Supporting Information

Cercosporin-Bioinspired Selective Photooxidation Reactions under Mild Conditions

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1. Materials and Methods

Cercosporin was biosynthesized by a new cercosporin producing strain in our laboratory.[1] Hypocrellin A and hypocrellin B were commercially available and used without further purification. All other 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 $CDCl_3$ 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. Gas chromatography (GC) and gas chromatography coupled to low-resolution mass spectrometry (GC–MS) analysis were performed through a capillary column (length: 30 m; diam.: 0.25 mm; film: 0.25 μM) using He gas as carrier. GC (TRACE 1300) was equipped with an FID detector. GC–MS (TSQ 8000) was performed on triple quadruple detector. UV–Vis and fluorescence measurements were performed with Shimadzu UV-3600plus spectrophotometer and F-2700 spectrofluorometer. The lifetime was measured on Edinburgh FLS920 fluorescence spectrometer. IR spectra was measured on Thermo Scientific Nicolet iS5 FTIR. Cyclic voltammetry (CV) was performed using an CHI600E electrochemical workstation: Au wire (φ = 1.6 mm) sealed in a Teflon jacket as working electrode, Pt wire as the counter electrode, Ag/AgCl (KCl, 3 M) electrode as the reference electrode, and ferrocenium/ferrocene (Fc^{+} /Fc) as the internal standard. Scan rate: 50 mV s^{-1} (in the range –1 to +2.2 V). Bu_4NPF_6 (0.1 M in MeCN) was used as the supporting electrolyte. Household CFLs (compact fluorescent lamps) were used as the light source. 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. The sample was placed at an approximate distance of 2 cm to the lamp. The light intensity was measured to be 21.3 mW/cm^2 for 23w CFL and

13.7 mW/cm^2 for 15w CFL, respectively. Additionally, the light intensity was also measured to be 6.51 mW/cm^2 for 5w blue LED and 2.39 mW/cm^2 for 5w green LED.

2. Biosynthesis of Cercosporin

Cercosporin was biosynthesized from microbial fermentation with cheap glucose as starting material by a new cercosporin producing strain in our laboratory.[1] Briefly, the neighbor-joining phylogenetic tree was constructed based on the 18S rDNA nucleotide sequences, showing that this new strain belongs to the genus *Cercospora*, thus designated as *Cercospora* sp. JNU001 (deposited to China Center for Type Culture Collection (CCTCCNo. M2017842). Next, cercosporin was produced by liquid fermentation using S7 medium (1 g/L Gluose, 6 g/L Fructose, 3g/L Sucrose, 1 g/L sodium acetate, 1 g/L soy peptone, 5 mg/L phenylalanine, 100 mg/L Sodium benzoate, 136 mg/L KH_2PO_4, 1 mg/L biotin, 6.5 mg/L $Ca(NO_3)_2$, 1 mg/L pyridoxal, 1 mg/L calcium pantothenate, 1 mg/L thiamine, 5 mg/L $MnCl_2$, 2 mg/L $FeCl_2$, 1 g/L $Cu(NO_3)_2$, 3.6 mg/L $MgSO_4$ and 2.5 mg/L $ZnSO_4$). A single colony of *Cercospora* sp. JNU001 was inoculated into 50 mL PDA medium and cultured for 7 days at 25 ℃. Then, they were inoculated into a 3 L Erlenmeyer flask containing 1L S-7 medium (pH=8.5) medium and shaked with 150 rpm at 25℃ under continuous light for 10 days. Cercosporin was purified by Sephadex LH-20 column after extraction by dichloromethane and identified by HPLC, LC-MS and NMR. A maximum of cercosporin production was obtained (128.2 mg/L), providing adequate amounts for further analysis.

3. Photostability Experiment of Cercosporin

The stability experiment of cercosporin under visible light Irradiation was performed. Upon irradiation with 23 W CFL for 48h, new signal related to the photolysis of cercosporin was not detected by HPLC. This result indicated the excellent stability of cercosporin as the photocatalyst.

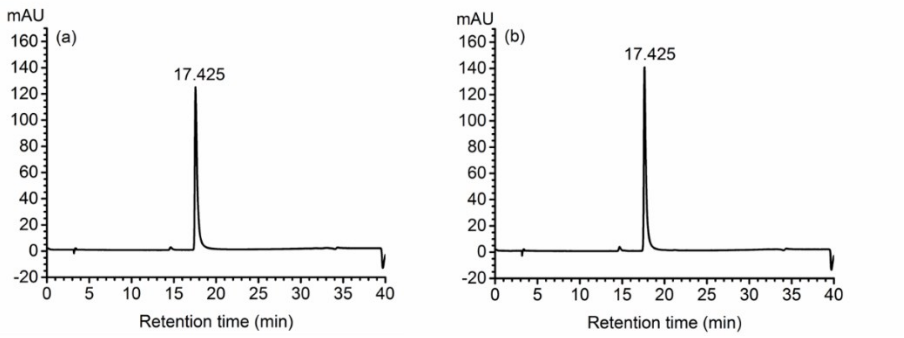


Fig. S1 High-performance liquid chromatogram analysis of photostability of cercosporin without irradiation (a) and with photoirradiation under 23 W CFL for 48h (b).

4. Spectra of the Light Source and Photochemical Reaction System

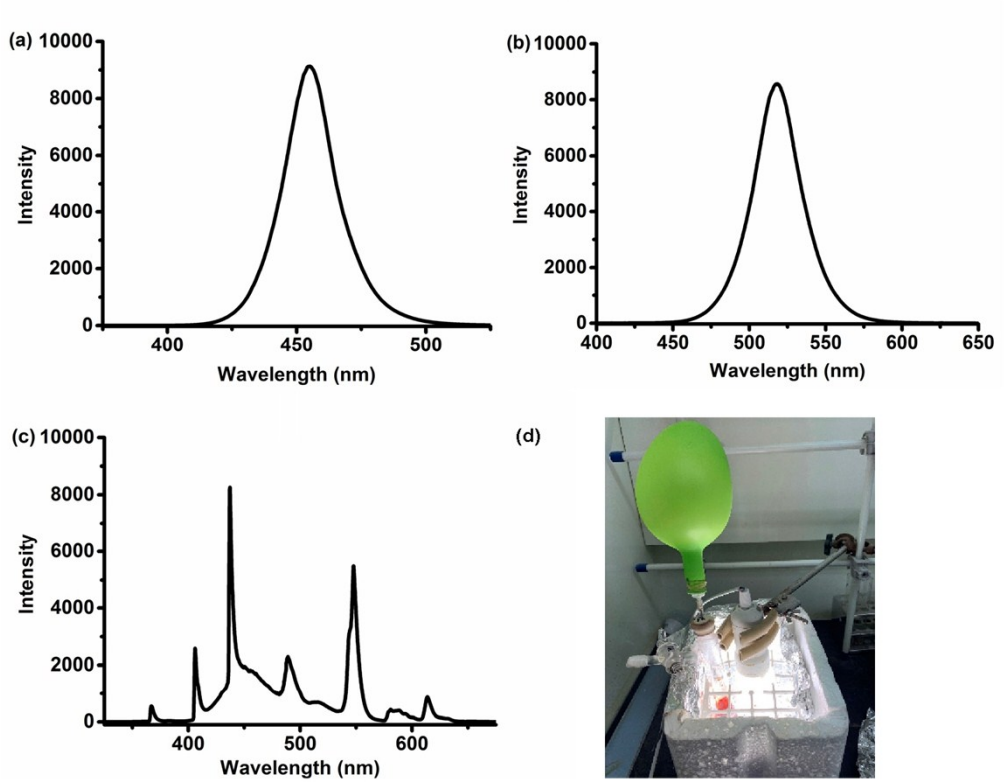


Fig. S2 Spectra of light source. (a) blue LED, (b) green LED, (c) CFL. (d) Photograph of the photochemical reaction set up.

5. Optimization of Reaction Conditions

5.1 Optimization of the reaction conditions for the selective oxidation of benzylic C–H bonds

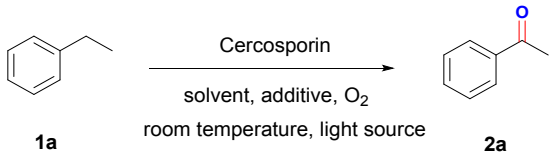


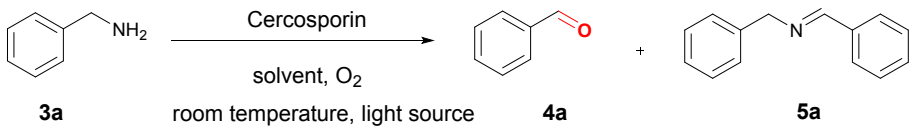
Table S1 Optimization of reaction conditions [a]

Entry	Photocatalyst (X mol%)	Additive	Solvent	Light source	Yield (%)[b]
1	CP (2)	—	DMSO	23 W CFL	Trace
2	CP (2)	—	Toluene	23 W CFL	Trace
3	CP (2)	—	DMF	23 W CFL	Trace
4	CP (2)	—	DCE	23 W CFL	Trace
5	CP (2)	—	CH_3CN	23 W CFL	5

6[c]	CP (2)	—	CH_3OH	23 W CFL	20
7	CP (2)	KBr (0.2 equiv)	CH_3OH	23 W CFL	78
8	CP (2)	LiBr (0.2 equiv)	CH_3OH	23 W CFL	26
9	CP (2)	NaBr (0.2 equiv)	CH_3OH	23 W CFL	25
10	CP (2)	CsBr (0.2 equiv)	CH_3OH	23 W CFL	20
11	CP (2)	KF (0.2 equiv)	CH_3OH	23 W CFL	30
12	CP (2)	KCl (0.2 equiv)	CH_3OH	23 W CFL	24
13	CP (2)	KI (0.2 equiv)	CH_3OH	23 W CFL	35
14	CP (2)	KO^{t}Bu (0.2 equiv)	CH_3OH	23 W CFL	29
15	CP (3)	KBr (0.2 equiv)	CH_3OH	23 W CFL	78
16	CP (1)	KBr (0.2 equiv)	CH_3OH	23 W CFL	72
17	CP (2)	KBr (0.1 equiv)	CH_3OH	23 W CFL	75
18	CP (2)	KBr (0.3 equiv)	CH_3OH	23 W CFL	75
19	CP (2)	KBr (0.4 equiv)	CH_3OH	23 W CFL	78
20	CP (2)	KBr (0.2 equiv)	CH_3OH	15 W CFL	75
21	CP (2)	KBr (0.2 equiv)	CH_3OH	5 W blue LED	70
22	CP (2)	KBr (0.2 equiv)	CH_3OH	5 W green LED	62
23	HA (2)	KBr (0.2 equiv)	CH_3OH	23 W CFL	30
24	HB (2)	KBr (0.2 equiv)	CH_3OH	23 W CFL	15
25	—	KBr (0.2 equiv)	CH_3OH	23 W CFL	trace
26	CP (2)	KBr (0.2 equiv)	CH_3OH	—	trace
27[d]	CP (2)	KBr (0.2 equiv)	CH_3OH	23 W CFL	trace

[a]Reaction conditions: **1a** (0.25 mmol), photocatalyst in solvent (2.0 mL) at room temperature in O_2 under irradiation for 30h. [b]Yields of isolated product. [c]Reaction time was 40h. [d]Reaction was conducted in nitrogen atmosphere.

5.2 Optimization of the reaction conditions for the selective oxidation of amines



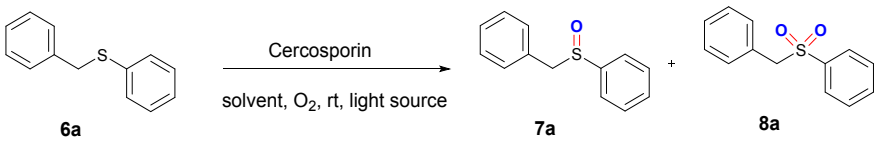
3a **4a** **5a**

Table S2 Optimization of reaction conditions [a]

Entry	Photocatalyst (X mol%)	Solvent	Light source	yield (%) [b]	
				4a	**5a**
1	CP (1)	$CHCl_3$	15 W CFL	60	23
2	CP (1)	THF	15 W CFL	59	31
3	CP (1)	CH_3CN	15 W CFL	49	29
4	CP (1)	CH_3OH	15 W CFL	95	0
5	CP (1)	DMF	15 W CFL	trace	trace
6	CP (1)	DMSO	15 W CFL	trace	trace
7	CP (1)	CH_3OH	5 W blue LED	8	35
8	CP (1)	CH_3OH	5 W green LED	0	20
9	CP (2)	CH_3OH	15 W CFL	95	0
10	CP (0.5)	CH_3OH	15 W CFL	0	79
11	HA (1)	CH_3OH	15 W CFL	80	5
12	HB (1)	CH_3OH	15 W CFL	62	23
13	—	CH_3OH	15 W CFL	0	0
14	CP (1)	CH_3OH	—	0	0
15[c]	CP (1)	CH_3OH	15 W CFL	0	trace

[a]All reactions were carried out on a scale of 0.25 mmol of **3a** in 2 mL of solvent under 15W CFL for 8h. [b] Yields of isolated product. [c] Reaction was conducted in nitrogen atmosphere.

5.3 Optimization of the reaction conditions for the selective oxidation of sulfides



6a **7a** **8a**

Table S3 Optimization of reaction conditions [a]

Entry	Photocatalyst (X mol%)	Solvent	Light source	yield (%) [b]	
				7a	**8a**
1	CP (1)	$CHCl_3$	15 W CFL	79	0
2	CP (1)	THF	15 W CFL	20	0
3	CP (1)	CH_3OH	15 W CFL	95	0
4	CP (1)	DMF	15 W CFL	18	0

5	CP (1)	DMSO	15 W CFL	trace	0
6	CP (1)	CH_3CN	15 W CFL	81	0
7	CP (1)	CH_3OH	5 W blue LED	35	8
8	CP (1)	CH_3OH	5 W green LED	20	0
9	CP (2)	CH_3OH	15 W CFL	95	0
10	CP (0.5)	CH_3OH	15 W CFL	79	0
11	—	CH_3OH	15 W CFL	0	0
12	CP (1)	CH_3OH	—	0	0
13[c]	CP (1)	CH_3OH	15 W CFL	trace	0

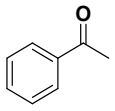
[a]All reactions were carried out on a scale of 0.25 mmol of **6a** in 2 mL of solvent under 15W CFL for 6h. [b] Yields of isolated product. [c] Reaction was conducted in nitrogen atmosphere.

6. General Procedures

6.1 General procedure for the selective oxidation benzylic C-H bonds with cercosporin

In a dried schlenk tube, benzylic derivatives **1** (0.25 mmol), potassium bromide (0.2 equiv) and cercosporin (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 23 W white CFL 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**.

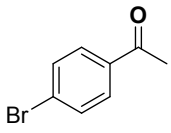
Acetophenone (**2a**)[2]



2a

The representative procedure was followed using ethylbenzene (**1a**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2a** (23 mg, 78%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.96 (d, 2H, J = 8 Hz, ArH), 7.58-7.55 (m, 1H, ArH), 7.48-7.44 (m, 2H, ArH), 2.58 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 198.04, 137.16, 133.05, 128.54, 128.27, 26.54.

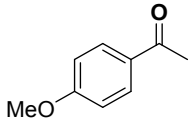
1-(4-Bromophenyl)ethan-1-one (**2b**)[3]



2b

The representative procedure was followed using 1-bromo-4-ethylbenzene (**1b**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2b** (32 mg, 65%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.82 (d, 2H, J = 8 Hz, ArH), 7.61 (d, 2H, J = 8 Hz, ArH), 2.59 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 196.89, 135.86, 131.87, 129.81, 128.25, 26.48.

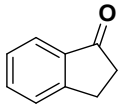
1-(4-Methoxyphenyl)ethan-1-one (**2c**)[4]



2c

The representative procedure was followed using 1-ethyl-4-methoxybenzene (**1c**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2c** (28 mg, 75%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.94 (d, 2H, J = 8 Hz, ArH), 6.94 (d, 2H, J = 12 Hz, ArH), 3.87 (s, 3H, OCH_3), 2.56 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 196.65, 163.48, 130.54, 130.36, 113.67, 55.42, 26.26.

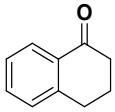
2,3-Dihydro-1*H*-inden-1-one (**2d**)[5]



2d

The representative procedure was followed using 2,3-dihydro-1*H*-indene (**1d**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2d** (24 mg, 73%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.77 (d, 1H, J = 8 Hz, ArH), 7.61-7.57 (m, 1H, ArH), 7.49 (d, 1H, J = 4 Hz, ArH), 7.39-7.36 (m, 1H, ArH), 3.17-3.14 (m, 2H, CH_2), 2.72-2.69 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 206.95, 155.12, 137.07, 134.56, 127.24, 126.68, 123.65, 36.20, 25.79.

3,4-Dihydronaphthalen-1(2*H*)-one (**2e**)[6]

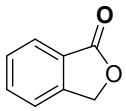


2e

The representative procedure was followed using 1,2,3,4-tetrahydronaphthalene (**1e**) (0.25 mmol) as

substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2e** (29 mg, 81%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.04 (d, 1H, *J* = 8 Hz, ArH), 7.49-7.45 (m, 1H, ArH), 7.33-7.29 (m, 1H, ArH), 7.25 (d, 1H, *J* = 8 Hz, ArH), 2.99-2.96 (m, 2H, CH_2), 2.68-2.65 (m, 2H, CH_2), 2.18-2.11 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 198.25, 144.46, 133.35, 132.63, 128.75, 127.13, 126.59, 39.15, 29.70, 23.29.

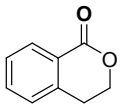
Isobenzofuran-1(3*H*)-one (**2f**)[3]



2f

The representative procedure was followed using 1,3-dihydroisobenzofuran (**1f**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2f** (23 mg, 71%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.93 (d, 1H, *J* = 8 Hz, ArH), 7.71-7.68 (m, 1H, ArH), 7.56-7.50 (m, 2H, ArH), 5.33 (s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.06, 146.59, 134.01, 128.95, 125.57, 125.48, 122.22, 69.69.

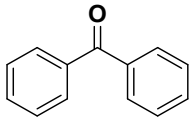
Isochroman-1-one (**2g**)[7]



2g

The representative procedure was followed using isochromane (**1g**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2g** (27 mg, 75%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.10 (d, 1H, *J* = 8 Hz, ArH), 7.56-7.52 (m, 1H, ArH), 7.41-7.38 (m, 1H, ArH), 7.27-7.26 (m, 1H, ArH), 4.55-4.52 (m, 2H, CH_2), 3.08-3.05 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 165.11, 39.64, 133.67, 130.16, 127.57, 127.53, 127.32, 125.21, 67.33, 27.75, 27.72, 27.56.

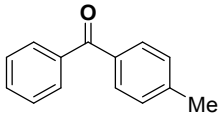
Benzophenone (**2h**)[8]



2h

The representative procedure was followed using diphenylmethane (**1h**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2h** (34 mg, 75%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.82-7.80 (m, 2H, ArH), 7.60-7.57 (m, 1H, ArH), 7.50-7.47 (m, 2H, ArH). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 196.67, 137.64, 132.39, 130.03, 128.28.

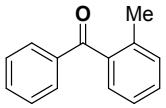
Phenyl (*p*-tolyl)methanone (**2i**)[9]



2i

The representative procedure was followed using 1-benzyl-4-methylbenzene (**1i**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2i** (38 mg, 78%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.78 (d, 2H, *J* = 8 Hz, ArH), 7.72 (d, 2H, *J* = 8 Hz, ArH), 7.59-7.55 (m, 1H, ArH), 7.49-7.45 (m, 2H, ArH), 7.28 (d, 2H, *J* = 8 Hz, ArH), 2.44 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 196.47, 143.22, 137.98, 134.91, 132.15, 130.30, 129.92, 128.98, 128.21, 21.65.

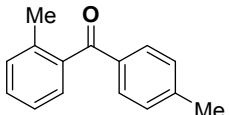
Phenyl (*o*-tolyl)methanone (**2j**)[10]



2j

The representative procedure was followed using 1-benzyl-2-methylbenzene (**1j**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2j** (37 mg, 77%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.81-7.79 (m, 2H, ArH), 7.59-7.56 (m, 1H, ArH), 7.47-7.43 (m, 2H, ArH), 7.41-7.37 (m, 1H, ArH), 7.32-7.22 (m, 3H, ArH), 2.33 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 197.60, 137.61, 136.73, 135.70, 132.08, 129.96, 129.19, 129.09, 127.47, 127.42, 124.16, 18.93.

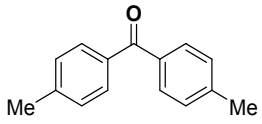
o-Tolyl(*p*-tolyl)methanone (**2k**)[11]



2k

The representative procedure was followed using 1-methyl-2-(4-methylbenzyl)benzene (**1k**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2k** (42 mg, 80%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.70 (d, 2H, *J* = 8 Hz, ArH), 7.39-7.36 (m, 1H, ArH), 7.30-7.22 (m, 5H, ArH), 2.42 (s, 3H, CH_3), 2.31 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 198.32, 144.07 , 139.03, 136.46, 135.21, 130.91, 130.30, 130.01, 129.20, 128.26, 125.19, 21.71, 19.90.

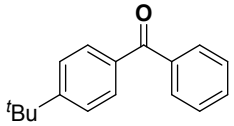
Di-*p*-tolylmethanone (**2l**)[12]



2l

The representative procedure was followed using di-*p*-tolylmethane (**1l**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2l** (39 mg, 76%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.70 (d, 2H, *J* = 8 Hz, ArH), 7.29 (d, 2H, *J* = 8 Hz, ArH), 2.44 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 196.23, 142.91, 135.25, 130.18, 128.90, 21.62.

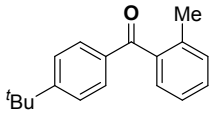
(4-(*tert*-Butyl) phenyl) (phenyl) methanone (**2m**)[13]



2m

The representative procedure was followed using 1-benzyl-4-(tert-butyl) benzene (**1m**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2m** (47 mg, 80%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.81-7.75 (m, 4H, ArH), 7.60-7.56 (m, 1H, ArH), 7.51-7.49 (m, 4H, ArH), 1.37 (s, 9H, $3CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 196. 42, 156.18, 137.97, 134.85, 132.16, 130.14, 129.96, 128.21, 125.25, 35.12, 31.17.

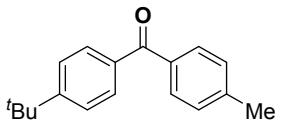
(4-(*tert*-Butyl) phenyl) (*o*-tolyl)methanone (**2n**)[14]



2n

The representative procedure was followed using 1-(4-(*tert*-butyl) benzyl)-2-methylbenzene (**1n**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2n** (49 mg, 79%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.75 (d, 2H, *J* = 8 Hz, ArH), 7.46 (d, 2H, *J* = 8 Hz, ArH), 7.39-7.36 (m, 1H, ArH), 7.31-7.21 (m, 3H, ArH), 2.33 (s, 3H, CH_3), 1.35 (s, 9H, $3CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 198.21, 156.96, 139.01, 136.54, 135.10, 130.91, 130.17, 129.99, 128.31, 125.43, 125.12, 35.17, 31.13, 19.90.

(4-*(tert*-Butyl) phenyl) (*p*-tolyl) methanone (**2o**)[11]

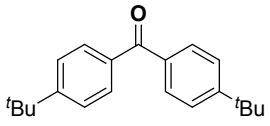


2o

The representative procedure was followed using 1-(*tert*-butyl)-4-(4-methylbenzyl) benzene (**1o**) (0.25

mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2o** (47 mg, 76%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.76-7.71 (m, 4H, ArH), 7.49 (d, 2H, J = 4 Hz, ArH), 7.27 (d, 2H, J = 8 Hz, ArH), 2.44 (s, 3H, CH_3), 1.36 (s, 9H, $3CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 196.15, 155.87, 142.90, 135.24, 135.19, 130.21, 130.00, 128.89, 125.16, 35.08, 31.17, 21.62.

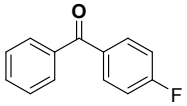
Bis (4-(*tert*-butyl)phenyl) methanone (**2p**)[15]



2p

The representative procedure was followed using bis(4-(*tert*-butyl) phenyl) methane (**1p**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2p** (60 mg, 82%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.76 (d, 2H, J = 8 Hz, ArH), 7.49 (d, 2H, J = 8 Hz, ArH), 1.37 (s, 9H, $3CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 196.13, 155.87, 135.18, 130.04, 125.16, 35.09, 31.18.

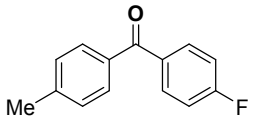
(4-Fluorophenyl) (phenyl) methanone (**2q**)[16]



2q

The representative procedure was followed using 1-benzyl-4-fluorobenzene (**1q**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2q** (31 mg, 62%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.87-7.83 (m, 2H, ArH), 7.78-7.76 (m, 2H, ArH), 7.61-7.58 (m, 1H, ArH), 7.51-7.47 (m, 2H, ArH), 7.18-7.14 (m, 2H, ArH). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 195.16, 166.64, 164.11, 137.53, 133.85, 133.82, 132.68, 132.59, 132.43, 129.84, 128.34, 115.54, 115.32.

(4-Fluorophenyl) (*p*-tolyl) methanone (**2r**)[17]

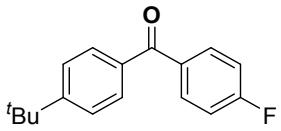


2r

The representative procedure was followed using 1-fluoro-4-(4-methylbenzyl)benzene (**1r**) (0.25 mmol)

as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2r** (32 mg, 60%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.84-7.81 (m, 2H, ArH), 7.69 (d, 2H, *J* = 8 Hz, ArH), 7.30-7.26 (m, 2H, ArH), 7.17-7.13 (m, 2H, ArH), 2.44 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 195.01, 166.50, 163.98, 143.31, 134.80, 134.17, 134.14, 132.54, 132.45, 130.12, 129.04, 115.46, 115.24, 21.63.

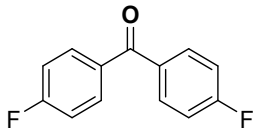
(4-(*tert*-Butyl)phenyl) (4-fluorophenyl) methanone (**2s**)[18]



2s

The representative procedure was followed using 1-(*tert*-butyl)-4-(4-fluorobenzyl) benzene (**1s**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2s** (44 mg, 69%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.86-7.83 (m, 2H, ArH), 7.43 (d, 2H, *J* = 8 Hz, ArH), 7.50 (d, 2H, *J* = 8 Hz, ArH), 7.17-7.13 (m, 2H, ArH), 1.37 (s, 9H, 3CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 194.94, 166.51, 163.99, 156.26, 134.74, 134.15, 134.12, 132.59, 132.50, 129.96, 125.32, 115.45, 115.23, 115.18, 114.97, 35.12, 31.14.

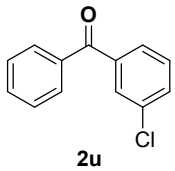
Bis (4-fluorophenyl) methanone (**2t**)[19]



2t

The representative procedure was followed using bis (4-fluorophenyl) methane (**1t**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2t** (26 mg, 48%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.83-7.80 (m, 2H, ArH), 7.19-7.15 (m, 2H, ArH). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 193.70, 166.65, 164.12, 133.74, 133.71, 132.50, 132.41, 115.64, 115.42.

(3-Chlorophenyl) (phenyl) methanone (**2u**)[20]

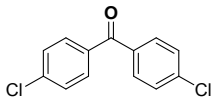


2u

The representative procedure was followed using 1-benzyl-3-chlorobenzene (**1u**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2u** (35 mg, 65%) as colorless

oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.79 (d, 2H, *J* = 8 Hz, ArH), 7.67 (d, 1H, *J* = 8 Hz, ArH), 7.61-7.55 (m, 3H, ArH), 7.52-7.48 (m, 2H, ArH), 7.42-7.40 (m, 1H, ArH). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 195.17, 139.30, 136.98, 134.58, 132.80, 132.32, 129.99, 129.88, 129.61, 128.45, 128.08.

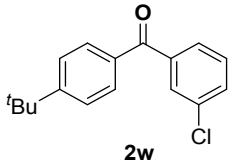
Bis (4-chlorophenyl) methanone (**2v**)[21]



2v

The representative procedure was followed using bis (4-chlorophenyl) methane (**1v**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2v** (36 mg, 58%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.73 (d, 2H, *J* = 8 Hz, ArH), 7.47 (d, 2H, *J* = 8 Hz, ArH). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 194.13, 139.14, 135.54, 131.29, 128.75.

(4-*(tert*-Butyl)phenyl) (3-chlorophenyl) methanone (**2w**)



2w

The representative procedure was followed using 1-(4-(tert-butyl)benzyl)-3-chlorobenzene (**1w**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 10/1) yielded **2w** (48 mg, 72%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.77-7.74 (m, 3H, ArH), 7.67-7.66 (m, 1H, ArH), 7.56-7.50 (m, 3H, ArH), 7.43-7.39 (m, 1H, ArH), 1.37 (s, 9H, $3CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 194.9, 156.7, 139.6, 134.5, 134.2, 132.1, 130.1, 129.8, 129.6, 128.0, 125.5, 35.2, 31.1. HRMS (ESI-Q-TOF) exact mass calcd for $C_{17}H_{18}ClO$ $[M+H]^+$ 273.1046, found 273.1023. IR: 3064.8, 2962.5, 2904.1, 2868.1, 1658.0, 1604.5, 1566.1, 1463.3, 1314.3, 1276.0, 945.5, 849.7, 761.5, 709.2 cm^{-1}.

6.2 General procedure for the selective oxidation of amines with cercosporin

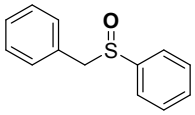
In a dried schlenk tube, amines **3** (0.25 mmol) and cercosporin (1 mol%) was added in 2.0 mL methanol. Next, a balloon was purged with oxygen and fixed on the top of the schlenk tube. The reaction mixture was stirred and irradiated by 15 W white CFL at room temperature under an atmospheric pressure oxygen atmosphere. The reaction progress was monitored by GC analysis. Photooxidation yields of **4** were calculated from GC measurements using internal standards.

6.3 General procedure for the selective oxidation of sulfides with cercosporin

In a dried schlenk tube, sulfides **6** (0.25 mmol) and cercosporin (1 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 15 W white CFL 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 **7**.

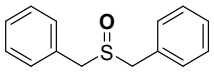
(Benzylsulfinyl)benzene (**7a**)[22]



7a

The representative procedure was followed using benzyl(phenyl)sulfane (**6a**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **7a** (51 mg, 95%) as a white viscous solid. ^{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 (101 MHz, $CDCl_3$) δ ppm 142.82, 131.15, 130.35, 129.16, 128.85, 128.44, 128.23, 124.43, 63.61.

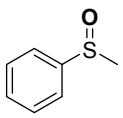
(Sulfinylbis(methylene))dibenzene (**7b**)[23]



7b

The representative procedure was followed using dibenzylsulfane (**6b**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **7b** (51 mg, 90%) as a white viscous solid. ^{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 (101 MHz, $CDCl_3$) δ ppm 130.15, 128.96, 128.36, 57.34.

(Methylsulfinyl)benzene (**7c**)[24]

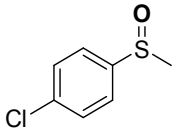


7c

The representative procedure was followed using methyl(phenyl)sulfane (**6c**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **7c** (32 mg, 94%) as a white viscous solid. ^{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 (101 MHz, $CDCl_3$) δ ppm 145.69, 131.00, 129.32, 123.45, 43.92.

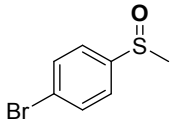
1-Chloro-4-(methylsulfinyl)benzene (**7d**)[25]



7d

The representative procedure was followed using (4-chlorophenyl)(methyl)sulfane (**6d**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **7d** (38 mg, 90%) as a white viscous solid. ^{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 (101 MHz, $CDCl_3$) δ ppm 144.26, 137.24, 129.64, 124.97, 44.03.

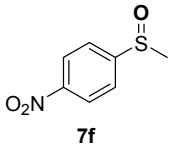
1-Bromo-4-(methylsulfinyl)benzene (**7e**)[26]



7e

The representative procedure was followed using (4-bromophenyl) (methyl)sulfane (**6e**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **7e** (47 mg, 87%) as a white viscous solid. ^{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 (101 MHz, $CDCl_3$) δ ppm 144.94, 132.56, 125.44, 125.14, 43.99.

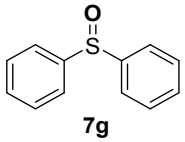
1-(Methylsulfinyl)-4-nitrobenzene (**7f**)[27]



7f

The representative procedure was followed using methyl (4-nitrophenyl) sulfane (**6f**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **7f** (37 mg, 80%) as a white viscous solid. ^{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 (101 MHz, $CDCl_3$) δ ppm 153.29, 149.49, 124.68, 124.45, 43.85.

Sulfinyldibenzene (**7g**)[28]

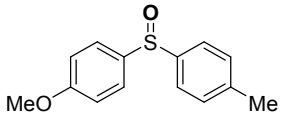


7g

The representative procedure was followed using diphenylsulfane (**6g**) (0.25 mmol) as substrate.

Isolation by column chromatography (PE/EtOAc: 5/1) yielded **7g** (45 mg, 90%) as a white viscous solid. ^{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 (75 MHz, $CDCl_3$) δ ppm 145.64, 131.08, 129.35, 124.80.

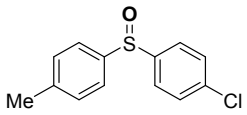
1-Methoxy-4-(*p*-tolylsulfinyl)benzene (**7h**)[29]



7h

The representative procedure was followed using (4-methoxyphenyl) (*p*-tolyl)sulfane (**6h**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **7h** (53 mg, 87%) as a white viscous solid. ^{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 (101 MHz, $CDCl_3$) δ ppm 161.91, 142.68, 141.24, 137.00, 129.90, 127.05, 124.73, 114.77, 55.47, 21.35.

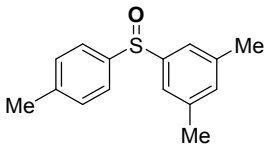
1-Chloro-4-(*p*-tolylsulfinyl)benzene (**7i**)[30]



7i

The representative procedure was followed using (4-chlorophenyl) (*p*-tolyl)sulfane (**6i**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **7i** (59 mg, 95%) as a white viscous solid. ^{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 (101 MHz, $CDCl_3$) δ ppm 144.44, 142.14, 142.02, 137.07, 130.16, 129.52, 126.01, 124.92, 21.41.

1,3-Dimethyl-5-(*p*-tolylsulfinyl)benzene (**7j**)[31]

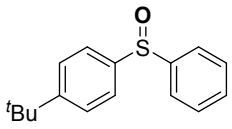


7j

The representative procedure was followed using (3,5-dimethyl phenyl) (*p*-tolyl)sulfane (**6j**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **7j** (54 mg, 90%) as a white viscous solid. ^{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 (101 MHz, $CDCl_3$) δ ppm 145.45,

142.65, 141.40, 139.19, 132.72, 129.96, 124.94, 122.17, 21.38, 21.28.

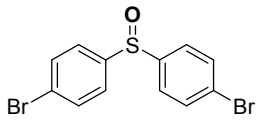
1-(tert-Butyl)-4-(phenylsulfinyl)benzene (**7k**)[32]



7k

The representative procedure was followed using (4-(*tert*-butyl) phenyl) (phenyl)sulfane (**6k**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **7k** (55 mg, 86%) as a white viscous solid. ^{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 (101 MHz, $CDCl_3$) δ ppm 154.64, 145.70, 142.41, 130.84, 129.22, 126.37, 124.80, 124.68, 34.91, 31.16.

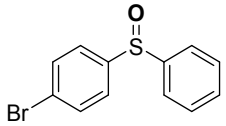
4,4'-Sulfinylbis(bromobenzene) (**7l**)[33]



7l

The representative procedure was followed using bis(4-bromophenyl) sulfane (**6l**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **7l** (83 mg, 93%) as a white viscous solid. ^{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 (101 MHz, $CDCl_3$) δ ppm 144.40, 132.69, 126.16, 125.92.

1-Bromo-4-(phenylsulfinyl)benzene (**7m**)[32]

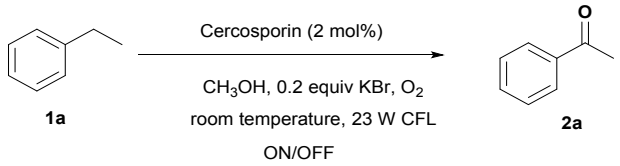


7m

The representative procedure was followed using (4-bromophenyl) (phenyl) sulfane (**6m**) (0.25 mmol) as substrate. Isolation by column chromatography (PE/EtOAc: 5/1) yielded **7m** (63 mg, 92%) as a white viscous solid. ^{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 (101 MHz, $CDCl_3$) δ ppm 145.23, 144.90, 132.46, 131.32, 129.45, 126.18, 125.46, 124.63.

7. Mechanism Research

7.1 Time profile of the photooxidation of benzylic C–H bond with and without visible light



In a dried schlenk tube, 4-ethylbenzene (**1a**) (0.25 mmol), potassium bromide (0.2 equiv) and cercosporin (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. Then, the reaction mixtures were placed under 23 W CFL at given time intervals. The yield was detected by GC using diphenyl as internal standard.

Table S4. On/off experiment for the photooxidation of benzylic C–H bond

Light ON/OFF	Time (h)	Yield of **2a**
0	0	0
2 hour on	2	20
1 hour off	3	22
2 hour on	5	45
1 hour off	6	46
2 hour on	8	68
1 hour off	9	70
2 hour on	11	83

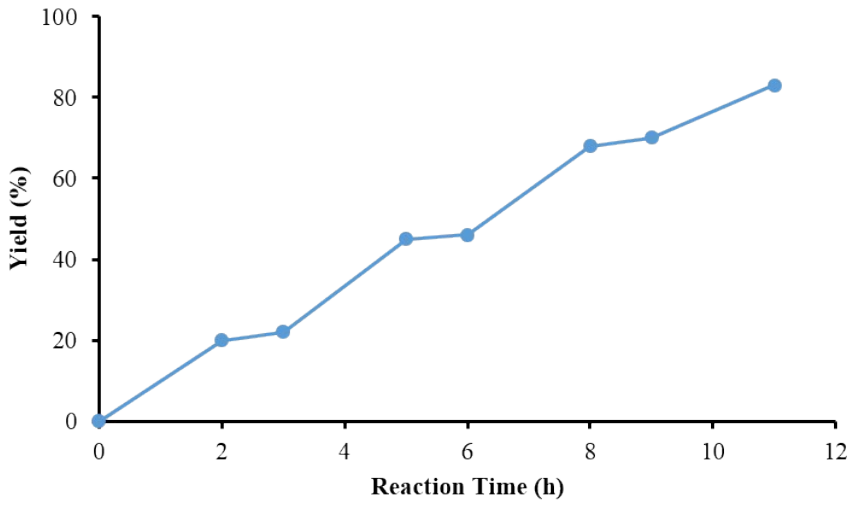
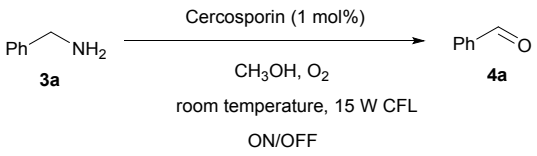


Fig. S3 Time profile of the photooxidation of benzylic C–H bond with and without visible light.

7.2 Time profile of the photooxidation of amine with and without visible light



In a dried schlenk tube, phenylmethanamine (**3a**) (0.2 mmol) and cercosporin (1 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 15 W CFL at given time intervals. The yield was detected by GC using diphenyl as internal standard.

Table S5. On/off experiment for the photooxidation of amine

Light ON/OFF	Time (h)	Yield of **4a**
0	0	0
2 hour on	2	26
1 hour off	3	29
2 hour on	5	52
1 hour off	6	55
2 hour on	8	72
1 hour off	9	75
2 hour on	11	95

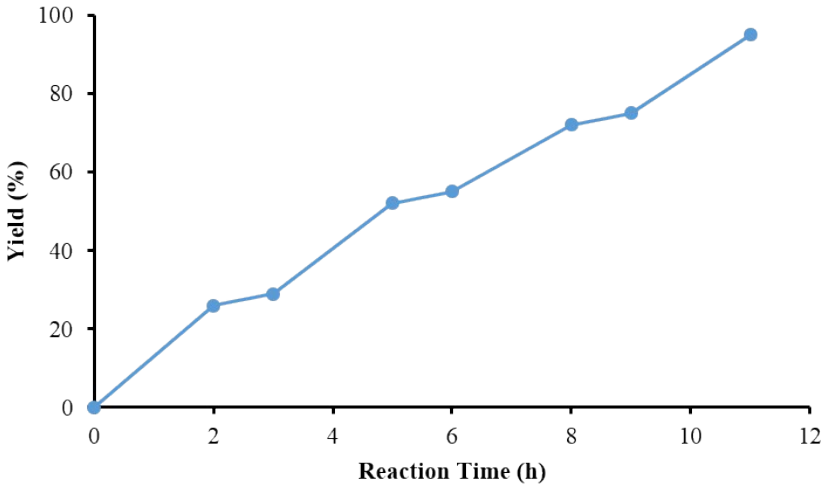
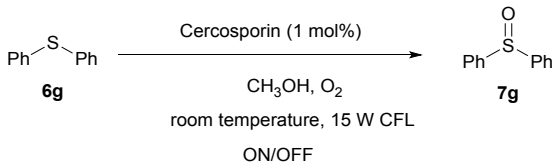


Fig. S4 Time profile of the photooxidation of amine with and without visible light.

7.3 Time profile of the photooxidation of sulfide with and without visible light



In a dried schlenk tube, diphenylsulfane (**6g**) (0.25 mmol) and cercosporin (1 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 15 W CFL at given time intervals. The yield was detected by GC using diphenyl as internal standard.

Table S6. On/off experiment for the photooxidation of sulfide.

Light ON/OFF	Time (h)	Yield of **7g**
0	0	0
2 hour on	2	30
1 hour off	3	32
2 hour on	5	55
1 hour off	6	57
2 hour on	8	75
1 hour off	9	77
2 hour on	11	95

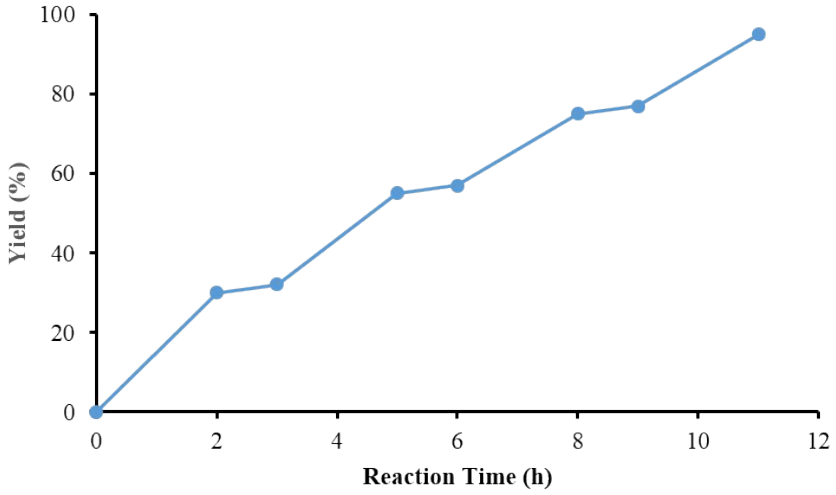


Fig. S5 Time profile of the photooxidation of sulfide with and without visible light.

7.4 Alkane radical capturing experiment in the photooxidation of benzylic C–H bond

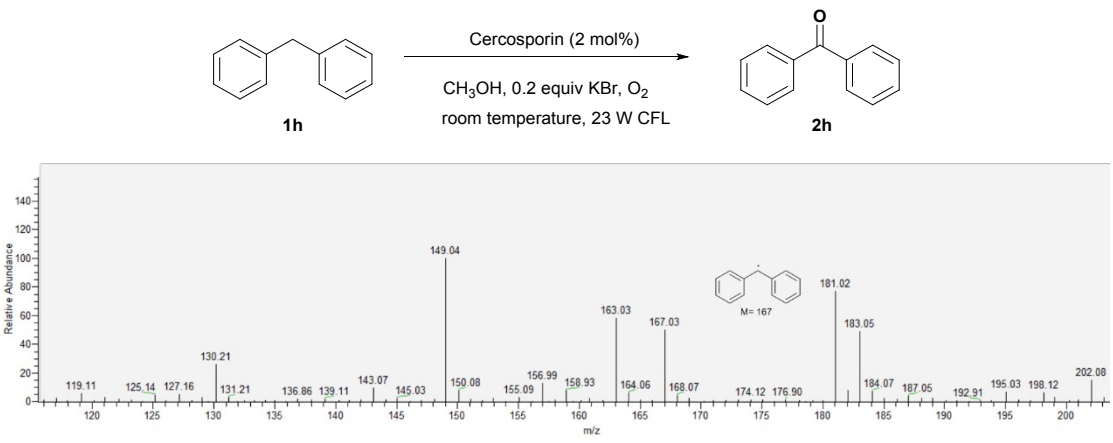


Fig. S6 Alkane radical capturing experiment in the photooxidation of benzylic C–H bond

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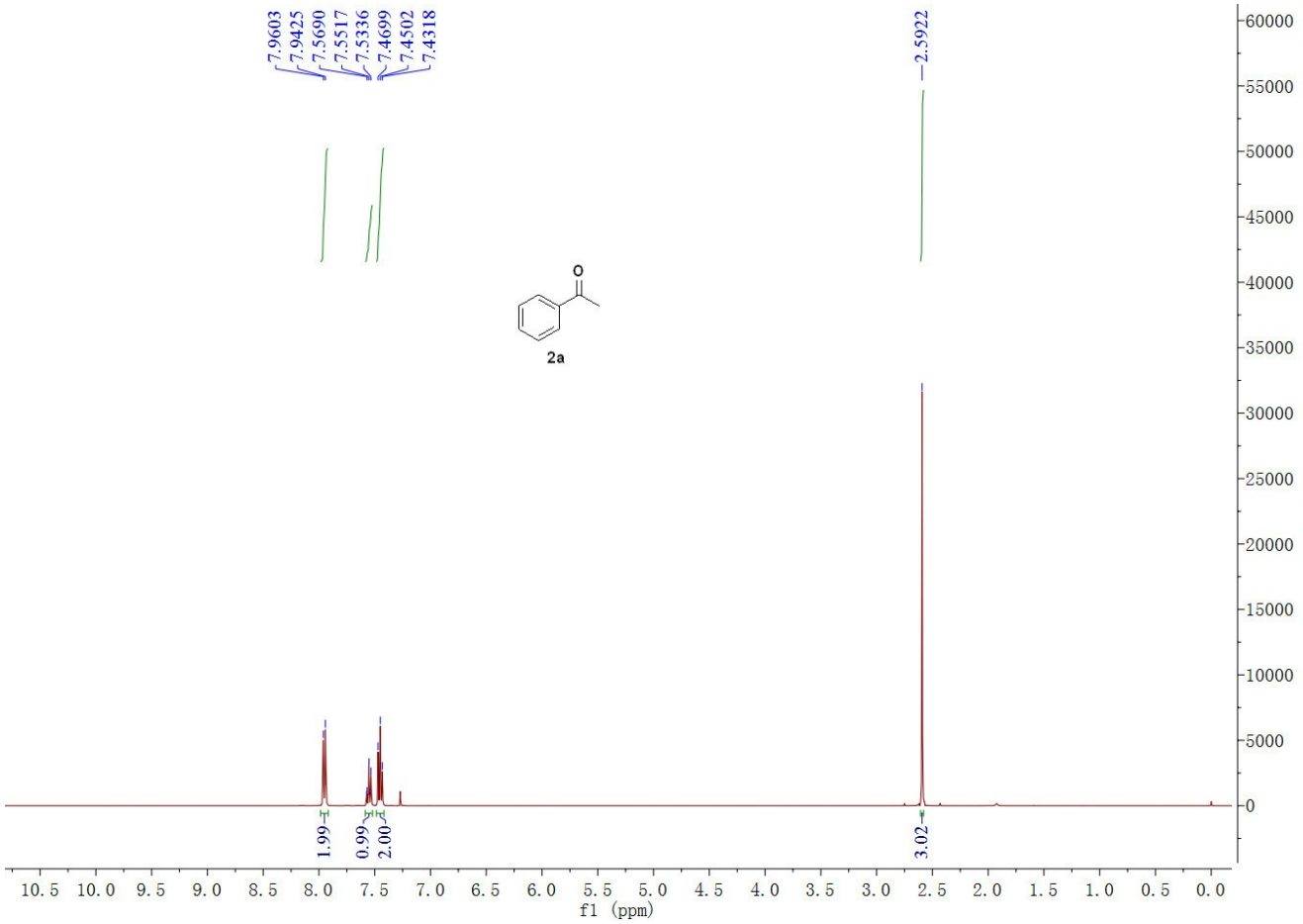
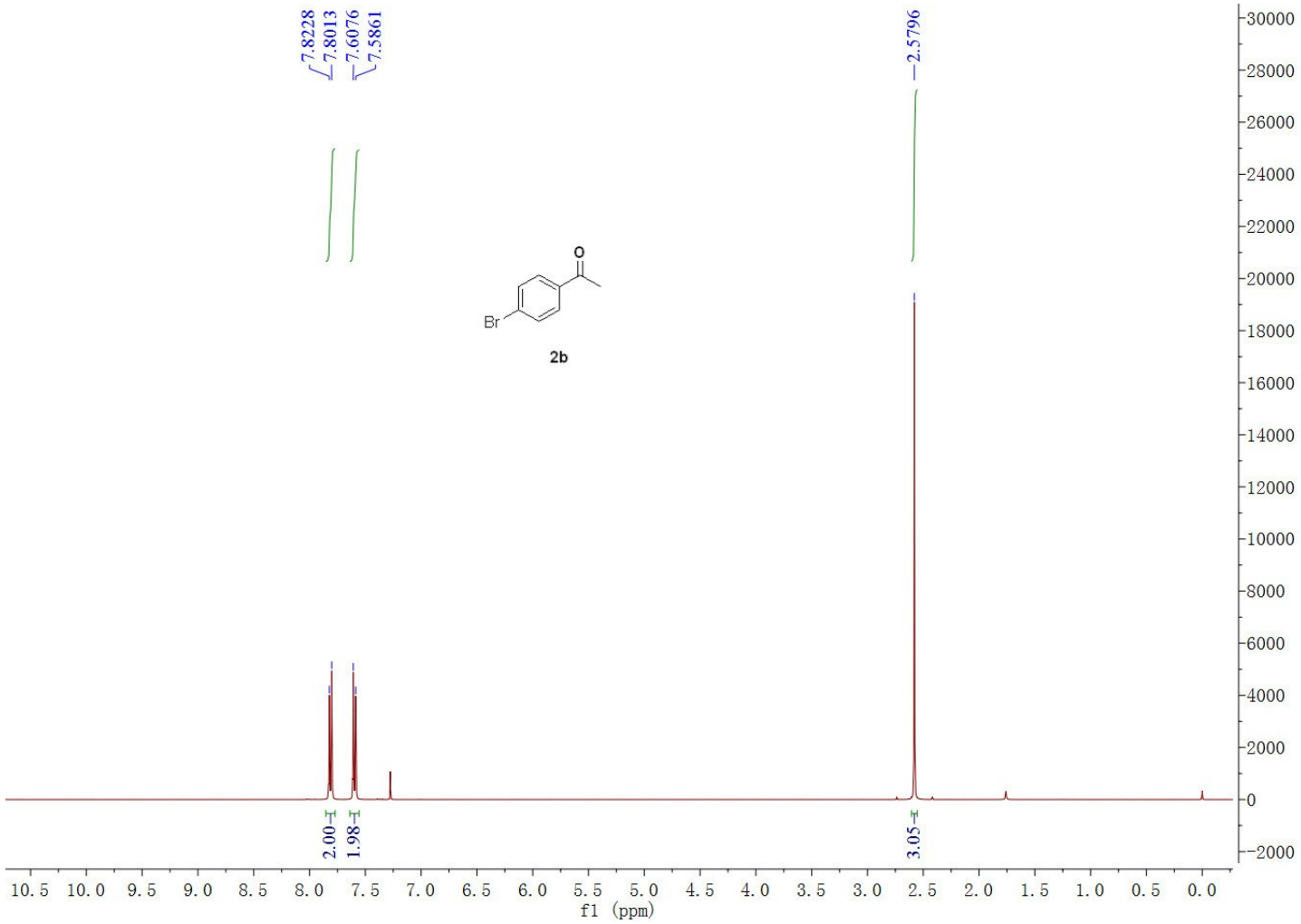
9. ^{1}H, ^{13}C and IR Spectra.

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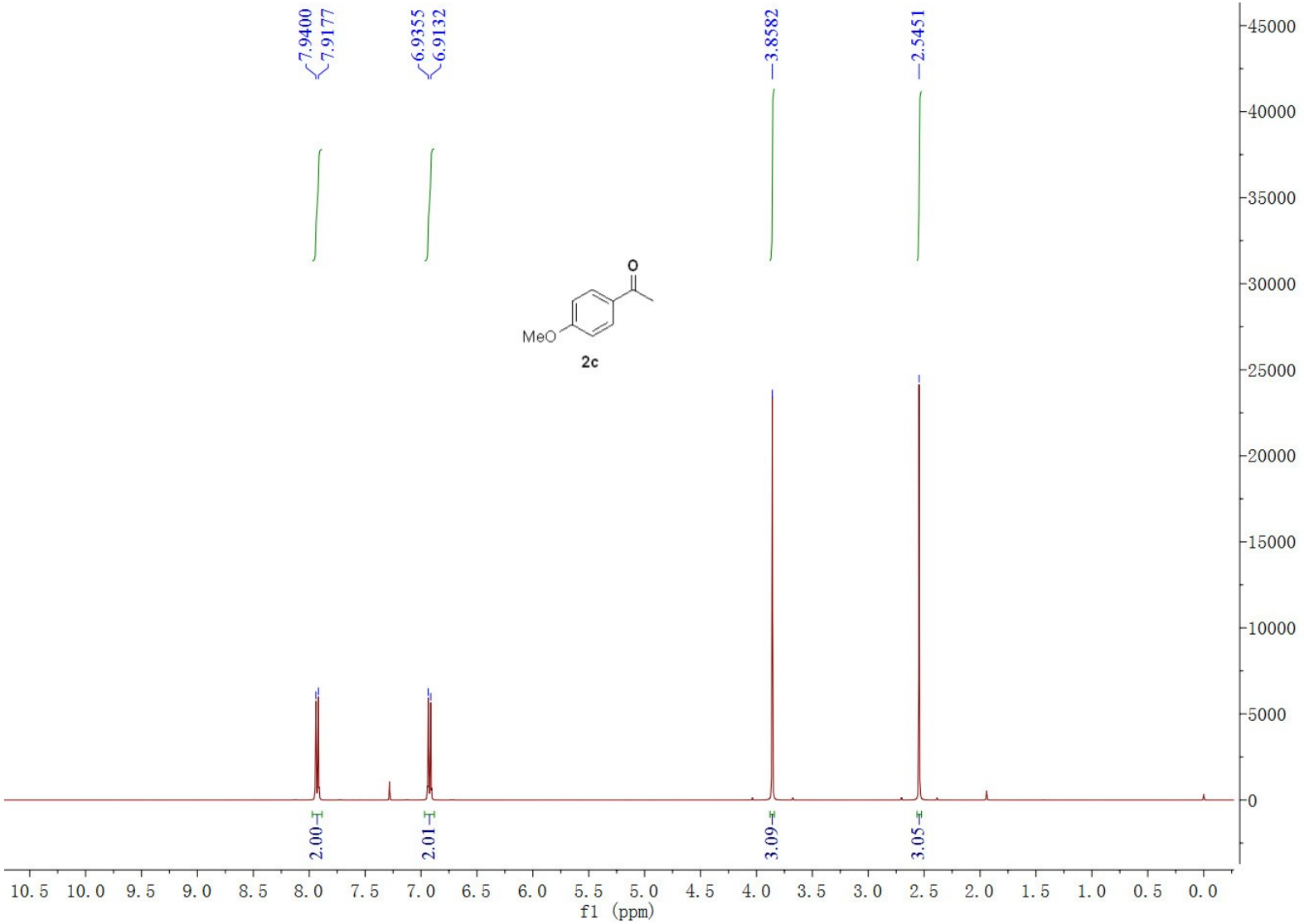
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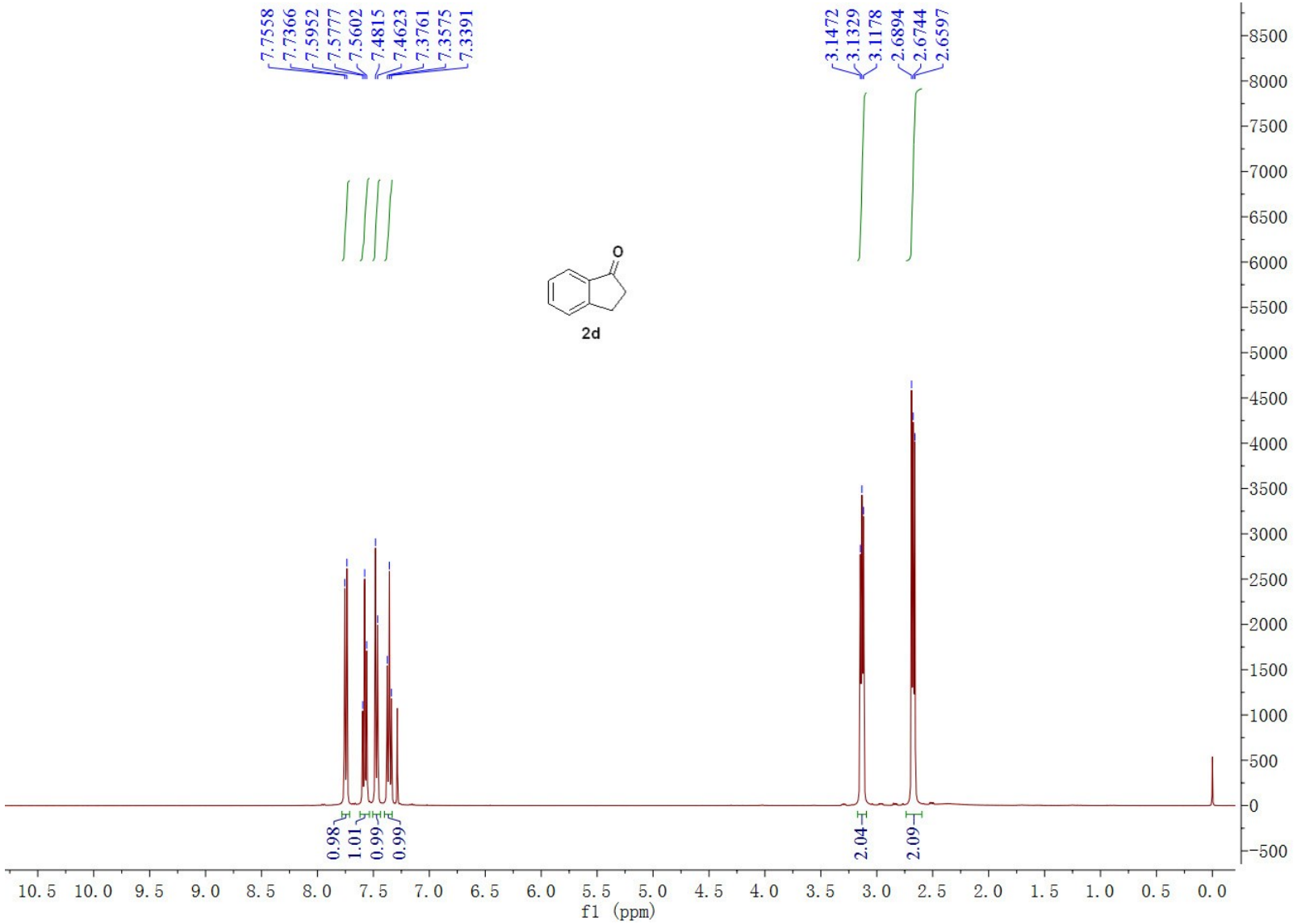
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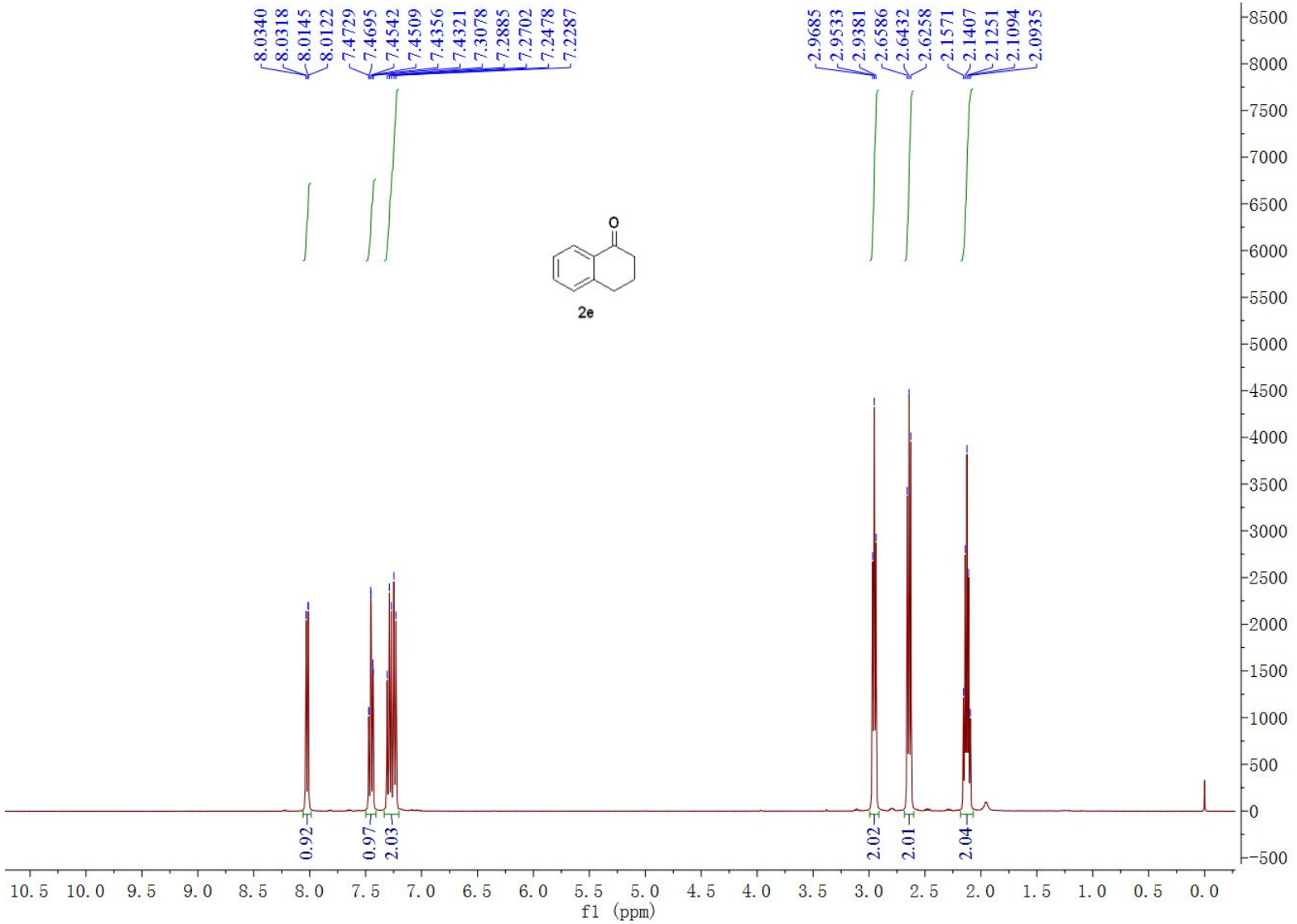
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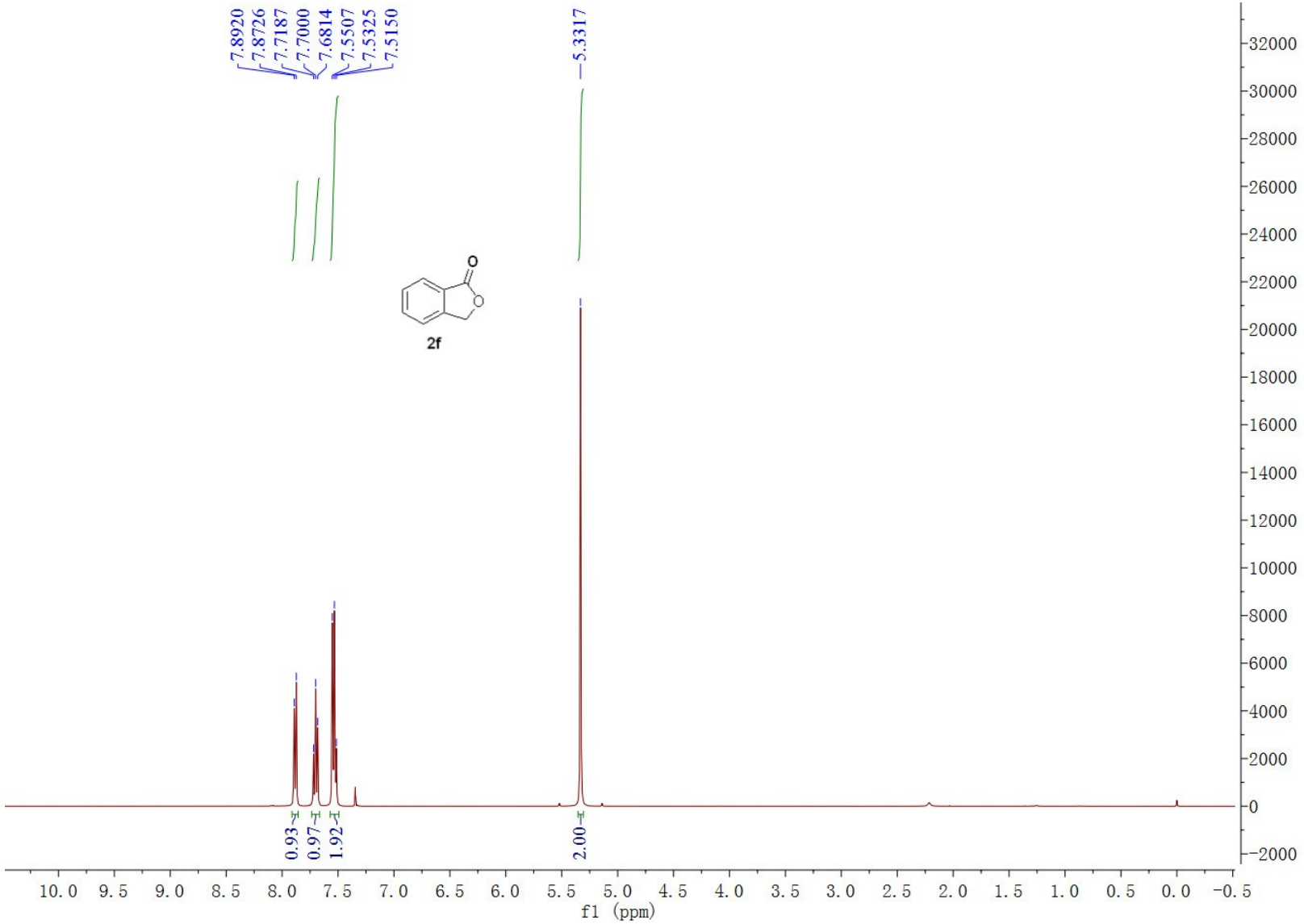
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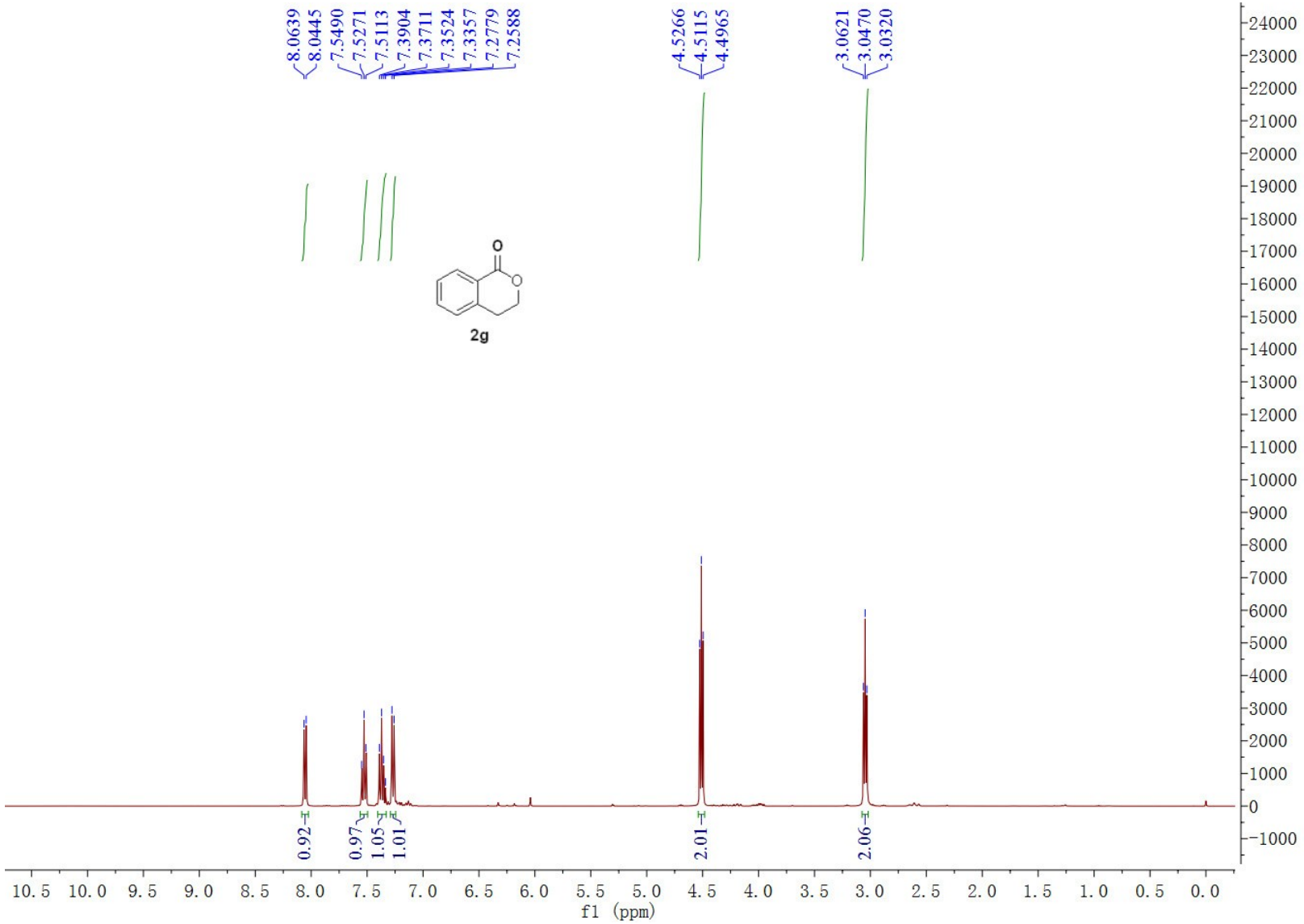
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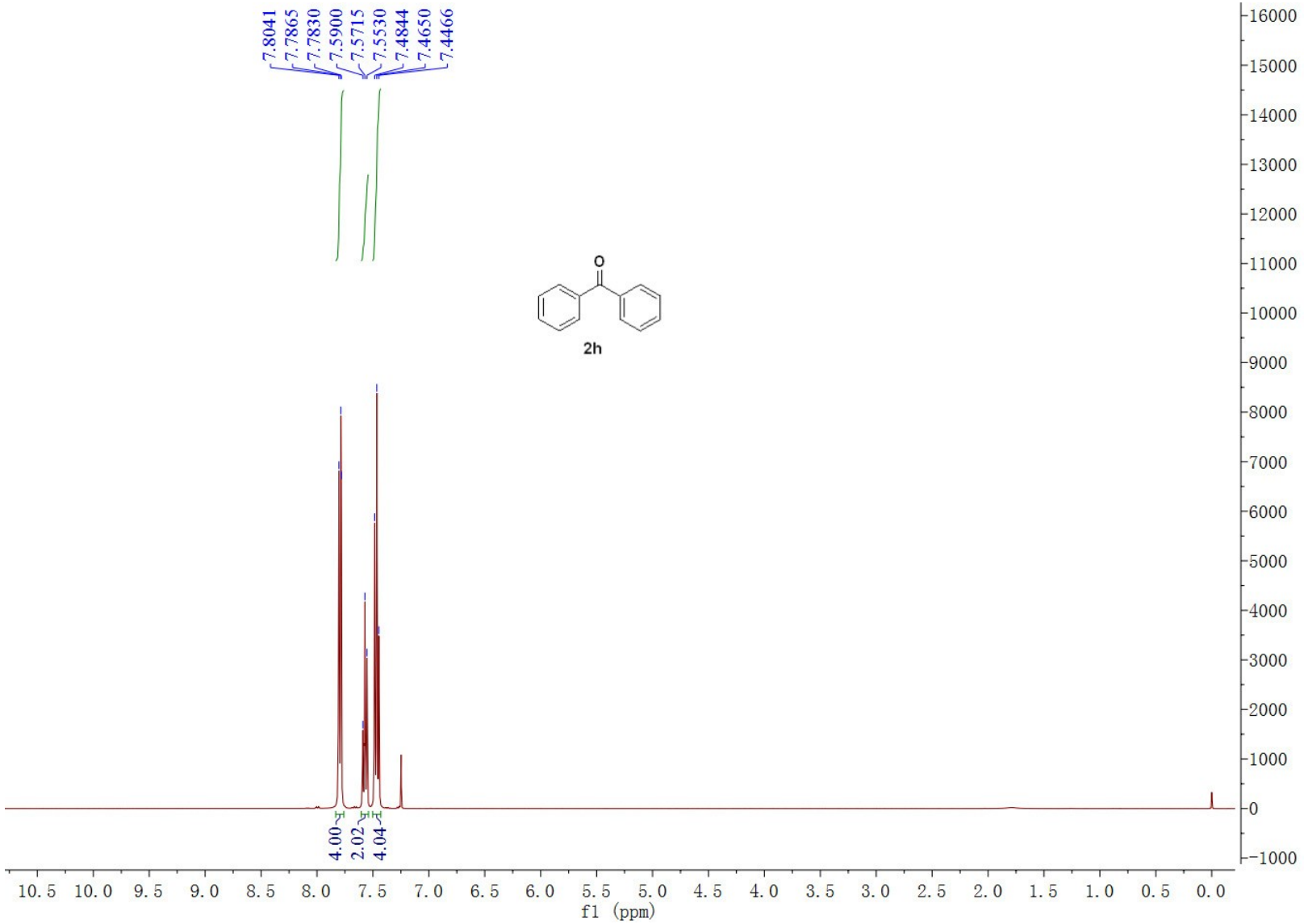
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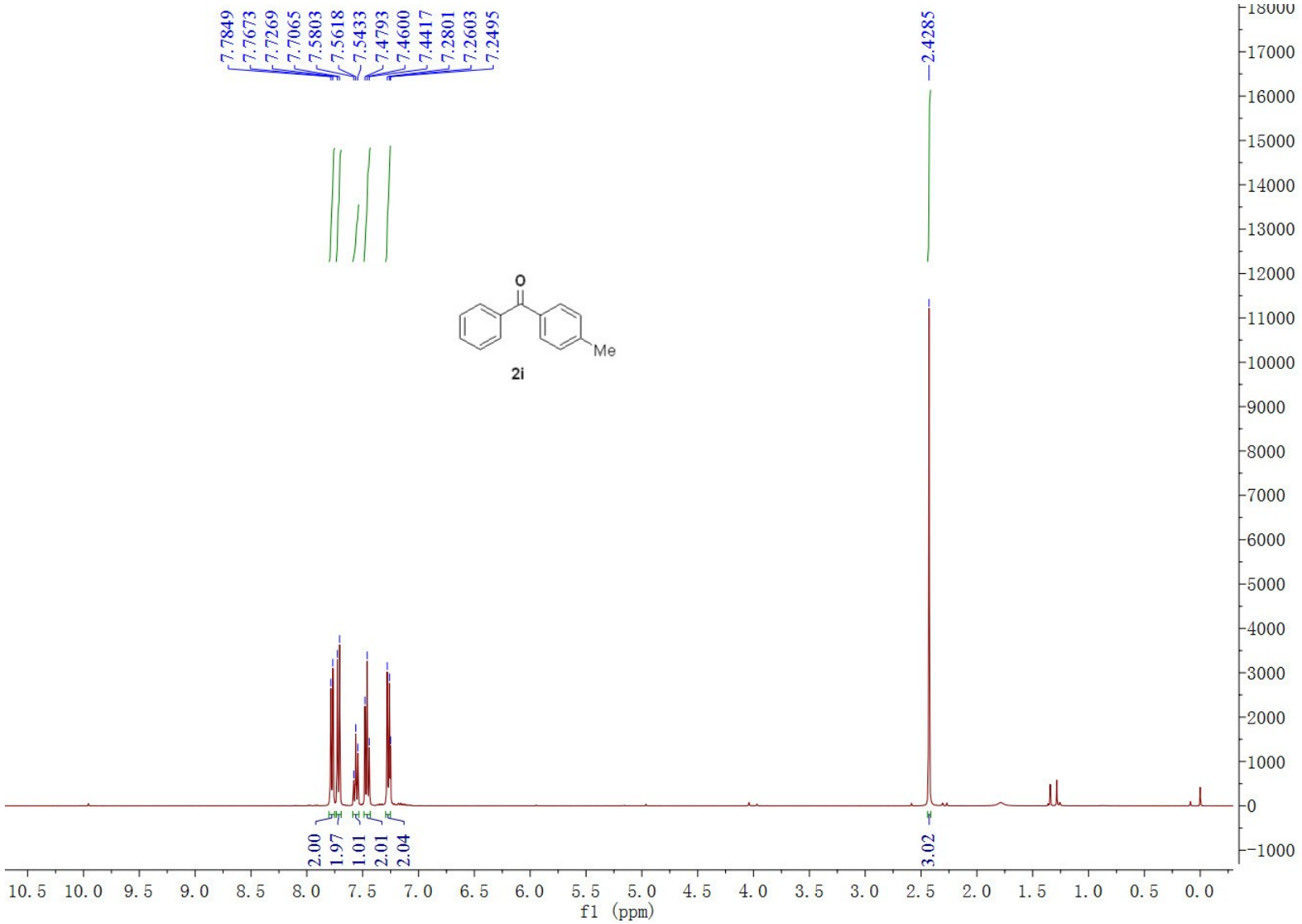
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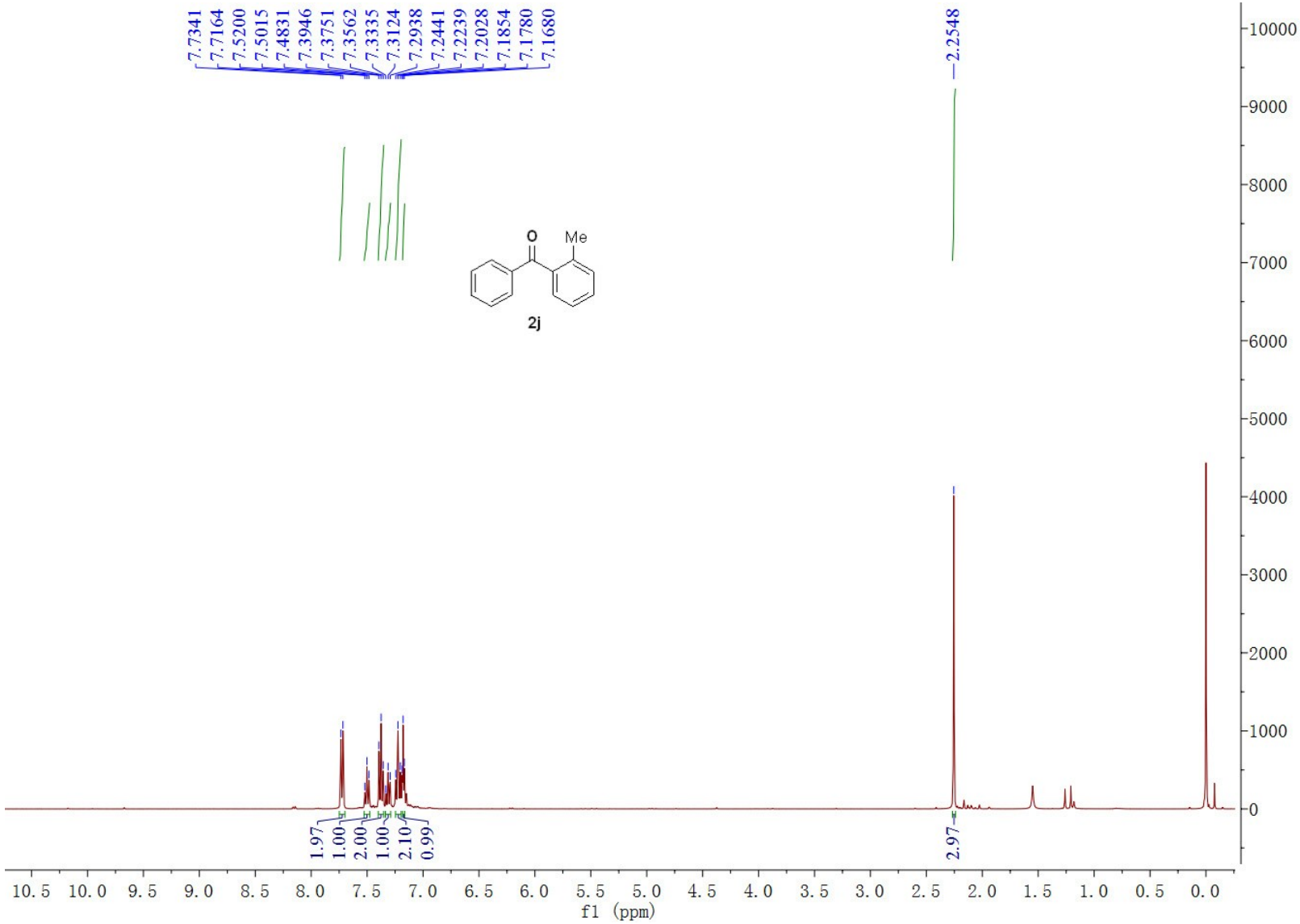
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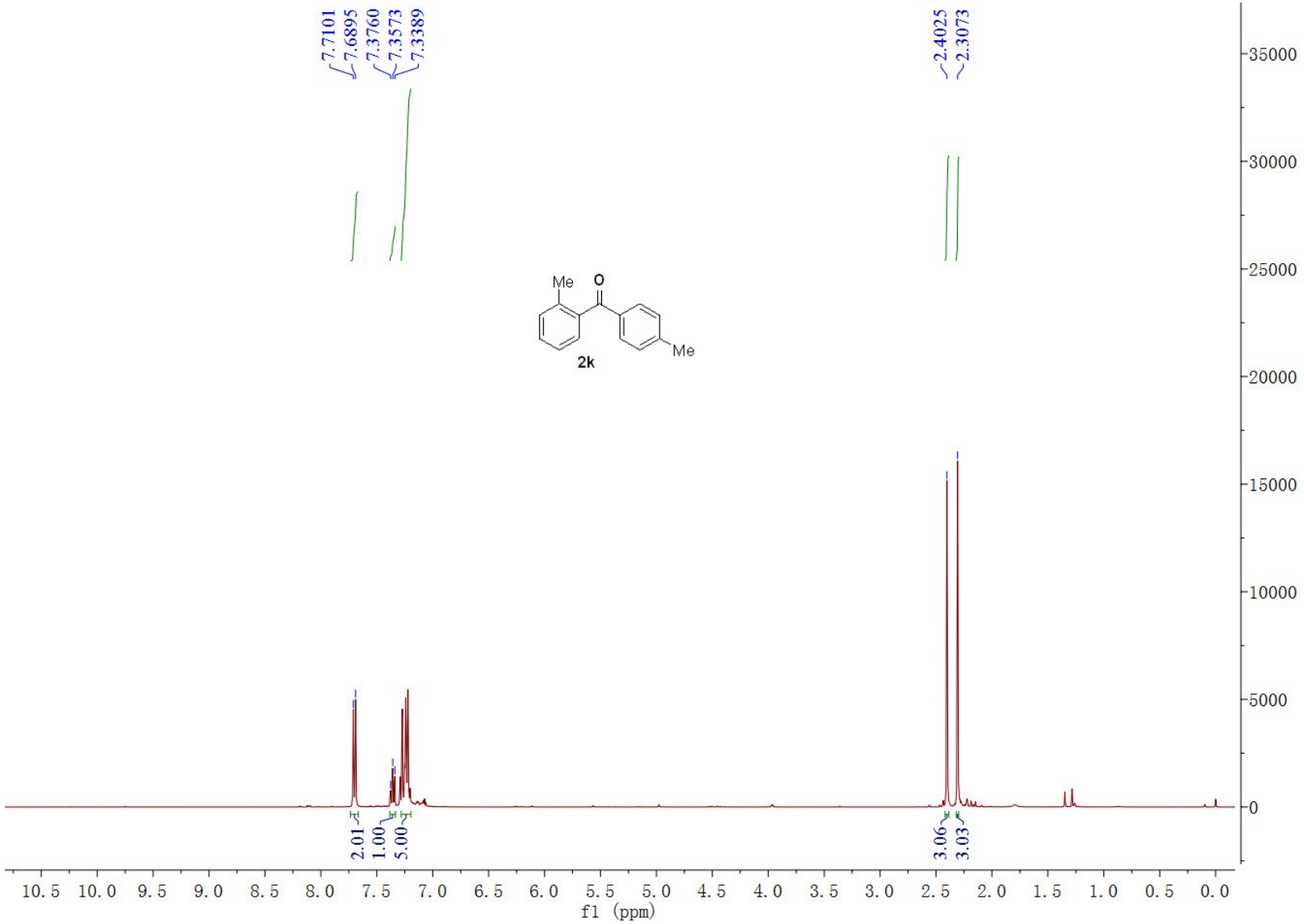
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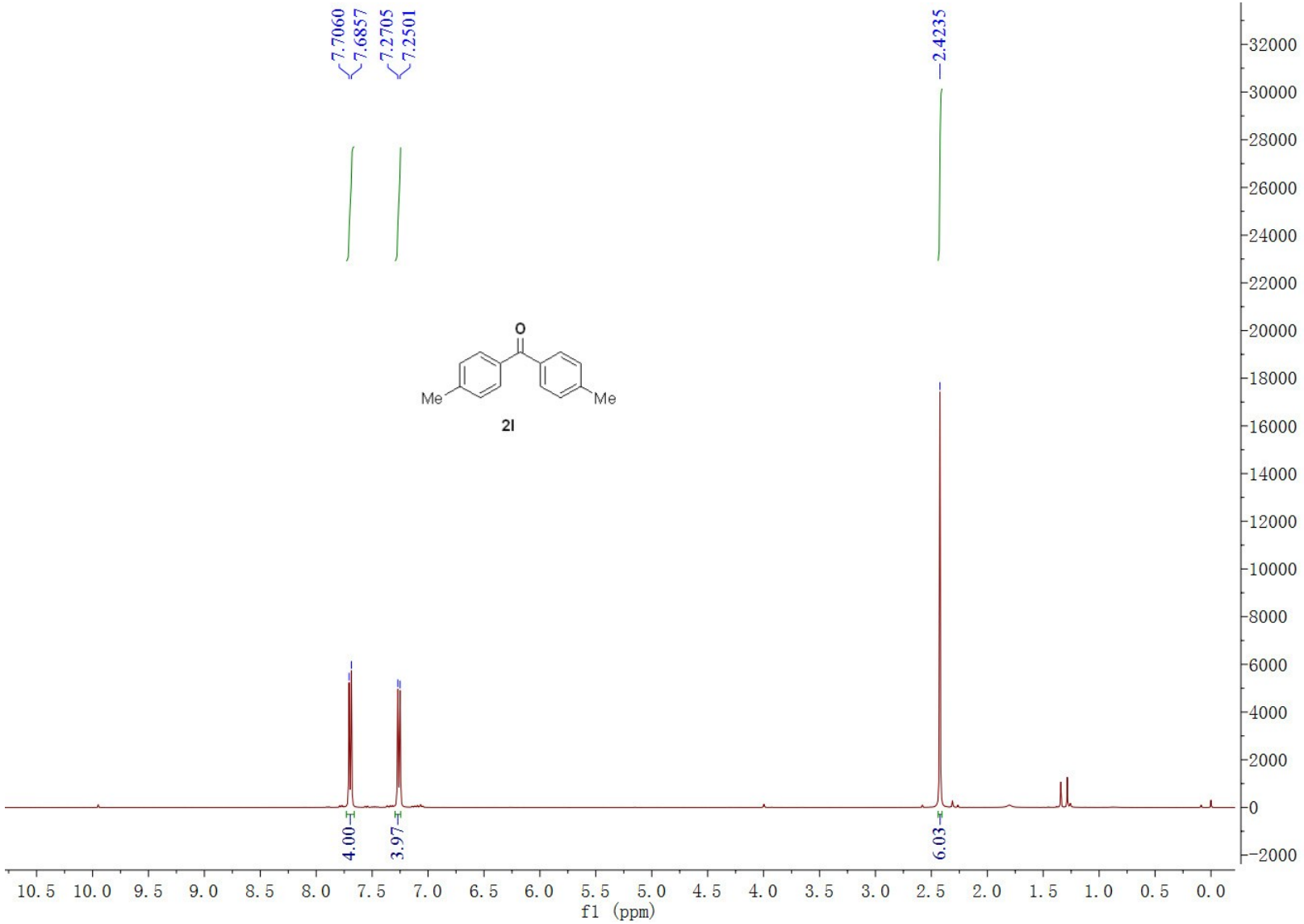
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.7060
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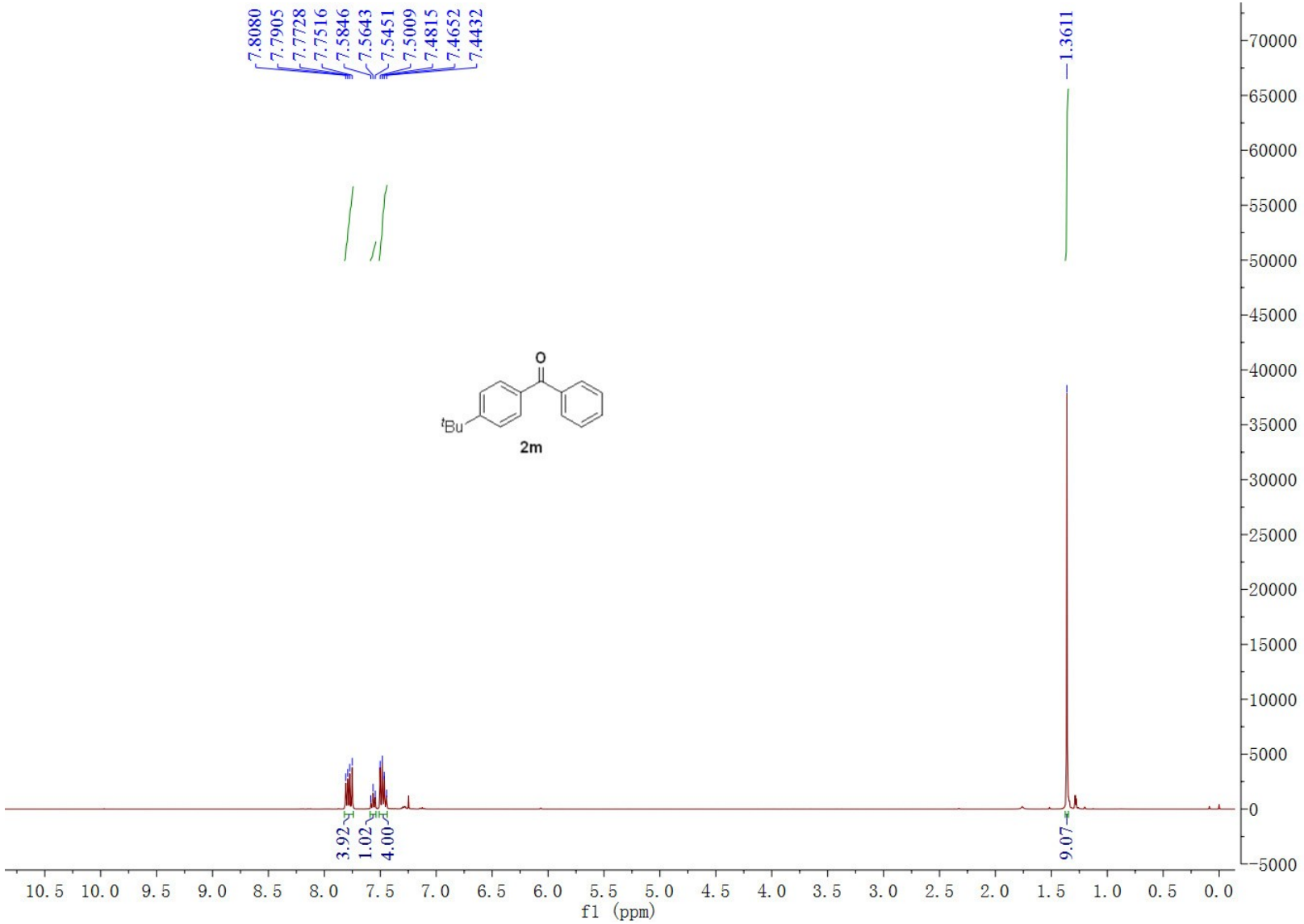
7.2501
2.4235
O
Me
Me
2l
4.00
3.97
6.03
f1 (ppm)


7.8080
7.7905
7.7728
7.7516
7.5846
7.5643
7.5451
7.5009
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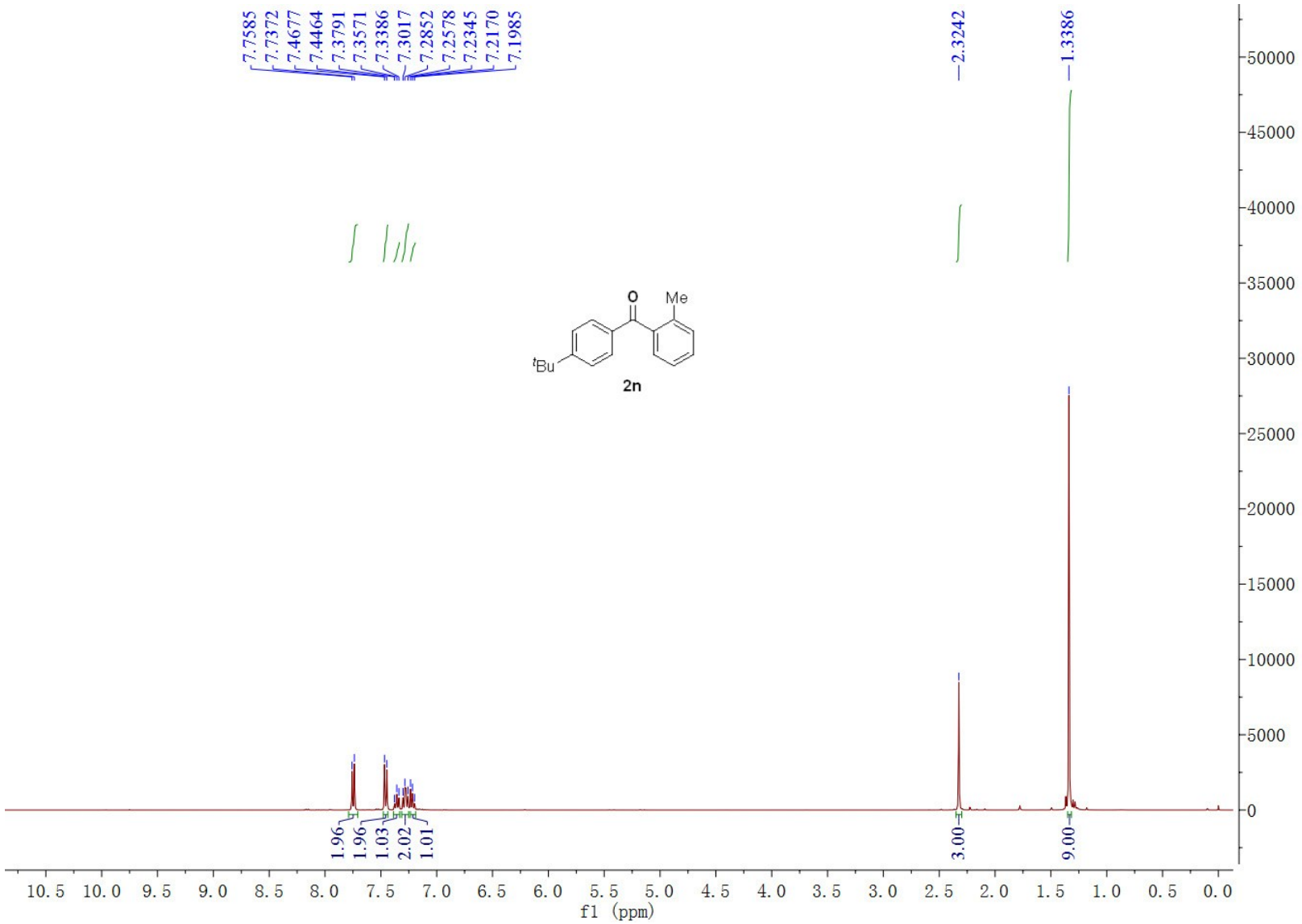
7.4652
7.4432
1.3611
O
tBu
2m
3.92
1.02
4.00
9.07
f1 (ppm)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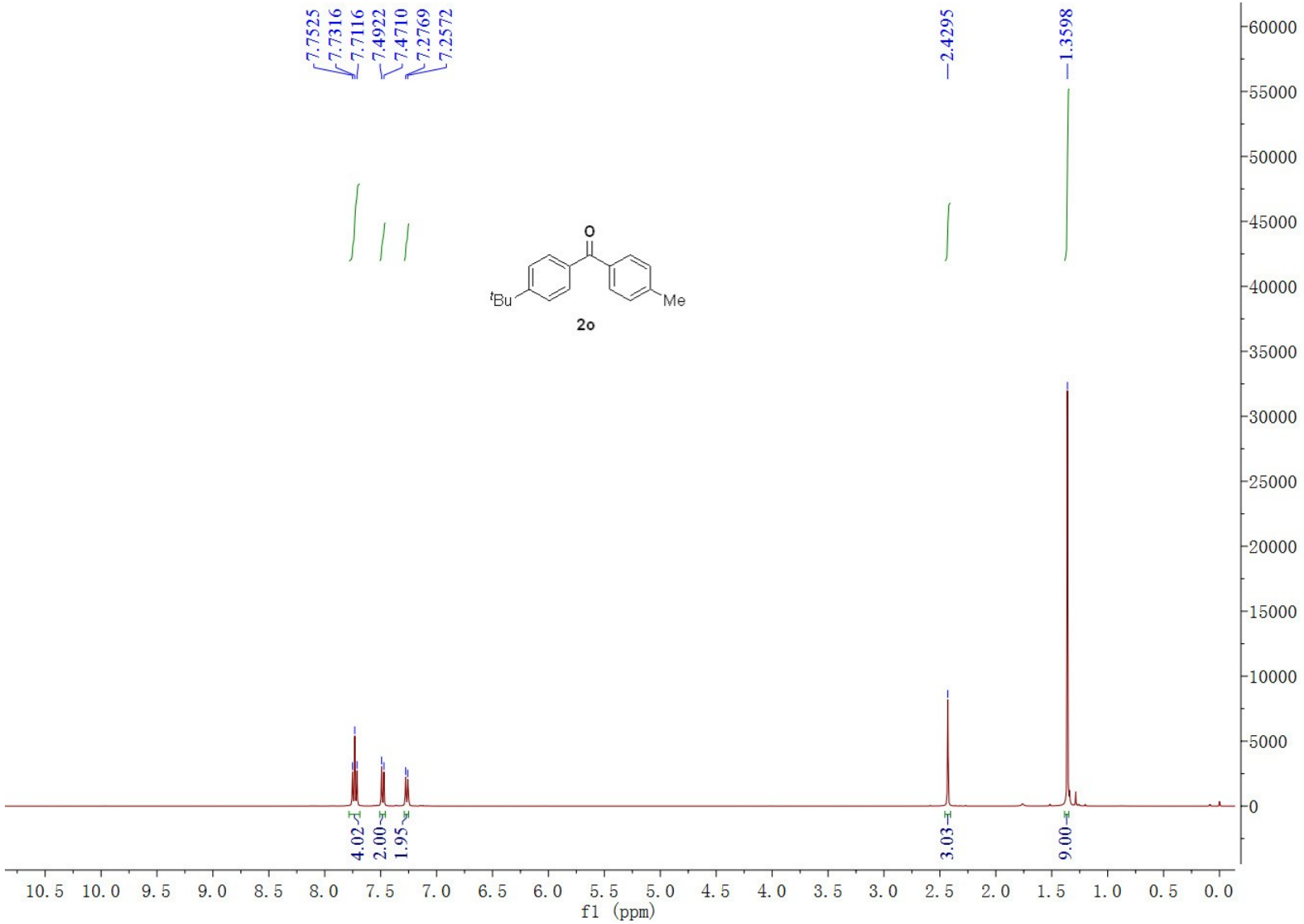
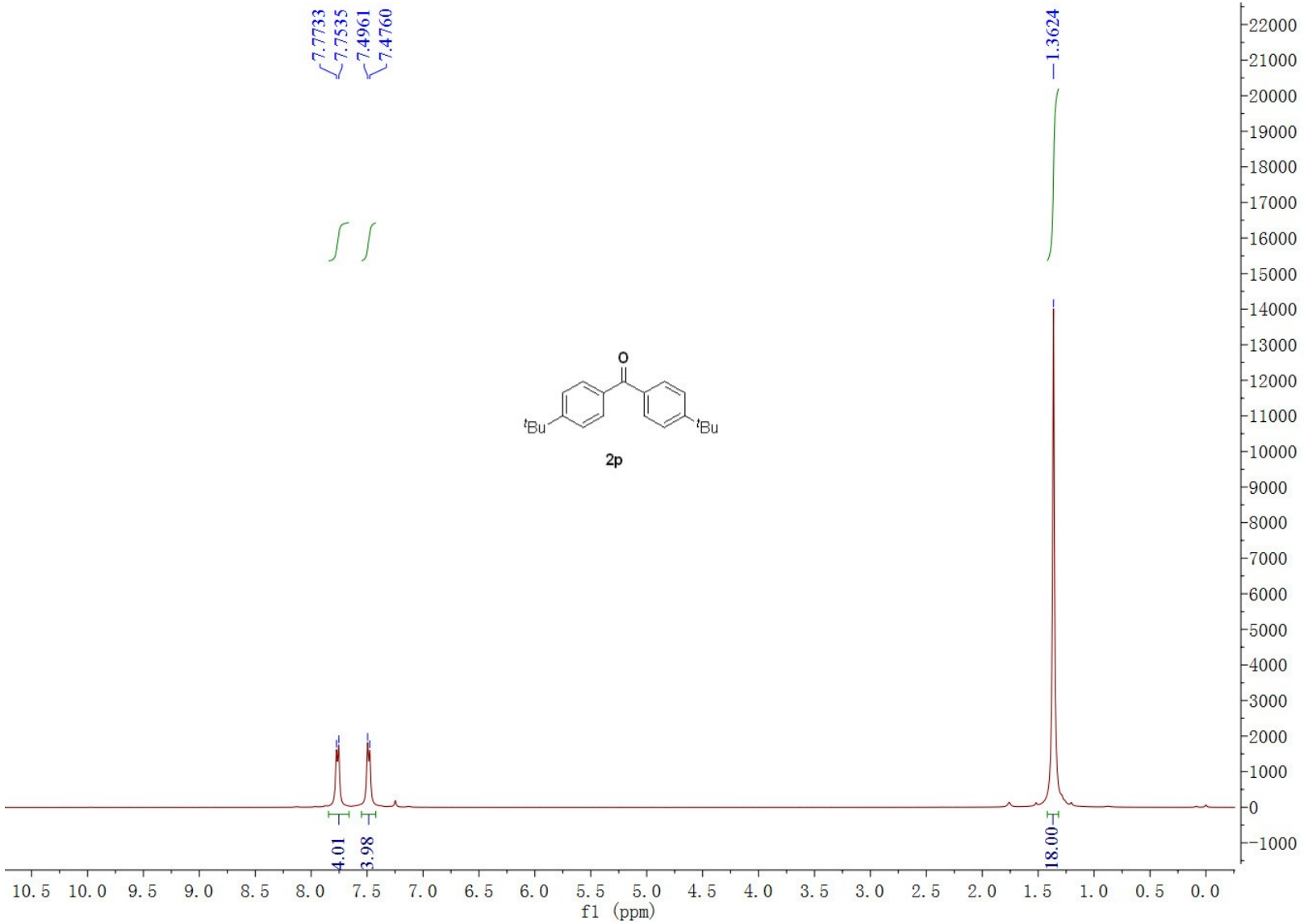
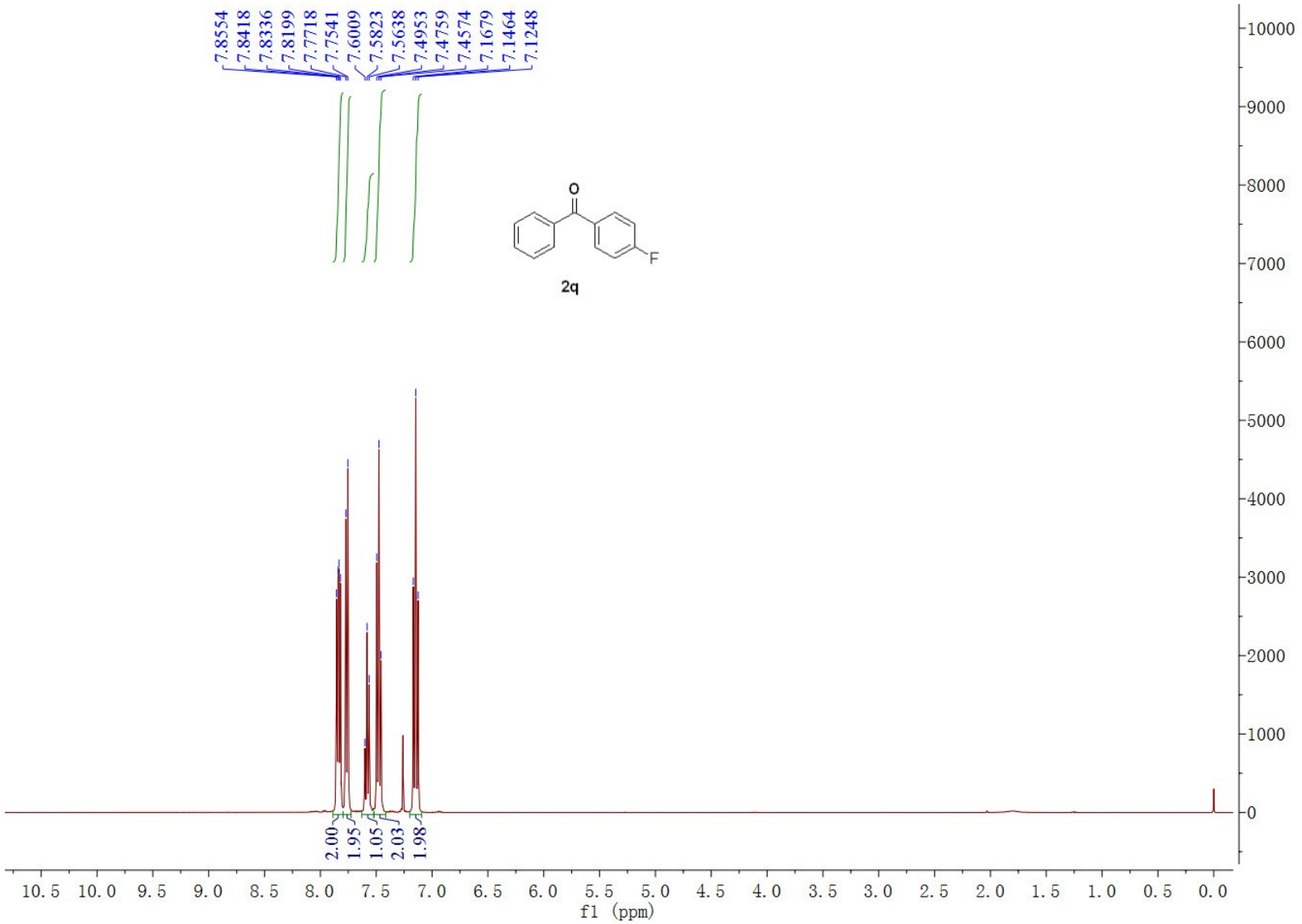
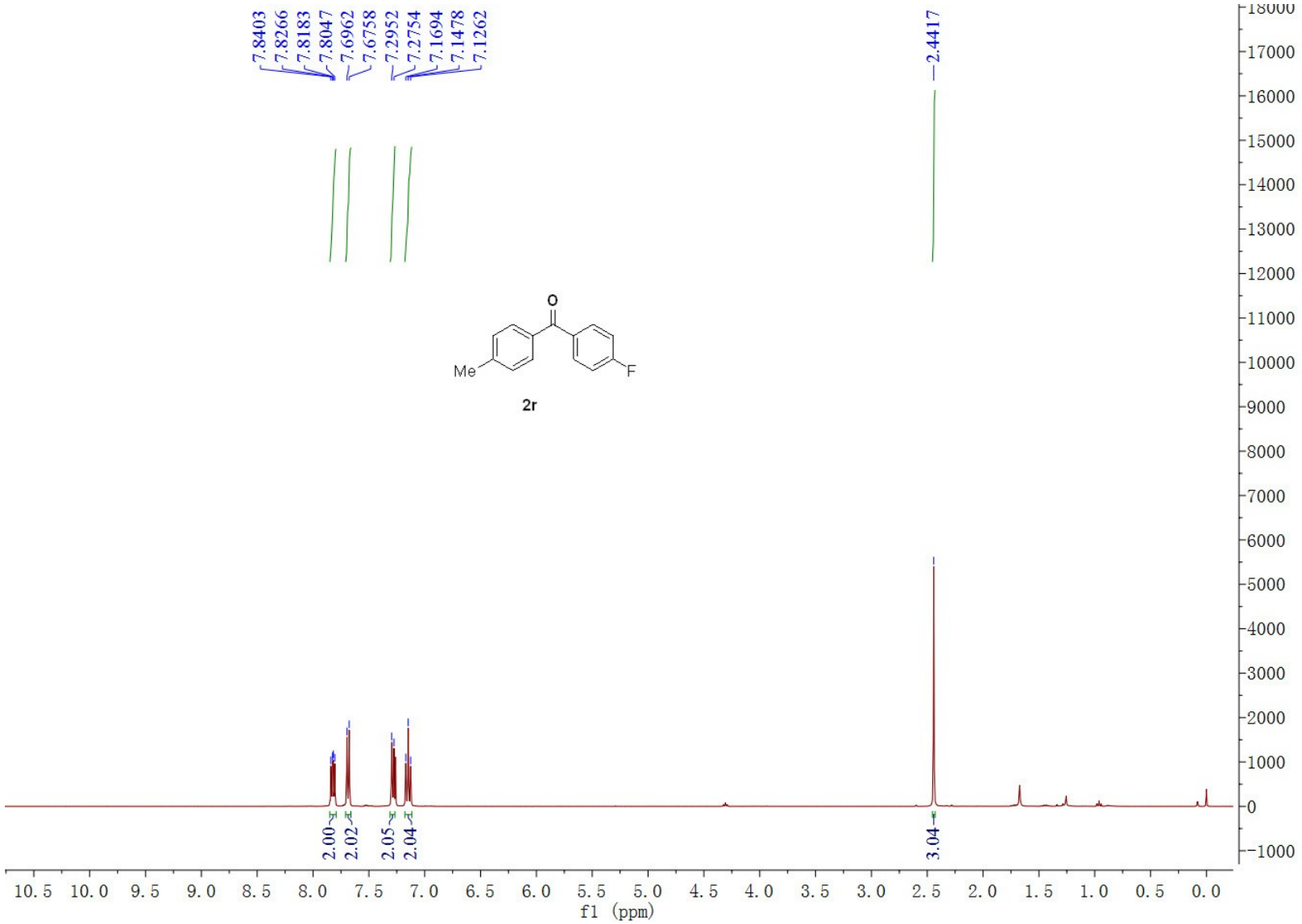
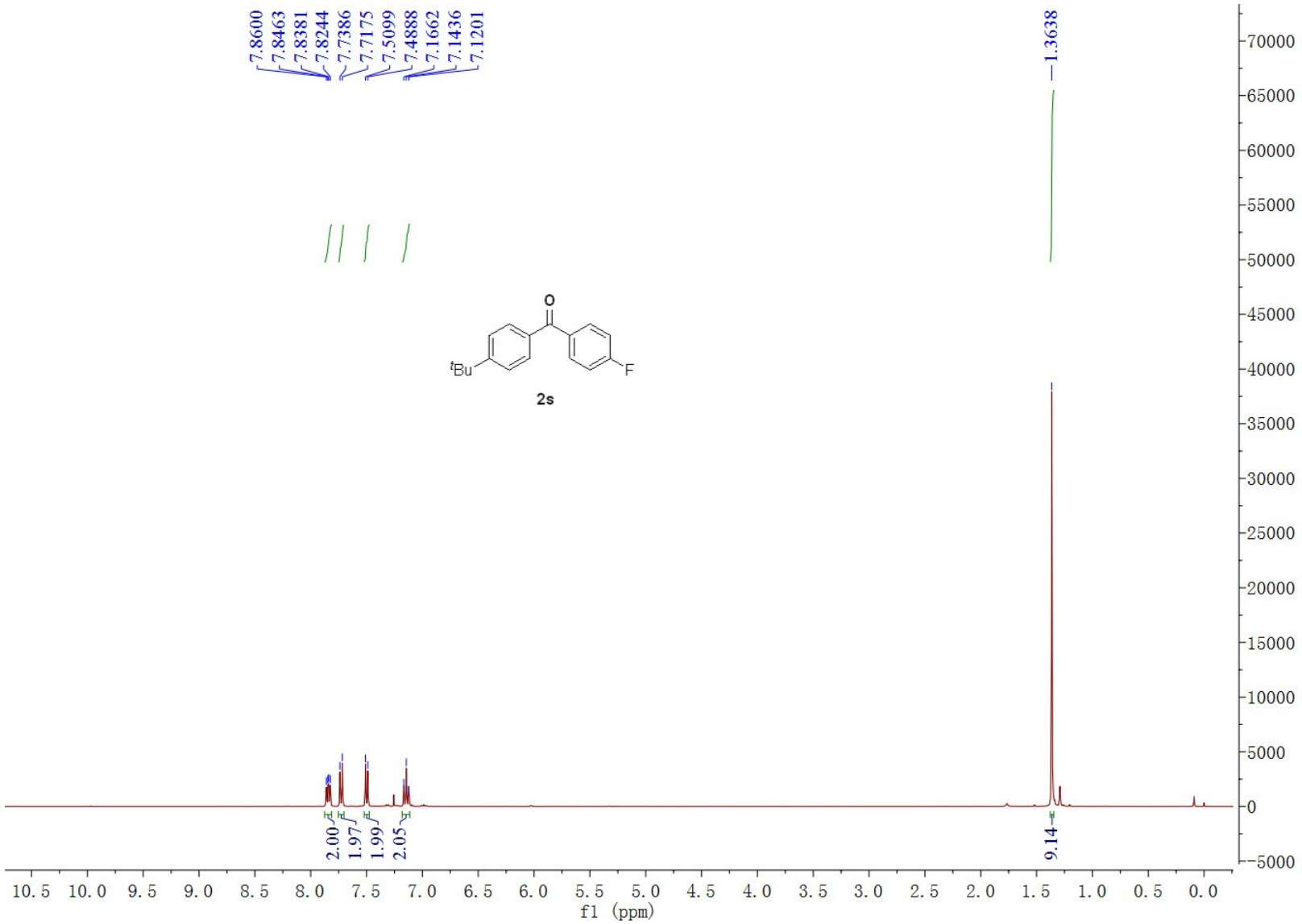
7.4677
7.4464
7.3791
7.3571
7.3386
7.3017
7.2852
7.2578
7.2345
7.2170
7.1985
2.3242
1.3386
O
Me
tBu
2n
1.96
1.96
1.03
2.02
1.01
3.00
9.00
f1 (ppm)


7.7525
7.7316
7.7116
7.4922
7.4710
7.2769
7.2572
2.4295
1.3598
O
tBu
Me
2o
4.02
2.00
1.95
3.03
9.00
f1 (ppm)


7.7733
7.7535
7.4961
7.4760
1.3624
O
tBu
tBu
2p
4.01
3.98
18.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
22000 21000 20000 19000 18000 17000 16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000


7.8554
7.8418
7.8336
7.8199
7.7718
7.7541
7.6009
7.5823
7.5638
7.4953
7.4759
7.4574
7.1679
7.1464
7.1248
O
F
2q
2.00
1.95
1.05
2.03
1.98
f1 (ppm)


7.8403
7.8266
7.8183
7.8047
7.6962
7.6758
7.2952
7.2754
7.1694
7.1478
7.1262
2.4417
O
Me
F
2r
2.00
2.02
2.05
2.04
3.04
f1 (ppm)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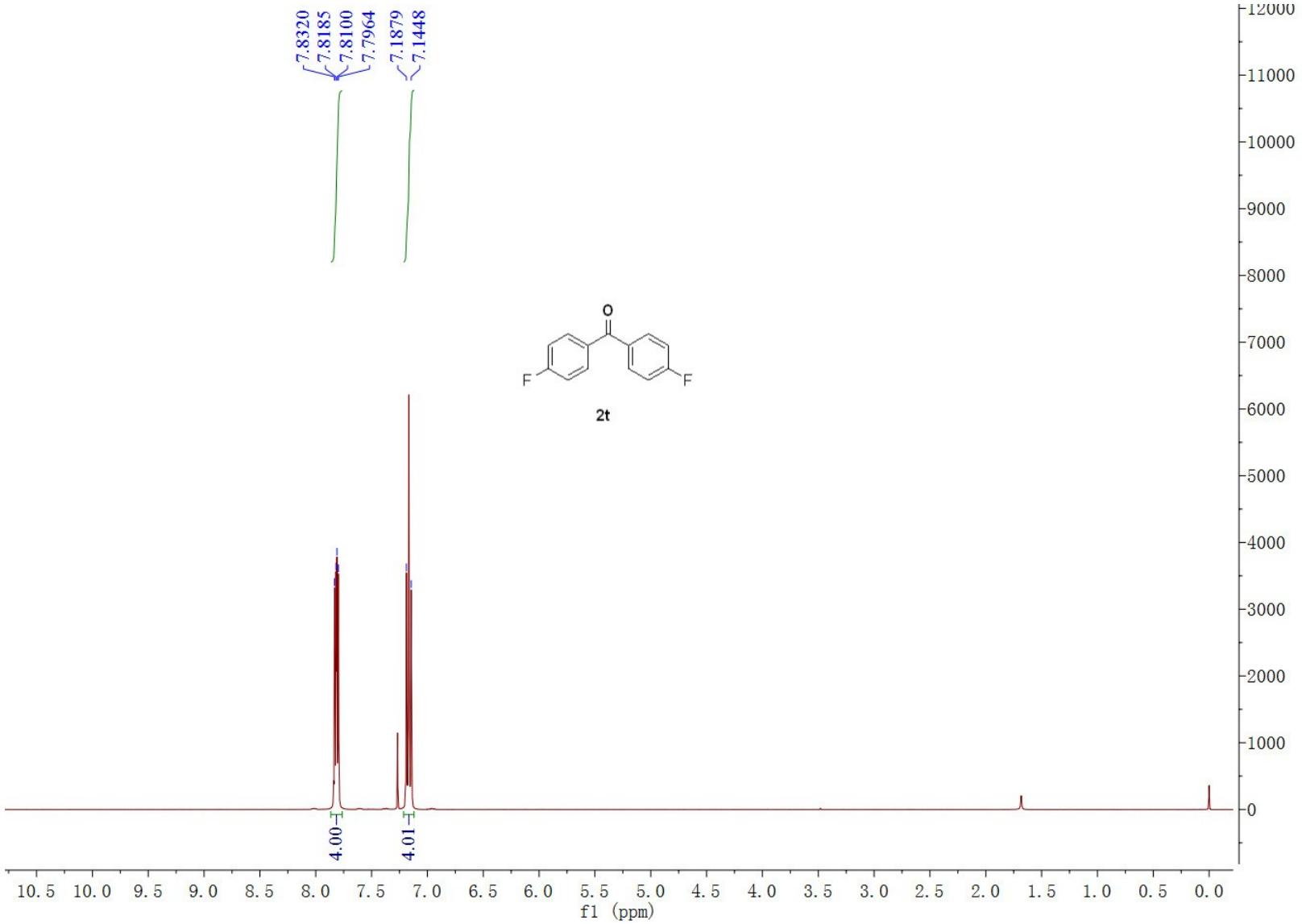
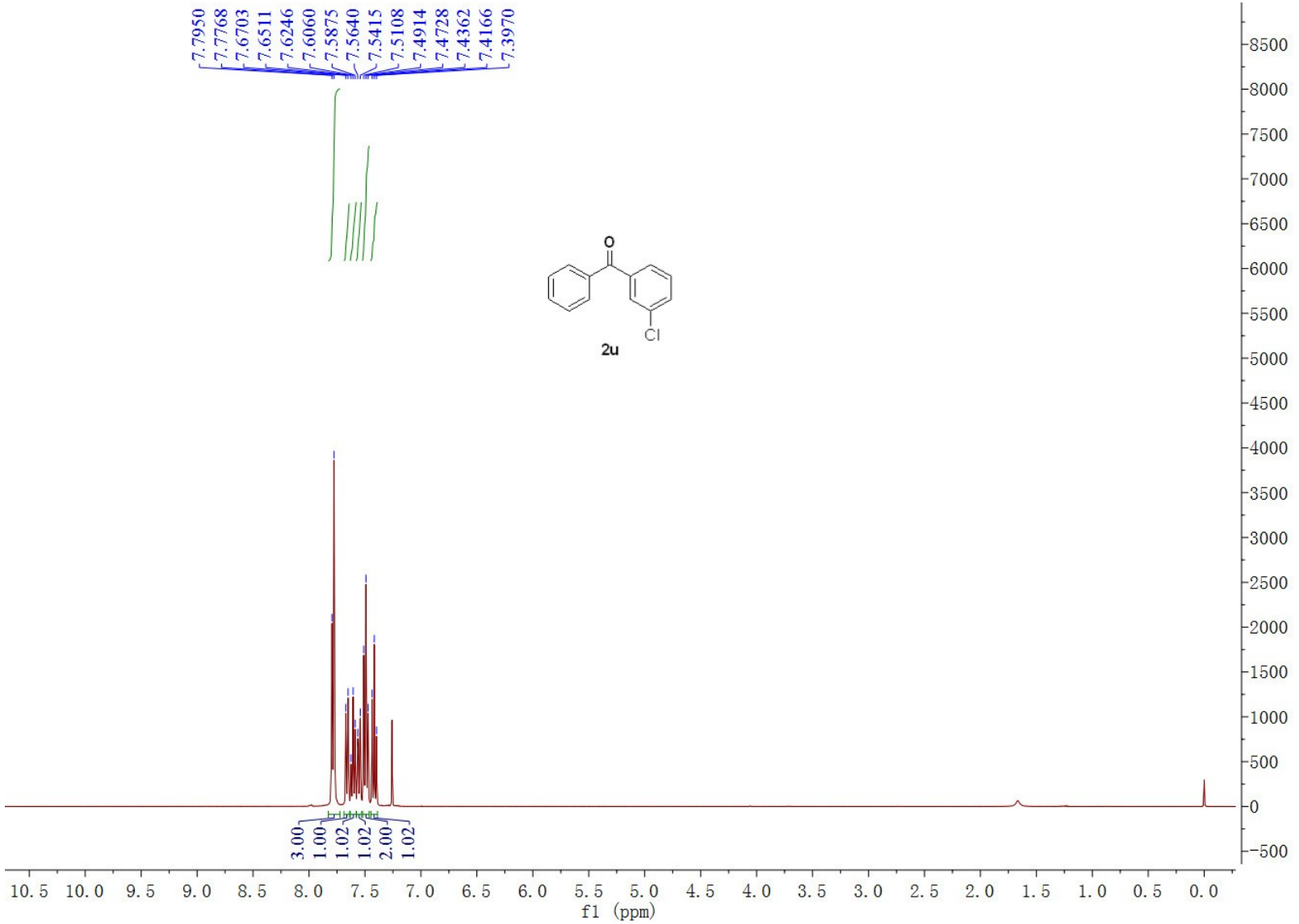
7.8463
7.8381
7.8244
7.7386
7.7175
7.5099
7.4888
7.1662
7.1436
7.1201
1.3638
O
tBu
F
2s
2.00
1.97
1.99
2.05
9.14
f1 (ppm)


7.8320
7.8185
7.8100
7.7964
7.1879
7.1448
O
F
F
2t
4.00
4.01
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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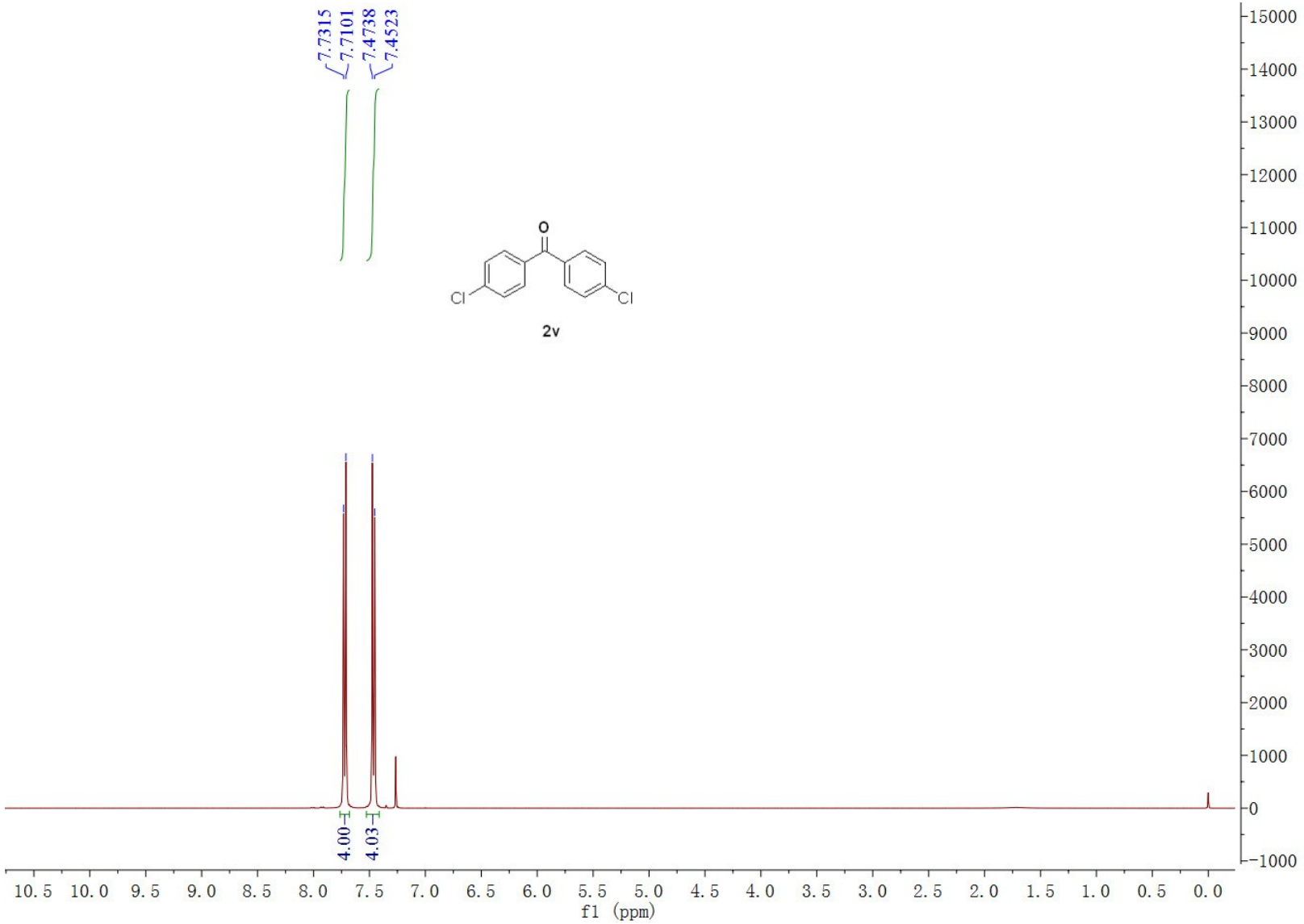
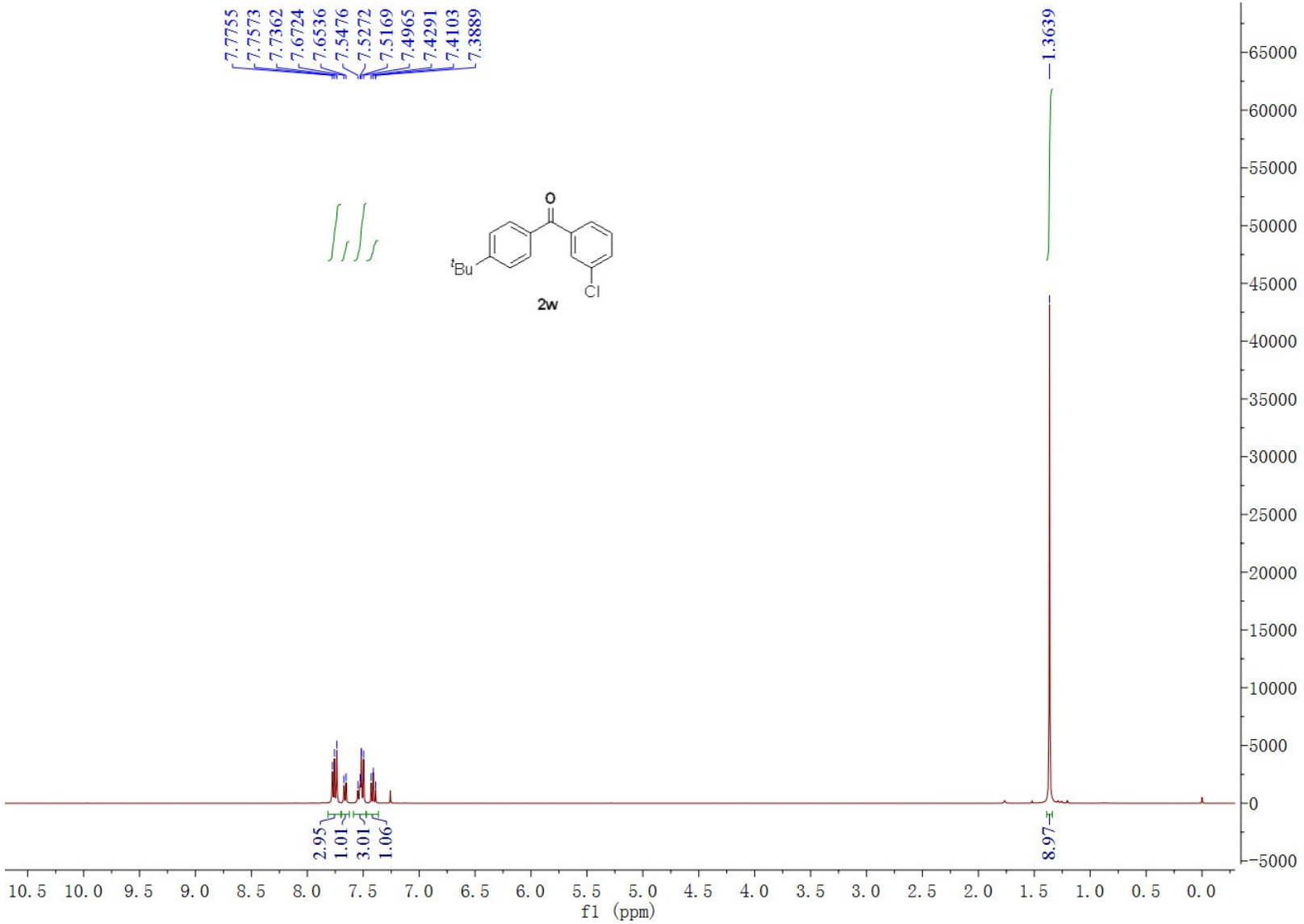
7.7768
7.6703
7.6511
7.6246
7.6060
7.5875
7.5640
7.5415
7.5108
7.4914
7.4728
7.4362
7.4166
7.3970
O
Cl
2u
3.00
1.00
1.02
1.02
2.00
1.02
f1 (ppm)


7.7315
7.7101
7.4738
7.4523
O
Cl
Cl
2v
4.00
4.03
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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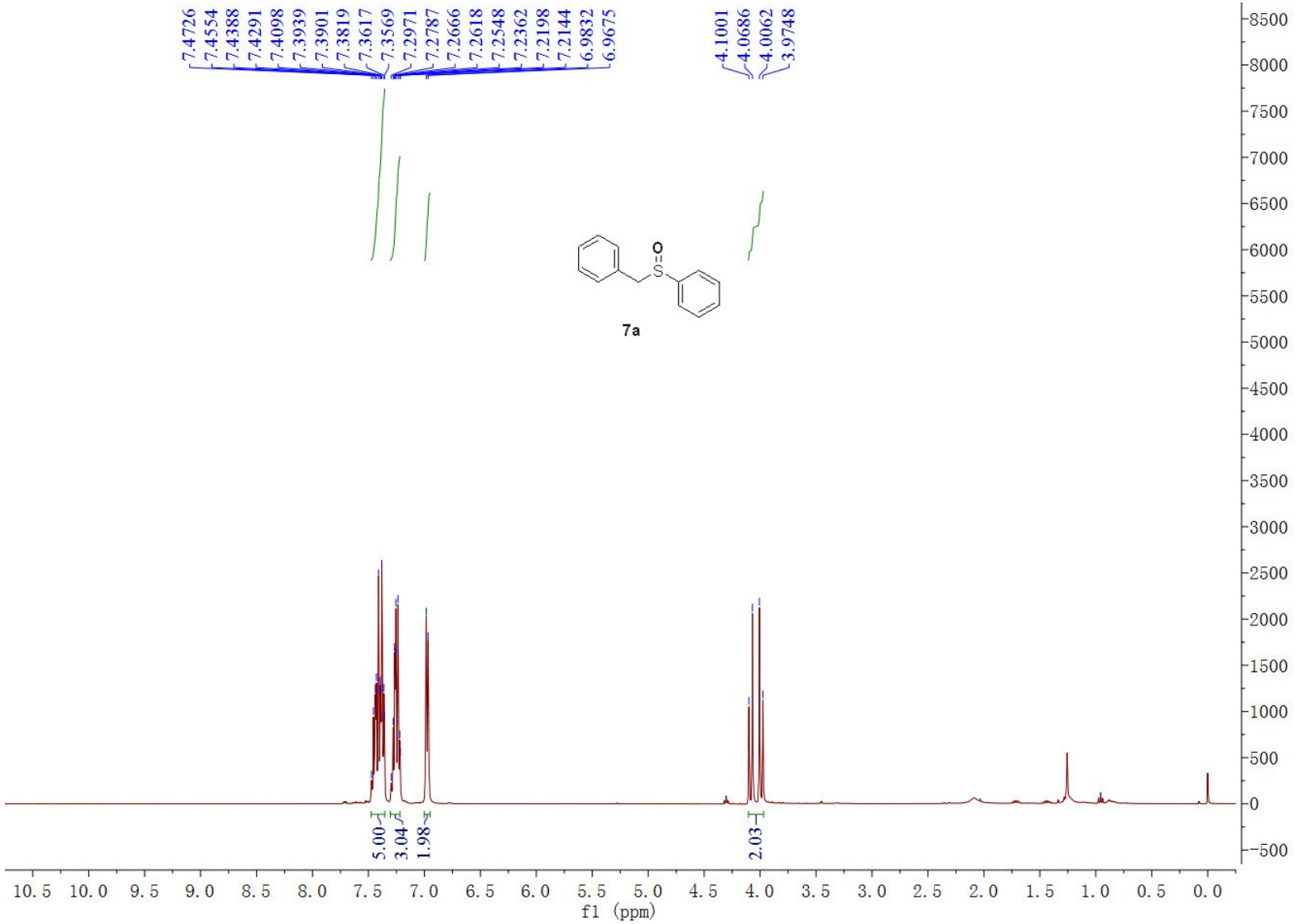
7.7573
7.7362
7.6724
7.6536
7.5476
7.5272
7.5169
7.4965
7.4291
7.4103
7.3889
1.3639
O
tBu
Cl
2w
2.95
1.01
3.01
1.06
8.97
f1 (ppm)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7.3939
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7.3617
7.3569
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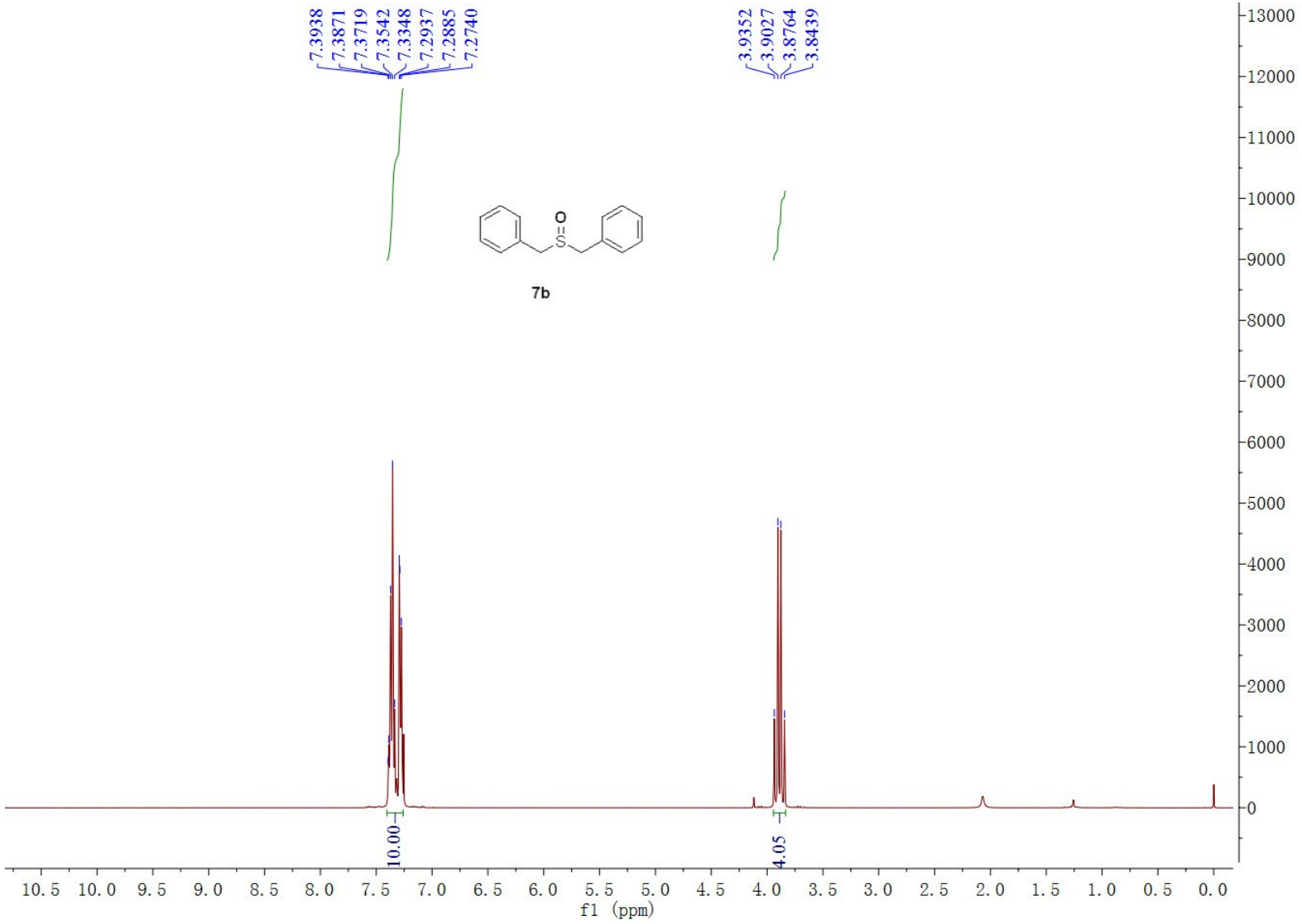
7.2787
7.2666
7.2618
7.2548
7.2362
7.2198
7.2144
6.9832
6.9675
4.1001
4.0686
4.0062
3.9748
O
S
7a
5.00
3.04
1.98
2.03
f1 (ppm)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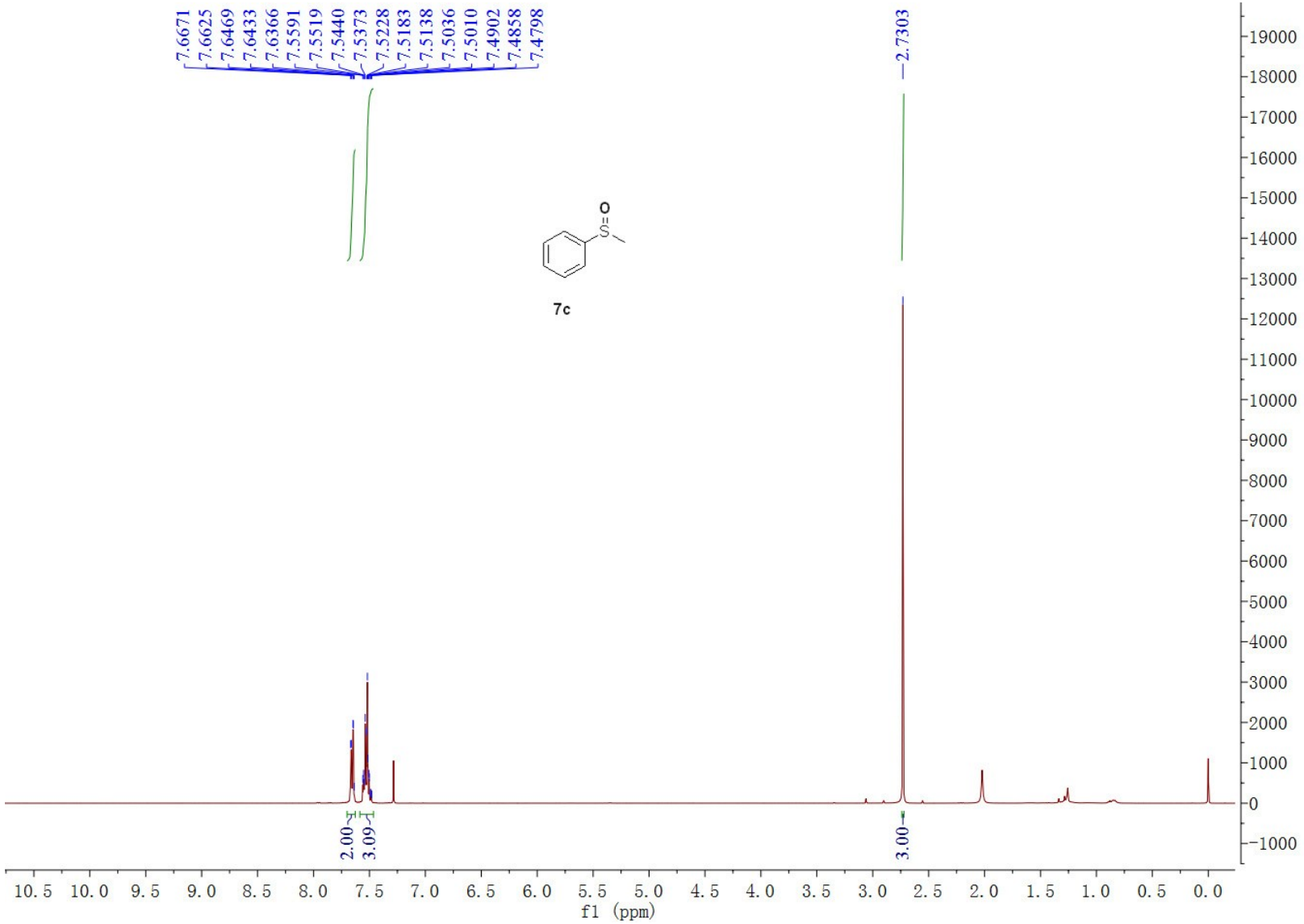
7.3871
7.3719
7.3542
7.3348
7.2937
7.2885
7.2740
3.9352
3.9027
3.8764
3.8439
O
S
7b
10.00
4.05
f1 (ppm)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7.6469
7.6433
7.6366
7.5591
7.5519
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7.5373
7.5228
7.5183
7.5138
7.5036
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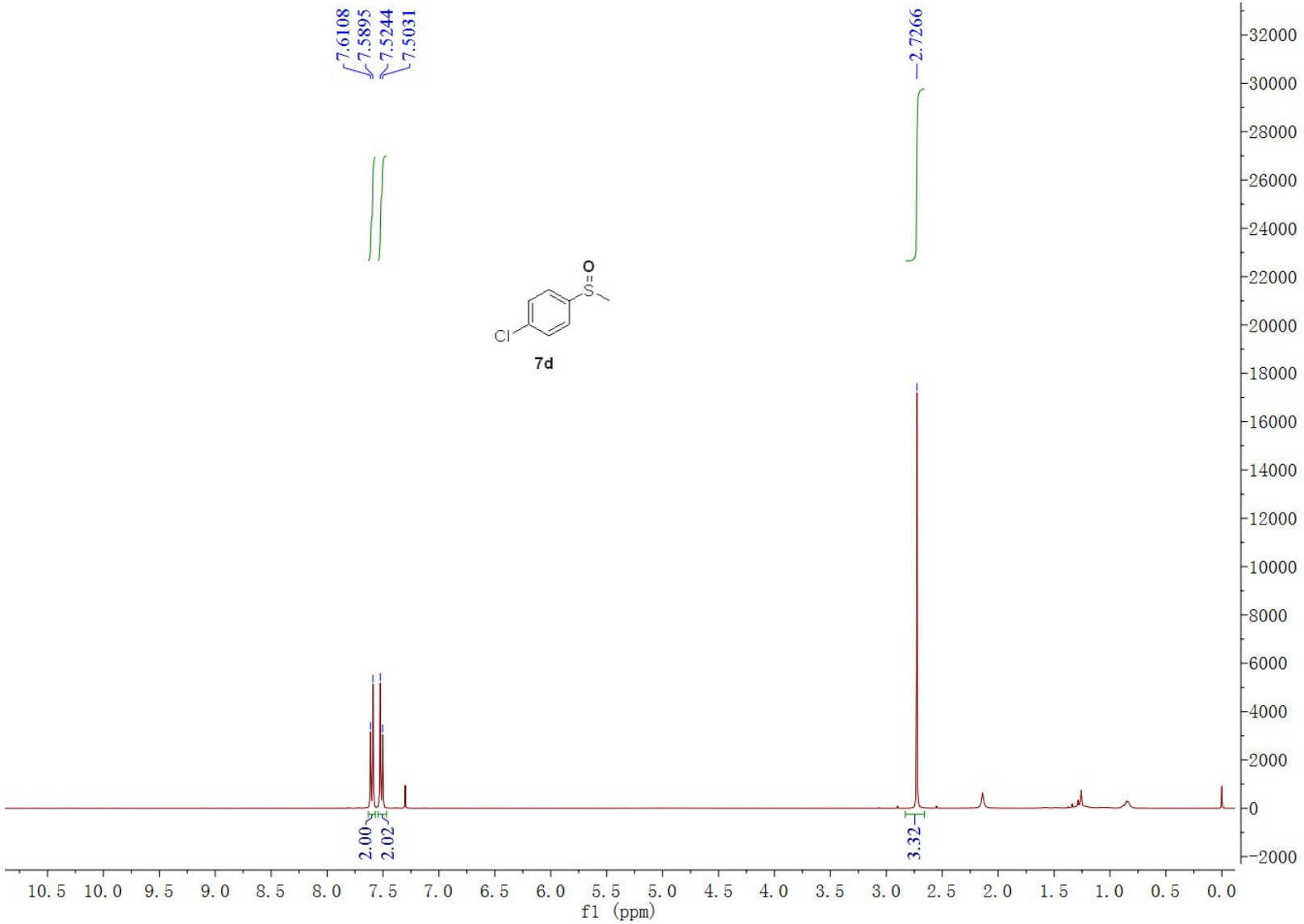
7.4858
7.4798
2.7303
O
S
7c
2.00
3.09
3.00
f1 (ppm)


7.6108
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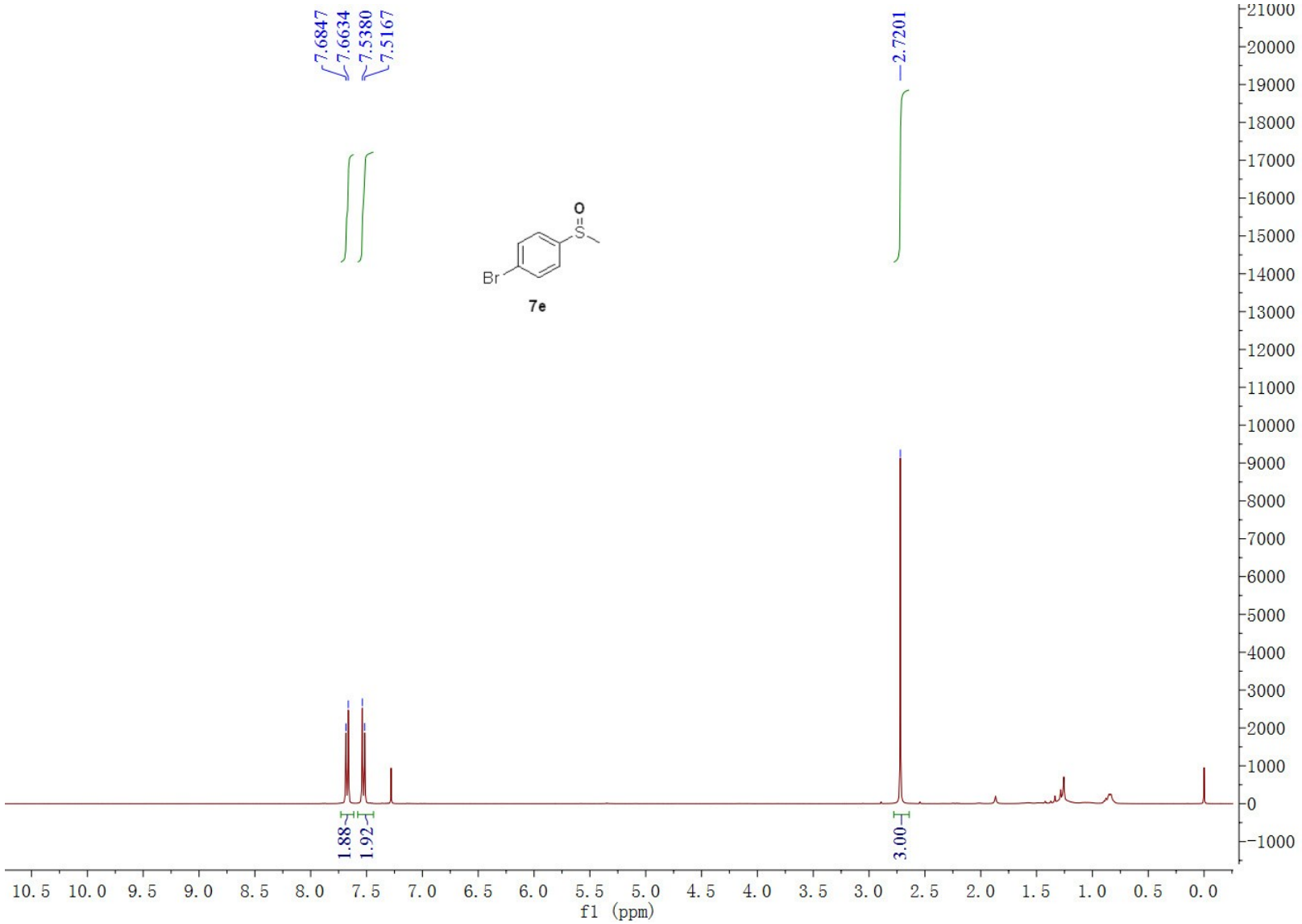
7.5244
7.5031
2.7266
O
S
Cl
7d
2.00
2.02
3.32
f1 (ppm)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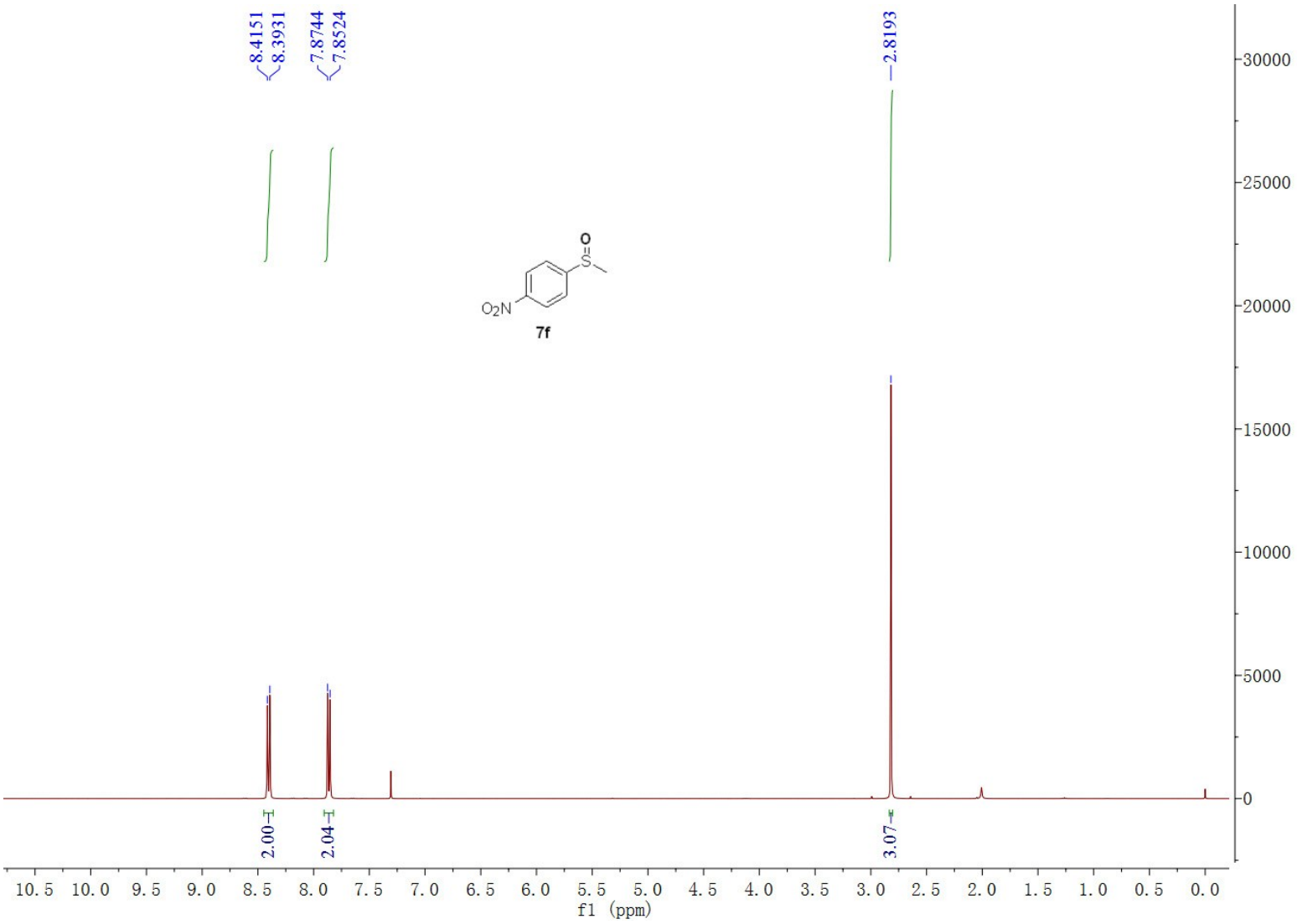
7.5167
2.7201
Br
O
S
7e
1.88
1.92
3.00
f1 (ppm)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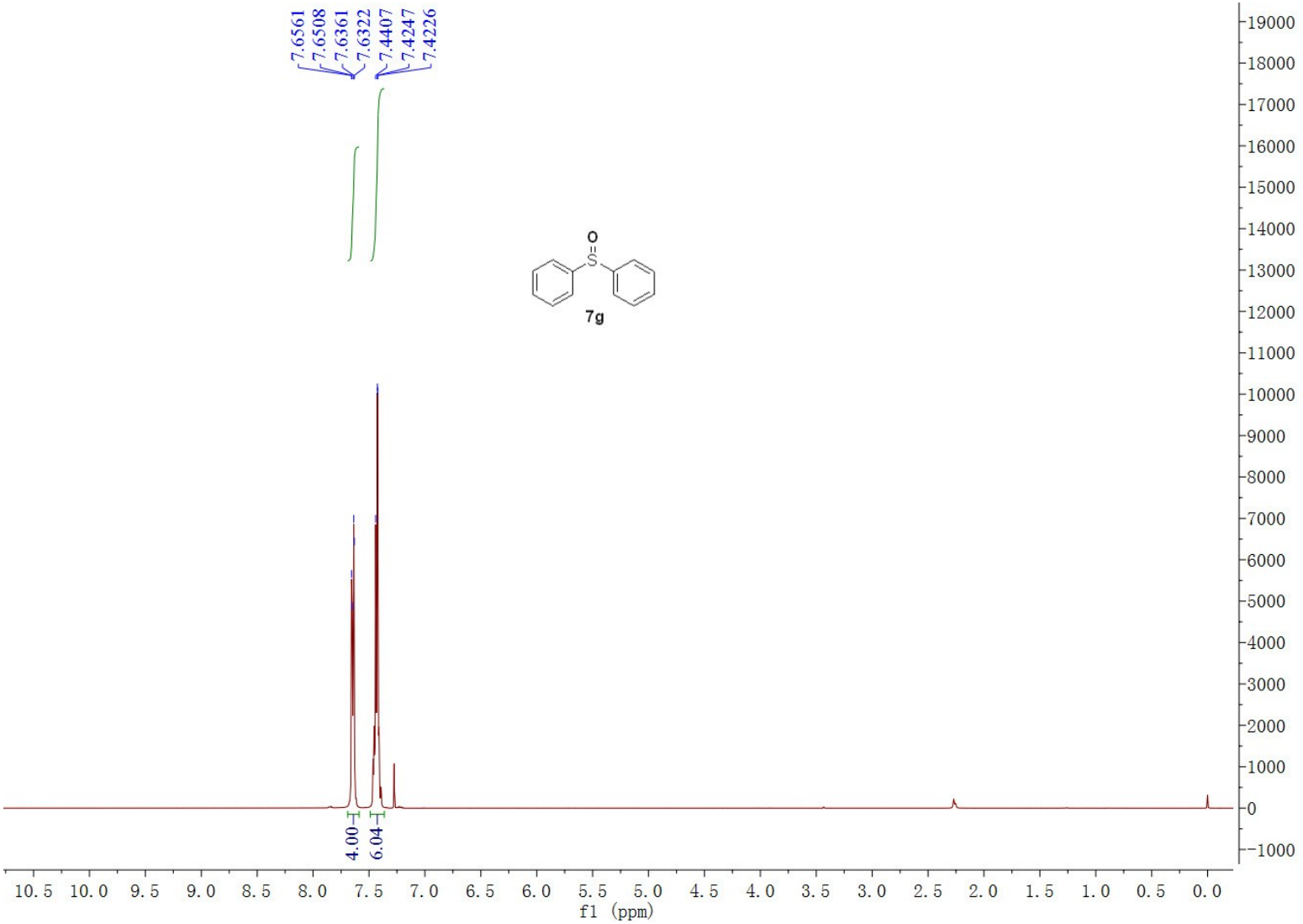
8.3931
7.8744
7.8524
2.8193
O
S
O2N
7f
30000
25000
20000
15000
10000
5000
0
2.00
2.04
3.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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7.6508
7.6361
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7.4407
7.4247
7.4226
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S
7g
4.00
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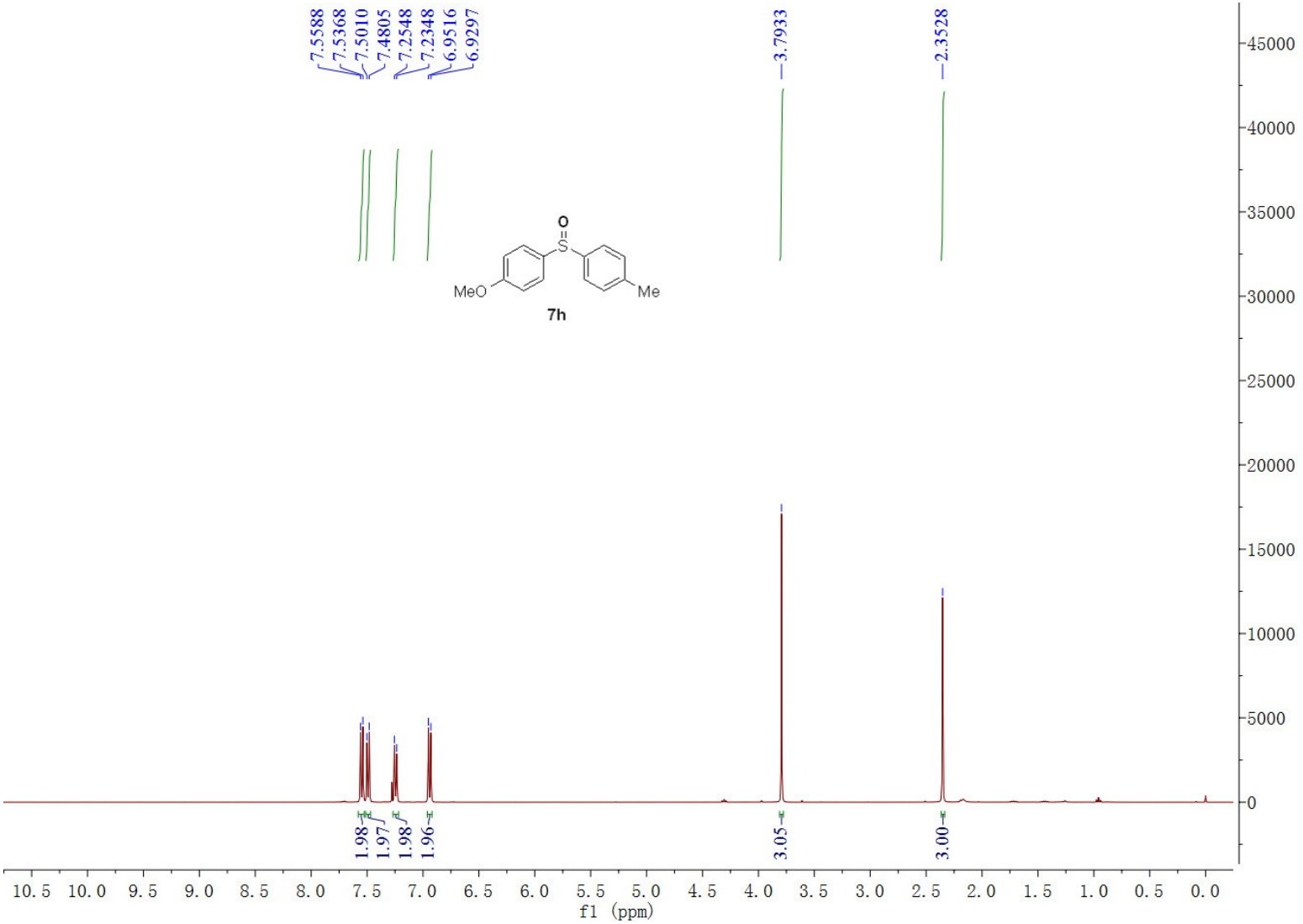
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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7.5010
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7.2548
7.2348
6.9516
6.9297
3.7933
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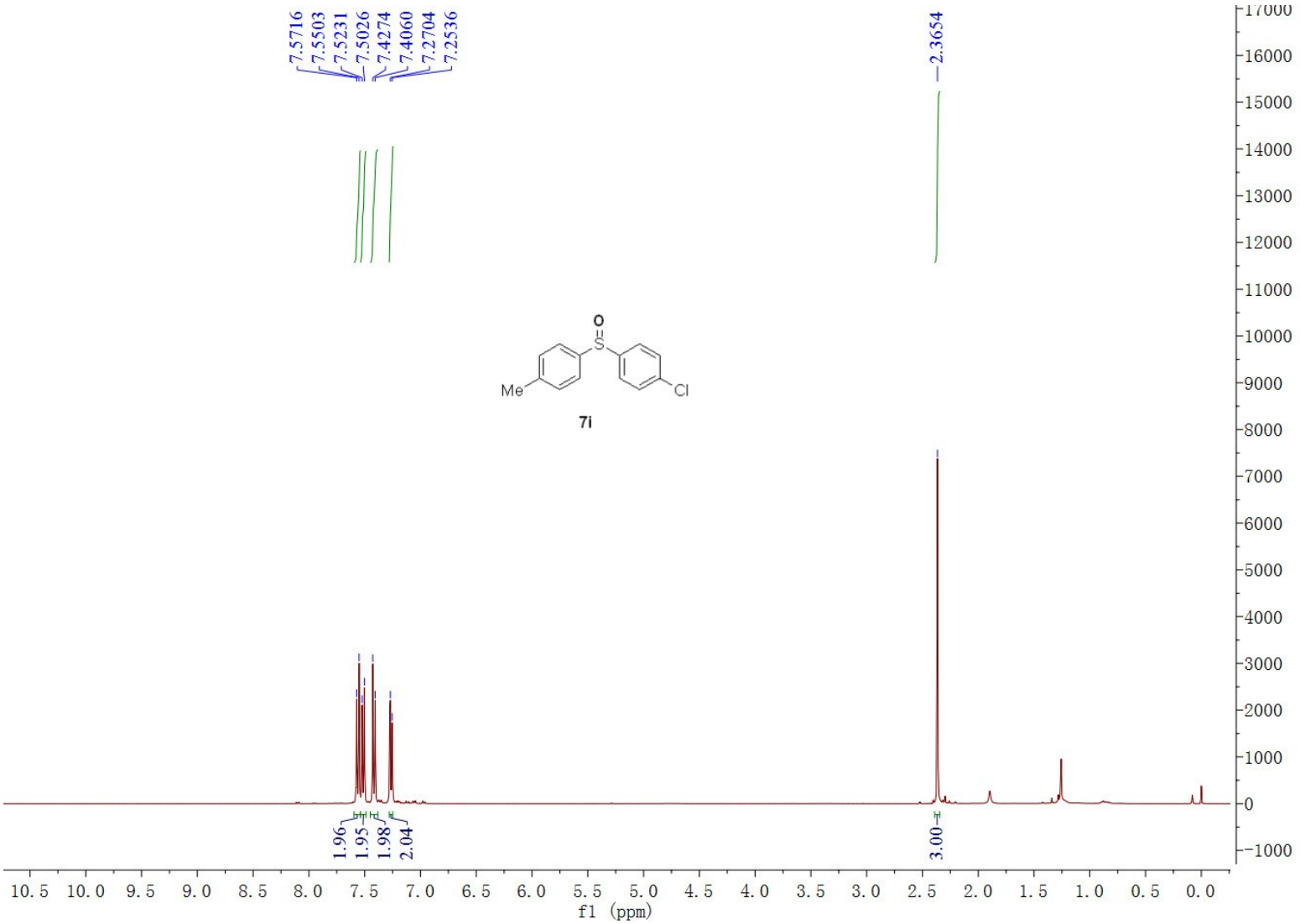
MeO
Me
7h
1.98
1.97
1.98
1.96
3.05
3.00
f1 (ppm)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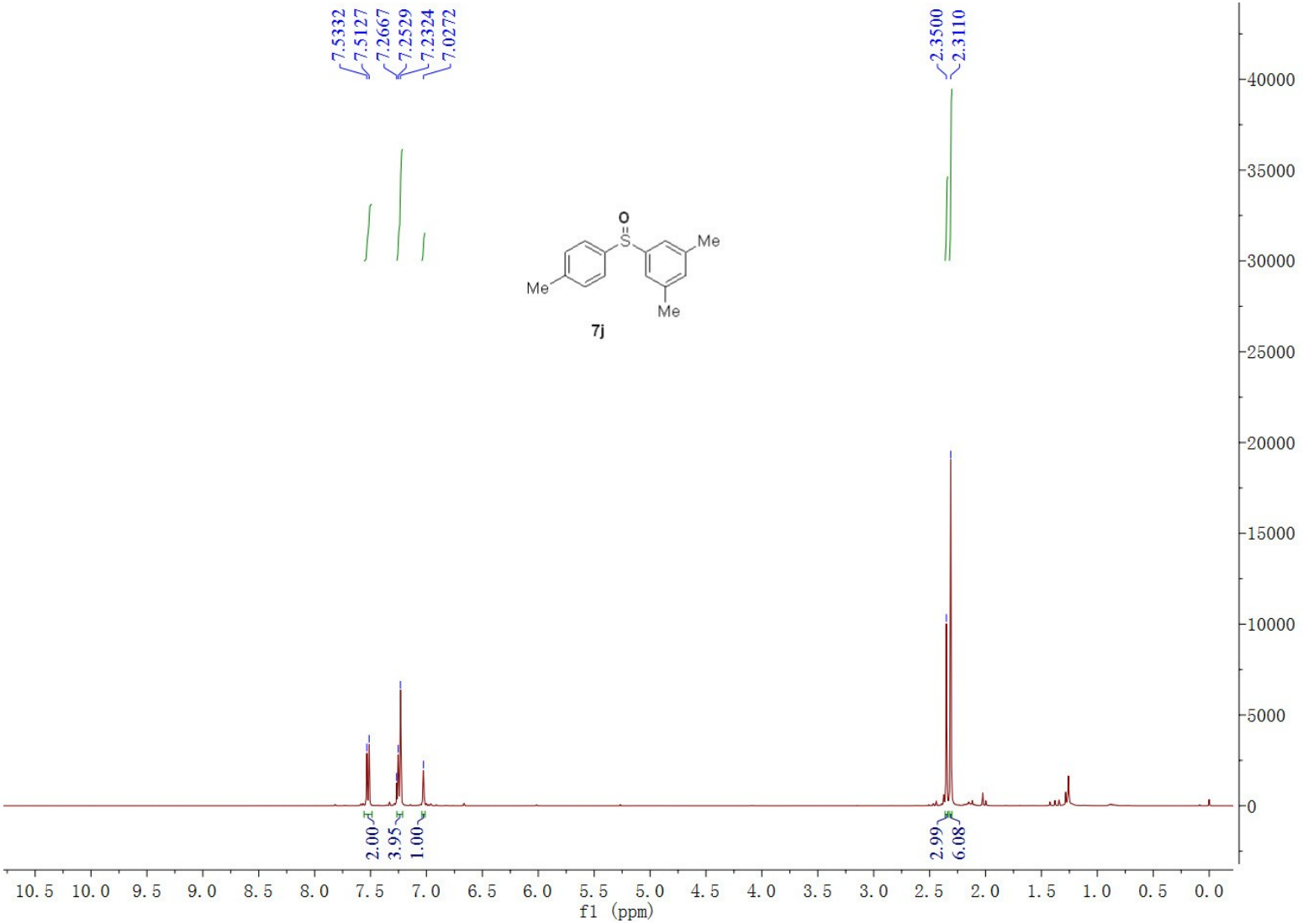
7.5231
7.5026
7.4274
7.4060
7.2704
7.2536
2.3654
O
S
Me
Cl
7i
1.96
1.95
1.98
2.04
3.00
f1 (ppm)


7.5332
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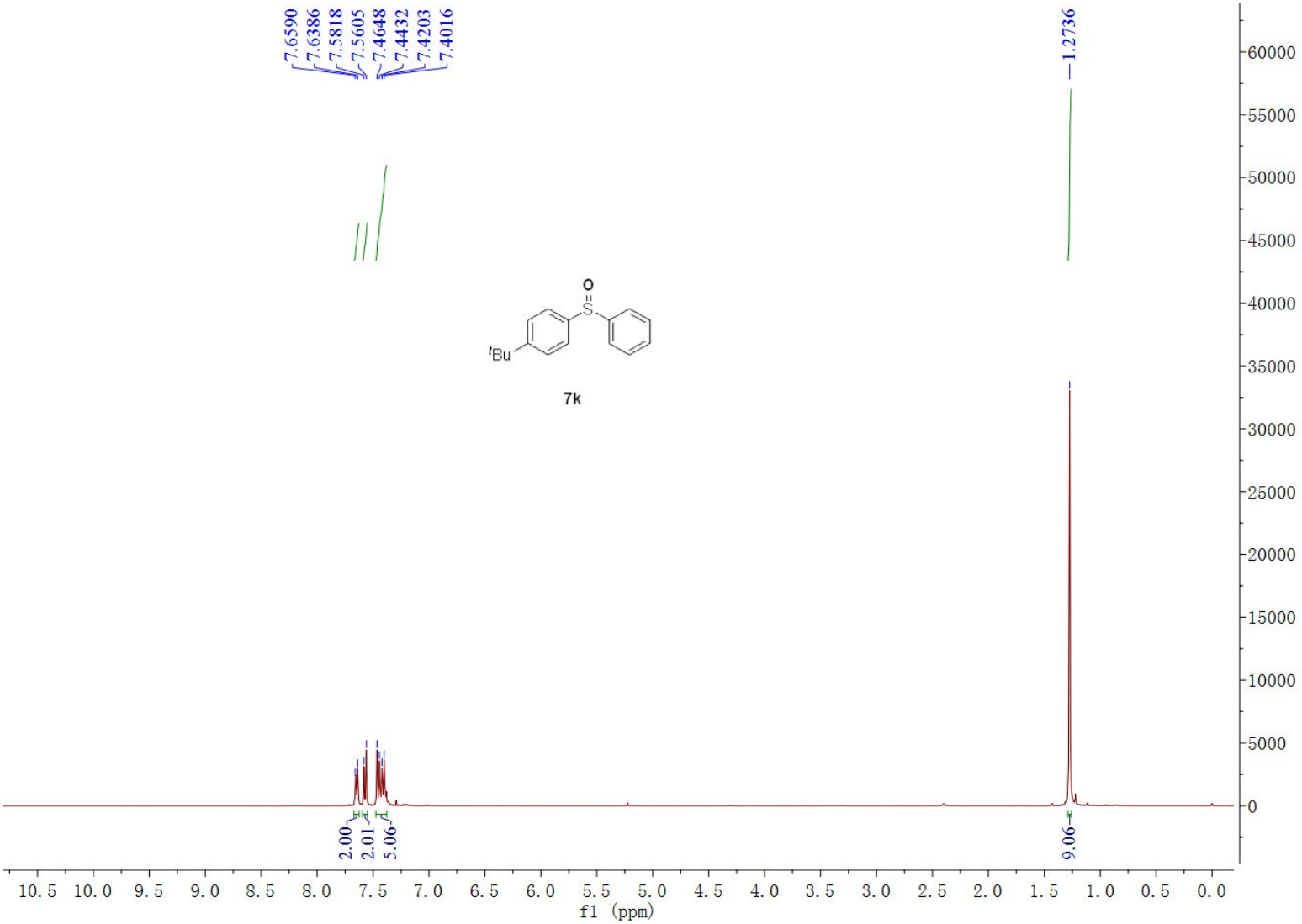
7.2324
7.0272
2.3500
2.3110
O
S
Me
Me
Me
7j
40000
35000
30000
25000
20000
15000
10000
5000
0
2.00
3.95
1.00
2.99
6.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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7.5605
7.4648
7.4432
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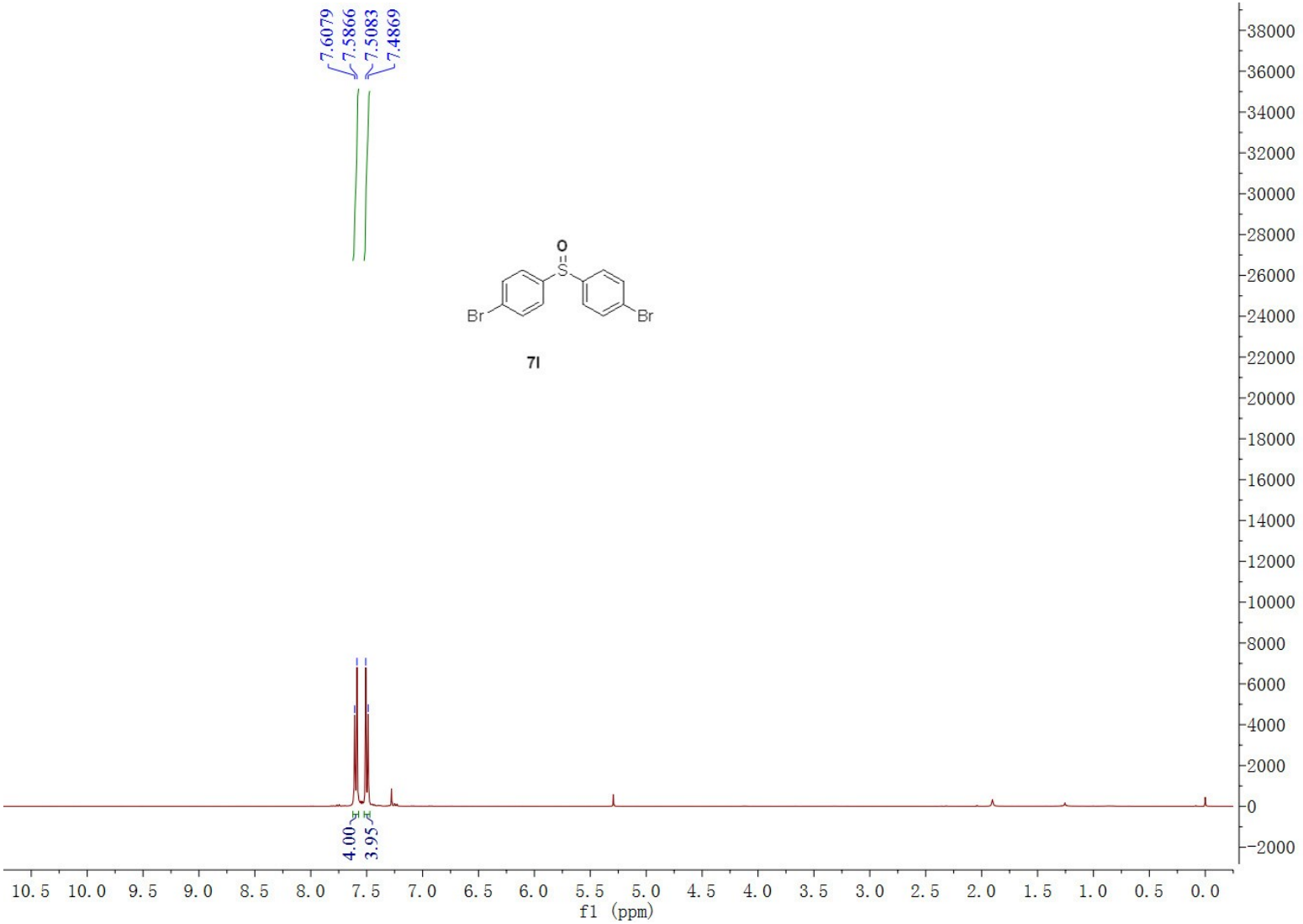
1.2736
O
S
tBu
7k
2.00
2.01
5.06
9.06
f1 (ppm)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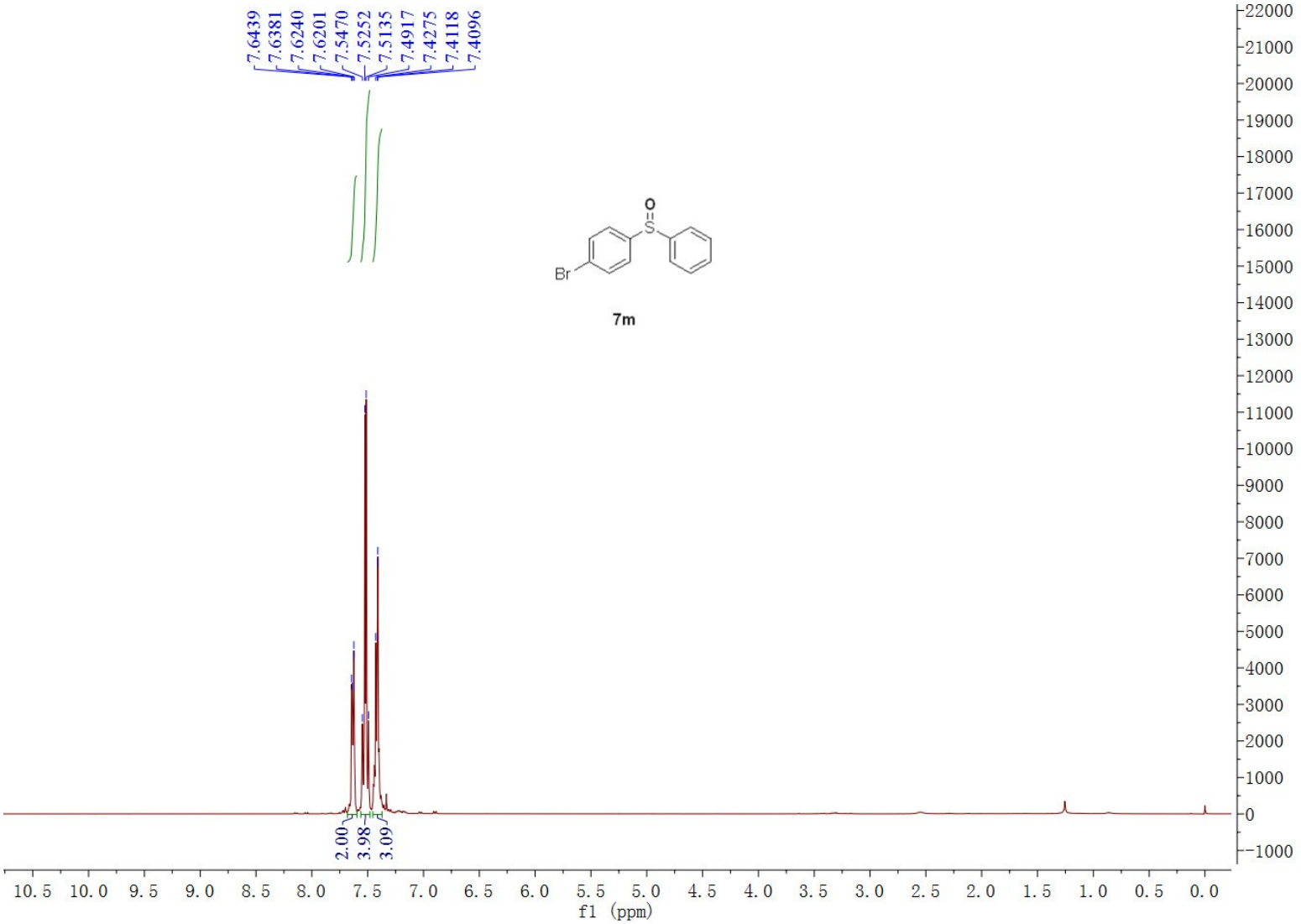
7.4869
O
S
Br
Br
7l
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
4.00
3.95
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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7.5135
7.4917
7.4275
7.4118
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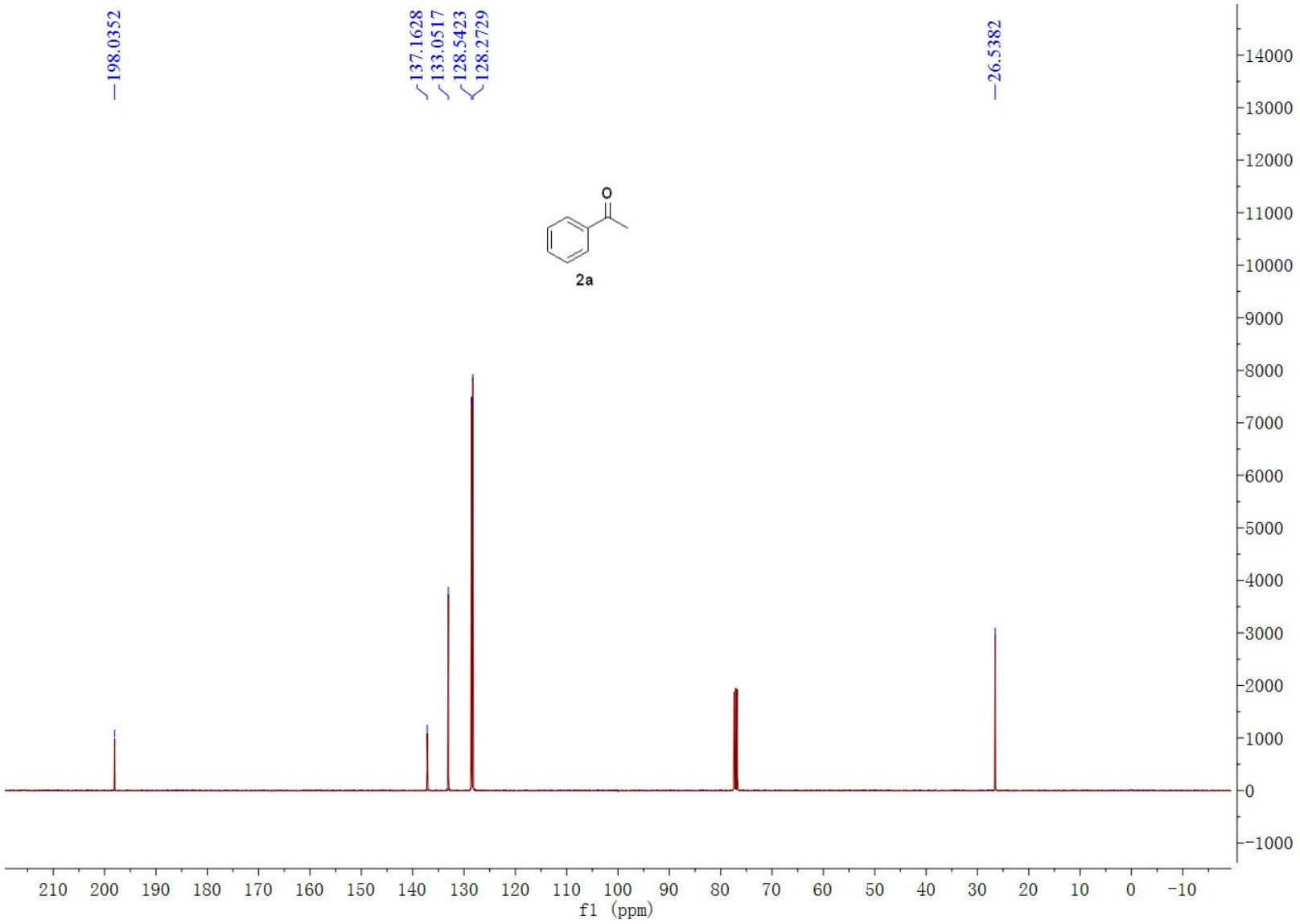
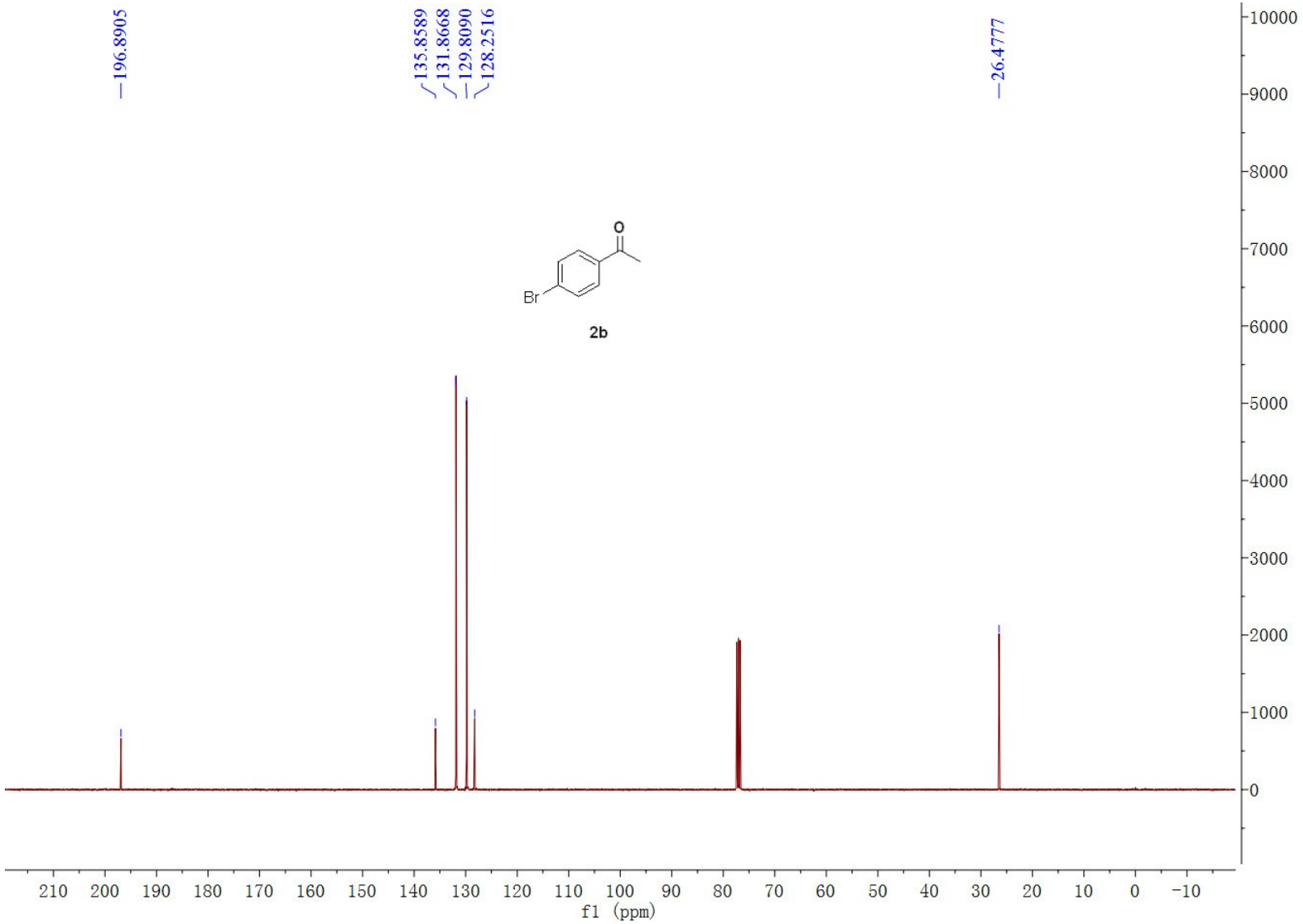
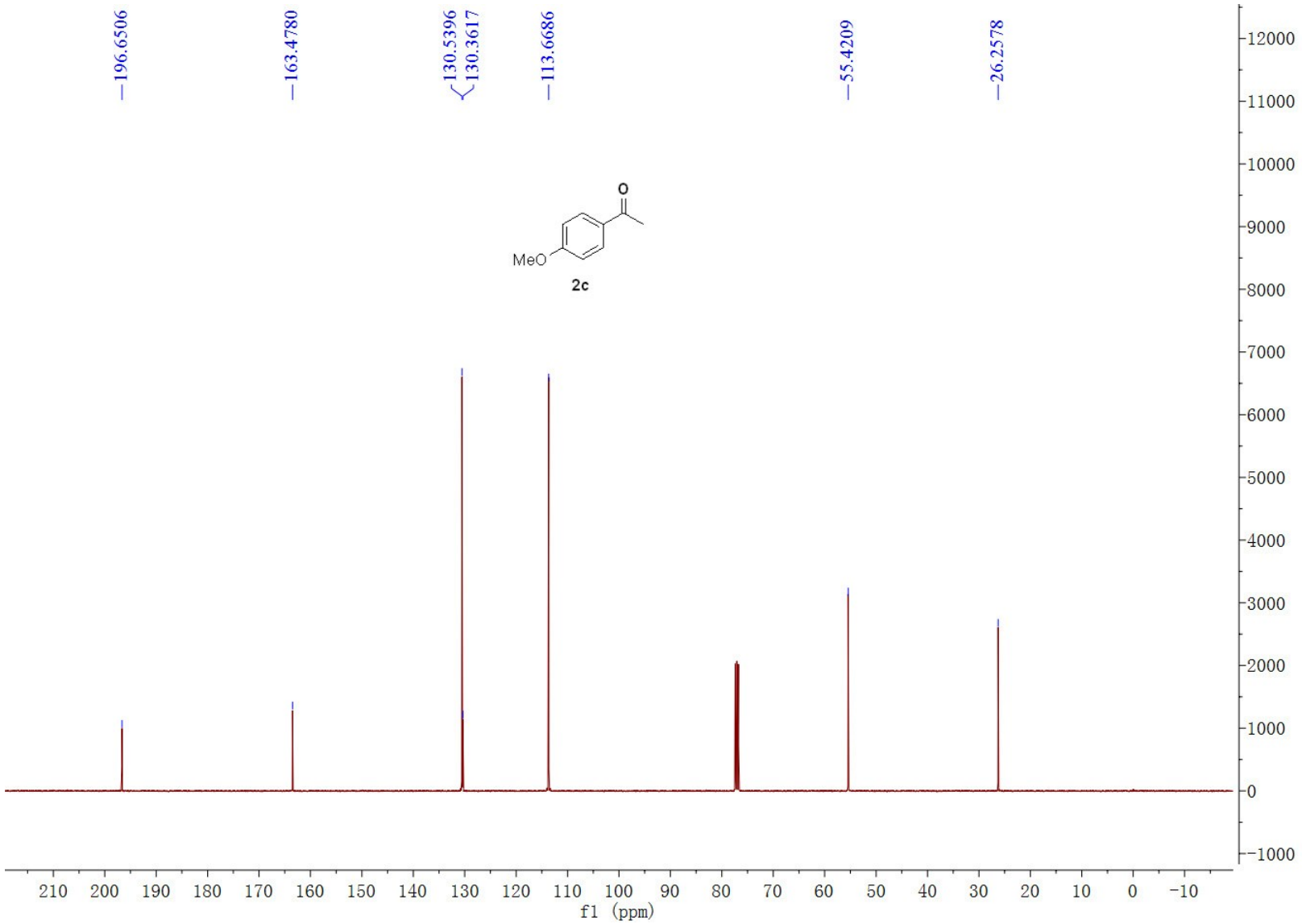
O
S
Br
7m
2.00
3.98
3.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000


198.0352
137.1628
133.0517
128.5423
128.2729
26.5382
O
2a
14000
13000
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)


196.8905
135.8589
131.8668
129.8090
128.2516
26.4777
O
Br
2b
10000
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)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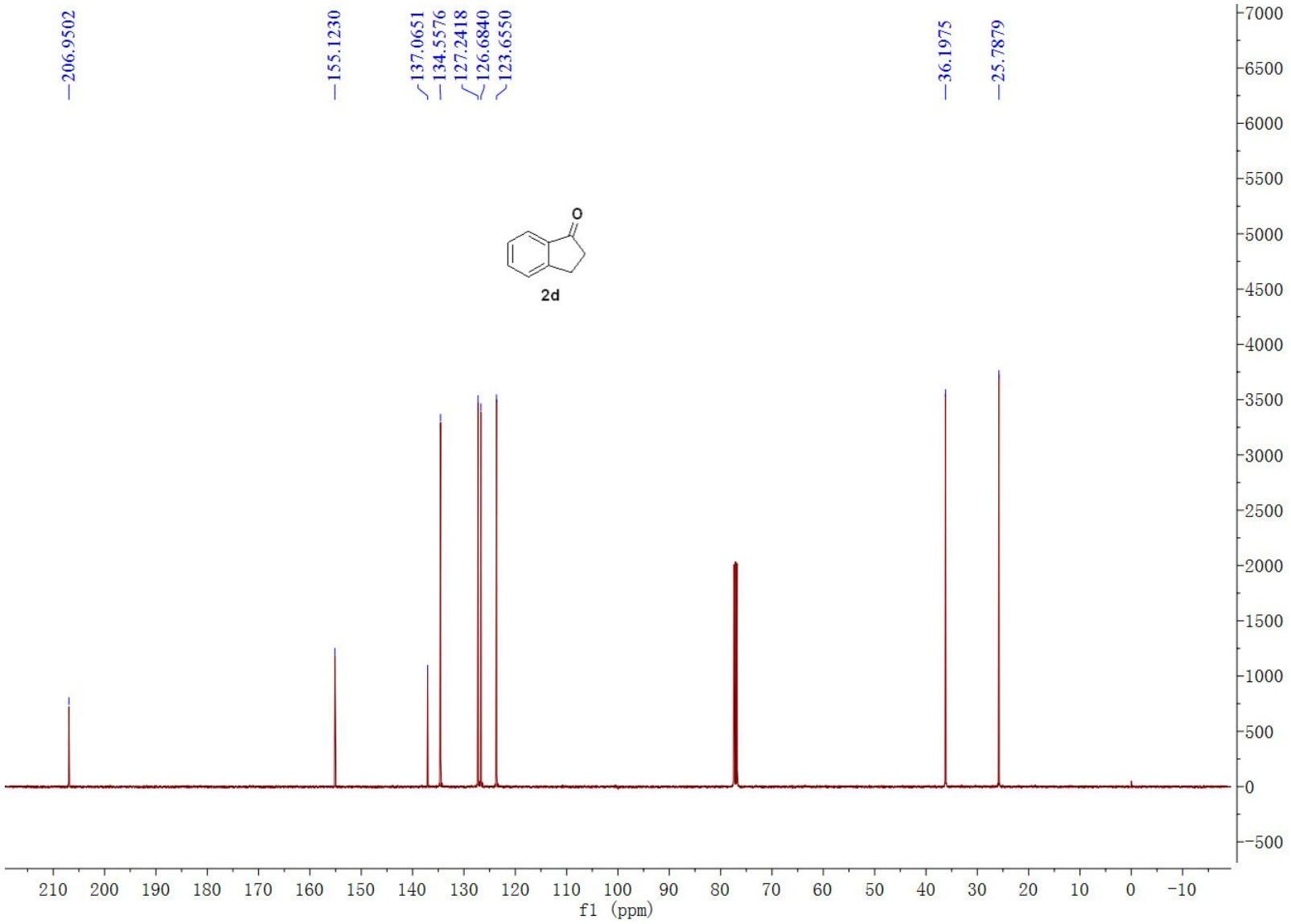
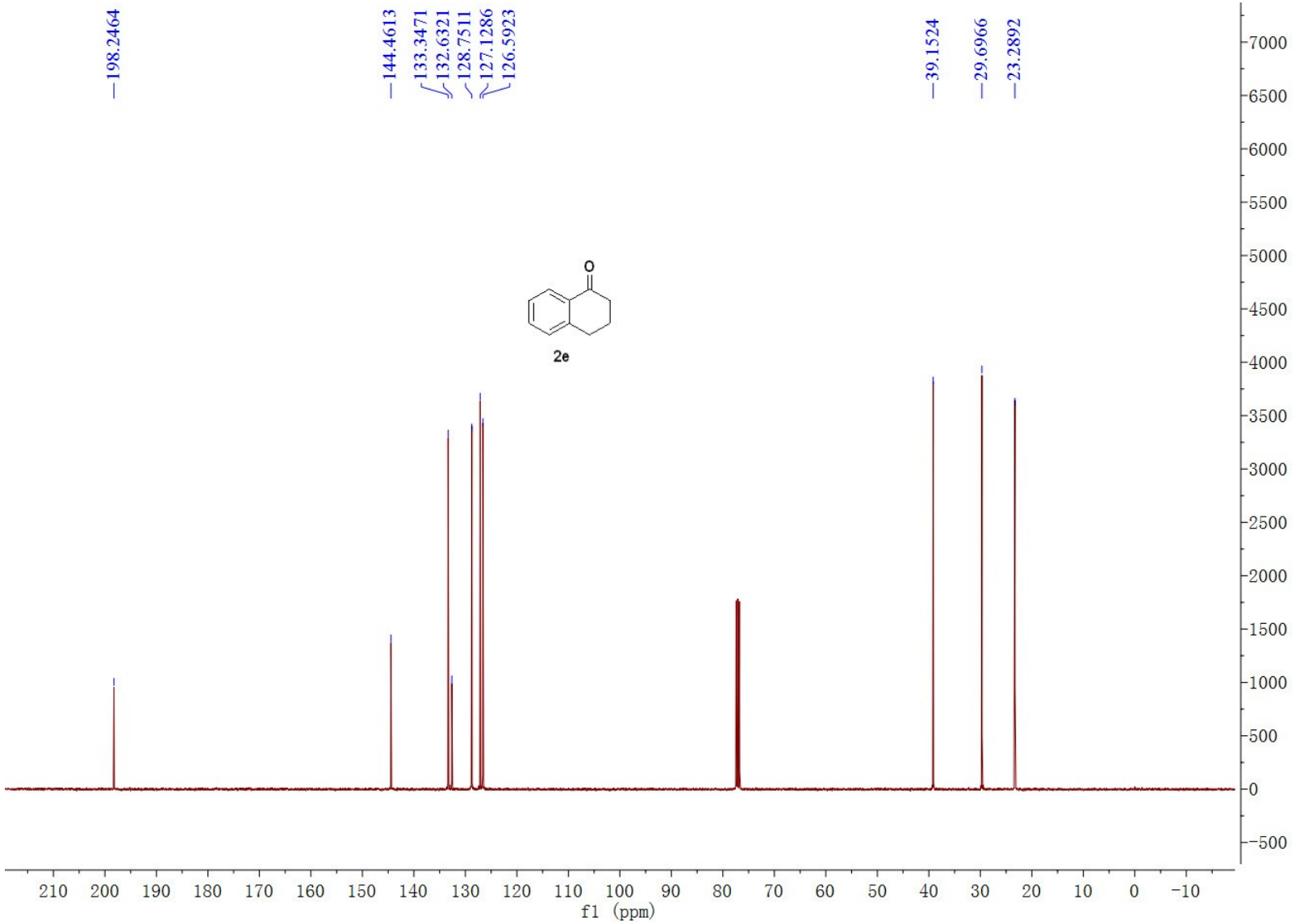
163.4780
130.5396
130.3617
113.6686
55.4209
26.2578
MeO
O
2c
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


206.9502
155.1230
137.0651
134.5576
127.2418
126.6840
123.6550
36.1975
25.7879
O
2d
f1 (ppm)


198.2464
144.4613
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132.6321
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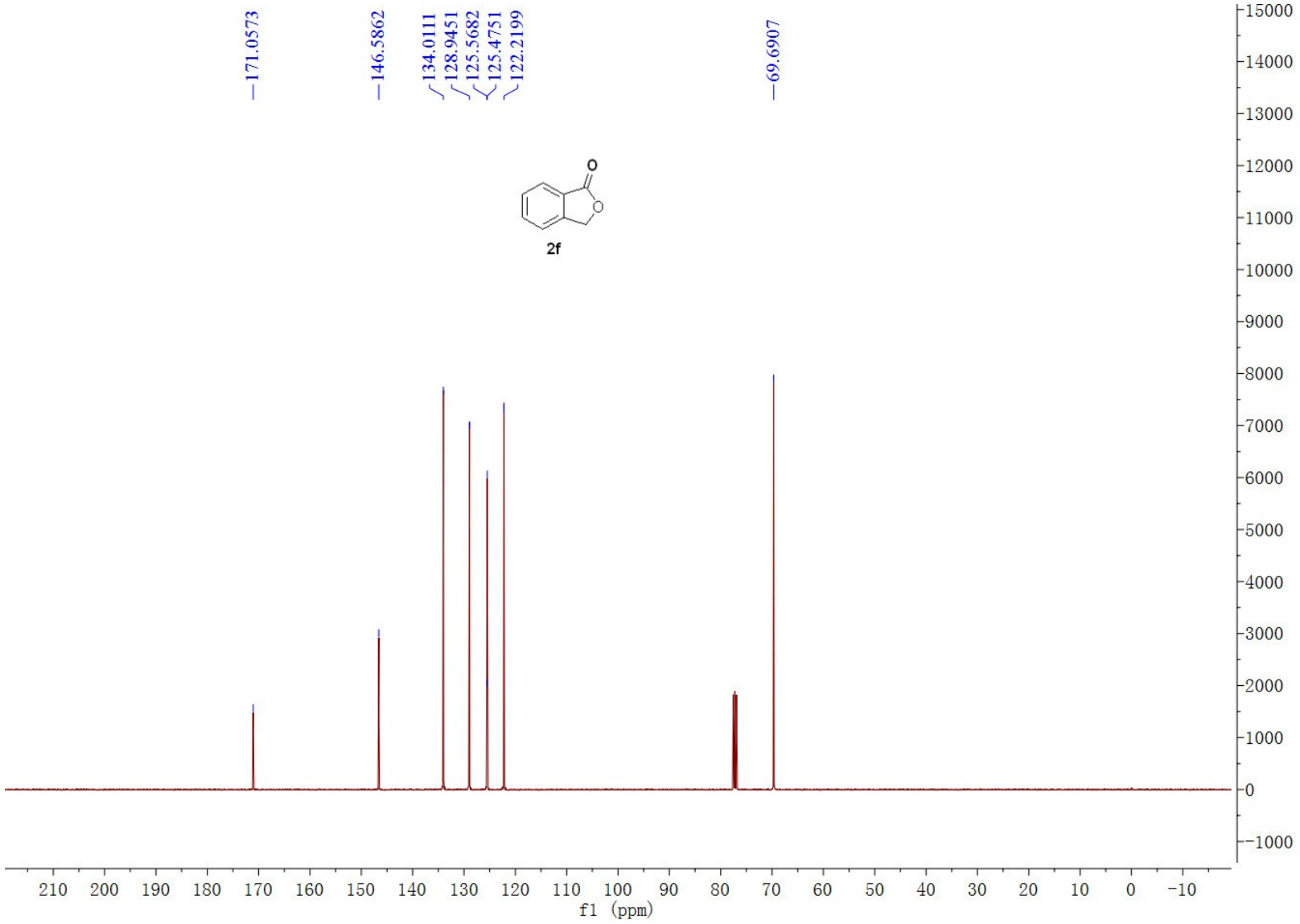
127.1286
126.5923
39.1524
29.6966
23.2892
O
2e
f1 (ppm)


171.0573
146.5862
134.0111
128.9451
125.5682
125.4751
122.2199
69.6907
O
O
2f
15000
14000
13000
12000
11000
10000
9000
8000
7000
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2000
1000
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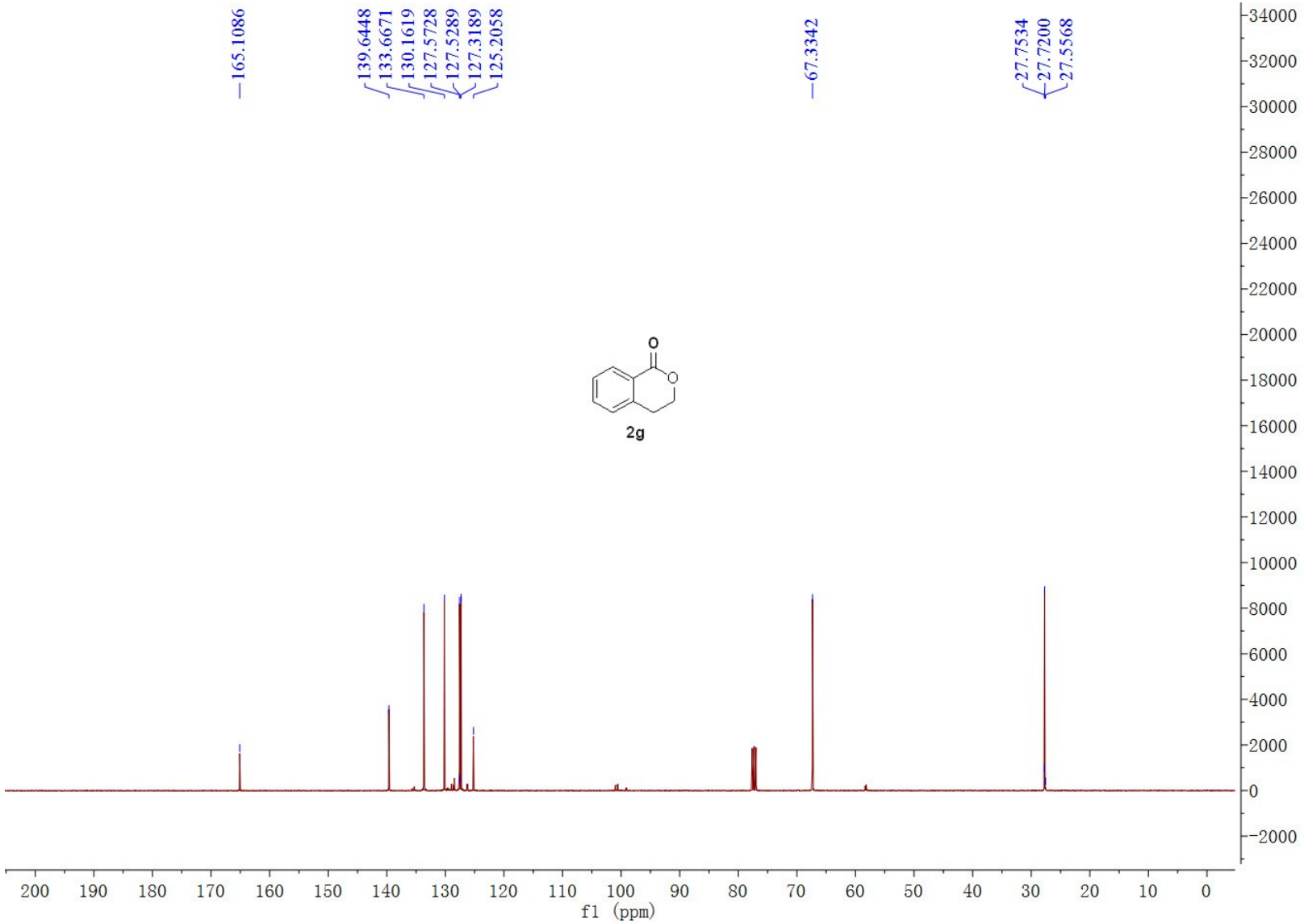
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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127.5728
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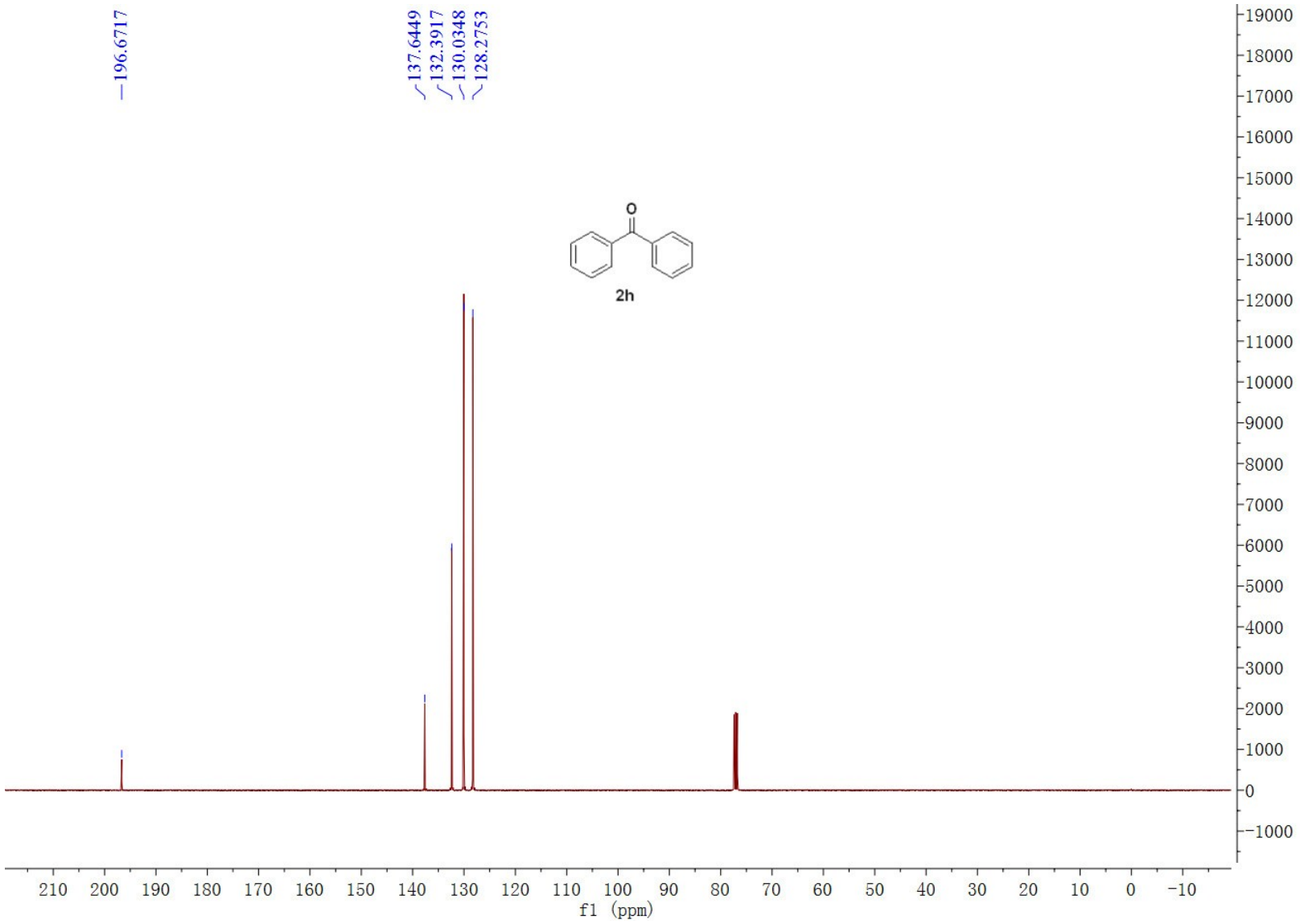
27.7534
27.7200
27.5568
O
O
2g
f1 (ppm)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2h
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16000
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12000
11000
10000
9000
8000
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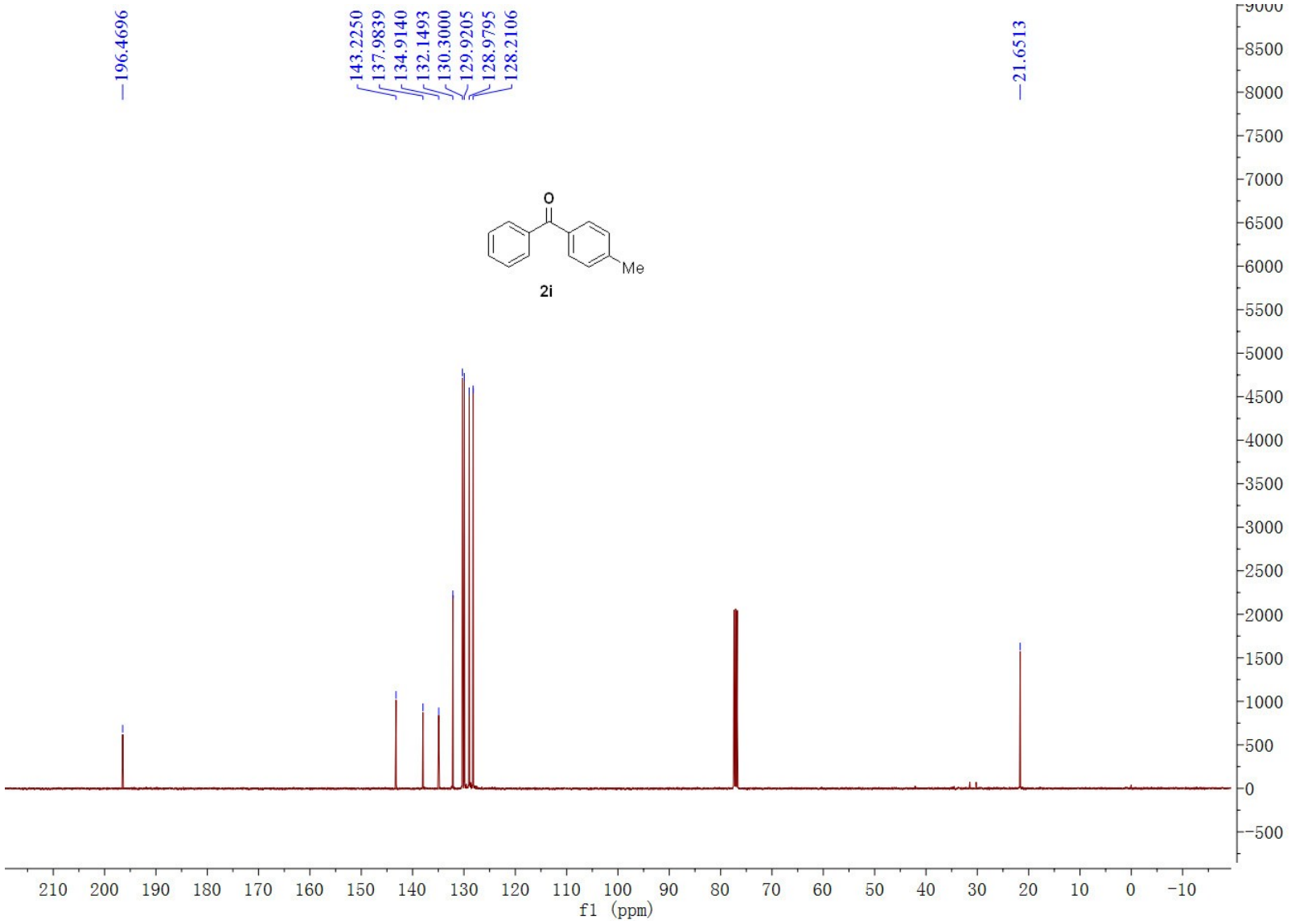
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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137.9839
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129.9205
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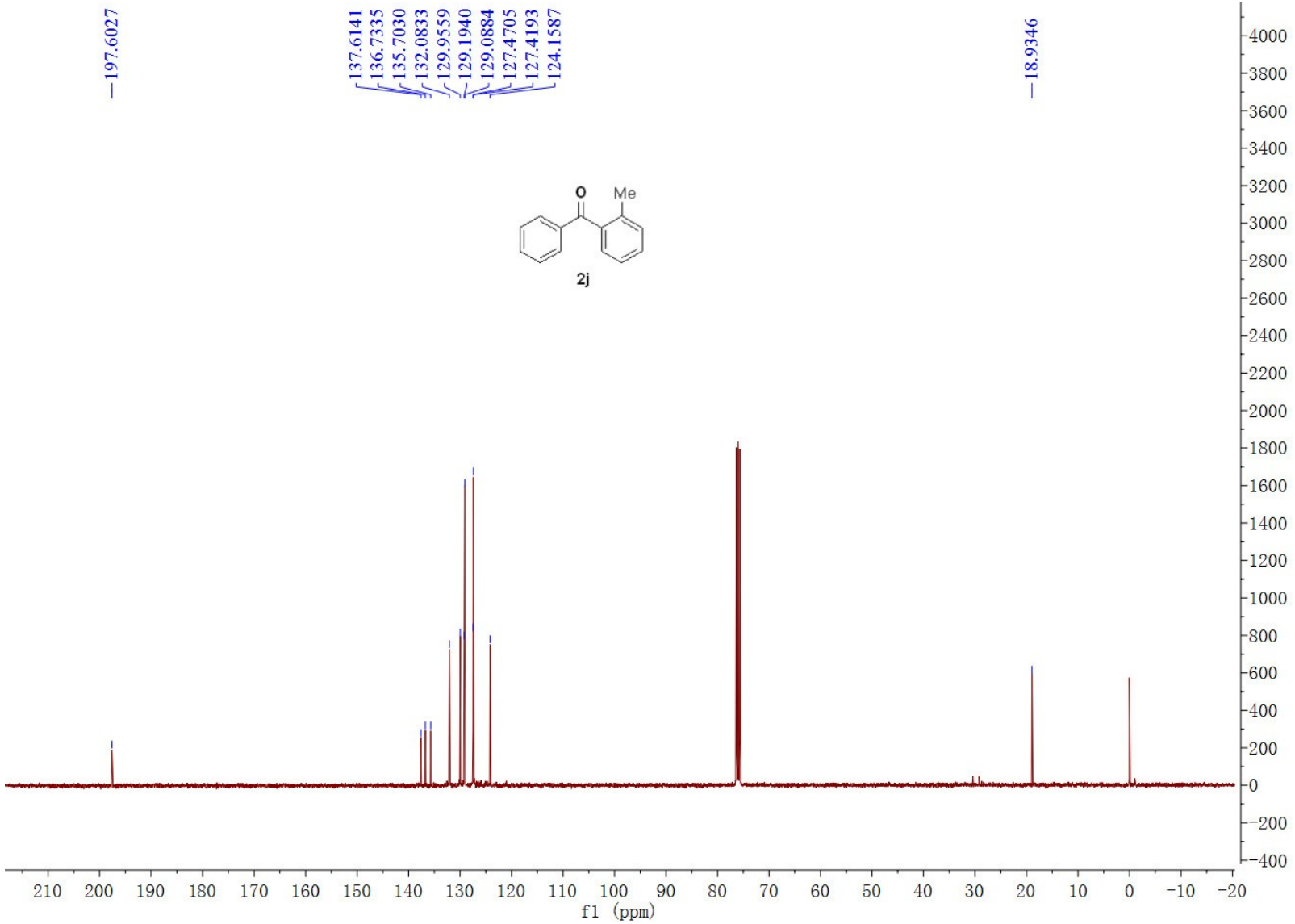
Me
2i
f1 (ppm)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135.7030
132.0833
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129.1940
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127.4193
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18.9346
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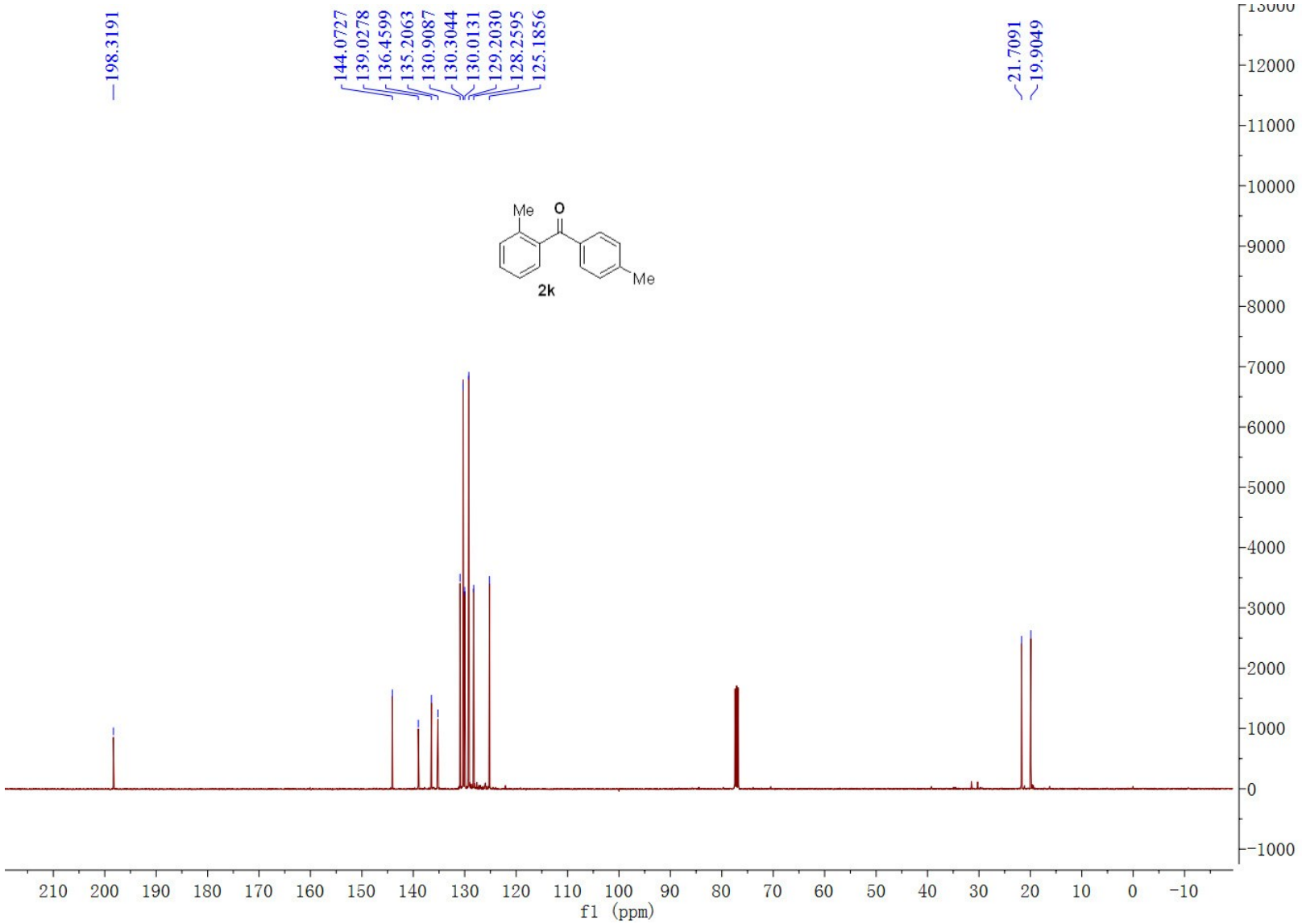
Me
2j
f1 (ppm)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139.0278
136.4599
135.2063
130.9087
130.3044
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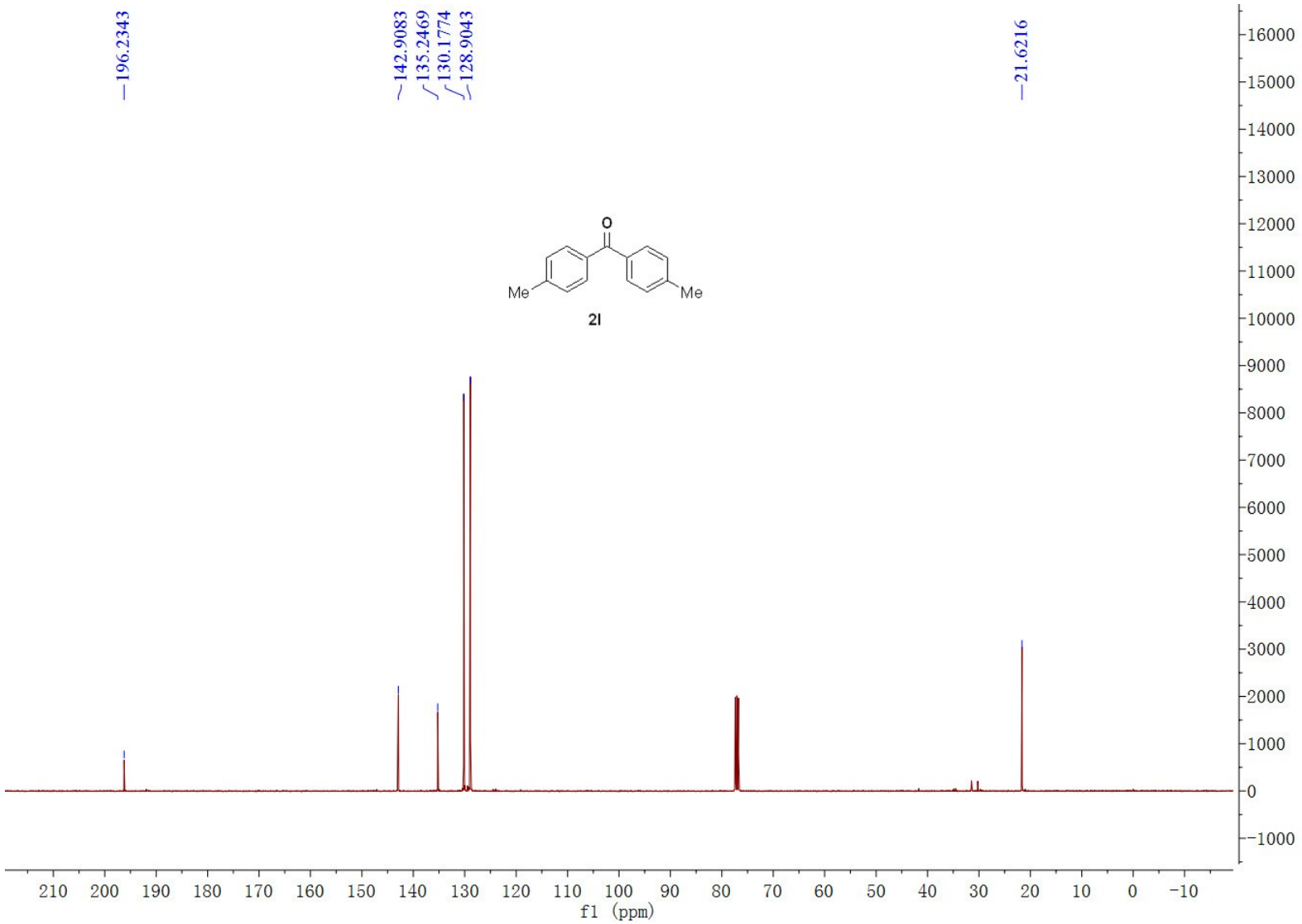
125.1856
21.7091
19.9049
Me
O
Me
2k
f1 (ppm)


196.2343
142.9083
135.2469
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128.9043
21.6216
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Me
Me
2l
16000
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13000
12000
11000
10000
9000
8000
7000
6000
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3000
2000
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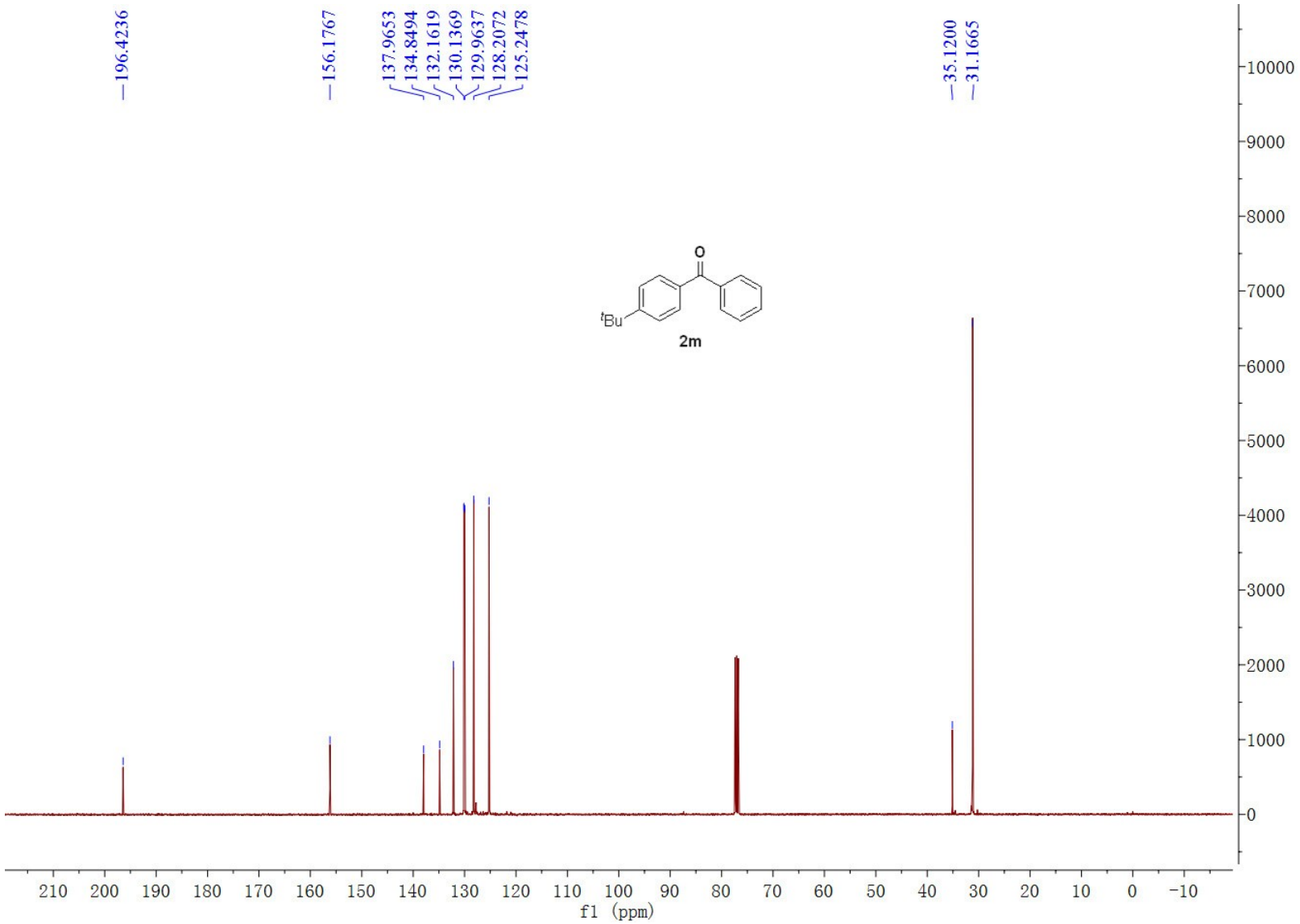
0
-1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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137.9653
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129.9637
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35.1200
31.1665
O
tBu
2m
10000
9000
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4000
3000
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0
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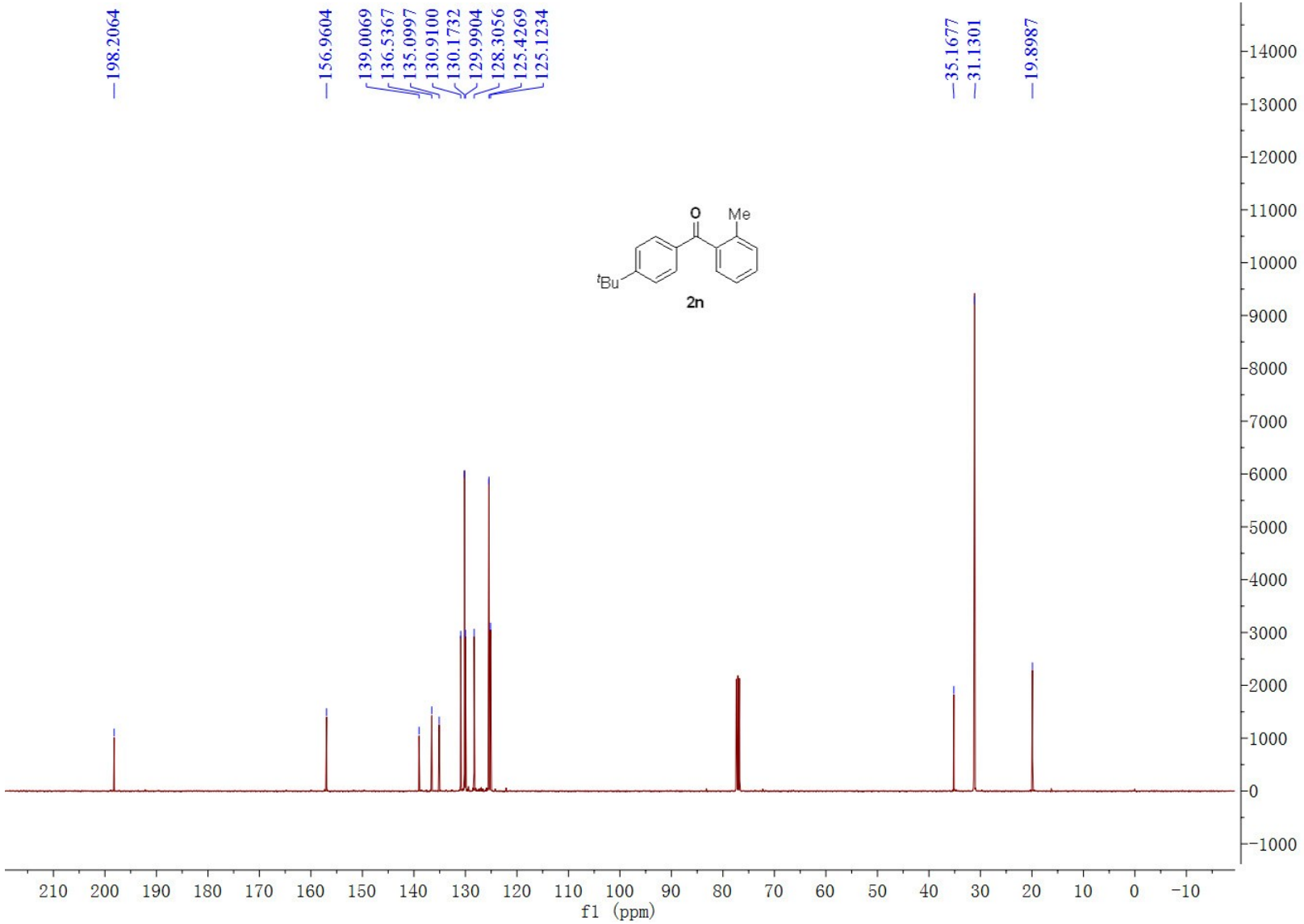
f1 (ppm)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125.1234
35.1677
31.1301
19.8987
O
Me
tBu
2n
14000
13000
12000
11000
10000
9000
8000
7000
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3000
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1000
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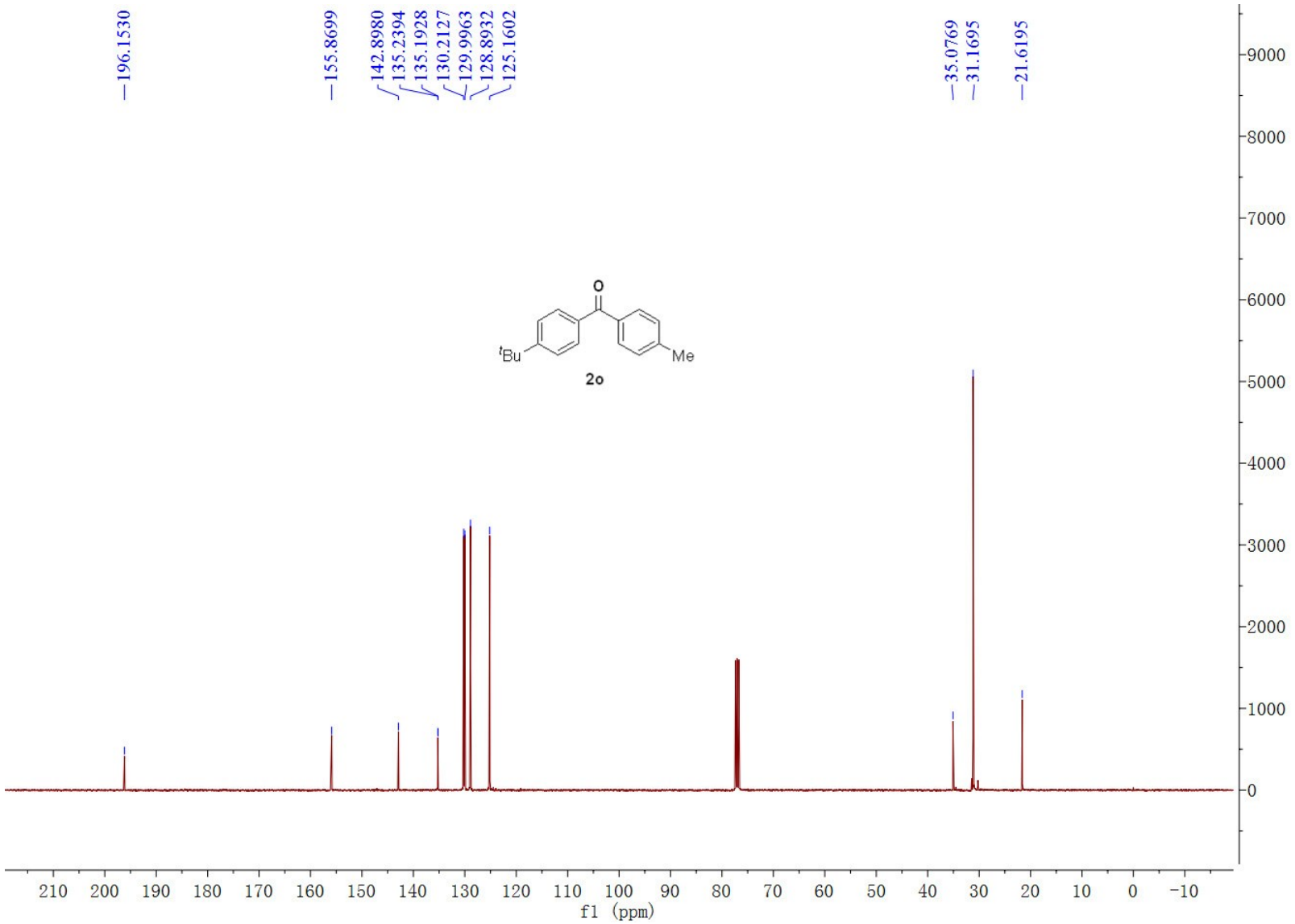
f1 (ppm)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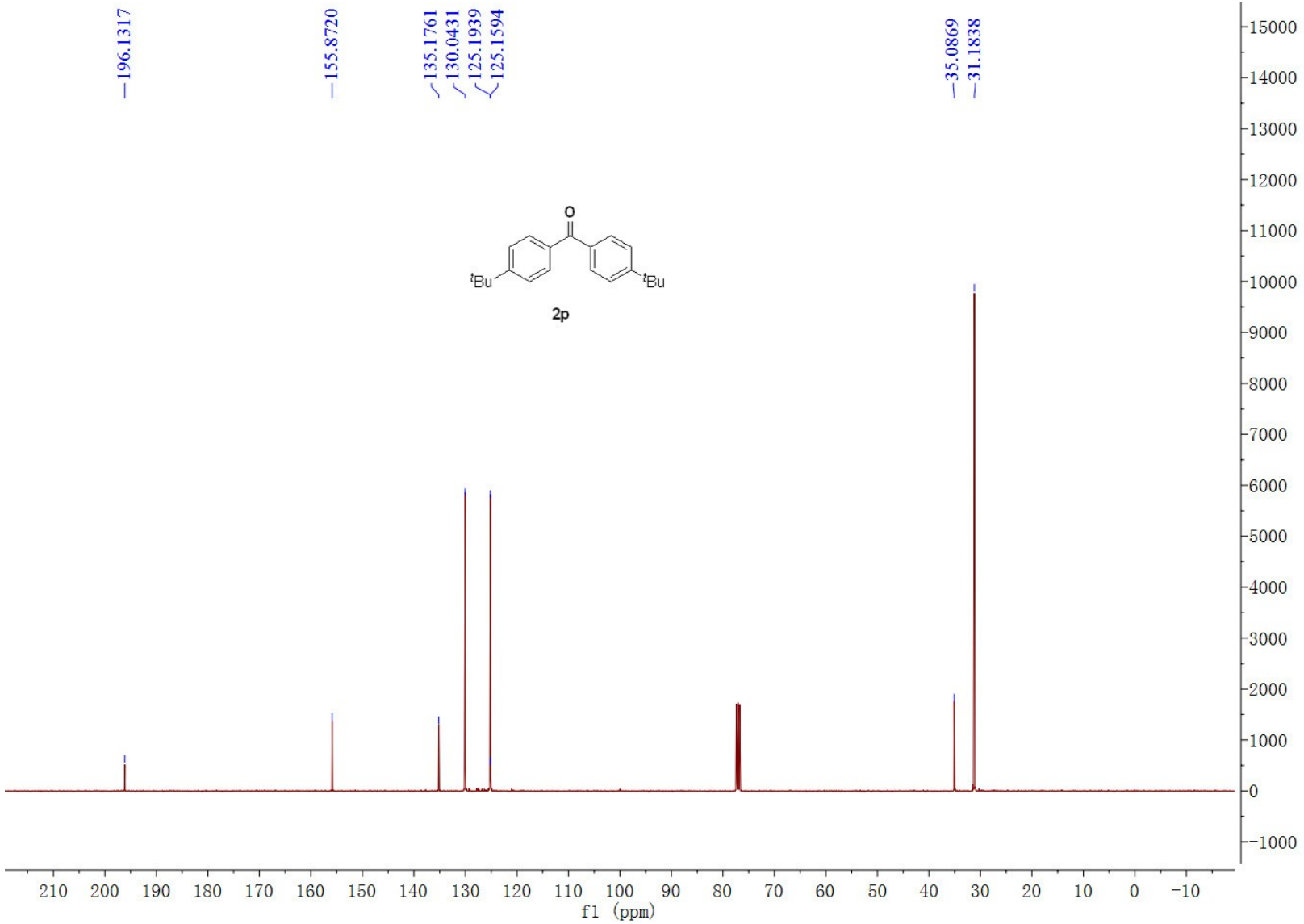
135.1928
130.2127
129.9963
128.8932
125.1602
35.0769
31.1695
21.6195
O
tBu
Me
2o
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


196.1317
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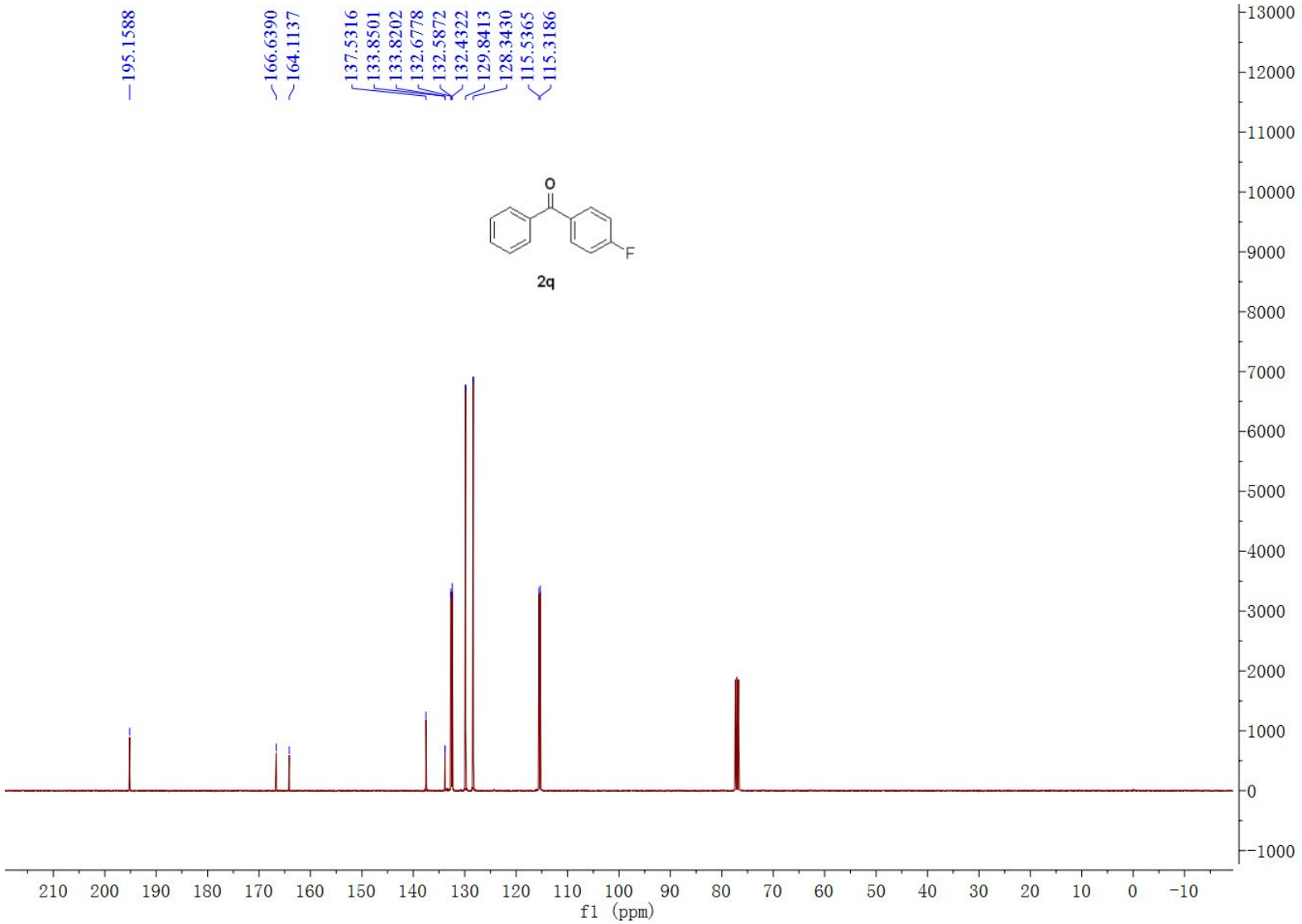
135.1761
130.0431
125.1939
125.1594
35.0869
31.1838
O
tBu
tBu
2p
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


195.1588
166.6390
164.1137
137.5316
133.8501
133.8202
132.6778
132.5872
132.4322
129.8413
128.3430
115.5365
115.3186
O
F
2q
13000
12000
11000
10000
9000
8000
7000
6000
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4000
3000
2000
1000
0
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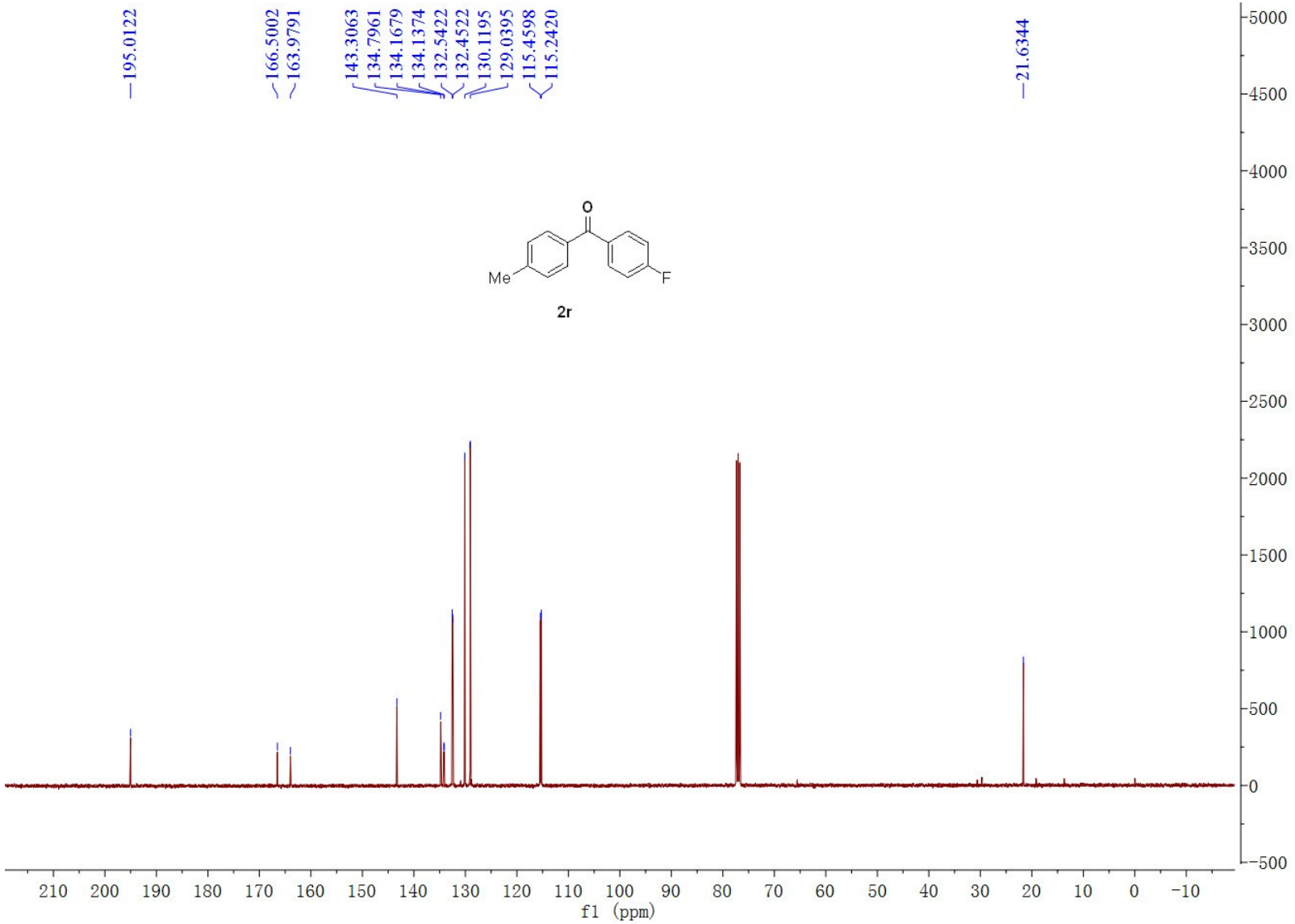
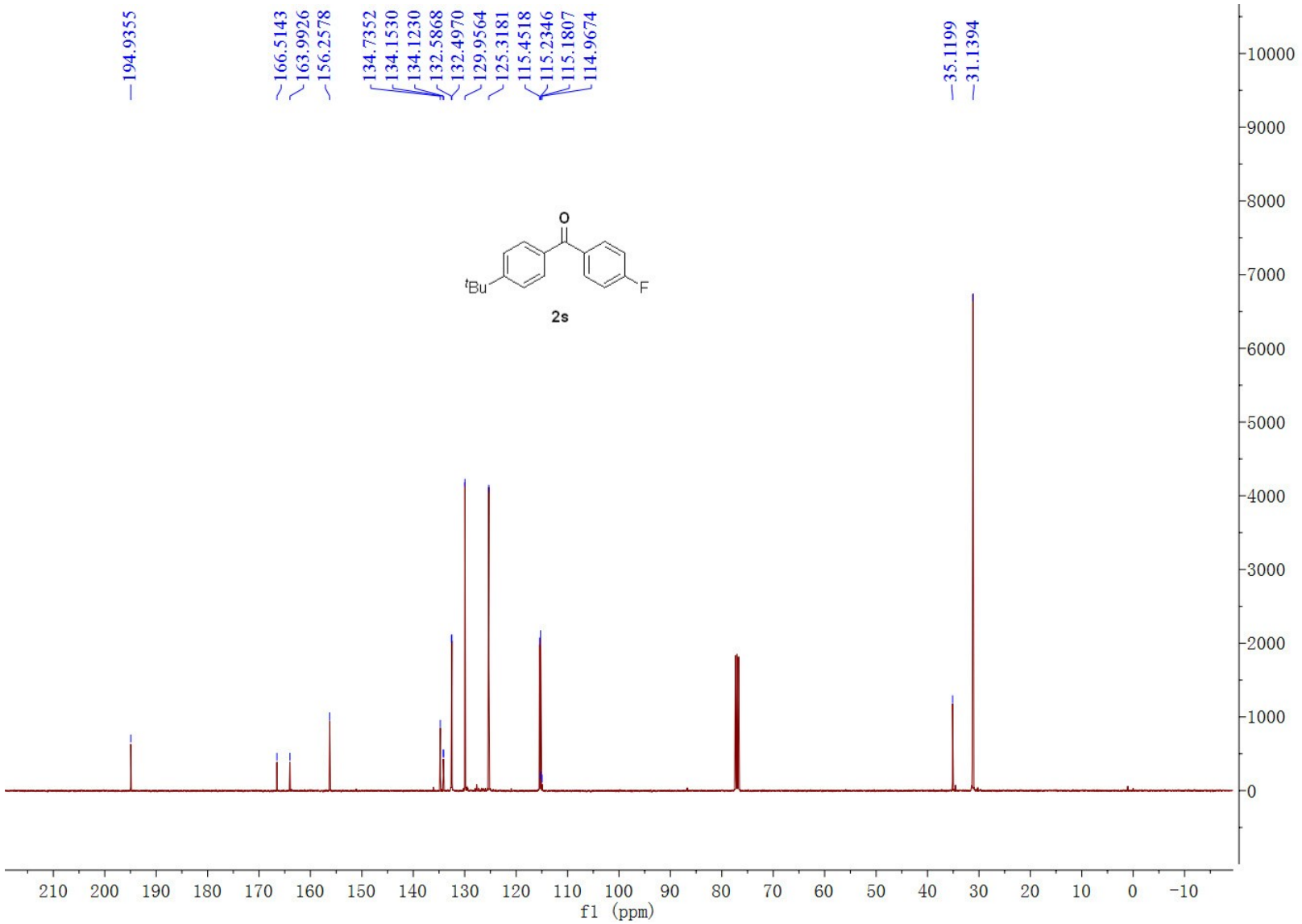
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


195.0122
166.5002
163.9791
143.3063
134.7961
134.1679
134.1374
132.5422
132.4522
130.1195
129.0395
115.4598
115.2420
21.6344
O
Me
F
2r
f1 (ppm)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125.3181
115.4518
115.2346
115.1807
114.9674
35.1199
31.1394
O
tBu
F
2s
10000
9000
8000
7000
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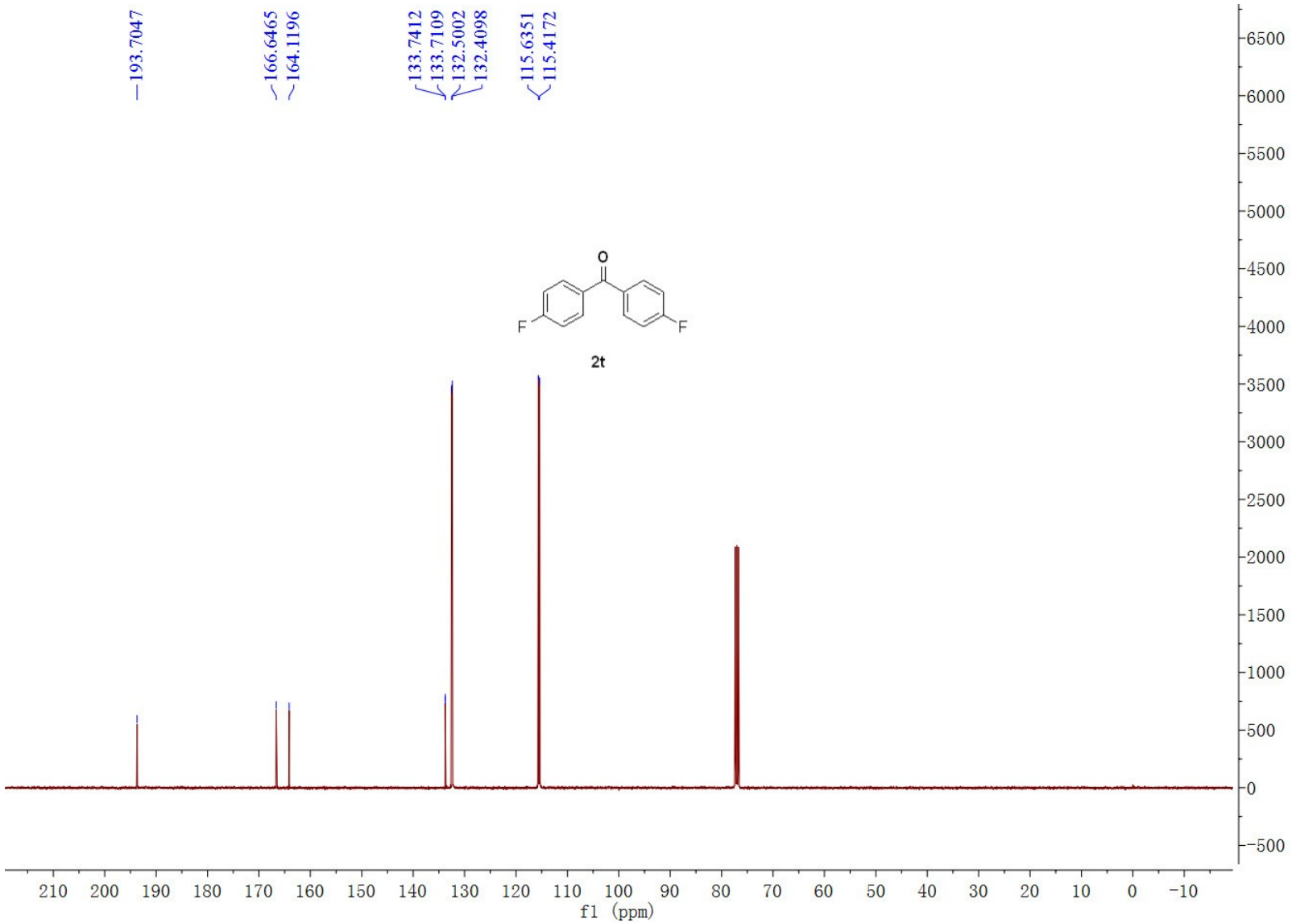
5000
4000
3000
2000
1000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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164.1196
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133.7109
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132.4098
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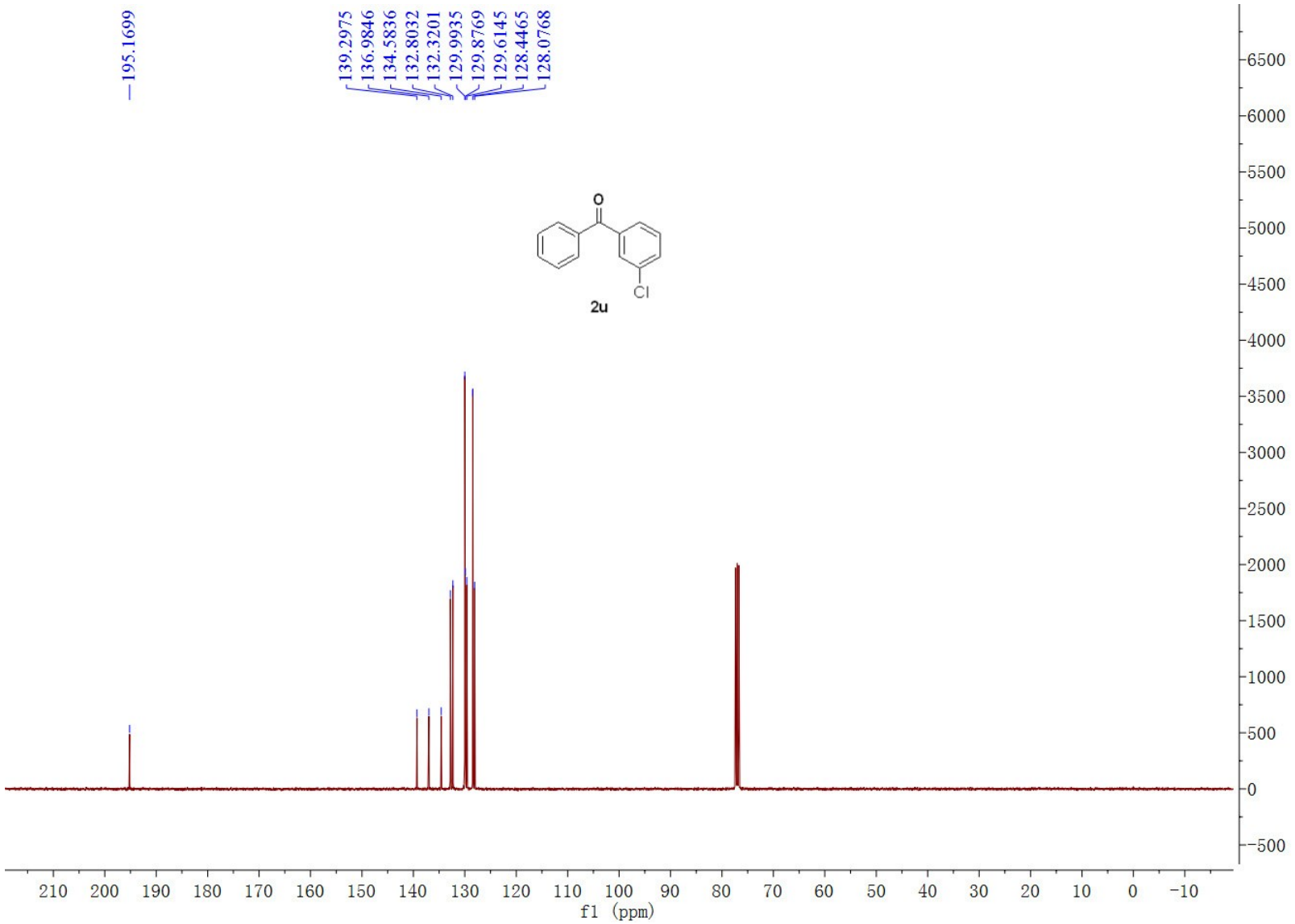
115.4172
O
F
F
2t
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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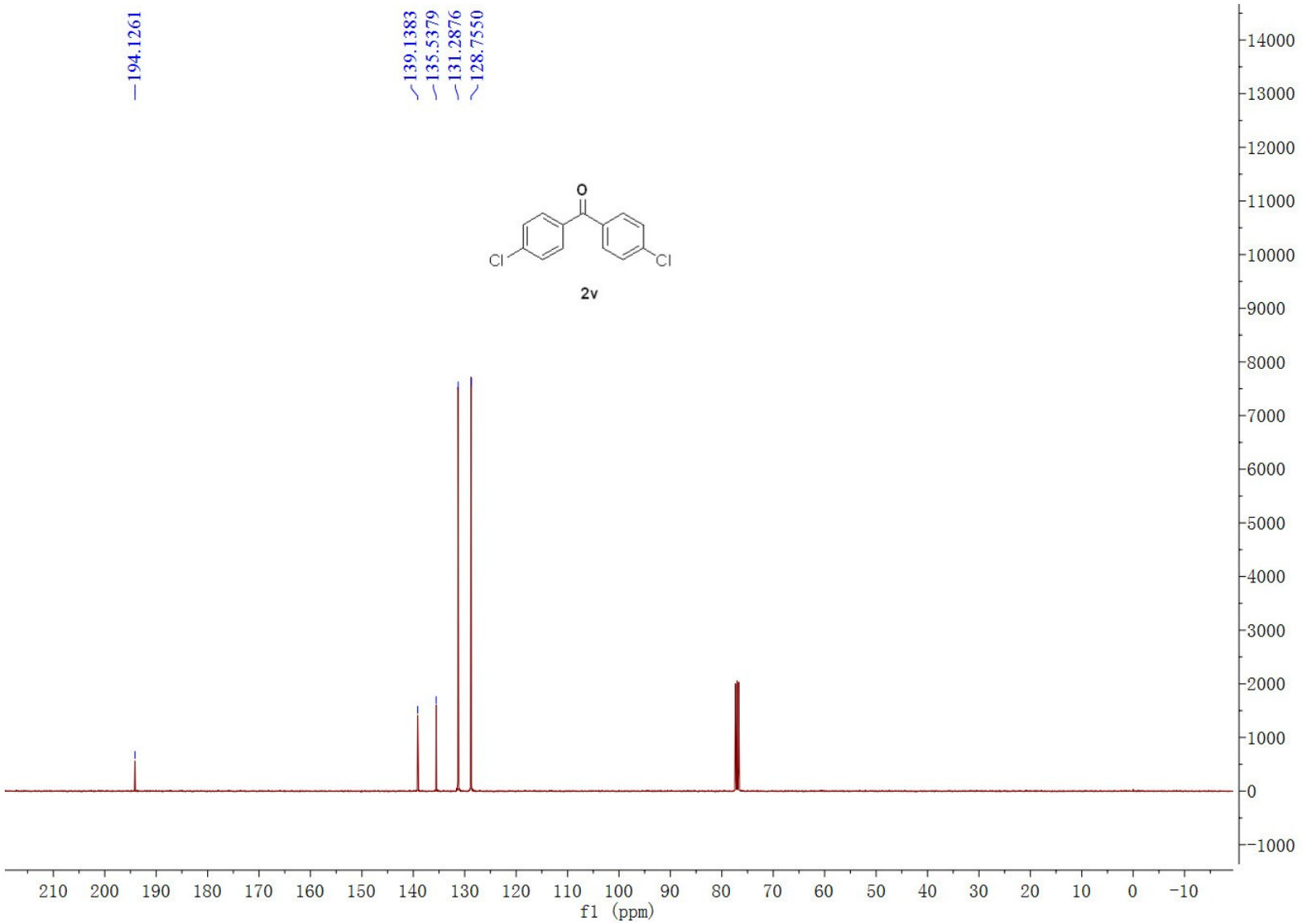
139.2975
136.9846
134.5836
132.8032
132.3201
129.9935
129.8769
129.6145
128.4465
128.0768
O
Cl
2u
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


194.1261
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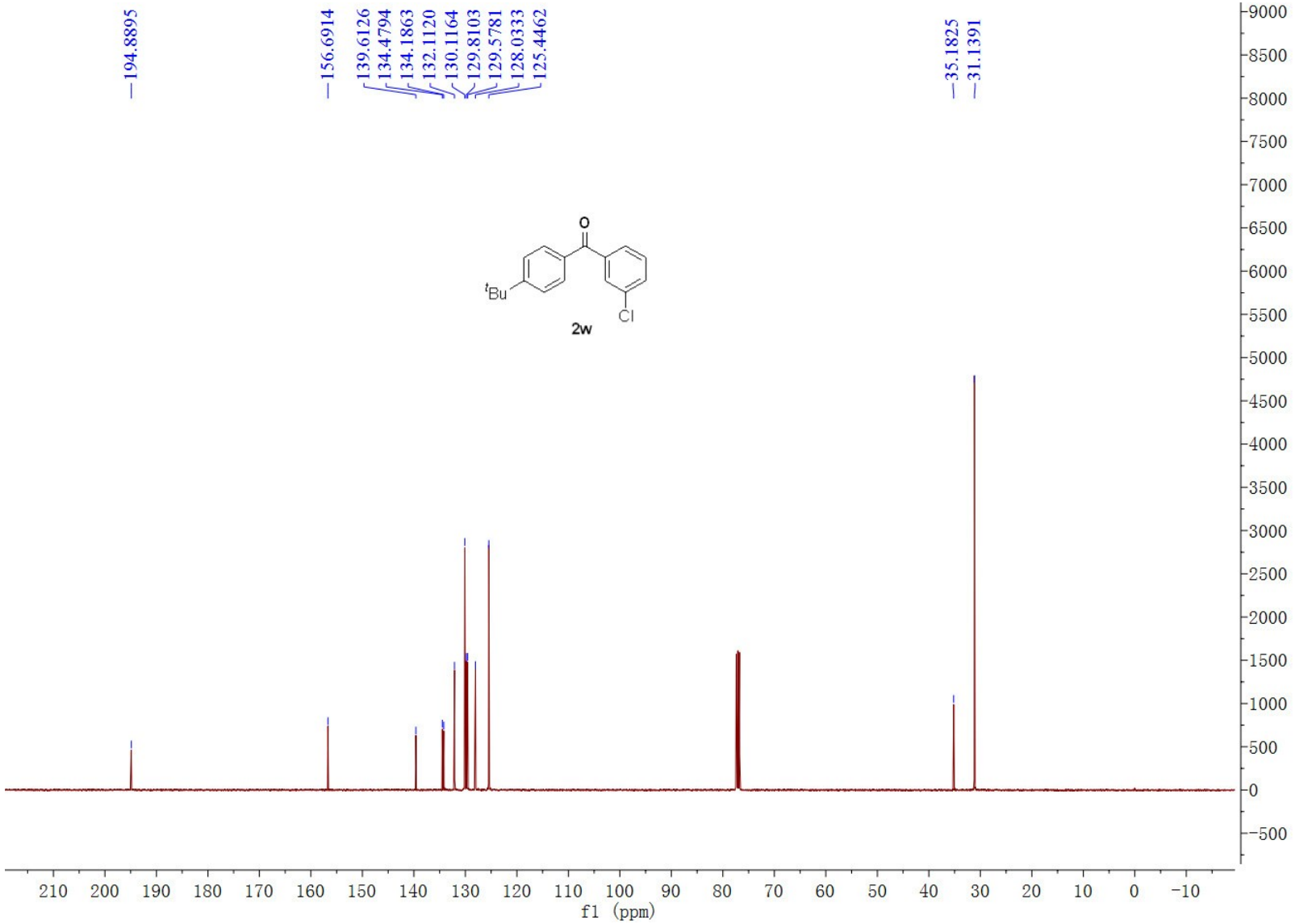
135.5379
131.2876
128.7550
O
Cl
Cl
2v
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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132.1120
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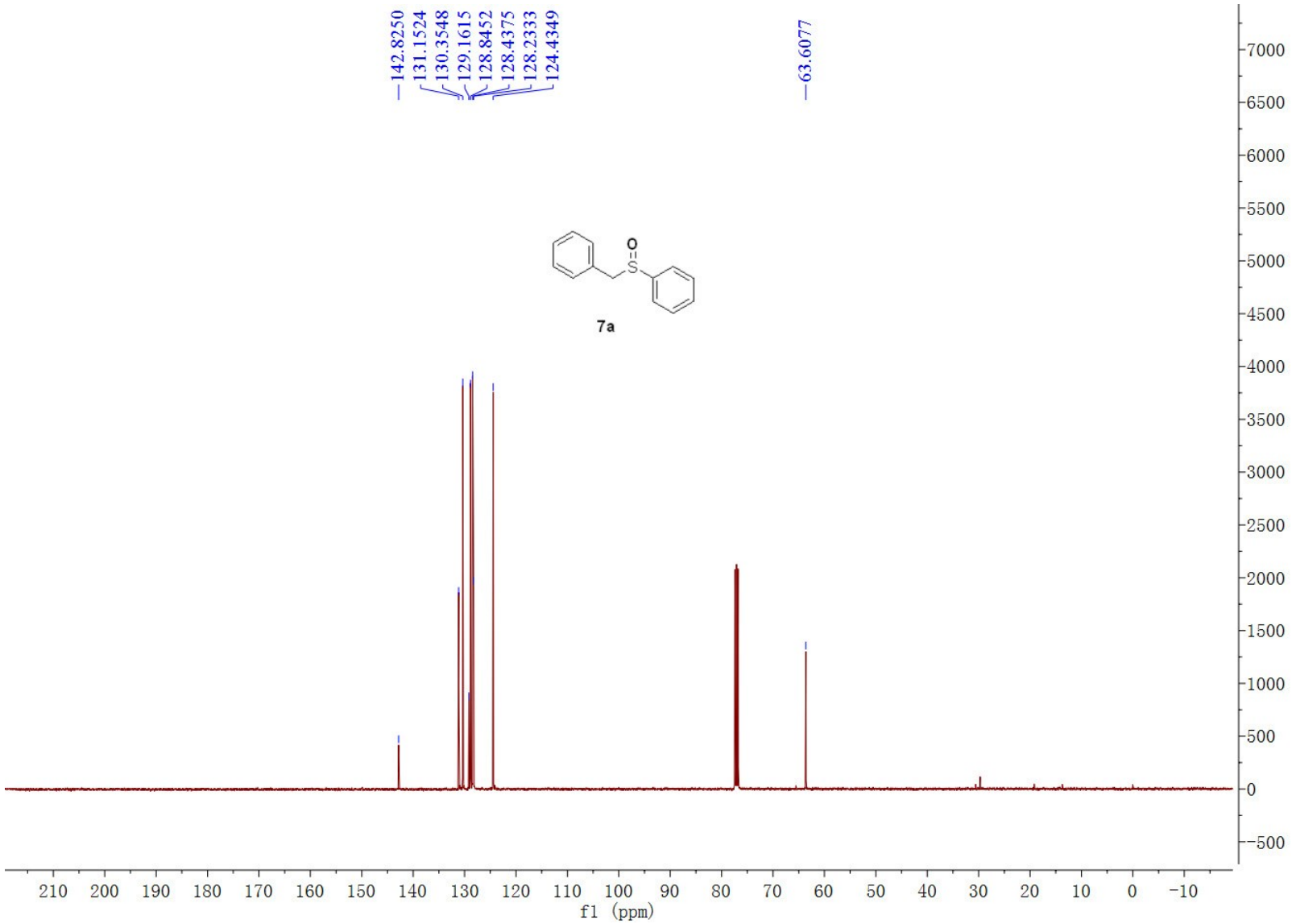
35.1825
31.1391
O
tBu
Cl
2w
f1 (ppm)


142.8250
131.1524
130.3548
129.1615
128.8452
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128.2333
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63.6077
O
S
7a
7000
6500
6000
5500
5000
4500
4000
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1500
1000
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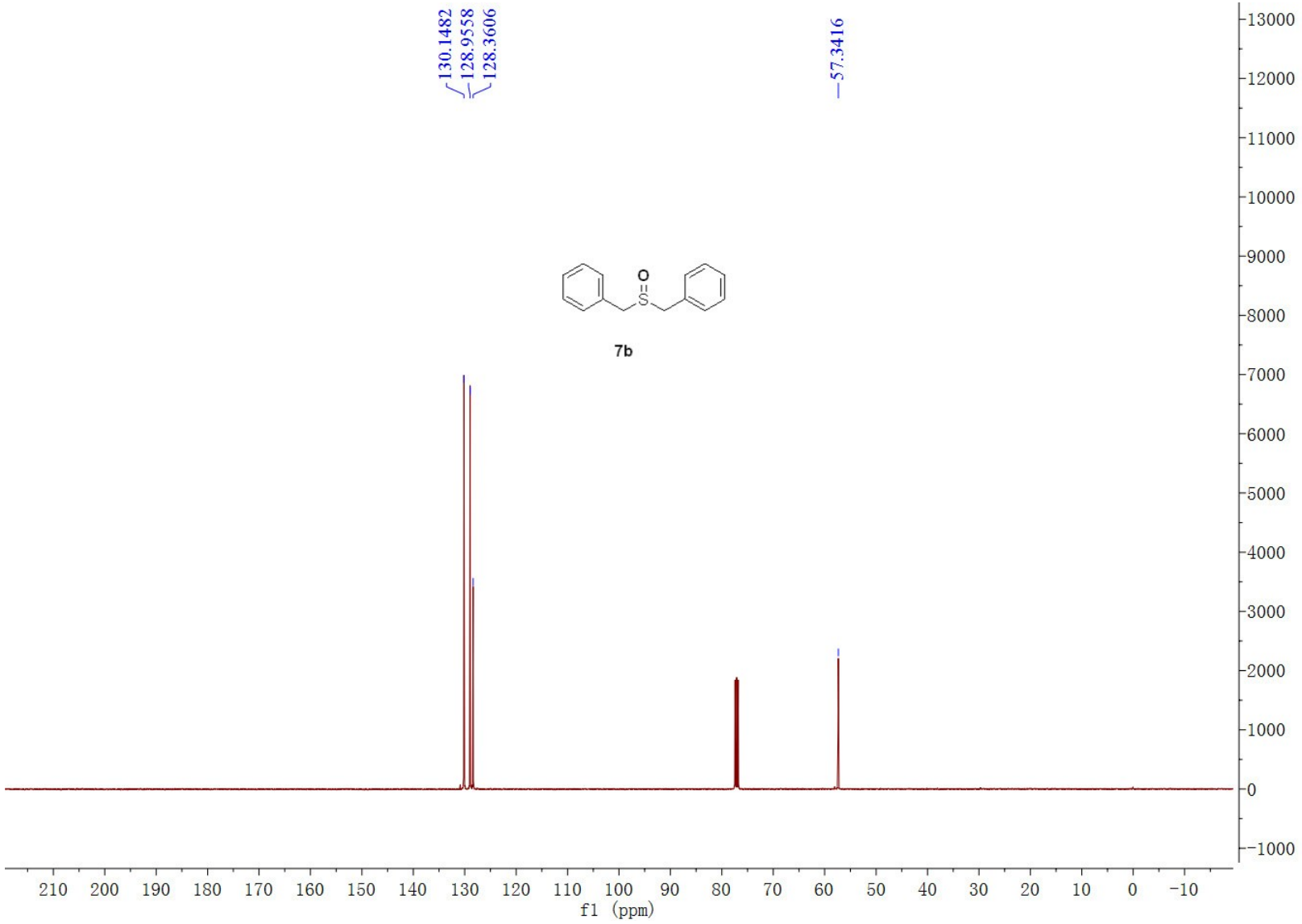
f1 (ppm)


130.1482
128.9558
128.3606
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O
S
7b
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11000
10000
9000
8000
7000
6000
5000
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3000
2000
1000
0
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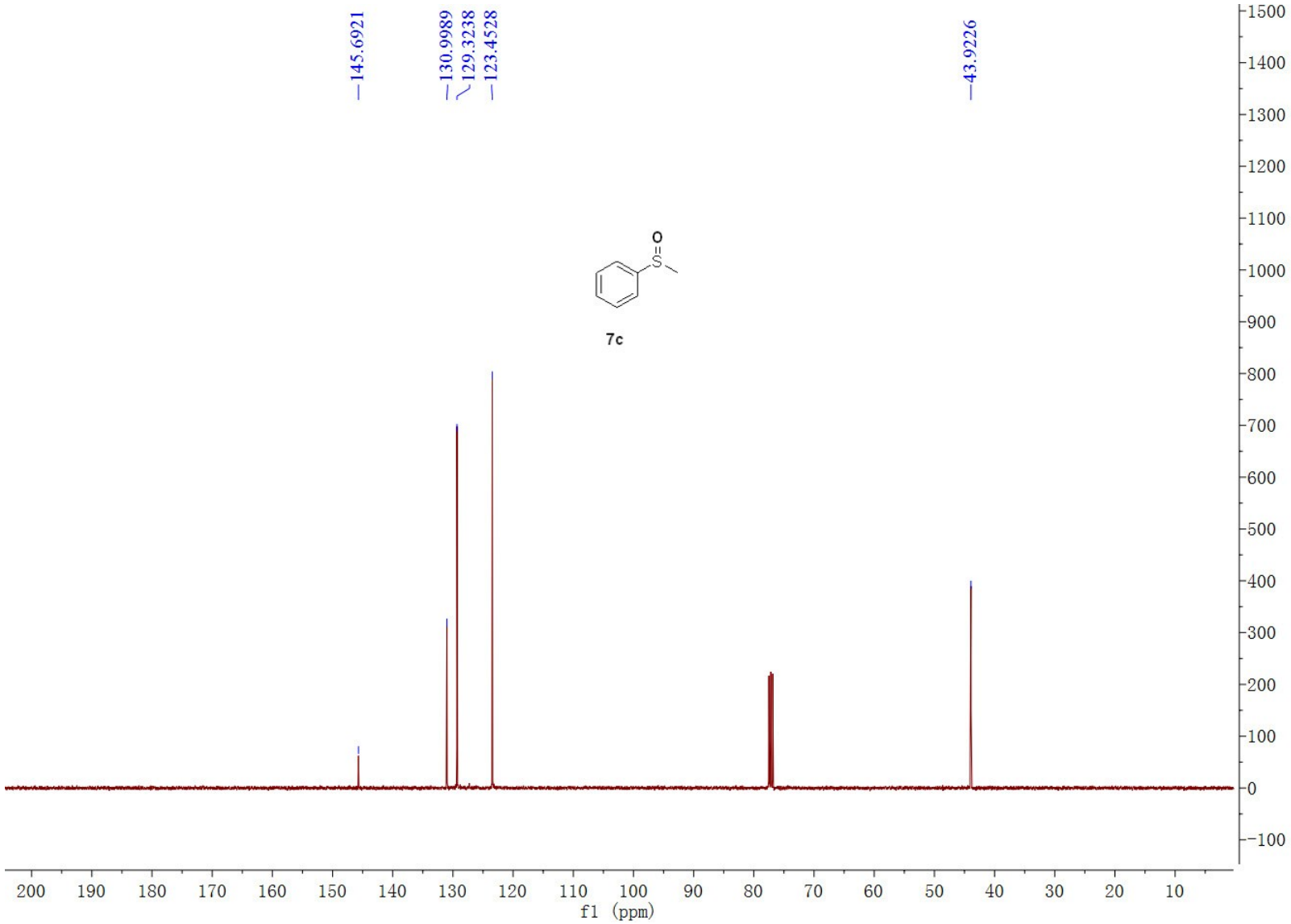
f1 (ppm)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129.3238
123.4528
43.9226
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S
7c
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1400
1300
1200
1100
1000
900
800
700
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500
400
300
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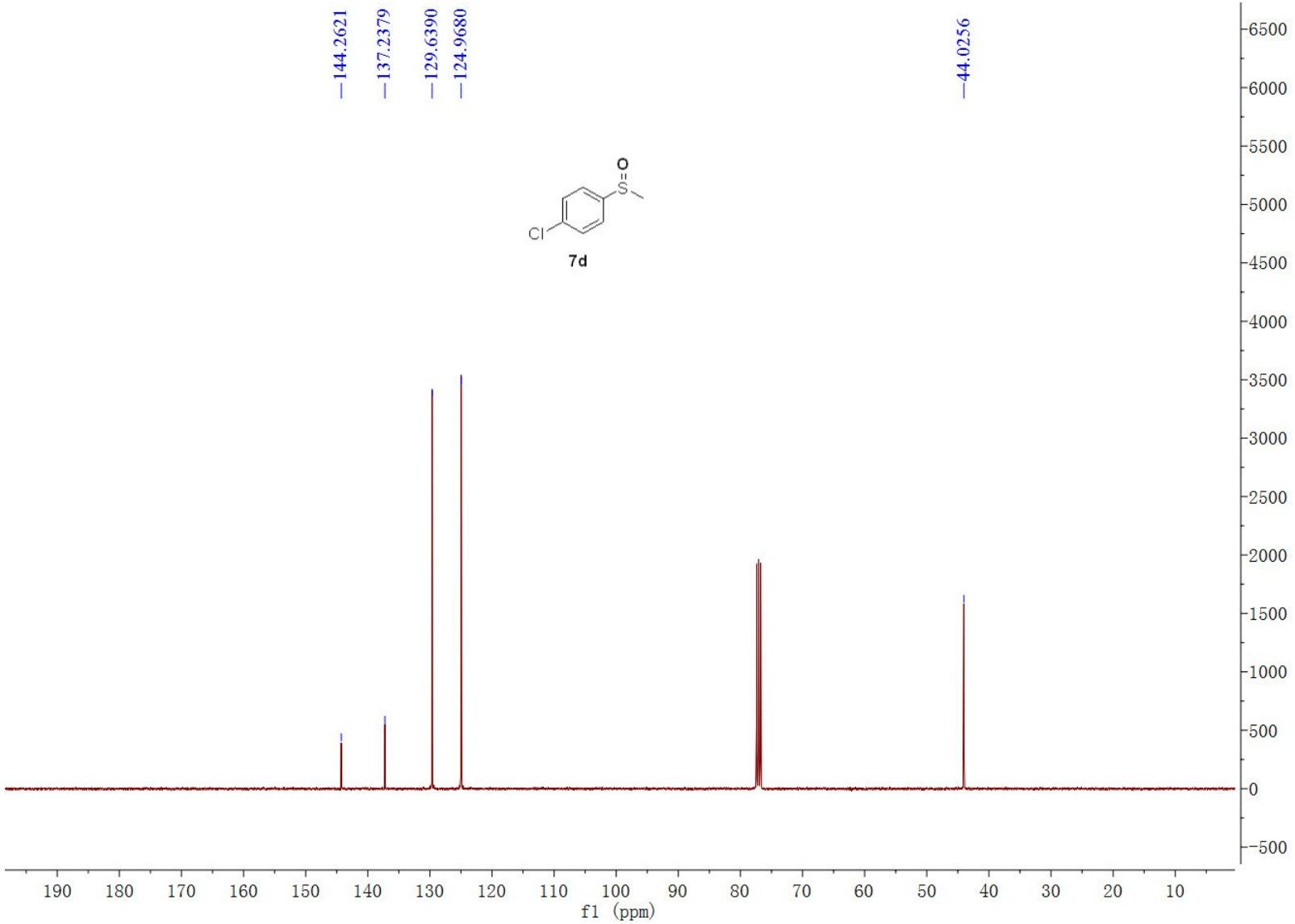
100
0
-100
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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137.2379
129.6390
124.9680
44.0256
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S
Cl
7d
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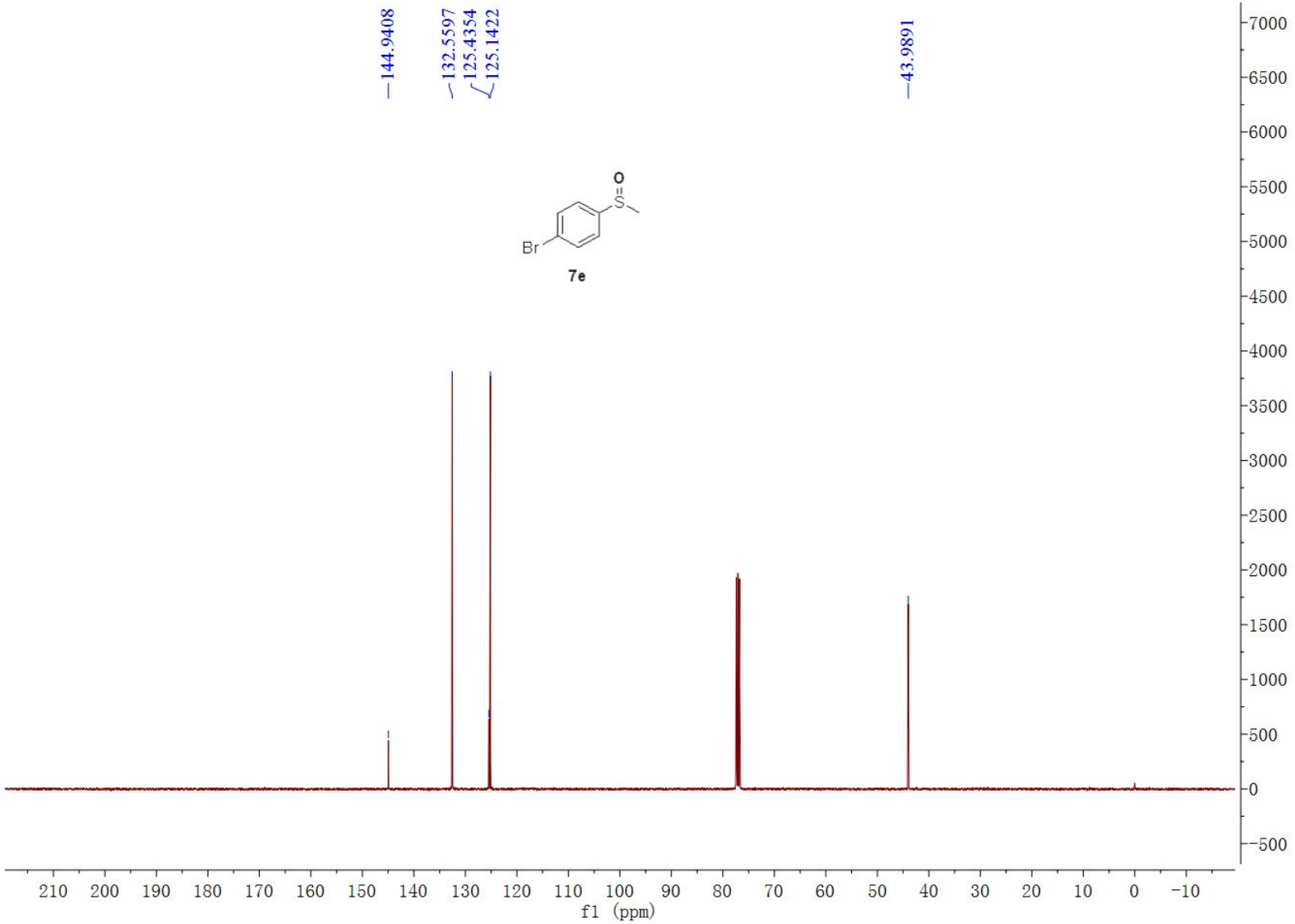
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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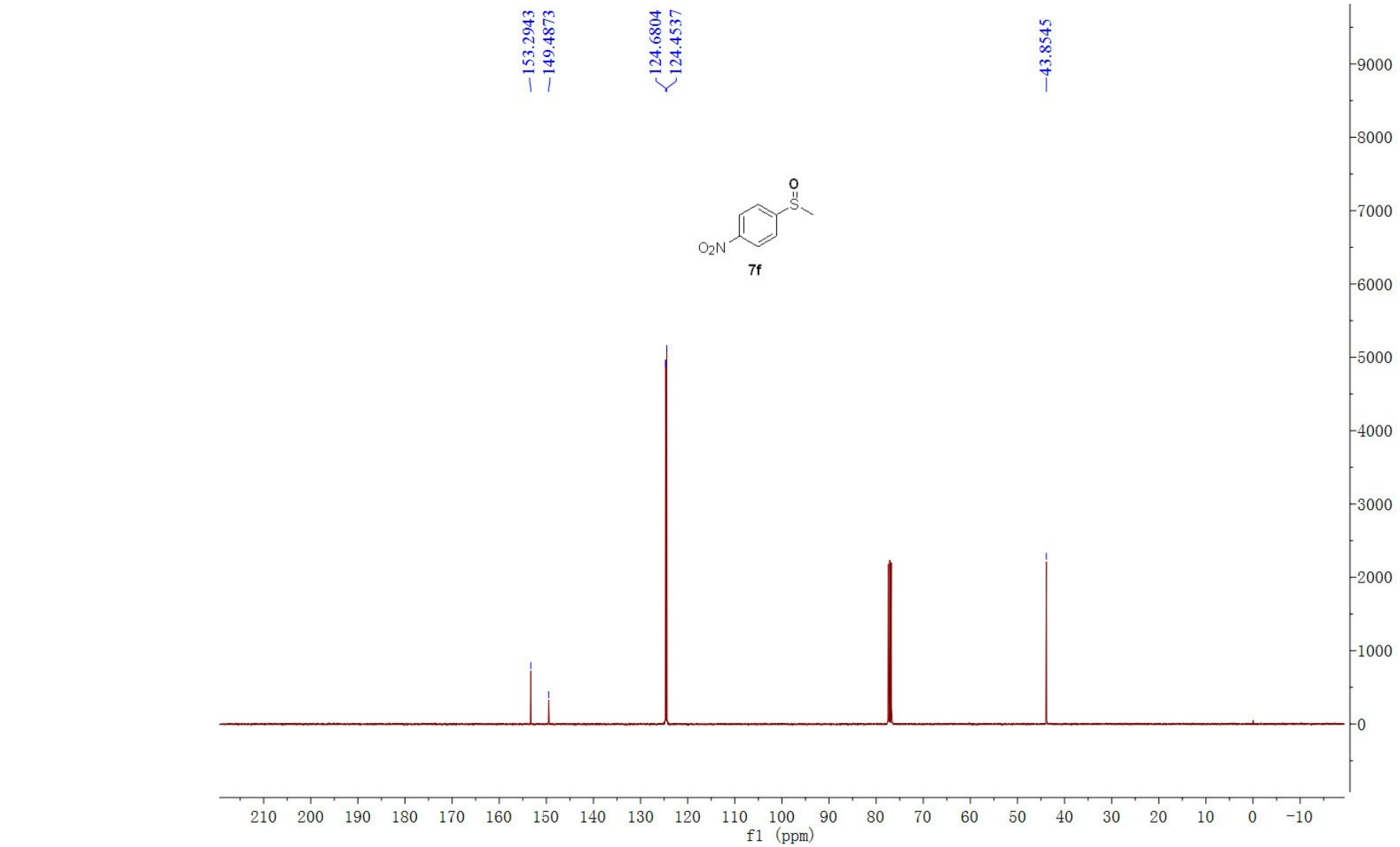
125.4354
125.1422
43.9891
O
S
Br
7e
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


153.2943
149.4873
124.6804
124.4537
43.8545
O2N
O
S
7f
9000
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7000
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4000
3000
2000
1000
0
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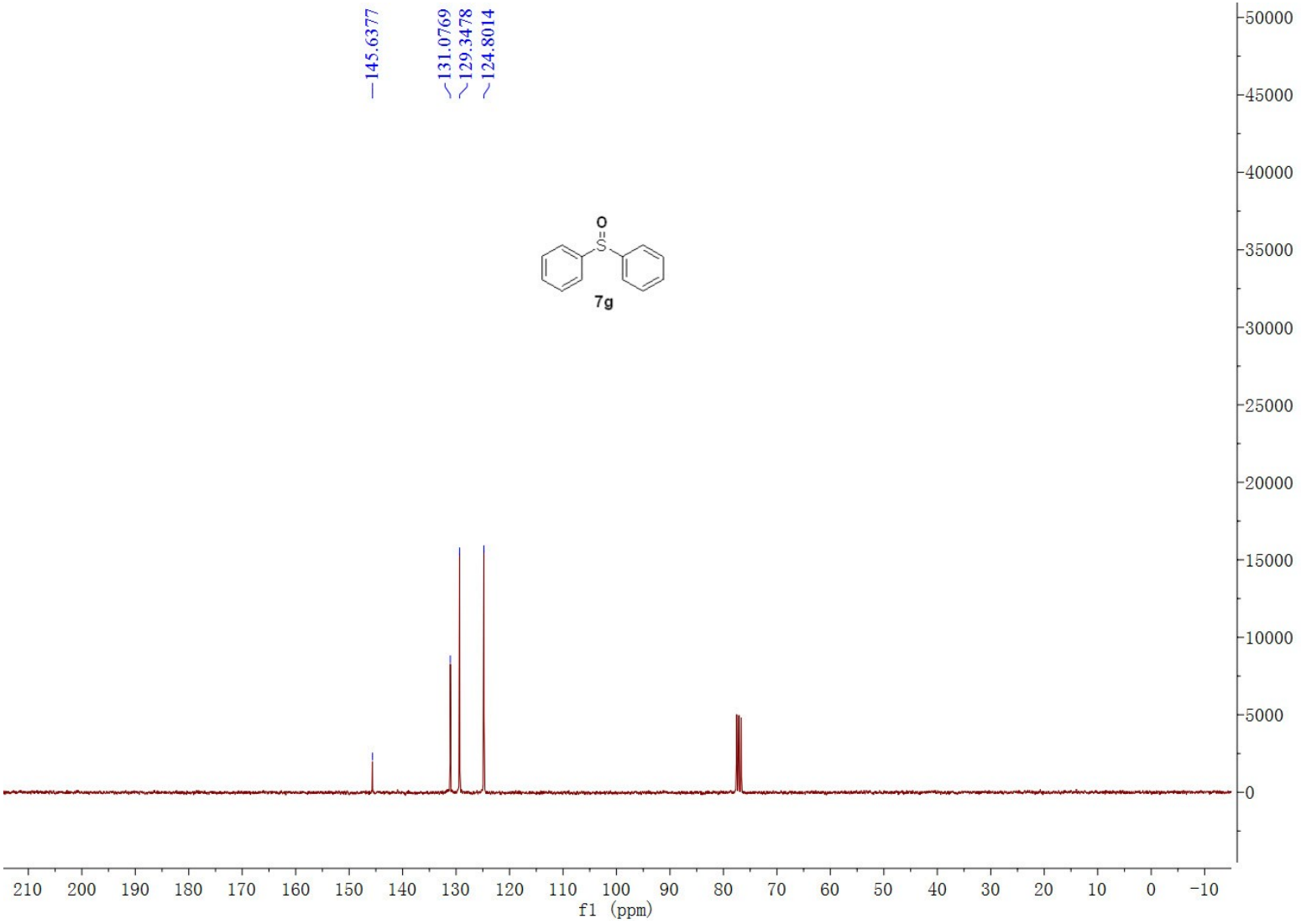
f1 (ppm)


145.6377
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129.3478
124.8014
O
S
7g
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40000
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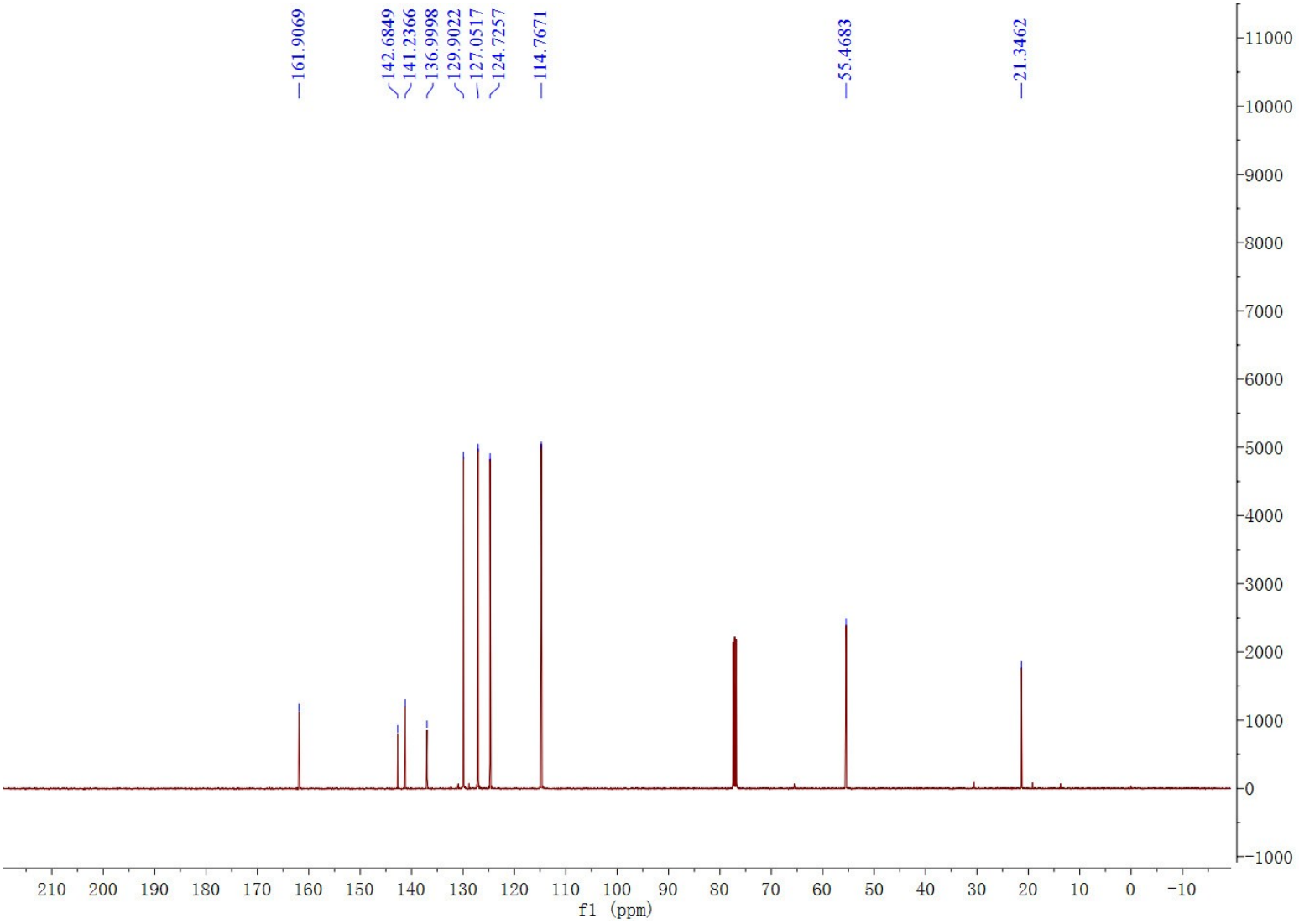
f1 (ppm)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21.3462
11000
10000
9000
8000
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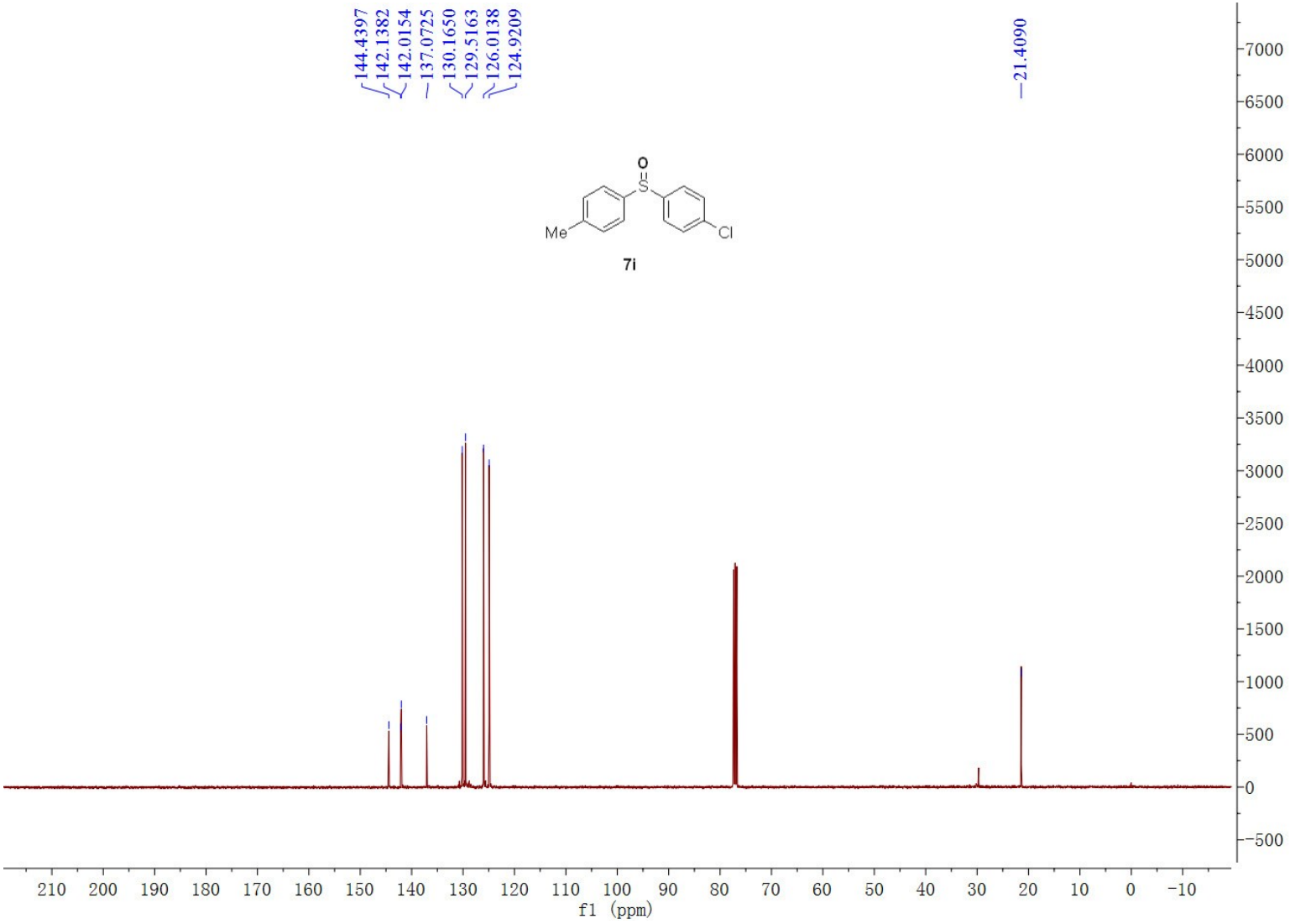
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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129.5163
126.0138
124.9209
21.4090
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S
Me
Cl
7i
7000
6500
6000
5500
5000
4500
4000
3500
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500
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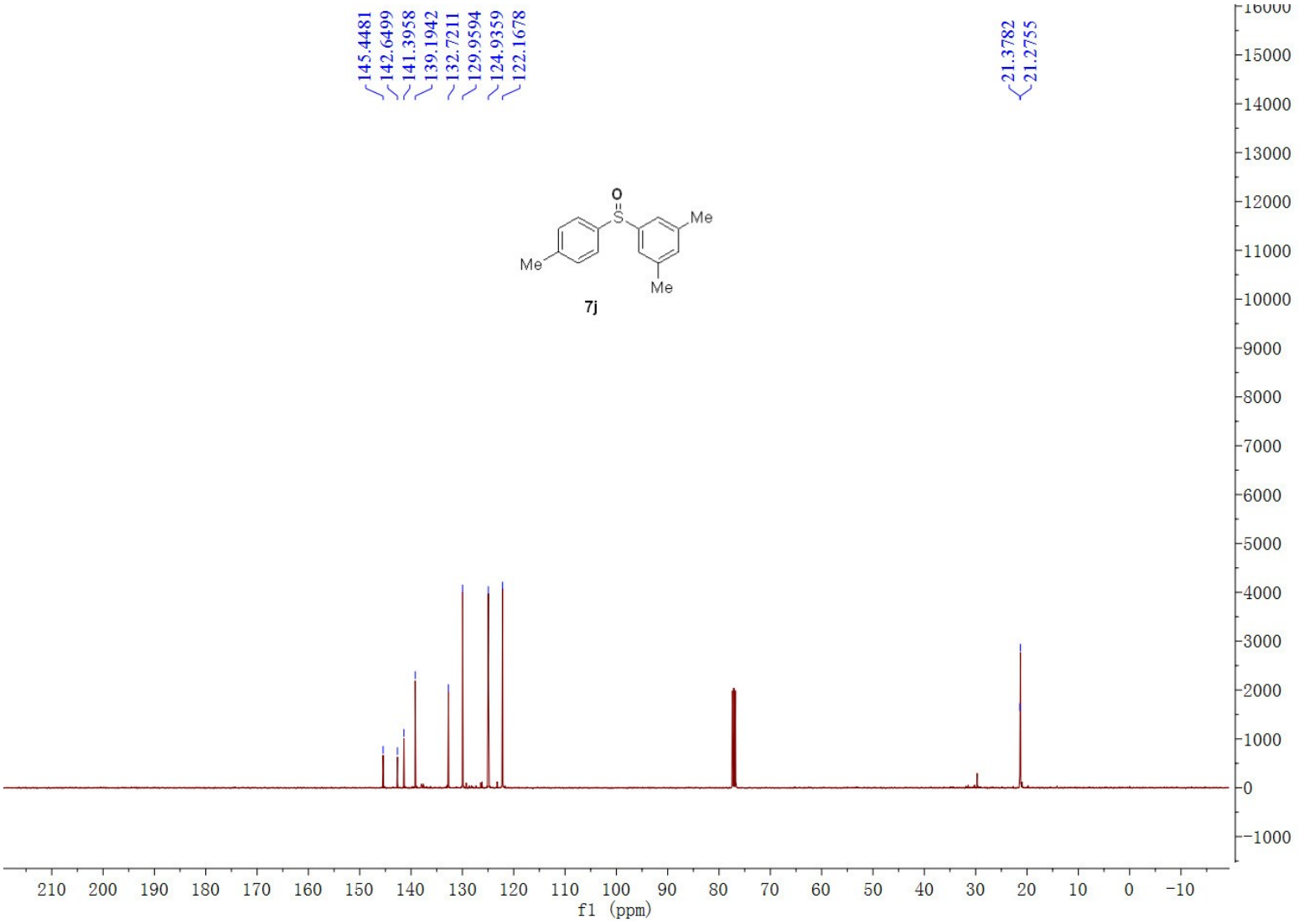
f1 (ppm)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124.9359
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21.3782
21.2755
O
S
Me
Me
Me
7j
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
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3000
2000
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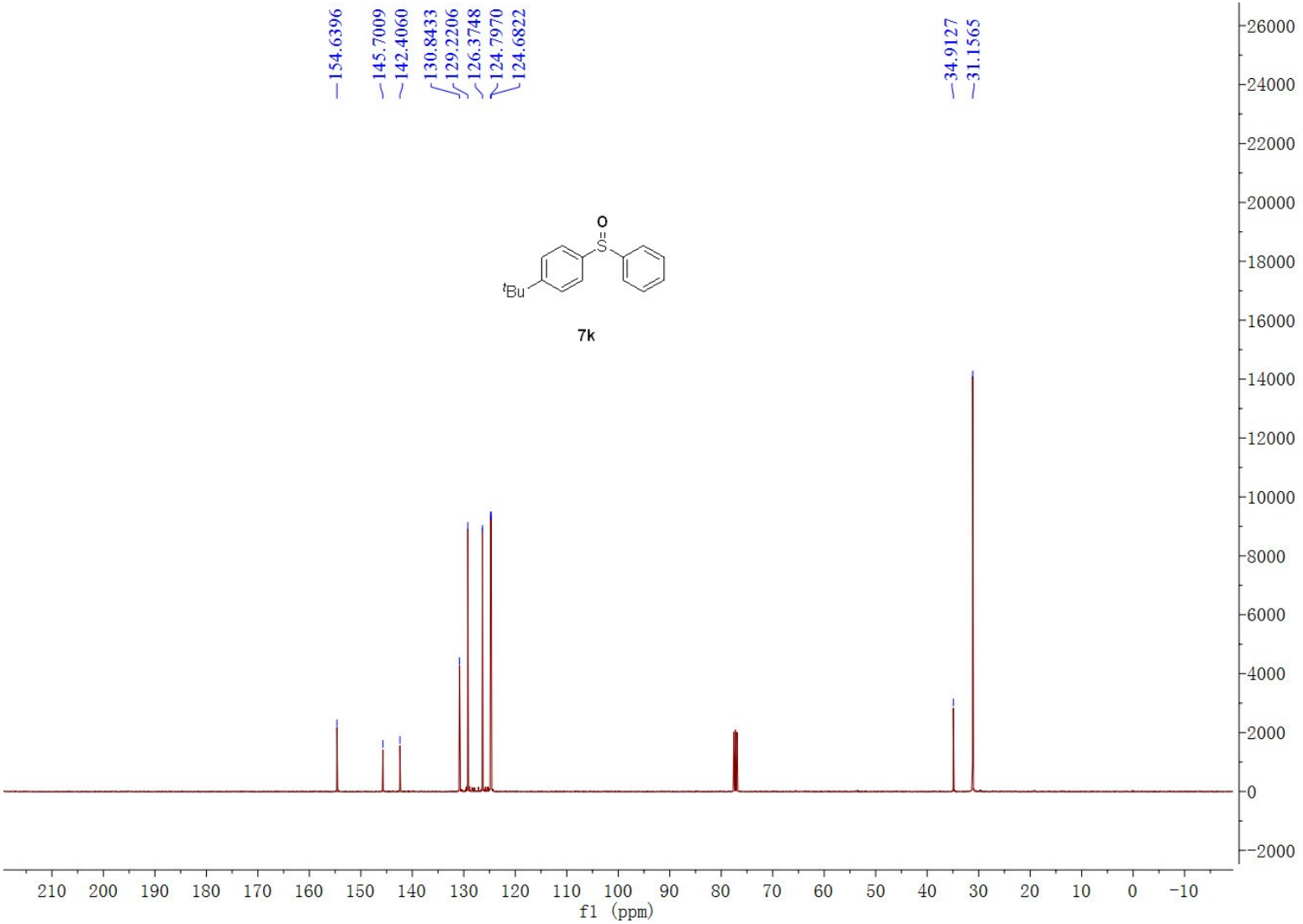
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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129.2206
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124.7970
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34.9127
31.1565
O
S
tBu
7k
26000
24000
22000
20000
18000
16000
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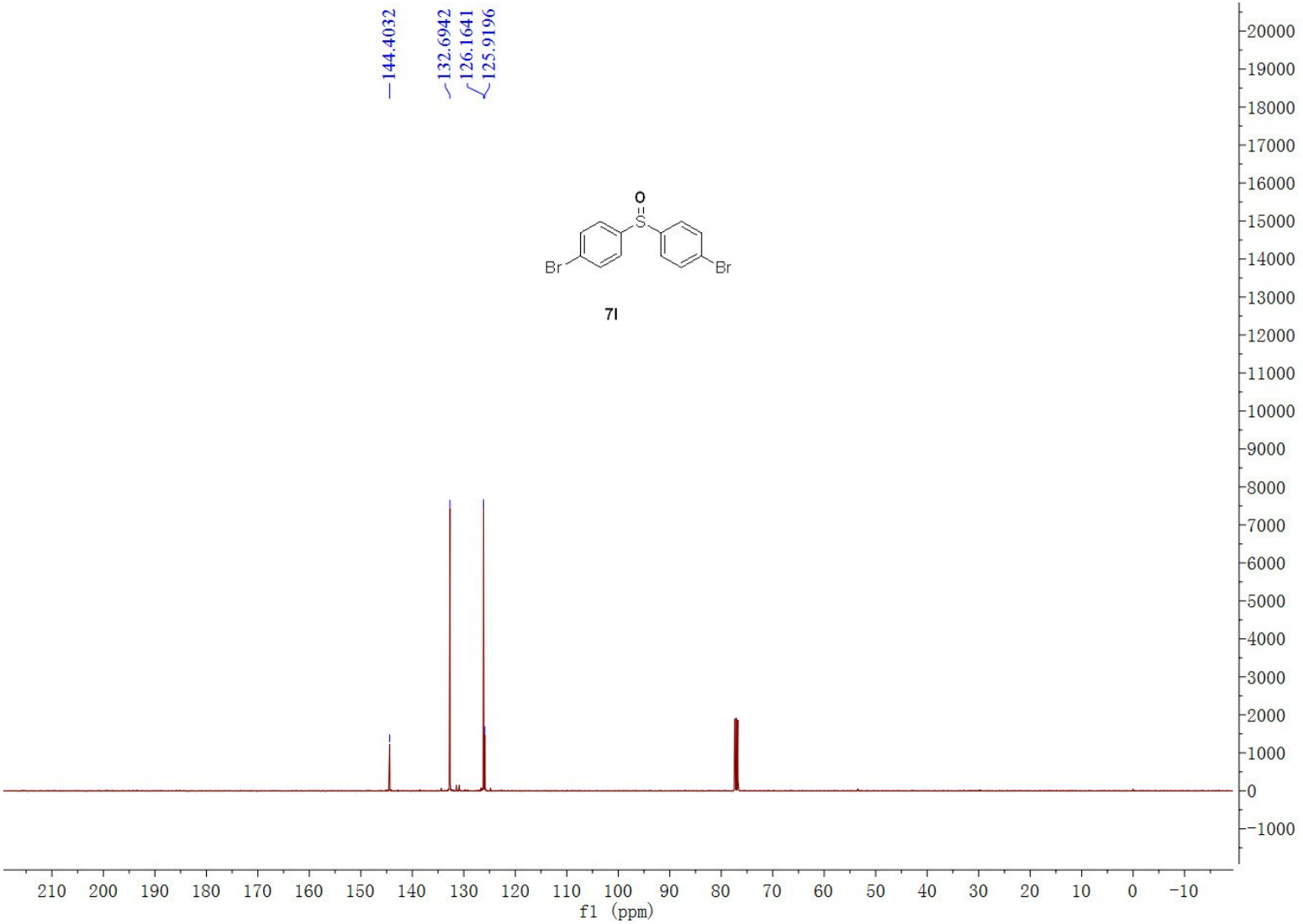
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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132.6942
126.1641
125.9196
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S
Br
Br
7l
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19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
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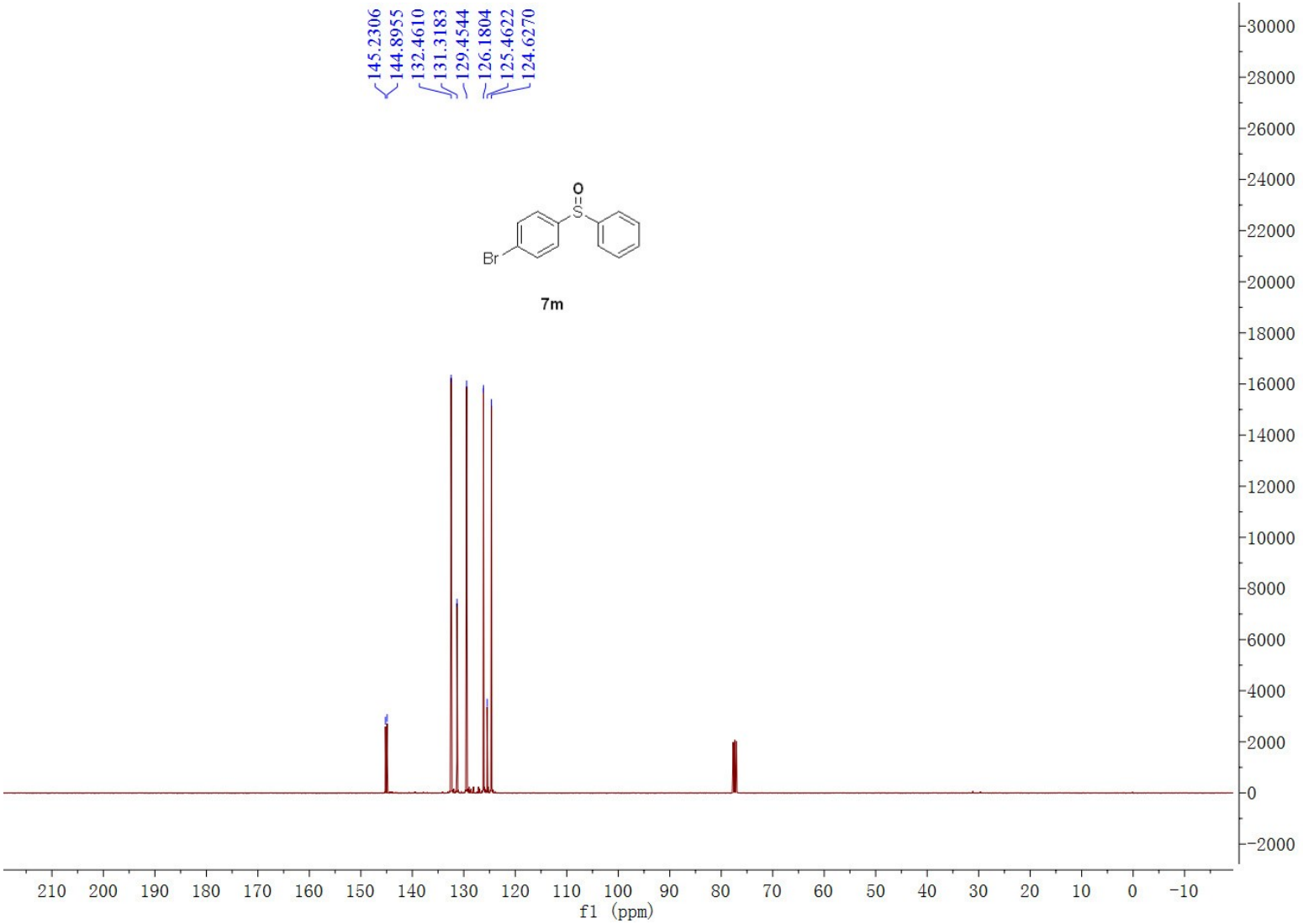
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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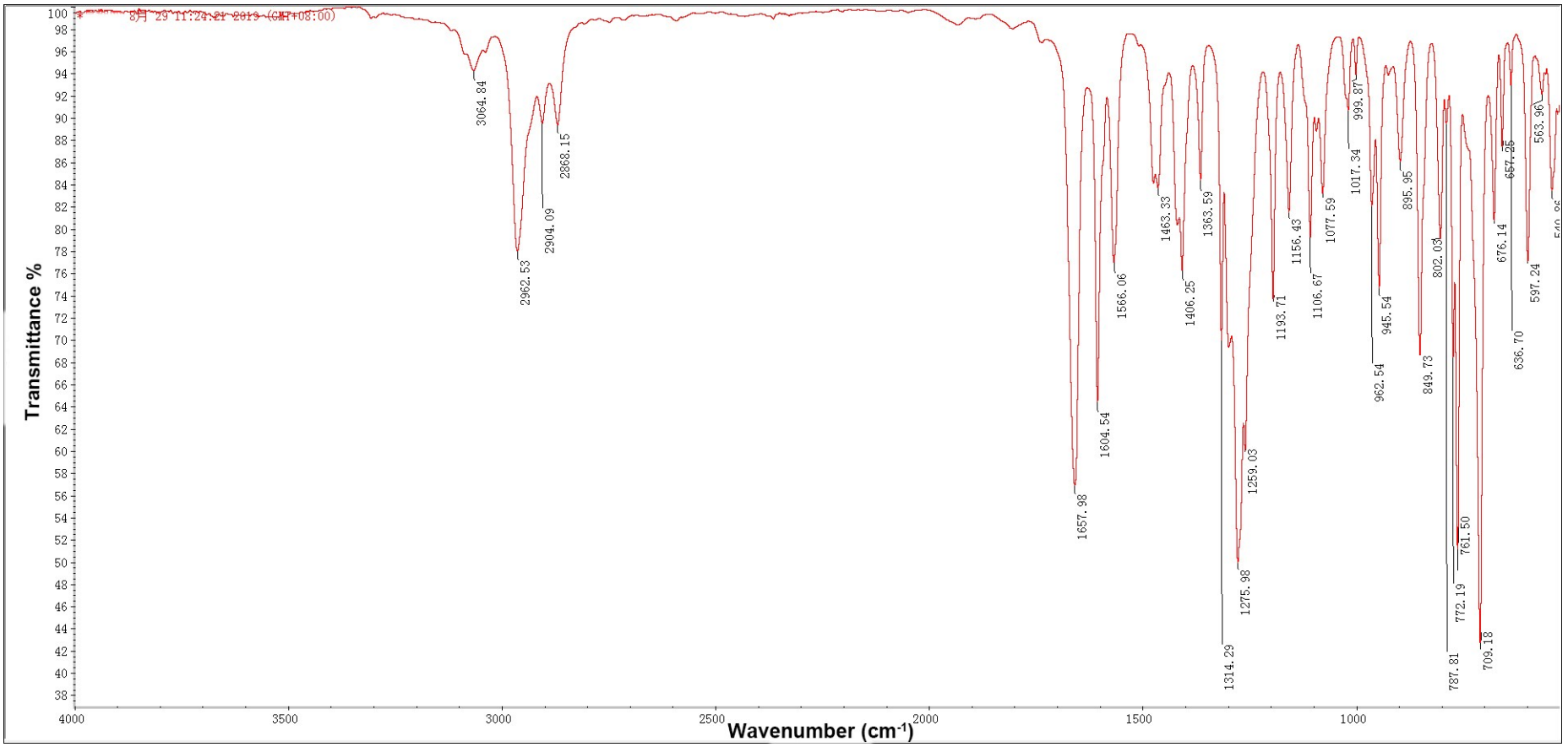
144.8955
132.4610
131.3183
129.4544
126.1804
125.4622
124.6270
O
S
Br
7m
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Transmittance %
Wavenumber (cm-1)
4000
3500
3000
2500
2000
1500
1000
3064.84
2962.53
2904.09
2868.15
1657.98
1604.54
1566.06
1463.33
1406.25
1383.59
1314.29
1275.98
1259.03
1193.71
1156.43
1106.67
1077.59
1017.34
999.87
962.54
945.54
895.95
849.73
802.03
787.81
772.19
761.50
709.18
676.14
657.85
636.70
597.24
563.96