Supporting Information

Perylenequinonoid-catalyzed Photoredox Activation for the Direct Arylation of (Het)Arenes with Sunlight

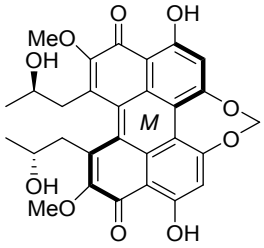
Shiwei Zhang, Zhaocheng Tang, Wenhao Bao, Jia Li, Baodang Guo, Shuping Huang, Yan Zhang and Yijian Rao

Table of Contents

1. Materials and Methods

Cercosporin was biosynthesized by a new cercosporin producing strain in our laboratory. Hypocrellin A and hypocrellin B were commercially available and used without further purification. The aryl diazonium tetrafluoroborates **2** were synthesized according to a previously described method.[1] 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 near UV 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. 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.

2. Biosynthesis of Cercosporin



Cercosporin

2.1 Isolation of a new cercosporin producing strain *Cercospora sp. JNU001*

Endophytic fungus *Cercospora sp. JNU001* strain used in this article was isolated from the barks of *Taxus chinensis* in Zhejiang Province, China. To isolate endophytic fungi, bark pieces (2.5×2.5cm) from *Taxus chinensis* were thoroughly washed using sterile distilled water, surface-sterilized by immersing in 70% aqueous ethyl alcohol (v/v) for 3 min to kill epiphytic microorganisms, rinsed 4–5 times in sterile distilled water and cut into small pieces (1×1cm). Using a flame-sterilized sharp blade to remove the outer layer of the surface-sterilized bark pieces. Small pieces of inner bark were placed on the surface of potato dextrose agar (PDA) plates with 50 mg/L streptomycin and 50 mg/L ampicillin to eliminate bacterial growth and incubate at 25 ^{o}C for 14-20 days. After fungal emergence in the plates, some fungal hyphal tips of the various fungi were transferred to new fresh PDA plates and this was repeated several times for fungus purity. Entophytic fungus were obtained from the bark of *Taxus chinensis* and only one colony (Figure S1) was found to produce cercosporin. The bottom of the plate has red pigment (Figure S1). It was designated as *Cercospora sp. JNU001* based on the 18S rDNA nucleotide sequences. The *Cercospora sp. JNU001* strain has been deposited to China Center for Type Culture Collection (CCTCCNo. M2017842). As shown in Figure S1, the pigments were red in acid solution, and turned green in alkaline solution. A light microscope and a scanning electronic microscope (SEM) (Figure S2) characterized the morphology of this strain.

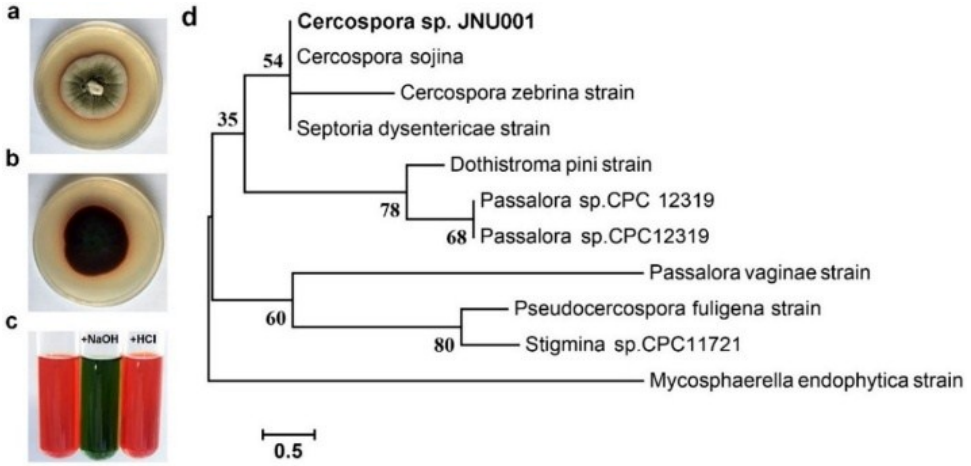


Figure S1. Characterization of Cercosporin-producing *Cercospora sp. JNU001* strain. (a) The bottom view of *Cercospora sp. JNU001* strain colony (7 days at 25 ^{o}C); (b) the top view of (a); (c) Cercosporin extractions at alkaline and acidic solution; (d) A neighbor-joining phylogenetic tree analysis of *Cercospora sp. JNU001* strain. Confidence values above 35% obtained from 1000-replicate bootstrap are indicated at the branch nodes. The scale bar indicates the number of base substitutions per site.

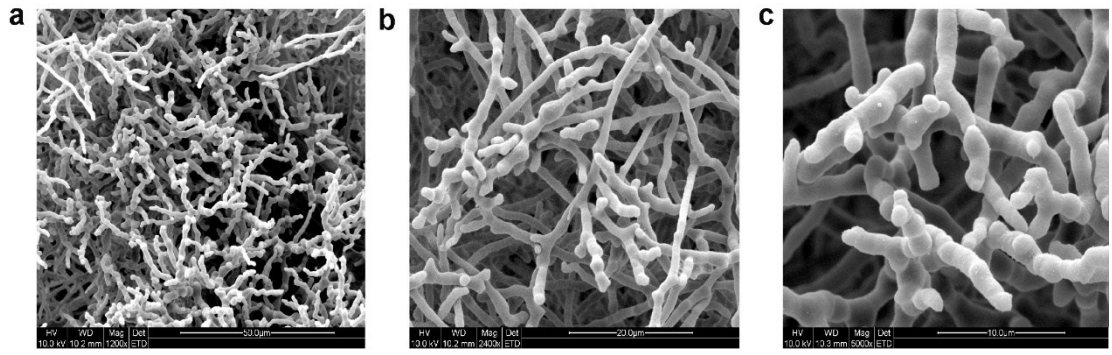


Figure S2. The morphological structure of *Cercospora sp. JNU001*. (A) SEM of pycnidium releasing conidia (1200×), (B) SEM of pycnidium on the mycelium (2400×); (C) SEM of pycnidium releasing conidia (5000×).

2.2 18S rDNA gene sequence analysis

The 18S rDNA sequence of *Cercospora sp. JNU001* was amplified using PCR with primer pairs: NS1 (5'-GTAGTCATATGCTTGTCTC-3') and NS4 (5'- CTTCCGTCAATTCCTTTAAG -3') and PCR products were sequenced. Its sequence was submitted to GenBank (MK077719). After homology searching against the GenBank, the 18S rDNA sequence of *Cercospora sp. JNU001* belongs to *Cercospora,* which was relatively close to *Cercospora sojina*. A phylogenetic relationship was

established through the alignment and cladistics analysis of homologous nucleotide sequence among these fungal species.

2.3 Liquid fermentation of cercosporin

Cercosporin was produced by liquid fermentation, extracted by dichloromethane, further purified by a sephadex LH-20 column and identified by HPLC (Figure S3), LC-MS, ^{1}HNMR, ^{13}C NMR. When *Cercospora sp. JNU001* was cultivated in continuous light with S-7 culture medium (pH = 8.5), a maximum of cercosporin production was obtained (128.2 mg/l).

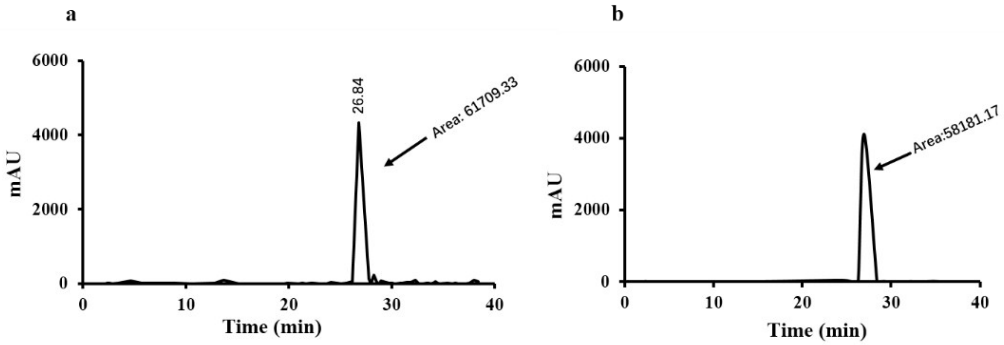
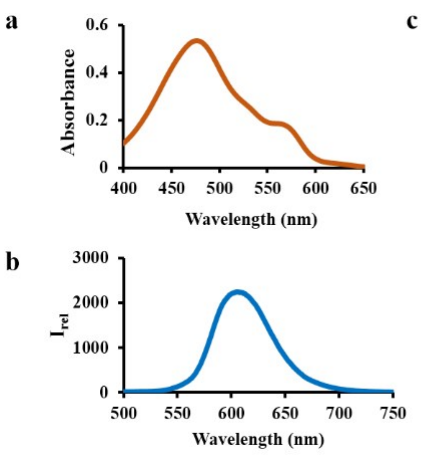


Figure S3. High-performance liquid chromatogram analysis of cercosporin. (a) crude cercosporin (b) purified cercosporin

Cercosporin identification: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 14.82 (s, 2H, ArH), 7.06 (s, 2H, ArH), 5.57 (s, 2H, CH_2), 4.20 (s, 6H, $2OCH_3$), 3.62-3.57 (m, 2H, CH_2), 3.42-3.37 (m, 2H, CH_2), 2.93-2.88 (m, 2H, CH_2), 0.63 (d, 6H, J = 8 Hz, $2CH_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.0, 181.8, 167.4, 163.4, 152.8, 135.4, 130.6, 127.9, 112.9, 109.3, 108.2, 92.6, 68.1, 61.2, 42.2, 23.3; HRMS (ESI-Q-TOF) exact mass calcd for $C_{29}H_{25}O_{10}$ $[M - H]^-$ 533.1448, found 533.1468.

3. Photochemical and Electrochemical Characterization.



c

Photochemical Properties
Absorption λ_{max}: 476 nm
ε = 19500 M^{-1} cm^{-1}
Singlet Energy: 2.33 eV
Triplet Energy: 1.30 eV
τ_0 (S_1)= 1.00 ns
Emission (Fl) λ_{max}: 605 nm

Redox Properties
$E_{1/2}(CP/CP^{\bullet-})$ = -0.46 V vs. SCE
$E_{1/2}(CP^{\bullet+}/CP)$ = 1.56 V vs. SCE
$E_{1/2}(CP^{*}/CP^{\bullet-})$ = 1.87 V vs. SCE
$E_{1/2}(CP^{\bullet+}/CP^{*})$ = -0.77 V vs. SCE

Figure S4. Absorption spectra (a), fluorescence spectra (b) of cercosporin ($2.75*10^{-5}$ mol/L) in DMSO at room temperature; and photochemical and redox properties of cercosporin (c).

3.1 $E_{0,0}^{S1}$ and $E_{0,0}^{T1}$

The calculated vertical first singlet and triplet excited energies are 2.33 eV (532 nm) and 1.30 eV (953 nm), respectively. The density functional theory (DFT) calculations and time-dependent density functional theory (TD-DFT) calculations are performed using the Gaussian 09 package.[2] The geometry of cercosporin was optimized without imposing symmetry constraints at the B3LYP density functional level[3,4] using the 6-31+g(d,p) basis set. The minima were confirmed with all real frequencies.

3.2 Cyclic voltammogram of cercosporin

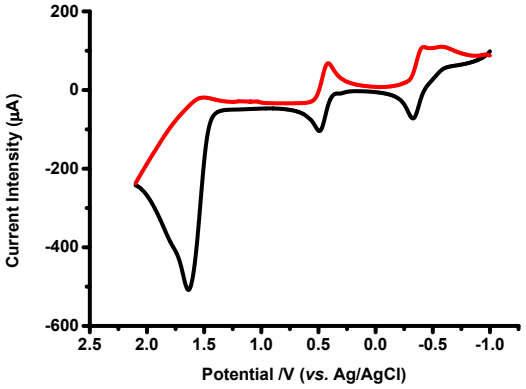


Figure S5. Cyclic voltammogram of cercosporin in CH_3CN with 0.1M TBAF (Bu_4NPF_6) as the supporting electrolyte and ferrocenium/ferrocene (Fc^+ /Fc) as the internal standard with a scan rate of 50 mV/s.

$E_{1/2}^{red}$ (CP/CP$^{\bullet-}$) = -0.46 V vs SCE

$E_{1/2}^{ox}$ (CP$^{\bullet+}$/CP) = 1.56 V vs SCE

E_{red}^{*} (CP*/CP$^{\bullet-}$) = $E_{1/2}^{red}$ (CP/CP$^{\bullet-}$) + $E_{0,0}^{S1}$= 1.87 V vs SCE

E_{ox}^{*} (CP$^{\bullet+}$/CP*) = $E_{1/2}^{ox}$ (CP$^{\bullet+}$/CP) - $E_{0,0}^{S1}$ = -0.77 V vs SCE

4. General Procedures

4.1 General procedure for the preparation of aryl diazonium tetrafluoroborates 2

The appropriate aniline (10 mmol) was dissolved in a mixture of 4 mL of distilled water and 3.4 mL of 50% hydrofluoroboric acid. After cooling the reaction mixture to 0°C using ice bath, the sodium nitrite

(0.69 g in 1.5 mL) was added dropwise in 5 min interval of time. The resulting mixture was stirred for 40 min and the precipitate was collected by filtration and re-dissolved in minimum amount of acetone. The product diazonium tetrafluoroborate was recrystallized and then washed several times with diethyl ether and dried under vacuum.

4.2 General procedure for the reaction of aryl diazonium tetrafluoroborates with (hetero)arenes

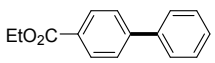
The reaction equipment is very simple (Figure S6). Three CD light disks are placed around the reaction tubes and then irradiated with sunlight at room temperature. (The light disks are for maximizing the amount of sunlight available to the reactions.)

Figure S6. Photograph of the photochemical reaction set up

4.2.1 General procedure for the reaction of aryl diazonium tetrafluoroborates with Arenes

In a 10 mL schlenk tube with magnetic stirring bar the cercosporin (0.01 equiv), aryl diazonium tetrafluoroborate **2** (1 equiv) and arene **1** (10 equiv) were dissolved in dry DMSO (2 mL) and the resulting mixture was degassed by "pump-freeze-thaw" cycles. Then, the reaction mixtures were placed under sunlight for 16 hours. 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 **3**.

Ethyl [1,1'-biphenyl]-4-carboxylate (**3aa**)[5]

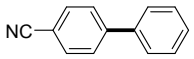


3aa

The representative procedure was followed using 4-(ethoxycarbonyl) phenyl diazonium tetrafluoroborate (**2a**) (0.20 mmol) and benzene (**1a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 100/1)

yielded **3aa** (26 mg, 58%) as a white oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.11 (d, 2H, *J* = 8 Hz, ArH), 7.67-7.62 (m, 4H, ArH), 7.49-7.45 (m, 2H, ArH), 7.42-7.38 (m, 1H, ArH), 4.43-4.38 (m, 2H, CH_2), 1.42 (t, 3H, *J* = 8 Hz, CH_3).

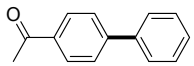
[1,1'-Biphenyl]-4-carbonitrile (**3ab**)[6]



3ab

The representative procedure was followed using 4-cyanophenyl diazonium tetrafluoroborate (**2i**) (0.20 mmol) and benzene (**1a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 100/1) yielded **3ab** (19 mg, 55%) as a white oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.74-7.67 (m, 4H, ArH), 7.59 (d, 2H, J = 8 Hz, ArH), 7.50-7.42 (m, 3H, ArH).

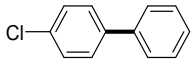
1-([1,1'-Biphenyl]-4-yl) ethan-1-one (**3ac**)[7]



3ac

The representative procedure was followed using 4-acetylphenyl diazonium tetrafluoroborate (**2m**) (0.20 mmol) and benzene (**1a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 100/1) yielded **3ac** (24 mg, 60%) as a white solid. M.p. = 116.9-118.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.04 (d, 2H, *J* = 8 Hz, ArH), 7.69 (d, 2H, *J* = 8 Hz, ArH), 7.63 (d, 2H, *J* = 8 Hz, ArH), 7.48-7.46 (m, 2H, ArH), 7.42-7.38 (m, 1H, ArH), 2.64 (s, 3H, CH_3).

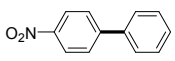
4-Chloro-1,1'-biphenyl (**3ad**)[5]



3ad

The representative procedure was followed using 4-chlorophenyl diazonium tetrafluoroborate (**2g**) (0.20 mmol) and benzene (**1a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 100/1) yielded **3ad** (20 mg, 53%) as a white oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.56-7.48 (m, 4H, ArH), 7.46-7.34 (m, 5H, ArH).

4-Nitro-1,1'-biphenyl (**3ae**)[5]

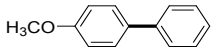


3ae

The representative procedure was followed using 4-nitrophenyl diazonium tetrafluoroborate (**2l**) (0.20 mmol) and benzene (**1a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 100/1) yielded **3ae**

(22 mg, 57%) as a yellow solid. M.p. = 107.1-110.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.30 (d, 2H, *J* = 8 Hz, ArH), 7.74 (d, 2H, *J* = 8 Hz, ArH), 7.63 (d, 2H, *J* = 4 Hz, ArH), 7.52-7.43 (m, 3H, ArH).

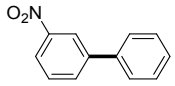
4-Methoxy-1,1'-biphenyl (**3af**)[6]



3af

The representative procedure was followed using 4-methoxyphenyl diazonium tetrafluoroborate (**2e**) (0.20 mmol) and benzene (**1a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 100/1) yielded **3af** (19 mg, 51%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.56-7.52 (m, 4H, ArH), 7.43-7.39 (m, 2H, ArH), 7.32-7.30 (m, 1H, ArH), 7.68 (d, 2H, *J* = 8 Hz, ArH), 3.85 (s, 3H, OCH_3).

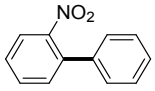
3-Nitro-1,1'-biphenyl (**3ag**)[8]



3ag

The representative procedure was followed using 3-nitrophenyl diazonium tetrafluoroborate (**2j**) (0.20 mmol) and benzene (**1a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 100/1) yielded **3ag** (22 mg, 56%) as a yellow solid. M.p. = 58.2-60.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.46 (s, 1H, ArH), 8.22-8.19 (m, 1H, ArH), 7.92 (d, 1H, *J* = 8 Hz, ArH), 7.64-7.59 (m, 3H, ArH), 7.53-7.41 (m, 3H, ArH).

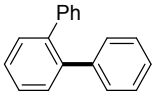
2-Nitro-1,1'-biphenyl (**3ah**)[9]



3ah

The representative procedure was followed using 2-nitrophenyl diazonium tetrafluoroborate (**2k**) (0.20 mmol) and benzene (**1a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 100/1) yielded **3ah** (19 mg, 48%) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.87-7.85 (m, 1H, ArH), 7.64-7.60 (m, 1H, ArH), 7.50-7.40 (m, 5H, ArH), 7.34-7.31 (m, 2H, ArH).

1,1':2',1''-Terphenyl (**3ai**)[10]

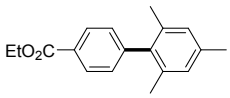


3ai

The representative procedure was followed using 2-phenyl phenyl diazonium tetrafluoroborate (**2o**) (0.20

mmol) and benzene (**1a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 100/1) yielded **3ai** (22 mg, 50%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.50-7.45 (m, 6H, ArH), 7.40-7.36 (m, 2H, ArH), 7.27-7.23 (m, 3H, ArH), 7.01-6.96 (m, 3H, ArH).

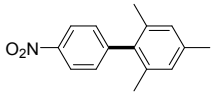
Ethyl 2',4',6'-trimethyl-[1,1'-biphenyl]-4-carboxylate (**3aj**)[11]



3aj

The representative procedure was followed using 4-(ethoxycarbonyl) phenyl diazonium tetrafluoroborate (**2a**) (0.20 mmol) and mesitylene (**1b**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **3aj** (38 mg, 71%) as a white oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.10 (d, 2H, *J* = 8 Hz, ArH), 7.22 (d, 2H, *J* = 8 Hz, ArH), 6.94 (s, 2H, ArH), 4.43-4.38 (m, 2H, CH_2), 2.33 (s, 3H, CH_3), 1.98 (s, 6H, $2CH_3$), 1.42 (t, 3H, *J* = 8 Hz, CH_3).

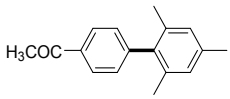
2,4,6-Trimethyl-4'-nitro-1,1'-biphenyl (**3ak**)[11]



3ak

The representative procedure was followed using 4-nitrophenyl diazonium tetrafluoroborate (**2l**) (0.20 mmol) and mesitylene (**1b**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **3ak** (33 mg, 68%) as a yellow solid. M.p. = 85.4-90.4 °C. ^{1}H NMR (400 MHz, CDCl3): 8.29 (d, 2H, *J* = 8 Hz, ArH), 7.33 (d, 2H, *J* = 8 Hz, ArH), 6.96 (s, 1H, ArH), 2.34 (s, 3H, CH_3), 1.98 (s, 6H, $2CH_3$).

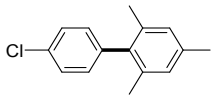
1-(2',4',6'-trimethyl-[1,1'-biphenyl]-4-yl) ethan-1-one (**3al**)[12]



3al

The representative procedure was followed using 4-acetylphenyl diazonium tetrafluoroborate (**2m**) (0.20 mmol) and mesitylene (**1b**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **3al** (30 mg, 62%) as a colorless solid. M.p. = 95.0-96.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.02 (d, 2H, *J* = 8 Hz, ArH), 7.25 (d, 2H, *J* = 8 Hz, ArH), 6.95 (s, 2H, ArH), 2.65 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 1.99 (s, 6H, $2CH_3$).

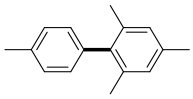
4'-Chloro-2,4,6-trimethyl-1,1'-biphenyl (**3am**)[11]



3am

The representative procedure was followed using 4-chlorophenyl diazonium tetrafluoroborate (**2g**) (0.20 mmol) and mesitylene (**1b**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **3am** (27 mg, 60%) as a white oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.38 (d, 2H, J = 8 Hz, ArH), 7.07 (d, 2H, J = 8 Hz, ArH), 6.93 (s, 2H, ArH), 2.32 (s, 3H, CH_3), 1.99 (s, 6H, $2CH_3$).

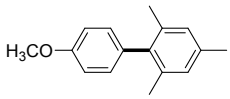
2,4,4',6-Tetramethyl-1,1'-biphenyl (**3an**)[11]



3an

The representative procedure was followed using 4-methylphenyl diazonium tetrafluoroborate (**2b**) (0.20 mmol) and mesitylene (**1b**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **3an** (24 mg, 57%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.21 (d, 2H, J = 8 Hz, ArH), 7.02 (d, 2H, J = 8 Hz, ArH), 6.93 (s, 2H, ArH), 2.40 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.00 (s, 6H, $2CH_3$).

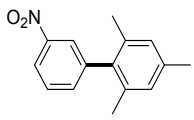
4'-Methoxy-2,4,6-trimethyl-1,1'-biphenyl (**3ao**)[11]



3ao

The representative procedure was followed using 4-methoxyphenyl diazonium tetrafluoroborate (**2e**) (0.20 mmol) and mesitylene (**1b**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **3ao** (24 mg, 54%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.06-7.03 (m, 2H, ArH), 6.96-6.93 (m, 4H, ArH), 3.85 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.01 (s, 6H, $2CH_3$).

2,4,6-Trimethyl-3'-nitro-1,1'-biphenyl (**3ap**)[11]

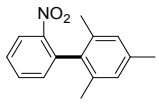


3ap

The representative procedure was followed using 3-nitrophenyl diazonium tetrafluoroborate (**2j**) (0.20 mmol) and mesitylene (**1b**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **3ap** (29 mg, 60%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.22-8.19 (m, 1H, ArH), 8.05-8.04 (m, 1H, ArH), 7.62-7.58 (m, 1H, ArH), 7.50-7.48 (m, 1H, ArH), 6.97 (s, 2H, ArH), 2.34 (s, 3H, CH_3),

1.99 (s, 6H, $2CH_3$).

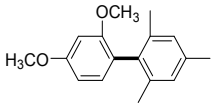
2,4,6-Trimethyl-2'-nitro-1,1'-biphenyl (**3aq**)[11]



3aq

The representative procedure was followed using 2-nitrophenyl diazonium tetrafluoroborate (**2k**) (0.20 mmol) and mesitylene (**1b**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **3aq** (24 mg, 50%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.00 (d, 1H, J = 8 Hz, ArH), 7.66-7.63 (m, 1H, ArH), 7.53-7.49 (m, 1H, ArH), 7.22 (d, 1H, J = 8 Hz, ArH), 6.92 (s, 2H, ArH).

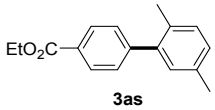
2',4'-Dimethoxy-2,4,6-trimethyl-1,1'-biphenyl (**3ar**)[13]



3ar

The representative procedure was followed using 2,4-dimethoxydiazonium tetrafluoroborate (**2q**) (0.20 mmol) and mesitylene (**1b**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **3ar** (27 mg, 52%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 6.92-6.90 (m, 3H, ArH), 3.86 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 2.31 (s, 3H, CH_3), 1.98 (s, 6H, $2CH_3$).

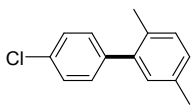
Ethyl 2',5'-dimethyl-[1,1'-biphenyl]-4-carboxylate (**3as**)[11]



3as

The representative procedure was followed using 4-(ethoxycarbonyl) phenyl diazonium tetrafluoroborate (**2a**) (0.20 mmol) and *p*-xylene (**1c**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 100/1) yielded **3as** (34 mg, 67%) as a white oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.08 (d, 2H, J = 8 Hz, ArH), 7.39 (d, 2H, J = 8 Hz, ArH), 7.17 (d, 1H, J = 8 Hz, ArH), 7.11-7.08 (m, 1H, ArH), 7.04 (s, 1H, ArH), 4.43-4.38 (m, 2H, ArH), 2.35 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 1.42 (t, 3H, J = 8 Hz, CH_3).

4'-Chloro-2,5-dimethyl-1,1'-biphenyl (**3at**)[14]

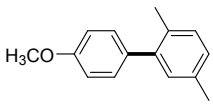


3at

The representative procedure was followed using 4-chlorophenyl diazonium tetrafluoroborate (**2g**) (0.20 mmol) and *p*-xylene (**1c**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 100/1) yielded **3at**

(27 mg, 62%) as a white oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.36 (d, 2H, *J* = 8 Hz, ArH), 7.24 (d, 2H, *J* = 8 Hz, ArH), 7.15 (d, 1H, *J* = 8 Hz, ArH), 7.08-7.07 (m, 1H, ArH), 7.01 (s, 1H, ArH), 2.34 (s, 3H, CH_3), 2.21 (s, 3H, CH_3).

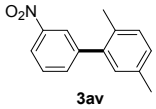
4'-Methoxy-2,5-dimethyl-1,1'-biphenyl (**3au**)[6]



3au

The representative procedure was followed using 4-methoxyphenyl diazonium tetrafluoroborate (**2e**) (0.20 mmol) and *p*-xylene (**1c**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 100/1) yielded **3au** (21 mg, 49%) as a white oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.22 (d, 2H, *J* = 8 Hz, ArH), 7.15-7.13 (m, 1H, ArH), 7.08-7.04 (m, 2H, ArH), 6.94 (d, 2H, *J* = 8 Hz, ArH), 3.85 (s, 3H, OCH_3), 2.34 (s, 3H, CH_3), 2.23 (s, 3H, CH_3).

2,5-Dimethyl-3'-nitro-1,1'-biphenyl (**3av**)[13]



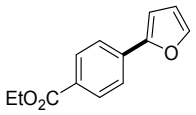
3av

The representative procedure was followed using 3-nitro phenyl diazonium tetrafluoroborate (**2k**) (0.20 mmol) and *p*-xylene (**1c**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 100/1) yielded **3av** (30 mg, 65%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.21-8.19 (m, 2H, ArH), 7.67-7.64 (m, 1H, ArH), 7.59-7.55 (m, 1H, ArH), 7.20-7.18 (m, 1H, ArH), 7.14-7.12 (m, 1H, ArH), 7.05 (s, 1H, ArH), 2.36 (s, 3H, CH_3), 2.23 (s, 3H, CH_3).

4.2.2 General procedure for the reaction of aryl diazonium tetrafluoroborates with furan

In a 10 mL schlenk tube with magnetic stirring bar the cercosporin (0.01 equiv), aryl diazonium tetrafluoroborate **2** (1 equiv) and furan **4a** (10 equiv) were dissolved in dry DMSO (2 mL) and the resulting mixture was degassed by "pump-freeze-thaw" cycles. Then, the reaction mixtures were placed under sunlight for 8 hours. 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 **5a**.

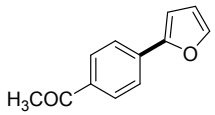
Ethyl 4-(furan-2-yl) benzoate (**5aa**)[5]



5aa

The representative procedure was followed using 4-(ethoxycarbonyl) phenyl diazonium tetrafluoroborate (**2a**) (0.20 mmol) and furan (**4a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **5aa** (31 mg, 72%) as a colorless solid. M.p. = 60.1-62.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.05 (d, 2H, *J* = 8 Hz, ArH), 7.72 (d, 2H, *J* = 8 Hz, ArH), 7.52 (s, 1H, ArH), 6.78 (d, 1H, *J* = 4 Hz, ArH), 6.51-6.50 (m, 1H, ArH), 4.41-4.35 (m, 2H, CH_2), 1.40 (t, 3H, *J* = 8 Hz, CH_3).

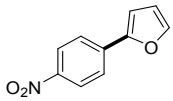
1-(4-(Furan-2-yl) phenyl) ethan-1-one (**5ab**)[12]



5ab

The representative procedure was followed using 4-acetylphenyl diazonium tetrafluoroborate (**2m**) (0.20 mmol) and furan (**4a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **5ab** (26 mg, 69%) as a colorless solid. M.p. = 77.1-78.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.98 (d, 2H, *J* = 8 Hz, ArH), 7.65 (d, 2H, *J* = 8 Hz, ArH), 7.53 (s, 1H, ArH), 6.81 (d, 1H, *J* = 4 Hz, ArH), 6.53-6.51 (m, 1H, ArH), 2.61 (s, 3H, CH_3).

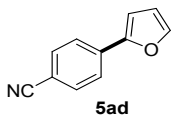
2-(4-Nitrophenyl) furan (**5ac**)[5]



5ac

The representative procedure was followed using 4-nitrophenyl diazonium tetrafluoroborate (**2l**) (0.20 mmol) and furan (**4a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **5ac** (28 mg, 75%) as a colorless solid. M.p. = 77.6-78.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.25 (d, 2H, *J* = 8 Hz, ArH), 7.80 (d, 2H, *J* = 8 Hz, ArH), 7.59-7.58 (m, 1H, ArH), 6.89 (d, 1H, *J* = 4 Hz, ArH), 6.56-6.55 (m, 1H, ArH).

4-(Furan-2-yl) benzonitrile (**5ad**)[5]

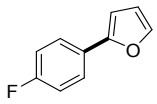


5ad

The representative procedure was followed using 4-cyanophenyl diazonium tetrafluoroborate (**2i**) (0.20 mmol) and furan (**4a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **5ad** (23

mg, 67%) as a colorless solid. M.p. = 54.2-55.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.74 (d, 2H, *J* = 8 Hz, ArH), 7.65 (d, 2H, *J* = 8 Hz, ArH), 7.54 (s, 1H, ArH), 6.82 (d, 1H, *J* = 4 Hz, ArH), 6.54-6.52 (m, 1H, ArH).

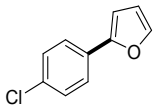
2-(4-Fluorophenyl) furan (**5ae**)[15]



5ae

The representative procedure was followed using 4-fluorophenyl diazonium tetrafluoroborate (**2f**) (0.20 mmol) and furan (**4a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **5ae** (19 mg, 60%) as a colorless solid. M.p. = 69.7-72.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.65-7.62 (m, 2H, ArH), 7.45-7.44 (m, 1H, ArH), 7.09-7.05 (m, 2H, ArH), 6.59-6.58 (m, 1H, ArH), 6.47-6.46 (m, 1H, ArH).

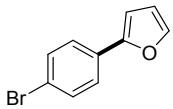
2-(4-Chlorophenyl) furan (**5af**)[16]



5af

The representative procedure was followed using 4-chlorophenyl diazonium tetrafluoroborate (**2g**) (0.20 mmol) and furan (**4a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **5af** (23 mg, 62%) as a colorless solid. M.p. = 65.5-68.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.59 (d, 2H, *J* = 8 Hz, ArH), 7.46 (s, 1H, ArH), 7.34 (d, 2H, *J* = 8 Hz, ArH), 6.64 (d, 1H, *J* = 4 Hz, ArH), 6.47-6.46 (m, 1H, ArH).

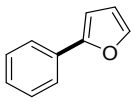
2-(4-Bromophenyl) furan (**5ag**)[5]



5ag

The representative procedure was followed using 4-bromophenyl diazonium tetrafluoroborate (**2h**) (0.20 mmol) and furan (**4a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 20/1) yielded **5ag** (28 mg, 63%) as a colorless solid. M.p. = 72.5-74.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.54-7.46 (m, 5H, ArH), 6.65 (d, 1H, *J* = 4 Hz, ArH), 6.47-6.46 (m, 1H, ArH).

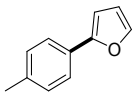
2-Phenylfuran (**5ah**)[12]



5ah

The representative procedure was followed using phenyl diazonium tetrafluoroborate (**2n**) (0.20 mmol) and furan (**4a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **5ah** (22 mg, 78%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.68-7.67 (m, 2H, ArH), 7.49-7.48 (m, 1H, ArH), 7.40-7.36 (m, 2H, ArH), 7.28-7.24 (m, 1H, ArH), 6.66 (d, 1H, *J* = 4 Hz, ArH), 6.48-6.47 (m, 1H, ArH).

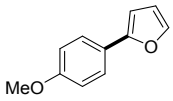
2-(*p*-Tolyl) furan (**5ai**)[16]



5ai

The representative procedure was followed using 4-methyl phenyl diazonium tetrafluoroborate (**2b**) (0.20 mmol) and furan (**4a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 20/1) yielded **5ai** (19 mg, 61%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.57 (d, 2H, *J* = 8 Hz, ArH), 7.45-7.44 (m, 1H, ArH), 7.19 (d, 2H, *J* = 8 Hz, ArH), 6.60-6.58 (m, 1H, ArH), 6.46-6.45 (m, 1H, ArH), 2.36 (s, 3H, CH_3).

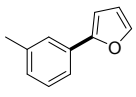
2-(4-Methoxyphenyl) furan (**5aj**)[16]



5aj

The representative procedure was followed using 4-methoxyphenyl diazonium tetrafluoroborate (**2e**) (0.20 mmol) and furan (**4a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **5aj** (23 mg, 67%) as a colorless solid. M.p. = 48.3-49.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.60 (d, 2H, *J* = 8 Hz, ArH), 7.42 (s, 1H, ArH), 6.92 (d, 2H, *J* = 8 Hz, ArH), 6.51 (d, 1H, *J* = 4 Hz, ArH), 6.45-6.43 (m, 1H, ArH), 3.82 (s, 3H, OCH_3).

2-(*m*-Tolyl) furan (**5ak**)[5]

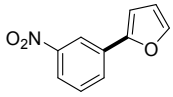


5ak

The representative procedure was followed using 3-methylphenyl diazonium tetrafluoroborate (**2p**) (0.20

mmol) and furan (**4a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **5ak** (24 mg, 78%) as red oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.50-7.46 (m, 3H, ArH), 7.29-7.23 (m, 1H, ArH), 7.08-7.07 (m, 1H, ArH), 7.64 (d, 1H, *J* = 4 Hz, ArH), 6.47-6.46 (m, 1H, ArH), 2.39 (s, 3H, CH_3).

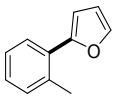
2-(3-Nitrophenyl) furan (**5al**)[5]



5al

The representative procedure was followed using 3-nitrophenyl diazonium tetrafluoroborate (2**j**) (0.20 mmol) and furan (**4a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 20/1) yielded **5al** (25 mg, 66%) as a colorless solid. M.p. = 72.6-74.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.49 (s, 1H, ArH), 8.10-8.07 (m, 1H, ArH), 7.96 (d, 1H, *J* = 8 Hz, ArH), 7.57-7.53 (m, 2H, ArH), 6.82 (d, 1H, *J* = 4 Hz, ArH), 6.54-6.52 (m, 1H, ArH).

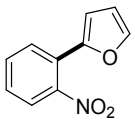
2-(*o*-Tolyl) furan (**5am**)[17]



5am

The representative procedure was followed using 2-methyl phenyl diazonium tetrafluoroborate (**2c**) (0.20 mmol) and furan (**4a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **5am** (22 mg, 70%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.69 (d, 1H, *J* = 8 Hz, ArH), 7.51-7.50 (m, 1H, ArH), 7.23-7.19 (m, 3H, ArH), 6.54-6.53 (m, 1H, ArH), 6.51-6.50 (m, 1H, ArH), 2.50 (s, 3H, CH_3).

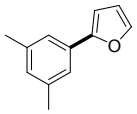
2-(2-Nitrophenyl) furan (**5an**)[18]



5an

The representative procedure was followed using 2-nitrophenyl diazonium tetrafluoroborate (**2k**) (0.20 mmol) and furan (**4a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **5an** (24 mg, 64%) as a colorless solid. M.p. = 73.3-77.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.72-7.66 (m, 2H, ArH), 7.59-7.55 (m, 1H, ArH), 7.51-7.50 (m, 1H, ArH), 7.43-7.38 (m, 1H, ArH), 6.68 (d, 1H, *J* = 4 Hz, ArH), 6.50-6.49 (m, 1H, ArH).

2-(3,5-Dimethylphenyl) furan (**5ao**)[19]



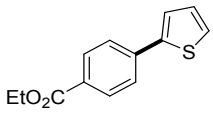
5ao

The representative procedure was followed using 3,5-dimethyl phenyl diazonium tetrafluoroborate (**2d**) (0.20 mmol) and furan (**4a**) (2 mmol). Isolation by column chromatography (PE/EtOAc: 20/1) yielded **5ao** (25 mg, 73%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.45 (s, 1H, ArH), 7.35 (s, 2H, ArH), 6.91 (s, 1H, ArH), 6.62 (d, 1H, *J* = 4 Hz, ArH), 6.46-6.45 (m, 1H, ArH), 2.34 (s, 6H, $2CH_3$).

4.2.3 General procedure for the reaction of aryl diazonium tetrafluoroborates with thiophene

In a 10 mL schlenk tube with magnetic stirring bar the cercosporin (0.01 equiv), aryl diazonium tetrafluoroborate **2** (1 equiv) and thiophene **4b** (8 equiv) were dissolved in dry DMSO (2 mL) and the resulting mixture was degassed by "pump-freeze-thaw" cycles. Then, the reaction mixtures were placed under sunlight for 8 hours. 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 **5b**.

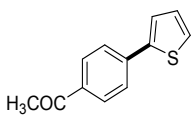
Ethyl 4-(thiophen-2-yl) benzoate (**5ba**)[16]



5ba

The representative procedure was followed using 4-(ethoxycarbonyl) phenyl diazonium tetrafluoroborate (**2a**) (0.20 mmol) and thiophen (**4b**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 20/1) yielded **5ba** (29 mg, 63%) as a colorless solid. M.p. = 66.8-70.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.04 (d, 2H, *J* = 12 Hz, ArH), 7.67 (d, 2H, *J* = 8 Hz, ArH), 7.42 (d, 1H, *J* = 4 Hz, ArH), 7.36 (d, 1H, *J* = 4 Hz, ArH), 7.12-7.10 (m, 1H, ArH), 4.41-4.36 (m, 2H, CH_2), 1.41 (t, 3H, *J* = 8 Hz, CH_3).

1-(4-(Thiophen-2-yl) phenyl) ethan-1-one (**5bb**)[12]

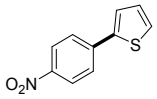


5bb

The representative procedure was followed using 4-acetylphenyl diazonium tetrafluoroborate (**2m**) (0.20 mmol) and thiophen (**4b**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 20/1) yielded

5bb (25 mg, 62%) as a colorless solid. M.p. = 118.4-121.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.97 (d, 2H, *J* = 8 Hz, ArH), 7.70 (d, 2H, *J* = 8 Hz, ArH), 7.44 (d, 1H, *J* = 4 Hz, ArH), 7.38 (d, 1H, *J* = 4 Hz, ArH), 7.13-7.11 (m, 1H, ArH), 2.62 (s, 3H, CH_3).

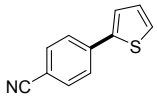
2-(4-Nitrophenyl) thiophene (**5bc**)[16]



5bc

The representative procedure was followed using 4-nitrophenyl diazonium tetrafluoroborate (**2l**) (0.20 mmol) and thiophen (**4b**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **5bc** (25 mg, 61%) as a colorless solid. M.p. = 134.1-137.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.25 (d, 2H, *J* = 8 Hz, ArH), 7.75 (d, 2H, *J* = 8 Hz, ArH), 7.49-7.44 (m, 2H, ArH), 7.17-7.14 (m, 1H, ArH).

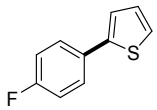
4-(Thiophen-2-yl) benzonitrile (**5bd**)[16]



5bd

The representative procedure was followed using 4-cyanophenyl diazonium tetrafluoroborate (**2i**) (0.20 mmol) and thiophen (**4b**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **5bd** (27 mg, 75%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.58-7.55 (m, 2H, ArH), 7.27-7.23 (m, 2H, ArH), 7.09-7.05 (m, 3H, ArH).

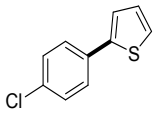
2-(4-Fluorophenyl) thiophene (**5be**)[5]



5be

The representative procedure was followed using 4-fluorophenyl diazonium tetrafluoroborate (**2f**) (0.20 mmol) and thiophen (**4b**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 20/1) yielded **5be** (20 mg, 57%) as a colorless solid. M.p. = 50.1-52.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.71-7.64 (m, 4H, ArH), 7.43-7.40 (m, 2H, ArH), 7.14-7.12 (m, 1H, ArH).

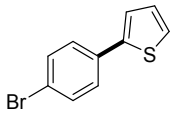
2-(4-Chlorophenyl) thiophene (**5bf**)[5]



5bf

The representative procedure was followed using 4-chlorophenyl diazonium tetrafluoroborate (**2g**) (0.20 mmol) and thiophen (**4b**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 20/1) yielded **5bf** (23 mg, 60%) as a colorless solid. M.p. = 79.6-81.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.53 (d, 2H, *J* = 8 Hz, ArH), 7.34 (d, 2H, *J* = 8 Hz, ArH), 7.29-7.28 (m, 2H, ArH), 7.09-7.06 (m, 1H, ArH).

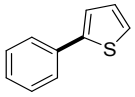
2-(4-Bromophenyl) thiophene (**5bg**)[16]



5bg

The representative procedure was followed using 4-bromophenyl diazonium tetrafluoroborate (**2h**) (0.20 mmol) and thiophen (**4b**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **5bg** (33 mg, 69%) as a colorless solid. M.p. = 82.1-84.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.51-7.46 (m, 4H, ArH), 7.30 (d, 2H, *J* = 4 Hz, ArH), 7.09-7.07 (m, 1H, ArH).

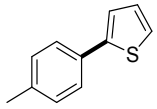
2-Phenylthiophene (**5bh**)[20]



5bh

The representative procedure was followed using phenyl diazonium tetrafluoroborate (**2n**) (0.20 mmol) and thiophen (**4b**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **5bh** (22 mg, 70%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.63-7.59 (m, 3H, ArH), 7.46-7.43 (m, 1H, ArH), 7.40-7.35 (m, 2H, ArH), 7.32-7.28 (m, 1H, ArH), 7.09-7.07 (m, 1H, ArH).

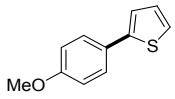
2-(*p*-Tolyl) thiophene (**5bi**)[16]



5bi

The representative procedure was followed using 4-methylphenyl diazonium tetrafluoroborate (**2b**) (0.20 mmol) and thiophen (**4b**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **5bi** (22 mg, 62%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.51 (d, 2H, *J* = 8 Hz, ArH), 7.27-7.24 (m, 2H, ArH), 7.18 (d, 2H, *J* = 8 Hz, ArH), 7.08-7.05 (m, 1H, ArH), 2.37 (s, 3H, CH_3).

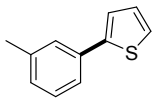
2-(4-Methoxyphenyl) thiophene (**5bj**)[5]



5bj

The representative procedure was followed using 4-methoxyphenyl diazonium tetrafluoroborate (**2e**) (0.20 mmol) and thiophen (**4b**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **5bj** (24 mg, 63%) as a colorless solid. M.p. = 105.9-107.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.54 (d, 2H, *J* = 8 Hz, ArH), 7.22-7.19 (m, 2H, ArH), 7.06-7.04 (m, 1H, ArH), 6.91 (d, 2H, *J* = 8 Hz, ArH), 3.84 (s, 3H, OCH_3).

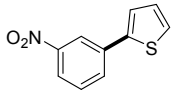
2-(*m*-Tolyl) thiophene (**5bk**)[21]



5bk

The representative procedure was followed using 3-methylphenyl diazonium tetrafluoroborate (**2p**) (0.20 mmol) and thiophen (**4b**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **5bk** (23 mg, 65%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.42 (d, 2H, *J* = 8 Hz, ArH), 7.31-7.27 (m, 2H, ArH), 7.25-7.21 (m, 1H, ArH), 7.16-7.06 (m, 2H, ArH), 2.39 (s, 3H, CH_3).

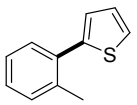
2-(3-Nitrophenyl) thiophene (**5bl**)[16]



5bl

The representative procedure was followed using 3-nitrophenyl diazonium tetrafluoroborate (**2j**) (0.20 mmol) and thiophen (**4b**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 20/1) yielded **5bl** (24 mg, 58%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.44 (s, 1H, ArH), 8.13-8.10 (m, 1H, ArH), 7.91 (d, 1H, *J* = 8 Hz, ArH), 7.59-7.53 (m, 1H, ArH), 7.44-7.43 (m, 1H, ArH), 7.39-7.38 (m, 1H, ArH), 7.15-7.13 (m, 1H, ArH).

2-(*o*-Tolyl) thiophene (**5bm**)[22]

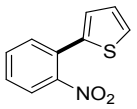


5bm

The representative procedure was followed using 2-methylphenyl diazonium tetrafluoroborate (**2c**) (0.20 mmol) and thiophen (**4b**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded

5bm (26 mg, 75%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.42-7.40 (m, 1H, ArH), 7.34 (d, 1H, *J* = 4 Hz, ArH), 7.28-7.27 (m, 1H, ArH), 7.25-7.20 (m, 2H, ArH), 7.11-7.06 (m, 2H, ArH), 2.43 (s, 3H, CH_3).

2-(2-Nitrophenyl) thiophene (**5bn**)[16]



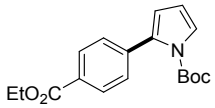
5bn

The representative procedure was followed using 2-nitrophenyl diazonium tetrafluoroborate (**2k**) (0.20 mmol) and thiophen (**4b**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 20/1) yielded **5bn** (27 mg, 67%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.75 (d, 1H, *J* = 8 Hz, ArH), 7.60-7.54 (m, 2H, ArH), 7.49-7.41 (m, 2H, ArH), 7.10-7.07 (m, 2H, ArH).

4.2.4 General procedure for the reaction of aryl diazonium tetrafluoroborates with *N*-Boc pyrrole

In a 10 mL schlenk tube with magnetic stirring bar the cercosporin (0.01 equiv), aryl diazonium tetrafluoroborate (1 equiv) **2** and *N*-Boc pyrrole **4c** (8 equiv) were dissolved in dry DMSO (2 mL) and the resulting mixture was degassed by "pump-freeze-thaw" cycles. Then, the reaction mixtures were placed under sunlight for 8 hours. 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 **5c**.

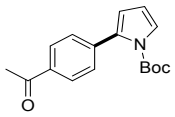
tert-Butyl 2-(4-(ethoxycarbonyl) phenyl)-1*H*-pyrrole-1-carboxylate (**5ca**)[23]



5ca

The representative procedure was followed using 4-(ethoxycarbonyl) phenyl diazonium tetrafluoroborate (**2a**) (0.20 mmol) and *N*-Boc pyrrole (**4c**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 50/1) yielded **5ca** (40 mg, 63%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.03 (d, 2H, *J* = 8 Hz, ArH), 7.41 (d, 2H, *J* = 8 Hz, ArH), 7.38-7.37 (m, 1H, ArH), 6.25-6.23 (m, 2H, ArH), 4.41-4.36 (m, 2H, CH_2), 1.42-1.38 (m, 12H, $4CH_3$).

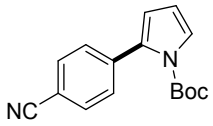
tert-Butyl 2-(4-acetylphenyl)-1*H*-pyrrole-1-carboxylate (**5cb**)[24]



5cb

The representative procedure was followed using 4-acetylphenyl diazonium tetrafluoroborate (**2m**) (0.20 mmol) and *N*-Boc pyrrole (**4c**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 50/1) yielded **5cb** (31 mg, 55%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.95 (d, 2H, *J* = 8 Hz, ArH), 7.45 (d, 2H, *J* = 8 Hz, ArH), 7.39-7.37 (m, 1H, ArH), 6.28-6.24 (m, 2H, ArH), 2.62 (s, 3H, CH_3), 1.40 (s, 9H, $3CH_3$).

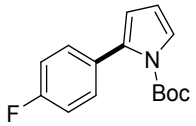
tert-Butyl 2-(4-cyanophenyl)-1*H*-pyrrole-1-carboxylate (**5cc**)[25]



5cc

The representative procedure was followed using 4-cyanophenyl diazonium tetrafluoroborate (**2i**) (0.20 mmol) and *N*-Boc pyrrole (**4c**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 50/1) yielded **5cc** (34 mg, 63%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.47 (d, 2H, *J* = 8 Hz, ArH), 7.35-7.34 (m, 1H, ArH), 7.22 (d, 2H, *J* = 8 Hz, ArH), 1.40 (s, 9H, $3CH_3$).

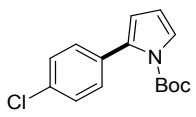
tert-Butyl 2-(4-fluorophenyl)-1*H*-pyrrole-1-carboxylate (**5cd**)[26]



5cd

The representative procedure was followed using 4-fluorophenyl diazonium tetrafluoroborate (**2f**) (0.20 mmol) and *N*-Boc pyrrole (**4c**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 50/1) yielded **5cd** (67 mg, 67%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.35-7.29 (m, 3H, ArH), 7.06-7.01 (m, 2H, ArH), 6.22-6.21 (m, 1H, ArH), 6.16-6.15 (m, 1H, ArH), 1.38 (s, 9H, $3CH_3$).

tert-Butyl 2-(4-chlorophenyl)-1*H*-pyrrole-1-carboxylate (**5ce**)[25]

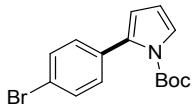


5ce

The representative procedure was followed using 4-chlorophenyl diazonium tetrafluoroborate (**2g**) (0.20 mmol) and *N*-Boc pyrrole (**4c**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 50/1)

yielded **5ce** (33 mg, 60%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.35-7.29 (m, 5H, ArH), 6.23-6.22 (m, 1H, ArH), 6.18-6.17 (m, 1H, ArH), 1.39 (s, 9H, $3CH_3$).

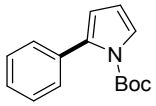
tert-Butyl 2-(4-bromophenyl)-1*H*-pyrrole-1-carboxylate (**5cf**)[24]



5cf

The representative procedure was followed using 4-bromophenyl diazonium tetrafluoroborate (**2h**) (0.20 mmol) and *N*-Boc pyrrole (**4c**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 50/1) yielded **5cf** (37 mg, 58%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.95 (d, 2H, J = 8 Hz, ArH), 7.45 (d, 2H, J = 8 Hz, ArH), 7.39-7.37 (m, 1H, ArH), 6.28-6.24 (m, 2H, ArH), 1.40 (s, 9H, $3CH_3$).

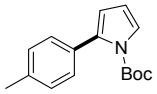
tert-Butyl 2-phenyl-1*H*-pyrrole-1-carboxylate (**5cg**)[26]



5cg

The representative procedure was followed using phenyl diazonium tetrafluoroborate (**2n**) (0.20 mmol) and *N*-Boc pyrrole (**4c**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 50/1) yielded **5cg** (29 mg, 59%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.36-7.32 (m, 6H, ArH), 6.25-6.22 (m, 1H, ArH), 6.19-6.18 (m, 1H, ArH), 1.35 (s, 9H, $3CH_3$).

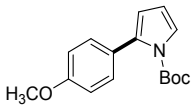
tert-Butyl 2-(*p*-tolyl)-1*H*-pyrrole-1-carboxylate (**5ch**)[27]



5ch

The representative procedure was followed using 4-methyl phenyl diazonium tetrafluoroborate (**2b**) (0.20 mmol) and *N*-Boc pyrrole (**4c**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 50/1) yielded **5ch** (31 mg, 61%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.33-7.31 (m, 1H, ArH), 7.24 (d, 2H, J = 8 Hz, ArH), 7.15 (d, 2H, J = 8 Hz, ArH), 6.22-6.20 (m, 1H, ArH), 6.16-6.15 (m, 1H, ArH), 2.37 (s, 3H, CH_3), 1.38 (s, 9H, $3CH_3$).

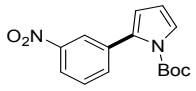
tert-Butyl 2-(4-methoxyphenyl)-1*H*-pyrrole-1-carboxylate (**5ci**)[12]



5ci

The representative procedure was followed using 4-methoxyphenyl diazonium tetrafluoroborate (**2e**) (0.20 mmol) and *N*-Boc pyrrole (**4c**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 50/1) yielded **5ci** (38 mg, 70%) as a colorless oil. Ratio: α: β = 15: 2. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.32-7.31 (m, 1H, ArH), 7.27 (d, 2H, *J* = 8 Hz, ArH), 6.89 (d, 2H, *J* = 8 Hz, ArH), 6.21-6.19 (m, 1H, ArH), 6.14-6.12 (m, 1H, ArH), 3.82 (s, 3H, OCH_3), 1.38 (s, 9H, $3CH_3$).

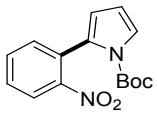
tert-Butyl 2-(3-nitrophenyl)-1*H*-pyrrole-1-carboxylate (**5cj**)[25]



5cj

The representative procedure was followed using 3-nitrophenyl diazonium tetrafluoroborate (**2j**) (0.20 mmol) and *N*-Boc pyrrole (**4c**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 50/1) yielded **5cj** (39 mg, 67%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.23 (s, 1H, ArH), 8.16 (d, 1H, *J* = 8 Hz, ArH), 7.69 (d, 1H, *J* = 8 Hz, ArH), 7.54-7.50 (m, 1H, ArH), 7.41-7.40 (m, 1H, ArH), 6.30-6.26 (m, 2H, ArH), 1.40 (s, 9H, $3CH_3$).

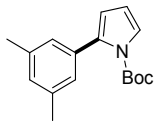
tert-Butyl 2-(2-nitrophenyl)-1*H*-pyrrole-1-carboxylate (**5ck**)[25]



5ck

The representative procedure was followed using 2-nitrophenyl diazonium tetrafluoroborate (**2k**) (0.20 mmol) and *N*-Boc pyrrole (**4c**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 50/1) yielded **5ck** (41 mg, 72%) as a colorless solid. M.p. = 77.4-80.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.09 (d, 1H, *J* = 8 Hz, ArH), 7.63-7.60 (m, 1H, ArH), 7.51-7.41 (m, 3H, ArH), 6.27-6.26 (m, 1H, ArH), 6.20-6.18 (m, 1H, ArH), 1.32 (s, 9H, $3CH_3$).

tert-Butyl 2-(3,5-dimethylphenyl)-1*H*-pyrrole-1-carboxylate (**5cl**)



5cl

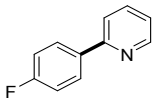
The representative procedure was followed using 3,5-dimethyl phenyl diazonium tetrafluoroborate (**2d**) (0.20 mmol) and *N*-Boc pyrrole (**4c**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 50/1) yielded **5cl** (34 mg, 60%) as a colorless oil. Ratio: α: β = 15: 2. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.35-7.34 (m, 0.11H, ArH, β), 7.32-7.31 (m, 0.83H, ArH, α), 7.06 (s, 0.2H, ArH), 6.97-6.94 (m, 2.5H,

ArH), 6.94 (s, 0.2H, ArH), 6.23-6.21 (m, 1H, ArH), 6.16-6.15 (m, 0.8H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 151.8, 138.8, 136.8, 128.7, 127.0, 122.5, 114.0, 110.4, 82.3, 28.2, 21.3. HRMS (ESI-Q-TOF) exact mass calcd for $C_{17}H_{22}NO_2$ $[M + H]^+$ 272.1650 found 272.1673.

4.2.5 General procedure for the reaction of aryl diazonium tetrafluoroborates with pyridines

In a 10 mL schlenk tube with magnetic stirring bar the cercosporin (0.01 equiv), aryl diazonium tetrafluoroborate **2** (1 equiv) and pyridine **6a** (or 2-chloropyridine **6aa**) (6 equiv) were dissolved in dry DMSO (2 mL) and the resulting mixture was degassed by "pump-freeze-thaw" cycles. Then, the reaction mixtures were placed under sunlight for 16 hours. 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 **7a**.

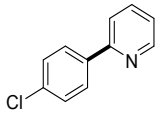
2-(4-Fluorophenyl) pyridine (**7aa**)[28]



7aa

The representative procedure was followed using 4-fluorophenyl diazonium tetrafluoroborate (**2f**) (0.20 mmol) and pyridine (**6a**) (1.2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **7aa** (23 mg, 67%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.68 (d, 1H, J = 4 Hz, ArH), 8.00-7.96 (m, 2H, ArH), 7.78-7.74 (m, 1H, ArH), 7.69 (d, 1H, J = 8 Hz, ArH), 7.25-7.22 (m, 1H, ArH), 7.18-7.14 (m, 2H, ArH).

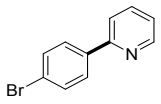
2-(4-Chlorophenyl) pyridine (**7ab**)[29]



7ab

The representative procedure was followed using 4-chlorophenyl diazonium tetrafluoroborate (**2g**) (0.20 mmol) and pyridine (**6a**) (1.2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **7ab** (22 mg, 58%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.69 (d, 1H, J = 4 Hz, ArH), 7.94 (d, 2H, J = 8 Hz, ArH), 7.76-7.69 (m, 2H, ArH), 7.44 (d, 2H, J = 8 Hz, ArH), 7.24 (d, 1H, J = 8 Hz, ArH).

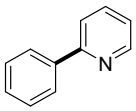
2-(4-Bromophenyl) pyridine (**7ac**)[29]



7ac

The representative procedure was followed using 4-bromophenyl diazonium tetrafluoroborate (**2h**) (0.20 mmol) and pyridine (**6a**) (1.2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **7ac** (26 mg, 57%) as a colorless solid. M.p. = 54.8-57.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.69 (d, 1H, *J* = 4 Hz, ArH), 7.87 (d, 2H, *J* = 8 Hz, ArH), 7.78-7.69 (m, 2H, ArH), 7.60 (d, 2H, *J* = 8 Hz, ArH), 7.25-7.24 (m, 1H, ArH).

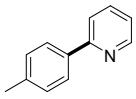
2-Phenylpyridine (**7ad**)[30]



7ad

The representative procedure was followed using phenyl diazonium tetrafluoroborate (**2n**) (0.20 mmol) and pyridine (**6a**) (1.2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **7ad** (16 mg, 53%) as a white solid. M.p. = 148.1-149.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.71 (d, 1H, *J* = 4 Hz, ArH), 7.99 (d, 2H, *J* = 8 Hz, ArH), 7.78-7.73 (m, 2H, ArH), 7.50-7.47 (m, 2H, ArH), 7.44-7.40 (m, 1H, ArH), 7.24-7.22 (m, 1H, ArH).

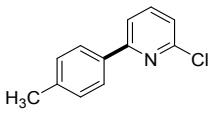
2-(*p*-Tolyl) pyridine (**7ae**)[31]



7ae

The representative procedure was followed using 4-methyl phenyl diazonium tetrafluoroborate (**2b**) (0.20 mmol) and pyridine (**6a**) (1.2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **7ae** (24 mg, 70%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.68 (d, 1H, *J* = 4 Hz, ArH), 7.89 (d, 2H, *J* = 8 Hz, ArH), 7.75-7.69 (m, 2H, ArH), 7.29 (d, 2H, *J* = 4 Hz, ArH), 7.22-7.19 (m, 1H, ArH), 2.41 (s, 3H, CH_3).

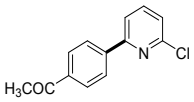
2-Chloro-6-(*p*-tolyl) pyridine (**7af**)[32]



7af

The representative procedure was followed using 4-methyl phenyl diazonium tetrafluoroborate (2**b**) (0.20 mmol) and 2-chloropyridine (**6aa**) (1.2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **7af** (28 mg, 69%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.90 (d, 2H, *J* = 8 Hz, ArH), 7.69-7.61 (m, 2H, ArH), 7.27 (d, 2H, *J* = 8 Hz, ArH), 7.23-7.22 (m, 1H, ArH), 2.40 (s, 3H, CH_3).

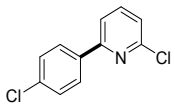
1-(4-(6-Chloropyridin-2-yl) phenyl) ethan-1-one (**7ag**)



7ag

The representative procedure was followed using 4-acetylphenyl diazonium tetrafluoroborate (**2m**) (0.20 mmol) and 2-chloropyridine (**6aa**) (1.2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **7ag** (25 mg, 58%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.12-8.05 (m, 4H, ArH), 7.78-7.70 (m, 2H, ArH), 7.34-7.31 (m, 1H, ArH), 2.65 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 197.7, 156.7, 151.7, 141.8, 139.4, 137.7, 128.8, 127.2, 123.5, 119.2, 26.8. HRMS (ESI-Q-TOF) exact mass calcd for $C_{13}H_{11}ClNO$ $[M + H]^+$ 232.0529, found 232.0545.

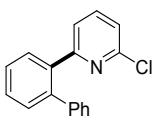
2-Chloro-6-(4-chlorophenyl) pyridine (**7ah**)



7ah

The representative procedure was followed using 4-chlorophenyl diazonium tetrafluoroborate (**2g**) (0.20 mmol) and 2-chloropyridine (**6aa**) (1.2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **7ah** (26 mg, 60%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.95 (d, 2H, *J* = 12 Hz, ArH), 7.73-7.69 (m, 1H, ArH), 7.63-7.61 (m, 1H, ArH), 7.44 (d, 2H, *J* = 8 Hz, ArH), 7.27 (d, 1H, *J* = 8 Hz, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 156.9, 151.6, 139.4, 136.1, 135.8, 129.0, 128.3, 122.8, 122.7, 118.4. HRMS (ESI-Q-TOF) exact mass calcd for $C_{11}H_8Cl_2N$ $[M + H]^+$ 224.0034, found 224.0051.

2-([1,1'-Biphenyl]-2-yl)-6-chloropyridine (**7ai**)



7ai

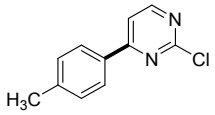
The representative procedure was followed using 2-phenyl phenyl diazonium tetrafluoroborate (**2o**) (0.20 mmol) and 2-chloropyridine (**6aa**) (1.2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1)

yielded **7ai** (25 mg, 48%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.81-7.80 (m, 1H, ArH), 7.73-7.70 (m, 2H, ArH), 7.59-7.57 (m, 1H, ArH), 7.52-7.45 (m, 3H, ArH), 7.43-7.36 (m, 4H, ArH), 7.04 (d, 1H, *J* = 8 Hz, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 155.0, 149.8, 147.5, 140.7, 139.0, 136.3, 130.9, 130.7, 129.4, 129.0, 128.3, 128.0, 127.5, 127.1, 123.6, 116.5, 115.9. HRMS (ESI-Q-TOF) exact mass calcd for $C_{17}H_{13}ClN$ $[M + H]^+$ 266.0736, found 266.0752.

4.2.6 General procedure for the reaction of aryl diazonium tetrafluoroborates with pyrimidine

In a 10 mL schlenk tube with magnetic stirring bar the cercosporin (0.01 equiv), aryl diazonium tetrafluoroborate **1** (1 equiv) and pyrimidine **6b** (6 equiv) were dissolved in dry DMSO (2 mL) and the resulting mixture was degassed by "pump-freeze-thaw" cycles. Then, the reaction mixtures were placed under sunlight for 16 hours. 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 **7b**.

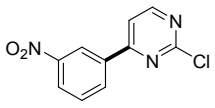
2-Chloro-4-(4-methylphenyl) pyrimidine (**7ba**)[33]



7ba

The representative procedure was followed using 4-methylphenyl diazonium tetrafluoroborate (**2e**) (0.20 mmol) and 2-chloropyrimidine (**6b**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 50/1) yielded **7ba** (26 mg, 63%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.60 (d, 1H, *J* = 8 Hz, ArH), 8.00 (d, 2H, *J* = 8 Hz, ArH), 7.62 (d, 1H, *J* = 4 Hz, ArH), 7.32 (d, 2H, *J* = 8 Hz, ArH), 2.43 (s, 3H, CH_3).

2-Chloro-4-(3-nitrophenyl) pyrimidine (**7bb**)[34]



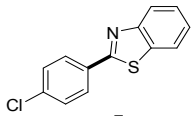
7bb

The representative procedure was followed using 4-methylphenyl diazonium tetrafluoroborate (**2e**) (0.20 mmol) and 2-chloropyrimidine (**6b**) (1.6 mmol). Isolation by column chromatography (PE/EtOAc: 50/1) yielded **7bb** (23 mg, 51%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.93 (s, 1H, ArH), 8.77 (d, 1H, *J* = 4 Hz, ArH), 8.49-8.47 (m, 1H, ArH), 8.43-8.41 (m, 1H, ArH), 7.76-7.72 (m, 2H, ArH).

4.2.7 General procedure for the reaction of aryl diazonium tetrafluoroborates with benzothiazole

In a 10 mL schlenk tube with magnetic stirring bar the cercosporin (0.01 equiv), aryl diazonium tetrafluoroborate **2** (1 equiv) and benzothiazole **6c** (6 equiv) were dissolved in dry DMSO (2 mL) and the resulting mixture was degassed by "pump-freeze-thaw" cycles. Then, the reaction mixtures were placed under sunlight for 8 hours. 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 **7c**.

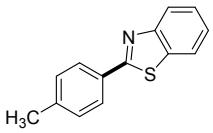
2-(4-Chlorophenyl) benzo[*d*]thiazole (**7ca**)[35]



7ca

The representative procedure was followed using 4-chlorophenyl diazonium tetrafluoroborate (**2g**) (0.20 mmol) and benzothiazole (**6c**) (1.2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **7ca** (29 mg, 60%) as a yellow solid. M.p. = 112.4-114.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.06 (d, 1H, *J* = 8 Hz, ArH), 8.03-8.01 (m, 2H, ArH), 7.99 (d, 1H, *J* = 8 Hz, ArH), 7.53-7.45 (m, 3H, ArH), 7.41-7.37 (m, 1H, ArH).

2-(*p*-Tolyl) benzo[*d*]thiazole (**7cb**)[35]



7cb

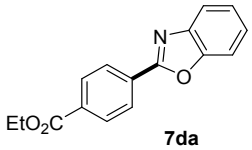
The representative procedure was followed using 4-methylphenyl diazonium tetrafluoroborate (**2b**) (0.20 mmol) and benzothiazole (**6c**) (1.2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **7cb** (29 mg, 61%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.05 (d, 1H, *J* = 8 Hz, ArH), 7.98 (d, 2H, *J* = 8 Hz, ArH), 7.88 (d, 1H, *J* = 8 Hz, ArH), 7.50-7.45 (m, 1H, ArH), 7.38-7.34 (m, 1H, ArH), 7.29 (d, 2H, *J* = 8 Hz, ArH), 2.42 (s, 3H, CH_3).

4.2.8 General procedure for the reaction of aryl diazonium tetrafluoroborates with benzoxazloe

In a 10 mL schlenk tube with magnetic stirring bar the cercosporin (0.01 equiv), aryl diazonium tetrafluoroborate **2** (1 equiv) and benzoxazole **6d** (6 equiv) were dissolved in dry DMSO (2 mL) and the

resulting mixture was degassed by "pump-freeze-thaw" cycles. Then, the reaction mixtures were placed under sunlight for 16 hours. 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 **7d**.

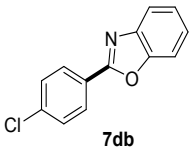
Ethyl 4-(benzo[*d*]oxazol-2-yl) benzoate (**7da**)[36]



7da

The representative procedure was followed using 4-(ethoxycarbonyl) phenyl diazonium tetrafluoroborate (**2a**) (0.20 mmol) and benzoxazole (**6d**) (1.2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **7da** (32 mg, 59%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.34 (d, 2H, J = 8 Hz, ArH), 8.20 (d, 2H, J = 8 Hz, ArH), 7.82-7.80 (m, 1H, ArH), 7.63-7.61 (m, 1H, ArH), 7.41-7.38 (m, 2H, ArH), 4.46-4.40 (m, 2H, CH_2), 1.44 (t, 3H, J = 8 Hz, CH_3).

2-(4-Chlorophenyl) benzo[*d*]oxazole (**7db**)[37]



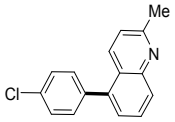
7db

The representative procedure was followed using 4-chlorophenyl diazonium tetrafluoroborate (**2g**) (0.20 mmol) and benzoxazole (**6d**) (1.2 mmol). Isolation by column chromatography (PE/EtOAc: 30/1) yielded **7db** (19 mg, 43%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.15 (s, 1H, ArH), 7.91 (d, 2H, J = 8 Hz, ArH), 7.60-7.57 (m, 1H, ArH), 7.55-7.45 (m, 4H, ArH).

4.2.9 General procedure for the reaction of aryl diazonium tetrafluoroborates with quinoline

In a 10 mL schlenk tube with magnetic stirring bar the Cercosporin (0.01 equiv), aryl diazonium tetrafluoroborate **2** (1 equiv) and substituted quinoline **6e** (6 equiv) were dissolved in dry DMSO (2 mL) and the resulting mixture was degassed by "pump-freeze-thaw" cycles. Then, the reaction mixtures were placed under sunlight for 16 hours. 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 **7e**.

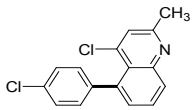
5-(4-chlorophenyl)-2-methylquinoline (**7ea**)



7ea

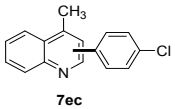
The representative procedure was followed using 4-chlorophenyl diazonium tetrafluoroborate (**2g**) (0.20 mmol) (0.20 mmol) and 2-methyl quinoline (**6ea**) (1.2 mmol). Isolation by column chromatography (PE/EtOAc: 10/1) yielded **7ea** (30 mg, 60%) as a red oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.07 (d, 1H, *J* = 8 Hz, ArH), 7.78-7.76 (m, 1H, ArH), 7.72 (d, 2H, *J* = 8 Hz, ArH), 7.69-7.67 (m, 1H, ArH), 7.54-7.50 (m, 1H, ArH), 7.44 (d, 2H, *J* = 8 Hz, ArH), 7.30 (d, 1H, *J* = 4 Hz, ArH), 2.68 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 158.9, 145.2, 138.6, 137.9, 136.4, 133.2, 132.3, 130.1, 127.9, 127.6, 127.0, 125.4, 122.0, 25.7. HRMS (ESI-Q-TOF) exact mass calcd for $C_{16}H_{13}ClN$ $[M + H]^+$ 254.0737, found 254.0751.

4-Chloro-5-(4-chlorophenyl)-2-methylquinoline (**7eb**)



7eb

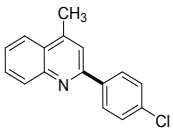
The representative procedure was followed using 4-chlorophenyl diazonium tetrafluoroborate (**2g**) (0.20 mmol) (0.20 mmol) and 2-methyl-4-chloroquinoline (**6eb**) (1.2 mmol). Isolation by column chromatography (PE/EtOAc: 10/1) yielded **7eb** (30 mg, 53%) as a red oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.22 (d, 1H, *J* = 8 Hz, ArH), 7.73 (d, 1H, *J* = 8 Hz, ArH), 7.67 (d, 2H, *J* = 8 Hz, ArH), 7.64-7.60 (m, 1H, ArH), 7.44 (d, 2H, *J* = 8 Hz, ArH), 7.42 (s, 1H, ArH), 2.66 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 158.6, 146.2, 142.5, 139.1, 137.7, 133.4, 132.3, 131.0, 128.0, 126.3, 125.2, 123.9, 121.9, 25.5. HRMS (ESI-Q-TOF) exact mass calcd for $C_{16}H_{12}Cl_2N$ $[M + H]^+$ 288.0347, found 288.0324.



7ec

The representative procedure was followed using 4-chlorophenyl diazonium tetrafluoroborate (**2g**) (0.20 mmol) (0.20 mmol) and 4-methylquinoline (**6ec**) (1.2 mmol). Isolation by column chromatography (PE/EtOAc: 10/1) yielded **7fc**-2-arylated (24 mg, 48%) and **7fc**-5-arylated (5 mg, 10%) as yellow oil in ratio 5:1.

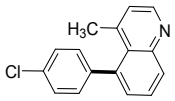
2-(4-Chlorophenyl)-4-methylquinoline (**7ec**)[38]



7ec-2-arylated

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.15 (d, 1H, *J* = 8 Hz, ArH), 8.11 (d, 2H, *J* = 8 Hz, ArH), 8.00 (d, 1H, *J* = 8 Hz, ArH), 7.75-7.70 (m, 1H, ArH), 7.68 (s, 1H, ArH), 7.58-7.52 (m, 1H, ArH), 7.49 (d, 2H, *J* = 8 Hz, ArH), 2.78 (s, 3H, CH_3).

5-(4-chlorophenyl)-4-methylquinoline (**7ec**)



7ec-5-arylated

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.80 (d, 1H, *J* = 4 Hz, ArH), 8.05-8.02 (m, 1H, ArH), 7.70-7.68 (m, 1H, ArH), 7.63-7.59 (m, 3H, ArH), 7.45 (d, 2H, *J* = 8 Hz, ArH), 7.26-7.24 (m, 1H, ArH), 2.75 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 150.0, 145.6, 144.3, 140.2, 138.4, 133.4, 132.0, 130.0, 128.7, 128.1, 125.9, 123.8, 122.0, 19.1. HRMS (ESI-Q-TOF) exact mass calcd for $C_{16}H_{13}ClN$ $[M + H]^+$ 254.0737, found 254.0746.

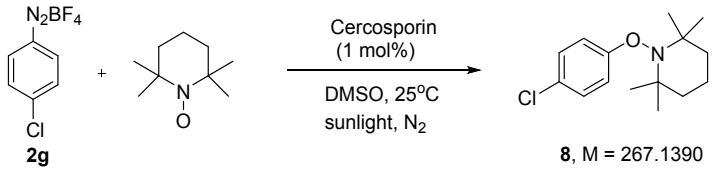
4.3 General procedure for the gram-scale synthesis with fermentation supernatant

To an oven-dried 200 mL flask equipped with a magnetic stir bar were added the cercosporin fermentation supernatant (2 mg/mL, 80 mL), aryl diazonium tetrafluoroborate 2 (5 mmol), arene or hetarene (10 equiv) and DMSO (10 mL) under N_2. Then, the reaction mixture was placed under 5 W blue LED. 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 products.

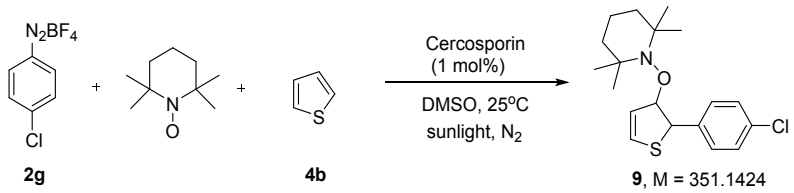
5. Radical Capturing Experiments

5.1 The experimental procedure for capturing radicals with TEMPO

In a 10 mL schlenk tube with magnetic stirring bar the cercosporin (0.01 equiv), aryl diazonium tetrafluoroborate **2g** (1 equiv) and TEMPO (2 equiv) were dissolved in dry DMSO (2 mL) and the resulting mixture was degassed by “pump-freeze-thaw” cycles. Then, the reaction mixtures were placed under sunlight. After 2 h of irradiation, a TEMPO trapped compound **8** was detected by mass spectra.



In a 10 mL schlenk tube with magnetic stirring bar the cercosporin (0.01 equiv), aryl diazonium tetrafluoroborate **2g** (1 equiv), thiophene (10 equiv) and TEMPO (2 equiv) were dissolved in dry DMSO (0.23 mmol/mL) and the resulting mixture was degassed by "pump-freeze-thaw" cycles. Then, the reaction mixtures were placed under sunlight. After 2 h of irradiation, a TEMPO trapped compound **9** was detected by mass spectra.



5.2 Mass spectra of radical trapped compounds with TEMPO

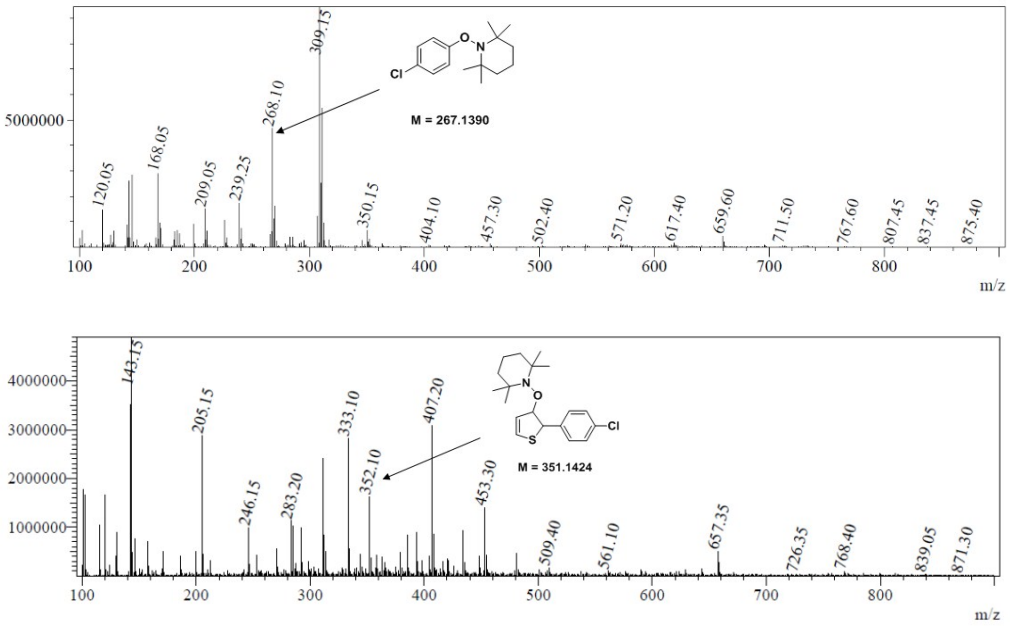
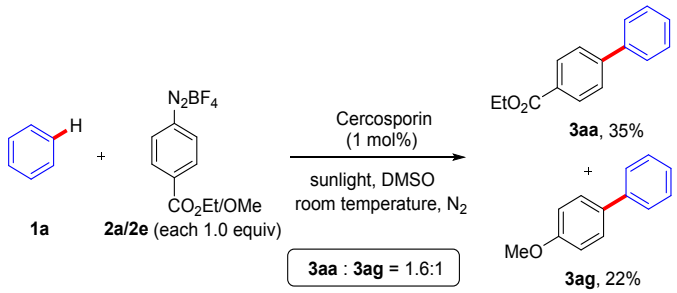


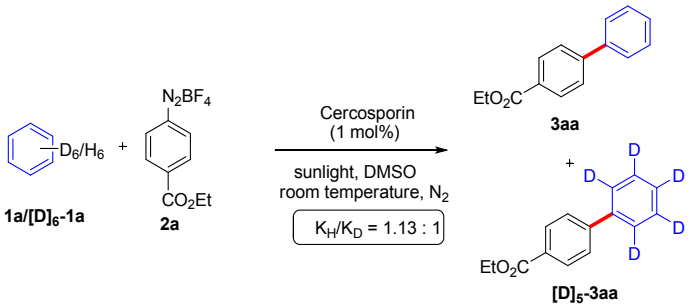
Figure S7. Mass spectra of radical trapped compounds with TEMPO

6. Intermolecular Competition Experiments



In a 10 mL schlenk tube with magnetic stirring bar the cercosporin (0.01 equiv), 4-(ethoxycarbonyl) phenyl diazonium tetrafluoroborate (**2a**) (0.2 mmol), 4-methoxyphenyl diazonium tetrafluoroborate (**2e**) (0.2 mmol), benzene **1a** (10 equiv) were dissolved in dry DMSO (2 mL) and the resulting mixture was degassed by "pump-freeze-thaw" cycles. Then, the reaction mixtures were placed under sunlight for the 16h. 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 product **3aa** (20 mg, 35%) and **3ag** (4 mg, 22%).

7. Intermolecular Kinetic Isotope Effect Experiment



In a 10 mL schlenk tube with magnetic stirring bar the cercosporin (0.01 equiv), 4-(ethoxycarbonyl) phenyl diazonium tetrafluoroborate (**2a**) (0.2 mmol), benzene **1a** (5 equiv), benzene (**1a**) -d_6 (5 equiv) were dissolved in dry DMSO (2 mL) and the resulting mixture was degassed by "pump-freeze-thaw" cycles. Then, the reaction mixtures were placed under sunlight. 8 Hours later, 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 product **3aa/[D]$_5$-3aa** (18 mg, 40%).

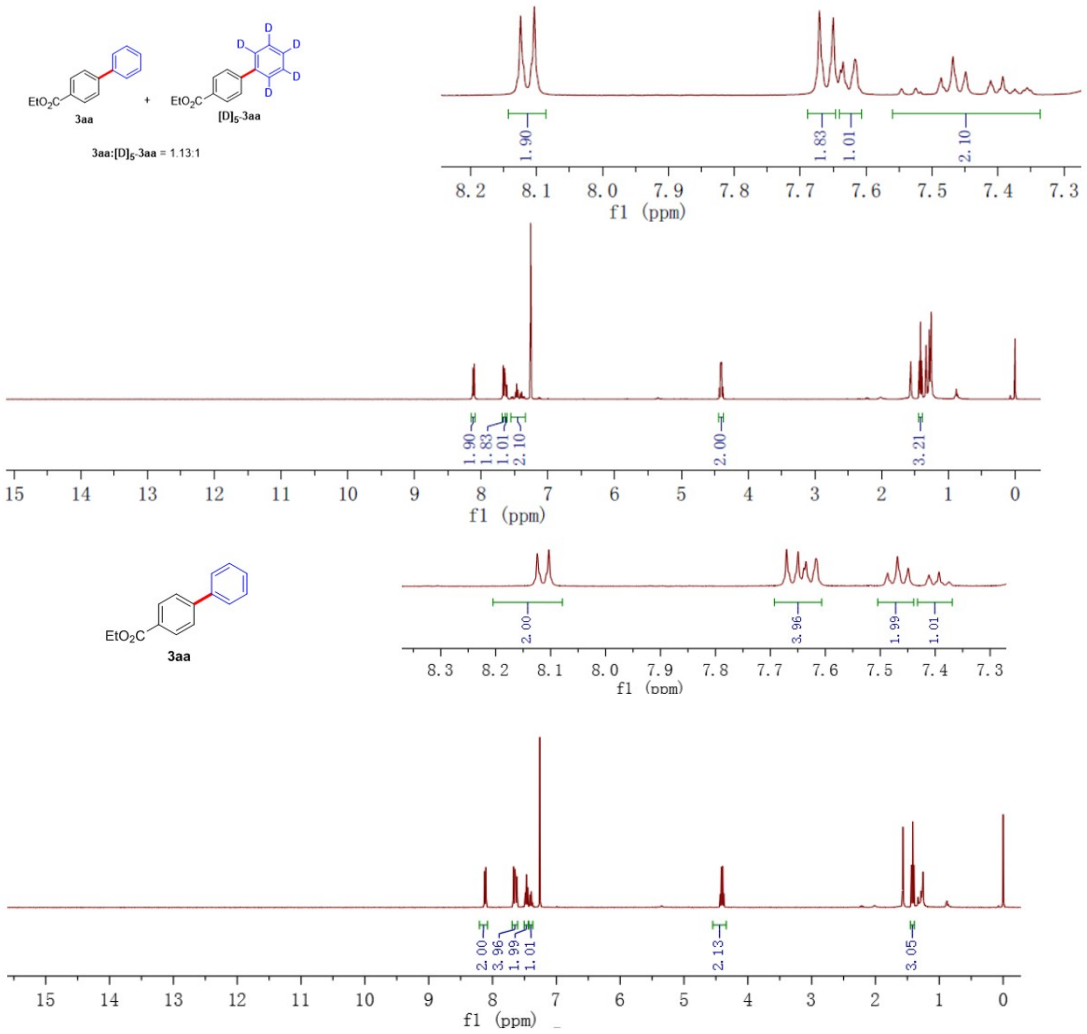


Figure S8. ^{1}H NMR of **3aa** and **3aa**+$[D]_5$-**3aa**

8. Spectroscopic Investigation of the Mechanism

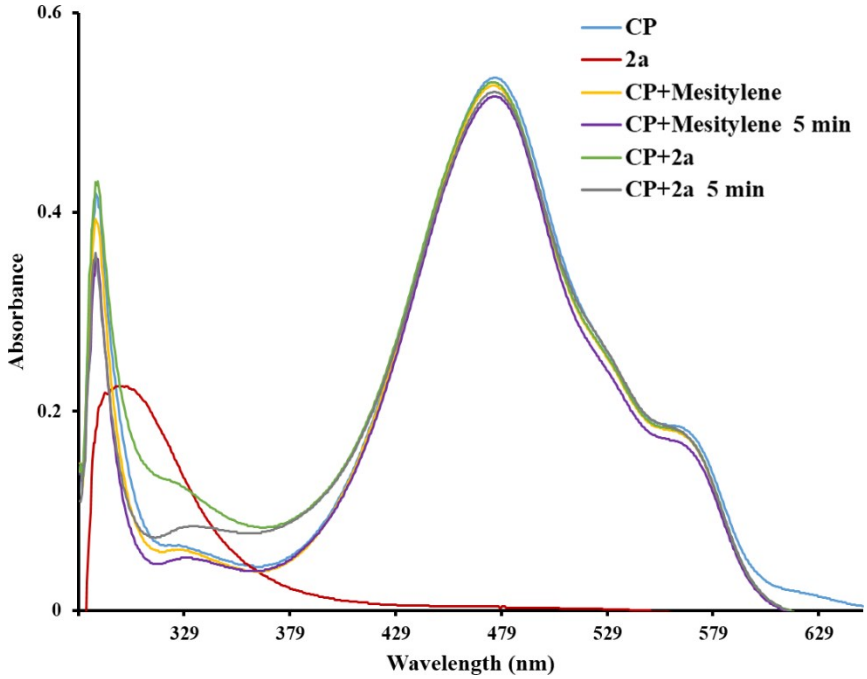


Figure S9. Absorption spectra of cercosporin (**CP**, 2.75*10^{-5} mol/L in DMSO, 2.5 mL), 4-(ethoxycarbonyl) phenyl diazonium tetrafluoroborate (**2a**, 2.65*10^{-3} mol/L in DMSO, 2.5 mL), cercosporin (2.75*10^{-5} mol/L in DMSO, 2.5 mL) + mesitylene **1b** (2.75*10^{-3} mol/L in DMSO, 40 µL), cercosporin (2.75*10^{-5} mol/L in DMSO, 2.5 mL) + mesitylene **1b** (2.75*10^{-3} mol/L in DMSO, 40 µL) with 5 minutes blue LED irradiation, cercosporin (2.75*10^{-5} mol/L in DMSO, 2.5 mL) +**2a** (2.65*10^{-3} mol/L in DMSO, 40 µL) and cercosporin (2.75*10^{-5} mol/L in DMSO, 2.5 mL) +**2a** (2.65*10^{-3} mol/L in DMSO, 40 µL) with 5 minutes blue LED irradiation.

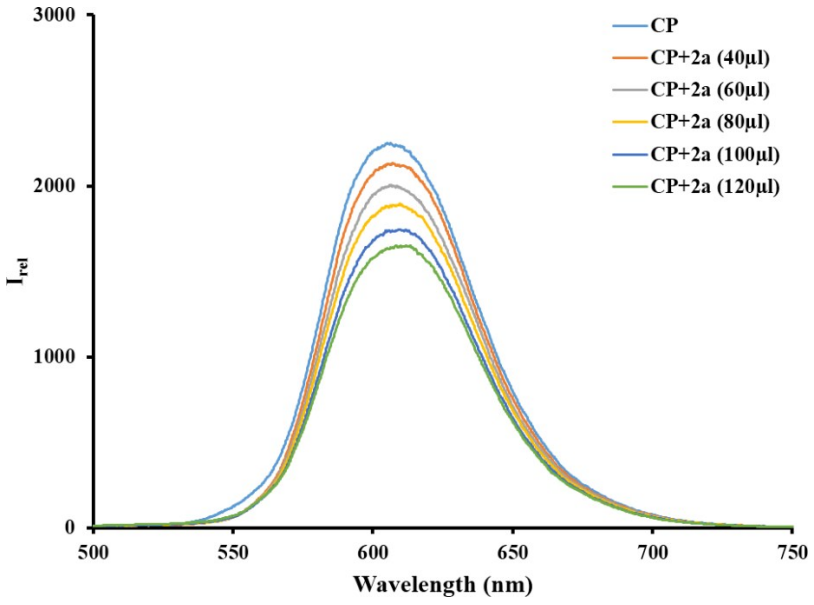


Figure S10. Fluorescence response of cercosporin (**CP**, 2.75*10^{-5} mol/L in DMSO) upon titration with 4-(ethoxycarbonyl) phenyl diazonium tetrafluoroborate (**2a**, 2.65*10^{-3} mol/L in DMSO).

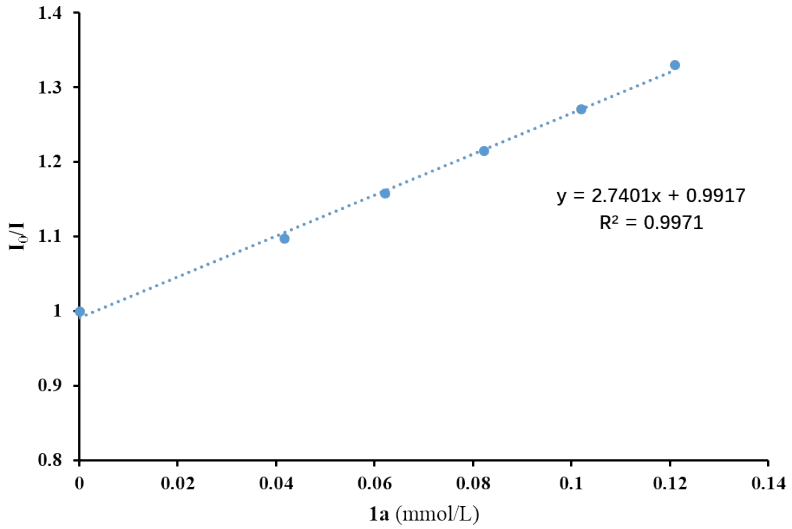
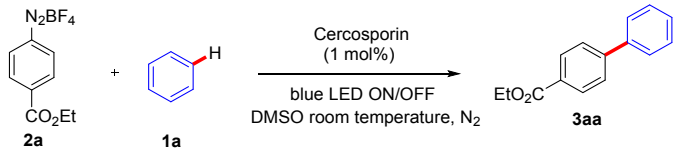


Figure S11. Stern–Volmer plots for the quenching of cercosporin (**CP**, 2.75*10^{-5} mol/L in DMSO) with with 4-(ethoxycarbonyl) phenyl diazonium tetrafluoroborate (**2a**, 2.65*10^{-3} mol/L in DMSO).

9. Light On/Off Experiments



Considering the time intervals, the light on/off experiments were irradiated with blue LED. In a 10 mL schlenk tube with magnetic stirring bar the cercosporin (0.01 equiv), 4-(ethoxycarbonyl) phenyl diazonium tetrafluoroborate (**2a**) (0.2 mmol), benzene (**1a**) (10 equiv) were dissolved in dry DMSO (2 mL) and the resulting mixture was degassed by "pump-freeze-thaw" cycles. Then, the reaction mixtures were placed under blue LED at given time intervals. The yield was detected by GC using diphenyl as internal standard.

Light On/Off	Time (h)	Yield of **3aa**
0	0	0
1 hour on	1	8
1 hour off	2	10
1 hour on	3	19
1 hour off	4	22

1 hour on	5	30
1 hour off	6	32
1 hour on	7	41
1 hour off	8	44
1 hour on	9	52
1 hour off	10	55

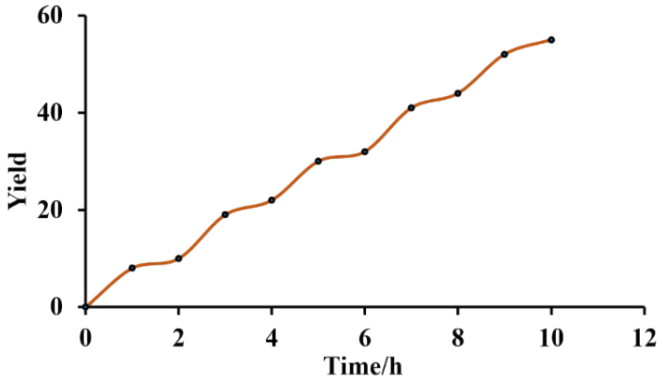


Figure S12. Light on/off experiment

10. References

1. W. Guo, L. Q. Lu, Y. Wang, Y. N. Wang, J. R. Chen and W. J. Xiao, *Angew. Chem. Int. Ed.* **2015**, *54*, 2265.
2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V.B akken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, **2013**.
3. A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
4. P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623.

5. Y. F. Liang, R. Steinbock, L. Yang and L. Ackermann, *Angew. Chem. Int. Ed*. **2018**, *57*, 10625.

6. H. Q. Zhao, X. W. Xu, W. Wu, W. Zhang and Y. X. Zhang, *Catal. Commun.* **2018**, *111*, 95.

7. H. N. Wang, B. Q. Wang and B. Li, *J. Org. Chem.* **2017**, *82*, 9560.

8. S. Chang, L. L. Dong, H. Q. Song and B. Feng, *Org. Biomol. Chem.,* **2018**, *16*, 3282.

9. A. Boelke, L. D. Caspers and B. J. Nachtsheim, *Org. Lett.* **2017**, *19*, 5344.

10. K. Okura, T. Teranishi, Y. Yoshida and E. Shirakawa, *Angew. Chem.* **2018**, *130*, 7304.

11. V. Gauchot, D. R. Sutherland and A.-L. Lee. *Chem. Sci*., **2017**, *8*, 2885.

12. S. Crespi, S. Protti and M. Fagnoni, *J. Org. Chem,* **2016**, *81*, 9612.

13. H. C. Bell, J. R. Kalman, G. L. May, J. T. Pinhey and S. Sternhell, *Aust. J. Chem.* **1979**, *32*, 1531.

14. T. E. Storr and M. F. Greaney, *Org. Lett.* **2013**, *15*, 1410.

15. H. G. Ghaleshahi, G. Antonacci, R. Madsen, *Eur. J. Org. Chem*. **2017**, 1331.

16. Y. S. Feng, X. S. Bu, B. Huang, C. Rong, J. J. Dai, J. Xu and H. J. Xu, *Tetrahedron Lett.* **2017**, *58*, 1939.

17. L. H. Zhi, H. L. Zhang, Z. Y. Yang, W. S. Liu and B. D. Wang, *Chem. Commun*., **2016**, *52*, 6431.

18. J. Ahmed, S. C. Sau, P. Sreejyothi, P. K. Hota, P. K. Vardhanapu, G. Vijaykumar and S. K. Mandal, *Eur. J. Org. Chem.* **2017**, 1004.

19. J. Y. Li, L. Lu, Q. Pan, Y. W. Ren, B. Liu and B. L. Yin, *Adv. Synth. Catal*. **2017**, *359*, 2001.

20. A. Affrose, P. Suresh, I. A. Azatha and K. Pitchumani, *RSC Adv*., **2015**, 5, 27533.

21. Z. Y. Lian, J. Yuan, M. Q. Yan, Y. Liu, X. Luo, Q. G. Wu, S. H. Liu, J. Chen, X. L. Zhu and G. A. Yu, *Org. Biomol. Chem*., **2016**, *14*, 10090.

22. J. F. Yang, S. J. Liu, J. F. Zheng and J. R. Zhou, *Eur. J. Org. Chem*. **2012**, 6248.

23. D. P. Hari, P. Schroll and B. König, *J. Am. Chem. Soc*. **2012**, *134*, 2958.

24. A. Honraedt, M. A. Raux, E. L. Grognec, D. Jacquemin and F. X. Felpin, *Chem. Commun*., **2014**, *50*, 5236.

25. M. D. Perretti, D. M. Monzón, F. P. Crisóstomo, V. S. and Martín and R. Carrillo, *Chem. Commun*., **2016**, *52*, 9036.

26. J. E. Zweig and T. R. Newhouse, *J. Am. Chem. Soc.,* **2017**, *139*, 10956.

27. P. H. Lee, *Bull. Korean Chem. Soc.* **2008**, *29*, 261.

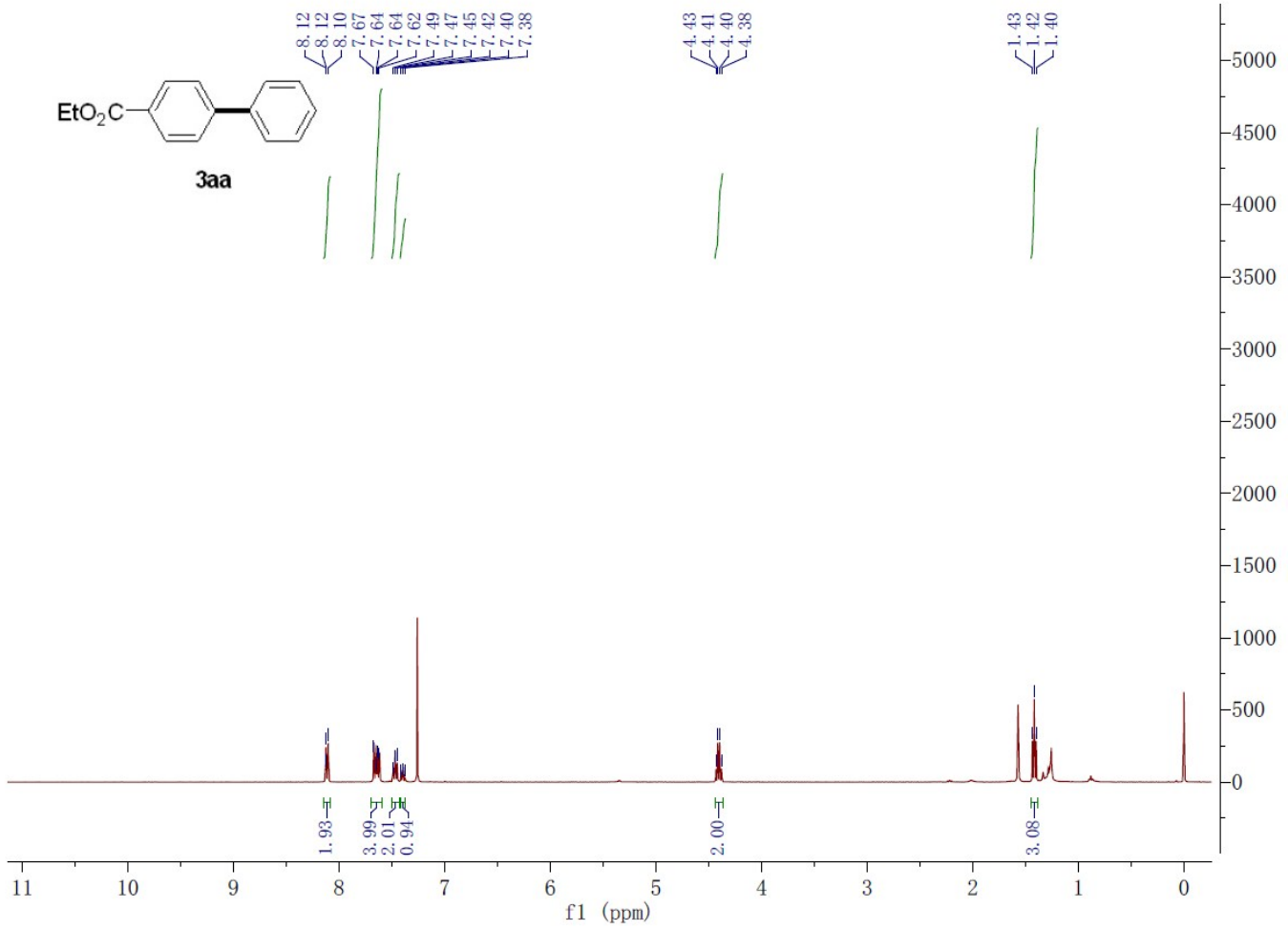
28. D. Hackenberger, P. Weber, D. C. Blakemore and L. J. Goossen, *J. Org. Chem.*, **2017**, *82*, 3917.

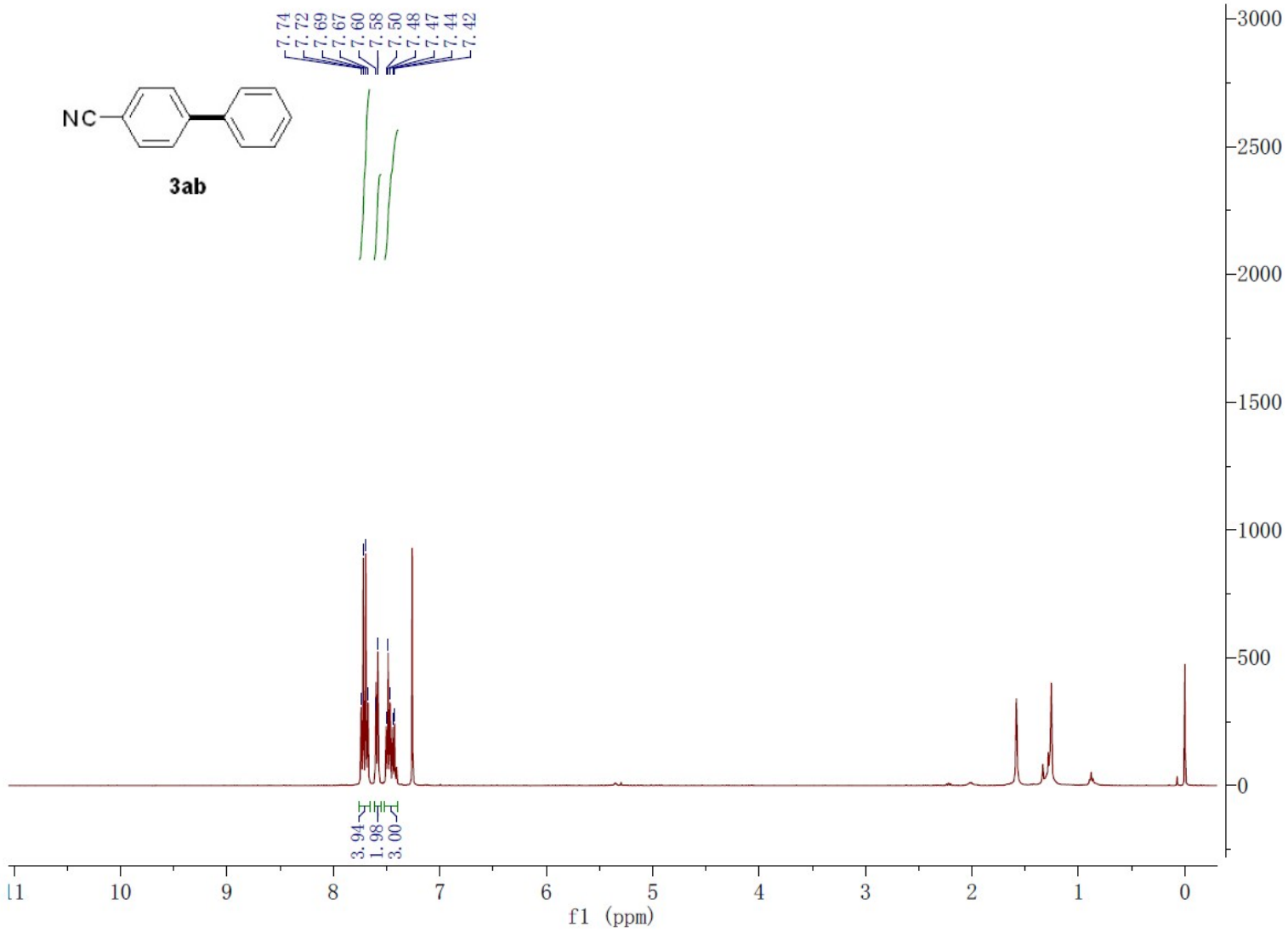
29. J. S. Ward, J. T. W. Bray, B. J. Aucott, C. Wagner, N. E. Pridmore, A. C. Whitwood, J. W. B. Moir,

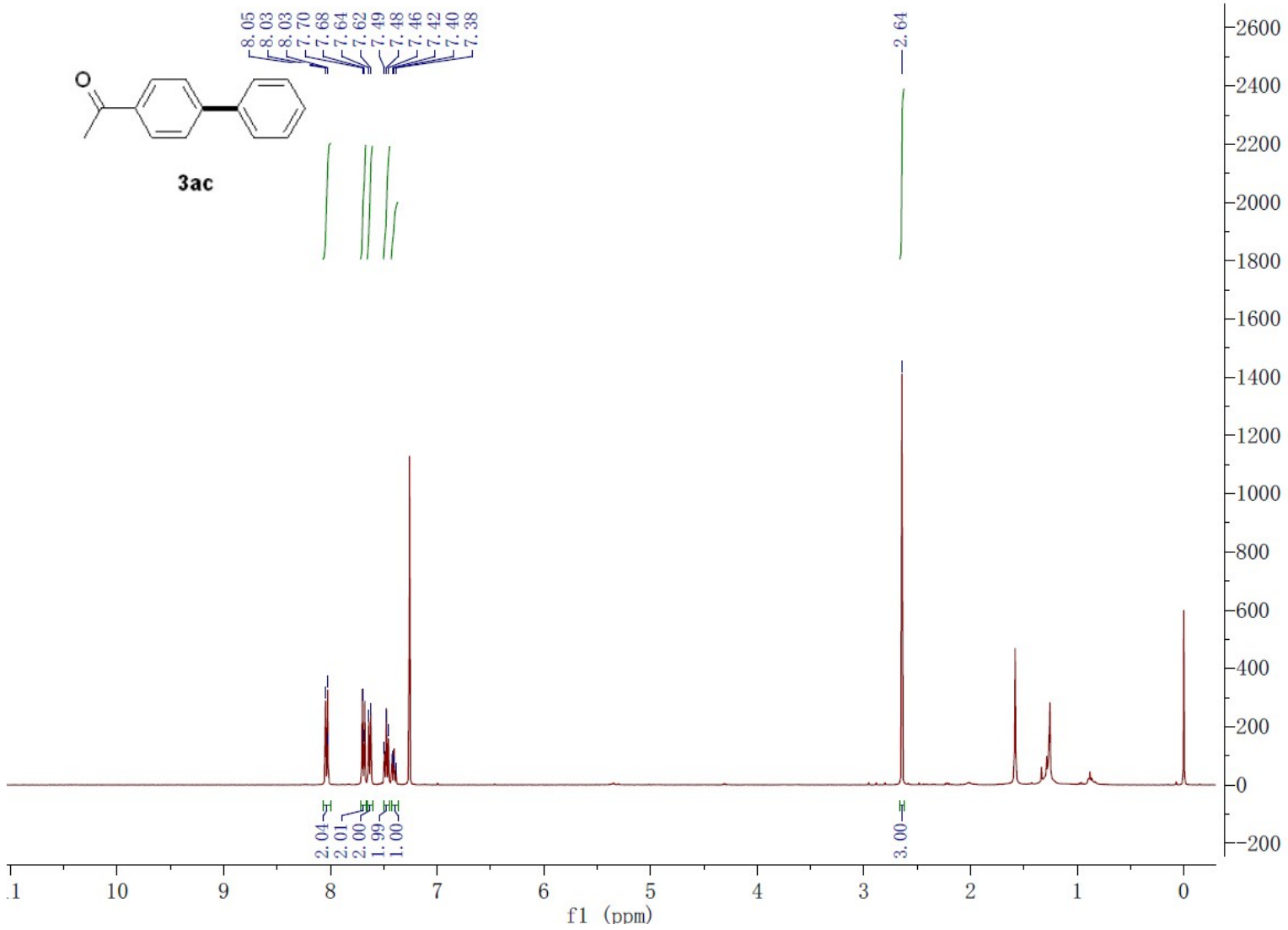
J. M. Lynam and I. J. S. Fairlamb, *Eur. J. Inorg. Chem*. **2016**, 5044.

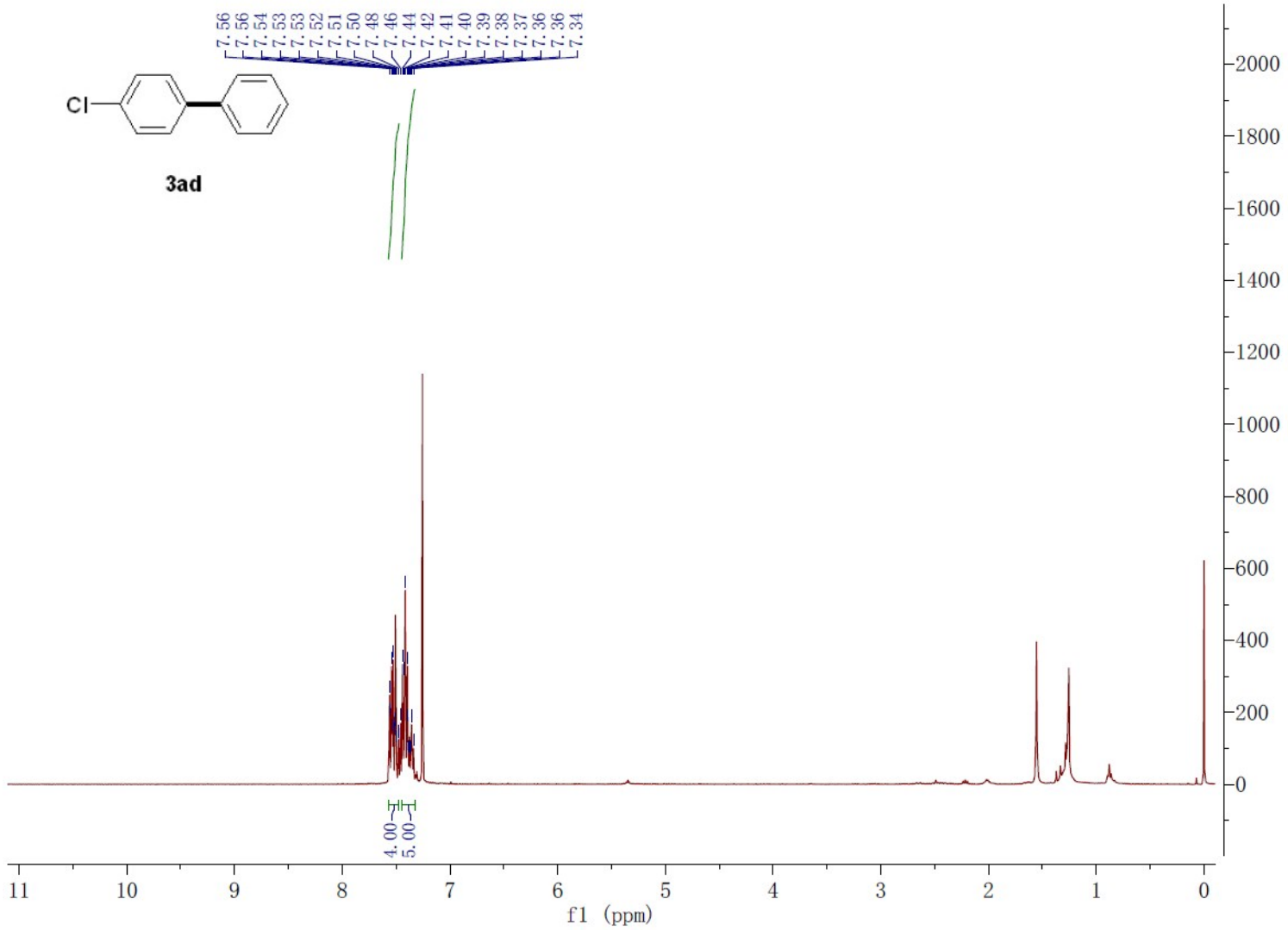
30. F. Schroeter and T. Strassner, *Eur. J. Inorg. Chem*. **2017**, 4231.
31. X. S. Ma, H. Dang, J. A. Rose, P. Rablen and S. B. Herzon, *J. Am. Chem. Soc*. **2017**, *139*, 5998.
32. D. X. Yang, S. L. Colletti, K. Wu, M. Y. Song, G. Y. Li and H. C. Shen, *Org. Lett.*, **2009**, *11*, 381.
33. R. Jain, M. Mathur, J. Lan, A. Costales, G. Atallah, S. Ramurthy, S. Subramanian, L. Setti, P. Feucht, B. Warne, L. Doyle, S. Basham, A. B. Jefferson, M. Lindvall, B. A. Appleton and C. M. Shafer, *J. Med. Chem.* **2015**, *58*, 6766.
34. L. Khurana, B. Q. Fu, A. L. Duddupudi, Y. H. Liao, S. S. Immadi, D. A. Kendall and D. Lu, *J. Med. Chem*. **2017**, *60*, 1089.
35. J. K. Laha, K. V. Patel, K. S. S. Tummalapalli, N. Dayal, *Chem. Commun*., **2016**, *52*, 10245.
36. W. Zhang, Q. L. Zeng, X. M. Zhang, Y. J. Tian, Y. Yue, Y. J. Guo and Z. H. Wang, *J. Org. Chem.*, **2011**, *76*, 4741.
37. D. H. Kim, K. Yoo, S. E. Kim, H. J. Cho, J. Lee, Y. Kim, M. Kim, *J. Org. Chem*. **2015**, *80*, 3670.
38. M. B. Zhong, S. Sun, J. Cheng and Y. Shao, *J. Org. Chem.* **2016**, *81*, 10825.

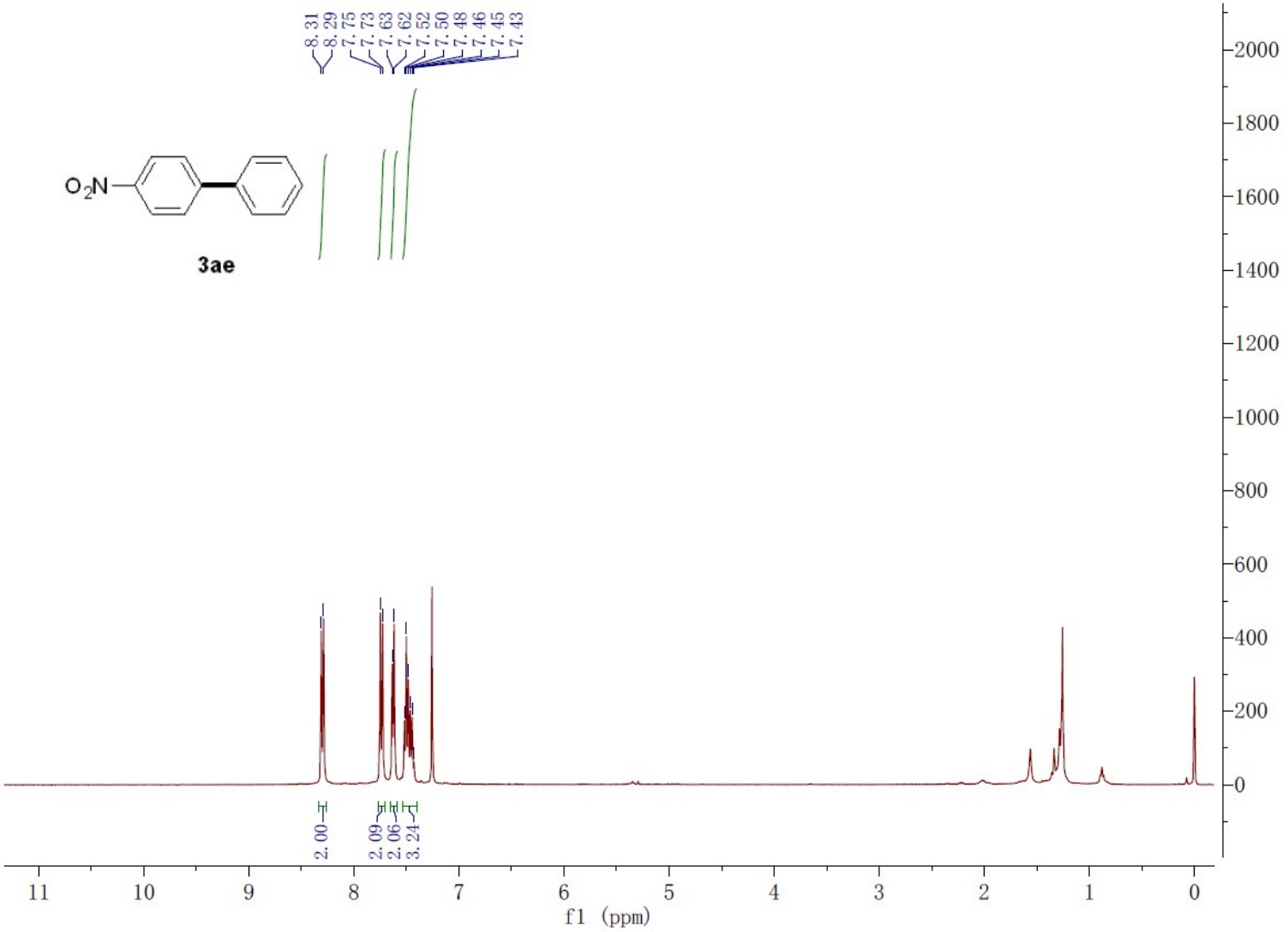
11. ^{1}H and ^{13}C Spectra

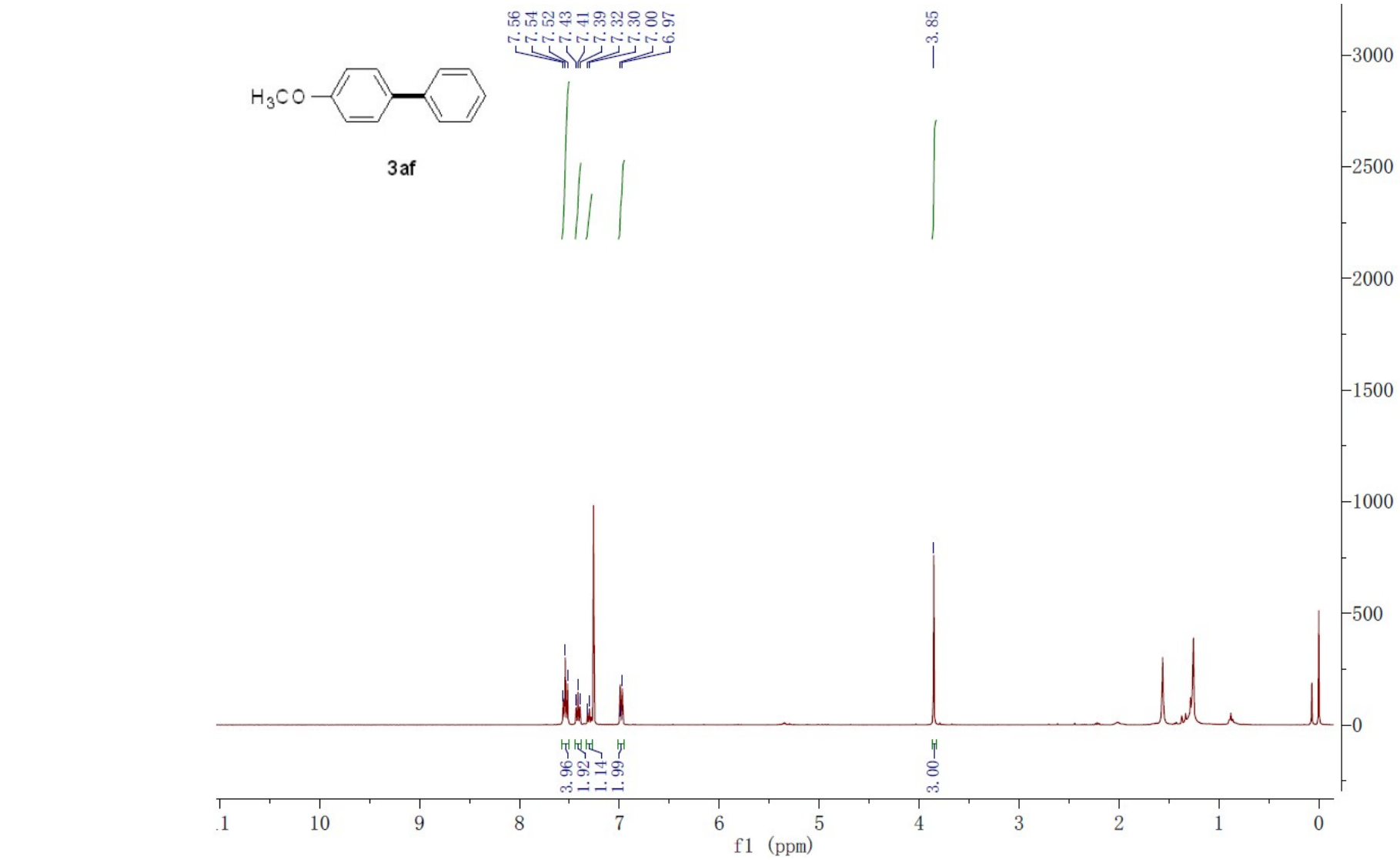


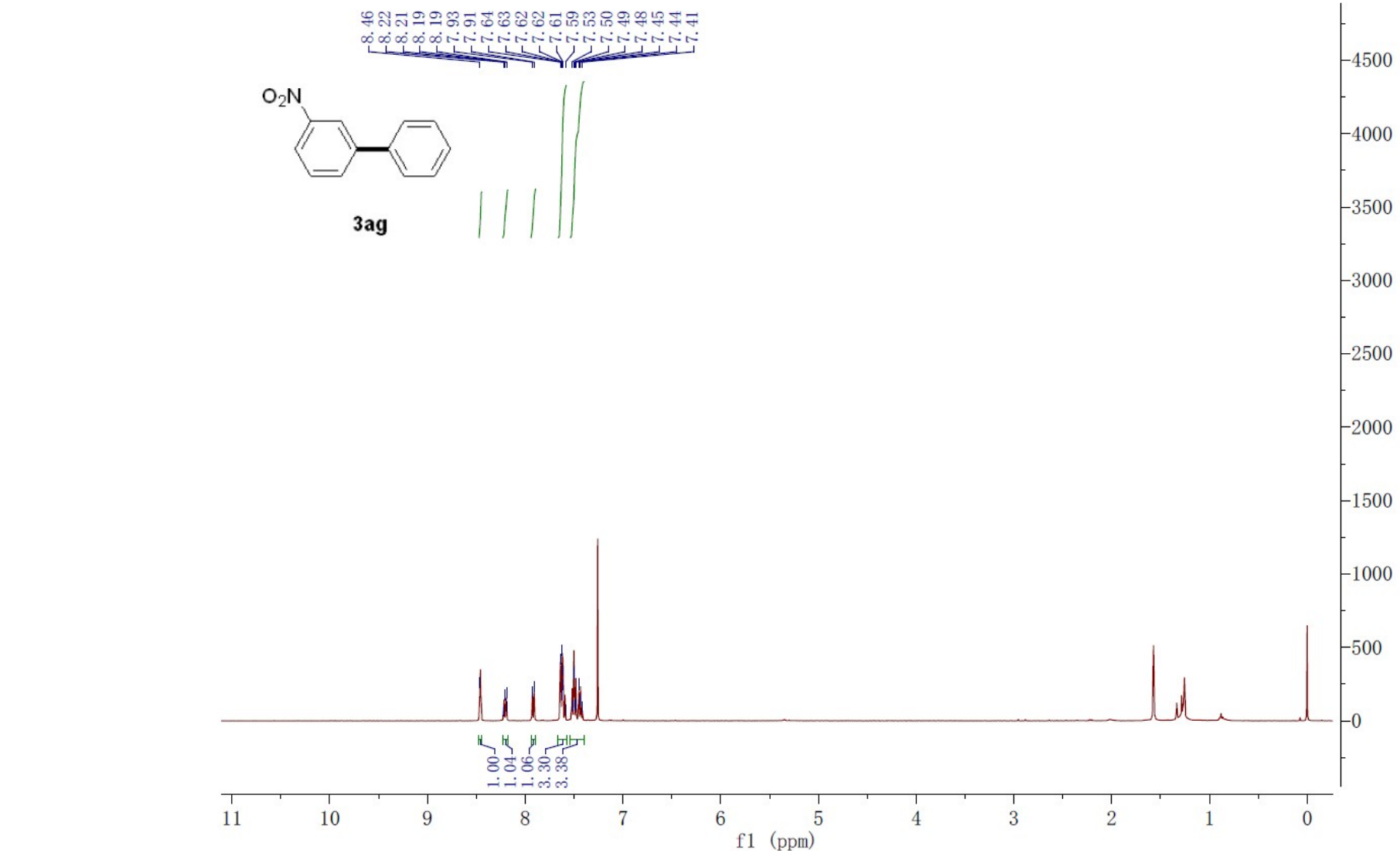

7.74
7.72
7.69
7.67
7.60
7.58
7.50
7.48
7.47
7.44
7.42
NC
3ab
3000
2500
2000
1500
1000
500
0
3.94
1.98
3.00
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

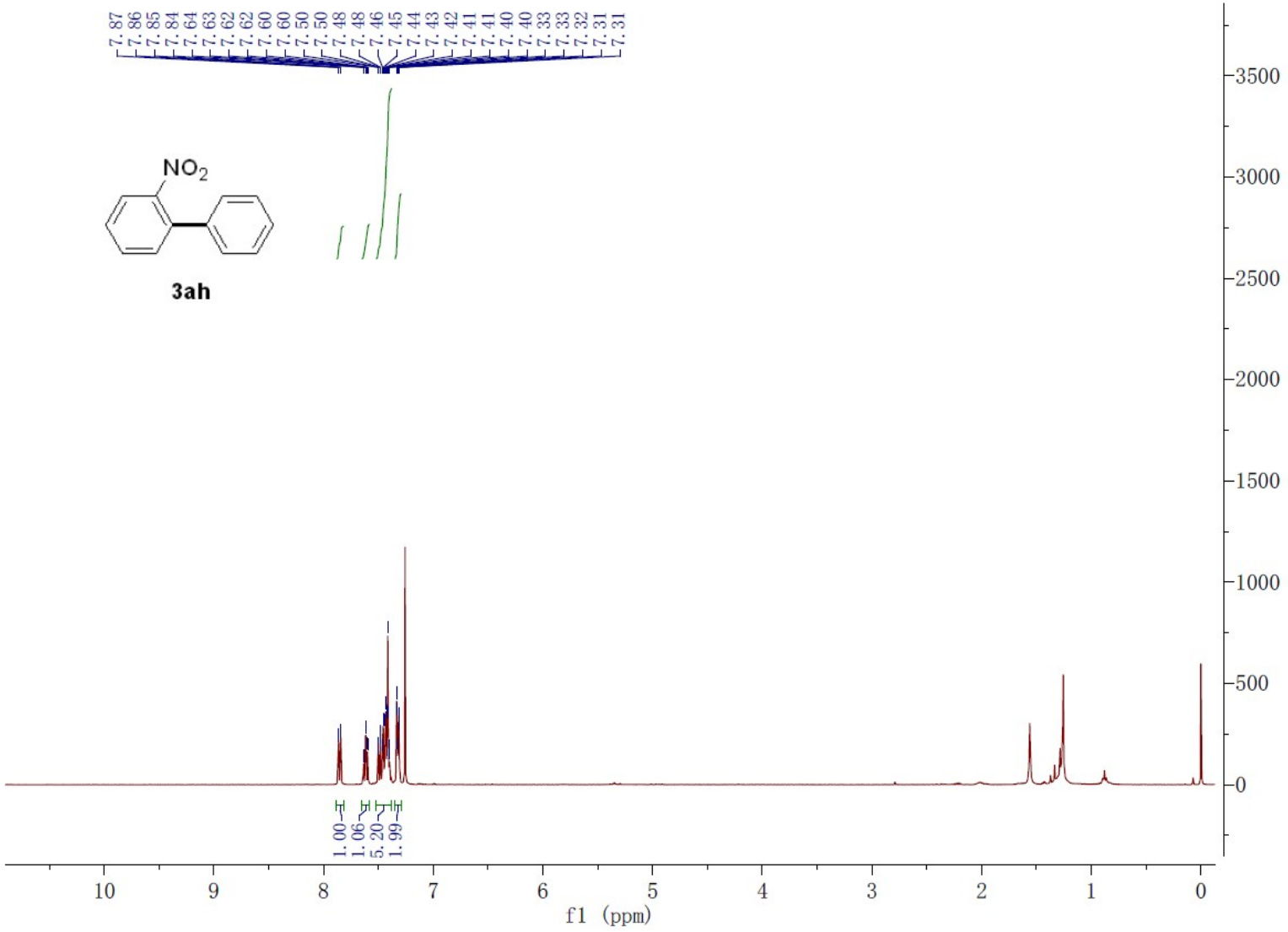

8.05
8.03
8.03
7.70
7.68
7.64
7.62
7.49
7.48
7.46
7.42
7.40
7.38
2.64
O
3ac
2.04
2.01
2.00
1.99
1.00
3.00
f1 (ppm)

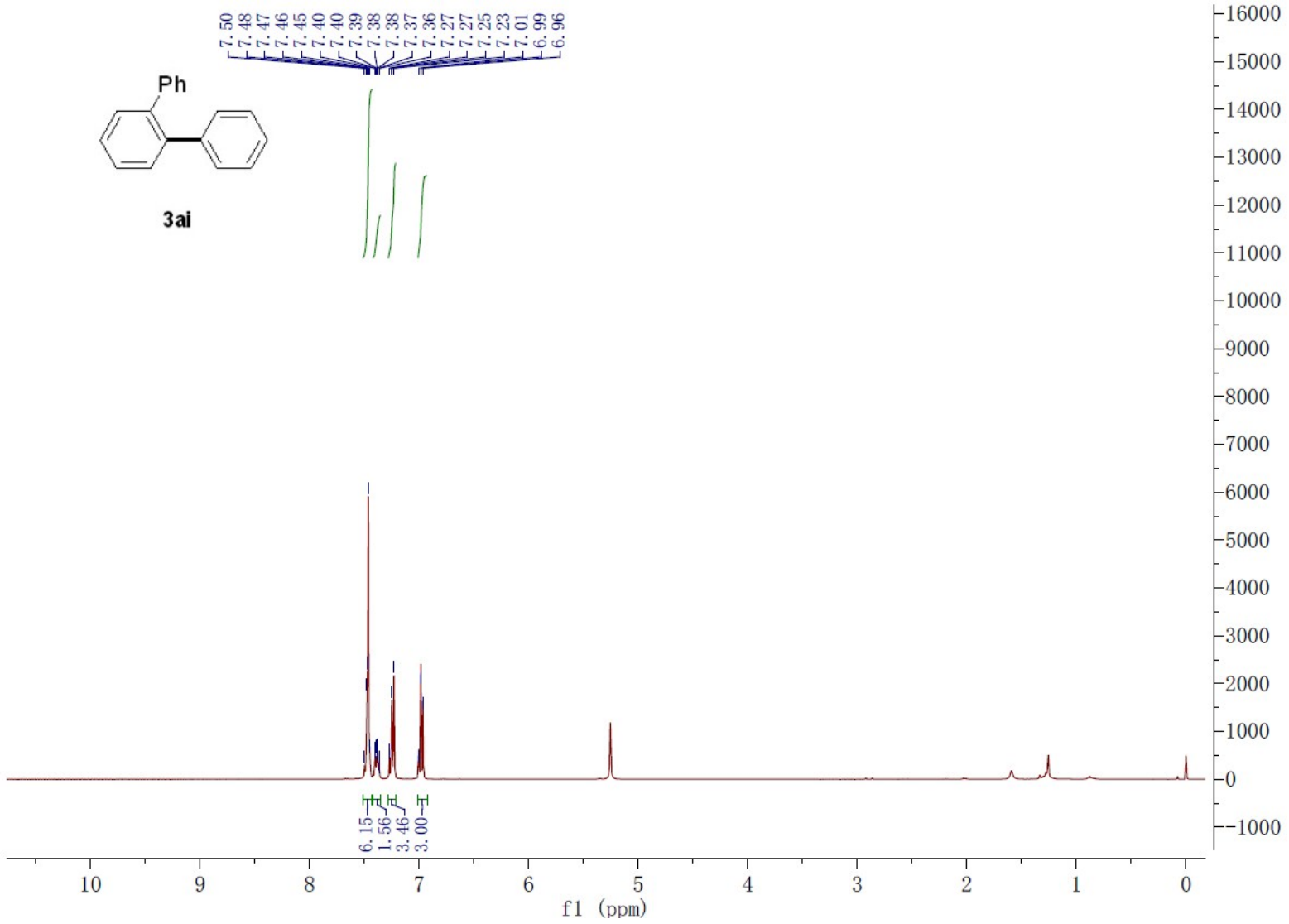

7.56
7.56
7.54
7.53
7.53
7.52
7.51
7.50
7.48
7.46
7.44
7.42
7.41
7.40
7.39
7.38
7.37
7.36
7.36
7.34
Cl
3ad
4.00
5.00
2000
1800
1600
1400
1200
1000
800
600
400
200
0
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

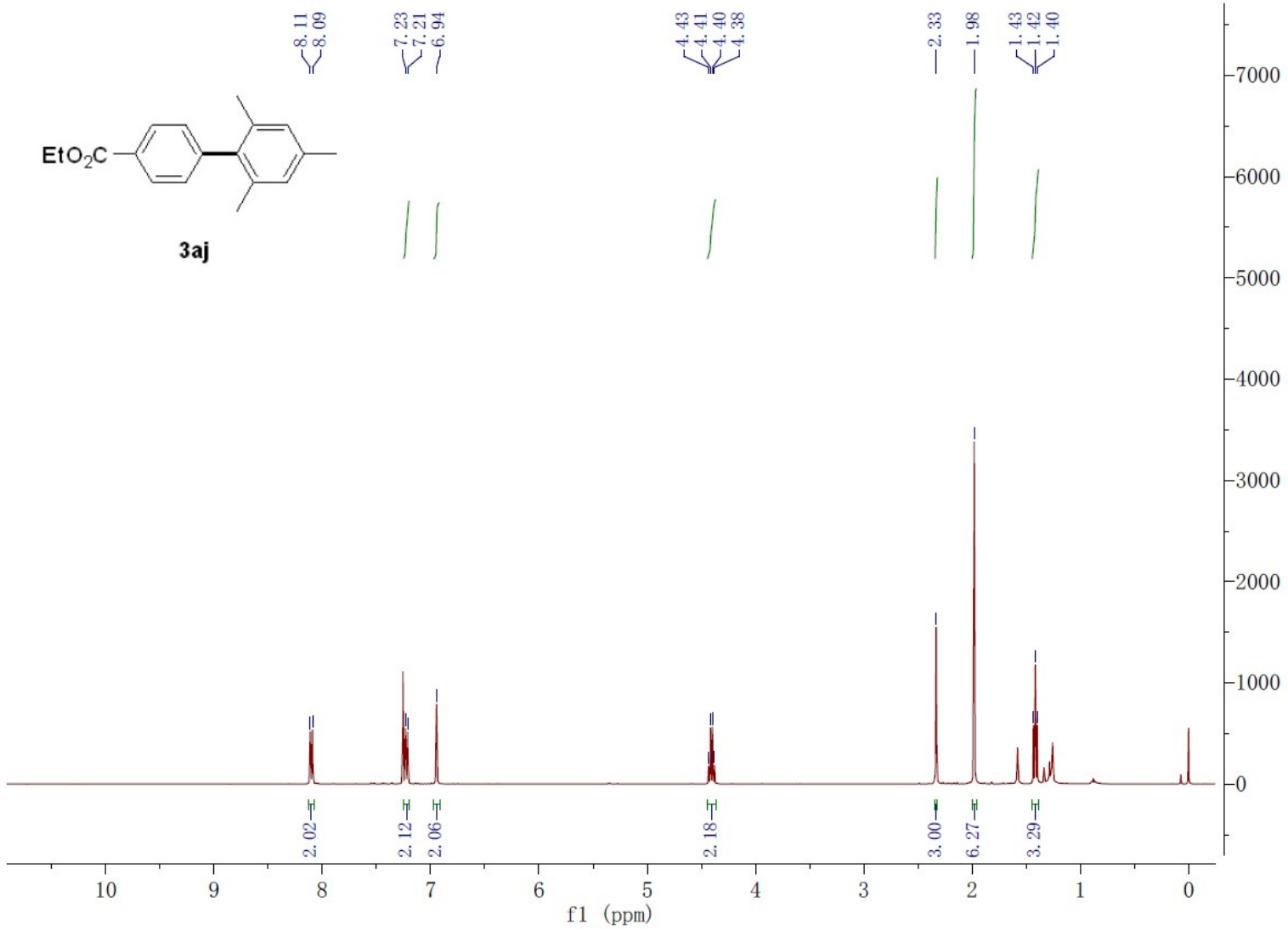

8.31
8.29
7.75
7.73
7.63
7.62
7.52
7.50
7.48
7.46
7.45
7.43
O2N
3ae
2.00
2.09
2.06
3.24
f1 (ppm)

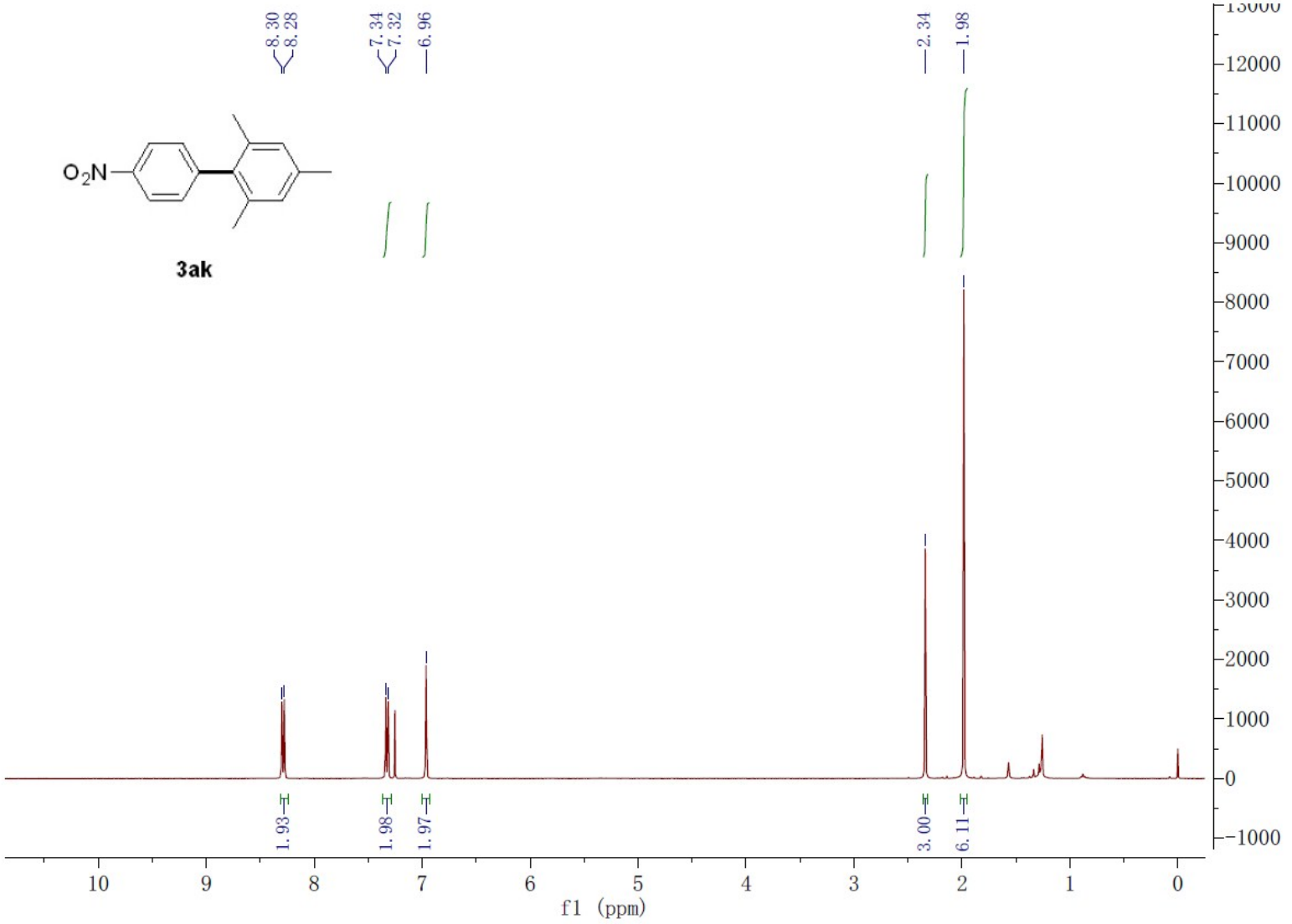

H3CO
3af
7.56
7.54
7.52
7.43
7.41
7.39
7.32
7.30
7.00
6.97
3.85
3000
2500
2000
1500
1000
500
0
3.96
1.92
1.14
1.99
3.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

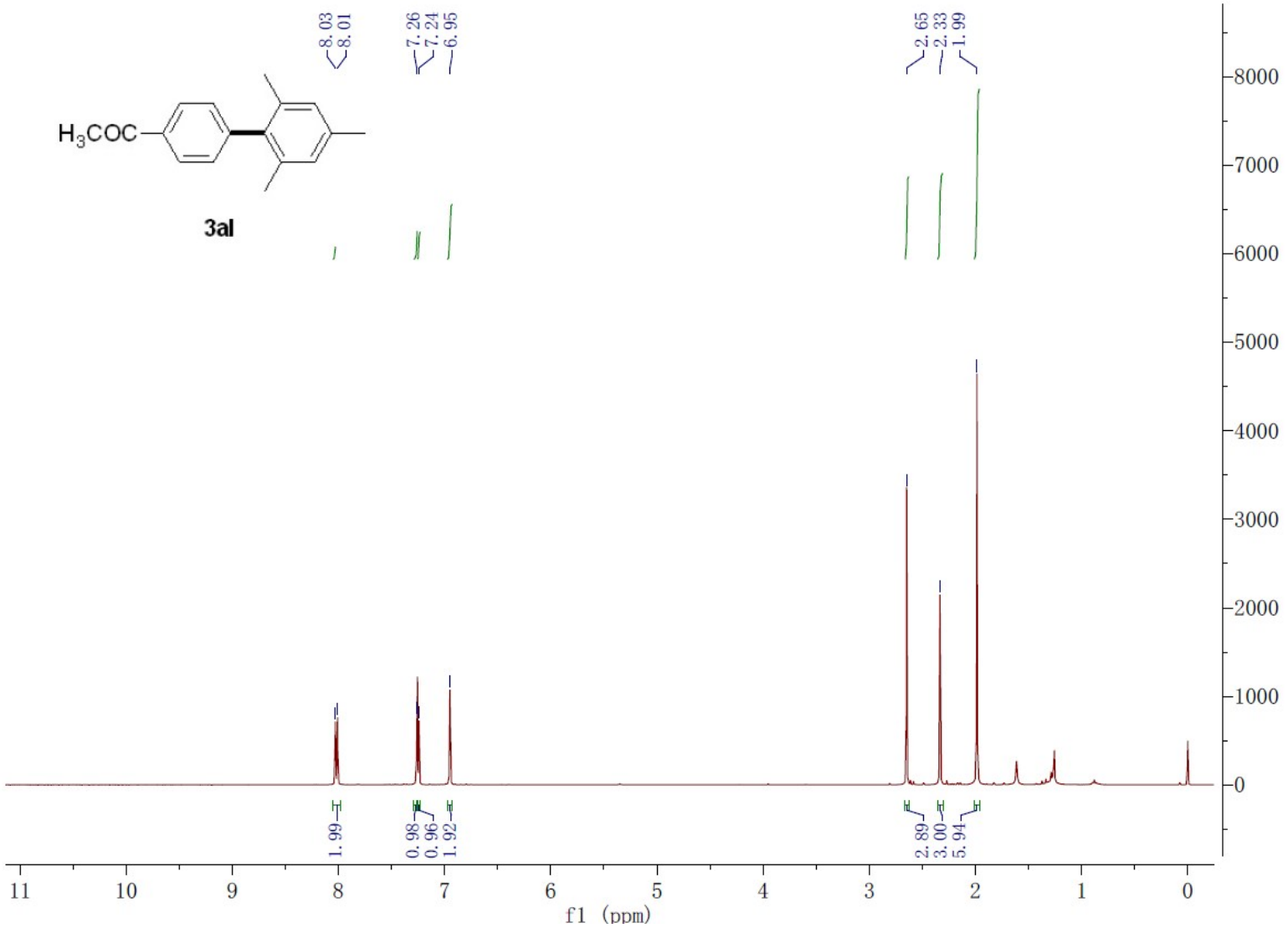

8.46
8.22
8.21
8.19
8.19
7.93
7.91
7.64
7.63
7.62
7.62
7.61
7.59
7.53
7.50
7.49
7.48
7.45
7.44
7.41
O2N
3ag
4500
4000
3500
3000
2500
2000
1500
1000
500
0
1.00
1.04
1.06
3.30
3.38
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

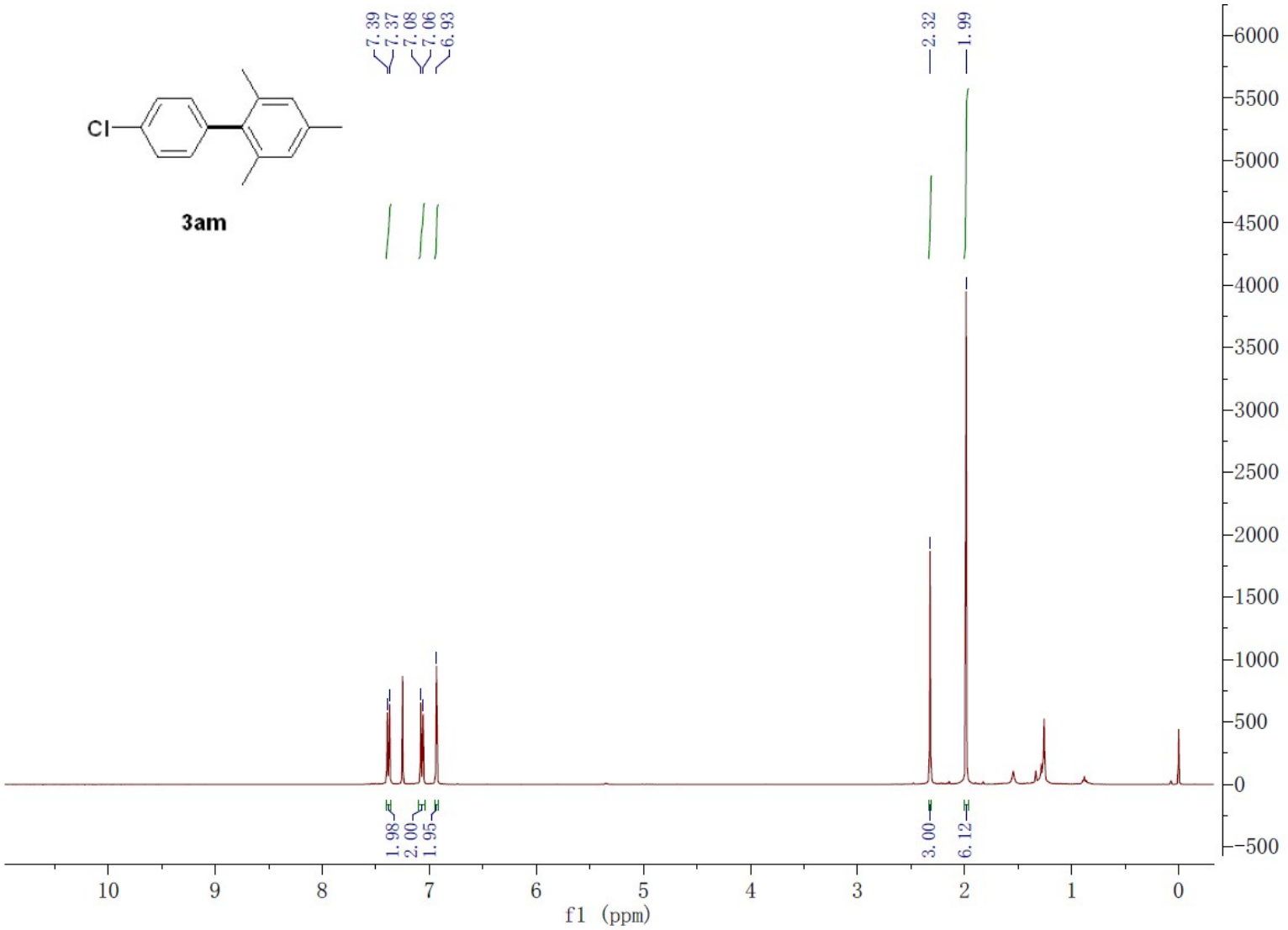

7.87
7.86
7.85
7.84
7.64
7.63
7.62
7.62
7.60
7.60
7.50
7.50
7.48
7.48
7.46
7.45
7.44
7.43
7.42
7.41
7.41
7.40
7.40
7.33
7.33
7.32
7.31
7.31
NO2
3ah
1.00
1.06
5.20
1.99
3500
3000
2500
2000
1500
1000
500
0
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

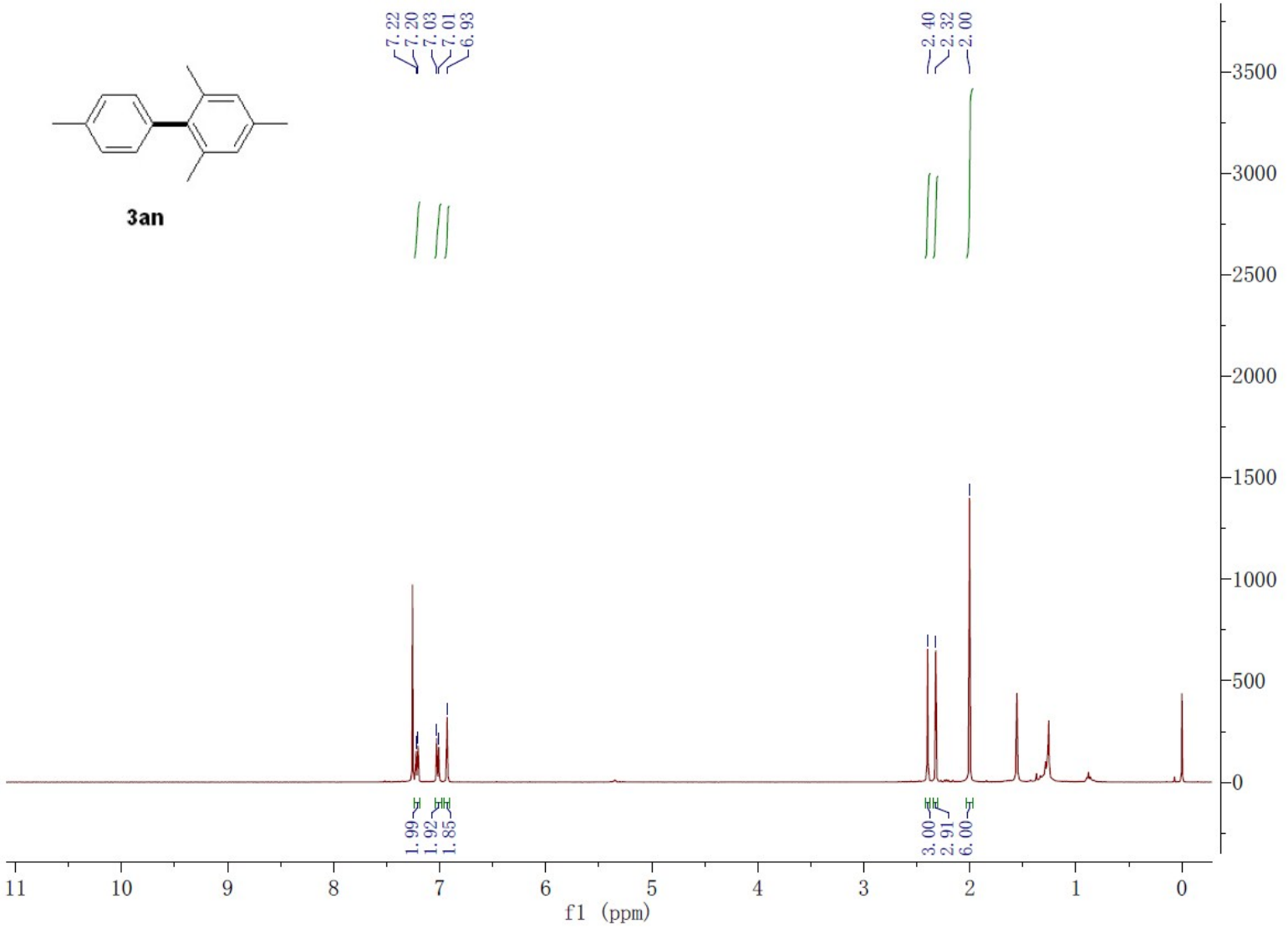

7.50
7.48
7.47
7.46
7.45
7.40
7.40
7.39
7.38
7.38
7.37
7.36
7.27
7.27
7.25
7.23
7.01
6.99
6.96
Ph
3ai
6.15
1.56
3.46
3.00
f1 (ppm)

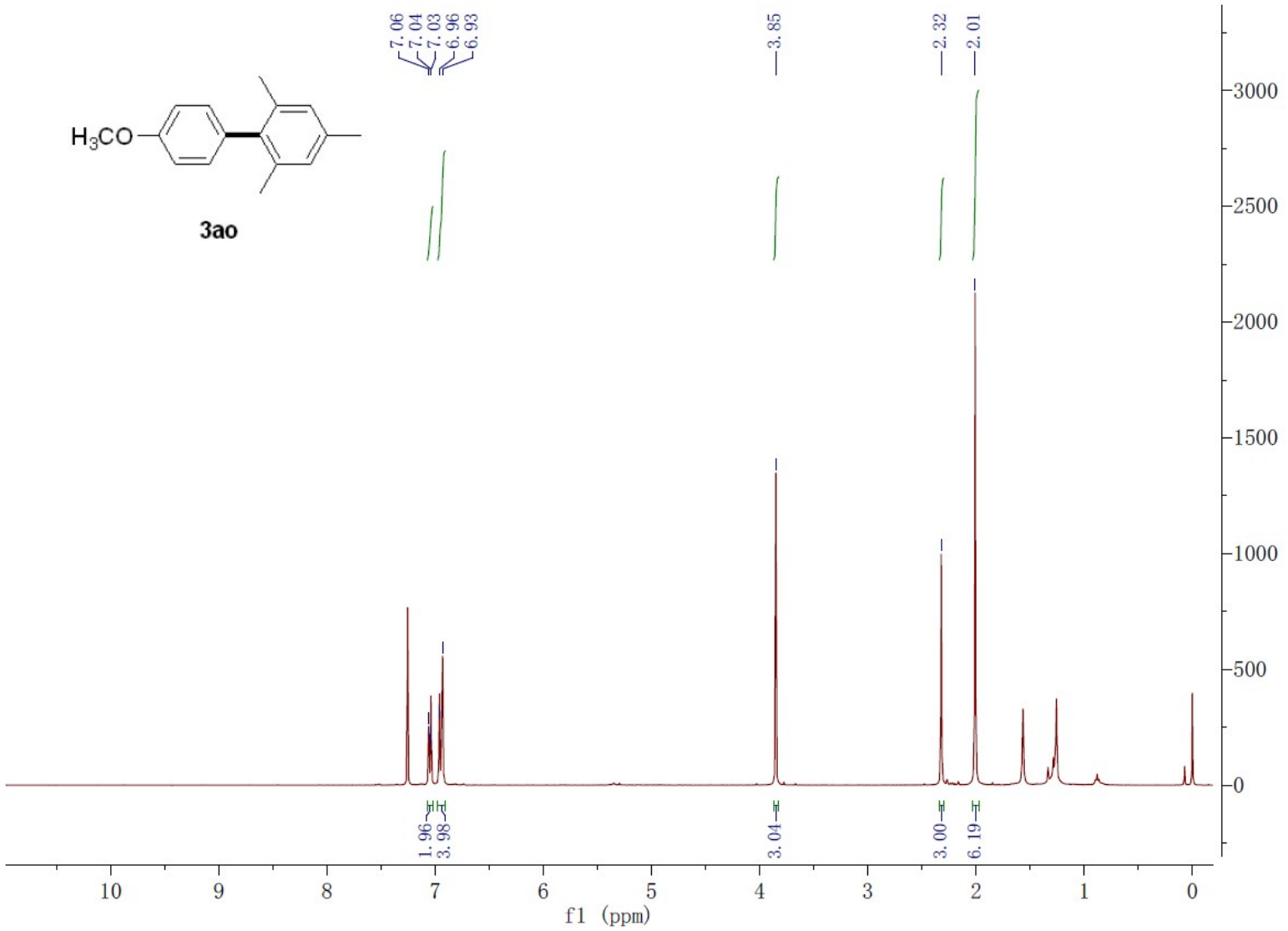

8.11
8.09
7.23
7.21
6.94
4.43
4.41
4.40
4.38
2.33
1.98
1.43
1.42
1.40
EtO2C
3aj
2.02
2.12
2.06
2.18
3.00
6.27
3.29
f1 (ppm)

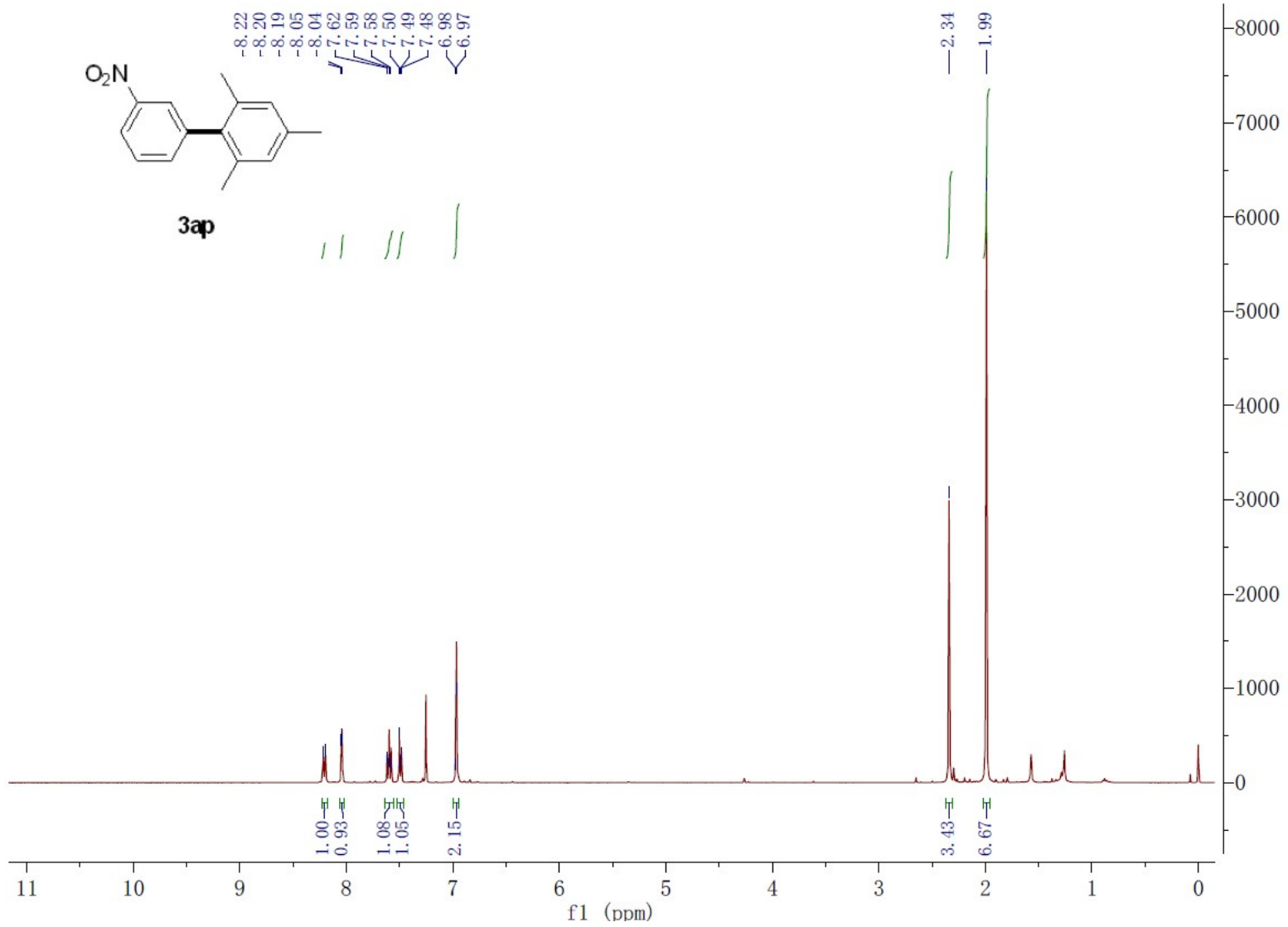

8.30
8.28
7.34
7.32
6.96
2.34
1.98
O2N
3ak
1.93
1.98
1.97
3.00
6.11
f1 (ppm)

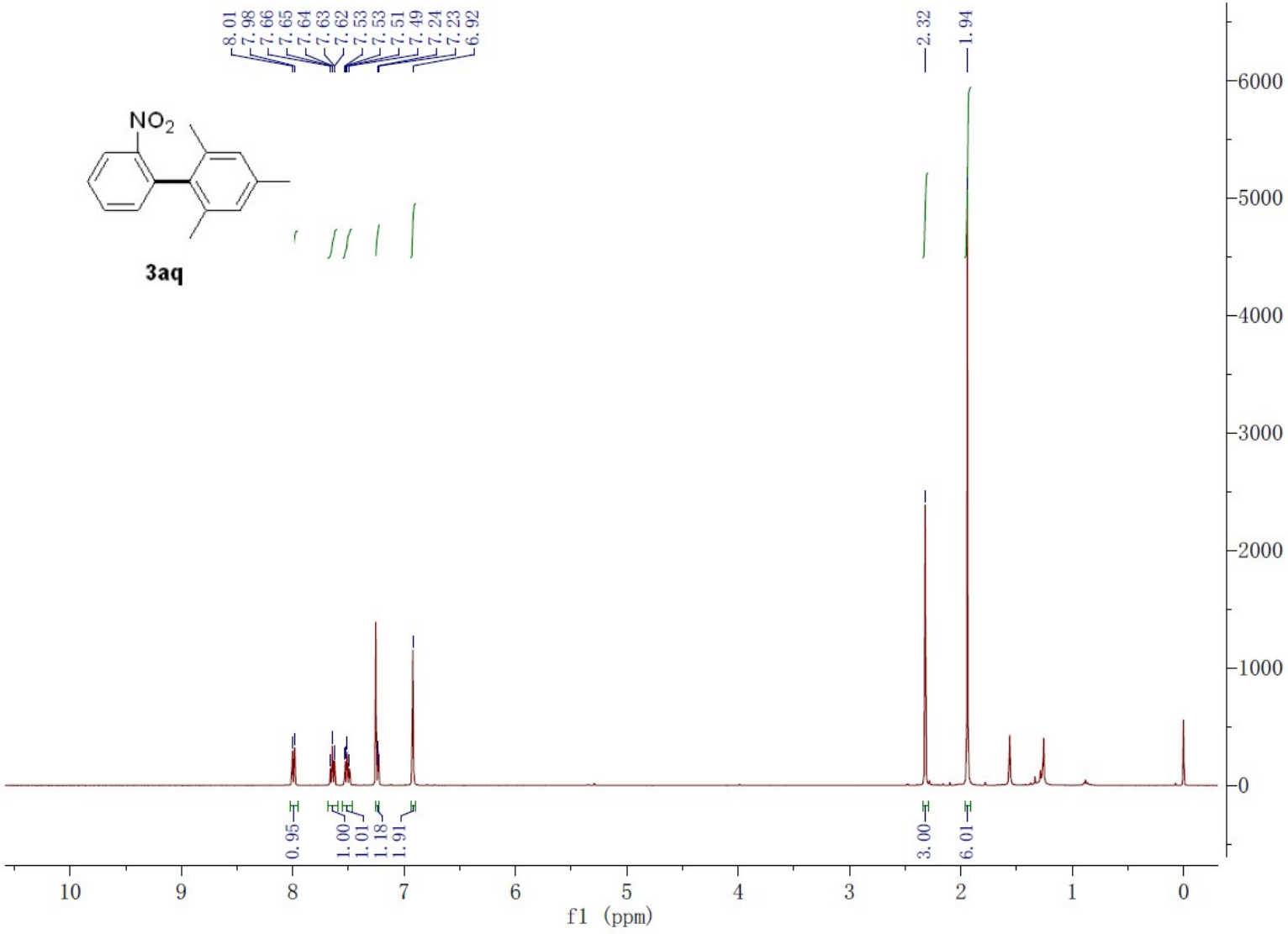

8.03
8.01
7.26
7.24
6.95
2.65
2.33
1.99
H3COC
3al
8000
7000
6000
5000
4000
3000
2000
1000
0
1.99
0.98
0.96
1.92
2.89
3.00
5.94
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

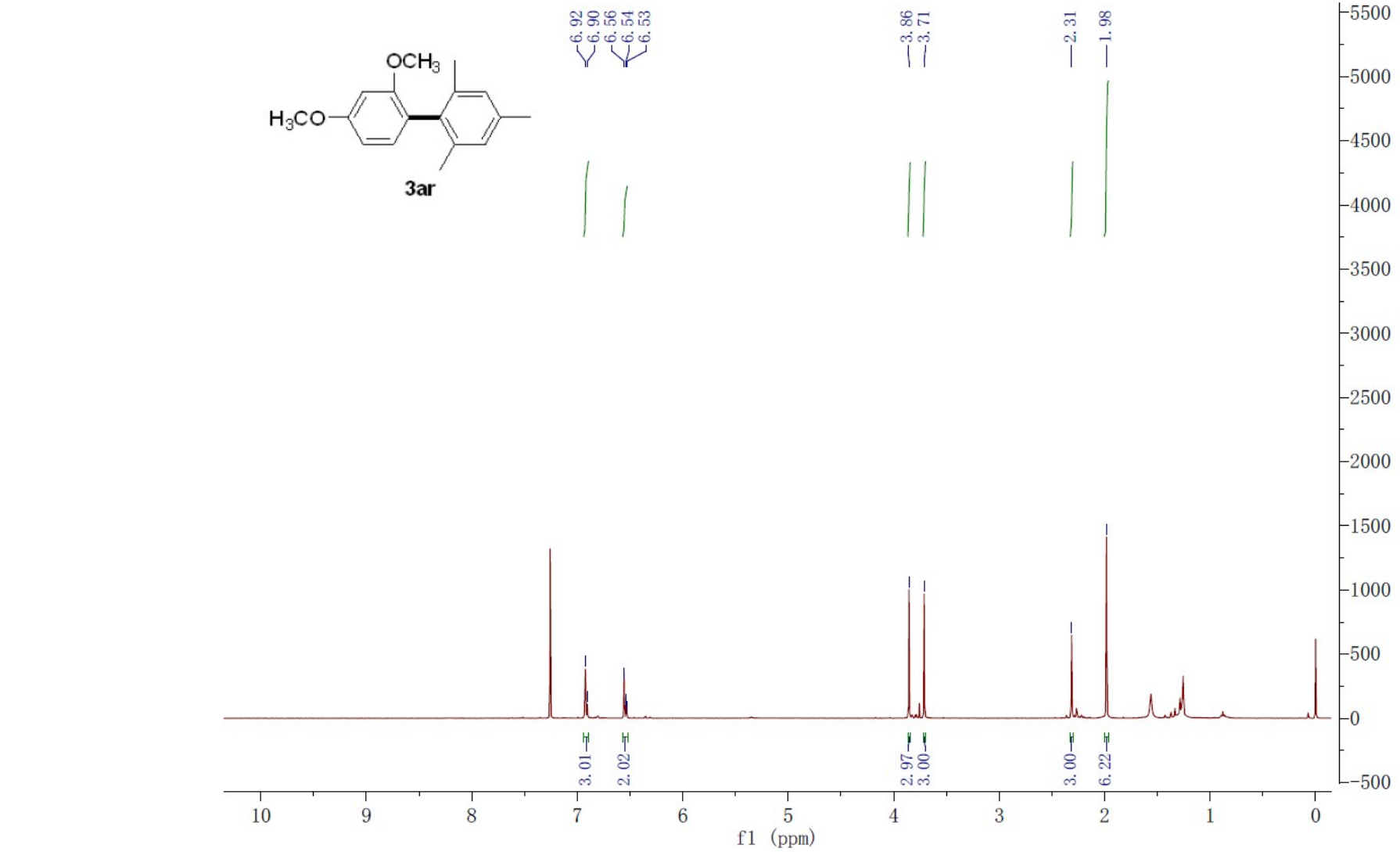

Cl
3am
7.39
7.37
7.08
7.06
6.93
2.32
1.99
1.98
2.00
1.95
3.00
6.12
f1 (ppm)

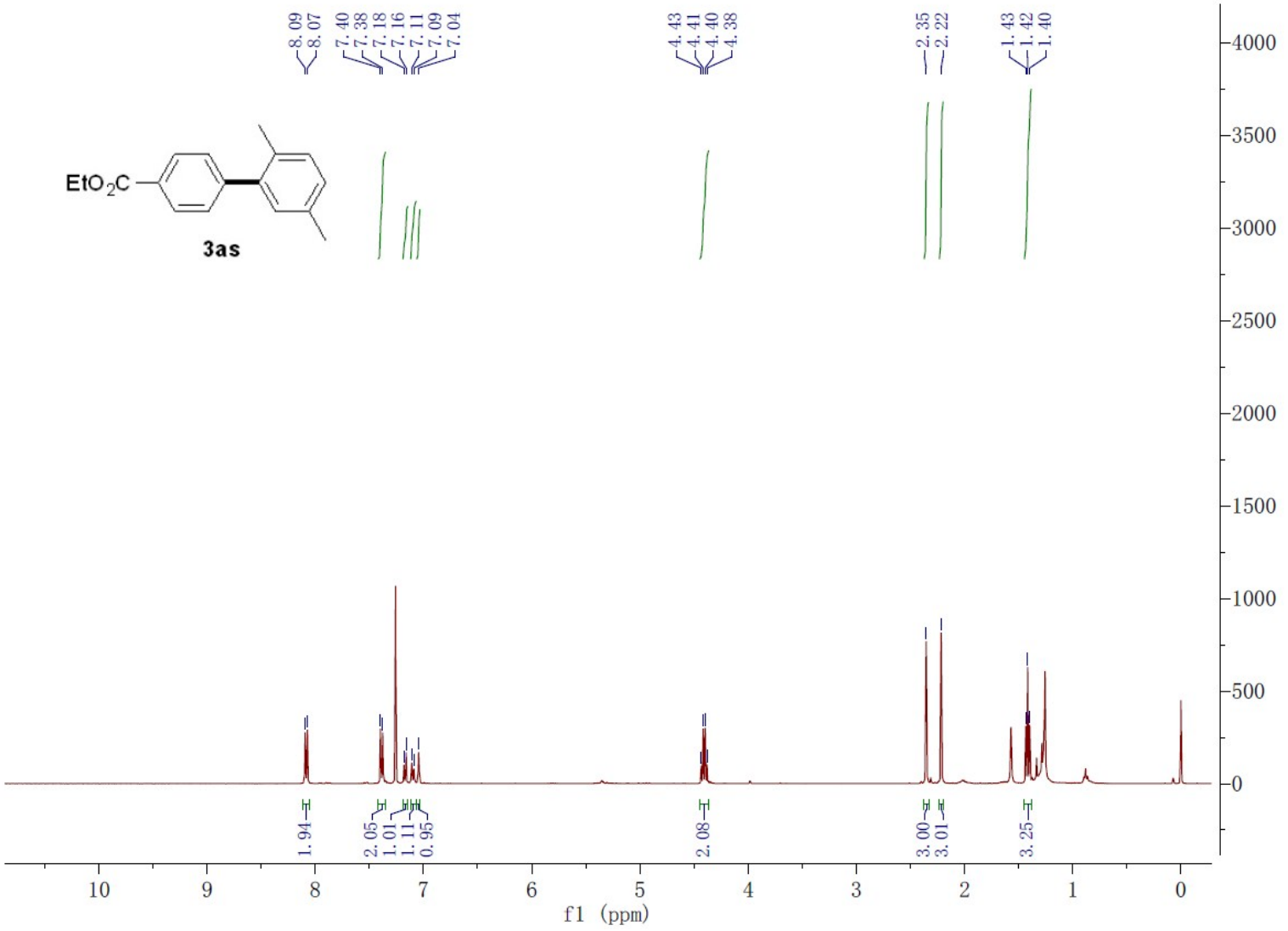

3an
7.22
7.20
7.03
7.01
6.93
2.40
2.32
2.00
1.99
1.92
1.85
3.00
2.91
6.00
f1 (ppm)

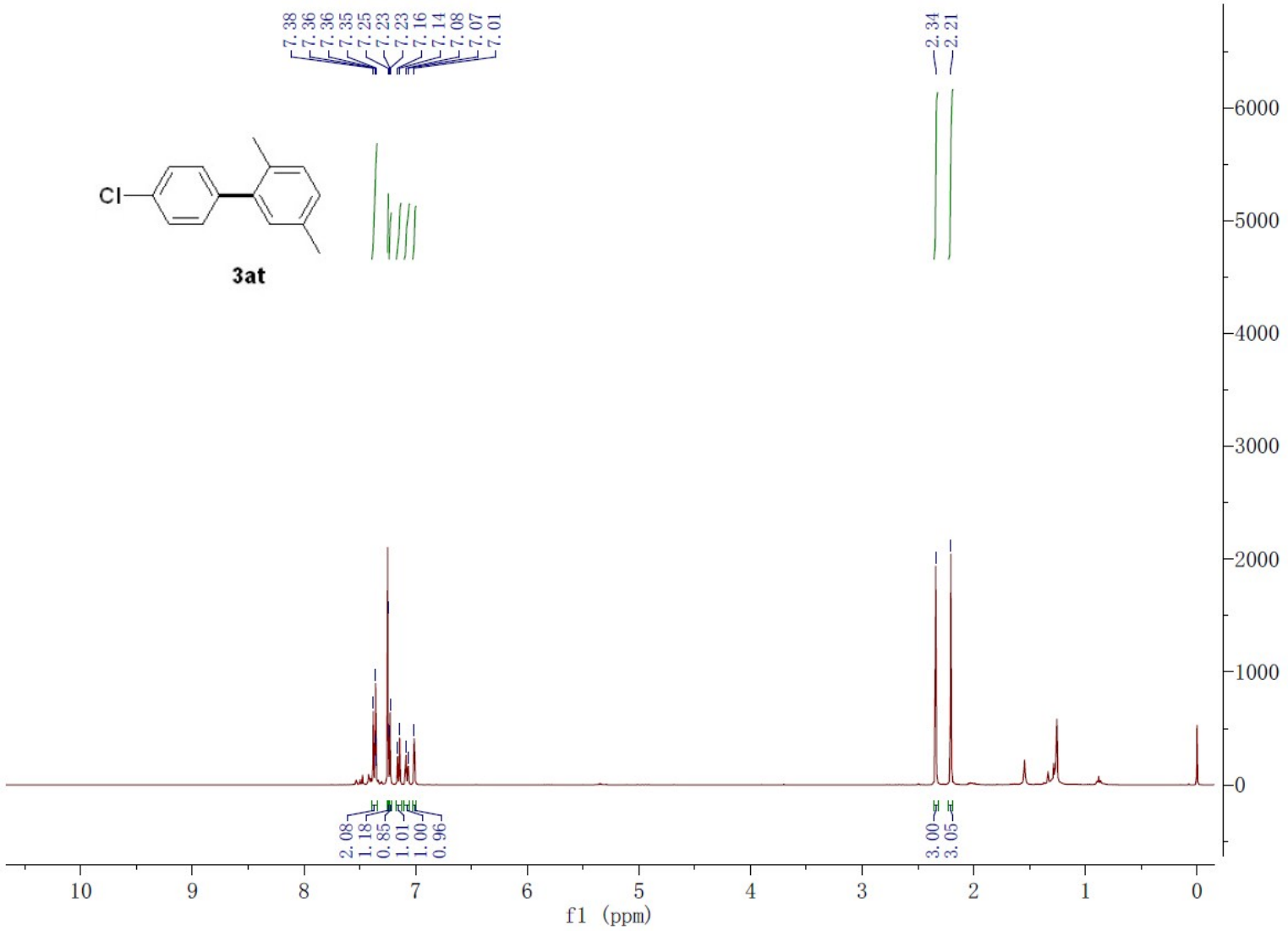

H3CO
3ao
7.06
7.04
7.03
6.96
6.93
3.85
2.32
2.01
1.96
3.98
3.04
3.00
6.19
f1 (ppm)

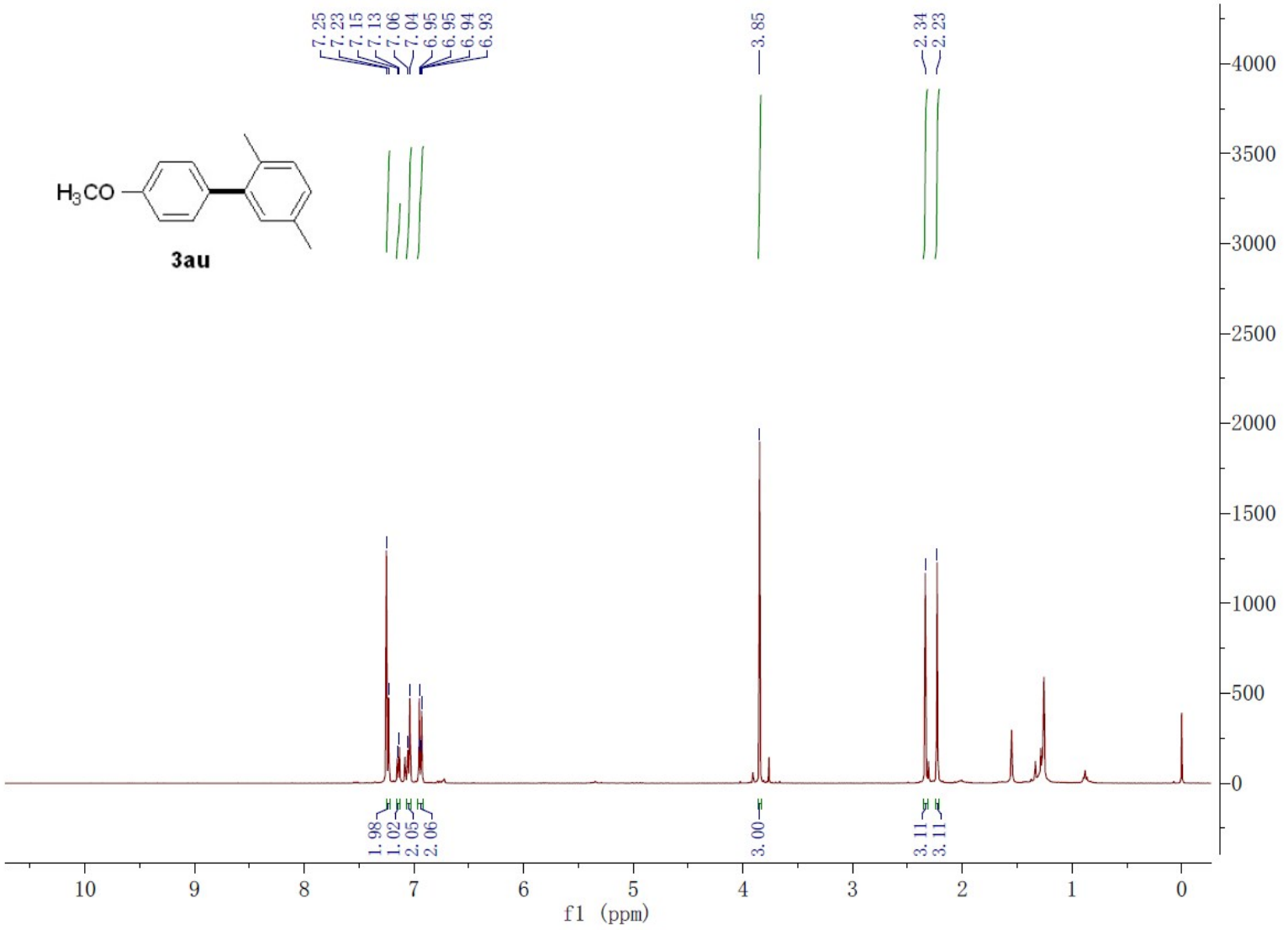

8.22
8.20
8.19
8.05
8.04
7.62
7.59
7.58
7.50
7.49
7.48
6.98
6.97
2.34
1.99
O2N
3ap
1.00
0.93
1.08
1.05
2.15
3.43
6.67
f1 (ppm)

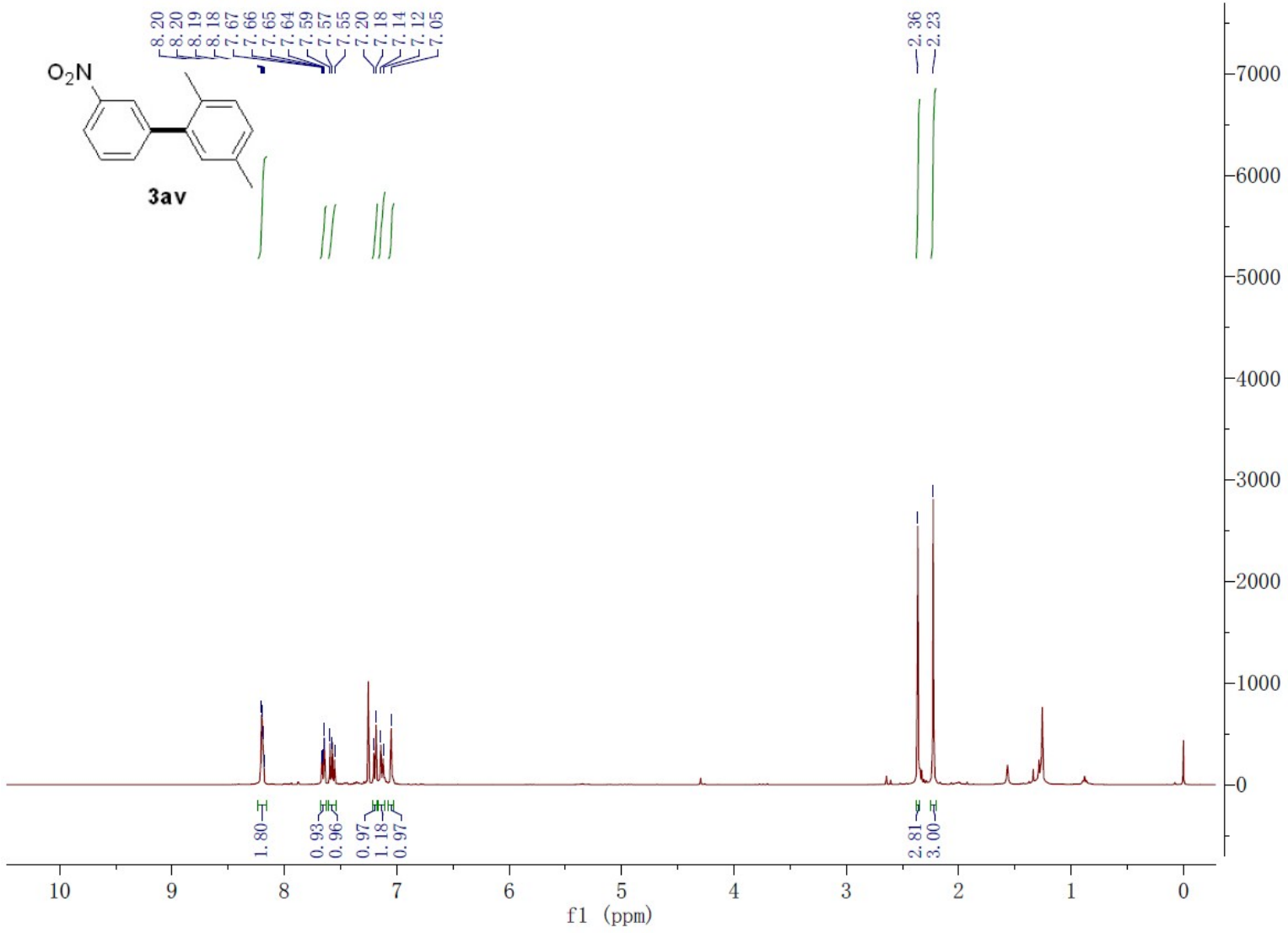

8.01
7.98
7.66
7.65
7.64
7.63
7.62
7.53
7.53
7.51
7.49
7.24
7.23
6.92
2.32
1.94
NO2
3aq
0.95
1.00
1.01
1.18
1.91
3.00
6.01
f1 (ppm)

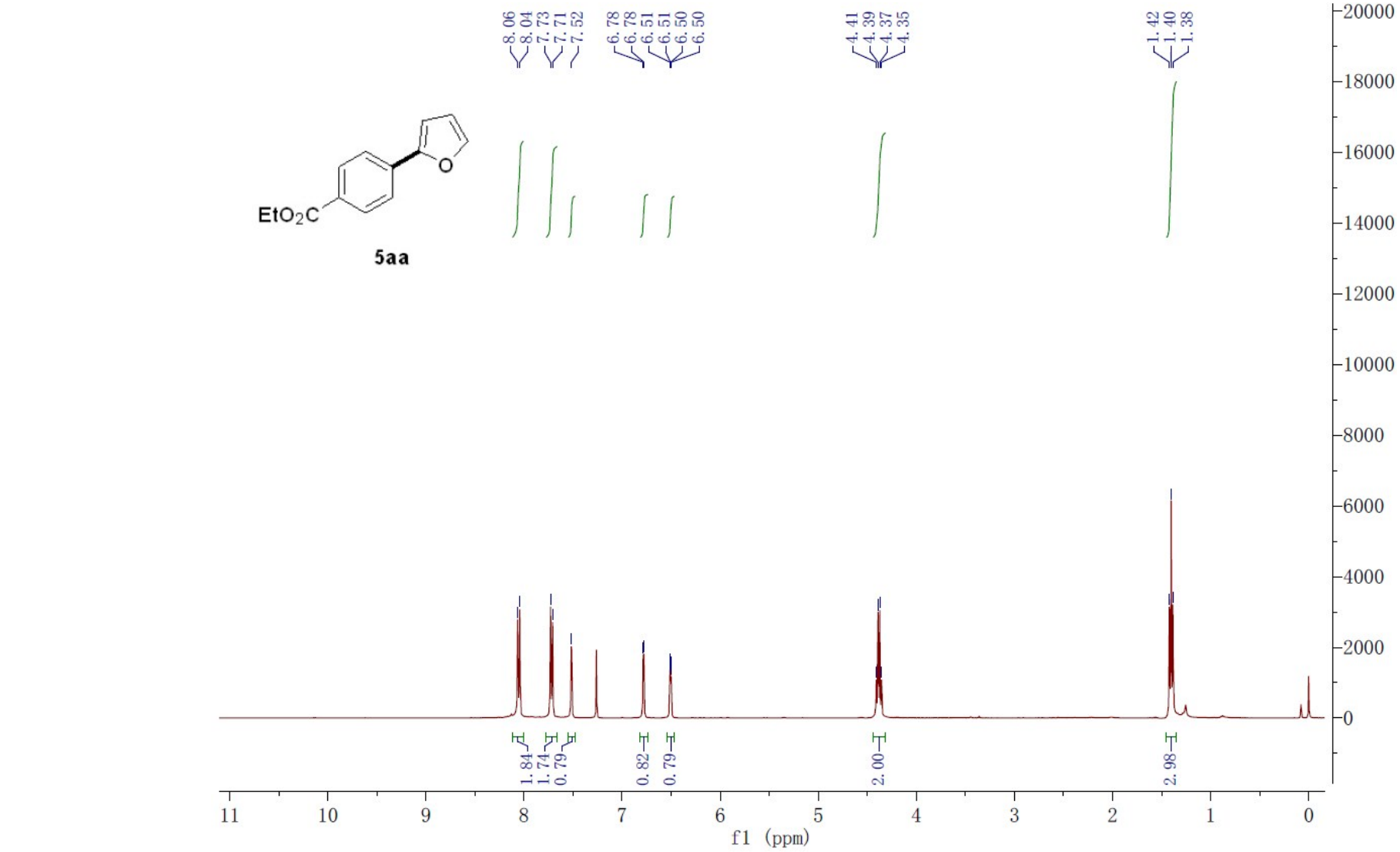

OCH3
H3CO
3ar
6.92
6.90
6.56
6.54
6.53
3.86
3.71
2.31
1.98
3.01
2.02
2.97
3.00
3.00
6.22
f1 (ppm)

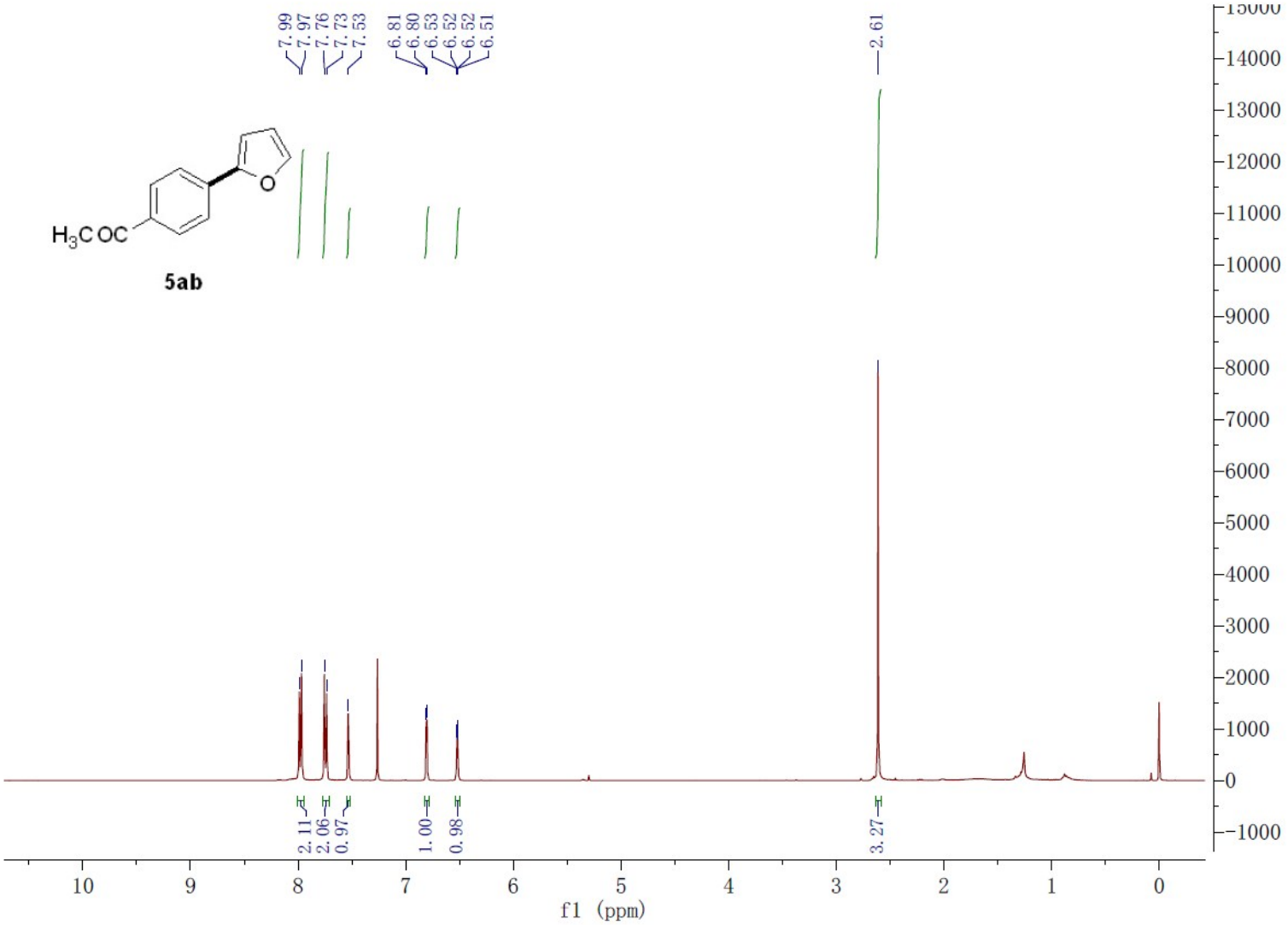

8.09
8.07
7.40
7.38
7.18
7.16
7.11
7.09
7.04
4.43
4.41
4.40
4.38
2.35
2.22
1.43
1.42
1.40
EtO2C
3as
1.94
2.05
1.01
1.11
0.95
2.08
3.00
3.01
3.25
f1 (ppm)

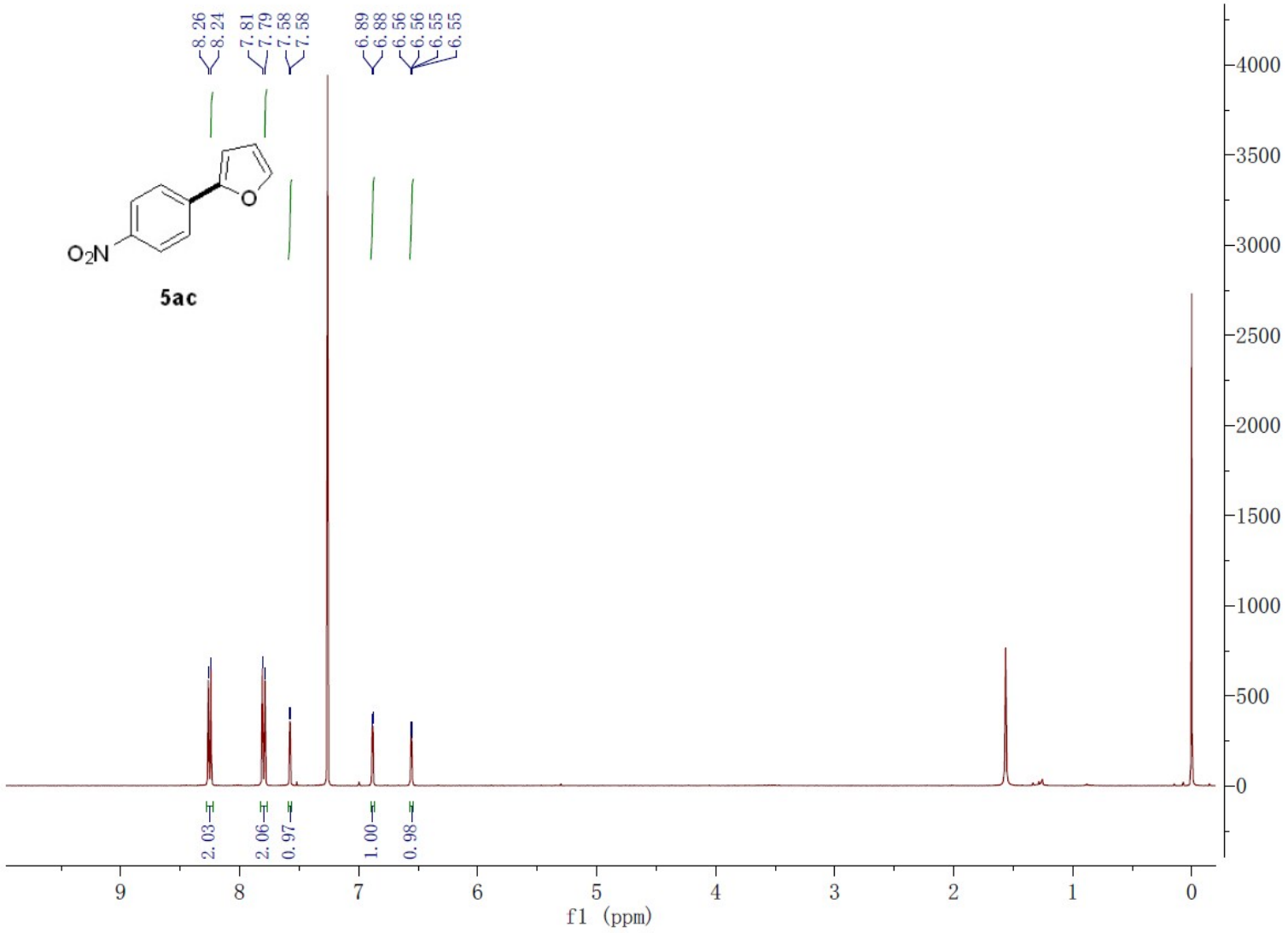

7.38
7.36
7.36
7.35
7.25
7.23
7.23
7.16
7.14
7.08
7.07
7.01
2.34
2.21
Cl
3at
6000
5000
4000
3000
2000
1000
0
2.08
1.18
0.85
1.01
1.00
0.96
3.00
3.05
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

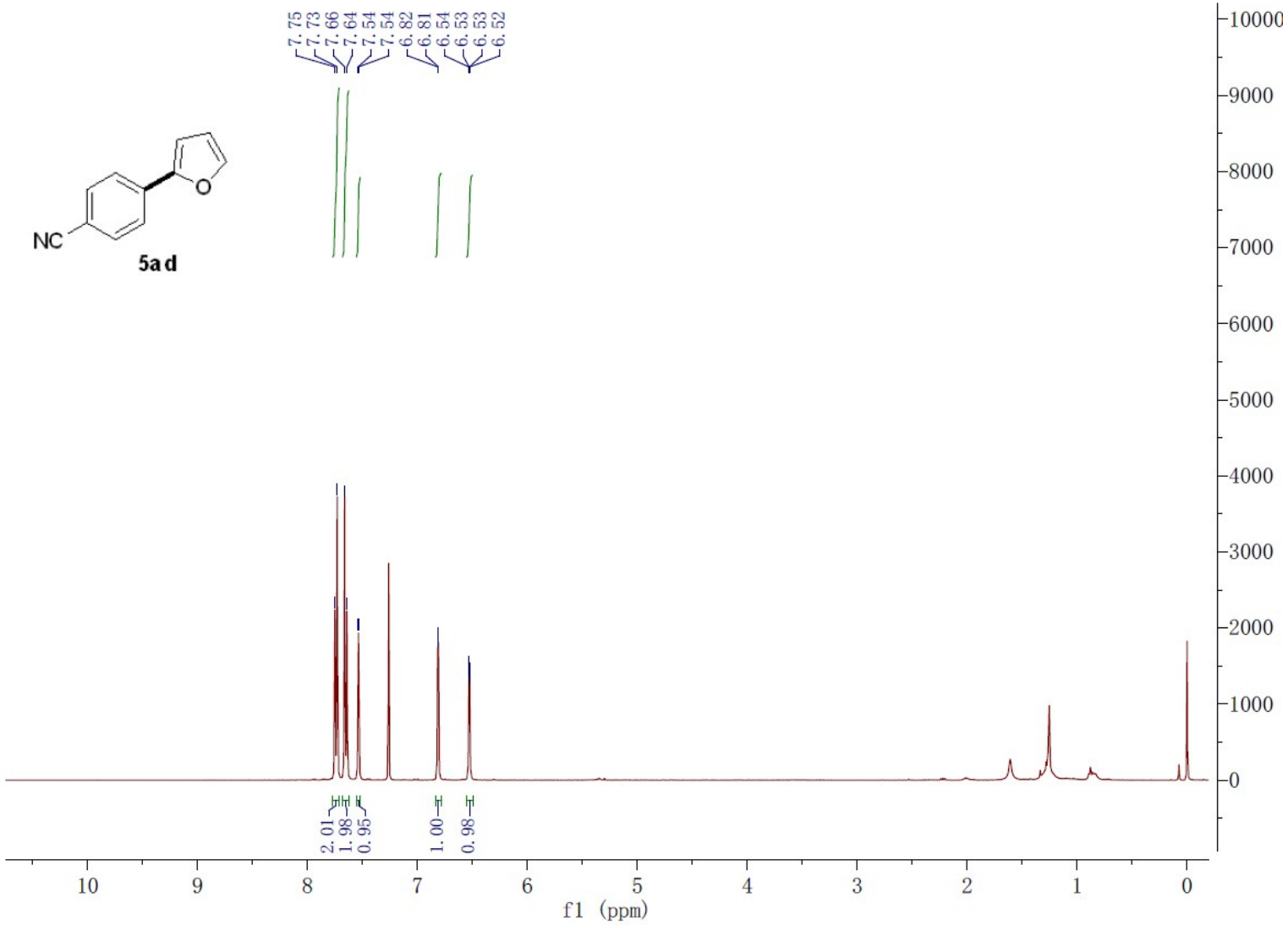

7.25
7.23
7.15
7.13
7.06
7.04
6.95
6.95
6.94
6.93
3.85
2.34
2.23
H3CO
3au
1.98
1.02
2.05
2.06
3.00
3.11
3.11
4000
3500
3000
2500
2000
1500
1000
500
0
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

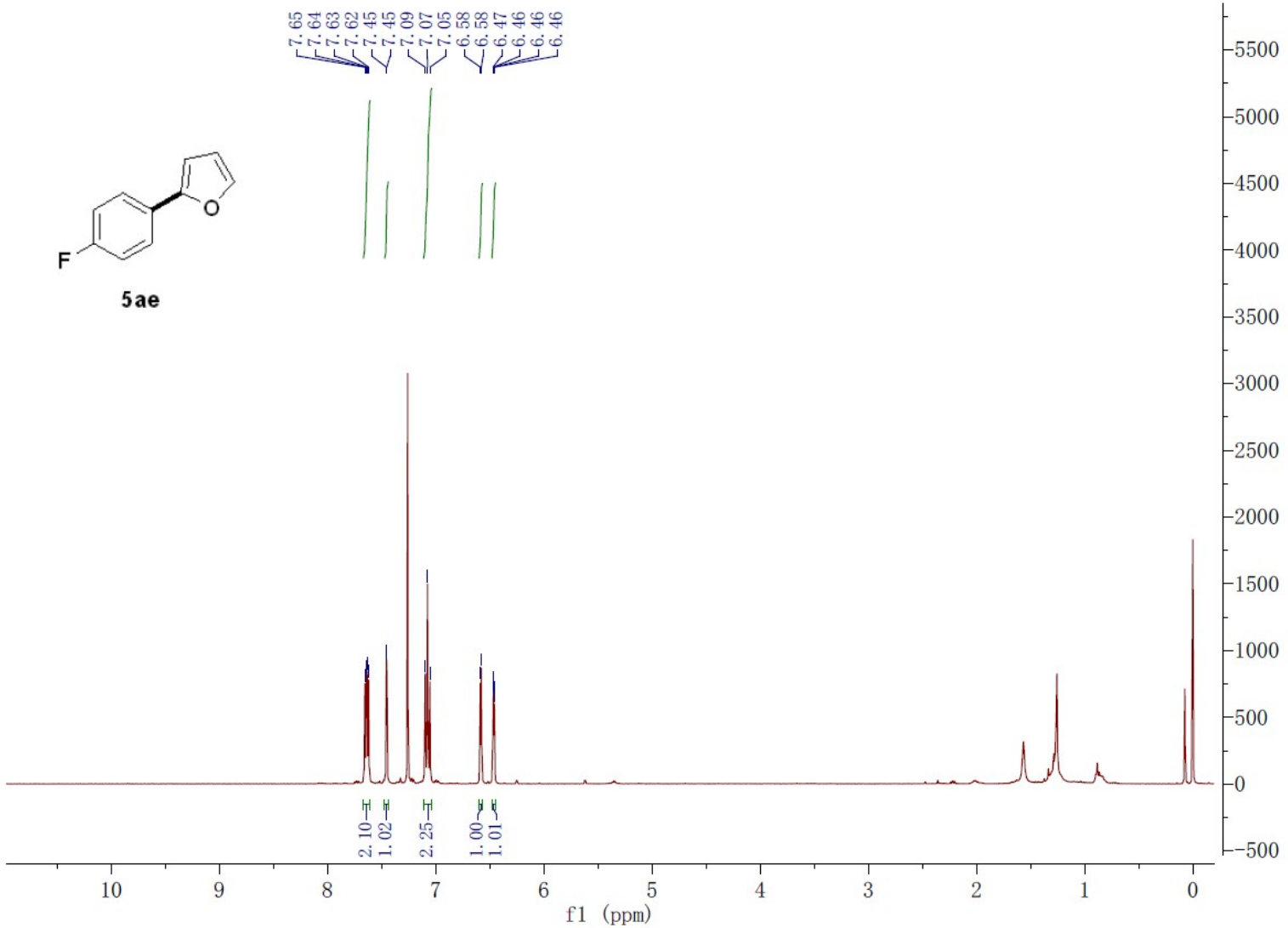

8.20
8.20
8.19
8.18
7.67
7.66
7.65
7.64
7.59
7.57
7.55
7.20
7.18
7.14
7.12
7.05
2.36
2.23
O2N
3av
7000
6000
5000
4000
3000
2000
1000
0
1.80
0.93
0.96
0.97
1.18
0.97
2.81
3.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

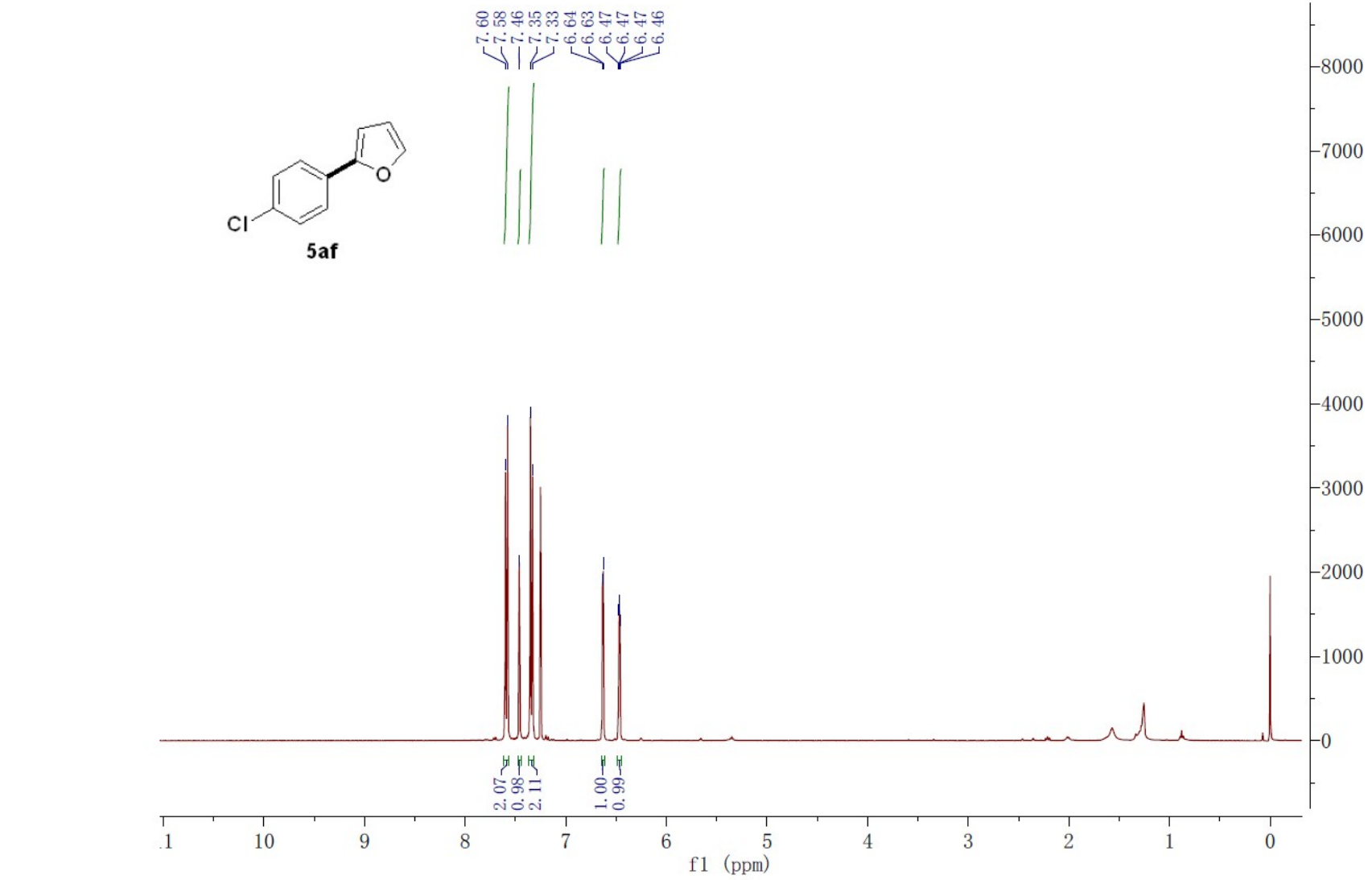

8.06
8.04
7.73
7.71
7.52
6.78
6.78
6.51
6.51
6.50
6.50
4.41
4.39
4.37
4.35
1.42
1.40
1.38
EtO2C
O
5aa
1.84
1.74
0.79
0.82
0.79
2.00
2.98
f1 (ppm)

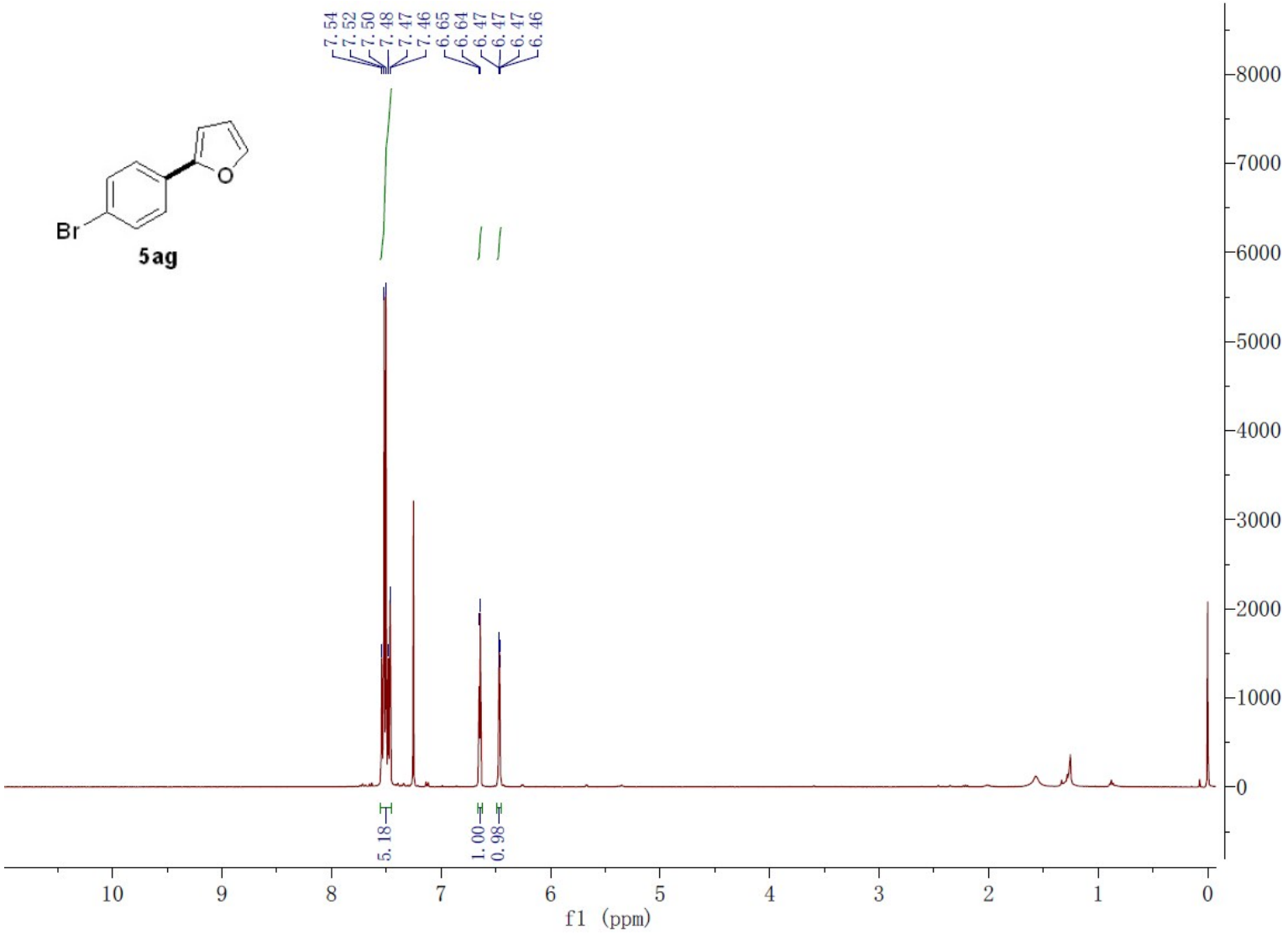

7.99
7.97
7.76
7.73
7.53
6.81
6.80
6.53
6.52
6.52
6.51
2.61
H3COC
O
5ab
2.11
2.06
0.97
1.00
0.98
3.27
f1 (ppm)

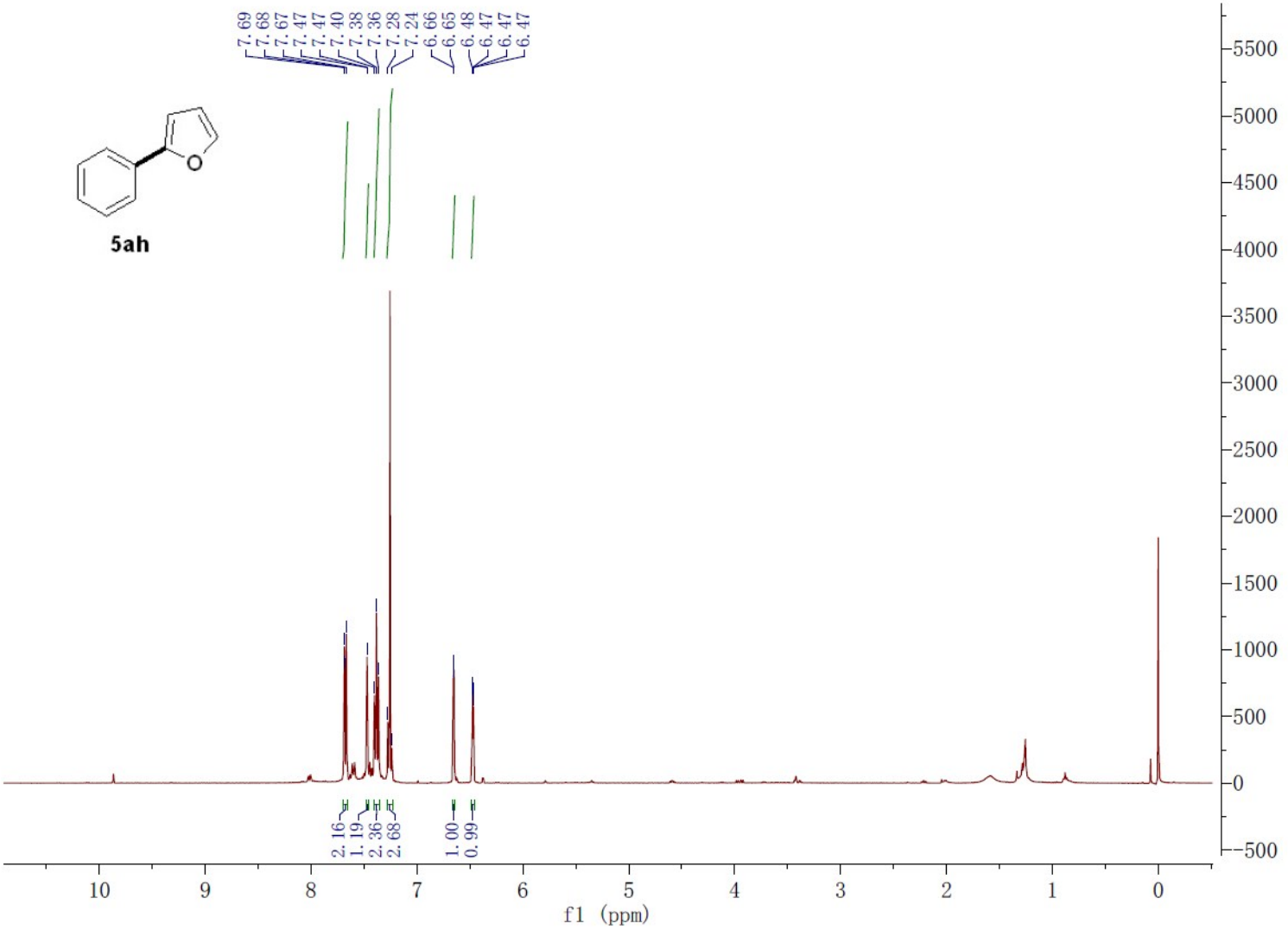

8.26
8.24
7.81
7.79
7.58
7.58
6.89
6.88
6.56
6.56
6.55
6.55
O2N
O
5ac
2.03
2.06
0.97
1.00
0.98
f1 (ppm)

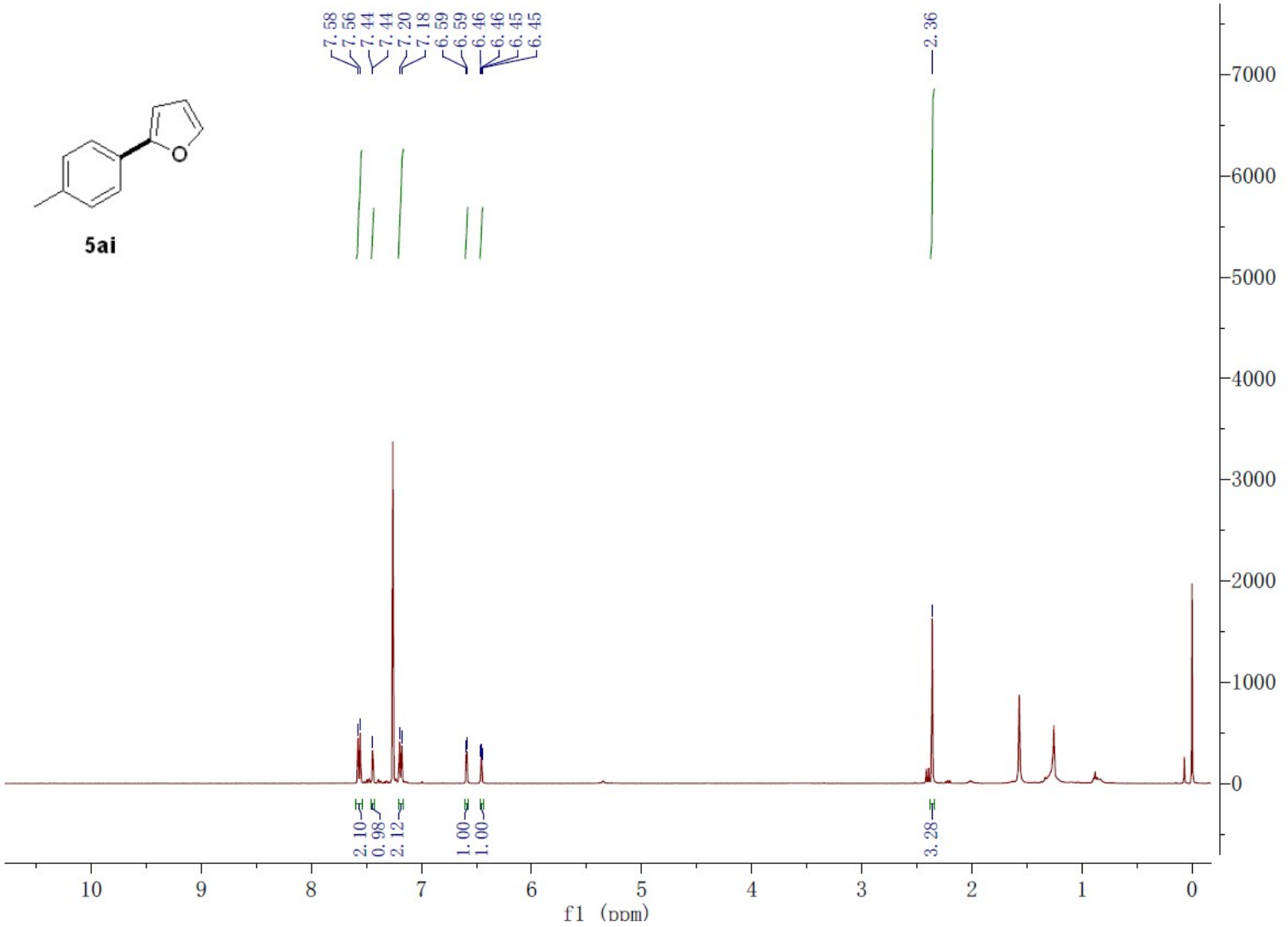

7.75
7.73
7.66
7.64
7.54
7.54
6.82
6.81
6.54
6.53
6.53
6.52
NC
O
5ad
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
2.01
1.98
0.95
1.00
0.98
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

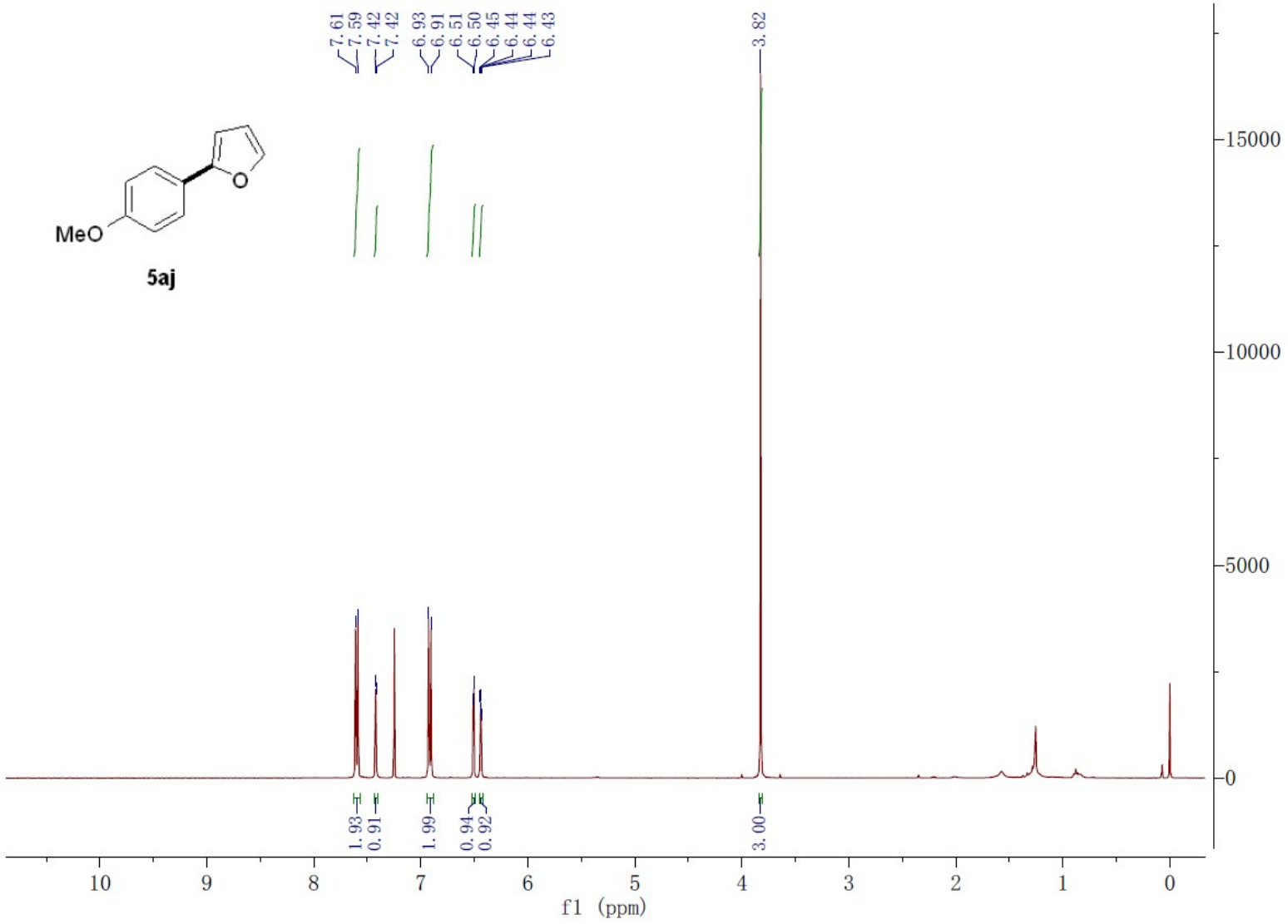

7.65
7.64
7.63
7.62
7.45
7.45
7.09
7.07
7.05
6.58
6.58
6.47
6.46
6.46
6.46
F
O
5ae
2.10
1.02
2.25
1.00
1.01
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

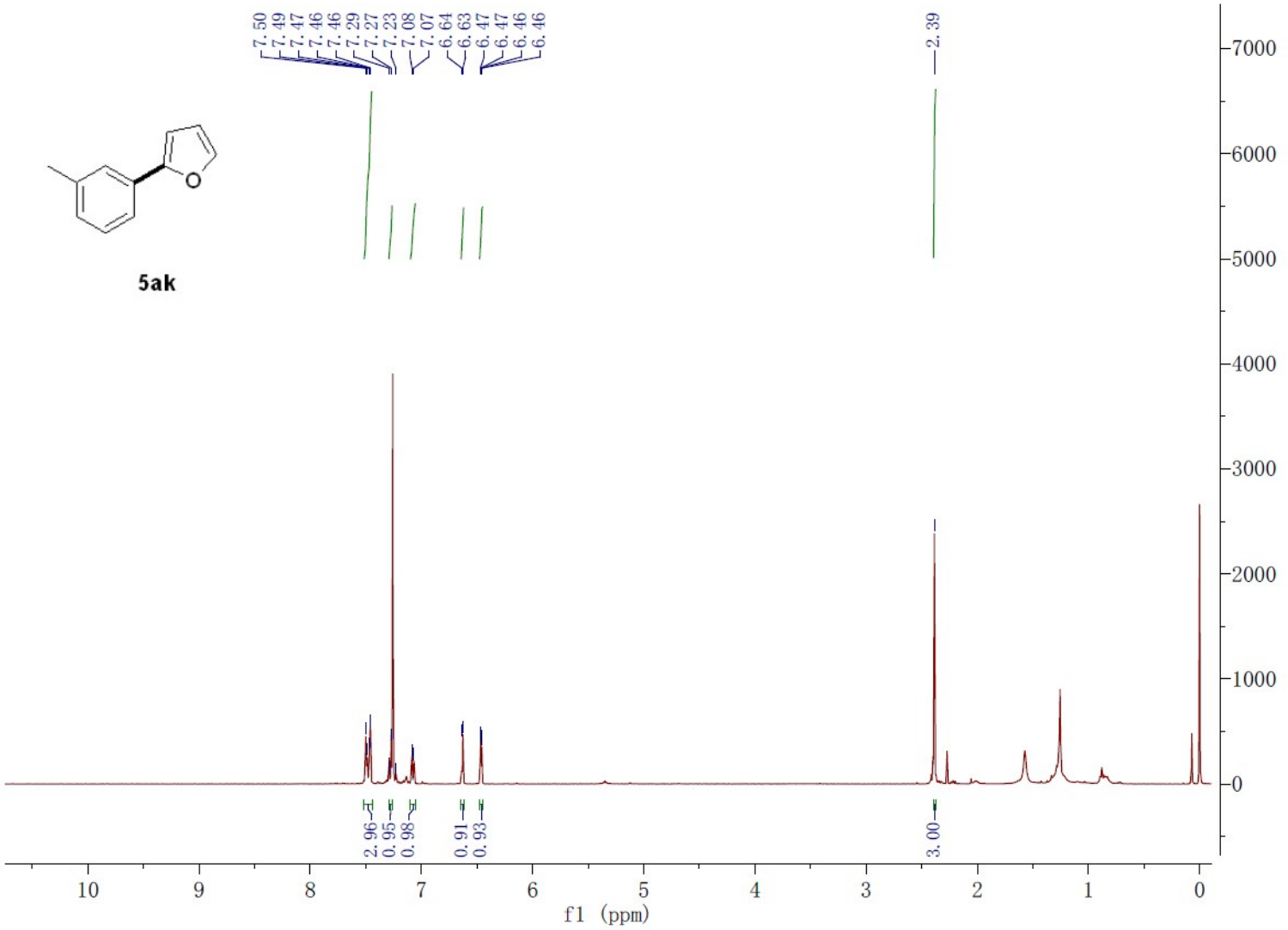

7.60
7.58
7.46
7.35
7.33
6.64
6.63
6.47
6.47
6.47
6.46
Cl
O
5af
8000
7000
6000
5000
4000
3000
2000
1000
0
2.07
0.98
2.11
1.00
0.99
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

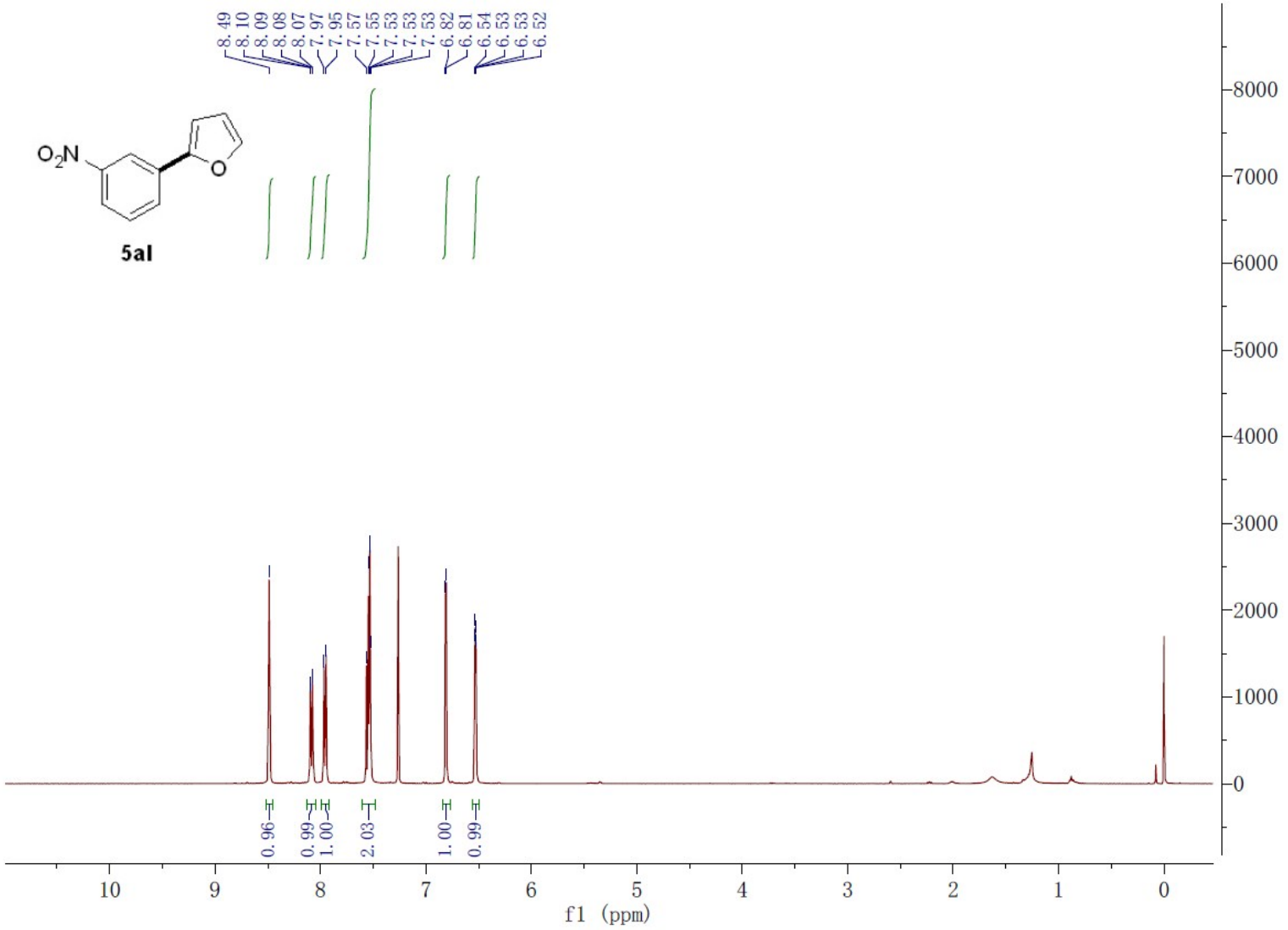

7.54
7.52
7.50
7.48
7.47
7.46
6.65
6.64
6.47
6.47
6.47
6.46
Br
O
5ag
8000
7000
6000
5000
4000
3000
2000
1000
0
5.18
1.00
0.98
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

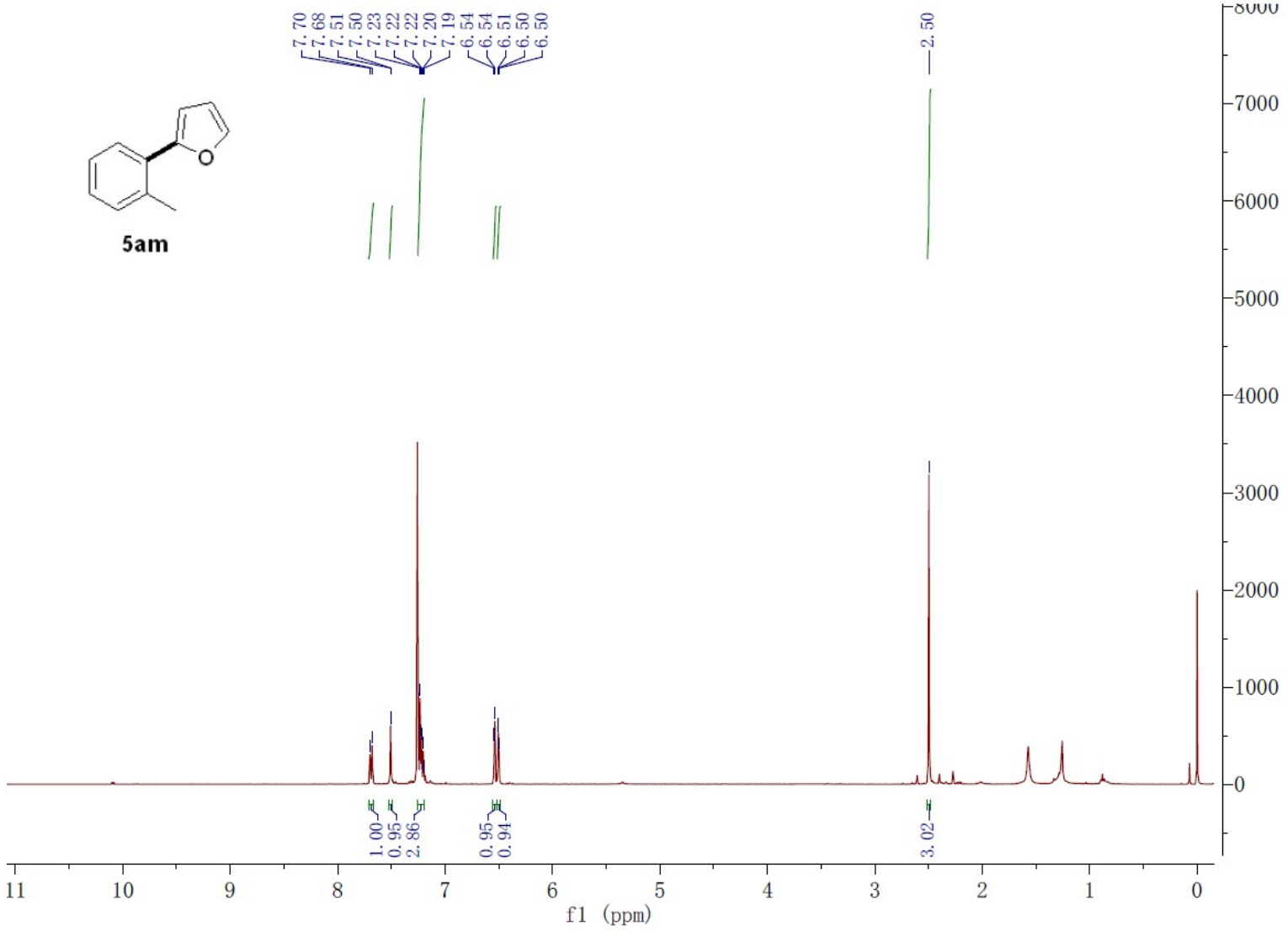

7.69
7.68
7.67
7.47
7.47
7.40
7.38
7.36
7.28
7.24
6.66
6.65
6.48
6.47
6.47
6.47
5ah
2.16
1.19
2.36
2.68
1.00
0.99
f1 (ppm)

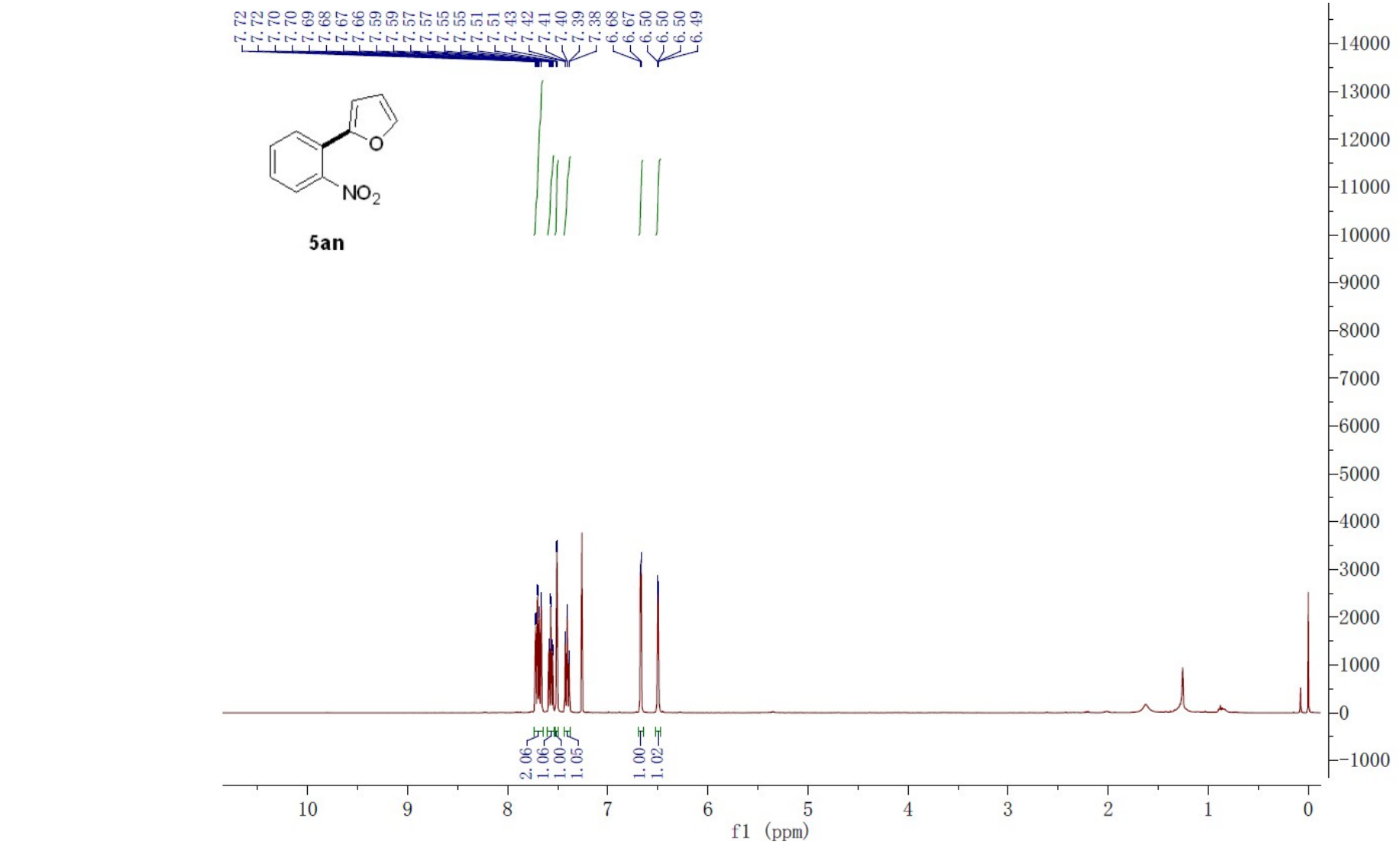

7.58
7.56
7.44
7.44
7.20
7.18
6.59
6.59
6.46
6.46
6.45
6.45
2.36
5ai
7000
6000
5000
4000
3000
2000
1000
0
2.10
0.98
2.12
1.00
1.00
3.28
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

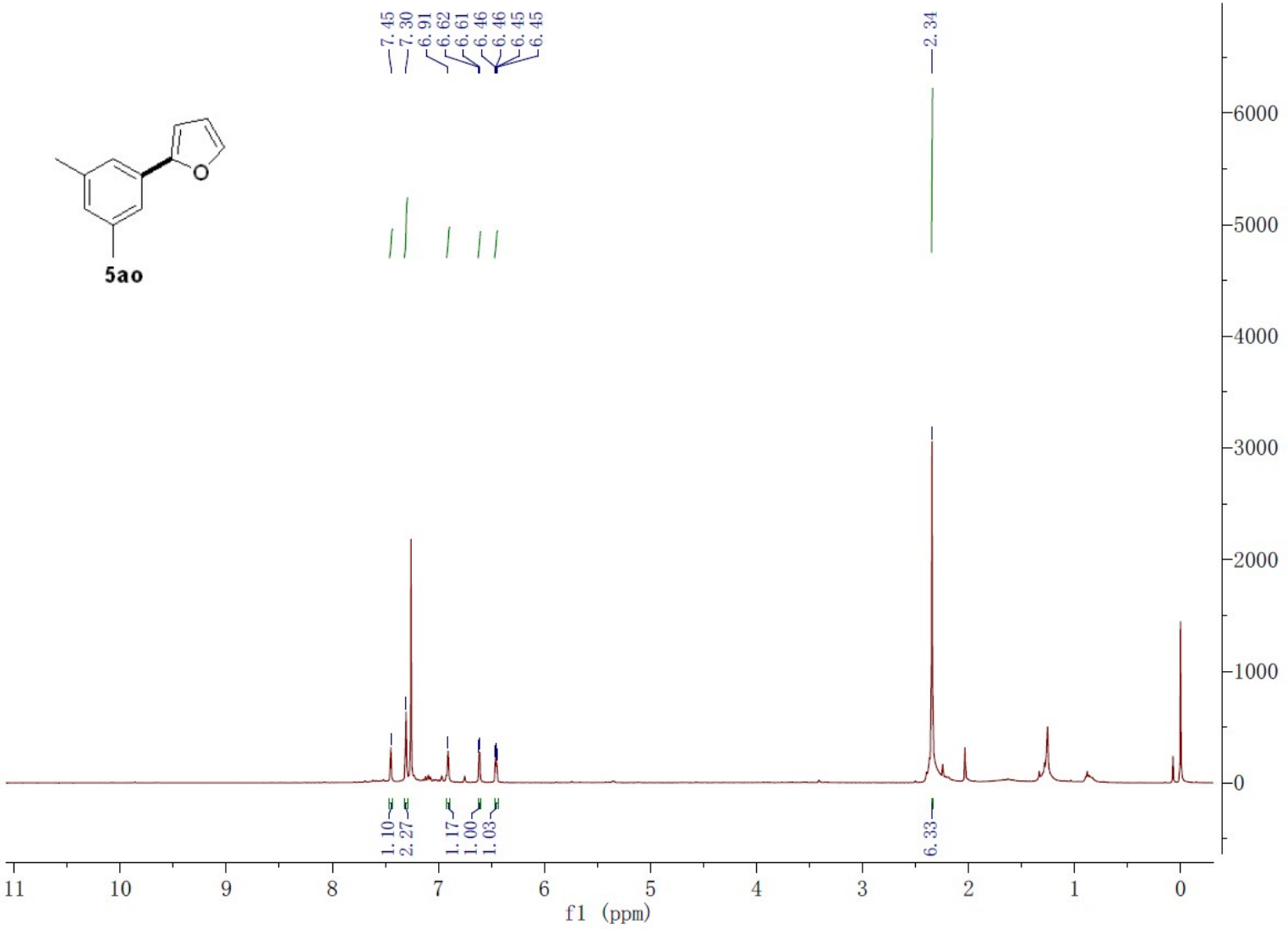

7.61
7.59
7.42
7.42
6.93
6.91
6.51
6.50
6.45
6.44
6.44
6.43
3.82
MeO
O
5aj
15000
10000
5000
0
1.93
0.91
1.99
0.94
0.92
3.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

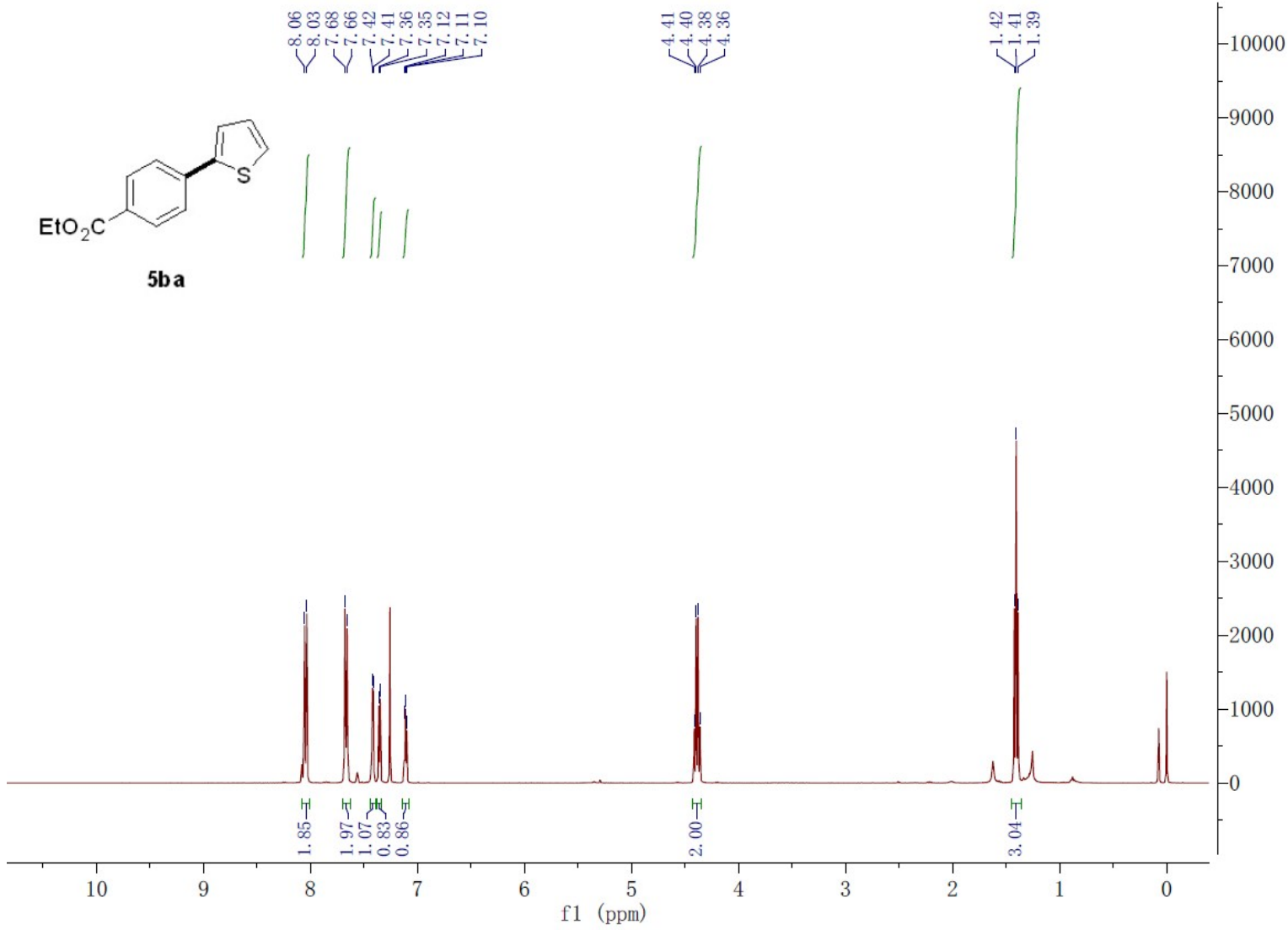

7.50
7.49
7.47
7.46
7.46
7.29
7.27
7.23
7.08
7.07
6.64
6.63
6.47
6.47
6.46
6.46
2.39
5ak
2.96
0.95
0.98
0.91
0.93
3.00
f1 (ppm)

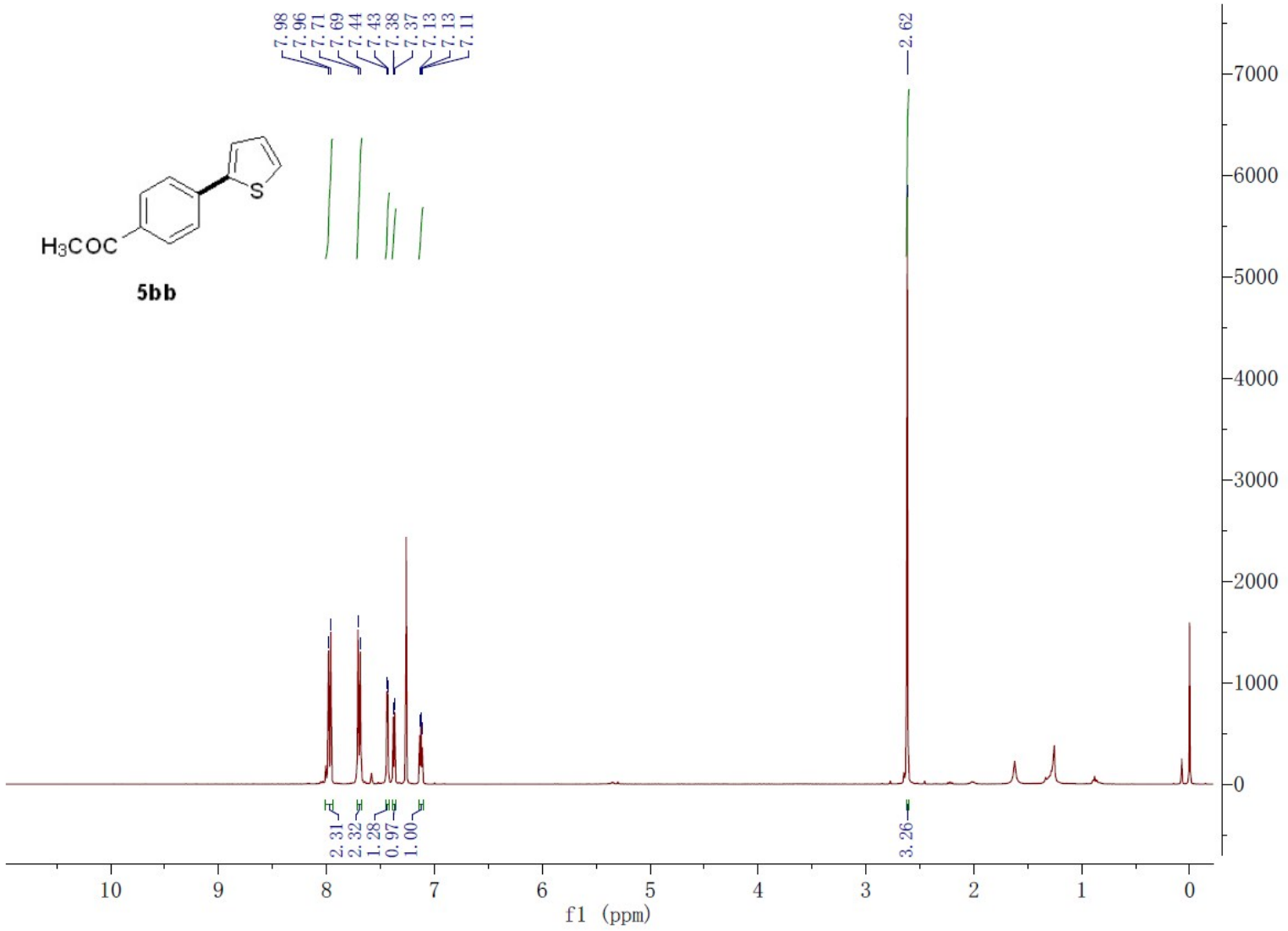

8.49
8.10
8.09
8.08
8.07
7.97
7.95
7.57
7.55
7.53
7.53
7.53
6.82
6.81
6.54
6.53
6.53
6.52
O2N
O
5al
8000
7000
6000
5000
4000
3000
2000
1000
0
0.96
0.99
1.00
2.03
1.00
0.99
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

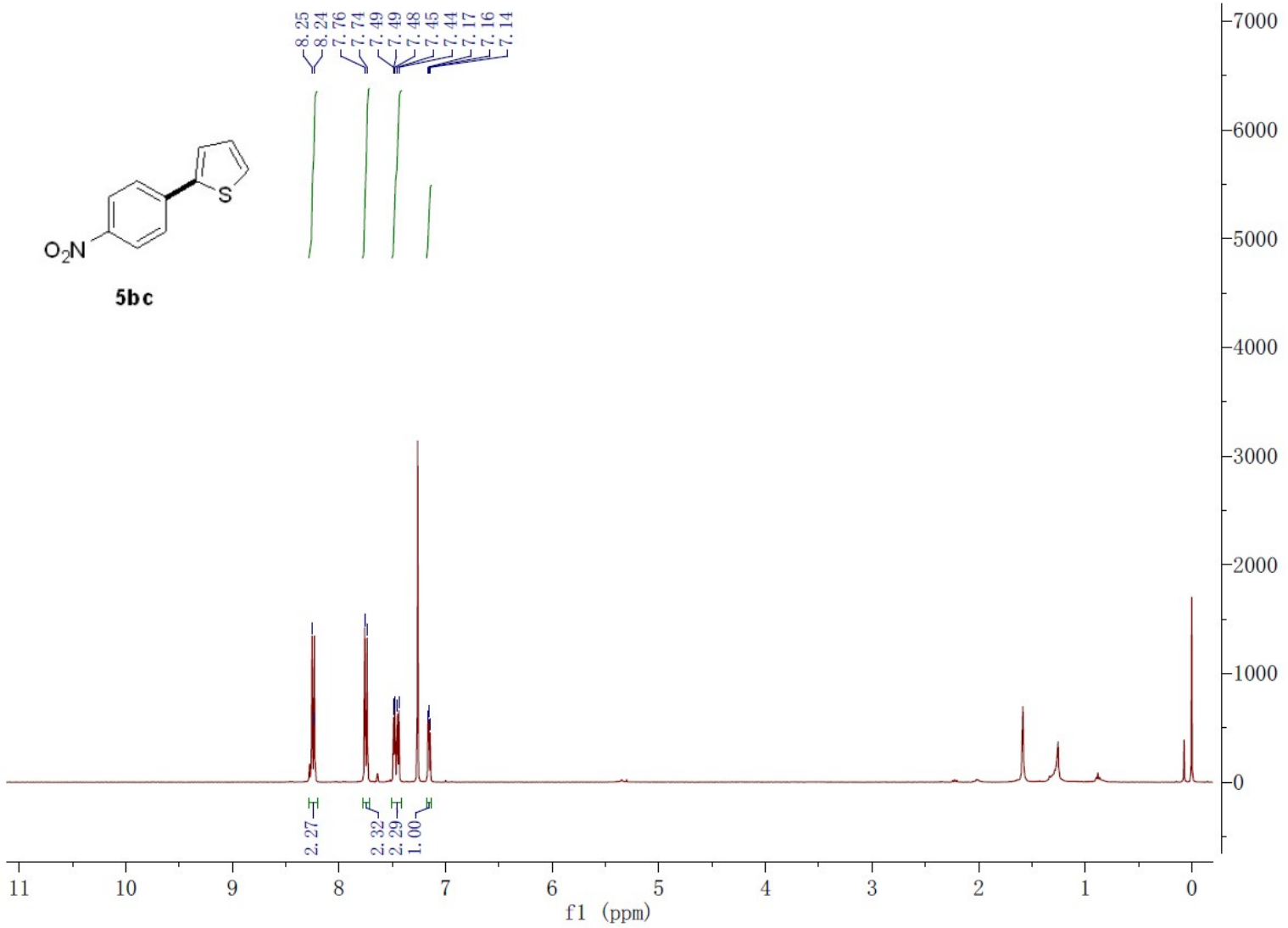

5am
7.70
7.68
7.51
7.50
7.23
7.22
7.22
7.20
7.19
6.54
6.54
6.51
6.50
6.50
2.50
1.00
0.95
2.86
0.95
0.94
3.02
f1 (ppm)

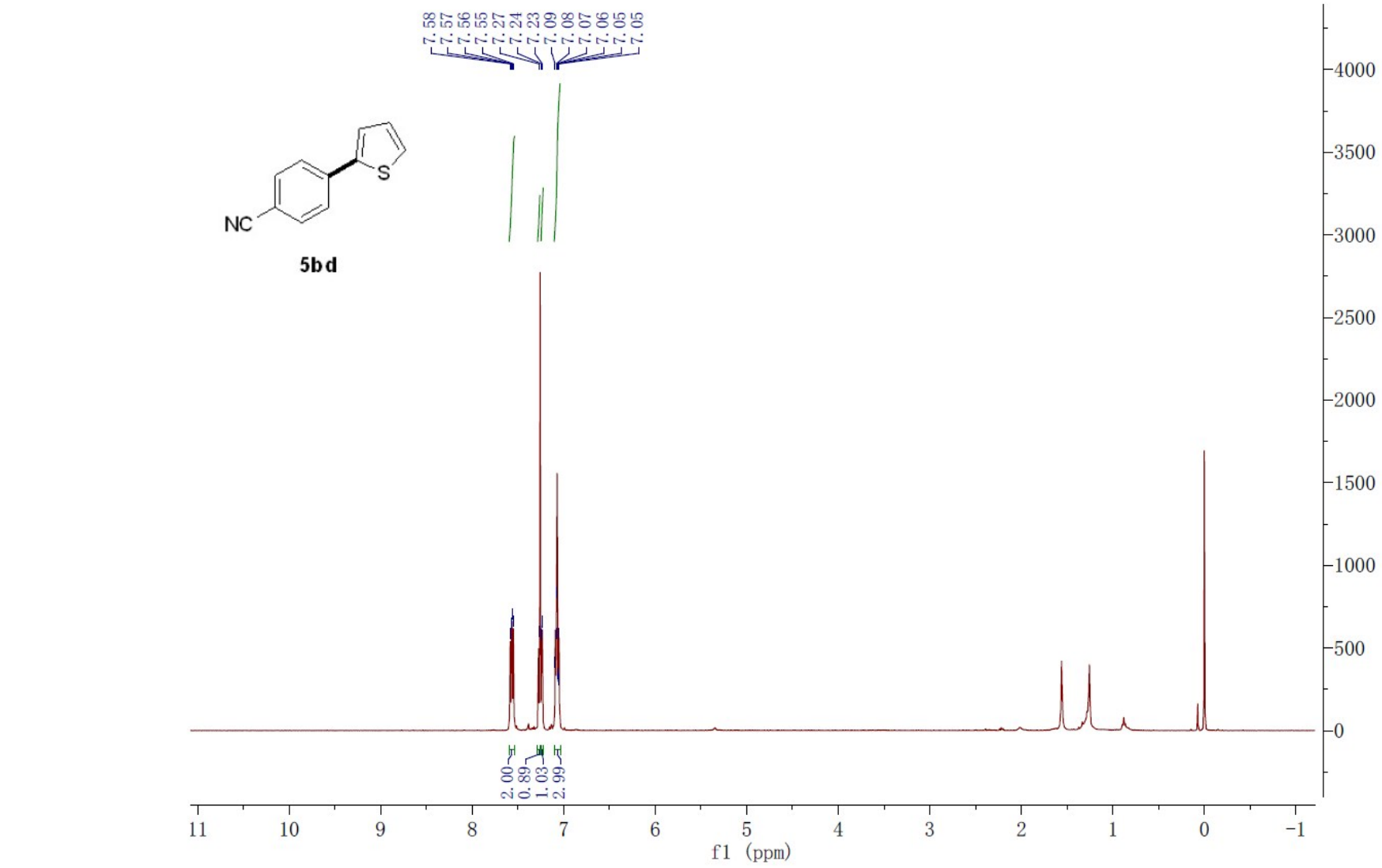

7.72
7.72
7.70
7.70
7.69
7.68
7.67
7.66
7.59
7.59
7.57
7.57
7.55
7.55
7.51
7.51
7.43
7.42
7.41
7.40
7.39
7.38
6.68
6.67
6.50
6.50
6.50
6.49
O
NO2
5an
2.06
1.06
1.00
1.05
1.00
1.02
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

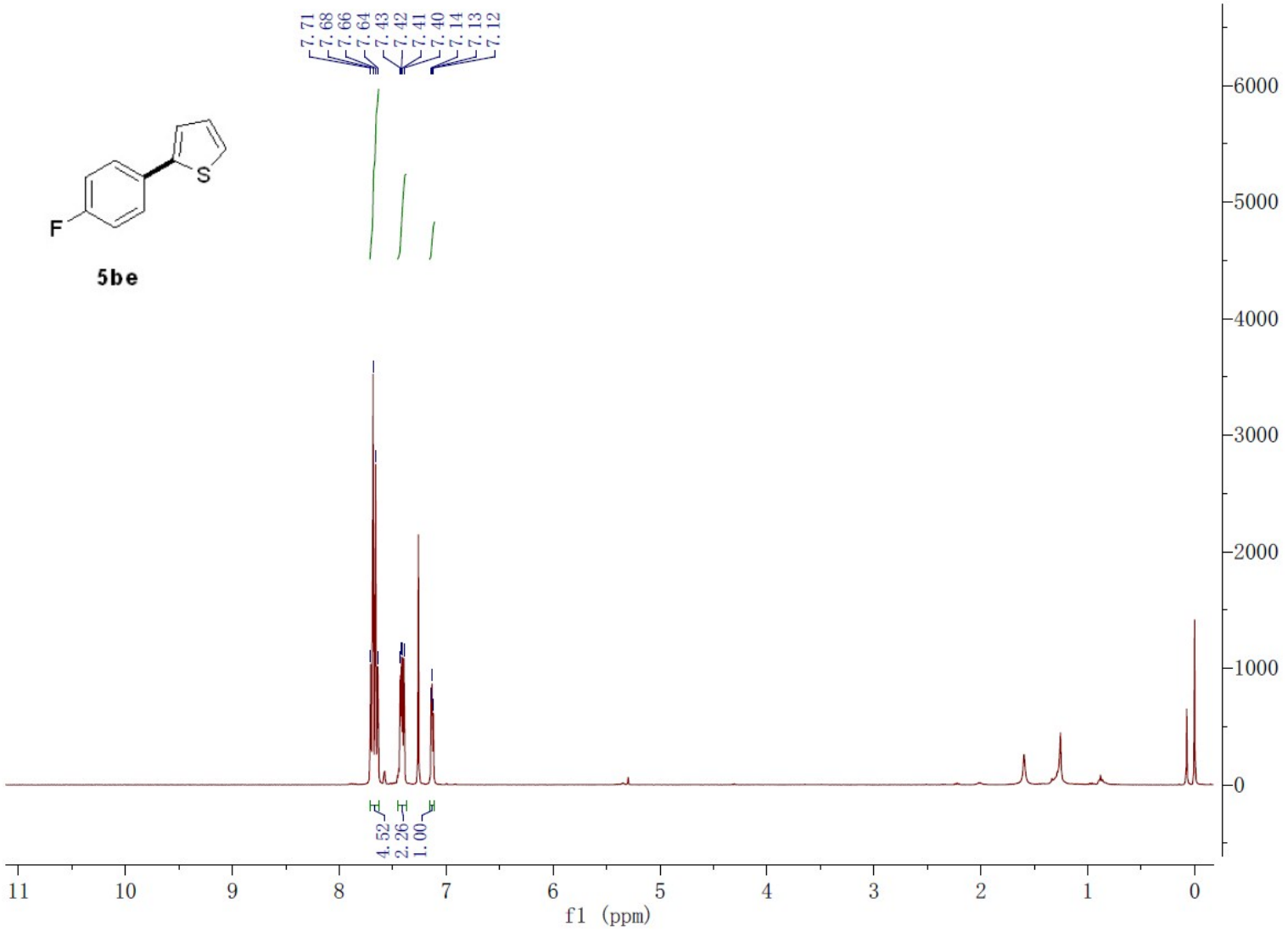

7.45
7.30
6.91
6.62
6.61
6.46
6.46
6.45
6.45
2.34
5ao
6000
5000
4000
3000
2000
1000
0
1.10
2.27
1.17
1.00
1.03
6.33
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

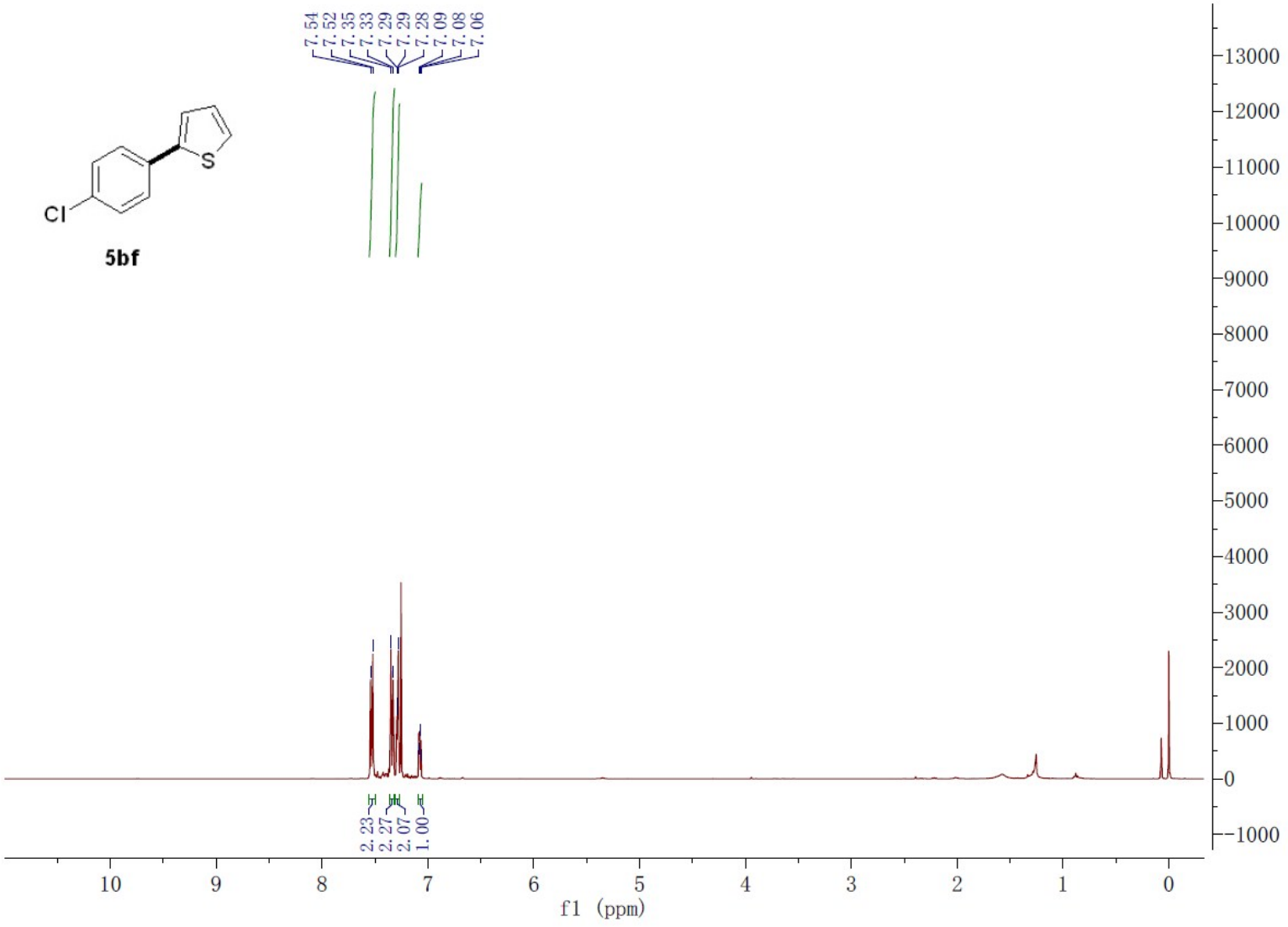

8.06
8.03
7.68
7.66
7.42
7.41
7.36
7.35
7.12
7.11
7.10
4.41
4.40
4.38
4.36
1.42
1.41
1.39
EtO2C
S
5ba
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
1.85
1.97
1.07
0.83
0.86
2.00
3.04
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

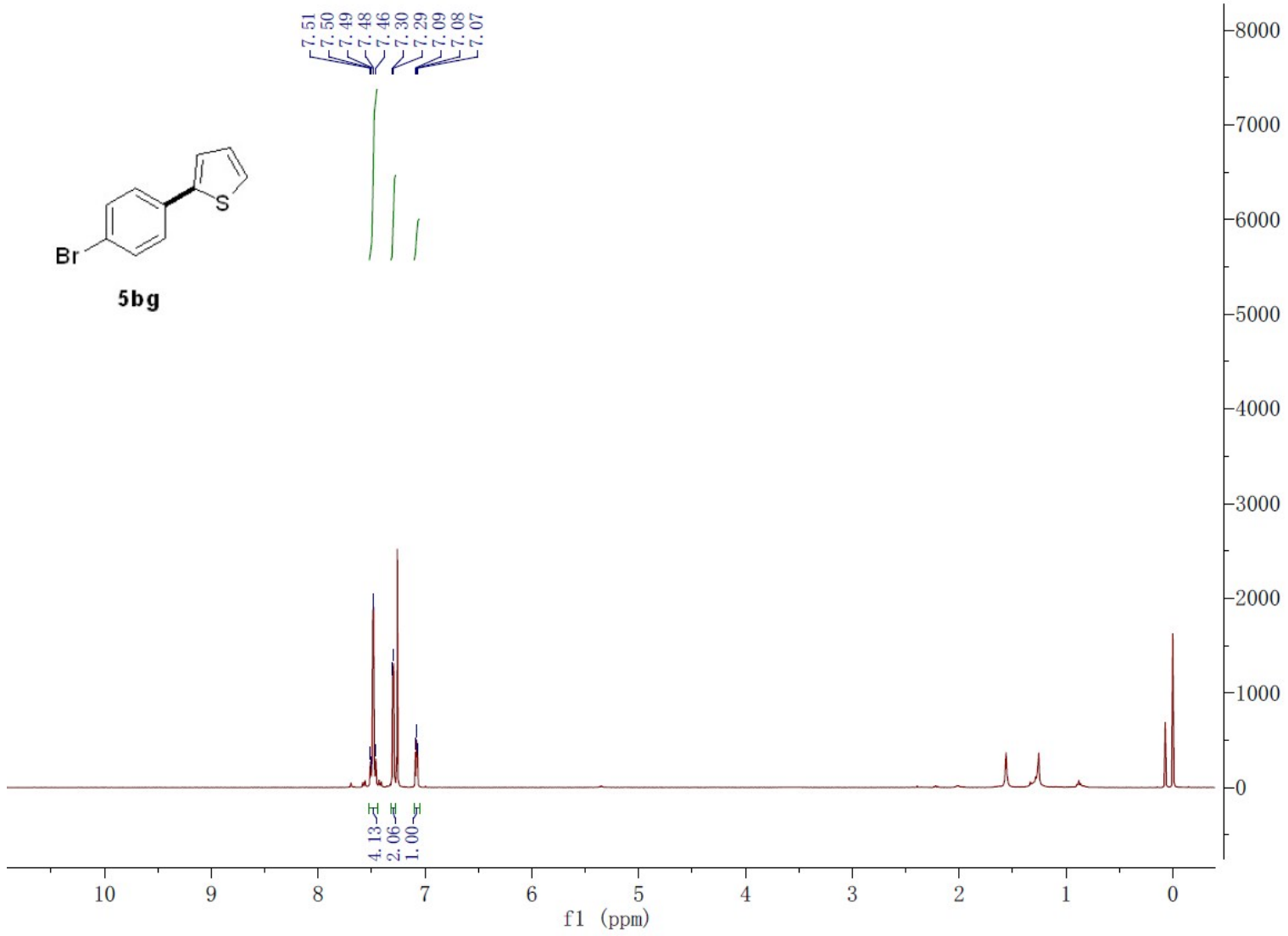

7.98
7.96
7.71
7.69
7.44
7.43
7.38
7.37
7.13
7.11
2.62
H3COC
S
5bb
2.31
2.32
1.28
0.97
1.00
3.26
f1 (ppm)

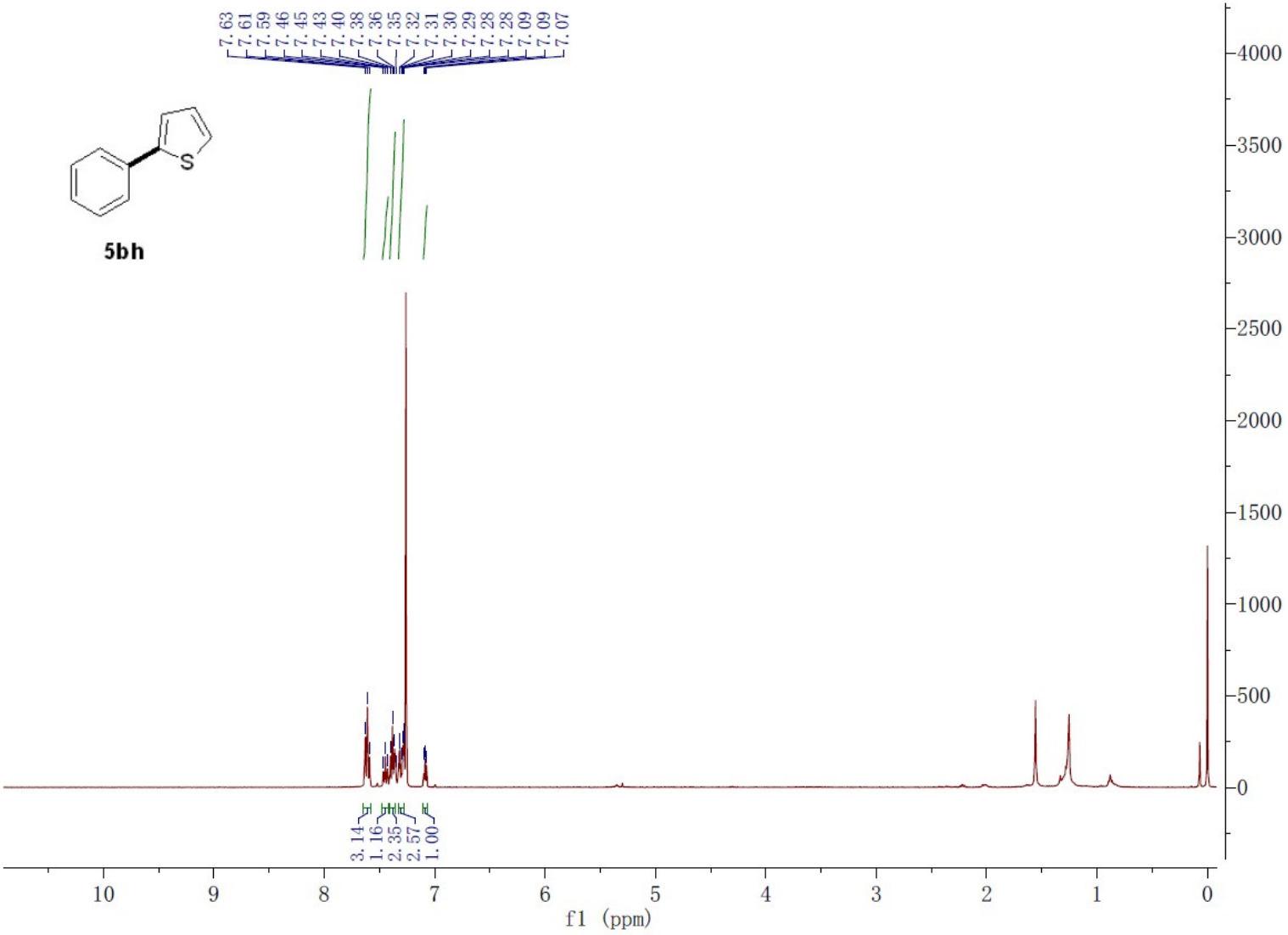

8.25
8.24
7.76
7.74
7.49
7.49
7.48
7.45
7.44
7.17
7.16
7.14
O2N
S
5bc
2.27
2.32
2.29
1.00
f1 (ppm)

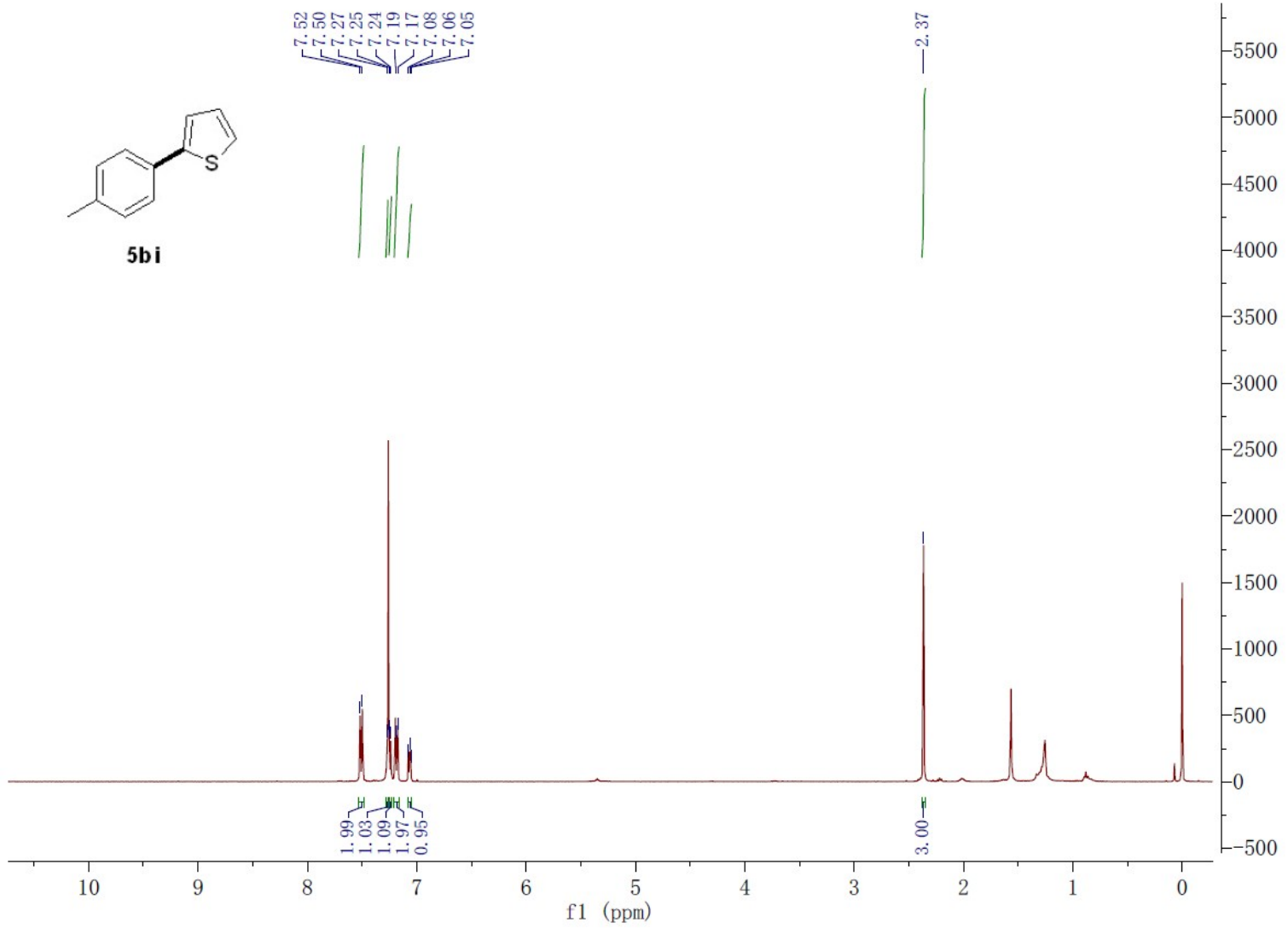

7.58
7.57
7.56
7.55
7.27
7.24
7.23
7.09
7.08
7.07
7.06
7.05
7.05
NC
S
5bd
2.00
0.89
1.03
2.99
4000
3500
3000
2500
2000
1500
1000
500
0
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

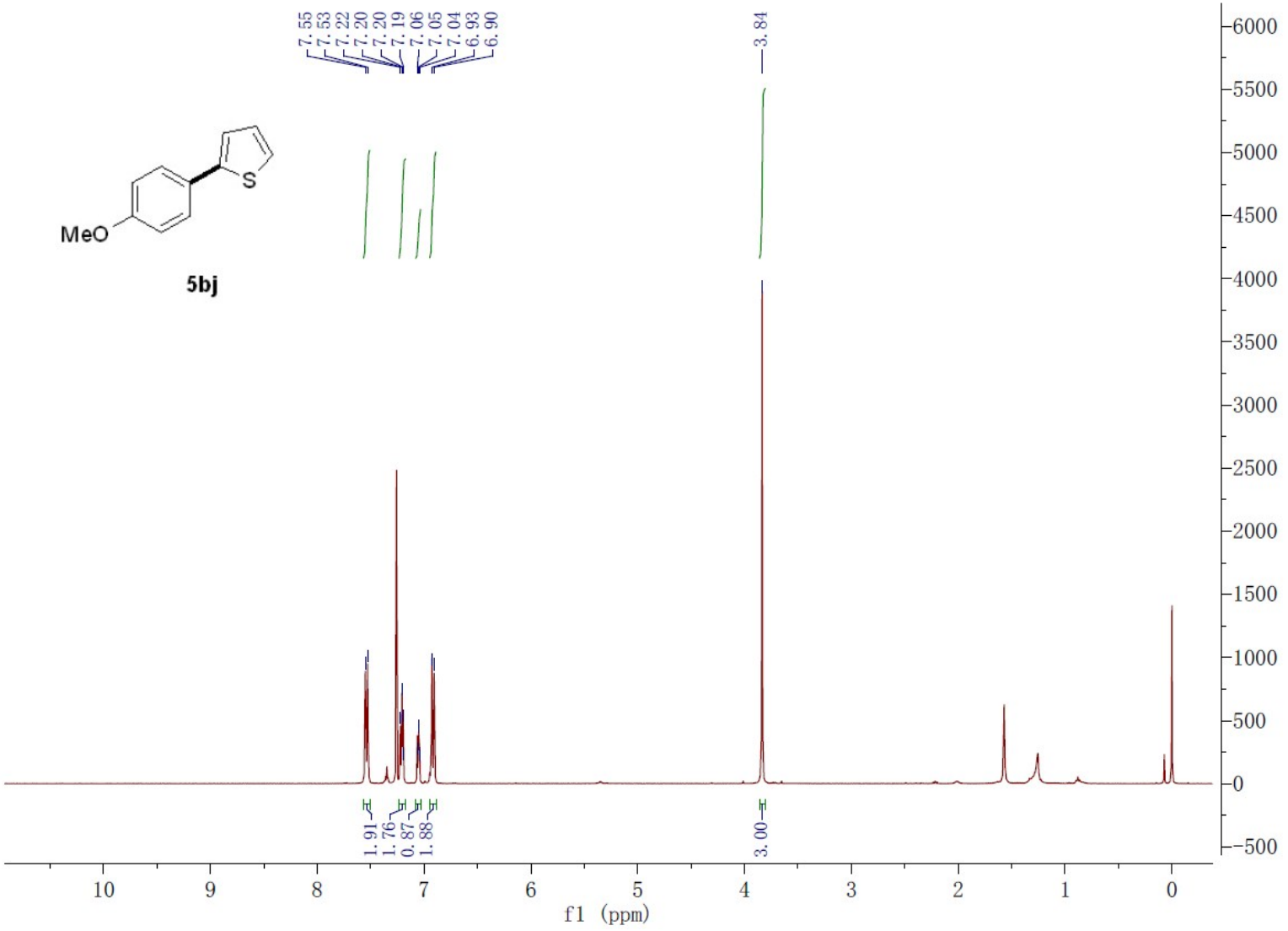

7.71
7.68
7.66
7.64
7.43
7.42
7.41
7.40
7.14
7.13
7.12
S
F
5be
6000
5000
4000
3000
2000
1000
0
4.52
2.26
1.00
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

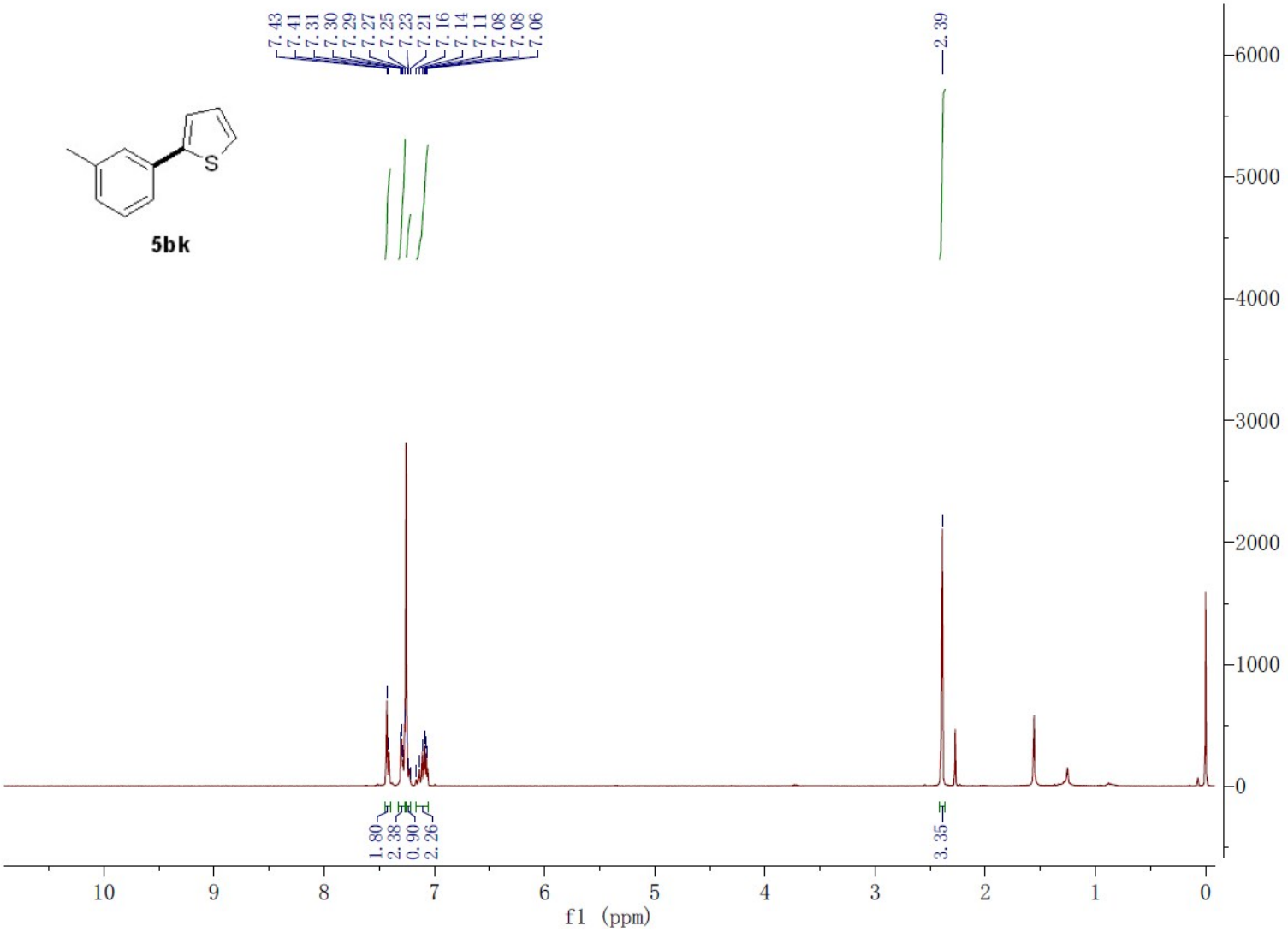

7.54
7.52
7.35
7.33
7.29
7.29
7.28
7.09
7.08
7.06
Cl
S
5bf
2.23
2.27
2.07
1.00
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

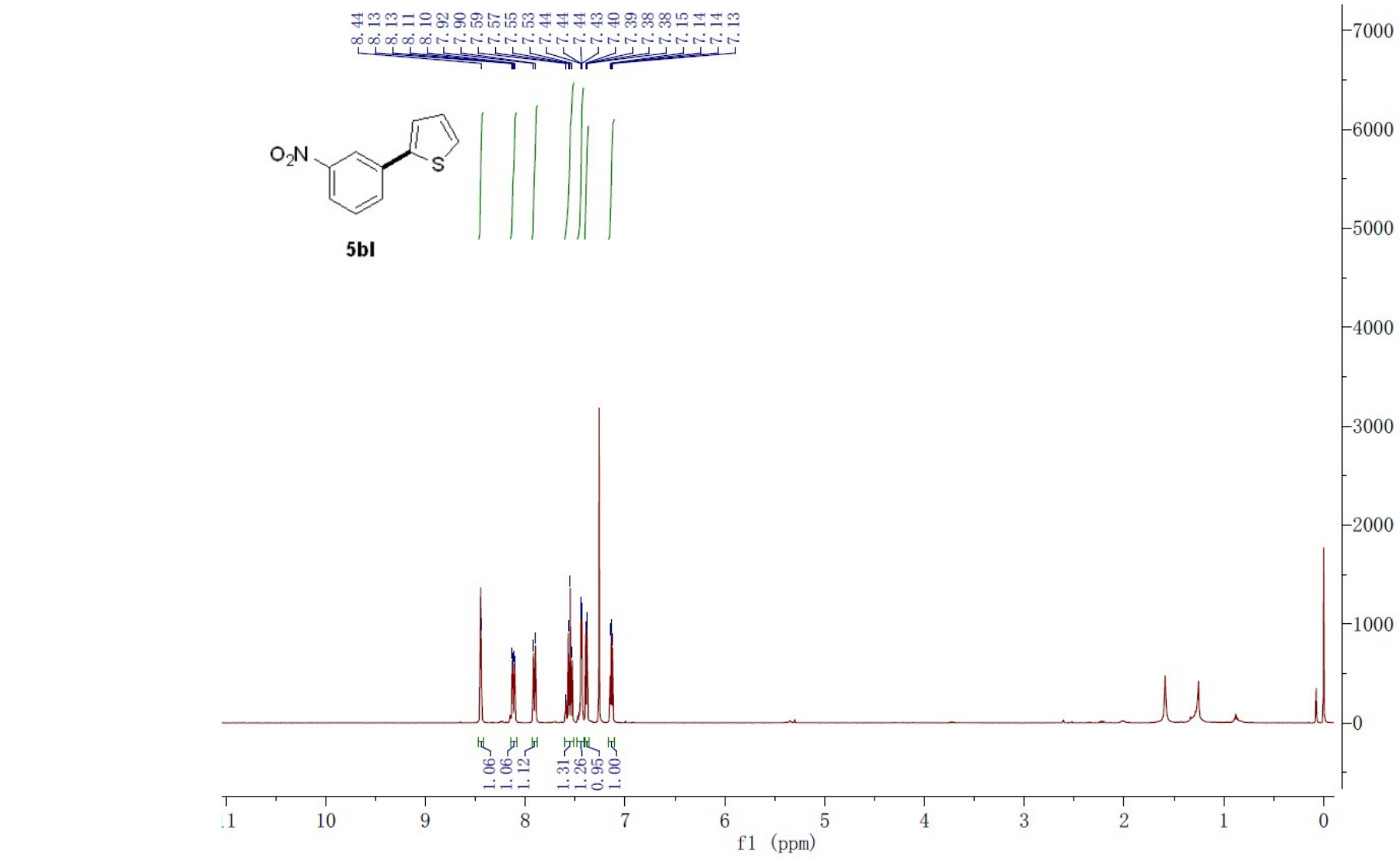

7.51
7.50
7.49
7.48
7.46
7.30
7.29
7.09
7.08
7.07
Br
S
5bg
8000
7000
6000
5000
4000
3000
2000
1000
0
4.13
2.06
1.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

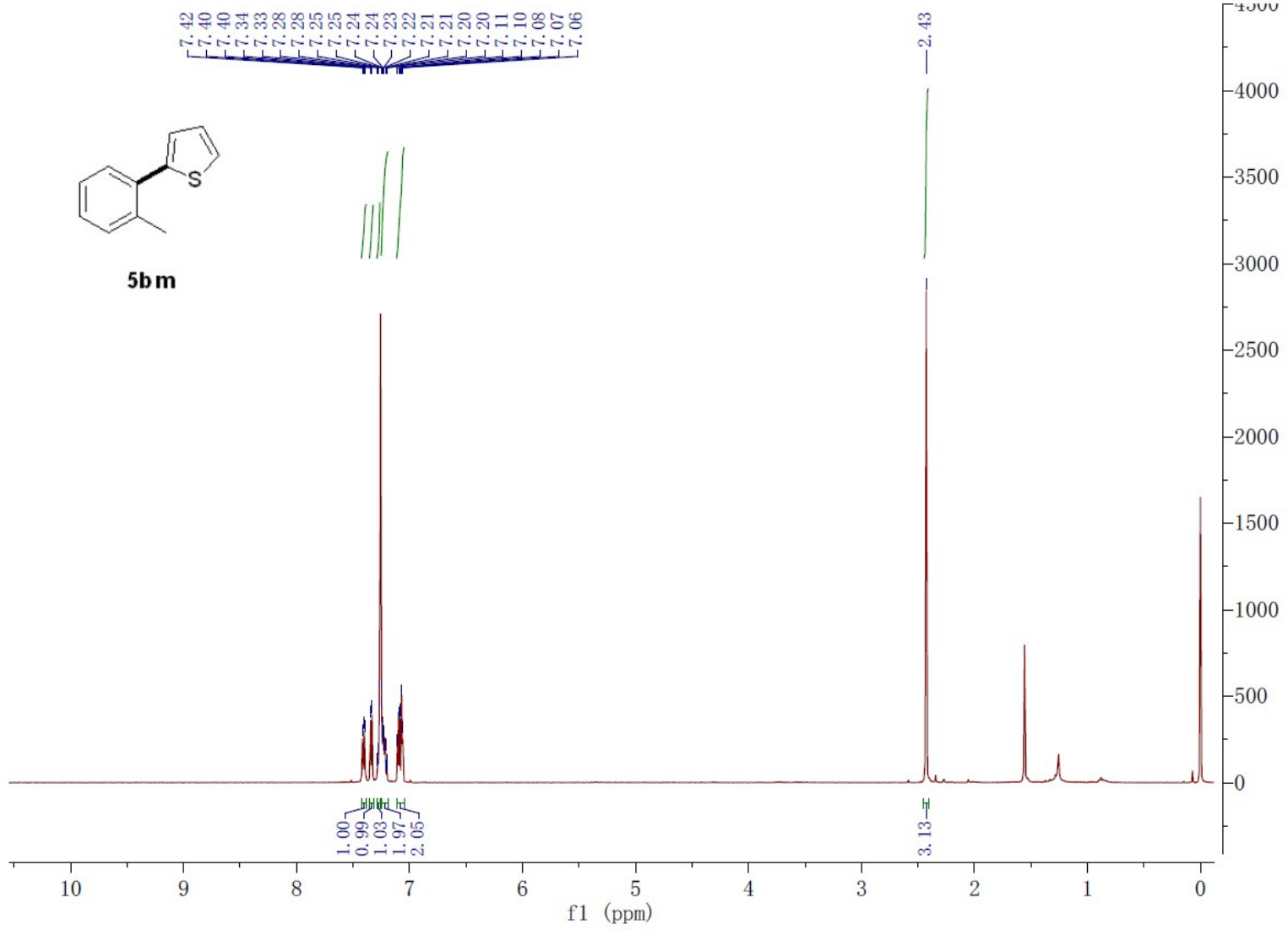

7.63
7.61
7.59
7.46
7.45
7.43
7.40
7.38
7.36
7.35
7.32
7.31
7.30
7.29
7.28
7.28
7.09
7.09
7.07
S
5bh
4000
3500
3000
2500
2000
1500
1000
500
0
3.14
1.16
2.35
2.57
1.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

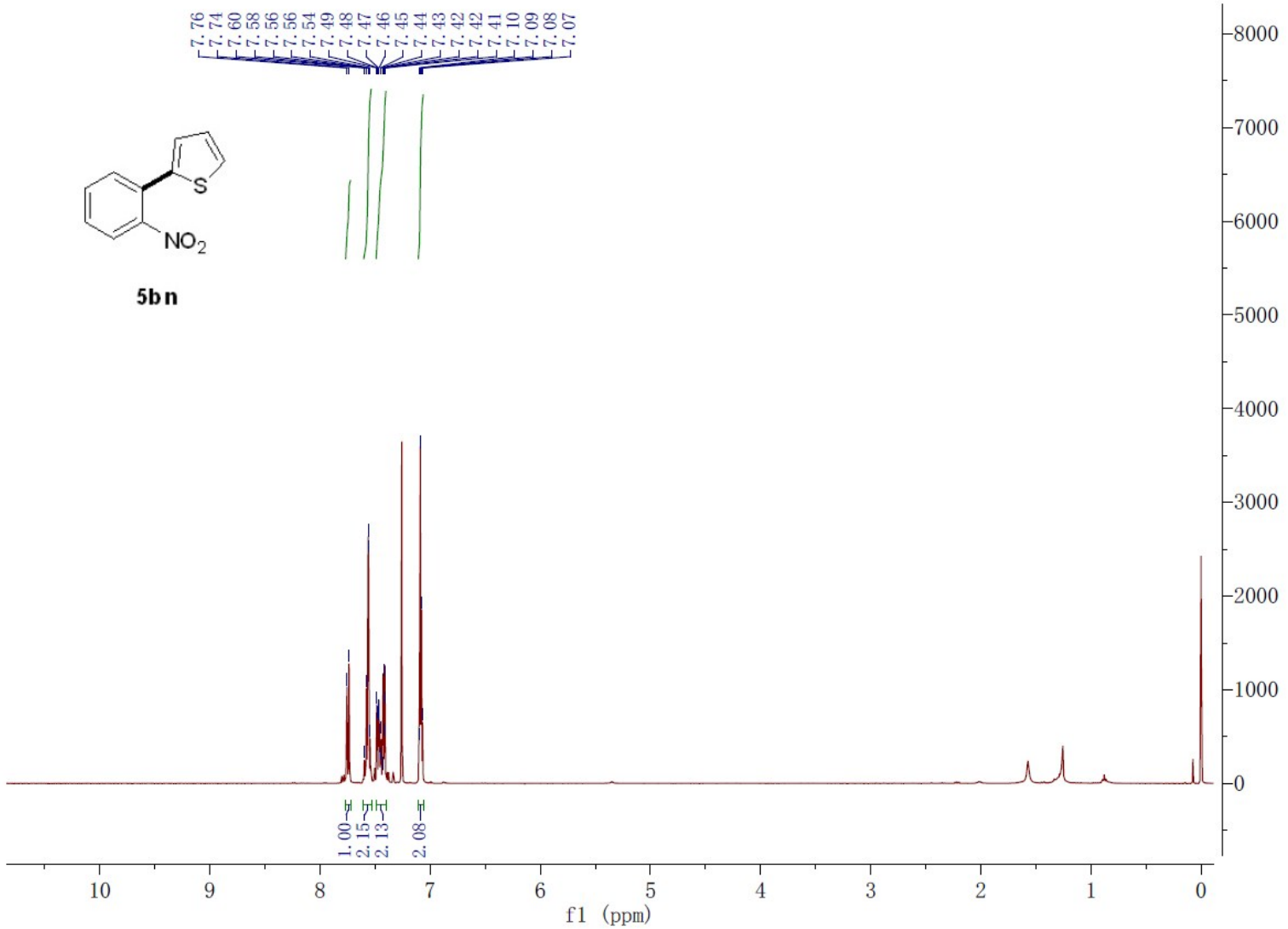

7.52
7.50
7.27
7.25
7.24
7.19
7.17
7.08
7.06
7.05
2.37
S
5bi
1.99
1.03
1.09
1.97
0.95
3.00
f1 (ppm)

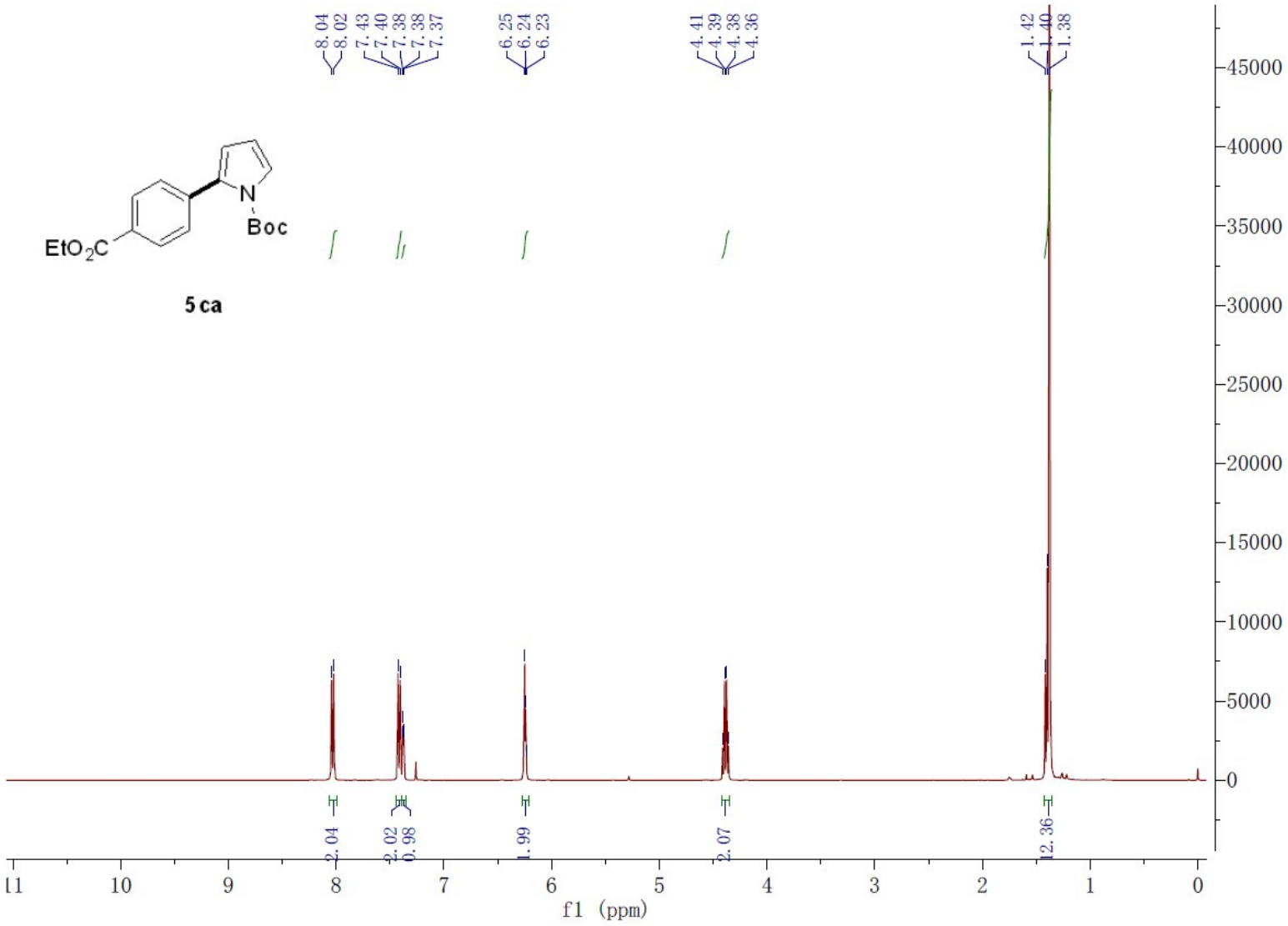

7.55
7.53
7.22
7.20
7.20
7.19
7.06
7.05
7.04
6.93
6.90
3.84
MeO
S
5bj
1.91
1.76
0.87
1.88
3.00
f1 (ppm)

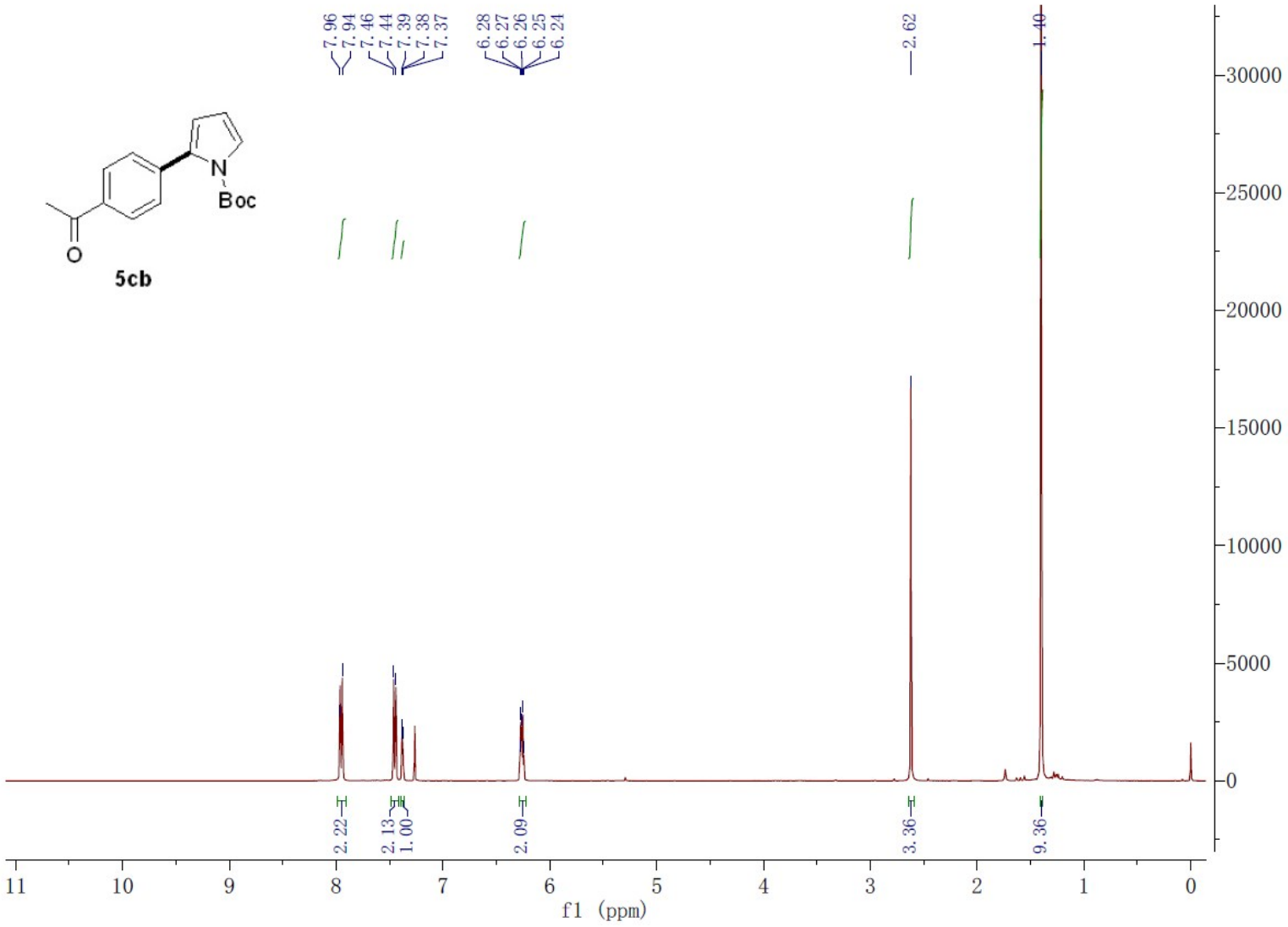

7.43
7.41
7.31
7.30
7.29
7.27
7.25
7.23
7.21
7.16
7.14
7.11
7.08
7.08
7.06
2.39
S
5bk
6000
5000
4000
3000
2000
1000
0
1.80
2.38
0.90
2.26
3.35
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

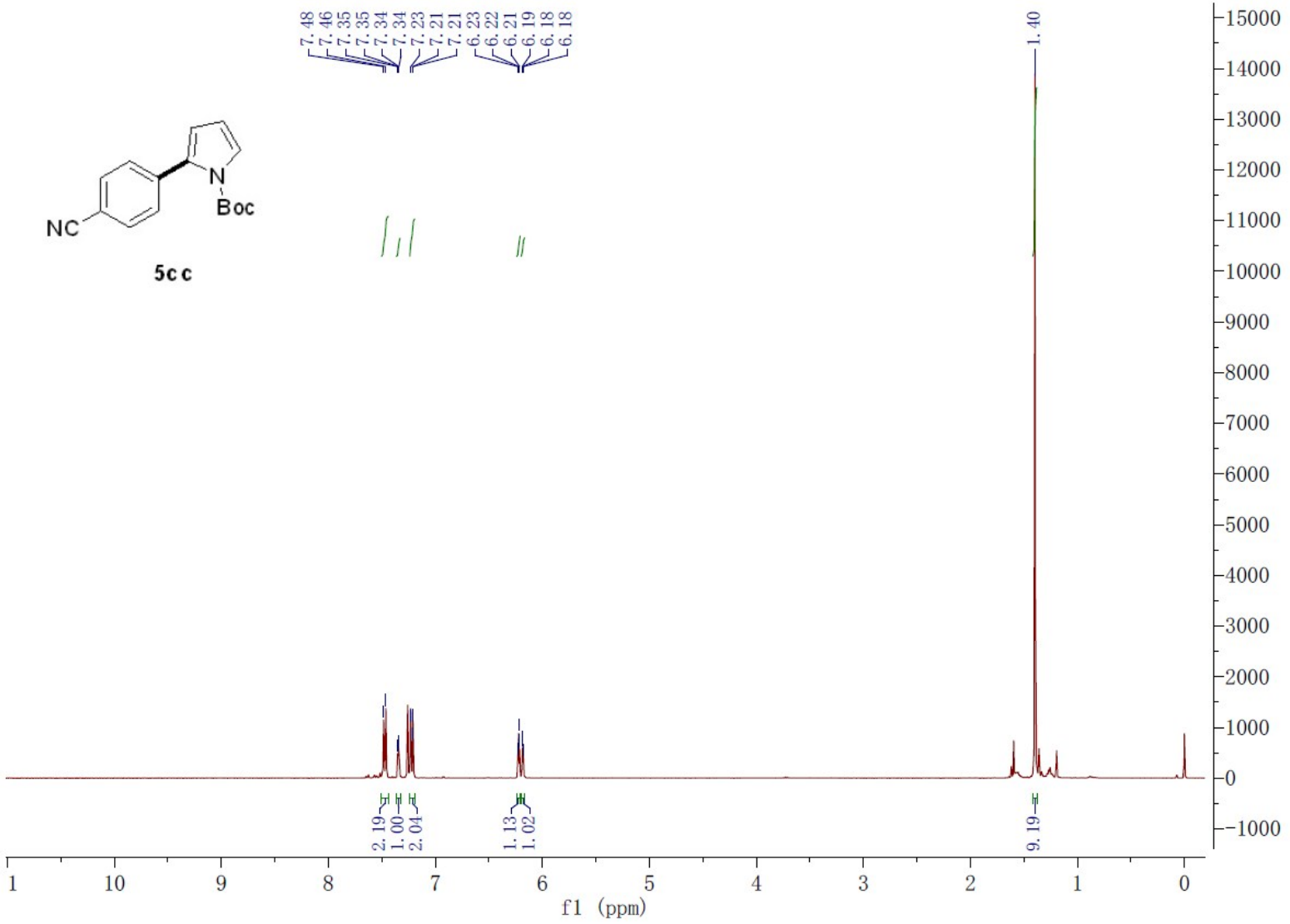

8.44
8.13
8.13
8.11
8.10
7.92
7.90
7.59
7.57
7.55
7.53
7.44
7.44
7.44
7.43
7.40
7.39
7.38
7.38
7.15
7.14
7.14
7.13
O2N
S
5bl
7000
6000
5000
4000
3000
2000
1000
0
1.06
1.06
1.12
1.31
1.26
0.95
1.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

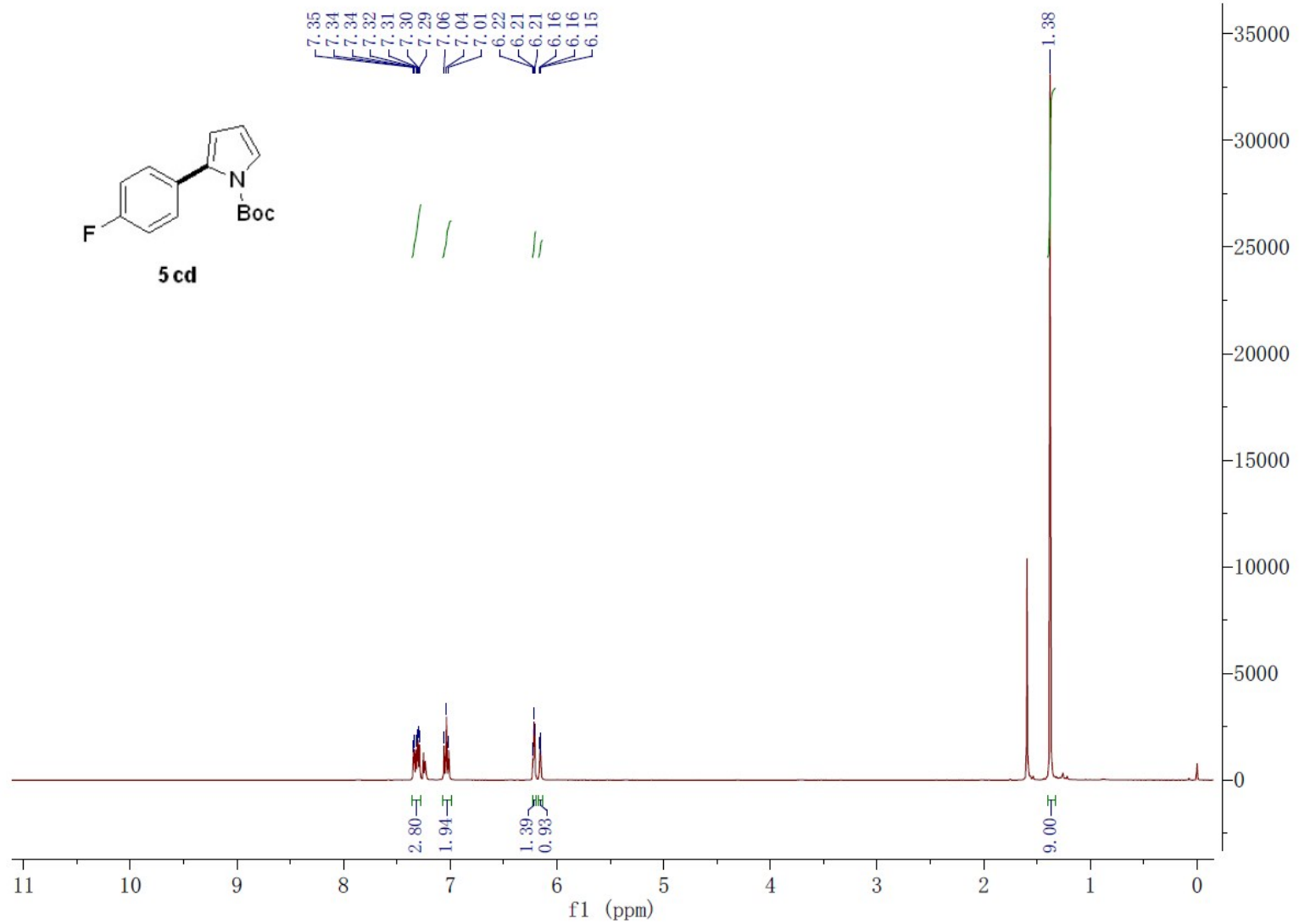

7.42
7.40
7.40
7.34
7.33
7.28
7.28
7.25
7.25
7.24
7.24
7.23
7.22
7.21
7.21
7.20
7.20
7.11
7.10
7.08
7.07
7.06
2.43
S
5bm
1.00
0.99
1.03
1.97
2.05
3.13
4000
3500
3000
2500
2000
1500
1000
500
0
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

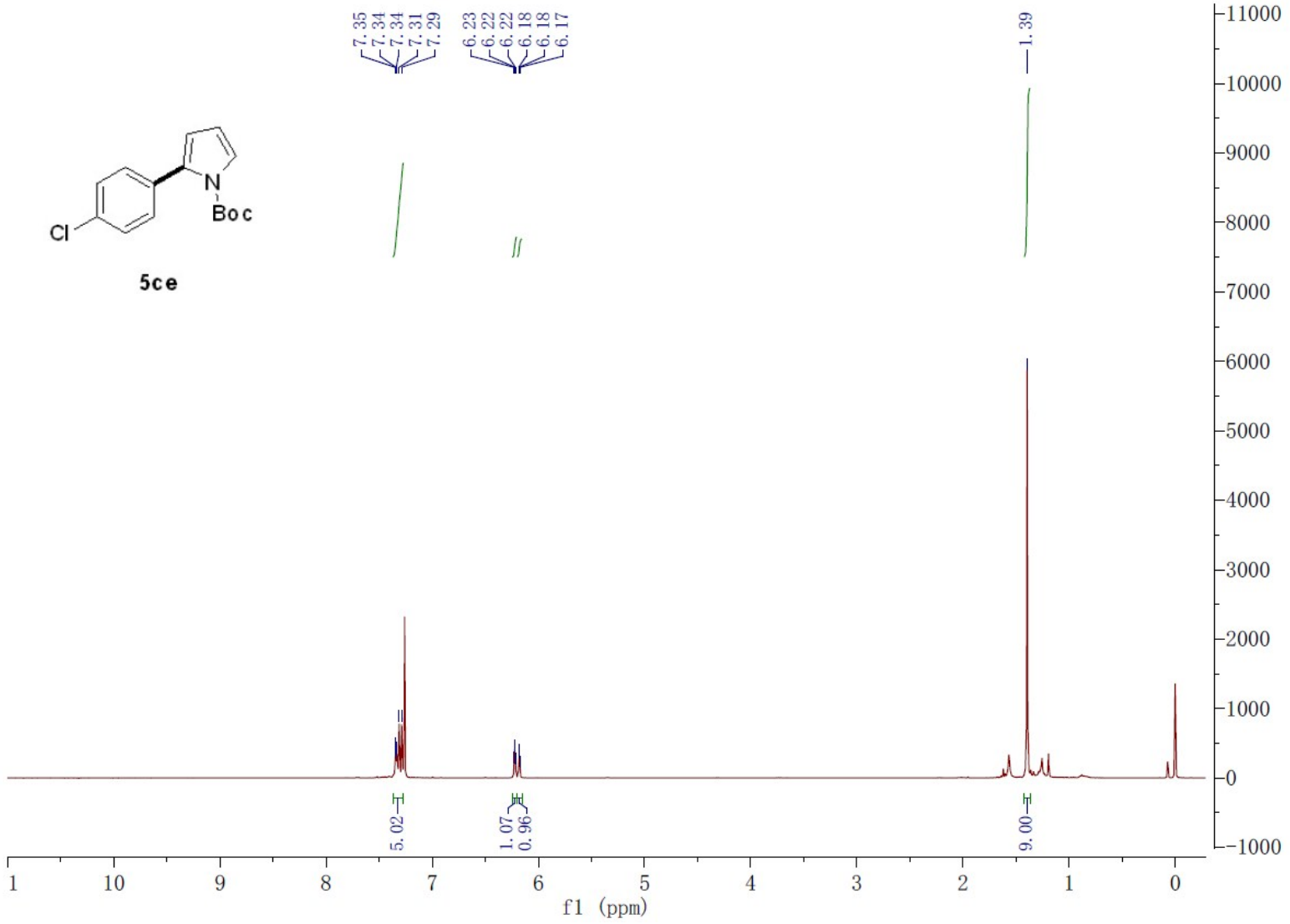

7.76
7.74
7.60
7.58
7.56
7.56
7.54
7.49
7.48
7.47
7.46
7.45
7.44
7.43
7.42
7.42
7.41
7.10
7.09
7.08
7.07
S
NO2
5bn
1.00
2.15
2.13
2.08
8000
7000
6000
5000
4000
3000
2000
1000
0
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

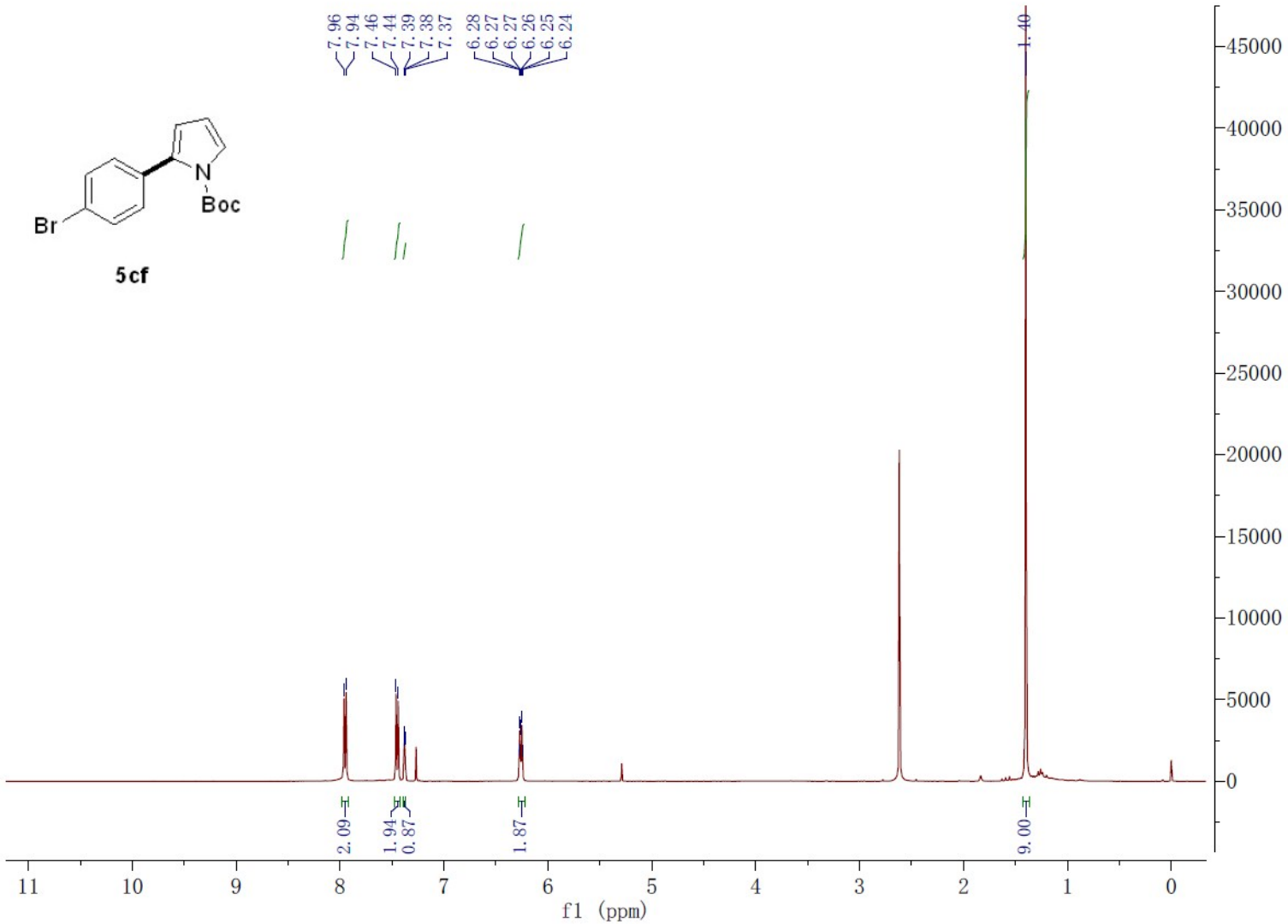

8.04
8.02
7.43
7.40
7.38
7.38
7.37
6.25
6.24
6.23
4.41
4.39
4.38
4.36
1.42
1.40
1.38
N
Boc
EtO2C
5ca
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
2.04
2.02
0.98
1.99
2.07
12.36
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

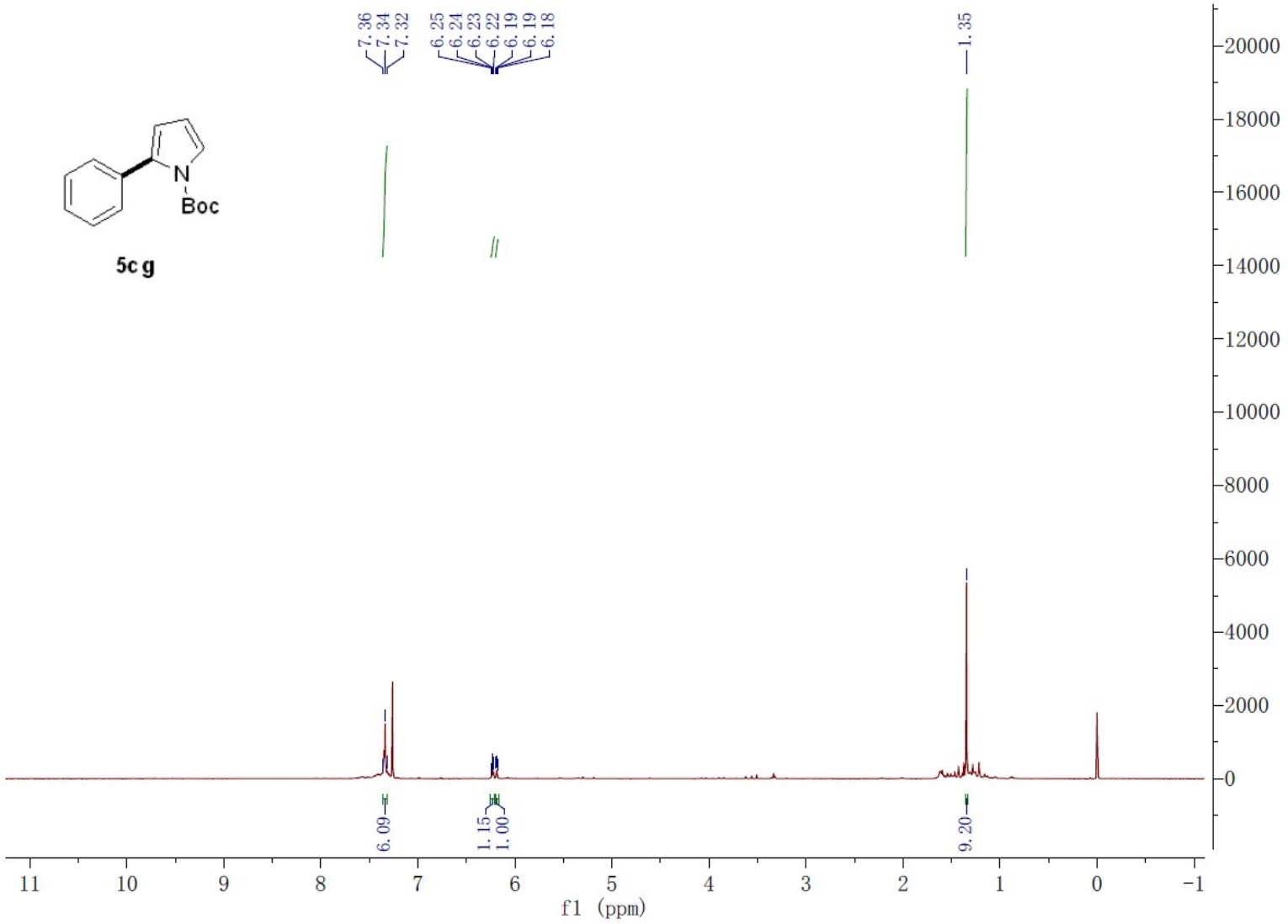

7.96
7.94
7.46
7.44
7.39
7.38
7.37
6.28
6.27
6.26
6.25
6.24
2.62
1.40
N
Boc
O
5cb
30000
25000
20000
15000
10000
5000
0
2.22
2.13
1.00
2.09
3.36
9.36
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

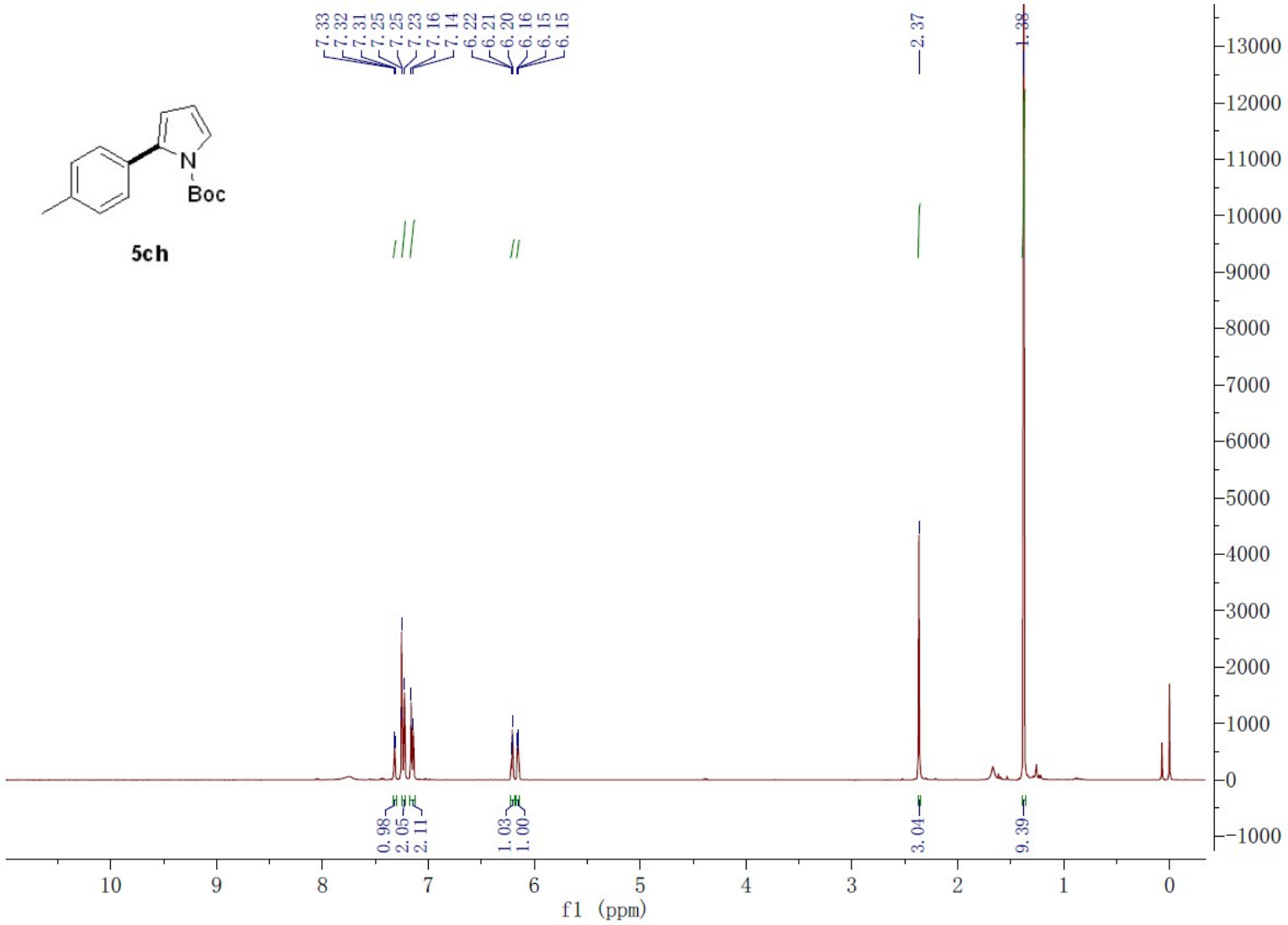

7.48
7.46
7.35
7.35
7.34
7.34
7.23
7.21
7.21
6.23
6.22
6.21
6.19
6.18
6.18
1.40
NC
N
Boc
5cc
2.19
1.00
2.04
1.13
1.02
9.19
f1 (ppm)

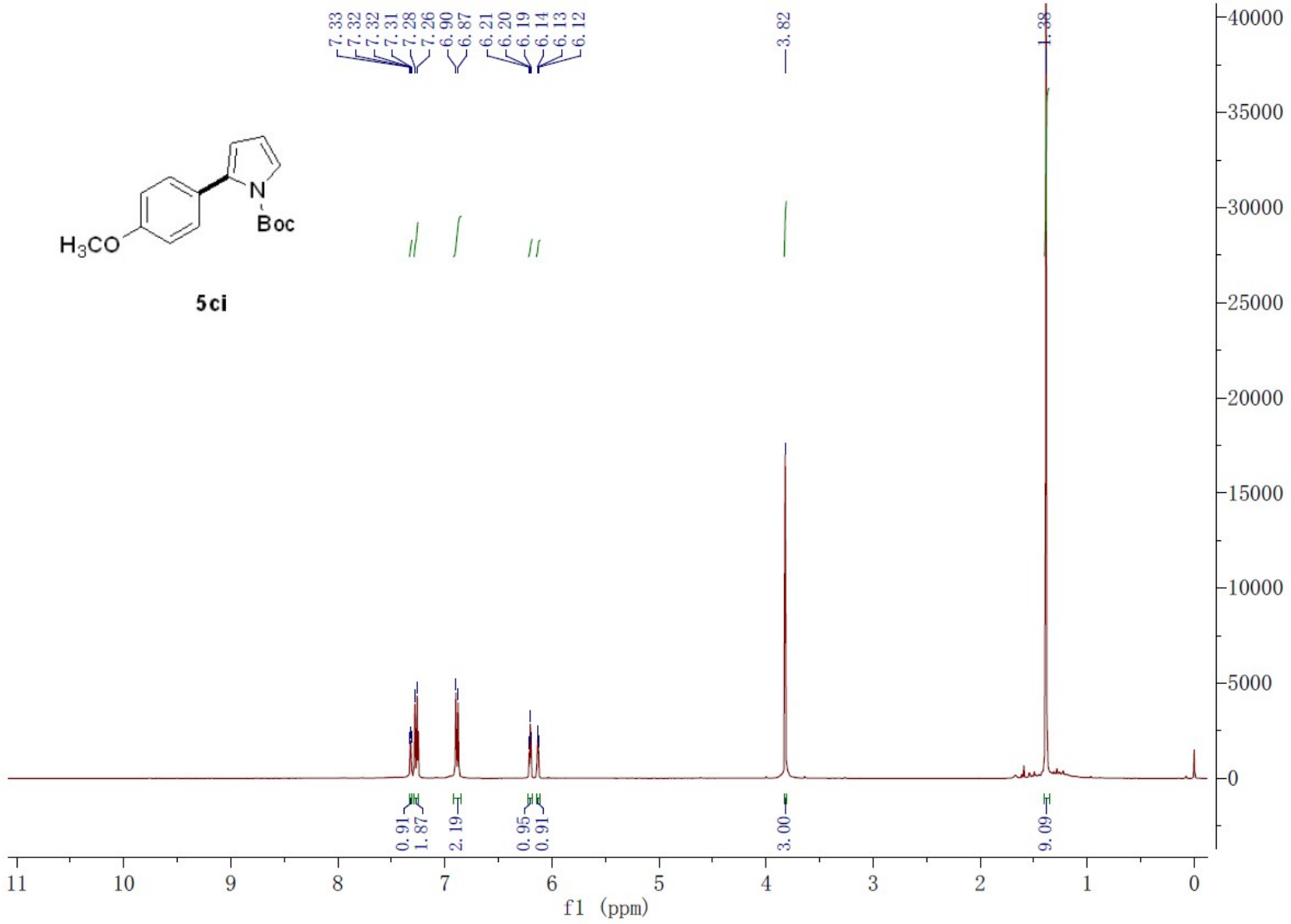

7.35
7.34
7.34
7.32
7.31
7.30
7.29
7.06
7.04
7.01
6.22
6.21
6.21
6.16
6.16
6.15
1.38
N
Boc
F
5cd
2.80
1.94
1.39
0.93
9.00
f1 (ppm)

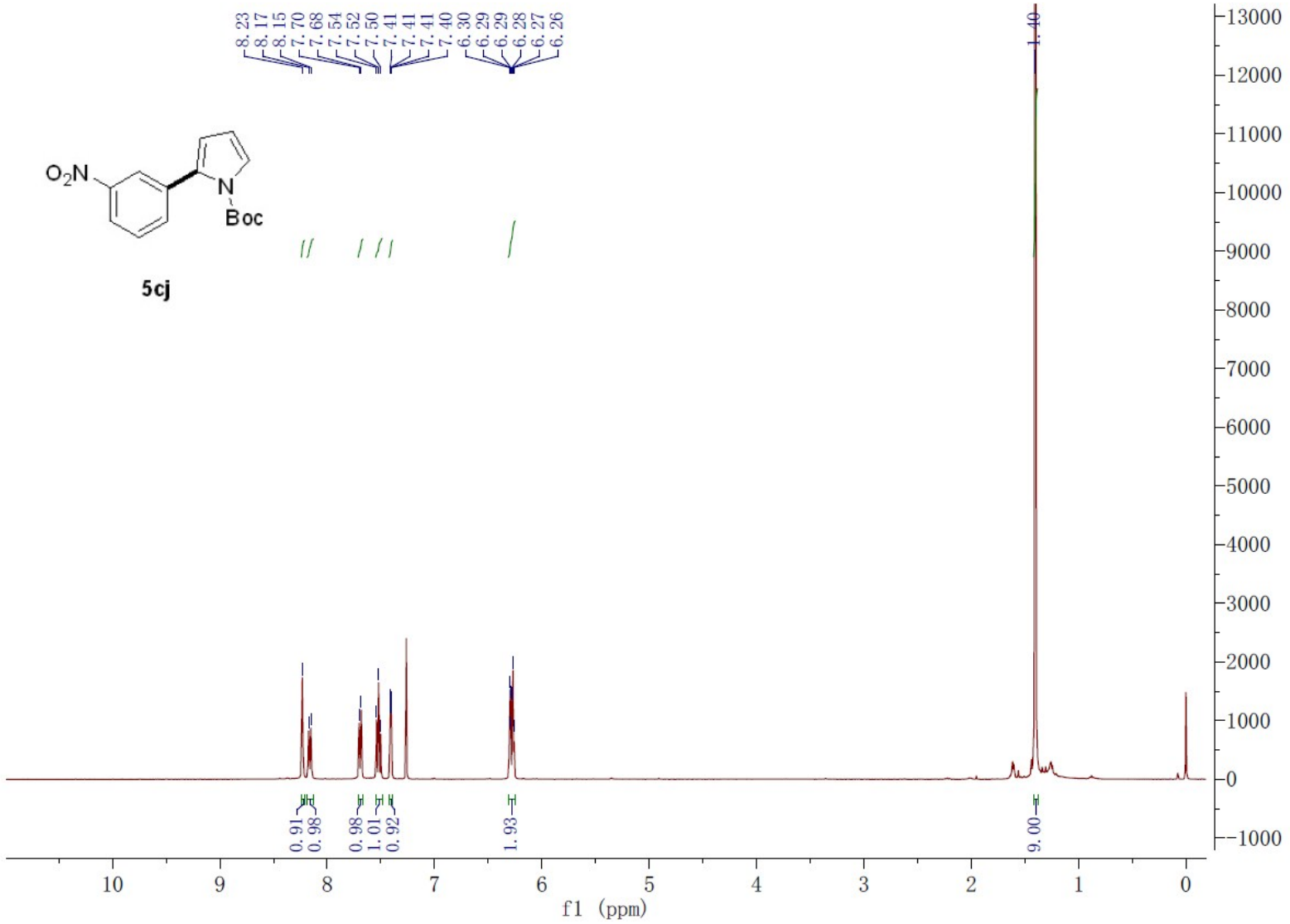

7.35
7.34
7.34
7.31
7.29
6.23
6.22
6.22
6.18
6.18
6.17
1.39
N
Boc
Cl
5ce
5.02
1.07
0.96
9.00
f1 (ppm)

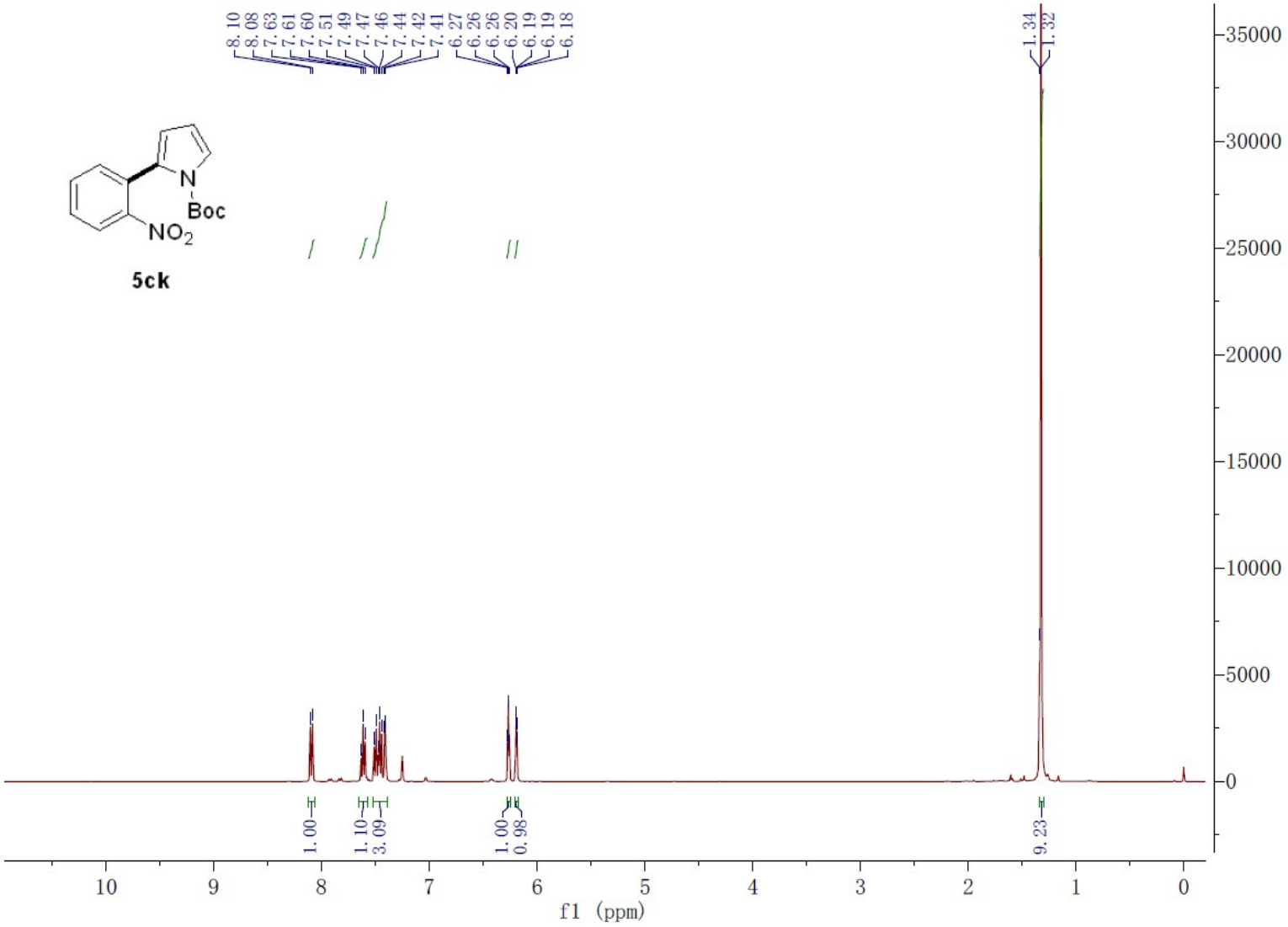

7.96
7.94
7.46
7.44
7.39
7.38
7.37
6.28
6.27
6.27
6.26
6.25
6.24
1.40
Br
N
Boc
5cf
2.09
1.94
0.87
1.87
9.00
f1 (ppm)

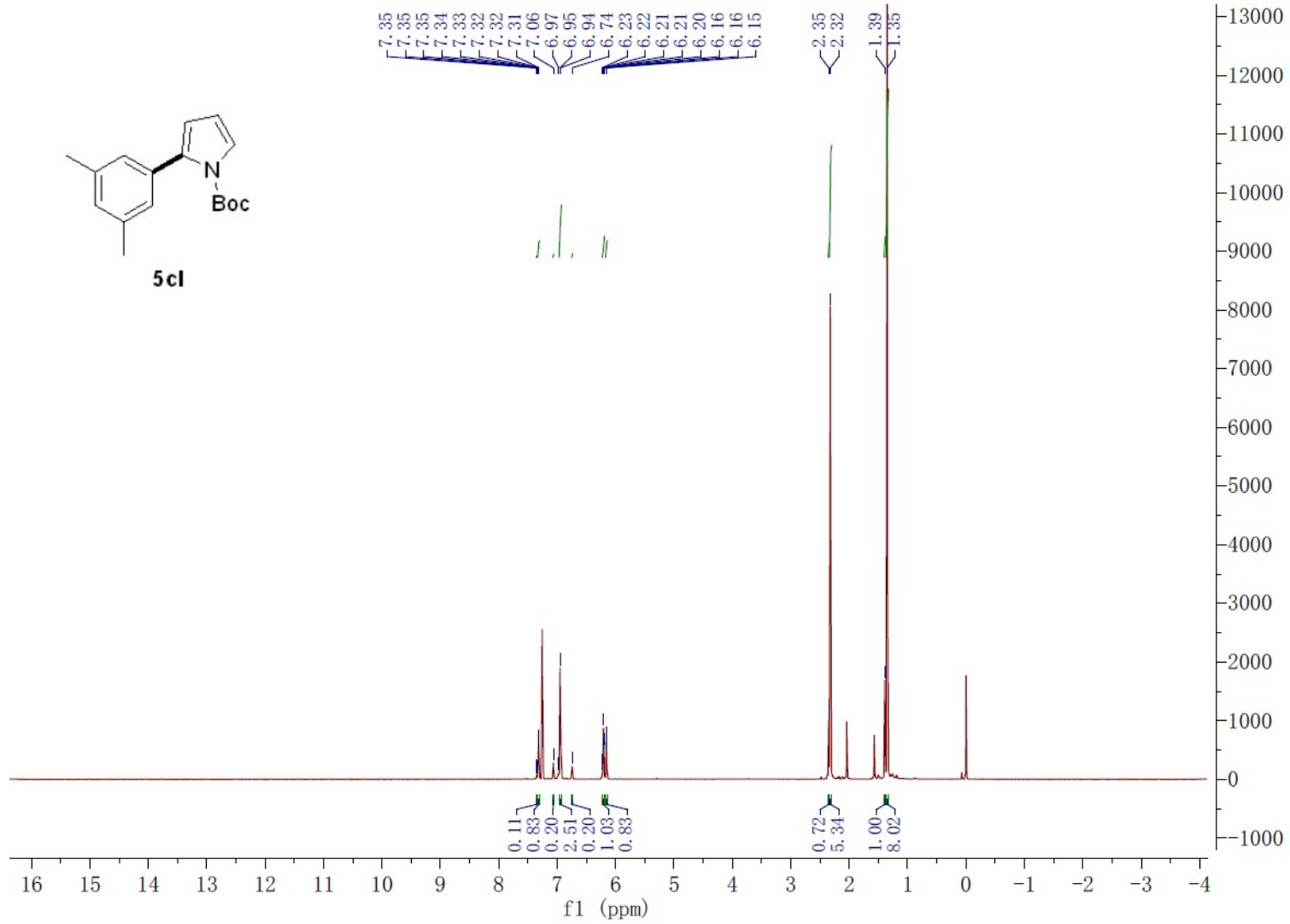

7.36
7.34
7.32
6.25
6.24
6.23
6.22
6.19
6.19
6.18
1.35
N
Boc
5cg
6.09
1.15
1.00
9.20
f1 (ppm)

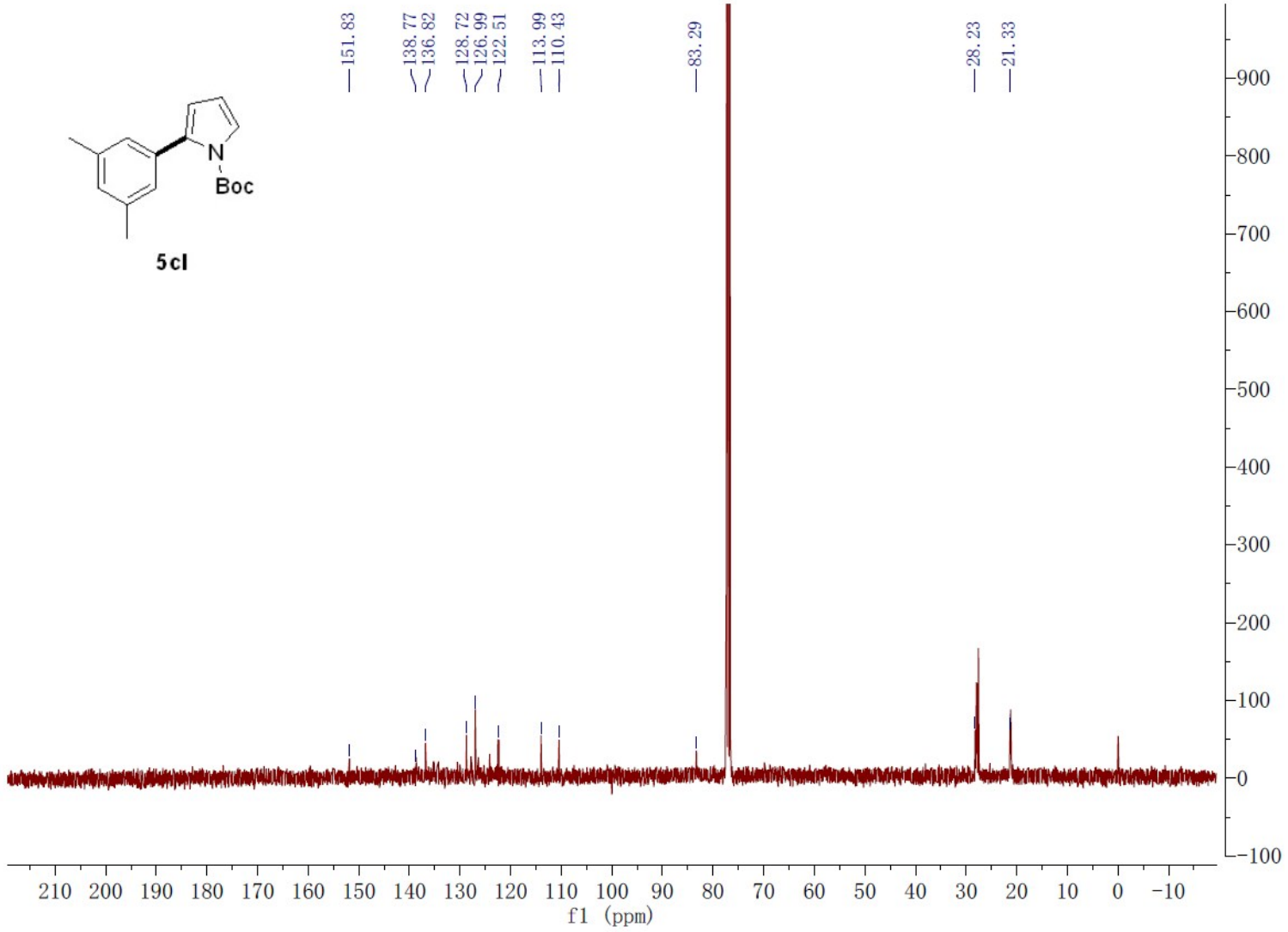

7.33
7.32
7.31
7.25
7.25
7.23
7.16
7.14
6.22
6.21
6.20
6.16
6.15
6.15
2.37
1.38
N
Boc
5ch
0.98
2.05
2.11
1.03
1.00
3.04
9.39
f1 (ppm)

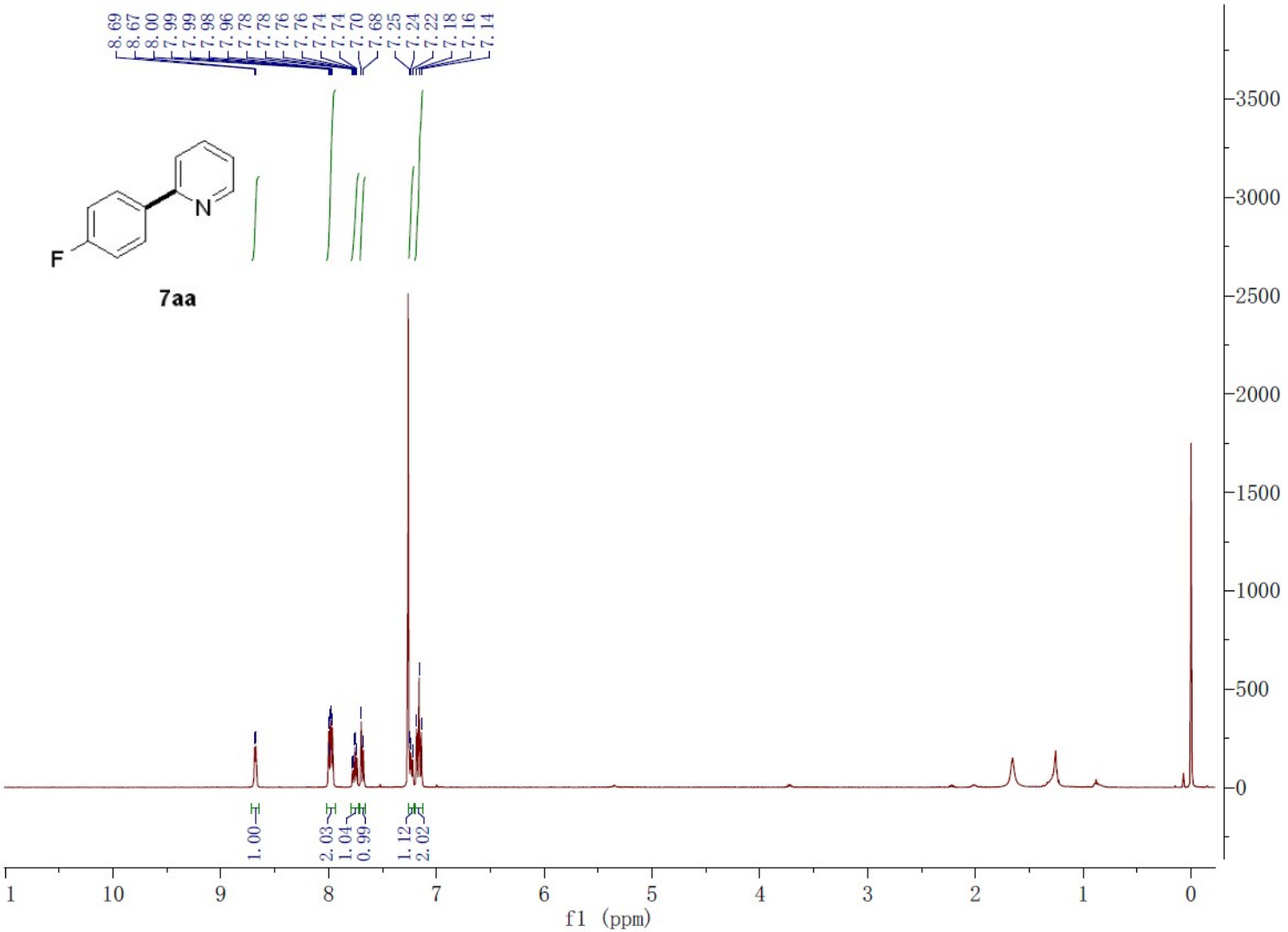

7.33
7.32
7.32
7.31
7.28
7.26
6.90
6.87
6.21
6.20
6.19
6.14
6.13
6.12
3.82
1.38
H3CO
N
Boc
5ci
0.91
1.87
2.19
0.95
0.91
3.00
9.09
f1 (ppm)

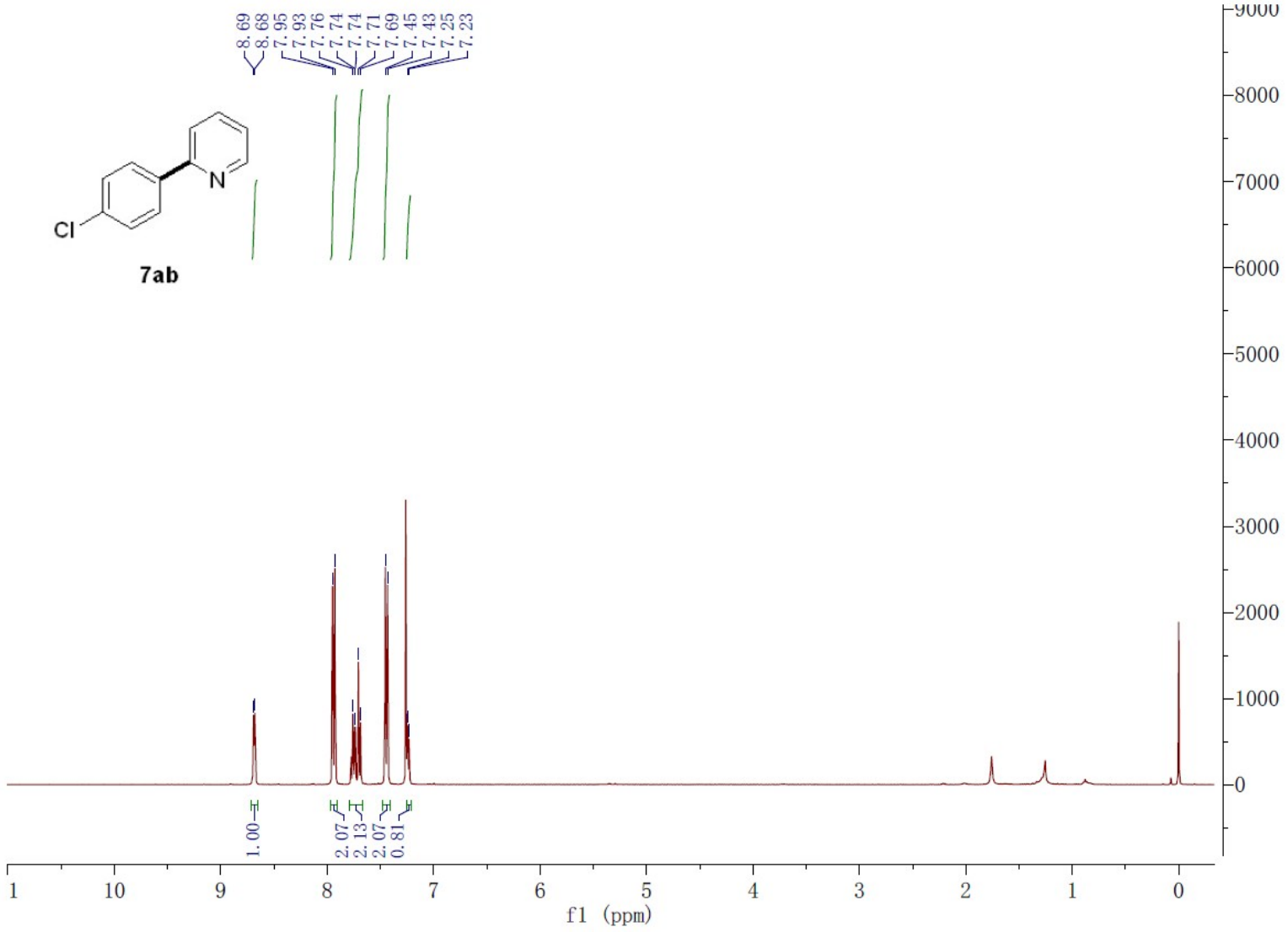

8.23
8.17
8.15
7.70
7.68
7.54
7.52
7.50
7.41
7.41
7.41
7.40
6.30
6.29
6.29
6.28
6.27
6.26
1.40
O2N
N
Boc
5cj
0.91
0.98
0.98
1.01
0.92
1.93
9.00
f1 (ppm)

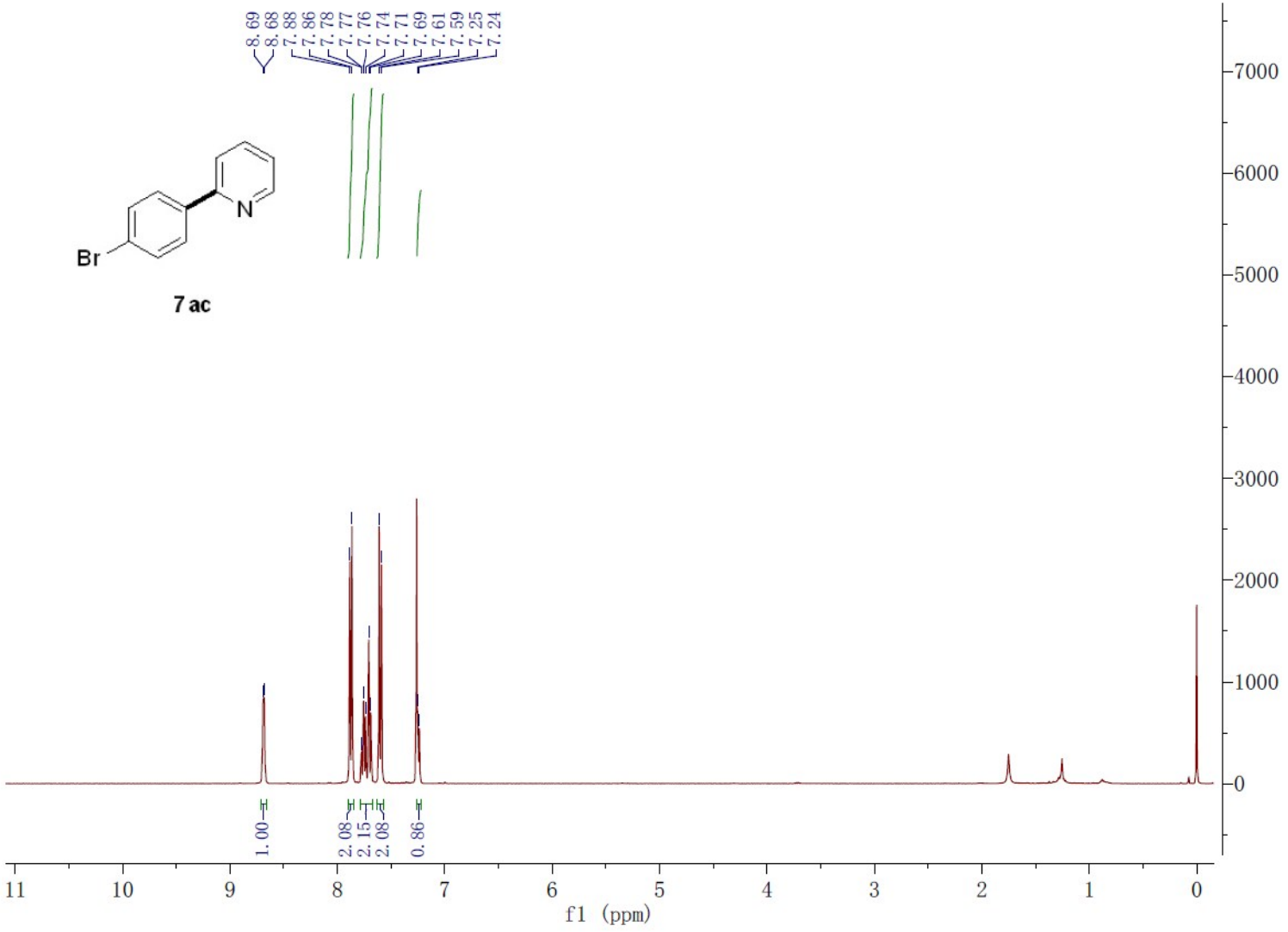

8.10
8.08
7.63
7.61
7.60
7.51
7.49
7.47
7.46
7.44
7.42
7.41
6.27
6.26
6.26
6.20
6.19
6.19
6.18
1.34
1.32
N
Boc
NO2
5ck
35000
30000
25000
20000
15000
10000
5000
0
1.00
1.10
3.09
1.00
0.98
9.23
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

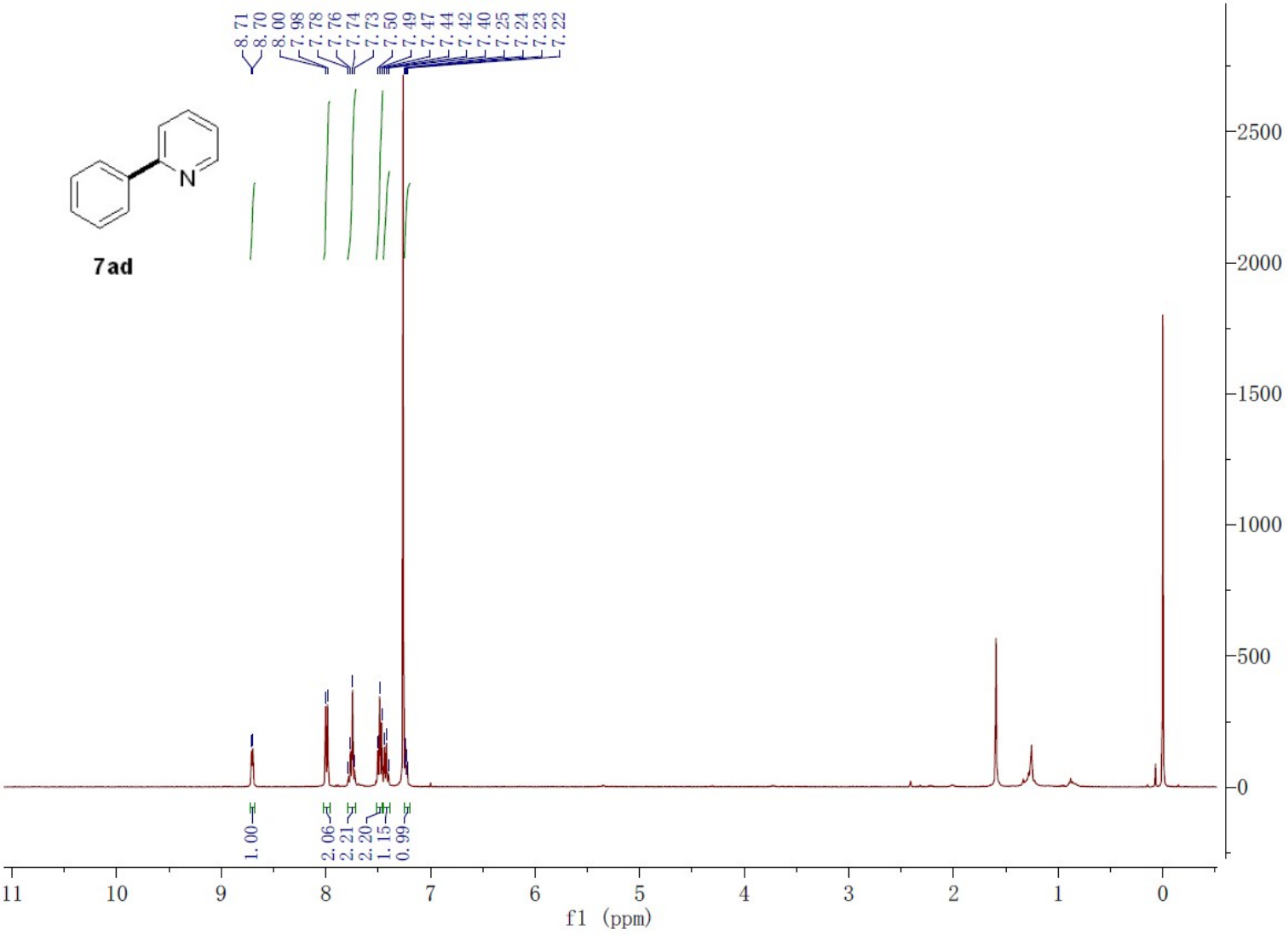

7.35
7.35
7.35
7.34
7.33
7.32
7.32
7.31
7.06
6.97
6.95
6.94
6.74
6.23
6.22
6.21
6.21
6.20
6.16
6.16
6.15
2.35
2.32
1.39
1.35
N
Boc
5cl
0.11
0.83
0.20
2.51
0.20
1.03
0.83
0.72
5.34
1.00
8.02
f1 (ppm)

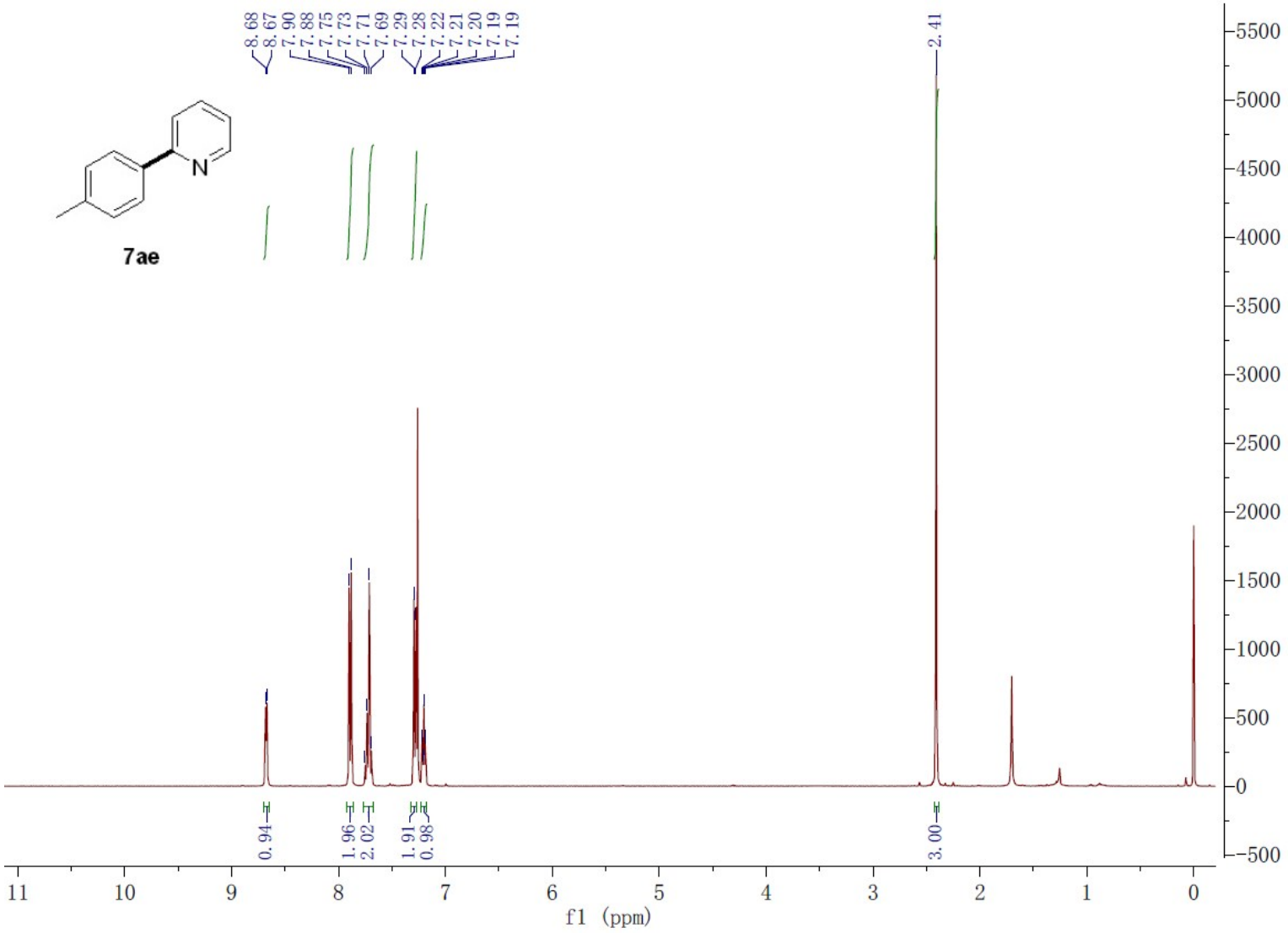

151.83
138.77
136.82
128.72
126.99
122.51
113.99
110.43
83.29
28.23
21.33
N
Boc
5cl
f1 (ppm)

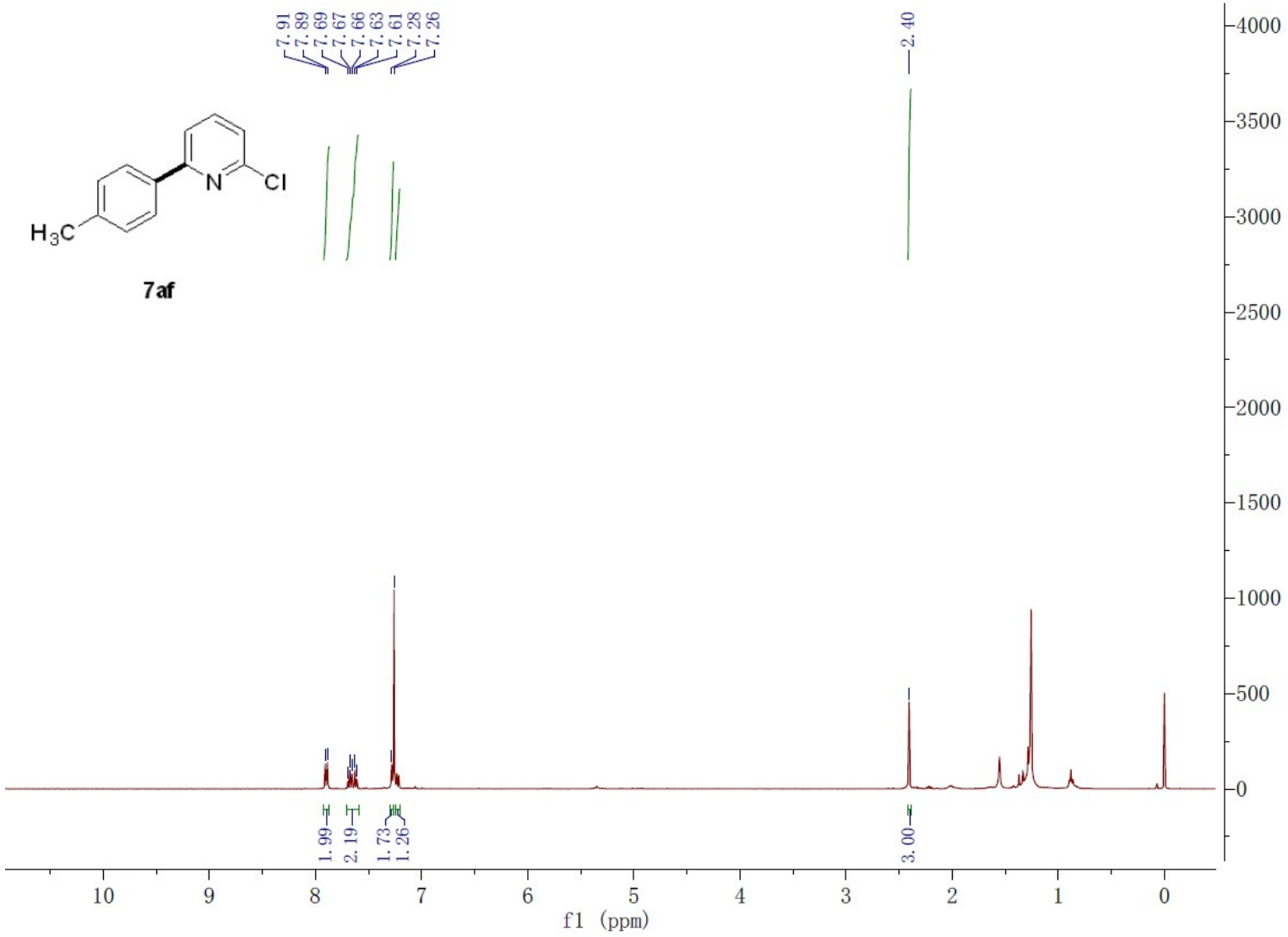

8.69
8.67
8.00
7.99
7.99
7.98
7.96
7.78
7.78
7.76
7.76
7.74
7.74
7.70
7.68
7.25
7.24
7.22
7.18
7.16
7.14
N
F
7aa
3500
3000
2500
2000
1500
1000
500
0
1.00
2.03
1.04
0.99
1.12
2.02
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

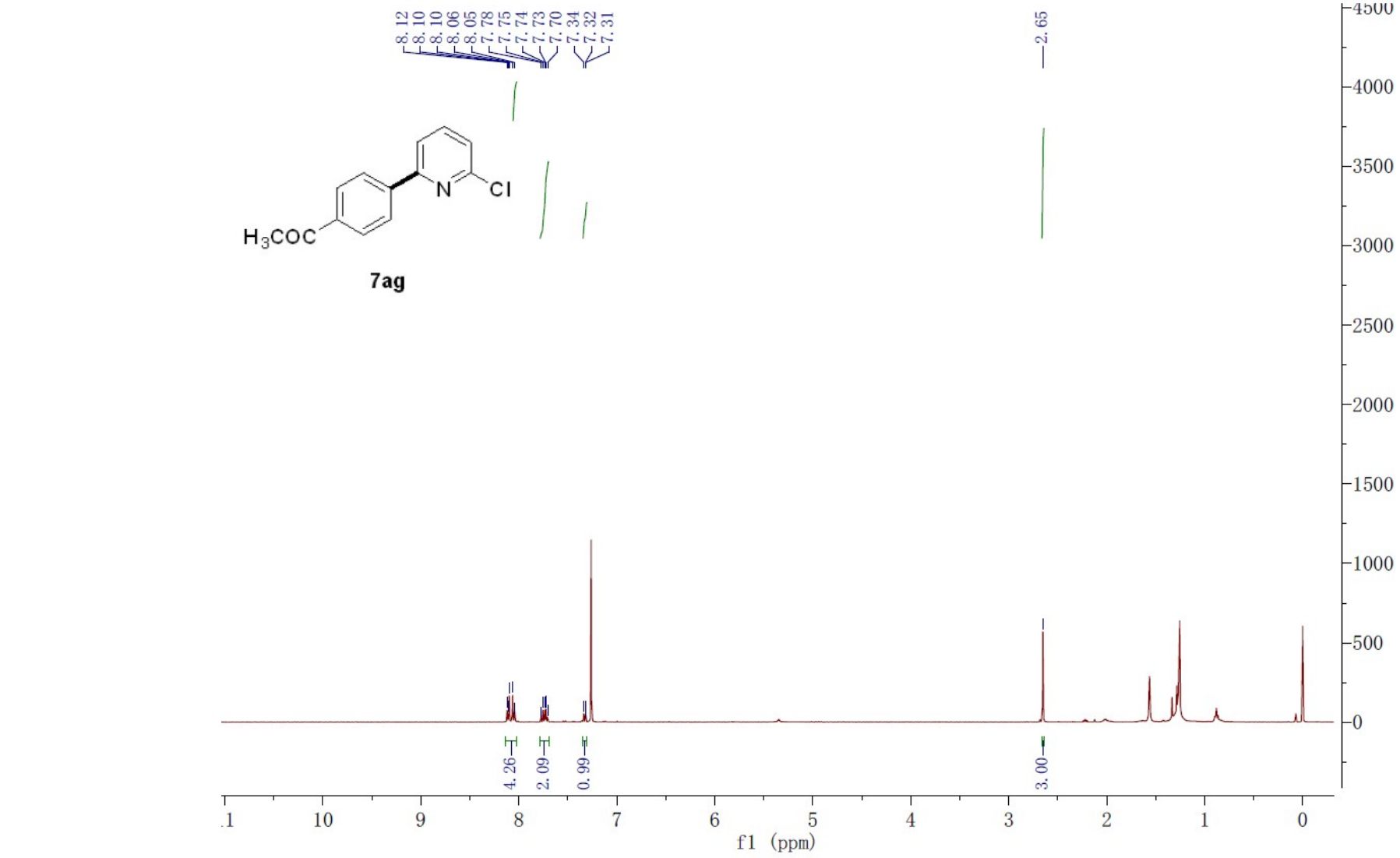

8.69
8.68
7.95
7.93
7.76
7.74
7.74
7.71
7.69
7.45
7.43
7.25
7.23
Cl
N
7ab
1.00
2.07
2.13
2.07
0.81
f1 (ppm)

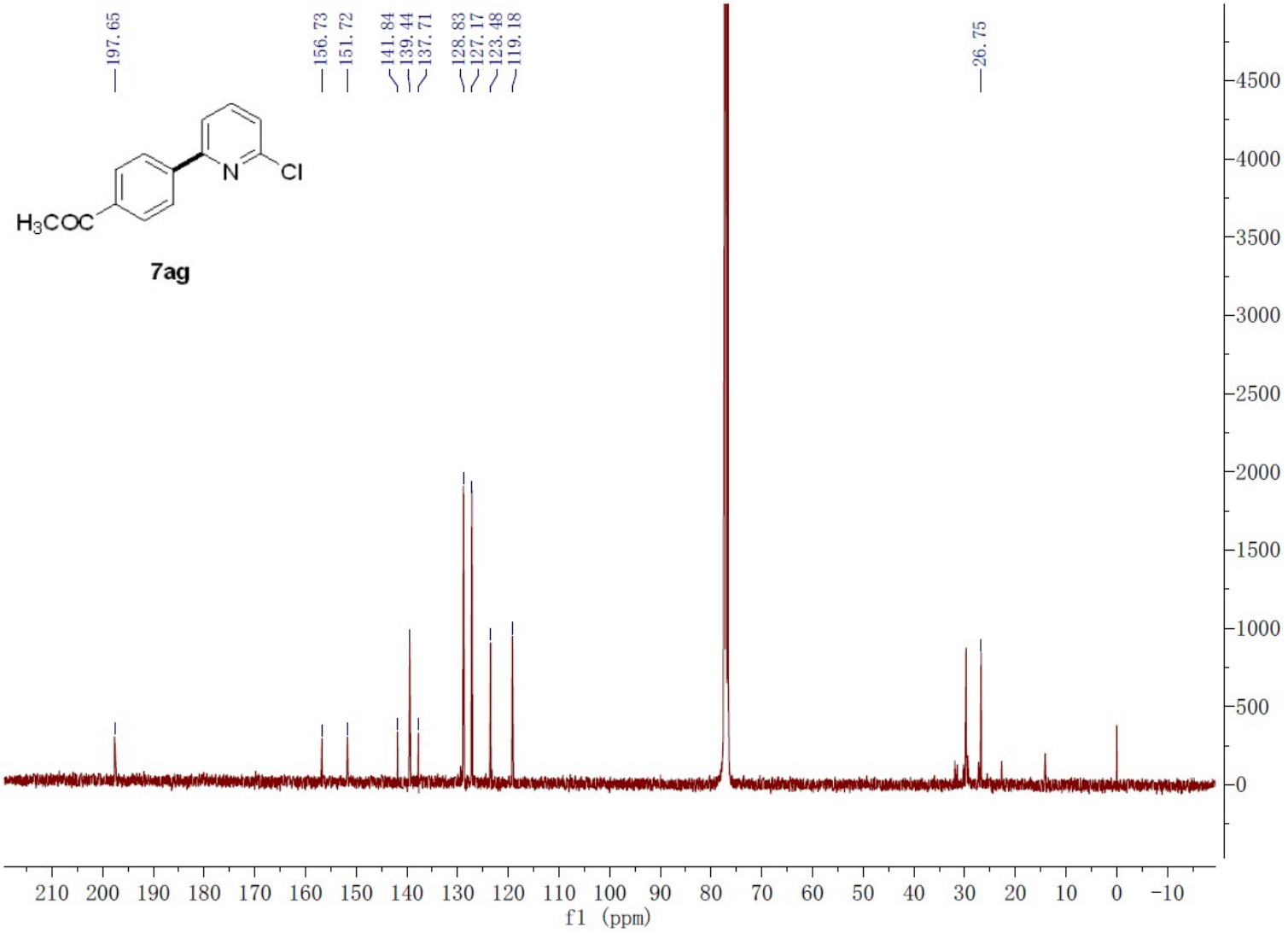

8.69
8.68
7.88
7.86
7.78
7.77
7.76
7.74
7.71
7.69
7.61
7.59
7.25
7.24
Br
N
7ac
7000
6000
5000
4000
3000
2000
1000
0
1.00
2.08
2.15
2.08
0.86
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

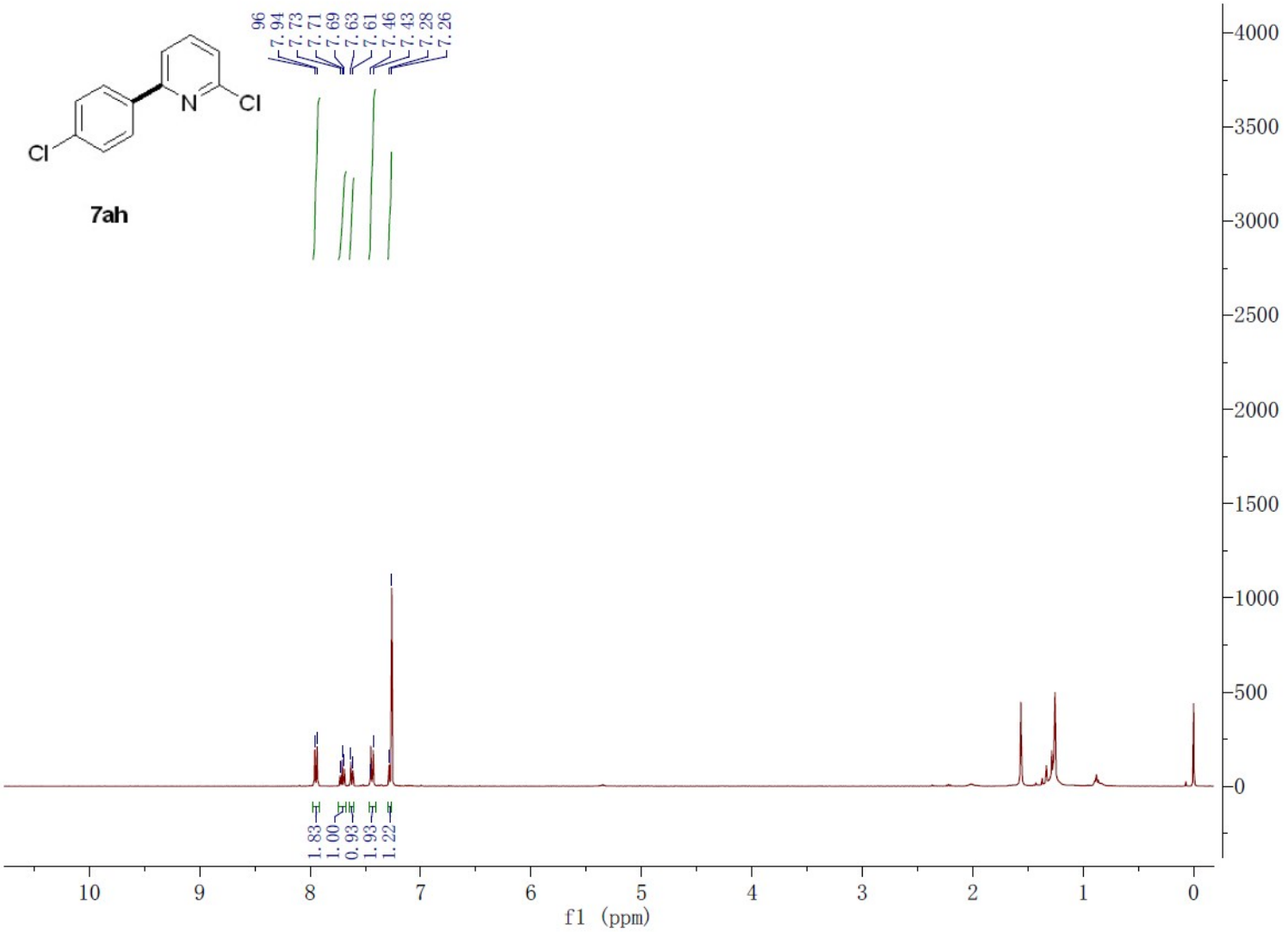

8.71
8.70
8.00
7.98
7.78
7.76
7.74
7.73
7.50
7.49
7.47
7.44
7.42
7.40
7.25
7.24
7.23
7.22
N
7ad
2500
2000
1500
1000
500
0
1.00
2.06
2.21
2.20
1.15
0.99
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

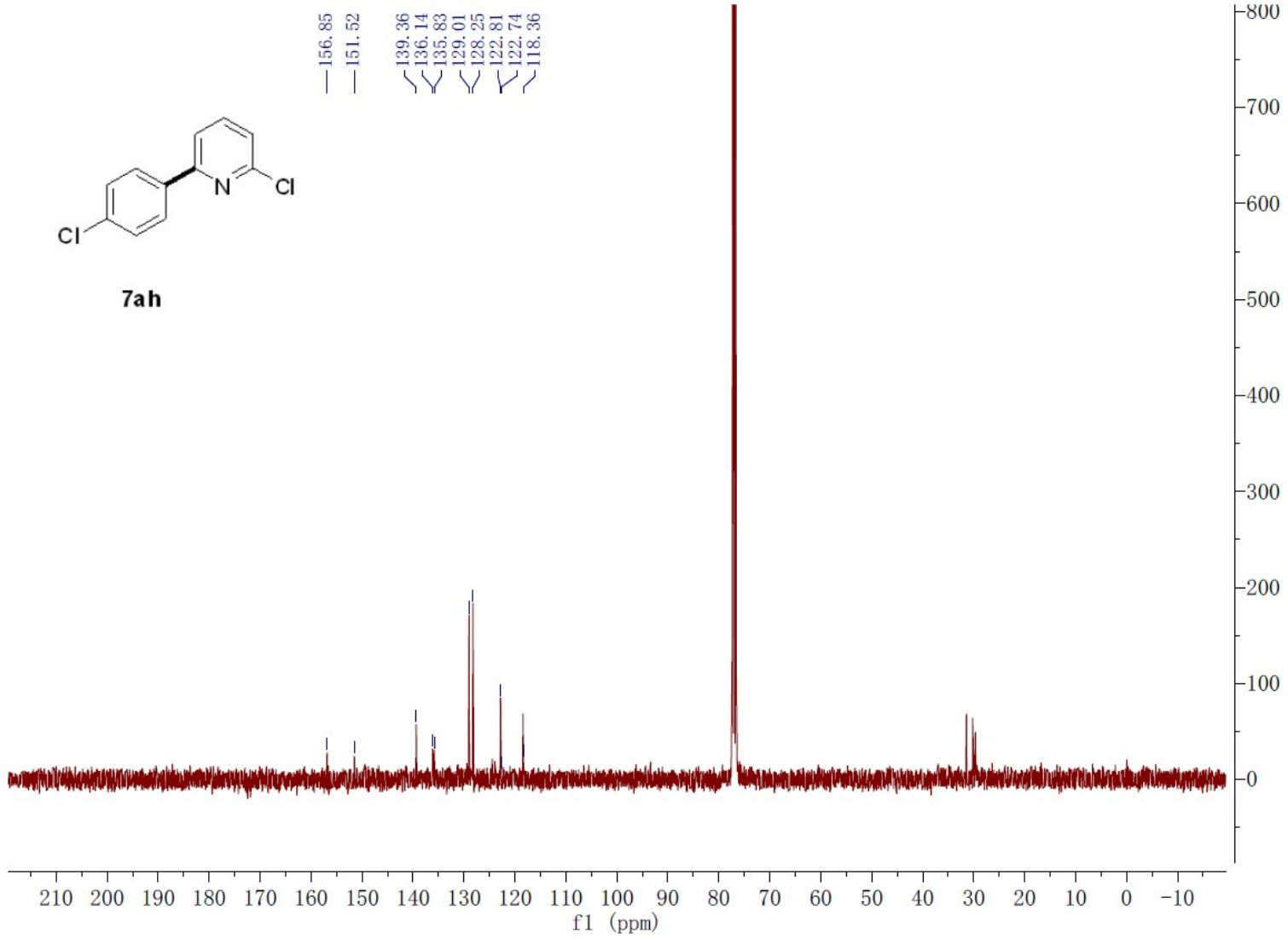

8.68
8.67
7.90
7.88
7.75
7.73
7.71
7.69
7.29
7.28
7.22
7.21
7.20
7.19
7.19
2.41
N
7ae
0.94
1.96
2.02
1.91
0.98
3.00
f1 (ppm)

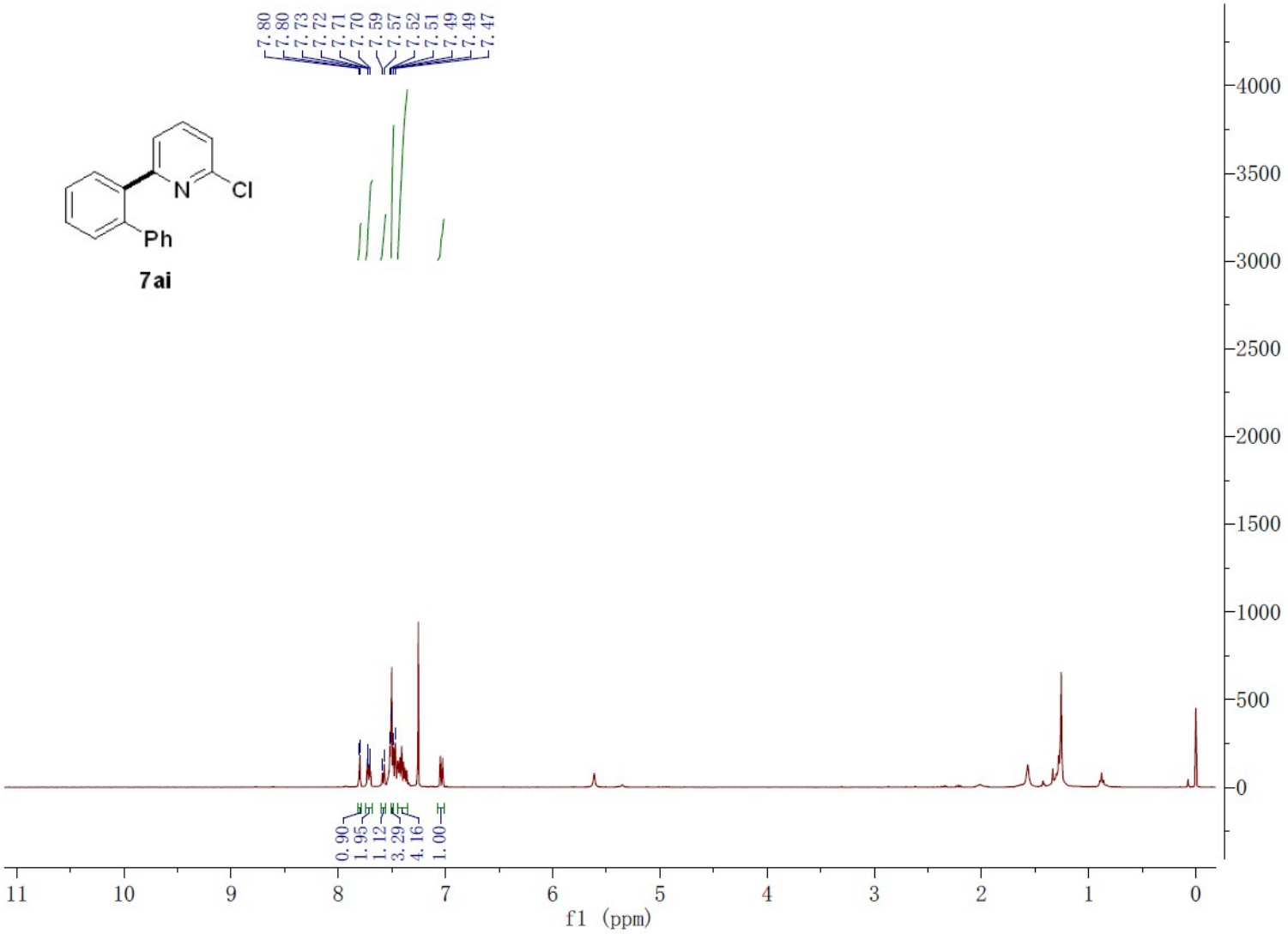

7.91
7.89
7.69
7.67
7.66
7.63
7.61
7.28
7.26
2.40
N
Cl
H3C
7af
1.99
2.19
1.73
1.26
3.00
f1 (ppm)

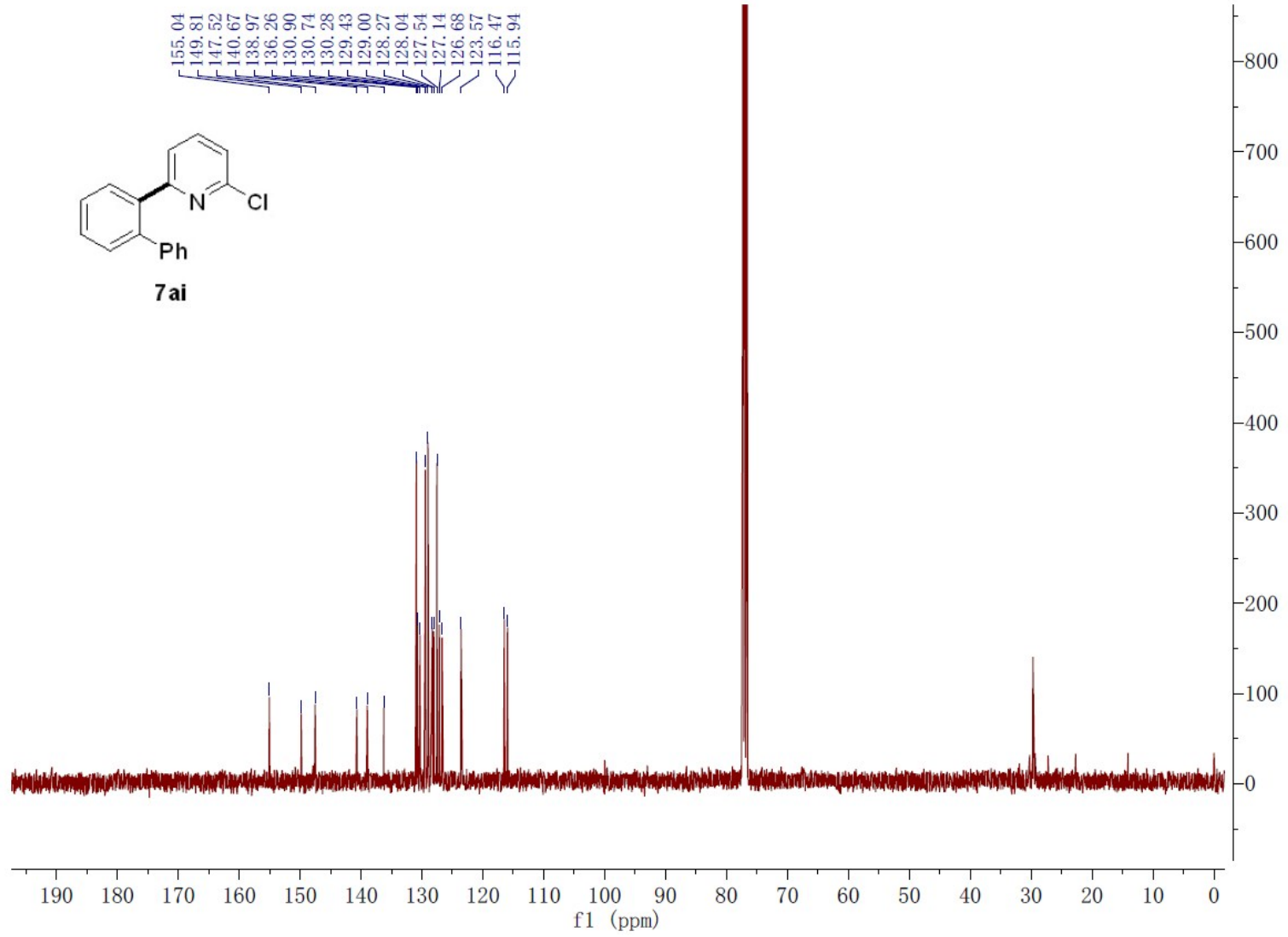

8.12
8.10
8.10
8.06
8.05
7.78
7.75
7.74
7.73
7.70
7.34
7.32
7.31
2.65
N
Cl
H3COC
7ag
4.26
2.09
0.99
3.00
f1 (ppm)

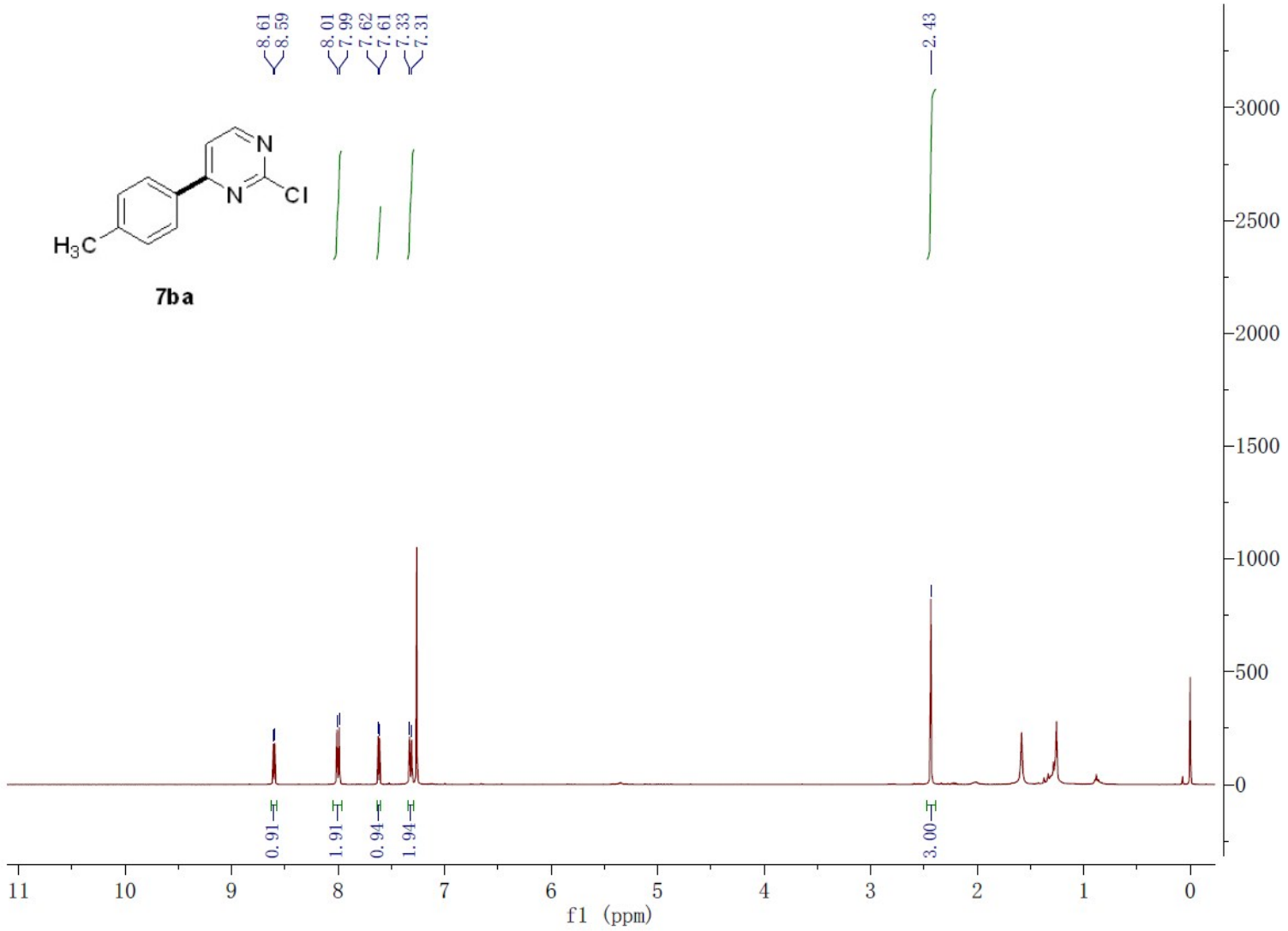

197.65
156.73
151.72
141.84
139.44
137.71
128.83
127.17
123.48
119.18
26.75
N
Cl
H3COC
7ag
4500
4000
3500
3000
2500
2000
1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

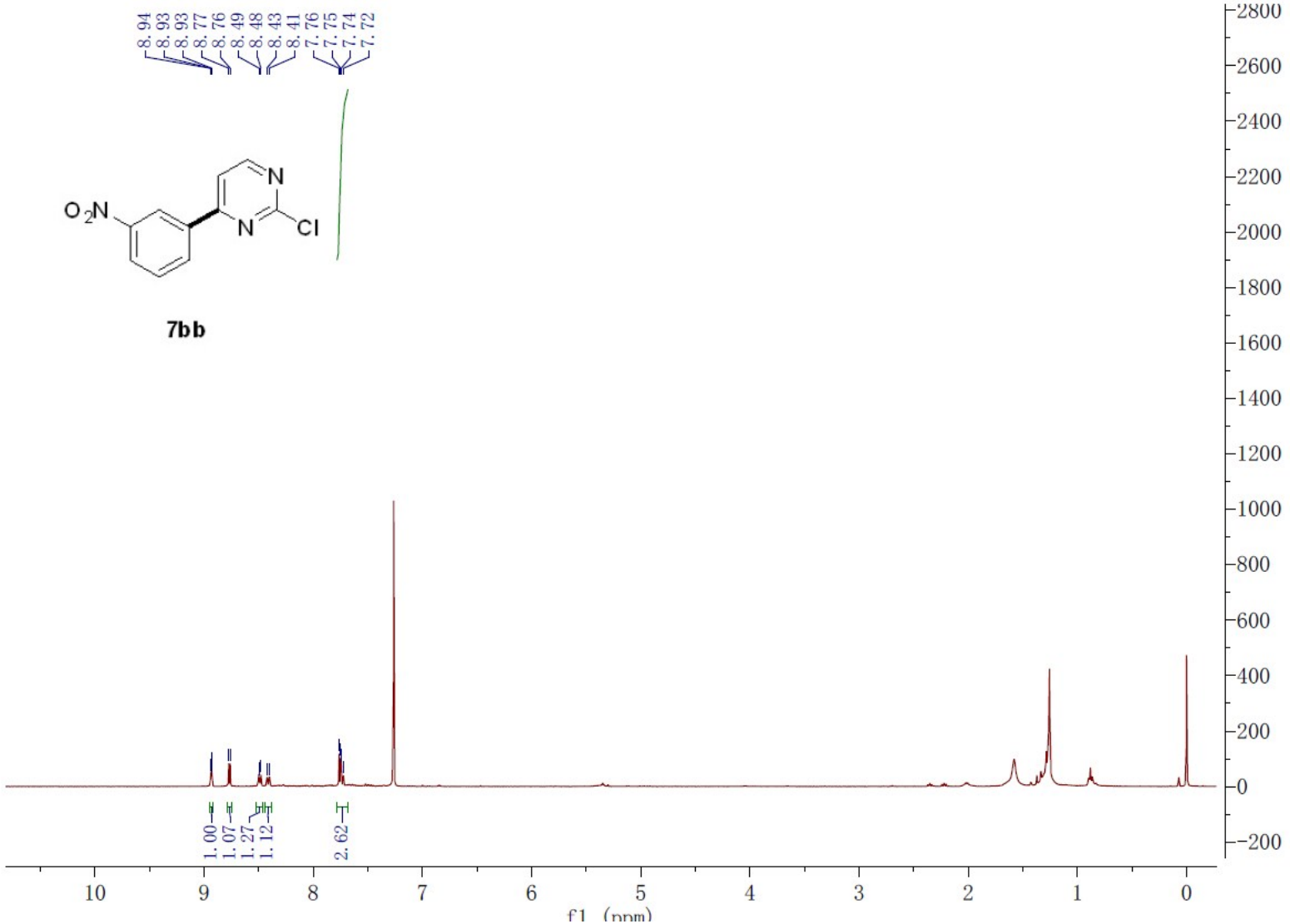

7ah
Cl
N
Cl
7.96
7.94
7.73
7.71
7.69
7.63
7.61
7.46
7.43
7.28
7.26
1.83
1.00
0.93
1.93
1.22
4000
3500
3000
2500
2000
1500
1000
500
0
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

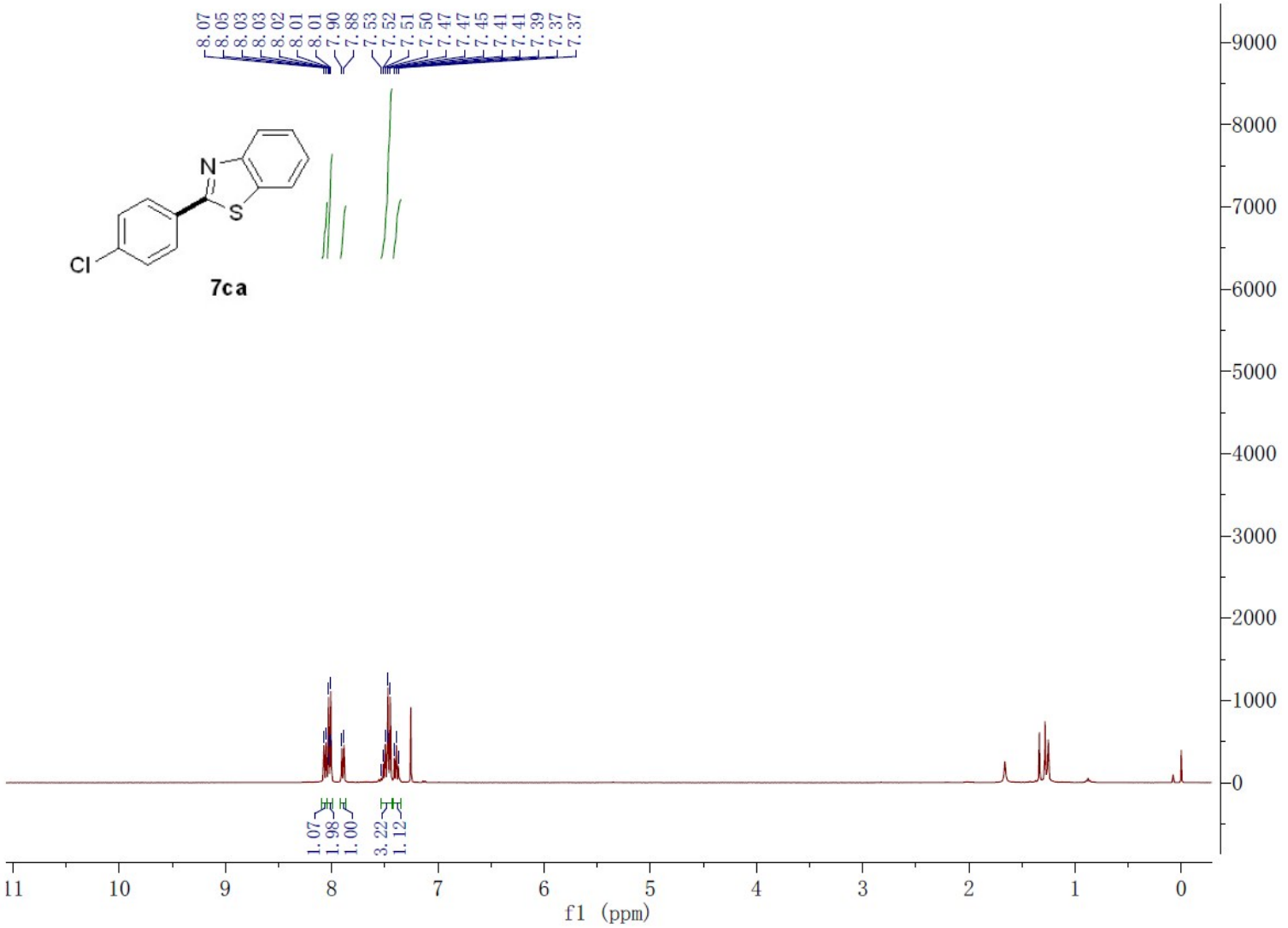

156.85
151.52
139.36
136.14
135.83
129.01
128.25
122.81
122.74
118.36
N
Cl
Cl
7ah
800
700
600
500
400
300
200
100
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

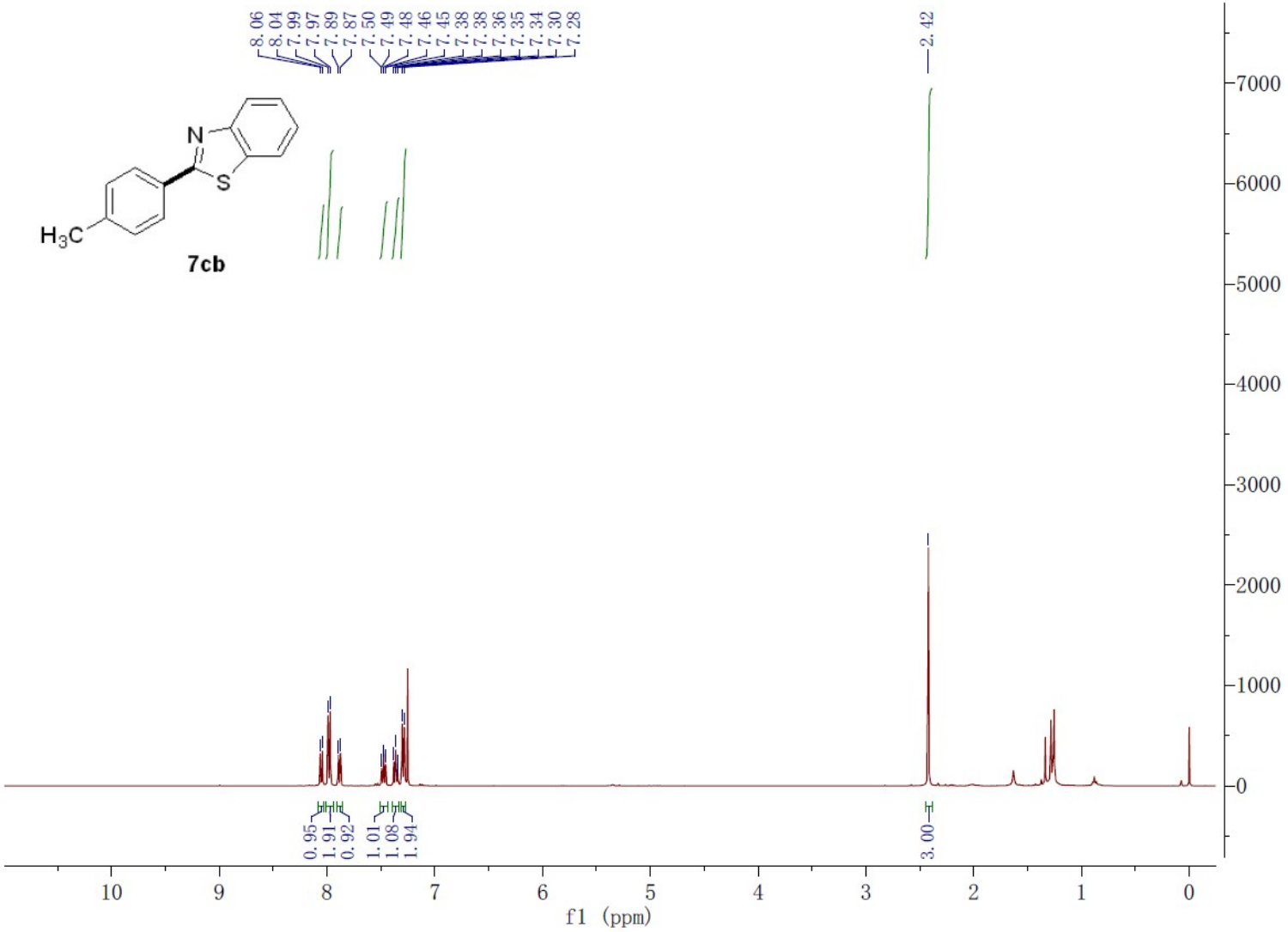

7.80
7.80
7.73
7.72
7.71
7.70
7.59
7.57
7.52
7.51
7.49
7.49
7.47
N
Cl
Ph
7ai
4000
3500
3000
2500
2000
1500
1000
500
0
0.90
1.95
1.12
3.29
4.16
1.00
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

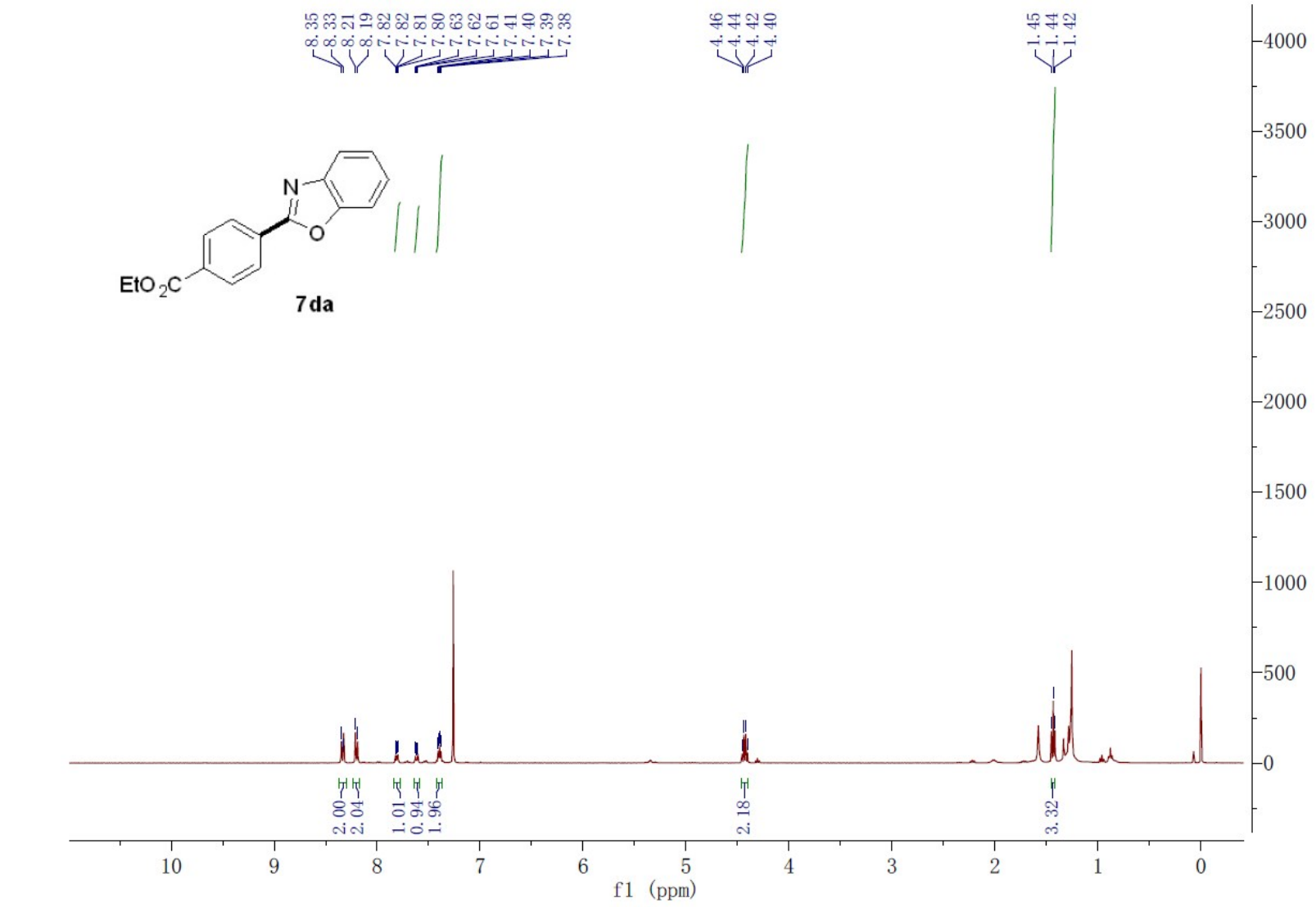

155.04
149.81
147.52
140.67
138.97
136.26
130.90
130.74
130.28
129.43
129.00
128.27
128.04
127.54
127.14
126.68
123.57
116.47
115.94
N
Cl
Ph
7ai
800
700
600
500
400
300
200
100
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

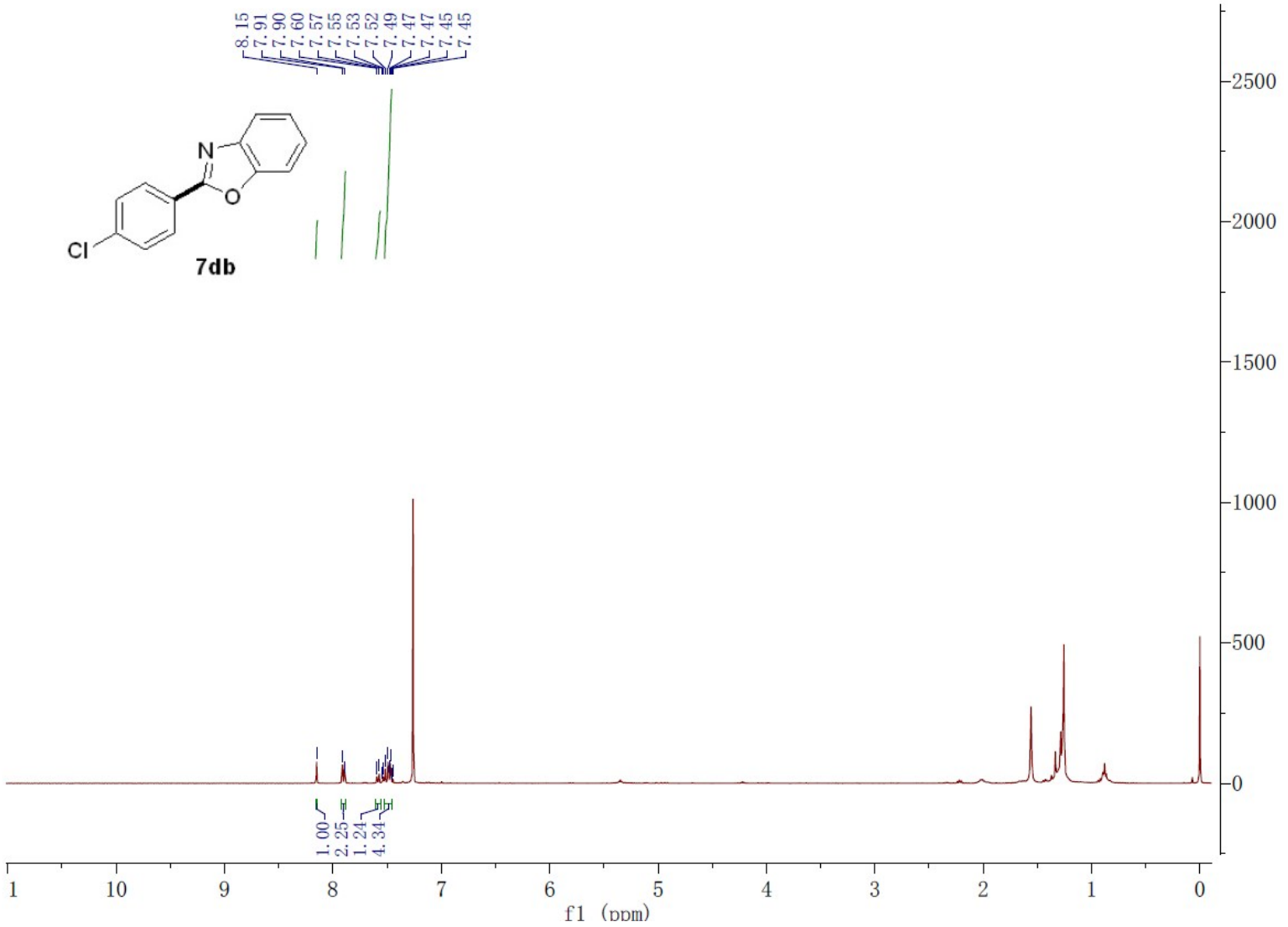

8.61
8.59
8.01
7.99
7.62
7.61
7.33
7.31
2.43
N
N
Cl
H3C
7ba
0.91
1.91
0.94
1.94
3.00
f1 (ppm)

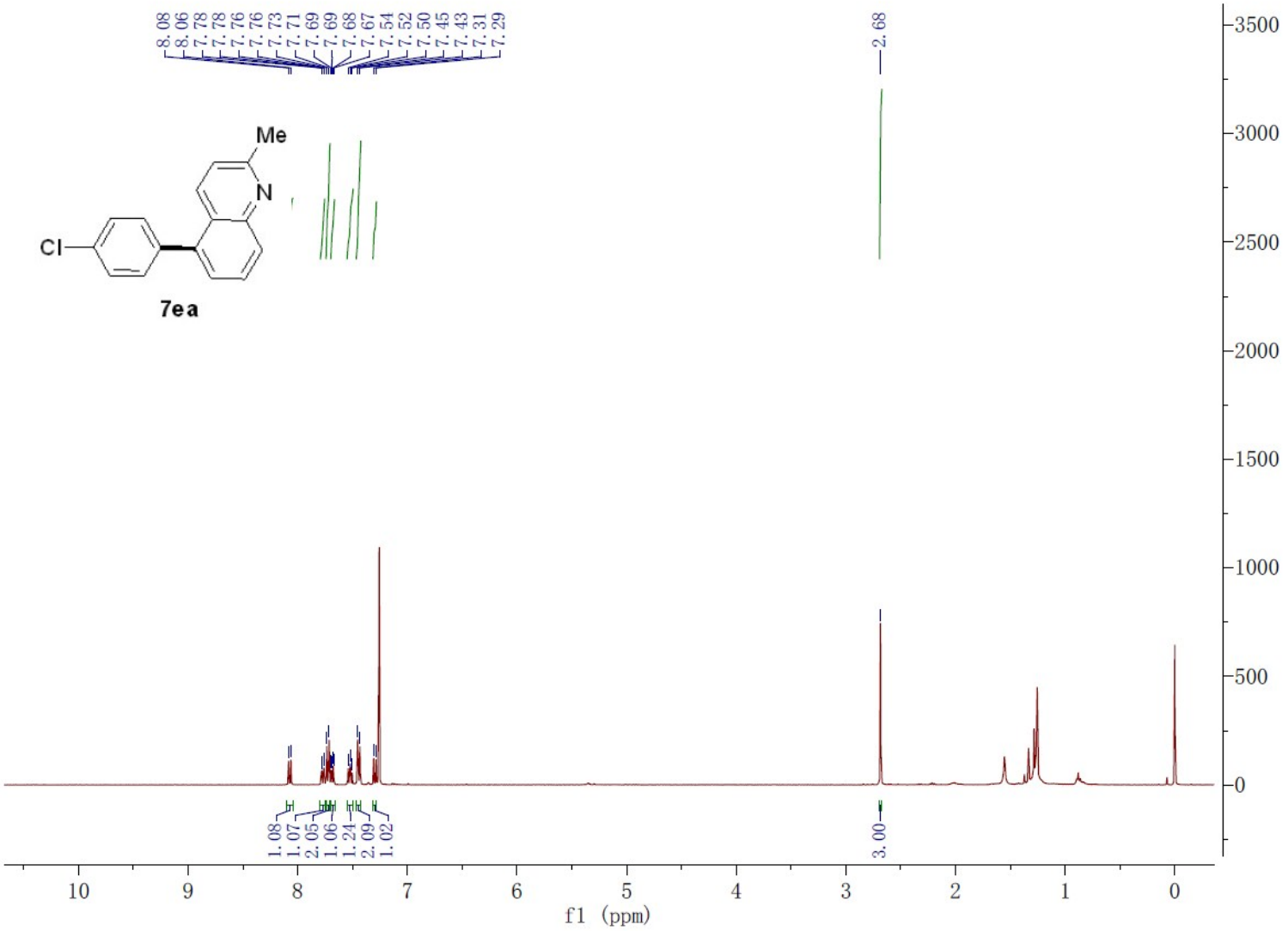

8.94
8.93
8.93
8.77
8.76
8.49
8.48
8.43
8.41
7.76
7.75
7.74
7.72
O2N
N
N
Cl
7bb
1.00
1.07
1.27
1.12
2.62
f1 (ppm)

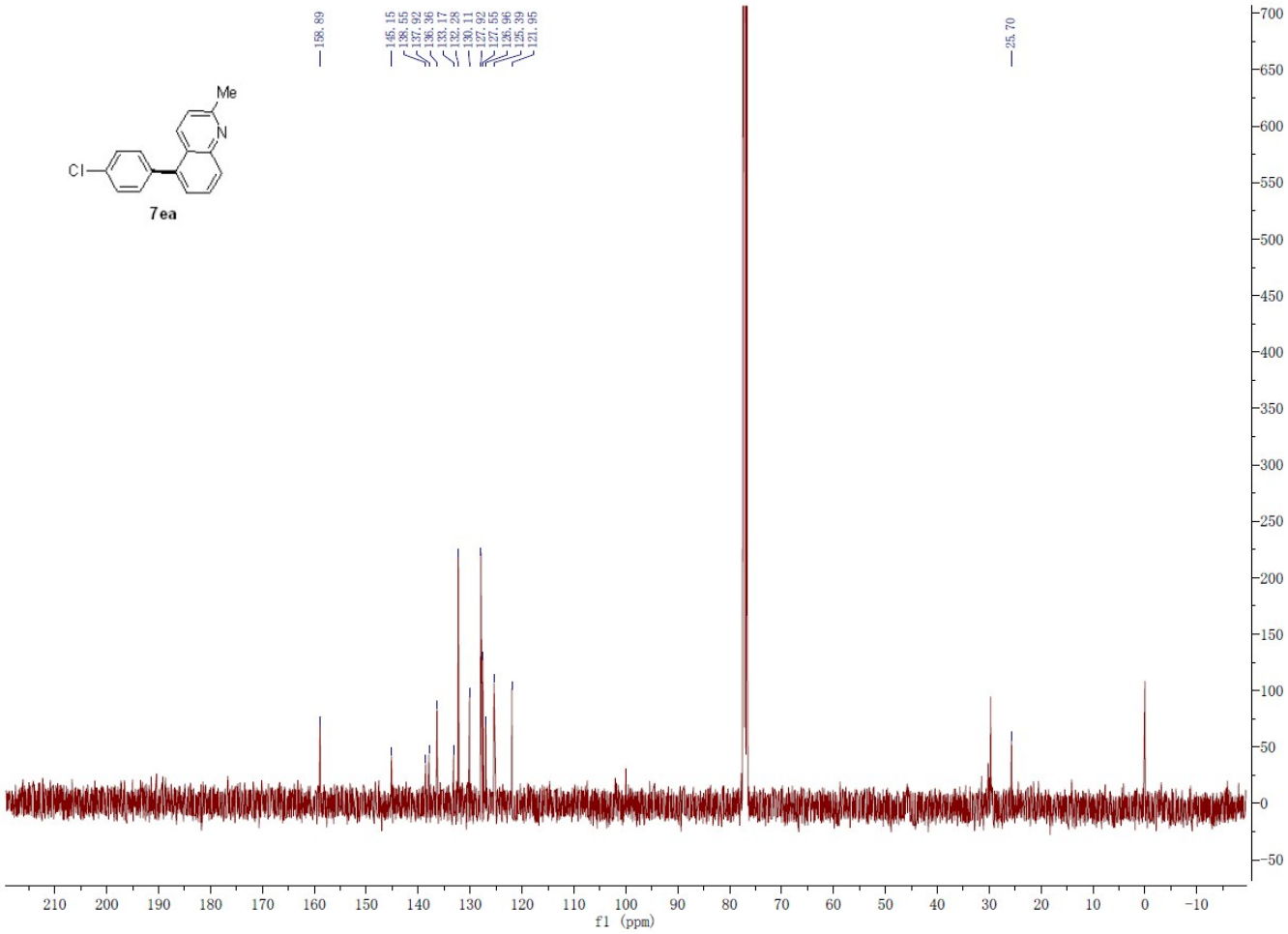

8.07
8.05
8.03
8.03
8.02
8.01
8.01
7.90
7.88
7.53
7.52
7.51
7.50
7.47
7.47
7.45
7.41
7.41
7.39
7.37
7.37
N
S
Cl
7ca
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
1.07
1.98
1.00
3.22
1.12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

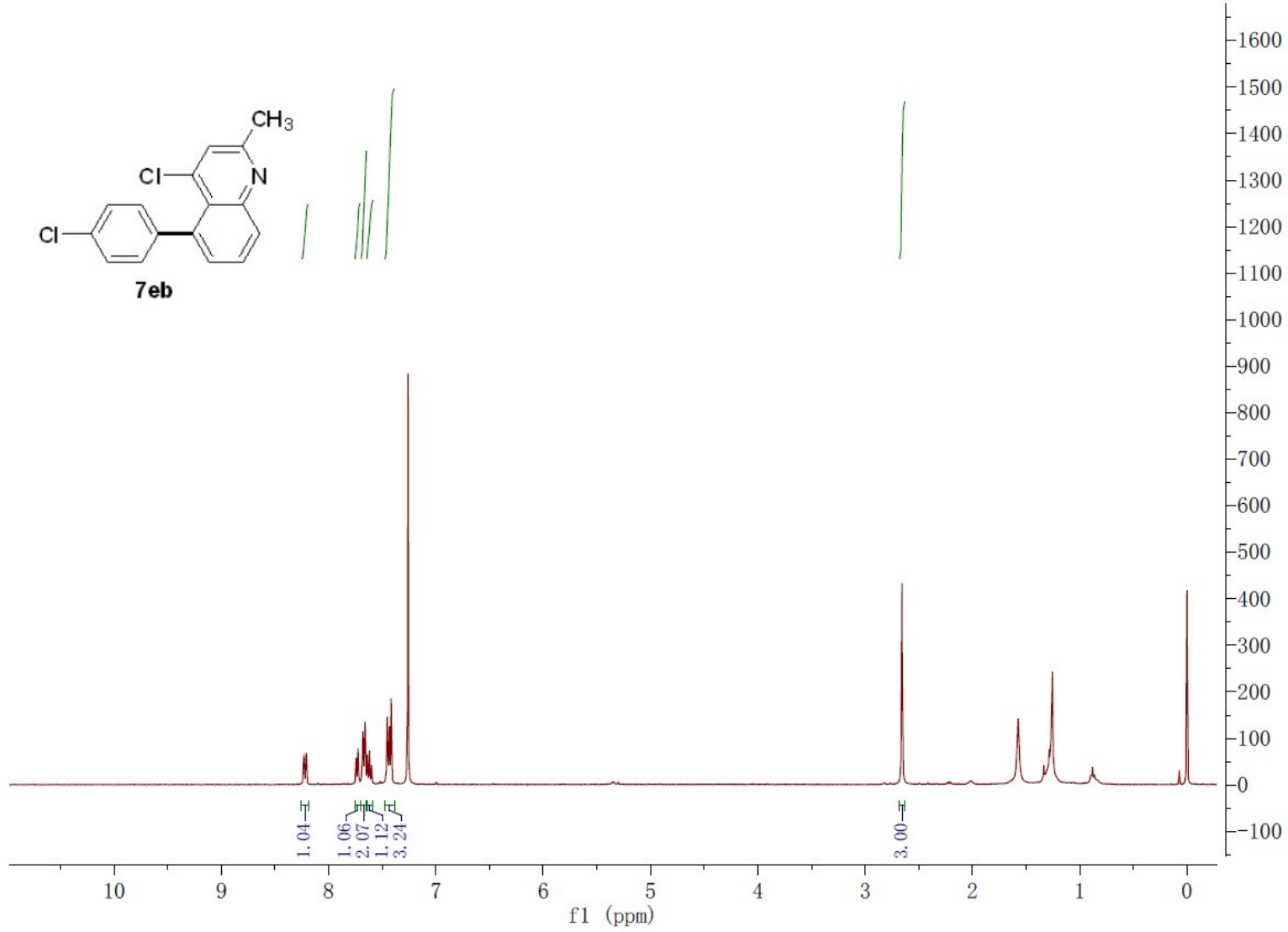

8.06
8.04
7.99
7.97
7.89
7.87
7.50
7.49
7.48
7.46
7.45
7.38
7.38
7.36
7.35
7.34
7.30
7.28
2.42
N
S
H3C
7cb
0.95
1.91
0.92
1.01
1.08
1.94
3.00
7000
6000
5000
4000
3000
2000
1000
0
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

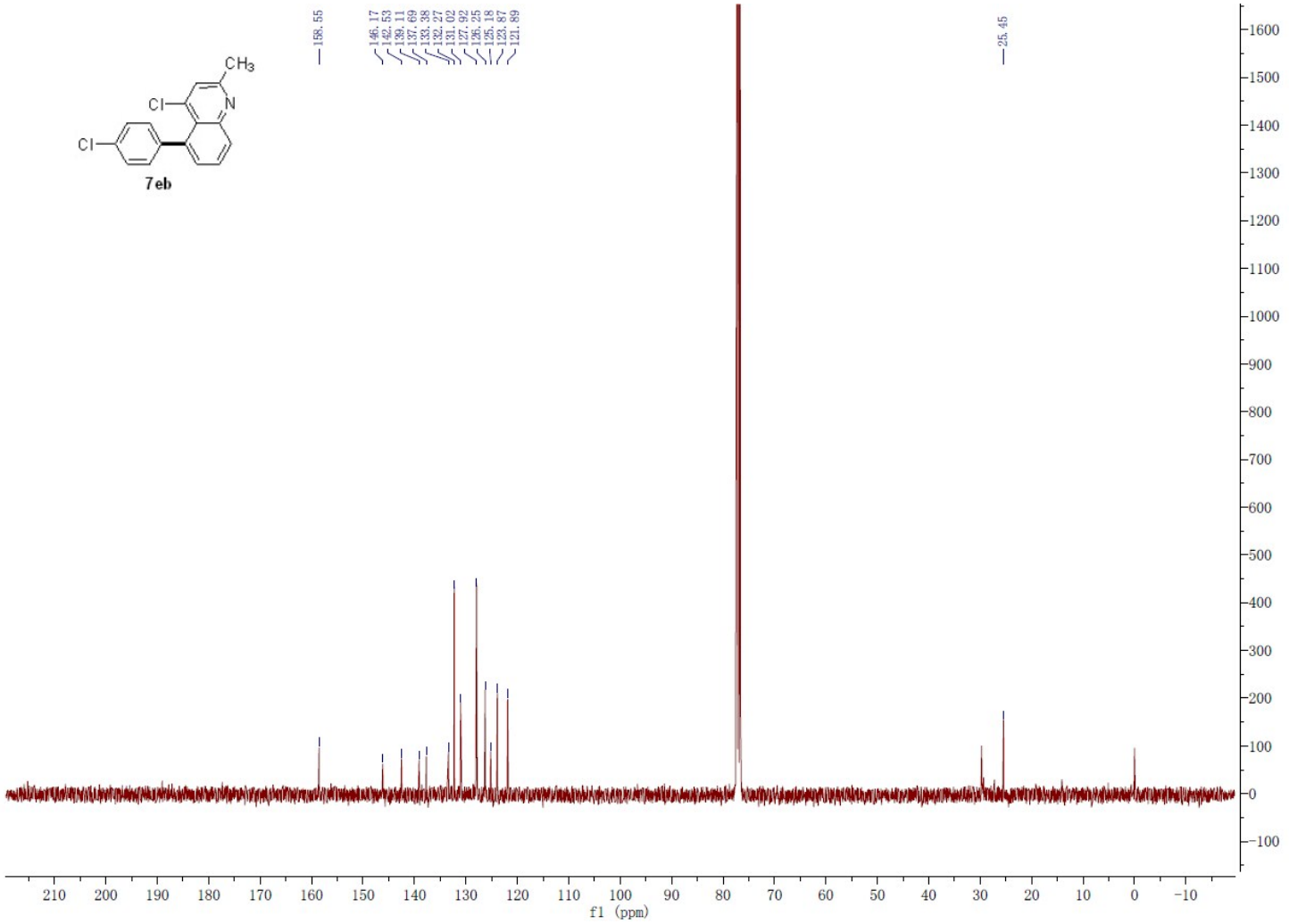

8.35
8.33
8.21
8.19
7.82
7.82
7.81
7.80
7.63
7.62
7.61
7.41
7.40
7.39
7.38
4.46
4.44
4.42
4.40
1.45
1.44
1.42
N
O
EtO2C
7da
4000
3500
3000
2500
2000
1500
1000
500
0
2.00
2.04
1.01
0.94
1.96
2.18
3.32
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

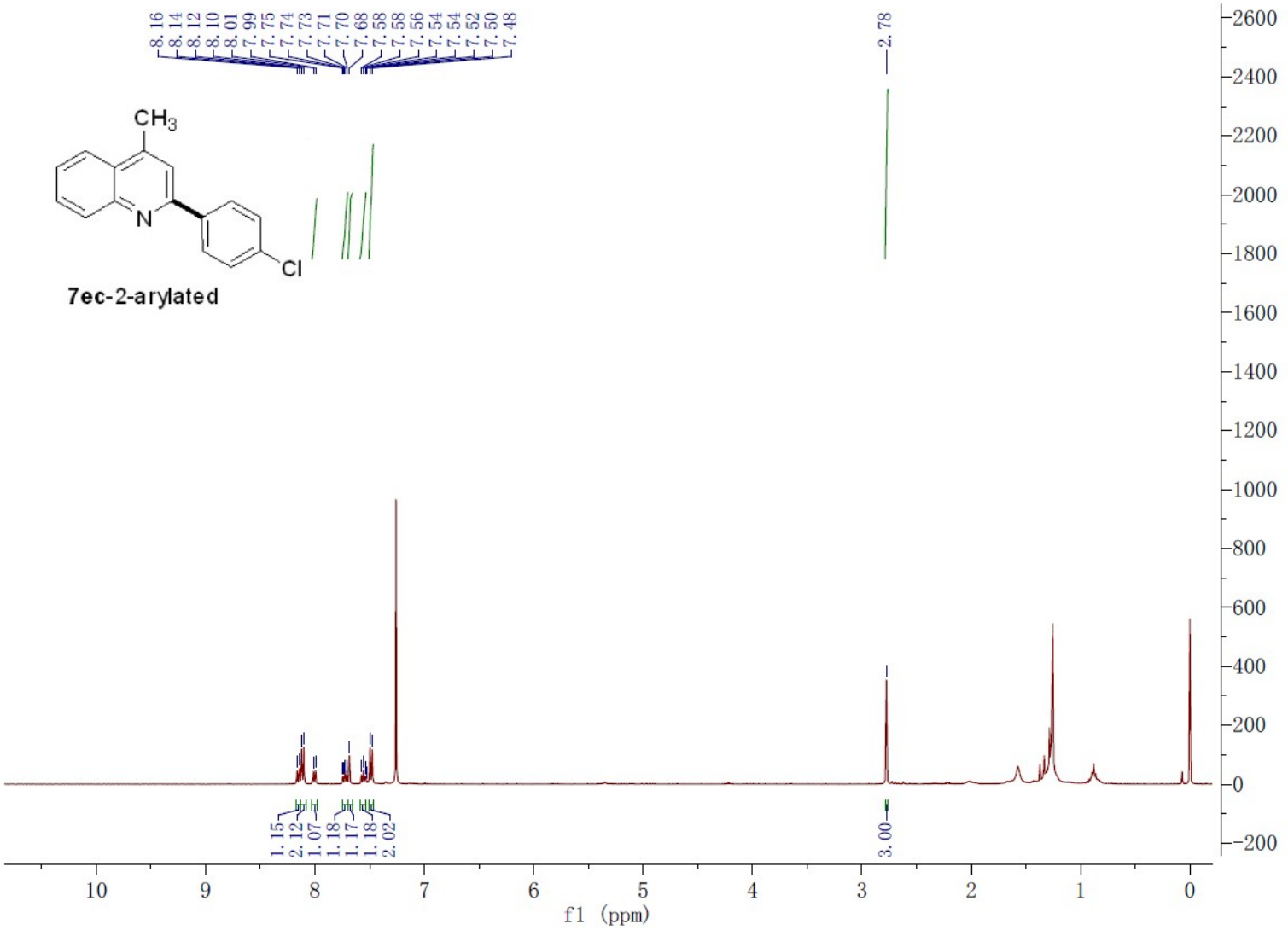

8.15
7.91
7.90
7.60
7.57
7.55
7.53
7.52
7.49
7.47
7.47
7.45
7.45
N
O
Cl
7db
2500
2000
1500
1000
500
0
1.00
2.25
1.24
4.34
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

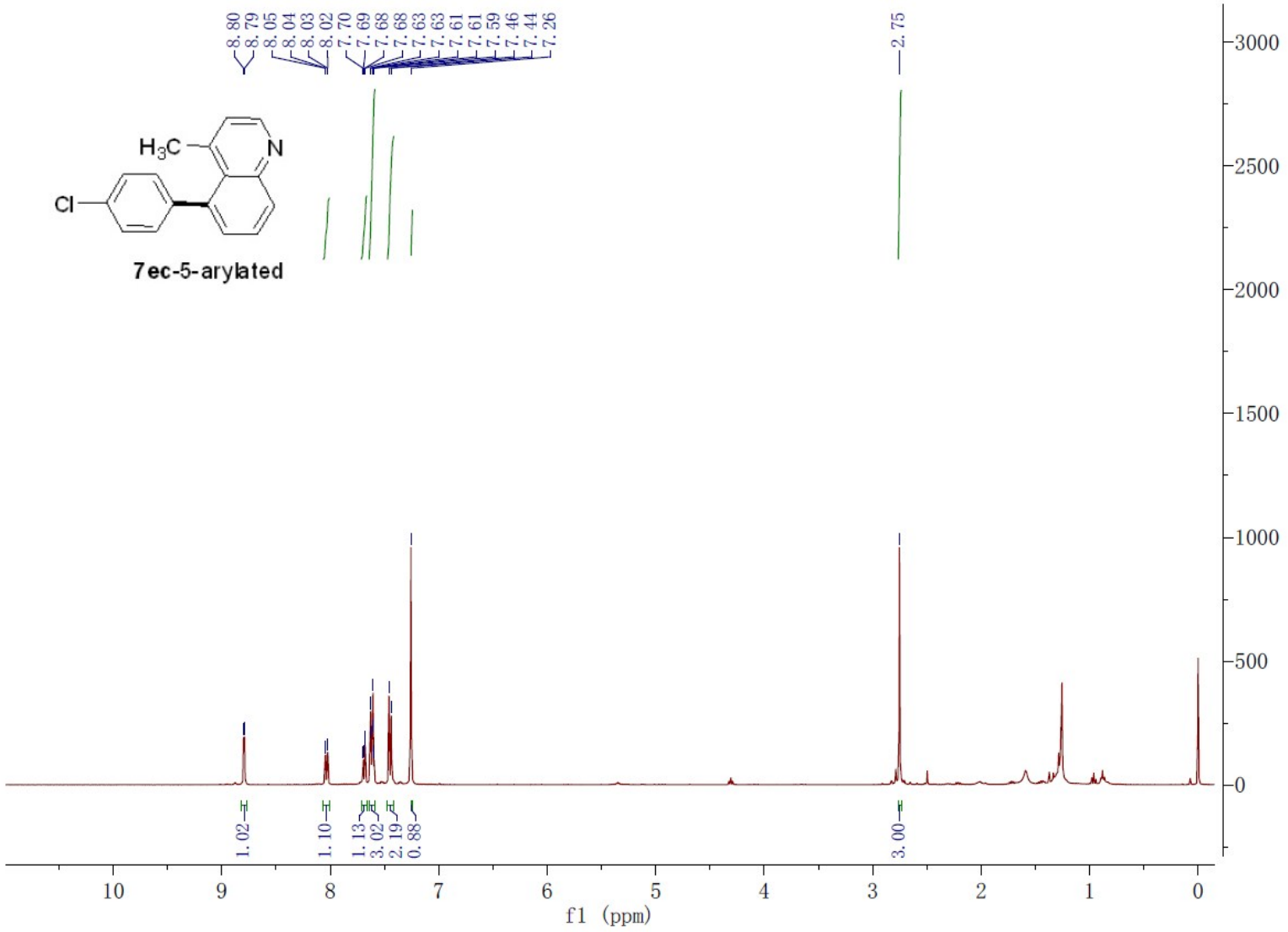

8.08
8.06
7.78
7.78
7.76
7.76
7.73
7.71
7.69
7.69
7.68
7.67
7.54
7.52
7.50
7.45
7.43
7.31
7.29
2.68
Me
N
Cl
7ea
3500
3000
2500
2000
1500
1000
500
0
1.08
1.07
2.05
1.06
1.24
2.09
1.02
3.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

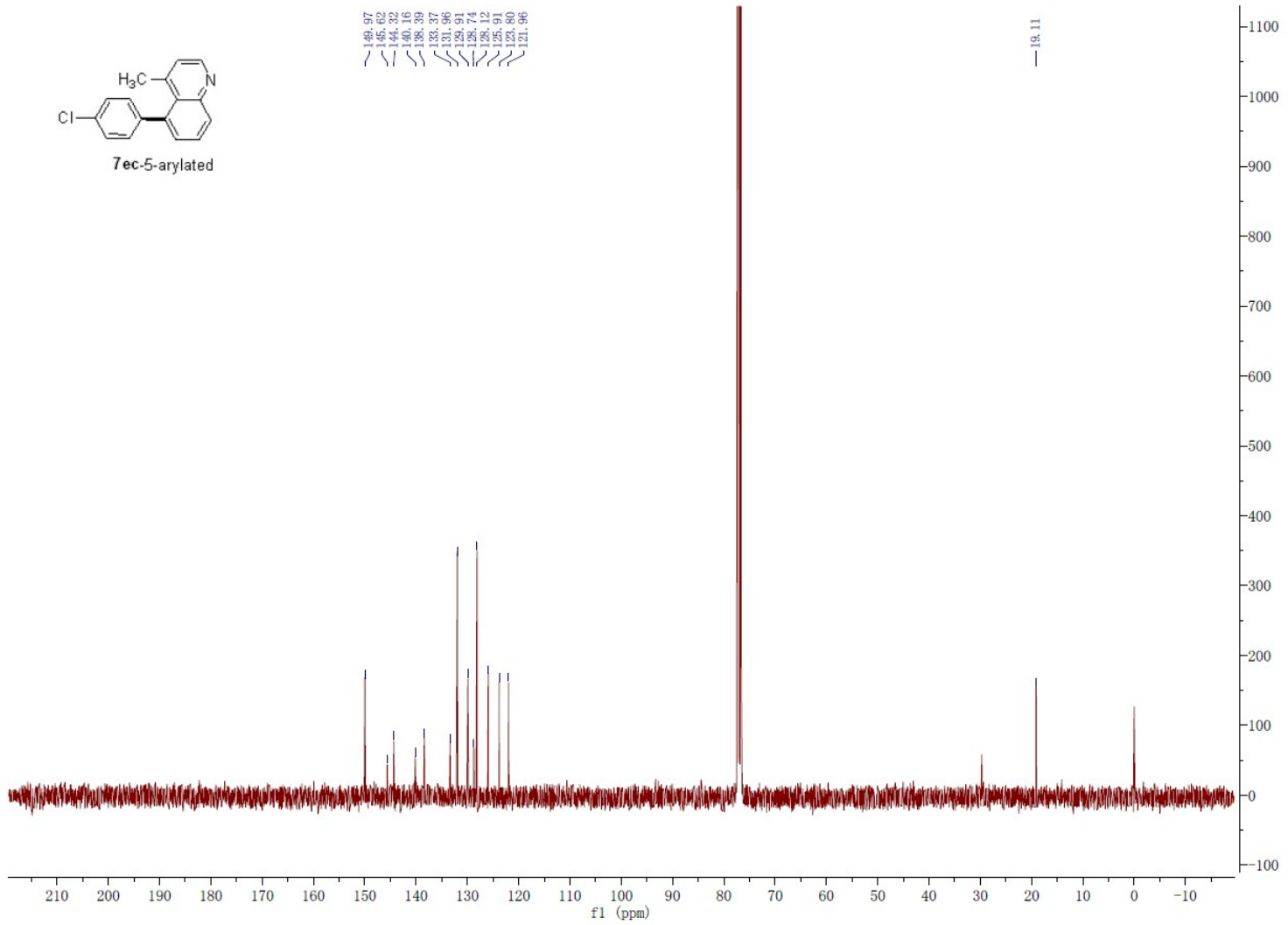

158.89
145.15
138.55
137.92
136.36
133.17
132.28
130.11
127.92
127.55
126.96
125.39
121.95
25.70
Me
N
Cl
7ea
f1 (ppm)


CH3
Cl
N
Cl
7eb
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
1.04
1.06
2.07
1.12
3.24
3.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


158.55
146.17
142.53
139.11
137.69
133.38
132.27
131.02
127.92
126.25
125.18
123.87
121.89
25.45
CH3
Cl
N
Cl
7eb
f1 (ppm)


8.16
8.14
8.12
8.10
8.01
7.99
7.75
7.74
7.73
7.71
7.70
7.68
7.58
7.58
7.56
7.54
7.54
7.52
7.50
7.48
2.78
CH3
N
Cl
7ec-2-arylated
1.15
2.12
1.07
1.18
1.17
1.18
2.02
3.00
f1 (ppm)


8.80
8.79
8.05
8.04
8.03
8.02
7.70
7.69
7.68
7.68
7.63
7.63
7.61
7.61
7.59
7.46
7.44
7.26
2.75
H3C
N
Cl
7ec-5-arylated
3000
2500
2000
1500
1000
500
0
1.02
1.10
1.13
3.02
2.19
0.88
3.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


149.97
145.62
144.32
140.16
138.39
133.37
131.96
129.91
128.74
128.12
125.91
123.80
121.96
19.11
H3C
N
Cl
7ec-5-arylated
f1 (ppm)