Metal- and Oxidant-Free Carbonylation of Benzylic and Allylic C−H Bonds with H_2O via Dual Oxidative Radical-Polar Crossover

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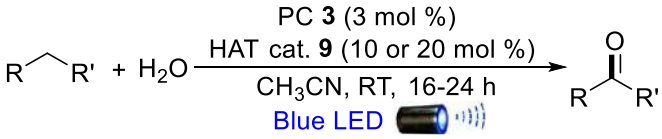
Table of Contents

I. General Information

Chemicals and solvents were purchased from commercial suppliers and used as received. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker AV-III400 (400 MHZ) spectrometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ (δ 7.26, 77.0 ppm) or benzene-d_6 (δ 7.16, 128.0 ppm) with tetramethylsilane (TMS) as the internal standard. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br s (broad singlet). All high resolution mass spectra (HRMS) were obtained by ESI mode with the mass analyzer of TOF used. The Blue LED strips (2.0 meter, 24 W, maximum emission at around 470 nm) were purchased from Shenzhen Lingke lighting Co., Ltd (China).

II. Typical Procedure for Carbonylation of Benzylic/Allylic C–H Bonds with Water



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfilled with argon for three times. After that anhydrous CH_3CN (1.5 mL), the corresponding benzylic/allylic substrate (0.2 mmol, 1.0 eq.), H_2O (4 mmol, 20 eq.), ethyl 2-mercaptopropanoate (HAT cat. **9**, 0.02 or 0.04 mmol) were added sequentially by means of syringe. Then the reaction was placed under blue LEDs with an argon balloon and irradiated for 16-24 h. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) or by prepared TLC to give the product.

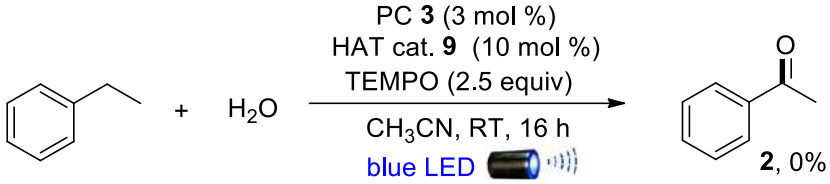
III. Typical Procedure for Oxidation of Benzylamines with H_2O

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation

and subsequent backfilled with argon for three times. After that anhydrous CH_3CN (1.5 mL), benzylamine (0.02 mmol), H_2O (4 mmol), ethyl 2-mercaptopropanoate (HAT cat. **9**, 0.04 mmol) were added sequentially by means of syringe. Then the reaction was placed under blue LEDs with an argon balloon and irradiated for 24 h. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) or by prepared TLC to give the product.

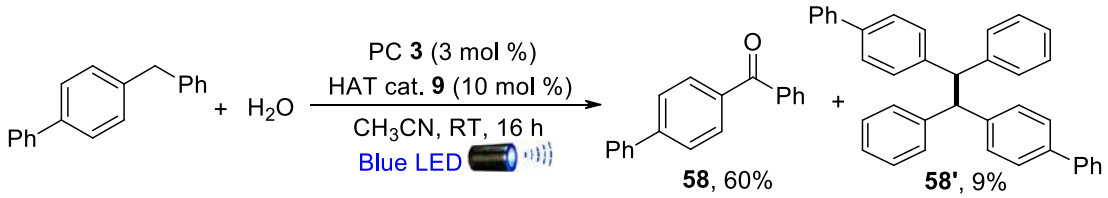
IV. Mechanistic Investigations

1) Control experiments



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol) and TEMPO (0.5 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After that anhydrous CH_3CN (1.5 mL), phenylethane (0.2 mmol), H_2O (4 mmol), ethyl 2-mercaptopropanoate (HAT cat. **9**, 2.6 μL, 0.02 mmol) were added sequentially by means of syringe. Then the reaction was placed under blue LEDs with an argon balloon and irradiated for 16 h. There is no corresponding product observed according to TLC analysis.

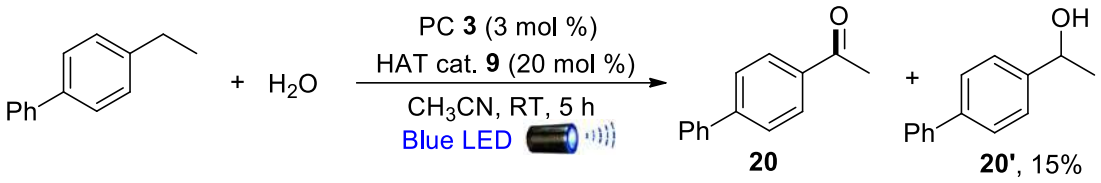
2) Benzyl radical validation experiment



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After that anhydrous CH_3CN (1.5 mL), 4-Benzylbiphenyl (0.2 mmol), H_2O (4 mmol), and ethyl 2-mercaptopropanoate (HAT cat. **9**, 2.6 μL, 0.02 mmol) were added sequentially by means of syringe. Then the reaction was placed under

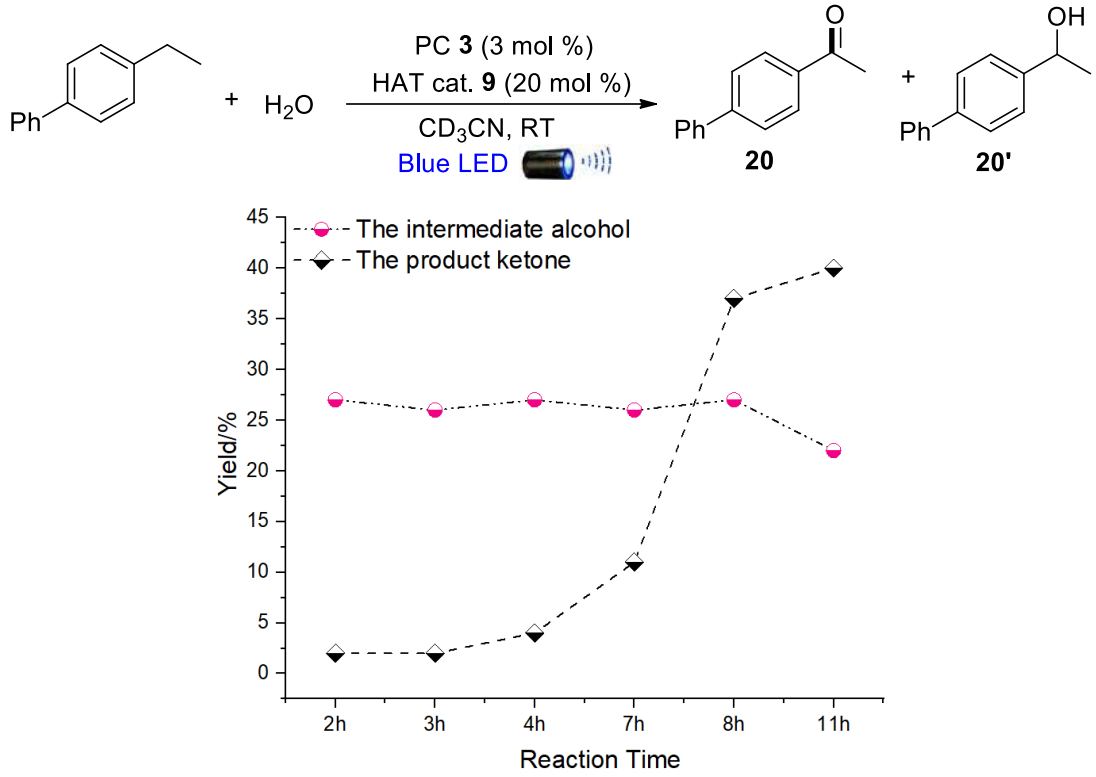
blue LEDs with an argon balloon and irradiated for 16 h. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by column chromatography isolation on silica gel to give the product **58** in 60% yield and the product **58′** in 9% yield.

3) Capture of the benzyl alcohol intermediary product



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After that anhydrous CH_3CN (1.5 mL), 4-benzylbiphenyl (0.2 mmol), H_2O (4 mmol), and ethyl 2-mercaptopropanoate (HAT cat. **9**, 5.2 μL, 0.04 mmol) were added sequentially by means of syringe. Then the reaction was placed under blue LEDs with an argon balloon and irradiated for 5 h. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by column chromatography isolation on silica gel to give the product **20′** in 15% yield.

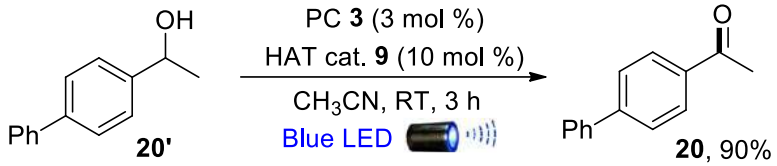
4) Experimental process monitoring



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst **3**

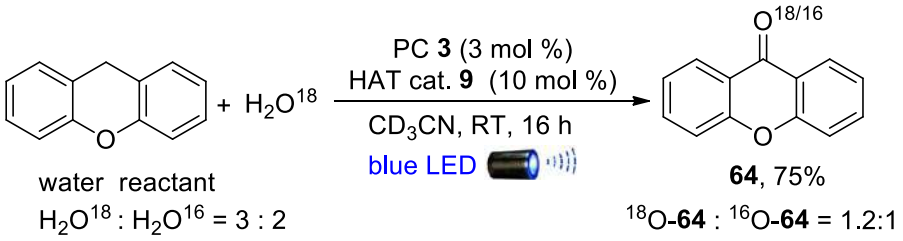
4CzIPN (4.7 mg, 0.006 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After that anhydrous CD_3CN (1.5 mL), 4-benzylbiphenyl (0.2 mmol), H_2O (4 mmol), and ethyl 2-mercaptopropanoate (HAT cat. **9**, 5.2 μL, 0.04 mmol) were added sequentially by means of syringe. Then the reaction was placed under blue LEDs with an argon balloon and irradiated for X h. After that, and the yield of product **20** and **20′** was determined by crude ^{1}HNMR analysis using 1,3,5-trimethoxybenzene as a internal standard.

5) Photocatalytic oxidation of the intermediary alcohol to carbonyl



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After that anhydrous CH_3CN (1.5 mL), 1-(4-biphenylyl)ethanol **20'** (0.1 mmol), and ethyl 2-mercaptopropanoate (HAT cat. **9**, 5.2 μL, 0.02 mmol) were added sequentially by means of syringe. Then the reaction was placed under blue LEDs with an argon balloon and irradiated for 3 h. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by column chromatography isolation on silica gel to give the product **20** in 90% yield.

6) Identification of the oxygen source



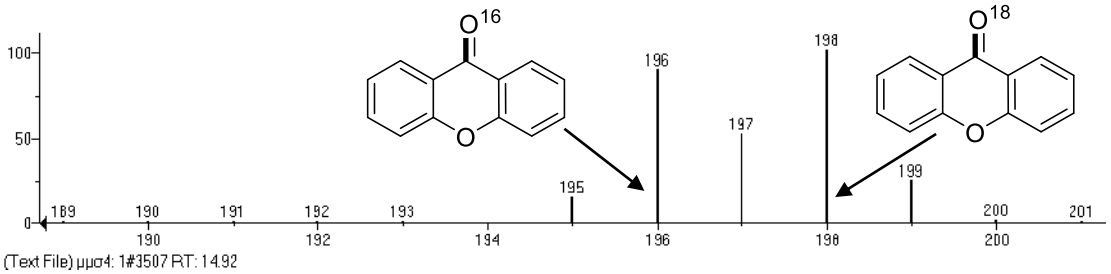
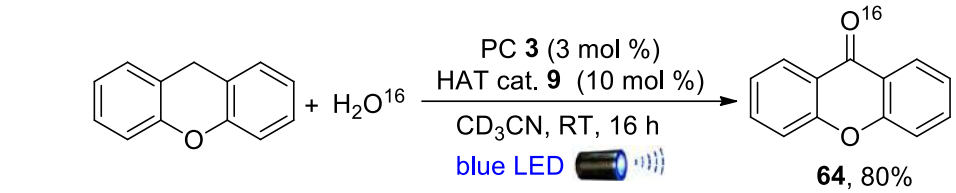


Figure S1. GC-MS spectrum of product of reaction of ^{18}O-labeled water and unlabeled water

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After that anhydrous CD_3CN (1.0 mL), xanthene (0.2 mmol), H_2O^{18} (43 μL, 2.4 mmol), H_2O^{16} (29 μL, 1.6 mmol) and ethyl 2-mercaptopropanoate (HAT cat. **9**, 2.6 μL, 0.02 mmol) were added sequentially by means of syringe. Then the reaction was placed under blue LEDs with an argon balloon and irradiated for 16 h. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by column chromatography isolation on silica gel to give the product **64** in 75% yield. The ratio of the $^{18}O/^{16}O$ labeled product was determined by GC-MS.



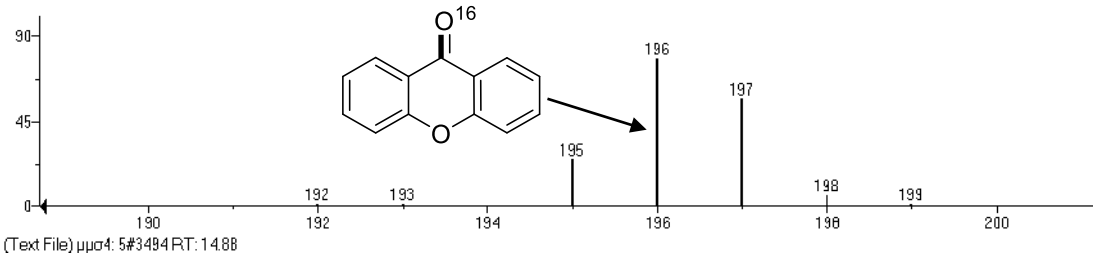


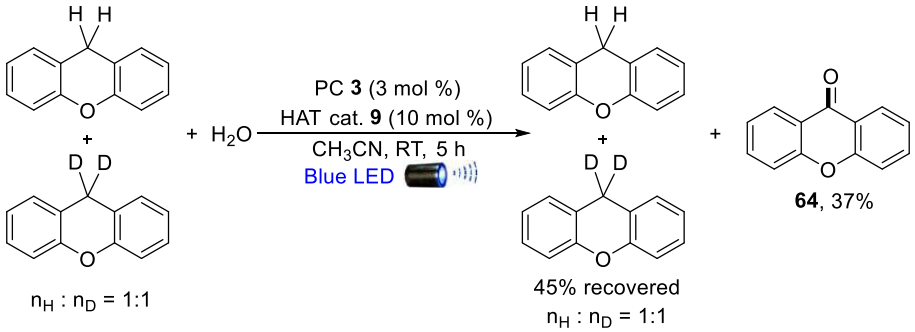
Figure S2. GC-MS spectrum of product of reaction of unlabeled water

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After that anhydrous CD_3CN (1.0 mL), xanthene (0.2 mmol), H_2O (72 μL, 4 mmol) and ethyl 2-mercaptopropanoate (HAT cat. **9**, 2.6 μL, 0.02 mmol) were added sequentially by means of syringe. Then the reaction was placed under blue LEDs with an argon balloon and irradiated for 16 h. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by column chromatography isolation on silica gel to give the product **64** in 80% yield. The product was determined by GC-MS.

7) KIE studies

The deuterated xanthene-d_2 (100%-*D* incorporation) was prepared according to a known

method. [S1]



To a 25 mL Schlenk tube equipped with a magnetic stir bar were added the photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), Xanthene (24 mg, 0.1 mmol) and Xanthene-d_2 (24 mg, 0.1 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After that anhydrous CH_3CN (1.5 mL), ethyl 2-mercaptopropanoate (HAT cat. **9**, 2.6 μL, 0.02 mmol) were added sequentially by means of syringe. Then the reaction was placed under blue LEDs with an argon balloon and irradiated for 5 h. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane/ethyl acetate (80:1 ~ 40:1) to give the product **64** in 37% yield and the recovered xanthene in 45% yield. A remained C–H/D ratio was observed in the recovered xanthene according to ^{1}H NMR analysis.

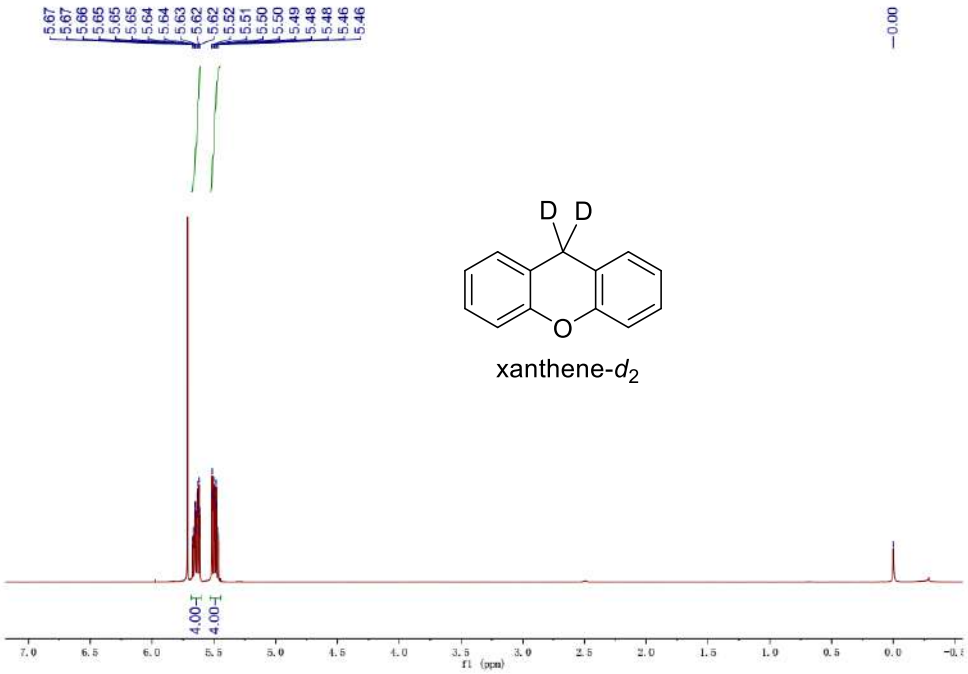


Figure S3. ^{1}H NMR spectra of the xanthene-d_2

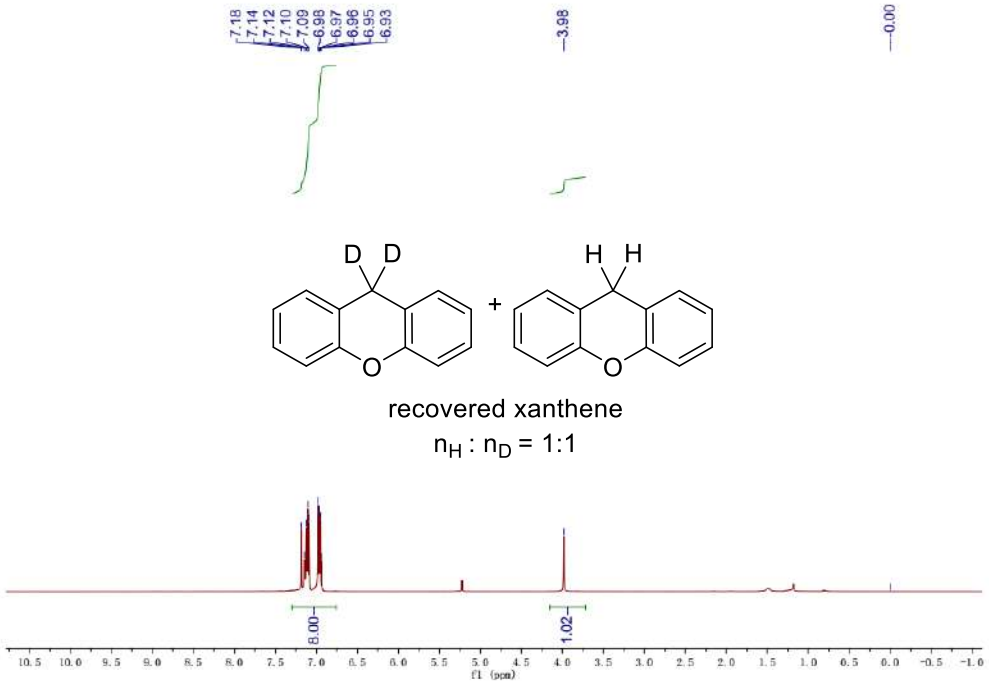


Figure S4. ^{1}H NMR spectra of the recovered xanthene (n_H : n_D = 1:1)

8) Light on-off experiments

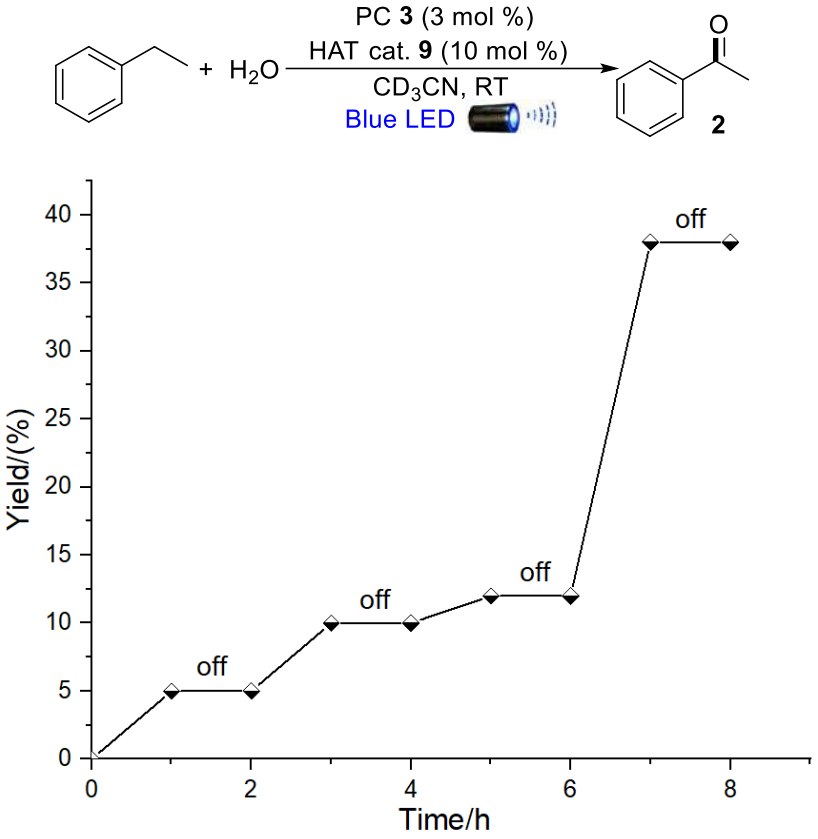
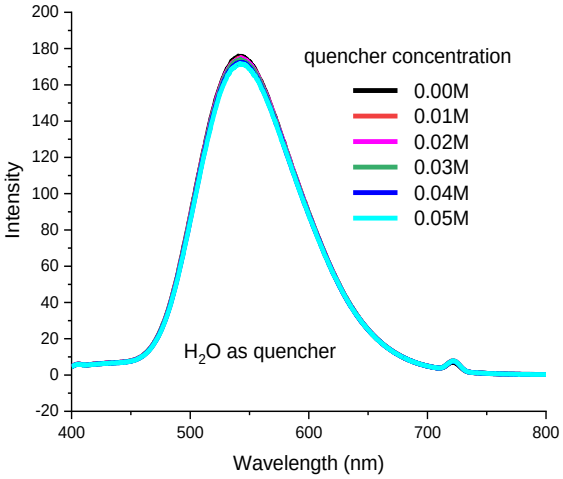
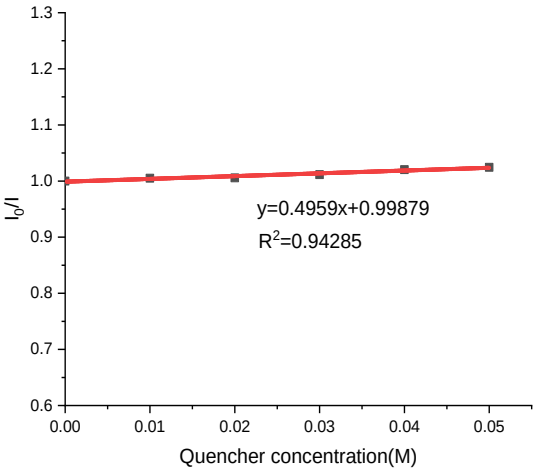


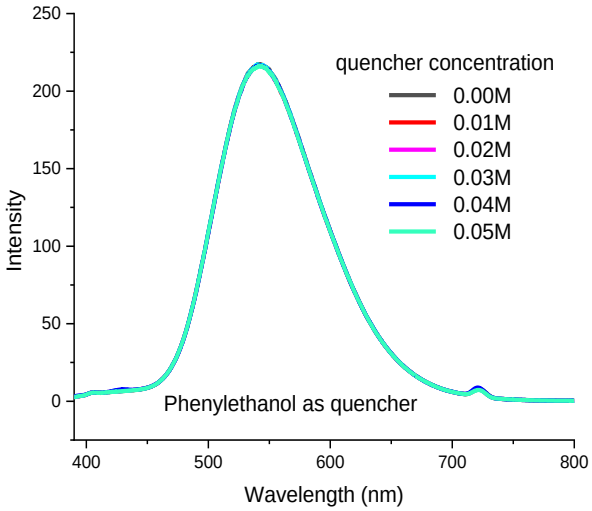
Figure S5. Light on-off experiments for carbonylation of ethylbenzene with H_2O

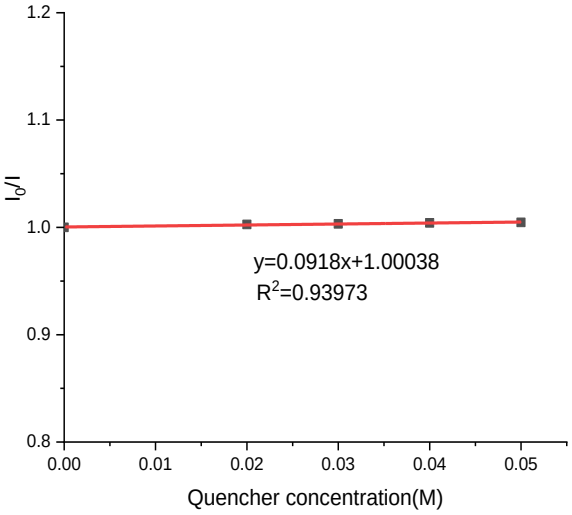
9) Stern-Volmer fluorescence quenching experiments

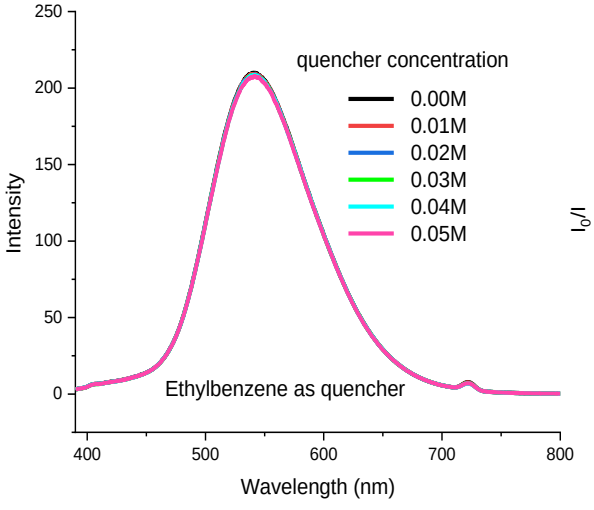
In a typical experiment, a solution of photocatalyst **3** 4CzIPN in anhydrous CH_3CN (1.25×10^{-4} M) was added with an appropriate amount of quencher in a quartz cuvette. Then the emission of the sample was collected. The emission intensity at 554 nm was collected with excited wavelength of 360 nm.

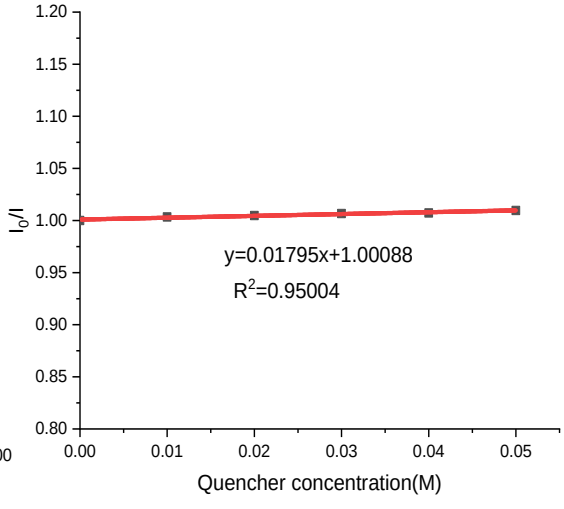












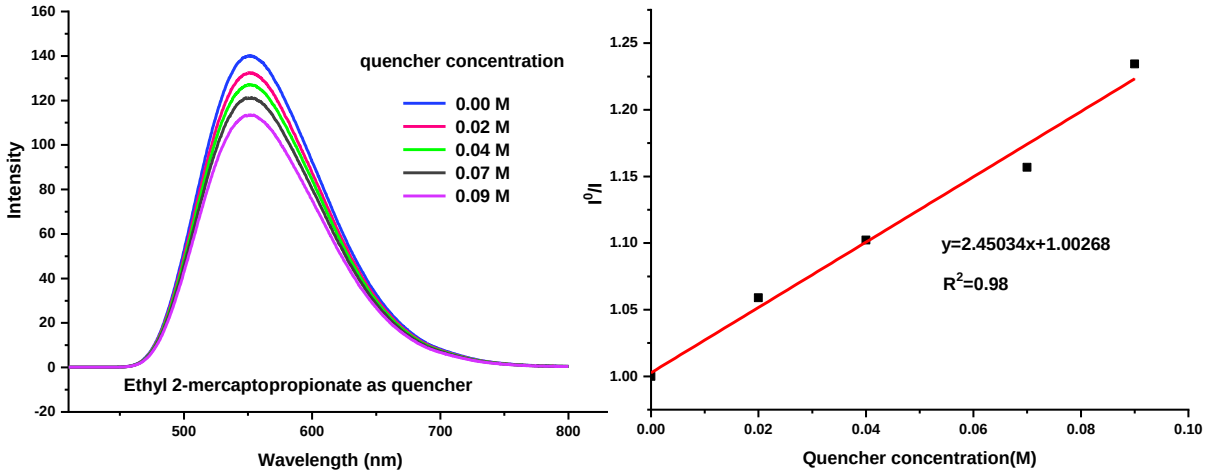


Figure S6. Stern-Volmer fluorescence quenching studies

10) Determination of quantum yields by standard ferrioxalate actinometry

Determination of the light intensity at 470 nm: Following Yoon's procedure[S2], the photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepapred by dissoving 50 mg of phenanthroline and 11.25 g of sodium aceate in 50 mL of 0.5 M H_2SO_4. Both solution were stored in the dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed solution was placed in a cuvette and irradiated for 93.0 second at λ = 470 nm with an emssion slit width at 10.0 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradinated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculates using eq (1).

$$molFe^{2+} = \frac{V \cdot \Delta A}{l\,\varepsilon} \qquad (1)$$

Where V is the total volume (0.00235 L) of the solution after of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solution, l is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1}). The photon flux can be calculated using eq (2).

$$Photo\ flux = \frac{\text{mol}\ Fe^{2+}}{\Phi\ t\ f} \qquad (2)$$

Where Φ is the quantum yield for the ferrioxalate actinometer (0.92 for a 0.15 M solution at λ = 468 nm), t is the time (60.0 s), and f is the fraction of light absorbed at λ = 470 nm (0.648, vide infra). The photo flux was calculated (average of three experiments) to be 4.705 × 10^{-9} einstein^{-1}.

$$molFe^{2+} = \frac{0.00235\ \text{L} \cdot 0.795}{1.000\ \text{cm} \cdot 11100\ \text{L}\ mol^{-1}\ cm^{-1}} = 1.6831 \times 10^{-7}\ mol$$

$$Photo\ flux = \frac{1.6831 \times 10^{-7}}{0.92 \cdot 60\ s \cdot 0.648} = 4.705 \times 10^{-9}\ mol$$

Determination of quantum yield:

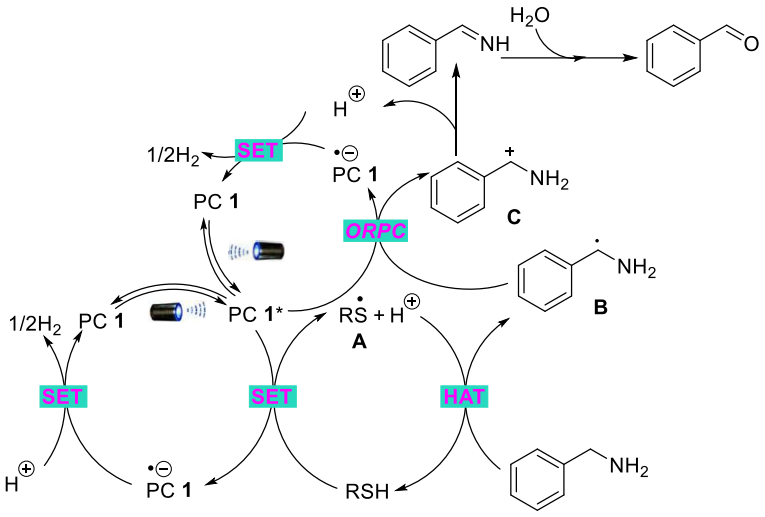
To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After that acetonitrile-d_3 (2.0 mL), ethylbenzene (0.2 mmol), H_2O (4 mmol) and ethyl 2-mercaptopropanoate (HAT cat. **9**, 2.6 μL, 0.02 mmol) were added sequentially by means of syringe. Then the reaction was placed under a blue LED (2 meter strips, 24 W) with an argon balloon and irradiated (λ = 470 nm, slit width = 10.0 nm) for 10800 s (180 min). After irradiation, the solvent was removed. The yield of product **2** was determined as 15% by crude ^{1}H NMR base on a 1,3,5-trimethoxybenzene standard. The quantum yield was determined using eq (3). Essentially all incident light (f > 0.999, vide infra) is absorbed by the 4CzIPN at the reaction conditions described above. Φ = 0.59.

$$\Phi = \frac{\text{mol product}}{\text{flux} \cdot\ t \cdot\ f} \qquad (3)$$

$$\Phi = \frac{3.0 \times 10^{-5}\ mol}{4.705 \times 10^{-9}\ \text{einstein s} \cdot 10800\ \text{s} \cdot 1.00} = 0.59$$

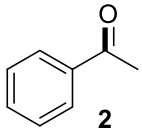
11) Proposed mechanism for the photocatalytic oxidation of amines to carbonyls

The oxidation of amines to carbonyls by this protocol was proposed to undergo a similar OPRC process on the basis of the experimental results and our previous studies on photocatalytic acceptorless alcohols oxidation (Scheme S1).[S3]

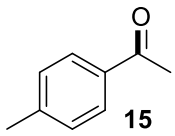


Scheme S1. Proposed mechanism for the photocatalytic oxidation of amine to carbonyl

V. Analytical Data of the Products

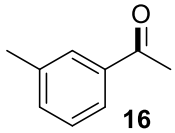


2; A known compound and the characterization data are in accordance with the literature[S4]. Following the typical procedure **II**, ethylbenzene (24 μL, 0.2 mmol), H_2O (72 μL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **2** (19 mg) in 80% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 – 7.78 (m, 2H), 7.53 – 7.45 (m, 1H), 7.39 (dd, *J* = 10.4, 4.7 Hz, 2H), 2.54 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.2, 137.1, 133.1, 128.5, 128.3, 26.6 ppm.



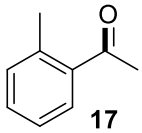
15; A known compound and the characterization data are in accordance with the literature[S4].

Following the typical procedure **II**, 4-ethyltoluene (28 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **15** (16 mg) in 60% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.22 – 7.14 (m, 2H), 2.51 (s, 3H), 2.34 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.8, 143.8, 134.7, 129.2, 128.4, 26.5, 21.6 ppm.



16

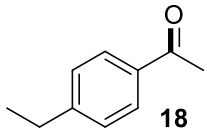
16; A known compound and the characterization data are in accordance with the literature[S5]. Following the typical procedure **II**, 3-ethyltoluene (28 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **16** (16 mg) in 60% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 10.5 Hz, 2H), 7.43 – 7.28 (m, 2H), 2.59 (s, 3H), 2.42 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.4, 138.3, 137.1, 133.8, 128.8, 128.4, 125.6, 26.7, 21.3 ppm.



17

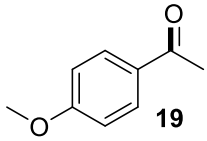
17; A known compound and the characterization data are in accordance with the literature[S5]. Following the typical procedure **II**, 2-ethyltoluene (27 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **17** (14 mg) in 52% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 – 7.58 (m, 1H), 7.31 (td, *J* = 7.5, 1.2 Hz, 1H), 7.19 (dd, *J* = 10.8,

8.2 Hz, 2H), 2.51 (d, *J* = 2.9 Hz, 3H), 2.46 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 201.7, 138.4, 137.6, 132.0, 131.5, 129.3, 125.7, 29.5, 21.6 ppm.



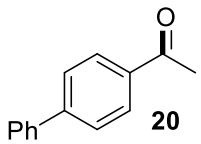
18

18; A known compound and the characterization data are in accordance with the literature[S6]. Following the typical procedure **II**, 1,4-diethylbenzene (31 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **18** (19 mg) in 64% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 2.61 (q, *J* = 7.6 Hz, 2H), 2.49 (s, 3H), 1.17 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.7, 149.9, 134.8, 128.4, 127.9, 28.8, 26.4, 15.1 ppm.



19

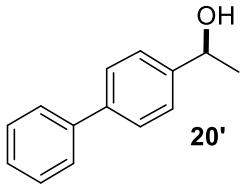
19; A known compound and the characterization data are in accordance with the literature[S7]. Following the typical procedure **II**, 4-ethylanisole (28 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **19** (20 mg) in 67% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (dd, *J* = 8.7, 1.5 Hz, 2H), 7.05 – 6.82 (m, 2H), 3.87 (d, *J* = 1.6 Hz, 3H), 2.56 (d, *J* = 1.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 196.6, 163.3, 130.4, 130.2, 113.5, 55.3, 26.2 ppm.



20

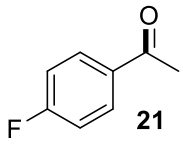
20; A known compound and the characterization data are in accordance with the literature[S8]. Following the typical procedure **II**, 4-ethylbiphenyl (37 µL, 0.2 mmol), H_2O (72 µL, 4 mmol),

photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 μL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **20** (32 mg) in 82% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 – 7.81 (m, 2H), 7.63 – 7.46 (m, 4H), 7.42 – 7.25 (m, 3H), 2.52 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.6, 145.6, 139.7, 135.7, 128.9, 128.8, 128.2, 127.2, 127.1, 26.6 ppm.



20'

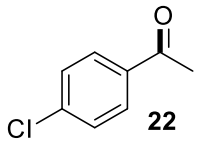
20′; A known compound and the characterization data are in accordance with the literature[S9]. Following the typical procedure **II**, 4-ethylbiphenyl (37 μL, 0.2 mmol), H_2O (72 μL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 μL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 5 h to give the product **20′** (6 mg) in 15 % yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 15:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.45 (m, 4H), 7.43 – 7.31 (m, 4H), 7.28 (ddd, *J* = 7.4, 3.9, 1.2 Hz, 1H), 4.89 (q, *J* = 6.5 Hz, 1H), 1.70 (s, 1H), 1.47 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.8, 140.8, 140.5, 128.8, 127.3, 127.1, 125.8, 70.2, 25.2 ppm.



21

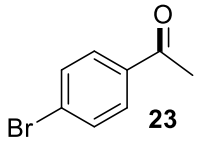
21; A known compound and the characterization data are in accordance with the literature[S10]. Following the typical procedure **II**, 1-ethyl-4-fluorobenzene (25 μL, 0.2 mmol), H_2O (72 μL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **21** (15 mg) in 54% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 – 7.81 (m, 2H), 7.06 (t, *J* = 8.6 Hz, 2H), 2.52 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.5, 167.0, 164.5, 133.6, 133.5, 131.0, 130.9, 115.7, 115.5, 26.5 ppm.



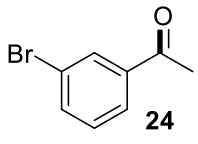
22

22; A known compound and the characterization data are in accordance with the literature[S10]. Following the typical procedure **II**, 1-chloro-4-ethylbenzene (27 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **22** (19 mg) in 63% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 2.47 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 196.5, 139.3, 135.2, 129.5, 128.7, 26.3 ppm.



23

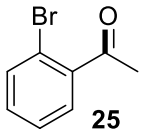
23; A known compound and the characterization data are in accordance with the literature[S10]. Following the typical procedure **II**, 4-bromoethylbenzene (28 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **23** (32 mg) in 80% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 – 7.77 (m, 2H), 7.65 – 7.56 (m, 2H), 2.59 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.0, 135.7, 131.8, 129.8, 128.3, 26.5 ppm.



24

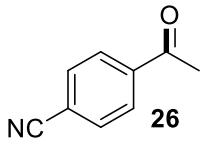
24; A known compound and the characterization data are in accordance with the literature[S11]. Following the typical procedure **II**, 1-bromo-3-ethylbenzene (27 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **24** (31 mg) in 78%

yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (t, *J* = 1.7 Hz, 1H), 7.94 – 7.83 (m, 1H), 7.69 (ddd, *J* = 7.9, 1.9, 1.0 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 2.60 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 196.6, 138.8, 135.9, 131.4, 130.2, 126.8, 122.9, 26.6 ppm.



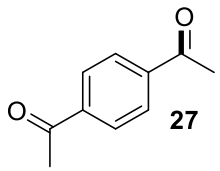
25

25; A known compound and the characterization data are in accordance with the literature[S11]. Following the typical procedure **II**, 2-bromoethylbenzene (28 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **25** (24 mg) in 60% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.9 Hz, 1H), 7.39 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.26 – 7.18 (m, 1H), 2.56 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 201.4, 141.5, 133.8, 131.8, 128.9, 127.4, 118.9, 30.3 ppm.



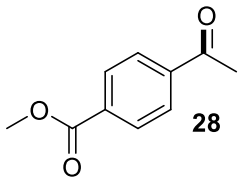
26

26; A known compound and the characterization data are in accordance with the literature[S6]. Following the typical procedure **II**, 4-ethylbenzonitrile (27 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **26** (15 mg) in 51% yield as a yellow powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 – 7.90 (m, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 2.58 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 196.5, 139.9, 132.5, 128.7, 117.9, 116.4, 26.7 ppm.



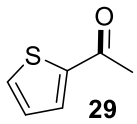
27

27; A known compound and the characterization data are in accordance with the literature[S12]. Following the typical procedure **II**, 4′-ethylacetophenone (30 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **27** (25 mg) in 77% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (s, 4H), 2.65 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.4, 140.1, 128.5, 26.9 ppm.



28

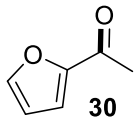
28; A known compound and the characterization data are in accordance with the literature[S12]. Following the typical procedure **II**, methyl 4-ethylbenzoate (32 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **28** (20 mg) in 56% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 – 8.09 (m, 2H), 8.04 – 7.96 (m, 2H), 3.95 (s, 3H), 2.65 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.5, 166.2, 140.2, 133.8, 129.8, 128.2, 52.4, 26.8 ppm.



29

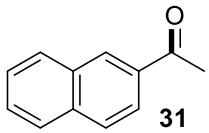
29; A known compound and the characterization data are in accordance with the literature[S10]. Following the typical procedure **II**, 2-ethylthiophene (23 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **29** (16 mg) in 63% yield

as a yellow oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 24.7 Hz, 2H), 7.06 (s, 1H), 2.50 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.7, 144.6, 133.7, 132.4, 128.1, 26.9 ppm.



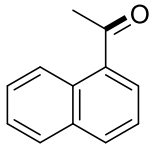
30

30; A known compound and the characterization data are in accordance with the literature[S13]. Following the typical procedure **II**, 2-ethylfuran (21 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **30** (14 mg) in 64% yield as a yellow oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.20 (dd, *J* = 3.6, 0.7 Hz, 1H), 6.55 (dd, *J* = 3.6, 1.7 Hz, 1H), 2.49 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 186.7, 152.7, 146.4, 117.2, 112.1, 25.9 ppm.



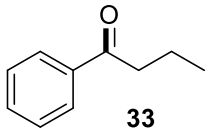
31

31; A known compound and the characterization data are in accordance with the literature[S5]. Following the typical procedure **II**, 2-ethylnaphthalene (31 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **31** (26 mg) in 76% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 8.01 – 7.71 (m, 4H), 7.61 – 7.39 (m, 2H), 2.66 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.1, 135.6, 134.5, 132.5, 130.2, 129.5, 128.5, 128.4, 127.8, 126.8, 123.9, 26.7 ppm.



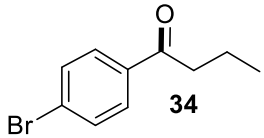
32

32; A known compound and the characterization data are in accordance with the literature[S5]. Following the typical procedure **II**, 1-ethylnaphthalene (31 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **32** (26 mg) in 75% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 8.7 Hz, 1H), 7.92 (ddd, *J* = 25.7, 23.7, 8.3 Hz, 3H), 7.64 – 7.40 (m, 3H), 2.73 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.9, 135.4, 134.3, 132.4, 130.1, 129.4, 128.3, 128.2, 127.6, 126.6, 123.7, 26.5 ppm.



33

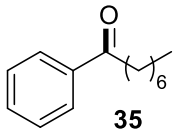
33; A known compound and the characterization data are in accordance with the literature[S5]. Following the typical procedure **II**, butylbenzene (31 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **33** (18 mg) in 61% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 – 7.85 (m, 2H), 7.62 – 7.50 (m, 1H), 7.48 – 7.36 (m, 2H), 3.04 – 2.85 (m, 2H), 1.85 – 1.68 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.4, 137.0, 132.8, 128.5, 128.0, 40.5, 17.7, 13.8 ppm.



34

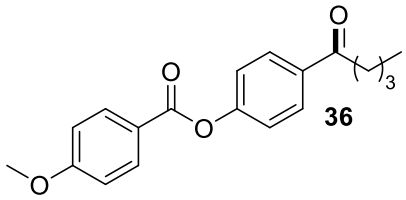
34; A known compound and the characterization data are in accordance with the literature[S14]. Following the typical procedure **II**, 1-bromo-4-n-butylbenzene (35 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL,

0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **34** (25 mg) in 56% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, *J* = 6.2, 4.6 Hz, 2H), 7.52 (dd, *J* = 6.2, 4.5 Hz, 2H), 2.83 (t, *J* = 7.3 Hz, 2H), 1.78 – 1.58 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.3, 135.7, 131.8, 129.5, 127.9, 40.4, 17.6, 13.8 ppm.



35

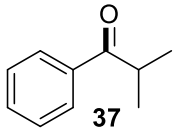
35; A known compound and the characterization data are in accordance with the literature[S15]. Following the typical procedure **II**, octylbenzene (44 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **35** (18 mg) in 45% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 – 7.88 (m, 2H), 7.54 (ddd, *J* = 6.7, 3.8, 1.2 Hz, 1H), 7.45 (dd, *J* = 10.3, 4.7 Hz, 2H), 3.06 – 2.83 (m, 2H), 1.82 – 1.61 (m, 2H), 1.43 – 1.13 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.5, 137.1, 132.8, 128.5, 128.0, 38.6, 31.7, 29.3, 29.1, 24.4, 22.6, 14.0 ppm.



36

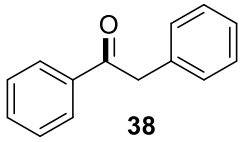
36; Following the typical procedure **II**, 4-pentylphenyl 4-methoxybenzoate (60 mg, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **36** (28 mg) in 45% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. Mp: 97 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.9 Hz, 2H), 8.04 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 8.9 Hz, 2H), 3.91 (s, 3H), 2.98 (t, *J* = 7.4 Hz, 2H), 1.74 (dt, *J* = 15.1, 7.5 Hz, 2H), 1.43 (dt, *J* = 15.0, 7.4 Hz, 2H), 0.96

(t, J = 7.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.4, 164.4, 164.1, 154.6, 134.5, 132.4, 129.7, 121.9, 121.3, 113.9, 55.5, 38.3, 26.5, 22.5, 13.9 ppm. HRMS m/z: calcd for $C_{19}H_{20}NO_4$ [M + Na]$^+$: 335.1254; Found: 335.1261.



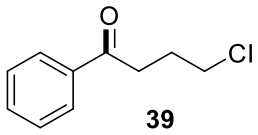
37

37; A known compound and the characterization data are in accordance with the literature[S15]. Following the typical procedure **II**, isobutylbenzene (31 μL, 0.2 mmol), H_2O (72 μL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **37** (19 mg) in 63% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 – 7.79 (m, 2H), 7.55 – 7.30 (m, 3H), 3.55 – 3.42 (m, 1H), 1.15 (d, J = 6.8 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 204.5, 136.2, 132.8, 128.6, 128.3, 35.3, 19.1 ppm.



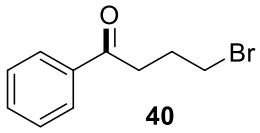
38

38; A known compound and the characterization data are in accordance with the literature[S10]. Following the typical procedure **II**, 1,2-diphenylethane (36 mg, 0.2 mmol), H_2O (72 μL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **38** (20 mg) in 50% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 – 7.88 (m, 2H), 7.54 – 7.44 (m, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.29 – 7.14 (m, 5H), 4.22 (s, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.6, 136.6, 134.5, 133.2, 129.5, 128.7, 128.63, 128.6, 126.9, 45.5 ppm.



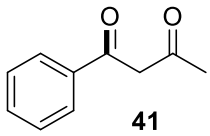
39

39; A known compound and the characterization data are in accordance with the literature[S16]. Following the typical procedure **II**, 1-chloro-4-phenylbutane (33 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **39** (27 mg) in 73% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.57 – 7.47 (m, 1H), 7.40 (dd, *J* = 10.5, 4.7 Hz, 2H), 3.62 (t, *J* = 6.2 Hz, 2H), 3.12 (t, *J* = 7.0 Hz, 2H), 2.26 – 2.05 (m, 2H) ppm;^{13}C NMR (101 MHz, $CDCl_3$): δ 199.0, 136.7, 133.2, 128.6, 128.0, 44.7, 35.3, 26.7 ppm.



40

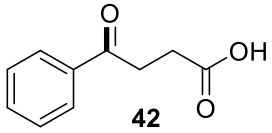
40; A known compound and the characterization data are in accordance with the literature[S17]. Following the typical procedure **II**, 1-bromo-4-phenylbutane (35 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **40** (32 mg) in 70% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 – 7.84 (m, 2H), 7.46 (dt, *J* = 15.2, 7.4 Hz, 3H), 3.49 (t, *J* = 6.3 Hz, 2H), 3.12 (t, *J* = 6.9 Hz, 2H), 2.25 (p, *J* = 6.6 Hz, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.8, 136.7, 133.2, 128.6, 128.0, 36.5, 33.6, 26.8 ppm.



41

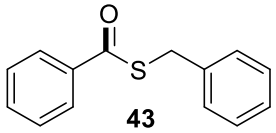
41; A known compound and the characterization data are in accordance with the literature[S18]. Following the typical procedure **II**, benzylacetone (30 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **41** (7 mg) in 23% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H

NMR (400 MHz, $CDCl_3$): δ 16.09 (s, 1H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.48 – 7.30 (m, 3H), 6.09 (s, 1H), 2.11 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 193.8, 183.3, 134.9, 132.3, 128.6, 127.0, 96.7, 25.9 ppm.



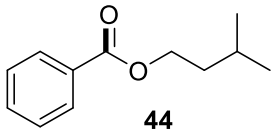
42

42; A known compound and the characterization data are in accordance with the literature[S19]. Following the typical procedure **II**, 1-bromo-4-phenylbutane (33 mg, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **42** (19 mg) in 52% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (40:1 ~ 10:1) to give the product. ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 – 7.90 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 3.32 (t, *J* = 6.5 Hz, 2H), 2.82 (t, *J* = 6.5 Hz, 2H) ppm;^{13}C NMR (101 MHz, $CDCl_3$): δ 197.8, 179.0, 136.3, 133.3, 128.6, 128.0, 33.1, 28.0 ppm.



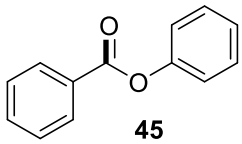
43

43; A known compound and the characterization data are in accordance with the literature[S20]. Following the typical procedure **II**, dibenzyl sulfide (43 mg, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **43** (23 mg) in 51% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 – 7.77 (m, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.42 – 7.12 (m, 7H), 4.25 (s, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.3, 137.4, 136.8, 133.4, 129.0, 128.7, 128.6, 127.3, 127.3, 33.3 ppm.



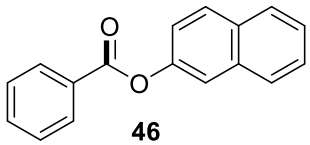
44

44; A known compound and the characterization data are in accordance with the literature[S21]. Following the typical procedure **II**, ((isopentyloxy)methyl) benzene (39 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **44** (25 mg) in 65% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 – 7.90 (m, 2H), 7.52 – 7.44 (m, 1H), 7.41 – 7.32 (m, 2H), 4.28 (t, *J* = 6.8 Hz, 2H), 1.80 – 1.67 (m, 1H), 1.60 (q, *J* = 6.8 Hz, 2H), 0.91 (d, *J* = 6.6 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.7, 132.8, 130.5, 129.5, 128.3, 63.6, 37.4, 25.2, 22.5 ppm.



45

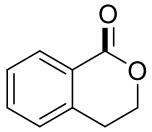
45; A known compound and the characterization data are in accordance with the literature[S22]. Following the typical procedure **II**, benzyl phenyl ether (37 mg, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **45** (21 mg) in 52% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.70 – 7.59 (m, 1H), 7.55 – 7.35 (m, 4H), 7.30 – 7.13 (m, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.2, 150.9, 133.6, 130.2, 129.6, 129.5, 128.6, 125.9, 121.7 ppm.



46

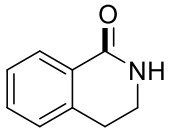
46; A known compound and the characterization data are in accordance with the literature[S22]. Following the typical procedure **II**, 1-(benzyloxy) naphthalene (47 mg, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **46** (24 mg) in 48% yield as a white powder. The crude product was purified by column chromatography isolation on

silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 – 8.08 (m, 2H), 7.76 (ddd, *J* = 15.4, 10.8, 8.0 Hz, 3H), 7.63 – 7.49 (m, 2H), 7.46 – 7.35 (m, 4H), 7.26 (dt, *J* = 13.4, 6.7 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.3, 148.6, 133.8, 133.6, 131.5, 130.2, 129.5, 129.4, 128.6, 127.8, 127.6, 126.5, 125.7, 121.2, 118.7 ppm.



47

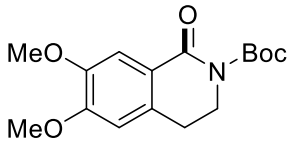
47; A known compound and the characterization data are in accordance with the literature[S23]. Following the typical procedure **II**, isochroman (25 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **47** (24 mg) in 81% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.54 (td, *J* = 7.5, 1.4 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.28 (s, 1H), 4.64 – 4.34 (m, 2H), 3.07 (t, *J* = 6.0 Hz, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.0, 139.5, 133.6, 130.2, 127.6, 127.2, 125.2, 67.2, 27.7 ppm.



48

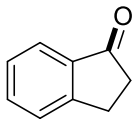
48; A known compound and the characterization data are in accordance with the literature[S24]. Following the typical procedure **II**, 1,2,3,4-tetrahydroisoquinoline (25 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **48** (9 mg) in 30% yield as a yellow powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (401 ~ 5:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.7 Hz, 1H), 7.45 (td, *J* = 7.4, 1.0 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 61.4 Hz, 1H), 3.58 (td, *J* = 6.7, 2.3 Hz, 2H),

3.01 (t, *J* = 6.6 Hz, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.5, 138.8, 132.1, 128.9, 127.9, 127.2, 127.1, 40.2, 28.3 ppm.



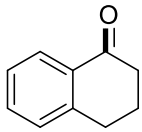
49

49; A known compound and the characterization data are in accordance with the literature [S24]. Following the typical procedure **II**, tert-butyl 6,7-dimethoxy-3,4-dihydroisoquinoline-2(1 H)-carboxylate (59 mg, 0.2 mmol), H_2O (72 μL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 m g, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 μL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **49** (18 mg) in 30% yield as a white powde r. The crude product was purified by column chromatography isolation on silica gel via gr adient elution with hexane to hexane/ethyl acetate (40:1 ~ 5:1) to give the product. ^{1}H N MR (400 MHz, $CDCl_3$): δ 7.65 (s, 1H), 6.64 (s, 1H), 4.01 – 3.96 (m, 2H), 3.92 (d, *J* = 9.5 Hz, 6H), 2.94 (t, *J* = 6.2 Hz, 2H), 1.59 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.9, 153.5, 152.9, 148.2, 133.9, 121.7, 111.2, 109.1, 83.1, 56.1, 56.0, 44.7, 28.1ppm.



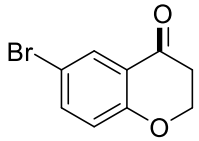
50

50; A known compound and the characterization data are in accordance with the literature[S10]. Following the typical procedure **II**, indan (24 μL, 0.2 mmol), H_2O (72 μL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **50** (17 mg) in 63% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.59 (td, *J* = 7.6, 1.1 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.42 – 7.32 (m, 1H), 3.20 – 3.09 (m, 2H), 2.74 – 2.63 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 206.7, 154.9, 136.8, 134.3, 127.0, 126.5, 123.3, 35.9, 25.5 ppm.



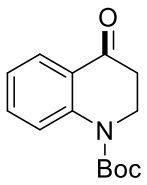
51

51; A known compound and the characterization data are in accordance with the literature[S4]. Following the typical procedure **II**, 1,2,3,4-tetrahydronaphthalene (27 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **51** (18 mg) in 63% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (t, *J* = 6.5 Hz, 1H), 7.48 (dd, *J* = 13.3, 7.1 Hz, 1H), 7.29 (dt, *J* = 24.3, 6.8 Hz, 2H), 2.98 (d, *J* = 5.7 Hz, 2H), 2.67 (dd, *J* = 12.8, 6.8 Hz, 2H), 2.15 (dd, *J* = 12.3, 6.1 Hz, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.4, 144.5, 133.4, 132.6, 128.7, 127.1, 126.6, 39.1, 29.7, 23.3 ppm.



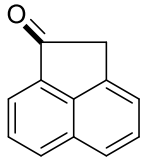
52

52; A known compound and the characterization data are in accordance with the literature[S26]. Following the typical procedure **II**, 6-bromochroman (29 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **52** (38 mg) in 83% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 2.5 Hz, 1H), 7.55 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 1H), 4.66 – 4.36 (m, 2H), 2.98 – 2.58 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.5, 160.7, 138.6, 129.6, 122.5, 120.0, 114.1, 67.1, 37.4 ppm.



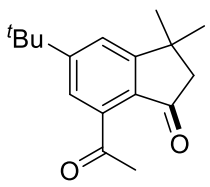
53

53; A known compound and the characterization data are in accordance with the literature[S27]. Following the typical procedure **II**, tert-butyl 3,4-dihydroquinoline-1(2H)-carboxylate (47 mg, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **53** (35 mg) in 71% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.50 (ddd, *J* = 8.7, 7.3, 1.7 Hz, 1H), 7.22 – 7.07 (m, 1H), 4.25 – 4.05 (m, 2H), 2.89 – 2.65 (m, 2H), 1.56 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 194.2, 152.7, 144.1, 133.9, 127.3, 124.9, 123.8, 123.7, 82.2, 44.3, 39.0, 28.3 ppm.



54

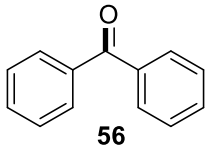
54; A known compound and the characterization data are in accordance with the literature[S28]. Following the typical procedure **II**, acenaphthene (31mg, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **54** (26 mg) in 78% yield as a yellow powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 7.0 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.65 (dd, *J* = 7.8, 7.3 Hz, 1H), 7.53 (dd, *J* = 8.3, 7.0 Hz, 1H), 7.40 (d, *J* = 6.8 Hz, 1H), 3.76 (s, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 203.0, 142.9, 135.0, 134.7, 131.5, 130.9, 128.4, 128.0, 123.9, 121.4, 121.0, 42.0 ppm.



55

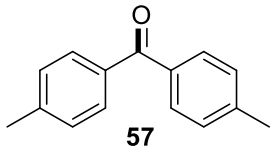
55; A known compound and the characterization data are in accordance with the literature[S29]. Following the typical procedure **II**, 4-acetyl-6-tert-butyl-1,1-dimethylindan (49 mg, 0.2 mmol),

H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **55** (30 mg) in 58% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.34 (s, 1H), 2.64 (d, *J* = 0.7 Hz, 3H), 2.62 (s, 2H), 1.44 (s, 6H), 1.37 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 204.7, 204.0, 164.5, 159.4, 139.1, 129.3, 123.2, 121.7, 53.2, 38.7, 35.7, 31.1, 30.9, 30.0 ppm.



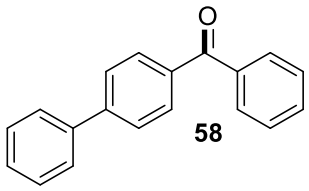
56

56; A known compound and the characterization data are in accordance with the literature[S4]. Following the typical procedure **II**, diphenylmethane (34 mg, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **56** (31 mg) in 85% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 – 7.71 (m, 4H), 7.64 – 7.55 (m, 2H), 7.53 – 7.42 (m, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 196.8, 137.5, 132.4, 130.1, 128.3 ppm.



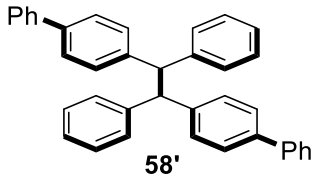
57

57; A known compound and the characterization data are in accordance with the literature[S11]. Following the typical procedure **II**, 4,4-dimethyldiphenylmethane (39 mg, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **57** (30 mg) in 71% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.2 Hz, 4H), 7.26 (d, *J* = 7.9 Hz, 4H), 2.42 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 196.2, 142.8, 135.1, 130.1, 128.8, 21.5 ppm.



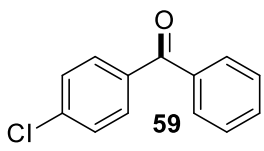
58

58; A known compound and the characterization data are in accordance with the literature[S30]. Following the typical procedure **II**, 4-benzylbiphenyl (49 mg, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **58** (31 mg) in 60% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 – 6.89 (m, 4H), 6.84 – 6.65 (m, 5H), 6.64 – 6.44 (m, 5H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 196.3, 145.2, 140.0, 137.7, 136.2, 132.4, 130.7, 130.0, 128.9, 128.3, 128.2, 127.3, 126.9 ppm.



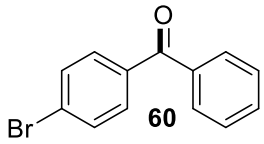
58'

58´; A known compound and the characterization data are in accordance with the literature[S31]. Following the typical procedure **II**, 4-benzylbiphenyl (49 mg, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **58´** (5 mg) in 9% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.38 (m, 4H), 7.32 – 7.27 (m, 7H), 7.23 – 7.11 (m, 11H), 7.06 (td, *J* = 7.5, 4.2 Hz, 4H), 6.96 (ddd, *J* = 7.4, 2.6, 1.3 Hz, 2H), 4.78 (s, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.4, 143.4, 142.6, 142.5, 140.8, 140.7, 138.6, 138.5, 128.9, 128.6, 128.5, 128.3, 128.2, 127.0, 126.9, 126.8, 126.0, 125.9, 56.0 ppm.



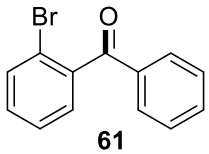
59

59; A known compound and the characterization data are in accordance with the literature[S32]. Following the typical procedure **II**, 4-chlorodiphenylmethane (37 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **59** (26 mg) in 60% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 – 7.71 (m, 4H), 7.67 – 7.39 (m, 5H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 195.5, 138.9, 137.2, 135.8, 132.6, 131.4, 129.9, 128.6, 128.4 ppm.



60

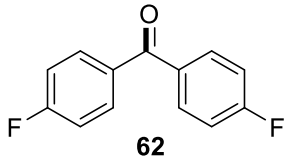
60; A known compound and the characterization data are in accordance with the literature[S33]. Following the typical procedure **II**, benzyl-4-bromobenzene (49 mg, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **60** (44 mg) in 85% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 – 7.73 (m, 2H), 7.70 – 7.65 (m, 2H), 7.64 – 7.56 (m, 3H), 7.52 – 7.42 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 195.5, 137.1, 136.2, 132.6, 131.6, 131.5, 129.9, 128.4, 127.4 ppm.



61

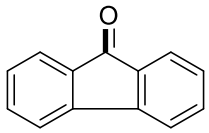
61; A known compound and the characterization data are in accordance with the literature[S34]. Following the typical procedure **II**, 2-bromodiphenylmethane (49 mg, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **61** (38 mg) in 73% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (100:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 – 7.76 (m, 2H), 7.60 (ddd, J = 19.2, 14.5, 10.1 Hz,

2H), 7.50 – 7.31 (m, 5H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 195.8, 140.6, 136.1, 133.7, 133.2, 131.1, 130.2, 129.0, 128.6, 127.2, 119.5 ppm.



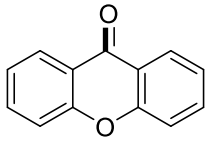
62

62; A known compound and the characterization data are in accordance with the literature[S11]. Following the typical procedure **II**, bis(4-fluorophenyl)methane (41 mg, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **62** (39 mg) in 89% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 – 7.77 (m, 4H), 7.24 – 7.09 (m, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 193.7, 166.6, 164.1, 133.7, 133.6, 132.5, 132.4, 115.6, 115.4 ppm.



63

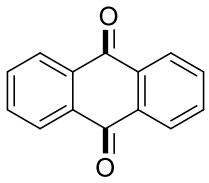
63; A known compound and the characterization data are in accordance with the literature[S35]. Following the typical procedure **II**, fluorene (33 mg, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **63** (30 mg) in 83% yield as a yellow powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.72 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 2H), 7.48 (dd, *J* = 8.4, 0.5 Hz, 2H), 7.43 – 7.30 (m, 2H) ppm;^{13}C NMR (101 MHz, $CDCl_3$): δ 177.2, 156.2, 134.8, 126.7, 123.9, 121.8, 118.0 ppm.



64

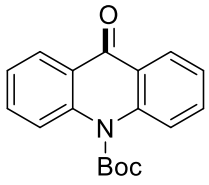
64; A known compound and the characterization data are in accordance with the literature[S10].

Following the typical procedure **II**, xanthene (36 mg, 0.2 mmol), H_2O (72 μL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **64** (32 mg) in 82% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.72 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 2H), 7.48 (dd, *J* = 8.4, 0.5 Hz, 2H), 7.43 – 7.30 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.2, 156.2, 134.8, 126.7, 123.9, 121.8, 118.0 ppm.



65

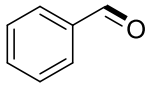
65; A known compound and the characterization data are in accordance with the literature[S29]. Following the typical procedure **II**, 9,10-dihydroanthracene (36 mg, 0.2 mmol), H_2O (72 μL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 16 h to give the product **65** (30 mg) in 72% yield as a yellow powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 – 8.14 (m, 4H), 7.94 – 7.61 (m, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 183.2, 134.1, 133.5, 127.2 ppm.



66

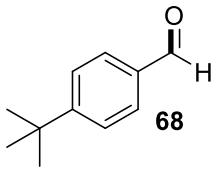
66; A known compound and the characterization data are in accordance with the literature[S36]. Following the typical procedure **II**, tert-butyl acridine-10(9H)-carboxylate (56 mg, 0.2 mmol), H_2O (72 μL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL, 0.02 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **66** (43 mg) in 73% yield as a yellow powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl

acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.68 (ddd, *J* = 8.6, 7.0, 1.6 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.29 (m, 2H), 1.69 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 178.6, 151.8, 139.5, 133.3, 127.2, 123.2, 122.9, 117.5, 86.3, 27.7 ppm.



67

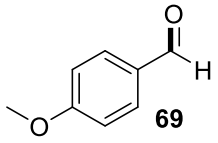
67; A known compound and the characterization data are in accordance with the literature[S4]. Following the typical procedure **II**, toluene (21 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **67** (7 mg) in 33% yield as a colorless oil or following the typical procedure **III**, benzylamine (22 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **67** (17 mg) in 80% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.88 – 7.77 (m, 2H), 7.63 – 7.53 (m, 1H), 7.51 – 7.41 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 192.4, 136.4, 134.5, 129.8, 129.0 ppm.



68

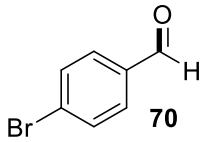
68; A known compound and the characterization data are in accordance with the literature[S35]. Following the typical procedure **II**, 4-tert-butyltoluene (35 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **68** (17 mg) in 52% yield as a colorless oil or following the typical procedure **III**, 4-tert-butylbenzylamine (35 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **68** (17 mg) in 52% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate

(80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.99 (s, 1H), 7.93 – 7.75 (m, 2H), 7.64 – 7.50 (m, 2H), 1.36 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 192.1, 158.5, 134.0, 129.7, 126.0, 35.4, 31.1 ppm.



69

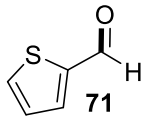
69; A known compound and the characterization data are in accordance with the literature[S8]. Following the typical procedure **II**, 4-methylanisole (25 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **69** (12 mg) in 44% yield as a colorless oil or following the typical procedure **III**, 4-methoxybenzylamine (26 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **69** (20 mg) in 73% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.76 (t, J = 5.5 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 3.81 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.8, 164.6, 131.9, 129.9, 114.3, 55.5 ppm.



70

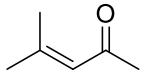
70; A known compound and the characterization data are in accordance with the literature[S8]. Following the typical procedure **II**, 4-bromotoluene (34 mg, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **70** (18 mg) in 48% yield as a white powder or following the typical procedure **III**, 4-bromobenzylamine (25 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **70** (30 mg) in 81% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl

acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.91 (s, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.1, 135.1, 132.4, 131.0, 129.8 ppm.



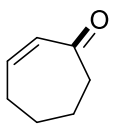
71

71; A known compound and the characterization data are in accordance with the literature[S35]. Following the typical procedure **II**, 2-methylthiophene (19 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **71** (10 mg) in 44% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.90 (t, *J* = 8.1 Hz, 1H), 7.83 – 7.60 (m, 2H), 7.15 (dd, *J* = 4.8, 3.8 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 183.0, 144.0, 136.3, 135.1, 128.3 ppm.



72

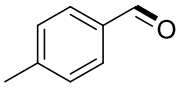
72; A known compound and the characterization data are in accordance with the literature[S37]. Following the typical procedure **II**, 2-methyl-2-pentene (24 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **72** (6 mg) in 31% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.09 (s, 1H), 2.12 (t, J = 24.3 Hz, 6H), 1.89 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.7, 155.1, 124.2, 31.6, 27.6, 20.6 ppm.



73

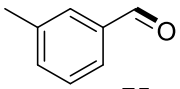
73; A known compound and the characterization data are in accordance with the literature[S38]. Following the typical procedure **II**, cycloheptene (23 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04

mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **73** (5 mg) in 23% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.52 (dt, *J* = 12.1, 5.5 Hz, 1H), 5.95 (dt, *J* = 12.1, 1.6 Hz, 1H), 2.55 (dd, *J* = 7.2, 5.1 Hz, 2H), 2.45 – 2.28 (m, 2H), 1.83 – 1.69 (m, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 204.5, 146.6, 132.5, 43.5, 30.2, 26.1, 21.7 ppm.



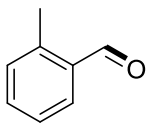
74

74; A known compound and the characterization data are in accordance with the literature[S39]. Following the typical procedure **III**, 4-methylbenzylamine (25 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **74** (17 mg) in 71% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.90 (s, 1H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 2.37 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 192.0, 145.6, 134.2, 129.9, 129.7, 21.9 ppm.



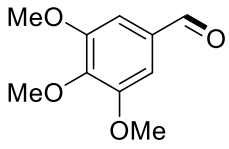
75

75; A known compound and the characterization data are in accordance with the literature[S39]. Following the typical procedure **III**, 3-methylbenzylamine (25 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **75** (20 mg) in 83% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.99 (s, 1H), 7.73 – 7.63 (m, 2H), 7.49 – 7.39 (m, 2H), 2.44 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 192.7, 138.9, 136.5, 135.3, 130.0, 128.9, 127.2, 21.2 ppm.



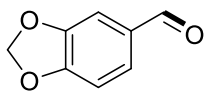
76

76; A known compound and the characterization data are in accordance with the literature[S4]. Following the typical procedure **III**, 2-methylbenzylamine (25 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **76** (18 mg) in 73% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.27 (d, *J* = 1.0 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 2.67 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 192.8, 140.6, 134.1, 133.6, 132.0, 131.7, 126.3, 19.6 ppm.



77

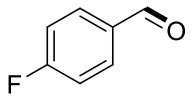
77; A known compound and the characterization data are in accordance with the literature[S39]. Following the typical procedure **III**, 3,4,5-trimethoxybenzylamine (34 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **77** (12 mg) in 30% yield as a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 7.06 (s, 2H), 3.91 – 3.80 (m, 9H) ppm;^{13}C NMR (101 MHz, $CDCl_3$): δ 191.1, 153.6, 143.5, 131.7, 106.6, 61.0, 56.2 ppm.



78

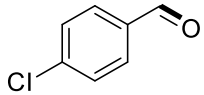
78; A known compound and the characterization data are in accordance with the literature[S4]. Following the typical procedure **III**, 3,4-methylenedioxybenzylamine (25 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **78** (23 mg) in 78% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.48 – 7.37 (m, 1H), 7.34 (s, 1H), 6.93 (dd, *J*

= 7.9, 0.9 Hz, 1H), 6.08 (s, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.3, 153.1, 148.7, 131.8, 128.7, 108.3, 106.9, 102.1 ppm.



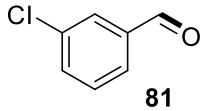
79

79; A known compound and the characterization data are in accordance with the literature[S39]. Following the typical procedure **III**, 4-fluorobenzylamine (23 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **79** (14 mg) in 56% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 8.00 – 7.81 (m, 2H), 7.22 (t, *J* = 8.5 Hz, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.5, 167.8, 165.3, 132.3, 132.2, 116.5, 116.3 ppm.



80

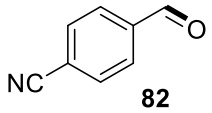
80; A known compound and the characterization data are in accordance with the literature[S8]. Following the typical procedure **III**, 4-chlorobenzylamine (24 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **80** (17 mg) in 60% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.92 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.9, 141.0, 134.7, 130.9, 129.5 ppm.



81

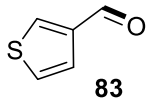
81; A known compound and the characterization data are in accordance with the literature[S35]. Following the typical procedure **III**, 3-chlorobenzylamine (24 µL, 0.2 mmol), H_2O (72 µL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 µL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **81** (21 mg) in 76%

yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.99 (s, 1H), 7.87 (t, *J* = 1.7 Hz, 1H), 7.77 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.61 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.9, 137.8, 135.5, 134.4, 130.4, 129.3, 128.0 ppm.



82

82; A known compound and the characterization data are in accordance with the literature[S4]. Following the typical procedure **III**, 4-(aminomethyl) benzonitrile (24 μL, 0.2 mmol), H_2O (72 μL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 μL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **82** (16 mg) in 60% yield a white powder. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.11 (s, 1H), 8.06 – 7.94 (m, 2H), 7.92 – 7.80 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.6, 138.7, 132.9, 129.9, 117.7, 117.6 ppm.



83

83; A known compound and the characterization data are in accordance with the literature[S35]. Following the typical procedure **III**, 3-thiophenemethylamine (20 μL, 0.2 mmol), H_2O (72 μL, 4 mmol), photocatalyst **3** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (5.2 μL, 0.04 mmol) in CH_3CN (1.5 mL) were employed for 24 h to give the product **83** (19 mg) in 83% yield as a colorless oil. The crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane/ethyl acetate (80:1 ~ 40:1) to give the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.94 (s, 1H), 8.33 – 7.94 (m, 1H), 7.55 (d, *J* = 5.1 Hz, 1H), 7.48 – 7.32 (m, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 184.9, 143.0, 136.7, 127.4, 125.3 ppm.

VI. References

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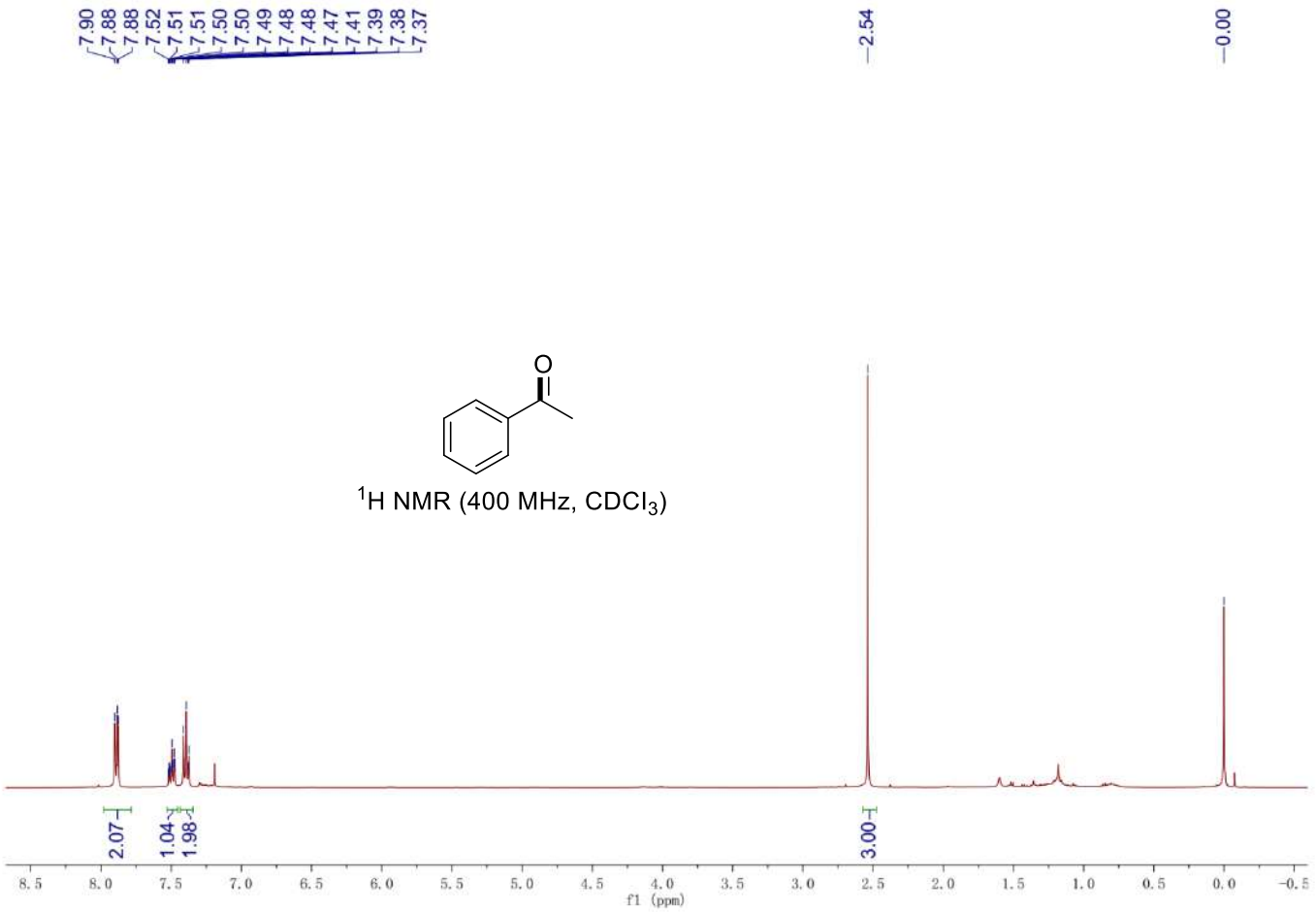
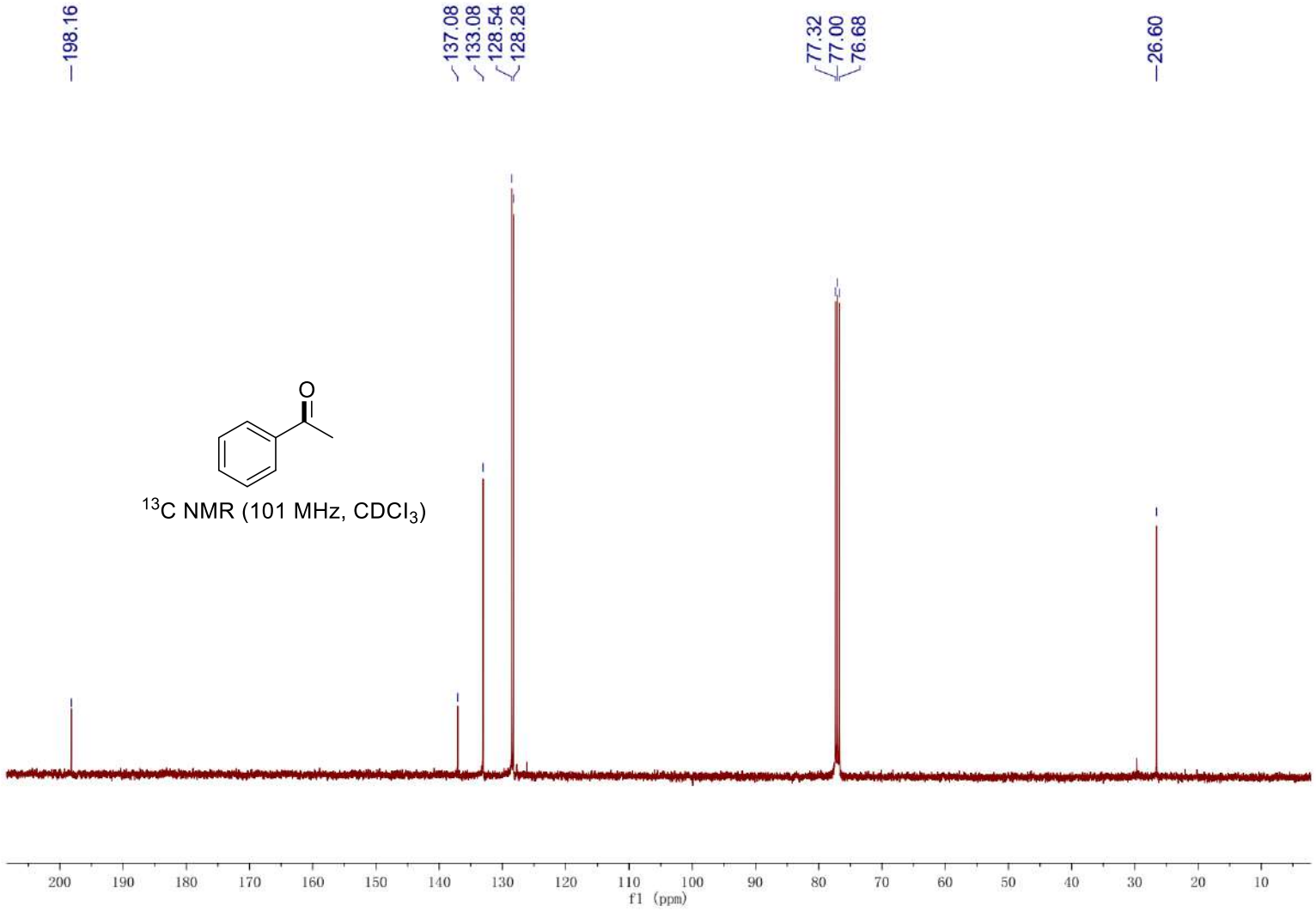
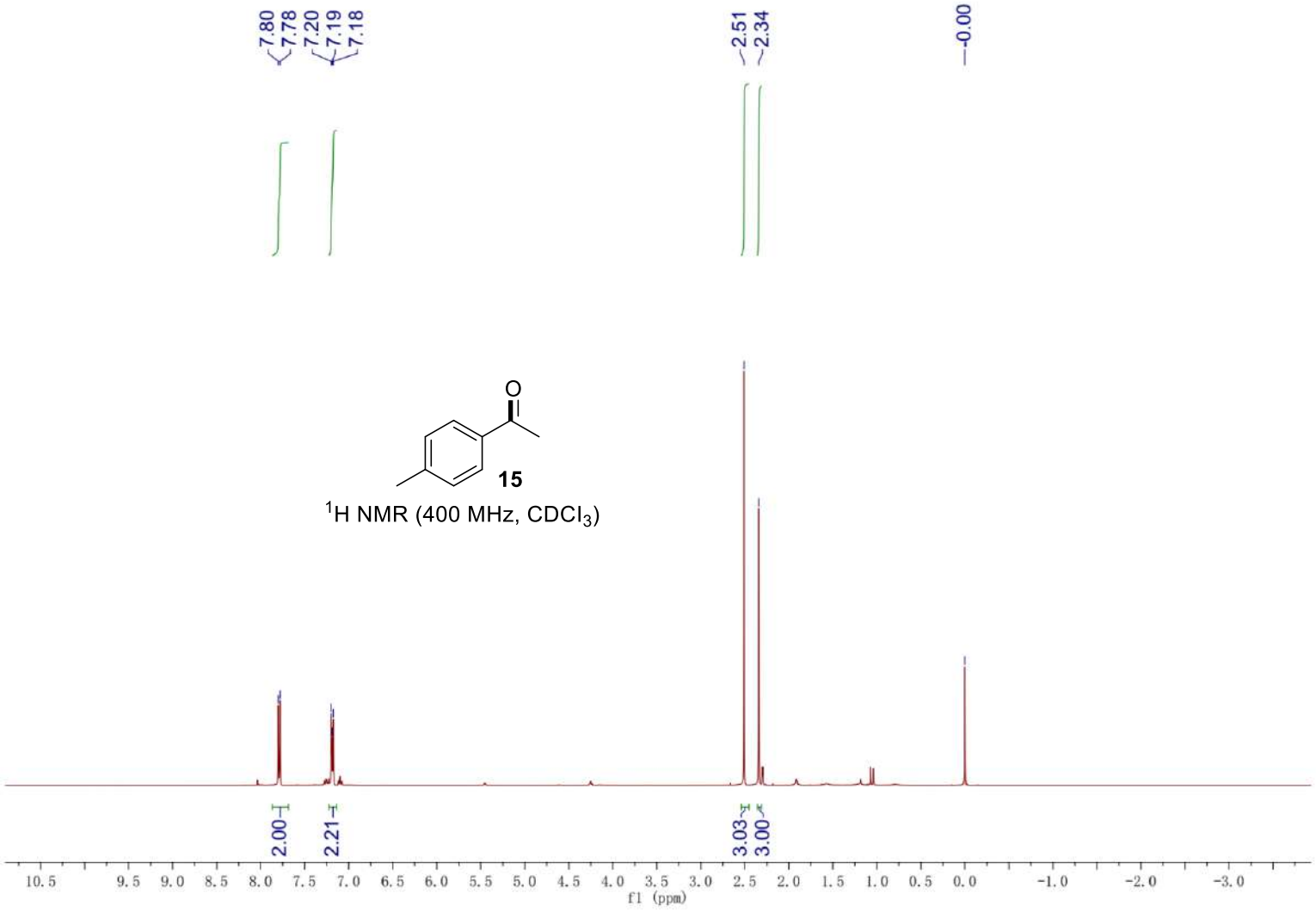
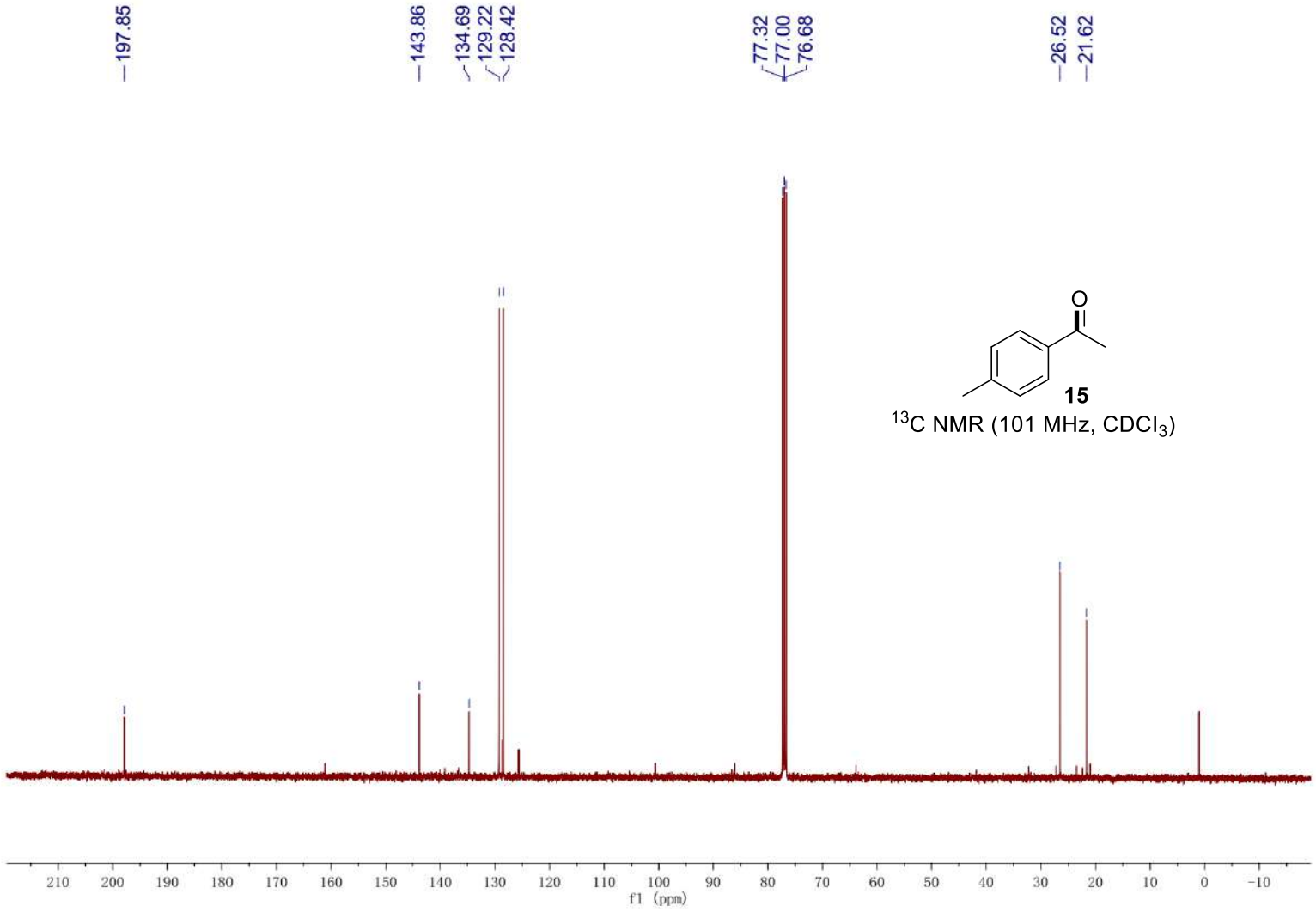
VII. ^{1}H, ^{13}C NMR Spectra of Products

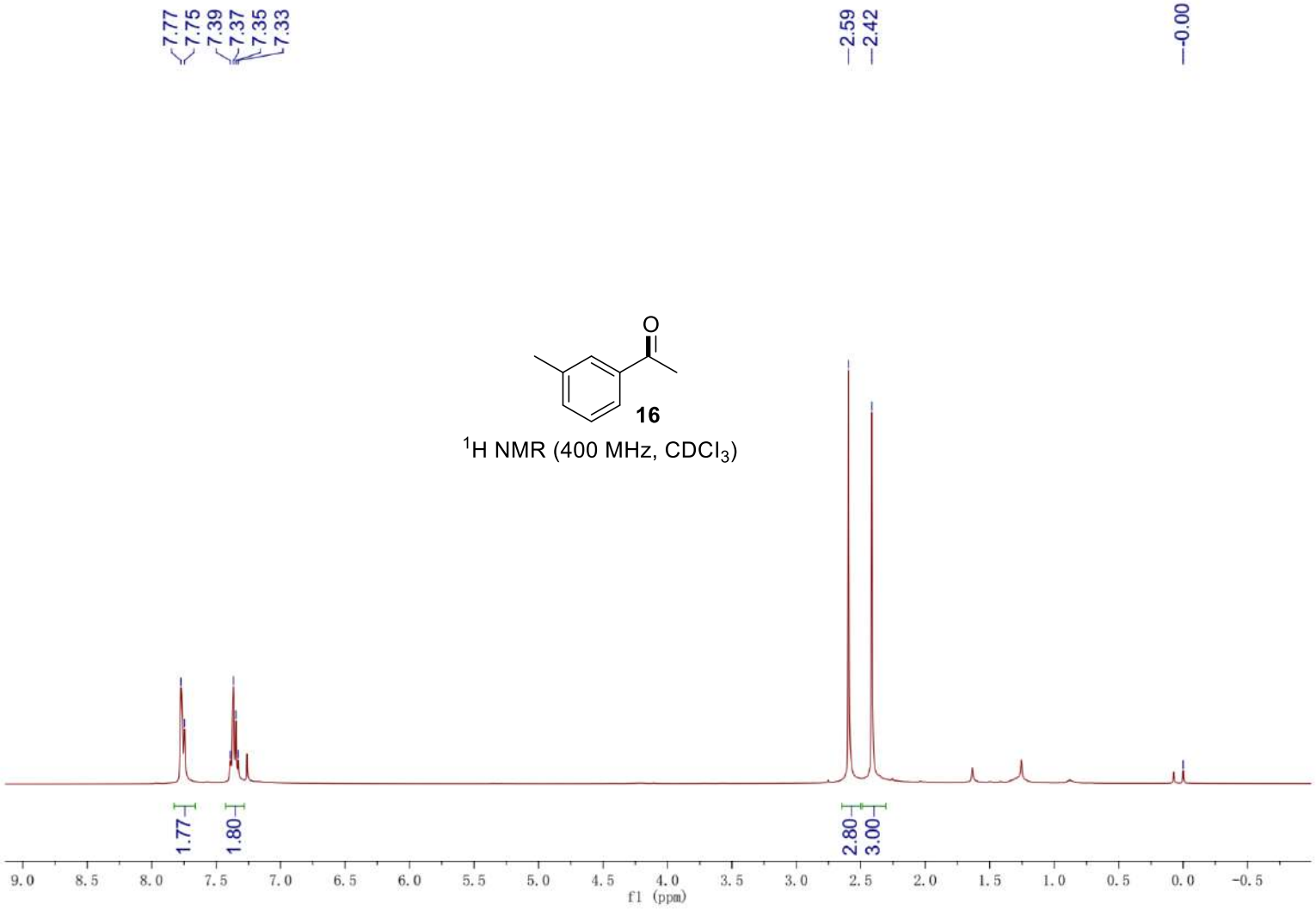


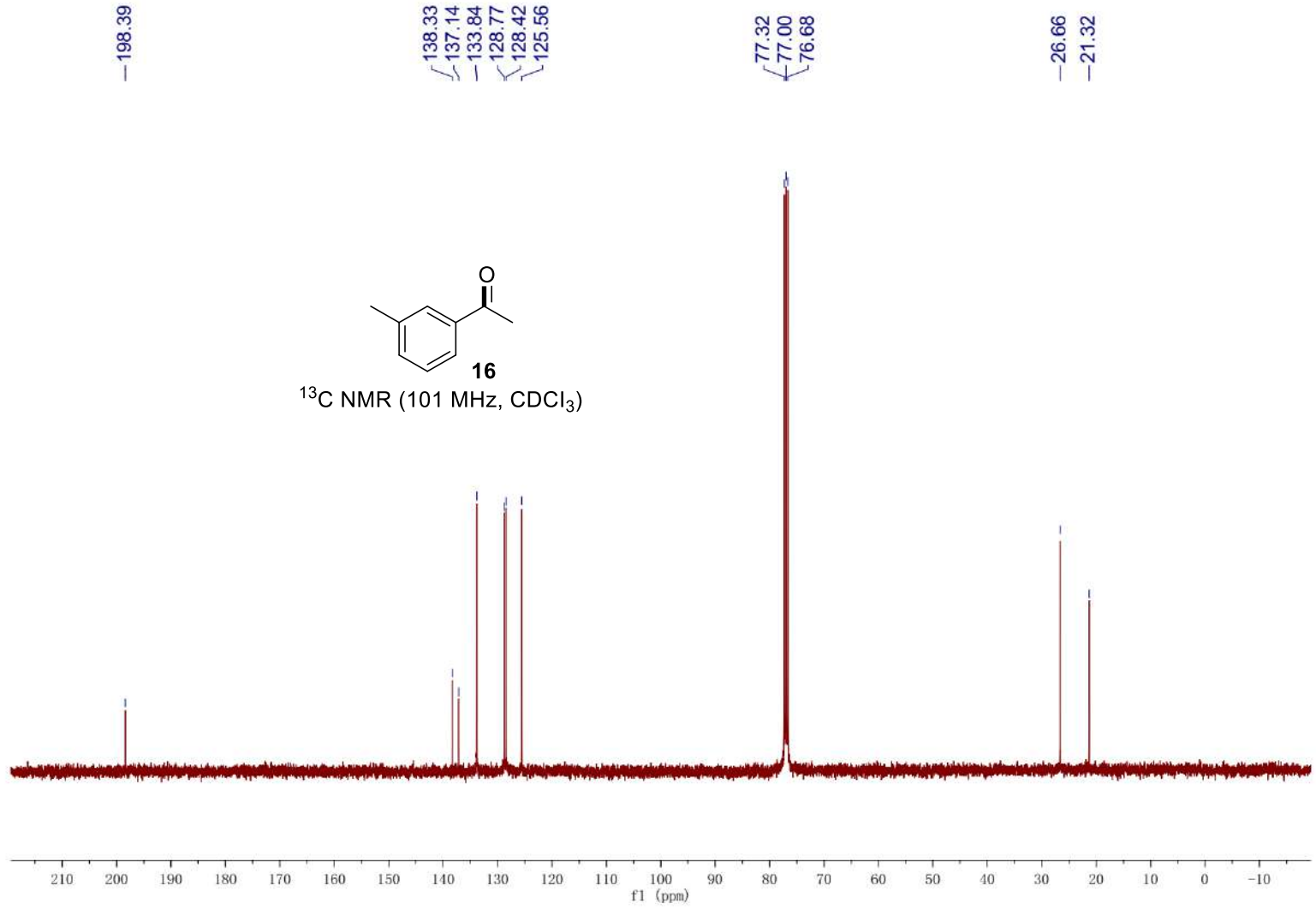

198.16
137.08
133.08
128.54
128.28
77.32
77.00
76.68
26.60
O
^{13}C NMR (101 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

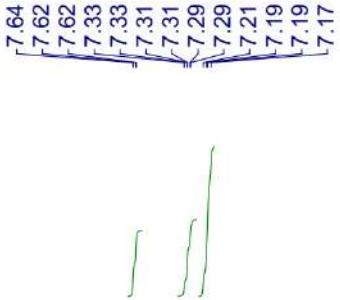


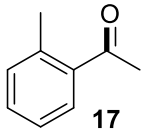
^{1}H NMR (400 MHz, $CDCl_3$)


197.85
143.86
134.69
129.22
128.42
77.32
77.00
76.68
26.52
21.62
O
15
13C NMR (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)


7.77
7.75
7.39
7.37
7.35
7.33
2.59
2.42
0.00
O
16
1H NMR (400 MHz, CDCl3)
1.77
1.80
2.80
3.00
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 -0.5
f1 (ppm)

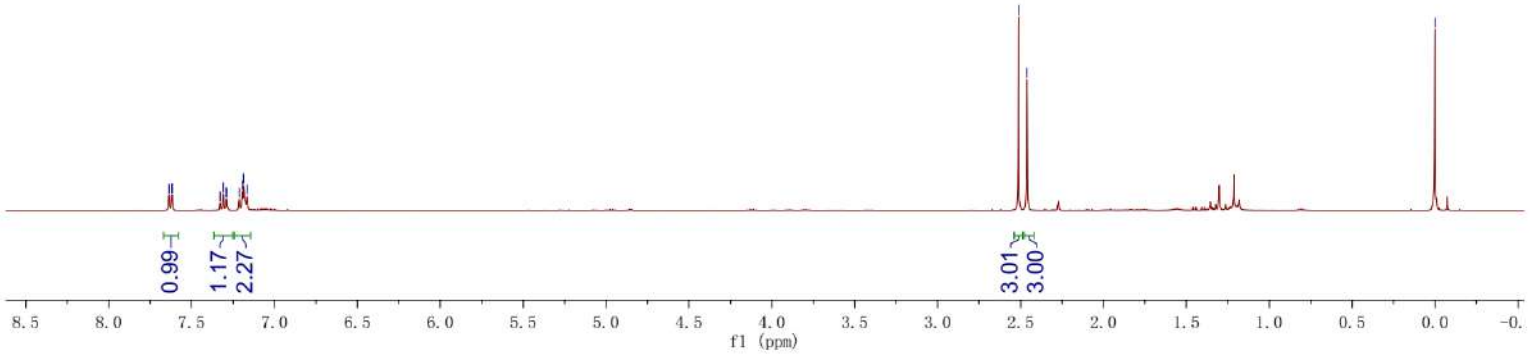

198.39
138.33
137.14
133.84
128.77
128.42
125.56
77.32
77.00
76.68
26.66
21.32
O
16
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

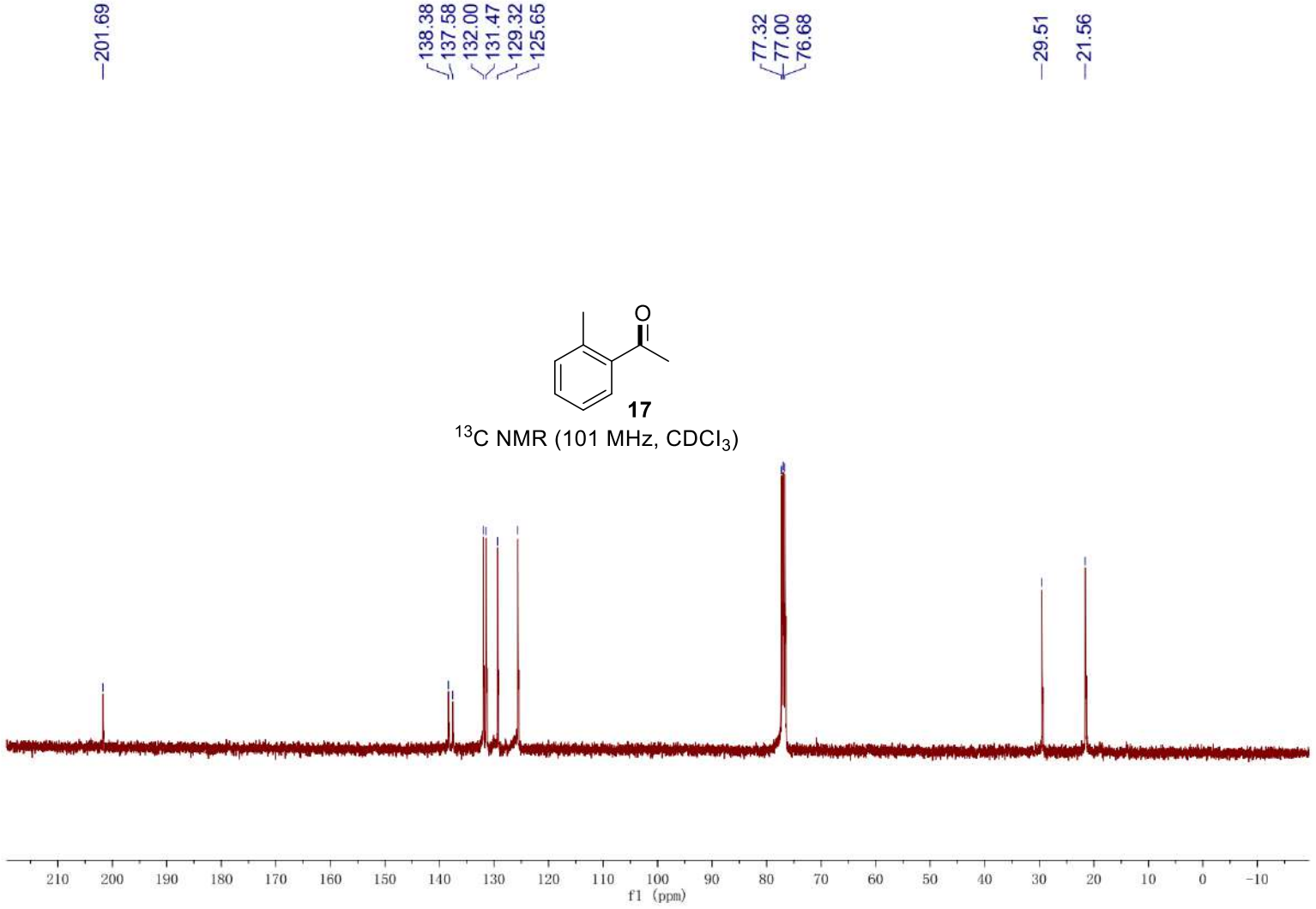


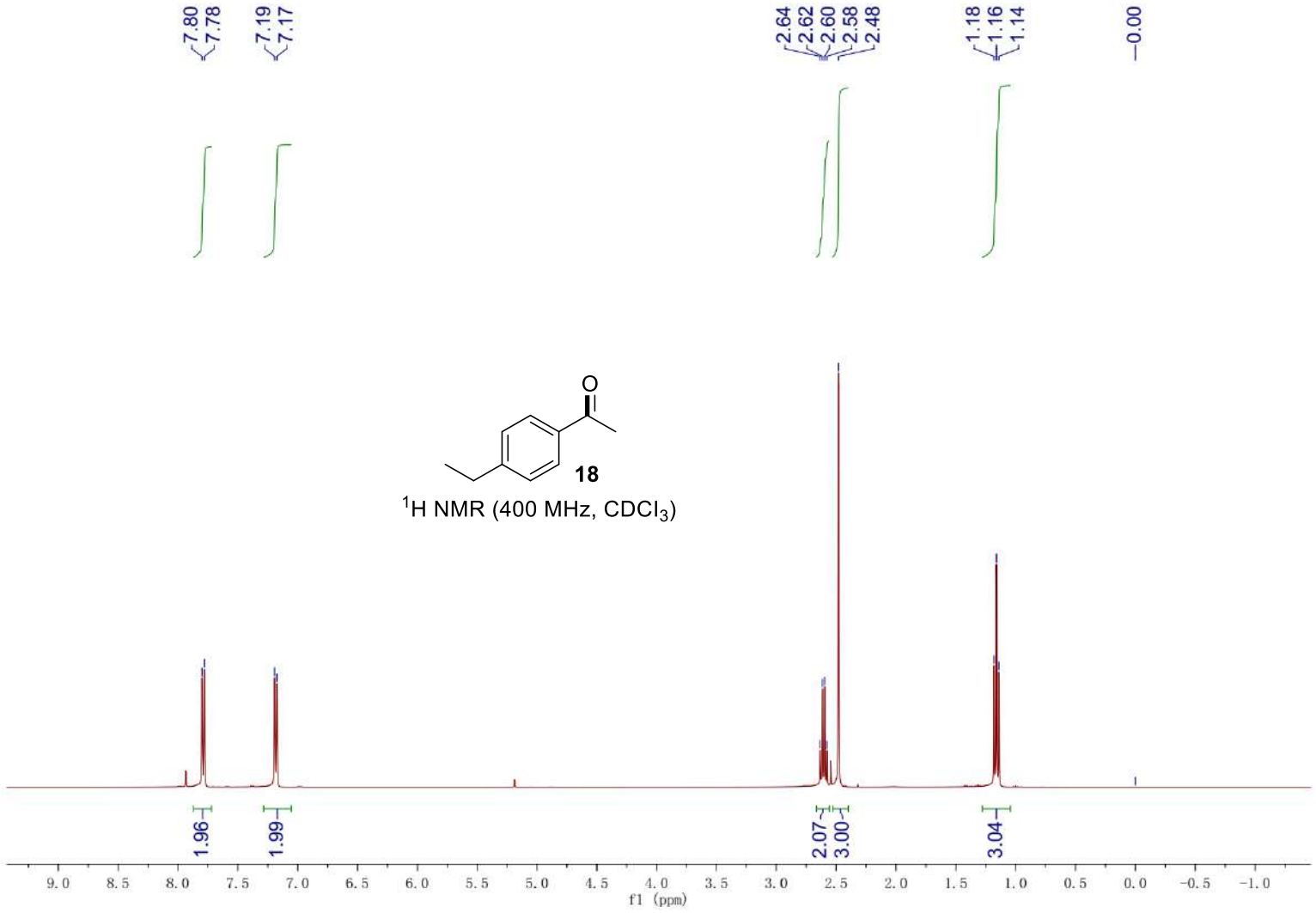


17

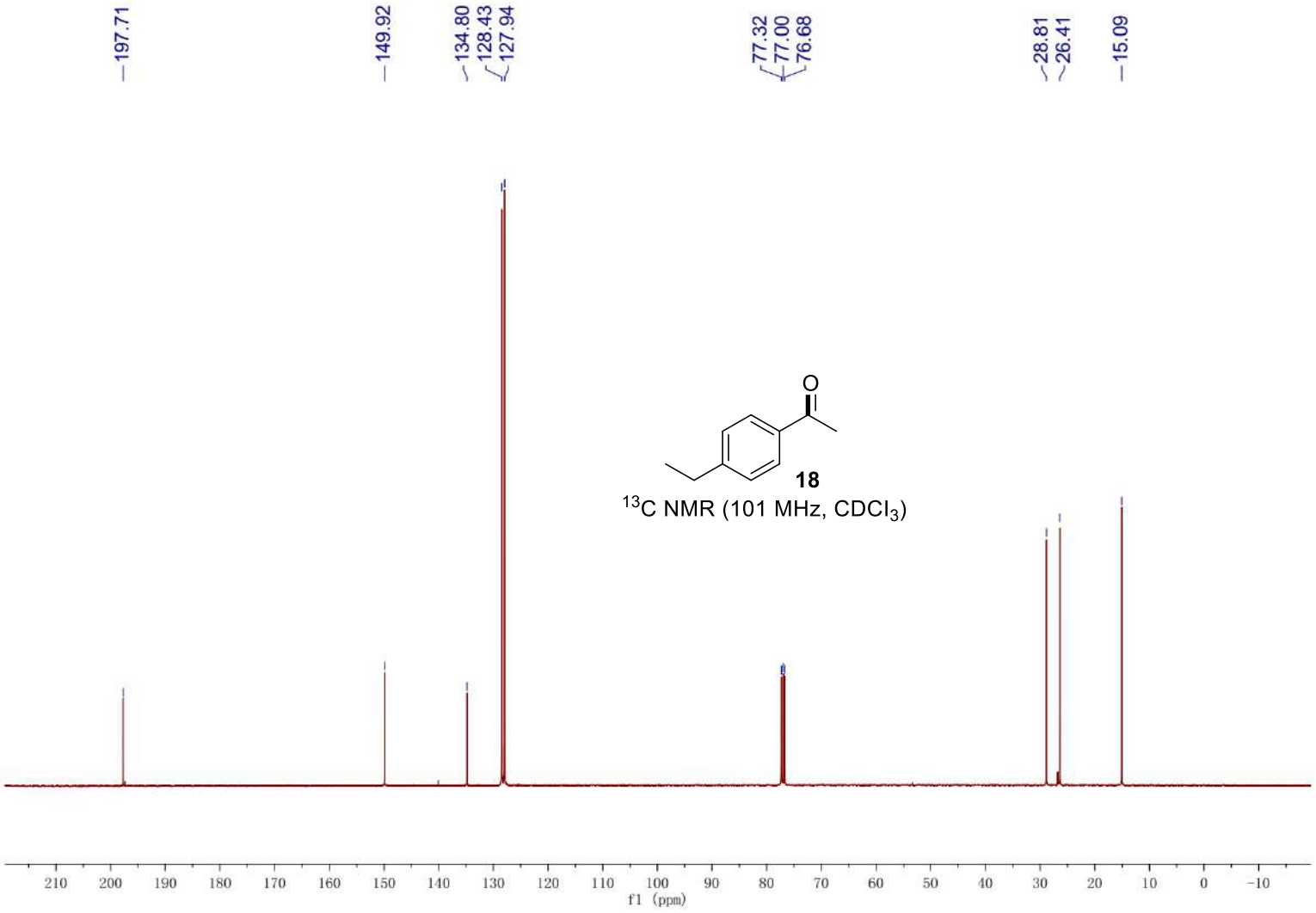
^{1}H NMR (400 MHz, $CDCl_3$)

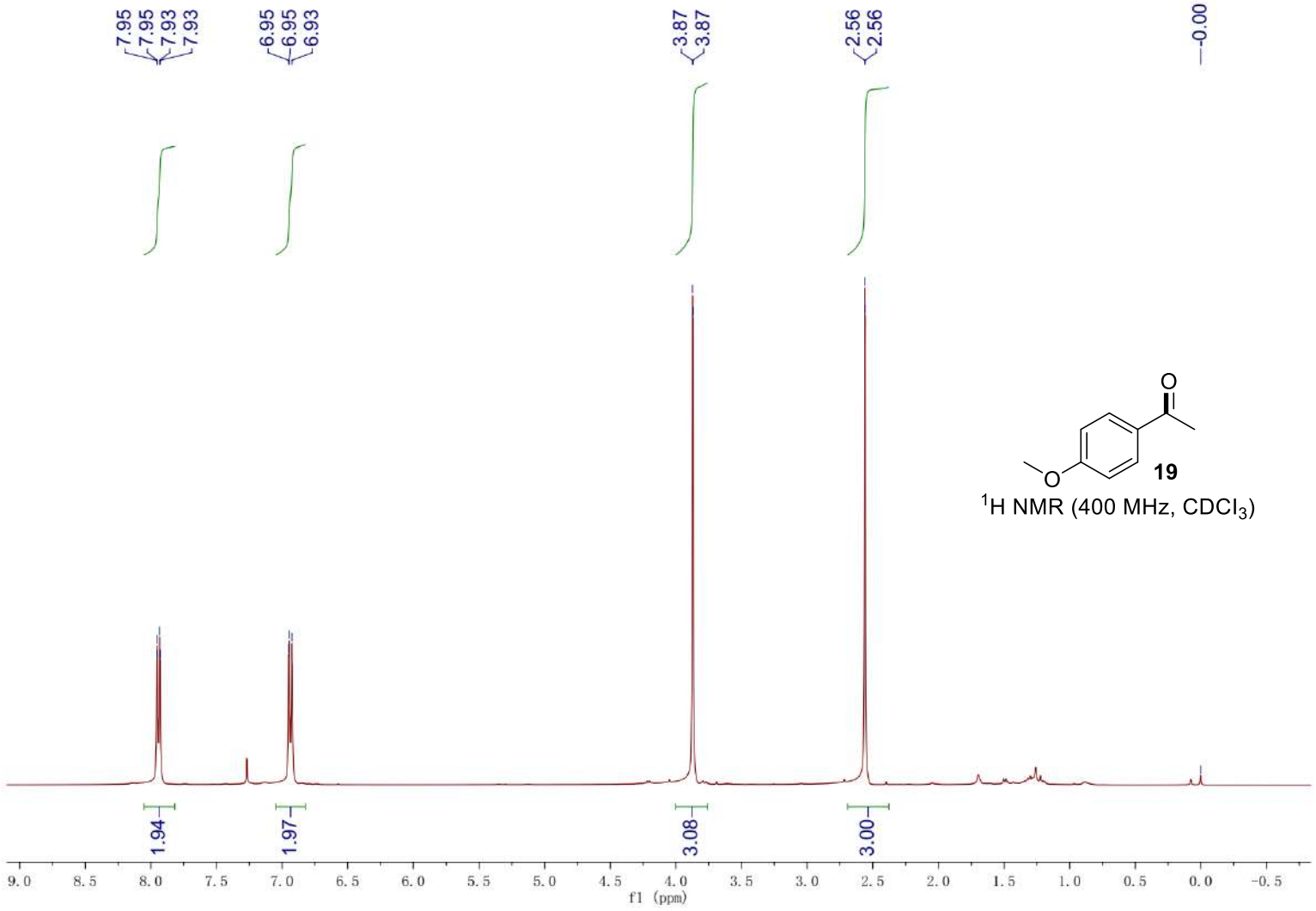


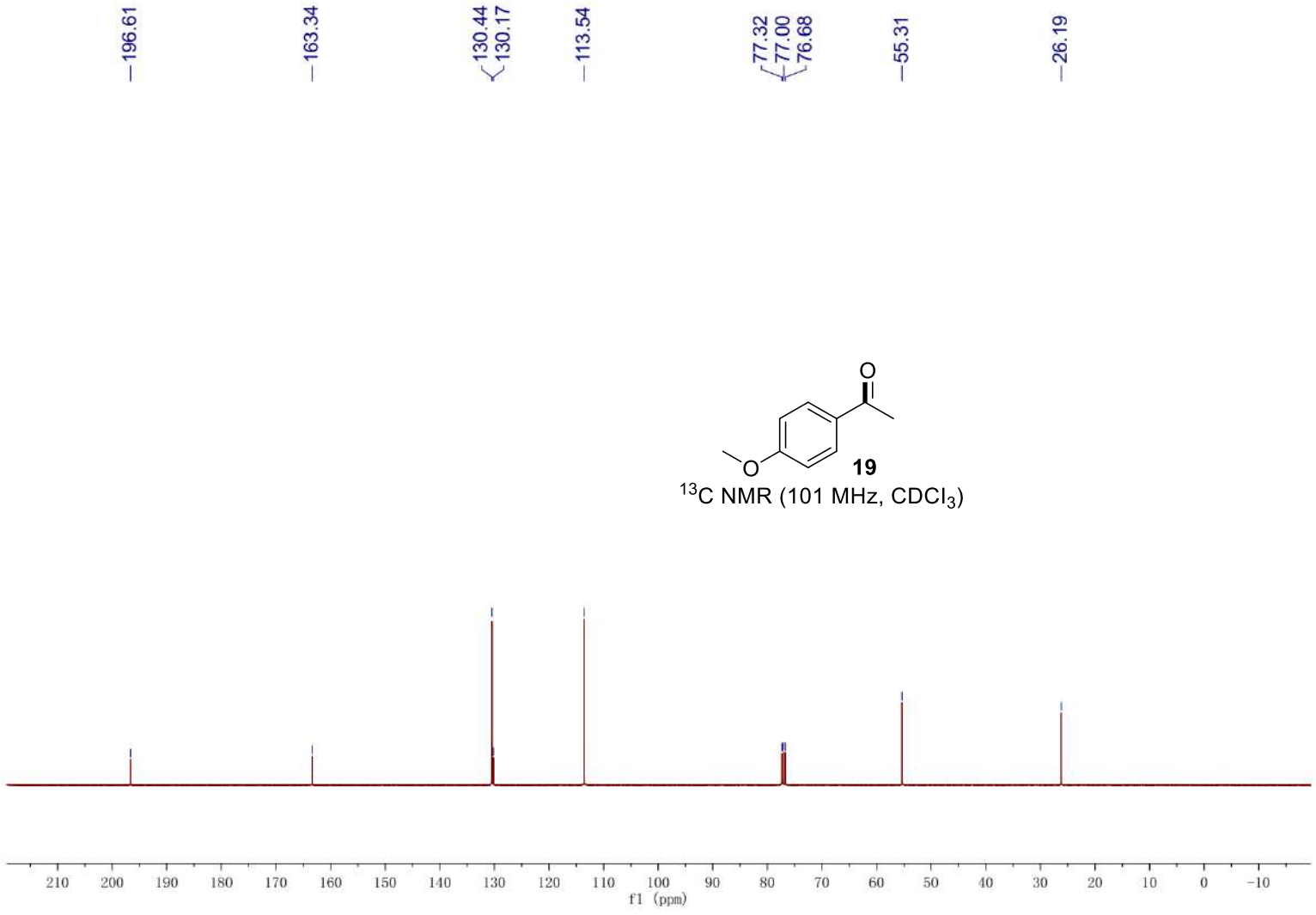

201.69
138.38
137.58
132.00
131.47
129.32
125.65
77.32
77.00
76.68
29.51
21.56
O
17
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

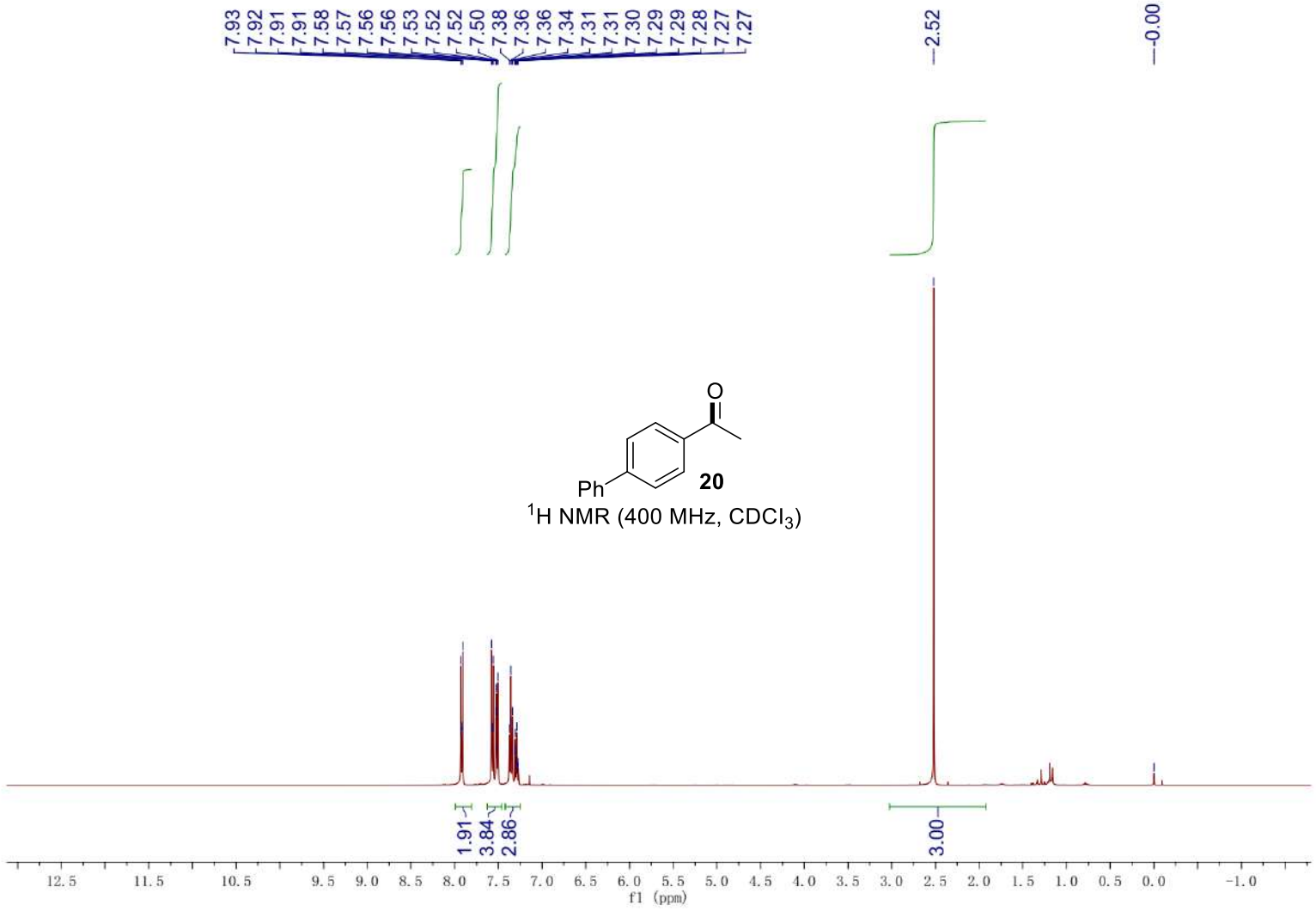


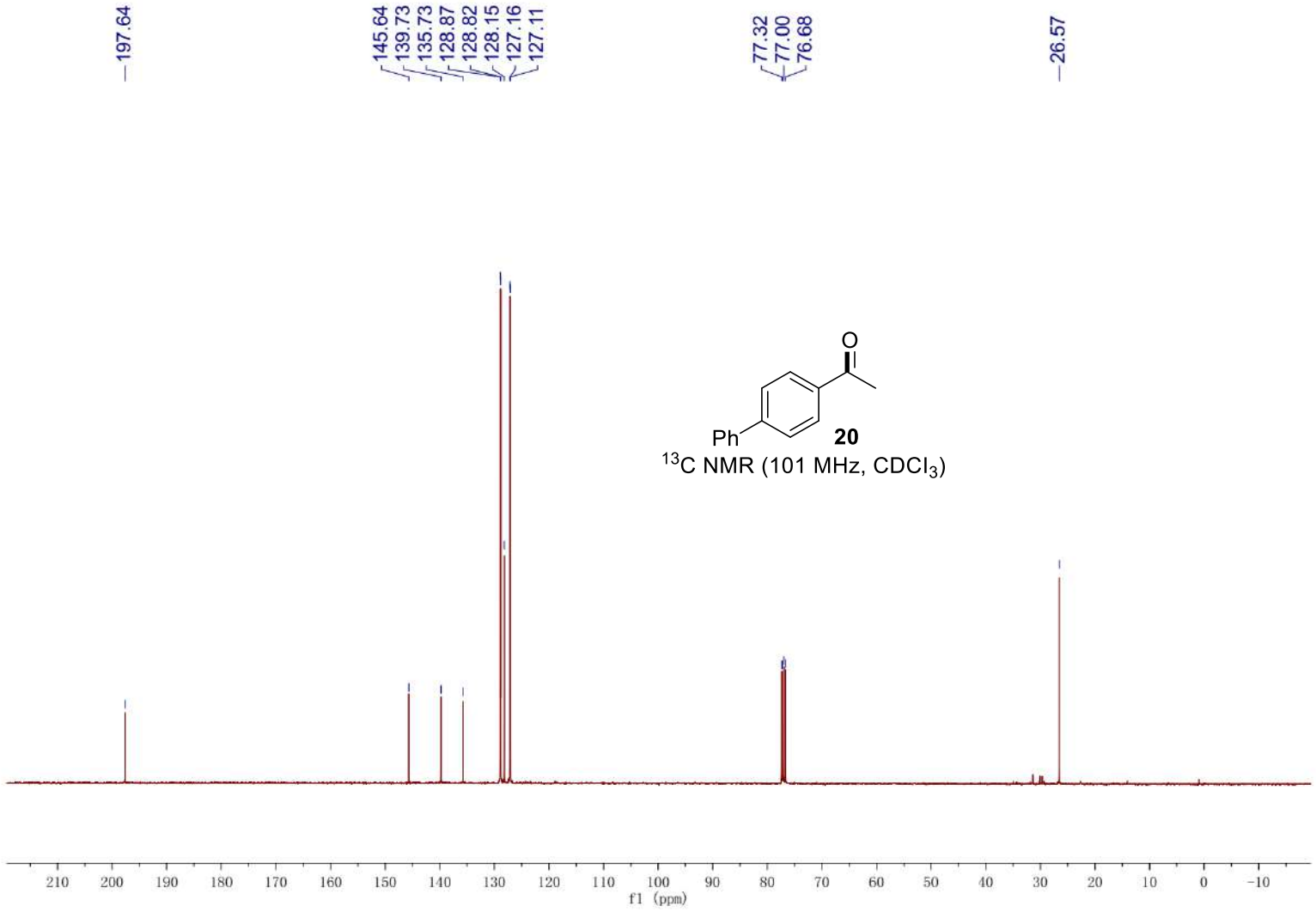
^{1}H NMR (400 MHz, $CDCl_3$)

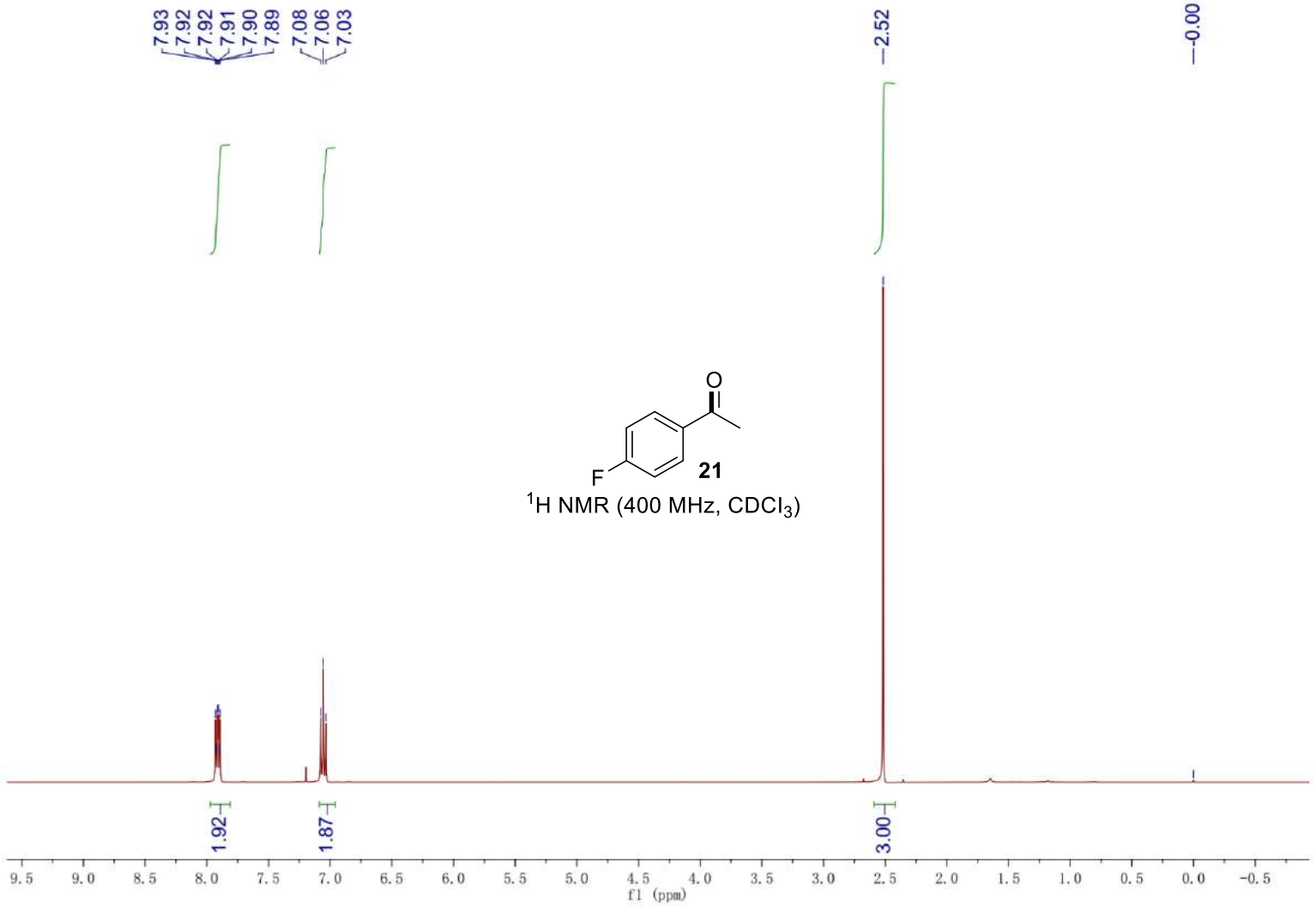

197.71
149.92
134.80
128.43
127.94
77.32
77.00
76.68
28.81
26.41
15.09
O
18
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

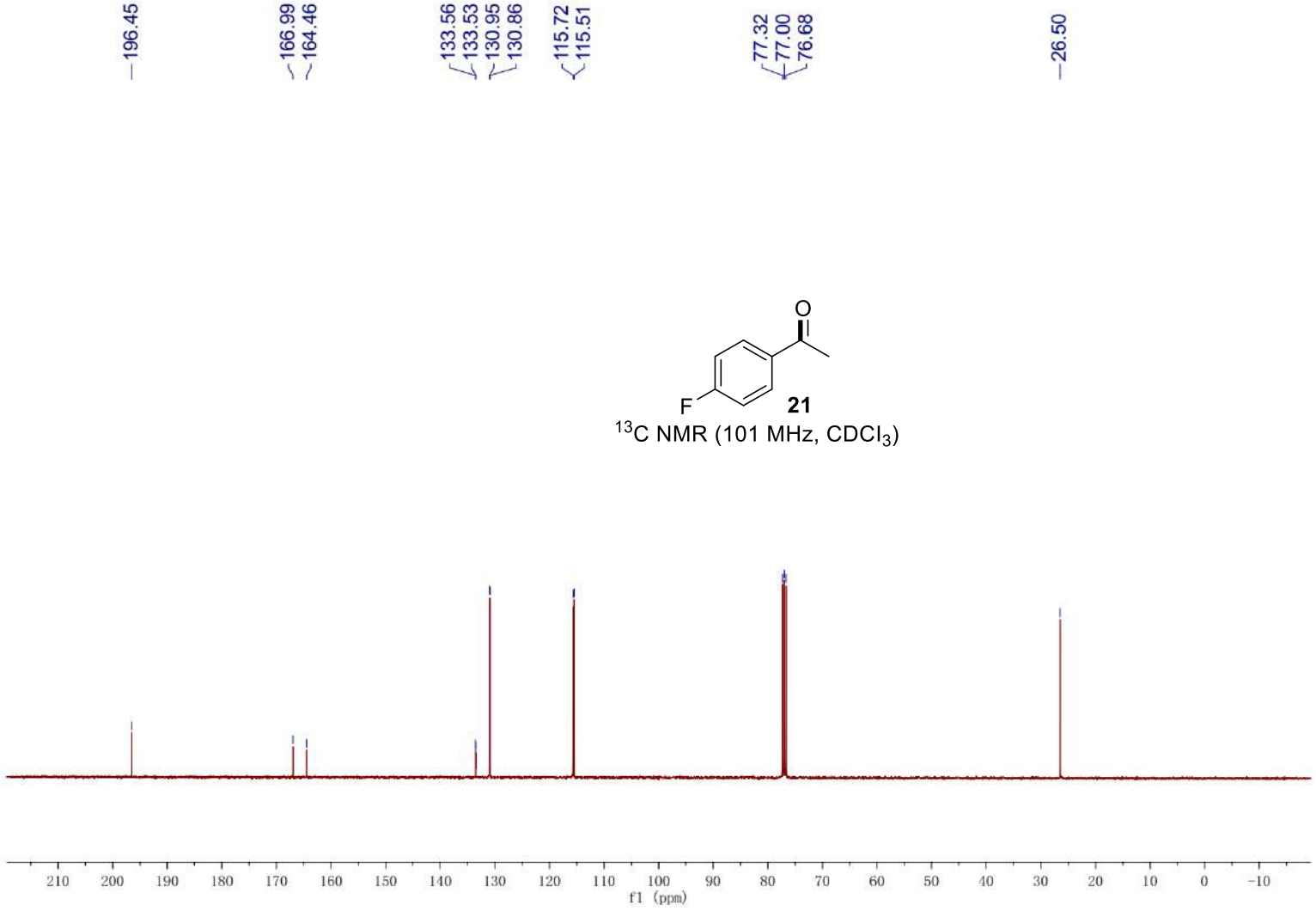

7.95
7.95
7.93
7.93
6.95
6.95
6.93
3.87
3.87
2.56
2.56
0.00
O
O
19
^{1}H NMR (400 MHz, $CDCl_3$)
1.94
1.97
3.08
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


196.61
163.34
130.44
130.17
113.54
77.32
77.00
76.68
55.31
26.19
O
O
19
13C NMR (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)


7.93
7.92
7.91
7.91
7.58
7.57
7.56
7.56
7.53
7.52
7.52
7.50
7.38
7.36
7.36
7.34
7.31
7.31
7.30
7.29
7.29
7.28
7.27
7.27
2.52
0.00
O
Ph
20
1H NMR (400 MHz, CDCl3)
1.91
3.84
2.86
3.00
12.5 11.5 10.5 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 -1.0
f1 (ppm)


197.64
145.64
139.73
135.73
128.87
128.82
128.15
127.16
127.11
77.32
77.00
76.68
26.57
O
Ph
20
13C NMR (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)


7.93
7.92
7.92
7.91
7.90
7.89
7.08
7.06
7.03
2.52
0.00
O
F
21
1H NMR (400 MHz, CDCl3)
1.92
1.87
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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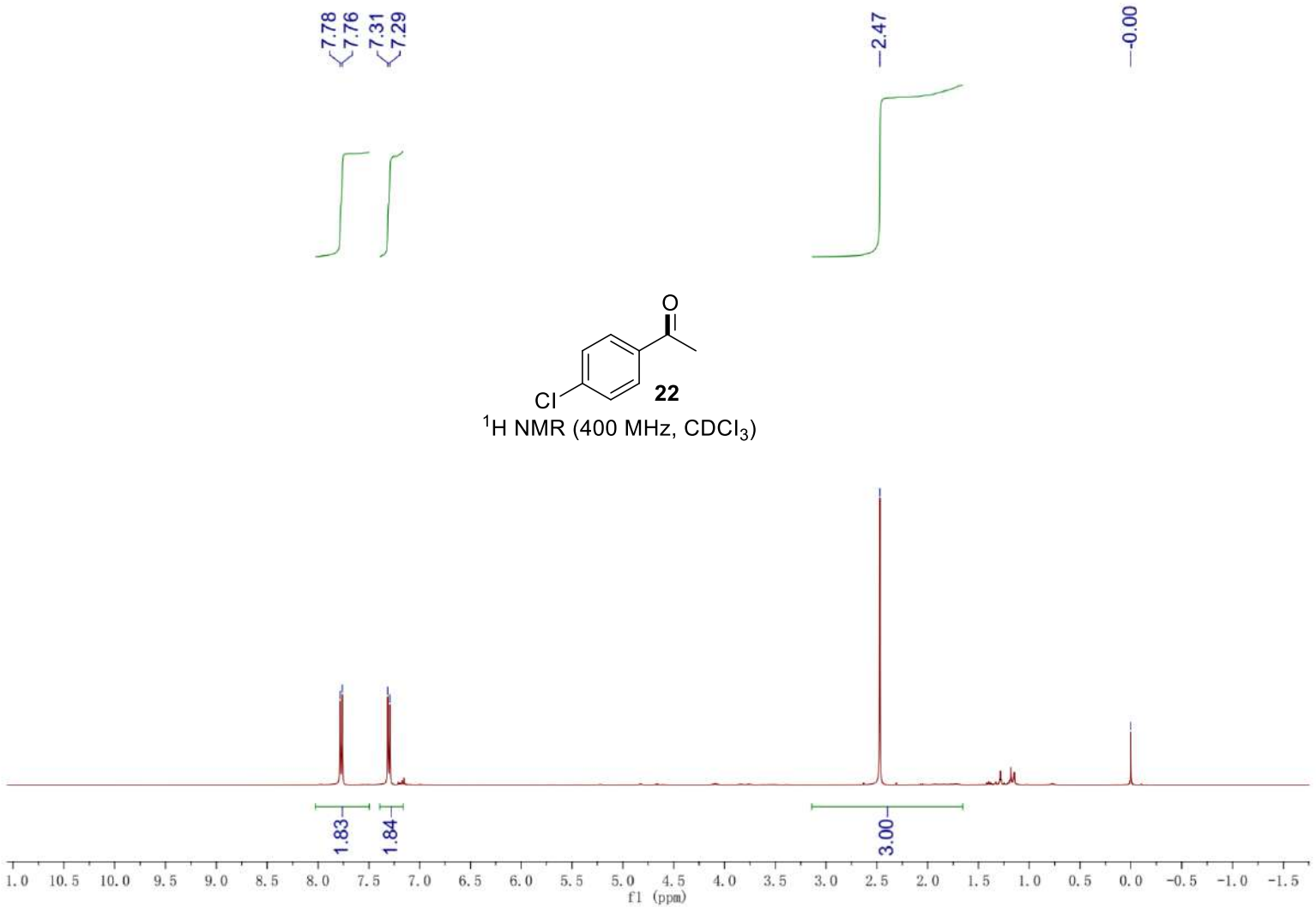
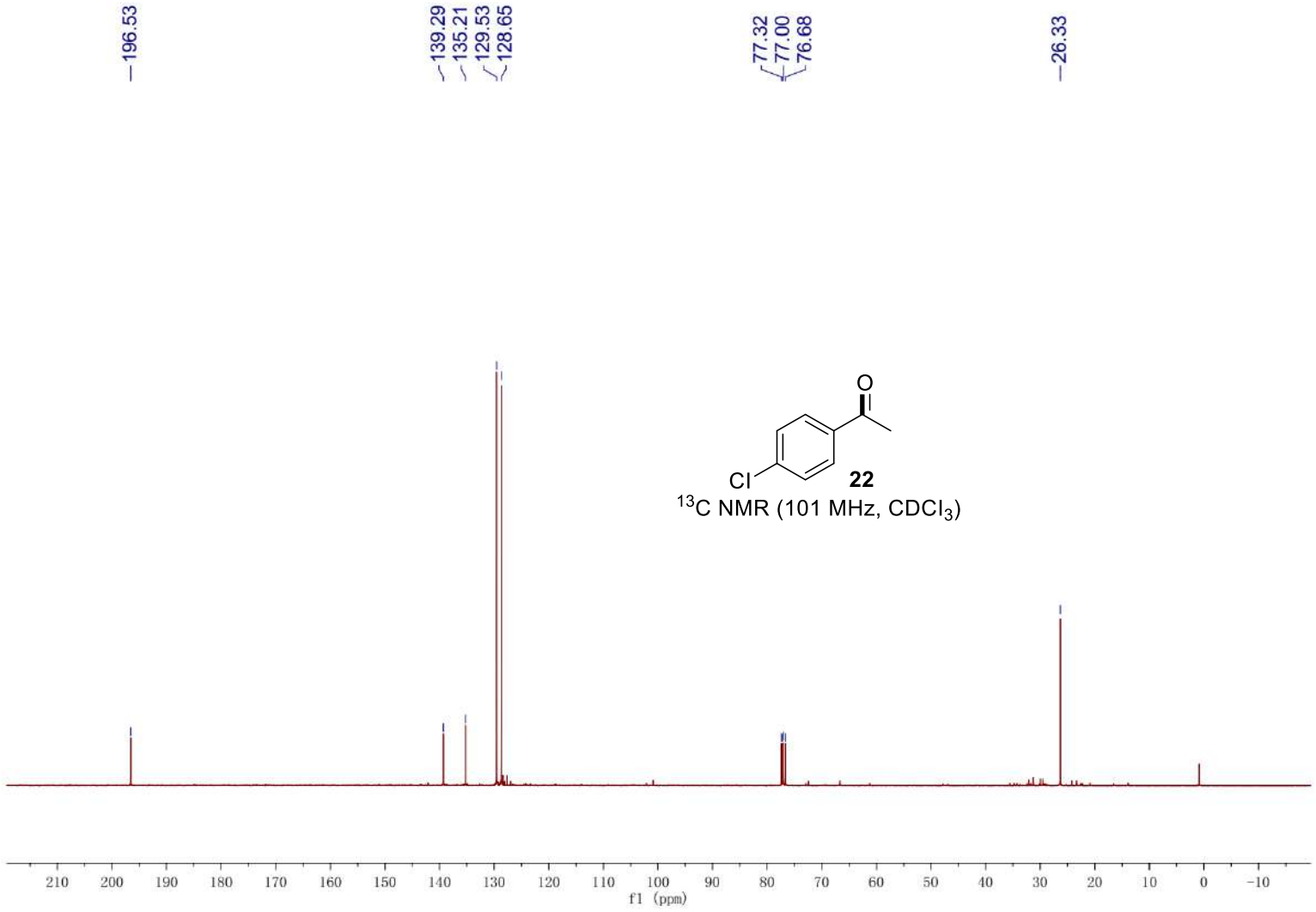
164.46
133.56
133.53
130.95
130.86
115.72
115.51
77.32
77.00
76.68
26.50
O
F
21
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



^{1}H NMR (400 MHz, $CDCl_3$)


196.53
139.29
135.21
129.53
128.65
77.32
77.00
76.68
26.33
O
Cl
22
13C NMR (101 MHz, CDCl3)
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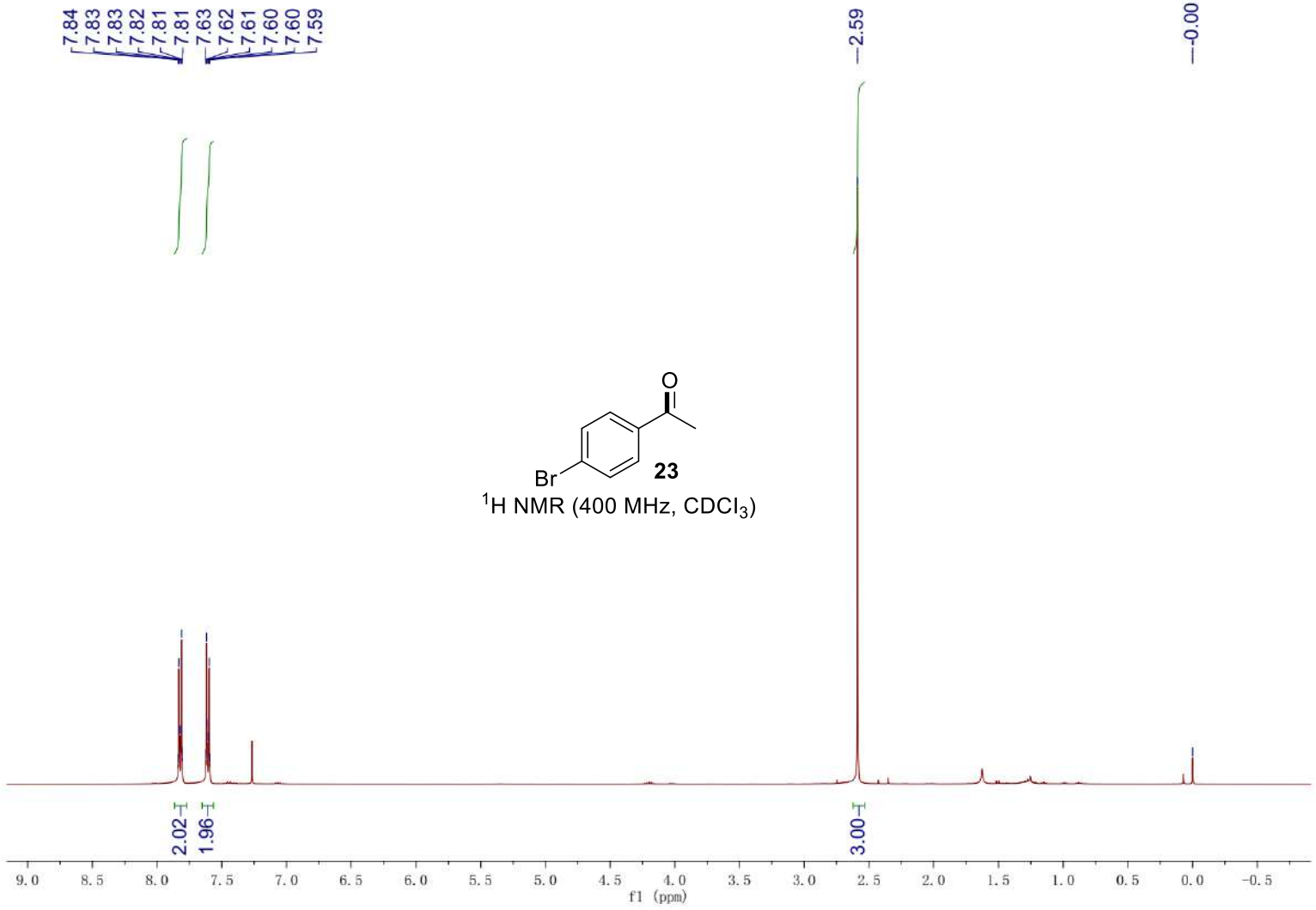
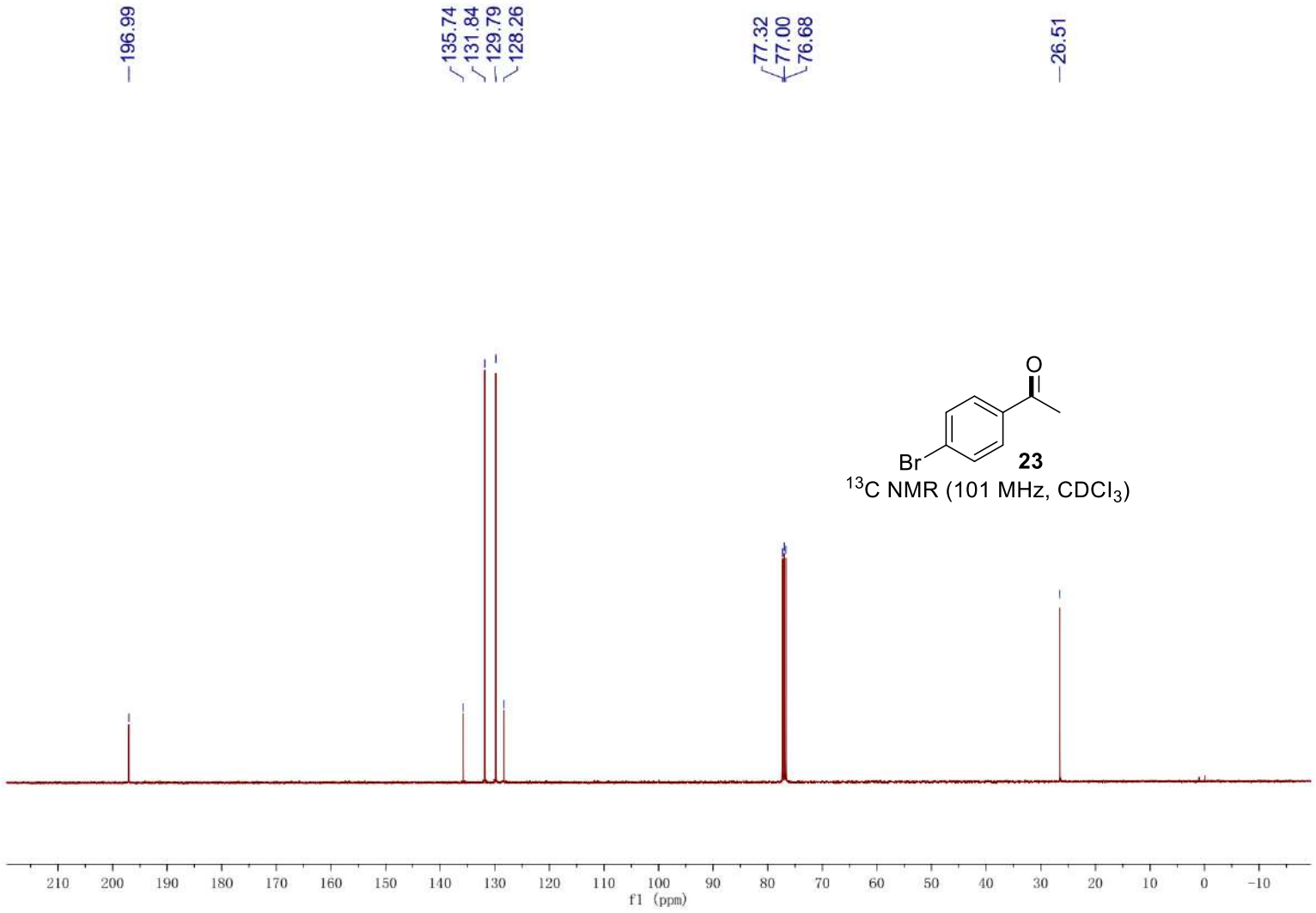
f1 (ppm)


7.84
7.83
7.83
7.82
7.81
7.81
7.63
7.62
7.61
7.60
7.60
7.59
2.59
0.00
O
Br
23
^{1}H NMR (400 MHz, $CDCl_3$)
2.02
1.96
3.00
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
-0.5
f1 (ppm)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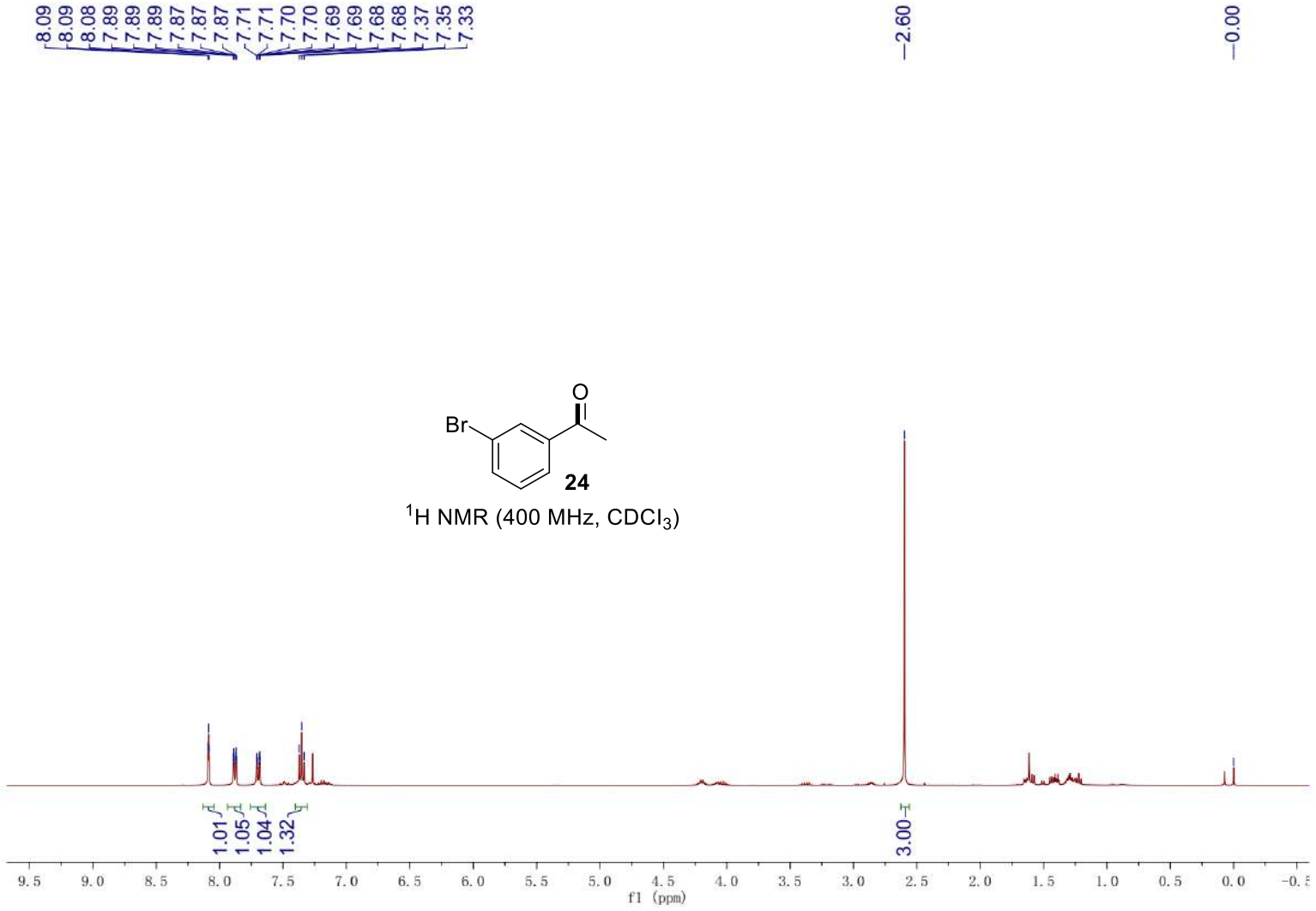
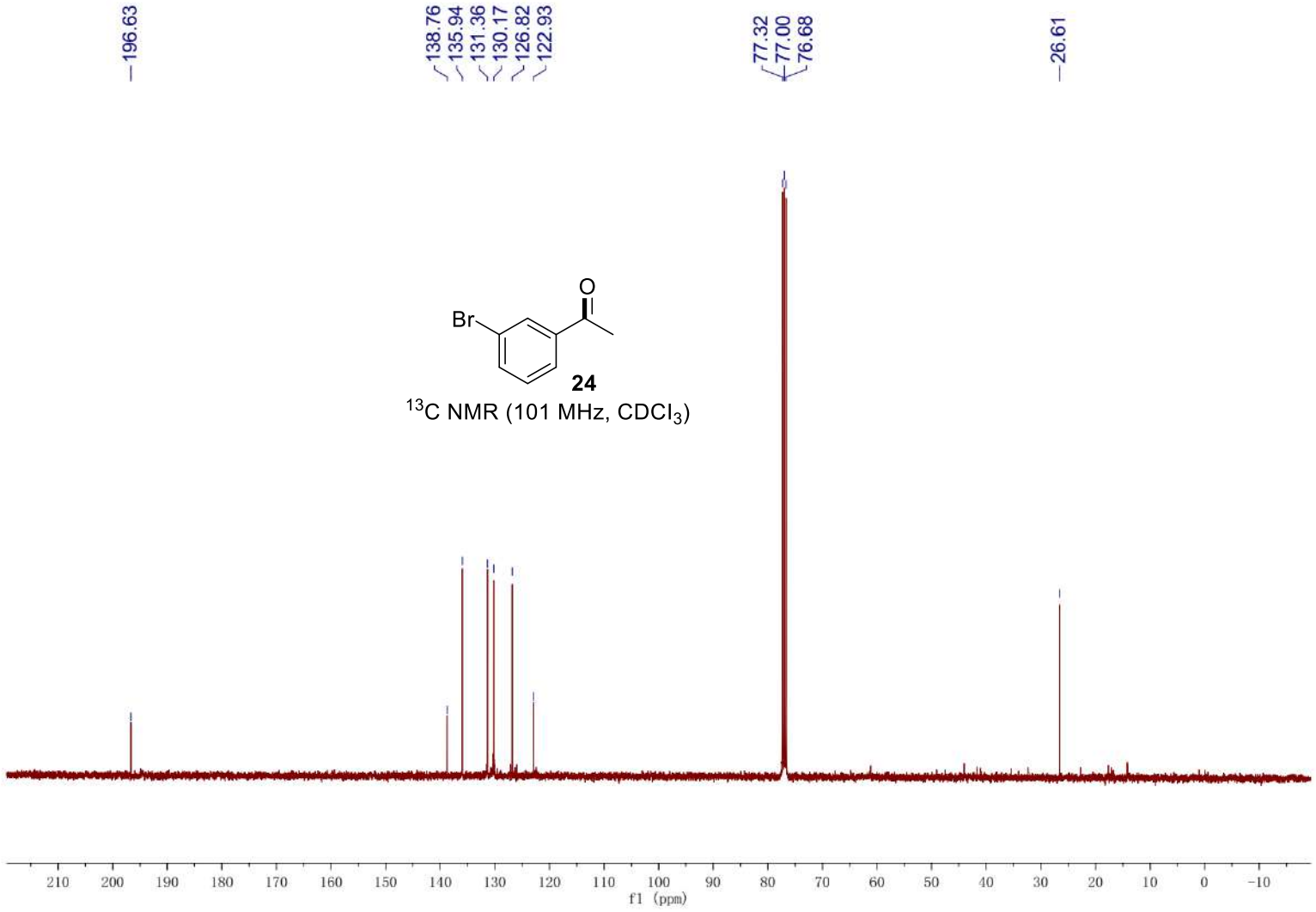
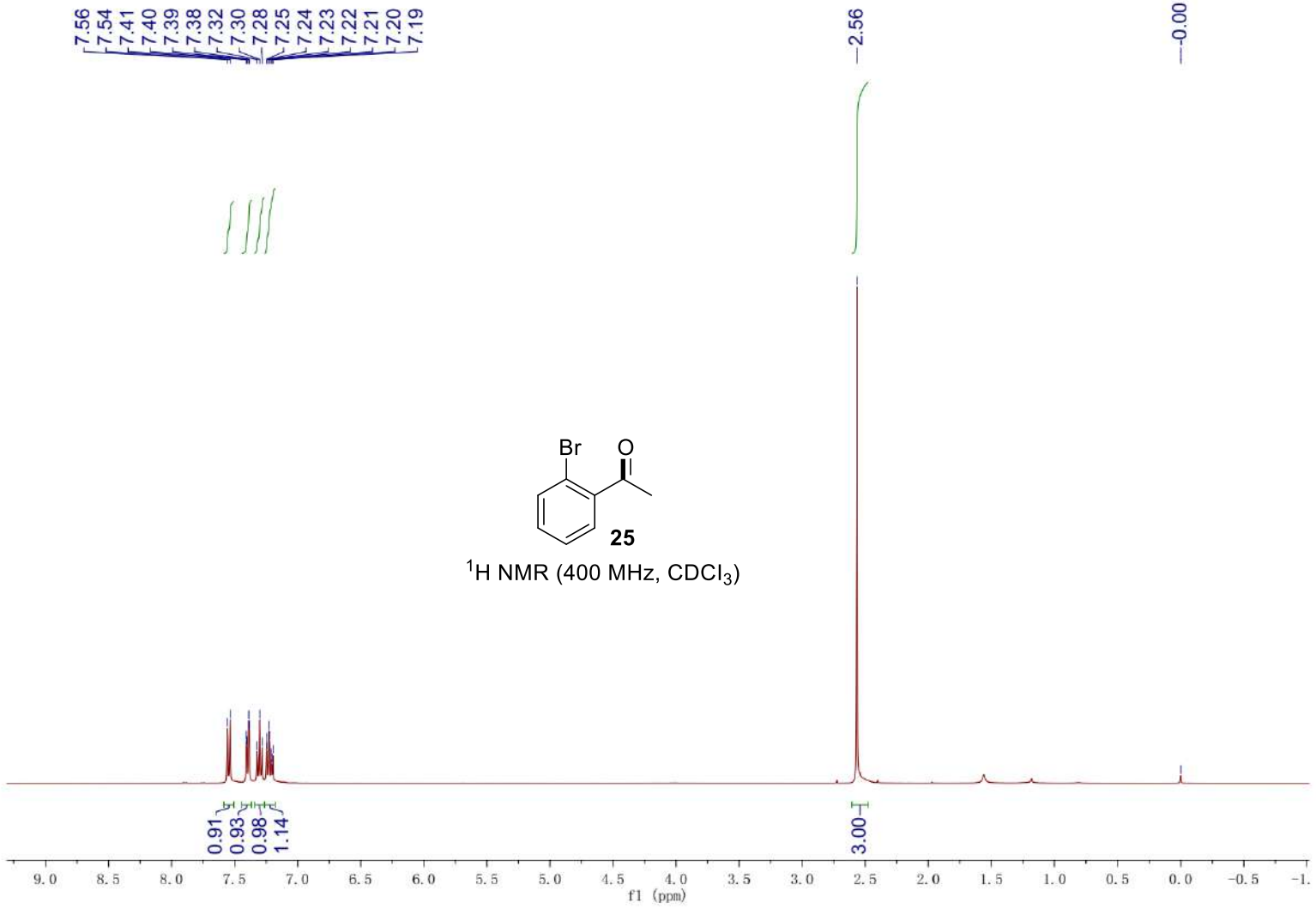
135.74
131.84
129.79
128.26
77.32
77.00
76.68
26.51
O
Br
23
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

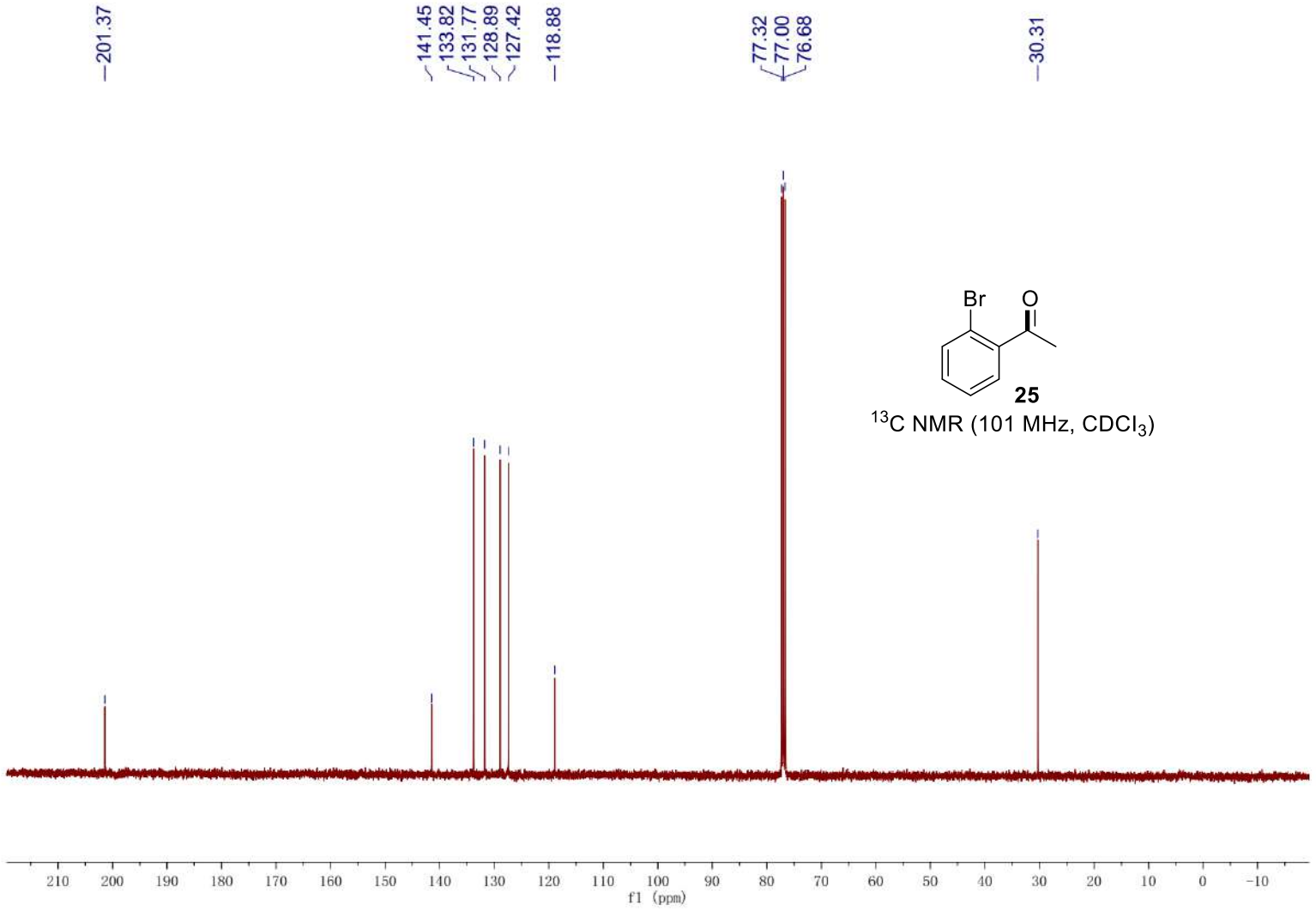

8.09
8.09
8.08
7.89
7.89
7.89
7.87
7.87
7.87
7.71
7.71
7.70
7.70
7.69
7.69
7.68
7.68
7.37
7.35
7.33
2.60
0.00
Br
O
24
1H NMR (400 MHz, CDCl3)
1.01
1.05
1.04
1.32
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

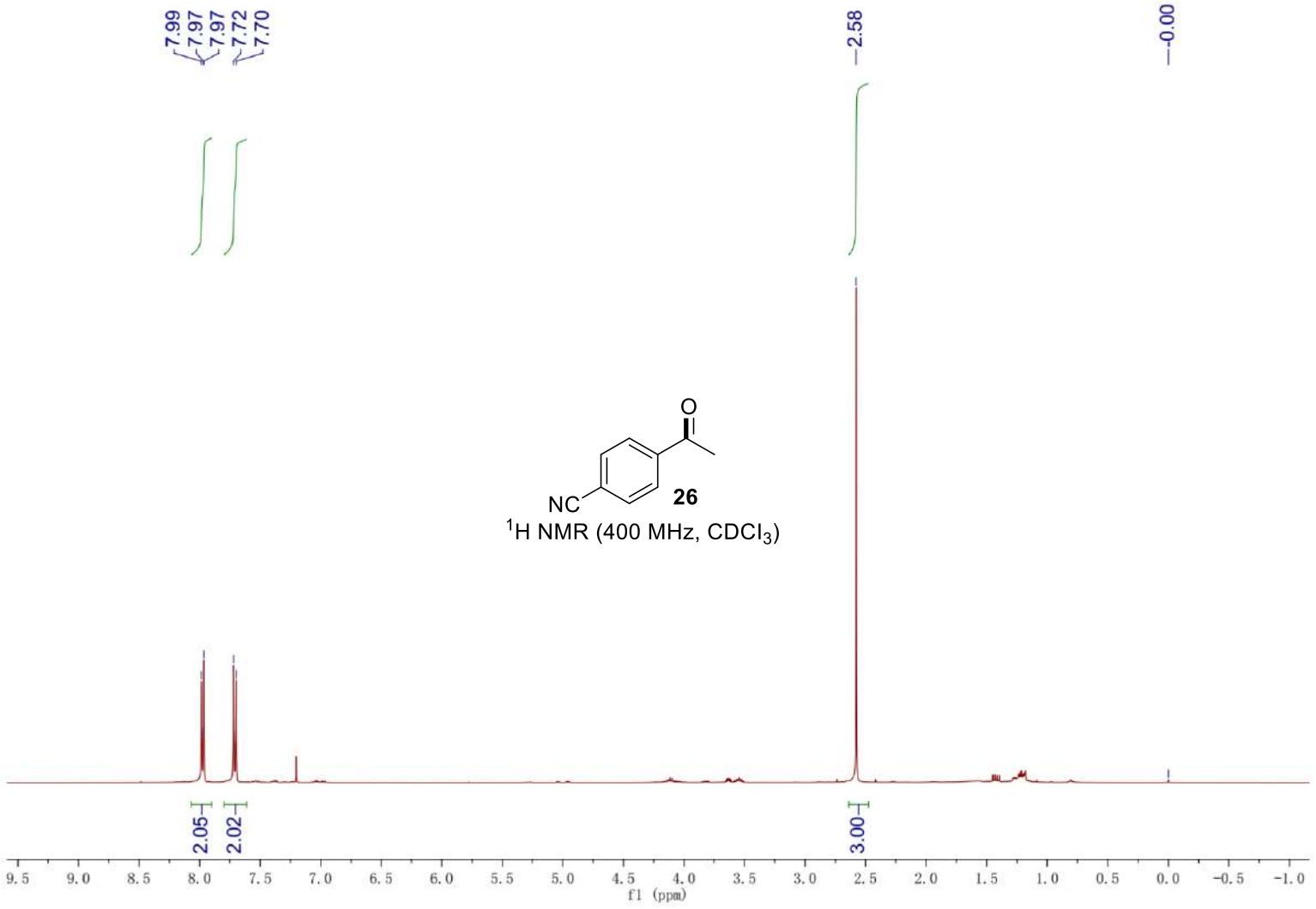

196.63
138.76
135.94
131.36
130.17
126.82
122.93
77.32
77.00
76.68
26.61
Br
O
24
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

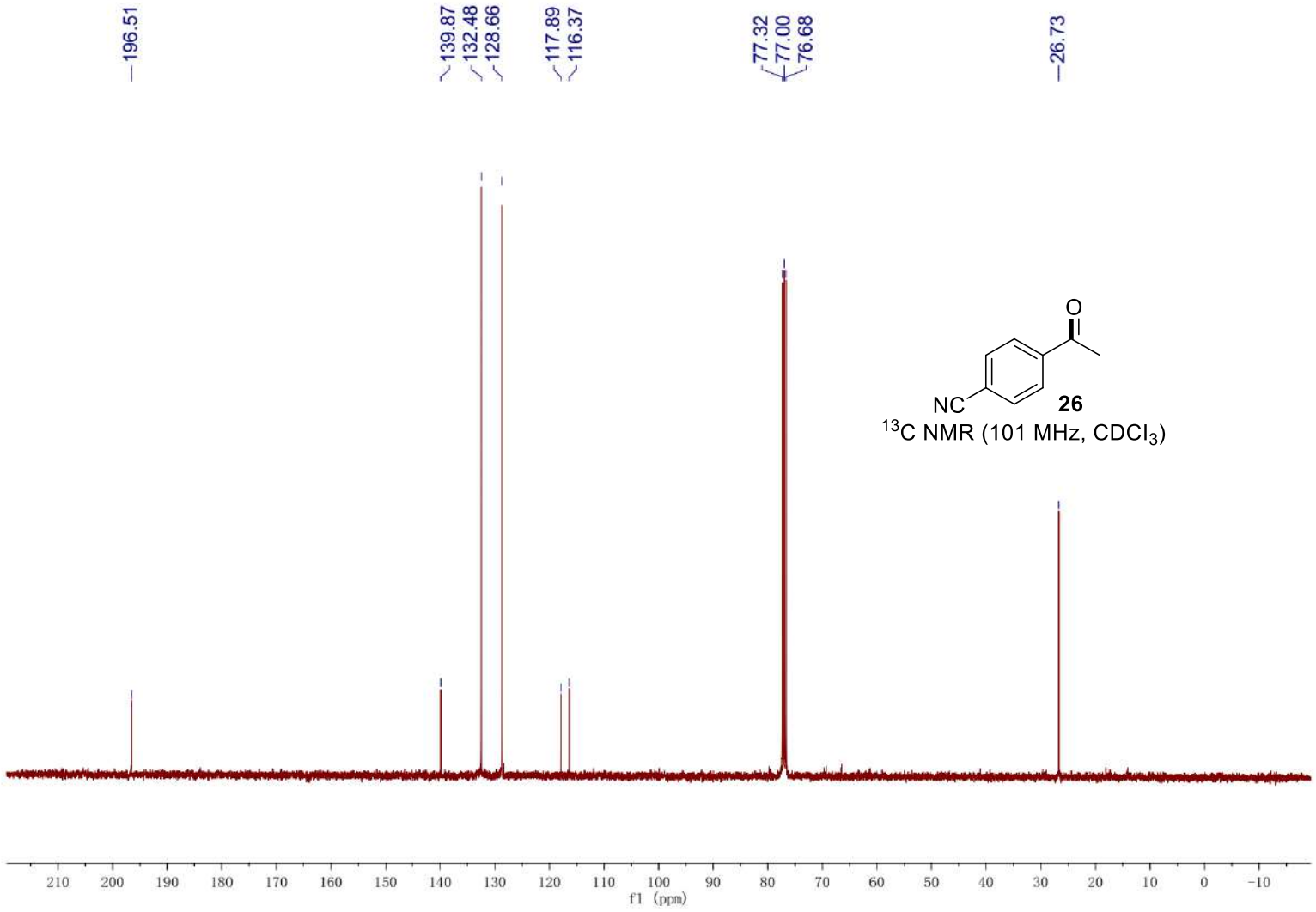


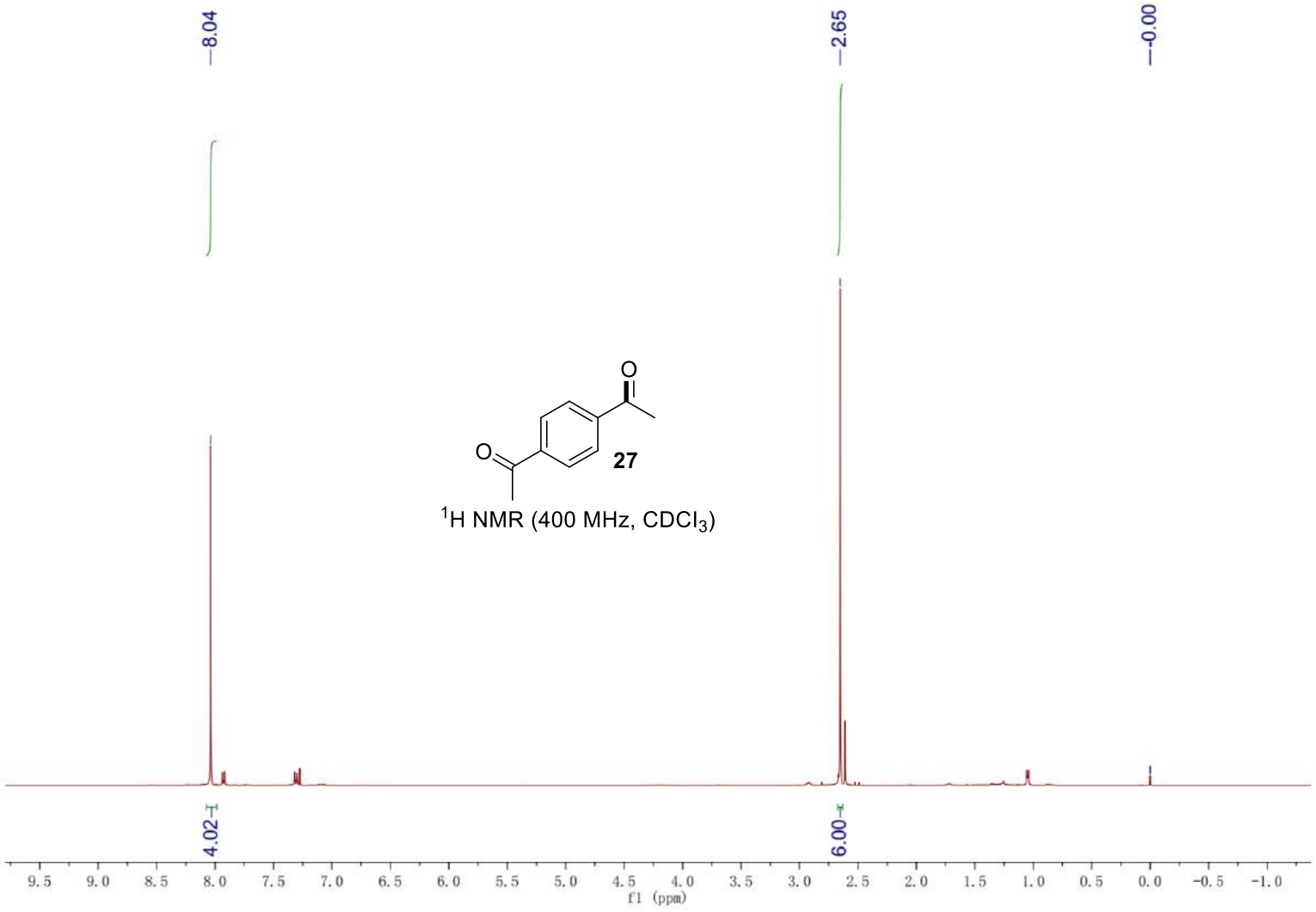
25

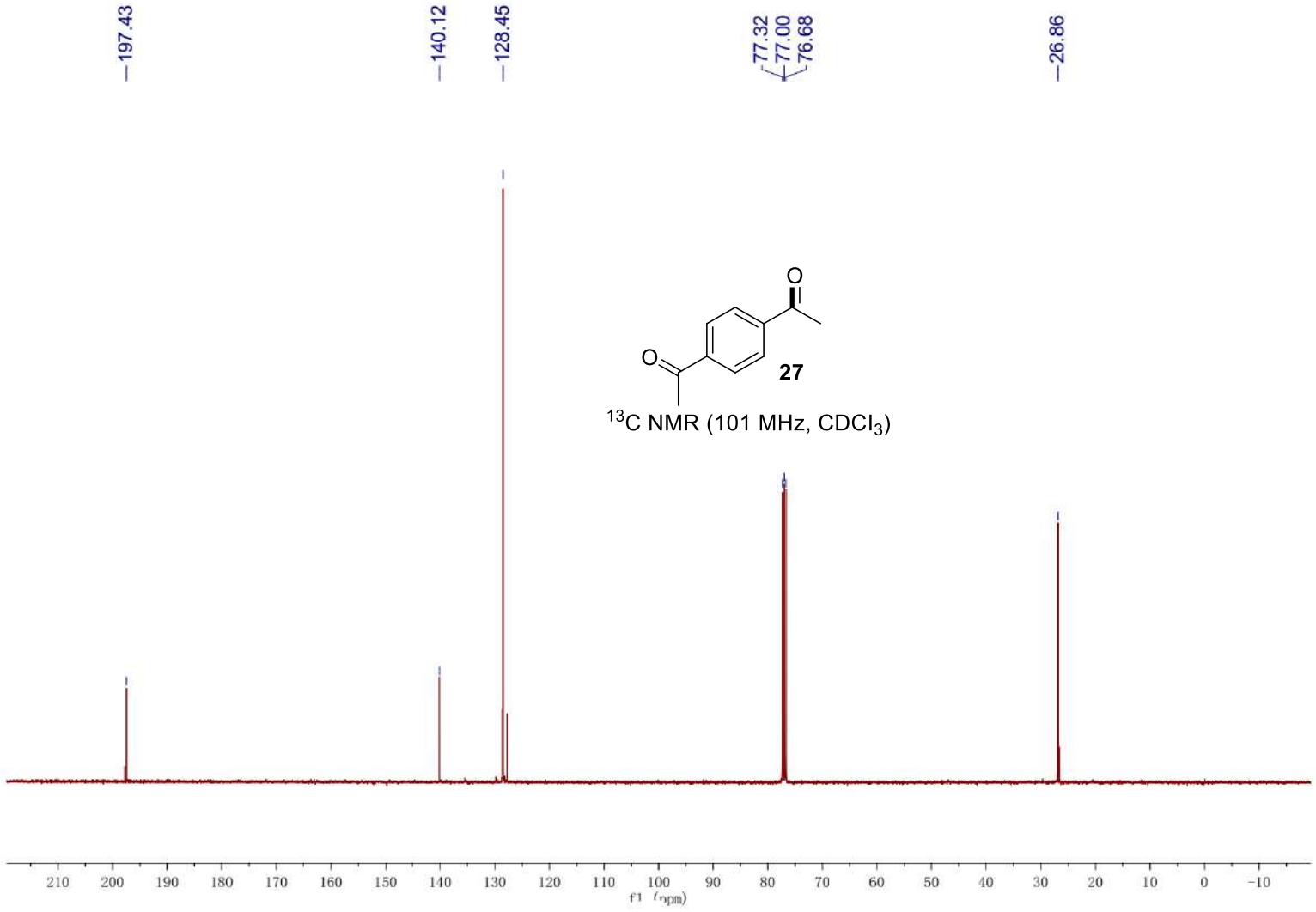
^{1}H NMR (400 MHz, $CDCl_3$)

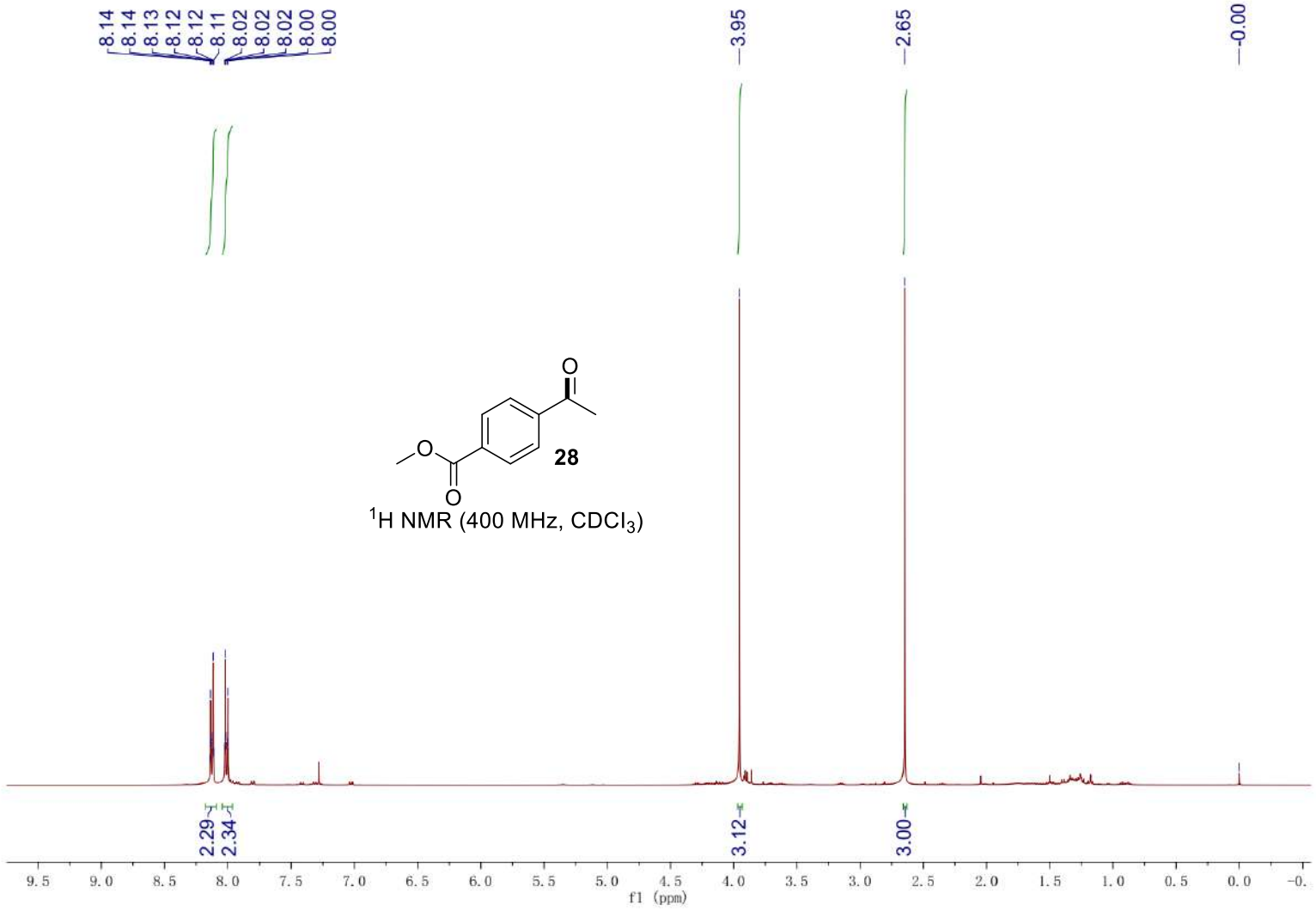

201.37
141.45
133.82
131.77
128.89
127.42
118.88
77.32
77.00
76.68
30.31
Br
O
25
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.99
7.97
7.97
7.72
7.70
2.58
0.00
O
NC
26
^{1}H NMR (400 MHz, $CDCl_3$)
2.05
2.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

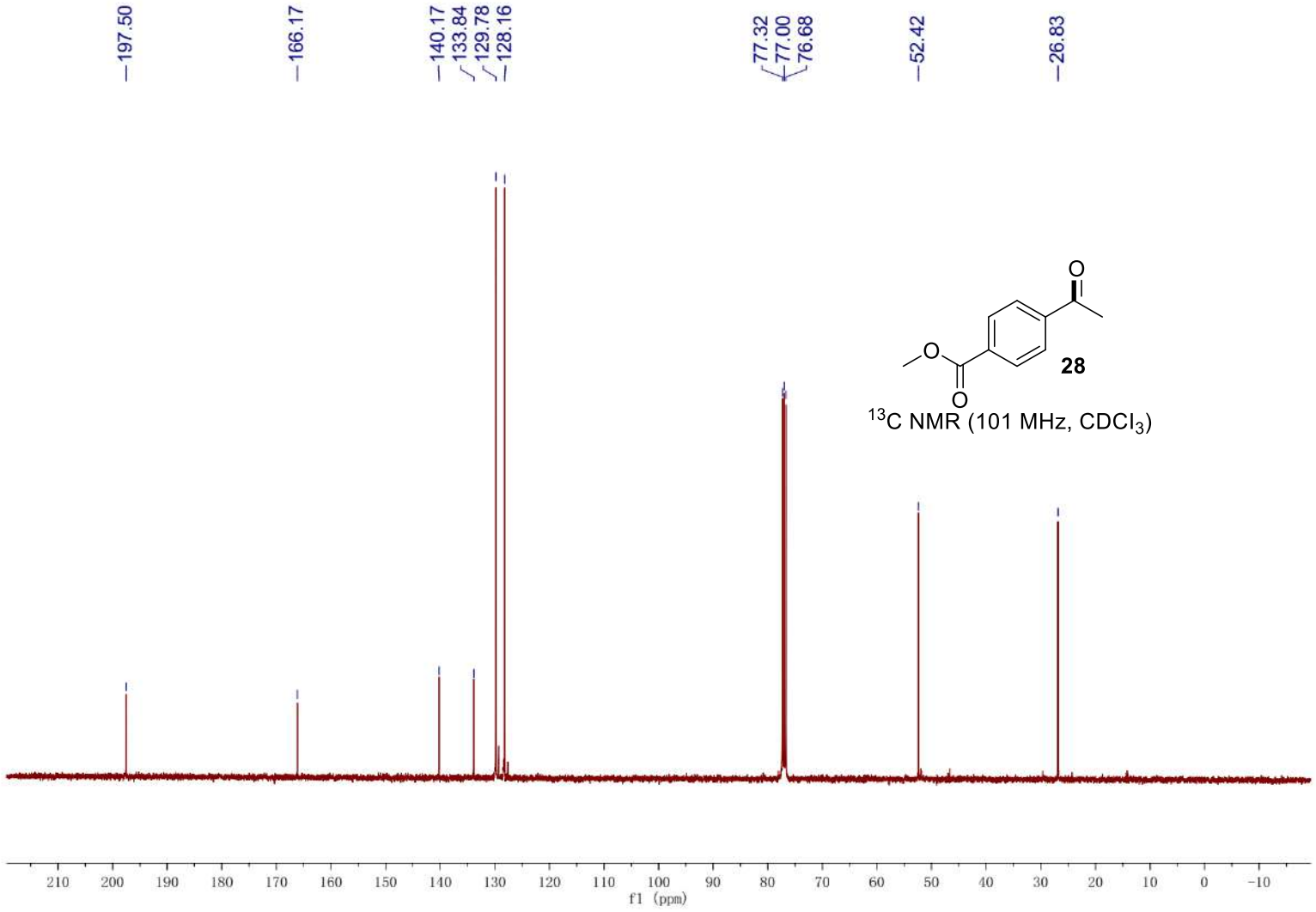

196.51
139.87
132.48
128.66
117.89
116.37
77.32
77.00
76.68
26.73
O
NC
26
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

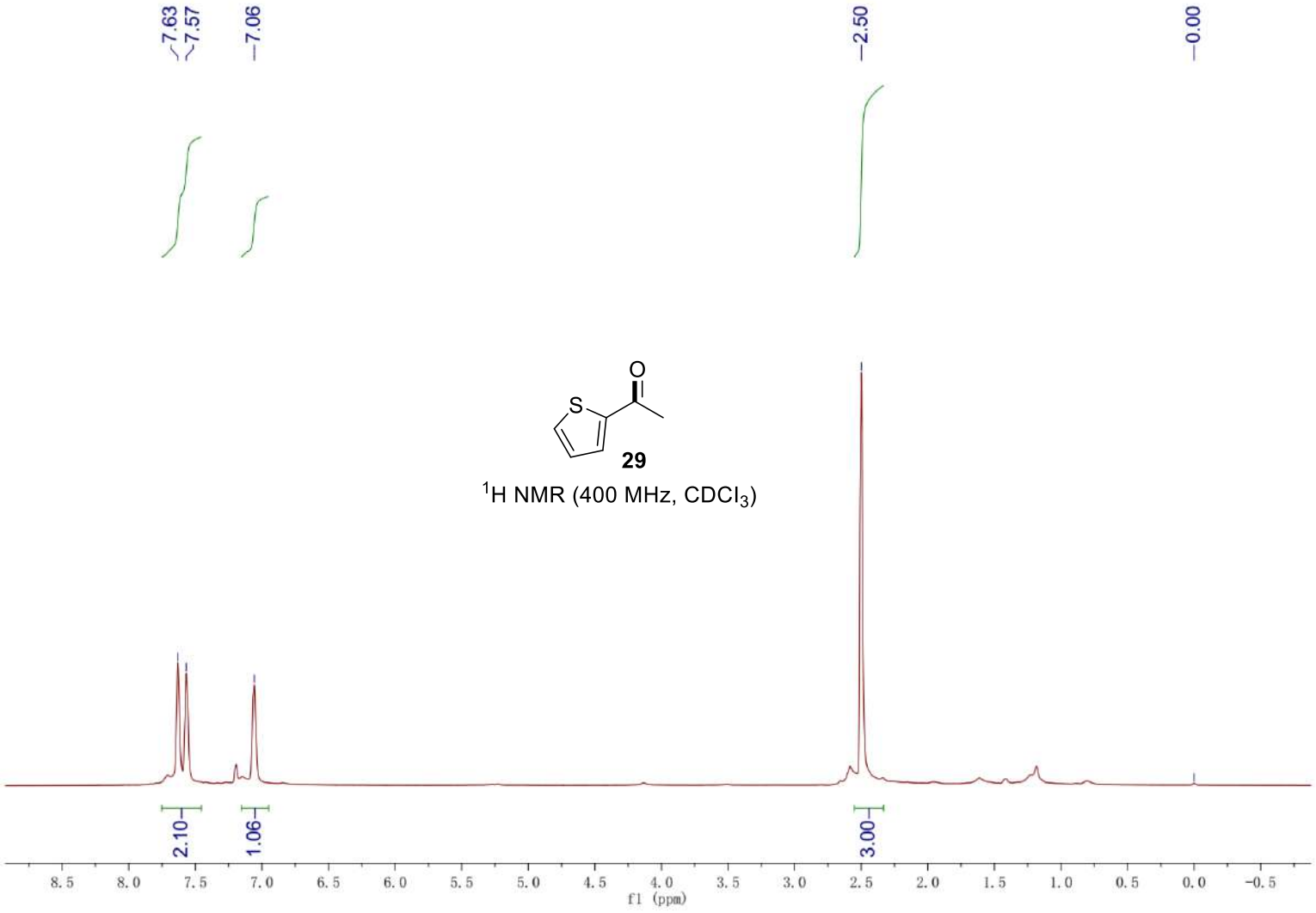

8.04
2.65
0.00
O
O
27
^{1}H NMR (400 MHz, $CDCl_3$)
4.02
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


197.43
140.12
128.45
77.32
77.00
76.68
26.86
O
O
27
^{13}C NMR (101 MHz, $CDCl_3$)
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)



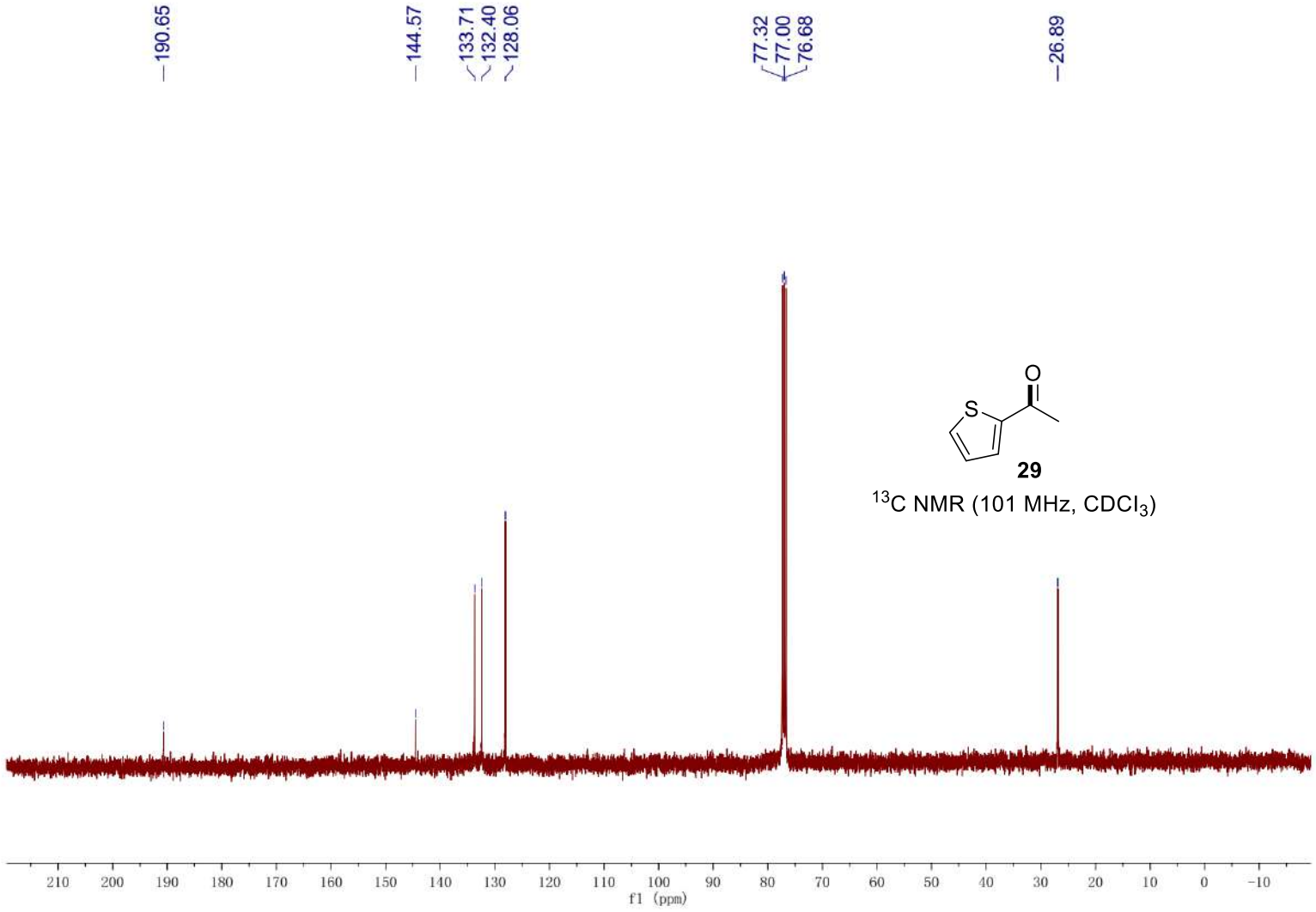
^{1}H NMR (400 MHz, $CDCl_3$)

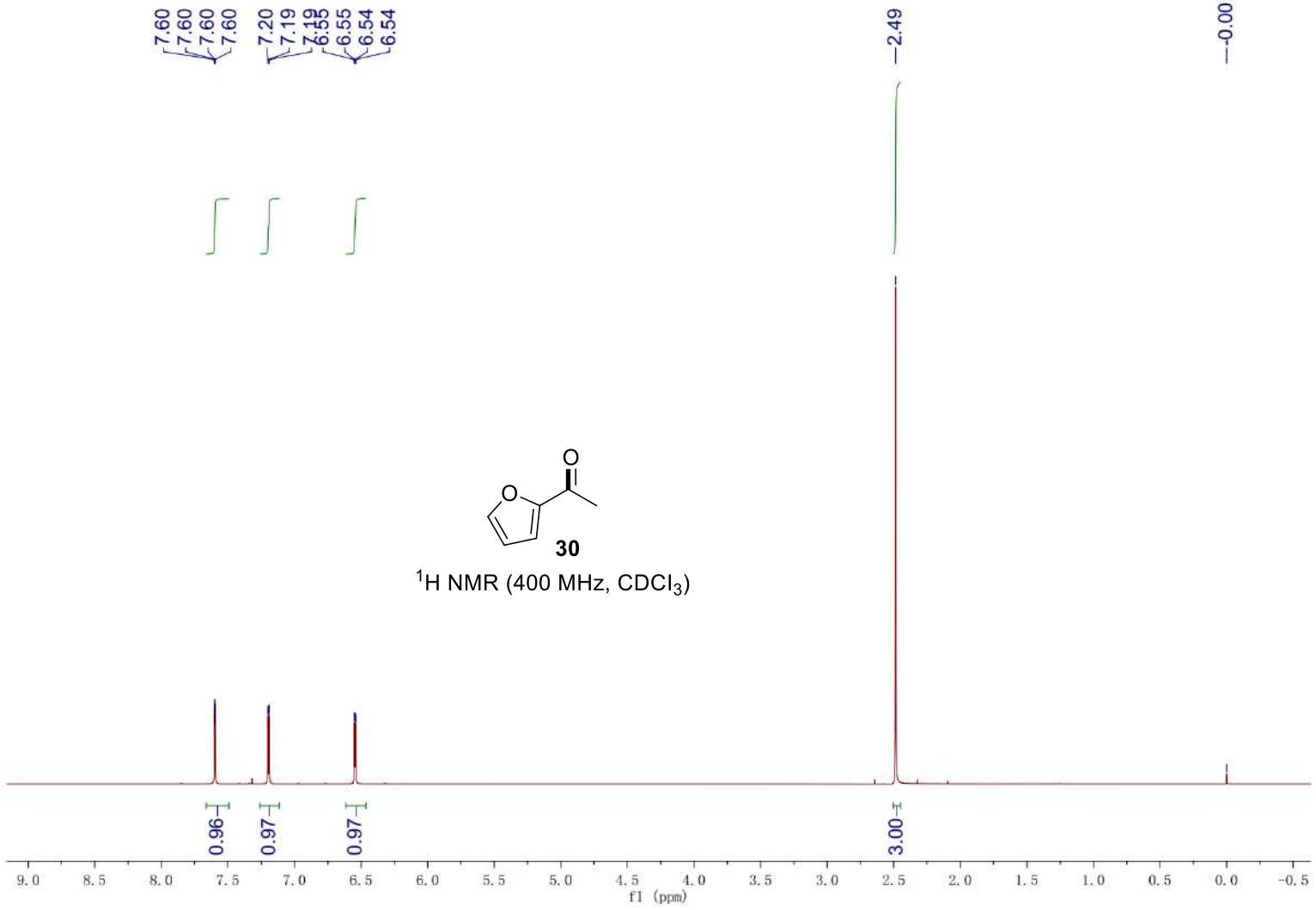

197.50
166.17
140.17
133.84
129.78
128.16
77.32
77.00
76.68
52.42
26.83
O
O
O
28
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



29

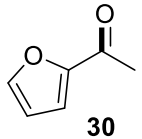
^{1}H NMR (400 MHz, $CDCl_3$)


190.65
144.57
133.71
132.40
128.06
77.32
77.00
76.68
26.89
O
S
29
^{13}C NMR (101 MHz, $CDCl_3$)
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)



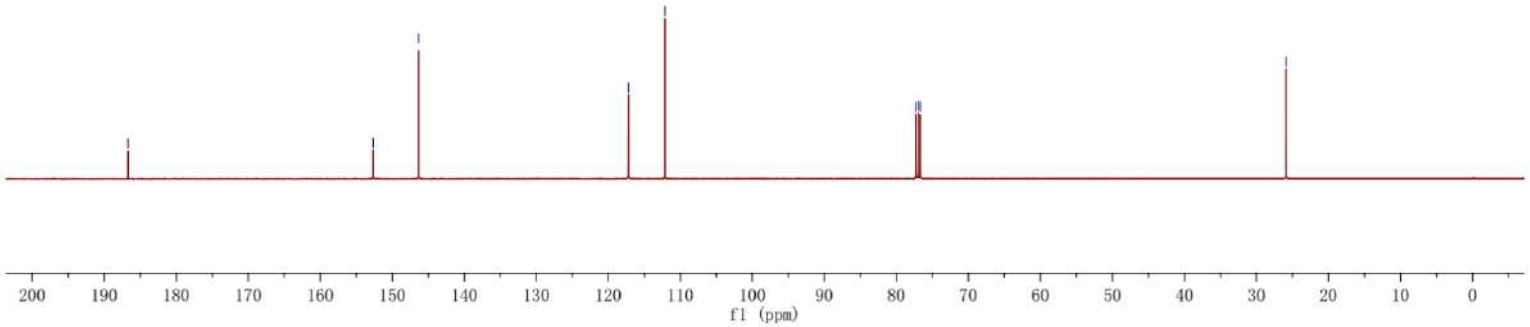
30

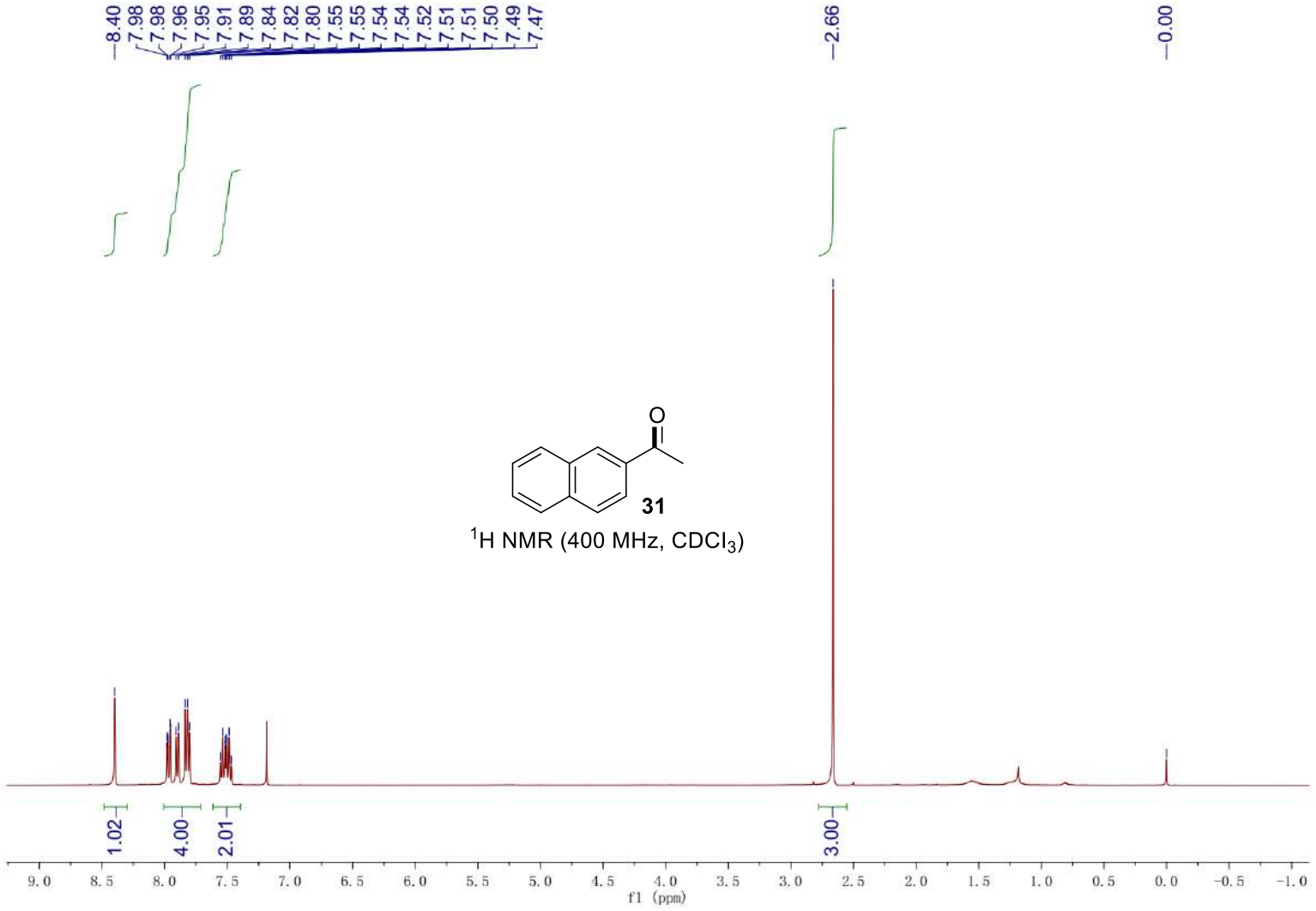
^{1}H NMR (400 MHz, $CDCl_3$)



30

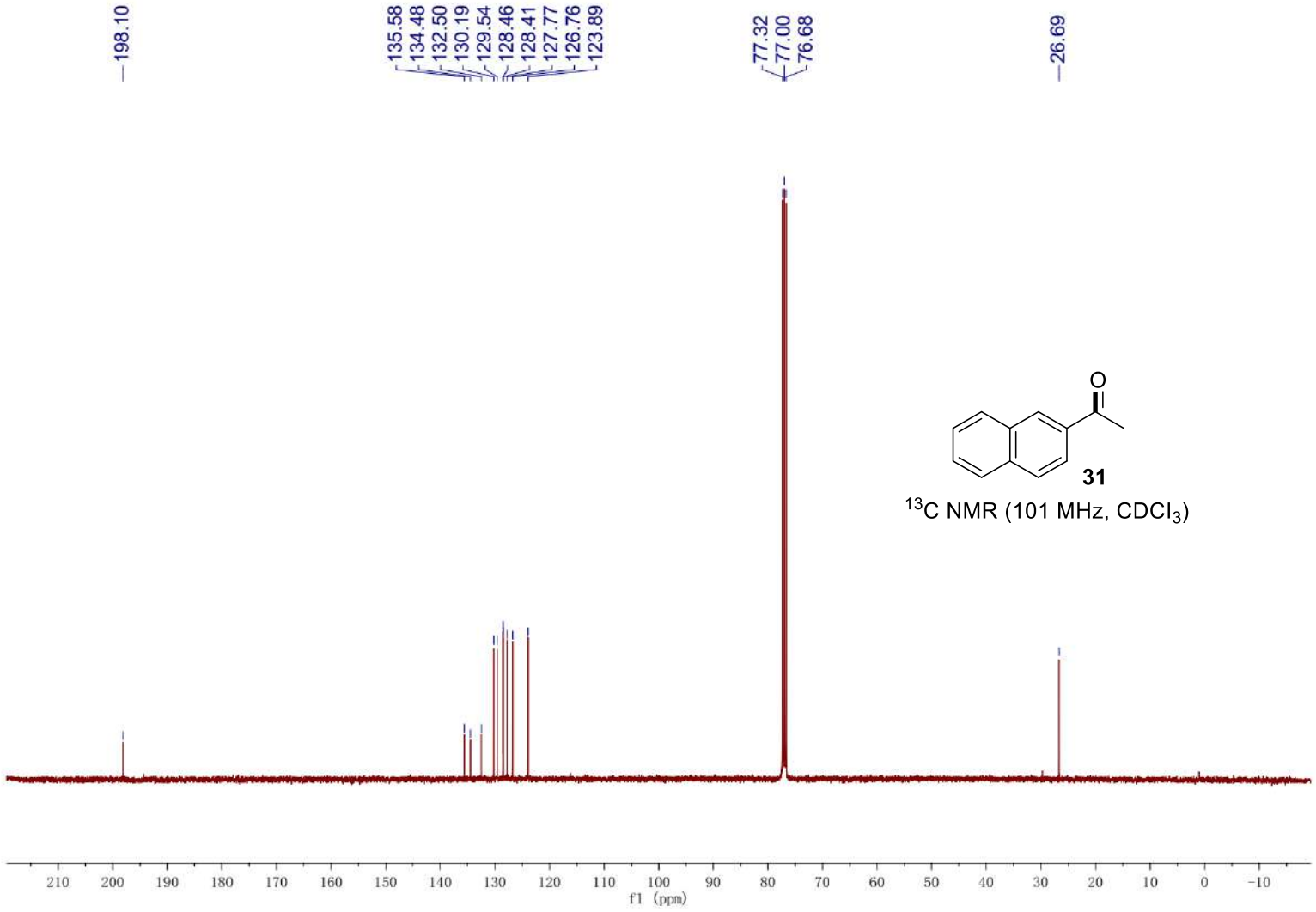
^{13}C NMR (101 MHz, $CDCl_3$)

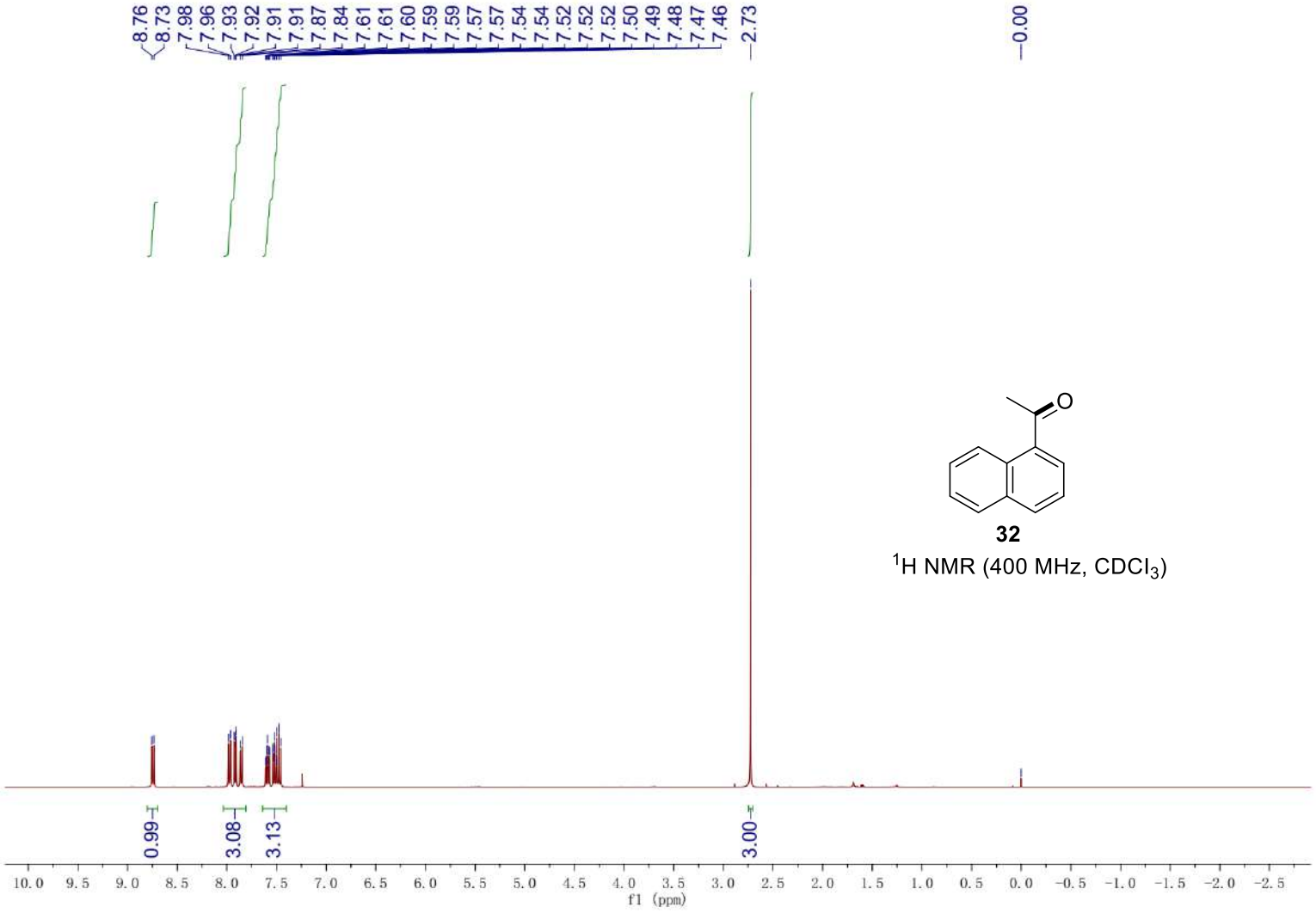




31

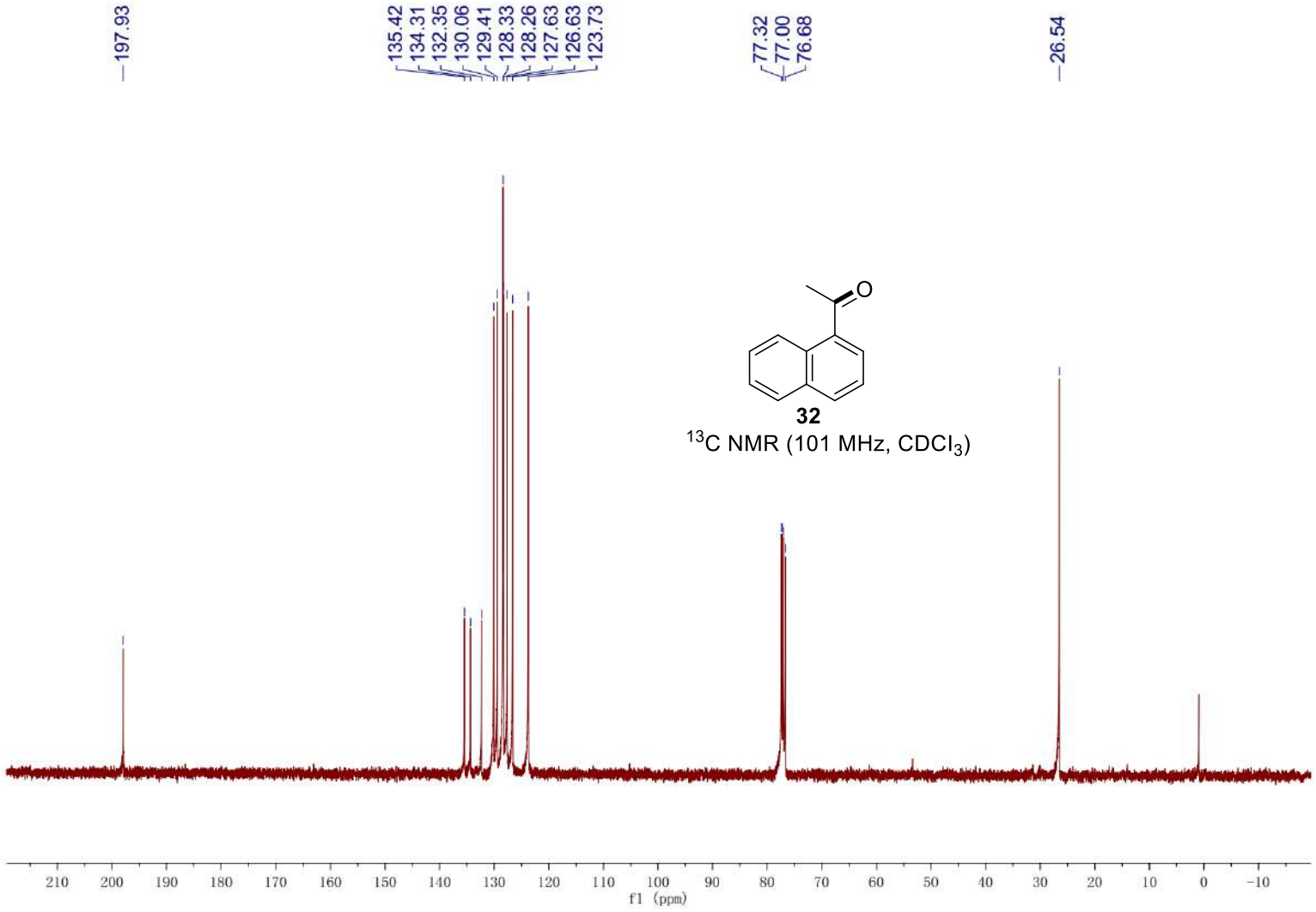
^{1}H NMR (400 MHz, $CDCl_3$)


198.10
135.58
134.48
132.50
130.19
129.54
128.46
128.41
127.77
126.76
123.89
77.32
77.00
76.68
26.69
O
31
13C NMR (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)



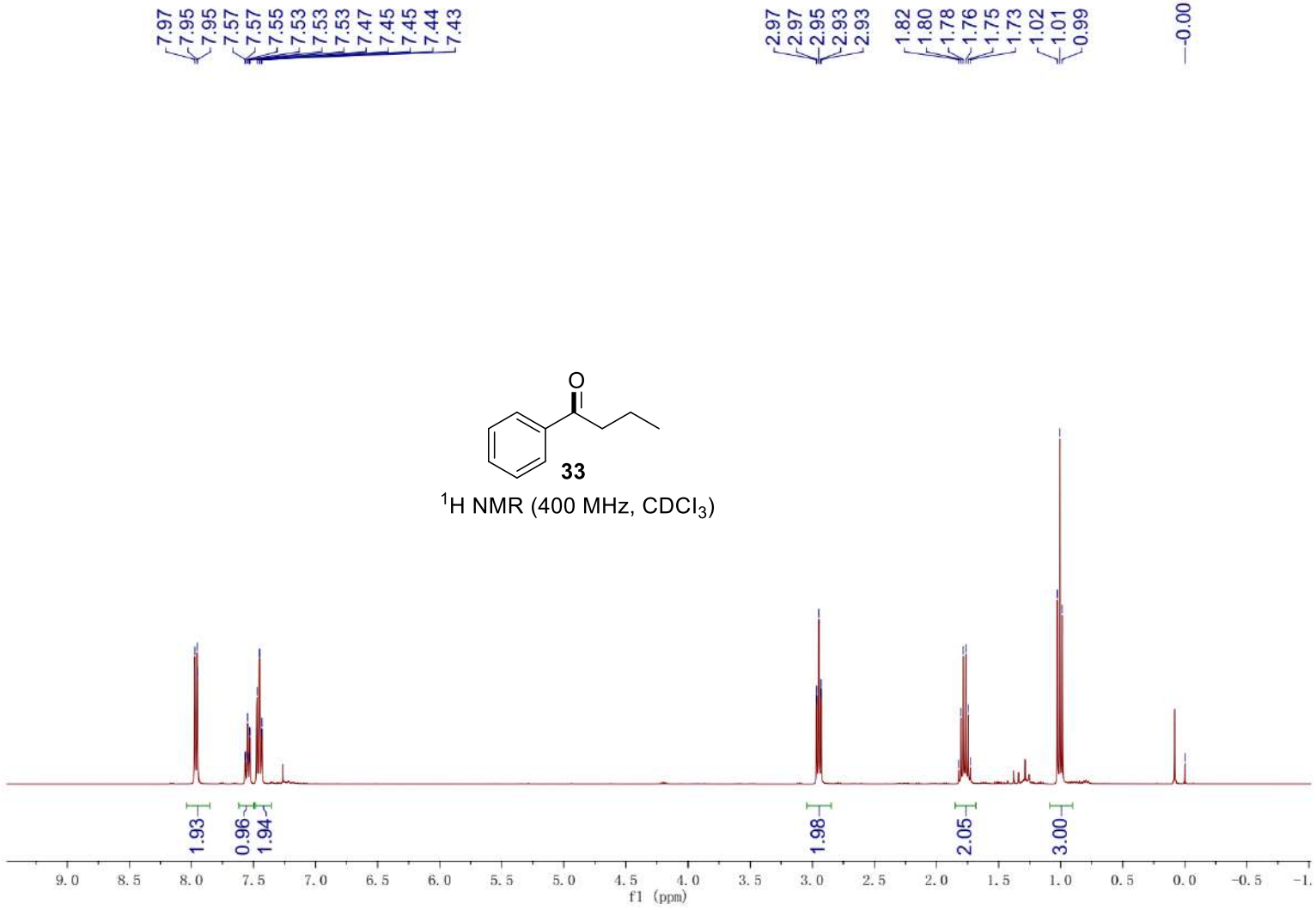
32

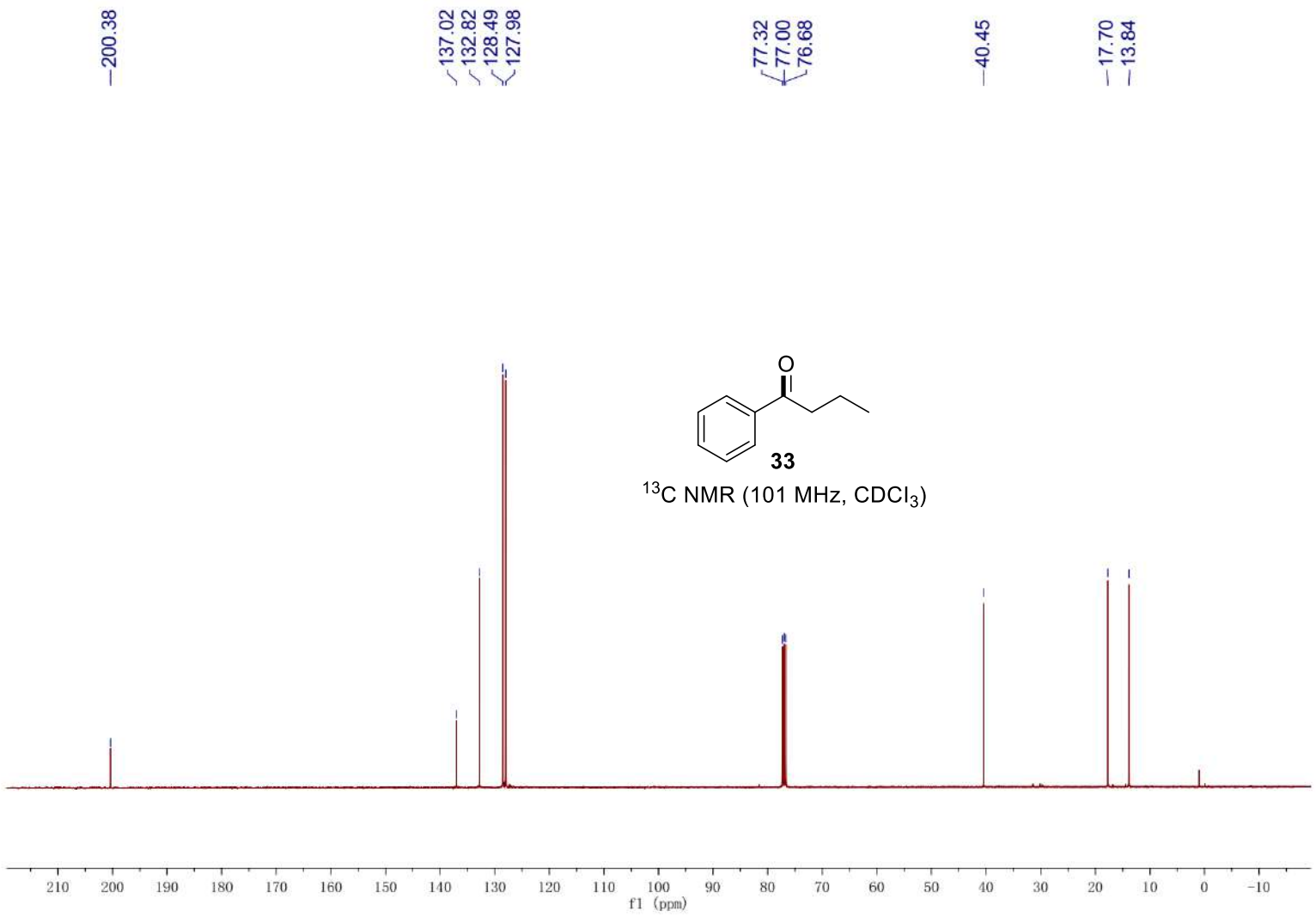
^{1}H NMR (400 MHz, $CDCl_3$)

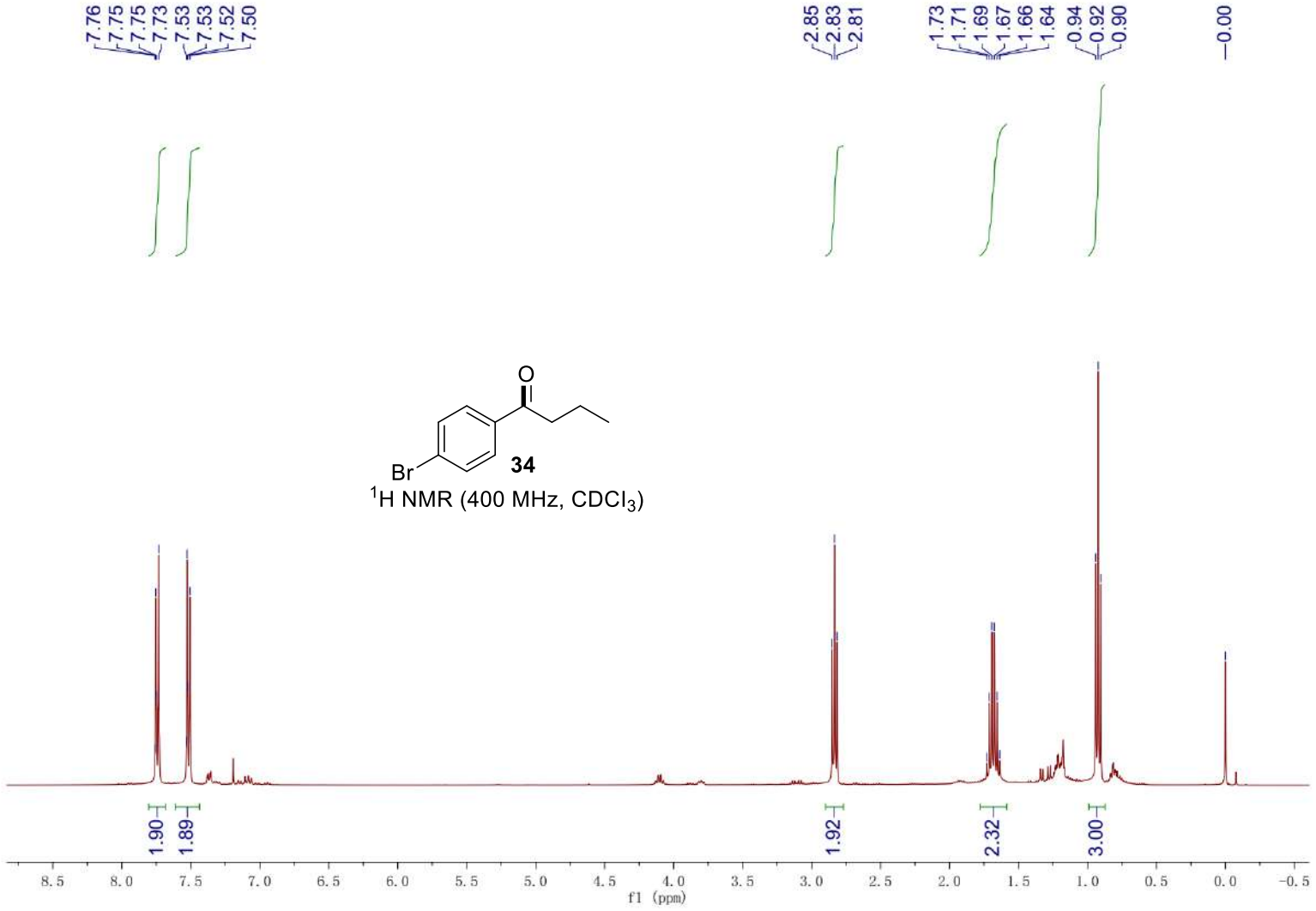


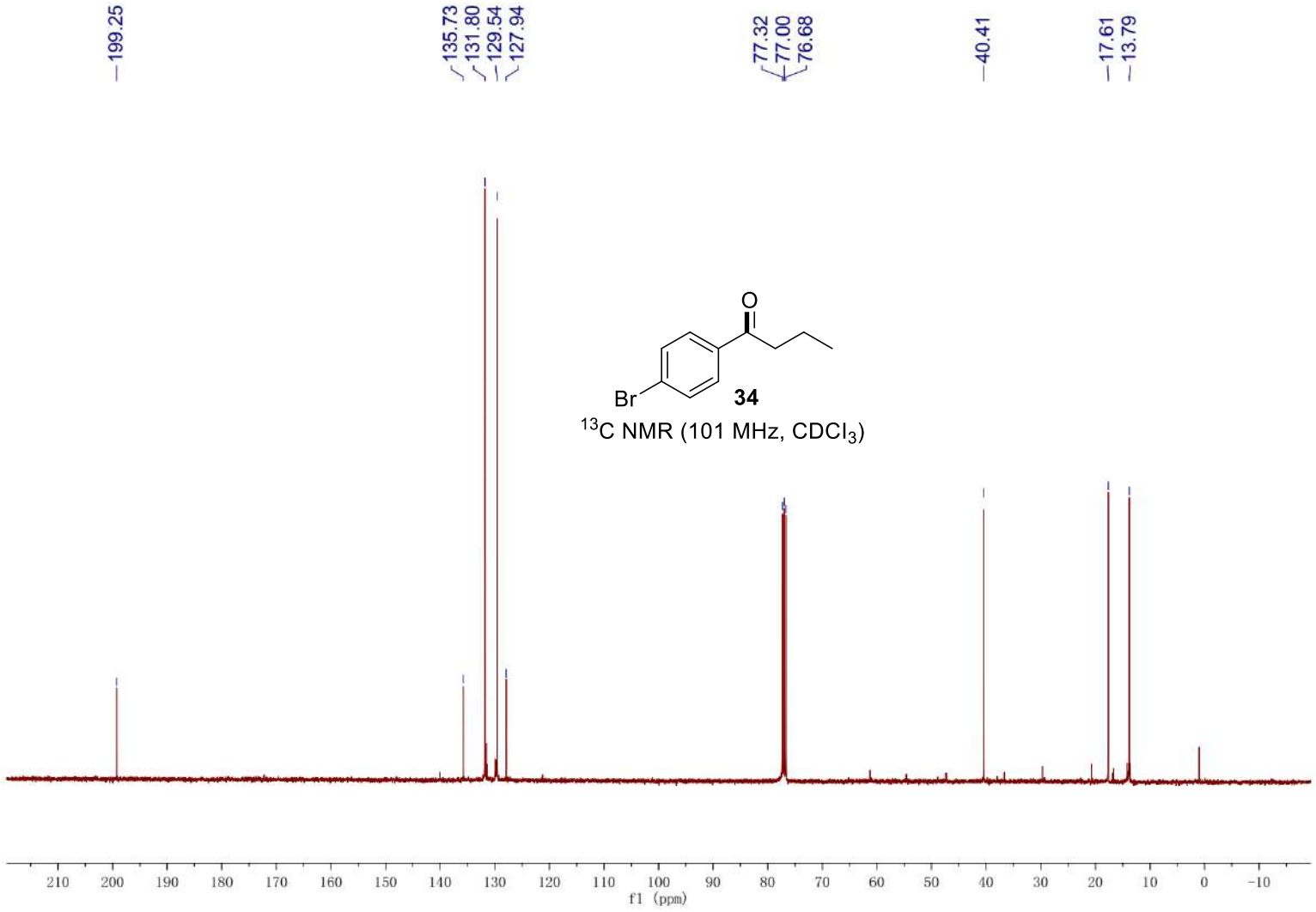
32

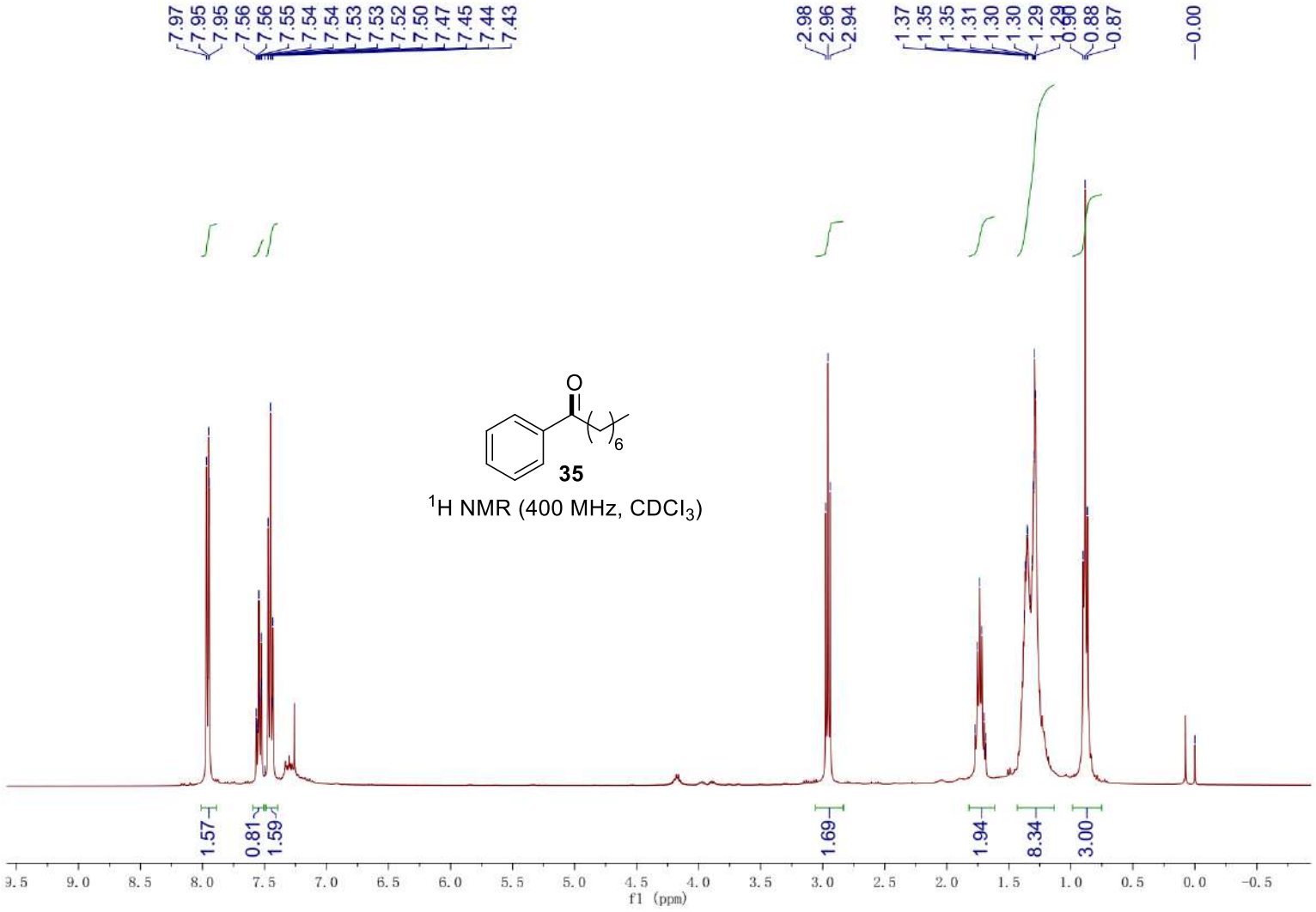
^{13}C NMR (101 MHz, $CDCl_3$)

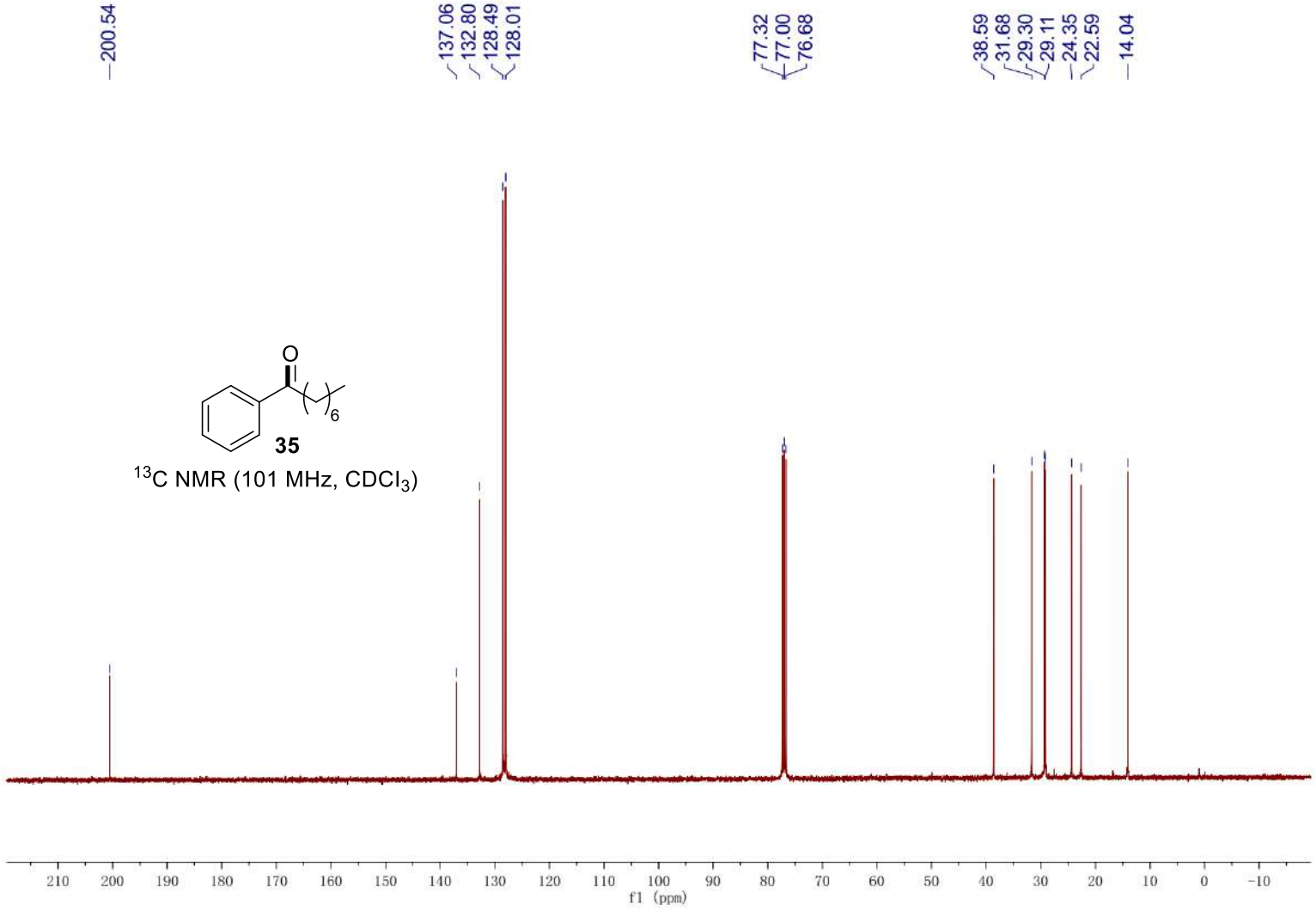

7.97
7.95
7.95
7.57
7.57
7.55
7.53
7.53
7.53
7.47
7.45
7.45
7.44
7.43
2.97
2.97
2.95
2.93
2.93
1.82
1.80
1.78
1.76
1.75
1.73
1.02
1.01
0.99
0.00
O
33
1H NMR (400 MHz, CDCl3)
1.93
0.96
1.94
1.98
2.05
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

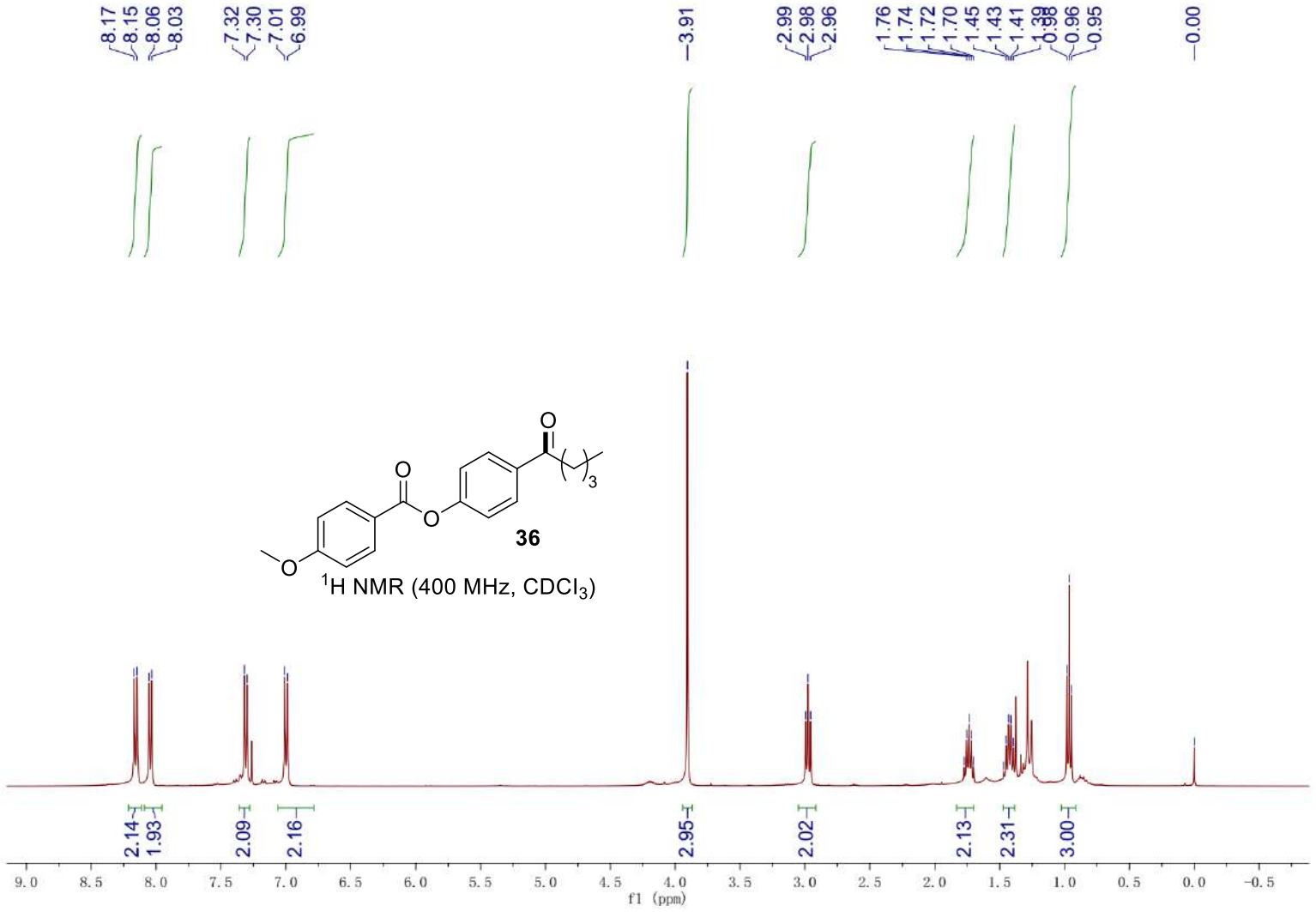

200.38
137.02
132.82
128.49
127.98
77.32
77.00
76.68
40.45
17.70
13.84
O
33
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

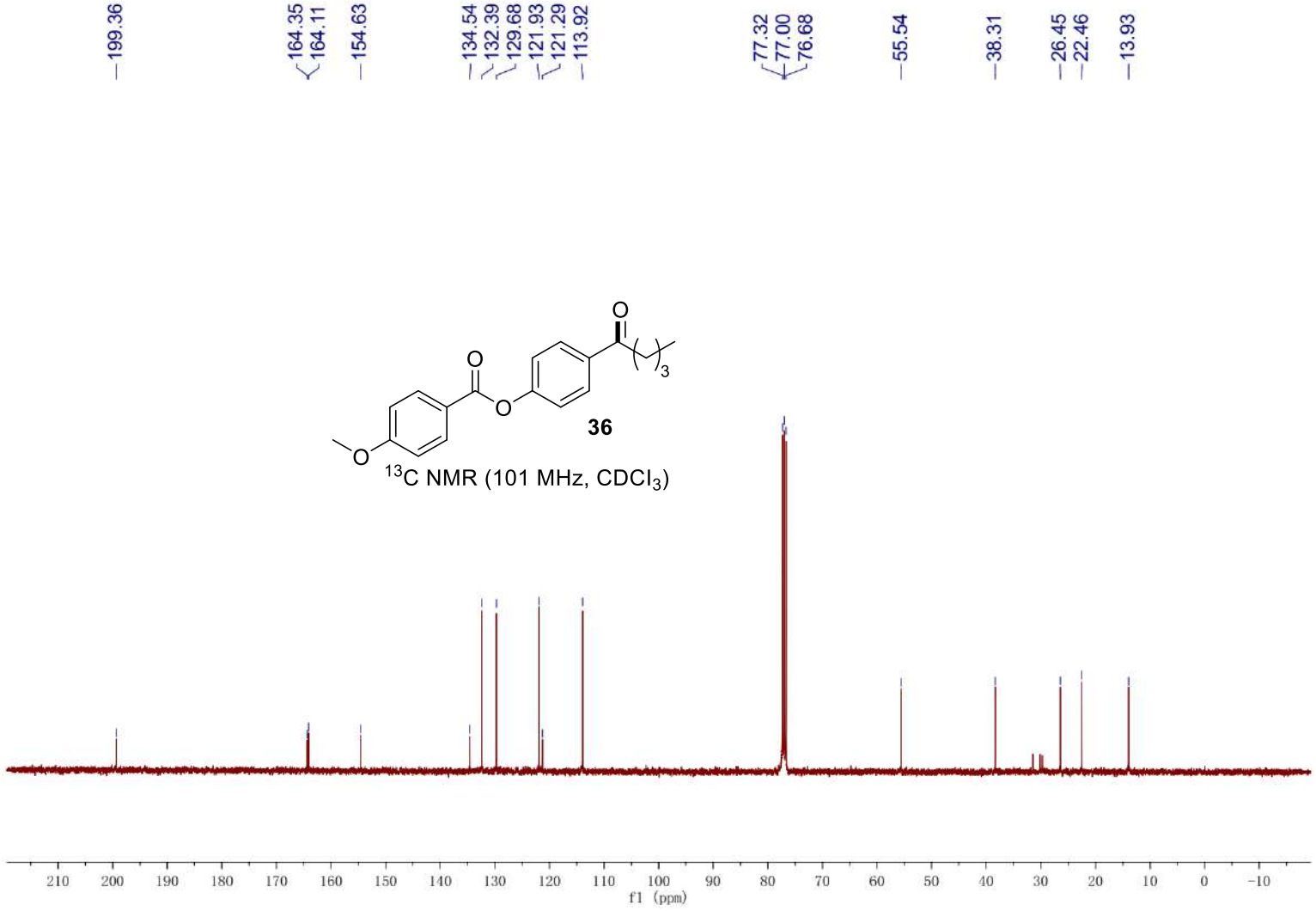

7.76
7.75
7.75
7.73
7.53
7.53
7.52
7.50
2.85
2.83
2.81
1.73
1.71
1.69
1.67
1.66
1.64
0.94
0.92
0.90
0.00
O
Br
34
1H NMR (400 MHz, CDCl3)
1.90
1.89
1.92
2.32
3.00
f1 (ppm)

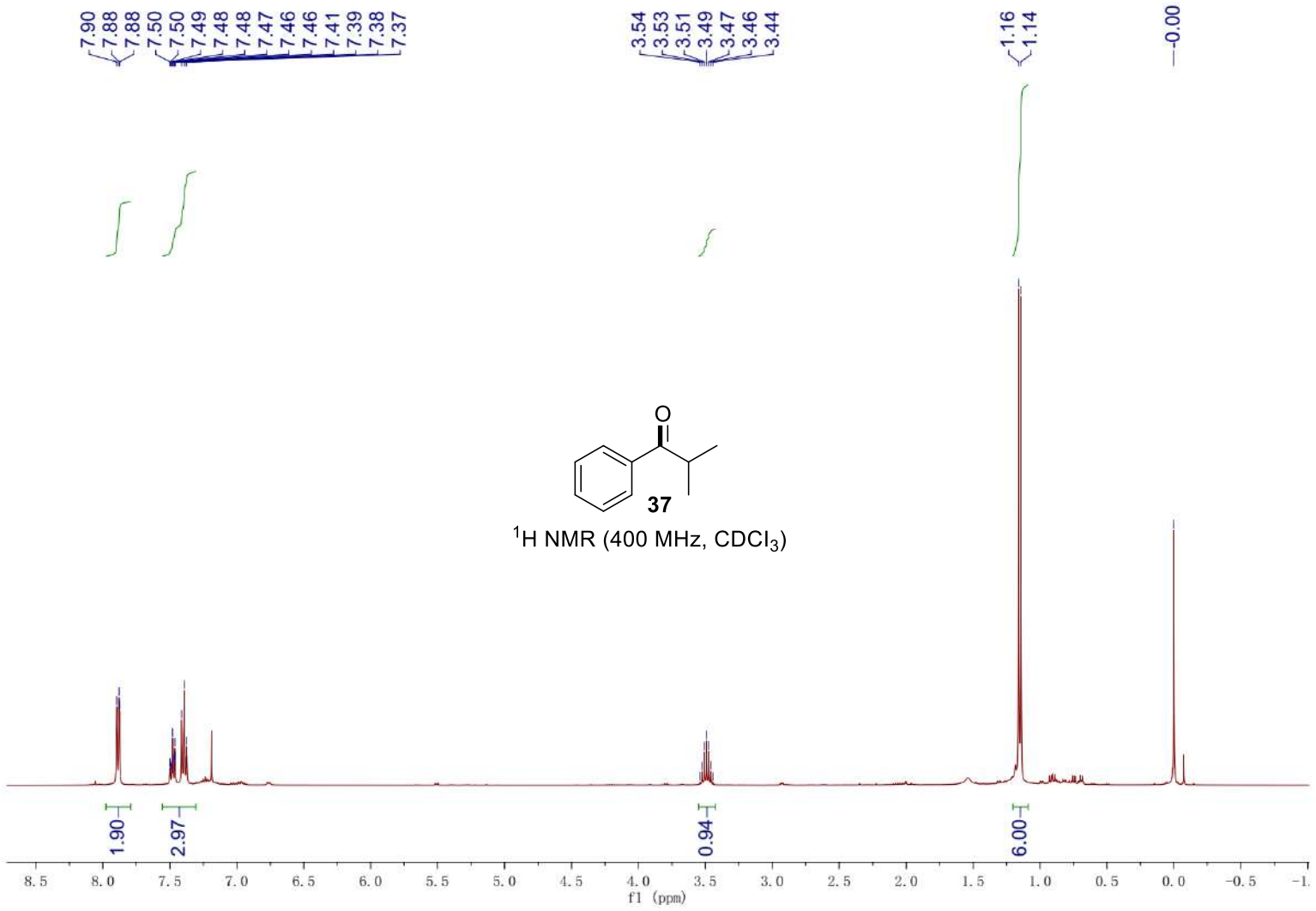

199.25
135.73
131.80
129.54
127.94
77.32
77.00
76.68
40.41
17.61
13.79
O
Br
34
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.97
7.95
7.95
7.56
7.56
7.55
7.54
7.54
7.53
7.53
7.52
7.50
7.47
7.45
7.44
7.43
2.98
2.96
2.94
1.37
1.35
1.35
1.31
1.30
1.30
1.29
0.90
0.88
0.87
0.00
O
6
35
1H NMR (400 MHz, CDCl3)
1.57
0.81
1.59
1.69
1.94
8.34
3.00
f1 (ppm)


200.54
137.06
132.80
128.49
128.01
77.32
77.00
76.68
38.59
31.68
29.30
29.11
24.35
22.59
14.04
O
6
35
^{13}C NMR (101 MHz, $CDCl_3$)
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)

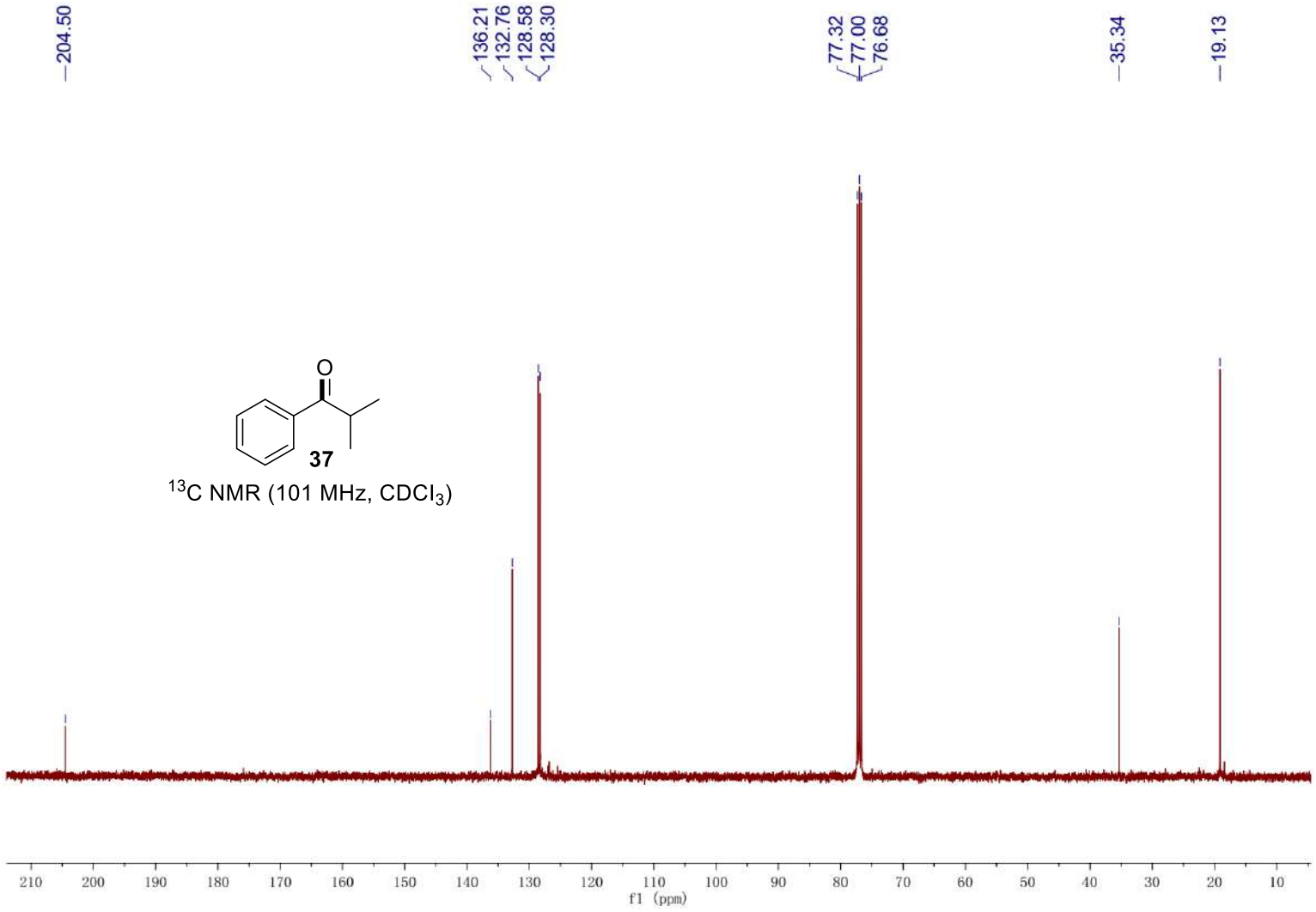

8.17
8.15
8.06
8.03
7.32
7.30
7.01
6.99
3.91
2.99
2.98
2.96
1.76
1.74
1.72
1.70
1.45
1.43
1.41
0.96
0.95
0.00
O
O
O
3
O
36
^{1}H NMR (400 MHz, CDCl$_3$)
2.14
1.93
2.09
2.16
2.95
2.02
2.13
2.31
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

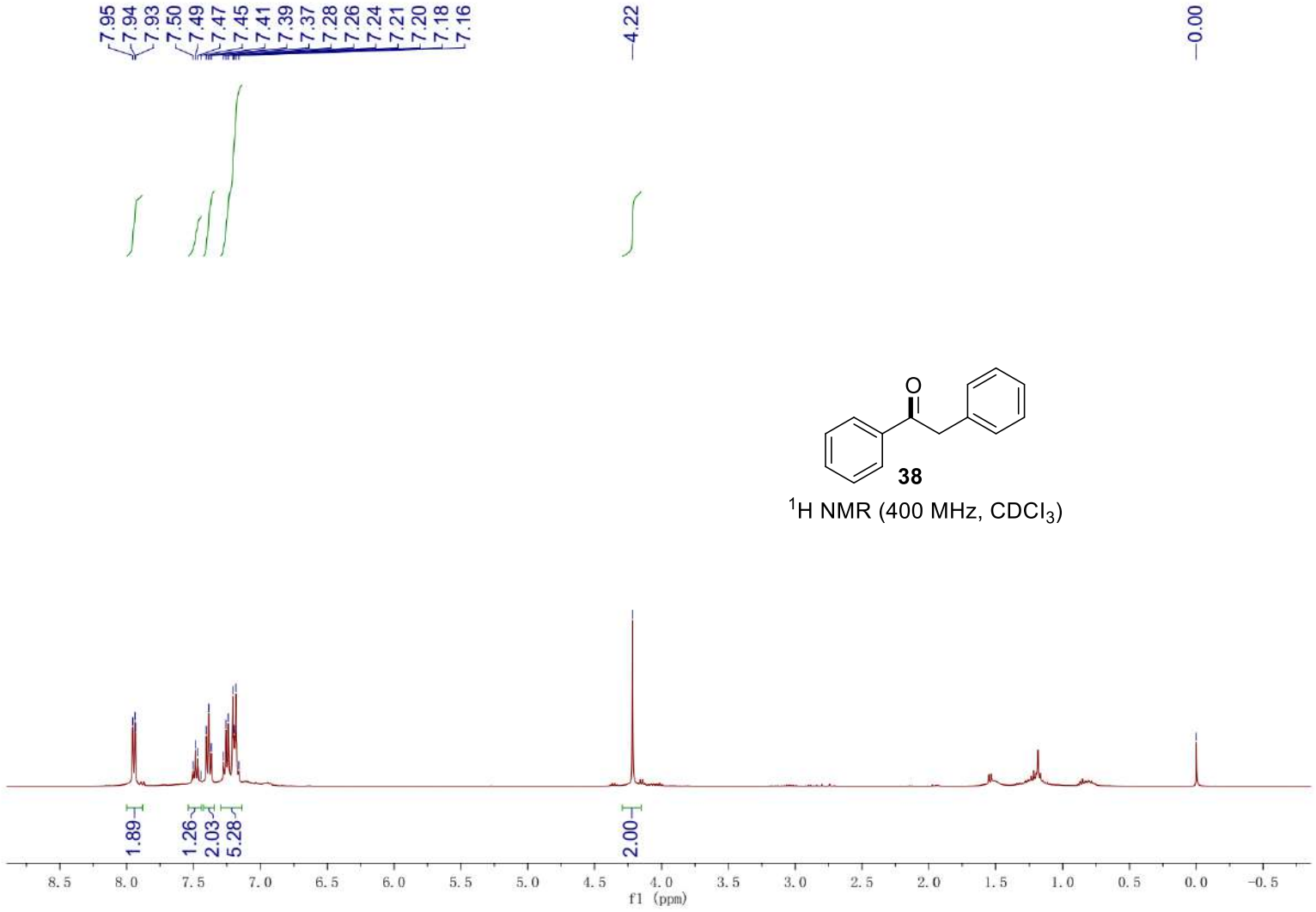

199.36
164.35
164.11
154.63
134.54
132.39
129.68
121.93
121.29
113.92
77.32
77.00
76.68
55.54
38.31
26.45
22.46
13.93
O
O
O
3
O
36
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

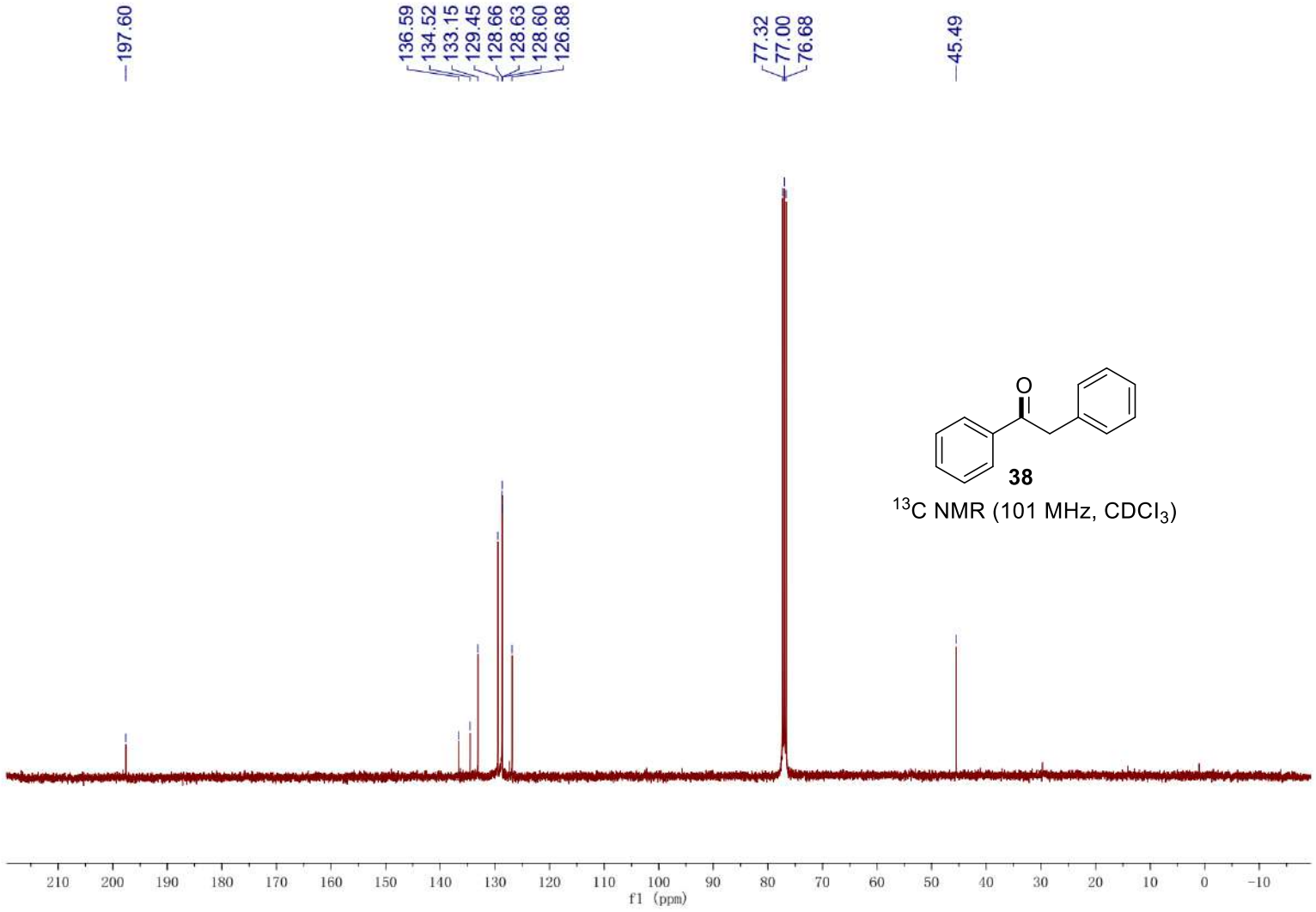


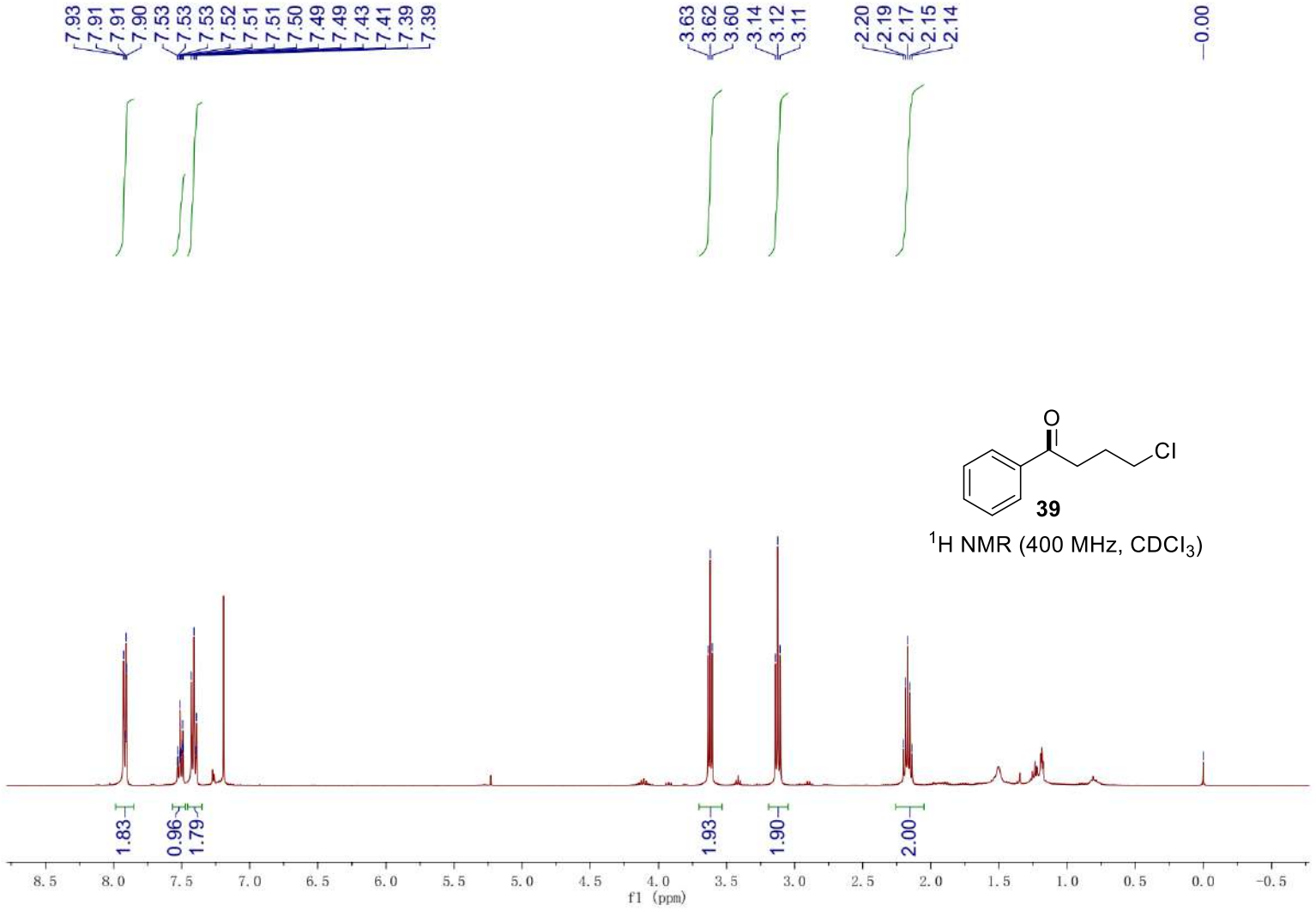
37

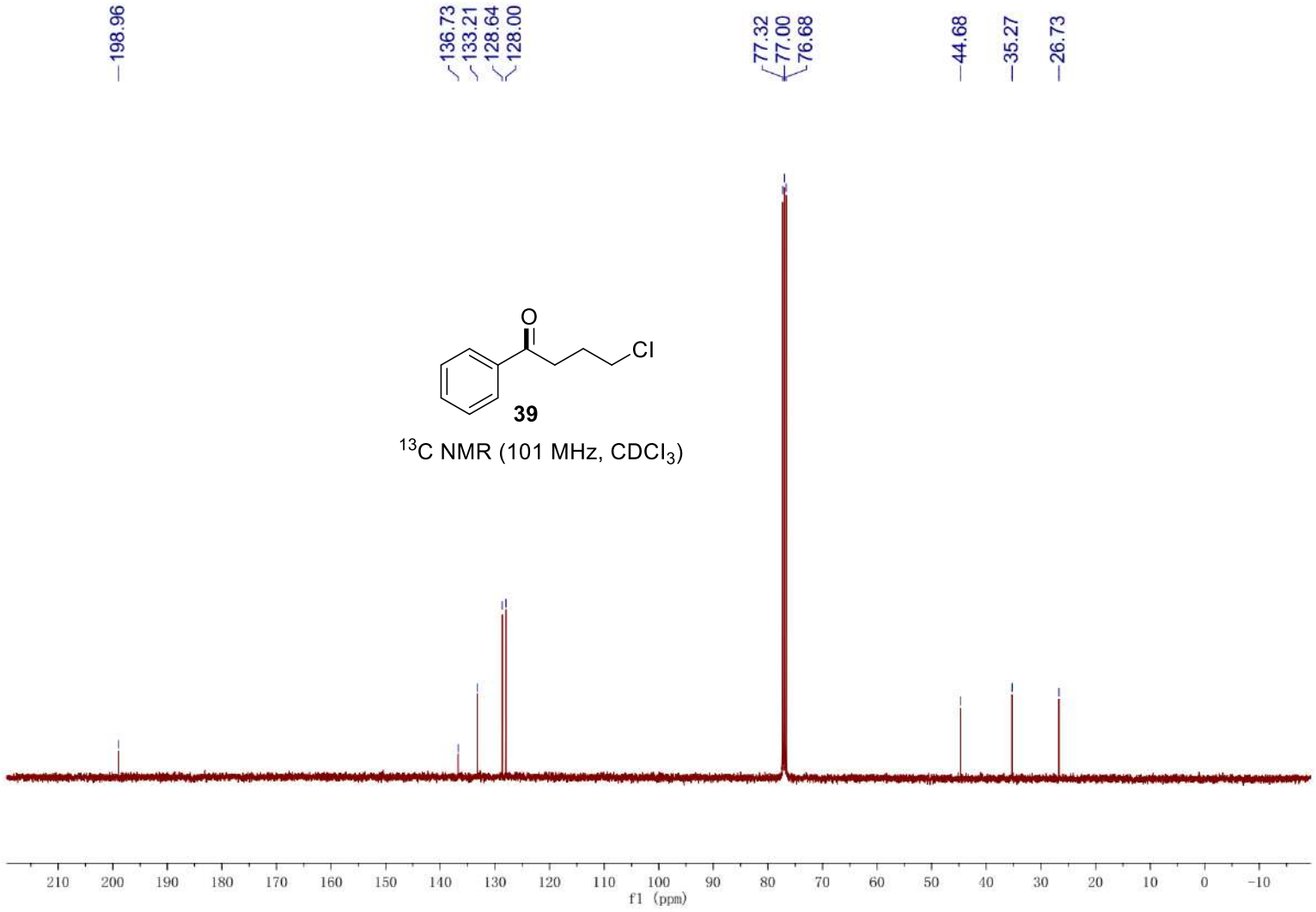
^{1}H NMR (400 MHz, $CDCl_3$)

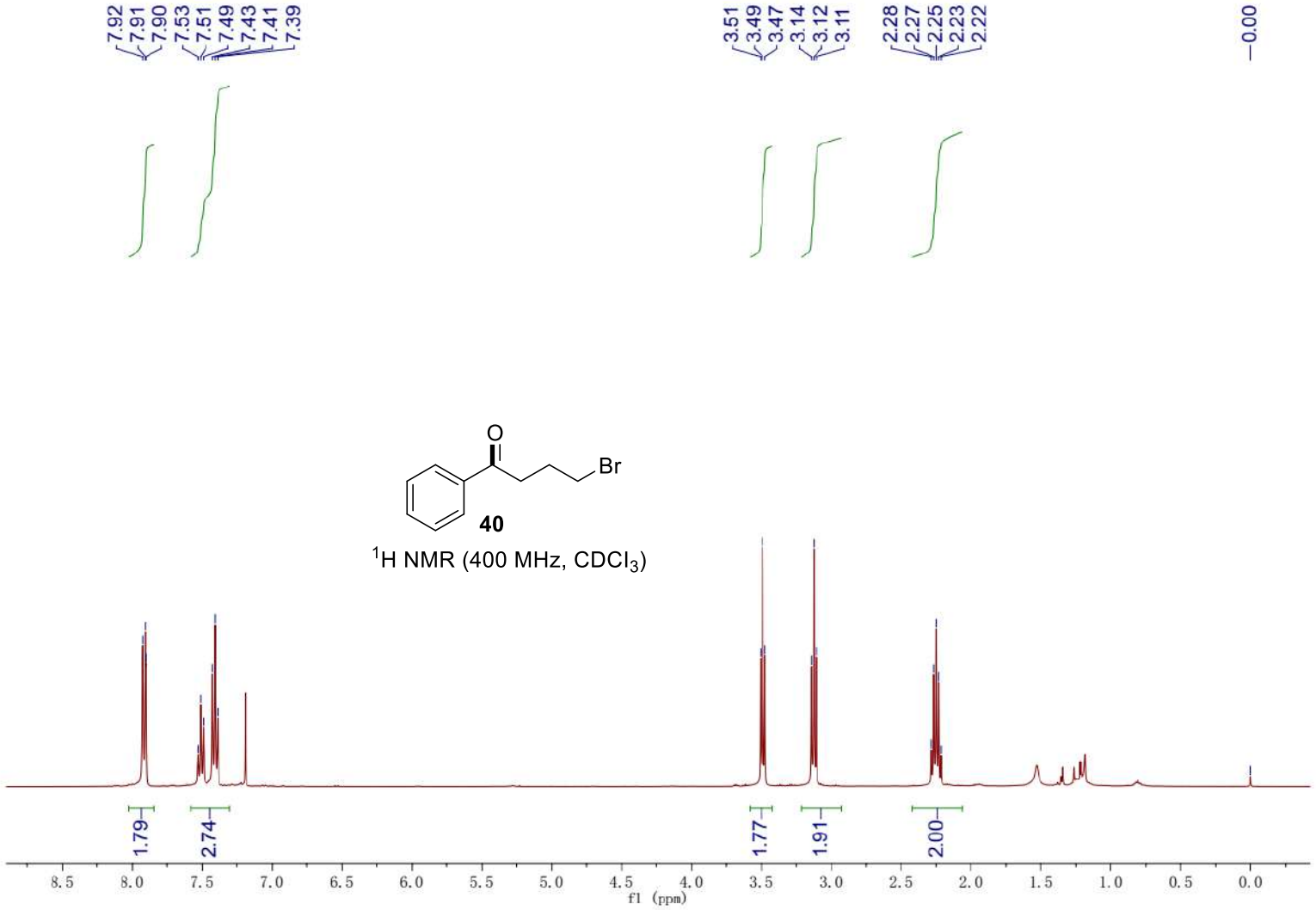

204.50
136.21
132.76
128.58
128.30
77.32
77.00
76.68
35.34
19.13
O
37
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

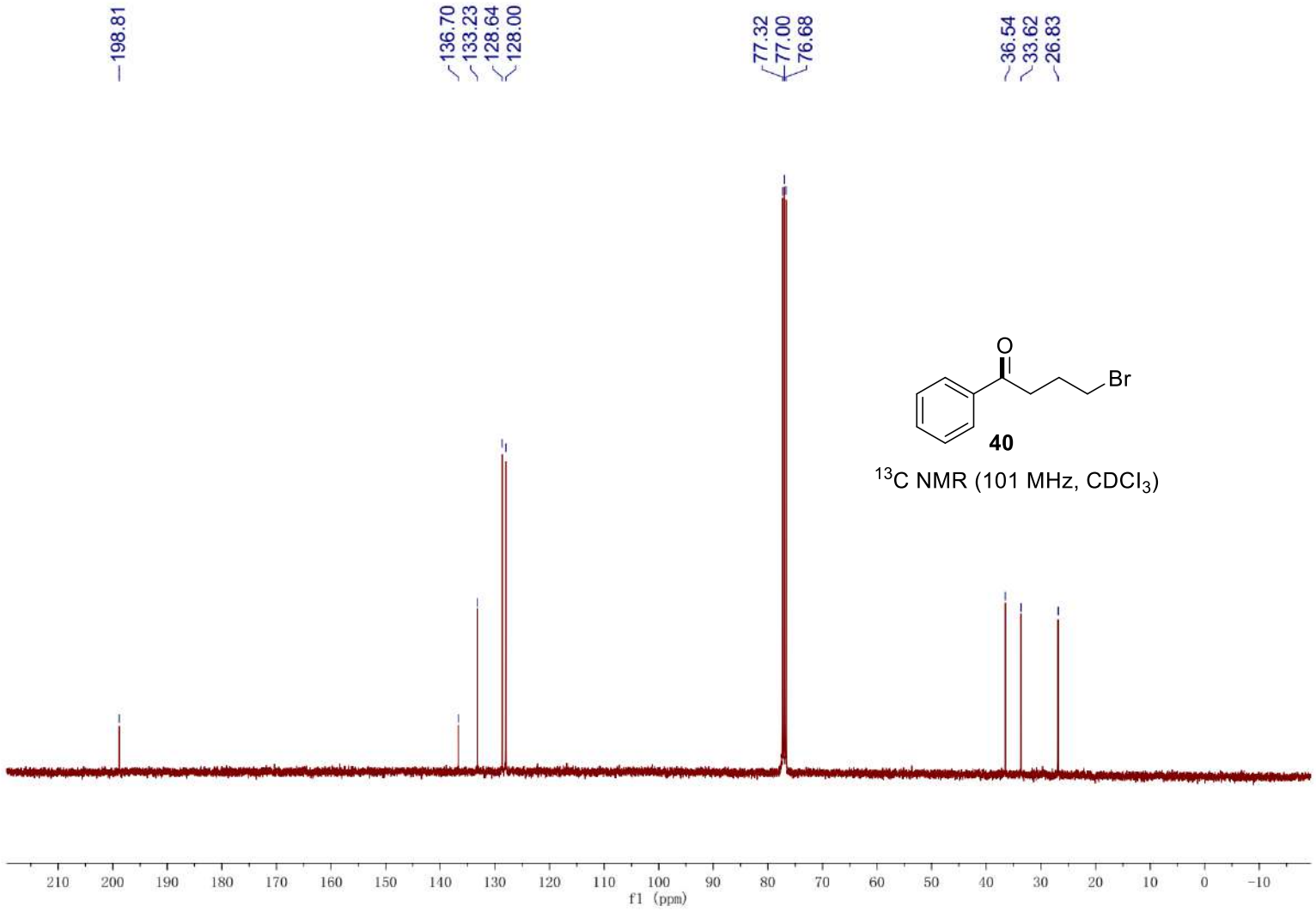

7.95
7.94
7.93
7.50
7.49
7.47
7.45
7.41
7.39
7.37
7.28
7.26
7.24
7.21
7.20
7.18
7.16
4.22
0.00
O
38
^{1}H NMR (400 MHz, $CDCl_3$)
1.89
1.26
2.03
5.28
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

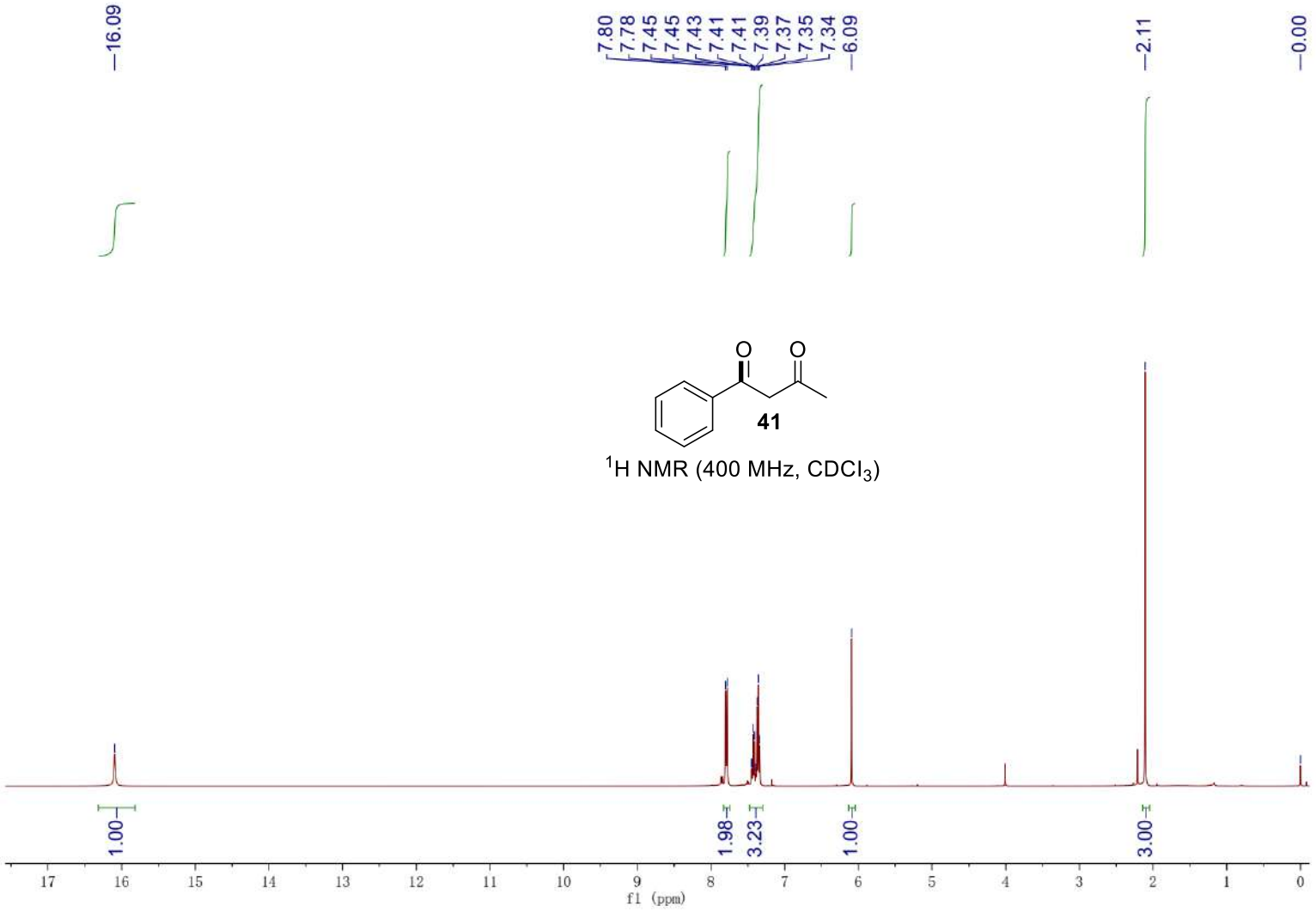

197.60
136.59
134.52
133.15
129.45
128.66
128.63
128.60
126.88
77.32
77.00
76.68
45.49
O
38
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.93
7.91
7.91
7.90
7.53
7.53
7.53
7.52
7.51
7.51
7.50
7.49
7.49
7.43
7.41
7.39
7.39
3.63
3.62
3.60
3.14
3.12
3.11
2.20
2.19
2.17
2.15
2.14
0.00
O
Cl
39
1H NMR (400 MHz, CDCl3)
1.83
0.96
1.79
1.93
1.90
2.00
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
-0.5
f1 (ppm)

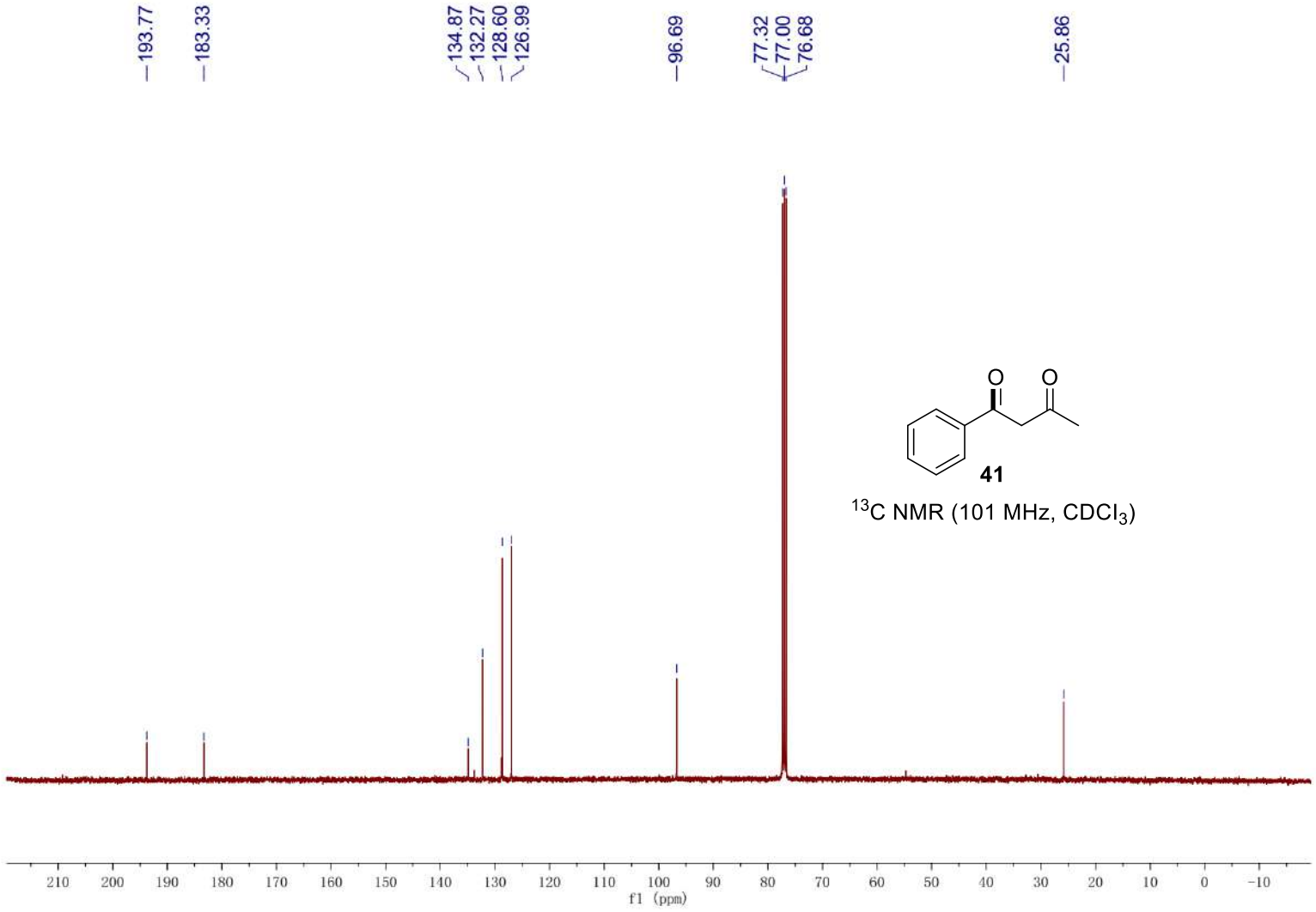

198.96
136.73
133.21
128.64
128.00
77.32
77.00
76.68
44.68
35.27
26.73
O
Cl
39
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

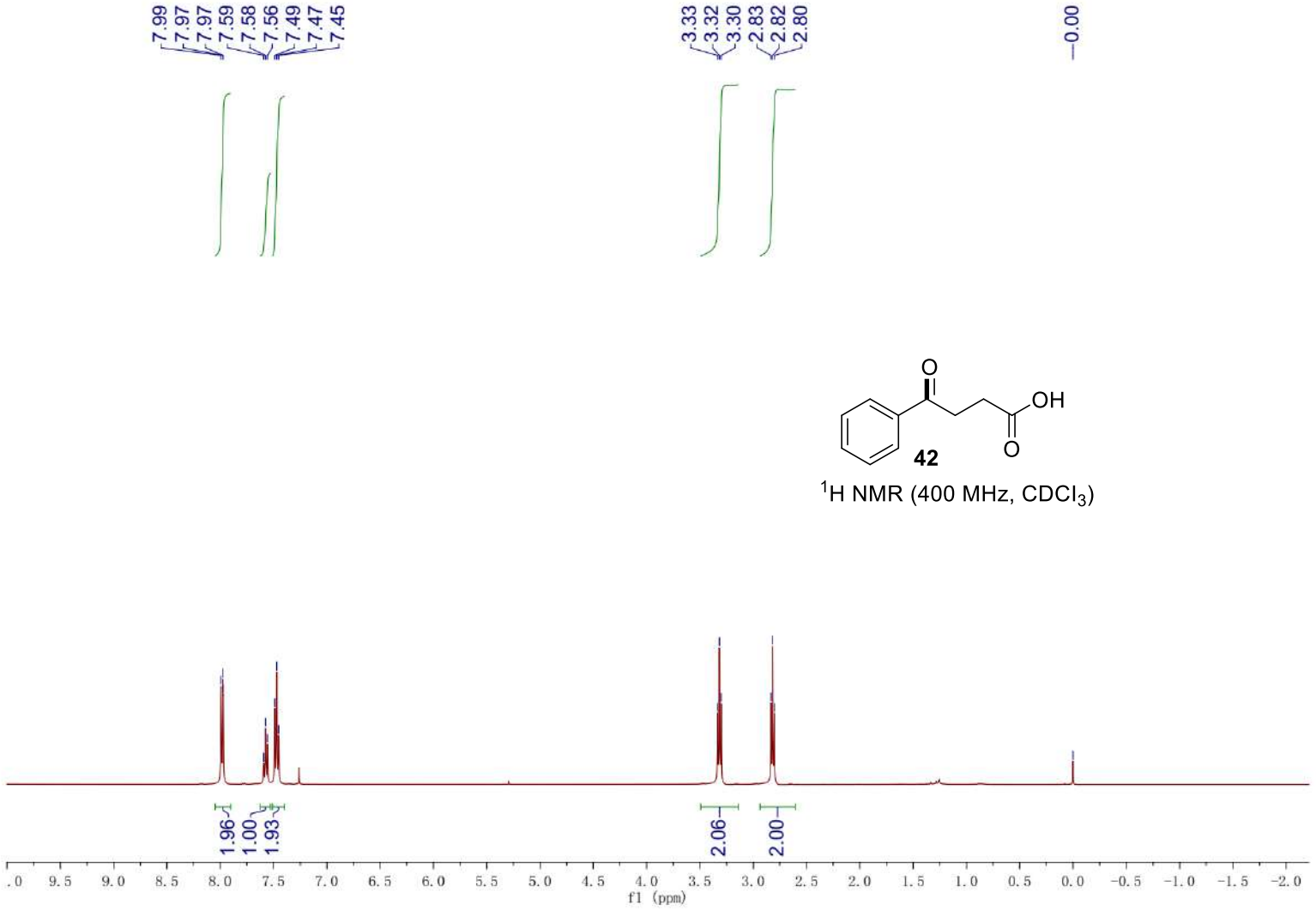

7.92
7.91
7.90
7.53
7.51
7.49
7.43
7.41
7.39
3.51
3.49
3.47
3.14
3.12
3.11
2.28
2.27
2.25
2.23
2.22
0.00
O
Br
40
1H NMR (400 MHz, CDCl3)
1.79
2.74
1.77
1.91
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


198.81
136.70
133.23
128.64
128.00
77.32
77.00
76.68
36.54
33.62
26.83
O
Br
40
^{13}C NMR (101 MHz, $CDCl_3$)
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)

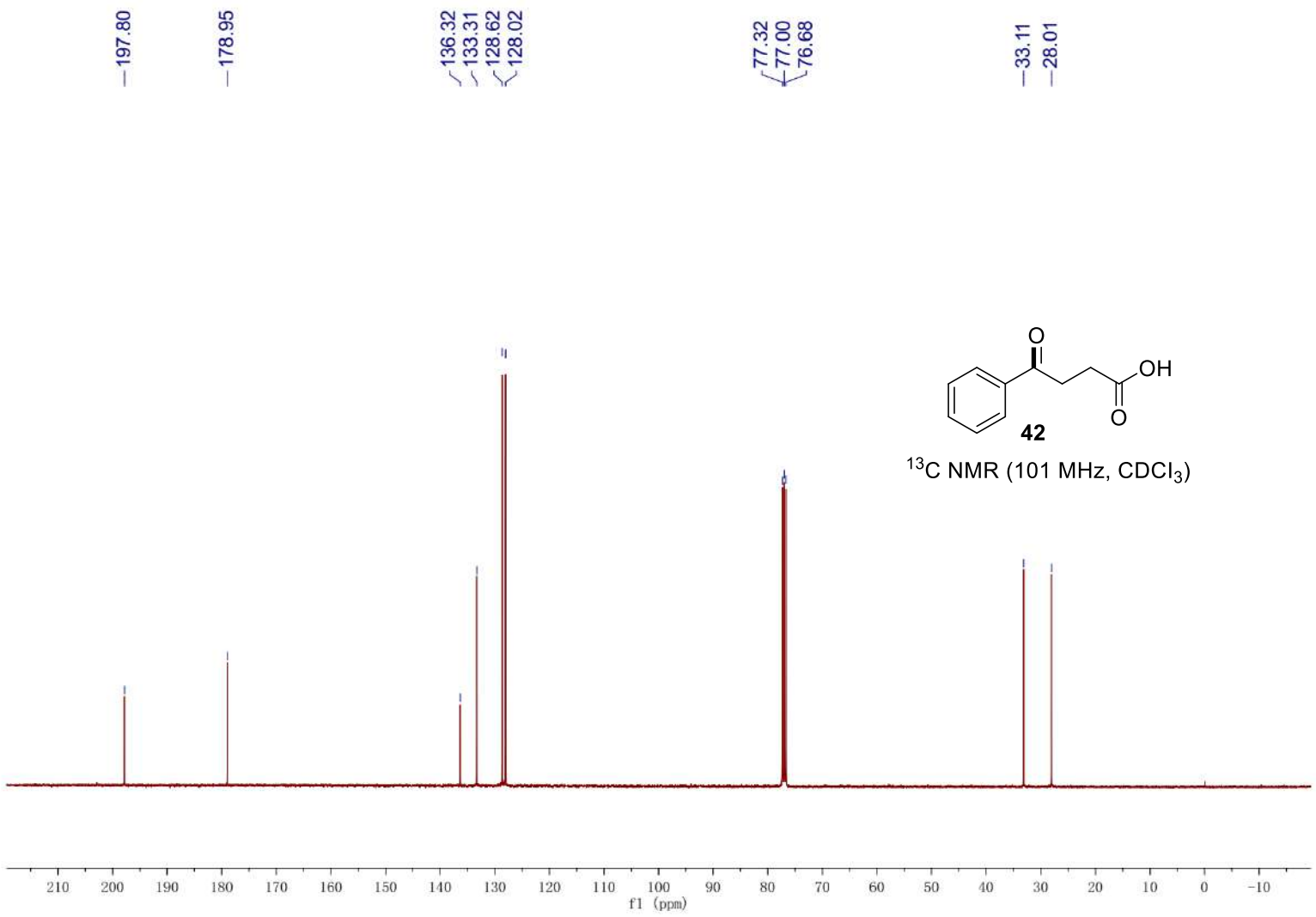


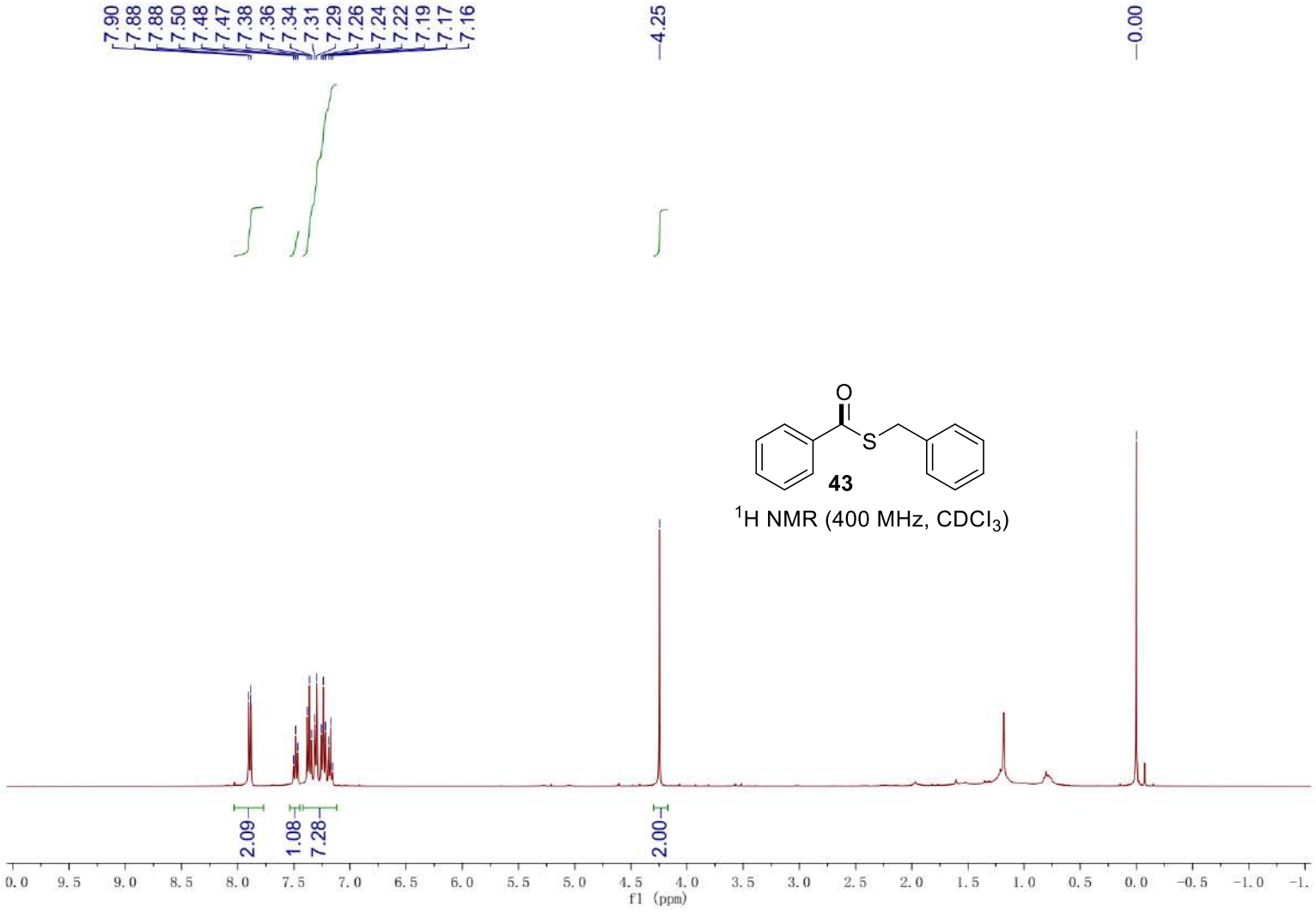
^{1}H NMR (400 MHz, $CDCl_3$)

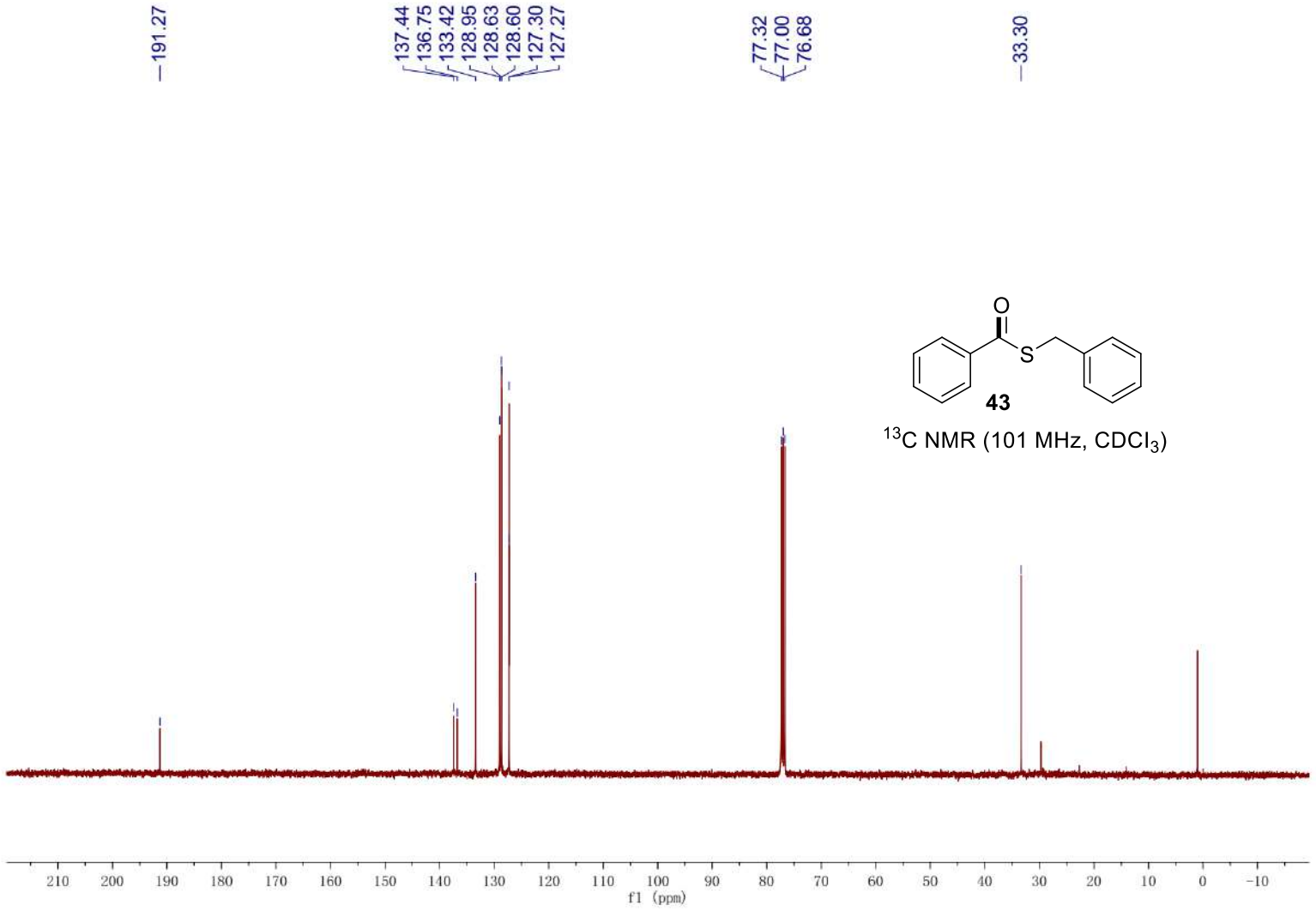

193.77
183.33
134.87
132.27
128.60
126.99
96.69
77.32
77.00
76.68
25.86
O
O
41
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

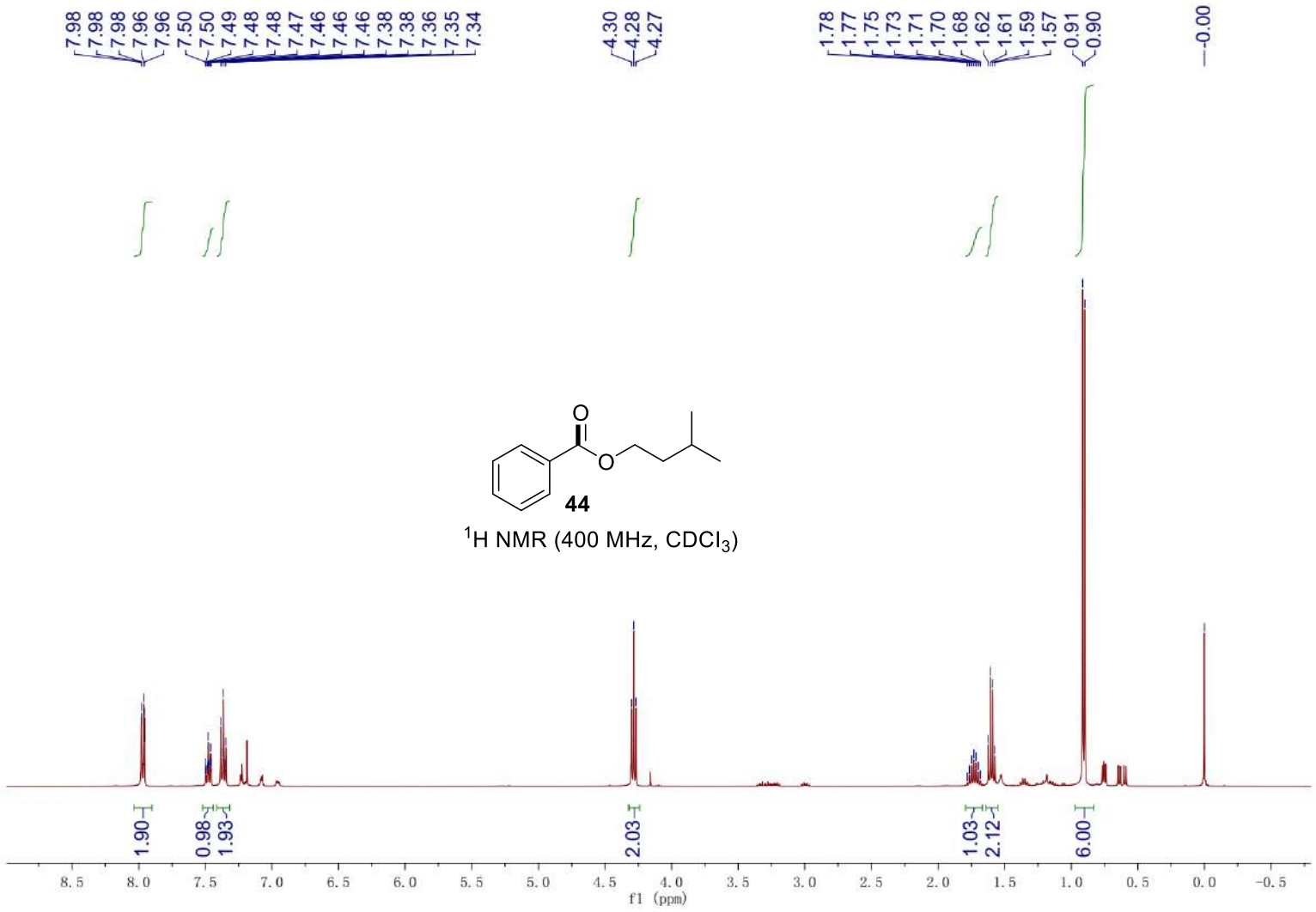


^{1}H NMR (400 MHz, $CDCl_3$)


197.80
178.95
136.32
133.31
128.62
128.02
77.32
77.00
76.68
33.11
28.01
O
OH
O
42
^{13}C NMR (101 MHz, $CDCl_3$)
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)

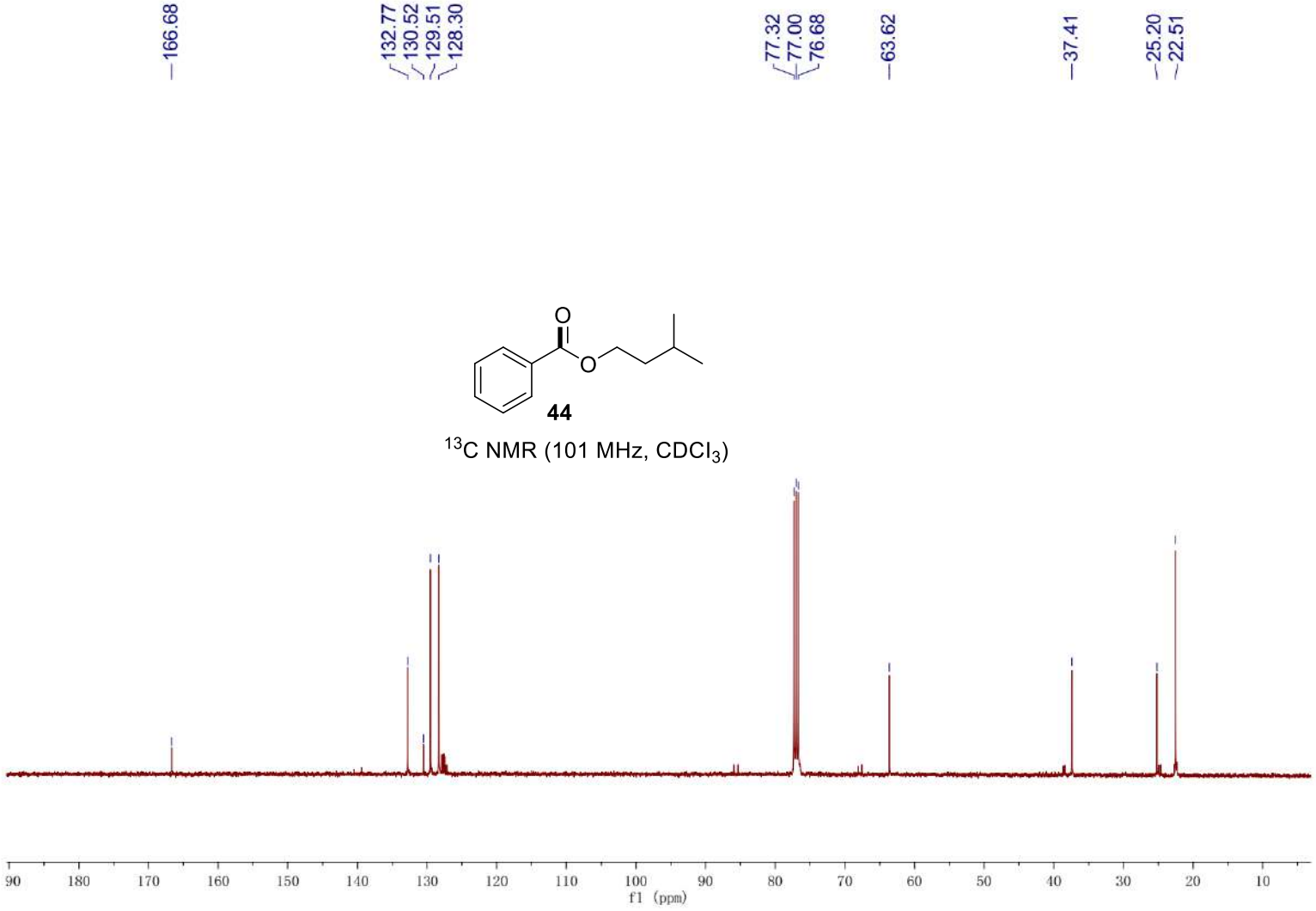

7.90
7.88
7.88
7.50
7.48
7.47
7.38
7.36
7.34
7.31
7.29
7.26
7.24
7.22
7.19
7.17
7.16
4.25
0.00
O
S
43
1H NMR (400 MHz, CDCl3)
2.09
1.08
7.28
2.00
f1 (ppm)

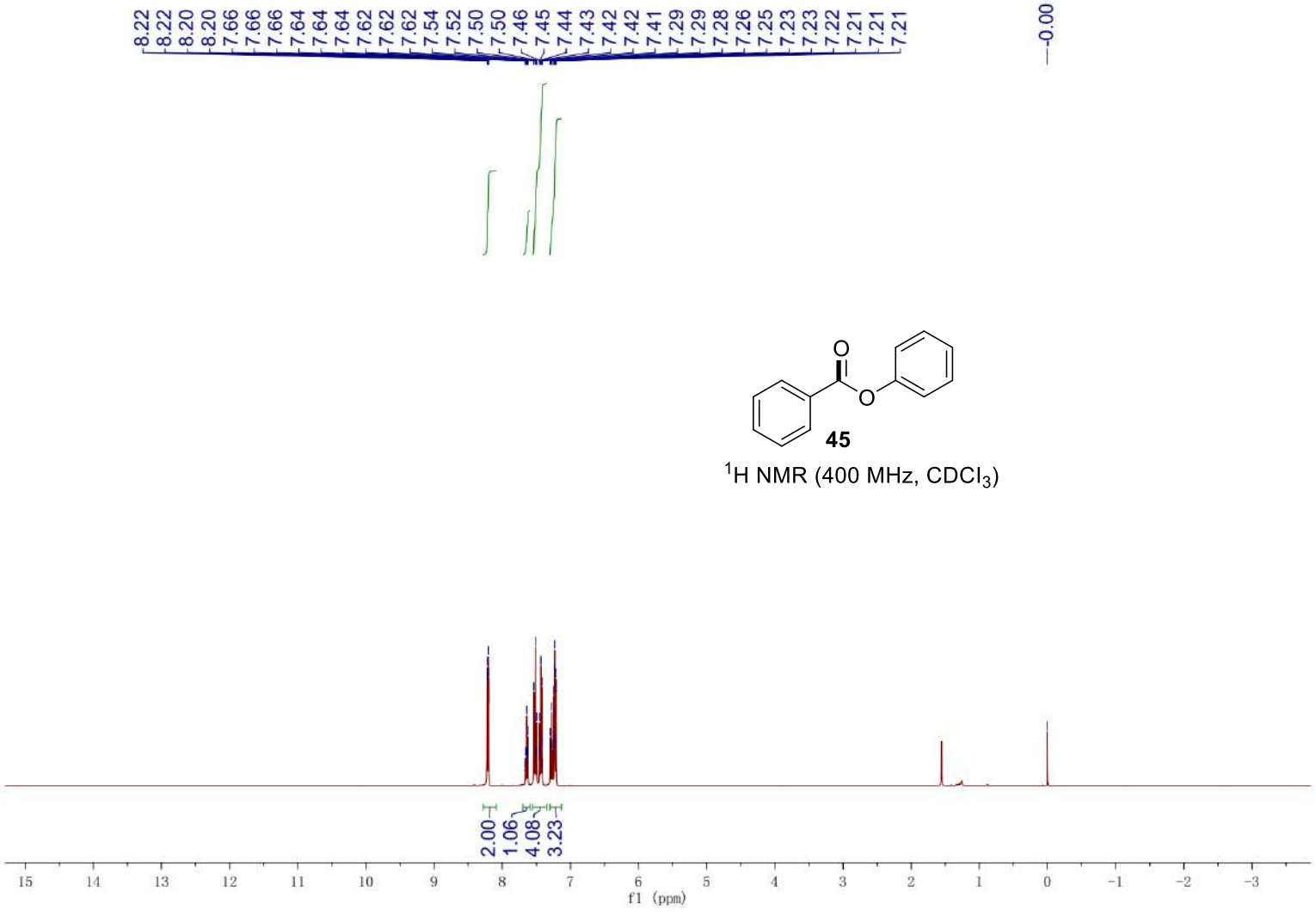

191.27
137.44
136.75
133.42
128.95
128.63
128.60
127.30
127.27
77.32
77.00
76.68
33.30
O
S
43
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

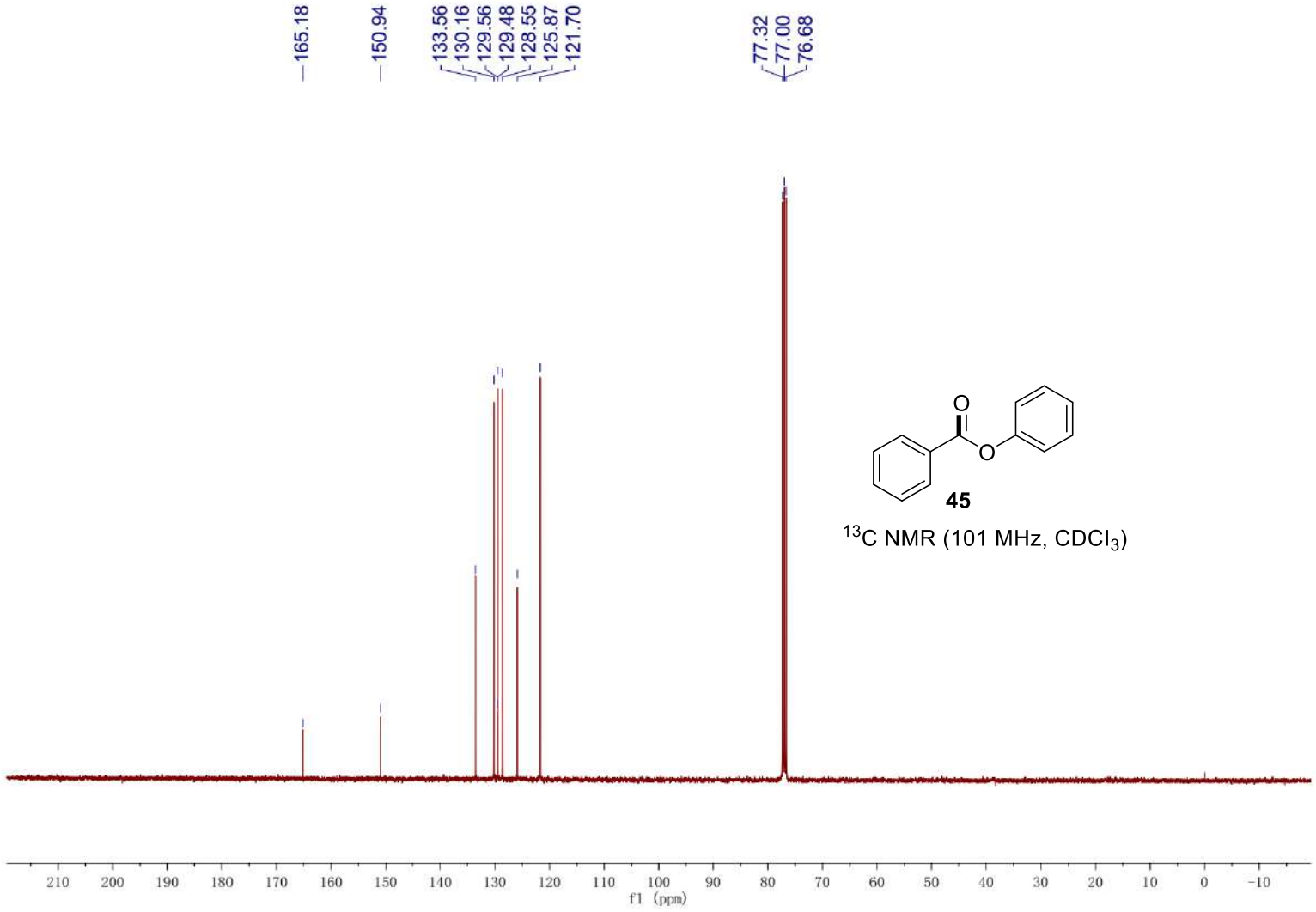


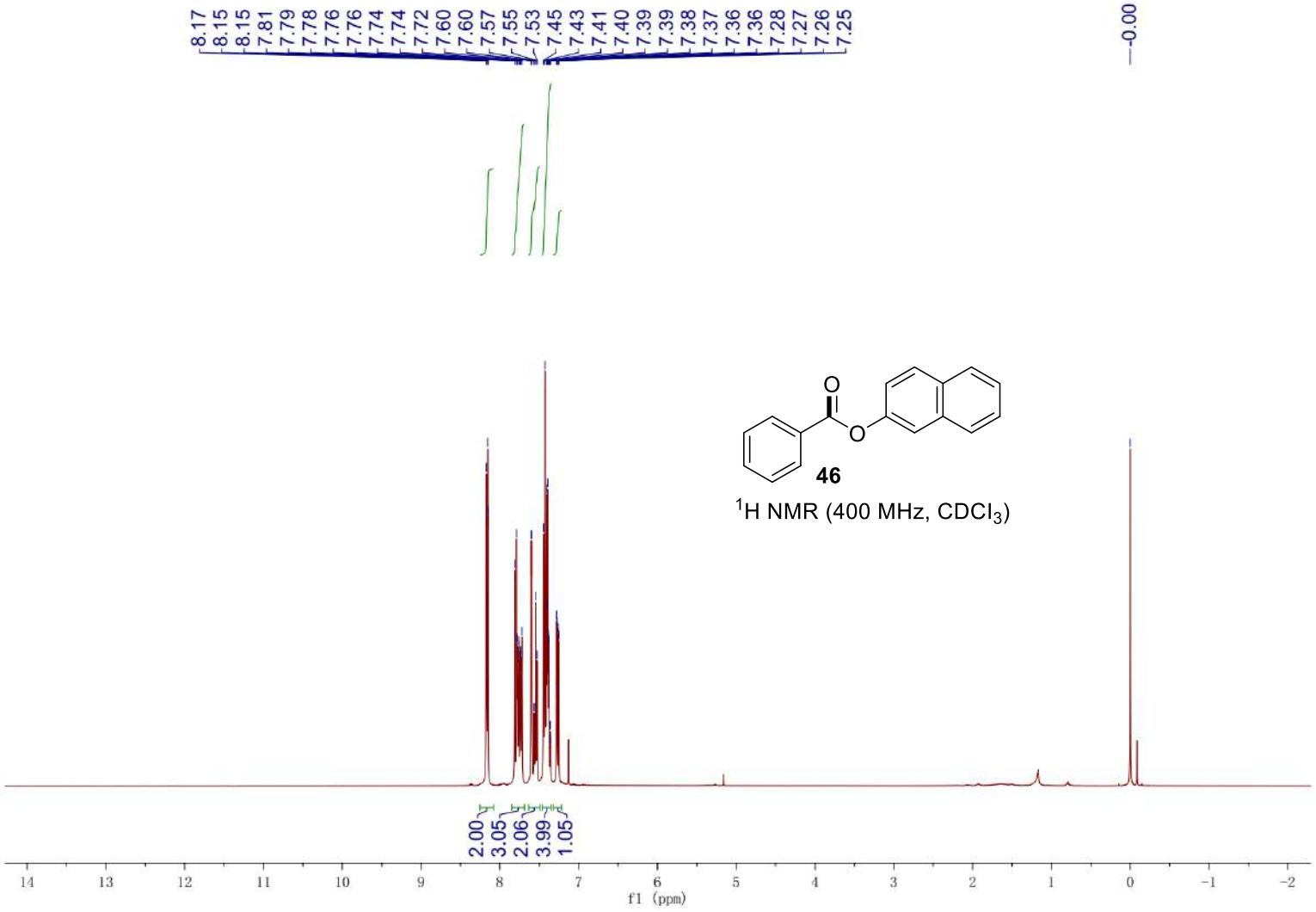
44

^{1}H NMR (400 MHz, $CDCl_3$)


166.68
132.77
130.52
129.51
128.30
77.32
77.00
76.68
63.62
37.41
25.20
22.51
O
O
44
^{13}C NMR (101 MHz, $CDCl_3$)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

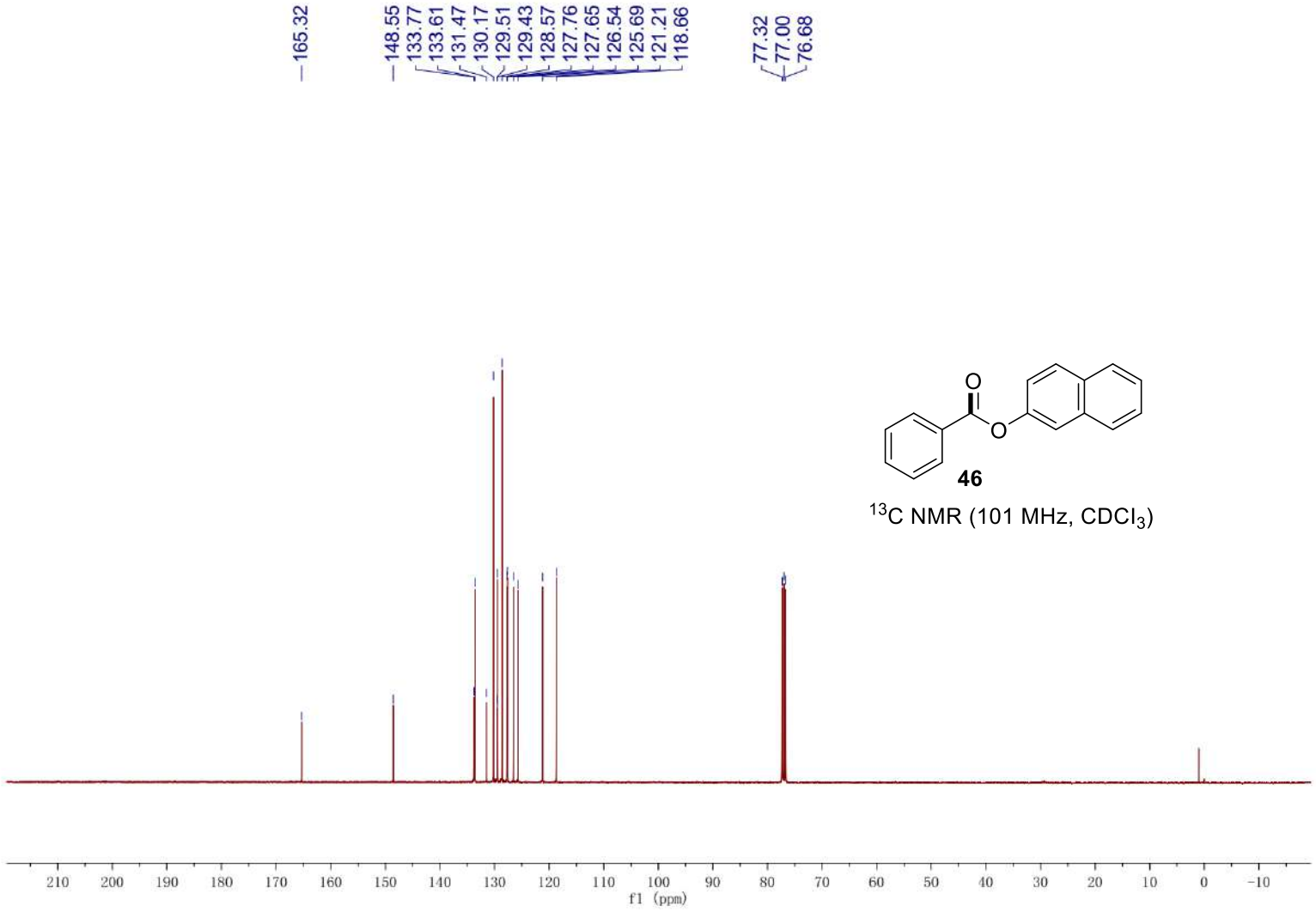

8.22
8.22
8.20
8.20
7.66
7.66
7.66
7.64
7.64
7.64
7.62
7.62
7.62
7.54
7.52
7.50
7.50
7.46
7.45
7.44
7.43
7.42
7.42
7.41
7.29
7.29
7.28
7.26
7.25
7.23
7.23
7.22
7.21
7.21
7.21
0.00
O
O
45
1H NMR (400 MHz, CDCl3)
2.00
1.06
4.08
3.23
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)

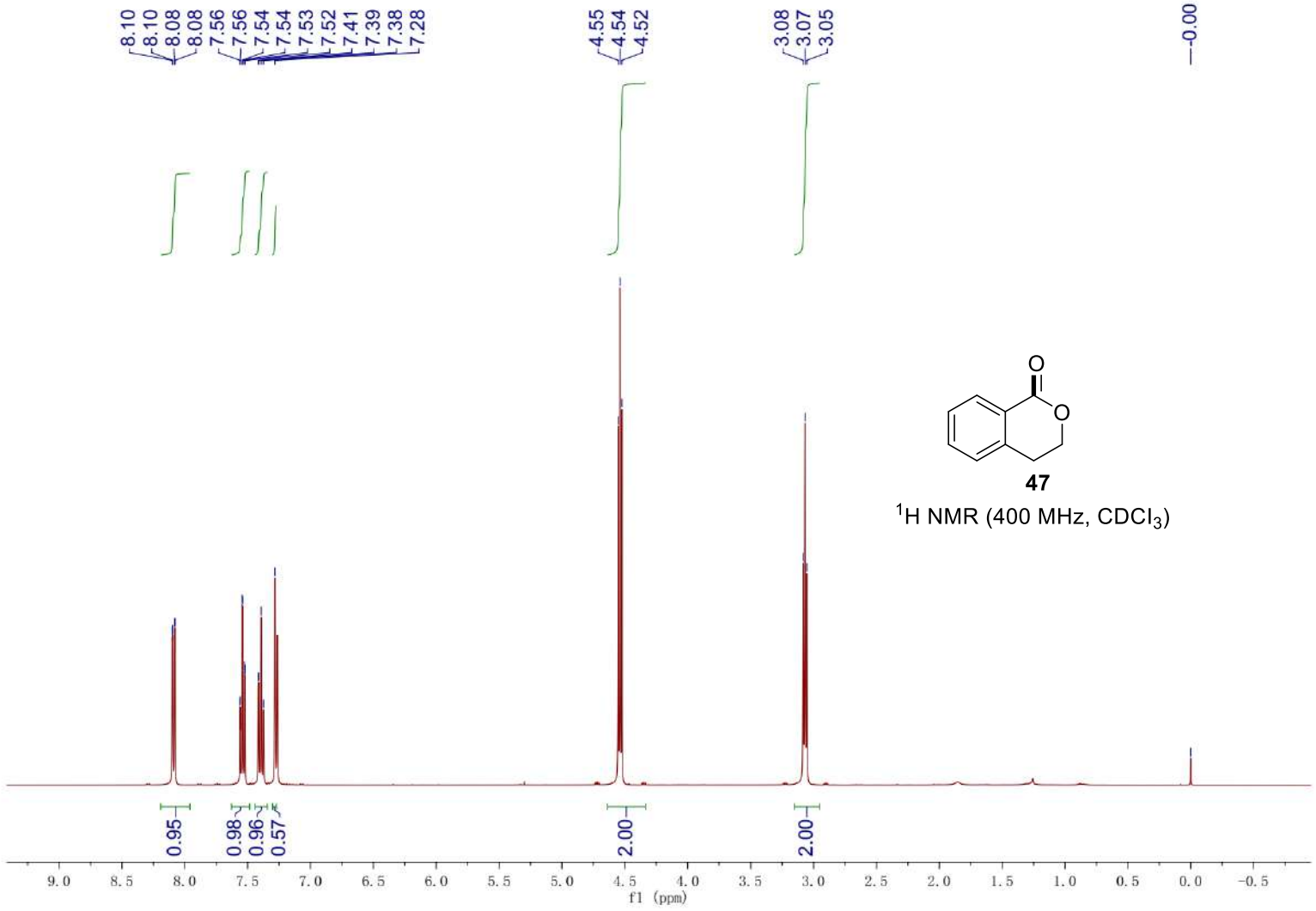

165.18
150.94
133.56
130.16
129.56
129.48
128.55
125.87
121.70
77.32
77.00
76.68
O
O
45
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



46

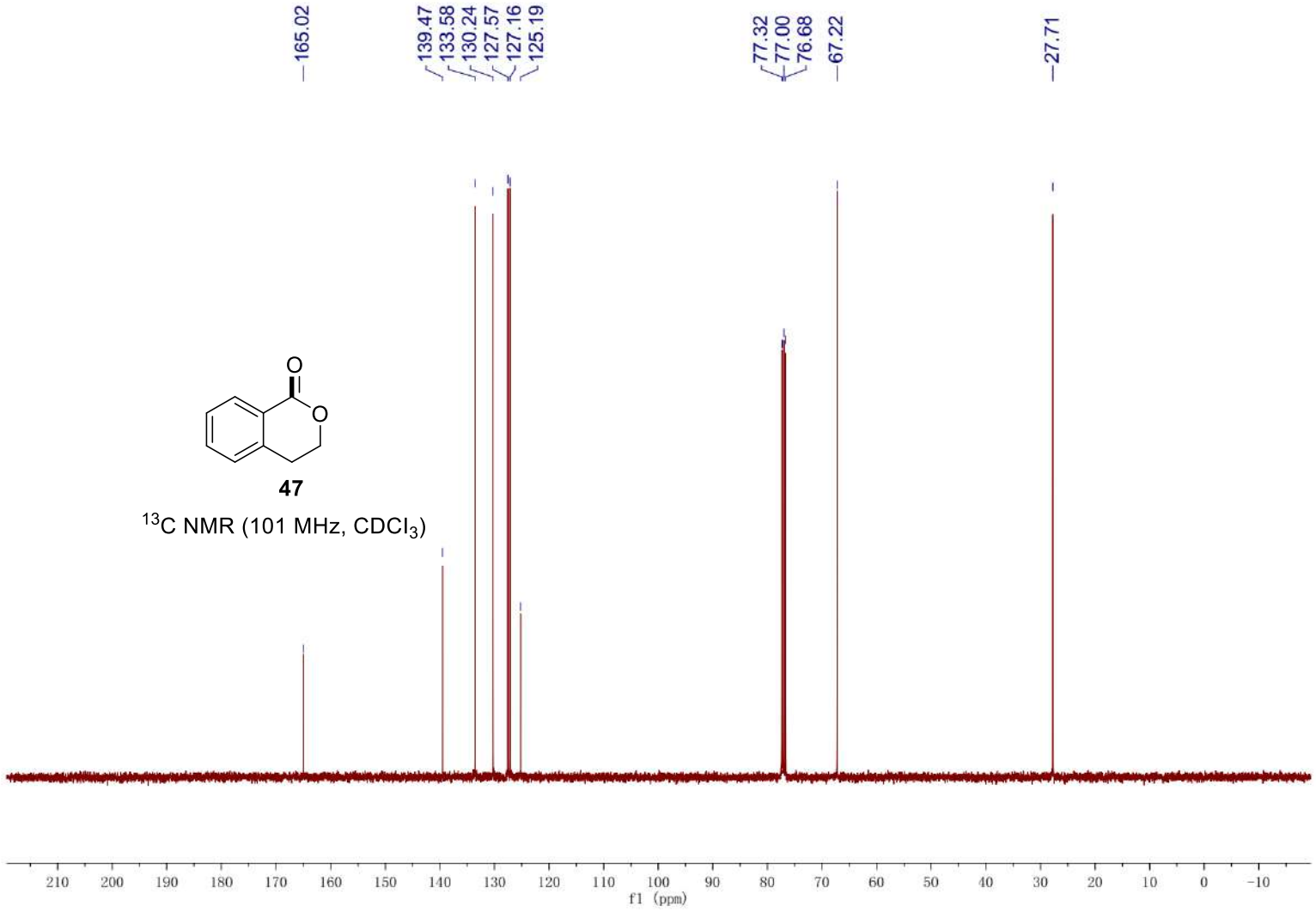
^{1}H NMR (400 MHz, $CDCl_3$)

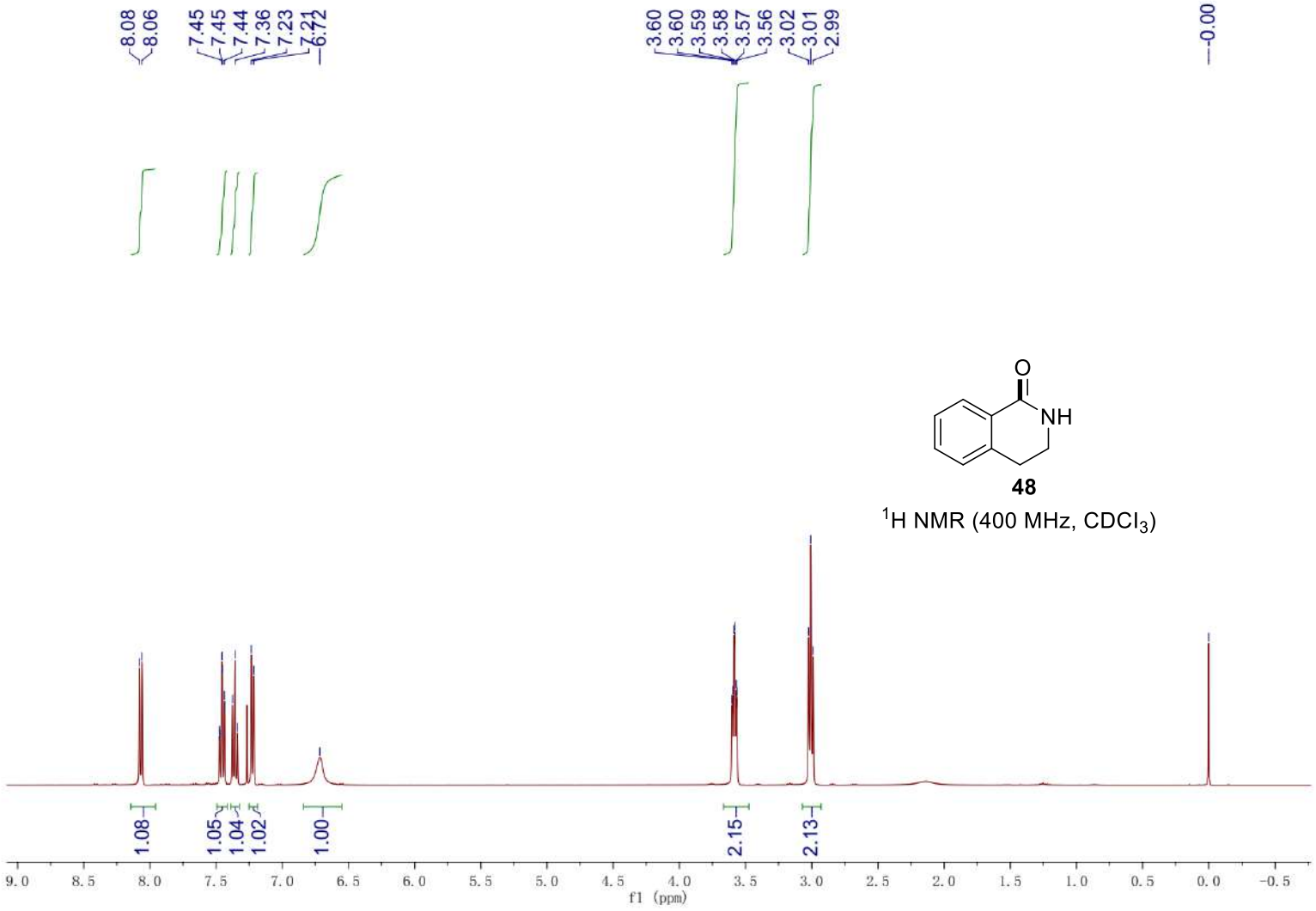

165.32
148.55
133.77
133.61
131.47
130.17
129.51
129.43
128.57
127.76
127.65
126.54
125.69
121.21
118.66
77.32
77.00
76.68
O
O
46
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

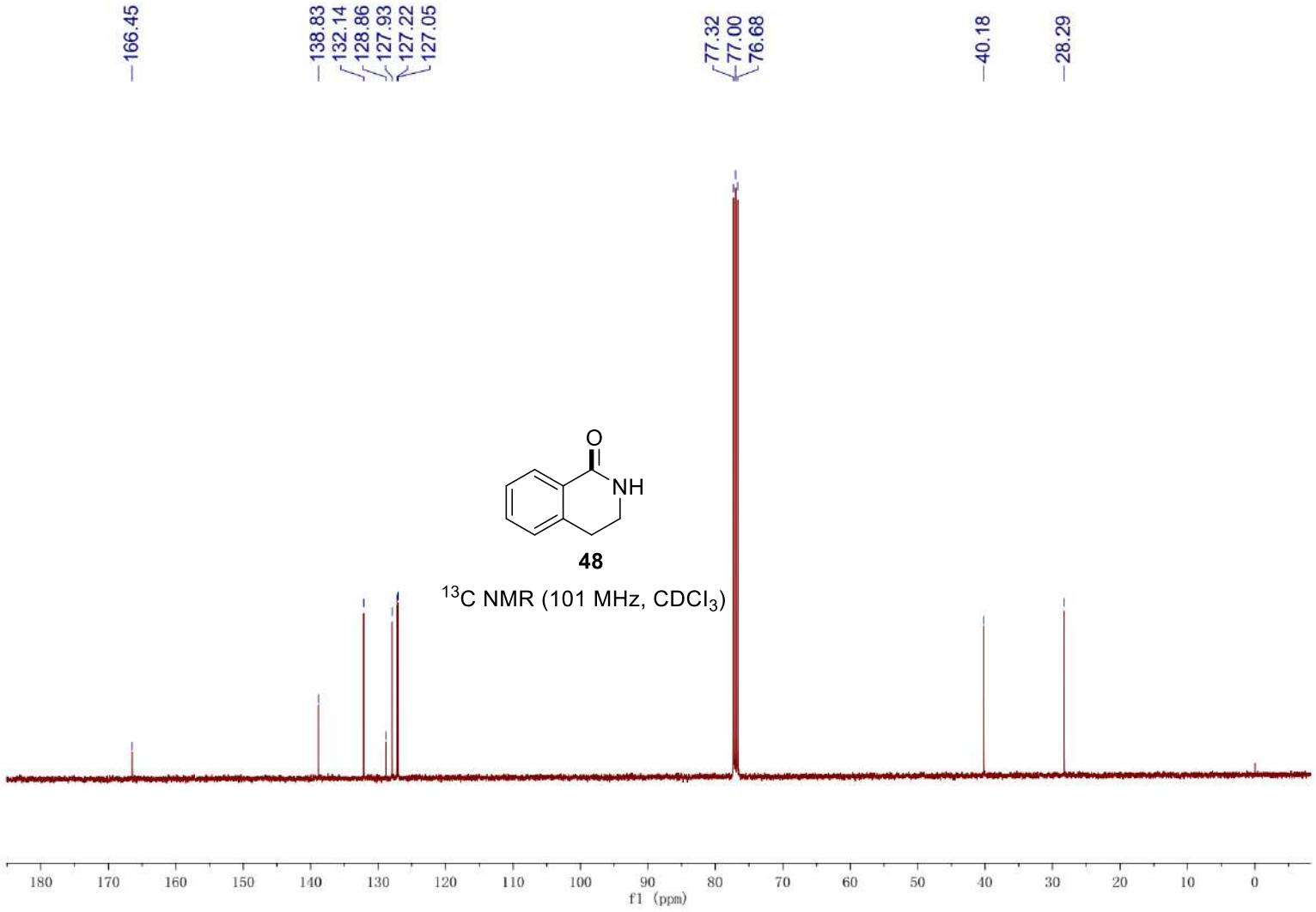


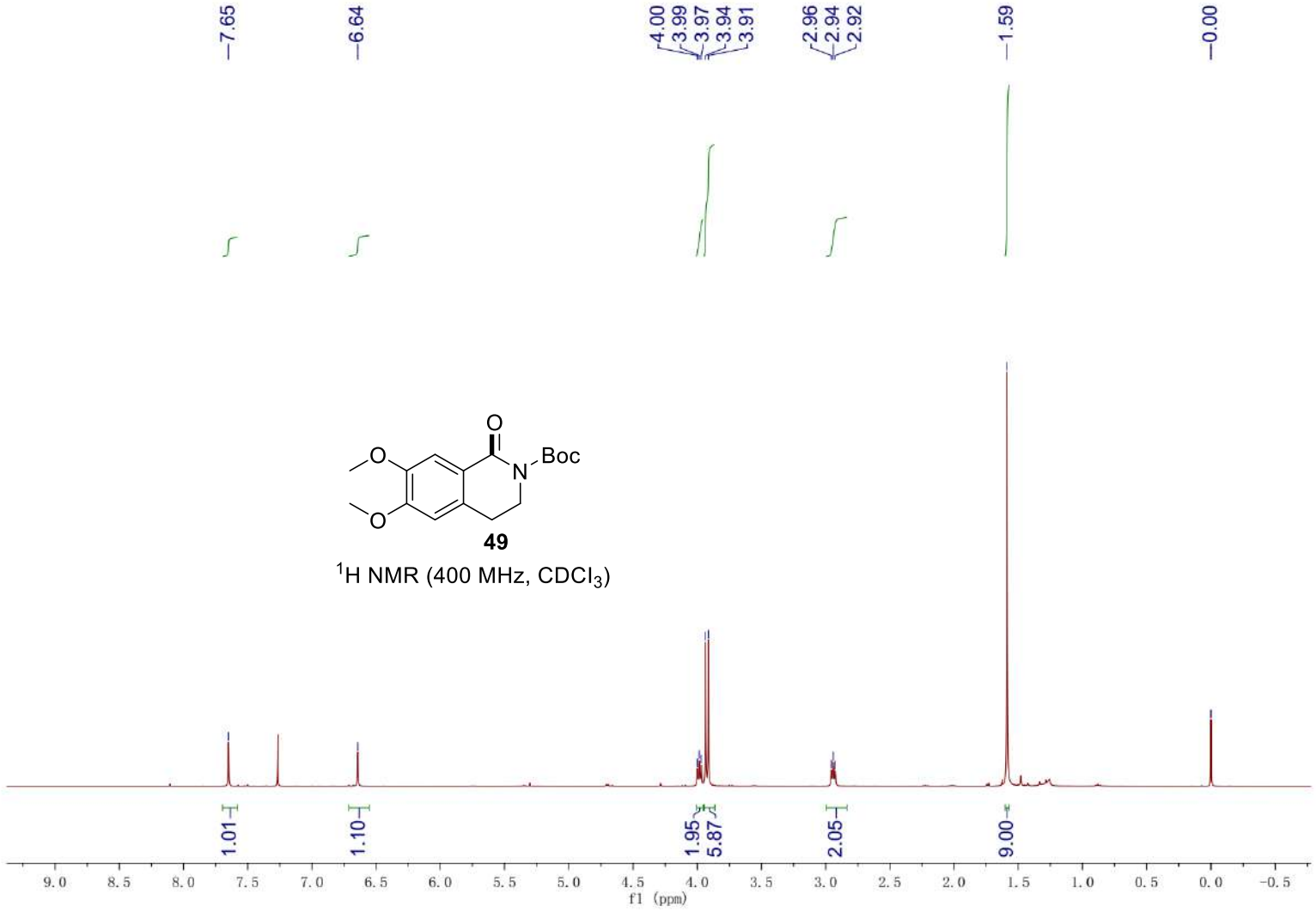
47

^{1}H NMR (400 MHz, $CDCl_3$)


165.02
139.47
133.58
130.24
127.57
127.16
125.19
77.32
77.00
76.68
67.22
27.71
O
O
47
^{13}C NMR (101 MHz, $CDCl_3$)
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)

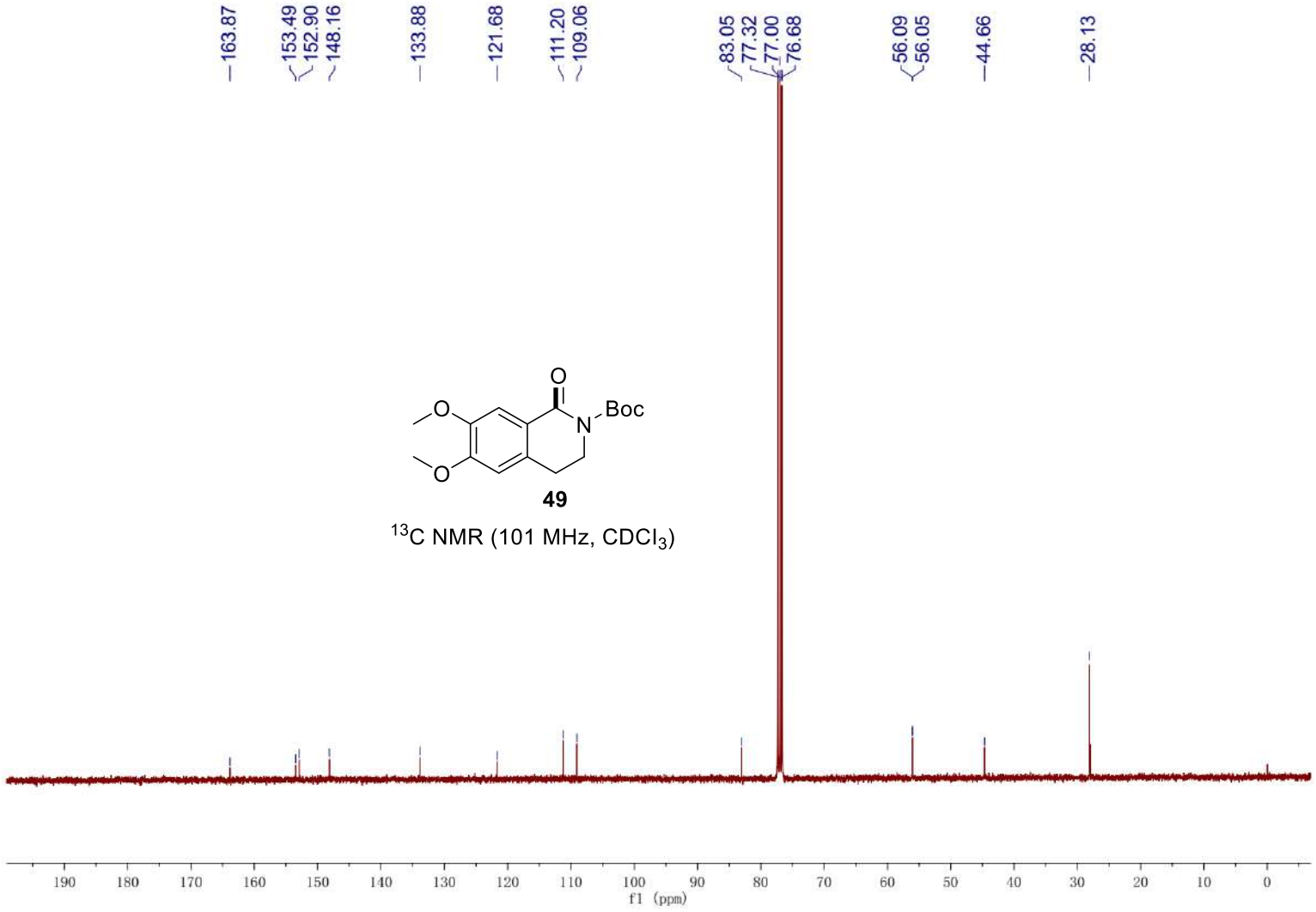

8.08
8.06
7.45
7.45
7.44
7.36
7.23
7.21
6.72
3.60
3.60
3.59
3.58
3.57
3.56
3.02
3.01
2.99
0.00
O
NH
48
1H NMR (400 MHz, CDCl3)
1.08
1.05
1.04
1.02
1.00
2.15
2.13
f1 (ppm)


166.45
138.83
132.14
128.86
127.93
127.22
127.05
77.32
77.00
76.68
40.18
28.29
O
NH
48
^{13}C NMR (101 MHz, $CDCl_3$)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



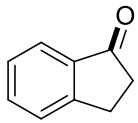
49

^{1}H NMR (400 MHz, $CDCl_3$)



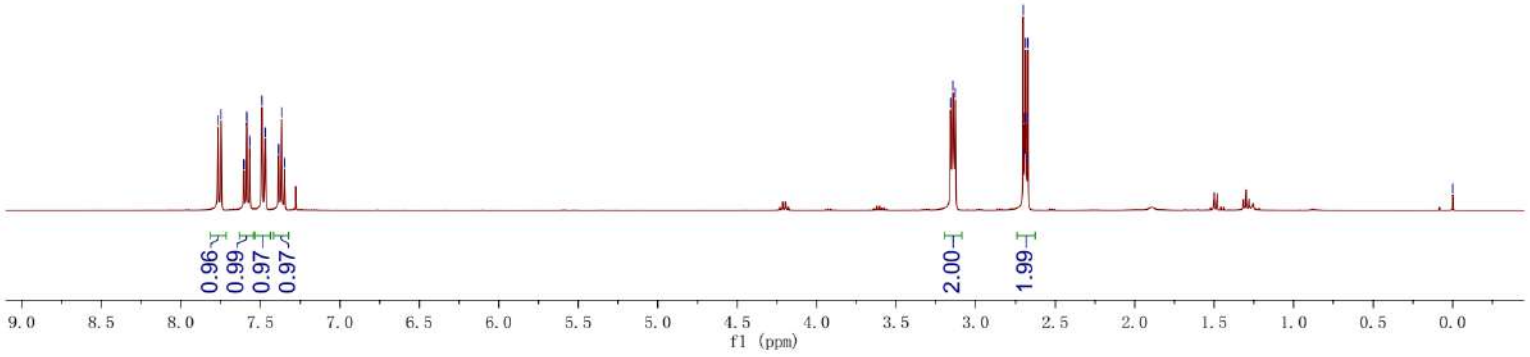
49

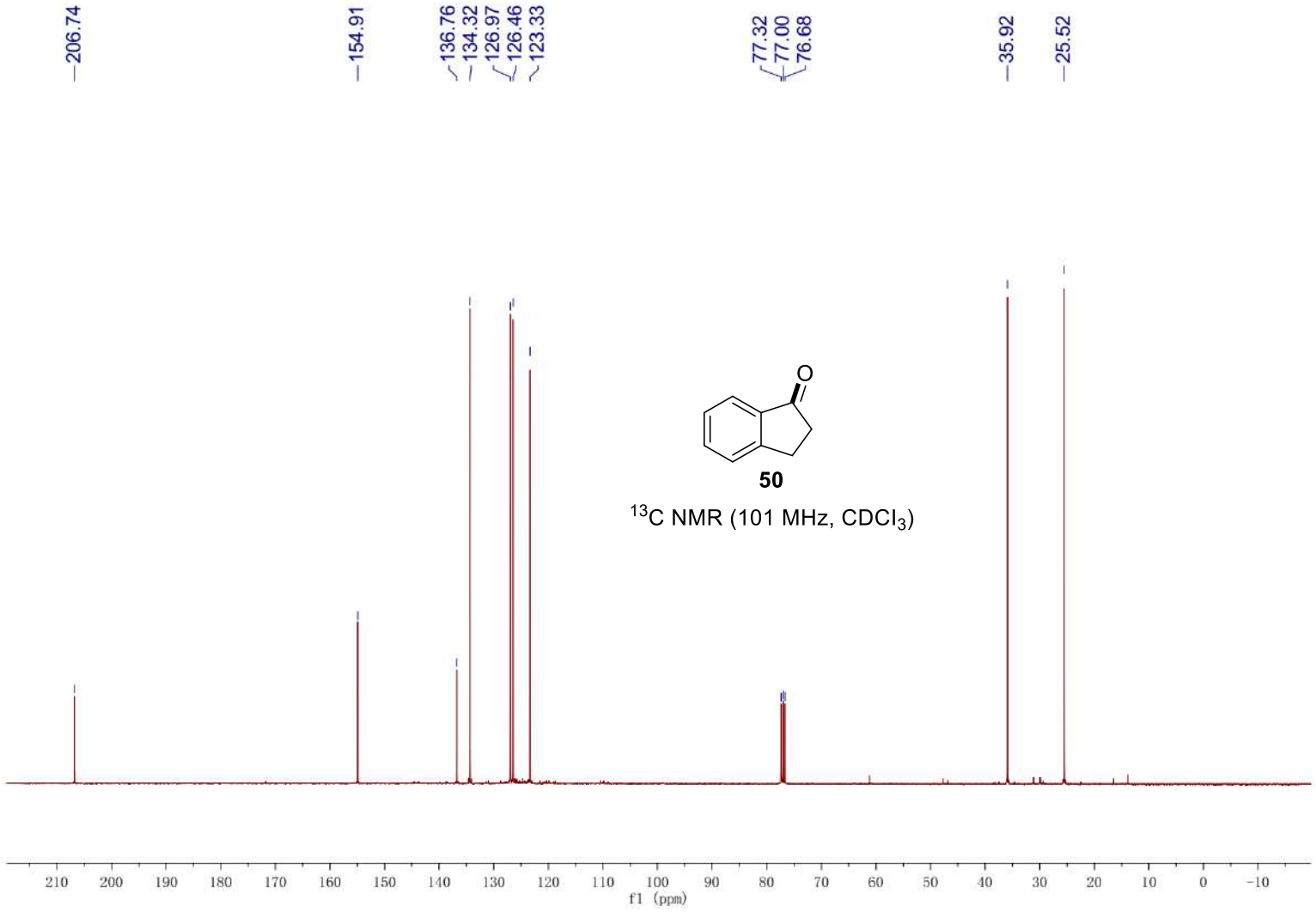
^{13}C NMR (101 MHz, $CDCl_3$)

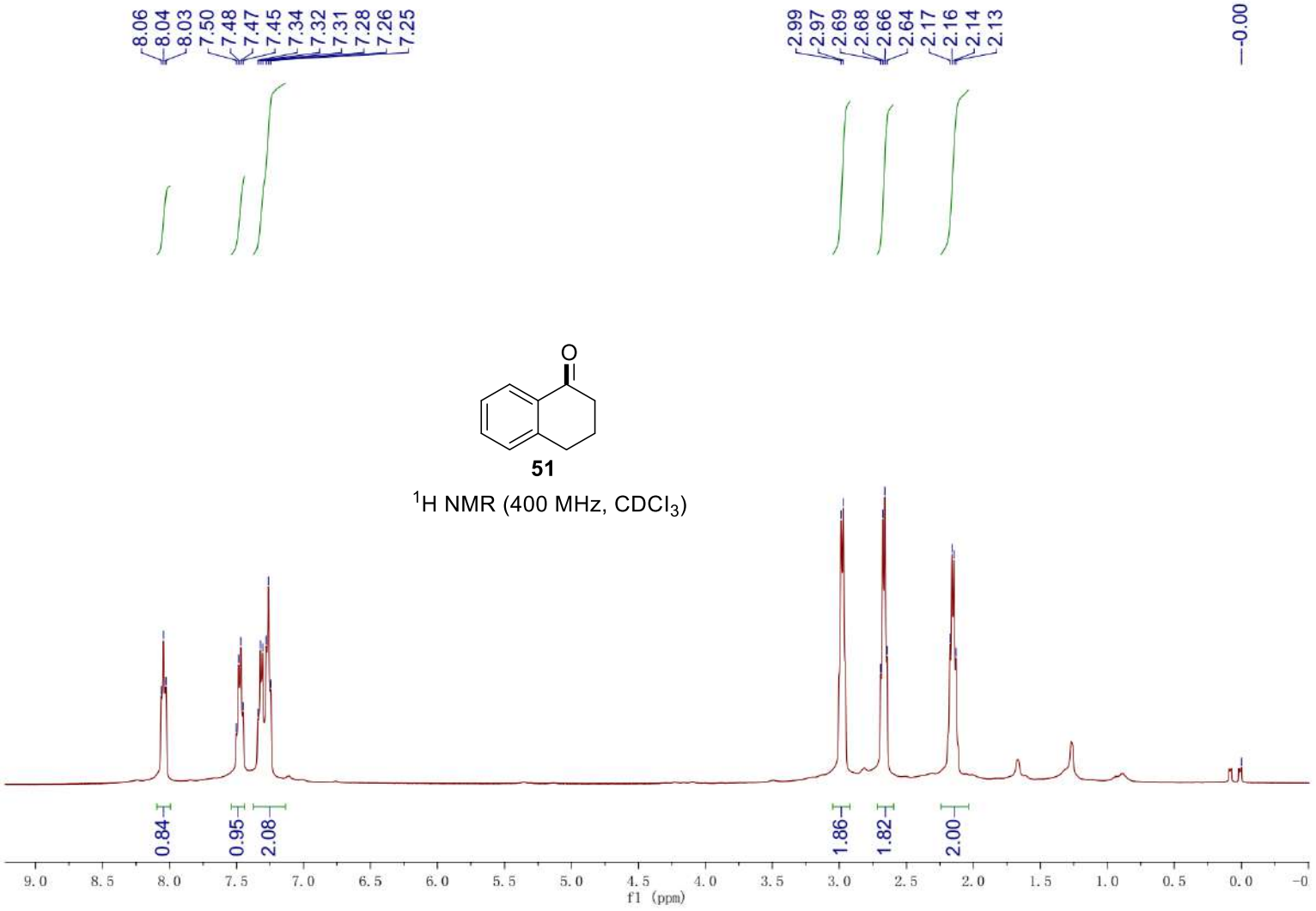


50

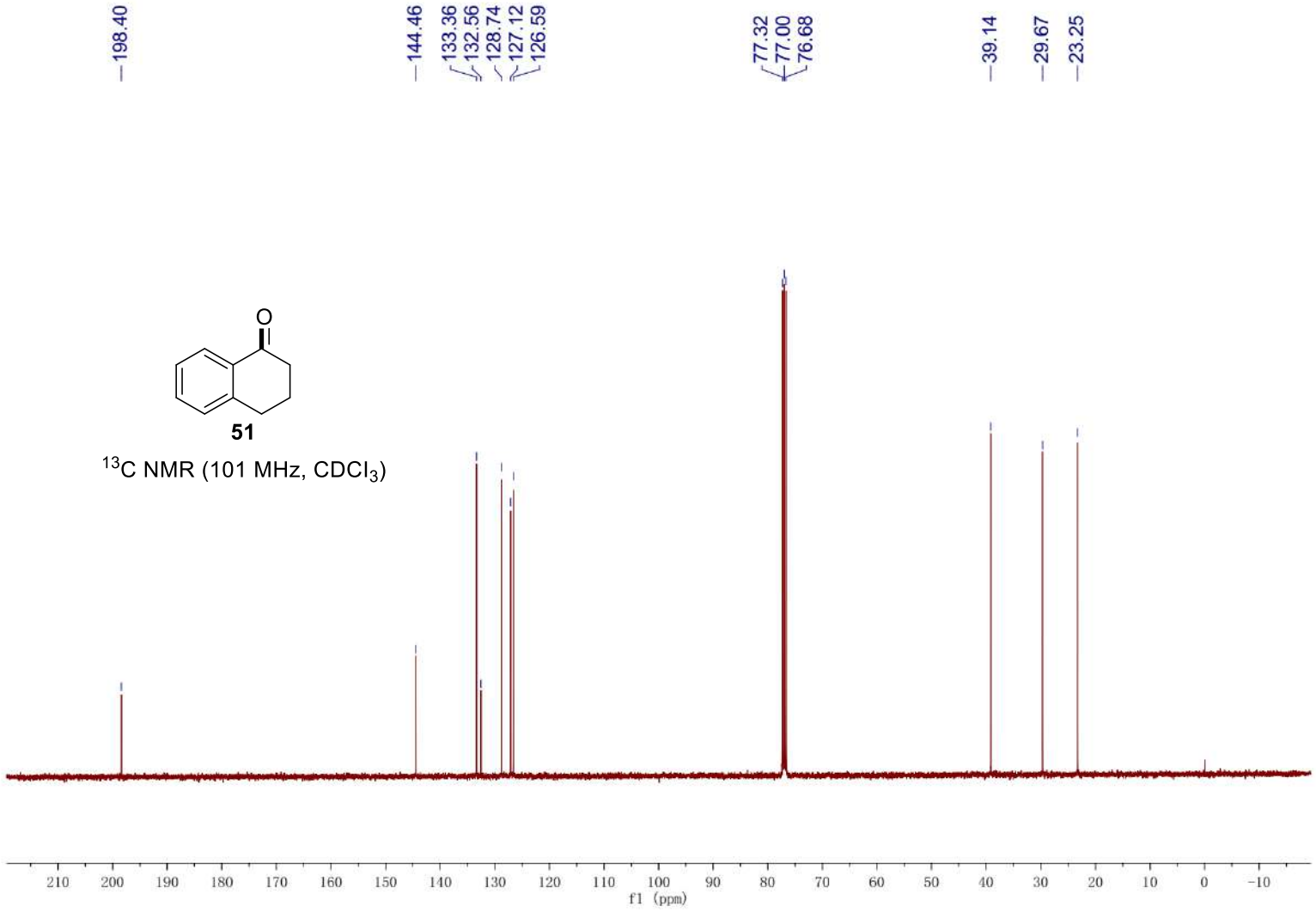
^{1}H NMR (400 MHz, $CDCl_3$)

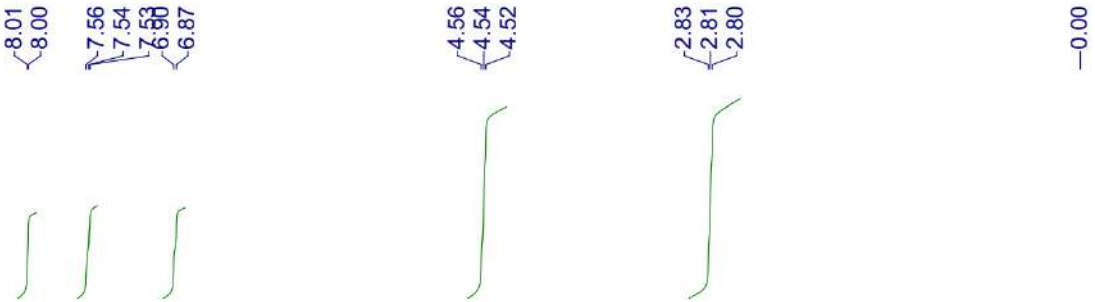


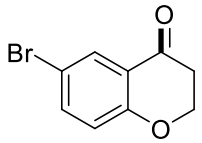

206.74
154.91
136.76
134.32
126.97
126.46
123.33
77.32
77.00
76.68
35.92
25.52
O
50
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



^{1}H NMR (400 MHz, $CDCl_3$)

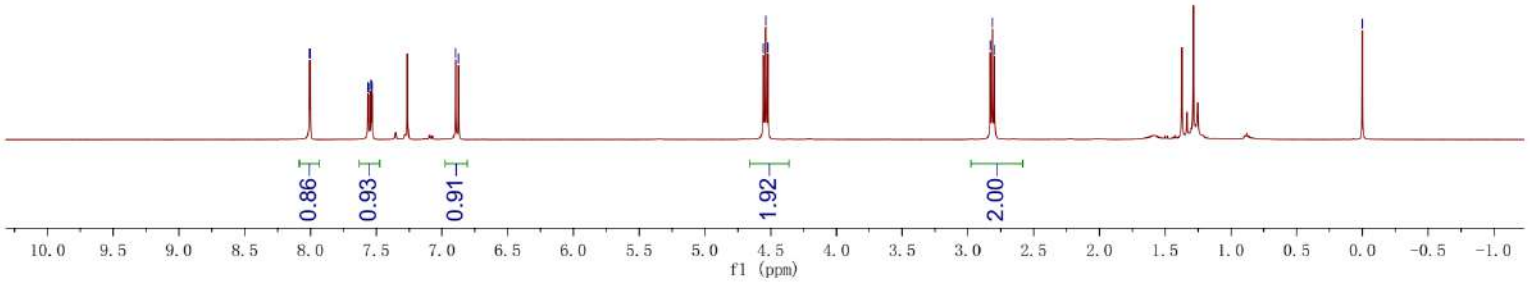

198.40
144.46
133.36
132.56
128.74
127.12
126.59
77.32
77.00
76.68
39.14
29.67
23.25
O
51
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

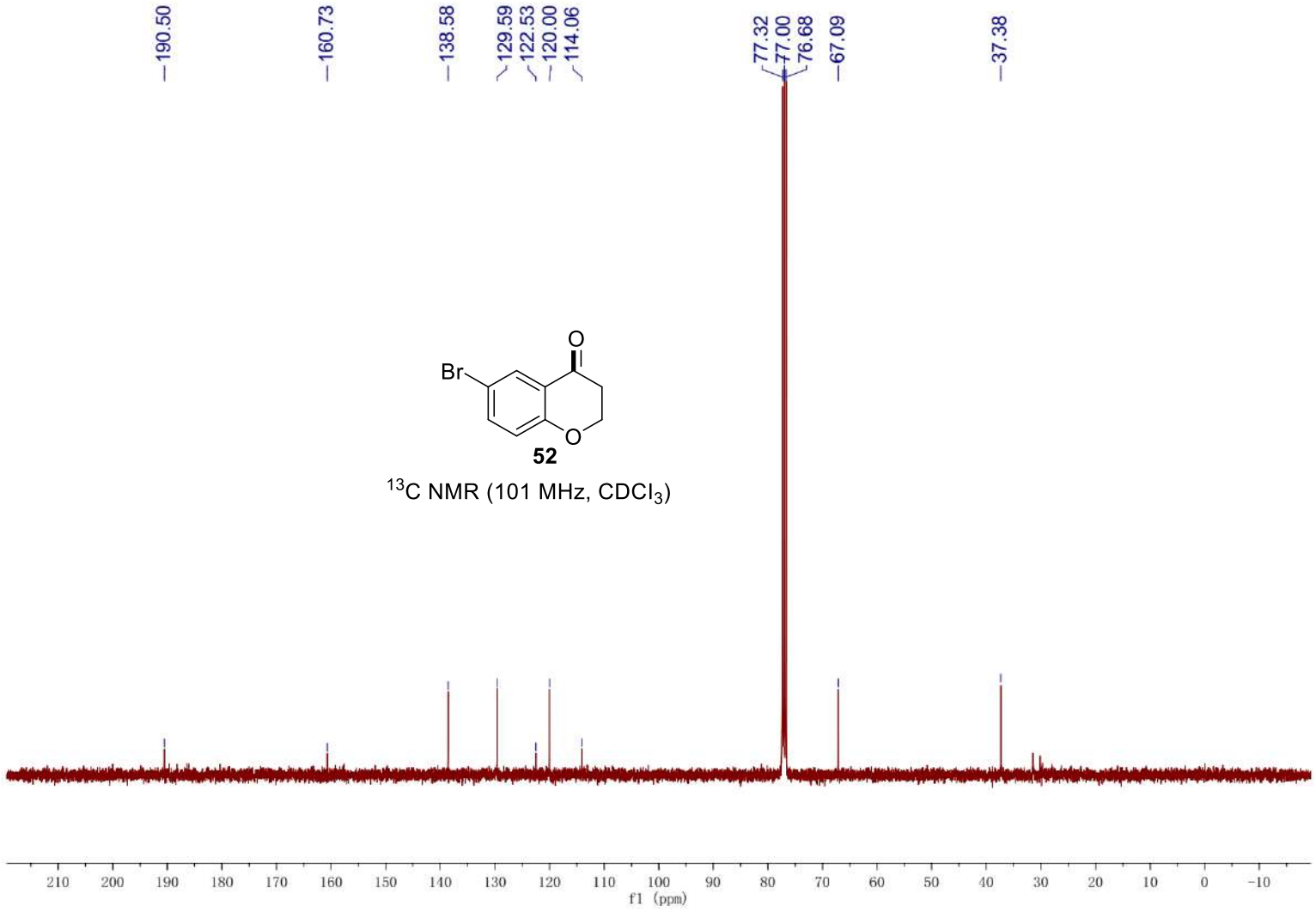




52

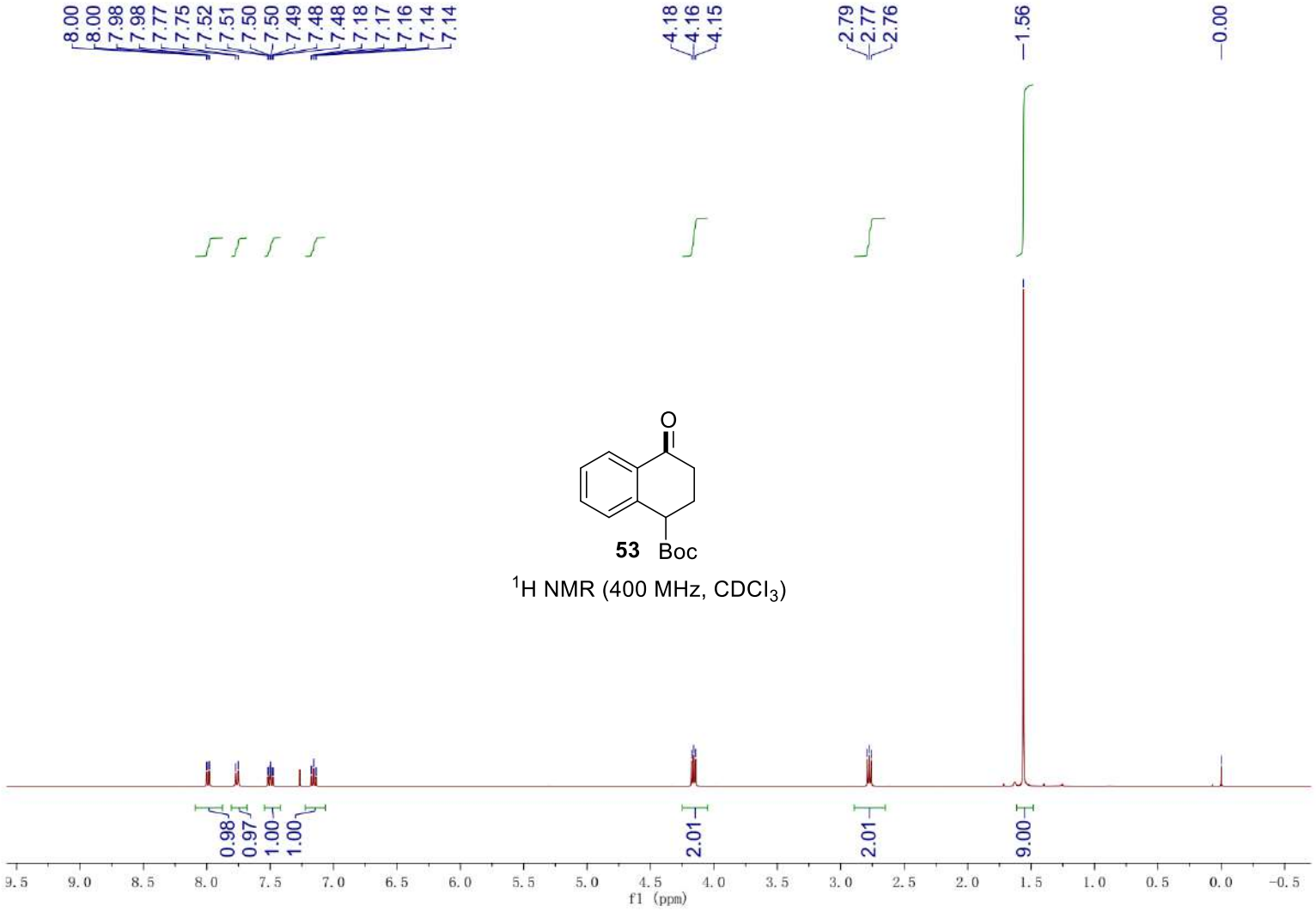
^{1}H NMR (400 MHz, $CDCl_3$)



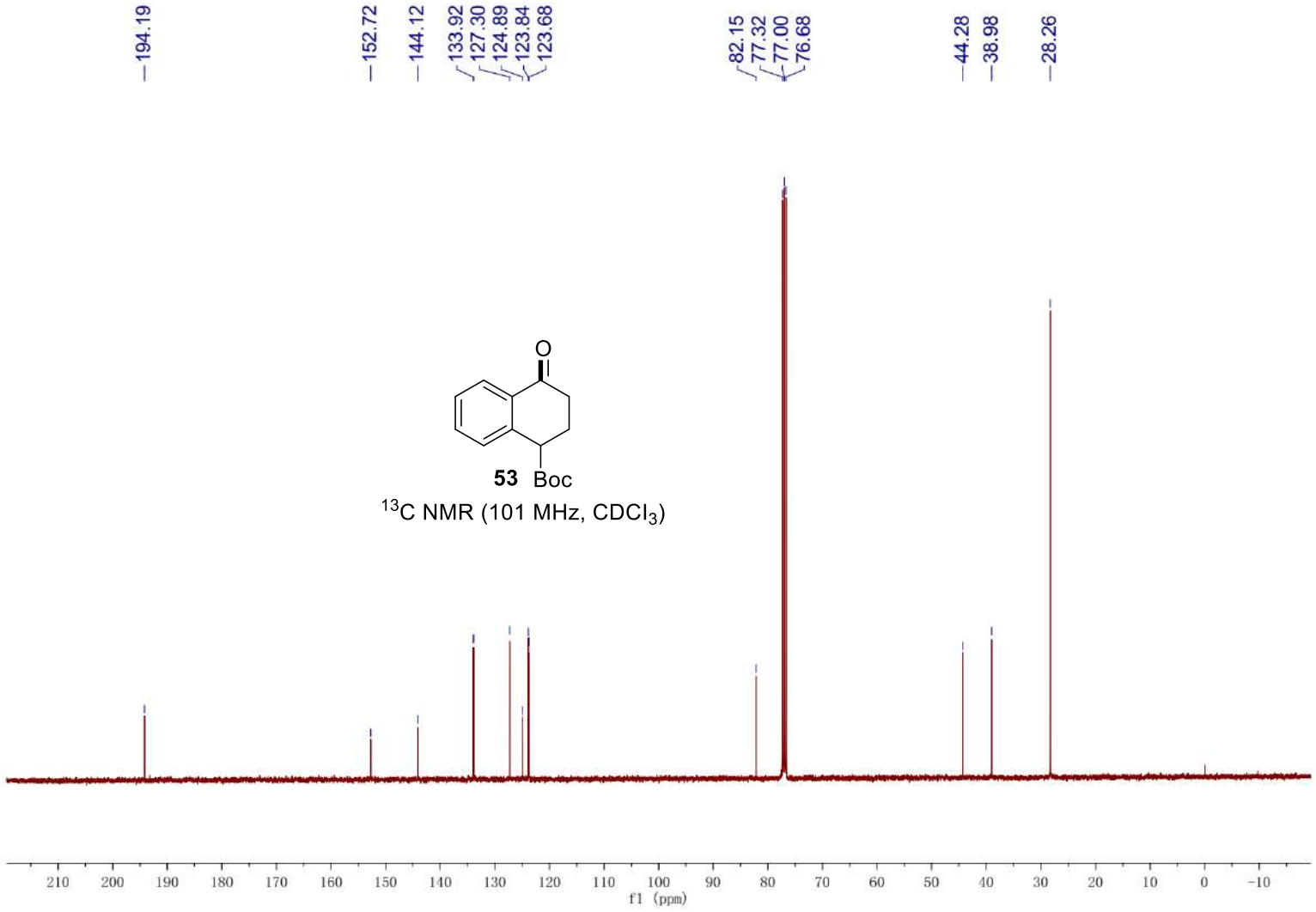


52

^{13}C NMR (101 MHz, $CDCl_3$)

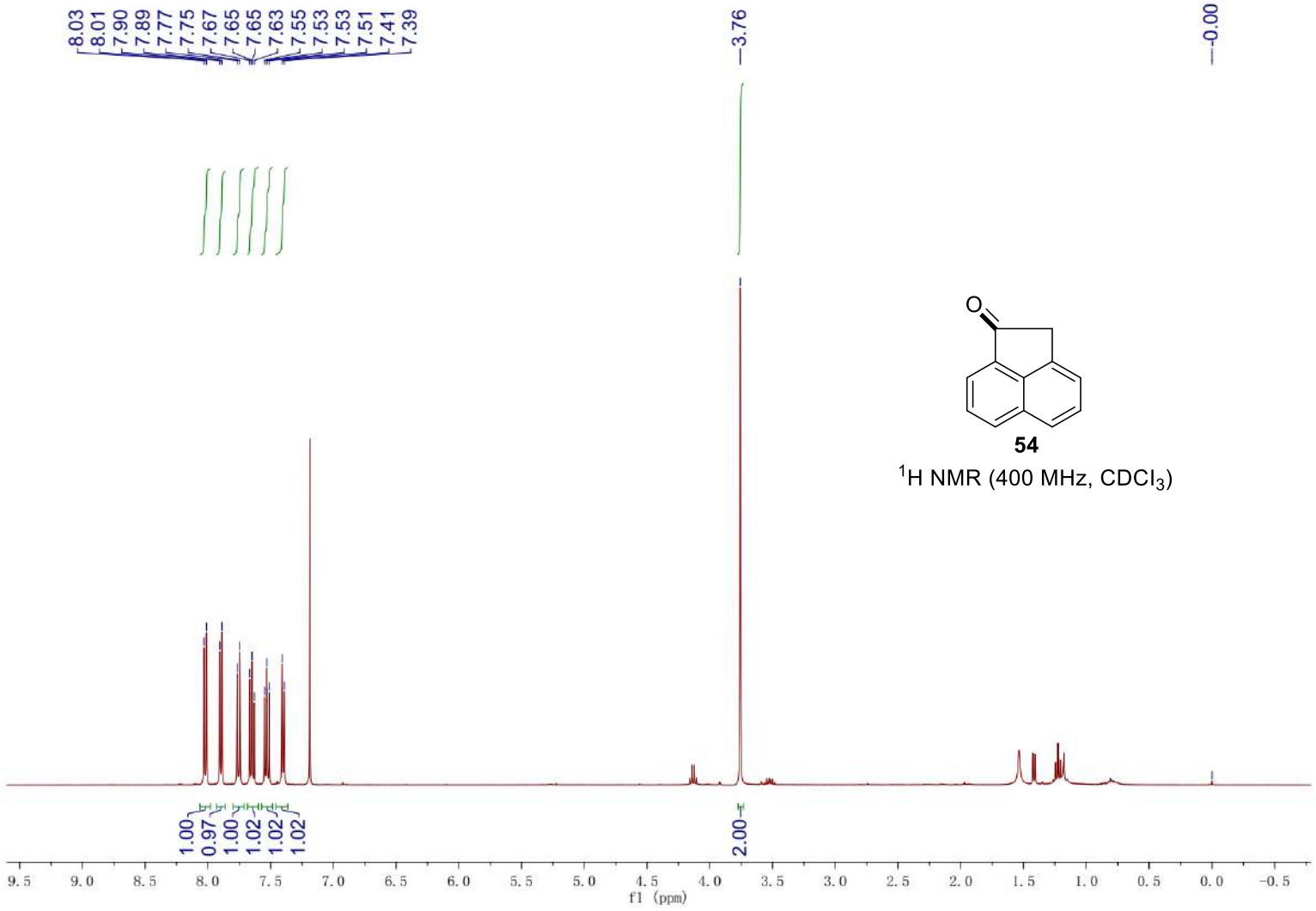


^{1}H NMR (400 MHz, $CDCl_3$)



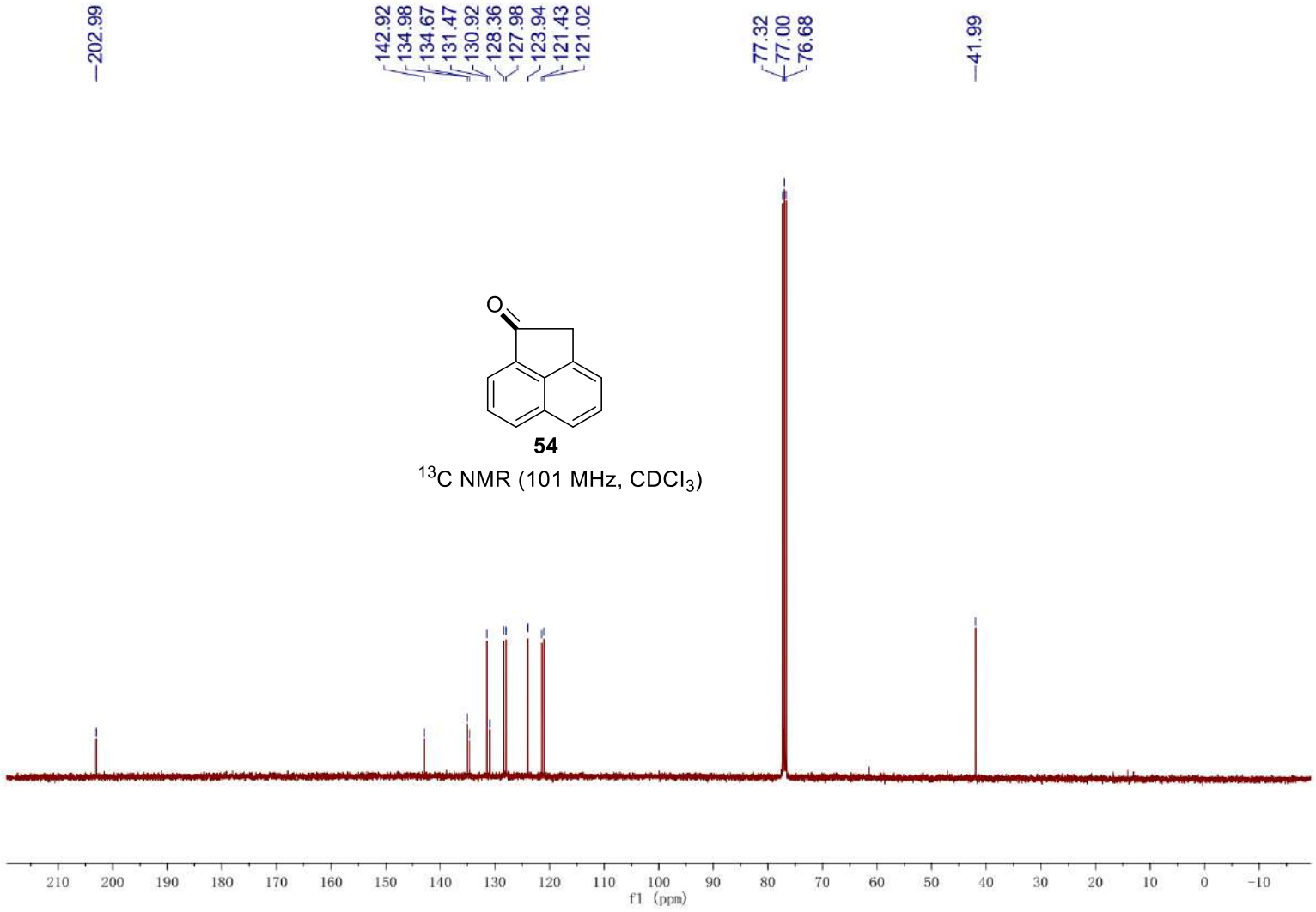
53

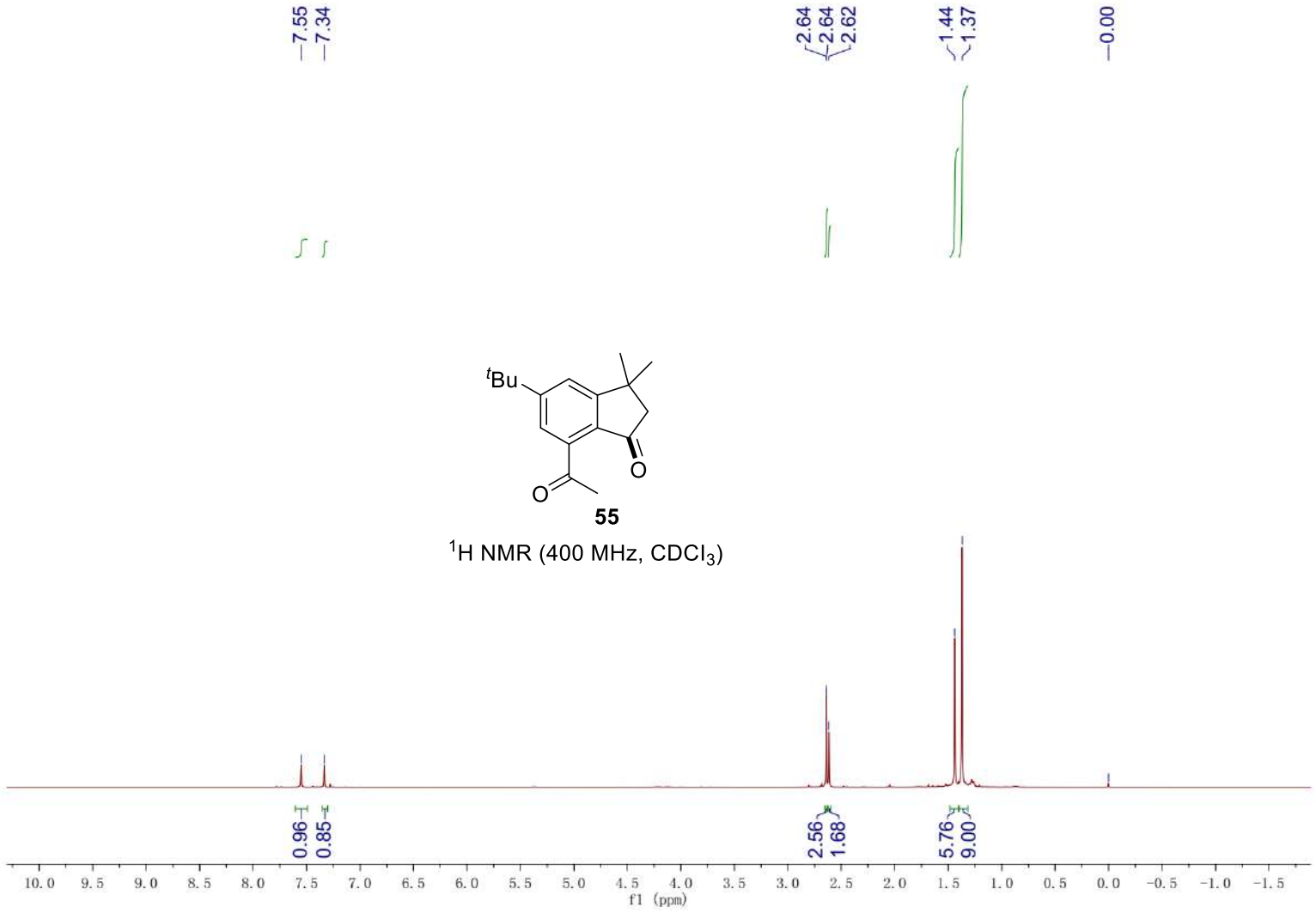
^{13}C NMR (101 MHz, $CDCl_3$)

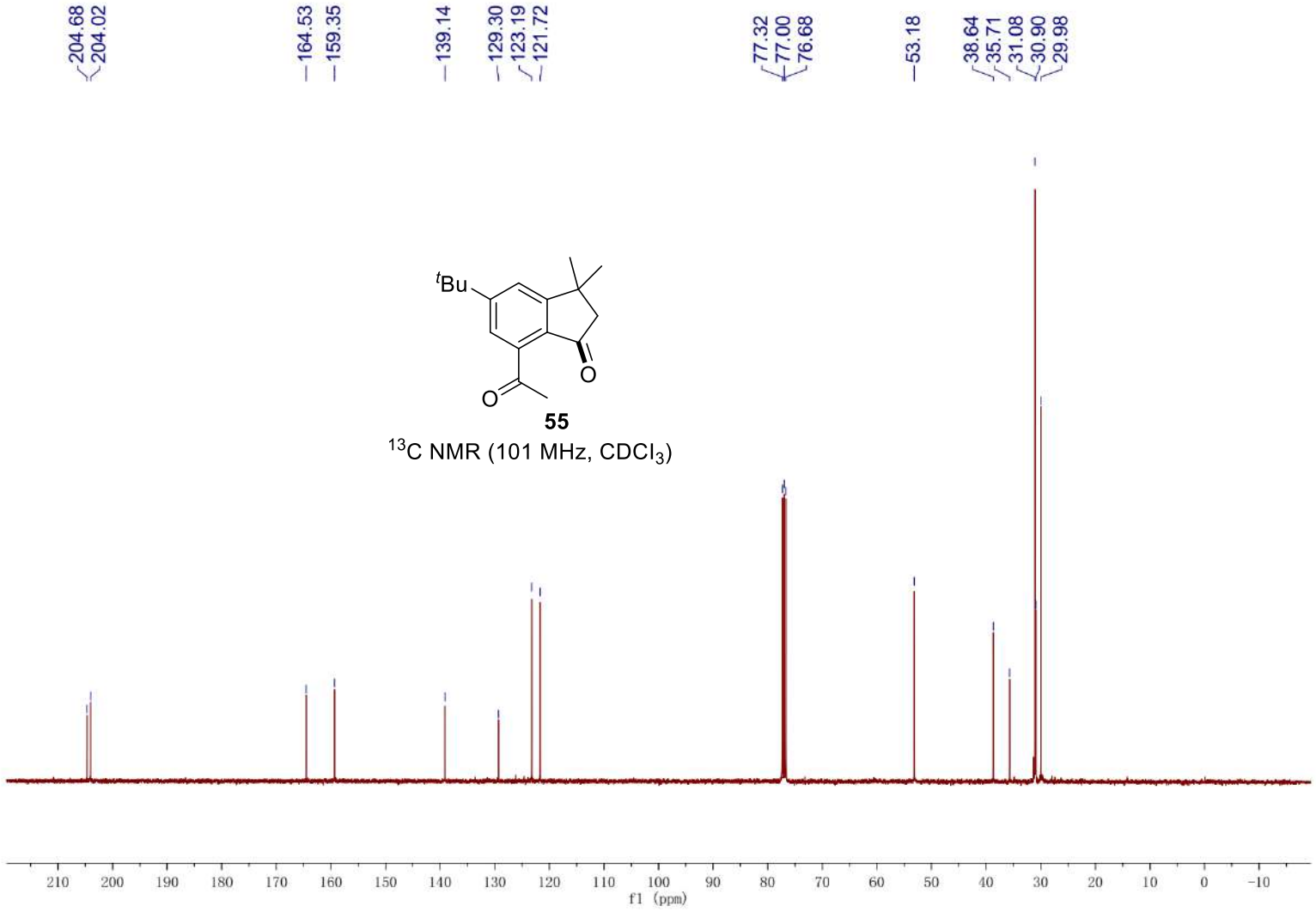


54

^{1}H NMR (400 MHz, $CDCl_3$)

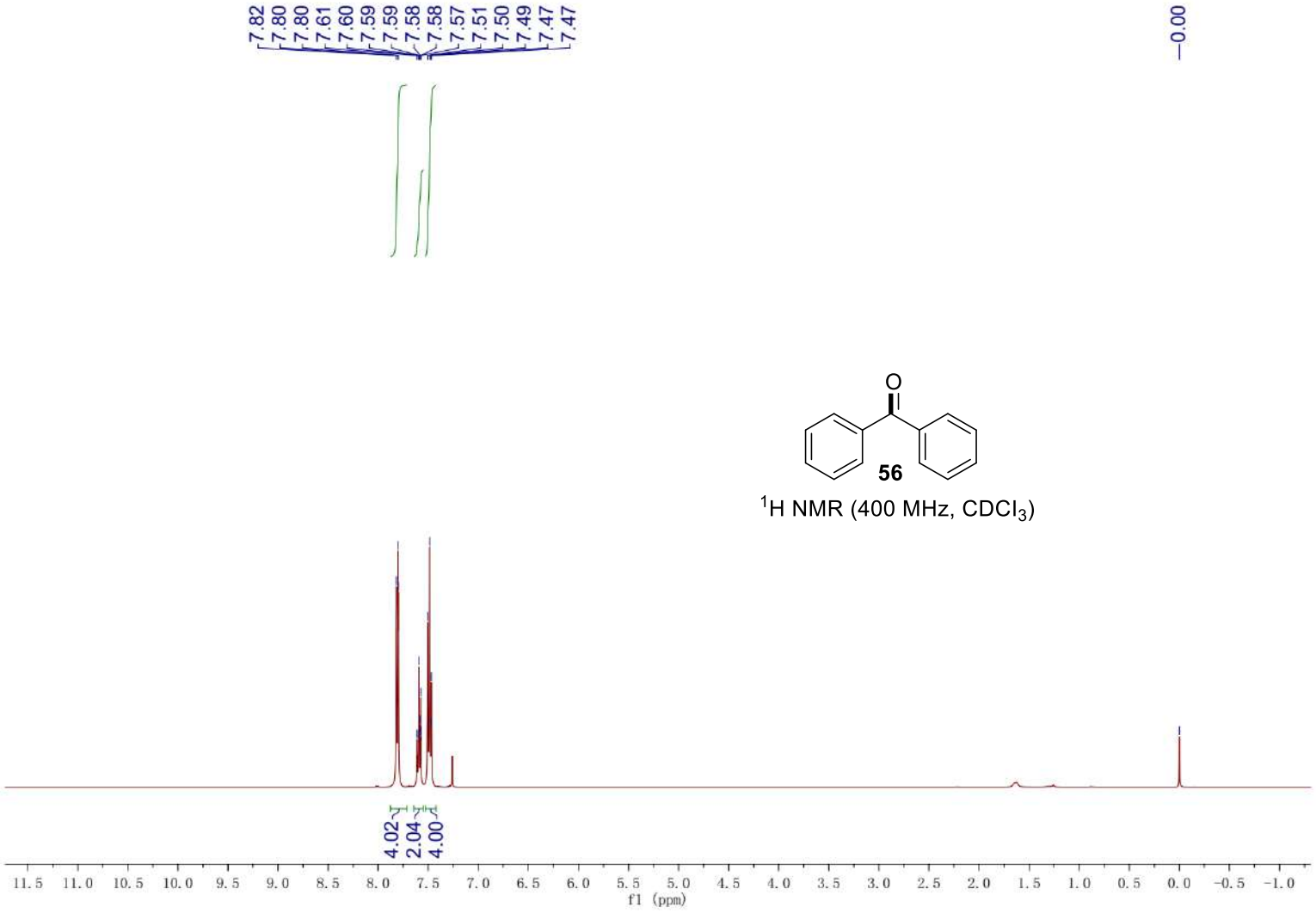

202.99
142.92
134.98
134.67
131.47
130.92
128.36
127.98
123.94
121.43
121.02
77.32
77.00
76.68
41.99
O
54
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

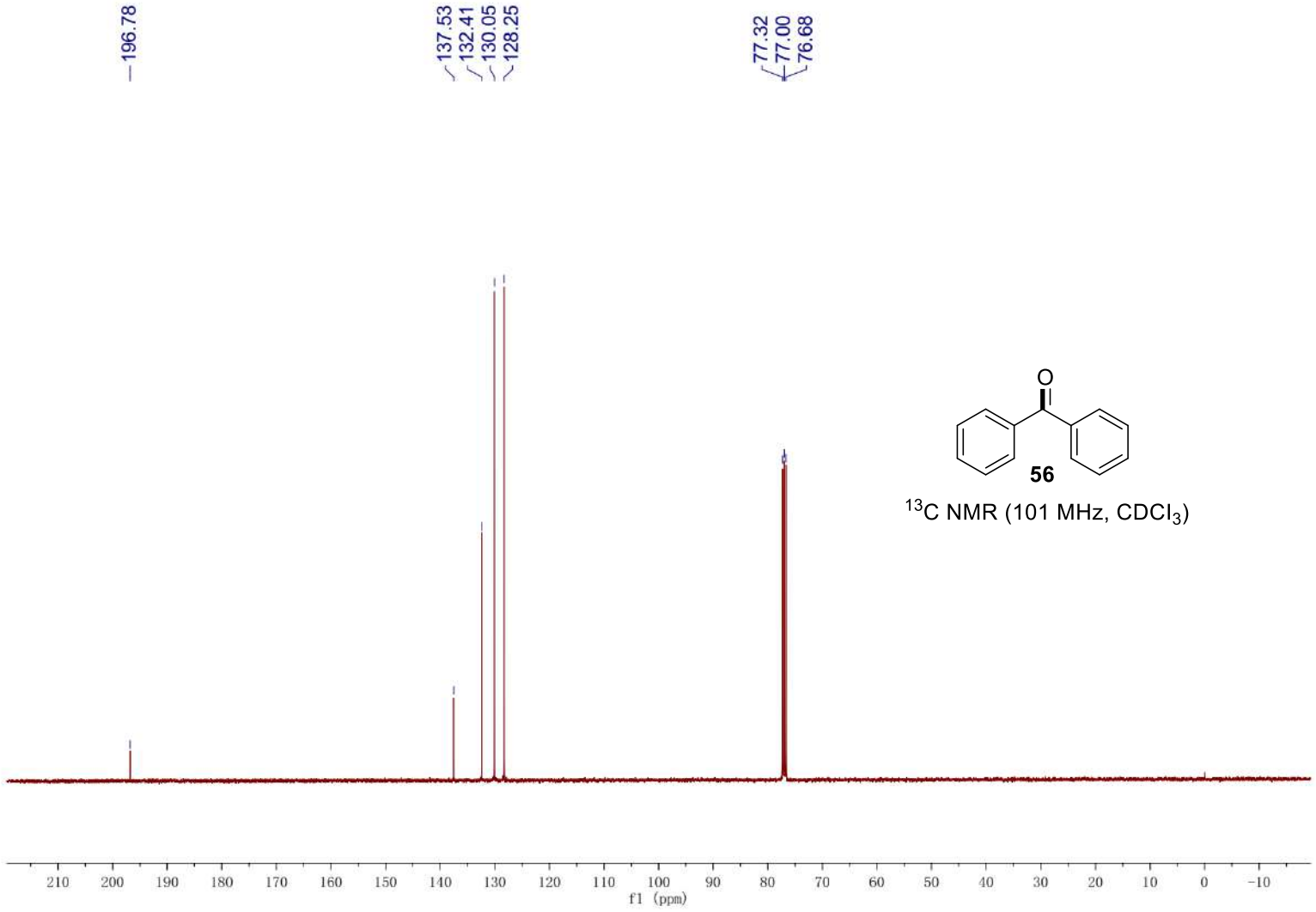

7.55
7.34
2.64
2.64
2.62
1.44
1.37
0.00
tBu
O
O
55
1H NMR (400 MHz, CDCl3)
0.96
0.85
2.56
1.68
5.76
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

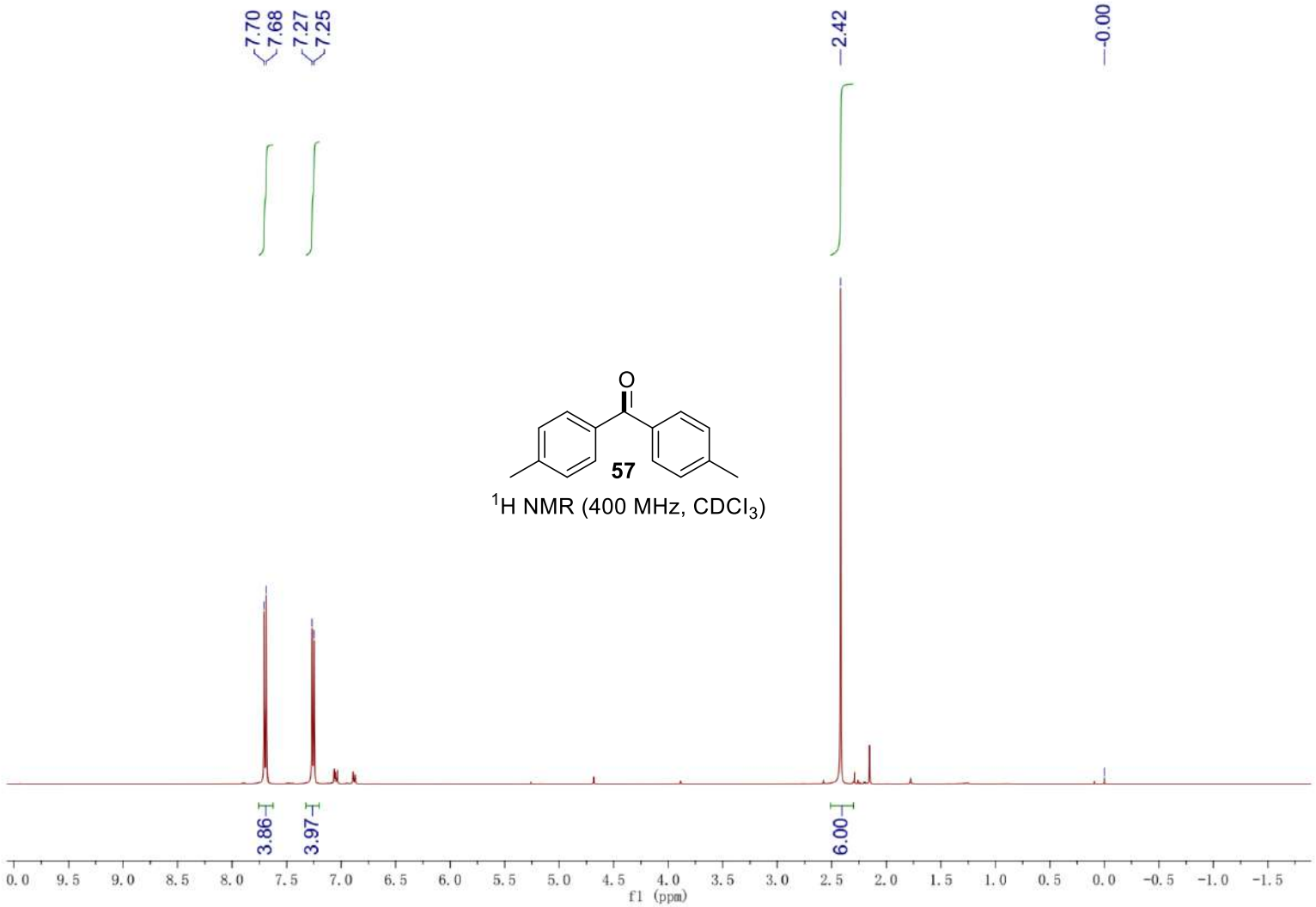


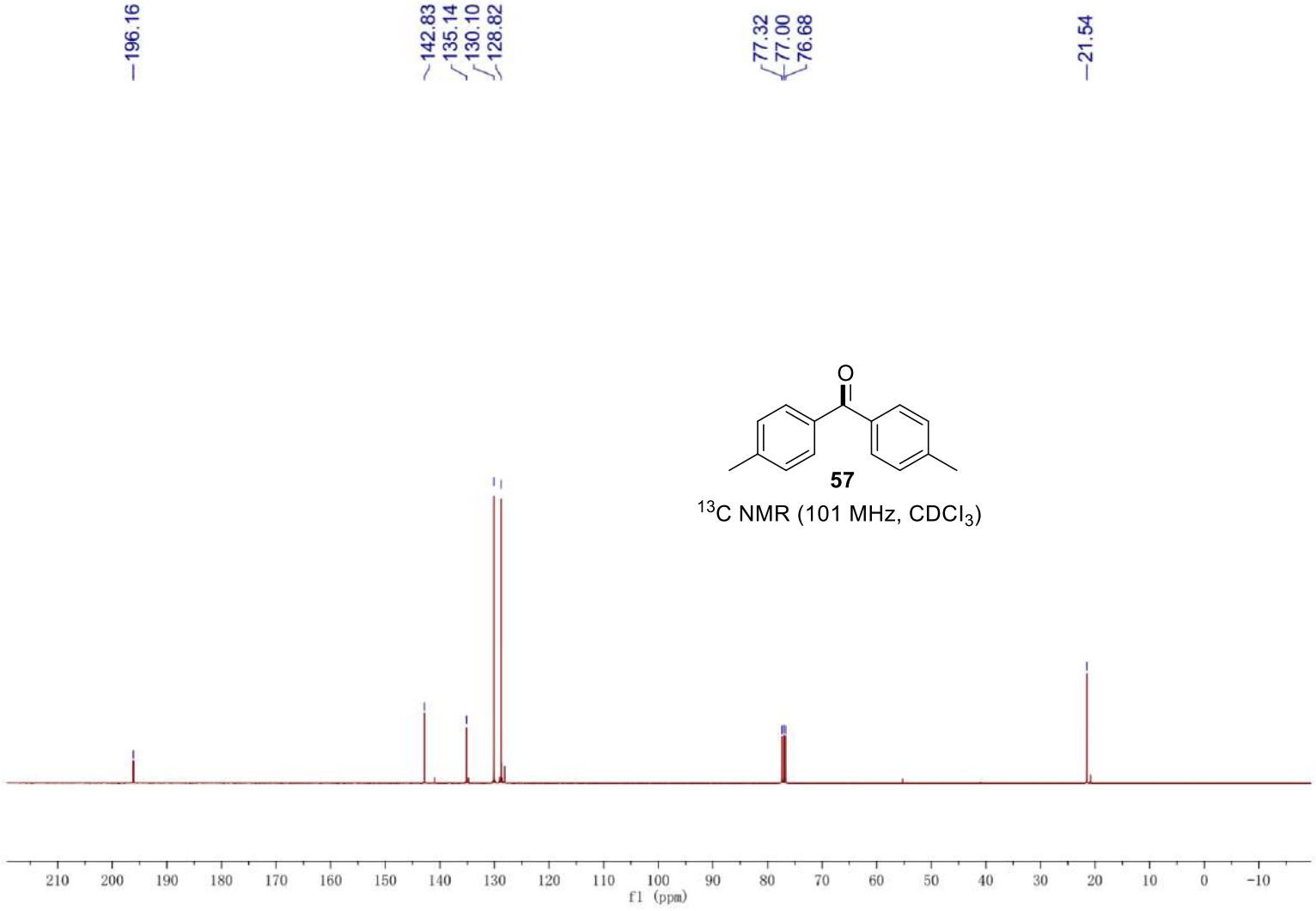
55

^{13}C NMR (101 MHz, $CDCl_3$)


7.82
7.80
7.80
7.61
7.60
7.59
7.59
7.58
7.58
7.57
7.51
7.50
7.49
7.47
7.47
0.00
O
56
^{1}H NMR (400 MHz, CDCl$_3$)
4.02
2.04
4.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

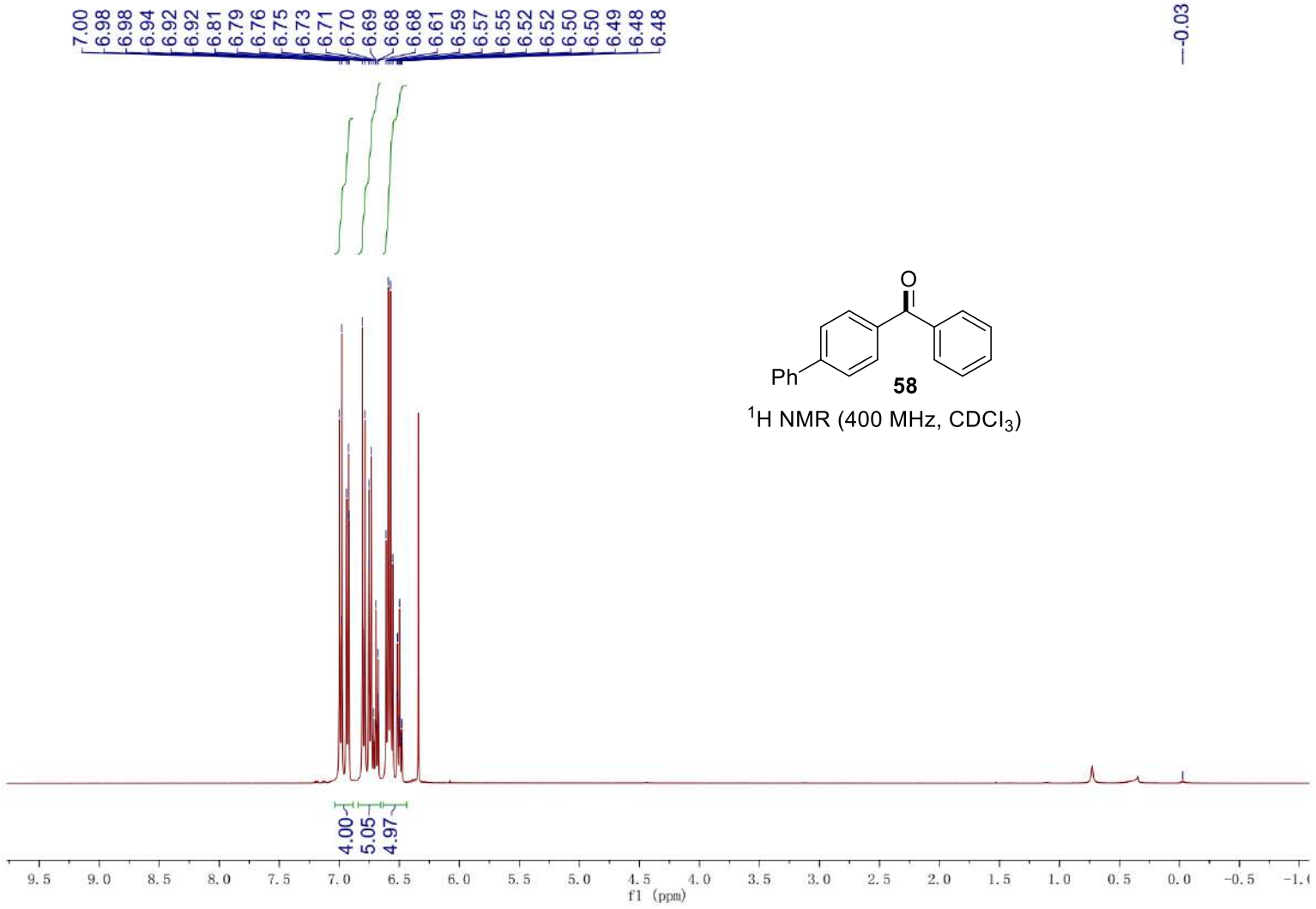

196.78
137.53
132.41
130.05
128.25
77.32
77.00
76.68
O
56
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.70
7.68
7.27
7.25
2.42
0.00
O
57
^{1}H NMR (400 MHz, $CDCl_3$)
3.86
3.97
6.00
f1 (ppm)



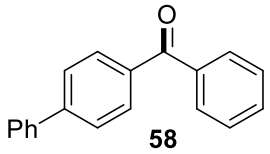
57

^{13}C NMR (101 MHz, $CDCl_3$)



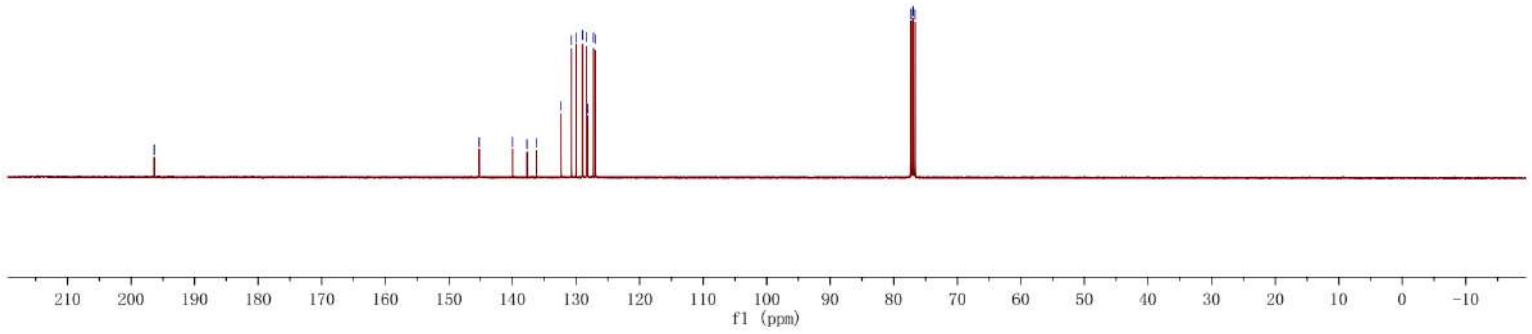
58

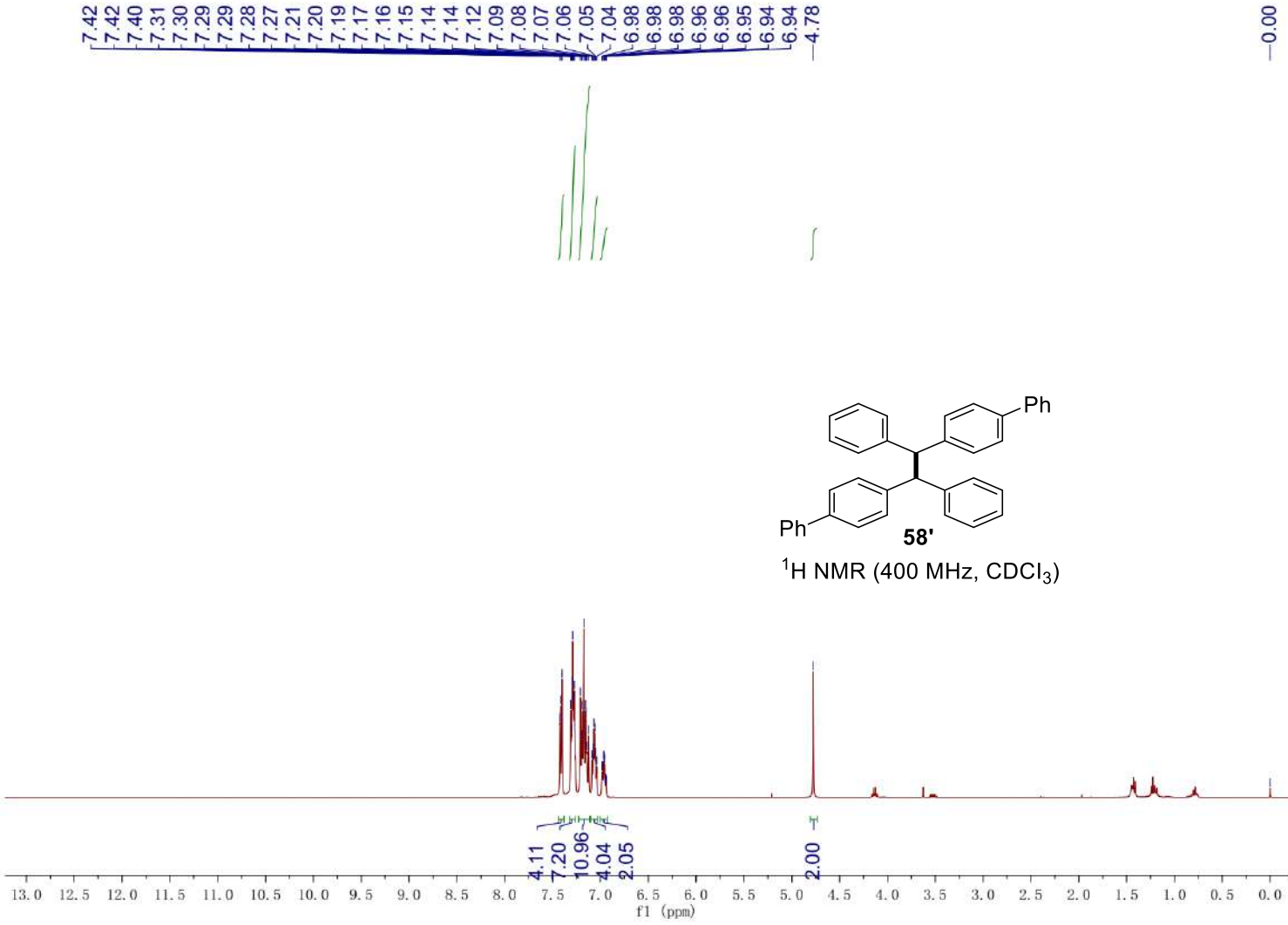
^{1}H NMR (400 MHz, $CDCl_3$)

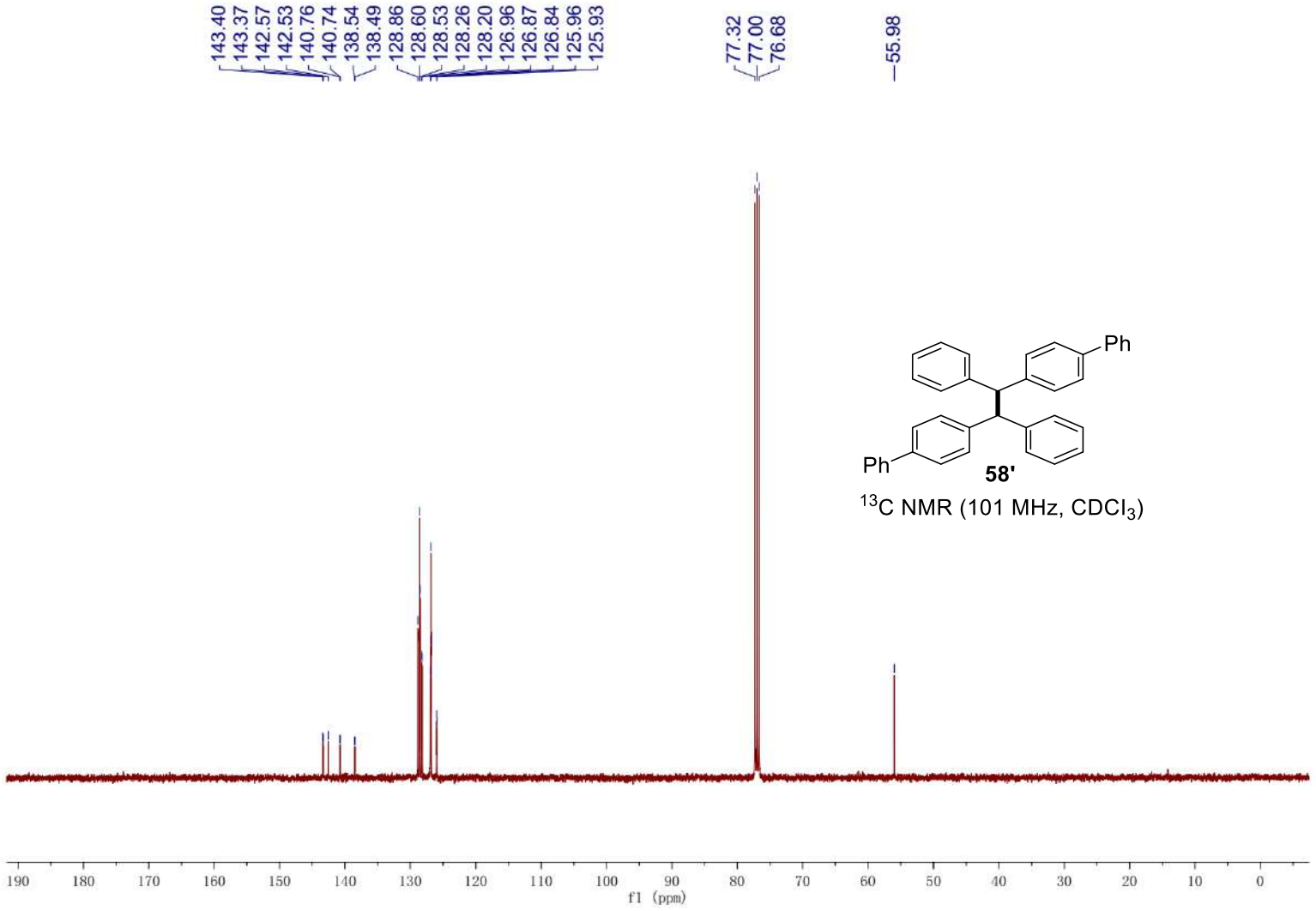


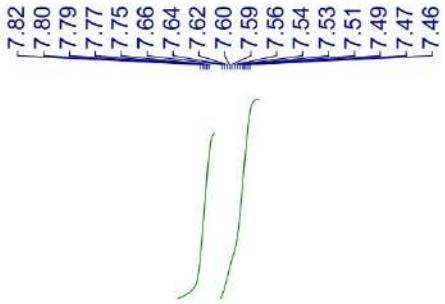
58

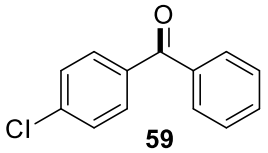
^{13}C NMR (101 MHz, $CDCl_3$)




7.42
7.42
7.40
7.31
7.30
7.29
7.29
7.28
7.27
7.21
7.20
7.19
7.17
7.16
7.15
7.14
7.14
7.12
7.09
7.08
7.07
7.06
7.05
7.04
6.98
6.98
6.98
6.96
6.96
6.95
6.94
6.94
4.78
0.00
Ph
Ph
58'
1H NMR (400 MHz, CDCl3)
4.11
7.20
10.96
4.04
2.05
2.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

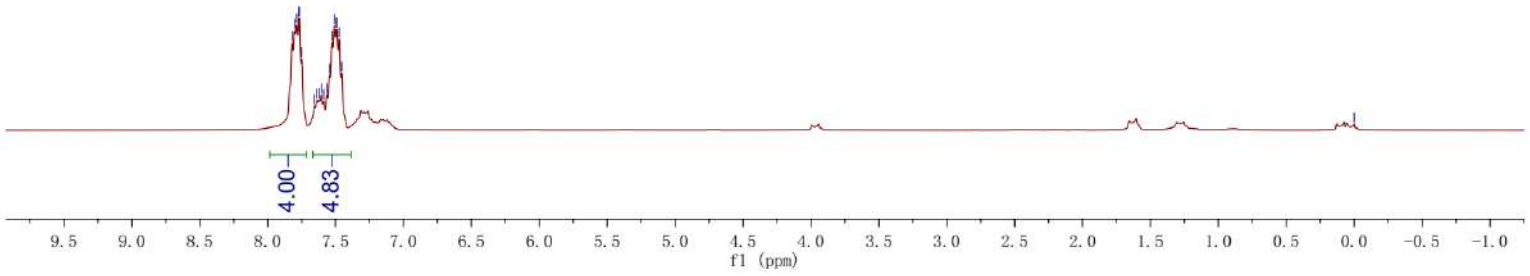

143.40
143.37
142.57
142.53
140.76
140.74
138.54
138.49
128.86
128.60
128.53
128.26
128.20
126.96
126.87
126.84
125.96
125.93
77.32
77.00
76.68
55.98
Ph
Ph
58'
^{13}C NMR (101 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

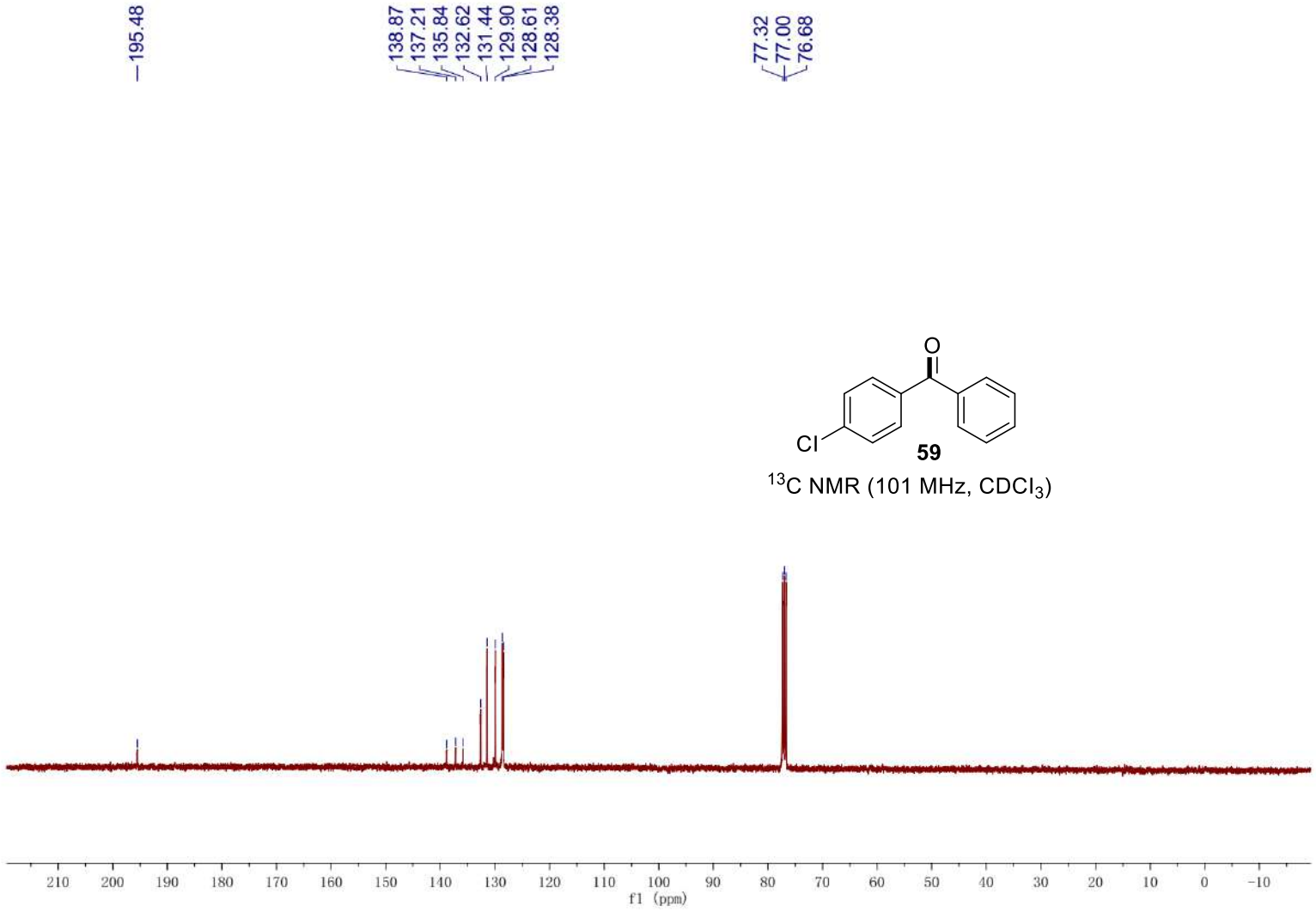


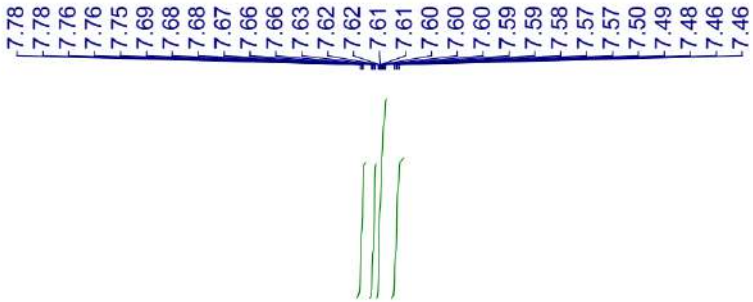


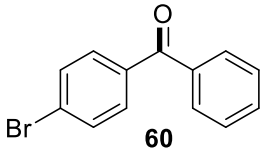
59

^{1}H NMR (400 MHz, $CDCl_3$)



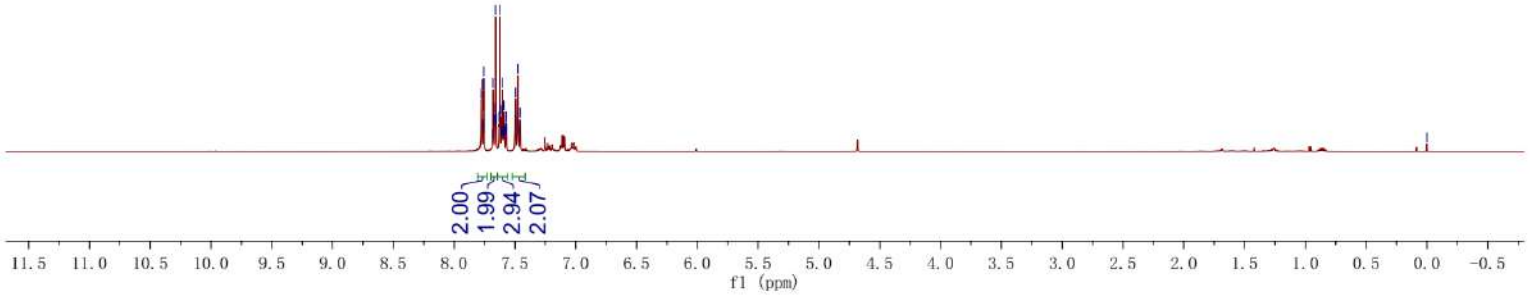

195.48
138.87
137.21
135.84
132.62
131.44
129.90
128.61
128.38
77.32
77.00
76.68
O
Cl
59
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

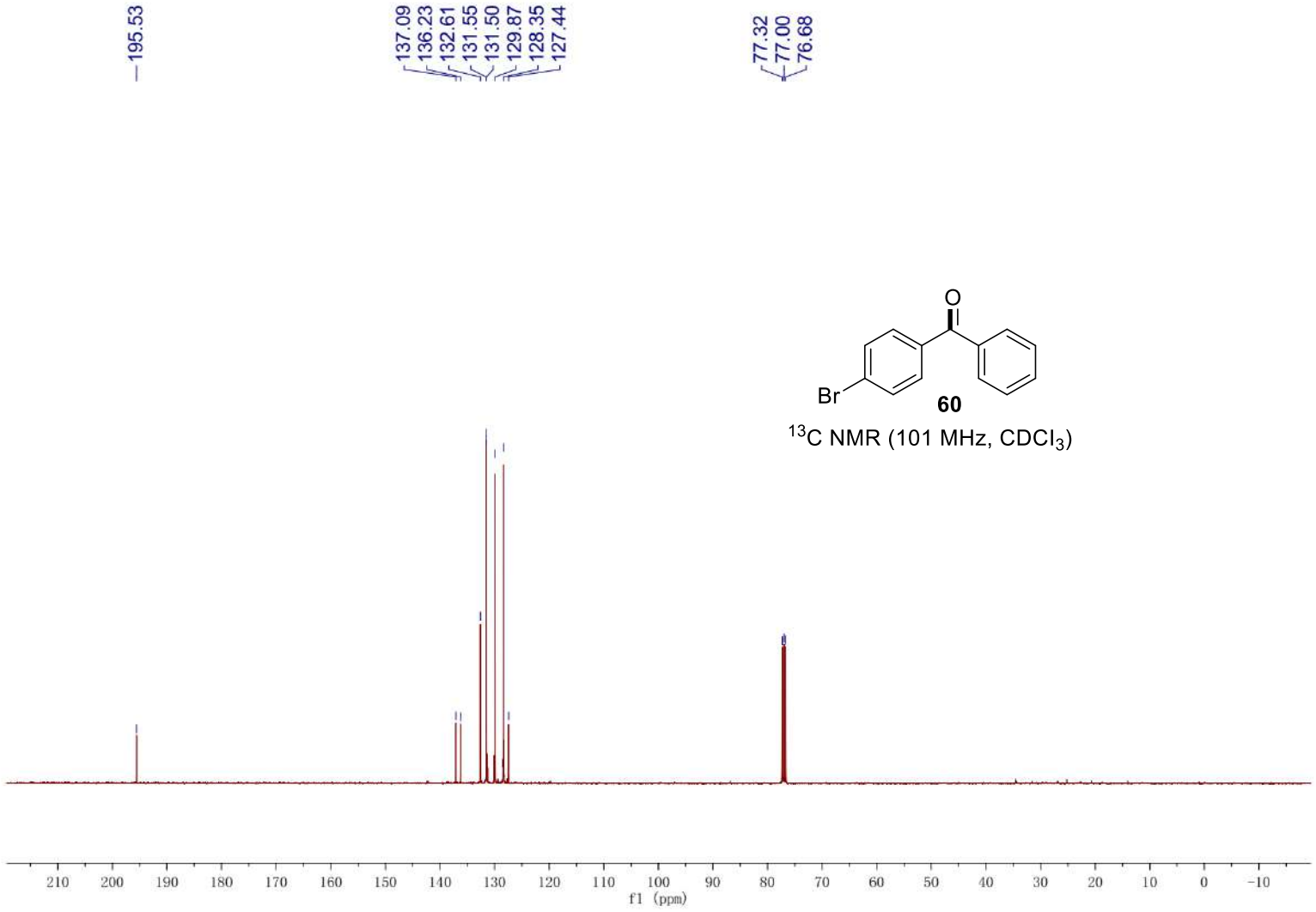


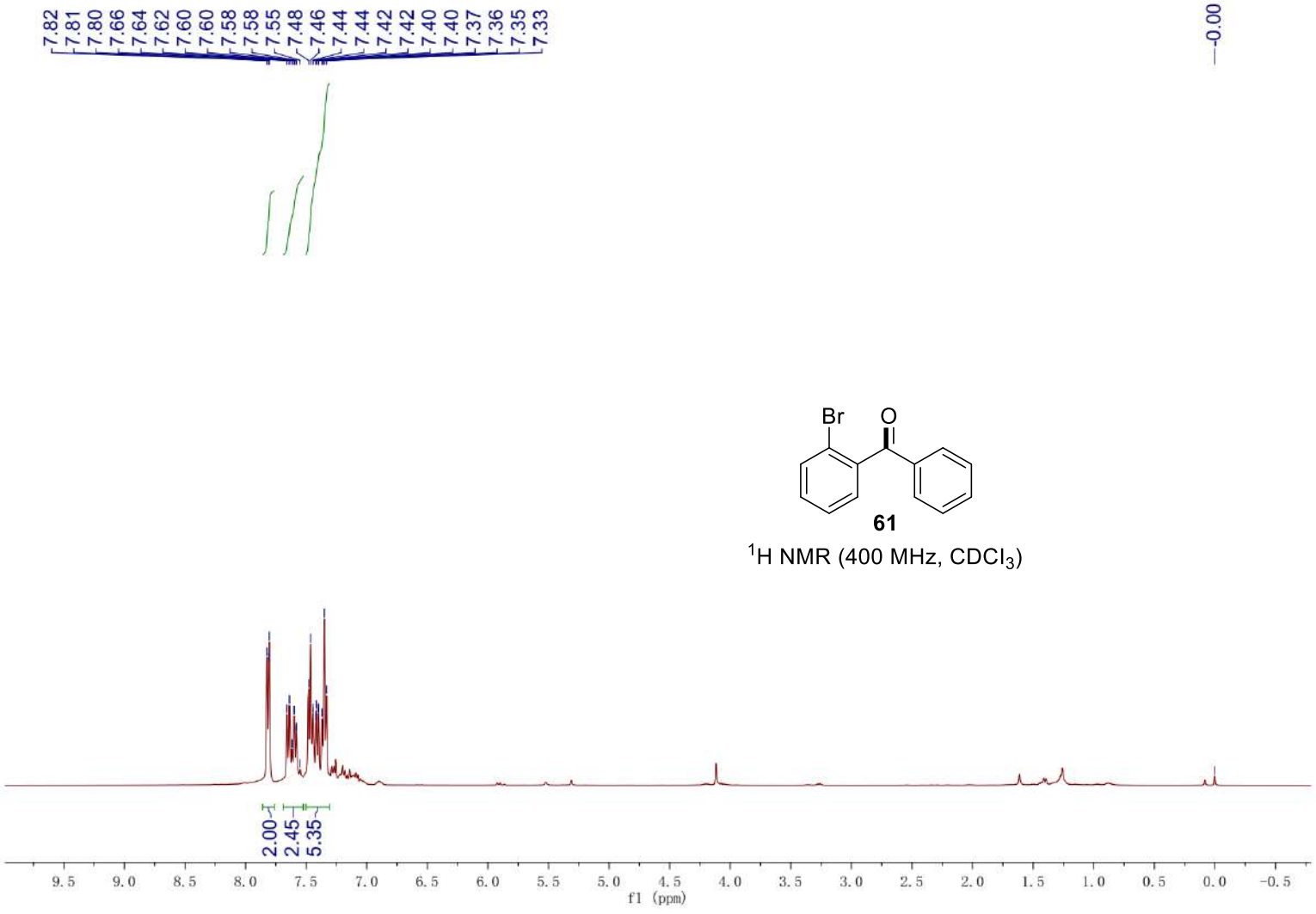


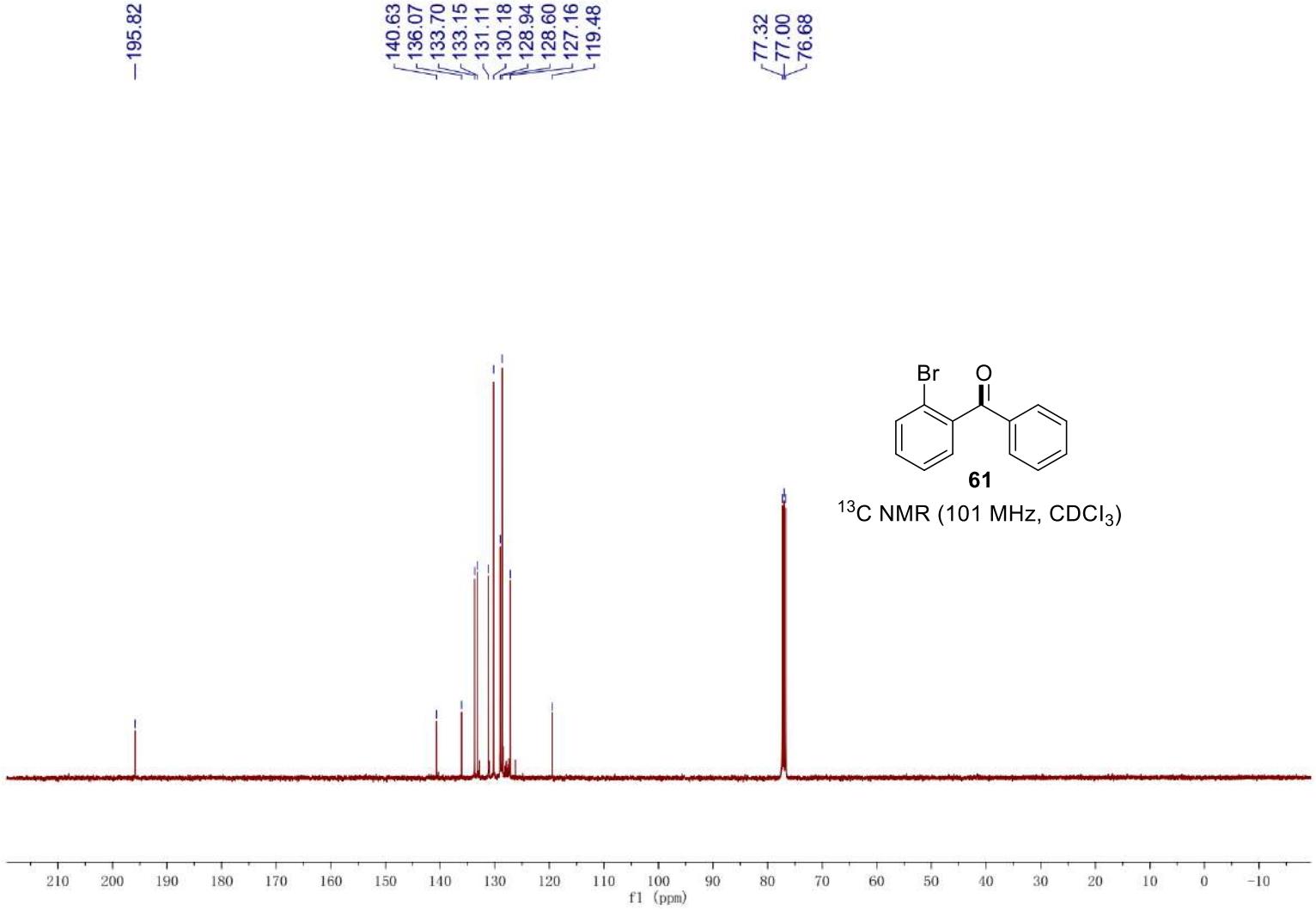
60

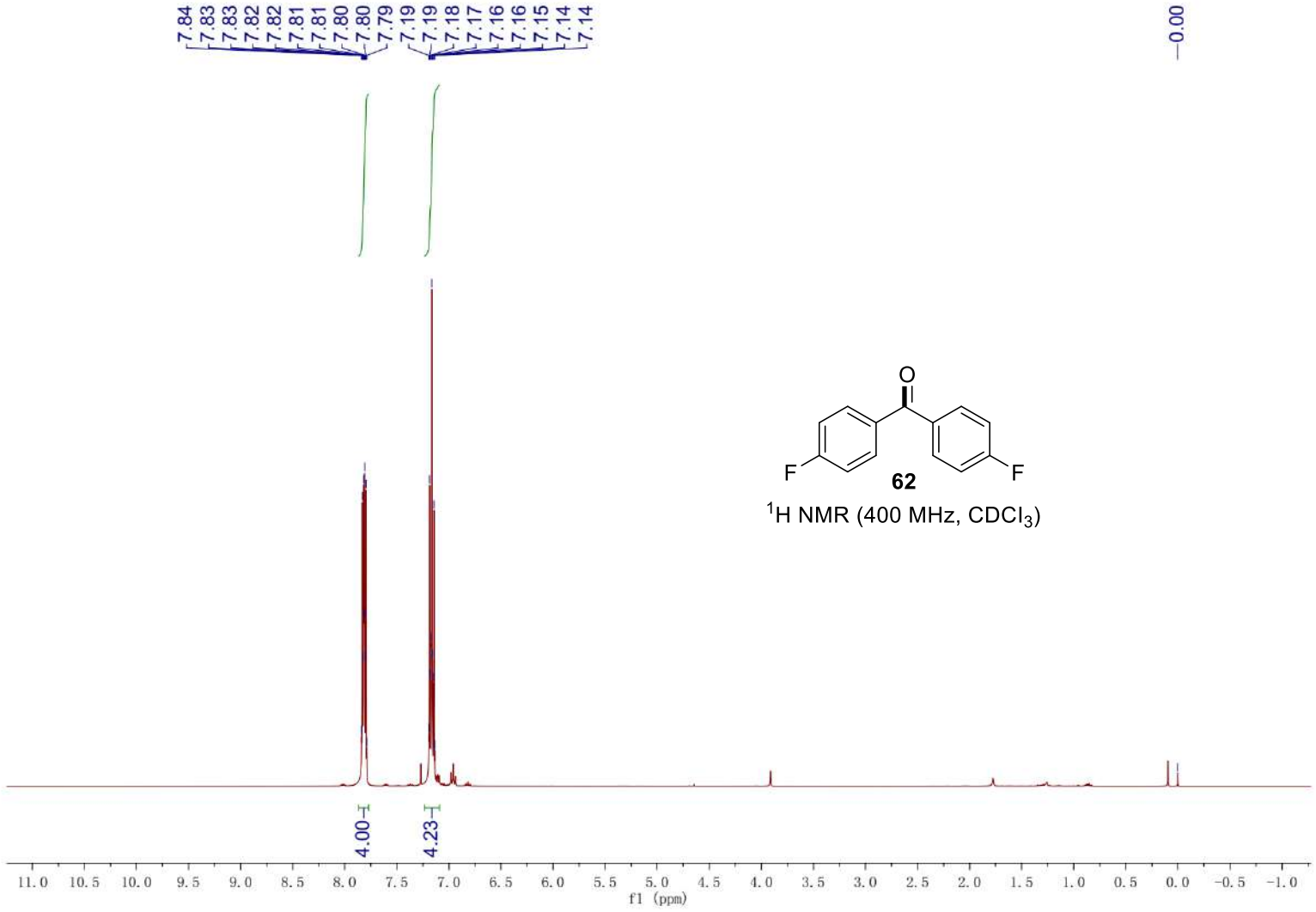
^{1}H NMR (400 MHz, $CDCl_3$)




195.53
137.09
136.23
132.61
131.55
131.50
129.87
128.35
127.44
77.32
77.00
76.68
O
Br
60
^{13}C NMR (101 MHz, $CDCl_3$)
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)

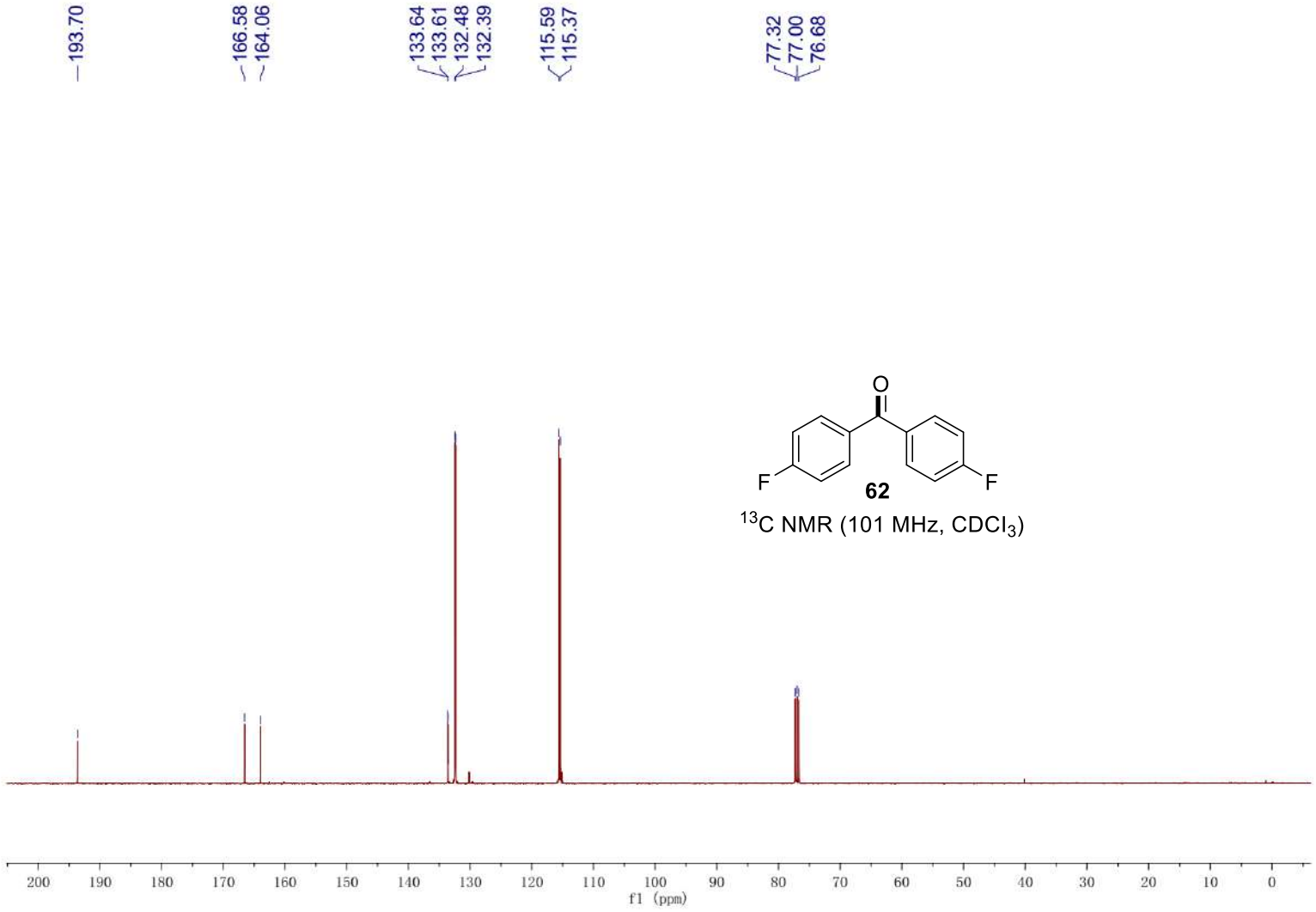

7.82
7.81
7.80
7.66
7.64
7.62
7.60
7.60
7.58
7.58
7.55
7.48
7.46
7.44
7.44
7.42
7.42
7.40
7.40
7.37
7.36
7.35
7.33
0.00
Br
O
61
1H NMR (400 MHz, CDCl3)
2.00
2.45
5.35
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

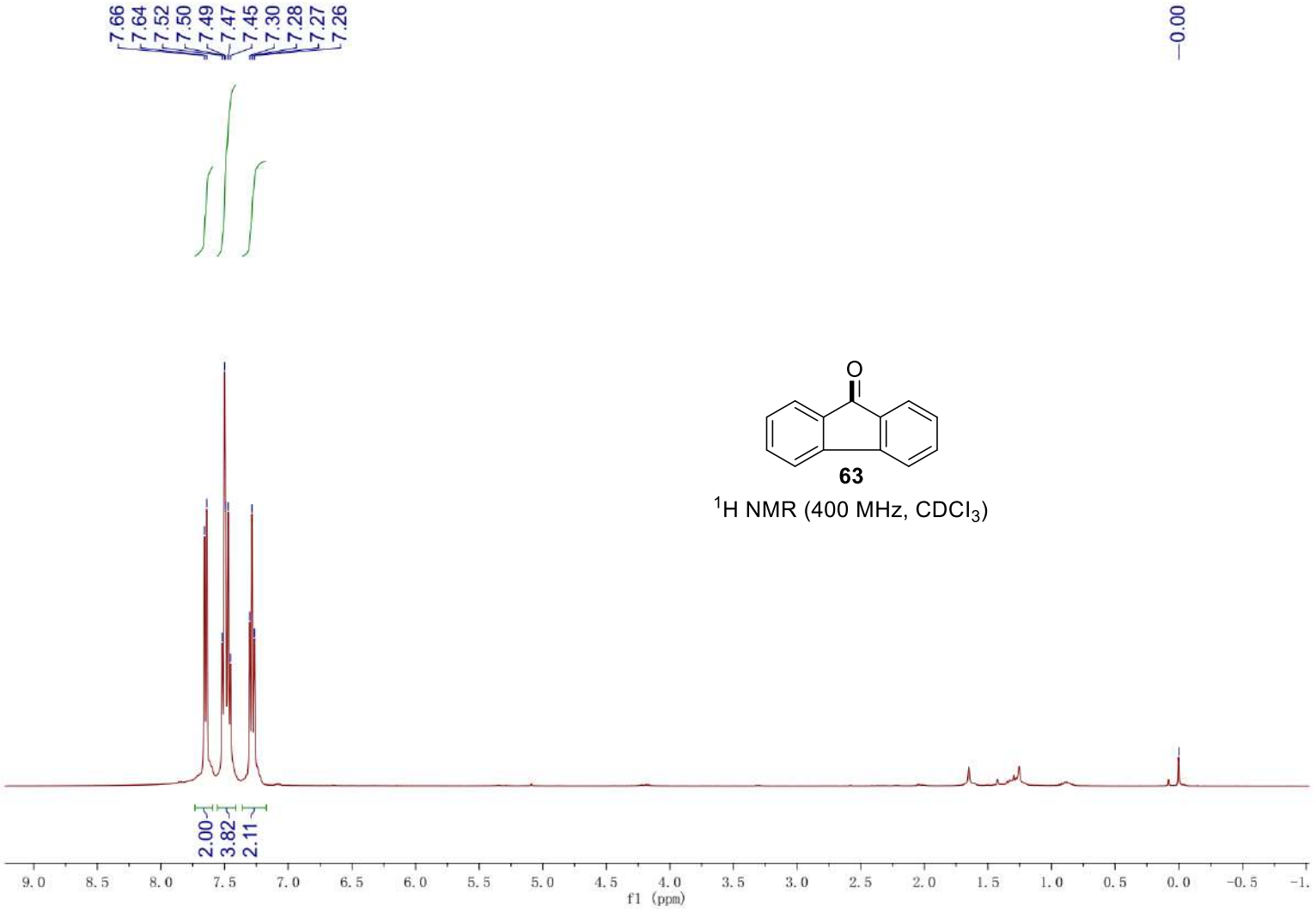

195.82
140.63
136.07
133.70
133.15
131.11
130.18
128.94
128.60
127.16
119.48
77.32
77.00
76.68
Br
O
61
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



62

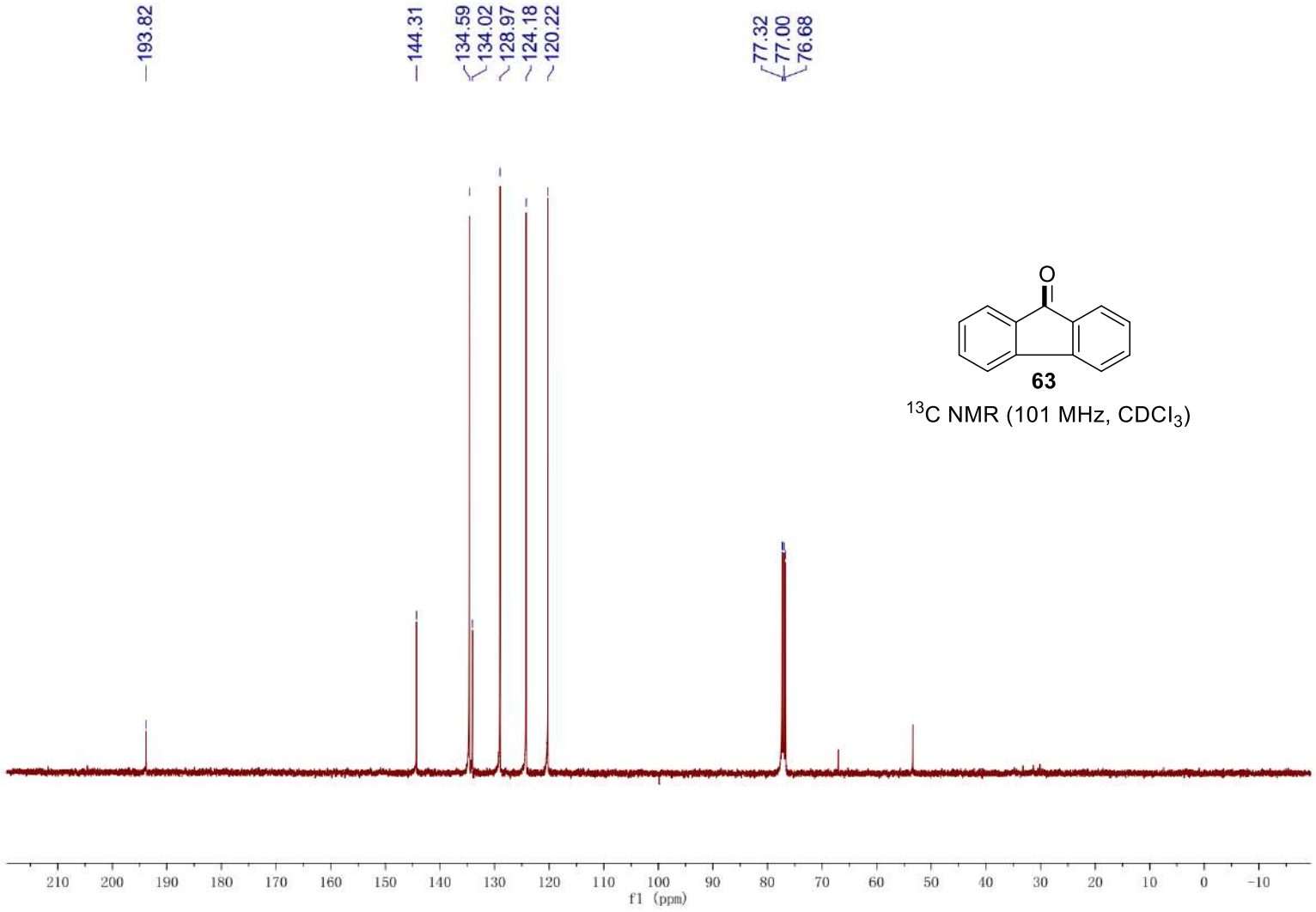
^{1}H NMR (400 MHz, $CDCl_3$)

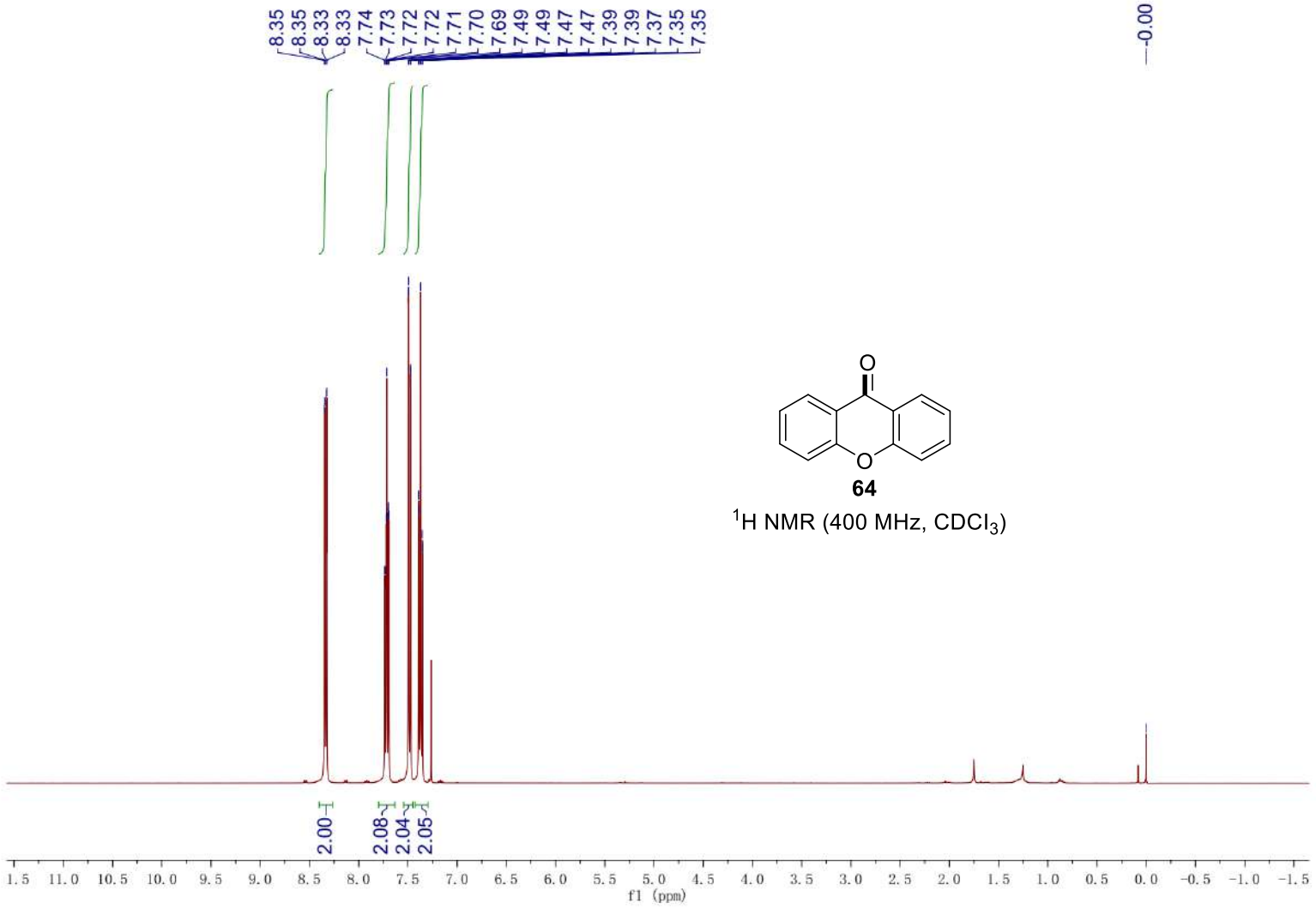

193.70
166.58
164.06
133.64
133.61
132.48
132.39
115.59
115.37
77.32
77.00
76.68
O
F
F
62
^{13}C NMR (101 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



63

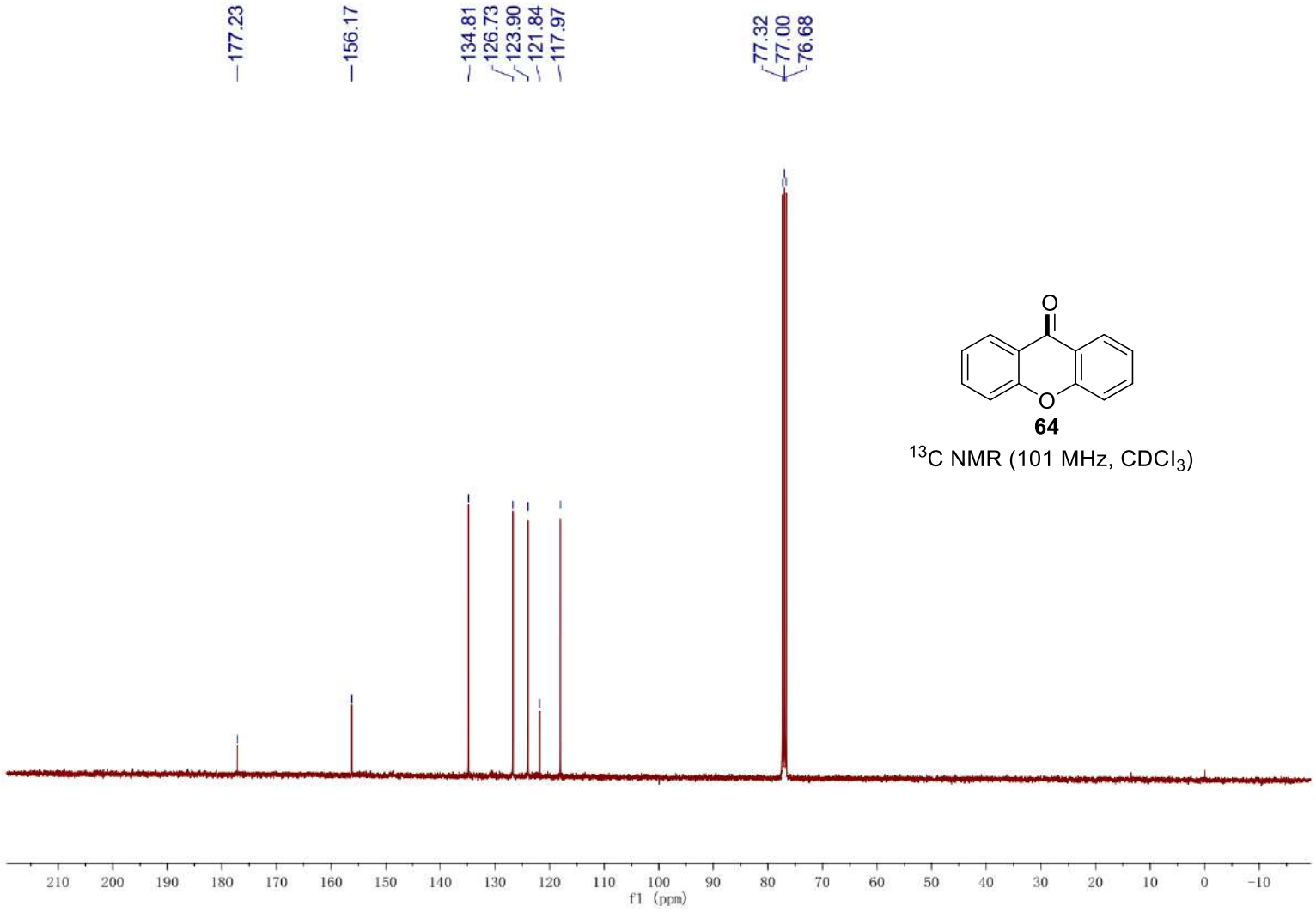
^{1}H NMR (400 MHz, $CDCl_3$)

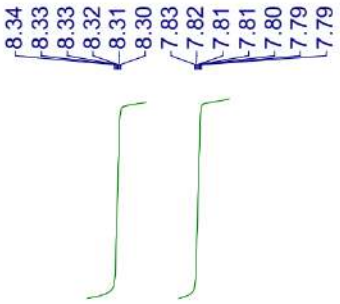

193.82
144.31
134.59
134.02
128.97
124.18
120.22
77.32
77.00
76.68
O
63
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

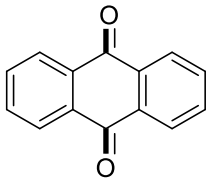


64

^{1}H NMR (400 MHz, $CDCl_3$)

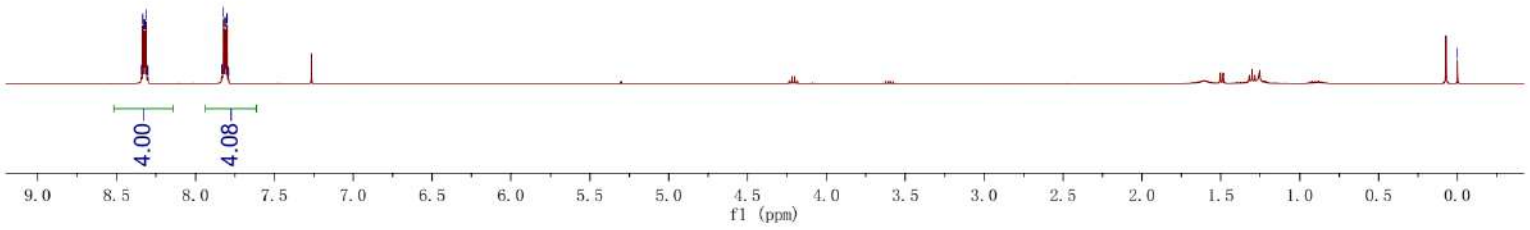

177.23
156.17
134.81
126.73
123.90
121.84
117.97
77.32
77.00
76.68
O
O
64
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

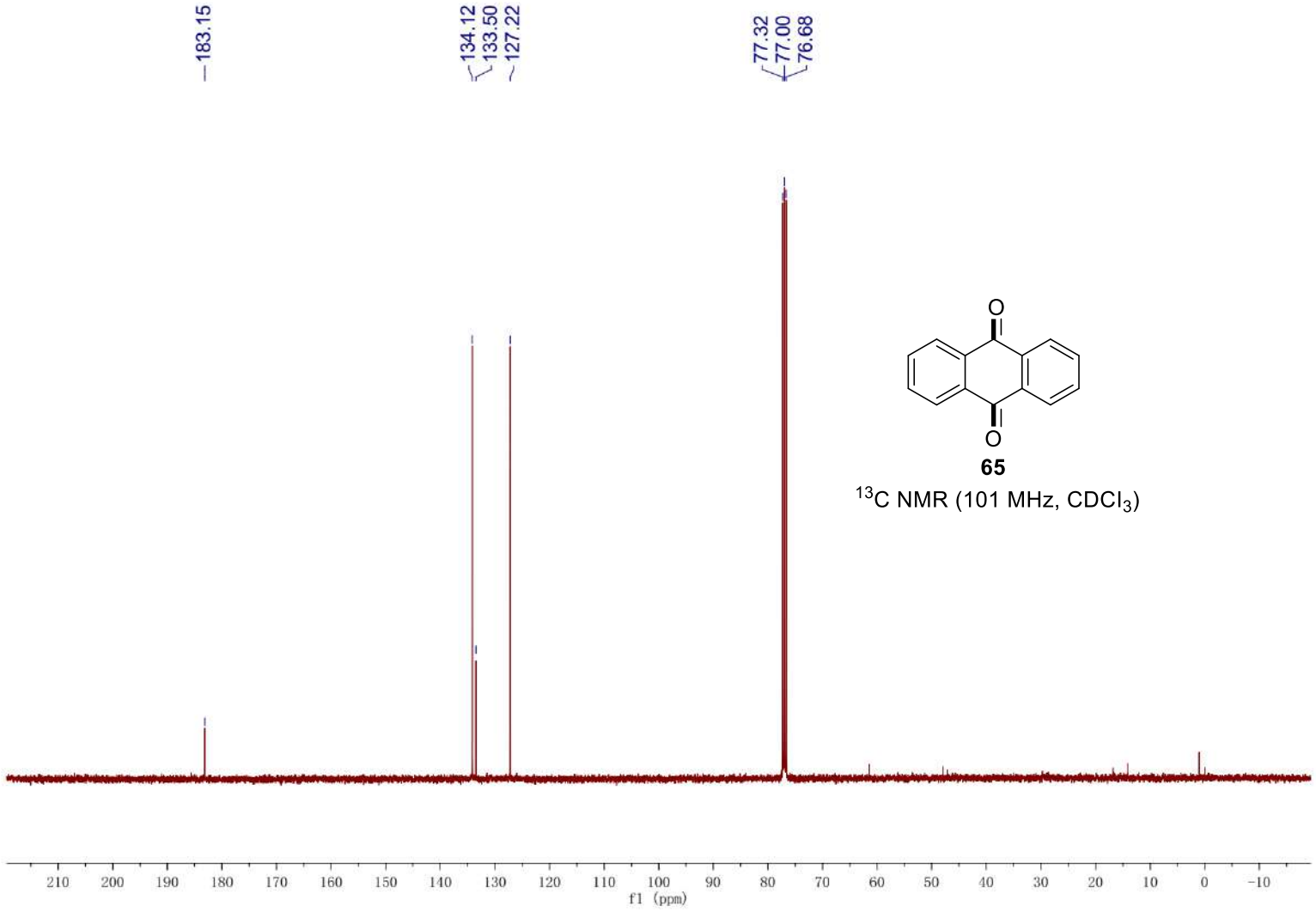




65

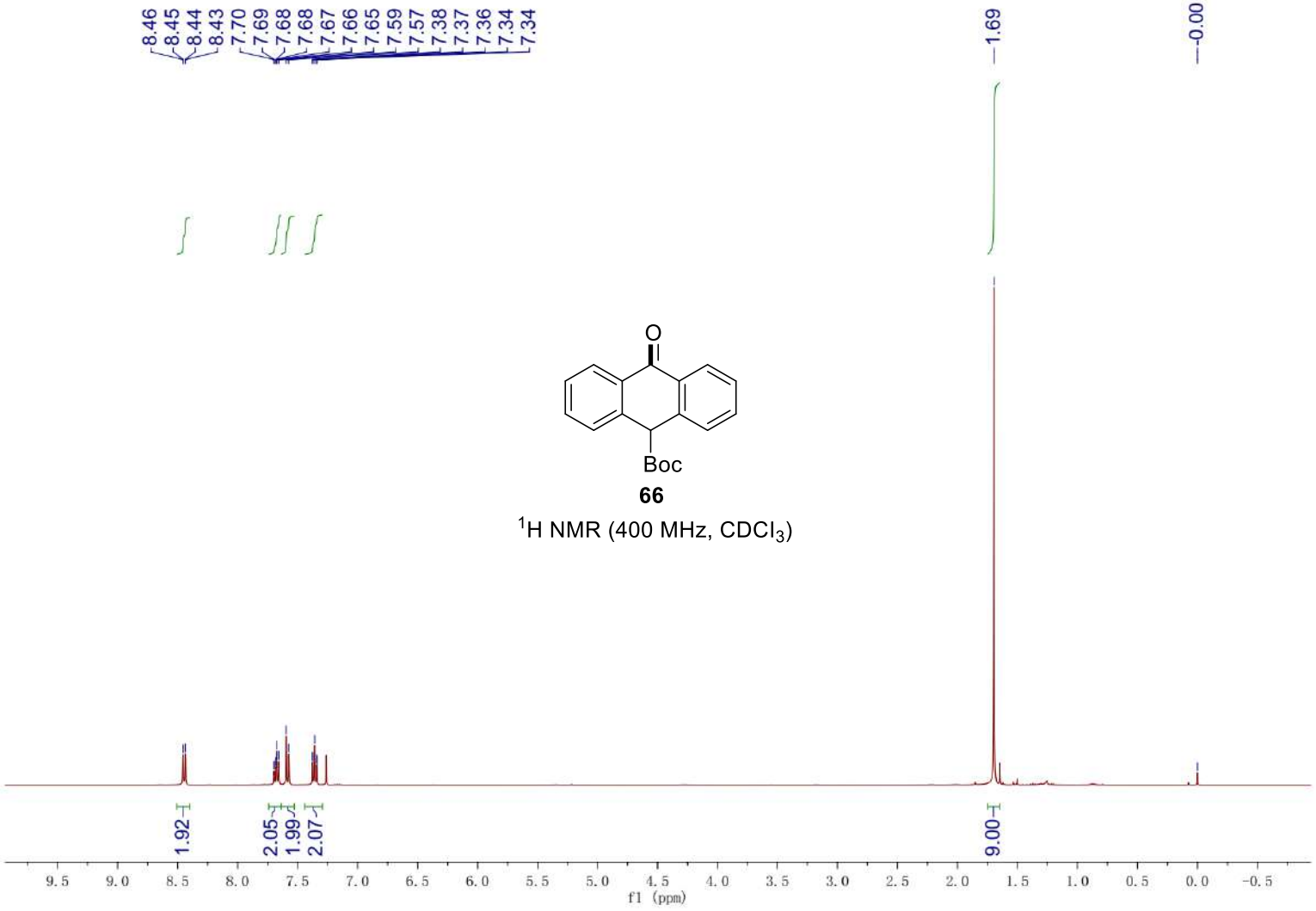
^{1}H NMR (400 MHz, $CDCl_3$)





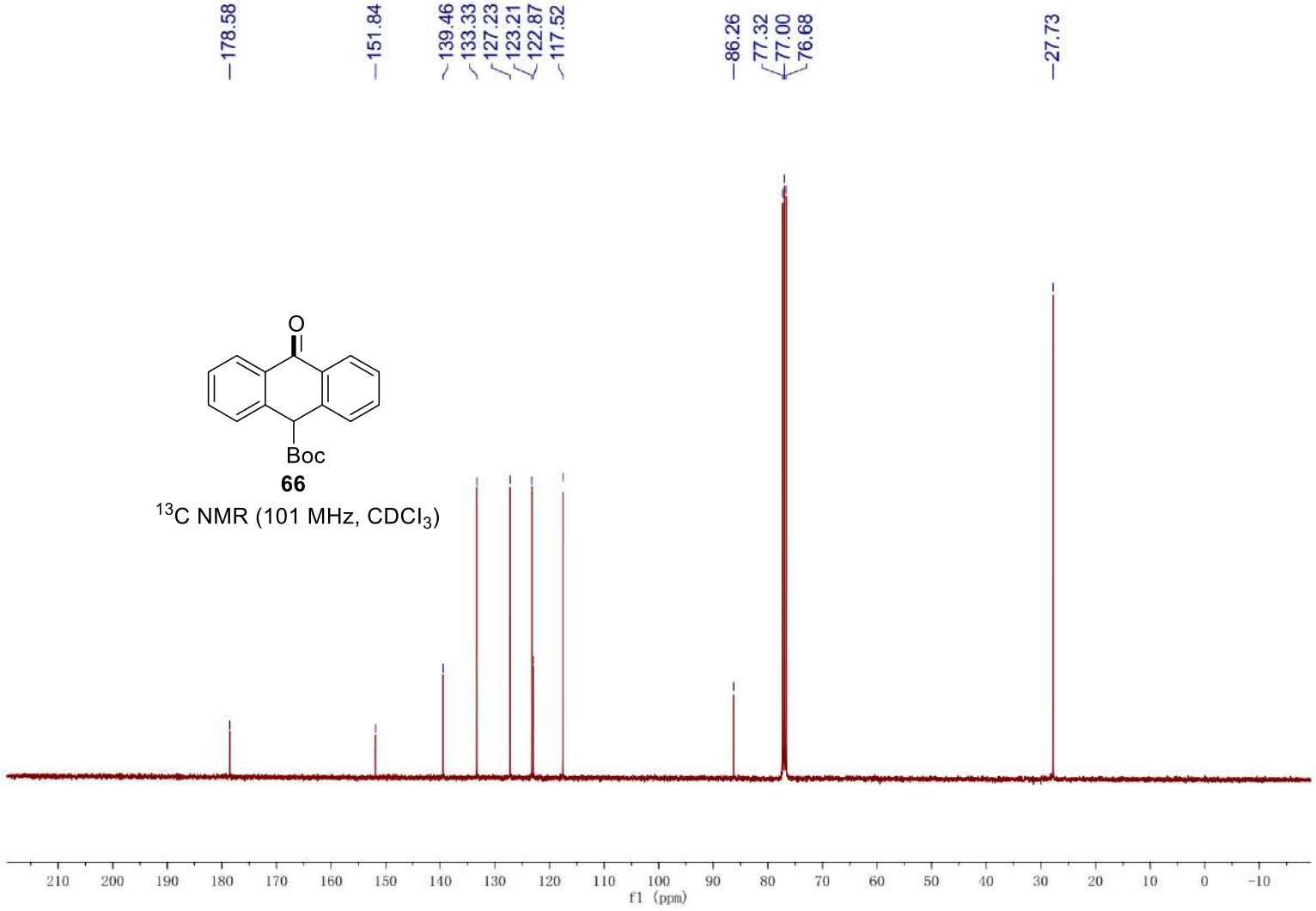
65

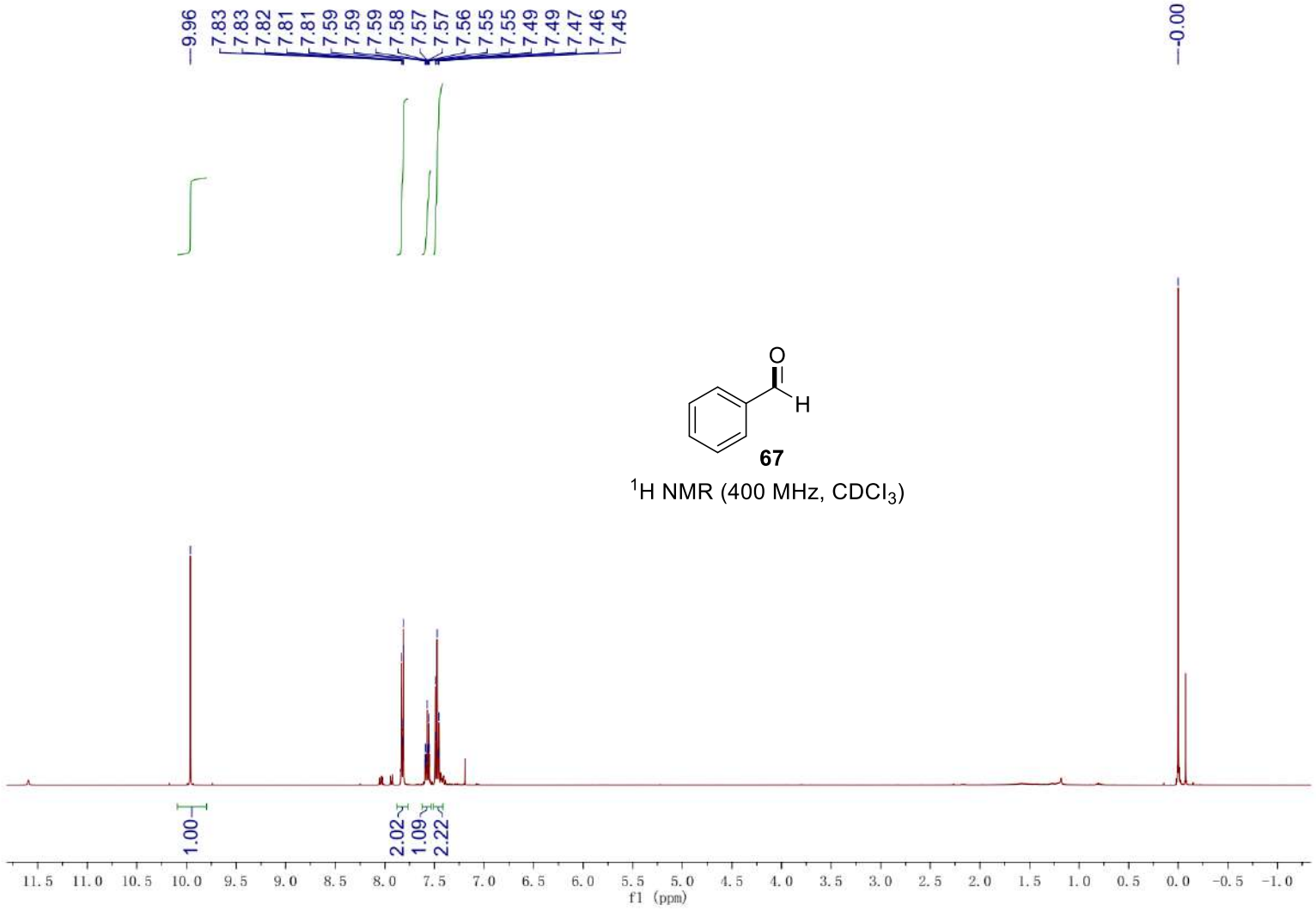
^{13}C NMR (101 MHz, $CDCl_3$)

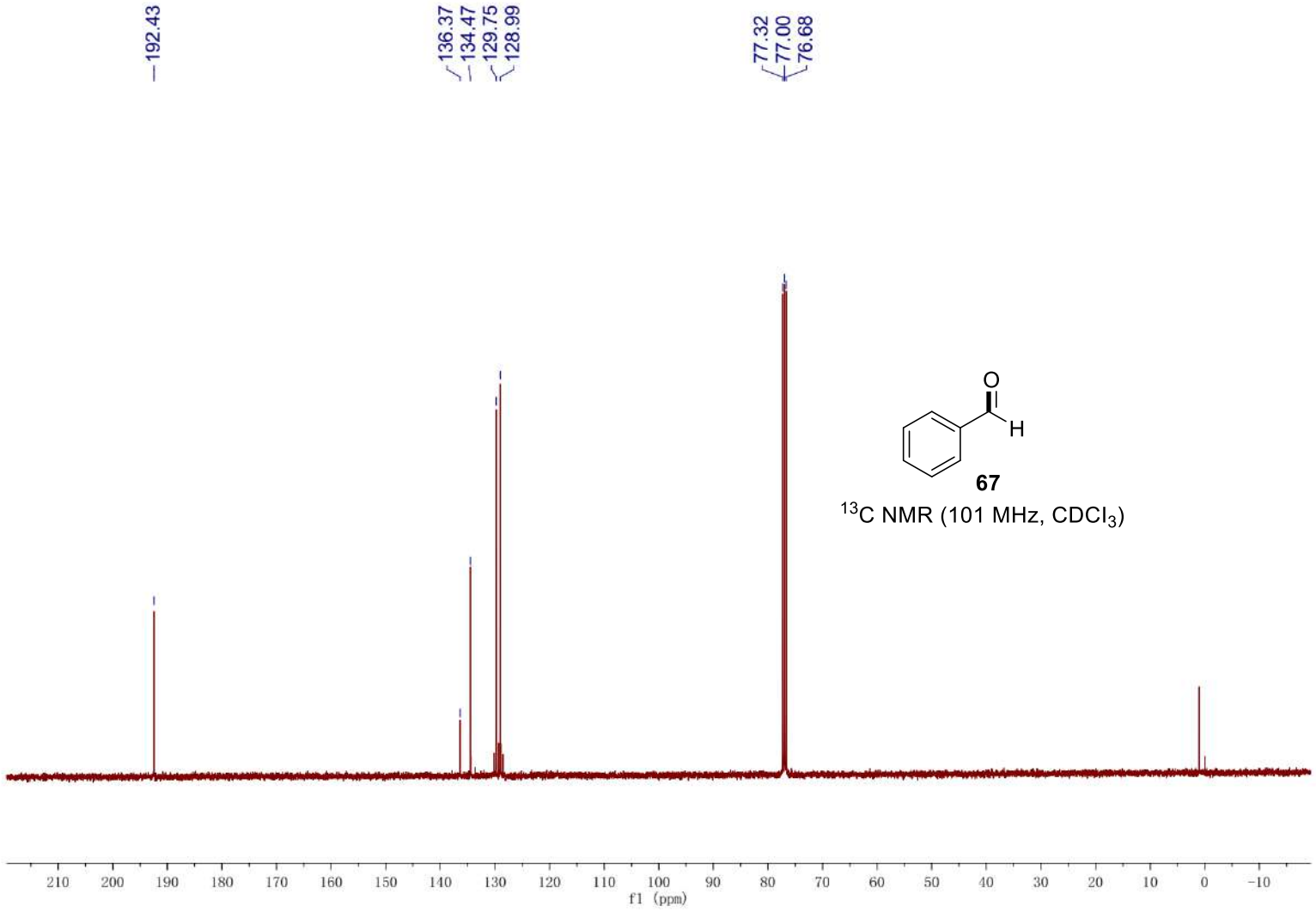


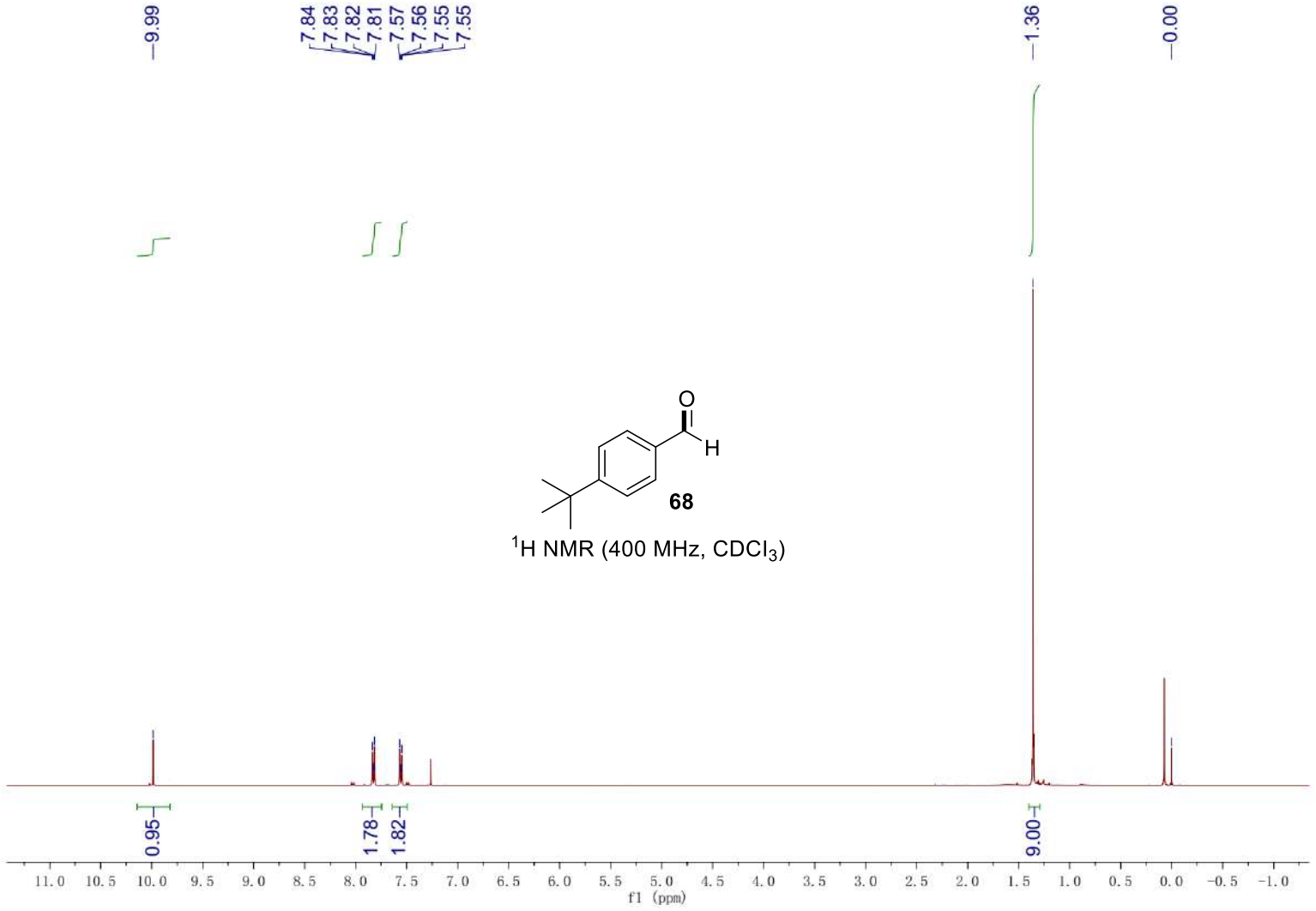
66

^{1}H NMR (400 MHz, $CDCl_3$)

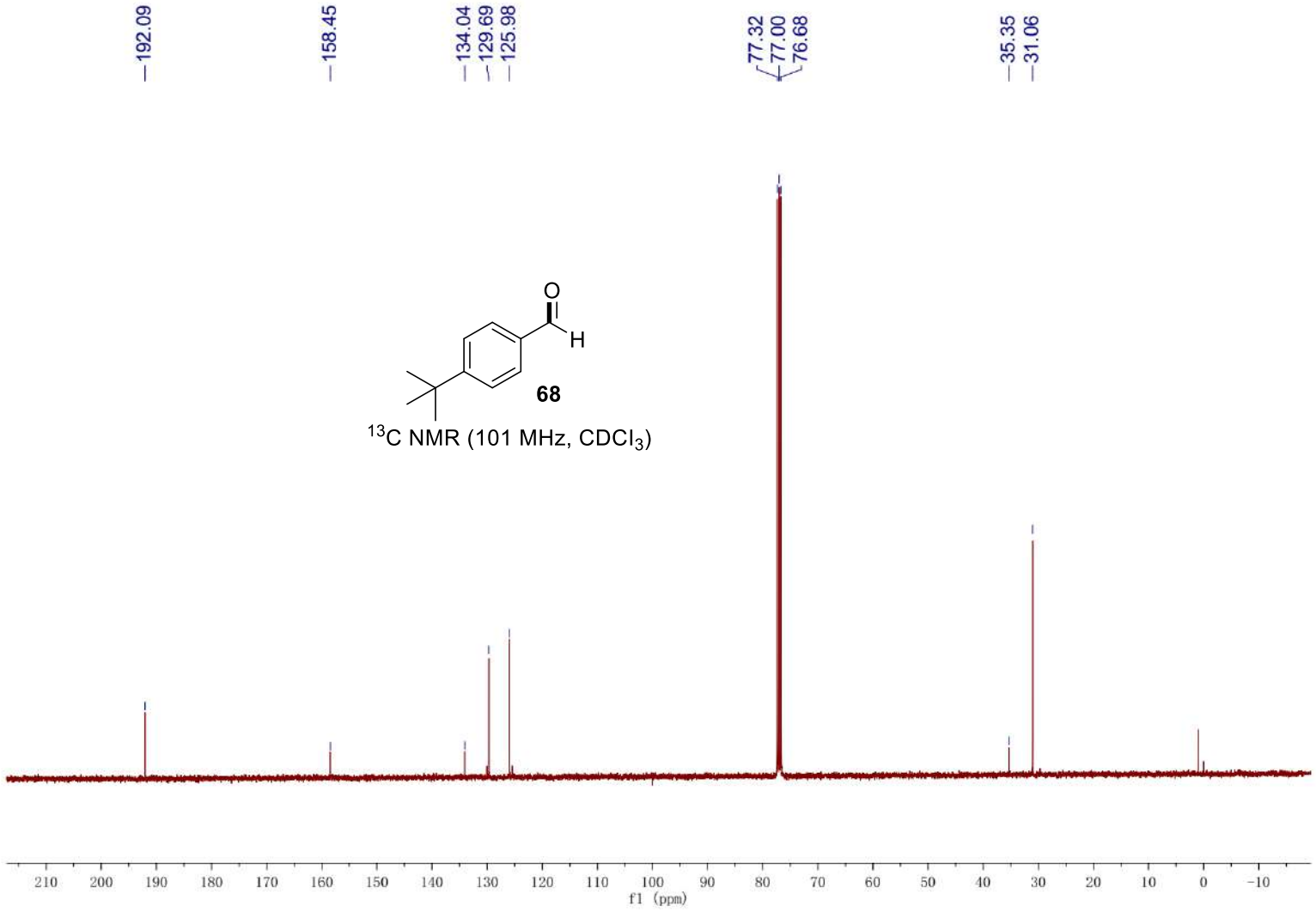

178.58
151.84
139.46
133.33
127.23
123.21
122.87
117.52
86.26
77.32
77.00
76.68
27.73
O
Boc
66
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

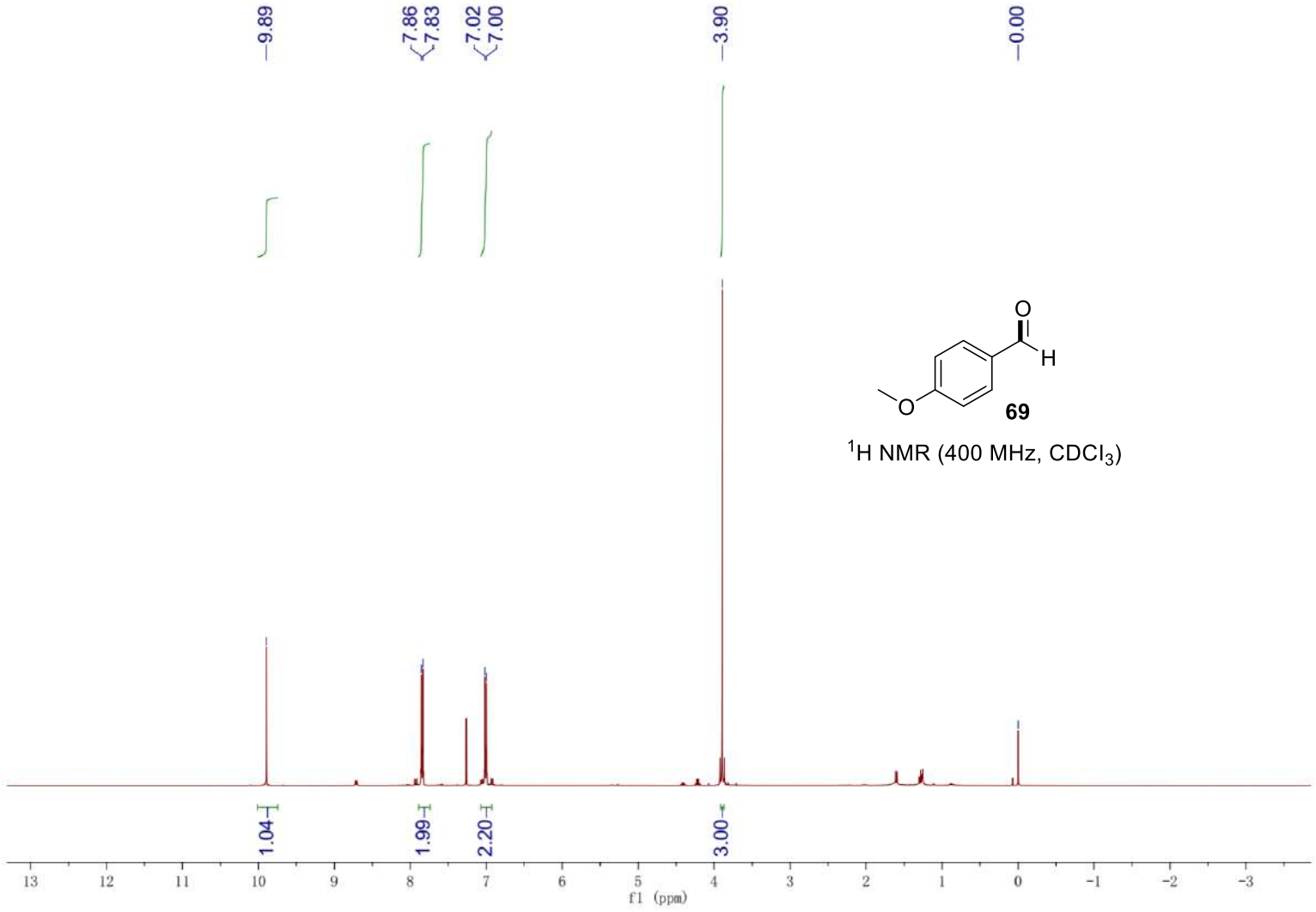

9.96
7.83
7.83
7.82
7.81
7.81
7.59
7.59
7.59
7.58
7.57
7.57
7.56
7.55
7.55
7.49
7.49
7.47
7.46
7.45
0.00
O
H
67
1H NMR (400 MHz, CDCl3)
1.00
2.02
1.09
2.22
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


192.43
136.37
134.47
129.75
128.99
77.32
77.00
76.68
O
H
67
^{13}C NMR (101 MHz, $CDCl_3$)
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)



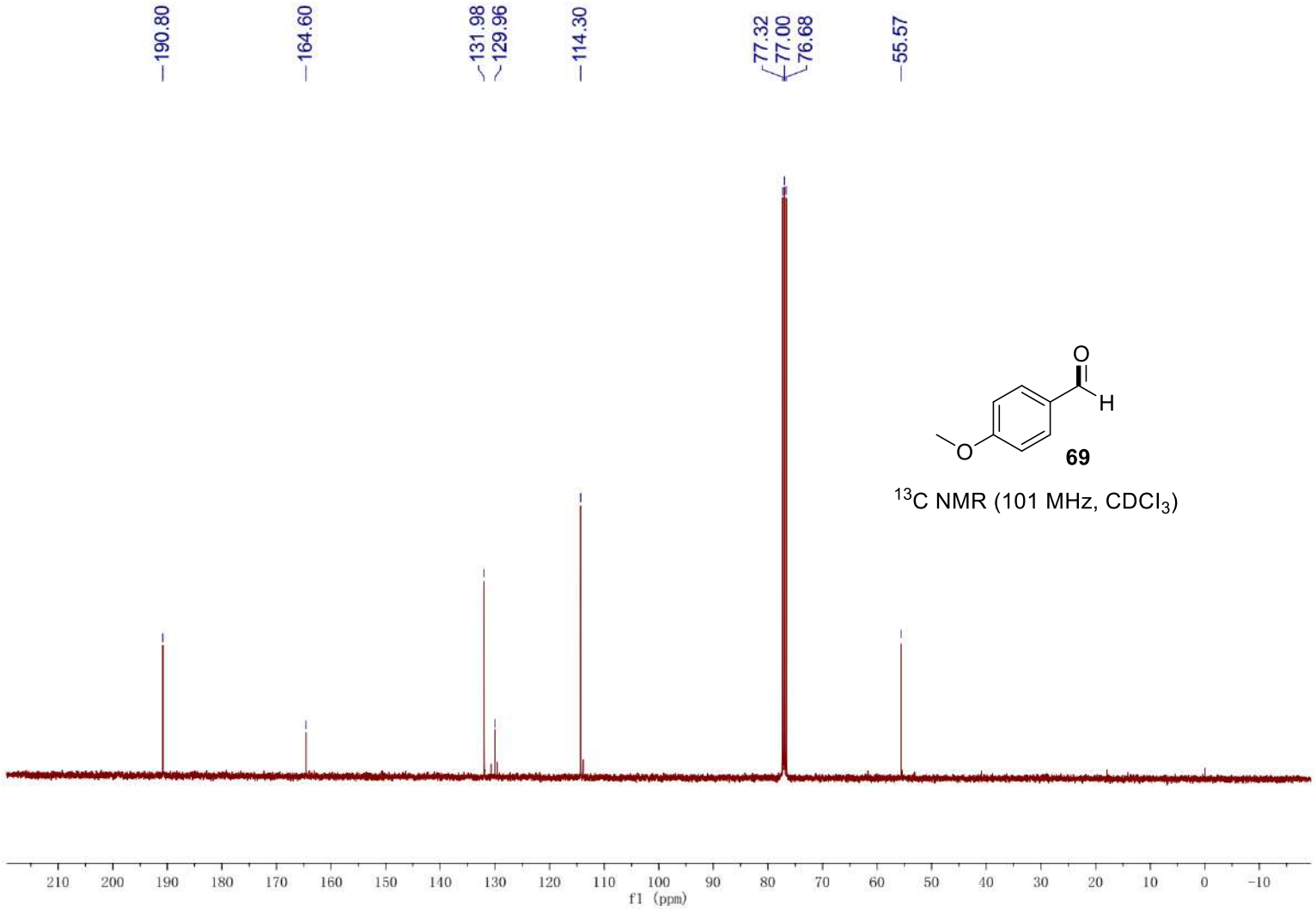
^{1}H NMR (400 MHz, $CDCl_3$)

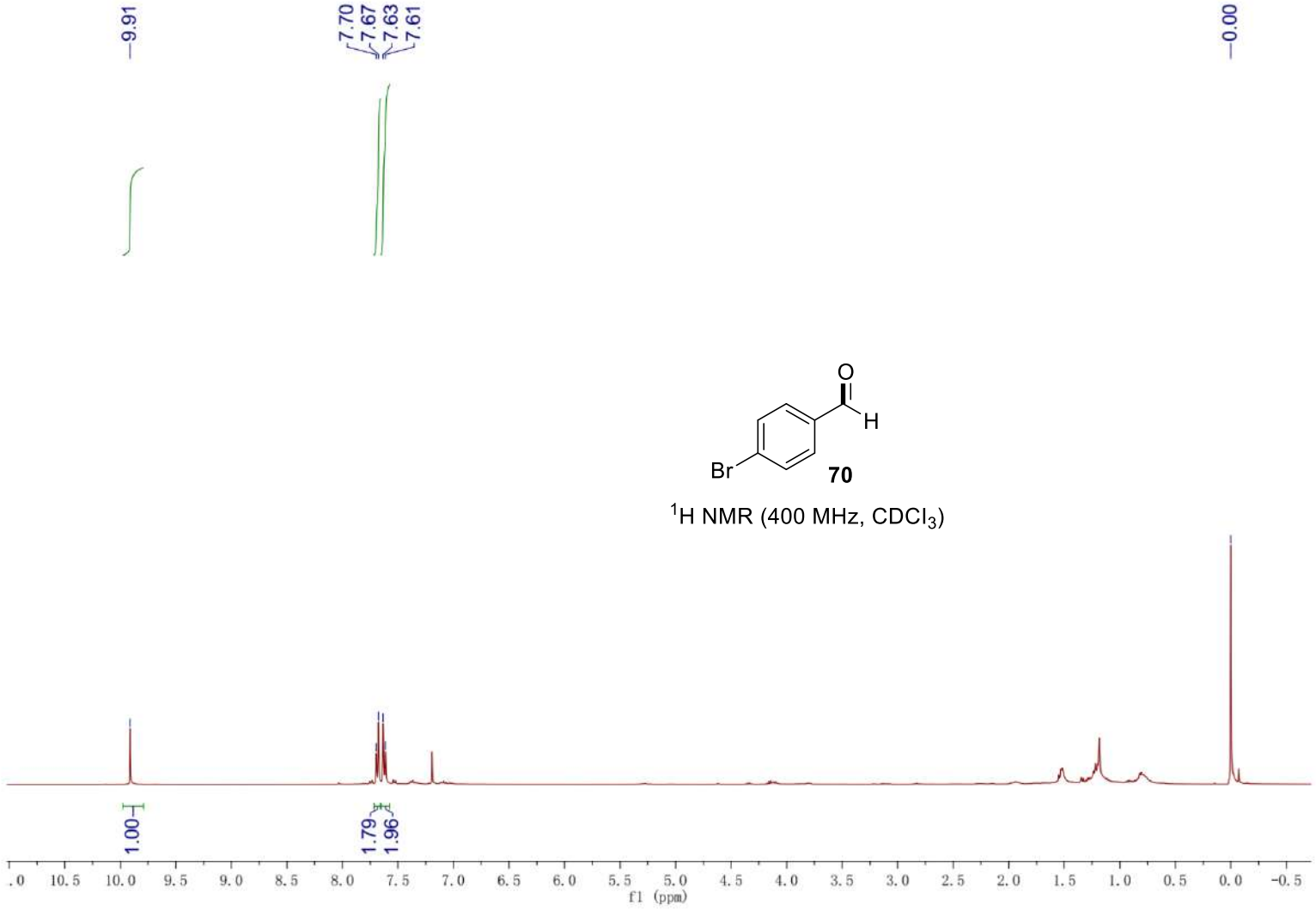

192.09
158.45
134.04
129.69
125.98
77.32
77.00
76.68
35.35
31.06
O
H
68
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

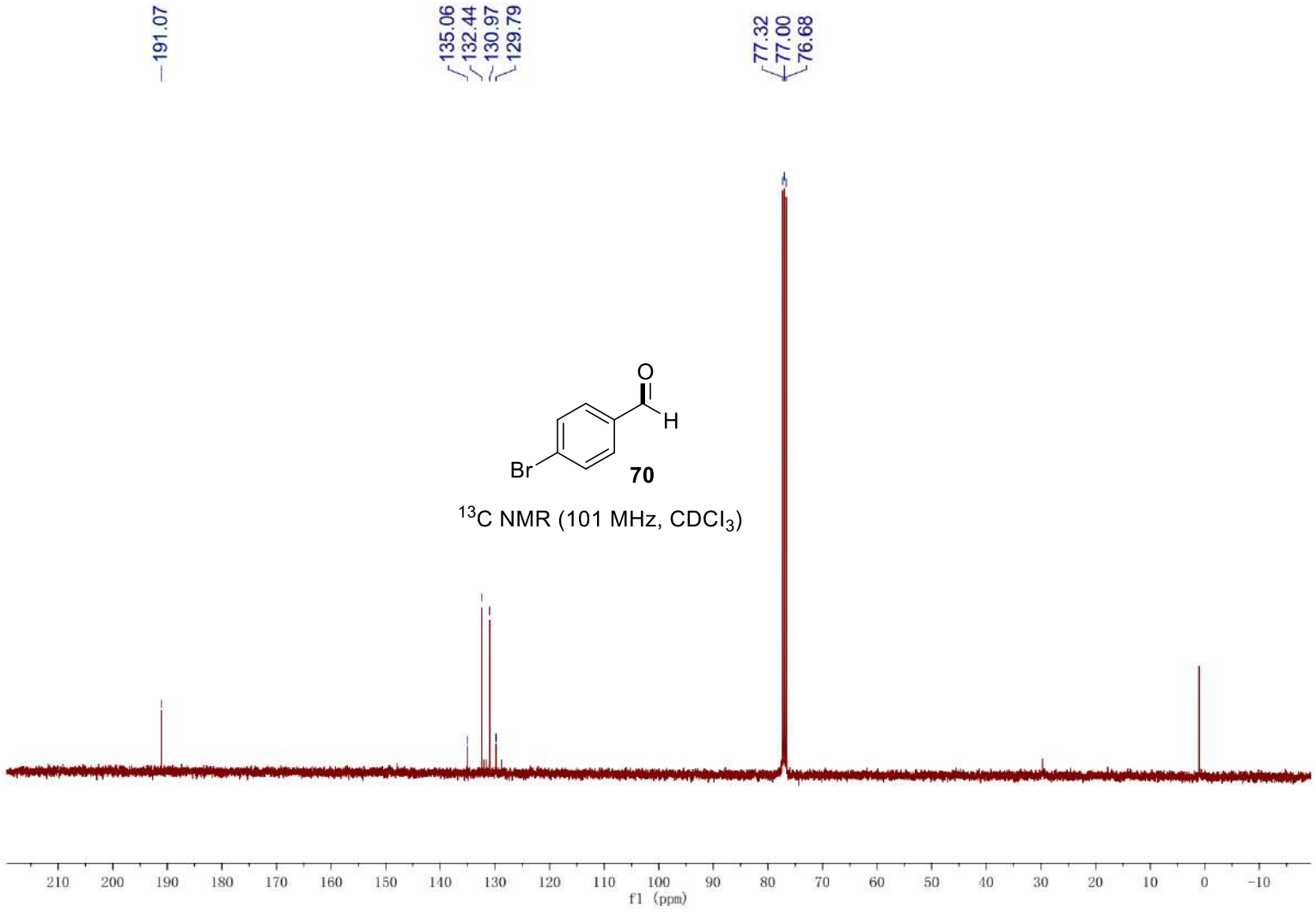


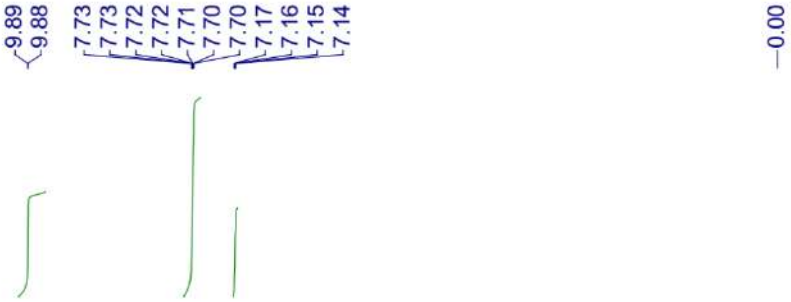
69

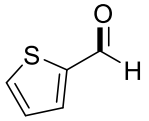
^{1}H NMR (400 MHz, $CDCl_3$)


190.80
164.60
131.98
129.96
114.30
77.32
77.00
76.68
55.57
O
H
O
69
^{13}C NMR (101 MHz, $CDCl_3$)
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)


9.91
7.70
7.67
7.63
7.61
0.00
O
H
Br
70
1H NMR (400 MHz, CDCl3)
1.00
1.79
1.96
f1 (ppm)

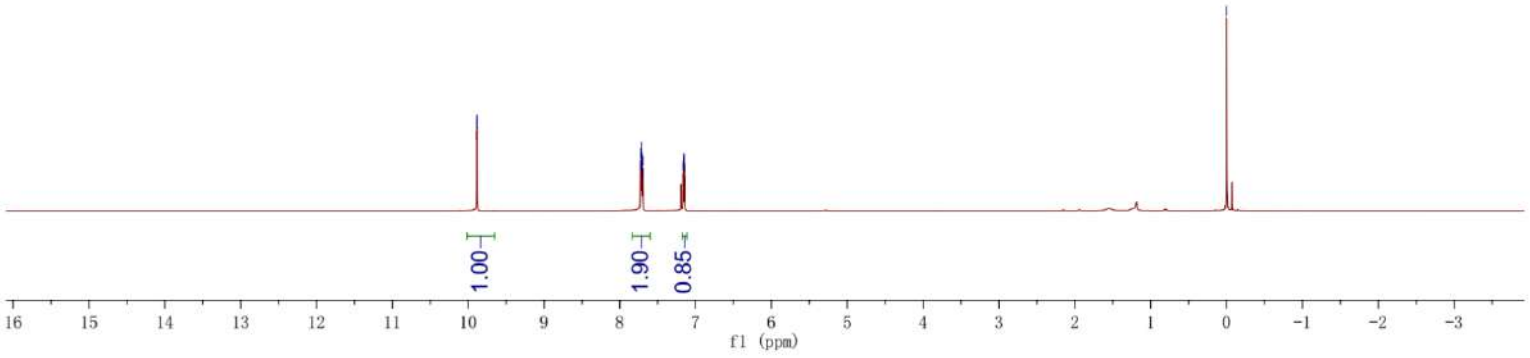

191.07
135.06
132.44
130.97
129.79
77.32
77.00
76.68
O
H
Br
70
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

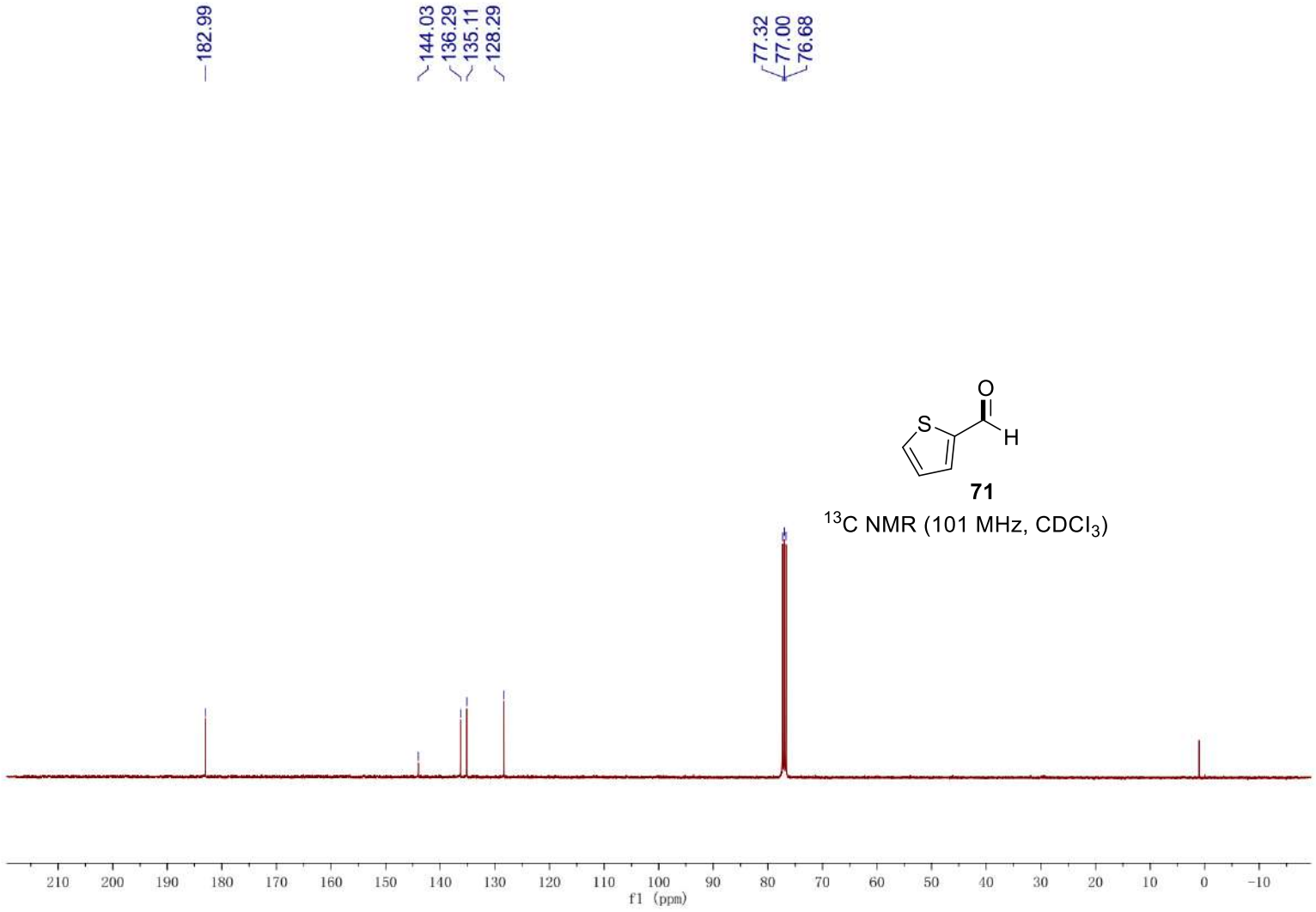


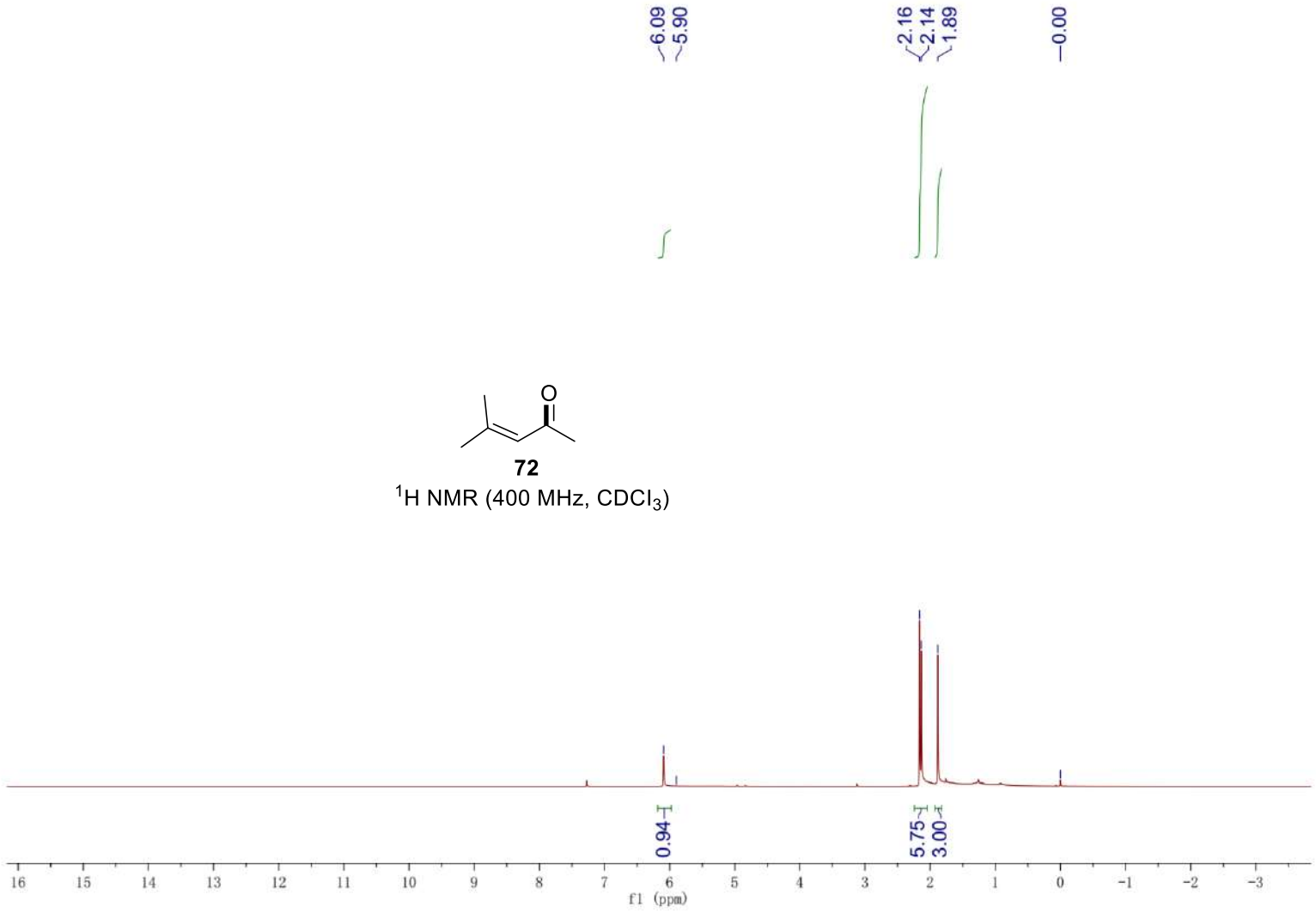


71

^{1}H NMR (400 MHz, $CDCl_3$)

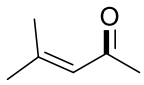



182.99
144.03
136.29
135.11
128.29
77.32
77.00
76.68
O
S
H
71
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



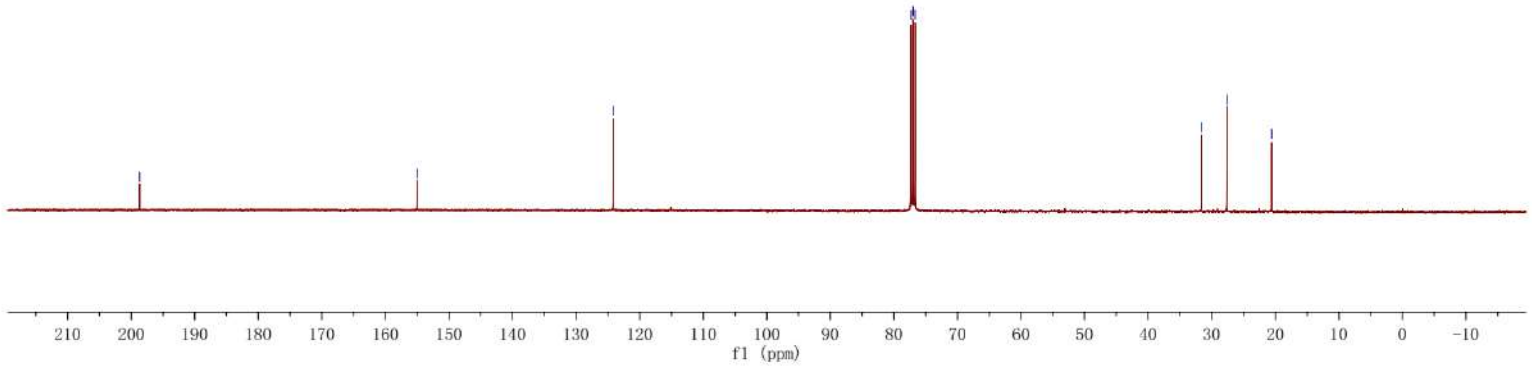
72

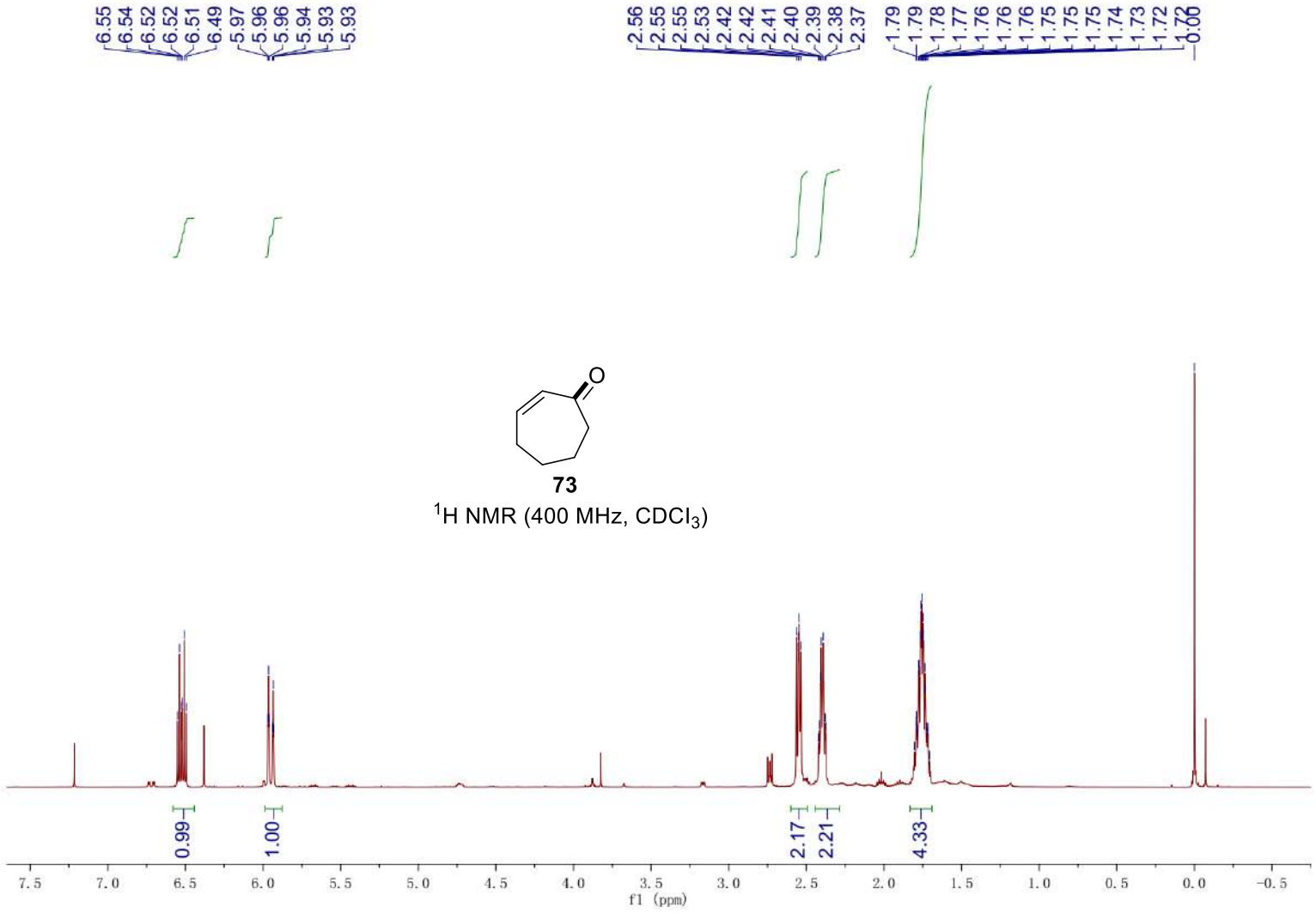
^{1}H NMR (400 MHz, $CDCl_3$)



72

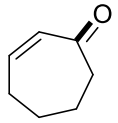
^{13}C NMR (101 MHz, $CDCl_3$)





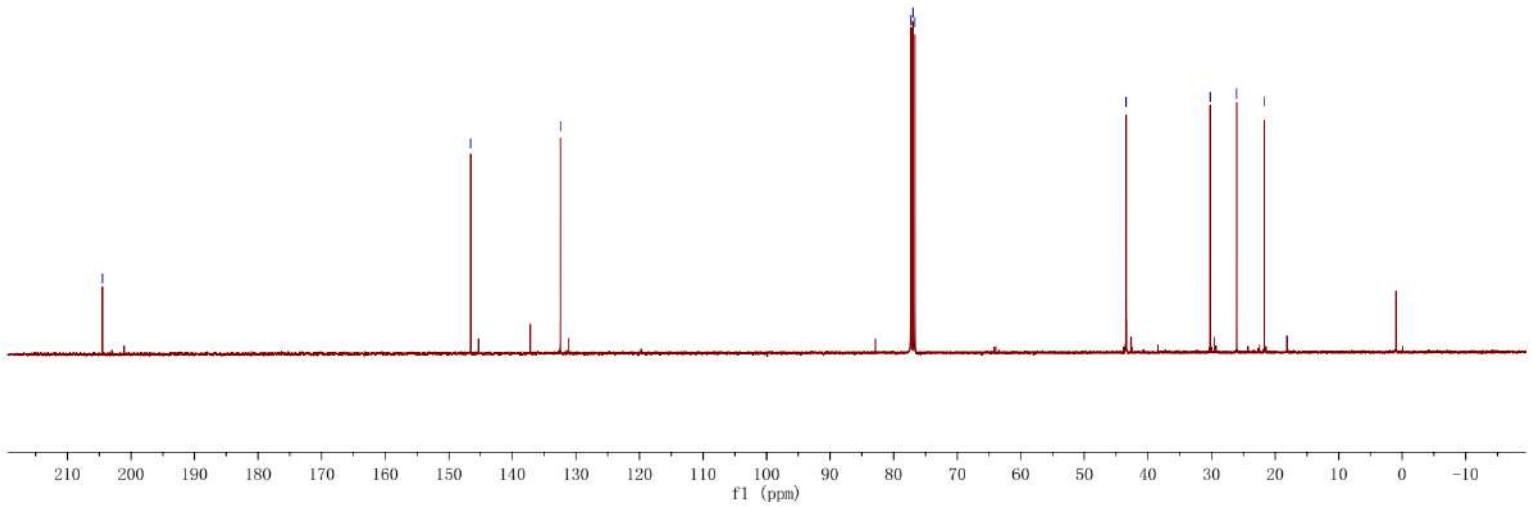
73

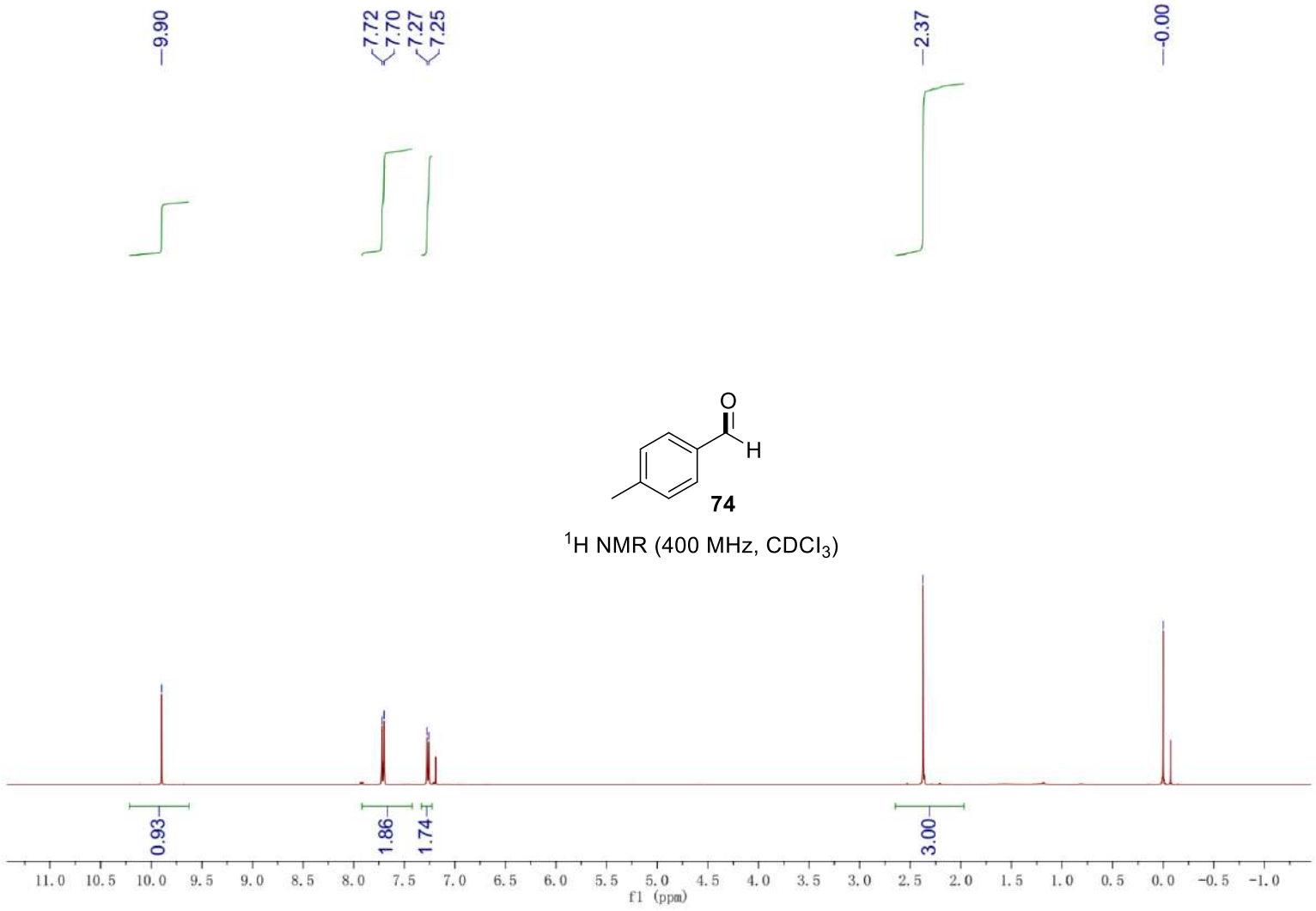
^{1}H NMR (400 MHz, $CDCl_3$)

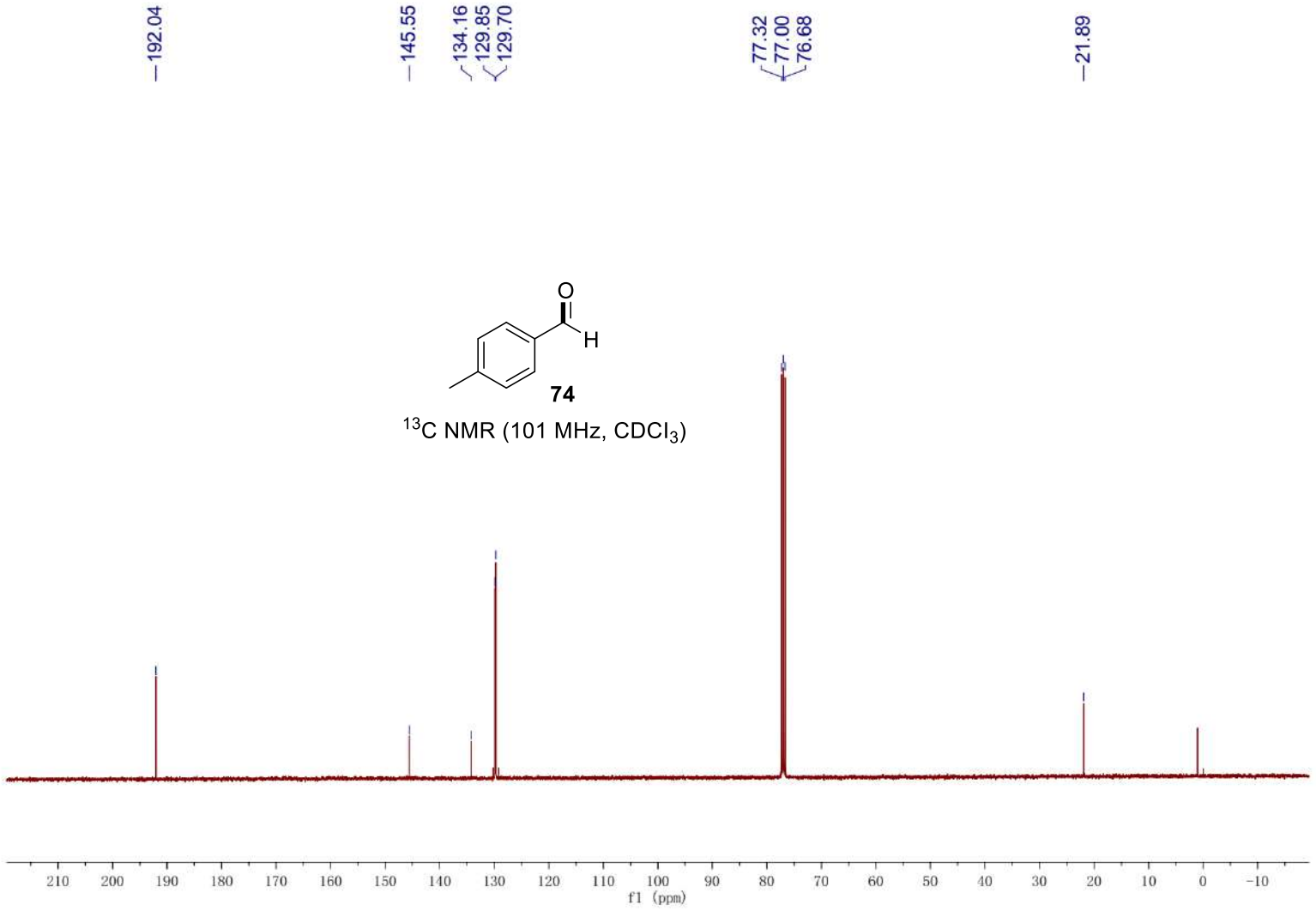


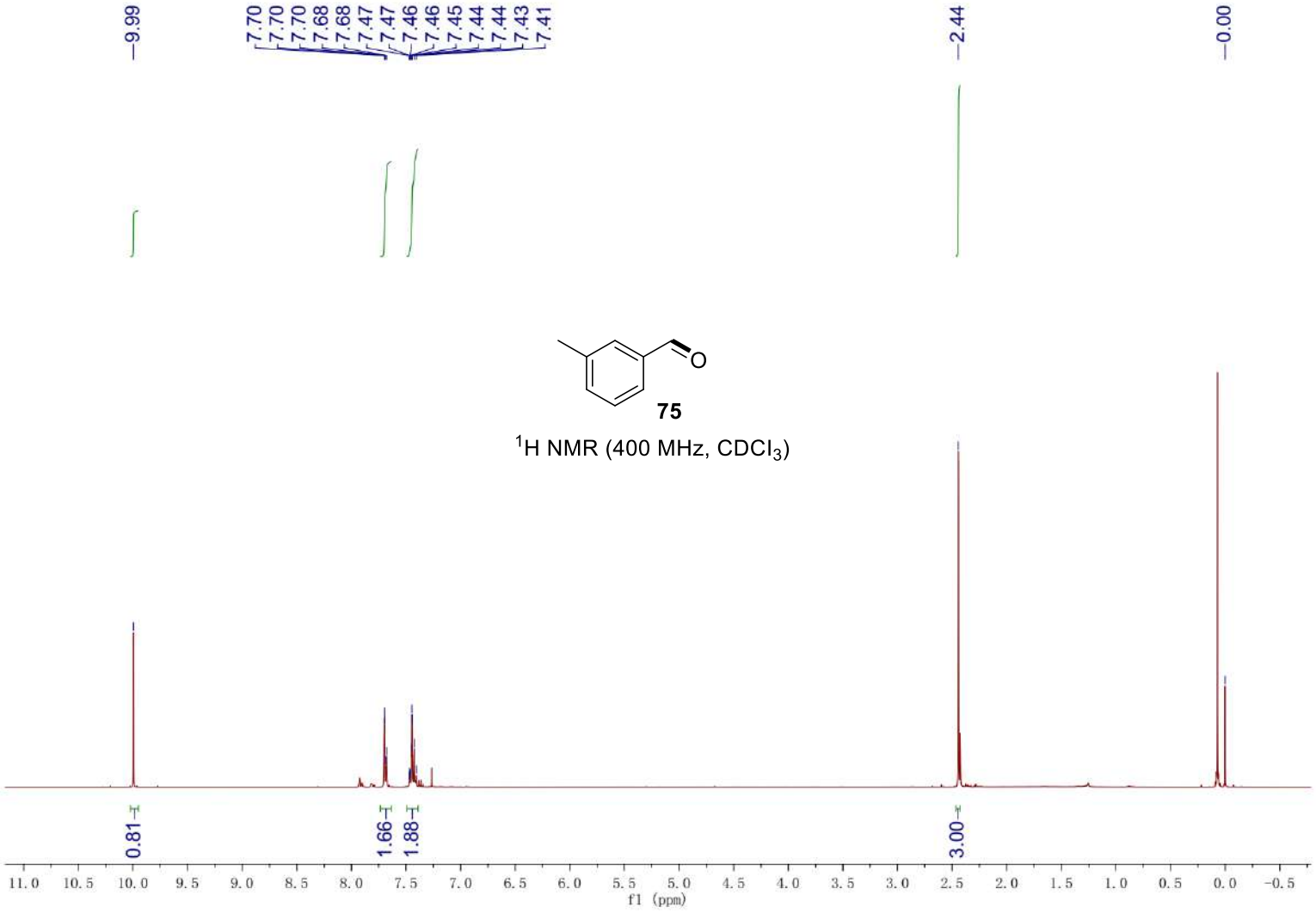
73

^{13}C NMR (101 MHz, $CDCl_3$)



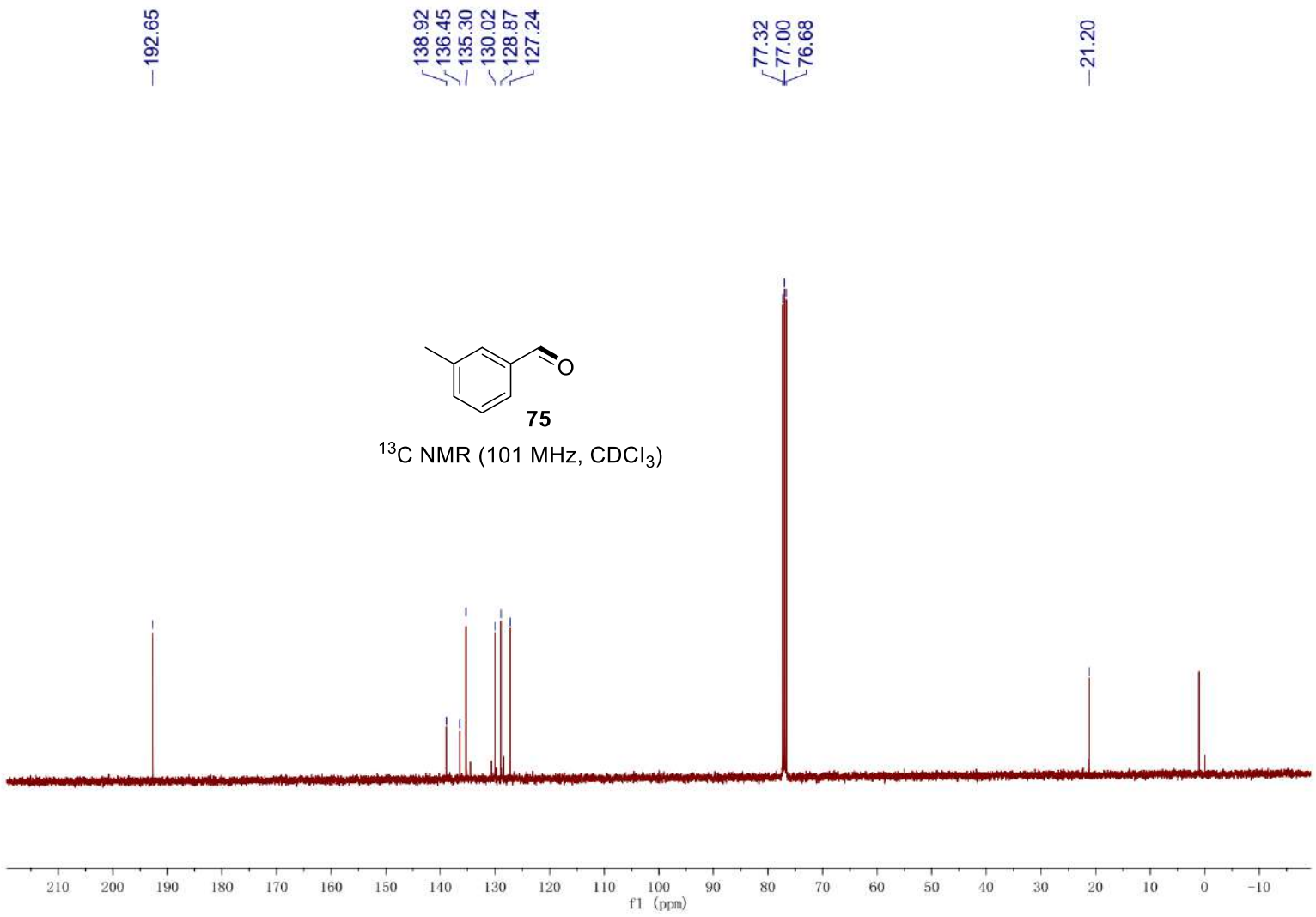

9.90
7.72
7.70
7.27
7.25
2.37
0.00
O
H
74
^{1}H NMR (400 MHz, $CDCl_3$)
0.93
1.86
1.74
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


192.04
145.55
134.16
129.85
129.70
77.32
77.00
76.68
21.89
O
H
74
^{13}C NMR (101 MHz, $CDCl_3$)
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)



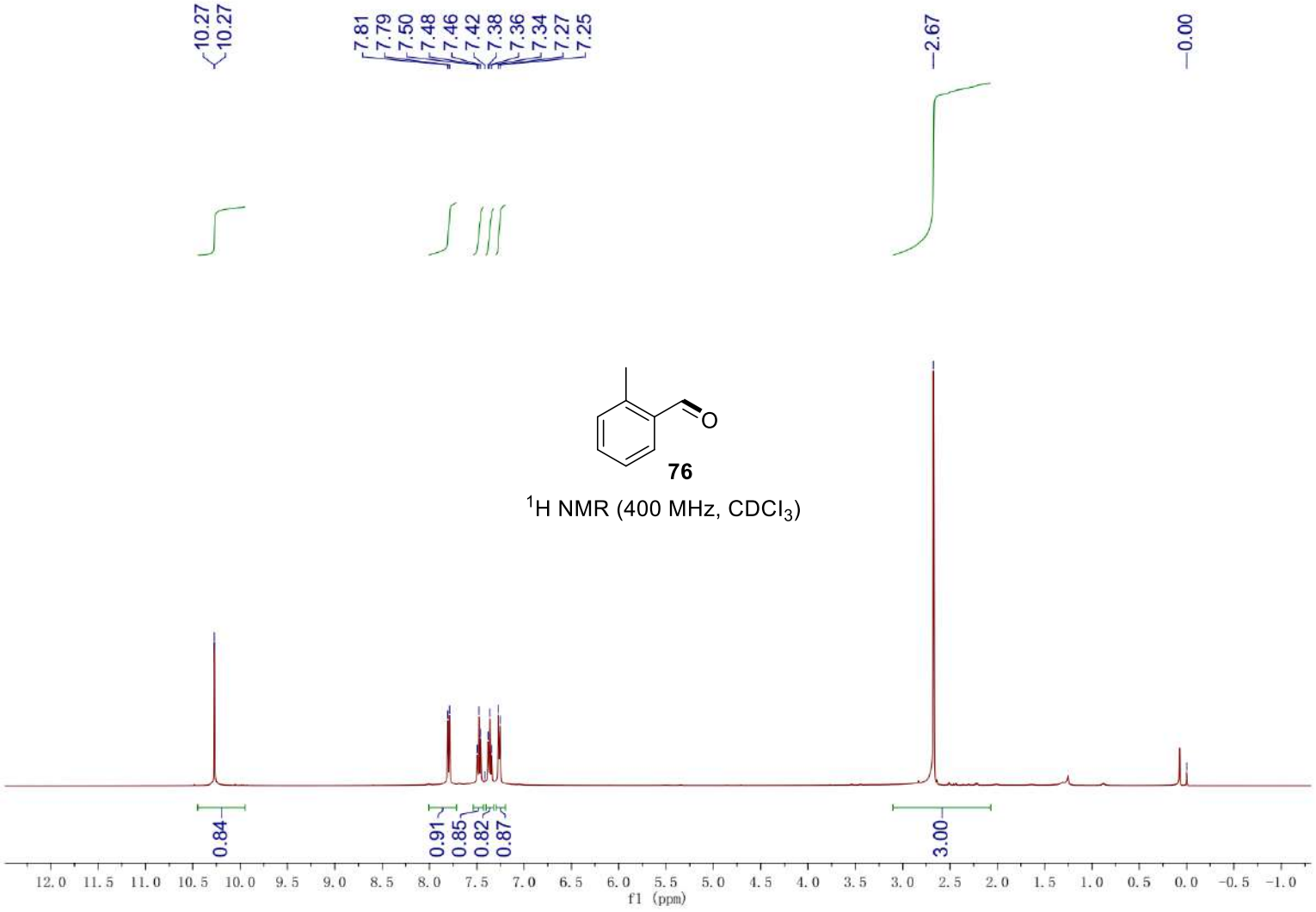
75

^{1}H NMR (400 MHz, $CDCl_3$)



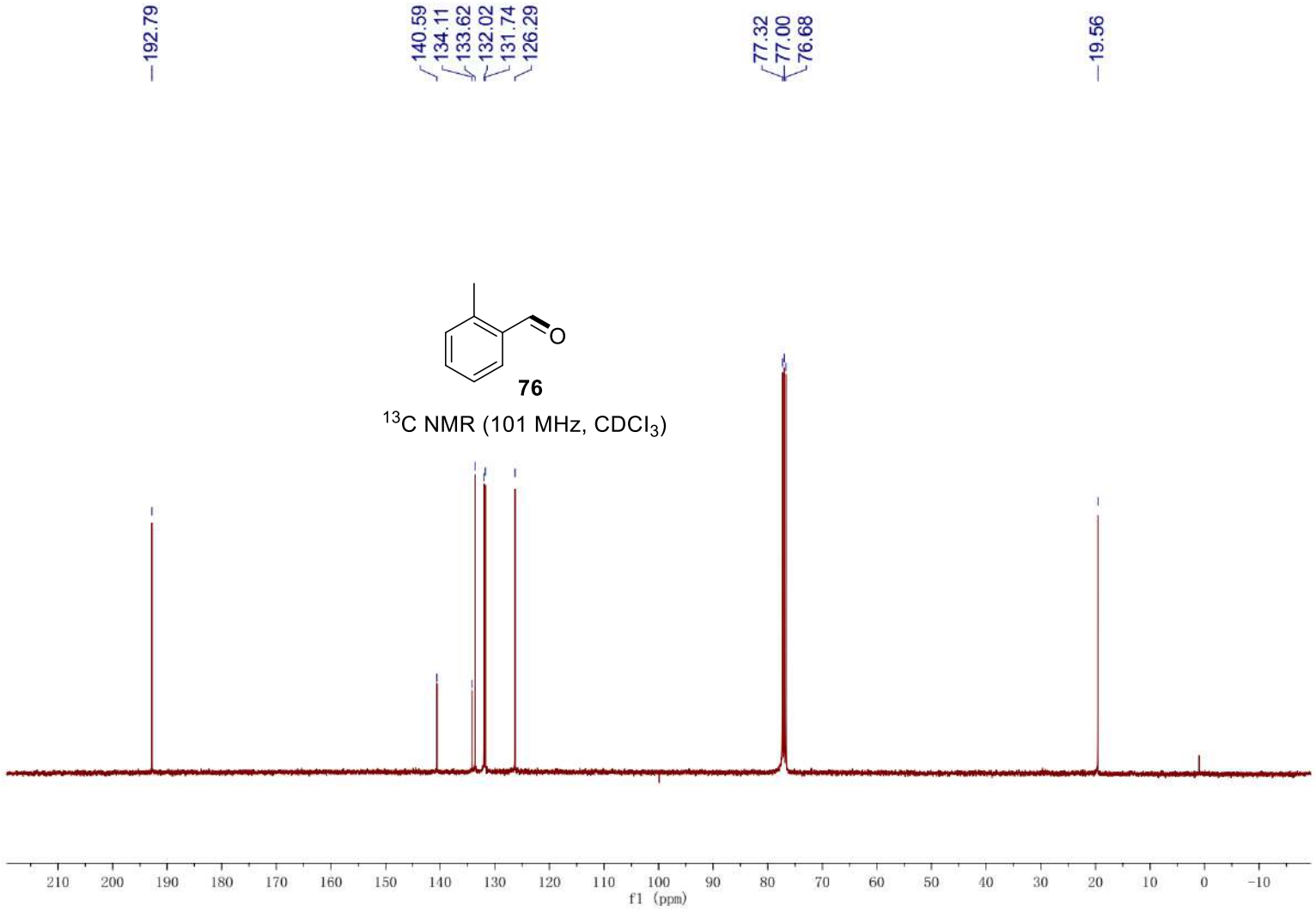
75

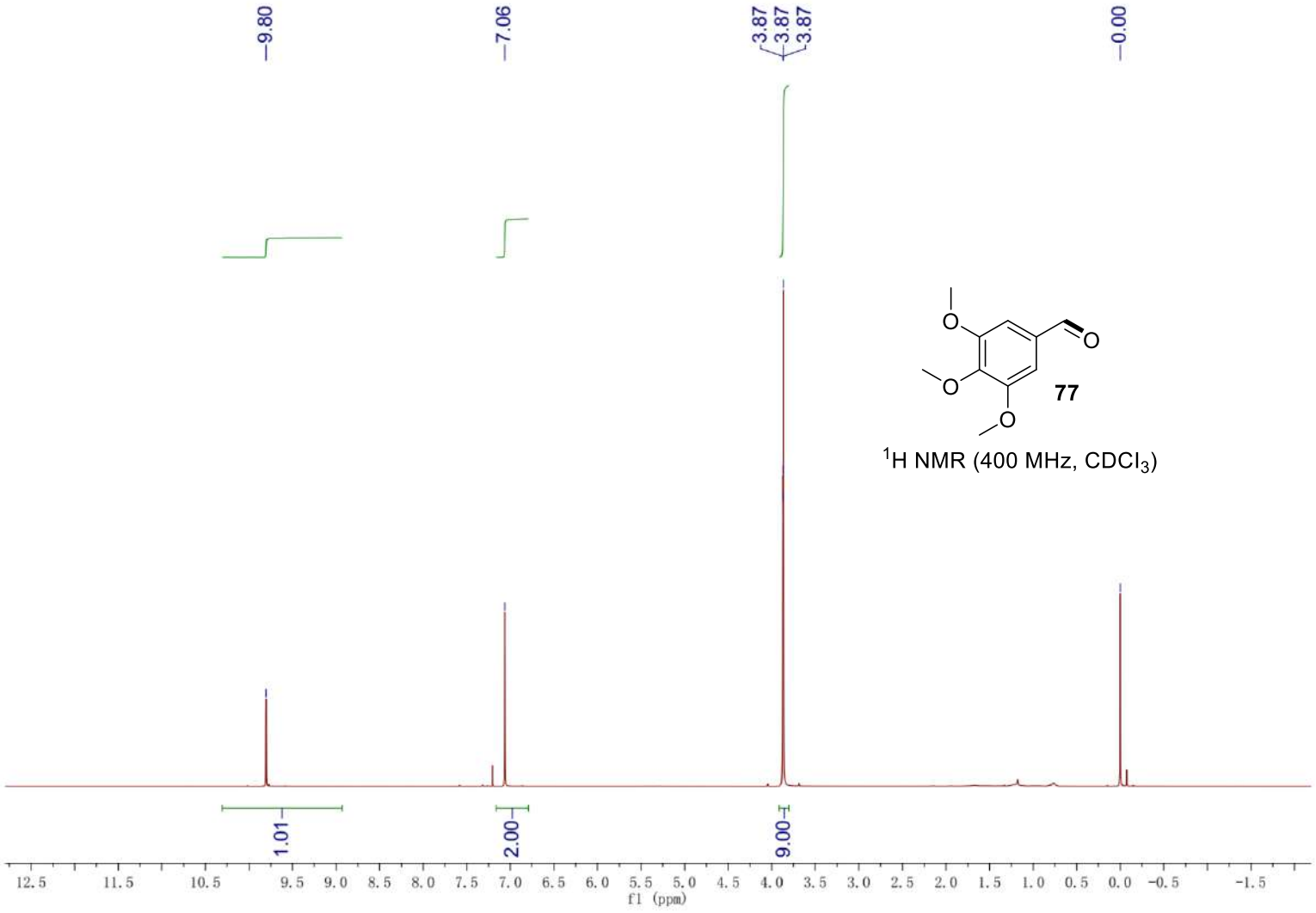
^{13}C NMR (101 MHz, $CDCl_3$)



76

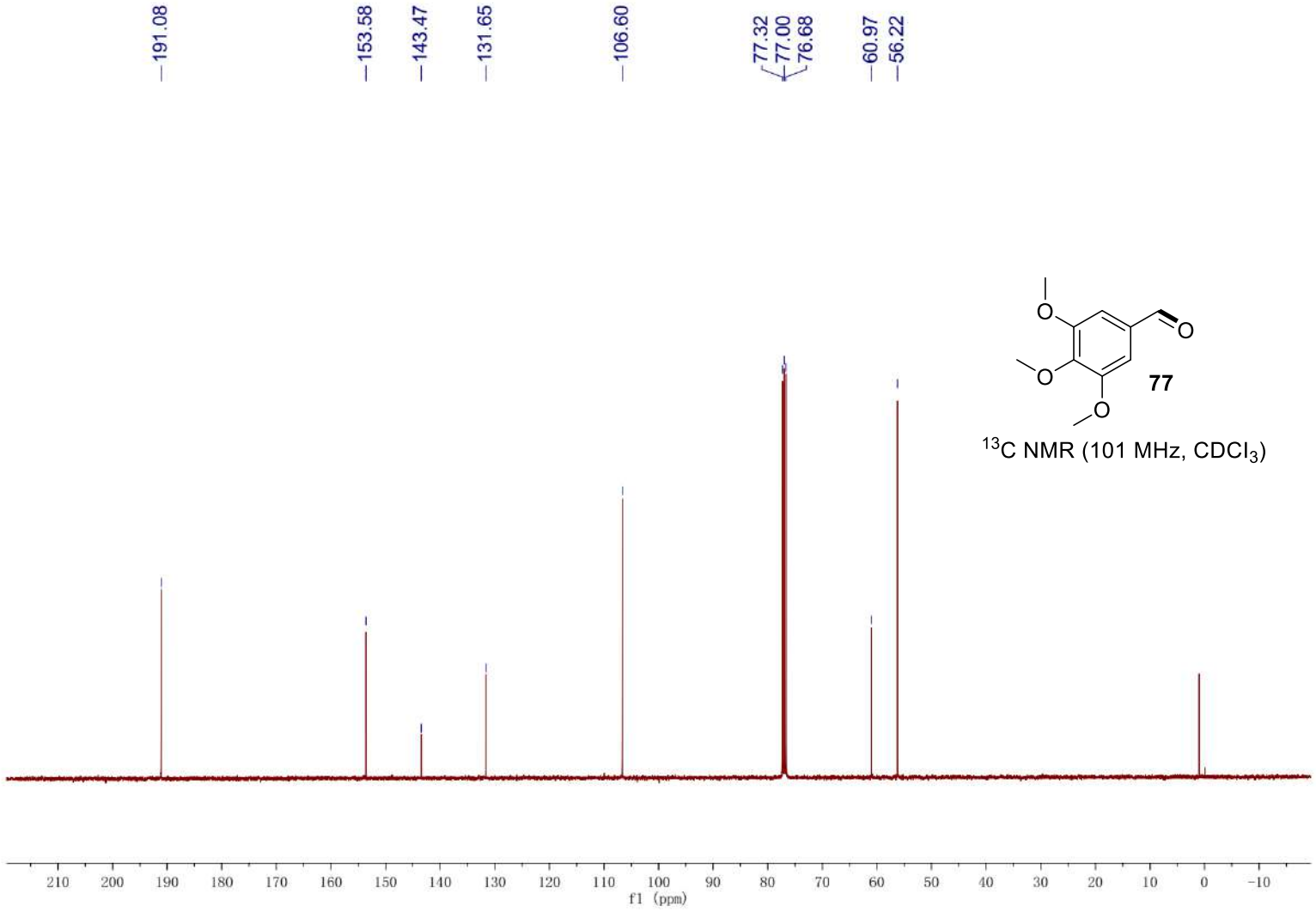
^{1}H NMR (400 MHz, $CDCl_3$)

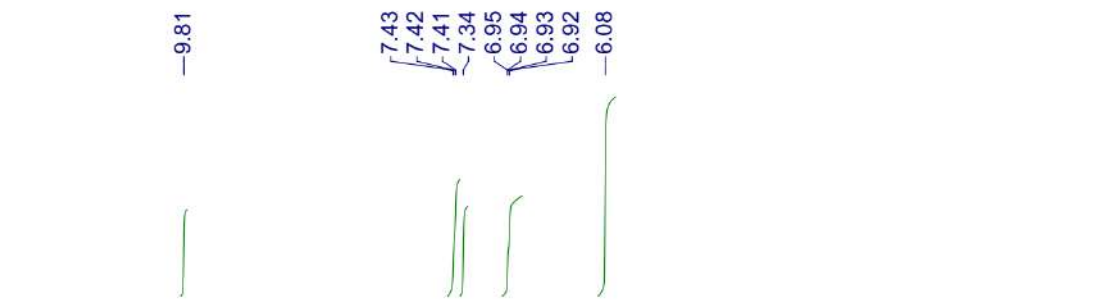

192.79
140.59
134.11
133.62
132.02
131.74
126.29
77.32
77.00
76.68
19.56
O
76
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

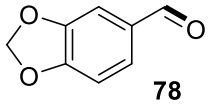


77

^{1}H NMR (400 MHz, $CDCl_3$)

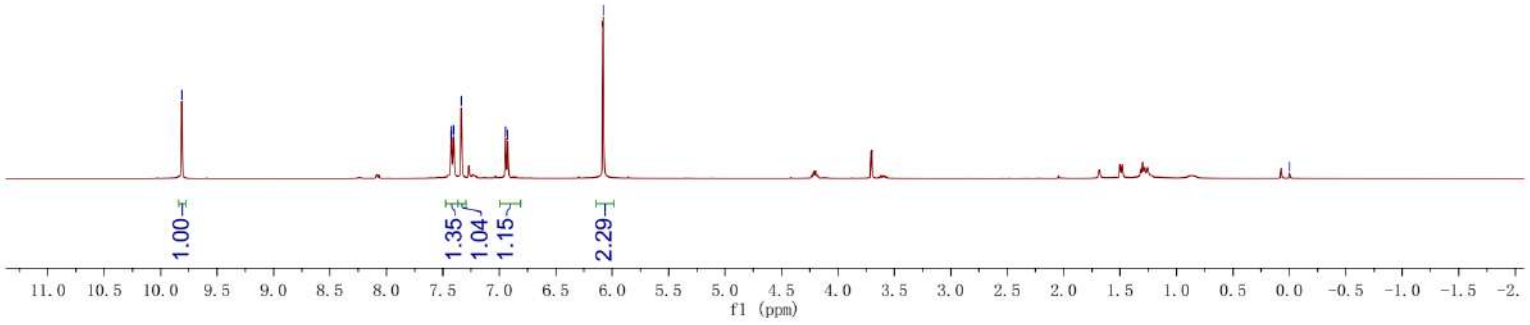

191.08
153.58
143.47
131.65
106.60
77.32
77.00
76.68
60.97
56.22
O
O
O
O
77
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

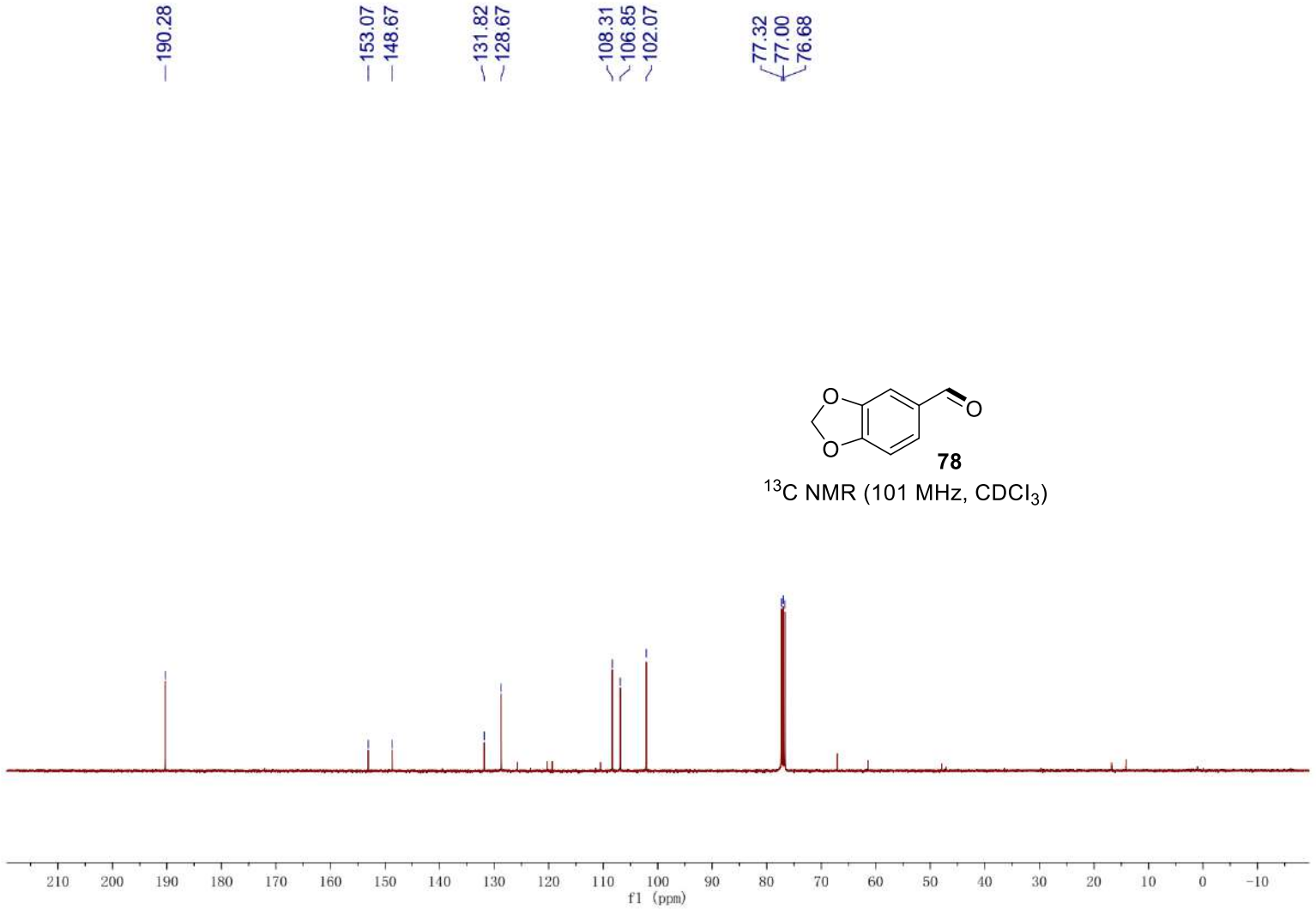


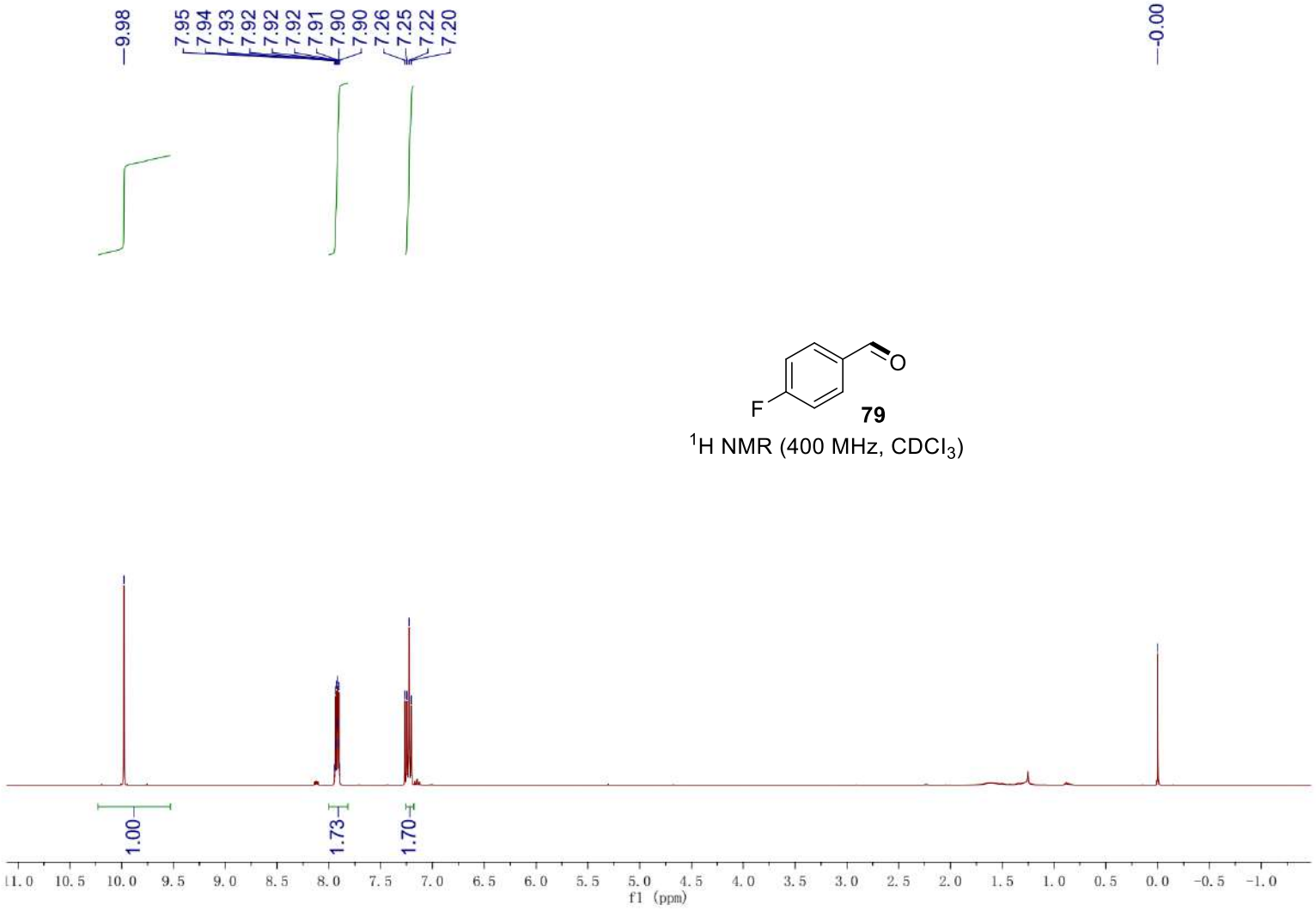


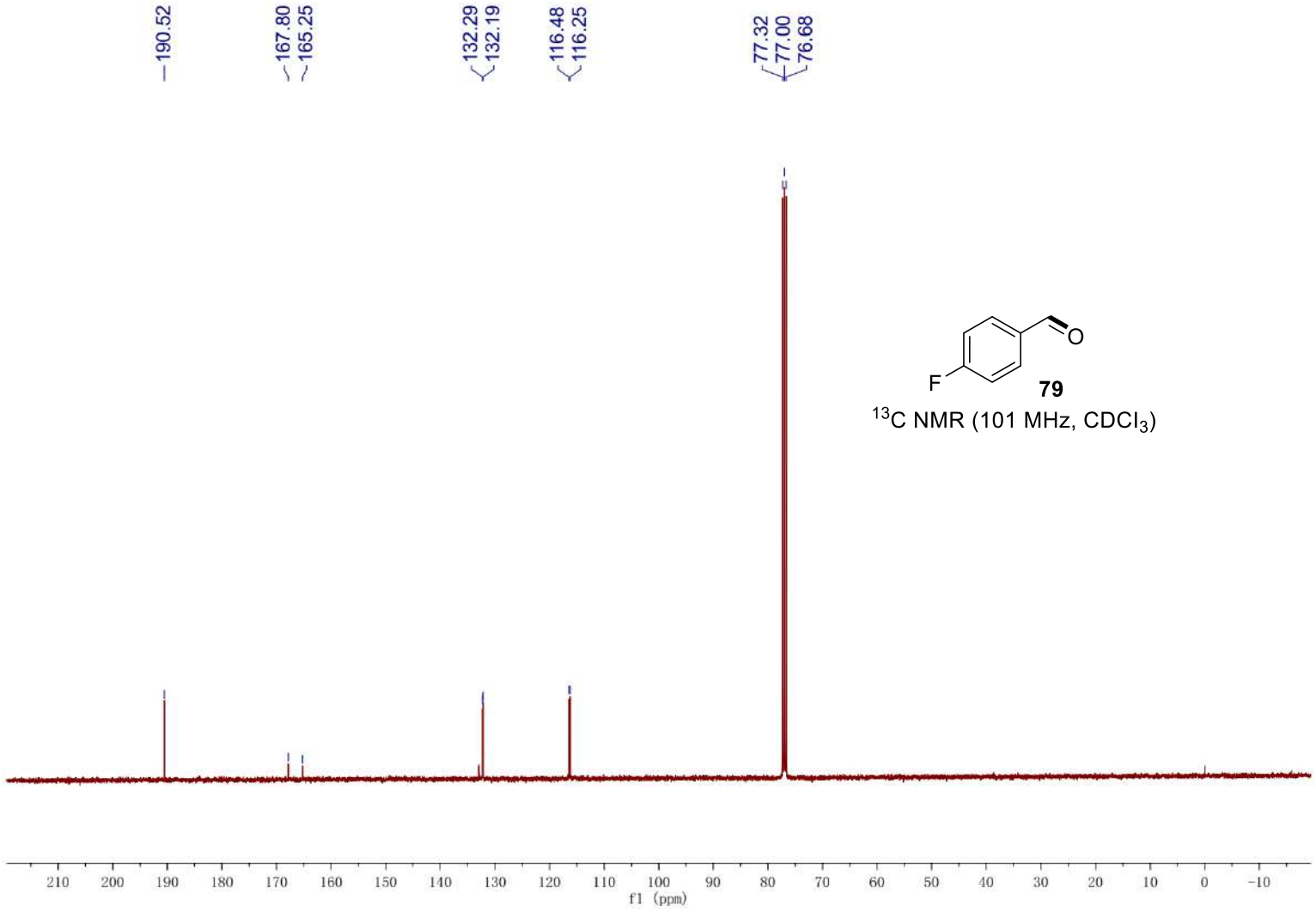
78

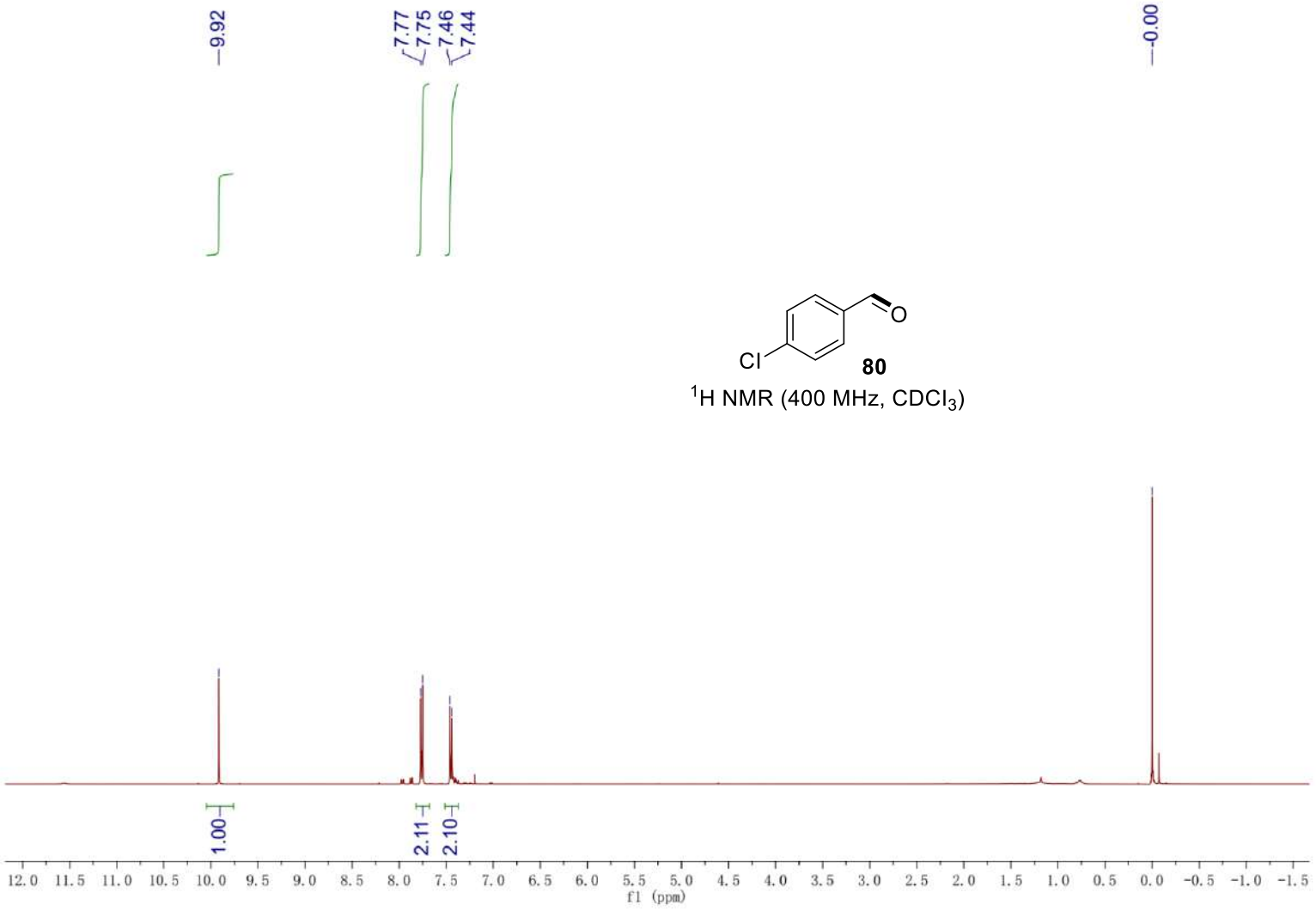
^{1}H NMR (400 MHz, $CDCl_3$)




190.28
153.07
148.67
131.82
128.67
108.31
106.85
102.07
77.32
77.00
76.68
O
O
O
78
13C NMR (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)

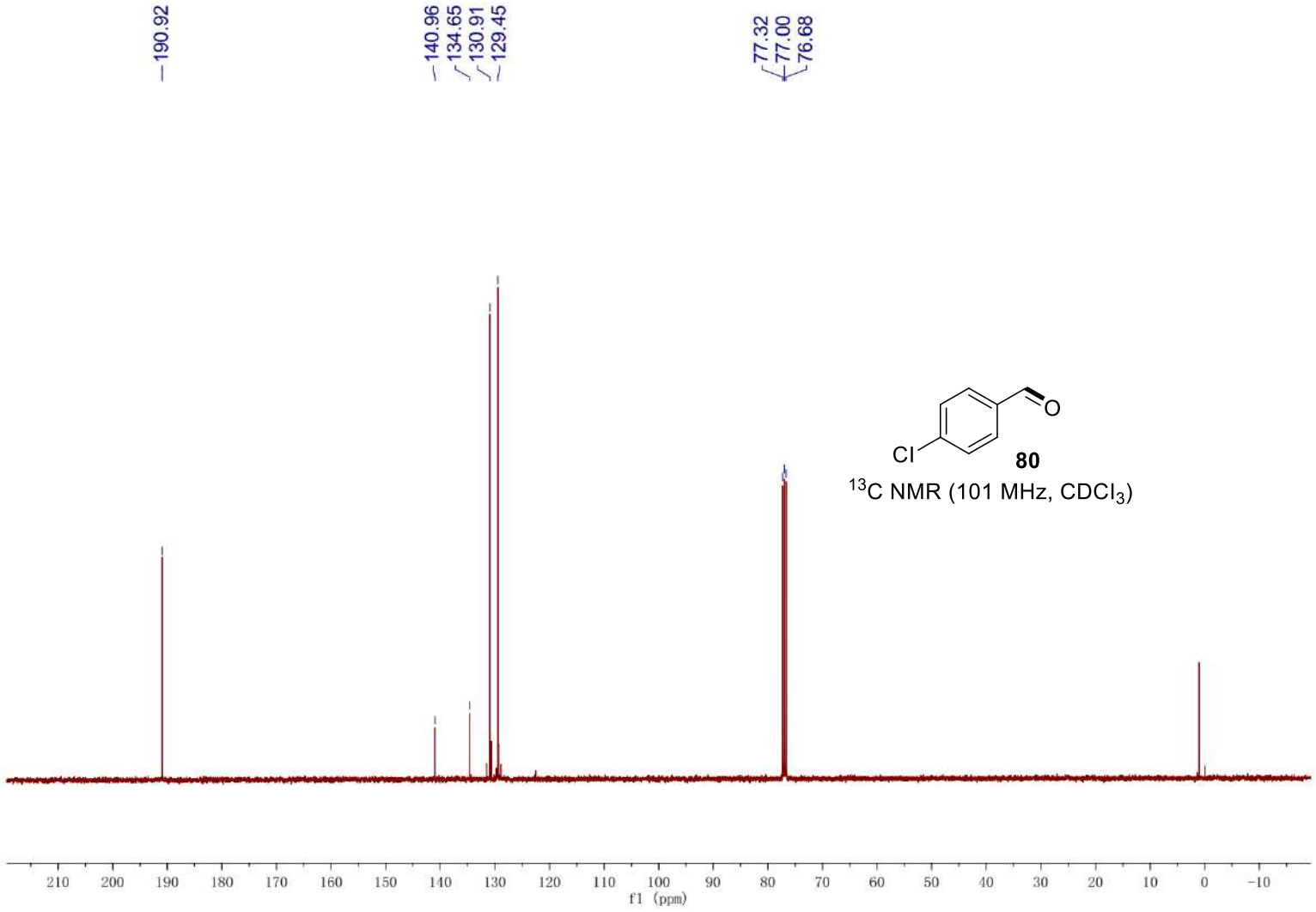

9.98
7.95
7.94
7.93
7.92
7.92
7.92
7.91
7.90
7.90
7.26
7.25
7.22
7.20
0.00
O
F
79
1H NMR (400 MHz, CDCl3)
1.00
1.73
1.70
f1 (ppm)

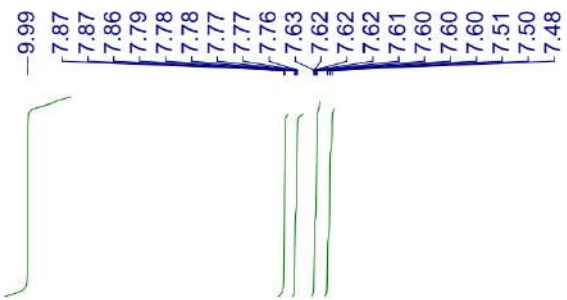

190.52
167.80
165.25
132.29
132.19
116.48
116.25
77.32
77.00
76.68
O
F
79
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

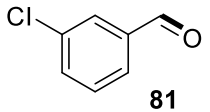


80

^{1}H NMR (400 MHz, $CDCl_3$)

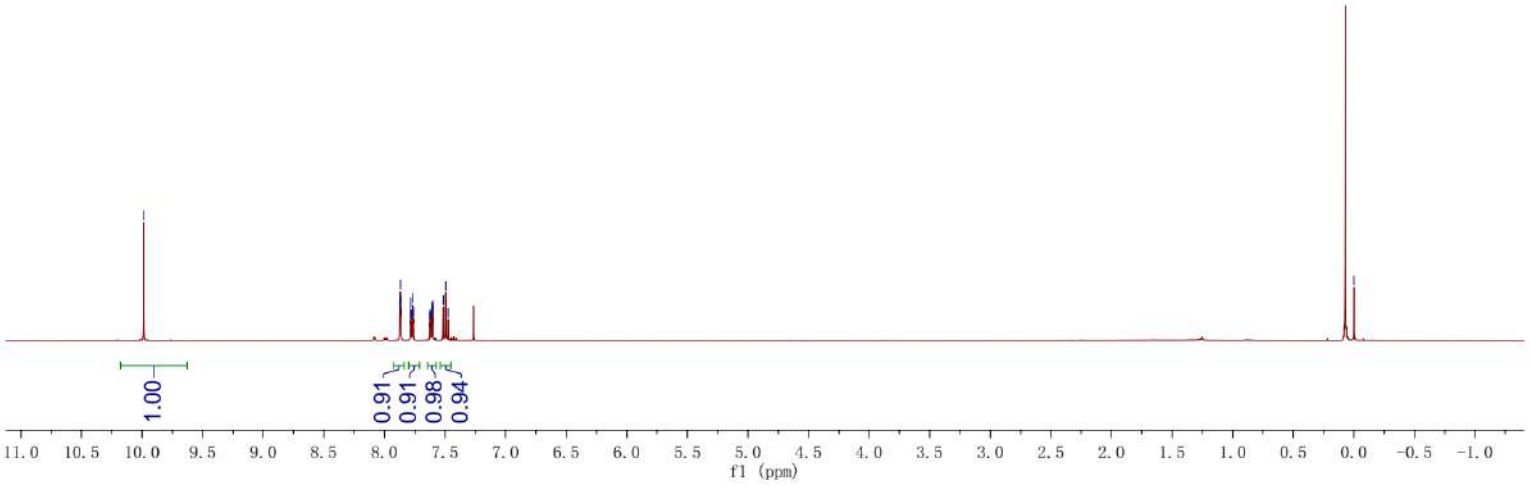

190.92
140.96
134.65
130.91
129.45
77.32
77.00
76.68
Cl
O
80
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

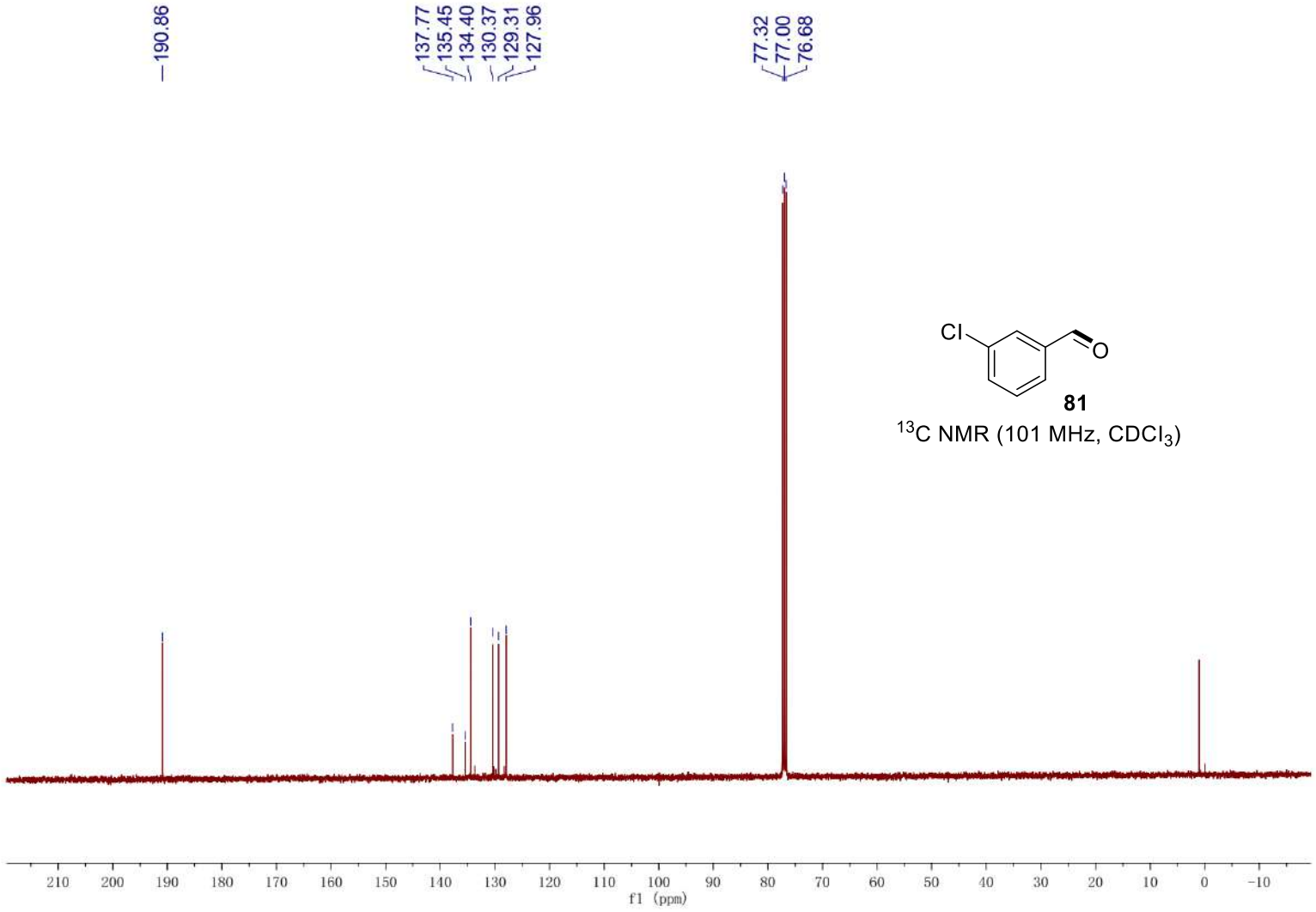


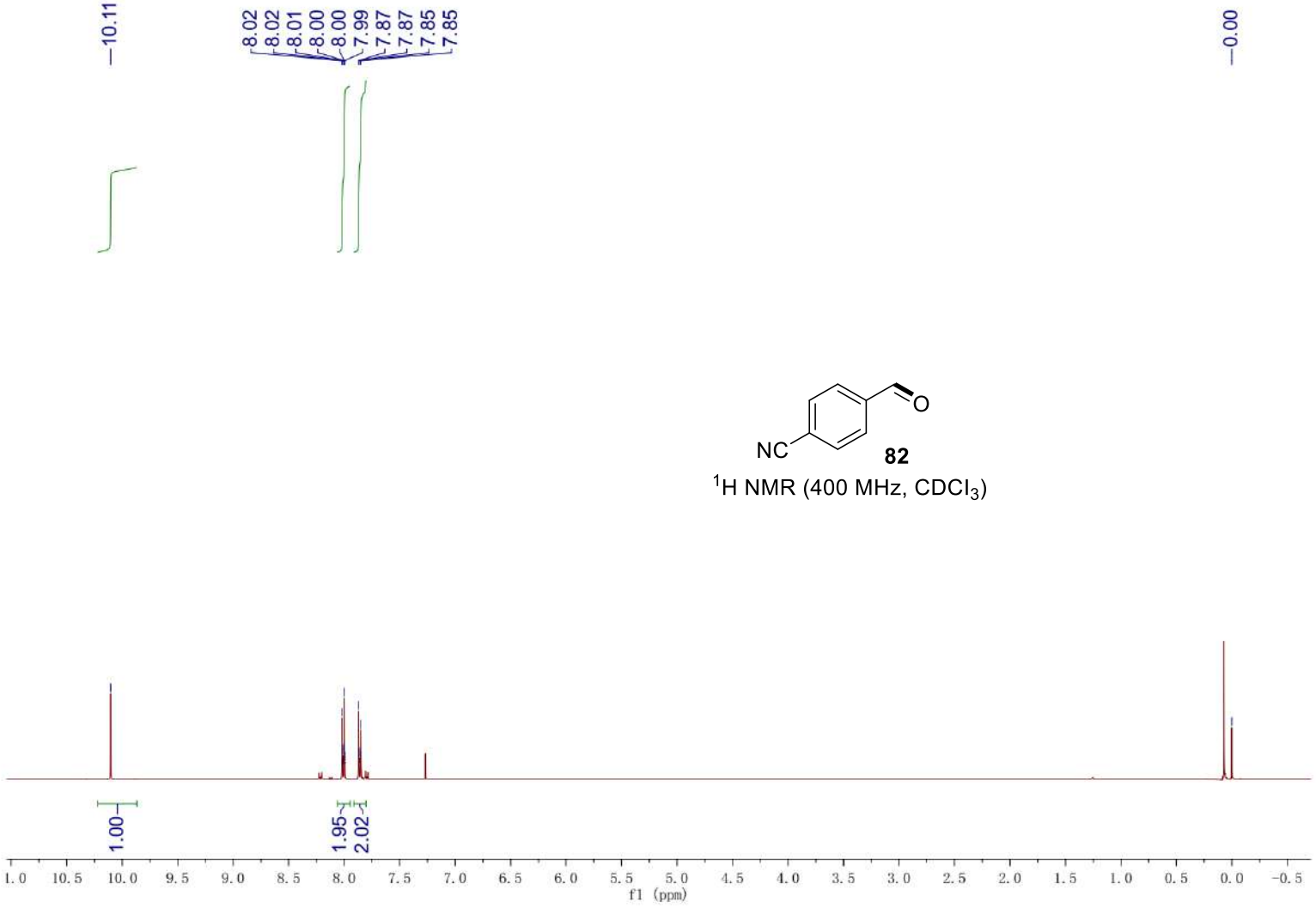


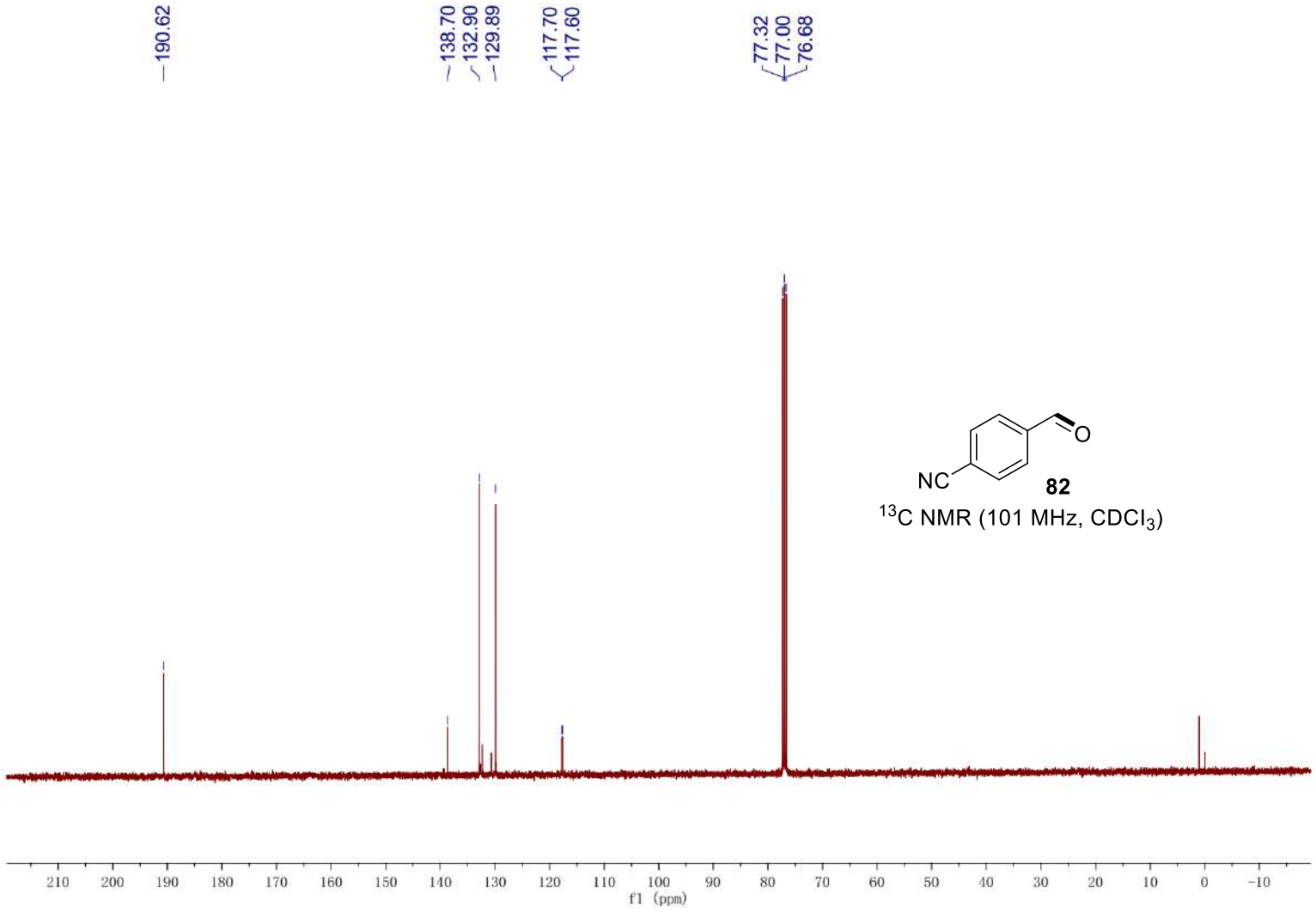
81

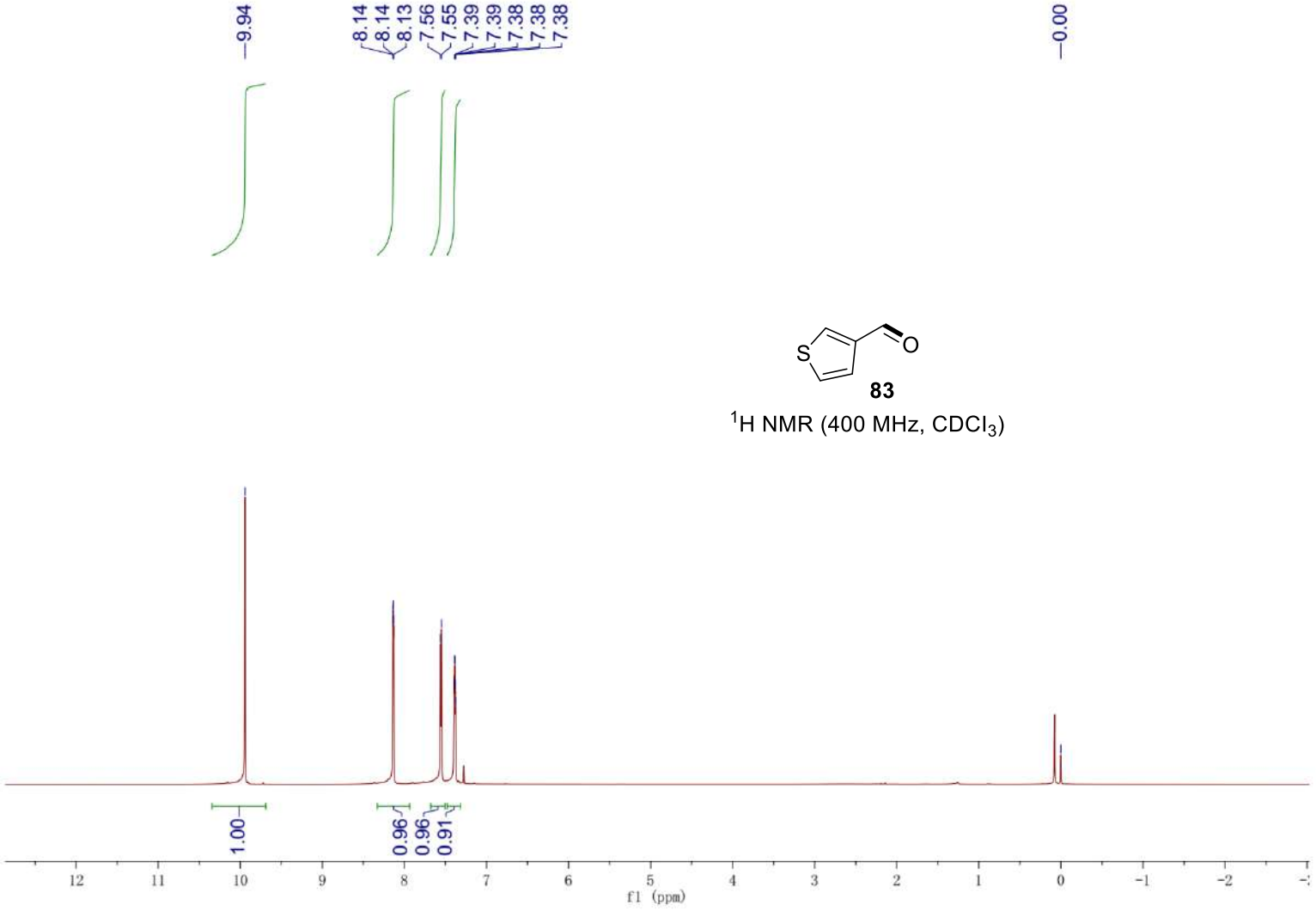
^{1}H NMR (400 MHz, $CDCl_3$)




190.86
137.77
135.45
134.40
130.37
129.31
127.96
77.32
77.00
76.68
Cl
O
81
^{13}C NMR (101 MHz, $CDCl_3$)
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)

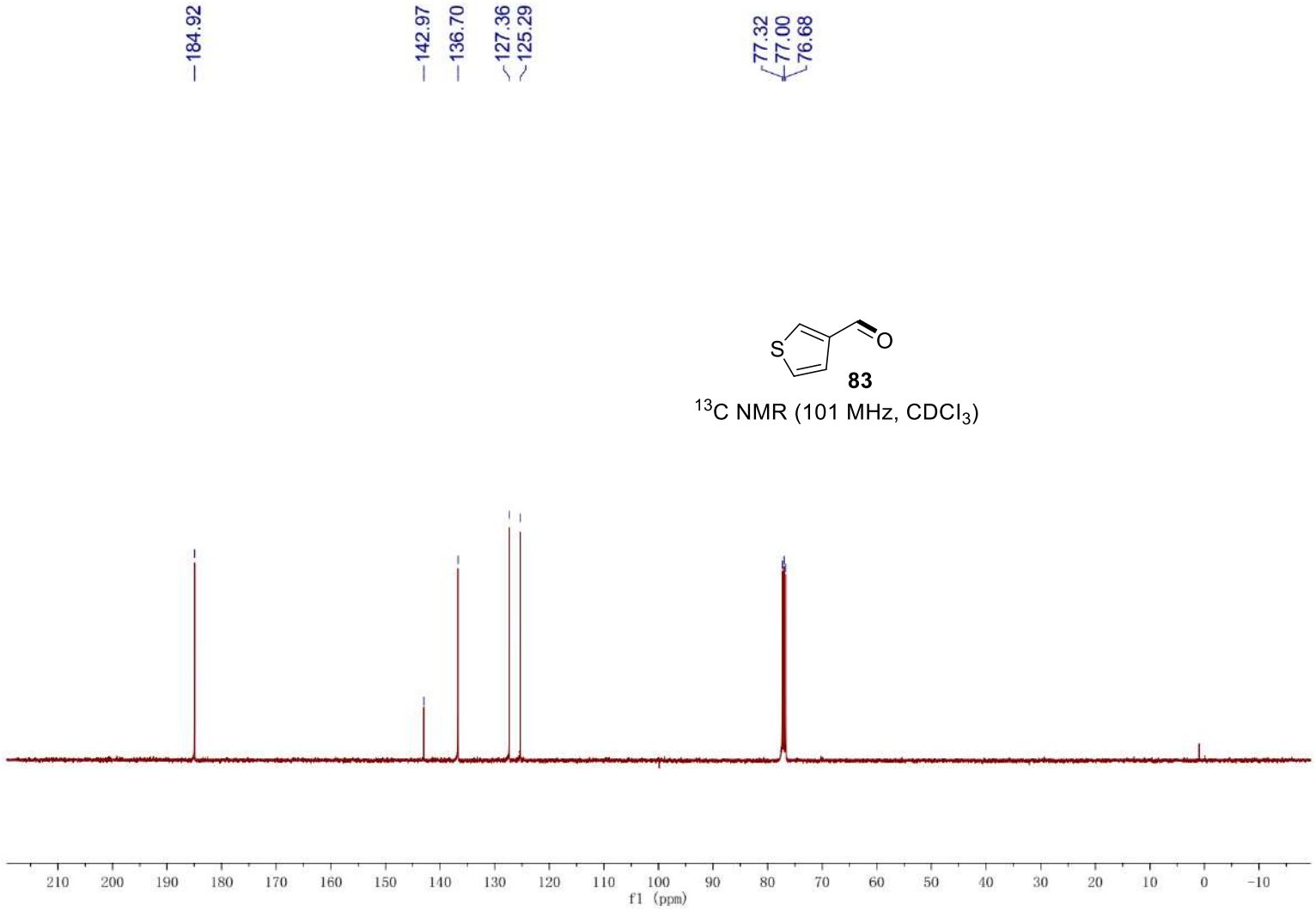

10.11
8.02
8.02
8.01
8.00
8.00
7.99
7.87
7.87
7.85
7.85
0.00
NC
O
82
1H NMR (400 MHz, CDCl3)
1.00
1.95
2.02
f1 (ppm)


190.62
138.70
132.90
129.89
117.70
117.60
77.32
77.00
76.68
NC
O
82
^{13}C NMR (101 MHz, $CDCl_3$)
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)



83

^{1}H NMR (400 MHz, $CDCl_3$)



83

^{13}C NMR (101 MHz, $CDCl_3$)