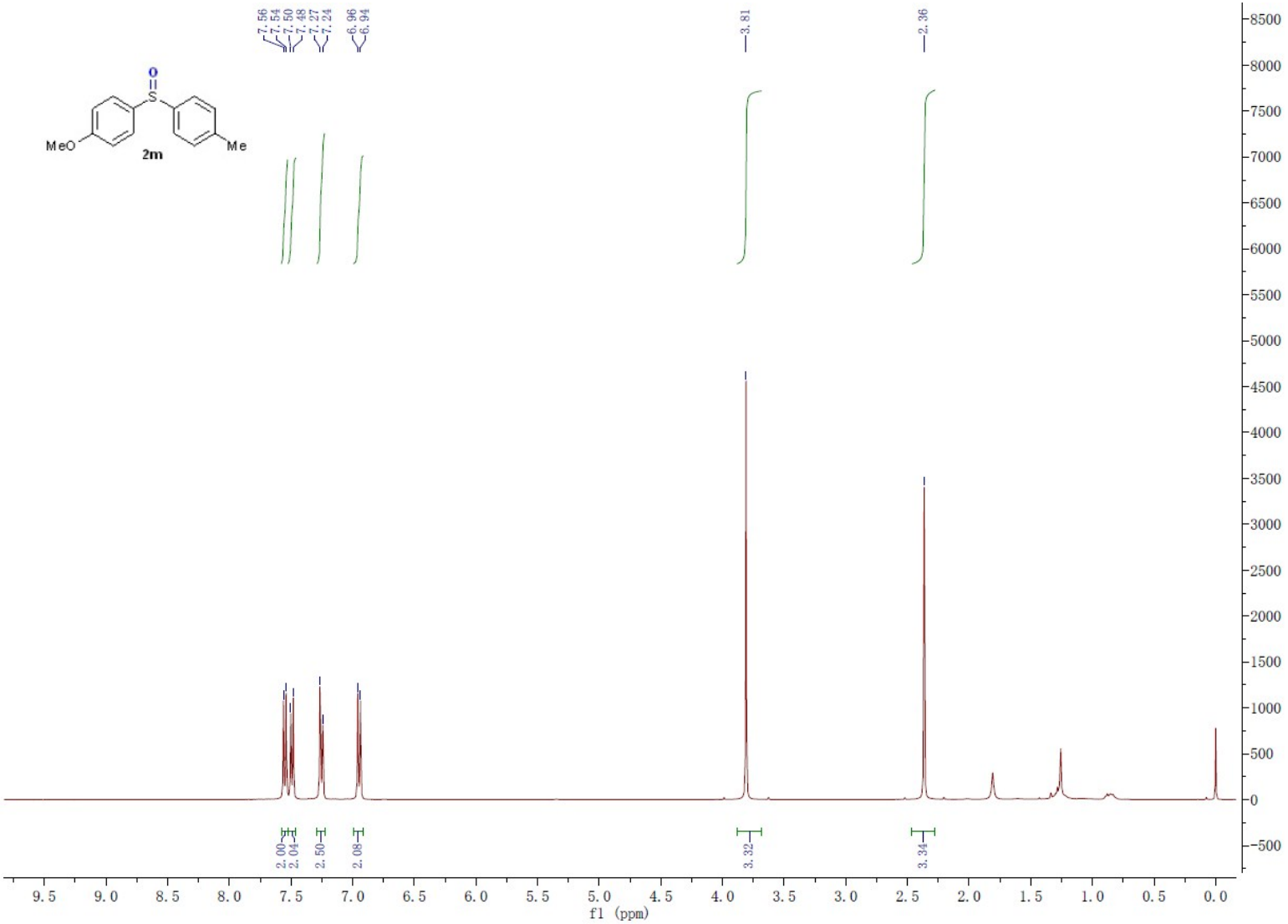

77.43
52.17
24.64
22.11
13.70
2j
f1 (ppm)

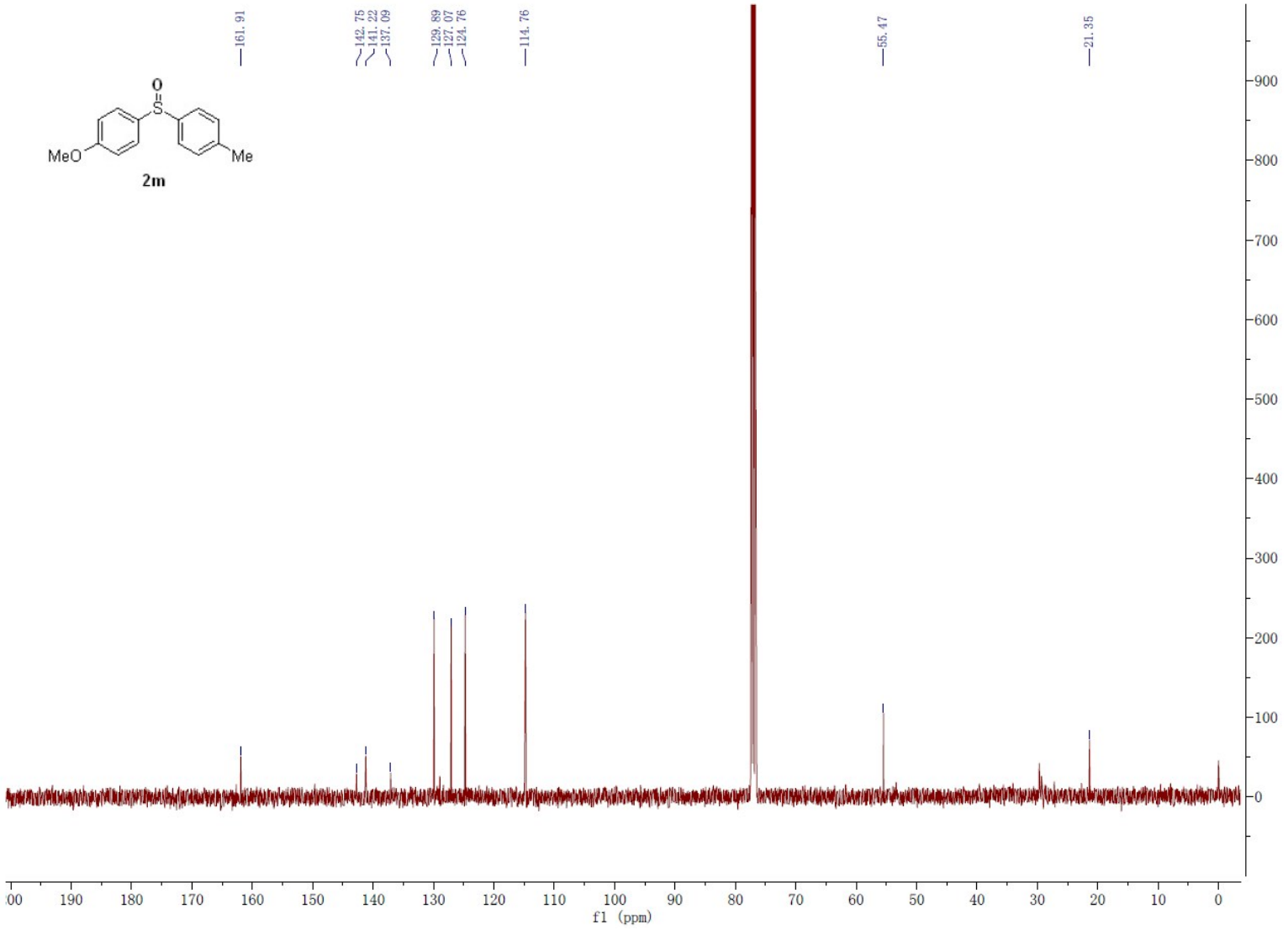

7.40
7.38
7.37
7.35
7.33
7.30
7.28
3.95
3.91
3.89
3.86
O
S
2k
5.92
3.75
4.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200

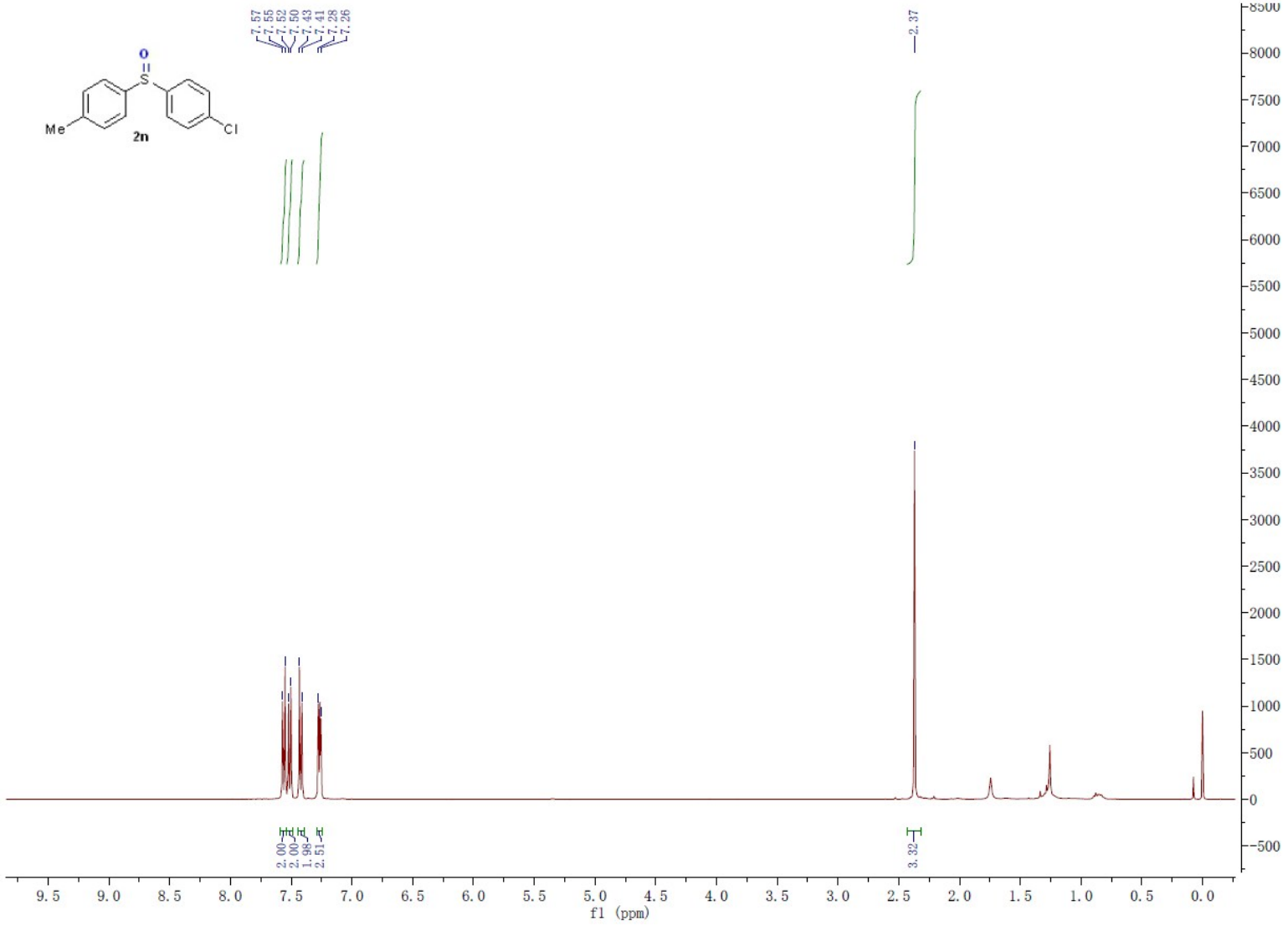

130.20
130.14
128.95
128.35
57.35
O
S
2k
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

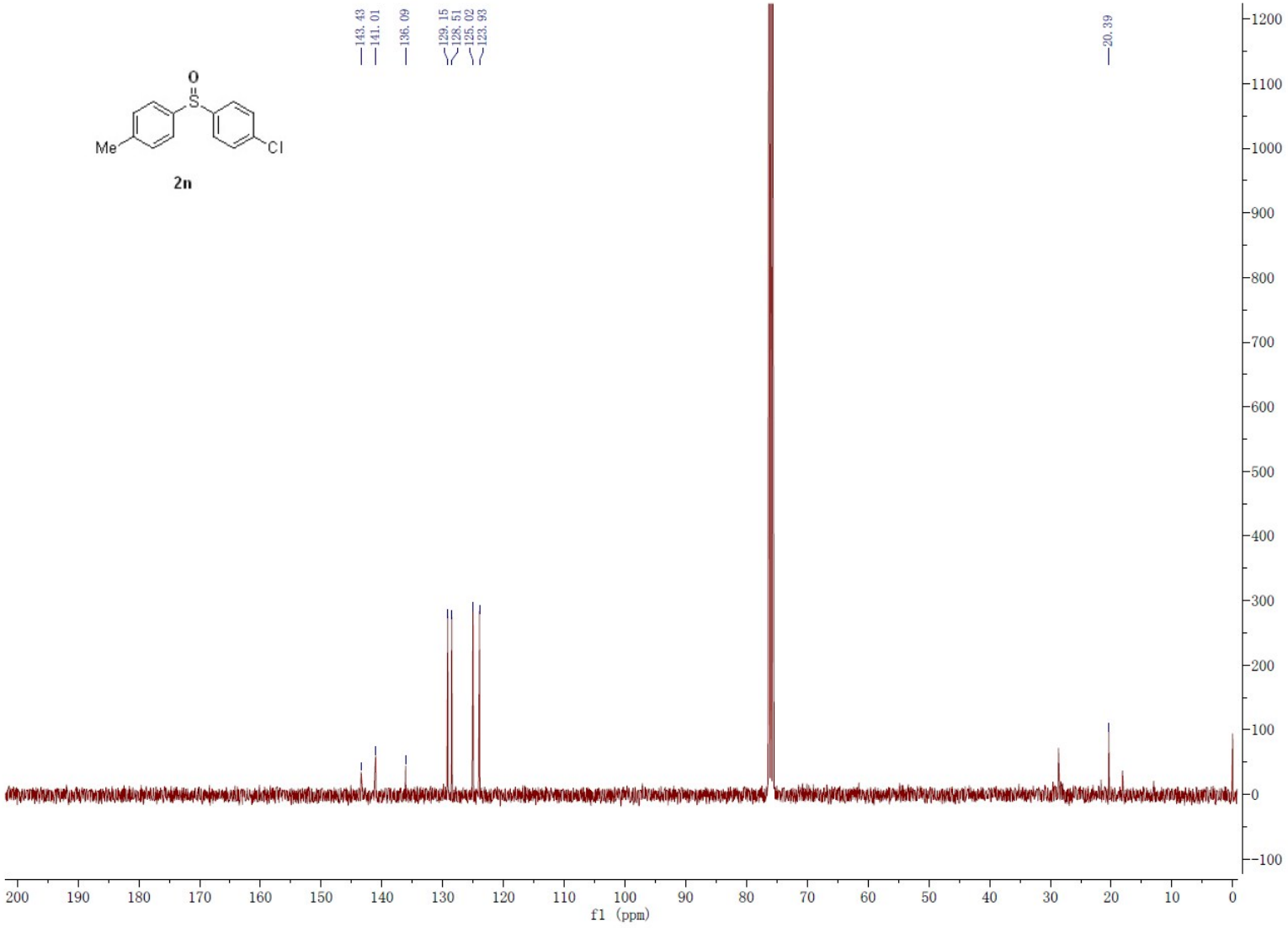

7.66
7.66
7.64
7.49
7.48
7.47
7.45
7.44
7.42
O
S
2l
3.93
6.00
f1 (ppm)

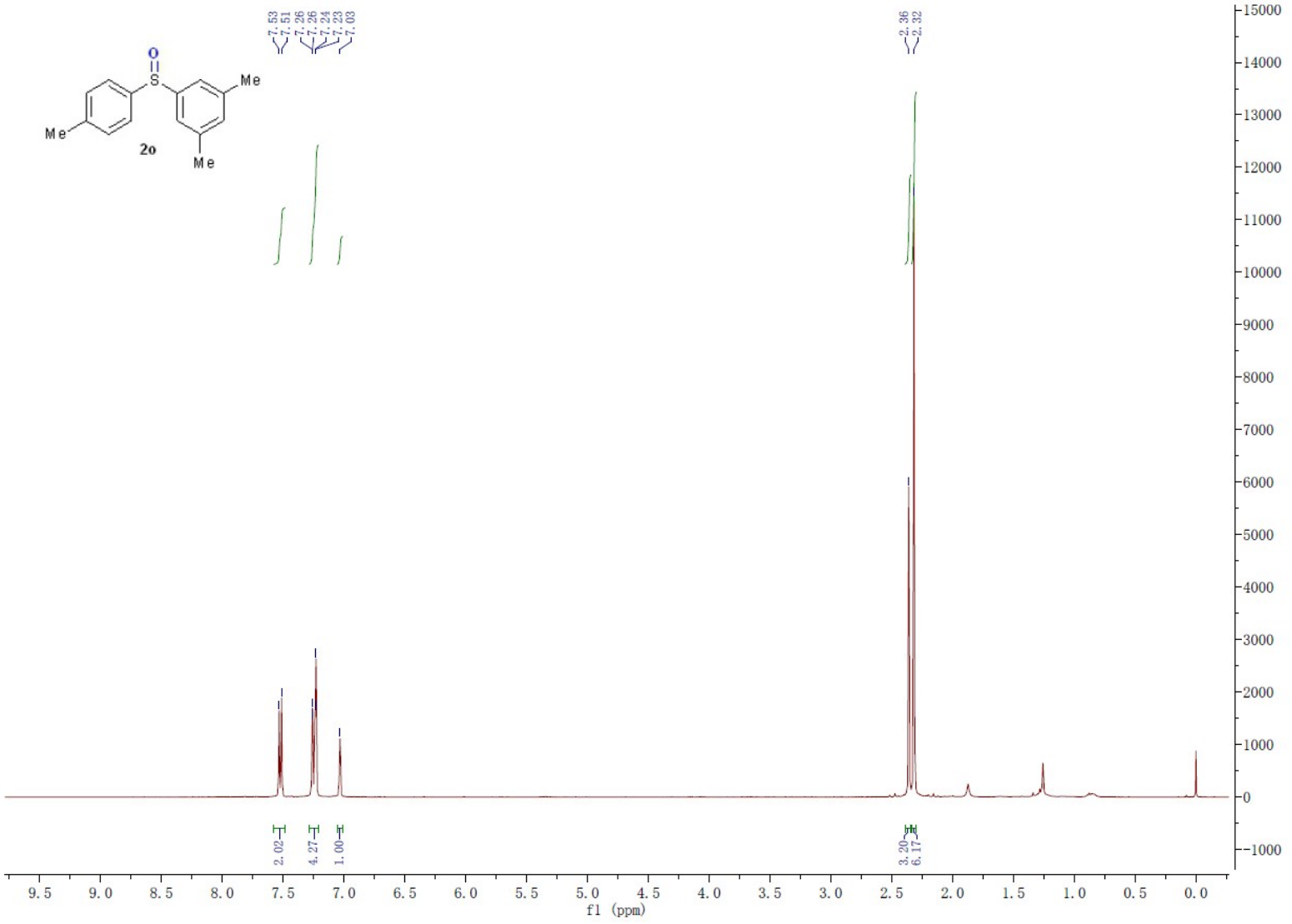

145.64
131.08
129.35
124.80
O
S
2l
f1 (ppm)

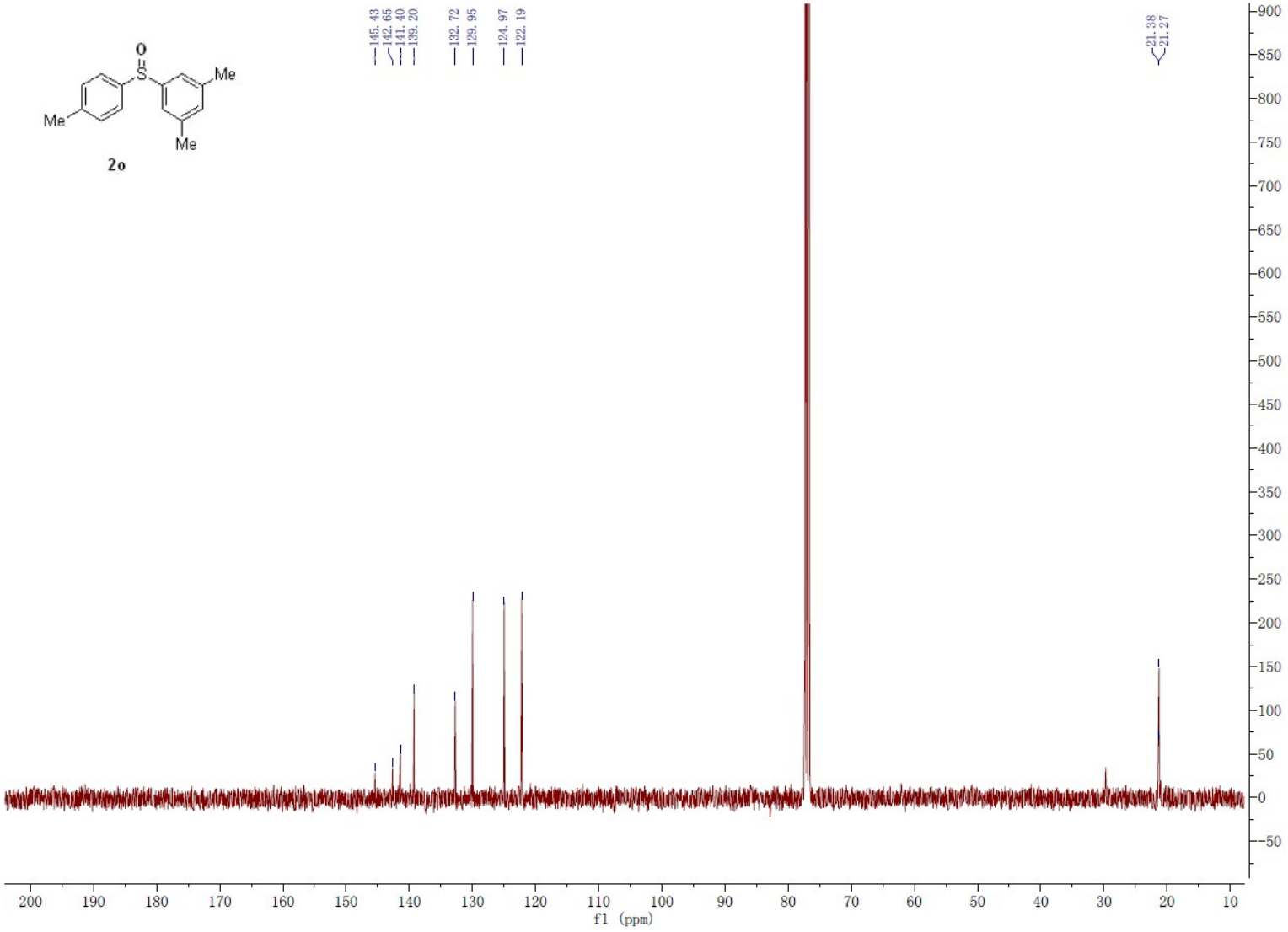

7.56
7.54
7.50
7.48
7.27
7.24
6.96
6.94
3.81
2.36
O
S
MeO
Me
2m
2.00
2.04
2.50
2.08
3.32
3.34
f1 (ppm)

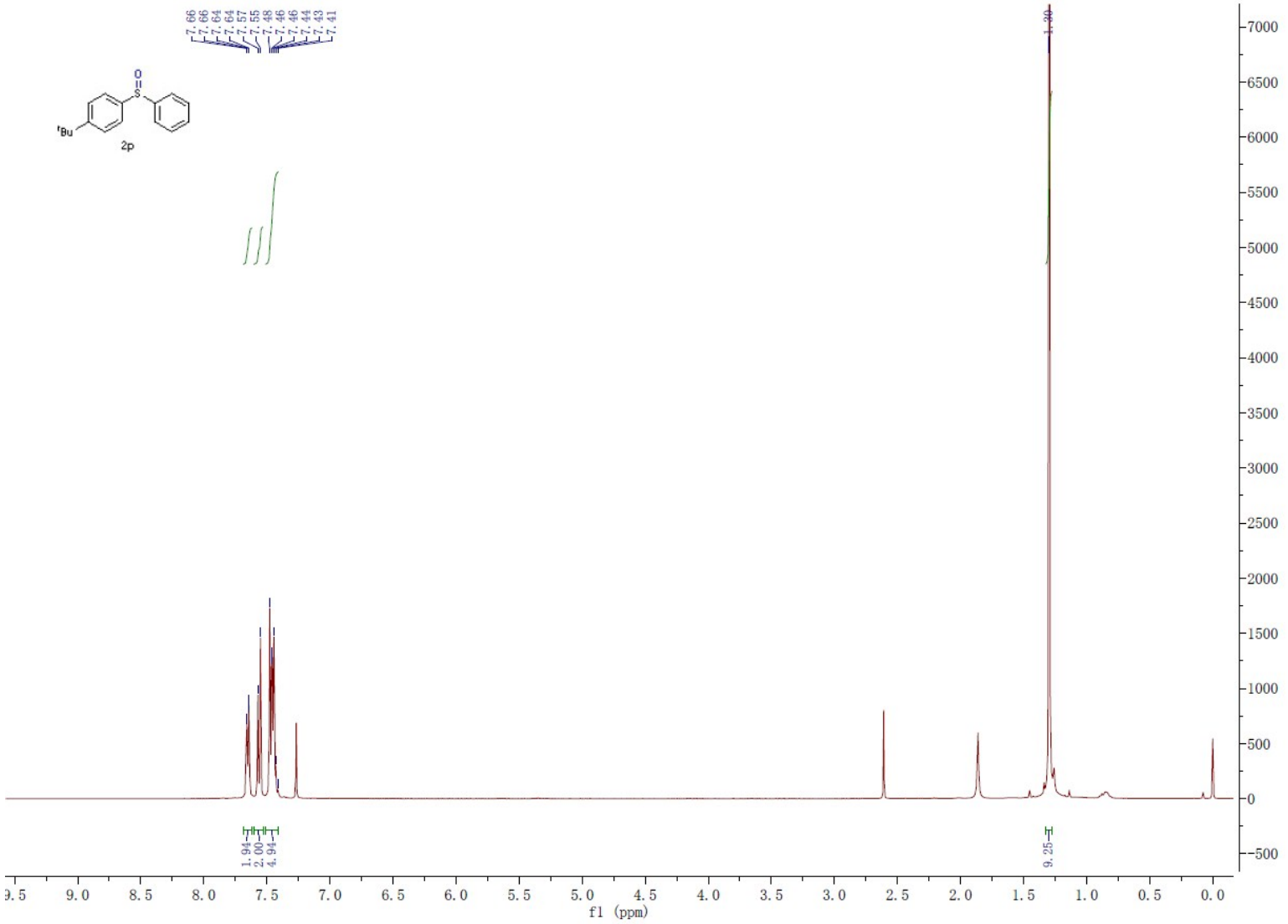

161.91
142.75
141.22
137.09
129.89
127.07
124.76
114.76
55.47
21.35
MeO
Me
2m
f1 (ppm)

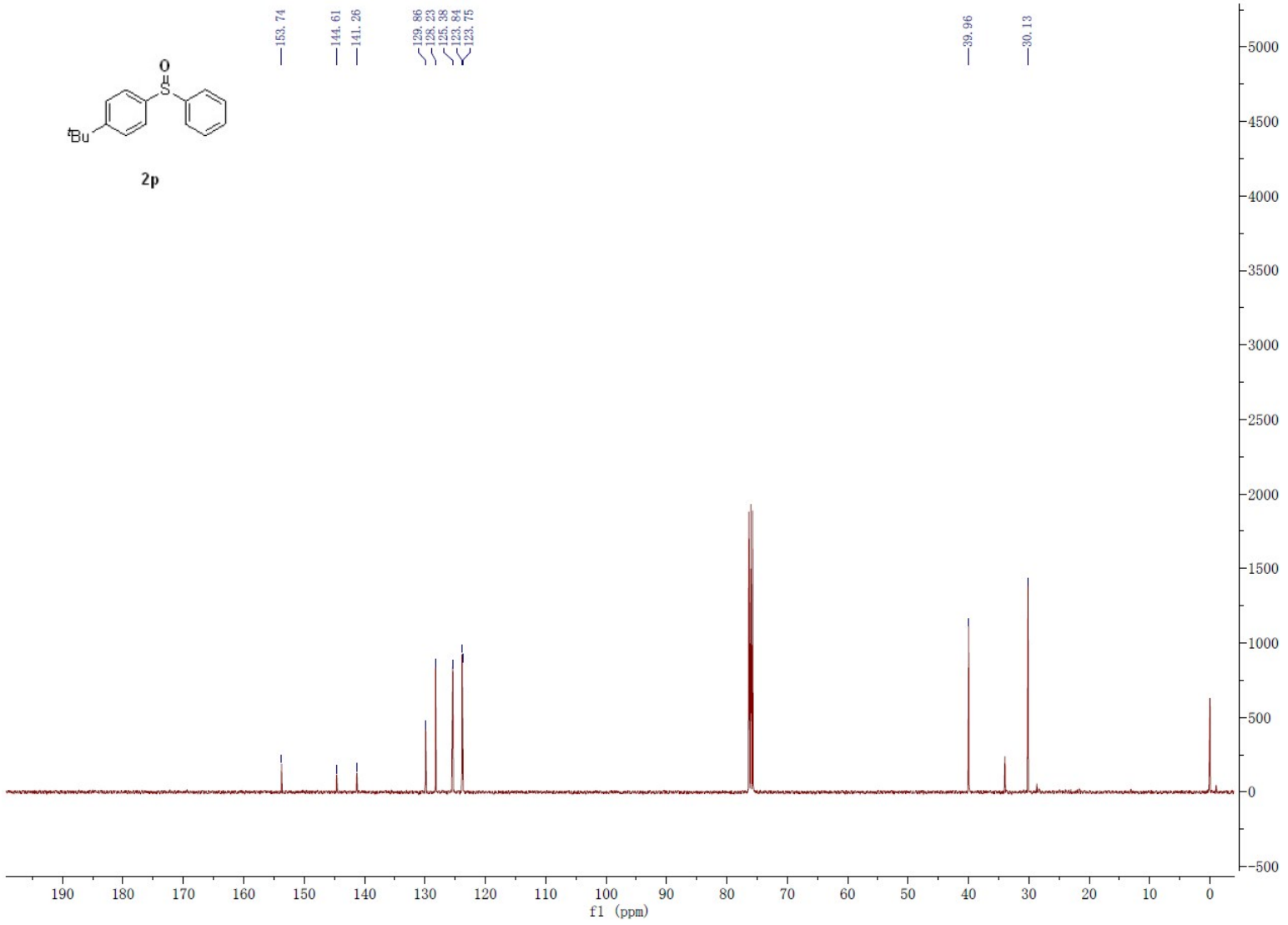

7.57
7.55
7.52
7.50
7.43
7.41
7.28
7.26
2.37
O
S
Me
Cl
2n
2.00
2.00
1.98
2.51
3.32
f1 (ppm)

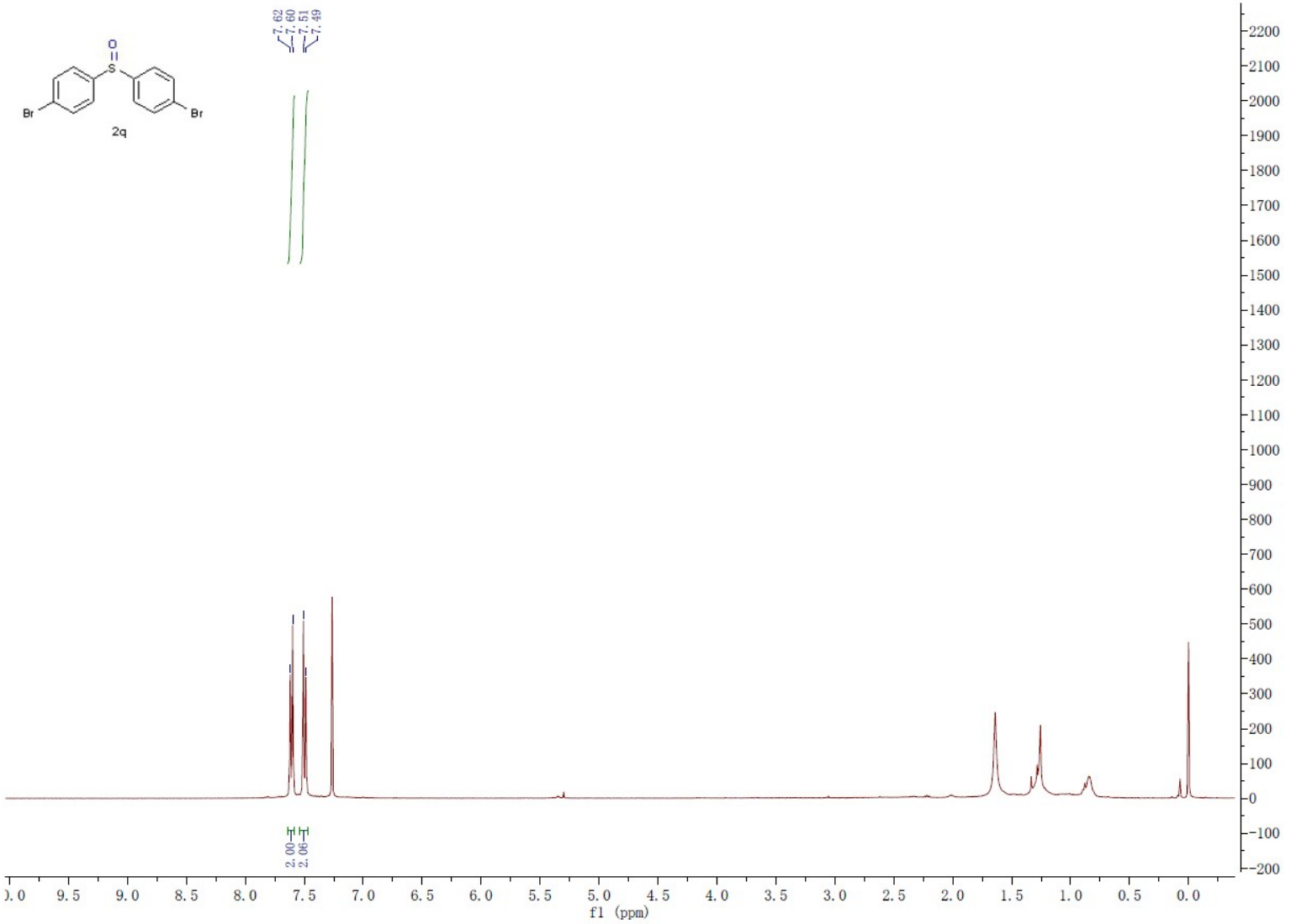

143.43
141.01
136.09
129.15
128.51
125.02
123.93
20.39
O
S
Me
Cl
2n
f1 (ppm)

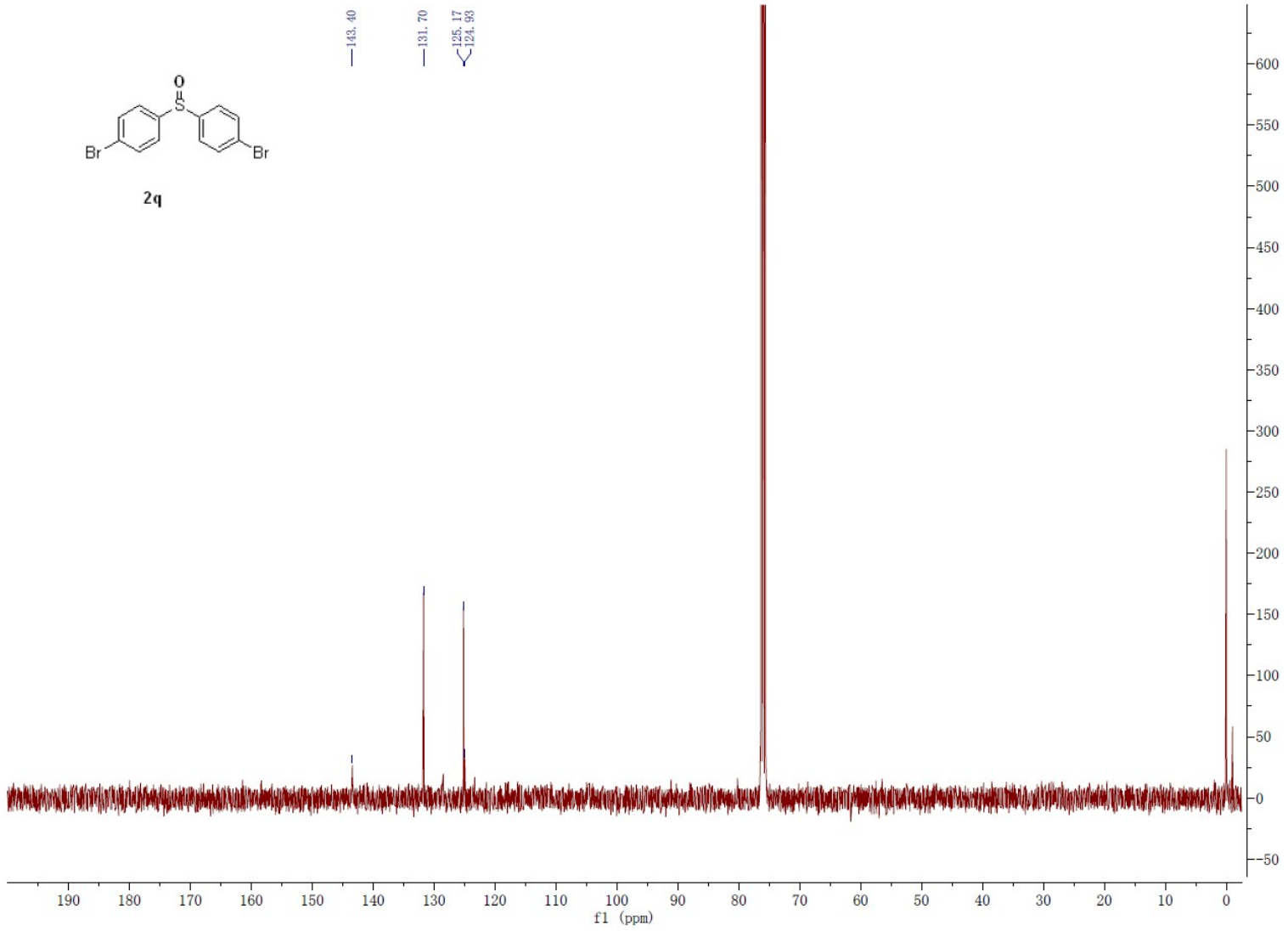

7.53
7.51
7.26
7.26
7.24
7.23
7.03
2.36
2.32
O
S
Me
Me
Me
2o
2.02
4.27
1.00
3.20
6.17
f1 (ppm)

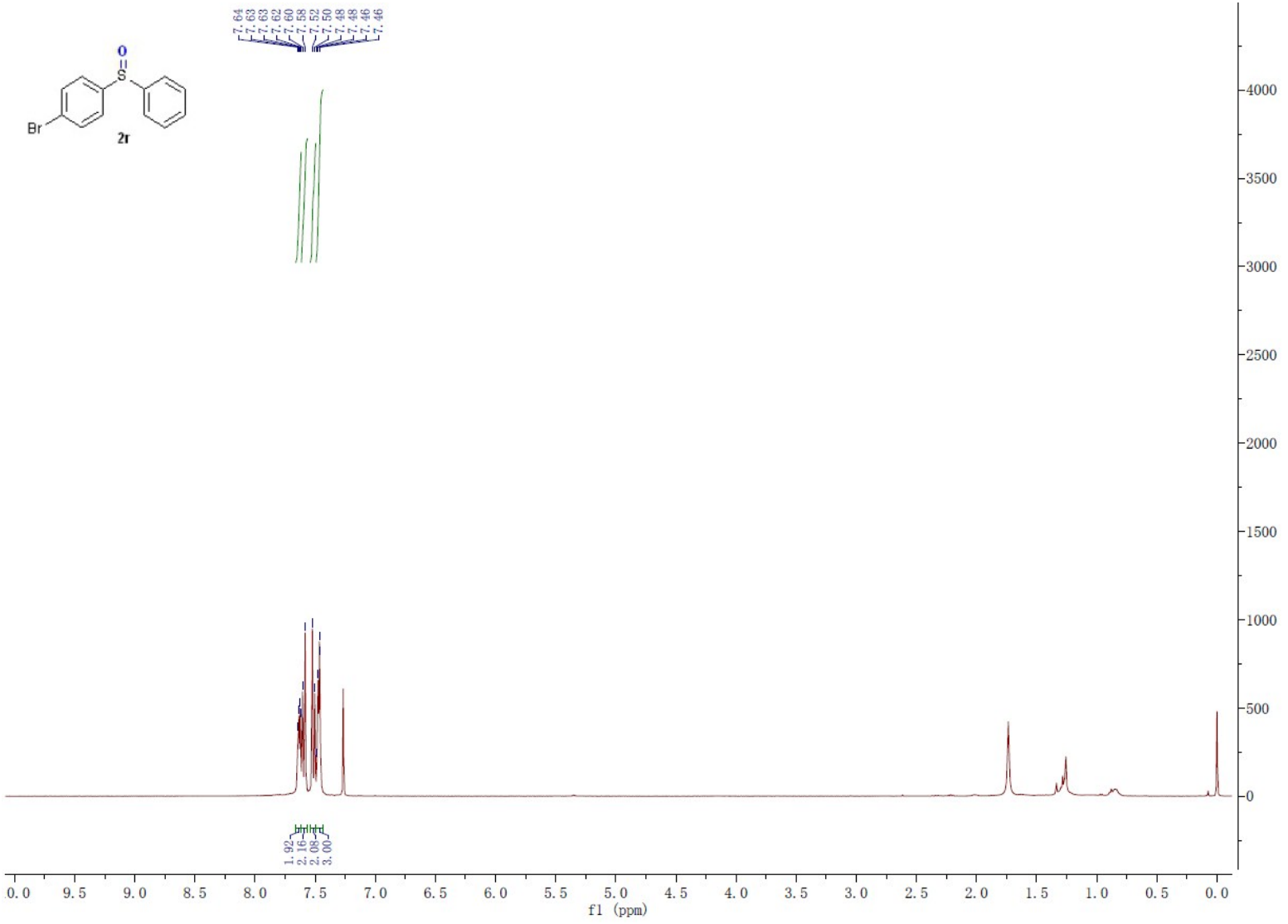

145.43
142.65
141.40
139.20
132.72
129.95
124.97
122.19
21.38
21.27
O
S
Me
Me
Me
2o
f1 (ppm)

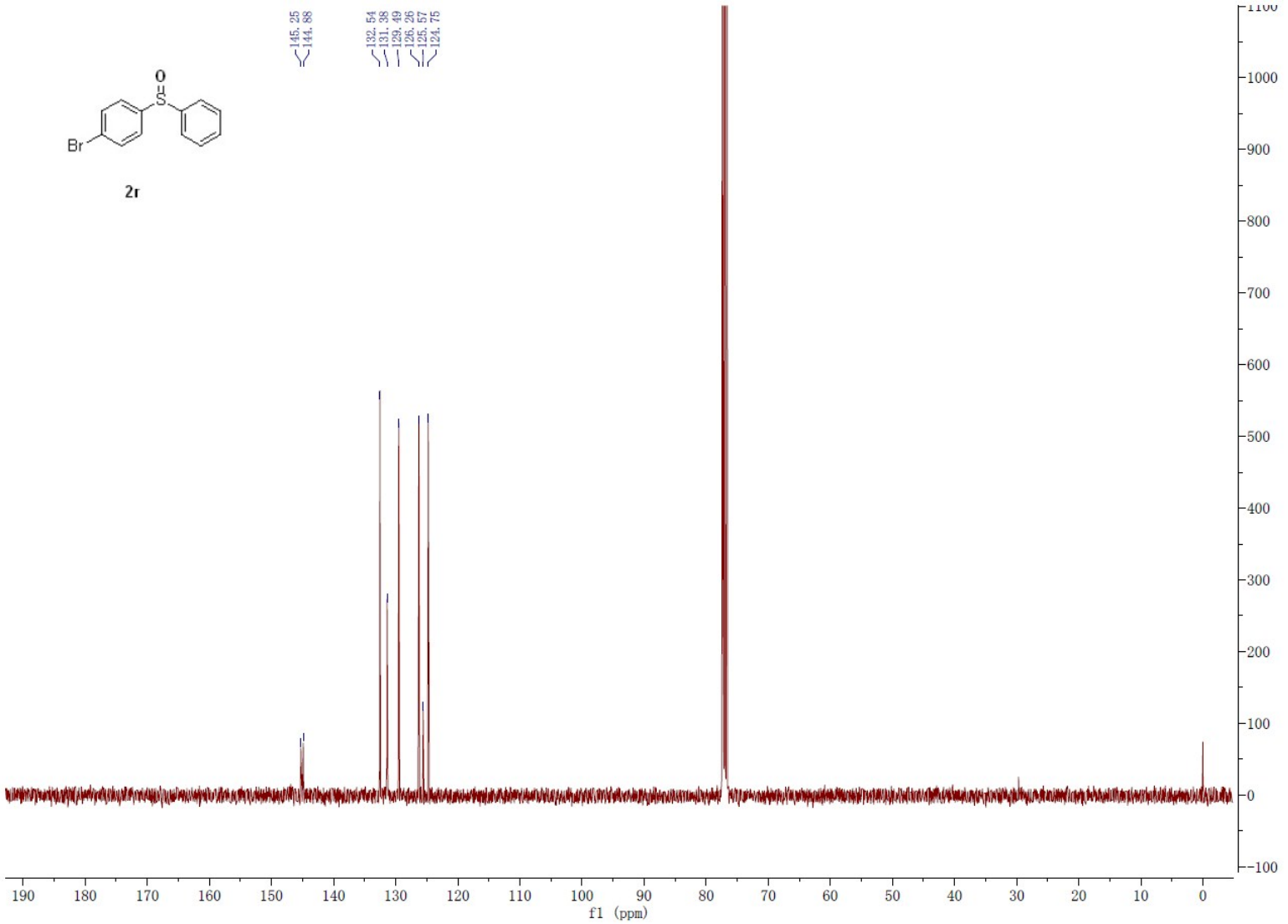

7.66
7.66
7.64
7.64
7.57
7.55
7.48
7.46
7.46
7.44
7.43
7.41
1.30
tBu
2p
1.94
2.00
4.94
9.25
f1 (ppm)

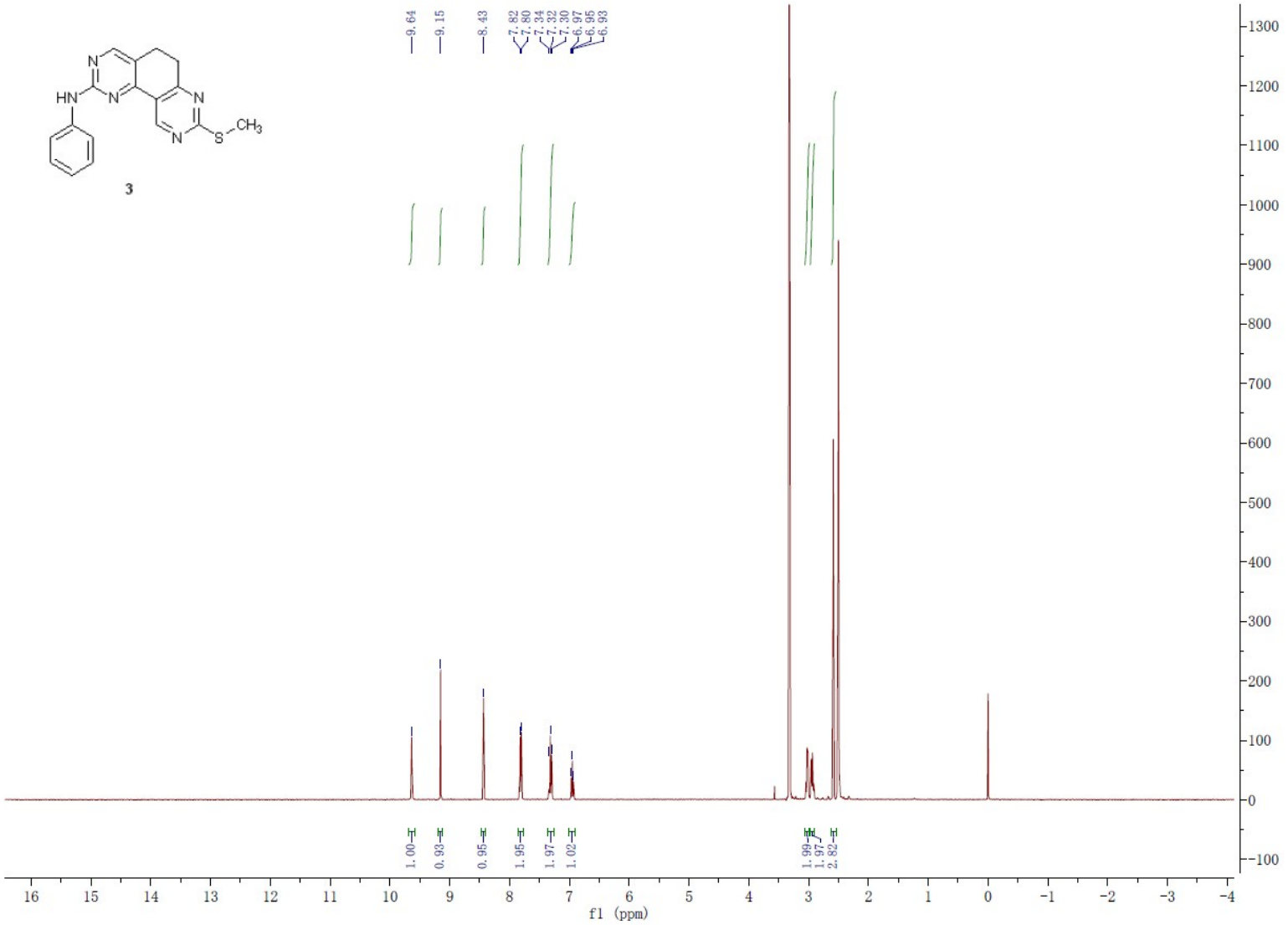

153.74
144.61
141.26
129.86
128.23
125.38
123.84
123.75
39.96
30.13
O
S
tBu
2p
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

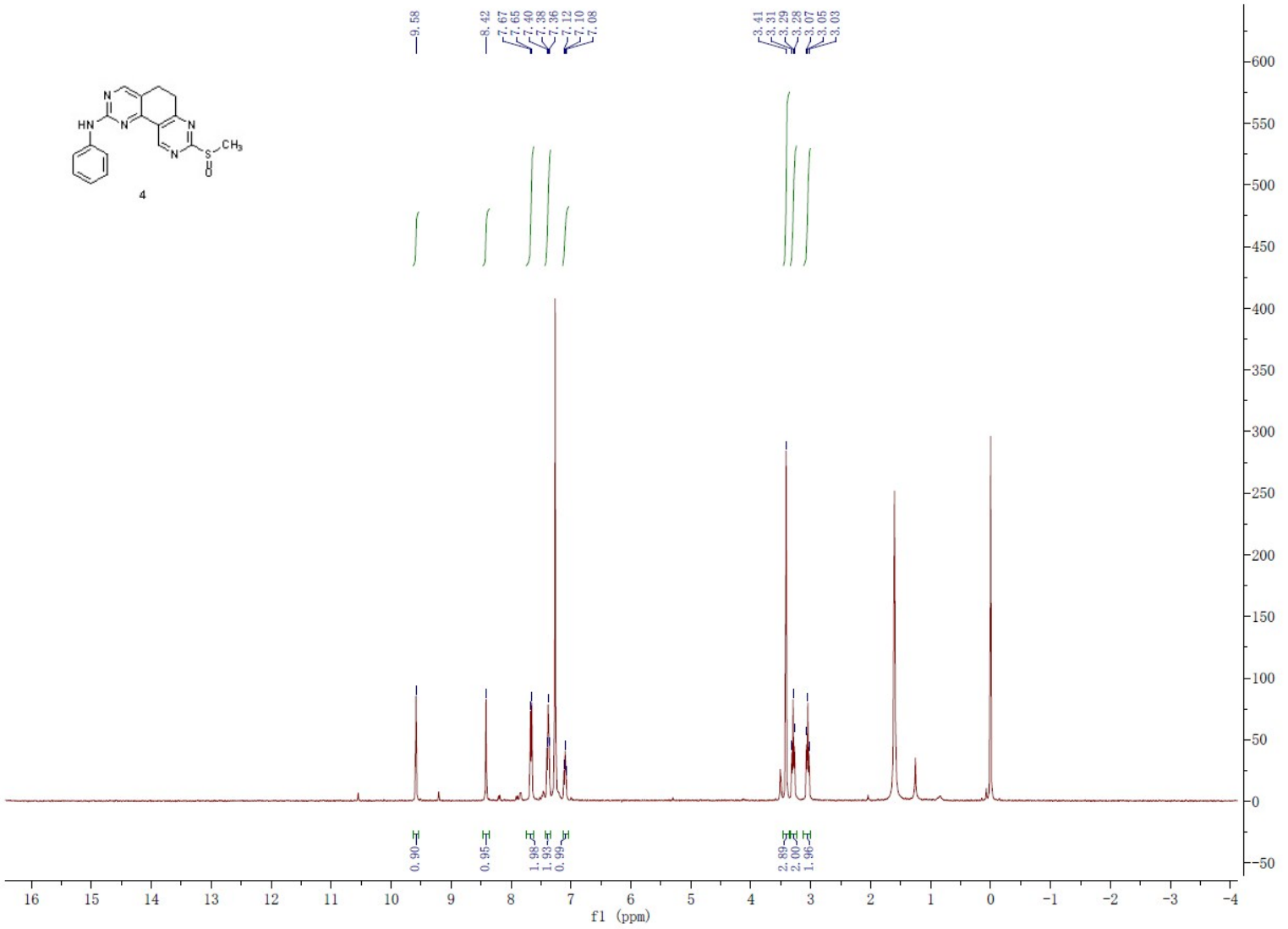

O
S
Br
Br
2q
7.62
7.60
7.51
7.49
2.00
2.06
f1 (ppm)

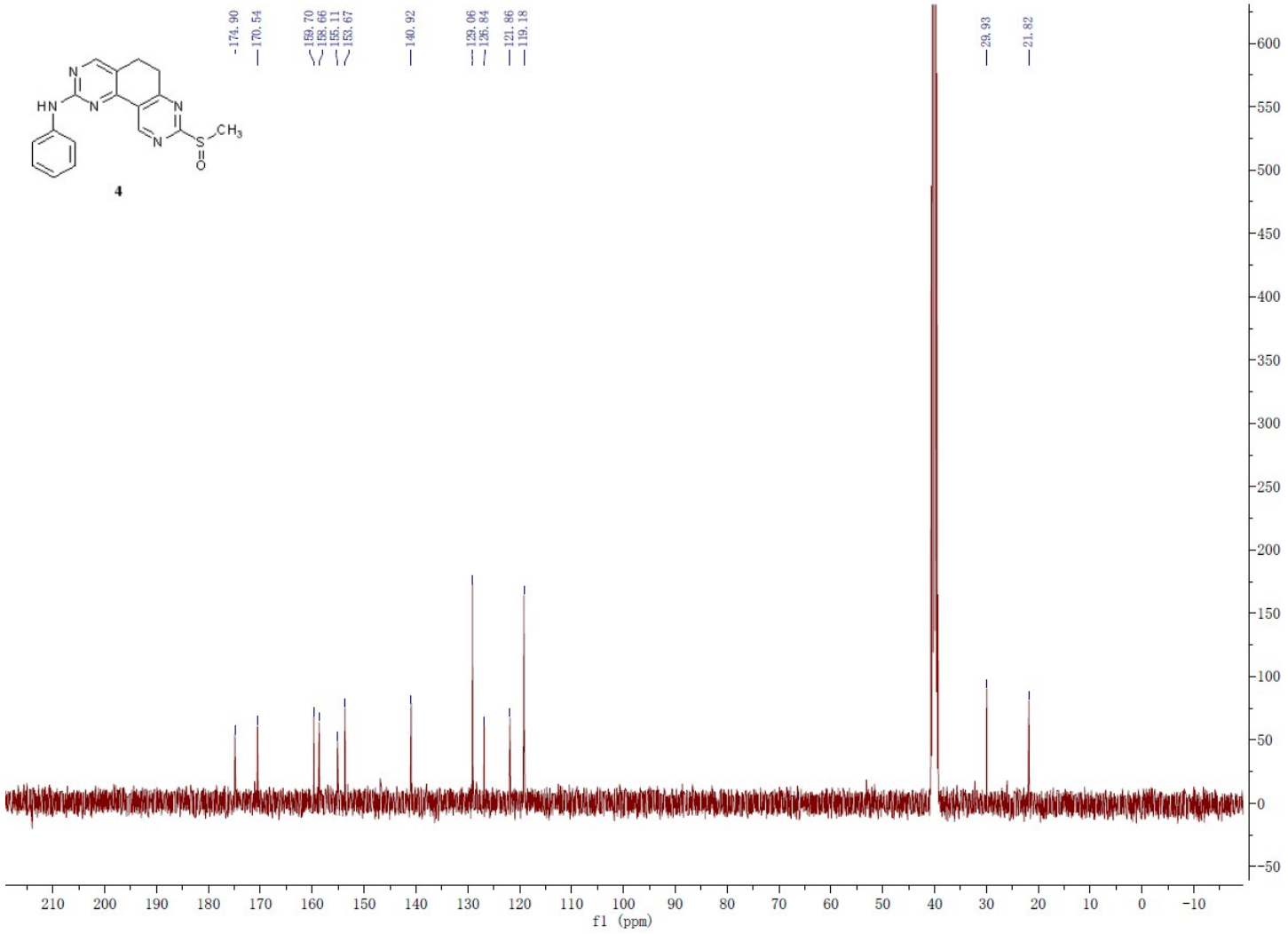

143.40
131.70
125.17
124.93
O
S
Br
Br
2q
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.64
7.63
7.63
7.62
7.60
7.58
7.52
7.50
7.48
7.48
7.46
7.46
O
S
Br
2r
4000
3500
3000
2500
2000
1500
1000
500
0
1.92
2.16
2.08
3.00
0.0
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)


145.25
144.88
132.54
131.38
129.49
126.26
125.57
124.75
O
S
Br
2r
f1 (ppm)


3
9.64
9.15
8.43
7.82
7.80
7.34
7.32
7.30
6.97
6.95
6.93
1.00
0.93
0.95
1.95
1.97
1.02
1.99
1.97
2.82
f1 (ppm)


9.58
8.42
7.67
7.65
7.40
7.38
7.36
7.12
7.10
7.08
3.41
3.31
3.29
3.28
3.07
3.05
3.03
HN
N
N
N
N
S
CH3
O
4
0.90
0.95
1.98
1.93
0.99
2.89
2.00
1.96
f1 (ppm)


174.90
170.54
159.70
158.66
155.11
153.67
140.92
129.06
126.84
121.86
119.18
29.93
21.82
HN
N
N
N
N
S
CH3
O
4
f1 (ppm)