Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photoinduced Oxidation of Benzylic Boronic Esters to Ketones/Aldehydes via α-Borylalkyl radicals

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Content

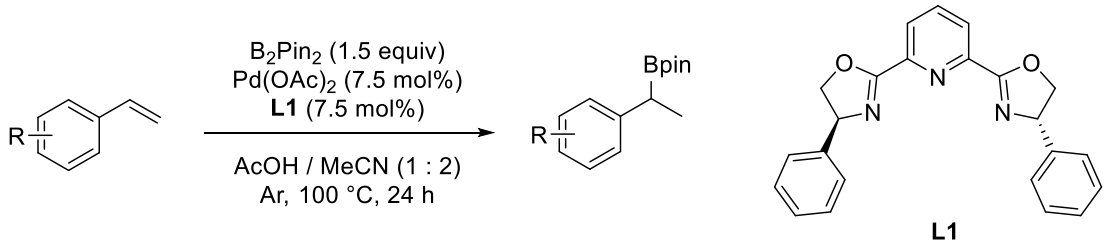
1. General considerations

General. Unless otherwise noted, all reactions were carried out under an air atmosphere. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator. Visualization was accomplished by exposure to a UV lamp. All the products in this article are compatible with standard silica gel chromatography. Column chromatography was performed on silica gel (200–300 mesh) using standard methods.

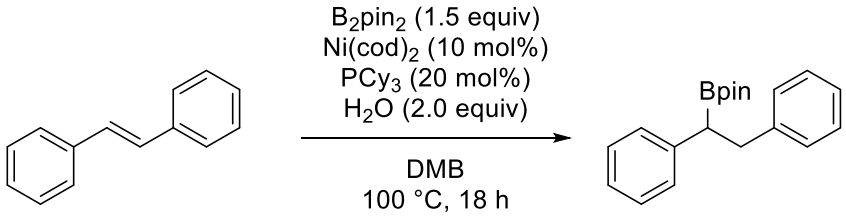
Structural analysis. NMR spectra were measured on a Bruker Ascend 400 spectrometer and chemical shifts (δ) are reported in parts per million (ppm). ^{1}H NMR spectra were recorded at 400 MHz in NMR solvents and referenced internally to corresponding solvent resonance, and ^{13}C NMR spectra were recorded at 101 MHz and referenced to corresponding solvent resonance. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Infrared spectra were collected on a Thermo Fisher Nicolet 6700 FT-IR spectrometer using ATR (Attenuated Total Reflectance) method. Absorption maxima (ν max) are reported in wavenumbers (cm^{-1}). High resolution mass spectra (HRMS) were acquired on Thermo Scientific LTQ Orbitrap XL with an ESI source.

Materials. Commercial reagents and solvent were purchased from Adamas, J&K, Energy, Sigma-Aldrich, Alfa Aesar, Acros Organics, TCI and used as received unless otherwise stated.

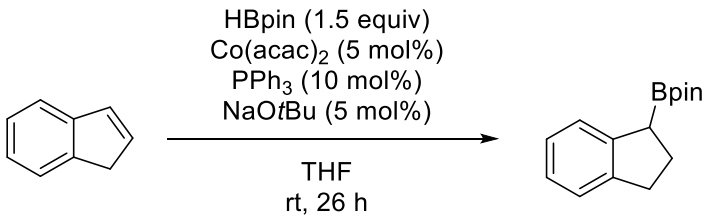
2. Preparation of boronic esters



General Procedure 1: Using a variation of the procedure of Jiang and co-workers,[1] an oven dried flask was charged with $Pd(OAc)_2$ (18.0 mg, 0.075 mmol, 7.5 mol%), B_2pin_2 (388.6 mg, 1.5 mmol, 1.5 equiv), ligand **L1** (27.7 mg, 0.075 mmol, 7.5 mol%) and purged with Ar. Then, styrene (116 μL, 1.0 mmol, 1.0 equiv), acetonitrile (1.6 mL) and acetic acid (0.80 mL) were added separately and the mixture was heated to 100 °C and stirred for 24 hours. Upon completion (as determined by TLC), the mixture was cooled to room temperature and concentrated in vacuo, and then purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to give the corresponding boronic esters.

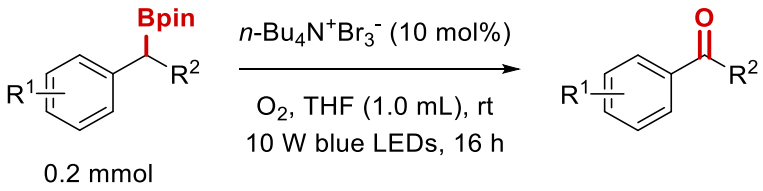


General Procedure 2: Using a variation of the procedure of Toyoshi Shimada and co-workers,[2] an oven dried flask was charged with stilbene (180.2 mg, 1.0 mmol, 1.0 equiv), $Ni(cod)_2$ (26.7 mg, 0.10 mmol, 10 mol%), B_2pin_2 (388.6 mg, 1.5 mmol, 1.5 equiv), PCy_3 (56.1 mg, 0.20 mmol, 20 mol%) and purged with Ar. Then, H_2O (36 μL, 2.0 mmol, 2.0 equiv) and xylene (3.0 mL) were added separately and the mixture was heated to 100 °C and stirred for 18 hours. Upon completion (as determined by TLC), the mixture was cooled to room temperature and concentrated in vacuo, and then purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to give the corresponding boronic esters.



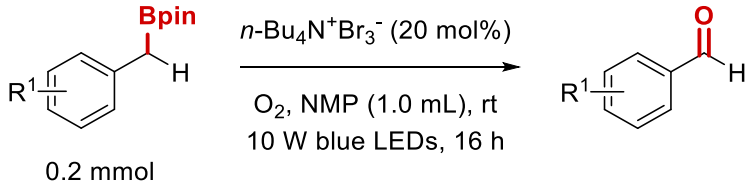
General Procedure 3: Using a variation of the procedure of Michael Findlater and co-workers,[3] an oven dried flask was charged with cobalt(II) acetylacetonate (12.8 mg, 0.050 mmol, 5.0 mol%), PPh_3 (26.2 mg, 0.10 mmol, 10 mol%), NaO*t*Bu (4.8 mg, 0.050 mmol, 5.0 mol%) and purged with Ar. Then, indene (116 μL, 1.0 mmol, 1.0 equiv), HBpin (218 μL, 1.5 mmol, 1.5 equiv) and anhydrous THF (2.0 mL) were added separately and the mixture was stirred at room temperature for 26 hours. Upon completion (as determined by TLC), the mixture was cooled to room temperature and concentrated in vacuo, and then purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to give the corresponding boronic esters.

3. General procedures for the conversions from boronic esters to the carbonyl groups



0.2 mmol

General Procedure A: A flame-dried 25 mL quartz column reaction tube was placed with a magnetic stir bar. Then, boronic esters (0.20 mmol, 1.0 equiv), tetrabutylammonium tribromide (9.6 mg, 0.020 mmol, 10 mol%), and THF (1.0 mL) were added. Then, the tube was charged with oxygen. The reaction tube was placed on a photocatalytic parallel reactor with 10 W blue LEDs (455 - 460 nm) at the bottom (**Figure S1**). Then the reaction tube (at approximately 0.3 cm away from the light source) was irradiated with the blue LEDs. After stirring for 16 hours at room temperature, the reaction mixture was concentrated under vacuum to afford the crude product, which was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to give the target products.



0.2 mmol

General Procedure B: A flame-dried 25 mL quartz column reaction tube was placed with a magnetic stir bar. Then, boronic esters (0.20 mmol, 1.0 equiv), tetrabutylammonium tribromide (19.2 mg, 0.040 mmol, 20 mol%), and NMP (1.0 mL) were added. Then, the tube was charged with oxygen. The reaction tube was placed on a photocatalytic parallel reactor with 10 W blue LEDs (455 - 460 nm) at the bottom (**Figure S1**). Then the reaction tube (at approximately 0.3 cm away from the light source) was irradiated with the blue LEDs. After stirring for 16 hours at room temperature, the reaction mixture was concentrated under vacuum to afford the crude

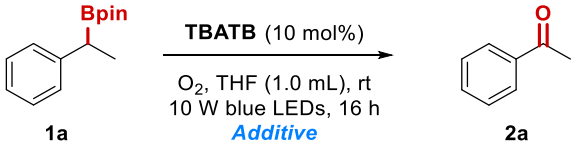
product, which was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to give the target products.

Figure S1. Picture of the reactor

4. Other controlled experiment

Other radical trapping reagents have also been used to test their influence on the reaction. For examples, in the presence of 2.0 equiv 2,6-di-tert-butyl-4-methylphenol (BHT) and 2.0 equiv *p*-benzoquinone (BQ), acetophenone was obtained in 18% and 15% HPLC yield, respectively. This supplementary radical trapping experiments also indicated the involvement of radical species.

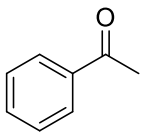
Table S1. Other controlled experiment



Entry	Additive	HPLC yield
1	BHT (2 equiv)	18%
2	BQ (2 equiv)	15%

5. Characterization data

(2a) acetophenone (CAS: 98-86-2)[4]



acetophenone
Chemical Formula: C_8H_8O
Exact Mass: 120.0575
Molecular Weight: 120.1510

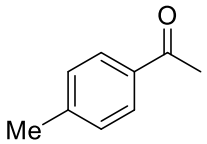
Following the General Procedure A with 4,4,5,5-tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (46.4 μL, 0.20 mmol), **2a** was obtained as colorless oil (22.6 mg, 94%).

This target product was purified by column chromatography on silica gel (PE : EA = 30 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.4 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 2.60 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3, 137.3, 133.3, 128.8, 128.5, 26.8.

(2b) 1-(*p*-tolyl)ethan-1-one (CAS: 122-00-9)[4]



1-(*p*-tolyl)ethan-1-one
Chemical Formula: $C_9H_{10}O$
Exact Mass: 134.0732
Molecular Weight: 134.1780

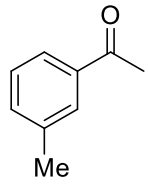
Following the General Procedure A with 4,4,5,5-tetramethyl-2-(1-(*p*-tolyl)ethyl)-1,3,2-dioxaborolane (49.2 μL, 0.20 mmol), **2b** was obtained as colorless oil (19.9 mg, 74%).

This target product was purified by column chromatography on silica gel (PE : EA = 30 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 2.56 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 143.9, 134.8, 129.3, 128.5, 26.5, 21.6.

(2c) 1-(*m*-tolyl)ethan-1-one (CAS: 585-74-0)[4]



1-(*m*-tolyl)ethan-1-one
Chemical Formula: $C_9H_{10}O$
Exact Mass: 134.0732
Molecular Weight: 134.1780

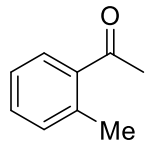
Following the General Procedure A with 4,4,5,5-tetramethyl-2-(1-(*m*-tolyl)ethyl)-1,3,2-dioxaborolane (49.2 μL, 0.20 mmol), **2c** was obtained as colorless oil (19.6 mg, 73%).

This target product was purified by column chromatography on silica gel (PE : EA = 30 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 2H), 7.40 – 7.32 (m, 2H), 2.59 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 138.5, 137.3, 134.0, 129.0, 128.6, 125.7, 26.8, 21.4.

(2d) 1-(*o*-tolyl)ethan-1-one (CAS: 577-16-2)[5]



1-(*o*-tolyl)ethan-1-one
Chemical Formula: $C_9H_{10}O$
Exact Mass: 134.0732
Molecular Weight: 134.1780

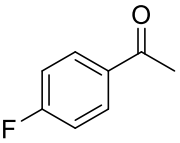
Following the General Procedure A with 4,4,5,5-tetramethyl-2-(1-(*o*-tolyl)ethyl)-1,3,2-dioxaborolane (49.2 μL, 0.20 mmol), **2d** was obtained as colorless oil (13.7 mg, 51%).

This target product was purified by column chromatography on silica gel (PE : EA = 30 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 6.8 Hz, 1H), 7.26 (dd, J = 11.2, 7.6 Hz, 2H), 2.58 (s, 3H), 2.53 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 138.6, 137.8, 132.2, 131.7, 129.5, 125.9, 29.7, 21.8.

(2e) 1-(4-fluorophenyl)ethan-1-one (CAS: 403-42-9)[6]



1-(4-fluorophenyl)ethan-1-one
Chemical Formula: C_8H_7FO
Exact Mass: 138.0481
Molecular Weight: 138.1414

Following the General Procedure A with 2-(1-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (50.0 μL, 0.20 mmol), **2e** was obtained as colorless oil (11.1 mg, 40%).

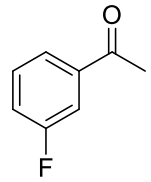
This target product was purified by column chromatography on silica gel (PE : EA = 30 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (q, J = 4.8 Hz, 2H), 7.13 (t, J = 8.6 Hz, 2H), 2.59 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 167.2, 164.7, 133.8, 133.8, 131.2, 131.1, 116.0, 115.7, 26.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -105.4.

(2f) 1-(3-fluorophenyl)ethan-1-one (CAS: 455-36-7)[6]



1-(3-fluorophenyl)ethan-1-one
Chemical Formula: C_8H_7FO
Exact Mass: 138.0481
Molecular Weight: 138.1414

Following the General Procedure A with 2-(1-(3-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (50.0 μL, 0.20 mmol), **2f** was obtained as colorless oil (15.5 mg, 56%).

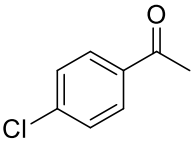
This target product was purified by column chromatography on silica gel (PE : EA = 30 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 9.6 Hz, 1H), 7.45 (dd, J = 13.6, 8.0 Hz, 1H), 7.27 (dd, J = 10.0, 8.4 Hz, 1H), 2.60 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 164.1, 161.6, 139.2, 139.2, 130.3, 130.2, 124.1, 120.2, 120.0, 115.1, 114.9, 26.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.0.

(2g) 1-(4-chlorophenyl)ethan-1-one (CAS: 99-91-2)[4]



1-(4-chlorophenyl)ethan-1-one
Chemical Formula: C_8H_7ClO
Exact Mass: 154.0185
Molecular Weight: 154.5930

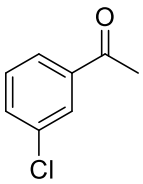
Following the General Procedure A with 2-(1-(4-chlorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (50.3 μL, 0.20 mmol), **2g** was obtained as colorless oil (15.7 mg, 51%).

This target product was purified by column chromatography on silica gel (PE : EA = 30 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H), 2.58 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 139.7, 135.6, 129.9, 129.1, 26.7.

(2h) 1-(3-chlorophenyl)ethan-1-one (CAS: 99-02-5)[6]



1-(3-chlorophenyl)ethan-1-one
Chemical Formula: C_8H_7ClO
Exact Mass: 154.0185
Molecular Weight: 154.5930

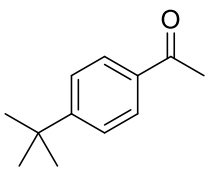
Following the General Procedure A with 2-(1-(3-chlorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (50.3 μL, 0.20 mmol), **2h** was obtained as colorless oil (15.7 mg, 51%).

This target product was purified by column chromatography on silica gel (PE : EA = 30 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.54 (dd, J = 8.0, 1.0 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 2.60 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 138.8, 135.1, 133.2, 130.1, 128.6, 126.6, 26.8.

(2i) 1-(4-(*tert*-butyl)phenyl)ethan-1-one (CAS: 943-27-1)[6]



1-(4-(*tert*-butyl)phenyl)ethan-1-one
Chemical Formula: $C_{12}H_{16}O$
Exact Mass: 176.1201
Molecular Weight: 176.2590

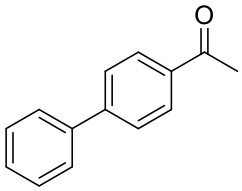
Following the General Procedure A with 2-(1-(4-(*tert*-butyl)phenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (57.6 μL, 0.20 mmol), **2i** was obtained as colorless oil (33.7 mg, 86%).

This target product was purified by column chromatography on silica gel (PE : EA = 30 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.6 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 2.58 (s, 3H), 1.34 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 156.8, 134.6, 128.3, 125.5, 35.1, 31.1, 26.6.

(2j) 1-([1,1'-biphenyl]-4-yl)ethan-1-one (CAS: 92-91-1)[7]



1-([1,1'-biphenyl]-4-yl)ethan-1-one
Chemical Formula: $C_{14}H_{12}O$
Exact Mass: 196.0888
Molecular Weight: 196.2490

Following the General Procedure A with 2-(1-([1,1'-biphenyl]-4-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (61.6 mg, 0.20 mmol), **2j** was obtained as white solid (29.8 mg, 76%).

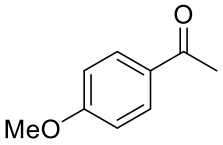
This target product was purified by column chromatography on silica gel (PE : EA = 30 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 7.2 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H), 2.64 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 145.8, 139.9, 135.9, 129.0, 128.9, 128.3, 127.3, 127.3, 26.7.

m.p. 155.6 – 156.8 °C

(2k) 1-(4-methoxyphenyl)ethan-1-one (CAS: 100-06-1)[5]



1-(4-methoxyphenyl)ethan-1-one
Chemical Formula: $C_9H_{10}O_2$
Exact Mass: 150.0681
Molecular Weight: 150.1770

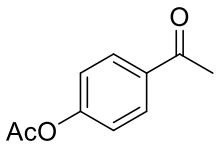
Following the General Procedure A with 2-(1-(4-methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (52.4 μL, 0.20 mmol), **2k** was obtained as colorless oil (26.4 mg, 88%).

This target product was purified by column chromatography on silica gel (PE : EA = 30 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 9.0 Hz, 2H), 6.92 (d, J = 9.0 Hz, 2H), 3.86 (s, 3H), 2.54 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 163.6, 130.7, 130.4, 113.8, 55.6, 26.4.

(2l) 4-acetylphenyl acetate (CAS: 2628-16-2)[8]



4-acetylphenyl acetate
Chemical Formula: $C_{10}H_{10}O_3$
Exact Mass: 178.0630
Molecular Weight: 178.1870

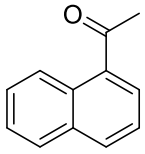
Following the General Procedure A with 4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl acetate (58.0 μL, 0.20 mmol), **2l** was obtained as colorless oil (26.4 mg, 88%).

This target product was purified by column chromatography on silica gel (PE : EA = 30 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.8 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 2.58 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 169.0, 154.5, 134.9, 130.1, 121.9, 26.8, 21.3.

(2m) 1-(naphthalen-1-yl)ethan-1-one (CAS: 941-98-0)[9]



1-(naphthalen-1-yl)ethan-1-one
Chemical Formula: $C_{12}H_{10}O$
Exact Mass: 170.0732
Molecular Weight: 170.2110

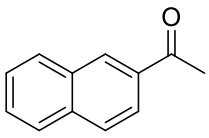
Following the General Procedure A with 4,4,5,5-tetramethyl-2-(1-(naphthalen-1-yl)ethyl)-1,3,2-dioxaborolane (56.4 μL, 0.20 mmol), **2m** was obtained as colorless oil (20.4 mg, 66%).

This target product was purified by column chromatography on silica gel (PE : EA = 30 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, J = 8.8 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H), 7.94 (dd, J = 7.2, 1.2 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.56 – 7.48 (m, 2H), 2.75 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 135.7, 134.2, 133.2, 130.3, 128.9, 128.6, 128.3, 126.6, 126.2, 124.5, 30.2.

(2n) 1-(naphthalen-2-yl)ethan-1-one (CAS: 34-18-4)[9]



1-(naphthalen-2-yl)ethan-1-one
Chemical Formula: $C_{12}H_{10}O$
Exact Mass: 170.0732
Molecular Weight: 170.2110

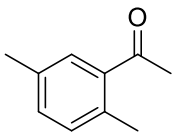
Following the General Procedure A with 4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane (56.4 μL, 0.20 mmol), **2n** was obtained as colorless oil (25.5 mg, 75%).

This target product was purified by column chromatography on silica gel (PE : EA = 30 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.04 (dd, J = 8.8, 2.0 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.91 – 7.87 (m, 2H), 7.63 – 7.53 (m, 2H), 2.73 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3, 135.8, 134.7, 132.7, 130.4, 129.8, 128.7, 128.6, 128.0, 127.0, 124.1, 26.9.

(2o) 1-(2,5-dimethylphenyl)ethan-1-one (CAS: 2142-73-6)[10]



1-(2,5-dimethylphenyl)ethan-1-one
Chemical Formula: $C_{10}H_{12}O$
Exact Mass: 148.0888
Molecular Weight: 148.2050

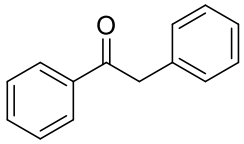
Following the General Procedure A with 2-(1-(2,5-dimethyl-phenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (52.0 μL, 0.20 mmol), **2o** was obtained as colorless oil (14.2 mg, 48%).

This target product was purified by column chromatography on silica gel (PE : EA = 30 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.15 (dd, J = 25.2, 7.6 Hz, 2H), 2.56 (s, 3H), 2.48 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 137.8, 135.4, 135.4, 132.4, 132.1, 130.1, 29.8, 21.3, 21.1.

(2p) 1,2-diphenylethan-1-one (CAS: 451-40-1)[4]



1,2-diphenylethan-1-one
Chemical Formula: $C_{14}H_{12}O$
Exact Mass: 196.0888
Molecular Weight: 196.2490

Following the General Procedure A with 2-(1,2-diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (61.6 mg, 0.20 mmol), **2p** was obtained as white solid (25.1 mg, 64%).

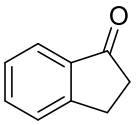
This target product was purified by column chromatography on silica gel (PE : EA = 30 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.35 – 7.22 (m, 5H), 4.28 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 136.8, 134.7, 133.4, 129.7, 128.9, 128.8, 128.8, 127.1, 45.7.

m.p. 56.2 – 57.7 °C

(2q) 2,3-dihydro-1*H*-inden-1-one (CAS: 83-33-0)[4]



2,3-dihydro-1*H*-inden-1-one
Chemical Formula: C_9H_8O
Exact Mass: 132.0575
Molecular Weight: 132.1620

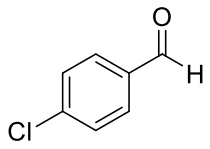
Following the General Procedure A with 2-(2,3-dihydro-1*H*-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (48.8 μL, 0.20 mmol), **2q** was obtained as colorless oil (21.1 mg, 80%).

This target product was purified by column chromatography on silica gel (PE : EA = 30 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 7.6 Hz, 1H), 7.57 (t, J = 7.2 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.36 (t, J = 7.4 Hz, 1H), 3.14 (t, J = 5.6 Hz, 2H), 2.68 (t, J = 5.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.2, 155.3, 137.3, 134.8, 127.5, 126.9, 123.9, 36.4, 26.0.

(2r) 4-chlorobenzaldehyde (CAS: 104-88-1)[9]



4-chlorobenzaldehyde
Chemical Formula: C_7H_5ClO
Exact Mass: 140.0029
Molecular Weight: 140.5660

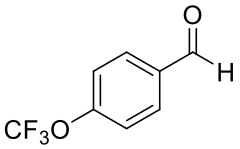
Following the General Procedure A with 2-(4-chlorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (46.8 μL, 0.20 mmol), **2r** was obtained as colorless oil (19.1 mg, 68%).

This target product was purified by column chromatography on silica gel (PE : EA = 30 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.0, 141.2, 134.9, 131.1, 129.7.

(2s) 4-(trifluoromethoxy)benzaldehyde (CAS: 659-28-9)[9]



4-(trifluoromethoxy)benzaldehyde
Chemical Formula: $C_8H_5F_3O_2$
Exact Mass: 190.0242
Molecular Weight: 190.1212

Following the General Procedure A with 4,4,5,5-tetramethyl-2-(4-(trifluoromethoxy)benzyl)-1,3,2-dioxaborolane (60.4 mg, 0.20 mmol), **2s** was obtained as colorless oil (14.9 mg, 51%).

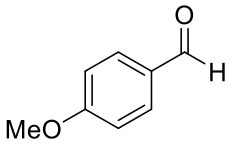
This target product was purified by column chromatography on silica gel (PE : EA = 30 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.94 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 167.2, 164.7, 133.8, 133.8, 131.2, 131.1, 116.0, 115.7, 26.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.6.

(2t) 4-methoxybenzaldehyde (CAS: 123-11-5)[9]



4-methoxybenzaldehyde
Chemical Formula: $C_8H_8O_2$
Exact Mass: 136.0524
Molecular Weight: 136.1500

Following the General Procedure A with 2-(4-methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (49.6 mg, 0.20 mmol), **2t** was obtained as colorless oil (22.4 mg, 92%).

This target product was purified by column chromatography on silica gel (PE : EA = 30 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.83 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 164.6, 132.0, 130.0, 114.3, 55.6.

6. HRMS spectrum

HRMS (ESI) m/z calcd for $C_8H_9{}^{18}O^+$ $(M+H)^+$ 123.0690, not found.

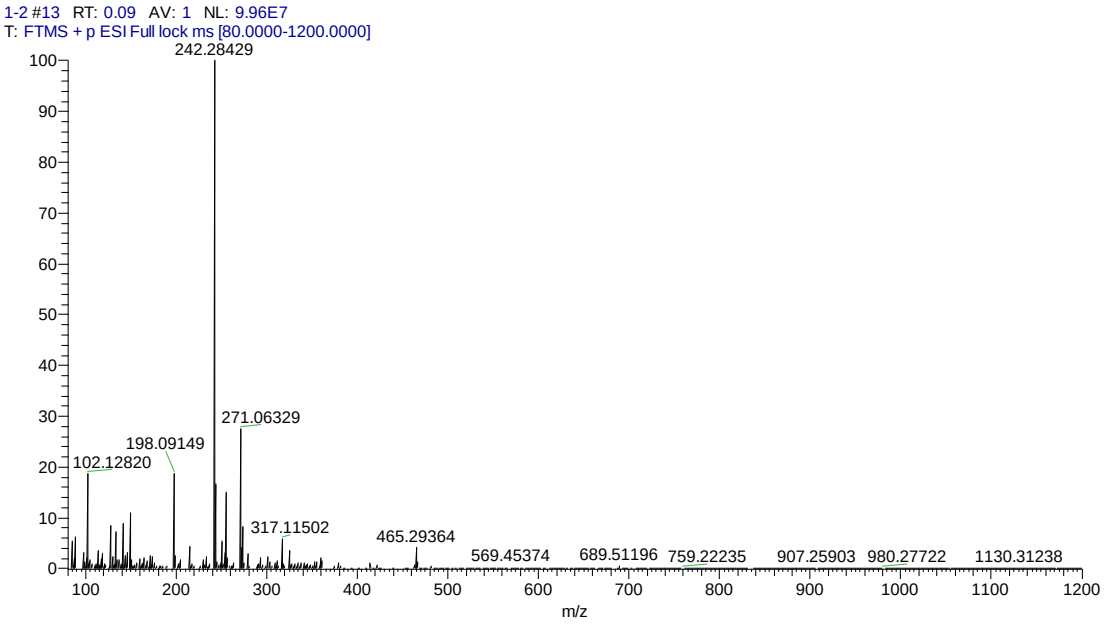


Figure S2. HRMS analysis of the product from the experiment using water-^{18}O.

7. References

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5. Xie, P.; Xue, C.; Du, D.; Shi, S., Photo-induced oxidative cleavage of C-C double bonds for the synthesis of biaryl methanone via $CeCl_3$ catalysis. *Organic Biomolecular Chemisrty* **2021,** *19* (31), 6781-6785.
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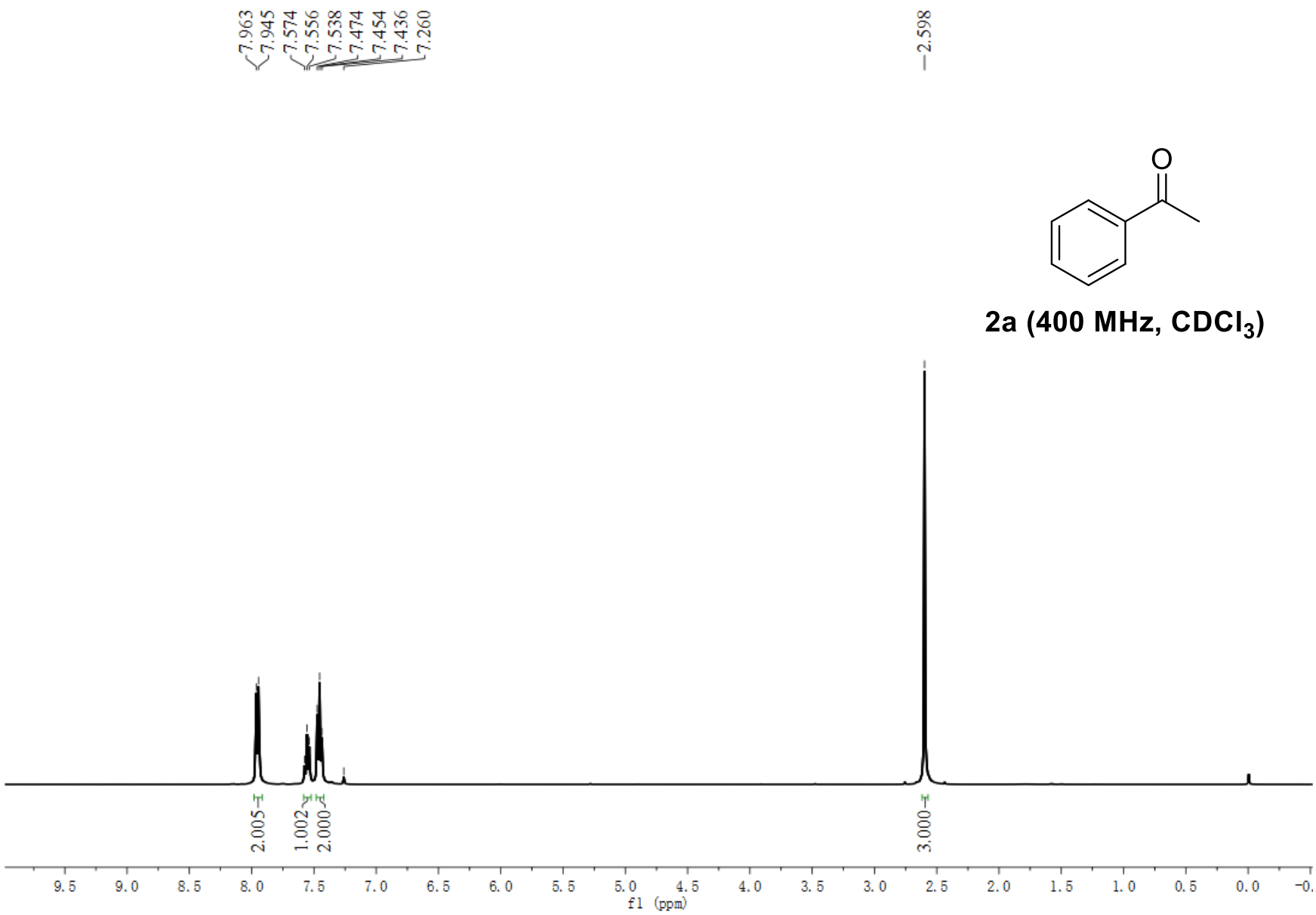
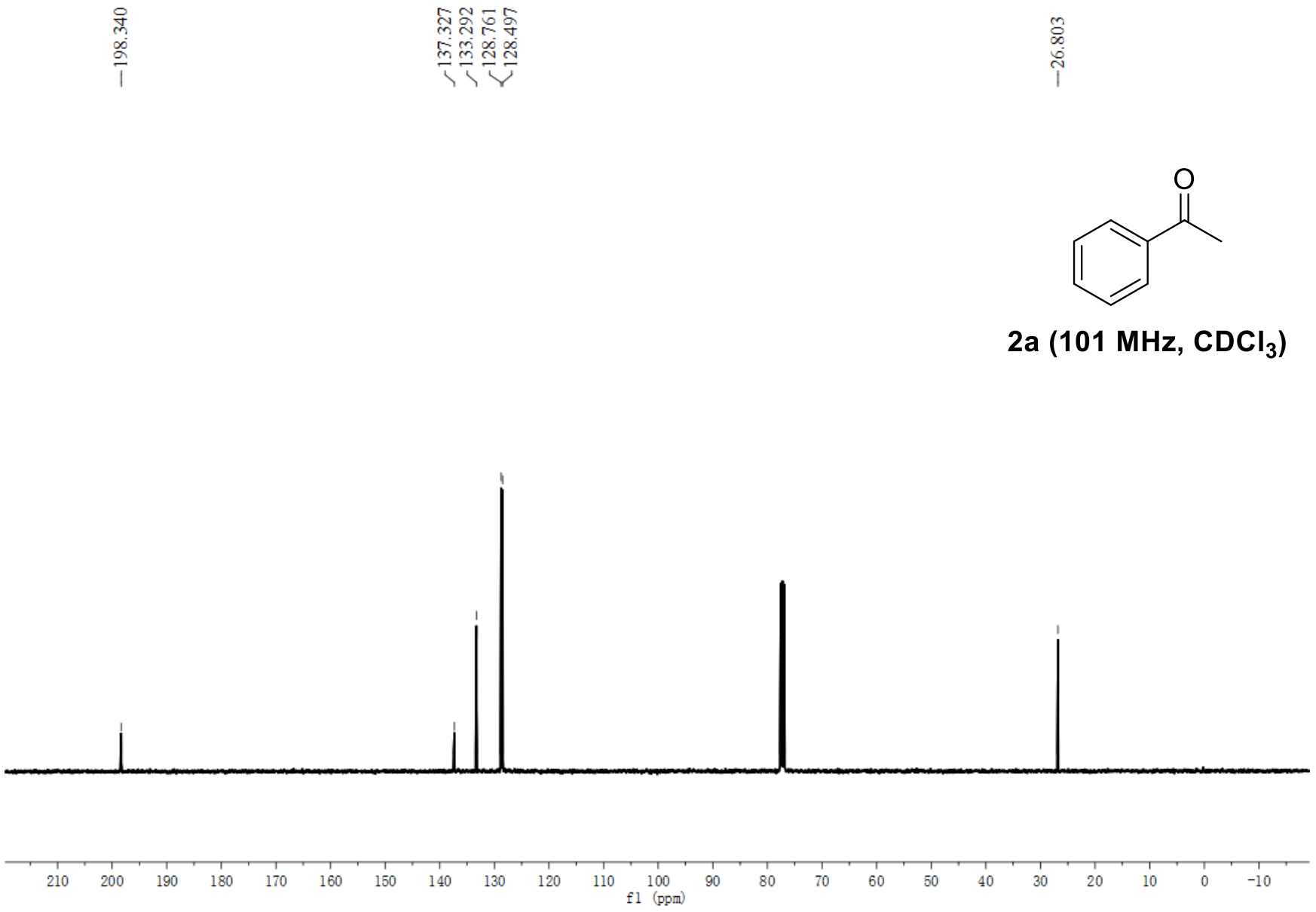
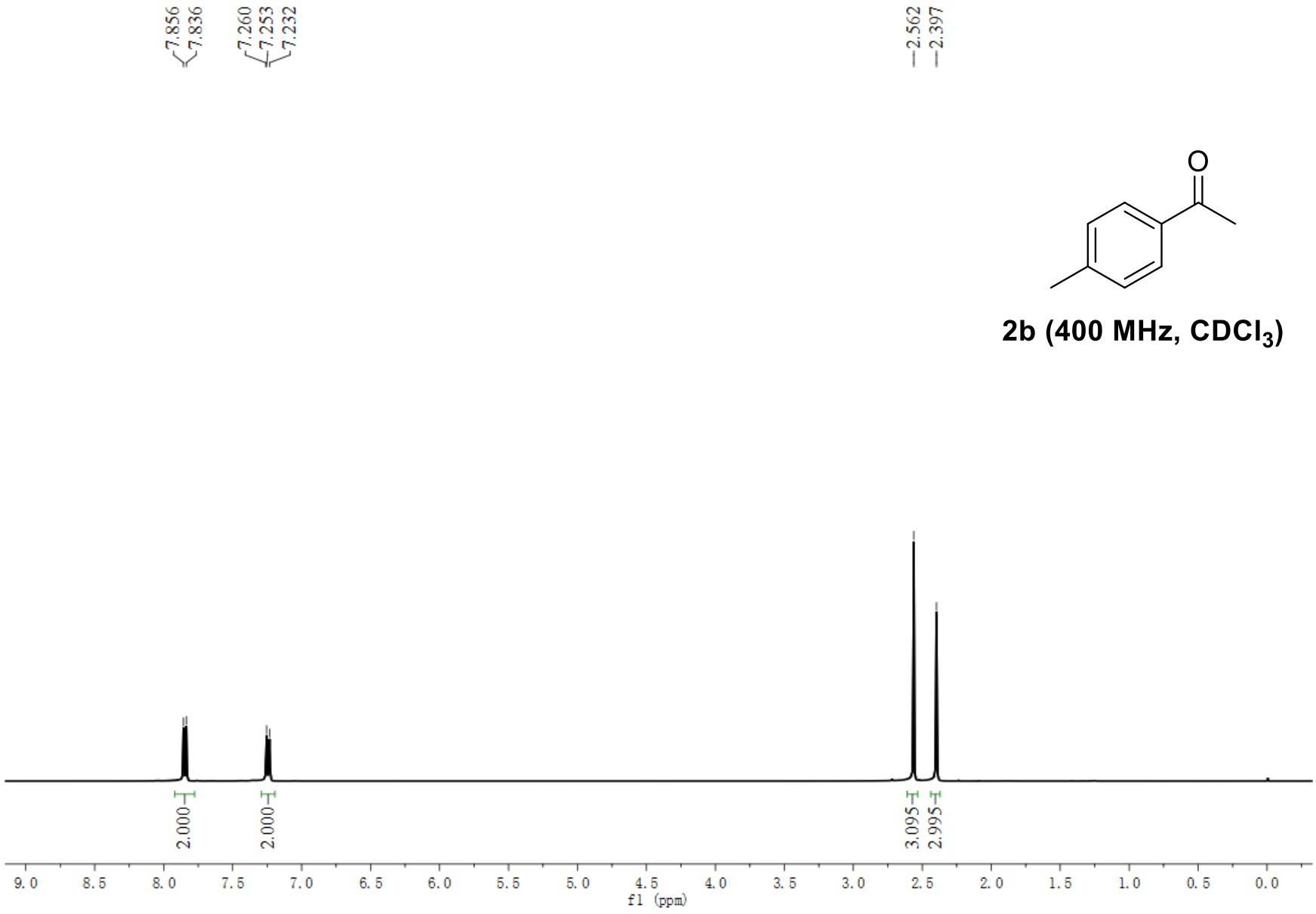
10. Pandey, G.; Tiwari, S. K.; Singh, B.; Vanka, K.; Jain, S., p-Selective (sp(2))-C-H functionalization for an acylation/alkylation reaction using organic photoredox catalysis. *Chemical Communications* **2017,** *53* (91), 12337-12340.

8. Copies of NMR spectra

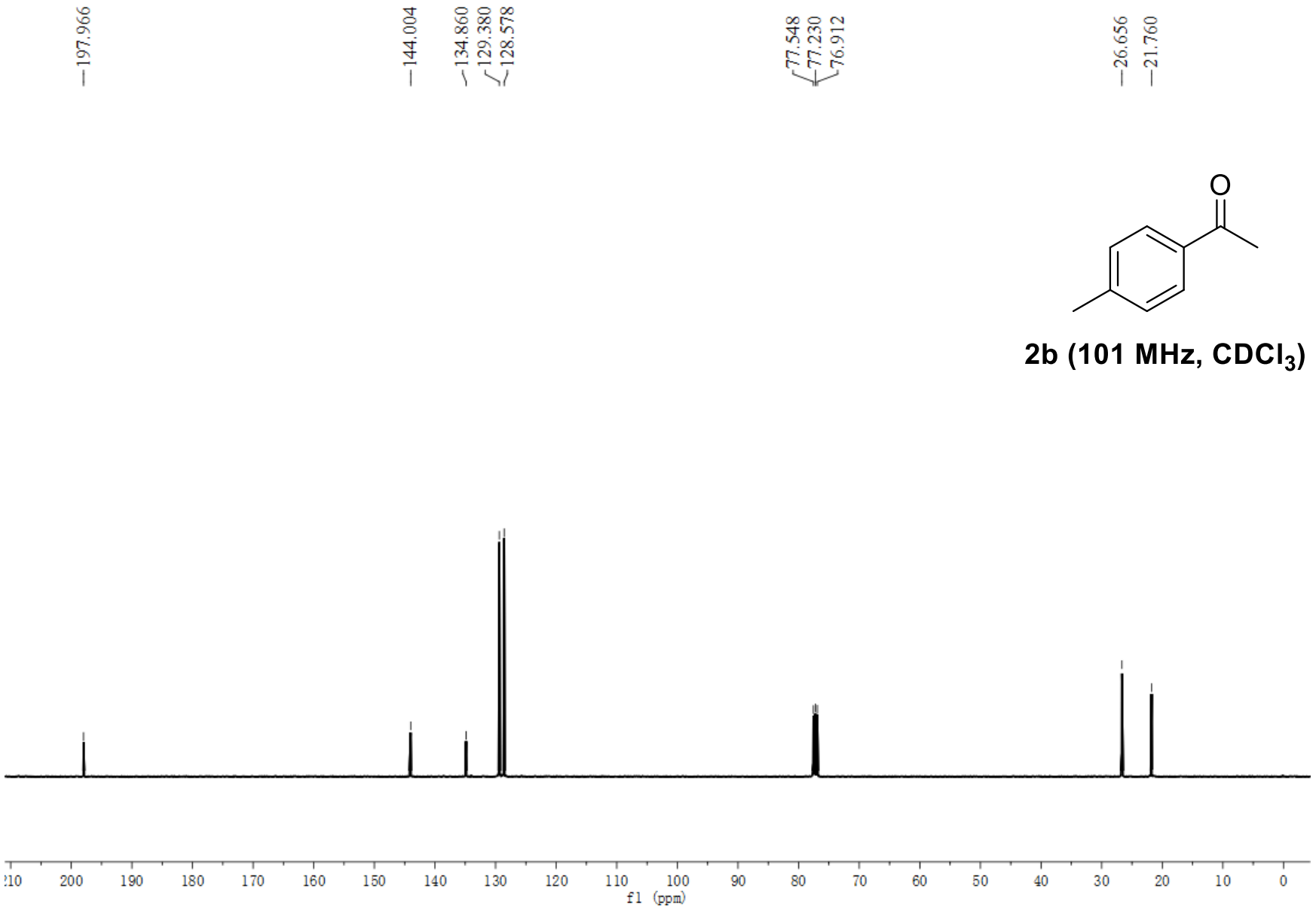

7.963
7.945
7.574
7.556
7.538
7.474
7.454
7.436
7.260
2.598
O
2a (400 MHz, CDCl3)
2.005
1.002
2.000
3.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



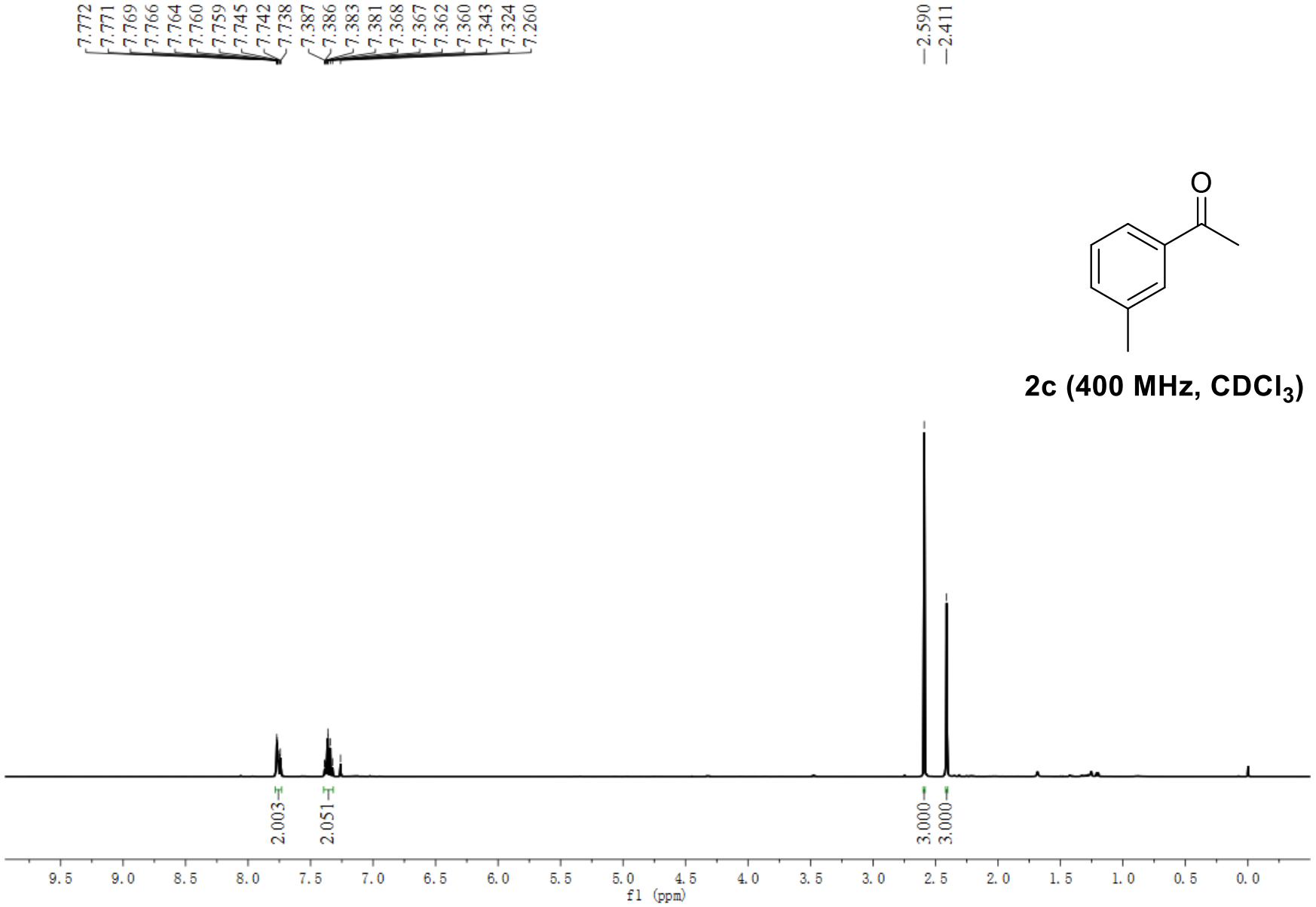
2a (101 MHz, $CDCl_3$)

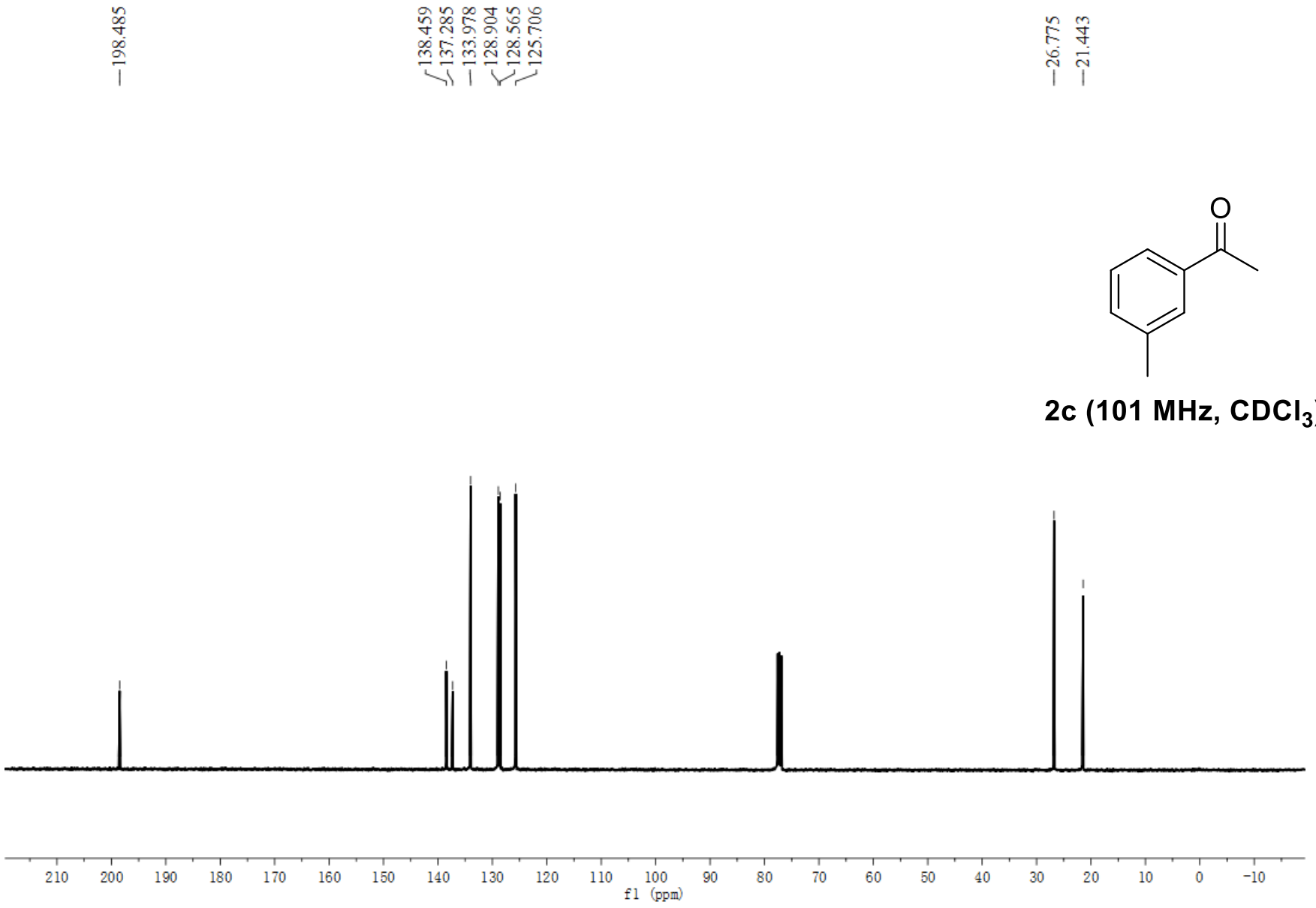


2b (400 MHz, $CDCl_3$)

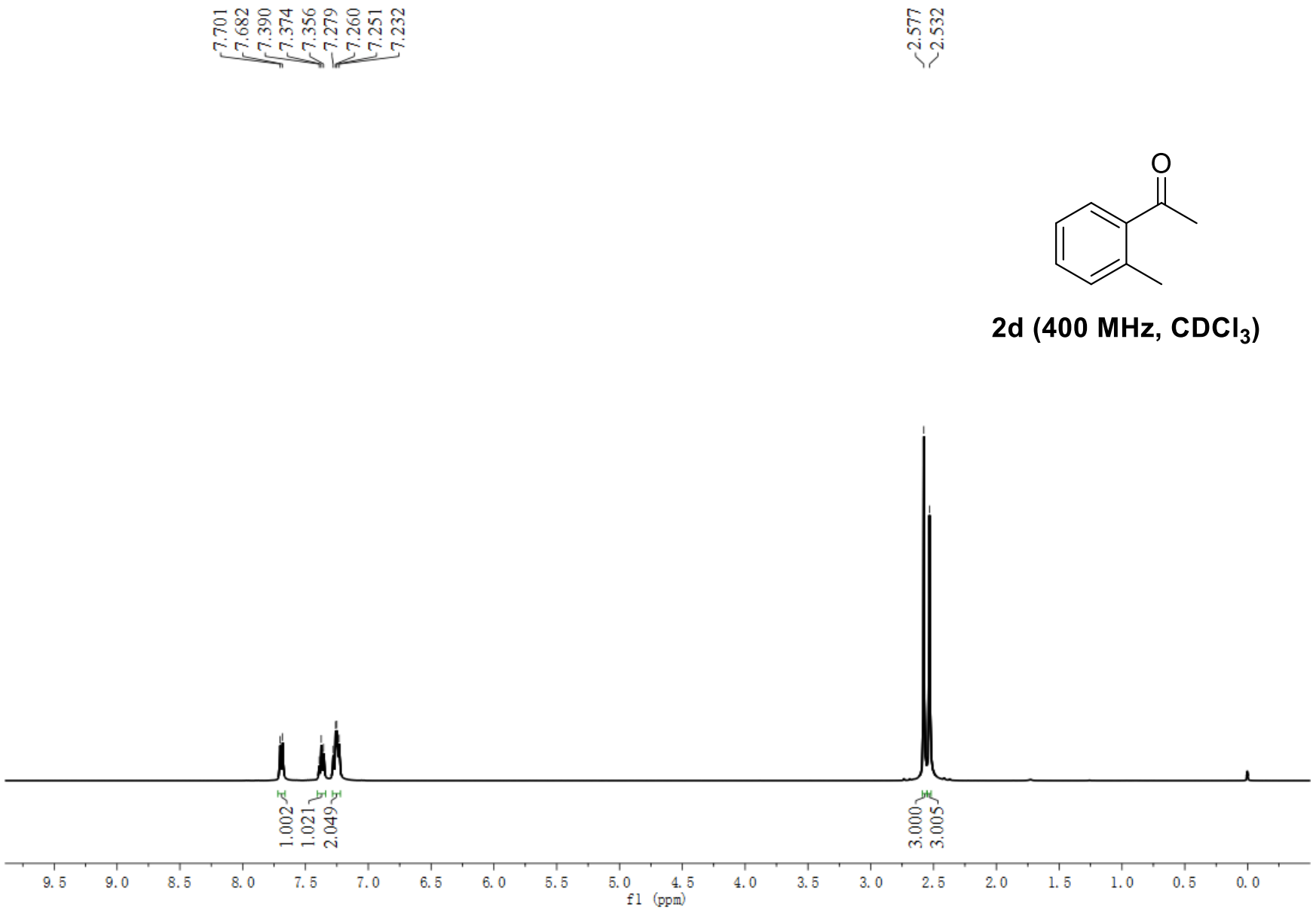


2b (101 MHz, $CDCl_3$)

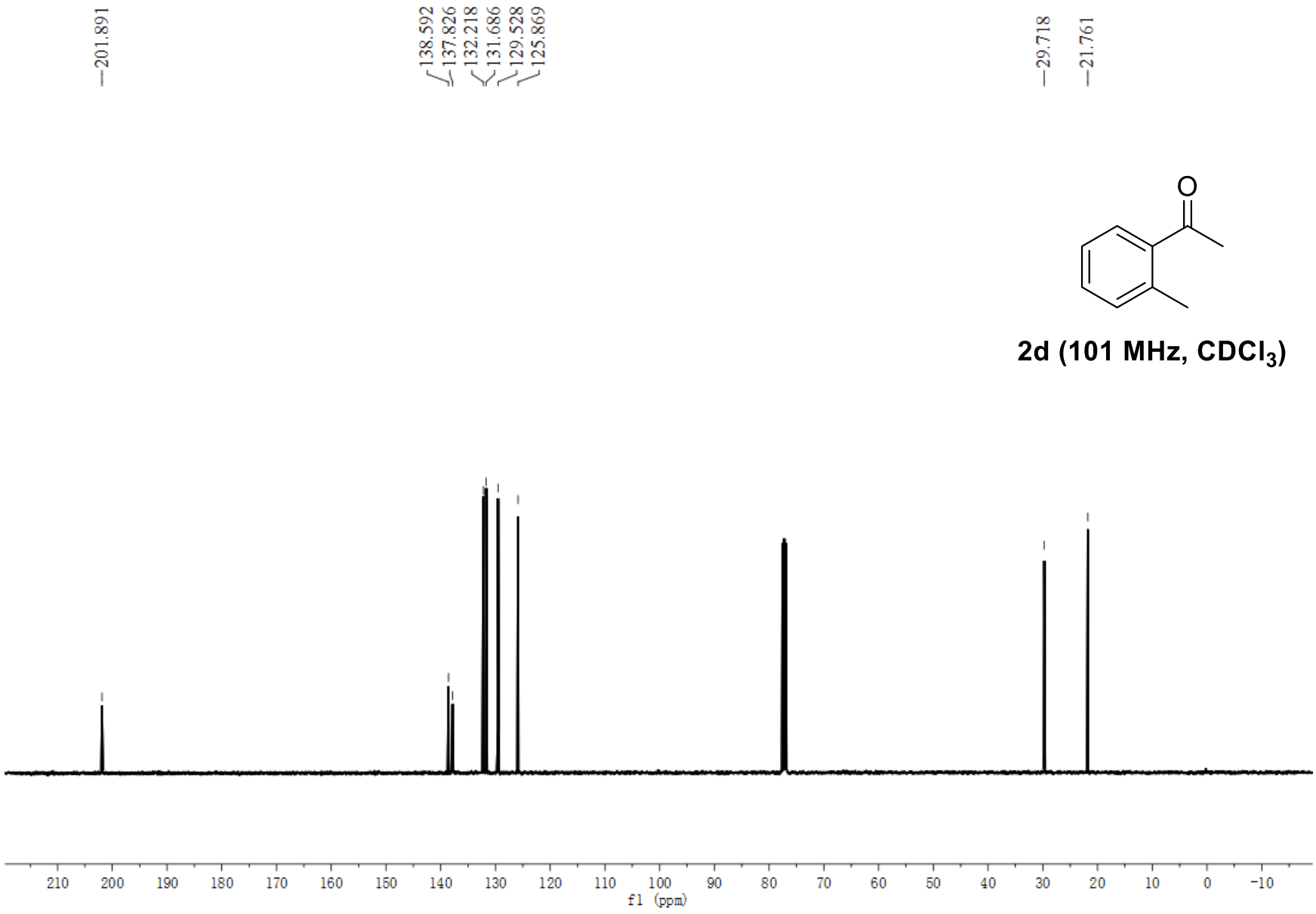

7.772
7.771
7.769
7.766
7.764
7.760
7.759
7.745
7.742
7.738
7.387
7.386
7.383
7.381
7.368
7.367
7.362
7.360
7.343
7.324
7.260
2.590
2.411
O
2c (400 MHz, CDCl3)
2.003
2.051
3.000
3.000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

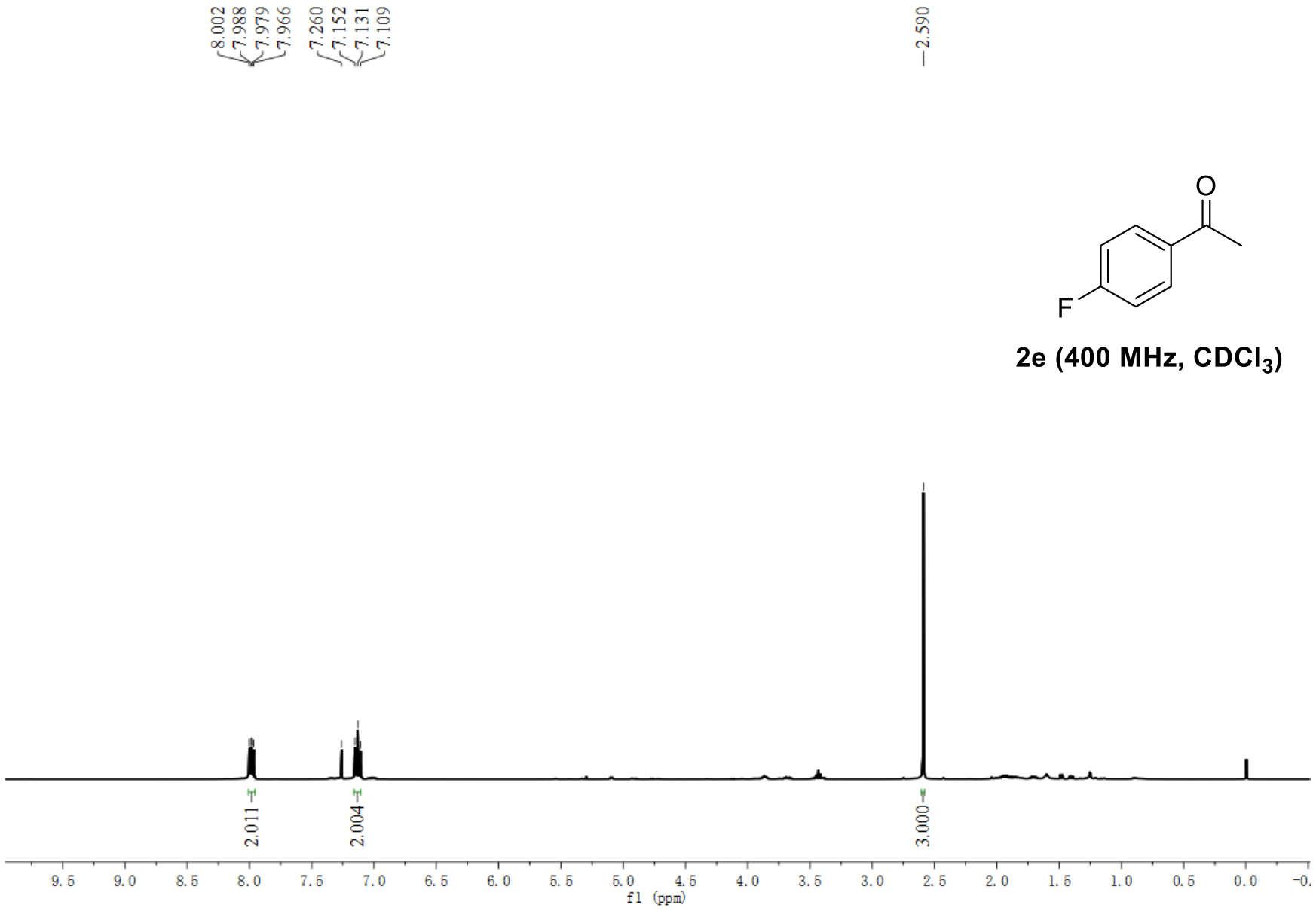


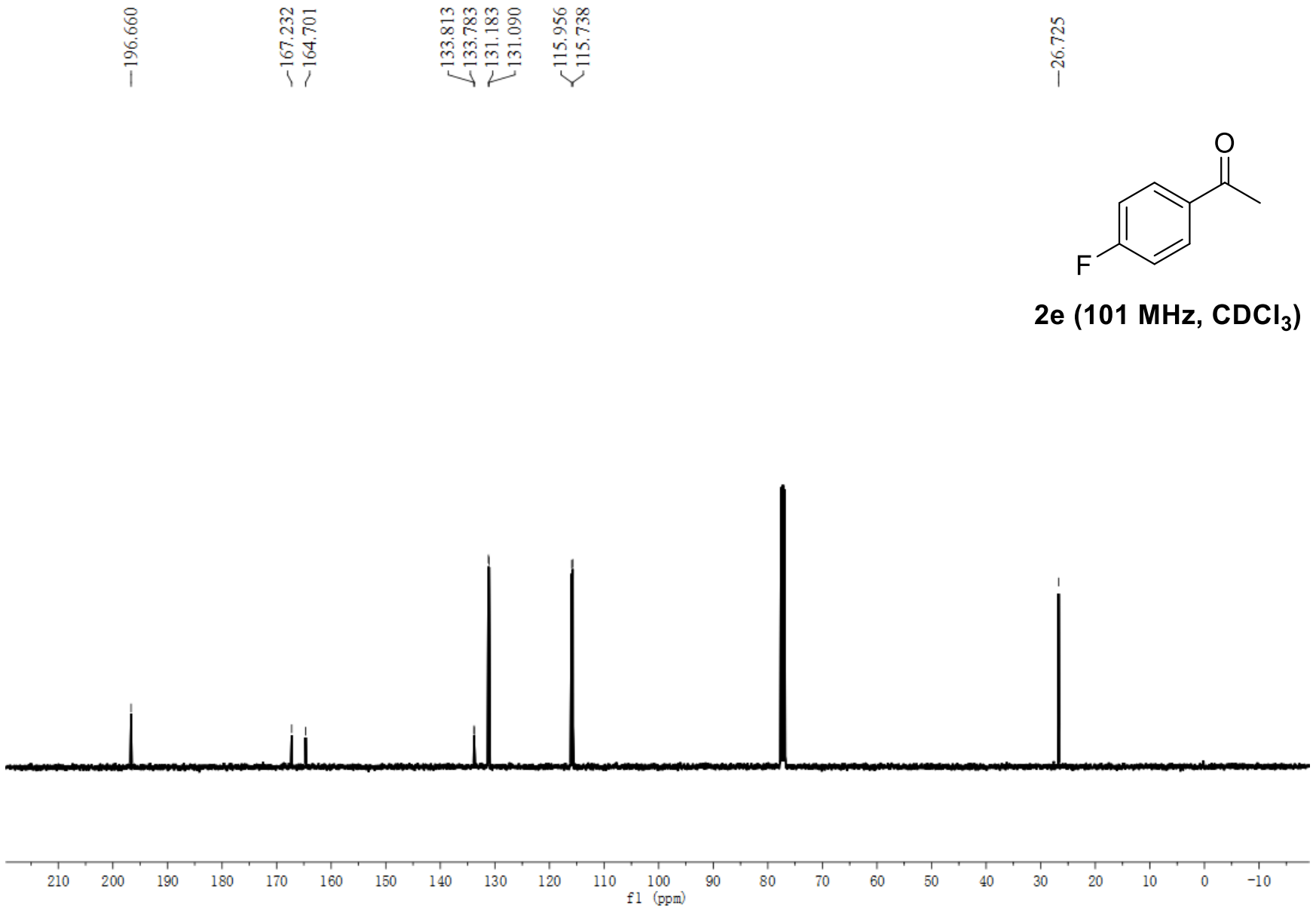
2c (101 MHz, $CDCl_3$)



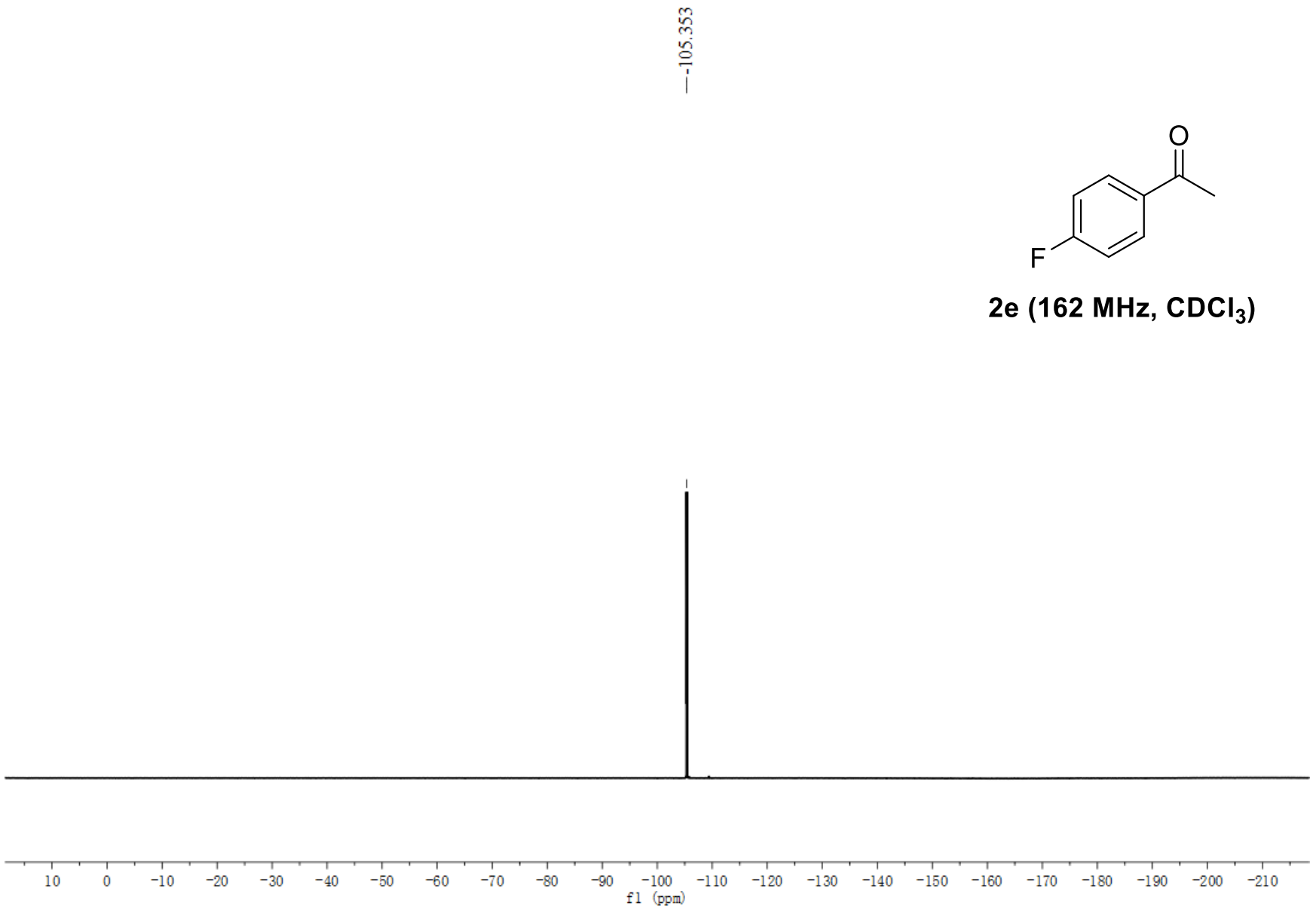
2d (400 MHz, $CDCl_3$)


201.891
138.592
137.826
132.218
131.686
129.528
125.869
29.718
21.761
O
2d (101 MHz, CDCl3)
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)

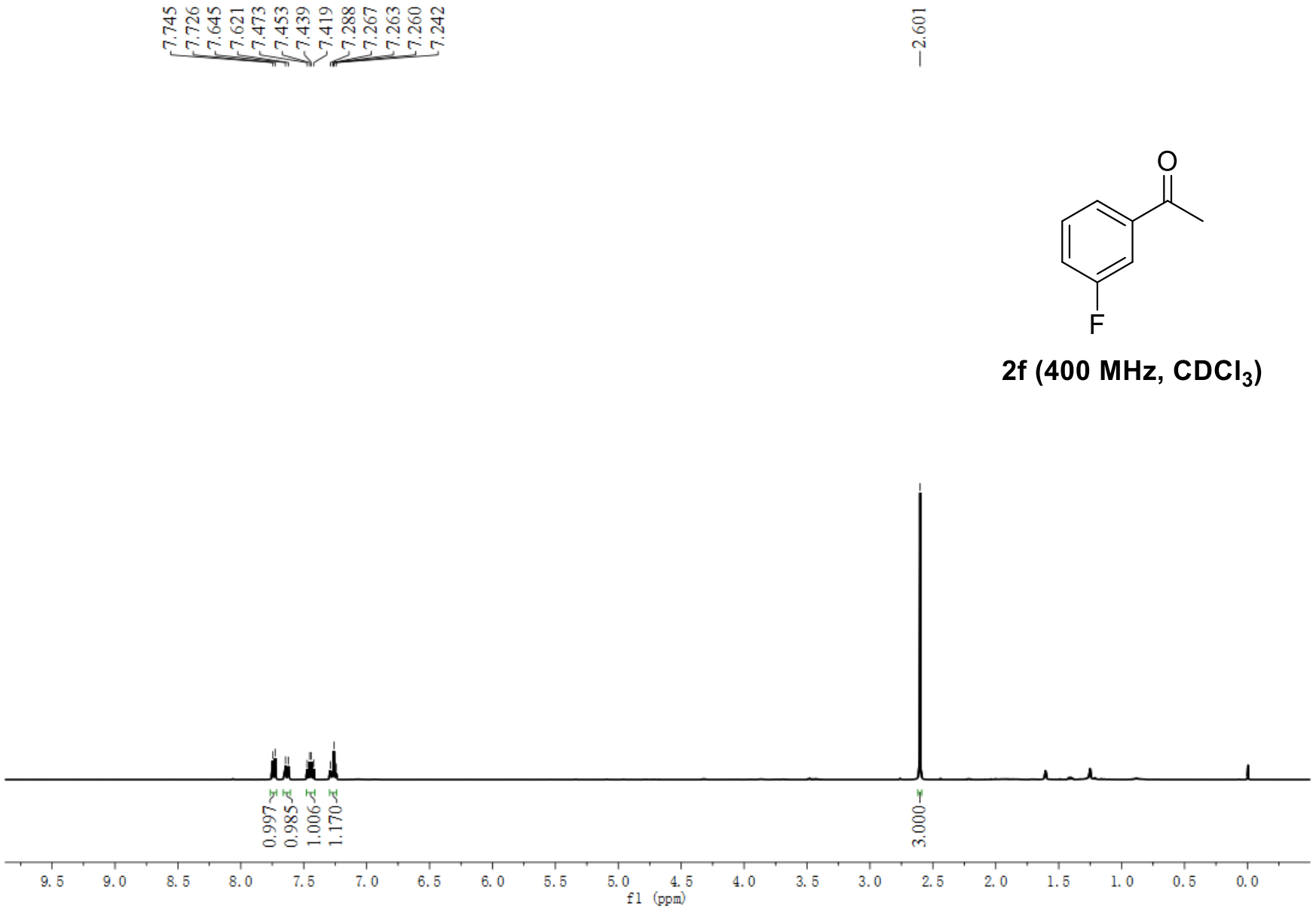

8.002
7.988
7.979
7.966
7.260
7.152
7.131
7.109
2.590
O
F
2e (400 MHz, CDCl3)
2.011
2.004
3.000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



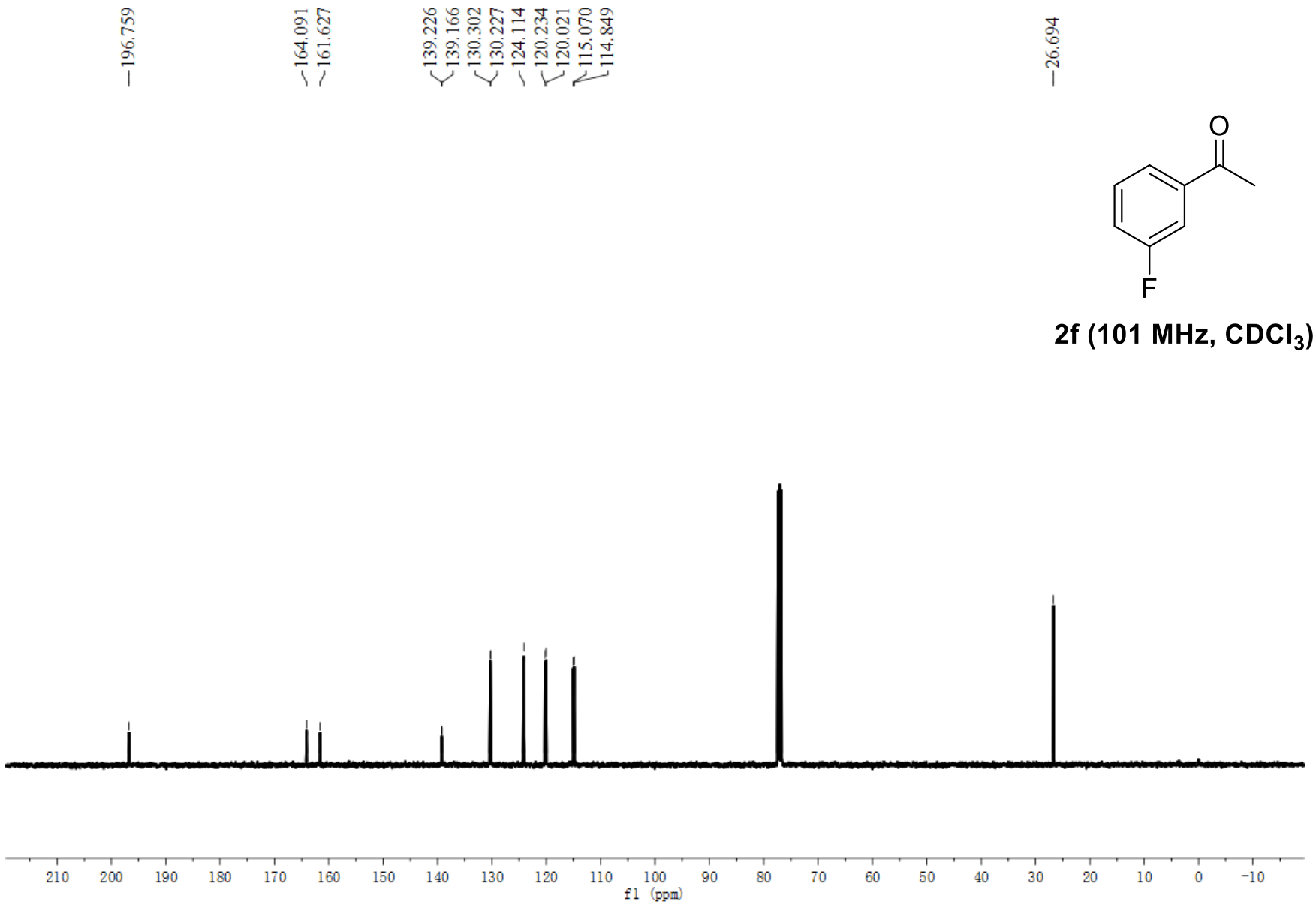
2e (101 MHz, $CDCl_3$)



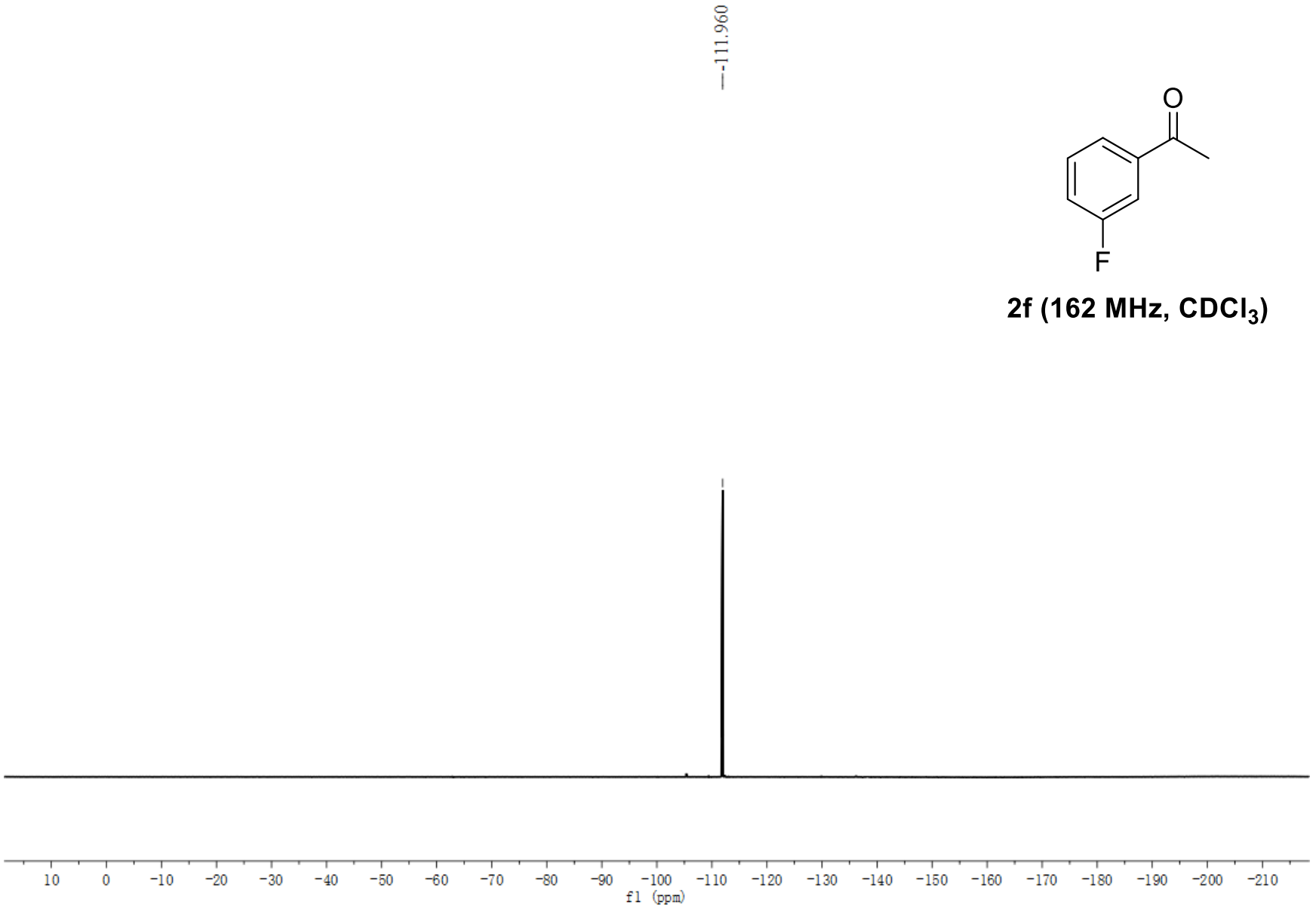
2e (162 MHz, $CDCl_3$)



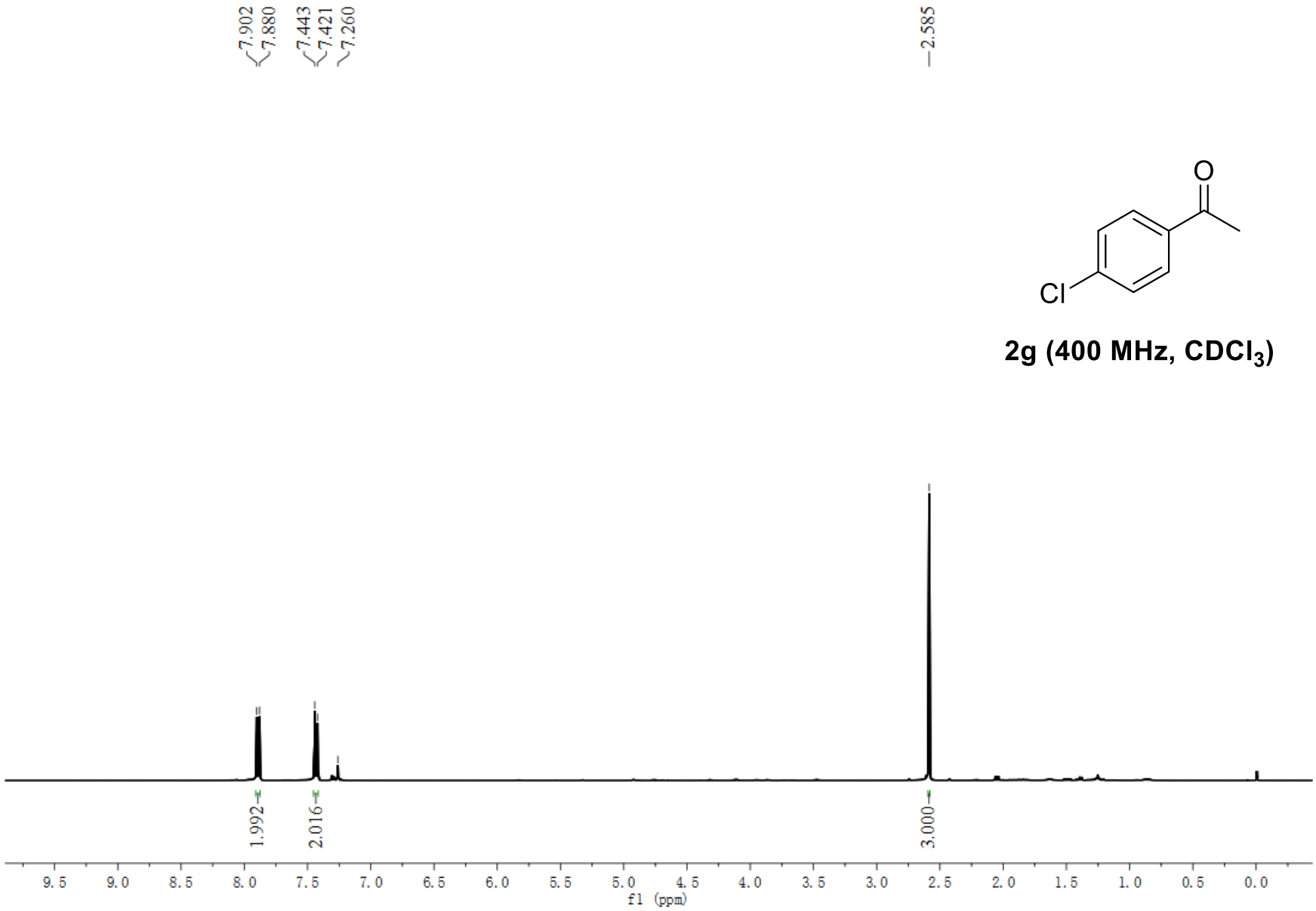
2f (400 MHz, $CDCl_3$)



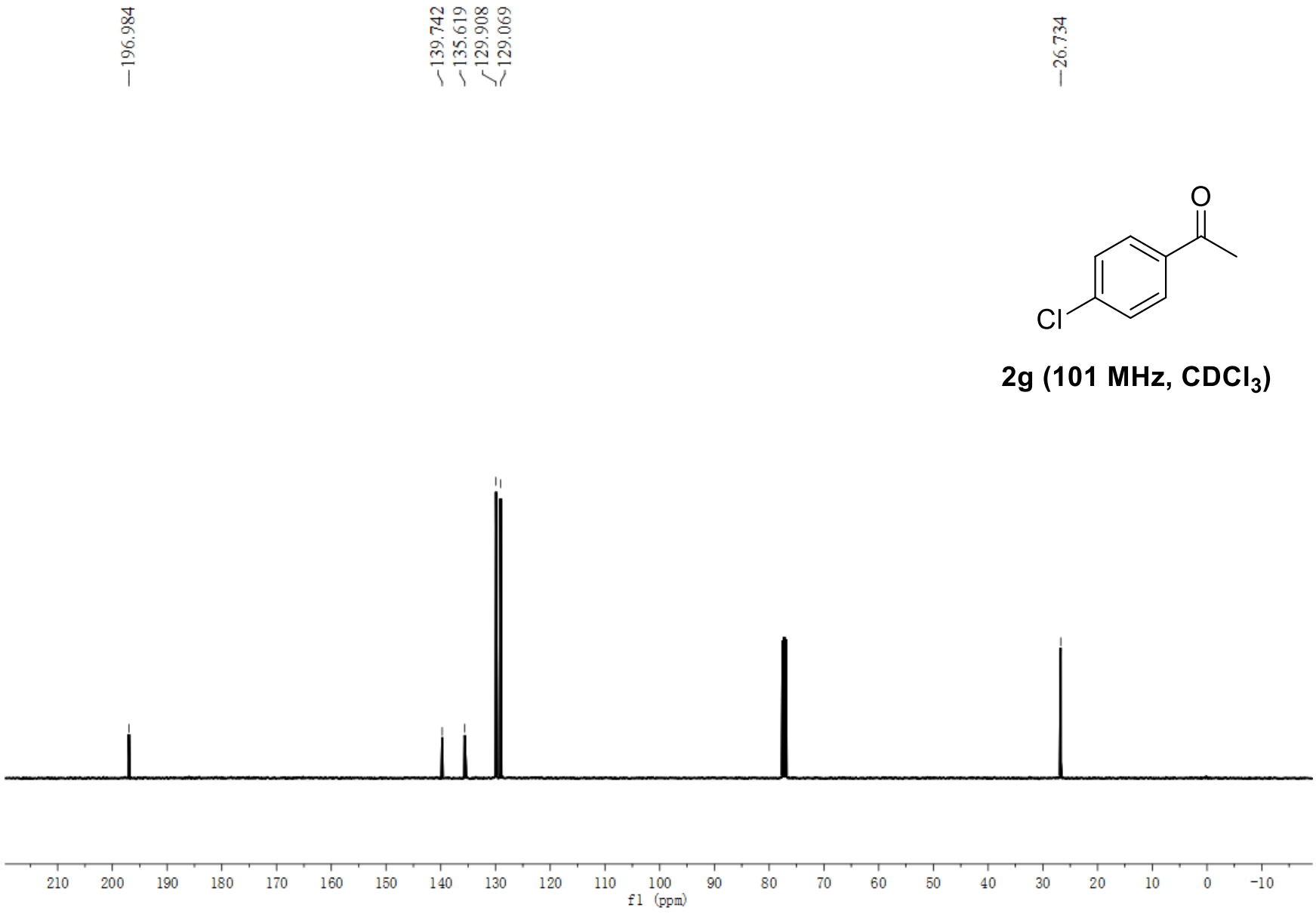
2f (101 MHz, $CDCl_3$)



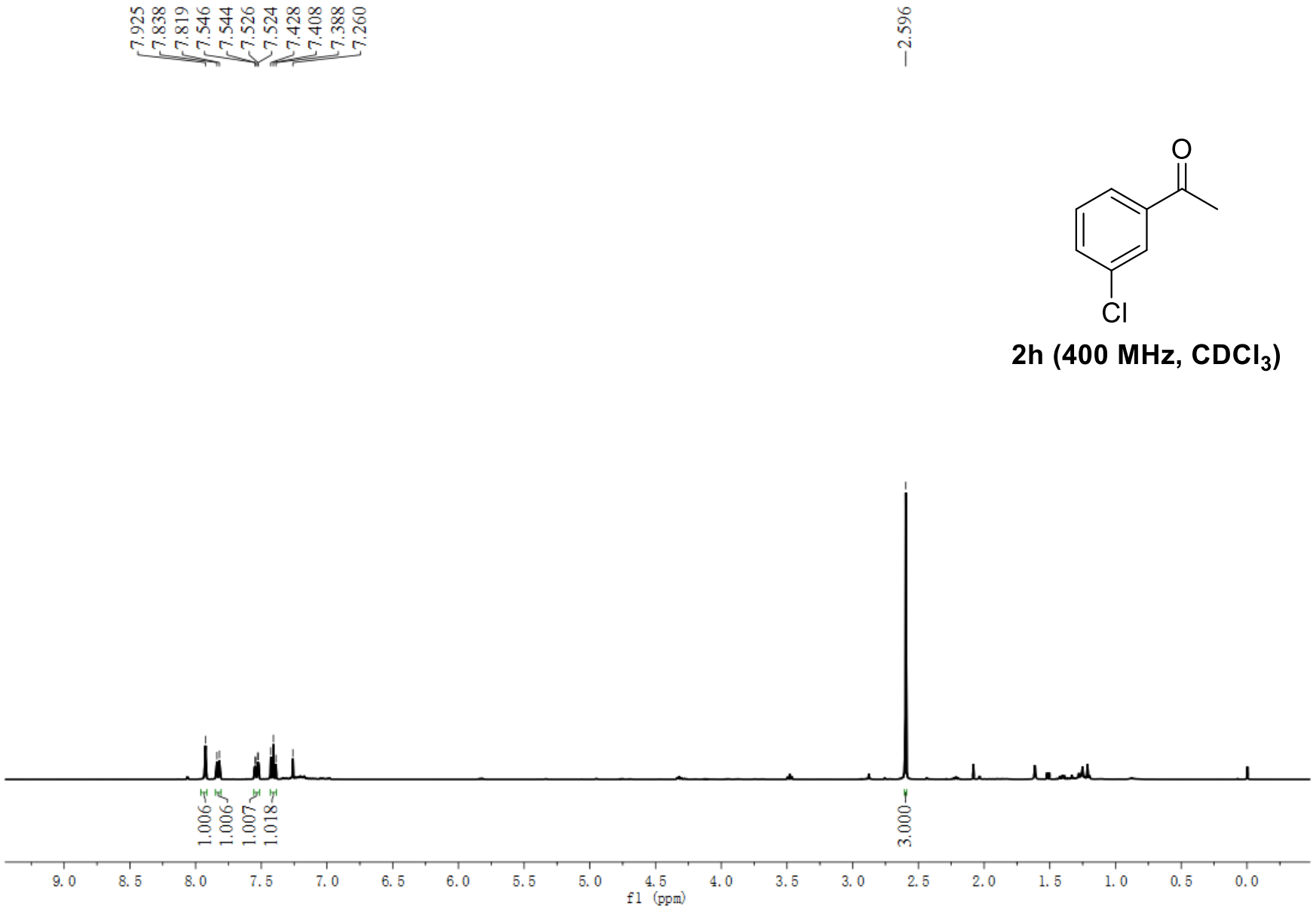
2f (162 MHz, $CDCl_3$)



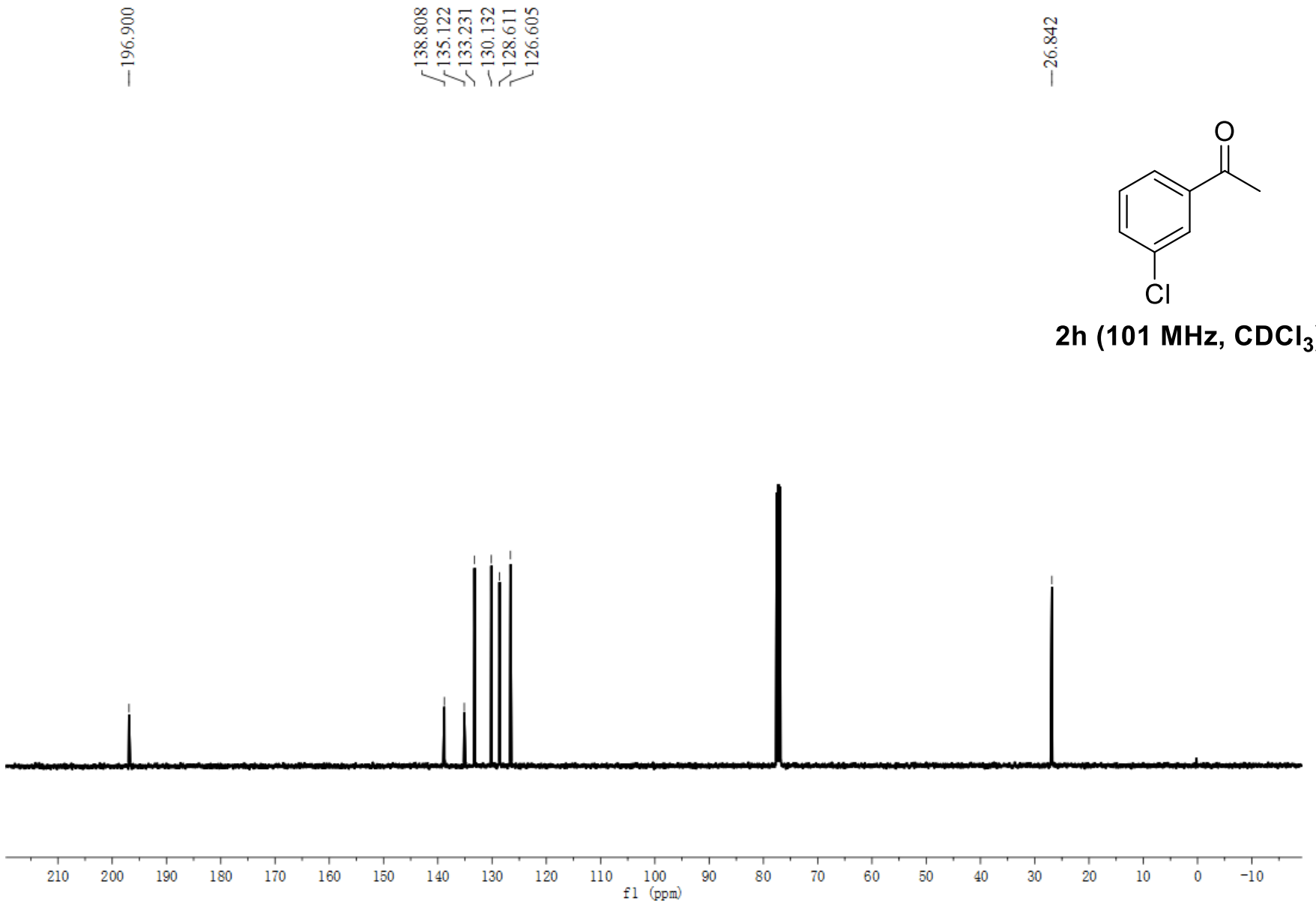
2g (400 MHz, $CDCl_3$)



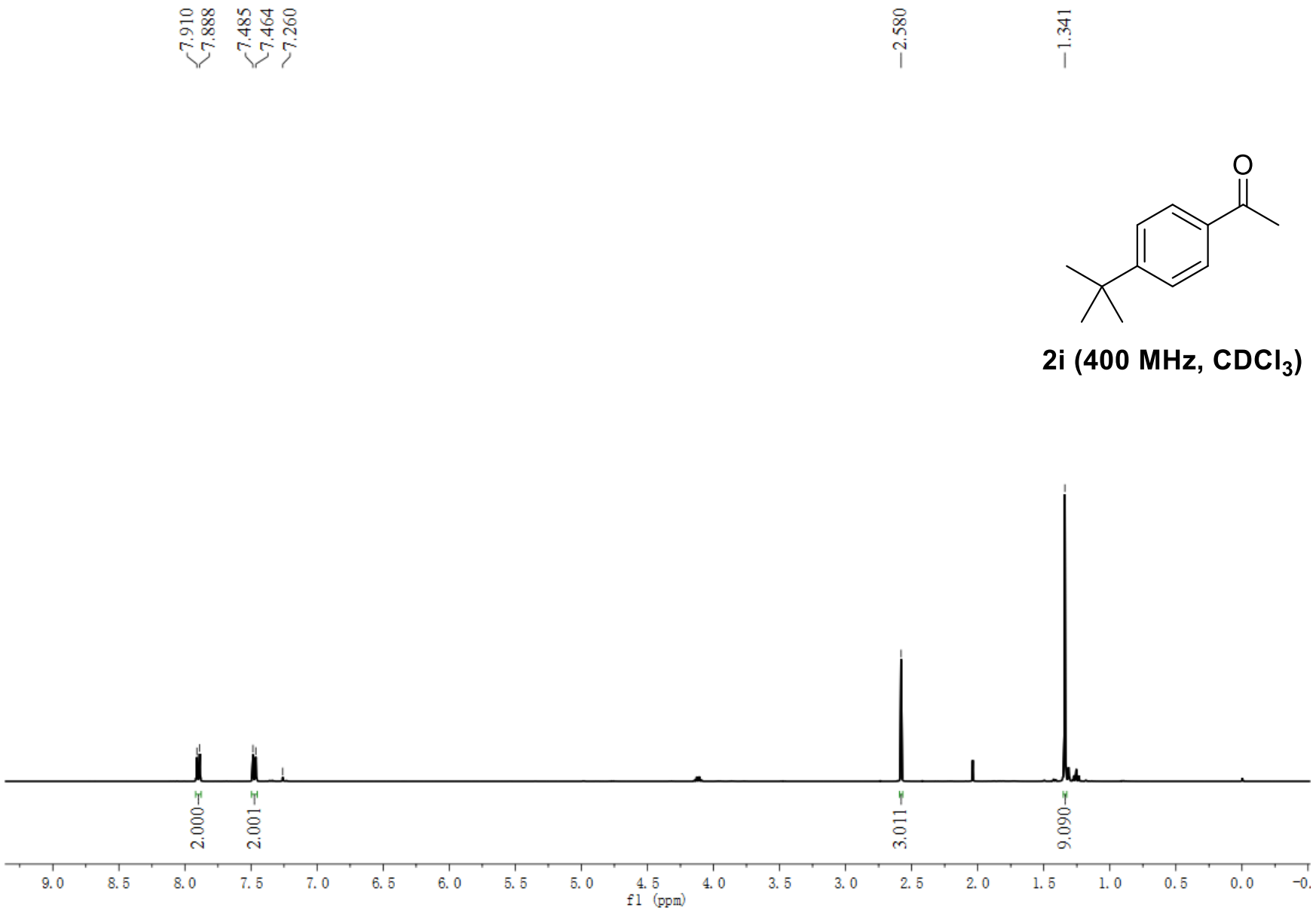
2g (101 MHz, $CDCl_3$)



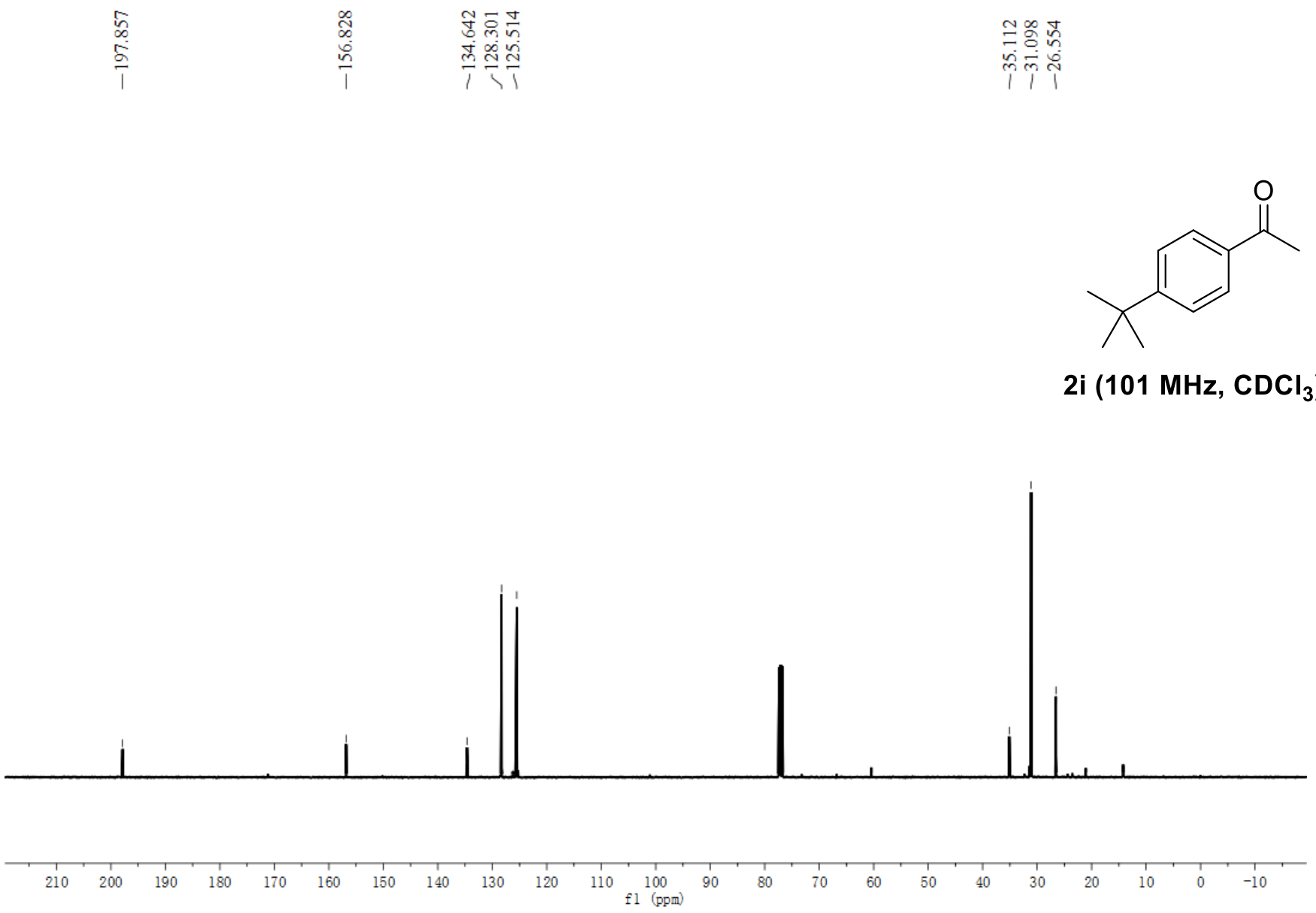
2h (400 MHz, $CDCl_3$)



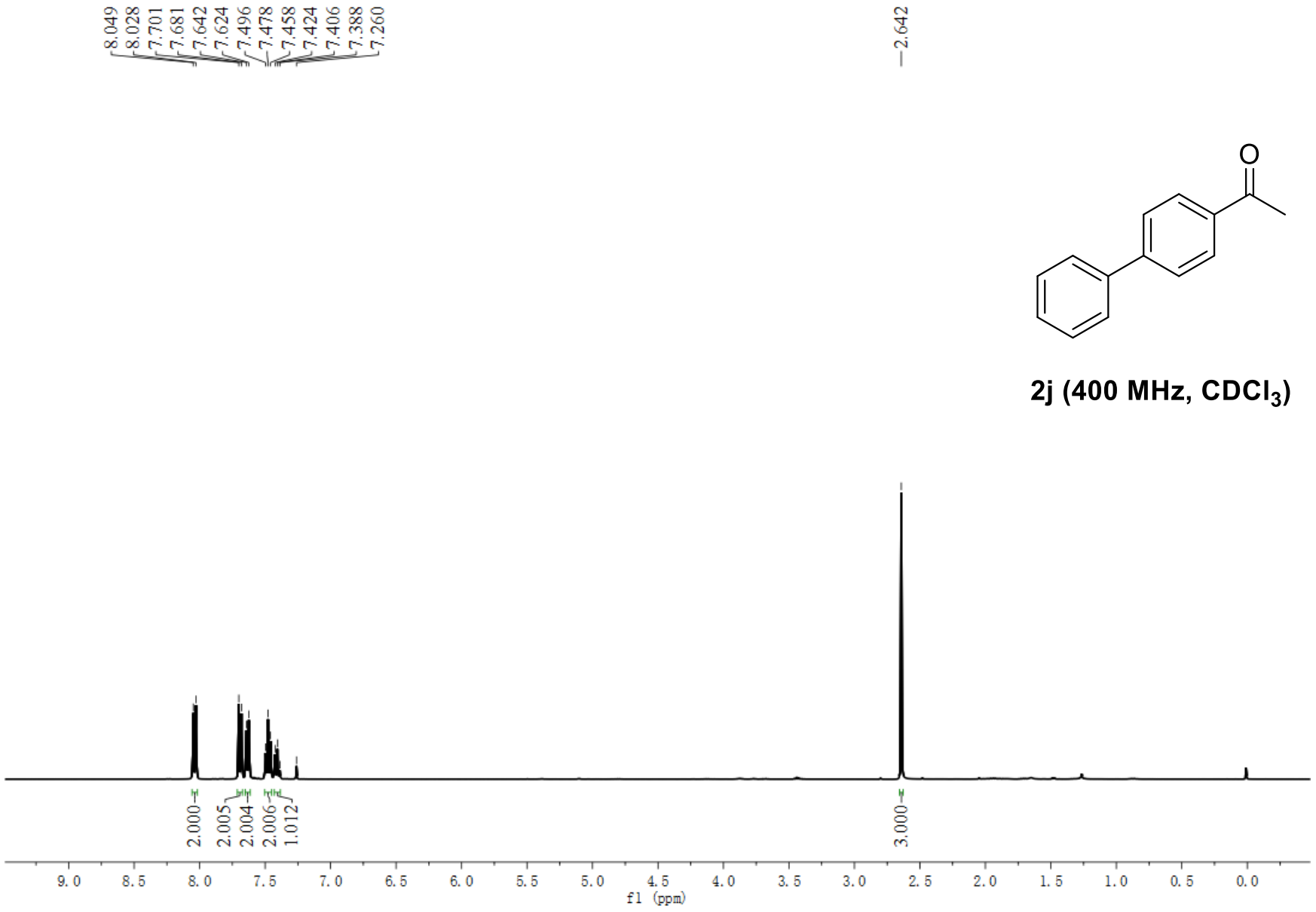
2h (101 MHz, $CDCl_3$)



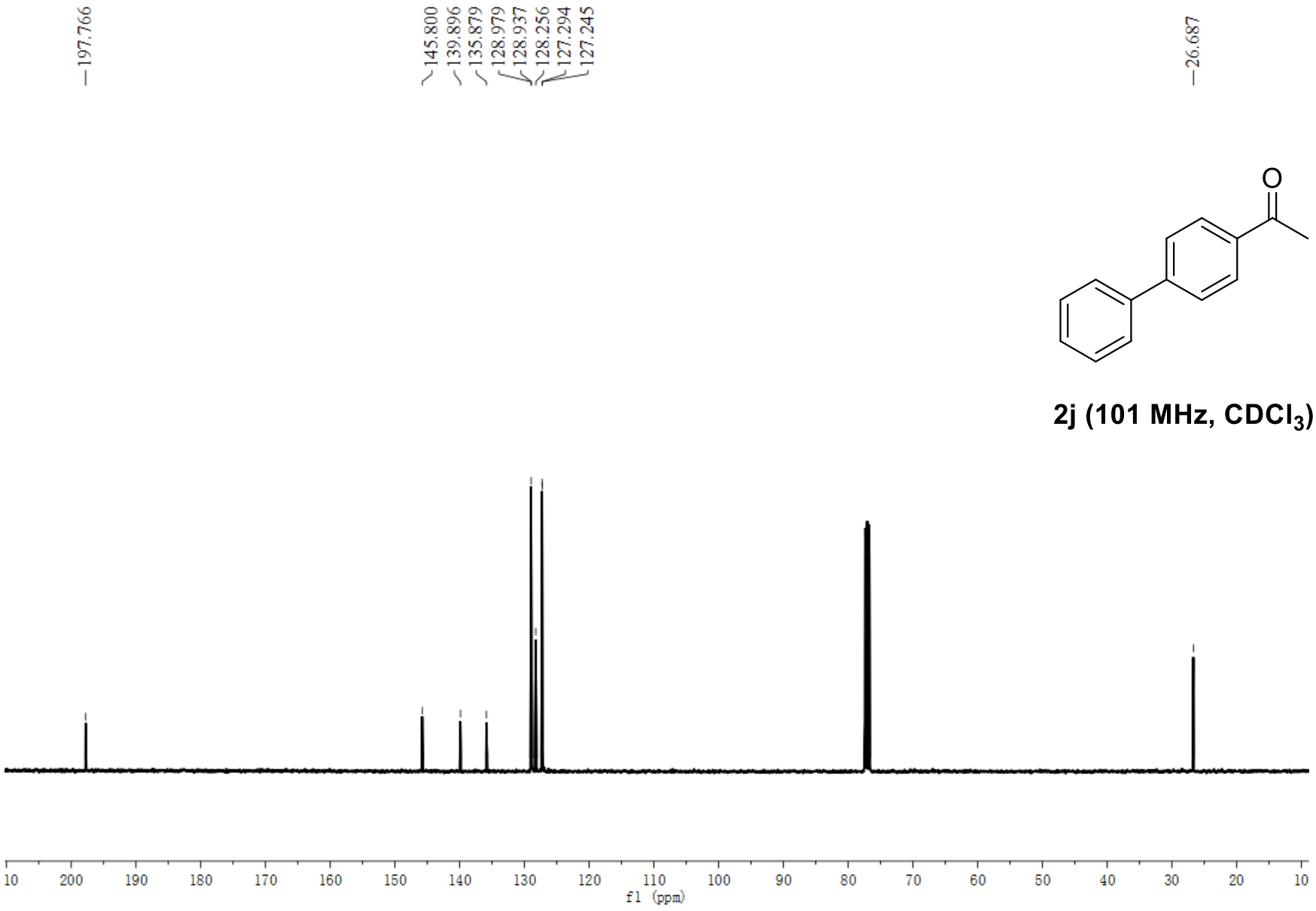
2i (400 MHz, $CDCl_3$)



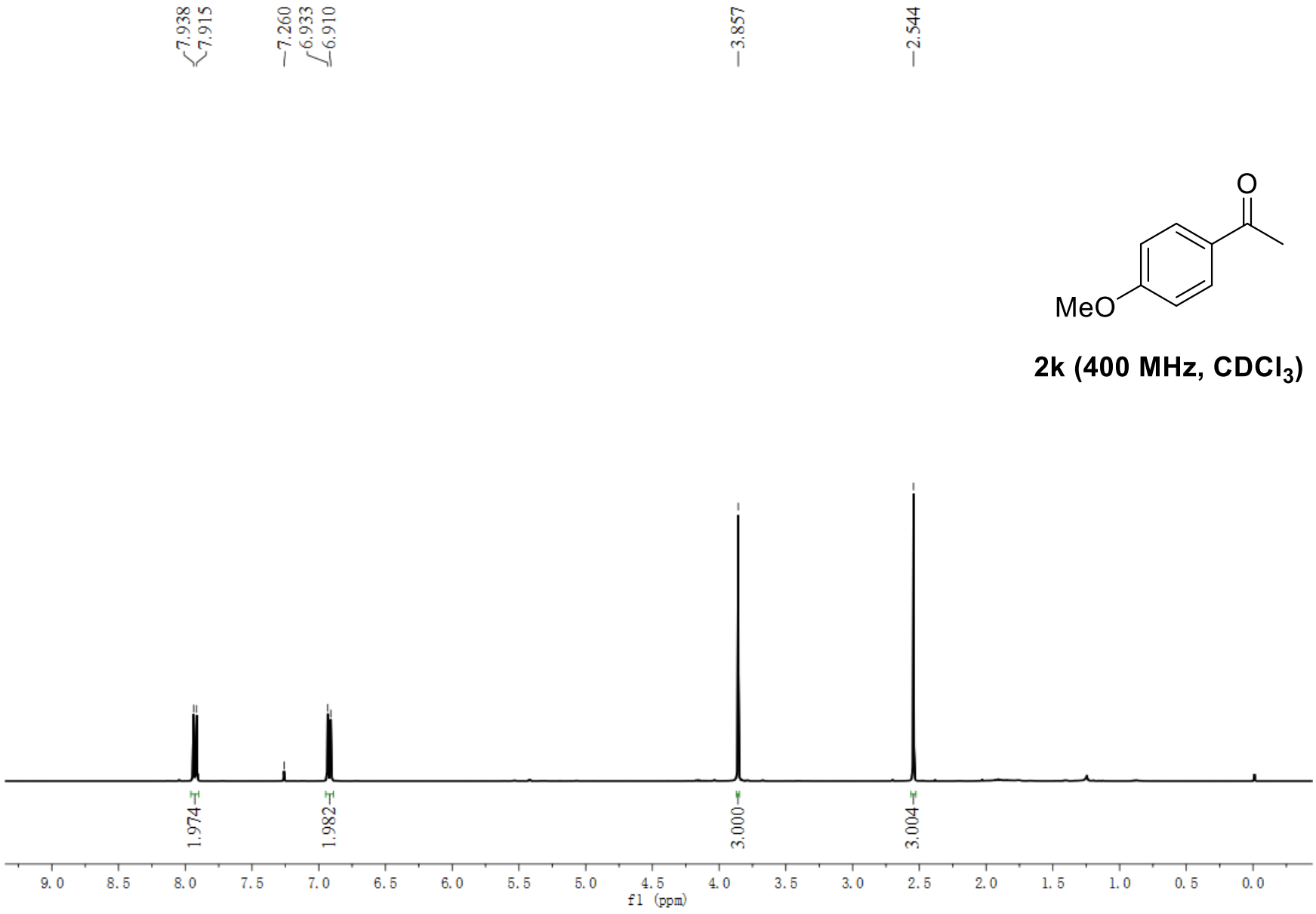
2i (101 MHz, $CDCl_3$)



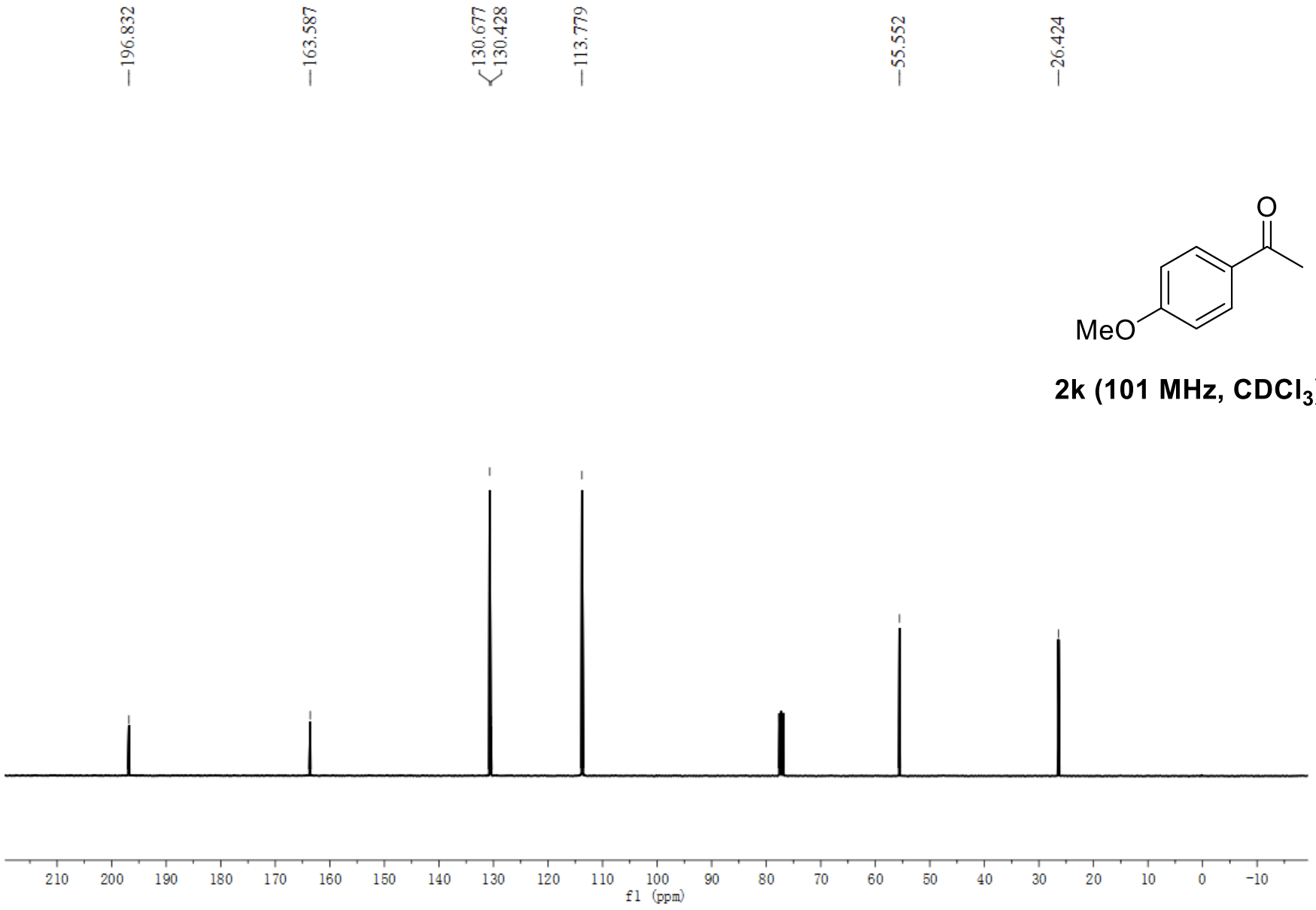
2j (400 MHz, $CDCl_3$)



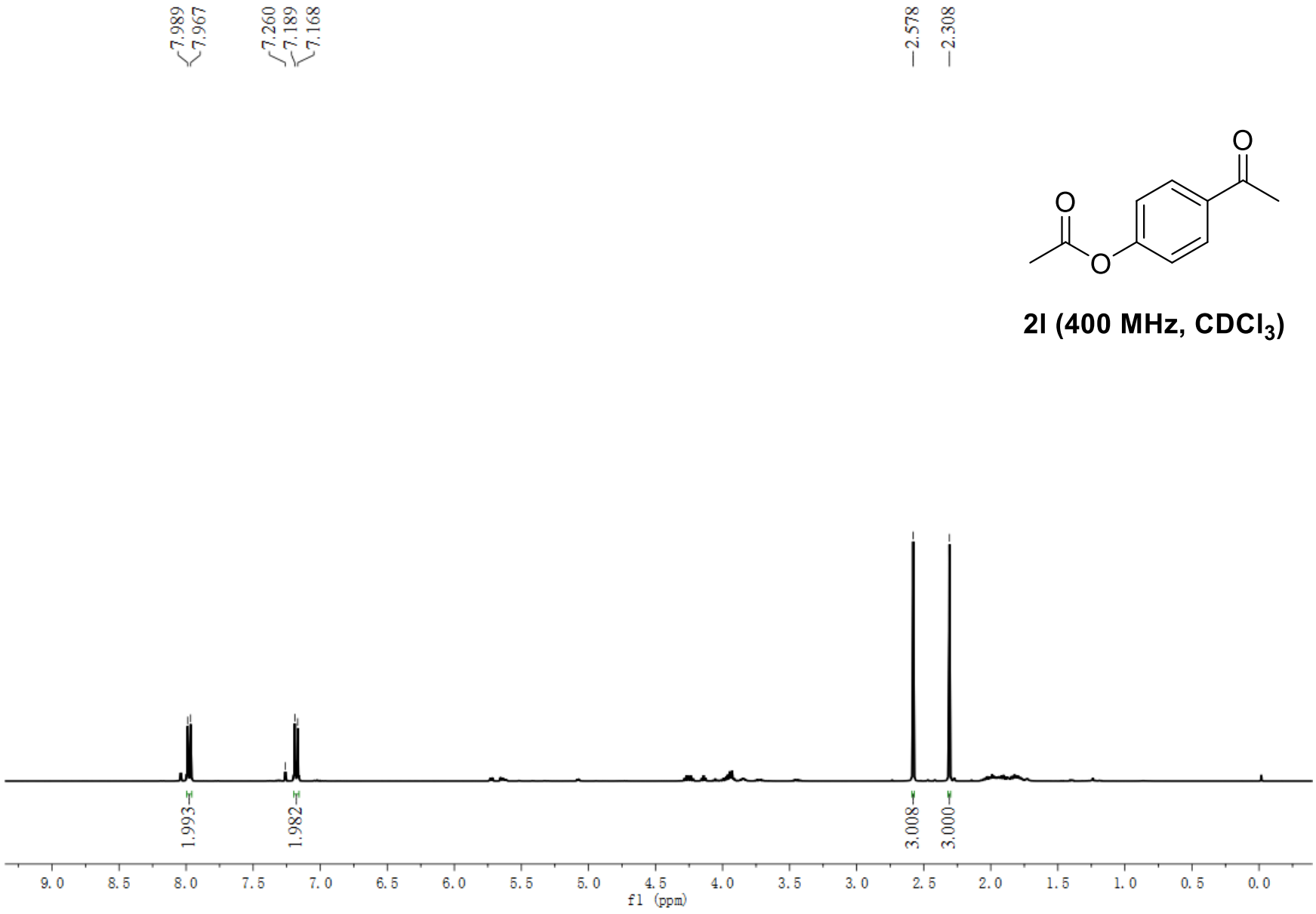
2j (101 MHz, $CDCl_3$)



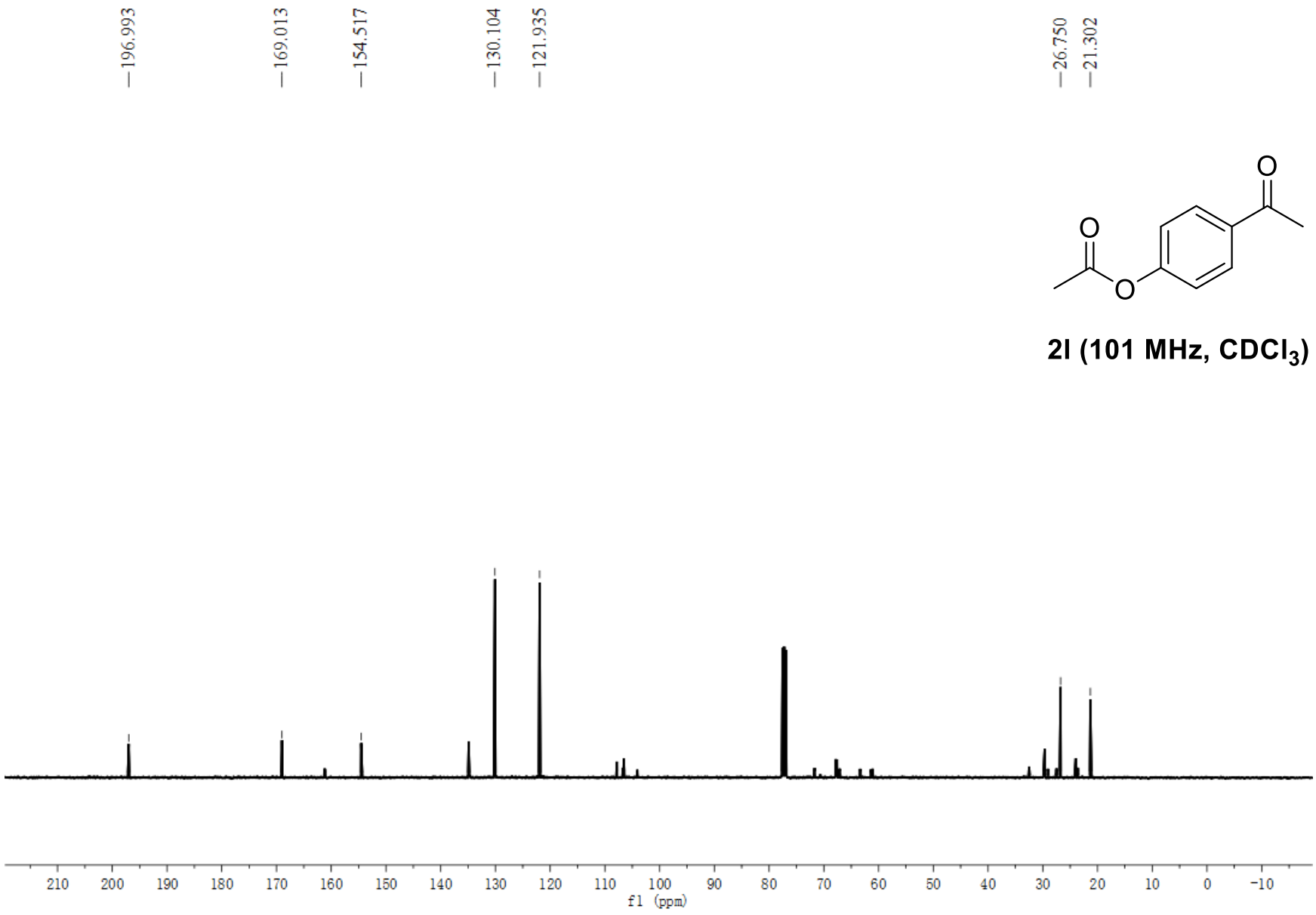
2k (400 MHz, $CDCl_3$)



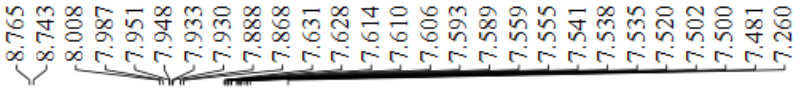
2k (101 MHz, $CDCl_3$)

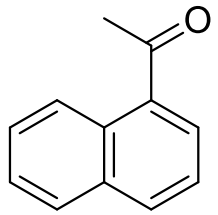


2l (400 MHz, $CDCl_3$)

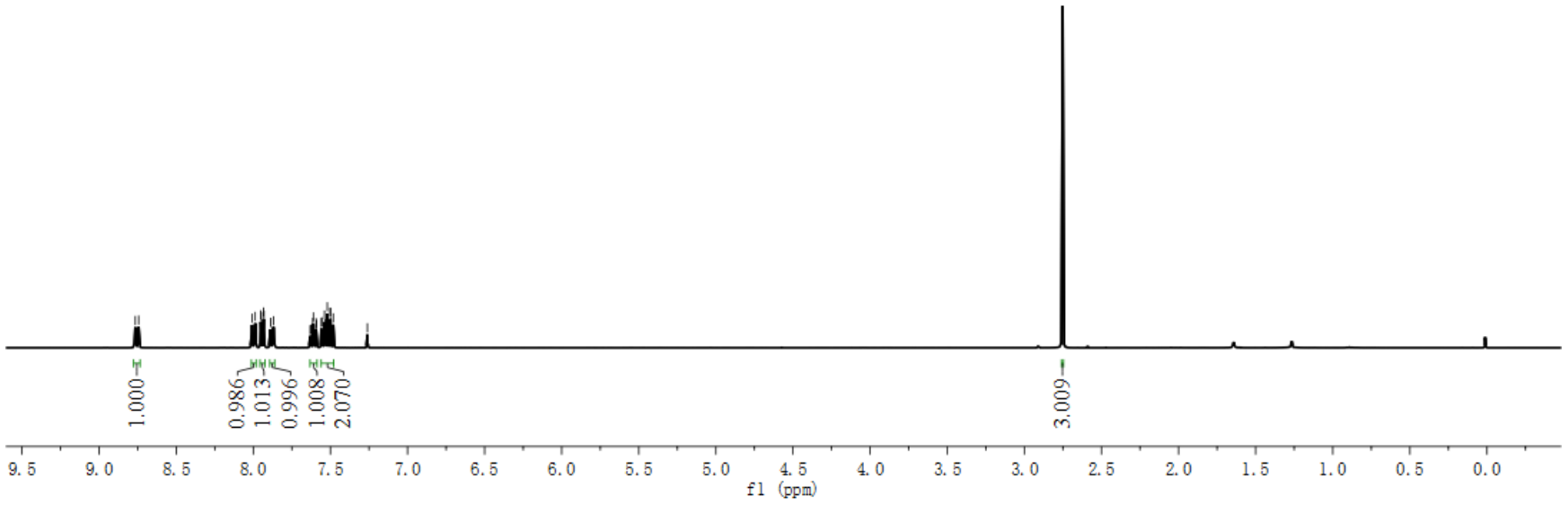


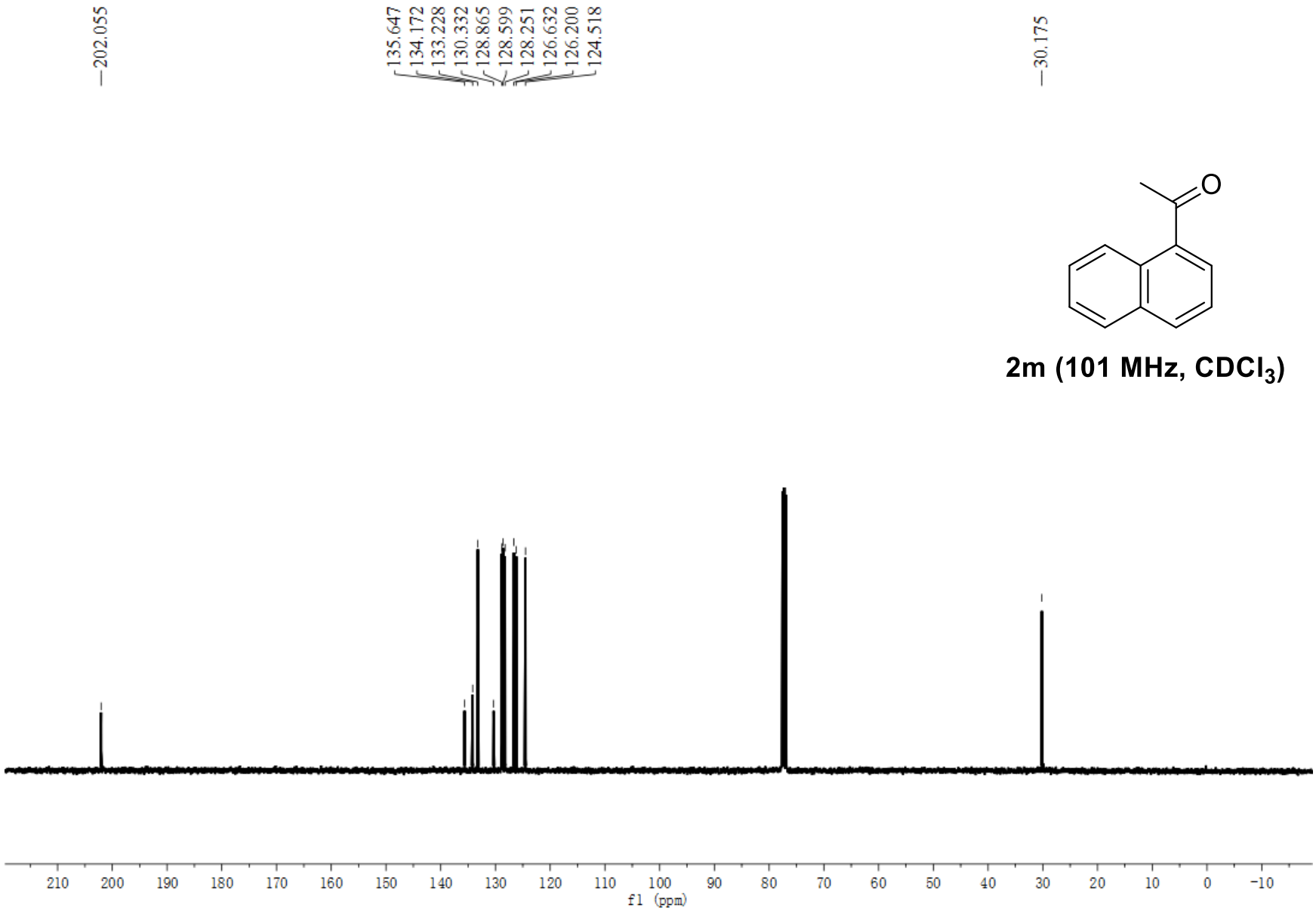
2l (101 MHz, $CDCl_3$)



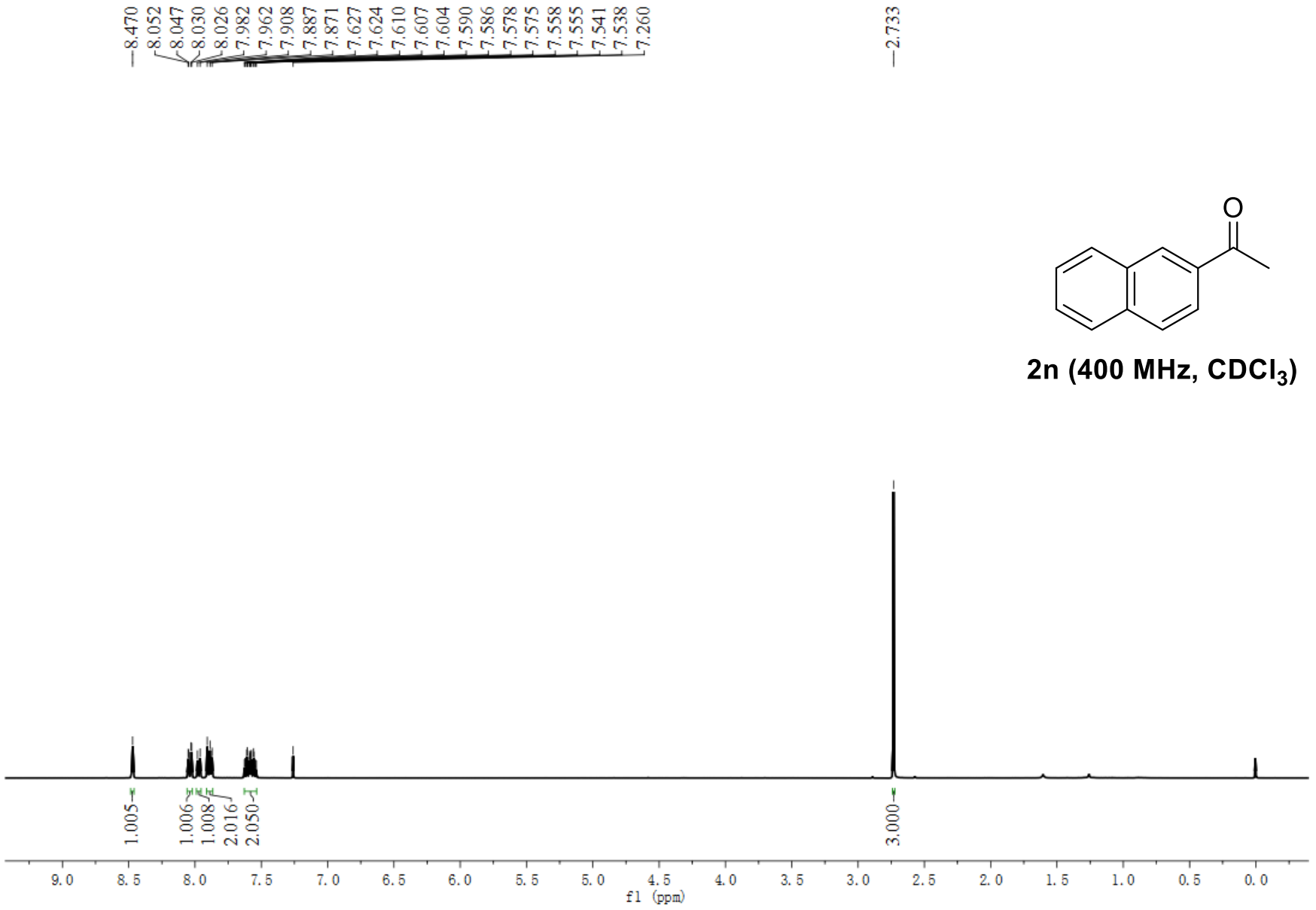


2m (400 MHz, $CDCl_3$)

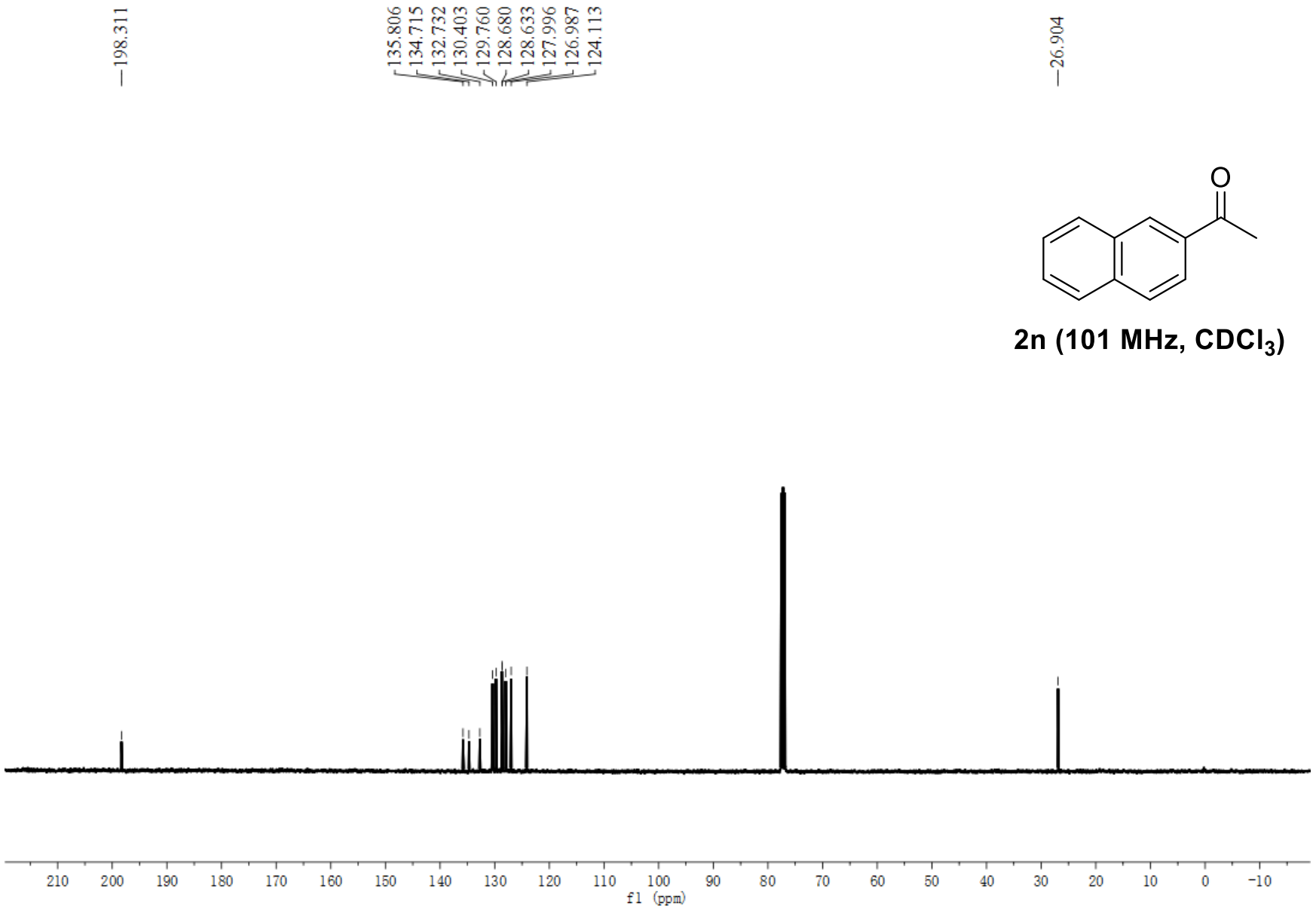




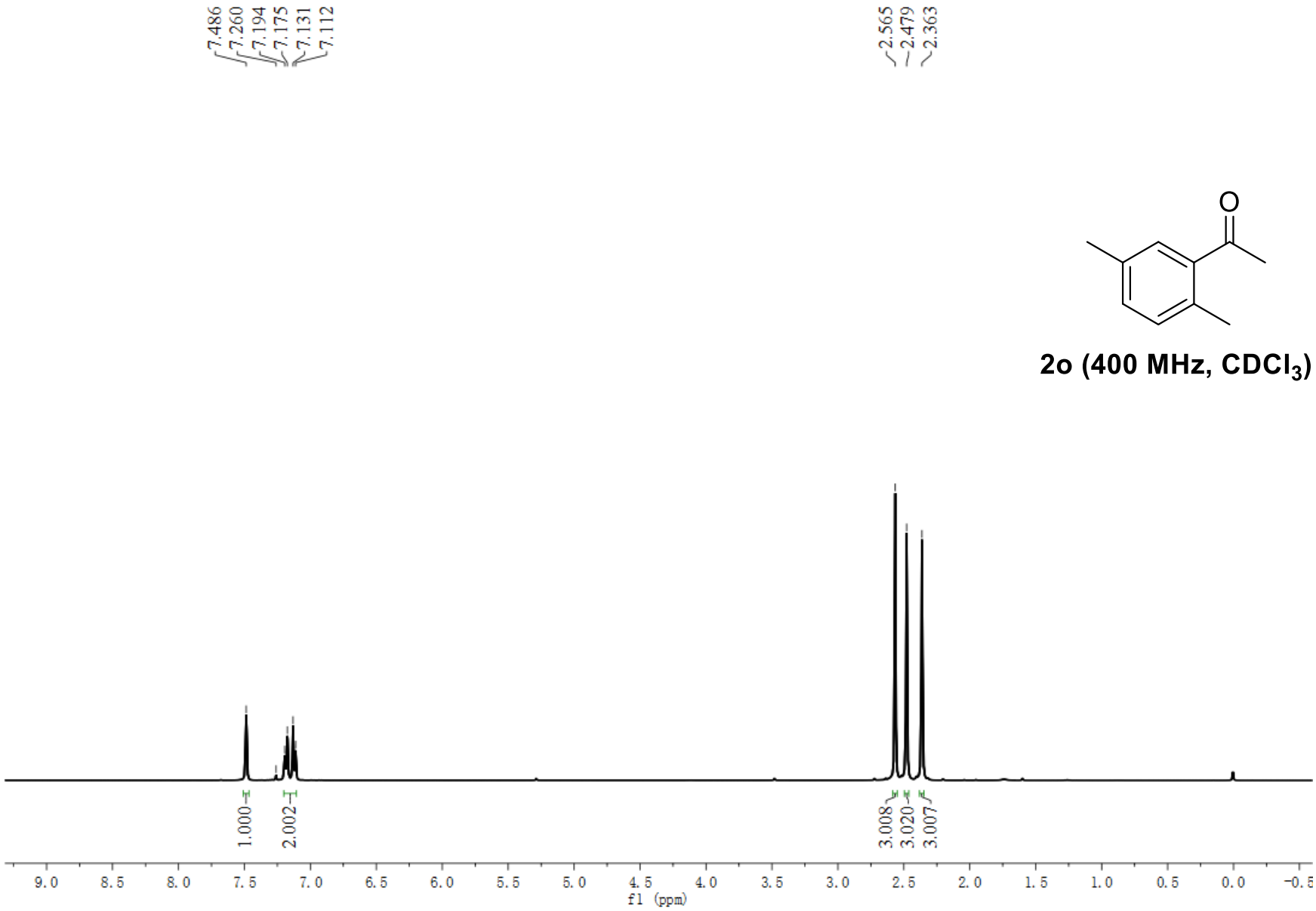
2m (101 MHz, $CDCl_3$)



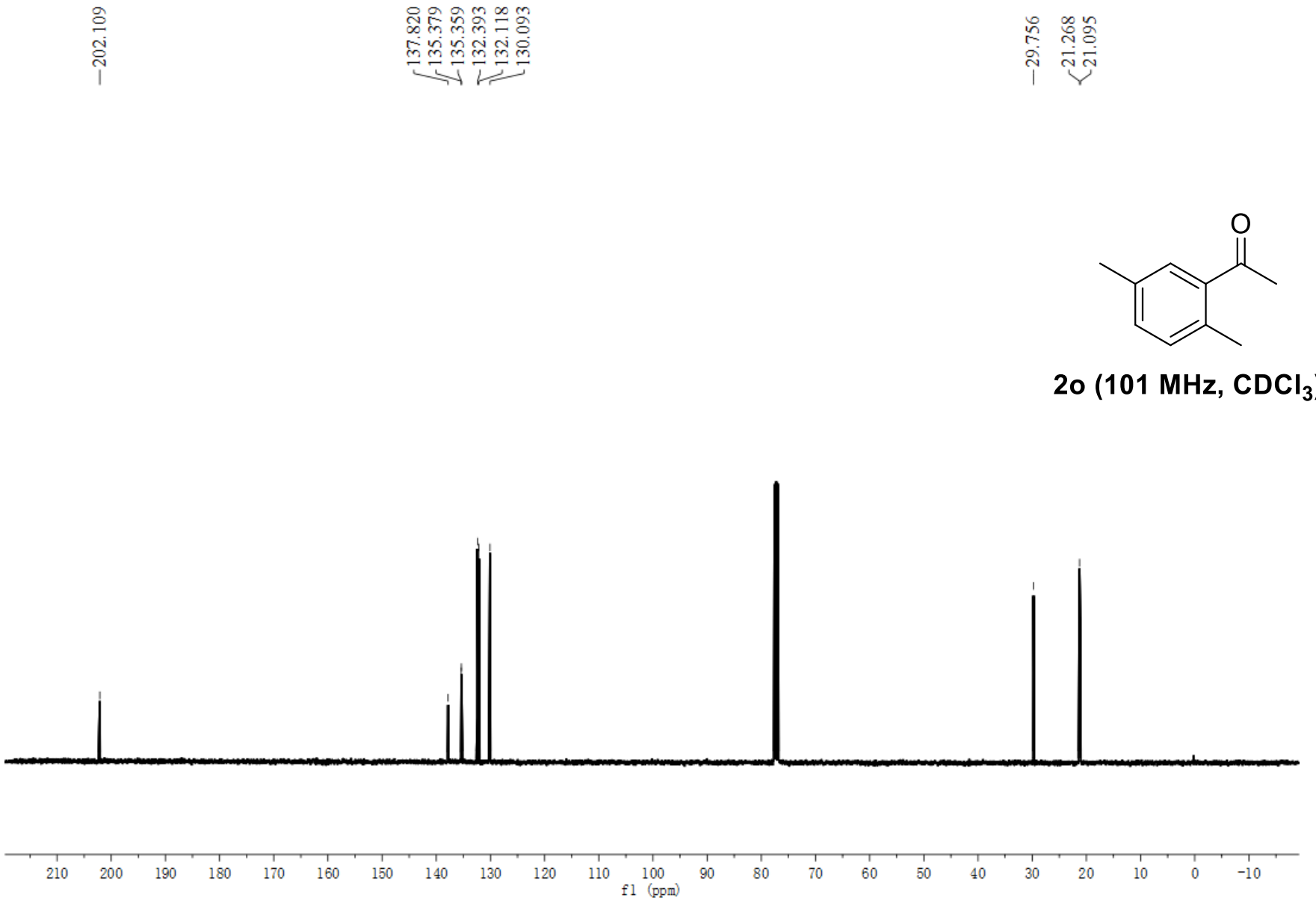
2n (400 MHz, $CDCl_3$)



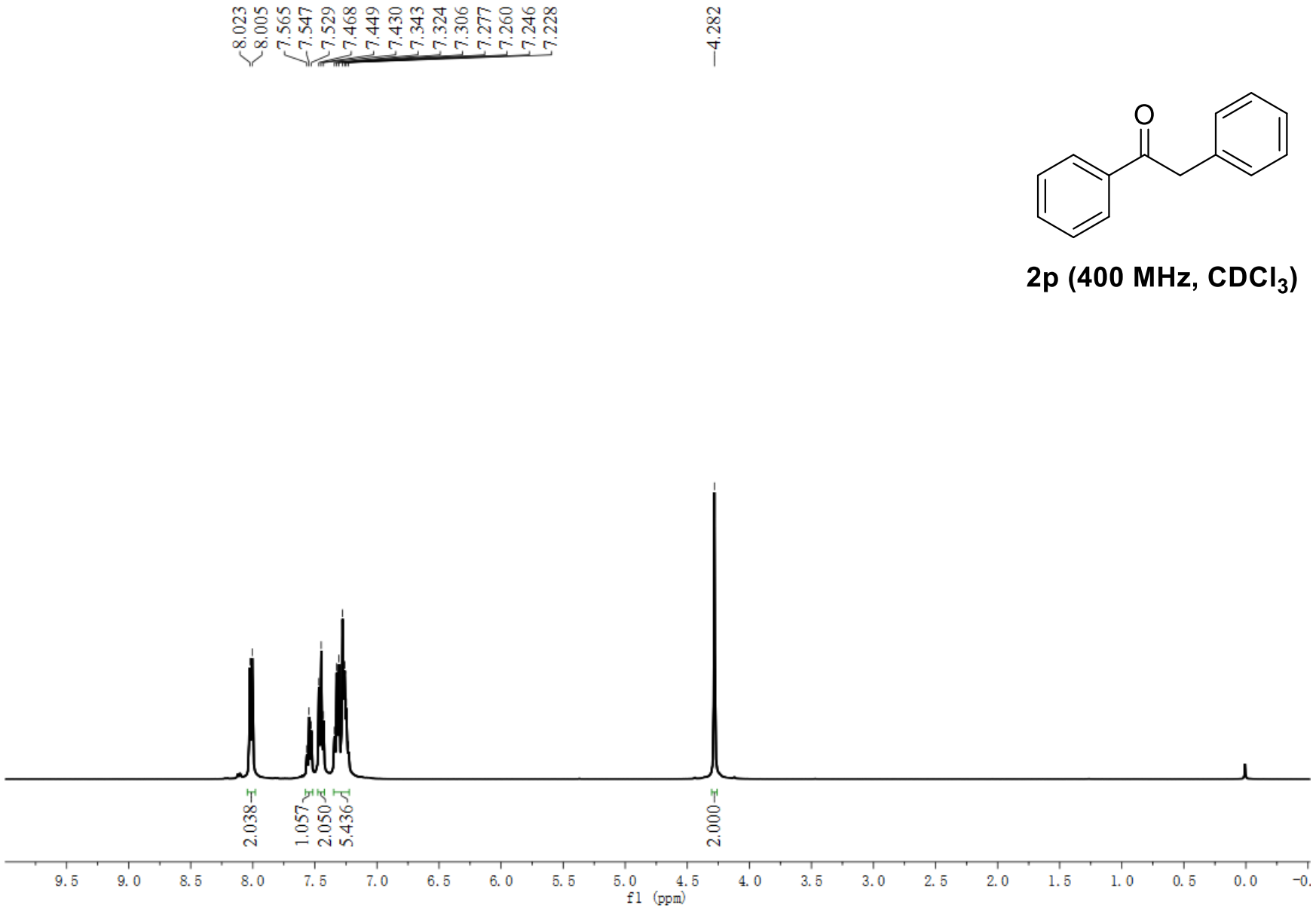
2n (101 MHz, $CDCl_3$)



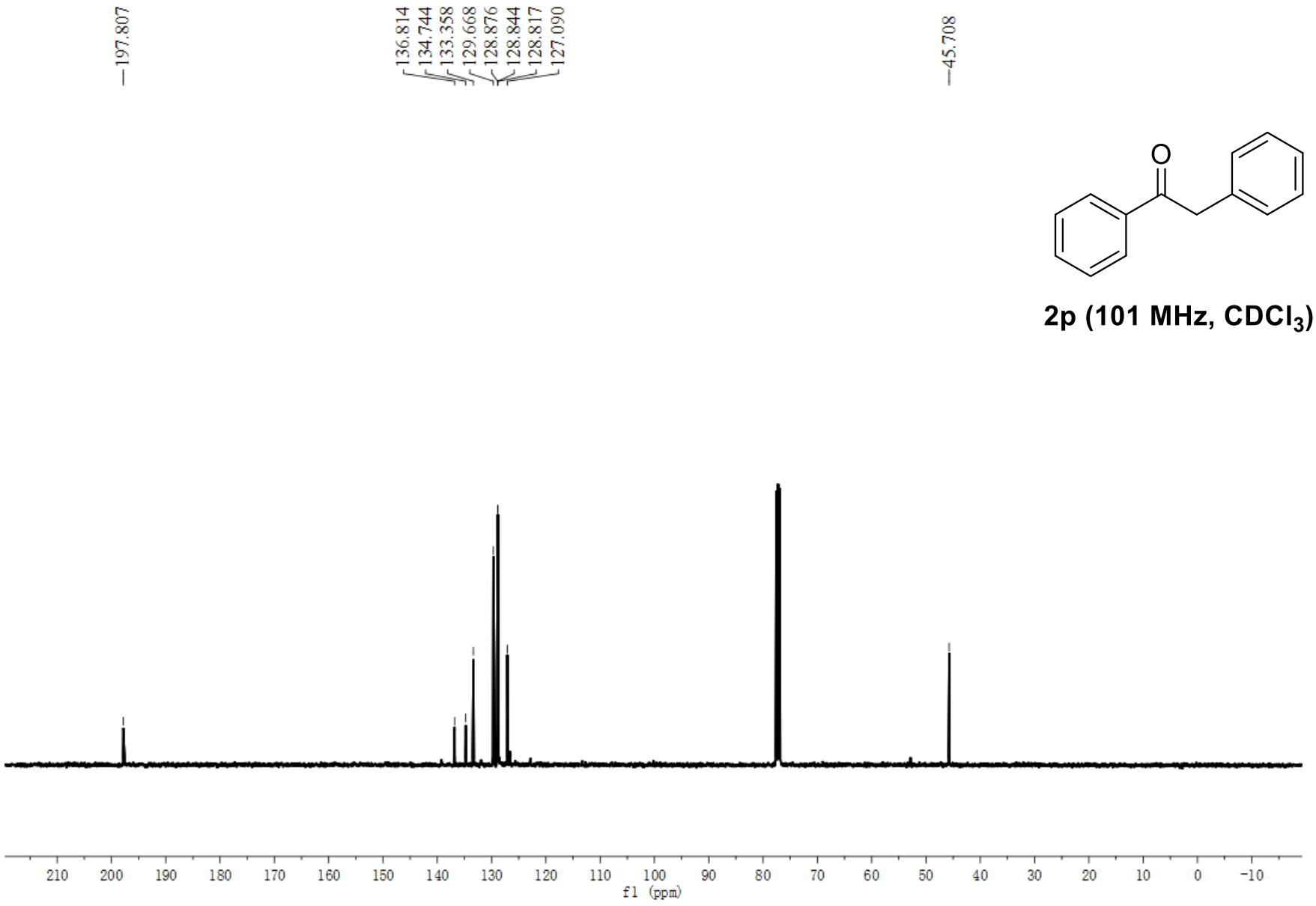
2o (400 MHz, $CDCl_3$)



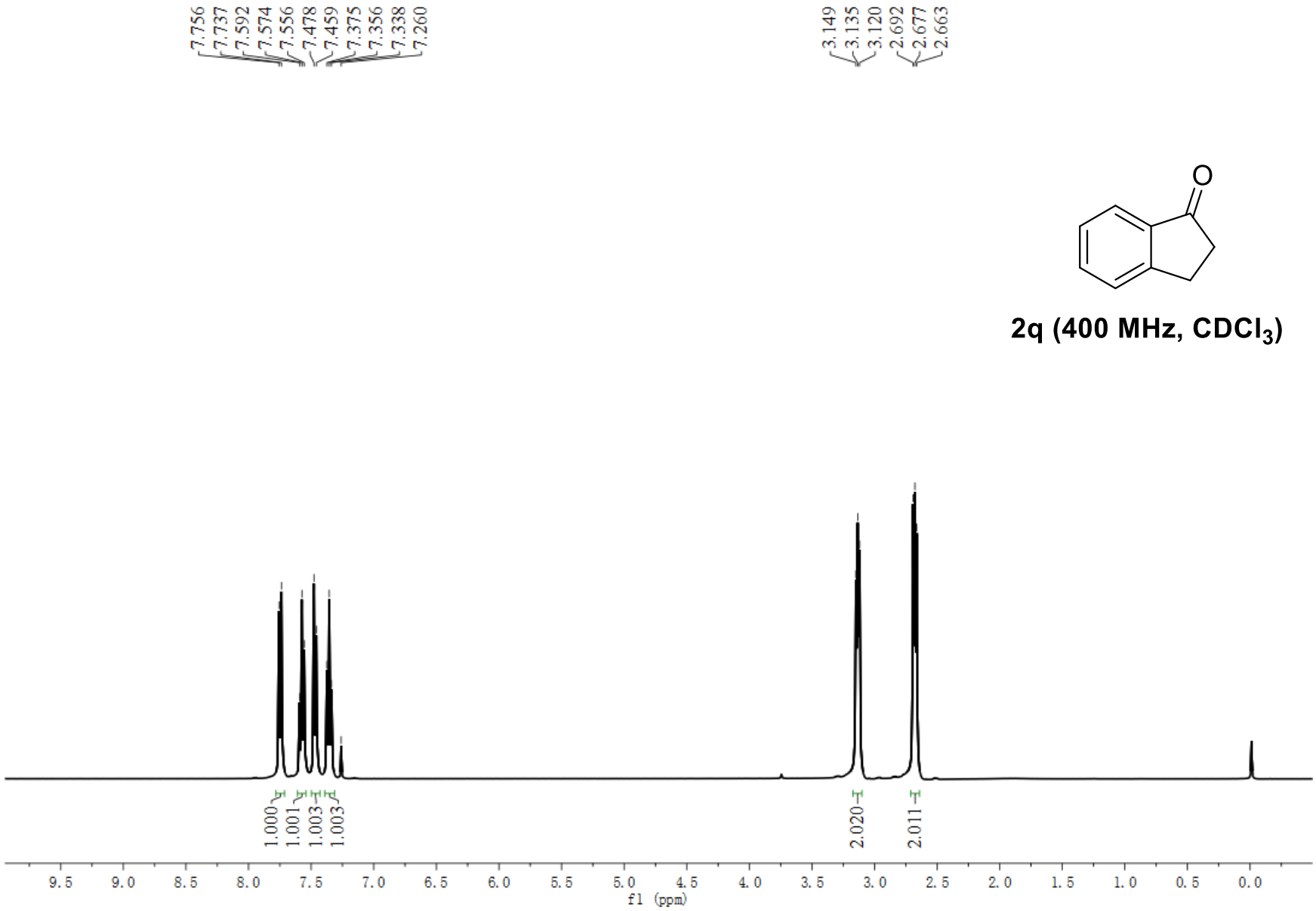
2o (101 MHz, $CDCl_3$)



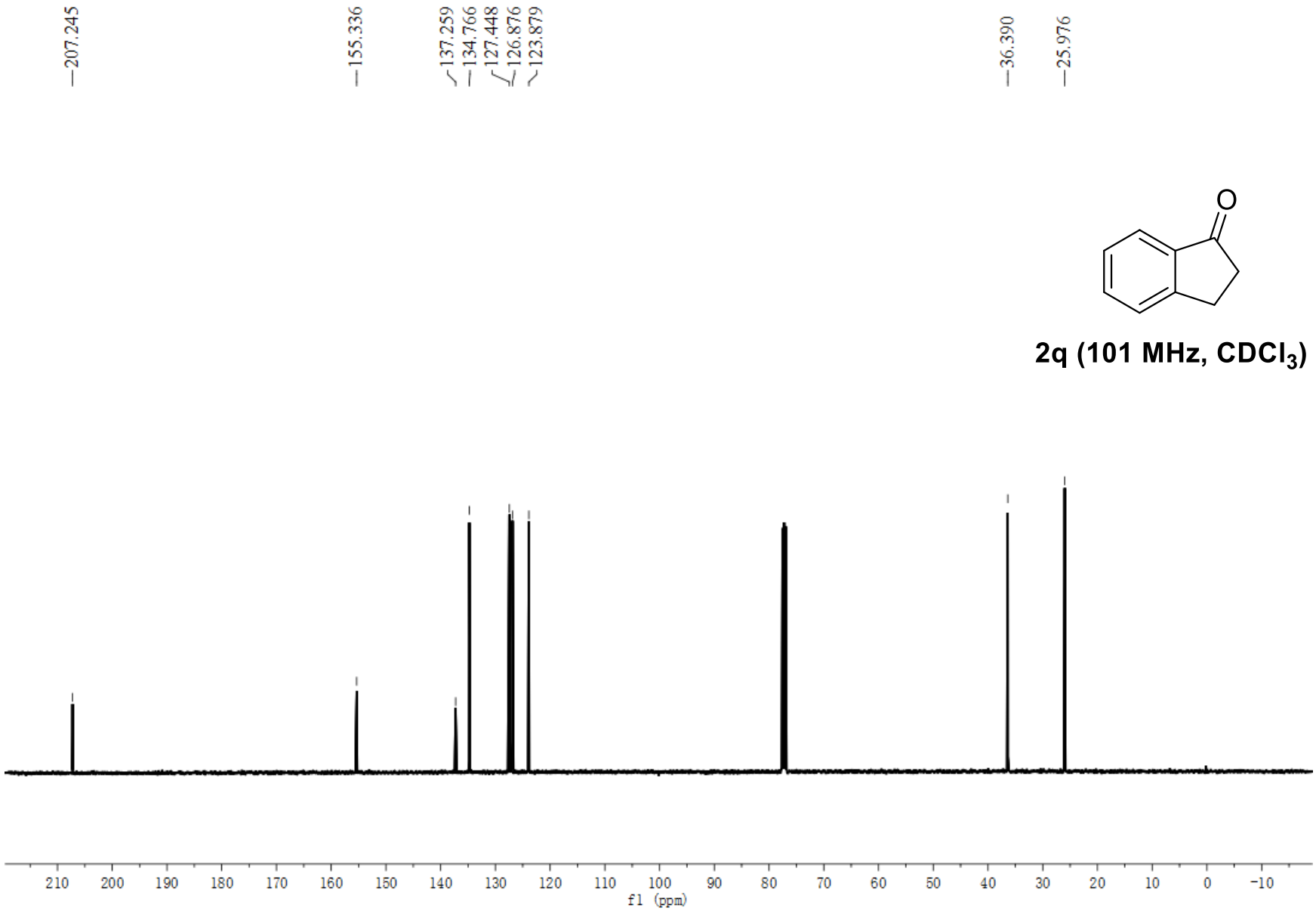
2p (400 MHz, $CDCl_3$)

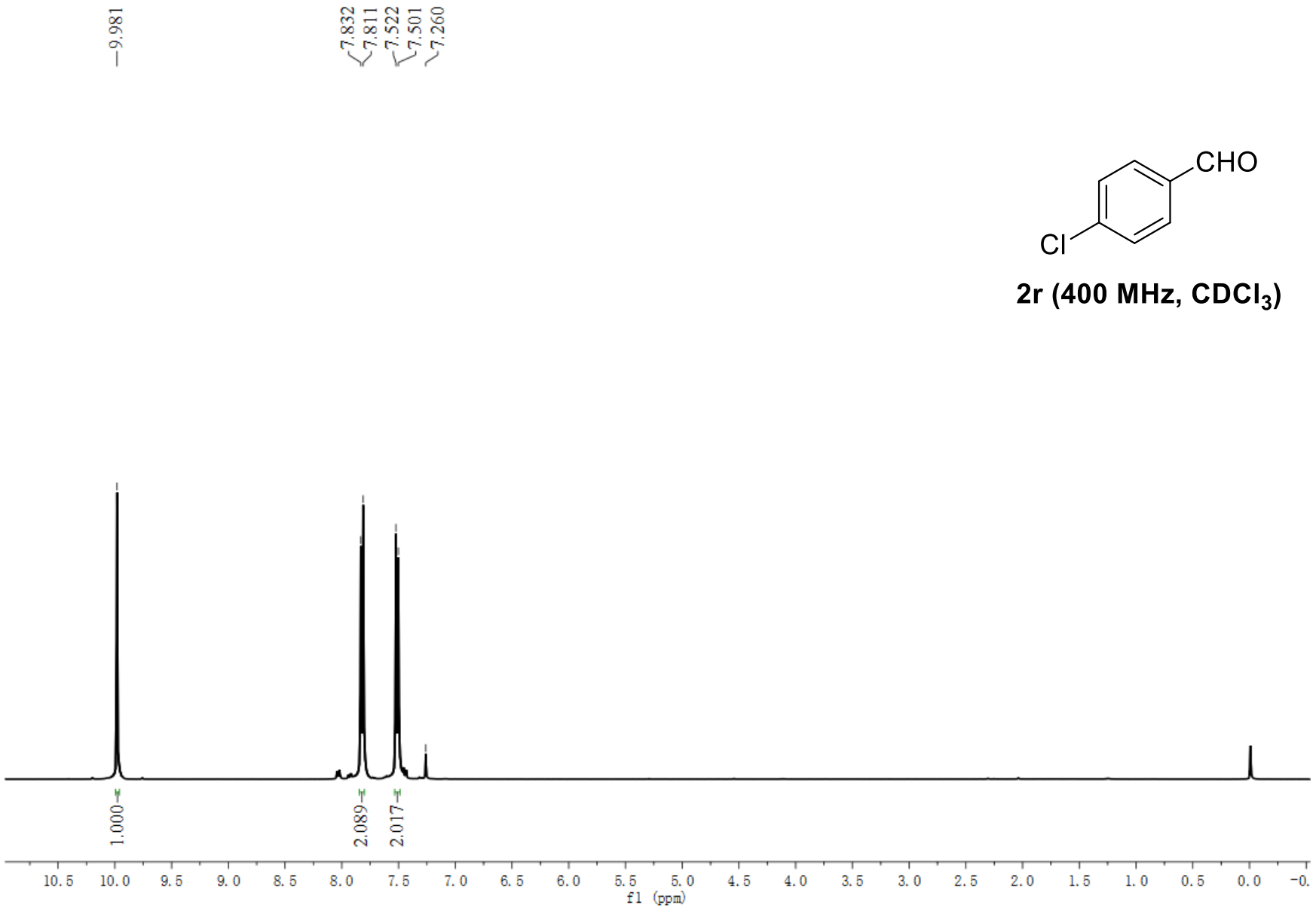


2p (101 MHz, $CDCl_3$)

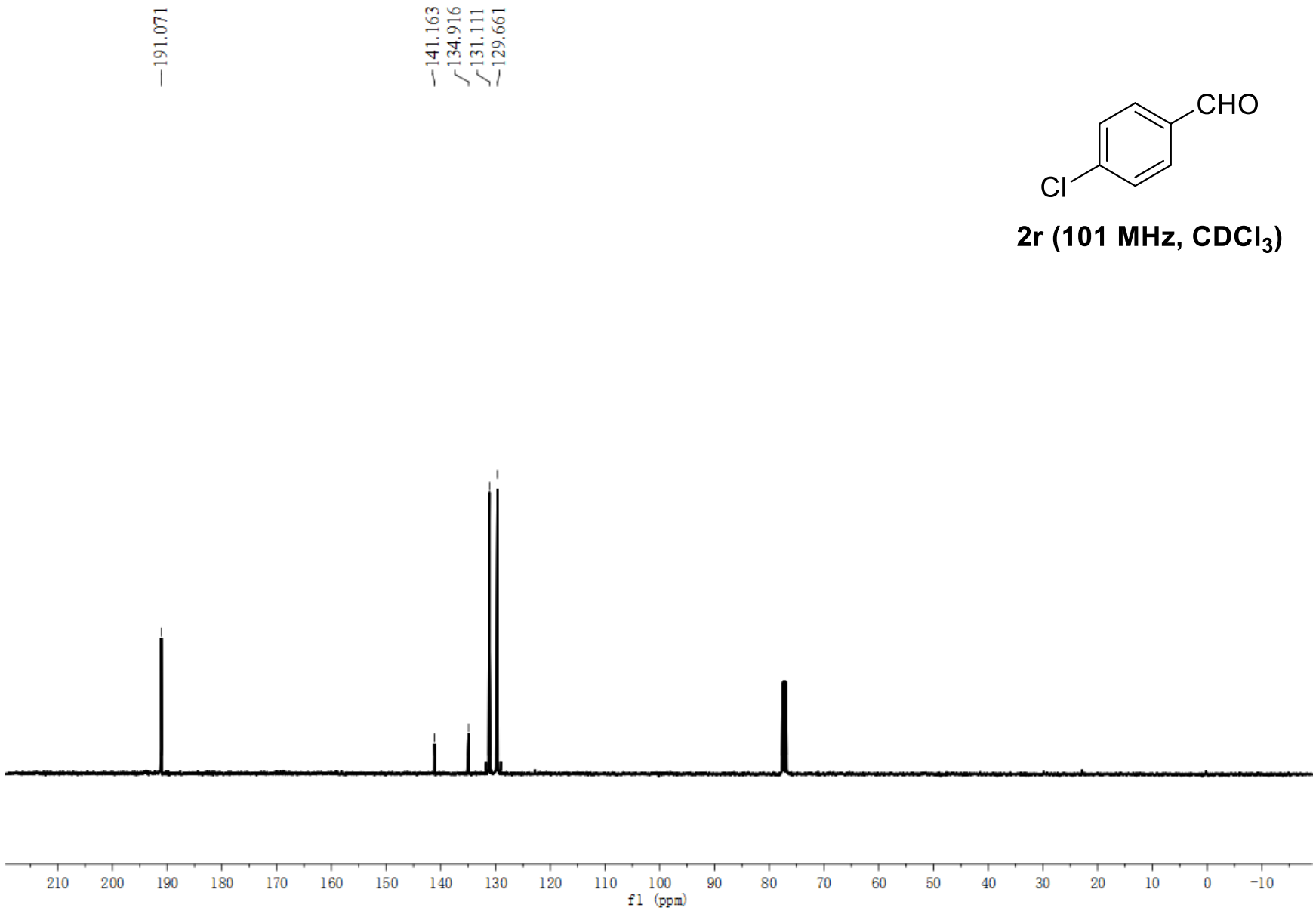


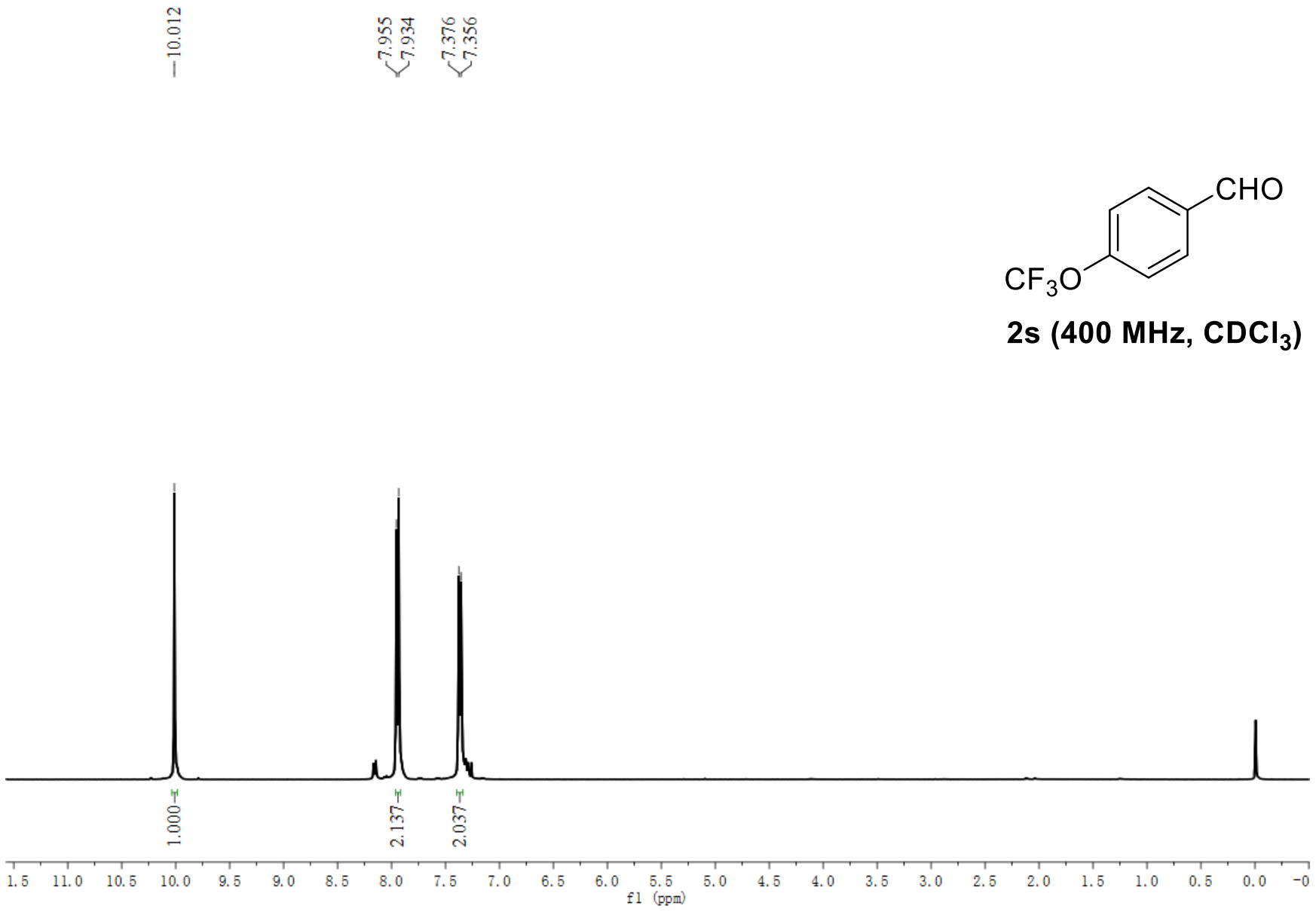
2q (400 MHz, $CDCl_3$)


207.245
155.336
137.259
134.766
127.448
126.876
123.879
36.390
25.976
O
2q (101 MHz, CDCl3)
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)

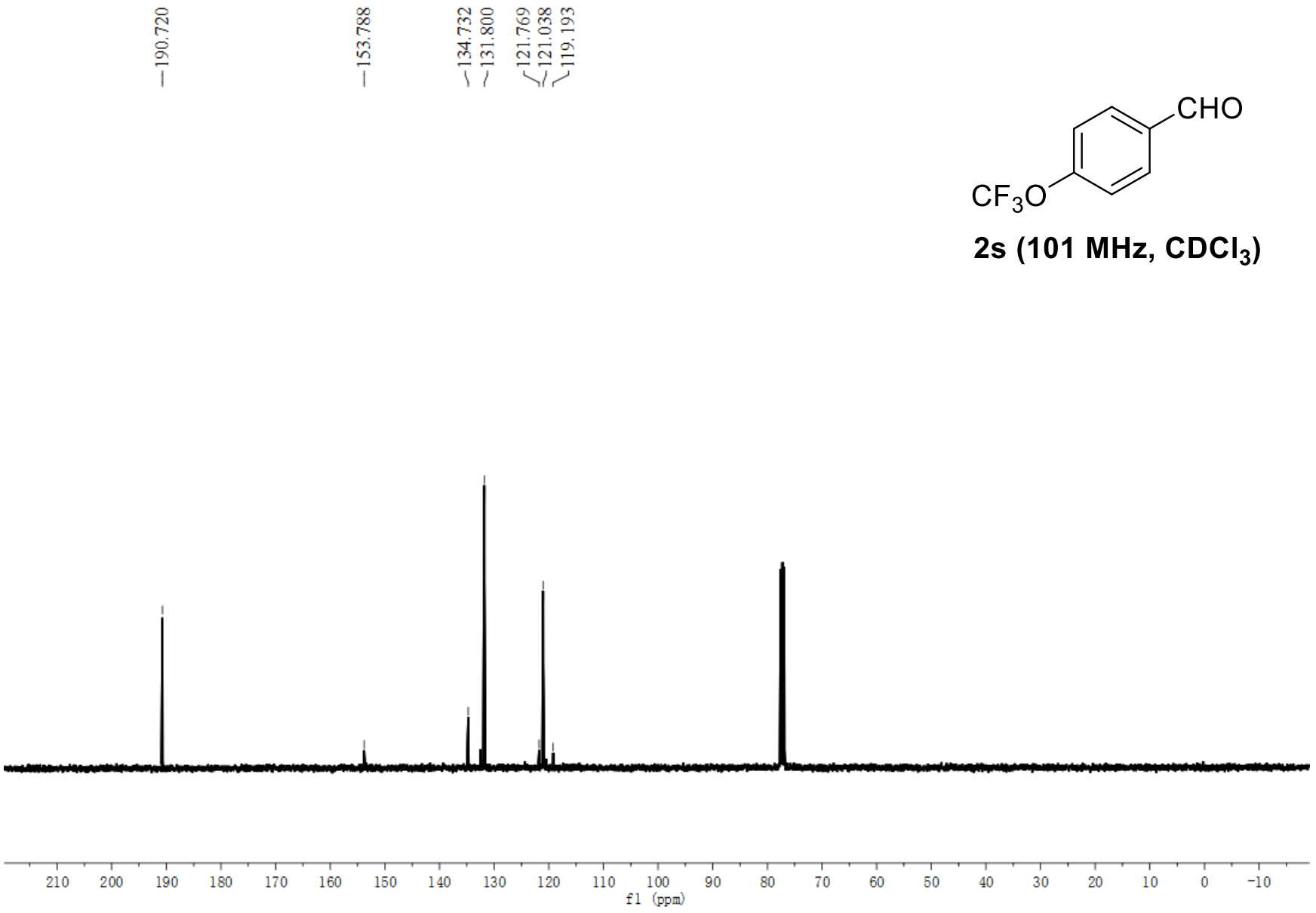


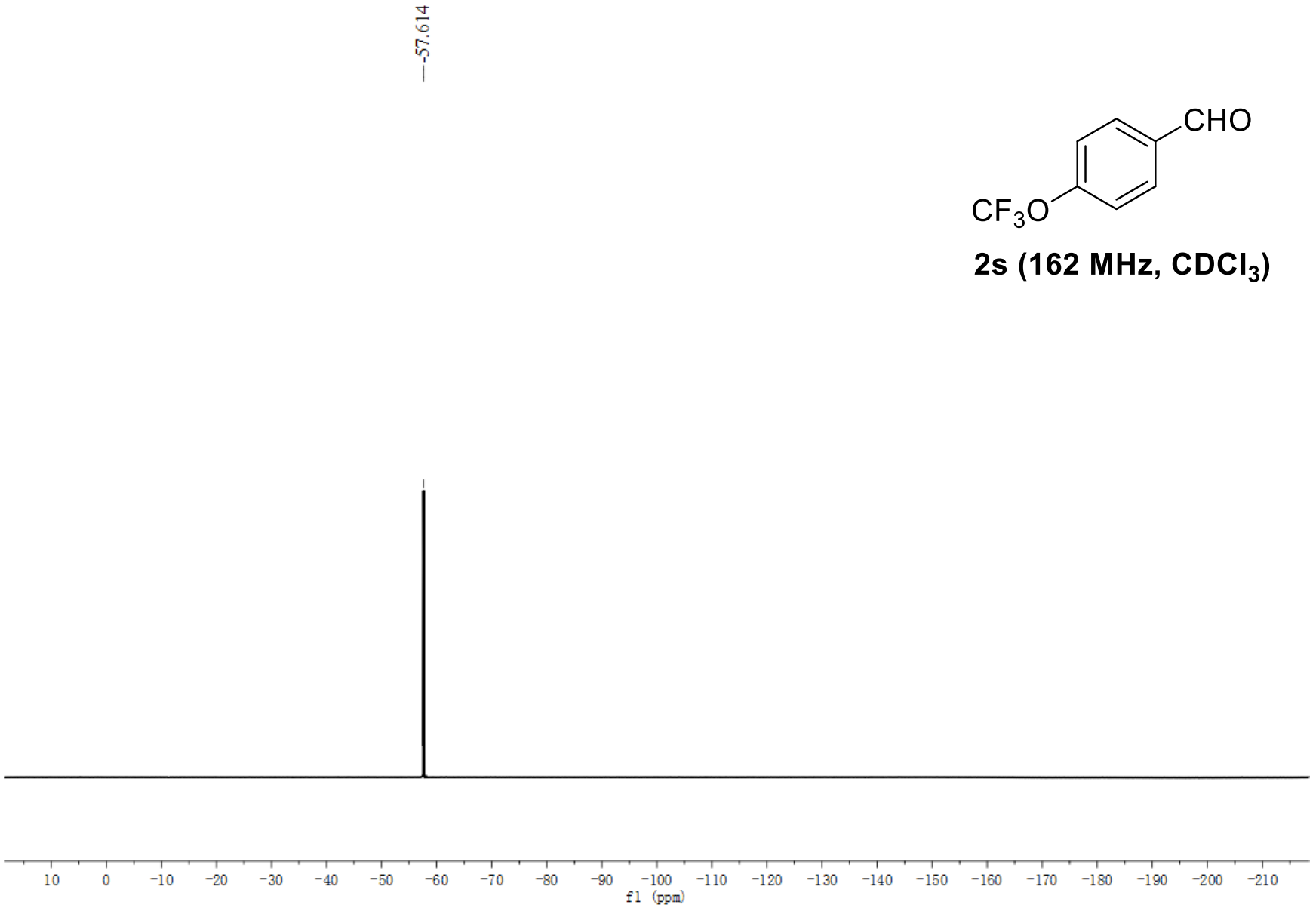
2r (400 MHz, $CDCl_3$)


191.071
141.163
134.916
131.111
129.661
CHO
Cl
2r (101 MHz, CDCl3)
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)

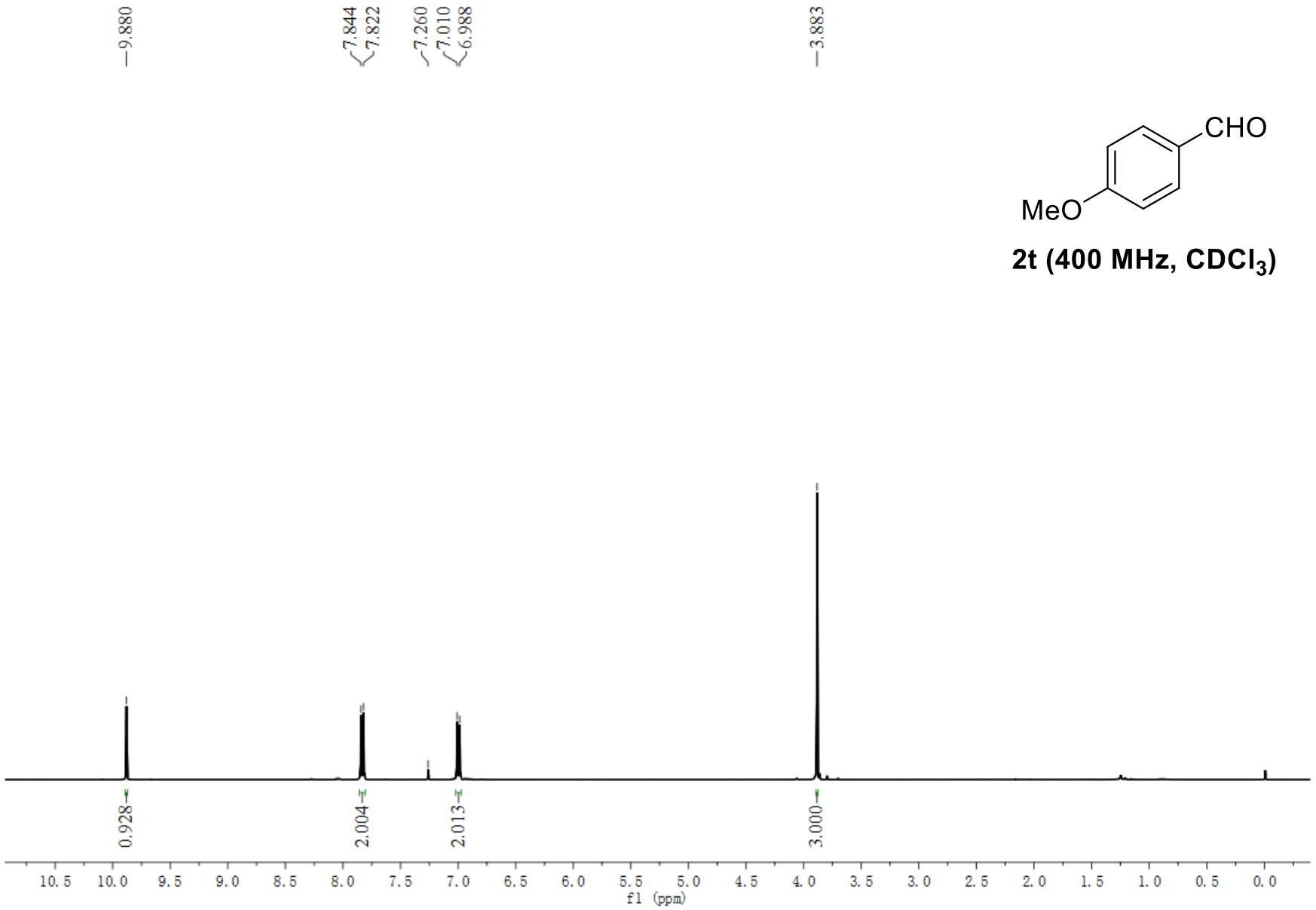


2s (400 MHz, $CDCl_3$)

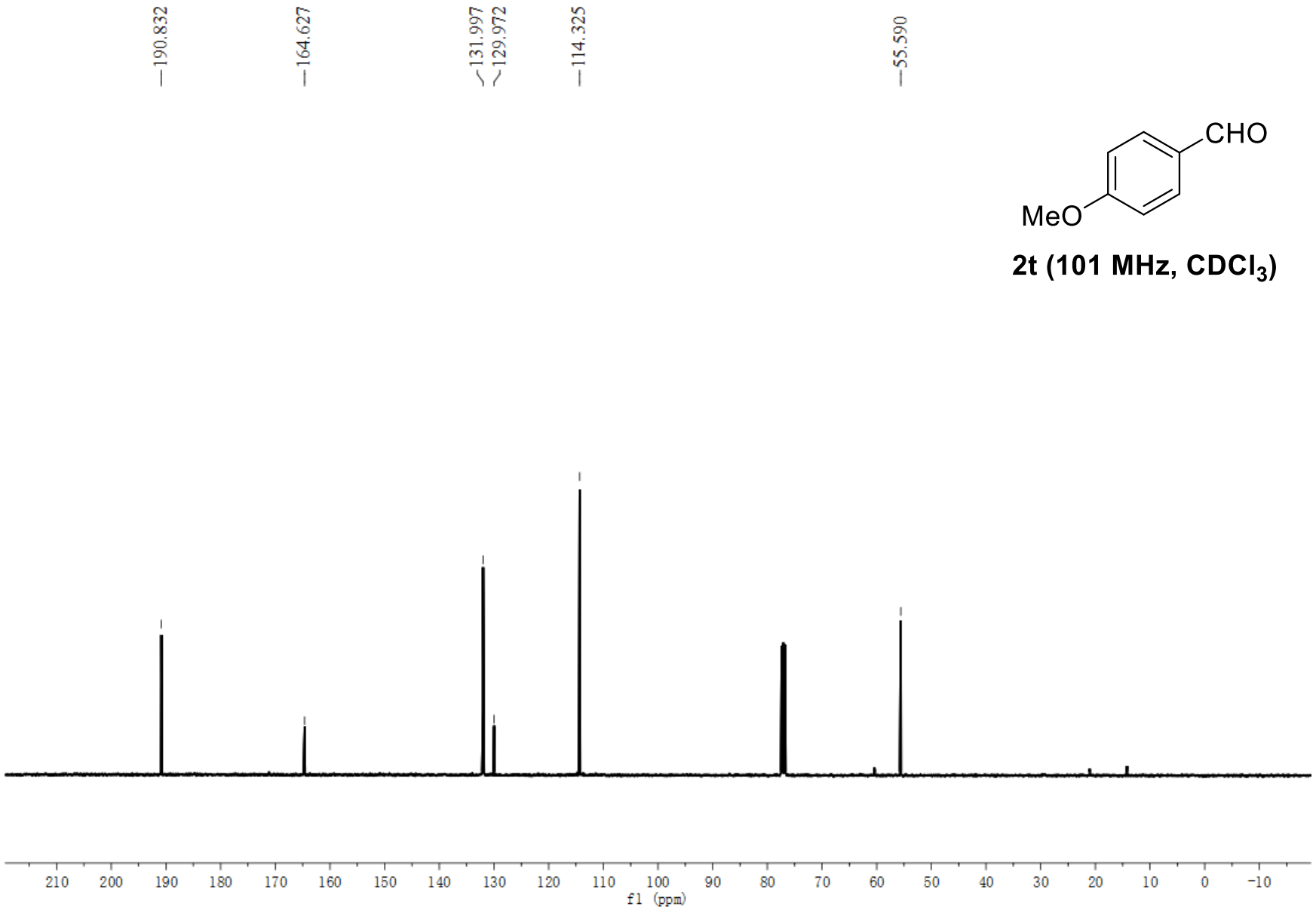

190.720
153.788
134.732
131.800
121.769
121.038
119.193
CHO
CF3O
2s (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



2s (162 MHz, $CDCl_3$)



2t (400 MHz, $CDCl_3$)



2t (101 MHz, $CDCl_3$)