Supporting Information

Visible Light-Induced Metal-Free Chemoselective Oxidative Cleav-age of Benzyl C−Heteroatom (N, S, Se) bonds Utilizing Organobo-ron Photocatalysts

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1. General considerations

General. Unless otherwise noted, all reactions were carried out under an O_2 atmosphere. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator. Visualization was accomplished by exposure to a UV lamp. All the products in this article are compatible with standard silica gel chromatography. Column chromatography was performed on silica gel (200–300 mesh) using standard methods.

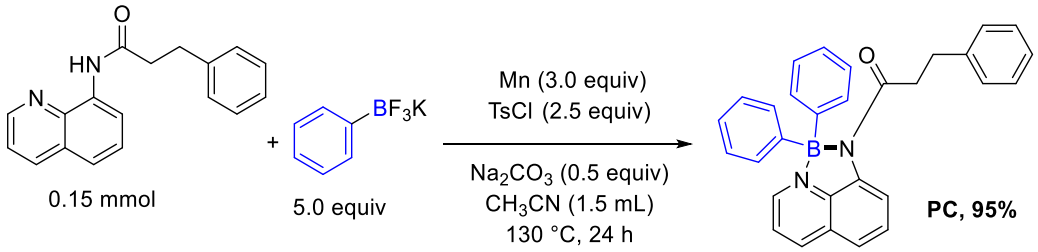
Structural analysis. NMR spectra were measured on a Bruker Ascend 400 spectrometer and chemical shifts (δ) are reported in parts per million (ppm). ^{1}H NMR spectra were recorded at 400 MHz in NMR solvents and referenced internally to corresponding solvent resonance, and ^{13}C NMR spectra were recorded at 101 MHz and referenced to corresponding solvent resonance. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad).

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

2. The synthesis of the photocatalyst used

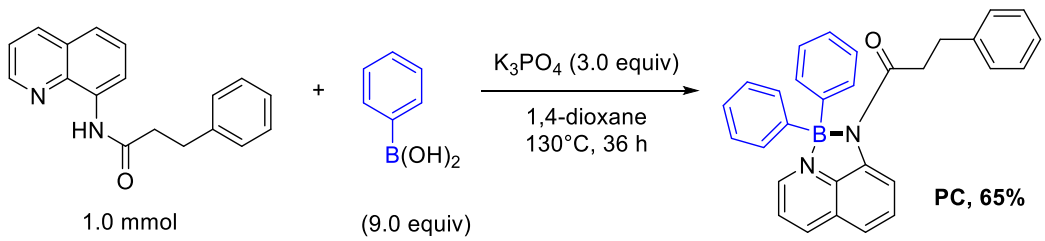
The photocatalyst was prepared via the methods that we have disclosed in the previous literatures (*Chemical Communications* **2020**, *56*, 8273; *ACS Sustainable Chemistry & Engineering* **2020**, *8*, 13894; *Green Chem* **2021**, *23*, 4446). The preparation procedure was recorded herein, for the sake of completeness. Also, the UV-vis the UV-vis, CV and fluorescence data have been disclosed (*Chemical Communications* **2020**, *56*, 8273).

(a) Method A for the synthesis of PC



A flame-dried 25 mL reaction tube was placed with a stirring bar. Then, 3-phenyl-N-(quinolin-8-yl)propanamide (41.4 mg, 0.15 mmol, 1.0 equiv), phenyl trifluoroborate (138.0 mg, 0.75 mmol, 5.0 equiv), Mn (24.7 mg, 0.45 mmol, 3.0 equiv), 4-toluenesulfonyl chloride (71.5 mg, 0.375 mmol, 2.5 equiv), Na_2CO_3 (7.9 mg, 0.075 mmol, 0.5 equiv) and CH_3CN (1.5 mL) were added. The resulting mixture was stirred at 130 ℃ for 24 hours. Then, the reaction mixture was filtered, concentrated and purified by column chromatography (silica gel) to give 62.7 mg of the target product in 95% yield.

(b) Method B for the synthesis of PC



A flame-dried 125 mL reaction tube was placed with a stirring bar. Then, 3-phenyl-N-(quinolin-8-yl)propanamide (276.3 mg, 1.0 mmol, 1.0 equiv), phenylboronic acid (1100.0 mg, 9.0 mmol, 9.0 equiv), K_3PO_4 (636.8 mg, 3.0 mmol, 3.0 equiv) and 1,4-

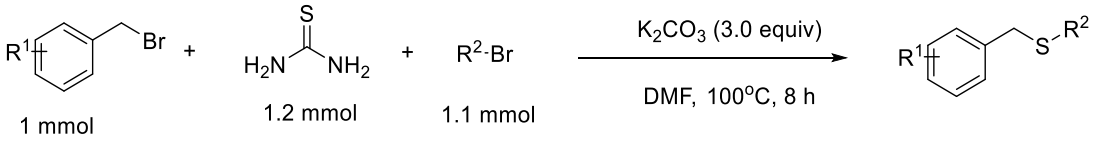
dioxane (15 mL) were added. The resulting mixture was stirred at 130 ℃ for 36 hours. Then, the reaction mixture was filtered, concentrated, and purified by column chromatography (silica gel) to give 286.2 mg of the target product in 65% yield.

(c) Characterization data of the photocatalyst

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, J = 7.6 Hz, 1H), 8.43 (dd, J = 5.2, 0.8 Hz, 1H), 8.38 (d, J = 8.4 Hz, 1H), 7.80 (t, J = 8.4 Hz, 1H), 7.56−7.52 (m, 1H), 7.52−7.46 (m, 5H), 7.30−7.24 (m, 6H), 7.13 (t, J = 7.2 Hz, 2H), 7.10−7.03 (m, 1H), 6.83 (d, J = 6.8 Hz, 2H), 2.60 (dd, J = 9.5, 4.9 Hz, 2H), 2.57−2.49 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 142.0, 141.5, 139.5, 139.1, 137.7, 133.5, 132.6, 128.5, 128.1, 127.9, 127.6, 127.2, 125.5, 122.5, 119.0, 117.2, 39.9, 31.5.

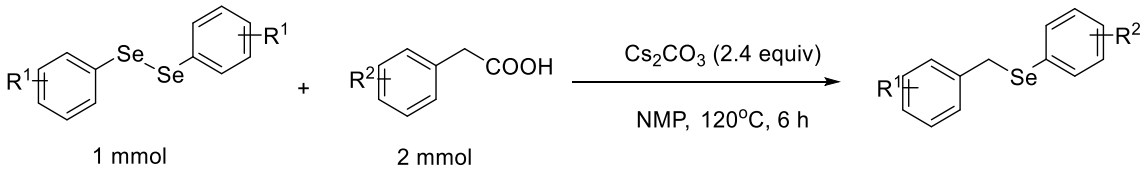
3. The synthesis of the raw materials used

(a) The synthesis of the sulfur compounds used



Benzylbromide (1 mmol), alkylhalide (1.1 mmol), thiourea (1.2 mmol), and K_2CO_3 (3 mmol) were added to 5 mL of DMF at 100°C. The reaction was stopped after the consumption of the benzyl bromide, which was monitored by gas chromatography (GC). Then, the reaction mixture was diluted with de-ionized water and extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation to generate a crude product. Purification by silica gel chromatography eluting with n-hexane afforded pure thioethers.

(b) The synthesis of the selenium compounds used



Diphenyl diselenide (0.25 mmol) and phenylacetic acid (0.5 mmol) were added to NMP (3 mL). The mixture was stirred at 120℃ for 6 h under air atmosphere. The progress of the reaction was monitored by TLC. Then, the reaction mixture was diluted with de-ionized water and extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation to generate a crude product. Purification by silica gel chromatography eluting with n-hexane afforded pure selenides.

4. General procedure for the oxidation reactions

(a) General Procedure A. The procedure for the C-N bond oxidation reactions.

A flame-dried 25 mL quartz reaction tube was placed with a magnetic stir bar. Then, p-tolylmethanamine (36.3 mg, 0.3 mmol, 1.0 equiv), PC (0.7 mg, 0.0015 mmol, 0.5 mol%), solvent were added to the tube. After that, charge the tube with oxygen. The reaction tube was placed on a photocatalytic parallel reactor with Blue LEDs (10 W) at the bottom (**Figure S1**). Then the reaction mixture was stirred and irradiated with the Blue LEDs for 36 hours at room temperature.

Figure S1. Picture of the reactor

After taking the reaction tube out, 10 mL water was added to the reaction mixture. Then, the reaction mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic phase was washed with brine (2 × 5.0 mL) and then dried over anhydrous Na_2SO_4. After concentration, the crude product was purified by column chromatography (silica gel) to give the target product, using petroleum ether/ethyl acetate as the eluent.

(b) General Procedure B. The procedure for the C-S bond oxidation reactions.

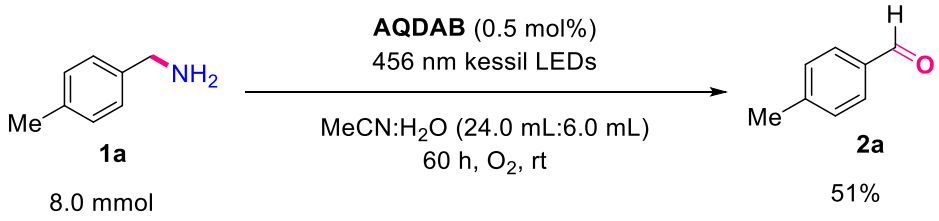
A flame-dried 25 mL quartz reaction tube was placed with a magnetic stir bar. Then, p-tolylmethanethiol (41.5 mg, 0.3 mmol, 1.0 equiv), PC (0.7 mg, 0.0015 mmol, 0.5 mol%), solvent were added to the tube. After that, charge the tube with oxygen. The reaction tube was placed on a photocatalytic parallel reactor with Blue LEDs (10 W) at the bottom. Then the reaction mixture was stirred and irradiated with the Blue LEDs for 10 hours at room temperature. After taking the reaction tube out, 10 mL water was added to the reaction mixture. Then, the reaction mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic phase was washed with brine (2 × 5.0 mL)

and then dried over anhydrous Na_2SO_4. After concentration, the crude product was purified by column chromatography (silica gel) to give the target product, using petroleum ether/ethyl acetate as the eluent.

(c) General Procedure C. The procedure for the C-Se bond oxidation reactions.

A flame-dried 25 mL quartz reaction tube was placed with a magnetic stir bar. Then, benzyl(phenyl)selane (74.2 mg, 0.3 mmol, 1.0 equiv), PC (0.7 mg, 0.0015 mmol, 0.5 mol%), solvent were added to the tube. After that, charge the tube with oxygen. The reaction tube was placed on a photocatalytic parallel reactor with Blue LEDs (10 W) at the bottom. Then the reaction mixture was stirred and irradiated with the Blue LEDs for 10 hours at room temperature. After taking the reaction tube out, 10 mL water was added to the reaction mixture. Then, the reaction mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic phase was washed with brine (2 × 5.0 mL) and then dried over anhydrous Na_2SO_4. After concentration, the crude product was purified by column chromatography (silica gel) to give the target product, using petroleum ether/ethyl acetate as the eluent.

(d) The procedure of the amplified reaction



A 120 mL flask was placed with a magnetic stir bar. Then, p-tolylmethanamine (969.4 mg, 8.0 mmol, 1.0 equiv), PC (17.6 mg, 0.04 mmol, 0.5 mol%), solvent were added to the tube. After that, charge the tube with oxygen. The reaction tube was placed on a reactor, where the flask was irradiated by two 456 nm Blue Kessil LEDs. A fan was used to cool the reaction mixture. Then the reaction mixture was stirred and irradiated for 60 hours at room temperature. After purification (the same procedure with 0.3 mmol scale reaction), 0.49 g of product was obtained in 51% yield.

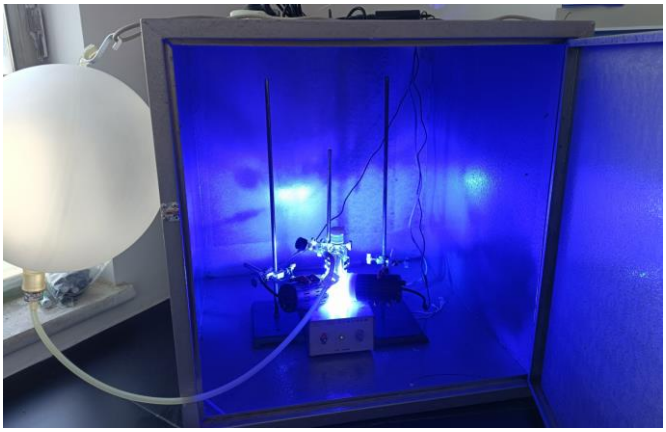


Figure S2. Reactor for mass synthesis expansion

5. Exploration of reaction mechanism

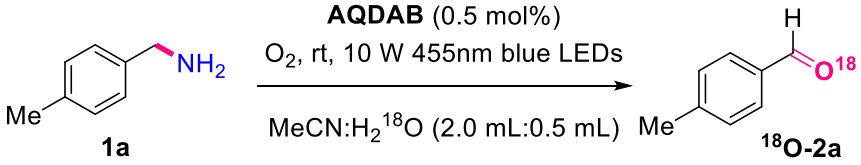
(a) Detection of free radical

Following the General Procedure A, used p-tolylmethanamine (36.4 mg, 0.3 mmol) as a raw material, and added TEMPO (93.7 mg, 0.6 mmol, 2.0 equiv) to the reaction mixture. 4.3 mg of the target product was obtained. The yield was 12%.

(b) Detection of superoxide radical

Following the General Procedure A, used p-tolylmethanamine (36.4 mg, 0.3 mmol) as a raw material, and added butylated hydroxytoluene (132.2 mg, 0.6 mmol, 2.0 equiv) to the reaction mixture. 6.5 mg of the target product was obtained. The yield was 18%.

(c) ^{18}O labelling experiment



A flame-dried 25 mL quartz reaction tube was placed with a magnetic stir bar. Then, p-tolylmethanamine (36.3 mg, 0.3 mmol, 1.0 equiv), PC (0.7 mg, 0.0015 mmol, 0.05 mol%), MeCN:$H_2{}^{18}O$ (2.0 mL:0.5 mL) were added to the tube. After that, charge the tube with oxygen. The reaction tube was placed on a photocatalytic parallel reactor with Blue LEDs (10 W) at the bottom. Then the reaction mixture was stirred and irradiated with the Blue LEDs for 36 hours at room temperature. After taking the reaction tube out, 10 mL water was added to the reaction mixture. Then, the reaction mixture was

extracted with ethyl acetate (3 × 10 mL). The combined organic phase was washed with brine (2 × 5.0 mL) and then dried over anhydrous Na_2SO_4. After concentration, the crude product was purified by column chromatography (silica gel) to give the target product, using petroleum ether/ethyl acetate as the eluent. The key peaks of ^{18}O labeled 4-methylbenzaldehyde was observed.

HRMS (ESI) m/z calcd for $C8H918O^+$ $(M+H)^+$ 123.06904, found

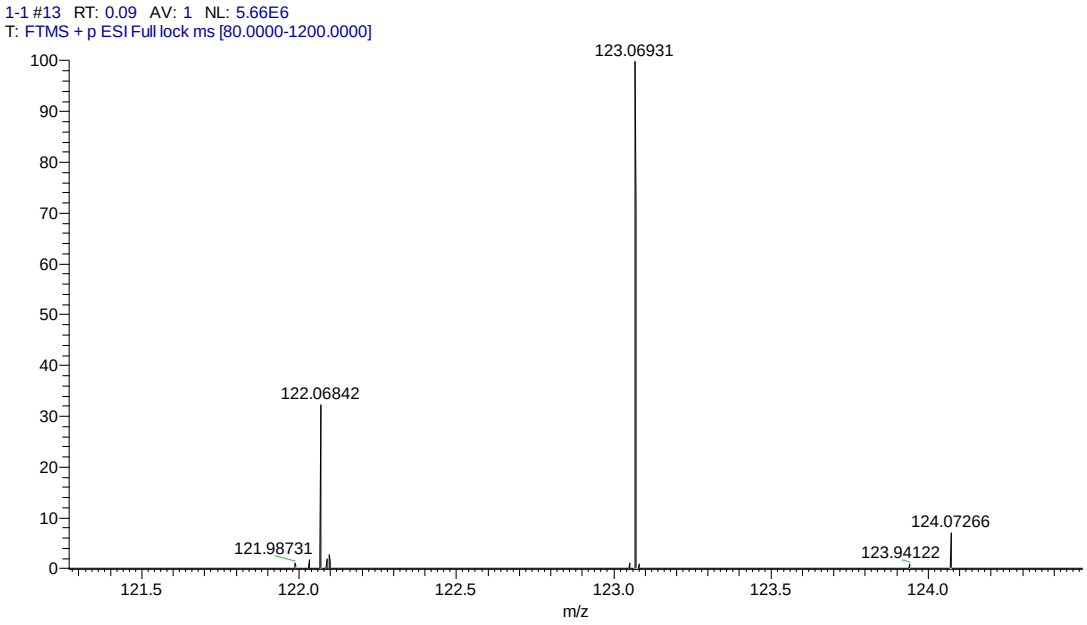
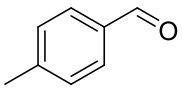


Figure S2. Picture of ^{18}O labeled 4-methylbenzaldehyde

6. Characterization data

All the obtained products are known compounds. The characterization data are in accordance with the reported literatures, which are referenced herein.

(2a) 4-methylbenzaldehyde (CAS: 104-87-0)[1]



4-methylbenzaldehyde
Chemical Formula: C_8H_8O
Exact Mass: 120.0575
Molecular Weight: 120.1510

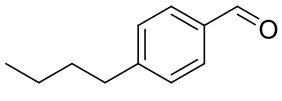
Following the General Procedure A with p-tolylmethanamine (36.4 mg, 0.3 mmol), **2a** was obtained as colorless liquid (31.0 mg, 86%).

Following the General Procedure B with p-tolylmethanethiol (41.5 mg, 0.3 mmol), **2a** was obtained as colorless liquid (26.7 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 145.6, 134.2, 129.9, 129.7, 21.9.

(2b) 4-butylbenzaldehyde (CAS: 1200-14-2)[2]



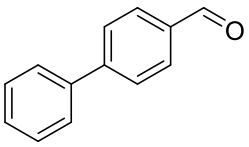
4-butylbenzaldehyde
Chemical Formula: $C_{11}H_{14}O$
Exact Mass: 162.1045
Molecular Weight: 162.2320

Following the General Procedure A with (4-butylphenyl)methanamine (49.0 mg, 0.3 mmol), **2b** was obtained as colorless liquid (38.1 mg, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 2.74 – 2.65 (m, 2H), 1.67 - 1.58 (m, 2H), 1.41 - 1.30 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 150.5, 134.4, 129.9, 129.1, 35.9, 33.2, 22.3, 13.9.

(2c) [1,1'-biphenyl]-4-carbaldehyde (CAS: 3218-36-8)[2]



[1,1'-biphenyl]-4-carbaldehyde
Chemical Formula: $C_{13}H_{10}O$
Exact Mass: 182.0732
Molecular Weight: 182.2220

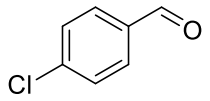
Following the General Procedure A with [1,1'-biphenyl]-4-ylmethanamine (54.9 mg, 0.3 mmol), **2c** was obtained as white solid (41.6 mg, 76%).

Following the General Procedure C with ([1,1'-biphenyl]-4-ylmethyl)(phenyl)selane (97.0 mg, 0.3 mmol), **2c** was obtained as white solid (49.2 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.96 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 7.6 Hz, 2H), 7.49 (t, J = 7.4 Hz, 2H), 7.42 (t, J = 7.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 147.2, 139.7, 135.2, 130.3, 129.1, 128.5, 127.7, 127.4.

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



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

Following the General Procedure A with (4-chlorophenyl)methanamine (42.5 mg, 0.3 mmol), **2d** was obtained as white solid (24.9 mg, 59%).

Following the General Procedure A with N-(4-chlorobenzyl)ethanamine (50.9 mg, 0.3 mmol), **2d** was obtained as white solid (24.5 mg, 58%).

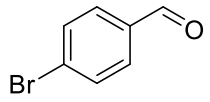
Following the General Procedure B with (4-chlorophenyl)methanethiol (47.6 mg, 0.3 mmol), **2d** was obtained as white solid (21.9 mg, 52%).

Following the General Procedure C with (4-chlorobenzyl)(phenyl)selane (84.5 mg, 0.3 mmol), **2d** was obtained as white solid (30.4 mg, 72%).

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

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 141.0, 134.7, 130.9, 129.5.

(2e) 4-bromobenzaldehyde (CAS: 1122-91-4)[3]



4-bromobenzaldehyde
Chemical Formula: C_7H_5BrO
Exact Mass: 183.9524
Molecular Weight: 185.0200

Following the General Procedure A with (4-bromophenyl)methanamine (55.8 mg, 0.3 mmol), **2e** was obtained as white solid (47.7 mg, 86%).

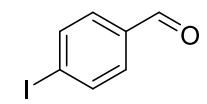
Following the General Procedure B with (4-bromophenyl)methanethiol (60.9 mg, 0.3 mmol), **2e** was obtained as white solid (31.1 mg, 56%).

Following the General Procedure C with (4-bromobenzyl)(phenyl)selane (97.8 mg, 0.3 mmol), **2e** was obtained as white solid (48.3 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.77 – 7.73 (m, 2H), 7.71 – 7.67 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1, 135.1, 132.5, 131.0, 129.8.

(2f) 4-iodobenzaldehyde (CAS: 15164-44-0)[4]



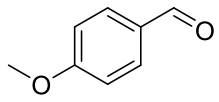
4-iodobenzaldehyde
Chemical Formula: C_7H_5IO
Exact Mass: 231.9385
Molecular Weight: 232.0205

Following the General Procedure A with (4-iodophenyl)methanamine (69.9 mg, 0.3 mmol), **2f** was obtained as white solid (37.6 mg, 54%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.92 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 138.4, 135.6, 130.8, 102.8.

(2g) 4-methoxybenzaldehyde (CAS: 123-11-5)[1]



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

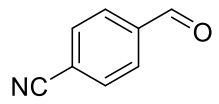
Following the General Procedure A with (4-methoxyphenyl)methanamine (41.2 mg, 0.3 mmol), **2g** was obtained as colorless liquid (26.2 mg, 64%).

Following the General Procedure B with (4-methoxyphenyl)methanethiol (46.3 mg, 0.3 mmol), **2g** was obtained as colorless liquid (24.5 mg, 60%)

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

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

(2h) 4-formylbenzonitrile (CAS: 105-07-7)[5]



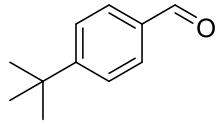
4-formylbenzonitrile
Chemical Formula: C_8H_5NO
Exact Mass: 131.0371
Molecular Weight: 131.1340

Following the General Procedure A with 4-(aminomethyl)benzonitrile (39.7 mg, 0.3 mmol), **2h** was obtained as white solid (28.3 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 7.99 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 138.8, 132.9, 129.9, 117.7, 117.6.

(2i) 4-(tert-butyl)benzaldehyde (CAS: 939-97-9)[1]



4-(*tert*-butyl)benzaldehyde
Chemical Formula: $C_{11}H_{14}O$
Exact Mass: 162.1045
Molecular Weight: 162.2320

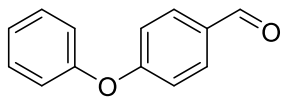
Following the General Procedure A with (4-(tert-butyl)phenyl)methanamine (49.0 mg, 0.3 mmol), **2i** was obtained as colorless liquid (31.2 mg, 64%).

Following the General Procedure B with (4-(tert-butyl)phenyl)methanethiol (54.1 mg, 0.3 mmol), **2i** was obtained as colorless liquid (34.1 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.82 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 158.5, 134.1, 129.7, 126.0, 35.37, 31.1.

(2j) 4-phenoxybenzaldehyde (CAS: 67-36-7)[6]



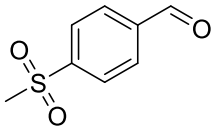
4-phenoxybenzaldehyde
Chemical Formula: $C_{13}H_{10}O_2$
Exact Mass: 198.0681
Molecular Weight: 198.2210

Following the General Procedure A with (4-phenoxyphenyl)methanamine (59.8 mg, 0.3 mmol), **2j** was obtained as white solid (37.5 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.8 Hz, 2H), 7.45 – 7.38 (m, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.12 – 7.03 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 163.3, 155.1, 132.0, 131.3, 130.2, 125.0, 120.4, 117.6.

(2k) 4-(methylsulfonyl)benzaldehyde (CAS: 5398-77-6)[4]

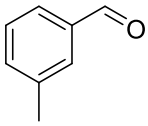


4-(methylsulfonyl)benzaldehyde
Chemical Formula: $C_8H_8O_3S$
Exact Mass: 184.0194
Molecular Weight: 184.2090

Following the General Procedure A with (4-(methylsulfonyl)phenyl)methanamine (55.6 mg, 0.3 mmol), **2k** was obtained as white solid (35.2 mg, 65%). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 10.13 (s, 1H), 8.15 (s, 4H), 3.34 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d$_6$) δ 193.1, 145.8, 139.8, 130.7, 128.2, 43.6.

(2l) 3-methylbenzaldehyde (CAS: 620-23-5)[1]

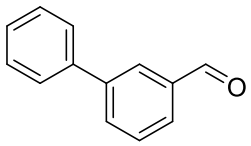


3-methylbenzaldehyde
Chemical Formula: C_8H_8O
Exact Mass: 120.0575
Molecular Weight: 120.1510

Following the General Procedure A with m-tolylmethanamine (36.4 mg, 0.3 mmol), **2l** was obtained as colorless liquid (22.4 mg, 62%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.67 (d, J = 6.8 Hz, 2H), 7.42 (d, J = 7.2 Hz, 2H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 138.9, 136.5, 135.3, 130.0, 128.9, 127.2, 21.2.

(2m) [1,1'-biphenyl]-3-carbaldehyde (CAS: 1204-60-0)[7]

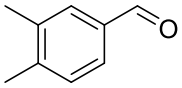


[1,1'-biphenyl]-3-carbaldehyde
Chemical Formula: $C_{13}H_{10}O$
Exact Mass: 182.0732
Molecular Weight: 182.2220

Following the General Procedure A with 6-fluoro-2-methyl-1,2,3,4-tetrahydroquinoline (55.0 mg, 0.3 mmol), **2m** was obtained as white solid (42.6 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 8.09 (t, J = 1.4 Hz, 1H), 7.85 (dd, J = 7.6, 1.6 Hz, 2H), 7.65 – 7.56 (m, 3H), 7.50 - 7.43 (m, 2H), 7.43 – 7.36 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.3, 142.2, 139.7, 137.0, 133.1, 129.5, 129.0, 128.7, 128.2, 128.0, 127.2.

(2n) 3,4-dimethylbenzaldehyde (CAS: 5973-71-7)[3]



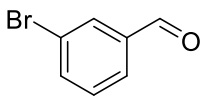
3,4-dimethylbenzaldehyde
Chemical Formula: $C_9H_{10}O$
Exact Mass: 134.0732
Molecular Weight: 134.1780

Following the General Procedure A with (3,4-dimethylphenyl)methanamine (40.6 mg, 0.3 mmol), **2n** was obtained as colorless liquid (26.6 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.65 – 7.58 (m, 2H), 7.28 (d, J = 7.6 Hz, 1H), 2.36 - 2.32 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.3, 144.3, 137.5, 134.6, 130.6, 130.3, 127.8, 20.3, 19.7.

(2o) 3-bromobenzaldehyde (CAS: 3132-99-8)[5]



3-bromobenzaldehyde
Chemical Formula: C_7H_5BrO
Exact Mass: 183.9524
Molecular Weight: 185.0200

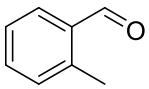
Following the General Procedure A with (3-bromophenyl)methanamine (55.8 mg, 0.3 mmol), **2o** was obtained as white solid (39.4 mg, 71%).

Following the General Procedure A with (3-bromophenyl)methanamine (55.8 mg, 0.3 mmol), **2o** was obtained as white solid (30.0 mg, 54%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.01 (s, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.78 – 7.72 (m, 1H), 7.42 (t, J = 7.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 138.0, 137.3, 132.4, 130.6, 128.4, 123.4.

(2p) 2-methylbenzaldehyde (CAS: 529-20-4)[1]



2-methylbenzaldehyde
Chemical Formula: C_8H_8O
Exact Mass: 120.0575
Molecular Weight: 120.1510

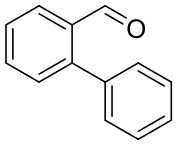
Following the General Procedure A with o-tolylmethanamine (36.4 mg, 0.3 mmol), **2p** was obtained as colorless liquid (20.6 mg, 57%).

Following the General Procedure B with o-tolylmethanethiol (41.5 mg, 0.3 mmol), **2p** was obtained as colorless liquid (17.3 mg, 48%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.48 (t, J = 7.4 Hz, 1H), 7.36 (t, J = 7.4 Hz, 1H), 7.26 (d, J = 7.6 Hz, 1H), 2.67 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.9, 140.6, 134.2, 133.7, 132.1, 131.8, 126.3, 19.6.

(2q) [1,1'-biphenyl]-2-carbaldehyde (CAS: 1203-68-5)[8]



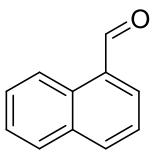
[1,1'-biphenyl]-2-carbaldehyde
Chemical Formula: $C_{13}H_{10}O$
Exact Mass: 182.0732
Molecular Weight: 182.2220

Following the General Procedure A with [1,1'-biphenyl]-2-ylmethanamine (55.0 mg, 0.3 mmol), **2q** was obtained as white solid (39.9 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (d, J = 0.8 Hz, 1H), 8.03 (dd, J = 7.6, 1.2 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.52 – 7.42 (m, 5H), 7.39 – 7.36 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.5, 146.0, 137.8, 133.7, 133.6, 130.8, 130.1, 128.5, 128.1, 127.8, 127.6.

(2r) 1-naphthaldehyde (CAS: 66-77-3)[1]



1-naphthaldehyde
Chemical Formula: $C_{11}H_8O$
Exact Mass: 156.0575
Molecular Weight: 156.1840

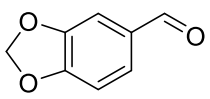
Following the General Procedure A with naphthalen-1-ylmethanamine (47.2 mg, 0.3 mmol), **2r** was obtained as white solid (25.8 mg, 55%).

Following the General Procedure C with (naphthalen-1-ylmethyl)(phenyl)selane (89.2 mg, 0.3 mmol), **2r** was obtained as white solid (28.6 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (s, 1H), 9.26 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.00 (dd, J = 7.2, 0.8 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.74 – 7.57 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 136.7, 135.3, 133.8, 131.5, 130.6, 129.1, 128.5, 127.0, 124.9, 124.9.

(2s) benzo[d][1,3]dioxole-5-carbaldehyde (CAS: 120-57-0)[5]



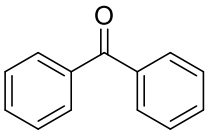
benzo[*d*][1,3]dioxole-5-carbaldehyde
Chemical Formula: $C_8H_6O_3$
Exact Mass: 150.0317
Molecular Weight: 150.1330

Following the General Procedure A with benzo[d][1,3]dioxol-5-ylmethanamine (45.4 mg, 0.3 mmol), **2s** was obtained as white solid (22.1 mg, 49%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.40 (dd, J = 8.0, 1.6 Hz, 1H), 7.32 (d, J = 1.6 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 6.07 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 153.1, 148.7, 131.9, 128.7, 108.4, 106.9, 102.1.

(2t) benzophenone (CAS: 119-61-9)[1]



benzophenone
Chemical Formula: $C_{13}H_{10}O$
Exact Mass: 182.0732
Molecular Weight: 182.2220

Following the General Procedure A with diphenylmethanamine (55.0 mg, 0.3 mmol), **2t** was obtained as colorless liquid (44.8 mg, 82%).

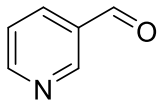
Following the General Procedure B with benzhydryl(phenyl)sulfane (82.9 mg, 0.3 mmol), **2t** was obtained as colorless liquid (39.9 mg, 73%).

Following the General Procedure C with (2,2-diphenylethyl)(phenyl)selane (101.2 mg, 0.3 mmol), **2t** was obtained as colorless liquid (25.2 mg, 46%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.77 (m, 4H), 7.63 – 7.54 (m, 2H), 7.54 – 7.45 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 137.6, 132.4, 130.1, 128.3.

(2u) nicotinaldehyde (CAS: 500-22-1)[9]



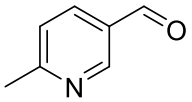
nicotinaldehyde
Chemical Formula: C_6H_5NO
Exact Mass: 107.04
Molecular Weight: 107.11

Following the General Procedure A with pyridin-3-ylmethanamine (32.5 mg, 0.3 mmol), **2u** was obtained as colorless liquid (14.5 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 1H), 9.10 (d, J = 1.6 Hz, 1H), 8.86 (dd, J = 4.8, 1.6 Hz, 1H), 8.19 (dt, J = 7.8, 2.0 Hz, 1H), 7.54 - 7.47 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 154.8, 152.1, 135.8, 131.4, 124.1.

(2v) 6-methylnicotinaldehyde (CAS: 53014-84-9)[10]



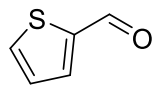
6-methylnicotinaldehyde
Chemical Formula: C_7H_7NO
Exact Mass: 121.05
Molecular Weight: 121.14

Following the General Procedure A with thiophen-2-ylmethanamine (36.7 mg, 0.3 mmol), **2v** was obtained as colorless liquid (24.0 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 8.96 (d, J = 2.0 Hz, 1H), 8.07 (dd, J = 8.0, 2.4 Hz, 1H), 7.34 (d, J = 8.4 Hz, 1H), 2.67 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 165.0, 152.1, 135.9, 129.3, 123.8, 25.1.

(2w) thiophene-2-carbaldehyde (CAS: 98-03-3)[11]



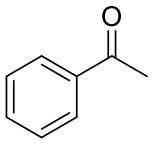
thiophene-2-carbaldehyde
Chemical Formula: C_5H_4OS
Exact Mass: 112.00
Molecular Weight: 112.15

Following the General Procedure A with diphenylmethanamine (34.0 mg, 0.3 mmol), **2w** was obtained as colorless liquid (26.9 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (d, J = 1.6 Hz, 1H), 7.82 – 7.74 (m, 2H), 7.24 - 7.19 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 183.0, 144.1, 136.4, 135.2, 128.4.

(4a) acetophenone (CAS: 98-86-2)[1]



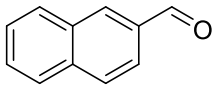
acetophenone
Chemical Formula: C_8H_8O
Exact Mass: 120.06
Molecular Weight: 120.15

Following the General Procedure B with 1-phenylethane-1-thiol (41.5 mg, 0.3 mmol), **4a** was obtained as colorless liquid (16.9 mg, 47%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.92 (m, 2H), 7.59 – 7.52 (m, 1H), 7.50 – 7.41 (m, 2H), 2.60 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2, 137.1, 133.1, 128.6, 128.3, 26.6.

(4b) 2-naphthaldehyde (CAS: 66-99-9)[1]



2-naphthaldehyde
Chemical Formula: $C_{11}H_8O$
Exact Mass: 156.0575
Molecular Weight: 156.1840

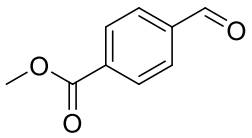
Following the General Procedure B with cyclohexyl(naphthalen-2-ylmethyl)sulfane (76.9 mg, 0.3 mmol), **4a** was obtained as colorless liquid (29.5 mg, 63%).

Following the General Procedure C with (naphthalen-2-ylmethyl)(phenyl)selane (89.2 mg, 0.3 mmol), **4a** was obtained as colorless liquid (37.0 mg, 79%)

^{1}H NMR (400 MHz, CDCl*3*) δ 10.15 (s, 1H), 8.32 (s, 1H), 8.03 – 7.86 (m, 4H), 7.67 - 7.55 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.3, 136.5, 134.6, 134.1, 132.7, 129.6, 129.1, 129.1, 128.1, 127.1, 122.8.

(4c) methyl 4-formylbenzoate (CAS: 1571-08-0)[5]



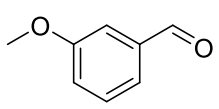
methyl 4-formylbenzoate
Chemical Formula: $C_9H_8O_3$
Exact Mass: 164.0473
Molecular Weight: 164.1600

Following the General Procedure B with methyl 4-((hexylthio)methyl)benzoate (79.9 mg, 0.3 mmol), 4b was obtained as white solid (27.1 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.20 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 8.4 Hz, 2H), 3.96 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 166.1, 139.2, 135.1, 130.2, 129.5, 52.6.

(6a) 3-methoxybenzaldehyde (CAS: 591-31-1)[12]



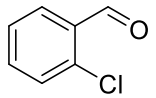
3-methoxybenzaldehyde
Chemical Formula: $C_8H_8O_2$
Exact Mass: 136.0524
Molecular Weight: 136.1500

Following the General Procedure C with (3-methoxybenzyl)(phenyl)selane (83.2 mg, 0.3 mmol), **6a** was obtained as colorless liquid (31.5 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.47 – 7.43 (m, 2H), 7.39 (d, J = 2.0 Hz, 1H), 7.20 - 7.14 (m, 1H), 3.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 160.2, 137.8, 130.1, 123.6, 121.5, 112.1, 55.5.

(6b) 2-chlorobenzaldehyde (CAS: 89-98-5)[1]



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

Following the General Procedure C with (2-chlorobenzyl)(phenyl)selane (84.5 mg, 0.3 mmol), **6b** was obtained as white solid (30.8 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.49 (d, J = 0.8 Hz, 1H), 7.93 (dd, J = 7.8, 1.8 Hz, 1H), 7.57 - 7.50 (m, 1H), 7.46 (dd, J = 8.0, 0.8 Hz, 1H), 7.43 – 7.36 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.8, 138.0, 135.1, 132.5, 130.6, 129.4, 127.3.

7. References

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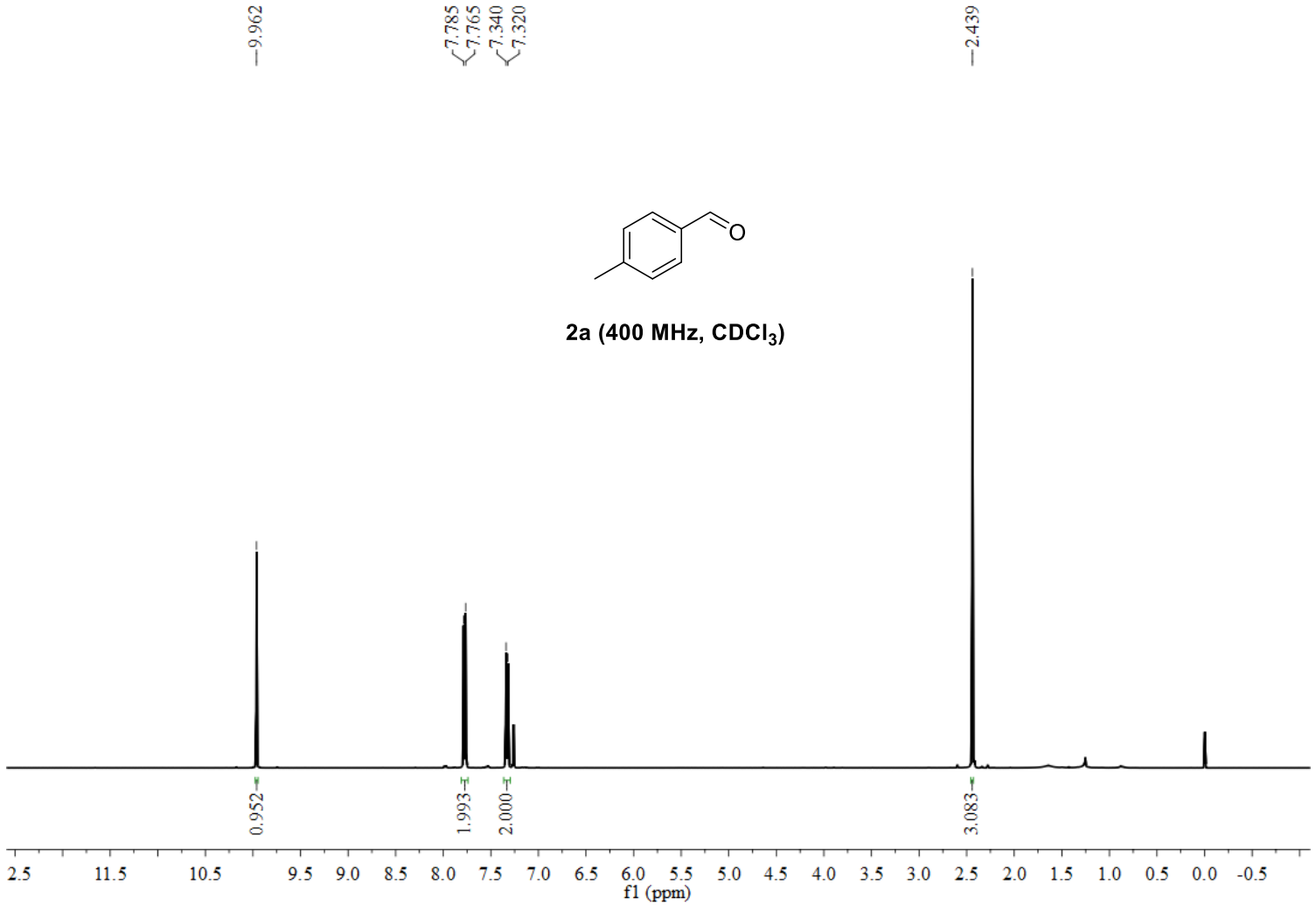
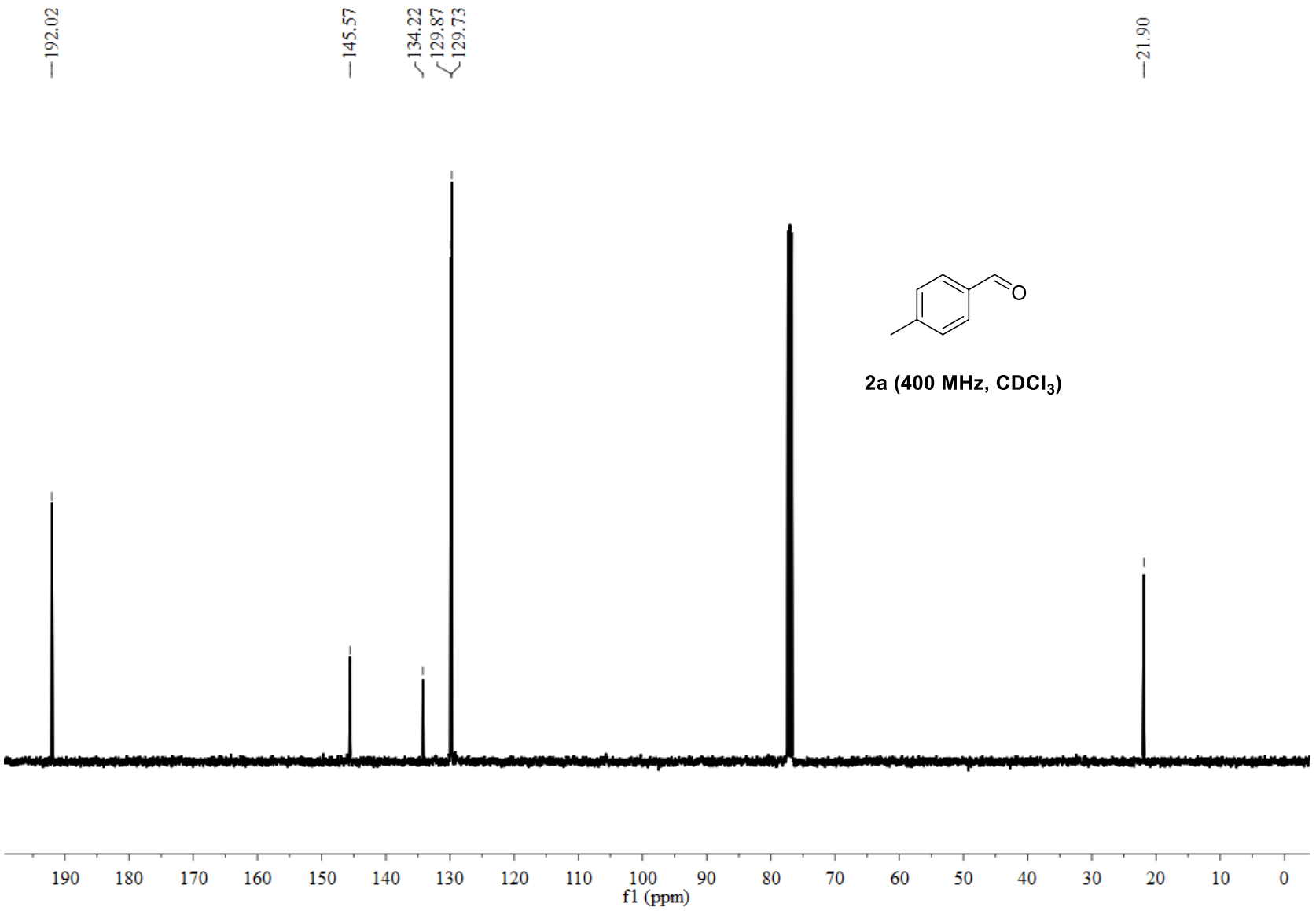
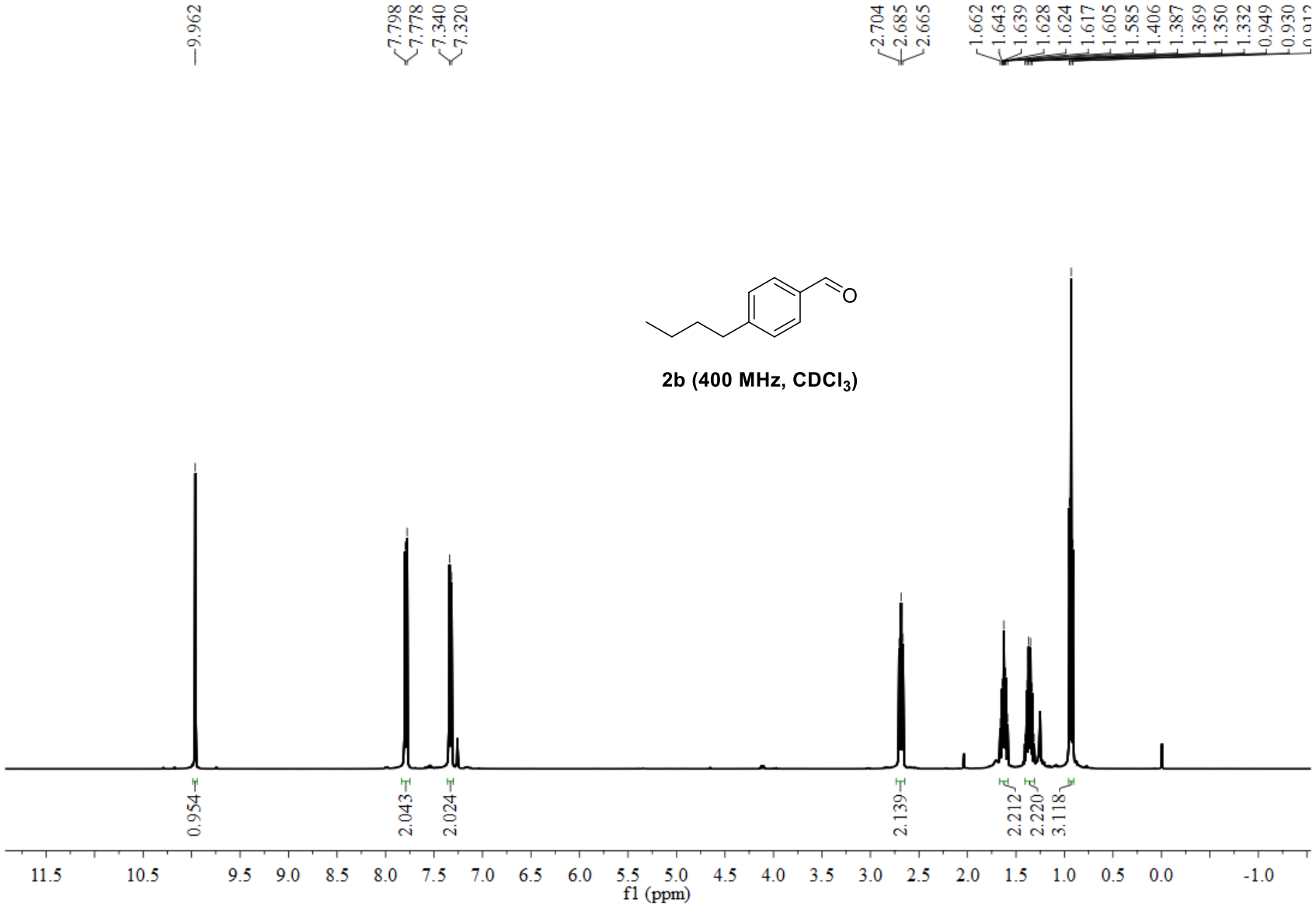
8. Copies of NMR spectra

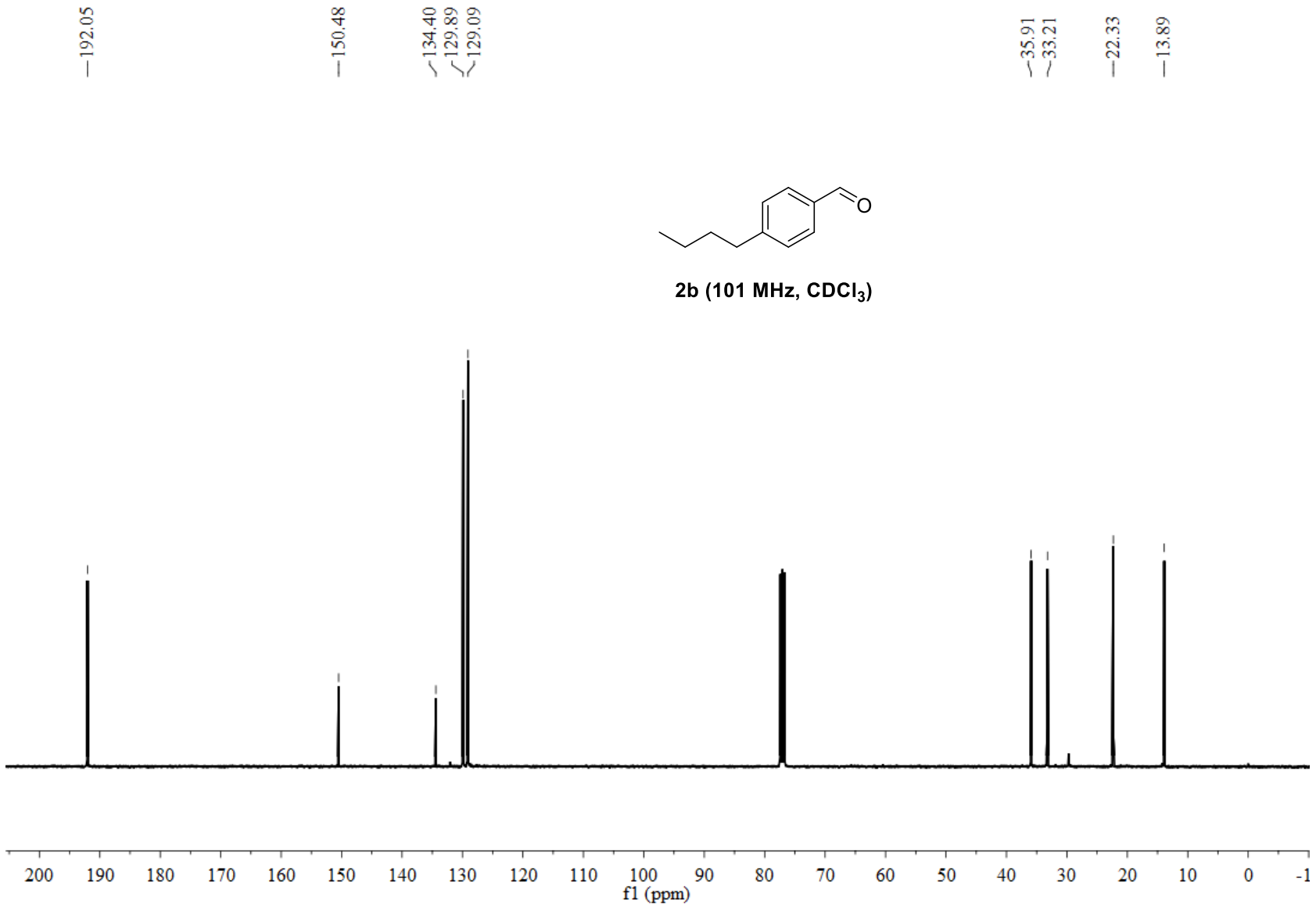


2a (400 MHz, $CDCl_3$)

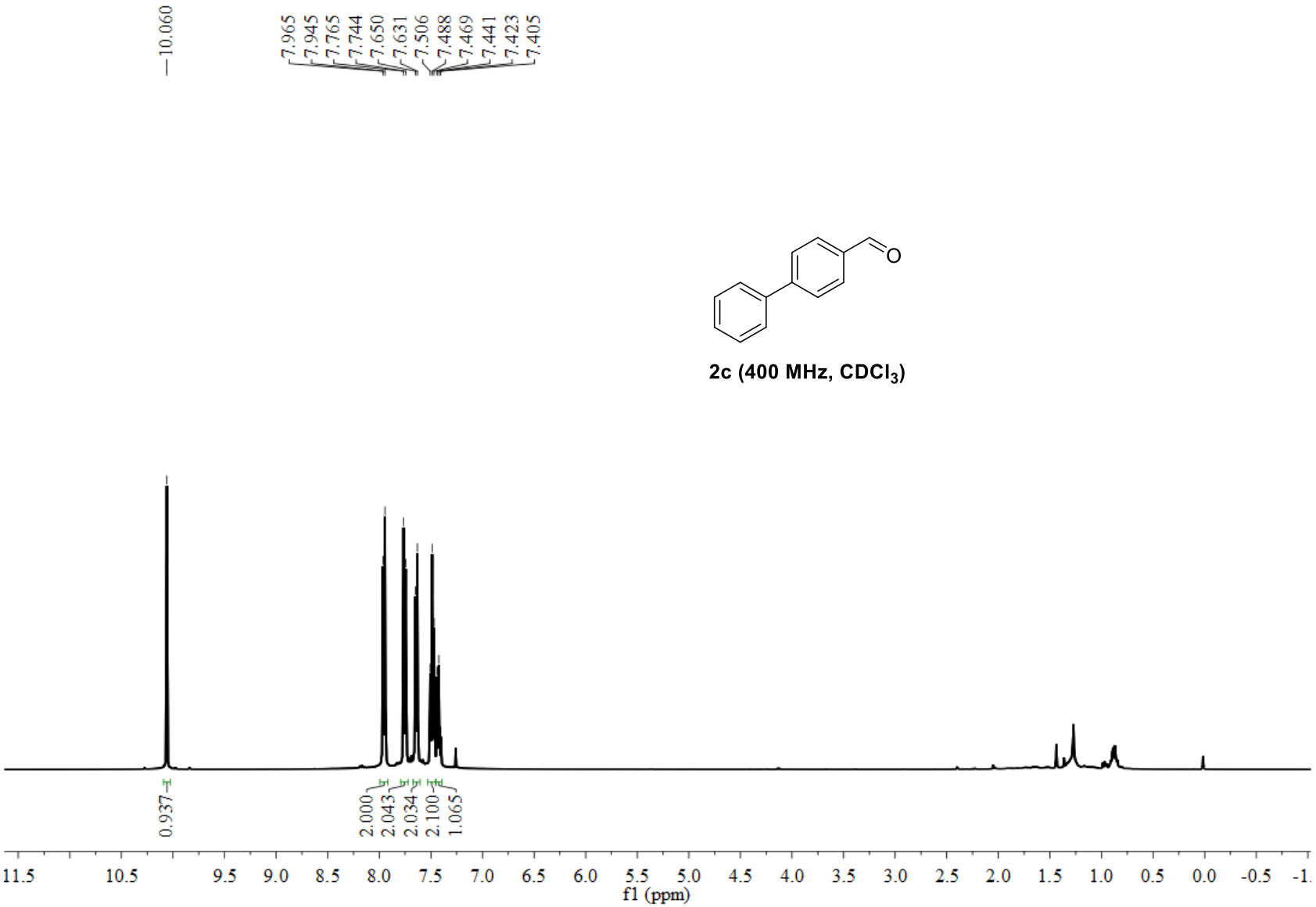

192.02
145.57
134.22
129.87
129.73
21.90
O
2a (400 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



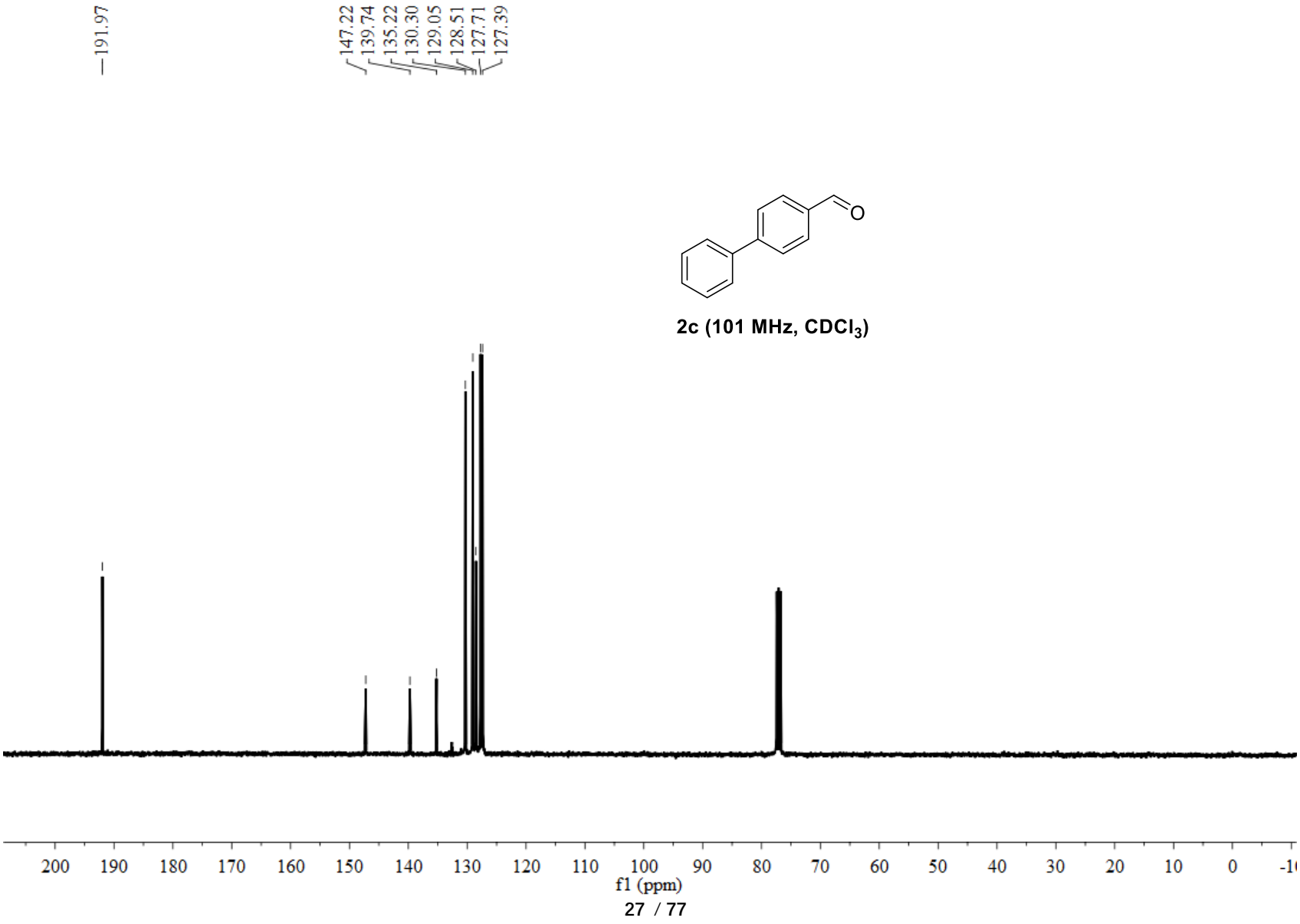
2b (400 MHz, $CDCl_3$)



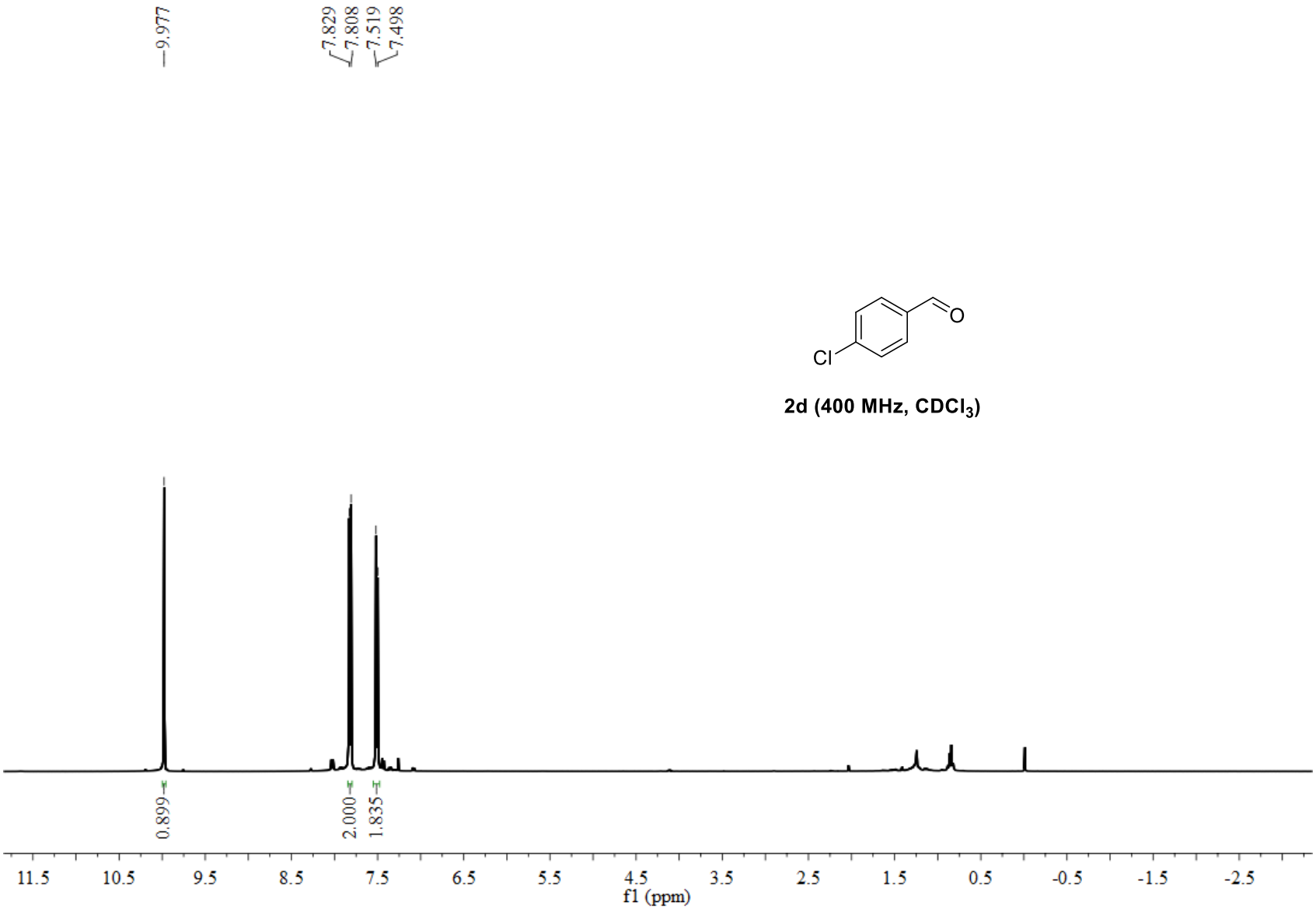
2b (101 MHz, $CDCl_3$)



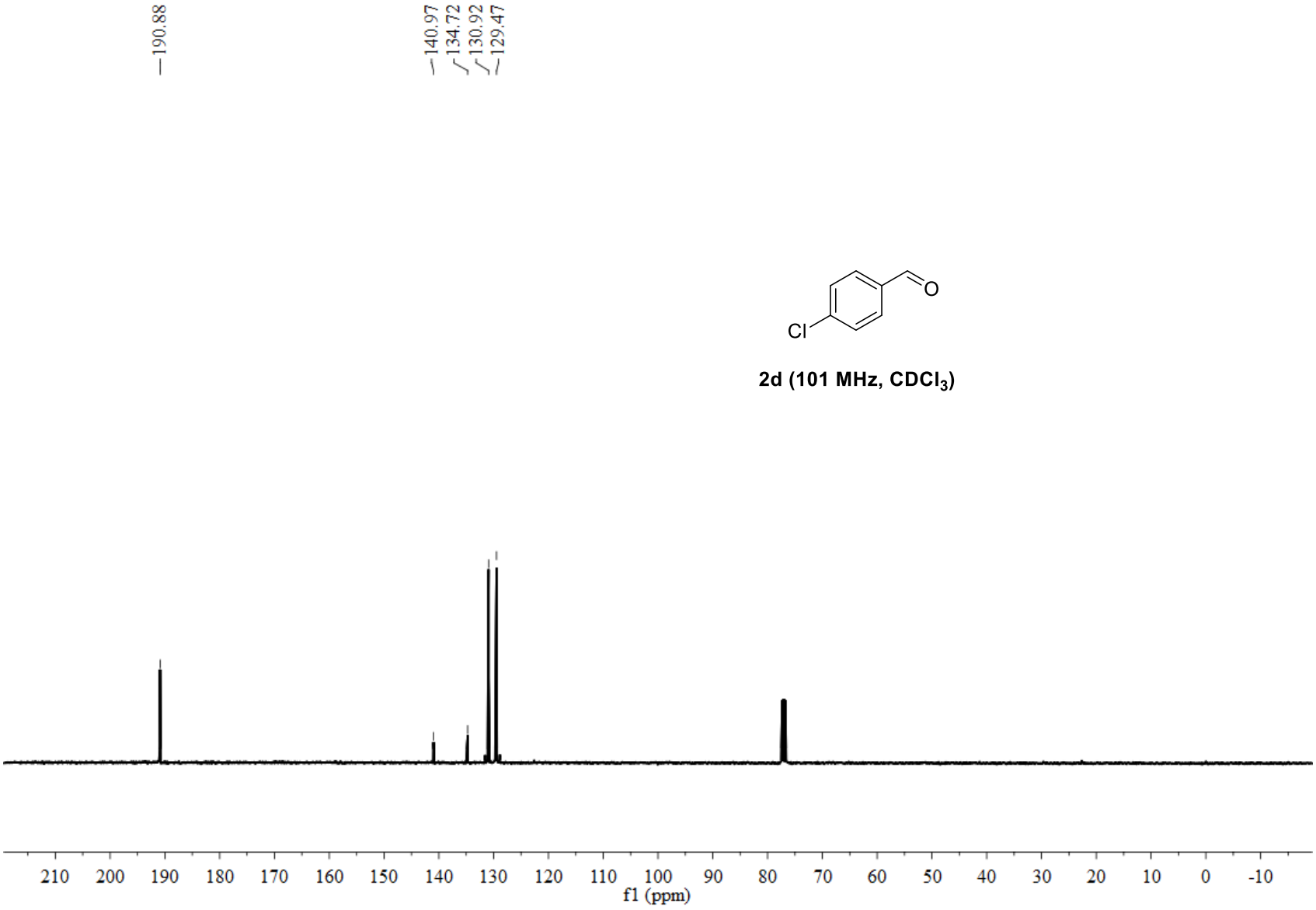
2c (400 MHz, $CDCl_3$)



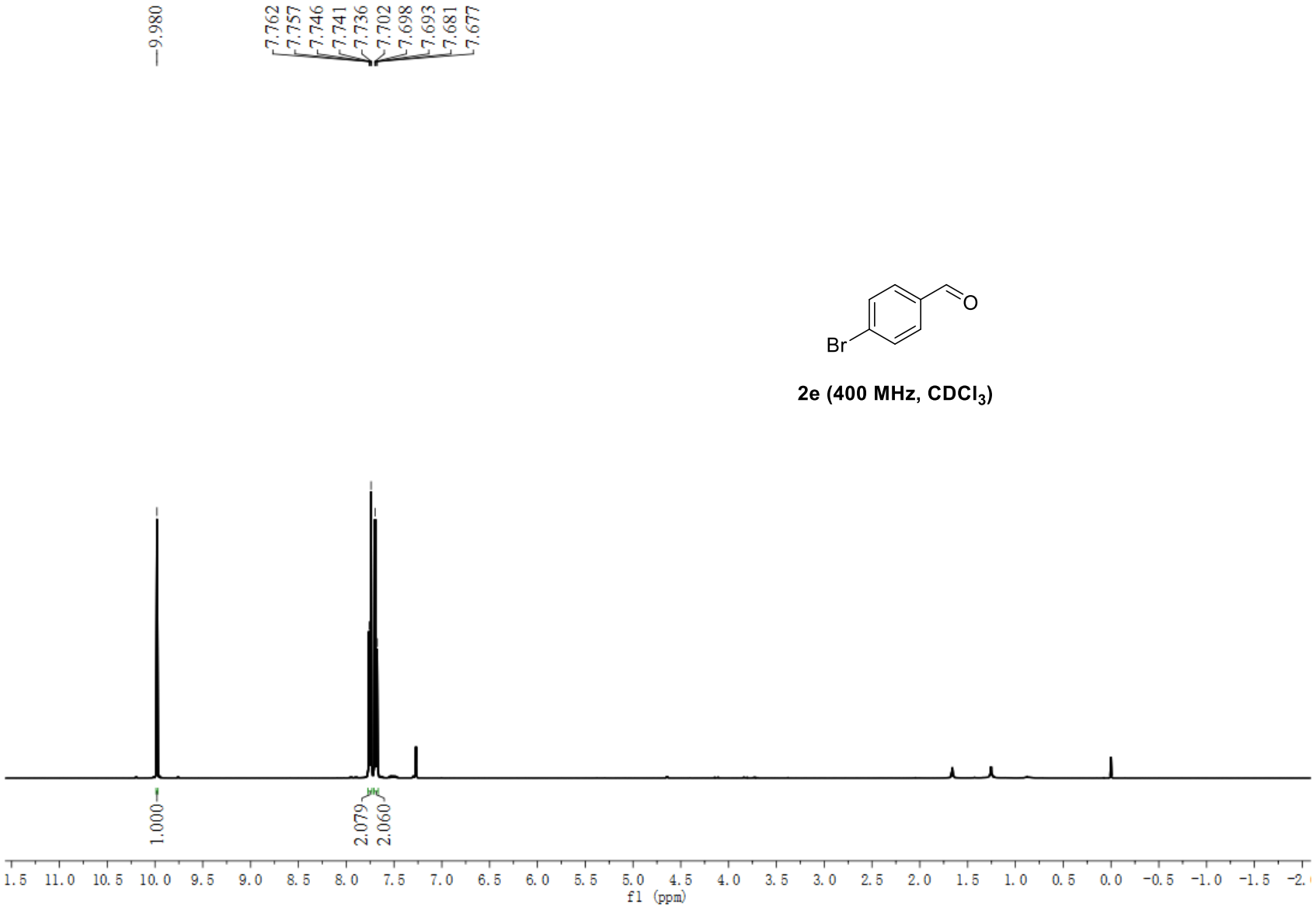
2c (101 MHz, $CDCl_3$)



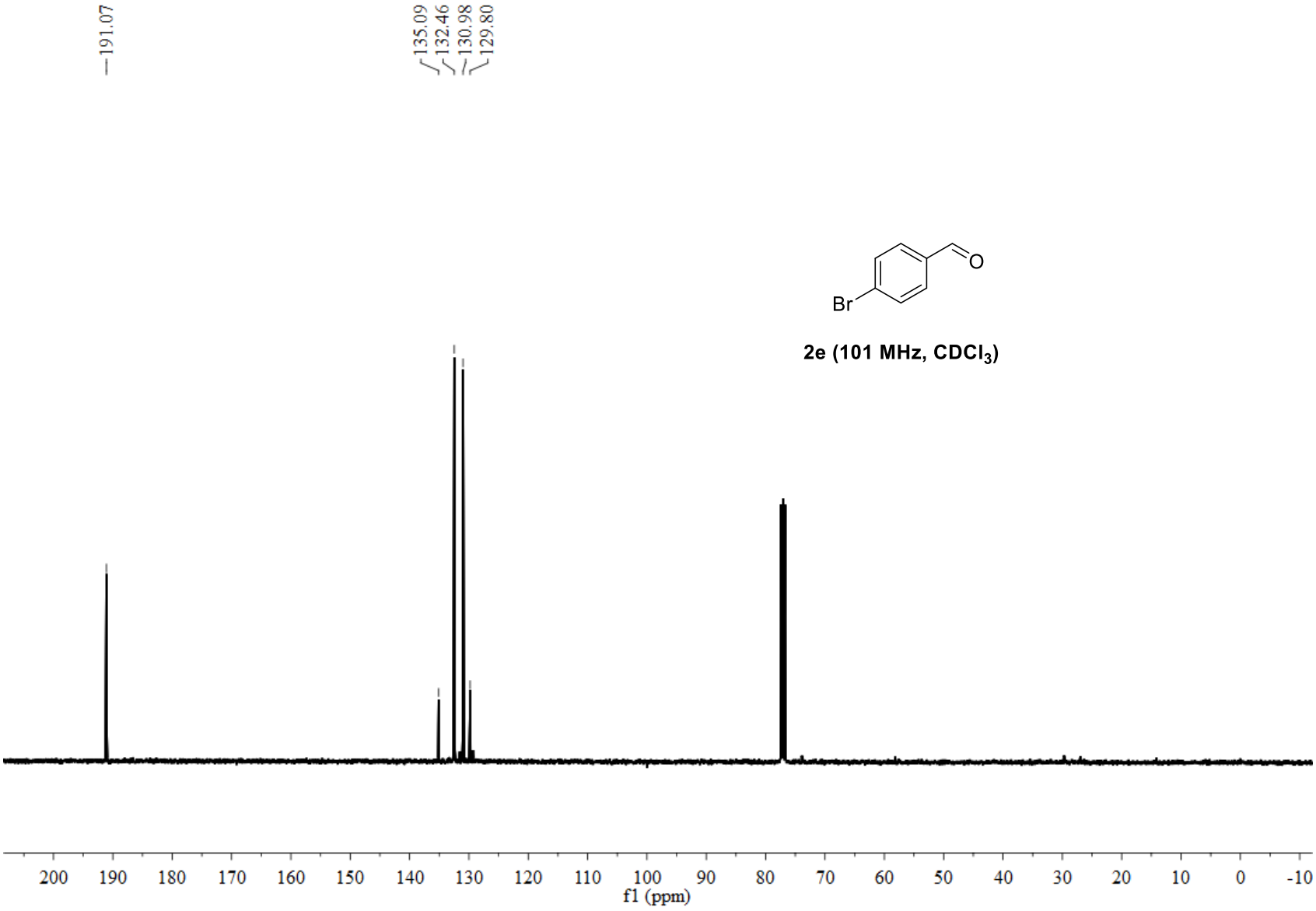
2d (400 MHz, $CDCl_3$)



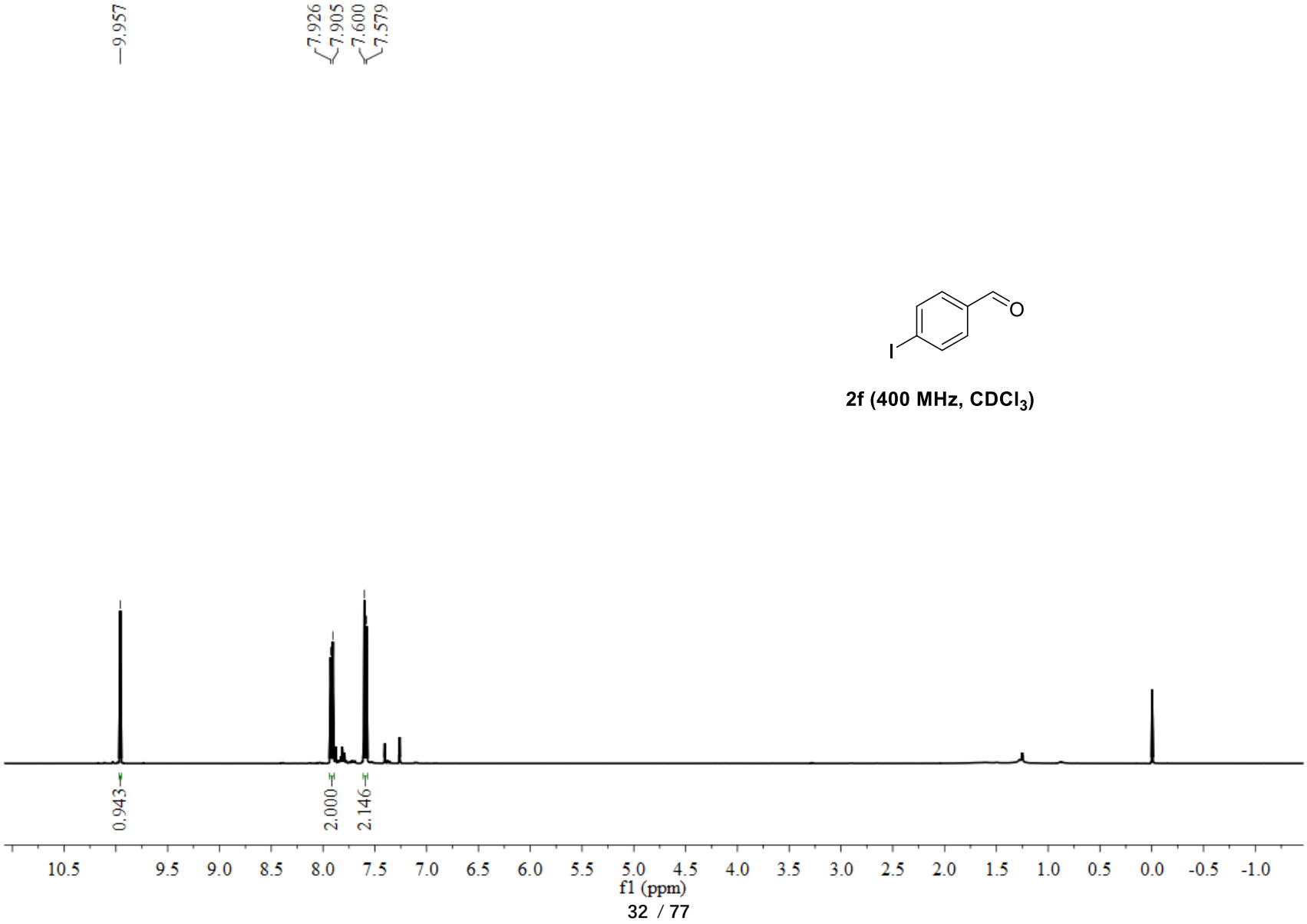
2d (101 MHz, $CDCl_3$)



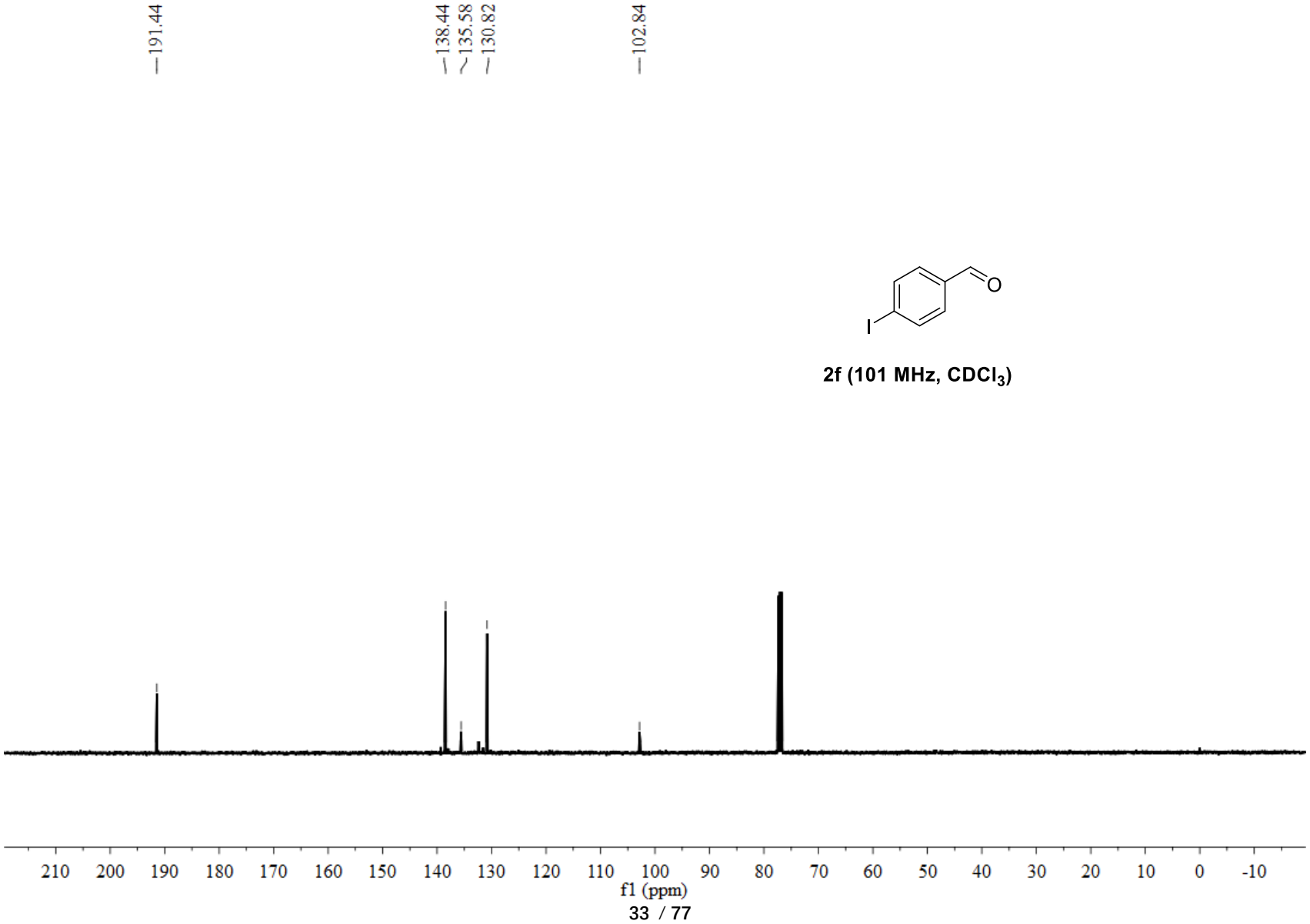
2e (400 MHz, $CDCl_3$)



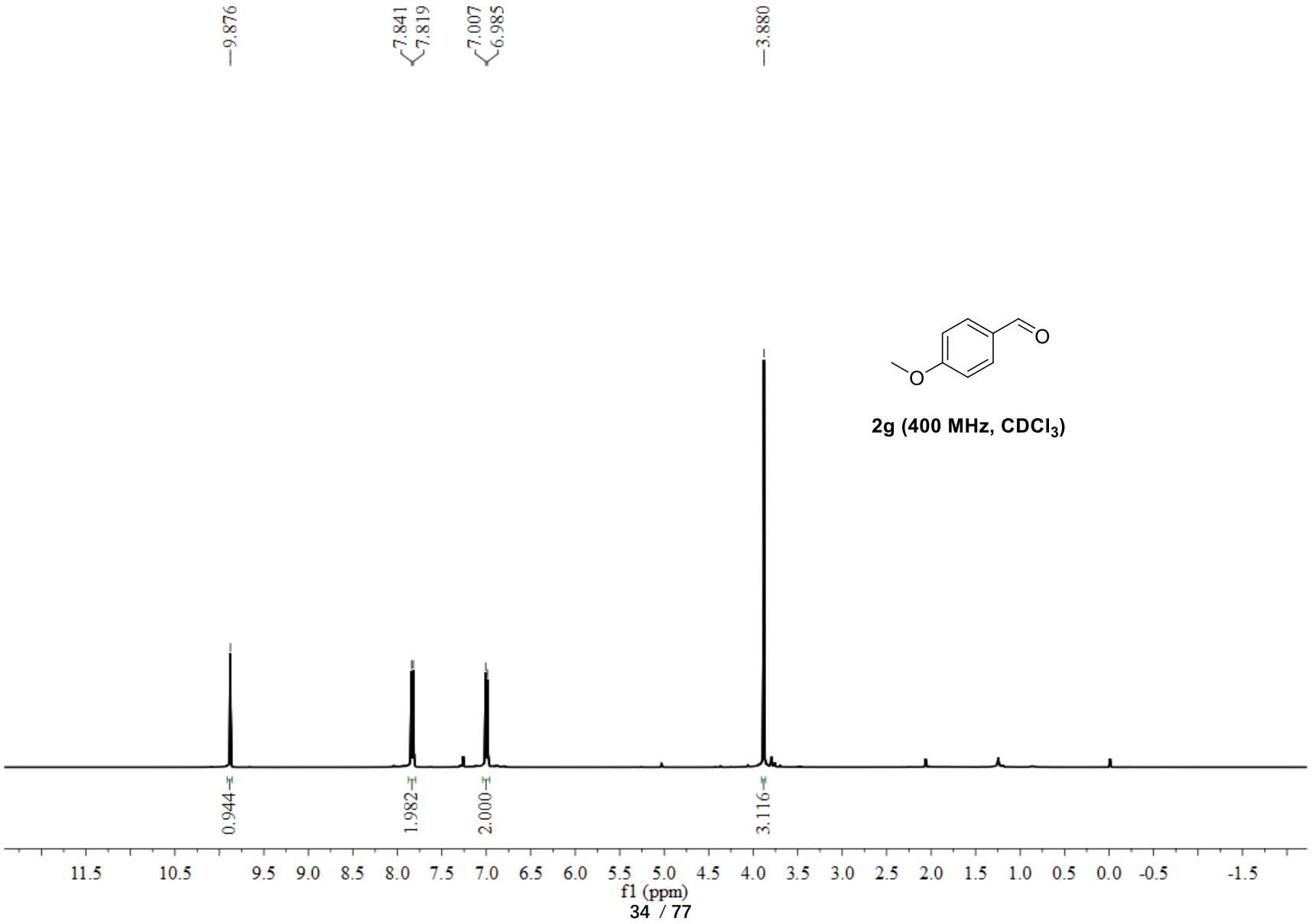
2e (101 MHz, $CDCl_3$)



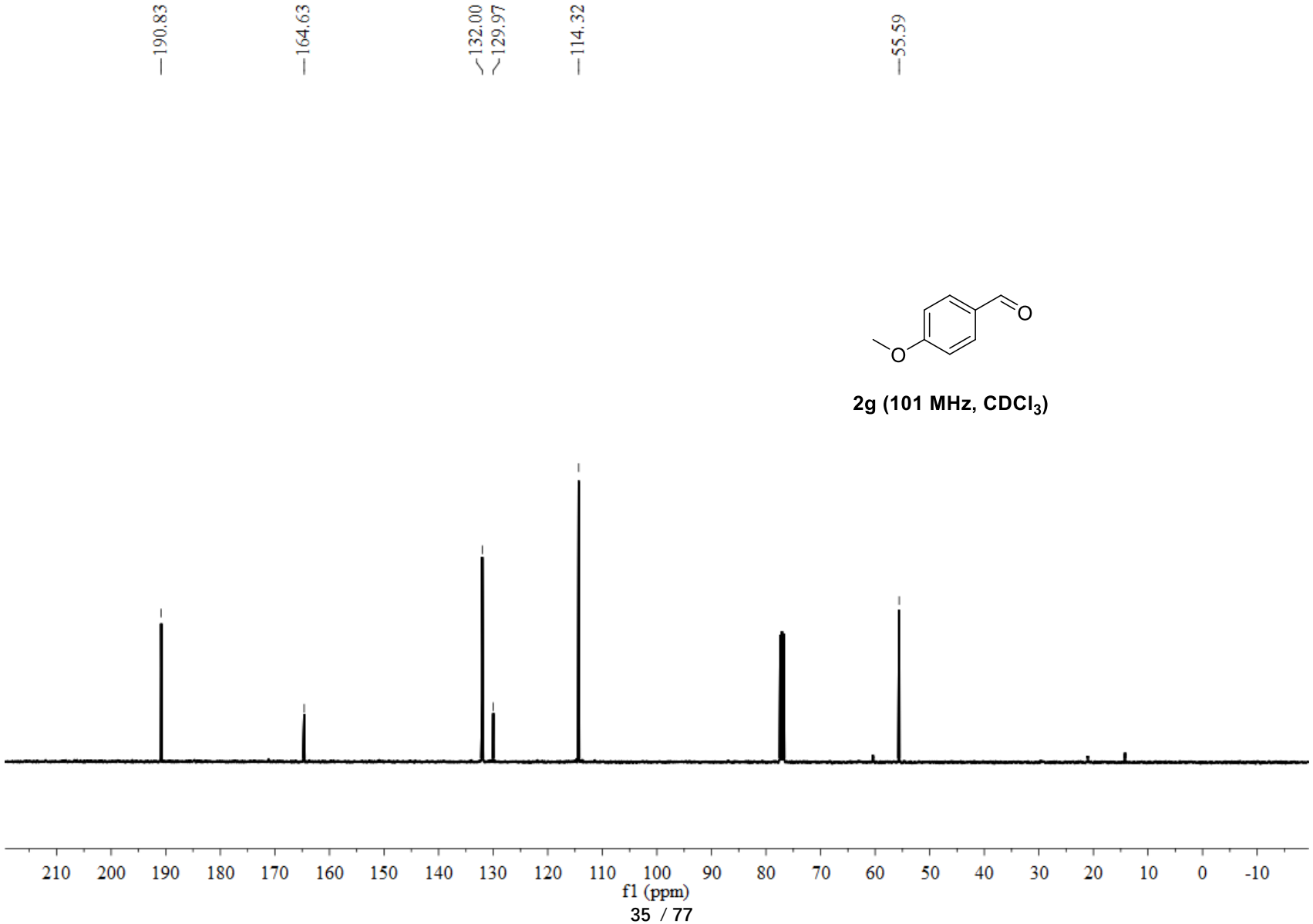
2f (400 MHz, $CDCl_3$)



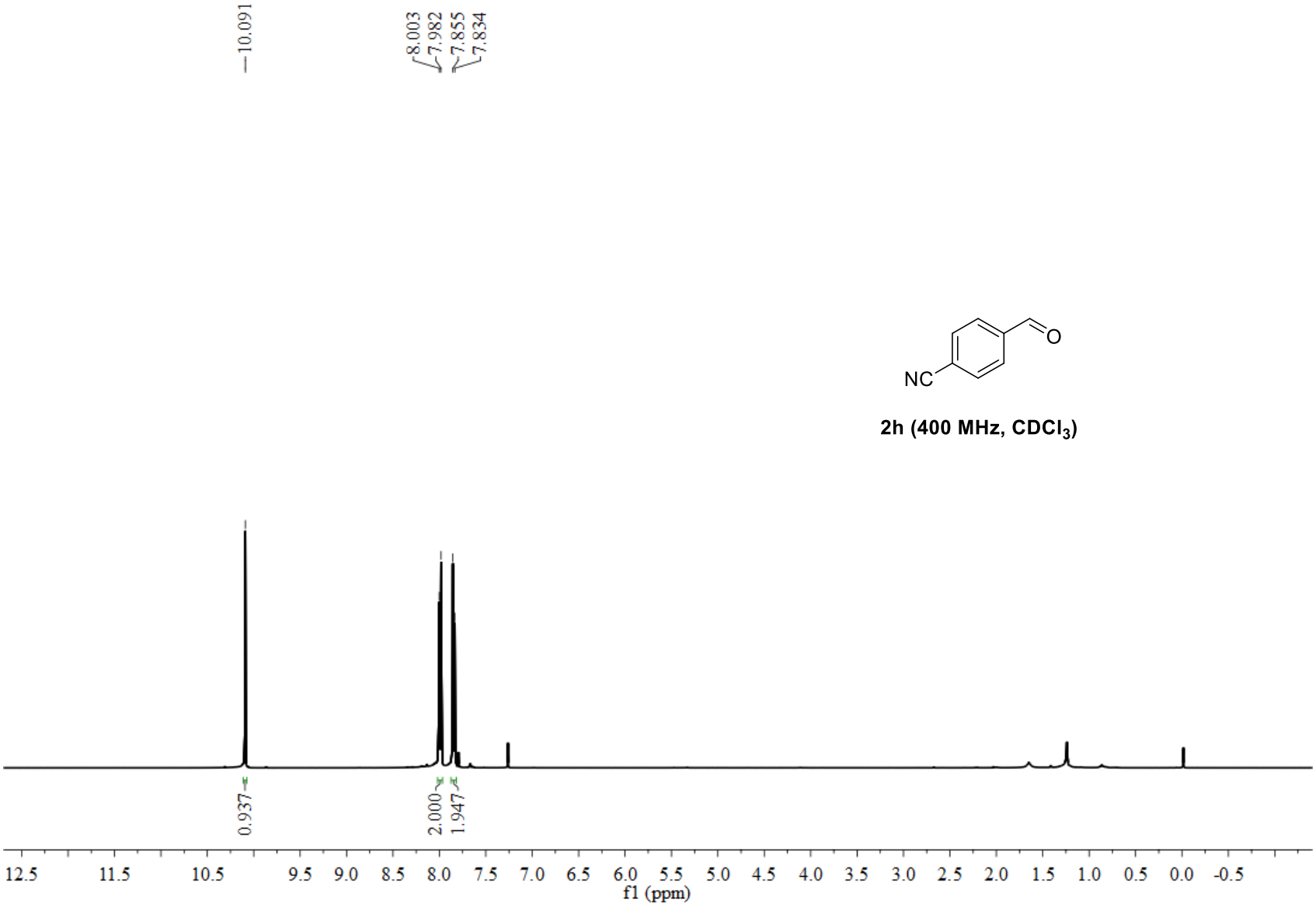
2f (101 MHz, $CDCl_3$)



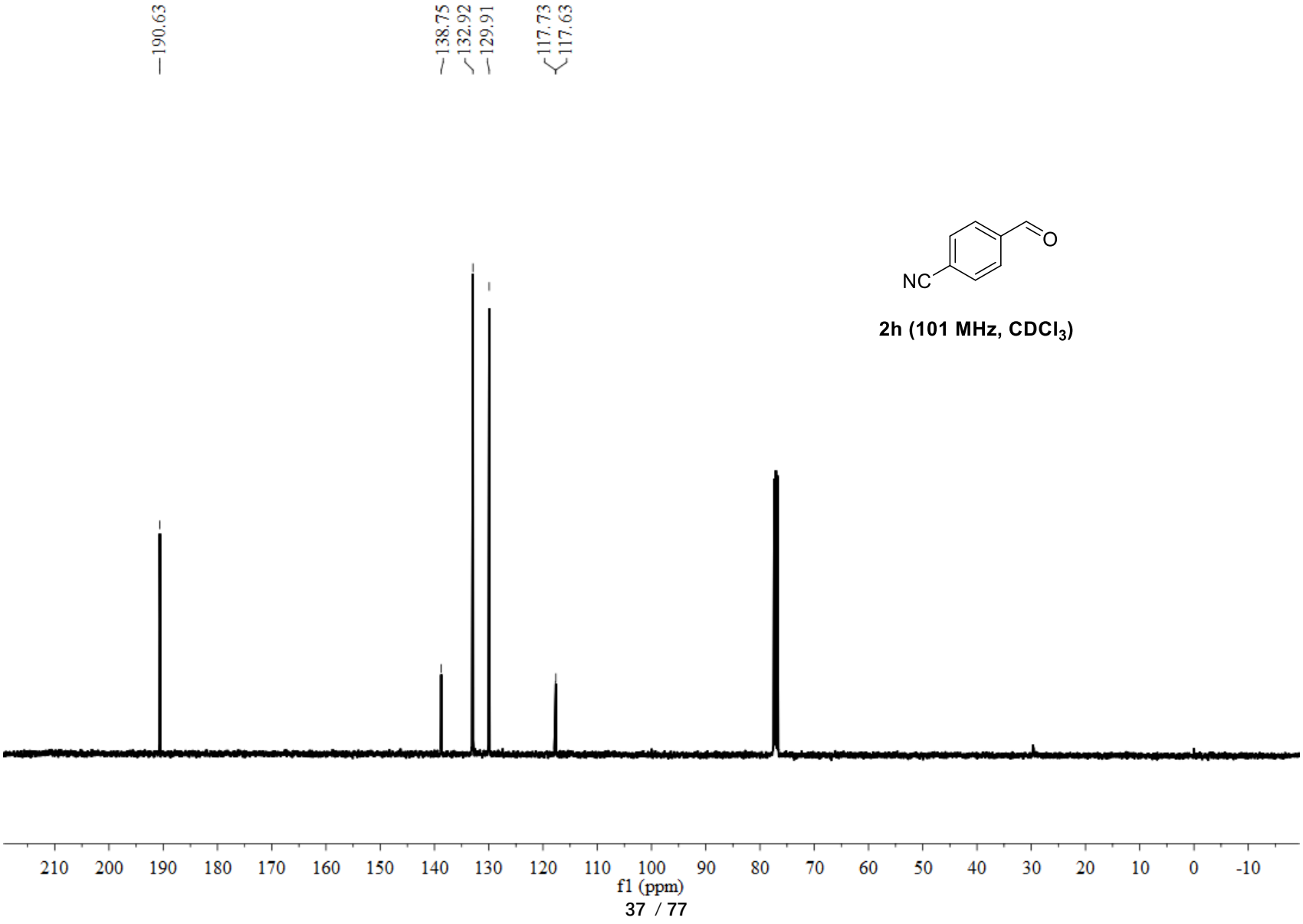
2g (400 MHz, $CDCl_3$)



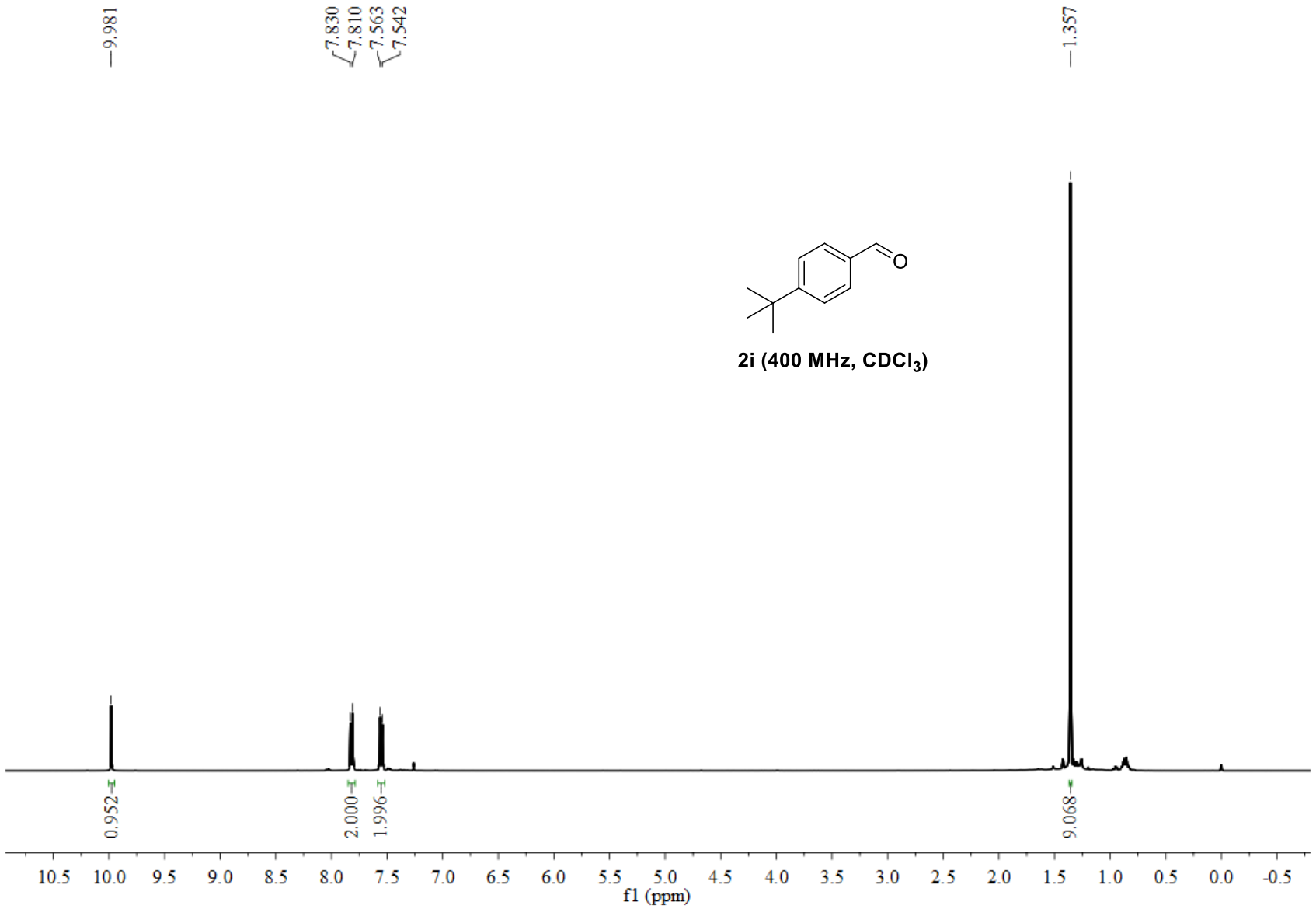
2g (101 MHz, $CDCl_3$)



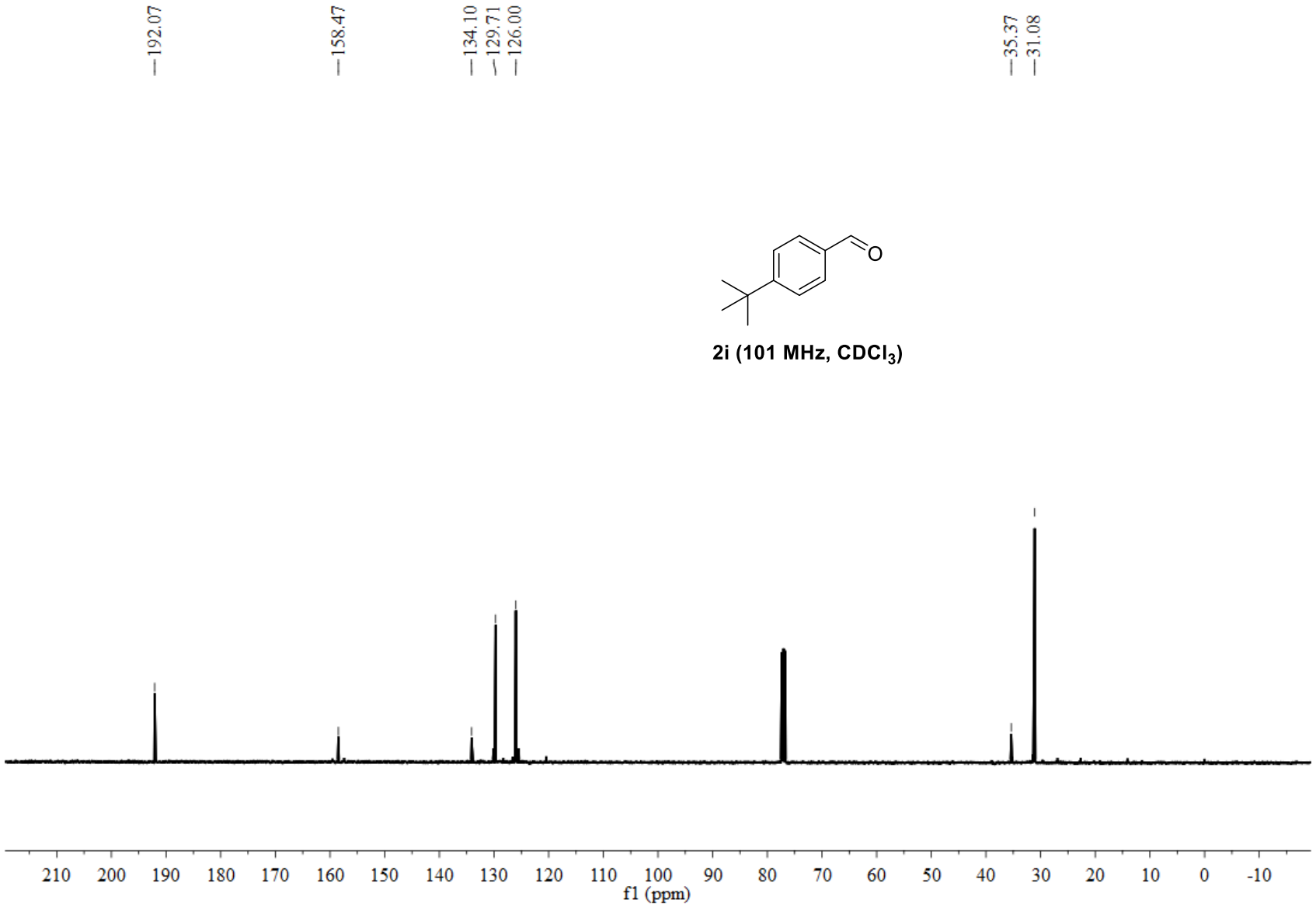
2h (400 MHz, $CDCl_3$)



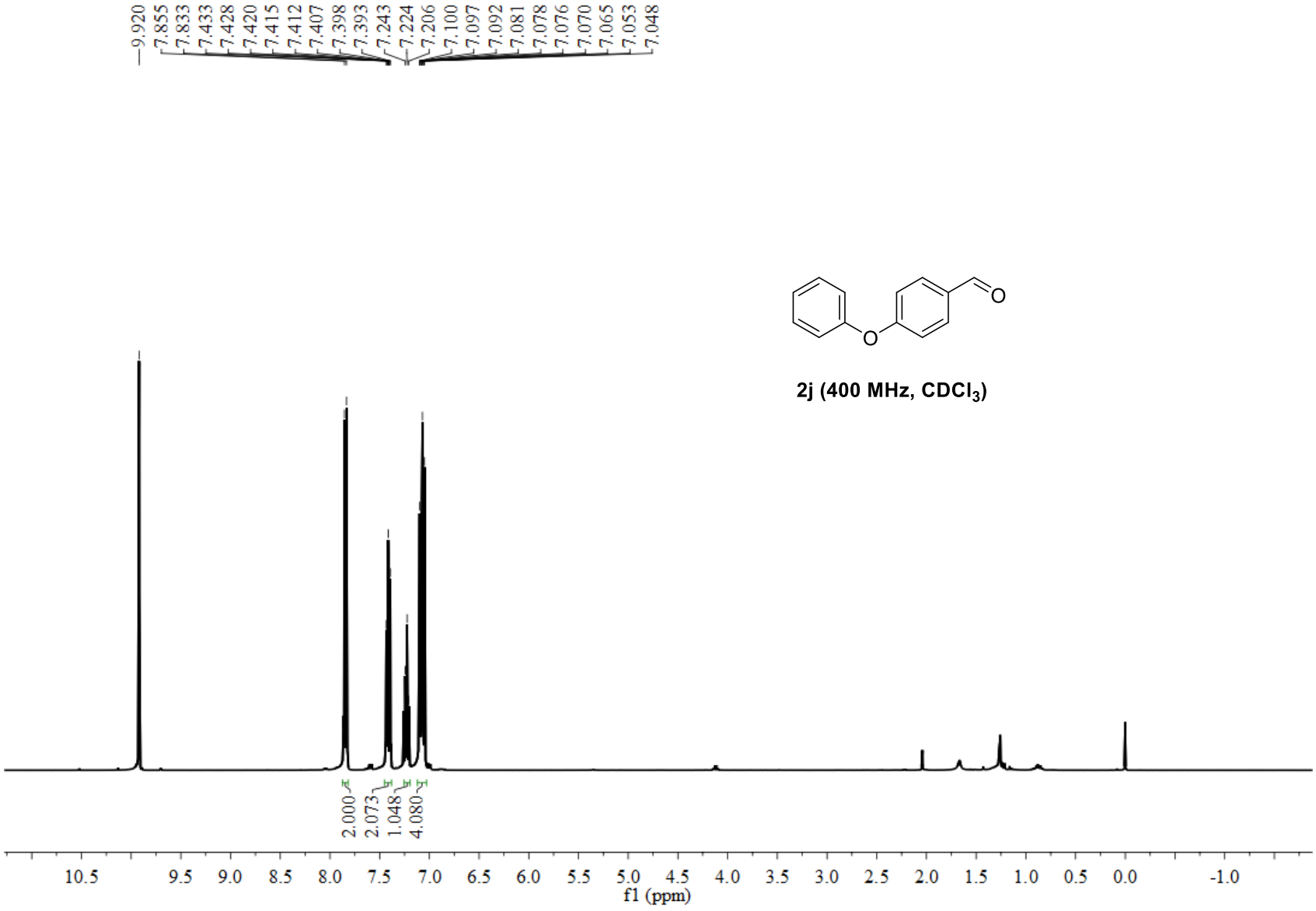
2h (101 MHz, $CDCl_3$)



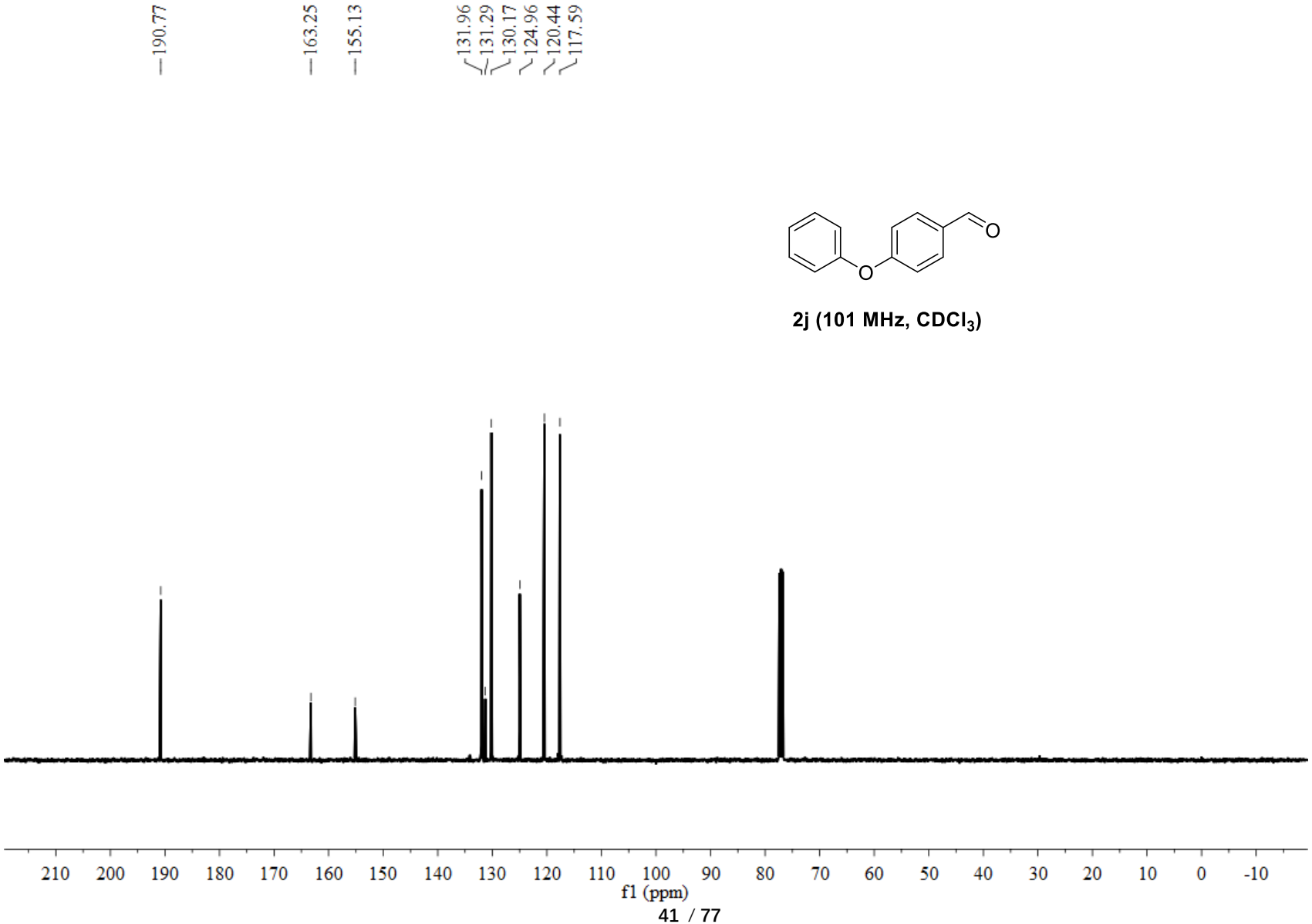
2i (400 MHz, $CDCl_3$)



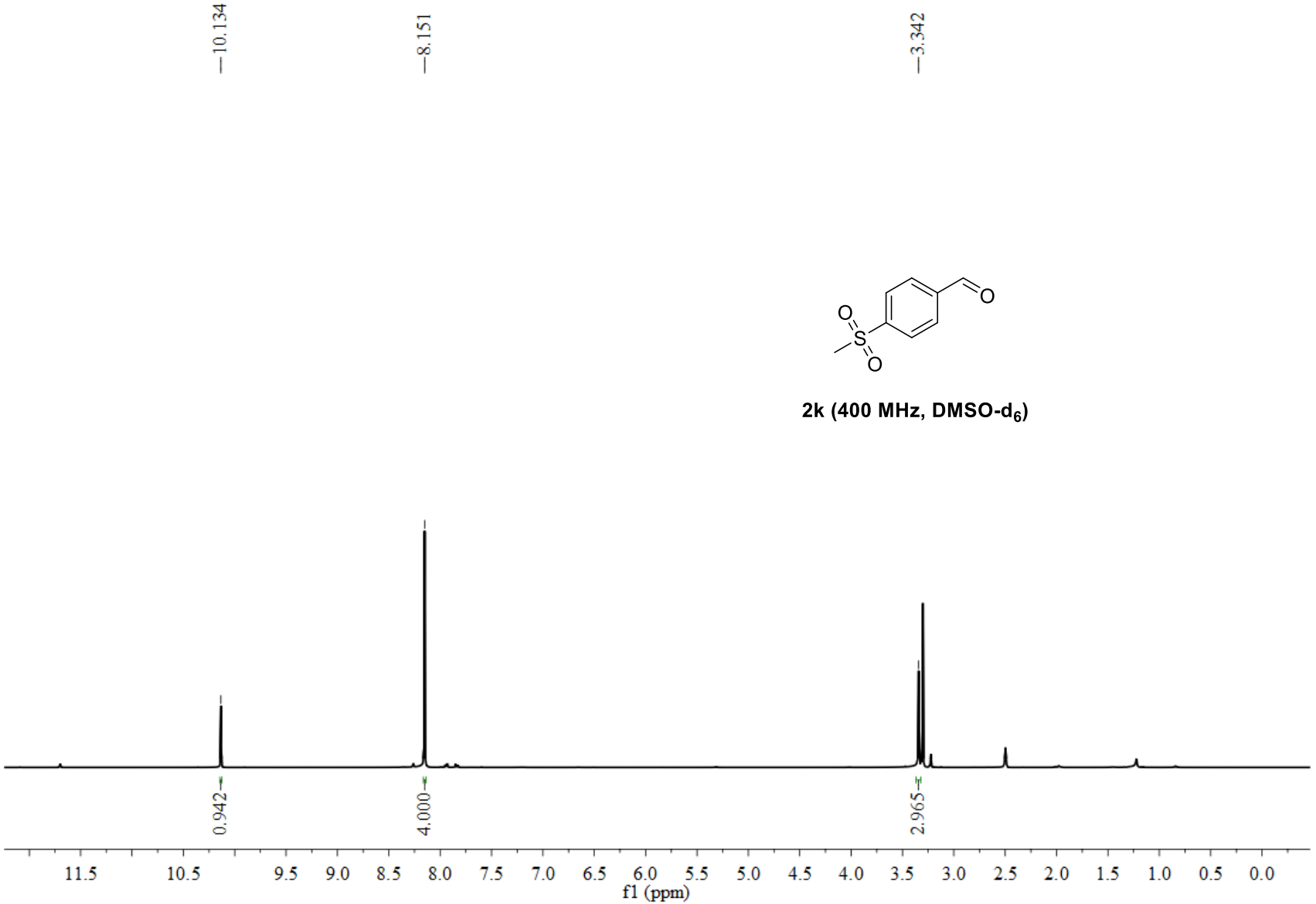
2i (101 MHz, $CDCl_3$)



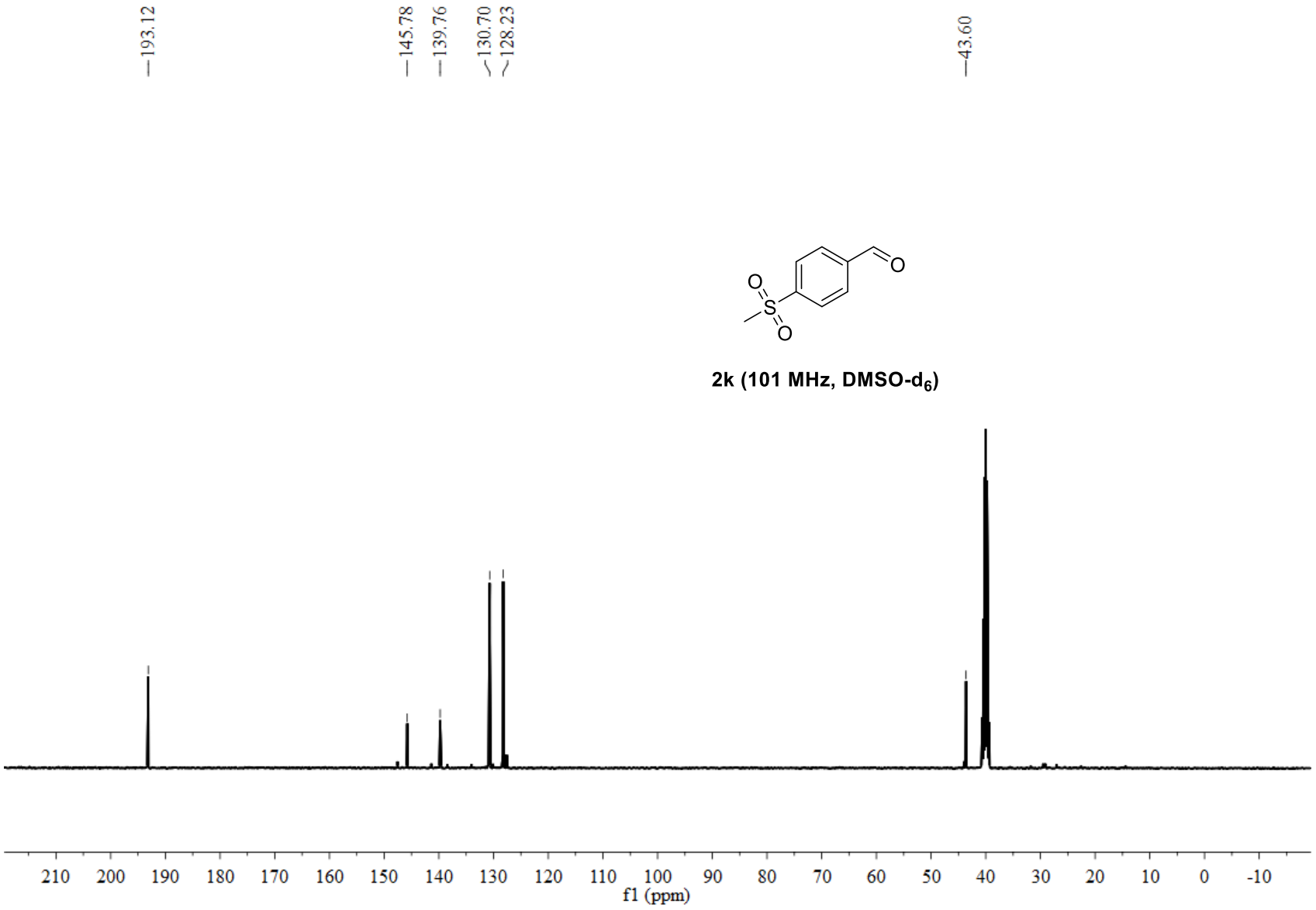
2j (400 MHz, $CDCl_3$)



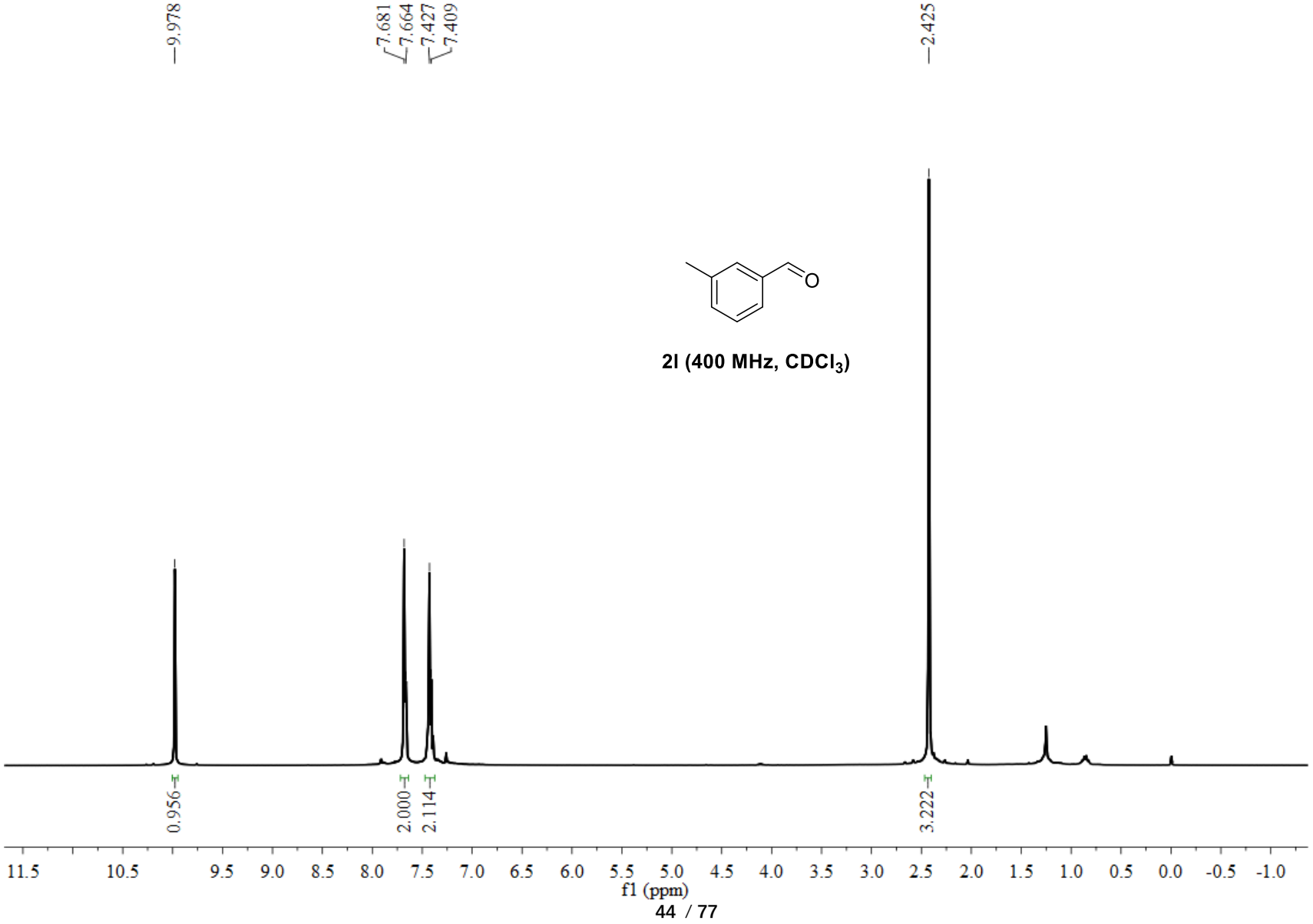
2j (101 MHz, $CDCl_3$)



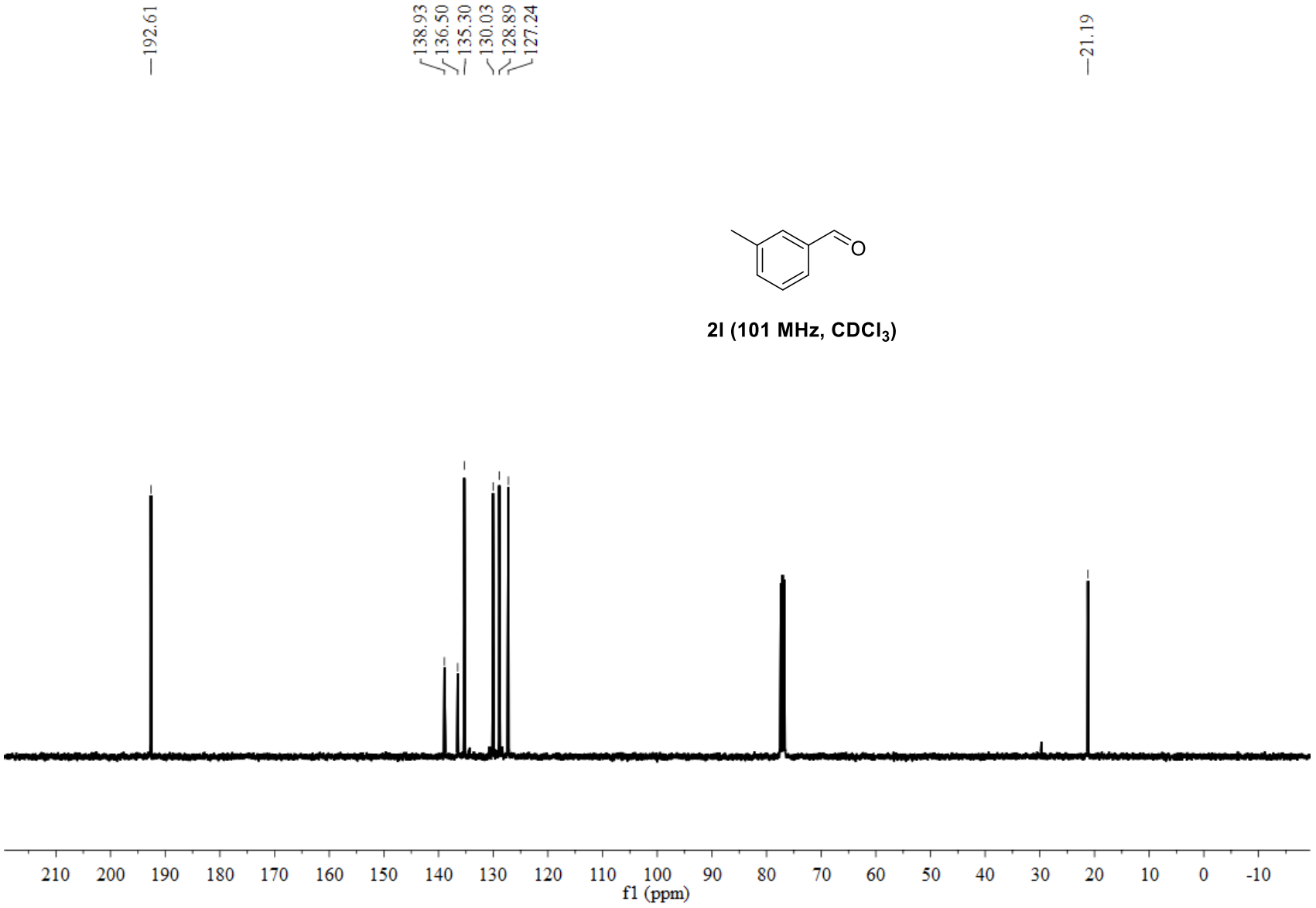
2k (400 MHz, DMSO-d_6)



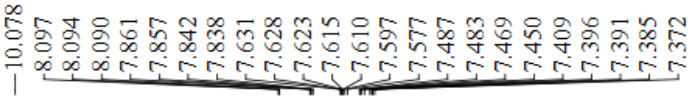
2k (101 MHz, DMSO-d_6)

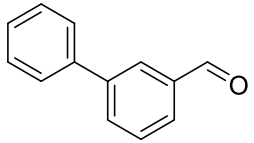


2l (400 MHz, $CDCl_3$)

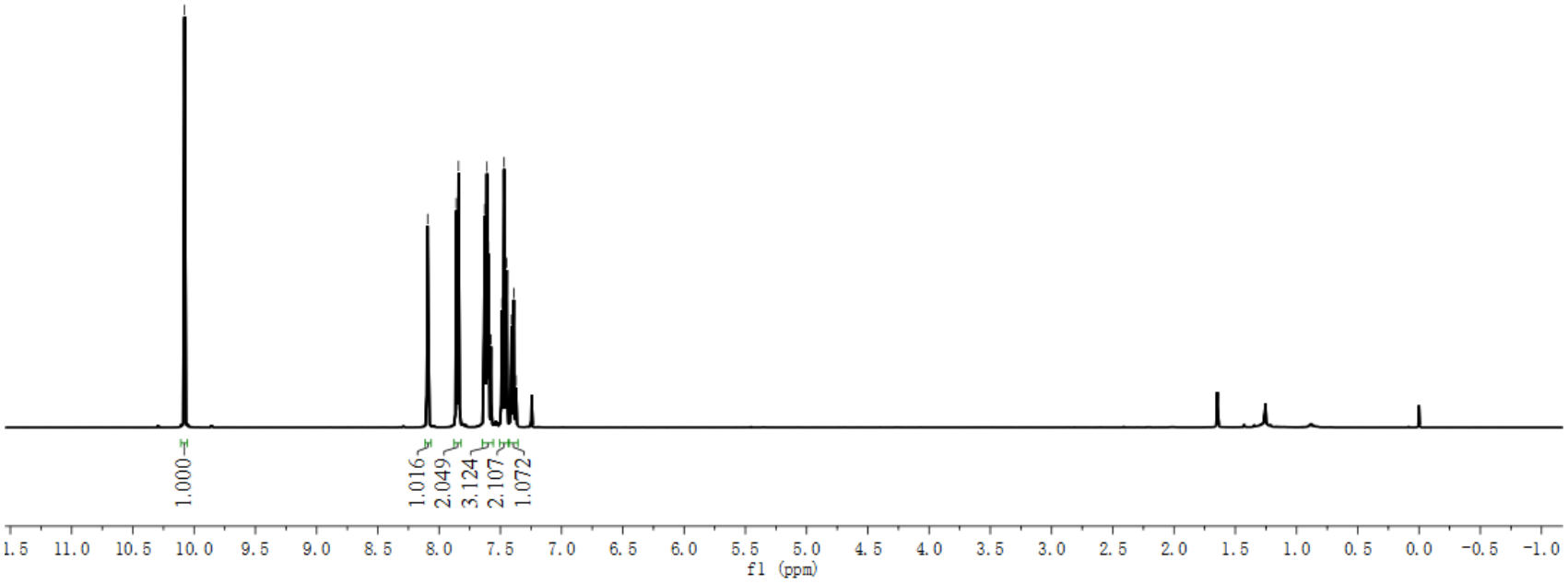


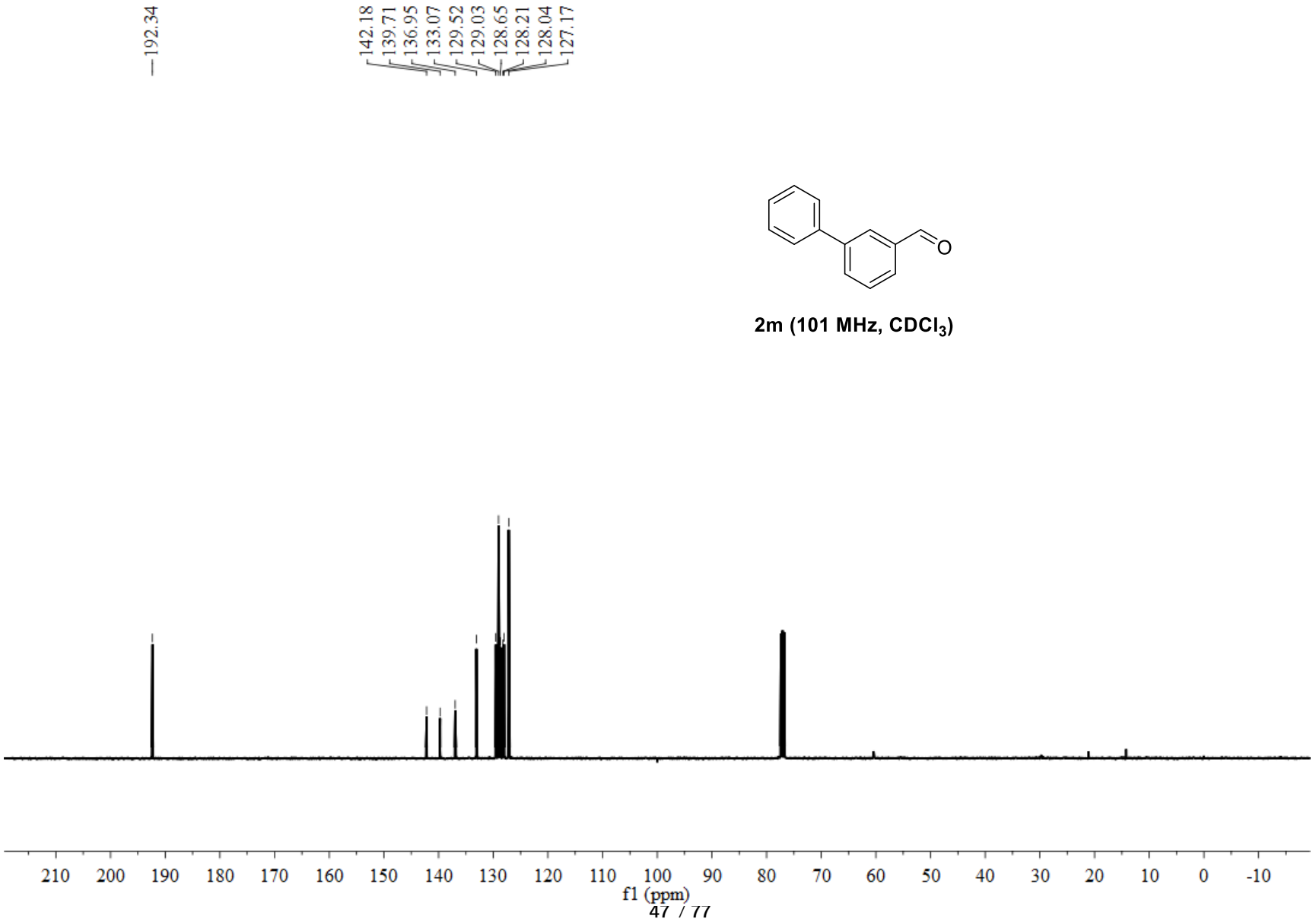
2l (101 MHz, $CDCl_3$)



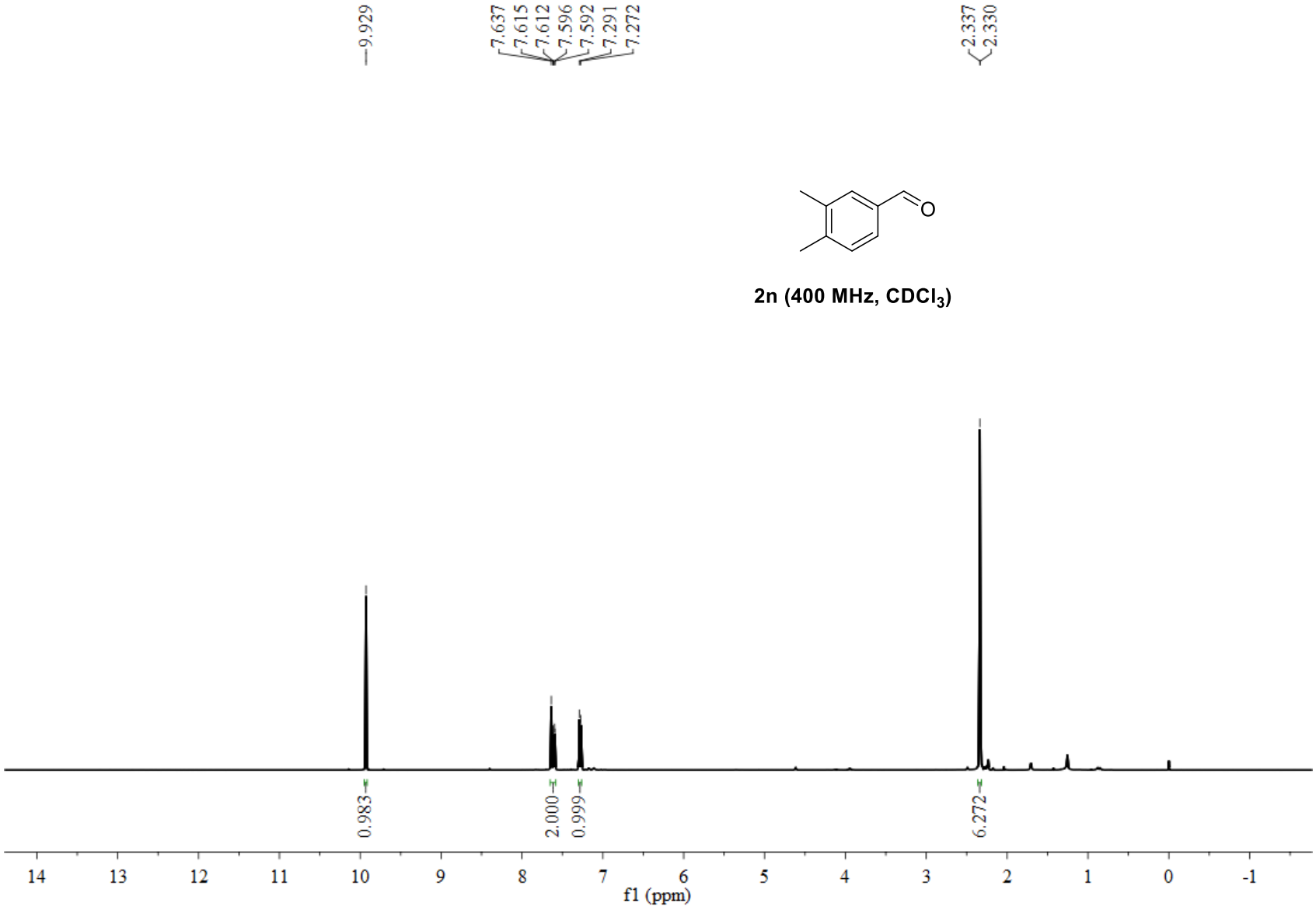


2m (400 MHz, $CDCl_3$)

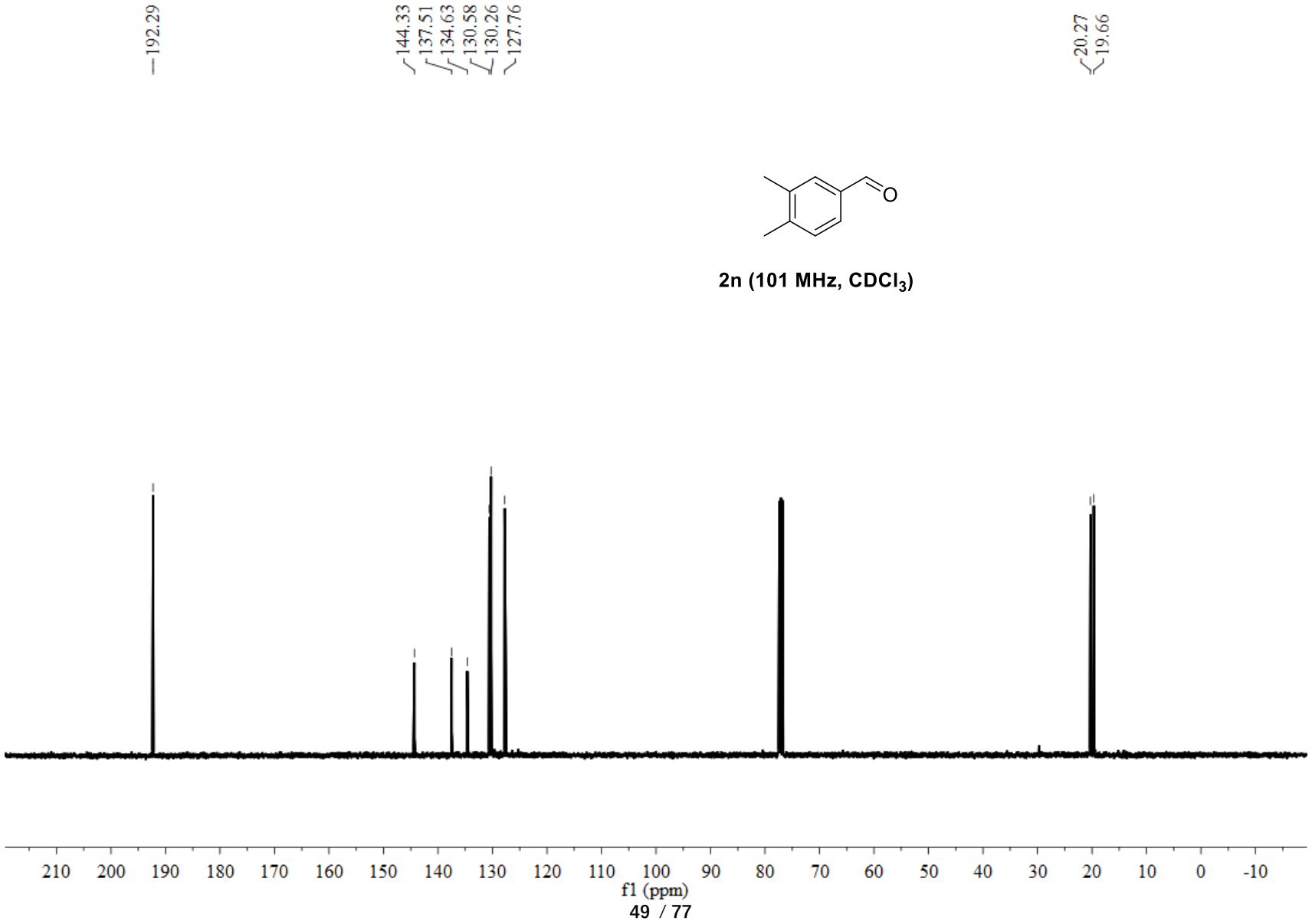




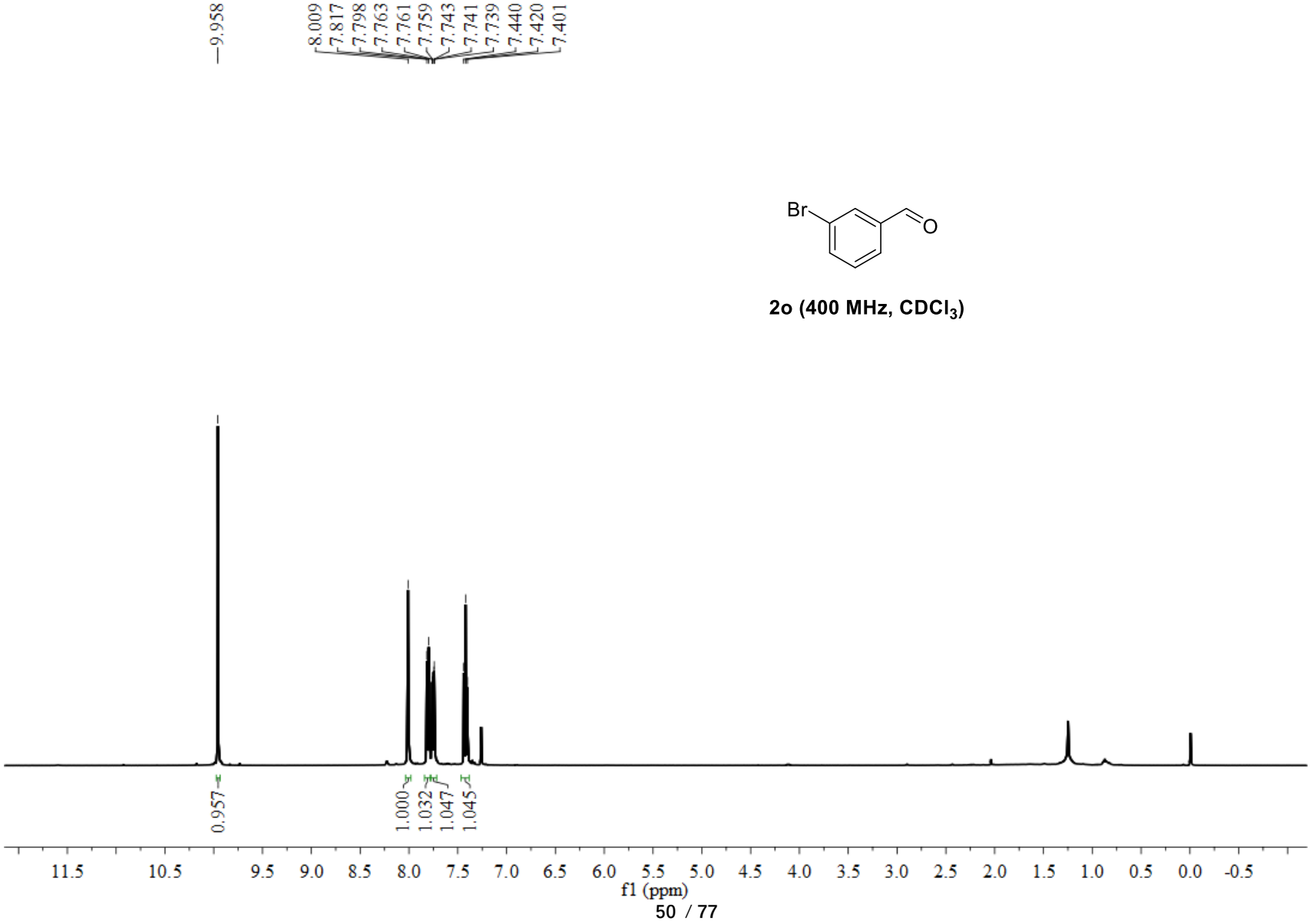
2m (101 MHz, $CDCl_3$)



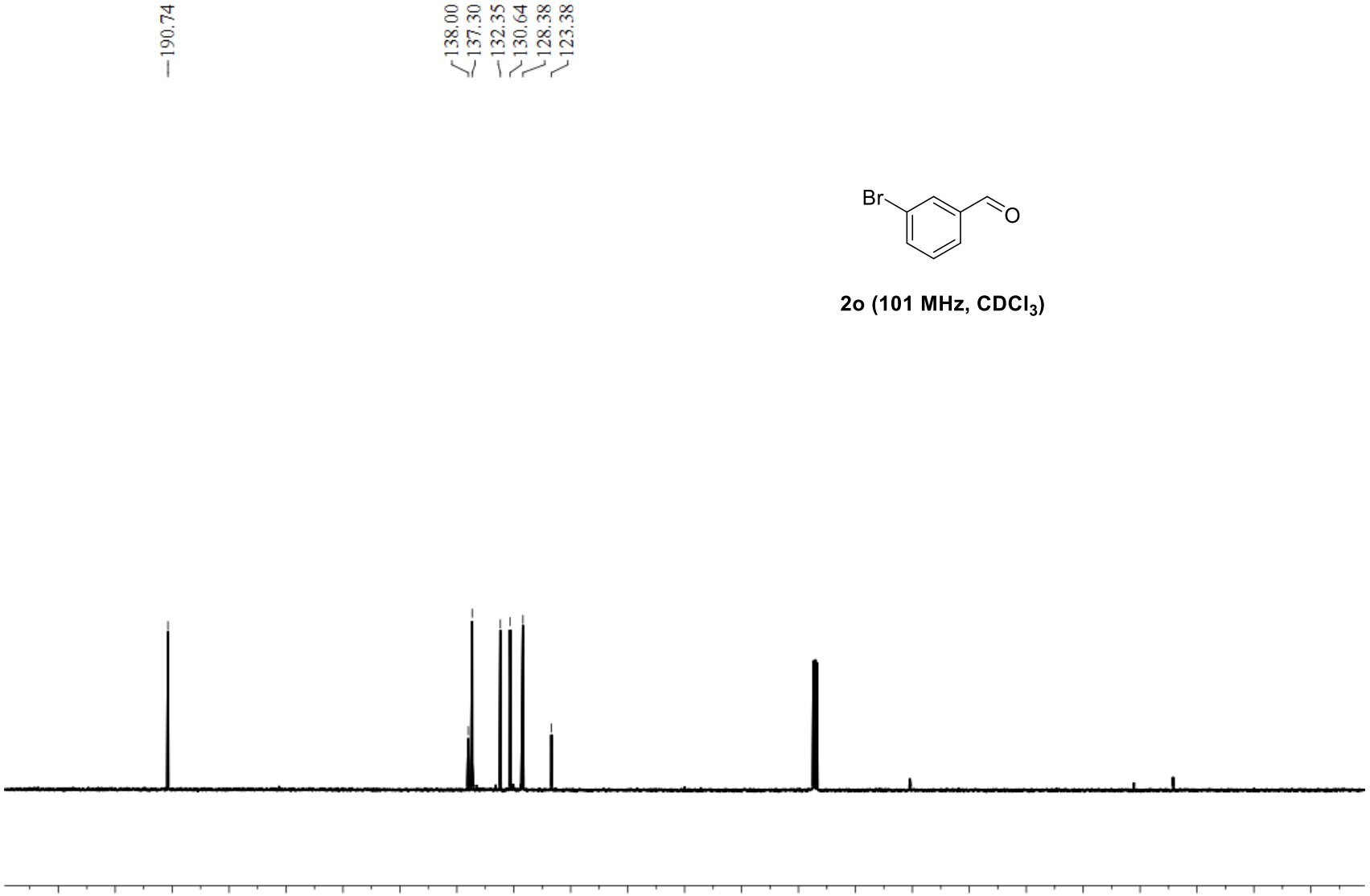
2n (400 MHz, $CDCl_3$)



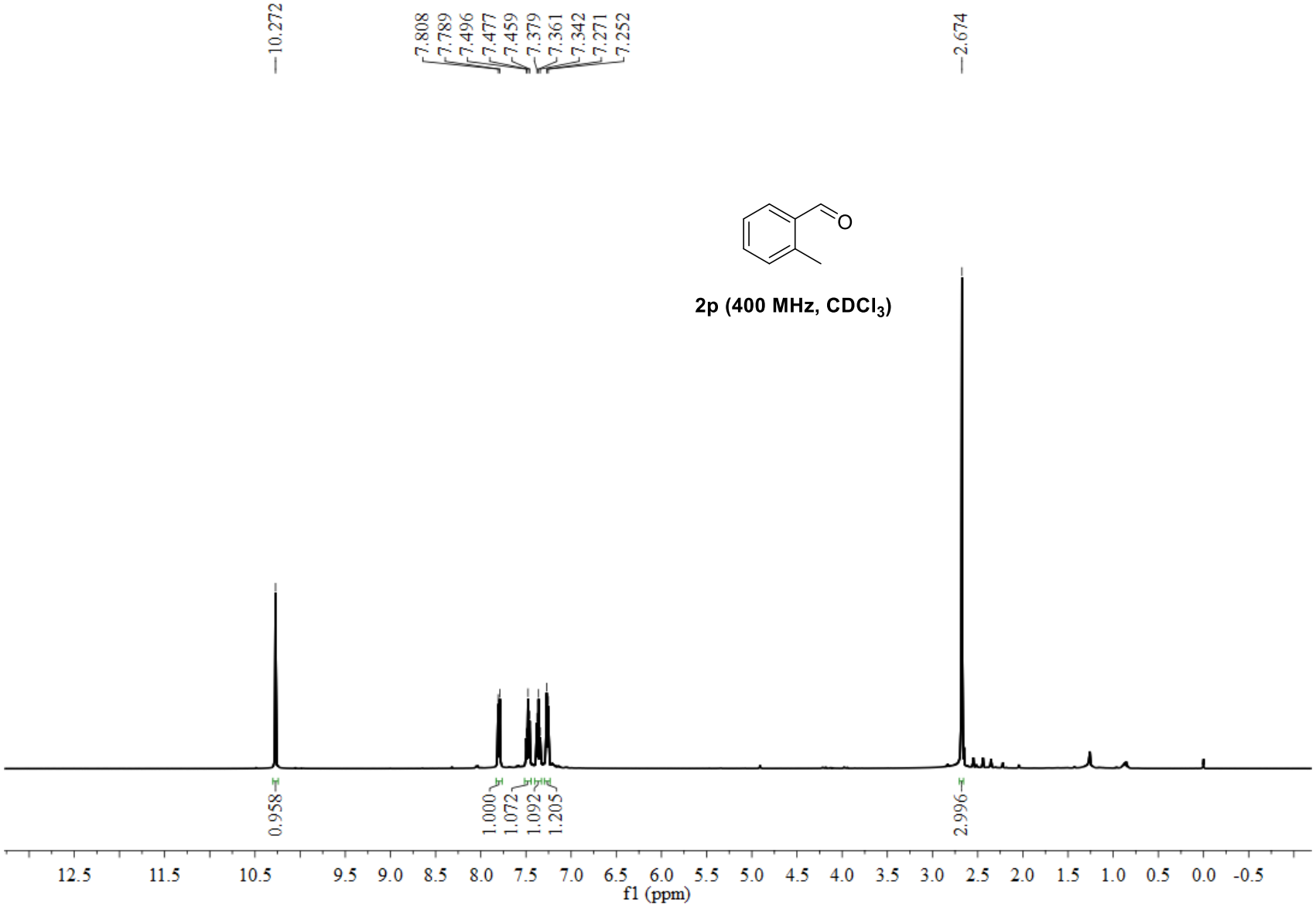
2n (101 MHz, $CDCl_3$)



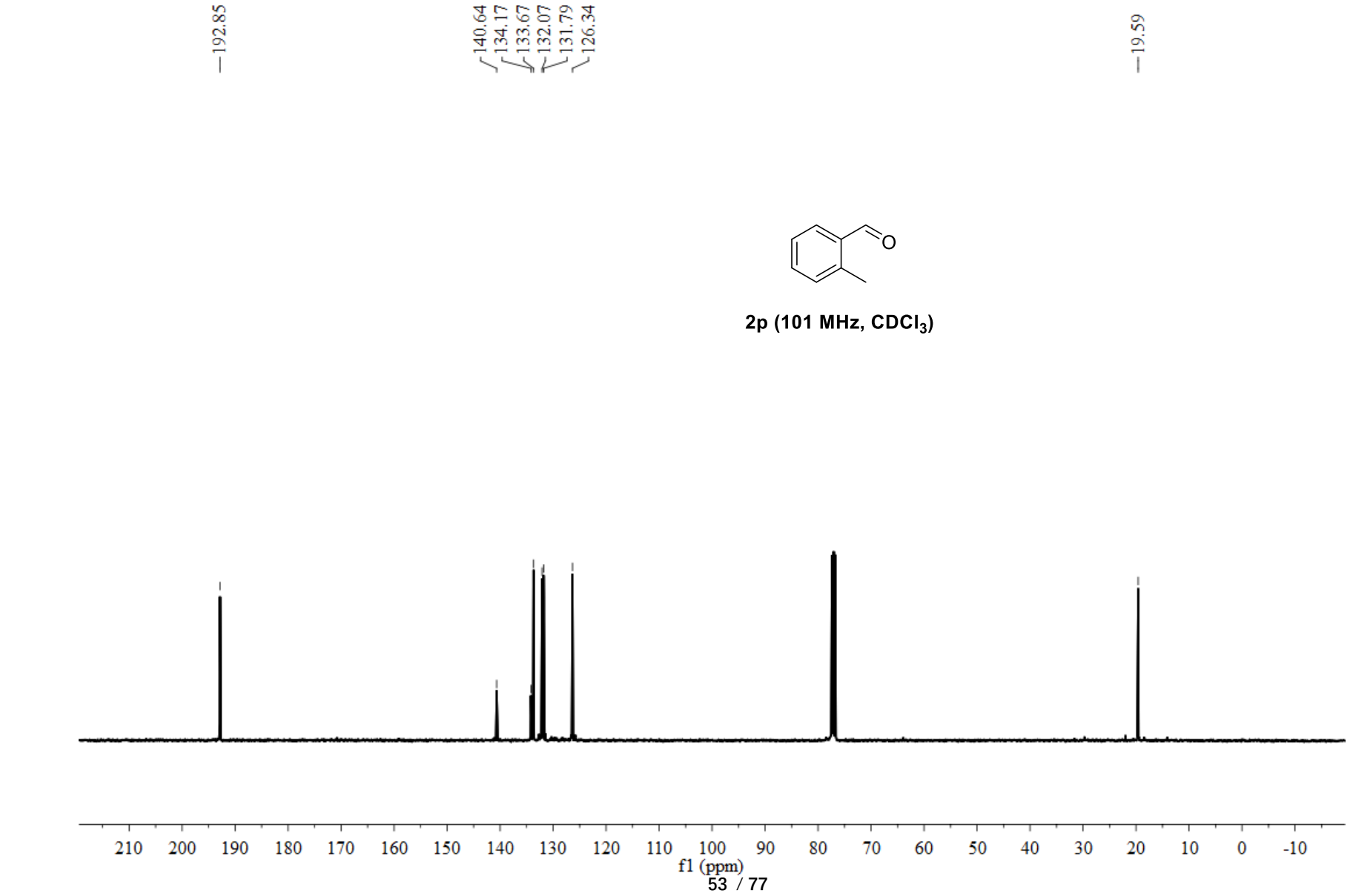
2o (400 MHz, $CDCl_3$)



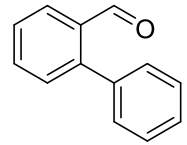
2o (101 MHz, $CDCl_3$)



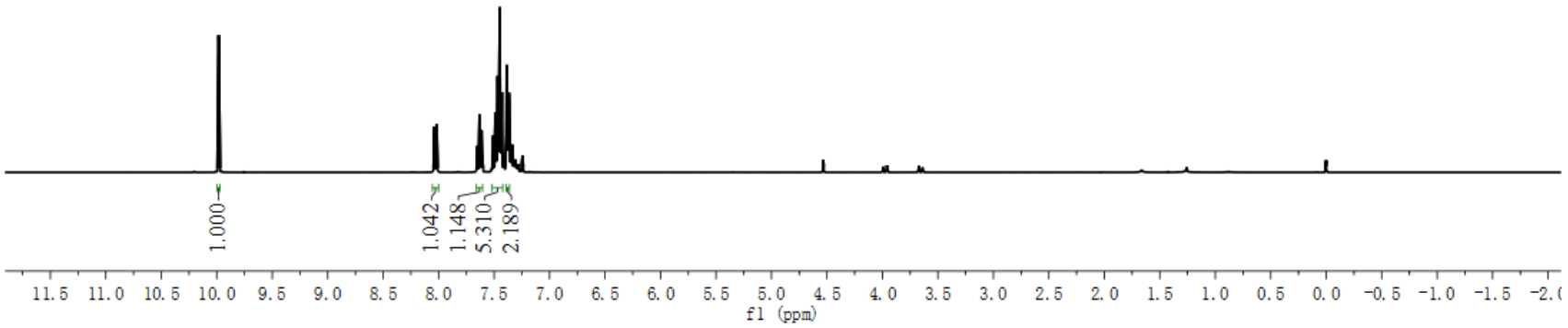
2p (400 MHz, $CDCl_3$)

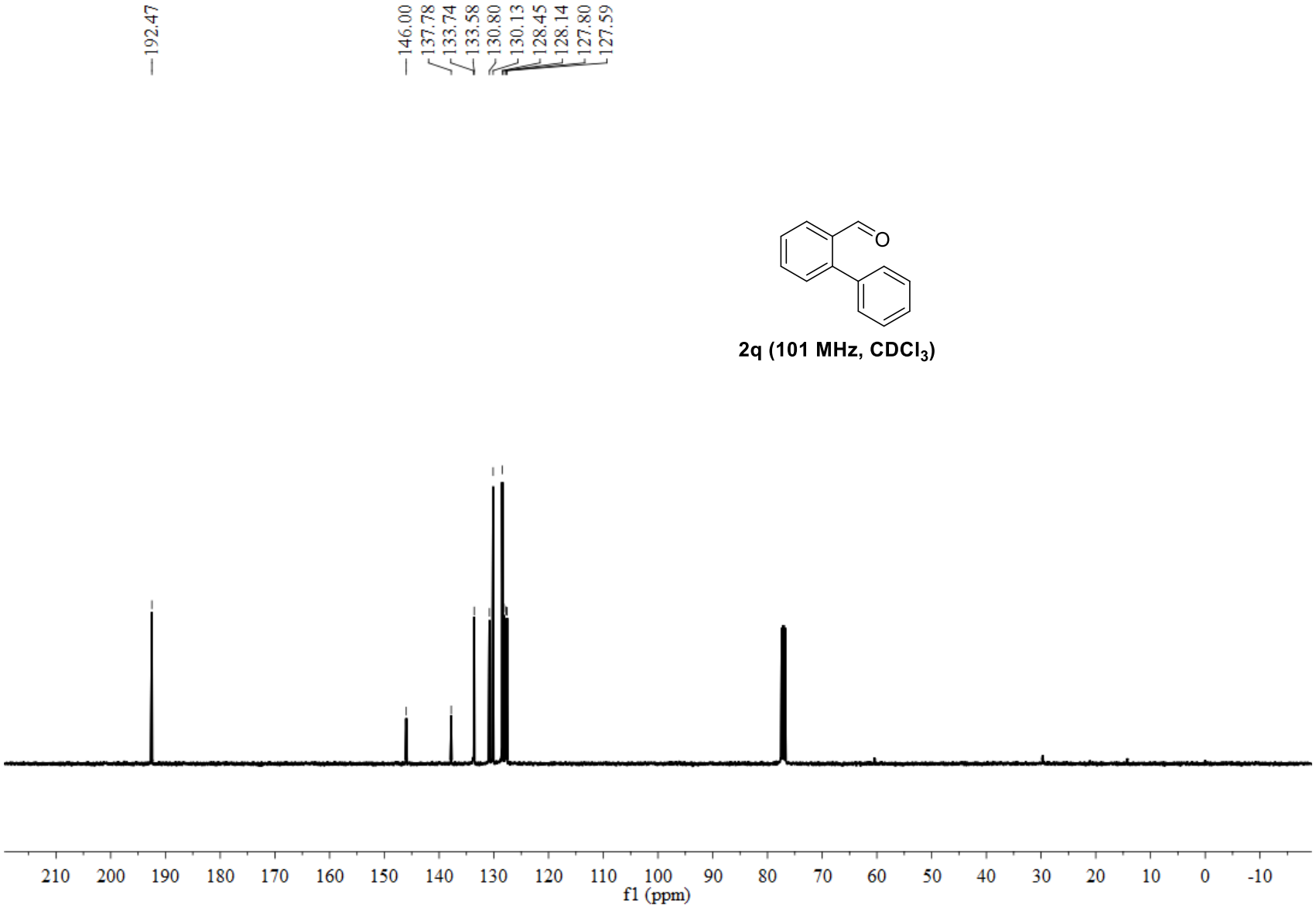


2p (101 MHz, $CDCl_3$)

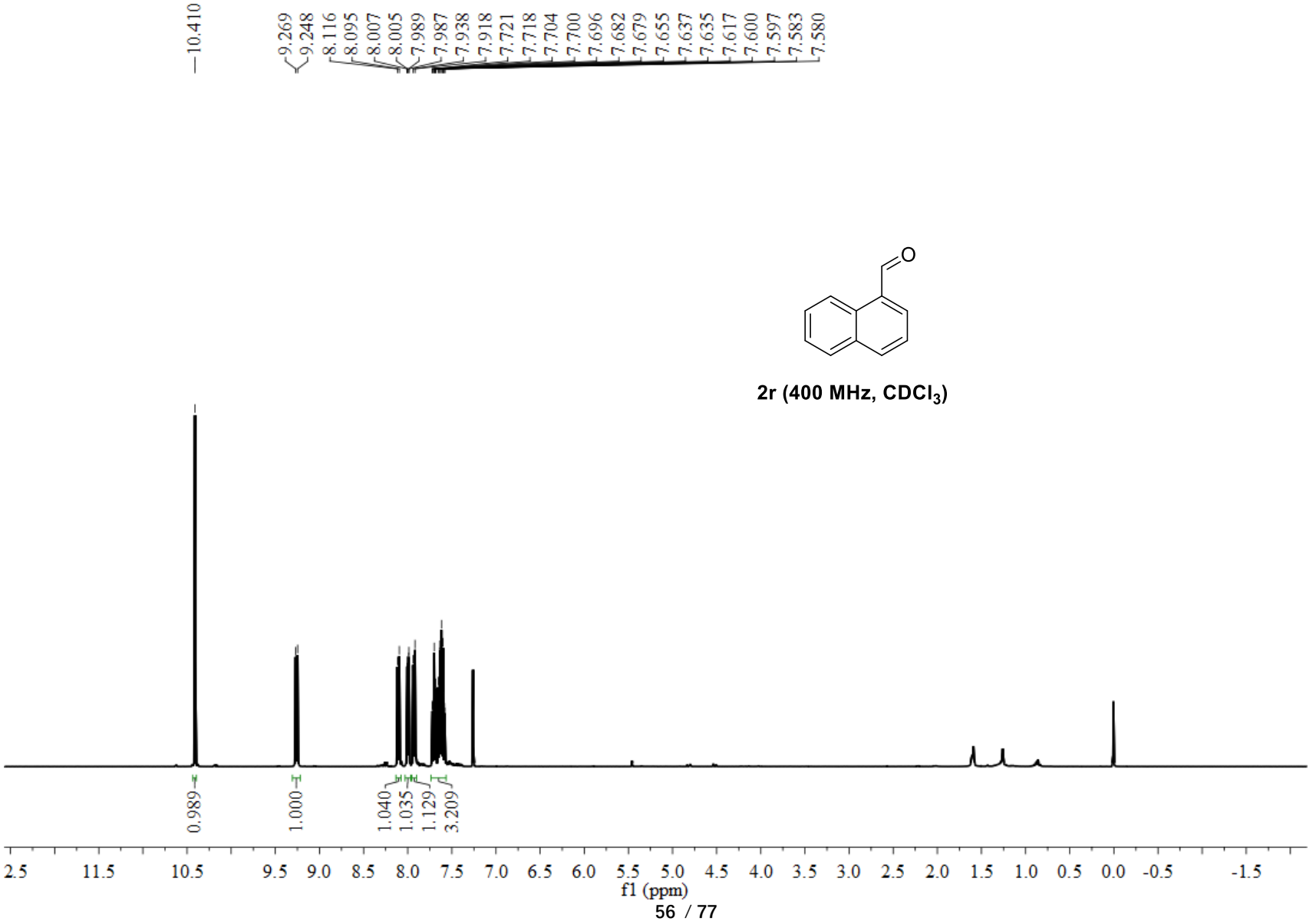


2q (400 MHz, $CDCl_3$)

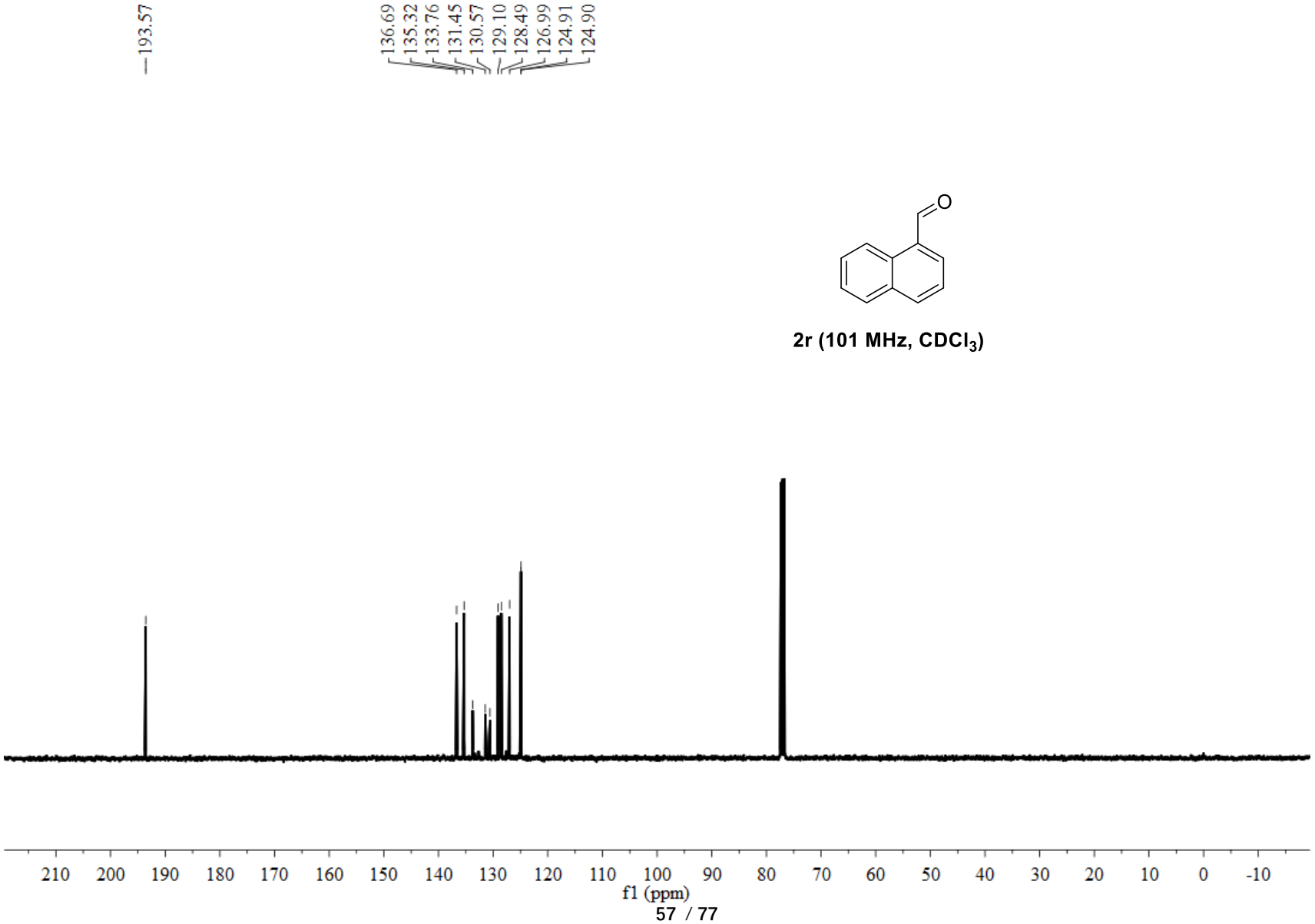




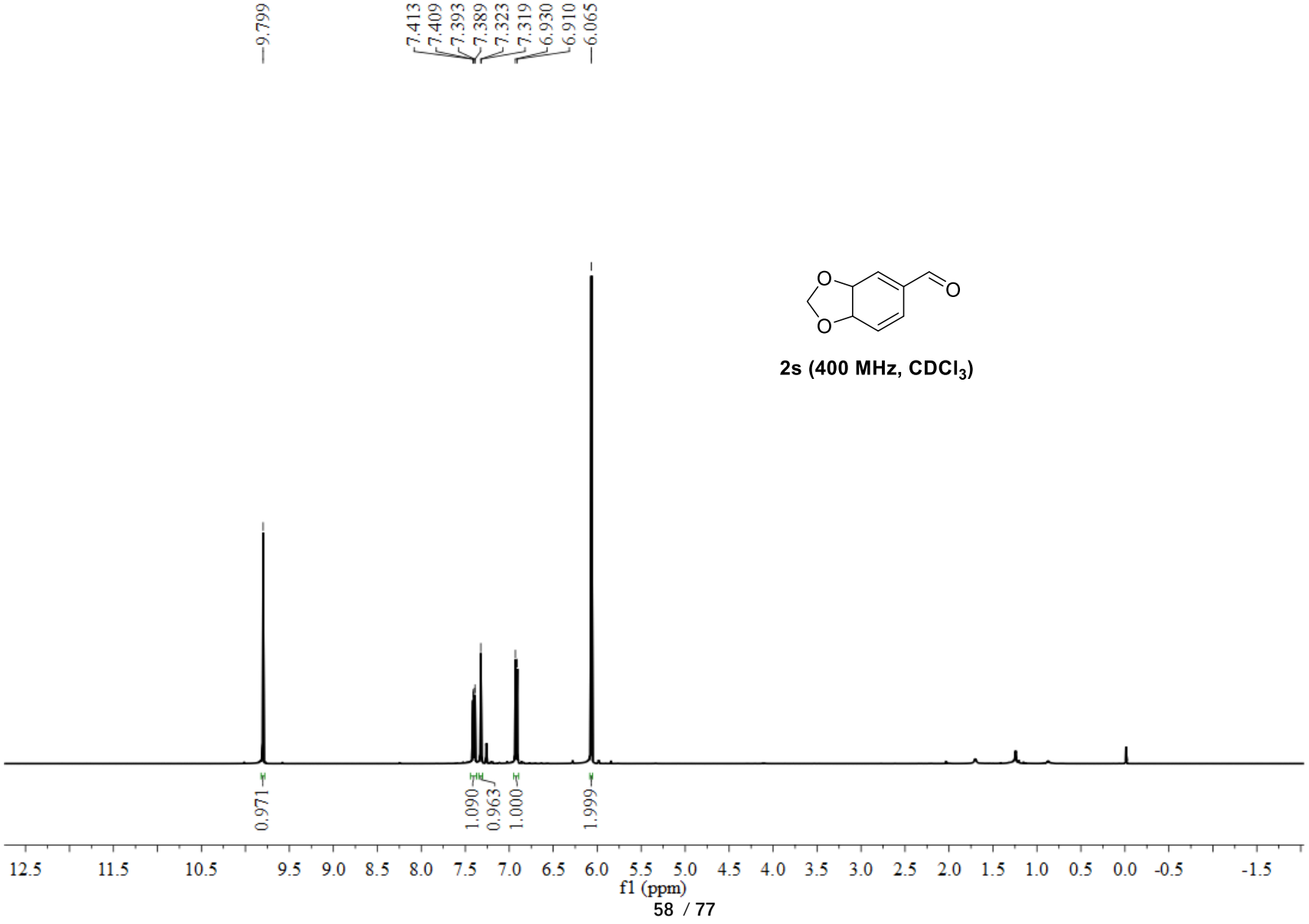
2q (101 MHz, $CDCl_3$)



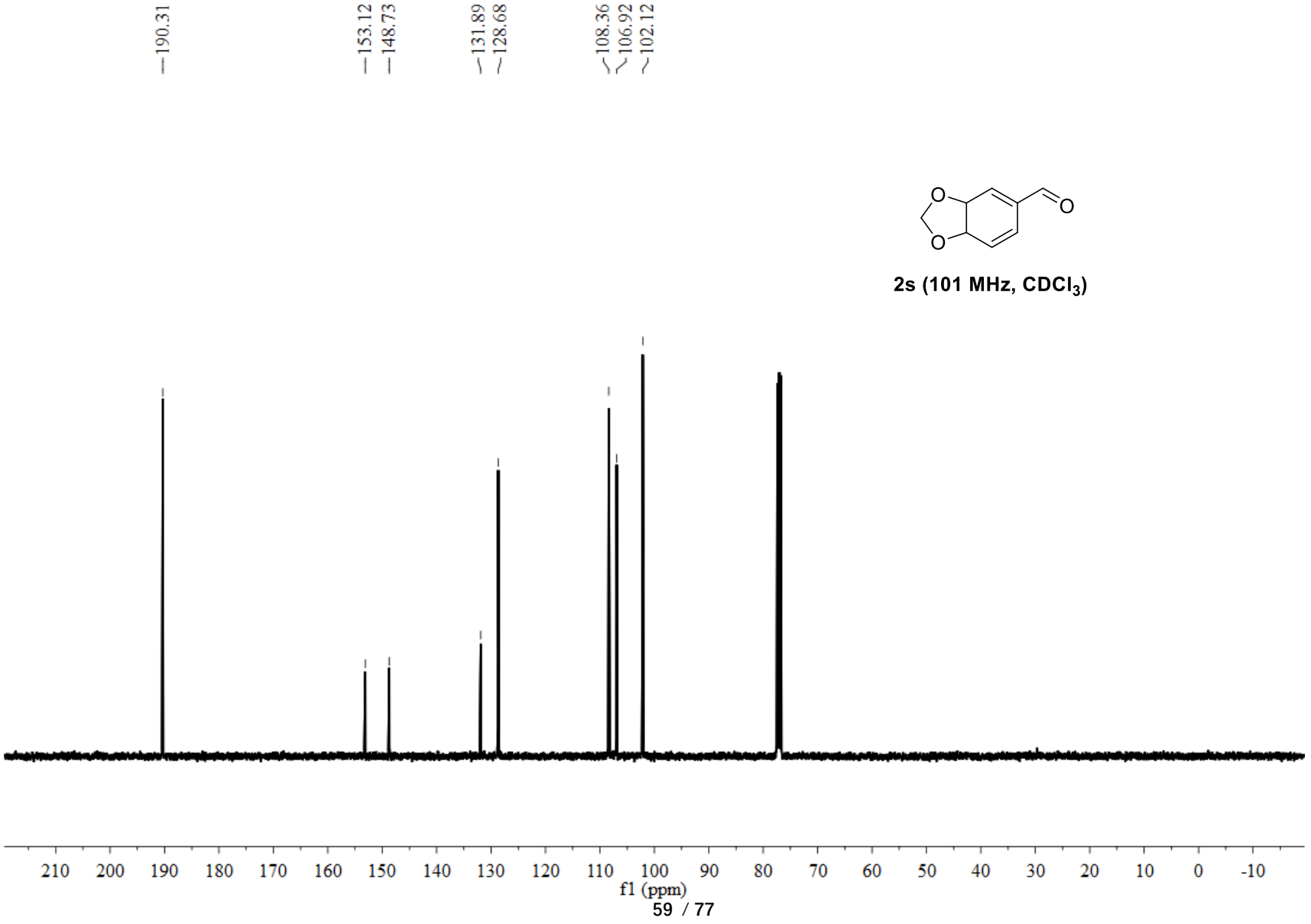
2r (400 MHz, $CDCl_3$)

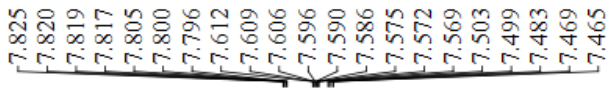


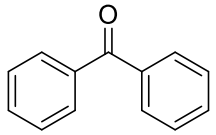
2r (101 MHz, $CDCl_3$)



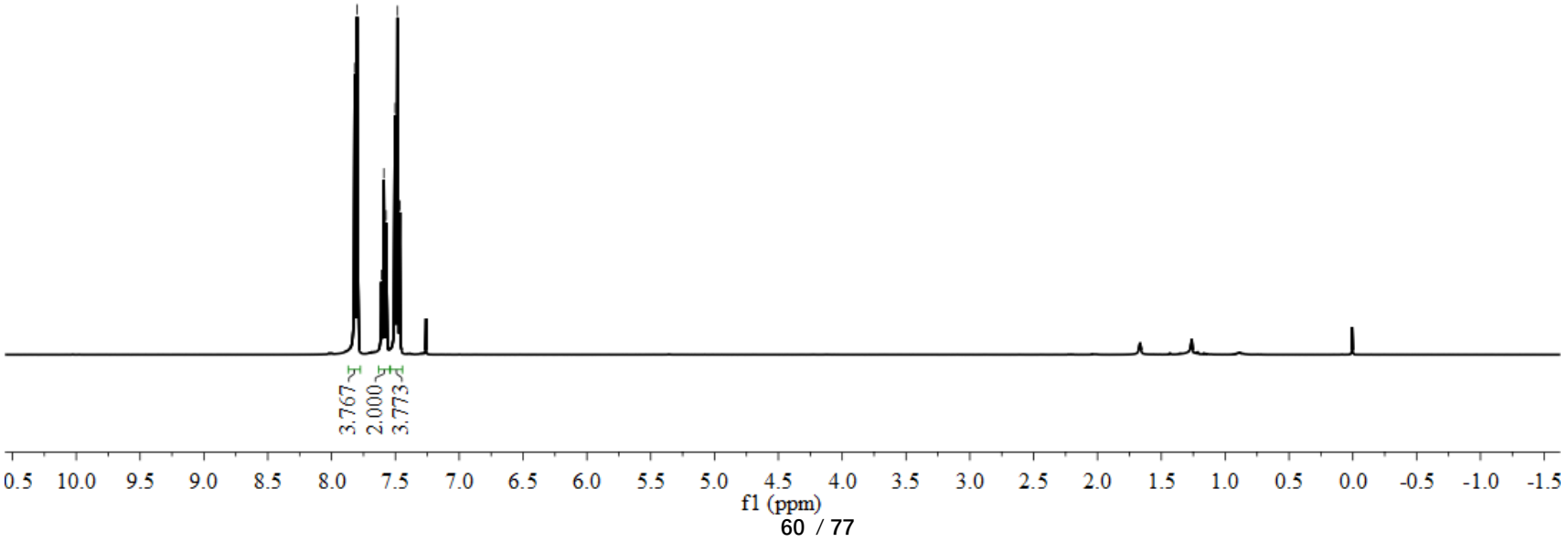
2s (400 MHz, $CDCl_3$)

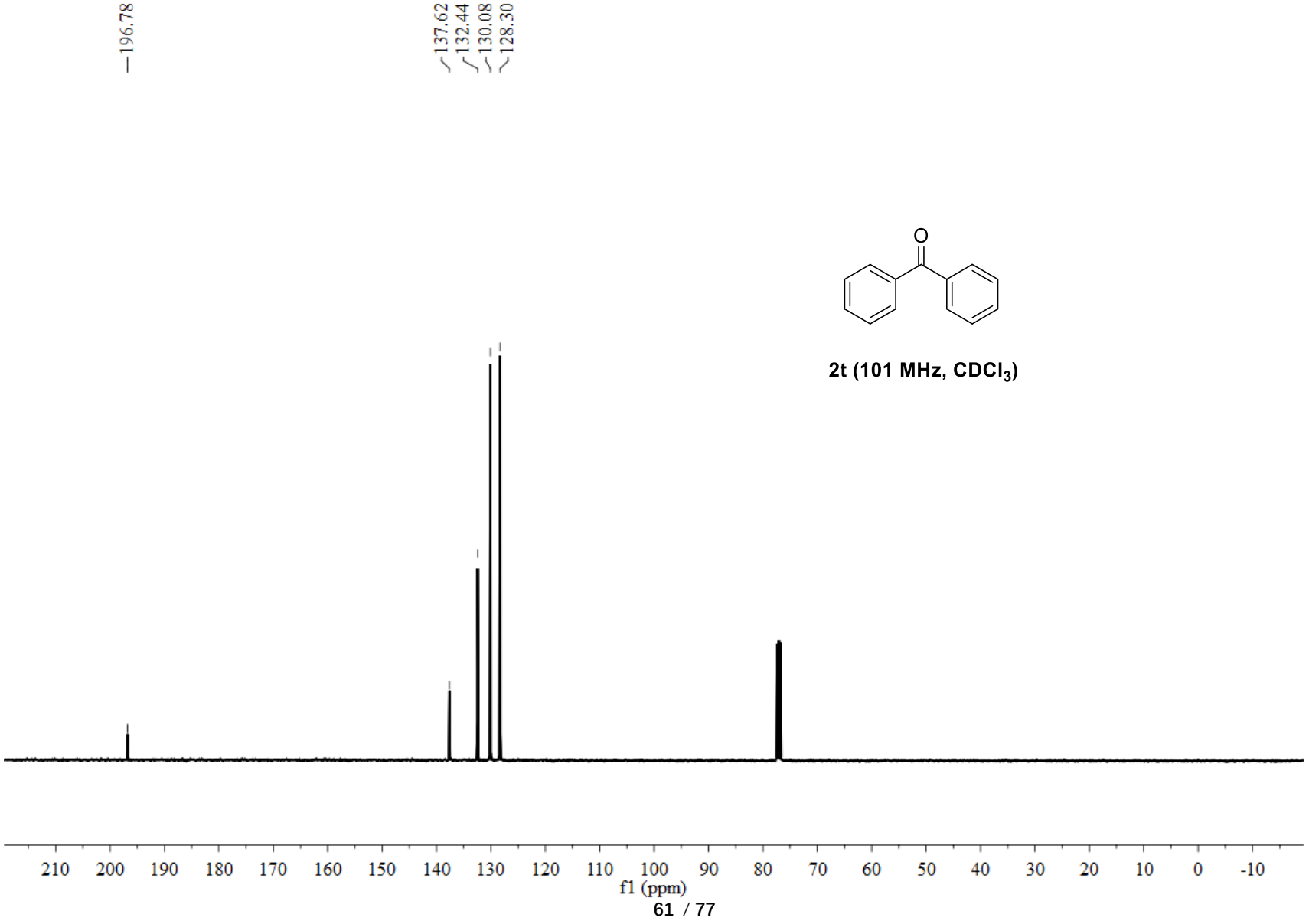

190.31
153.12
148.73
131.89
128.68
108.36
106.92
102.12
O
O
O
2s (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



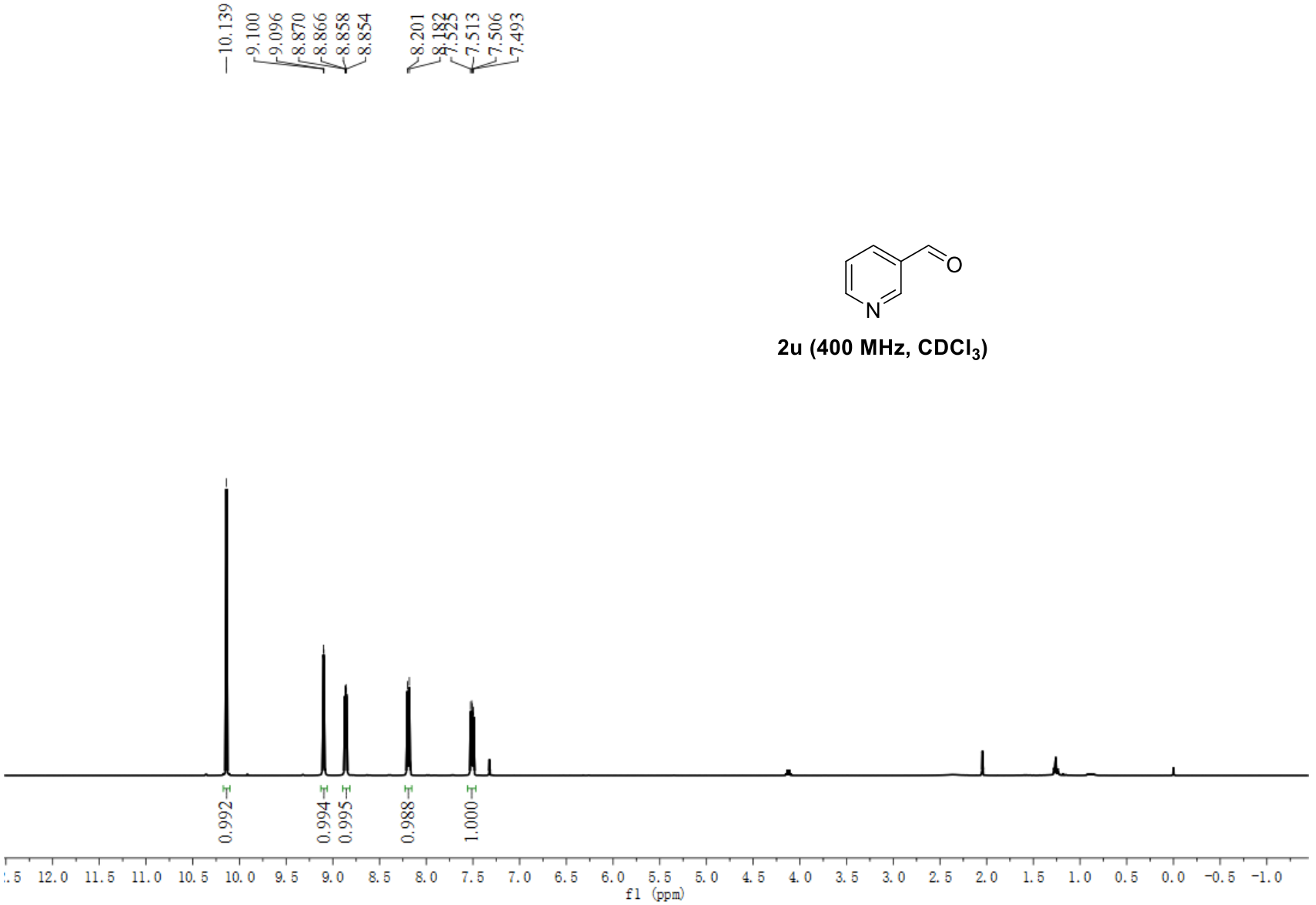


2t (400 MHz, $CDCl_3$)

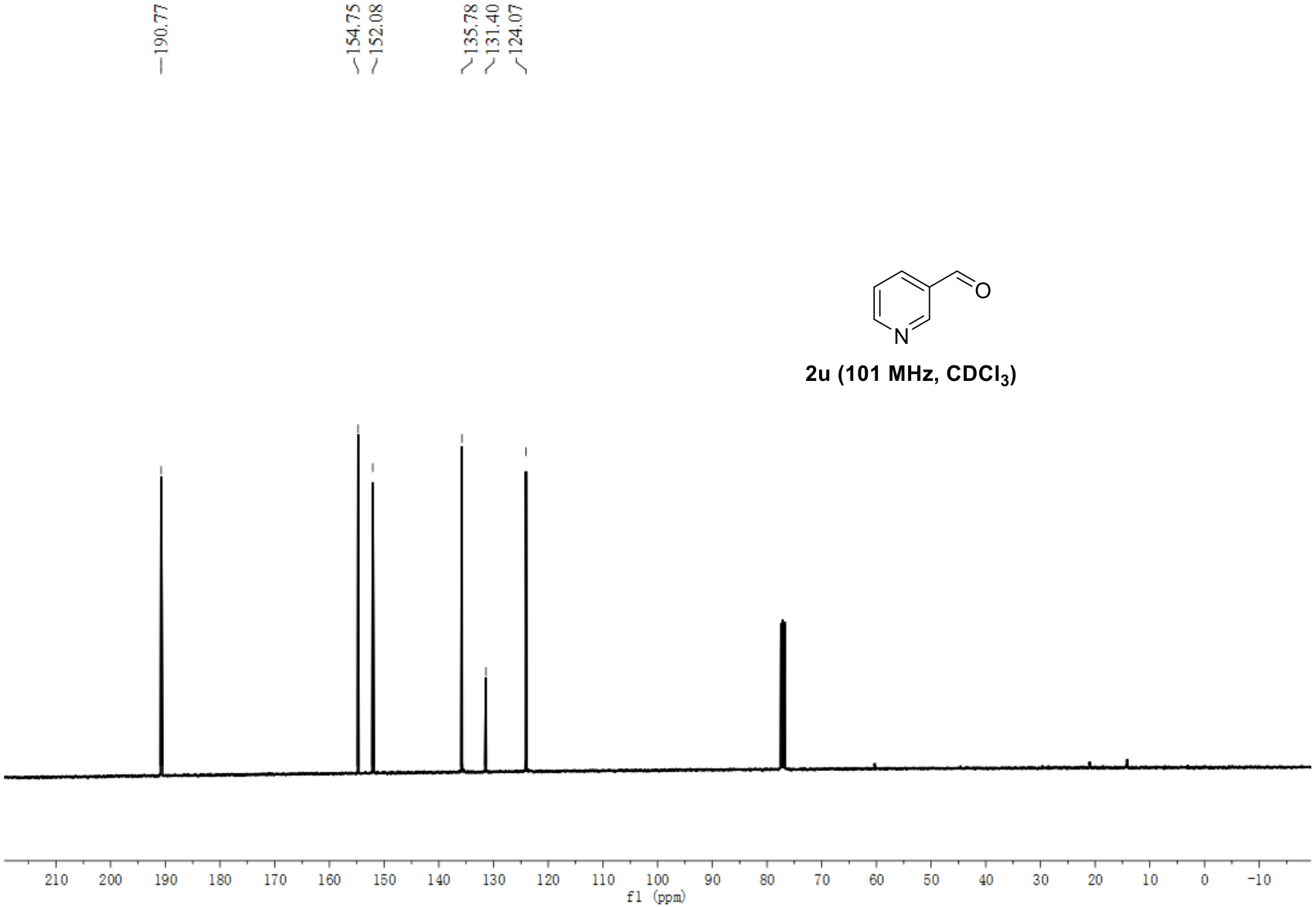




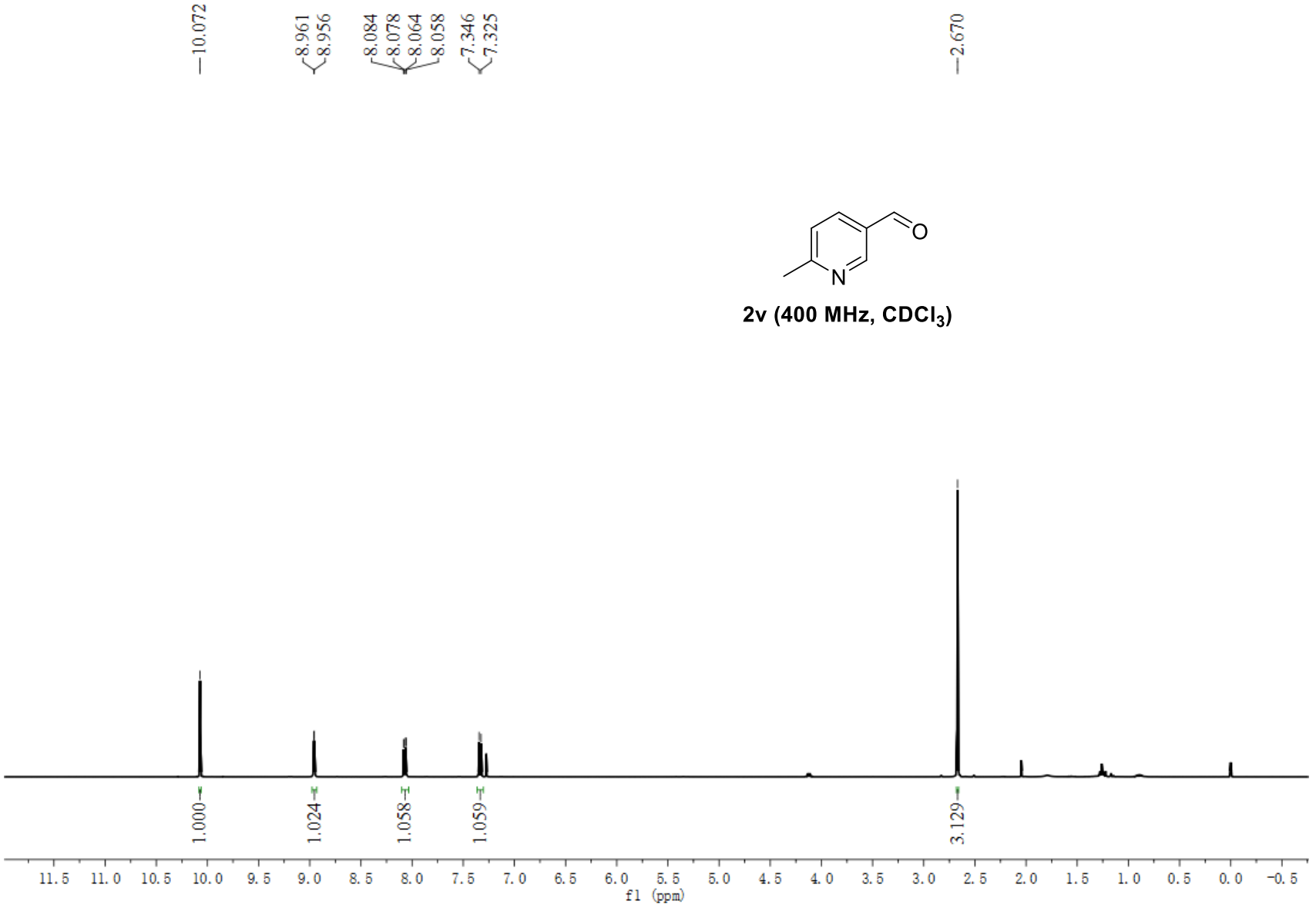
2t (101 MHz, $CDCl_3$)



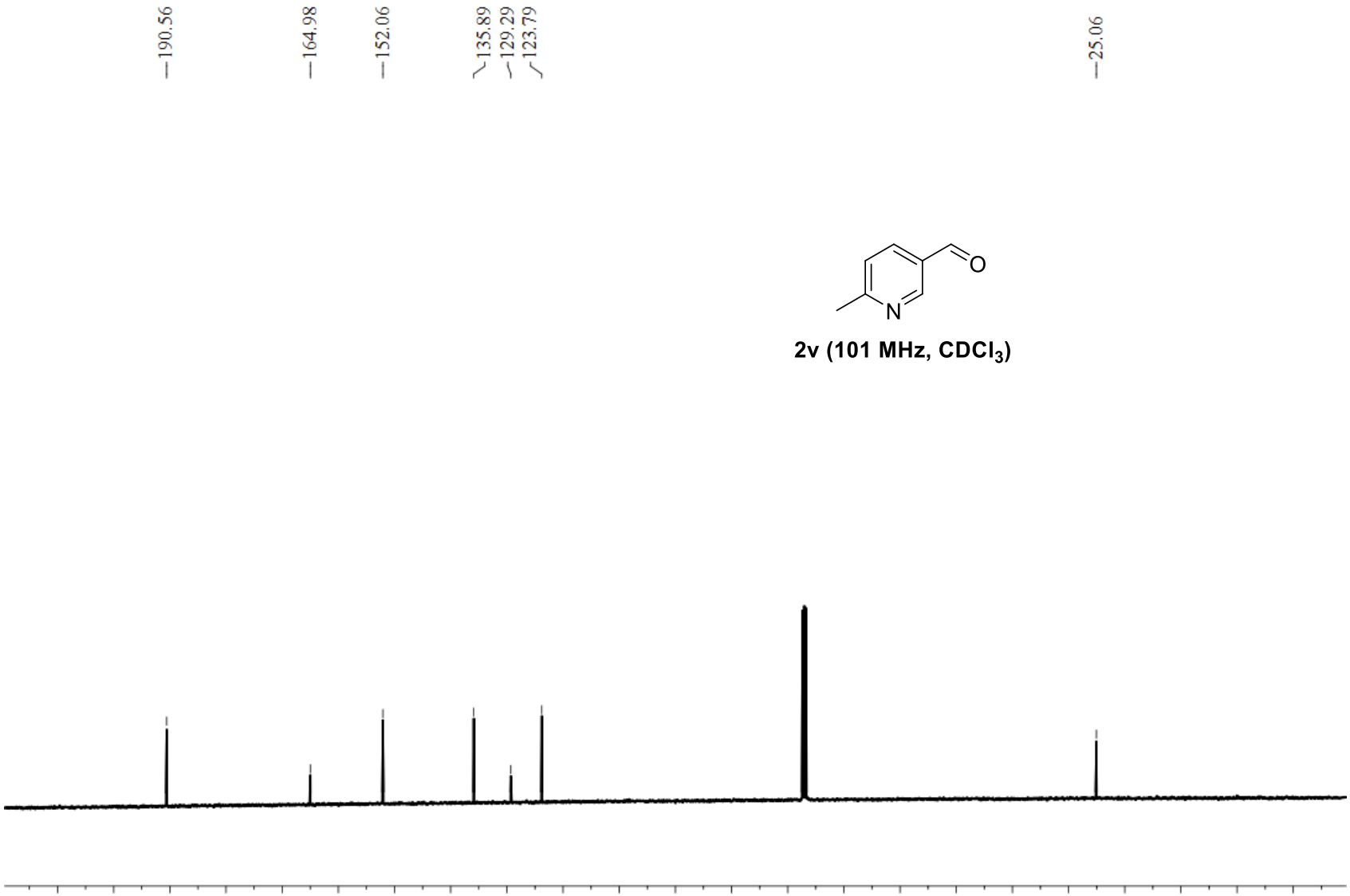
2u (400 MHz, $CDCl_3$)



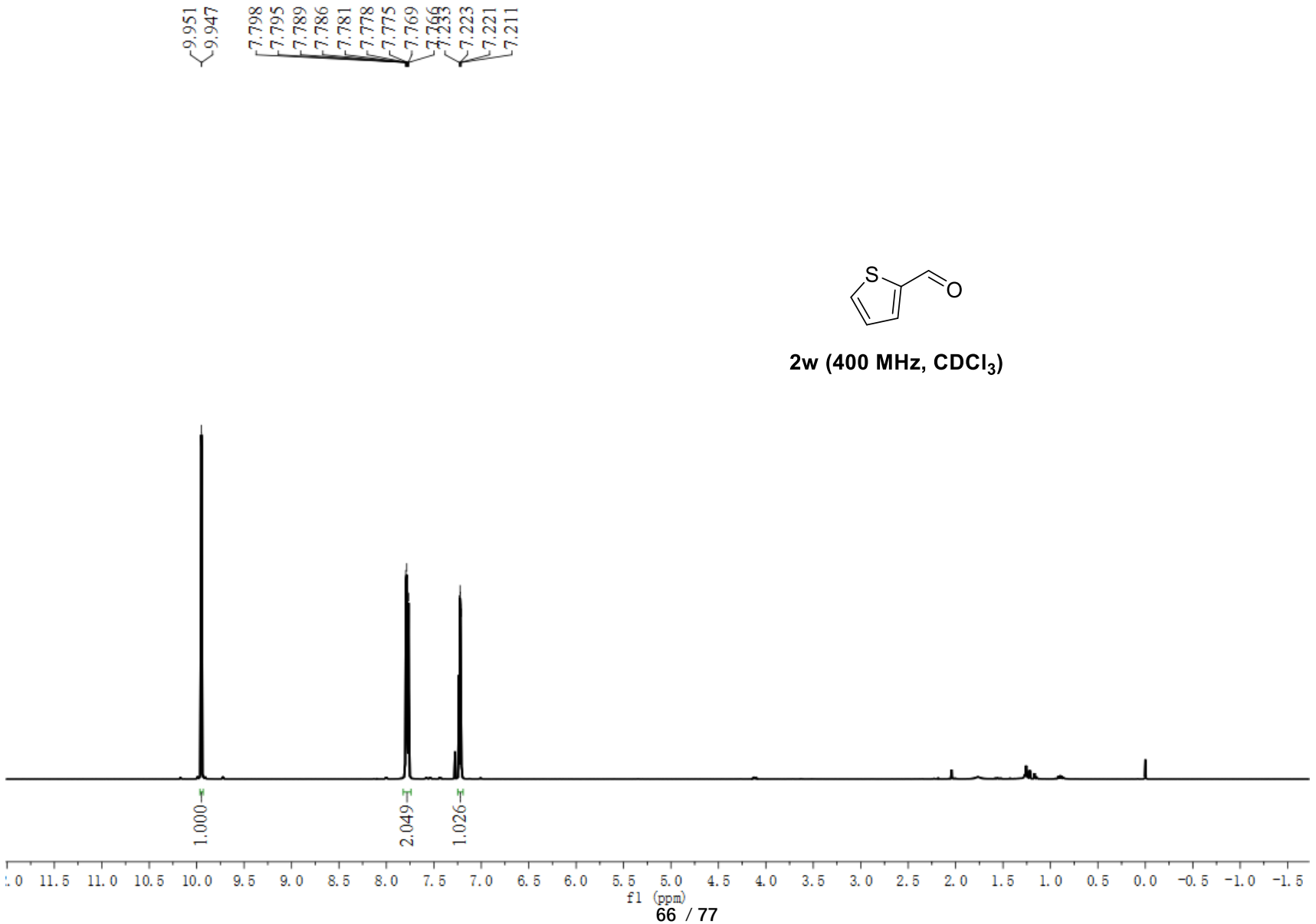
2u (101 MHz, $CDCl_3$)



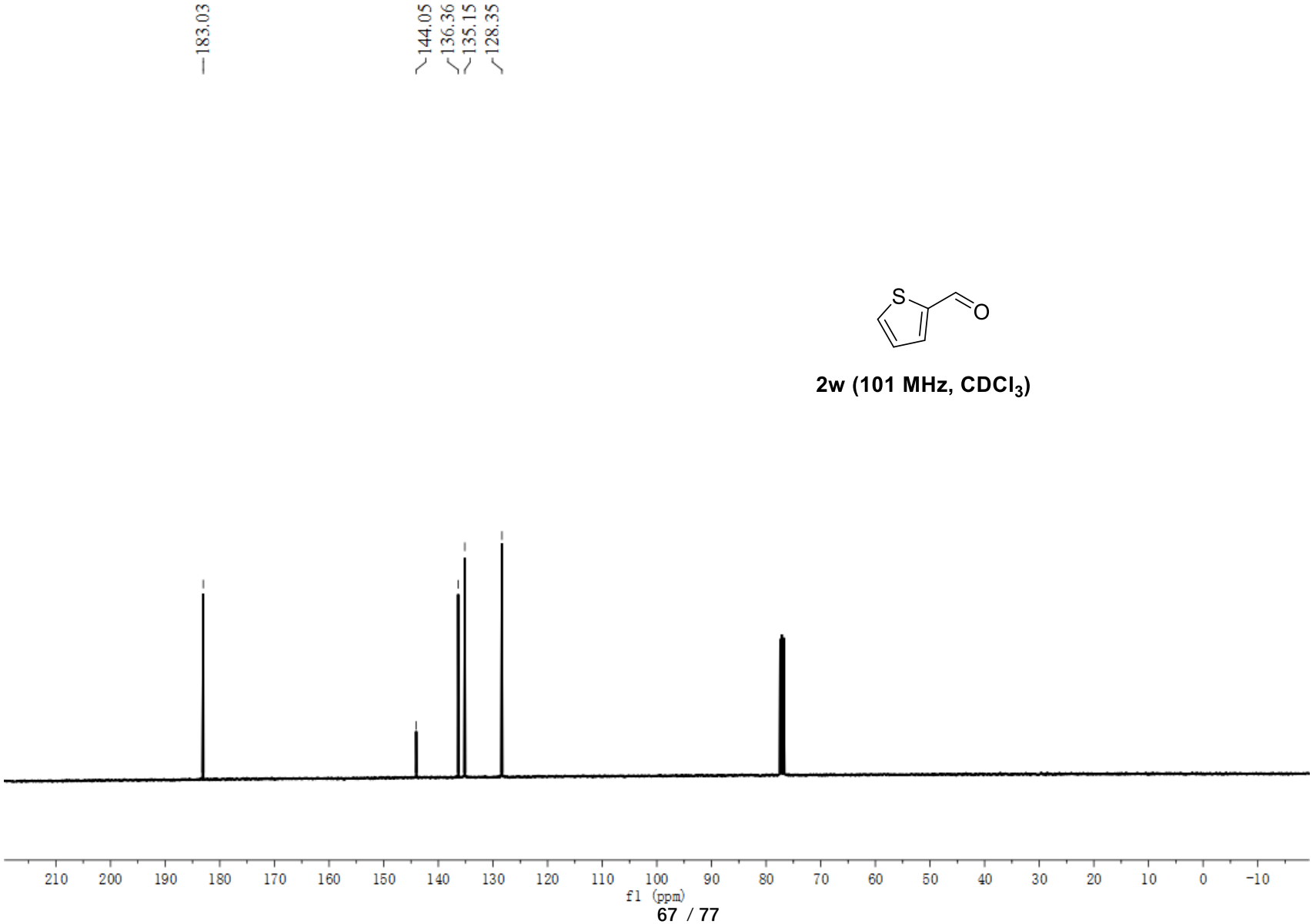
2v (400 MHz, $CDCl_3$)



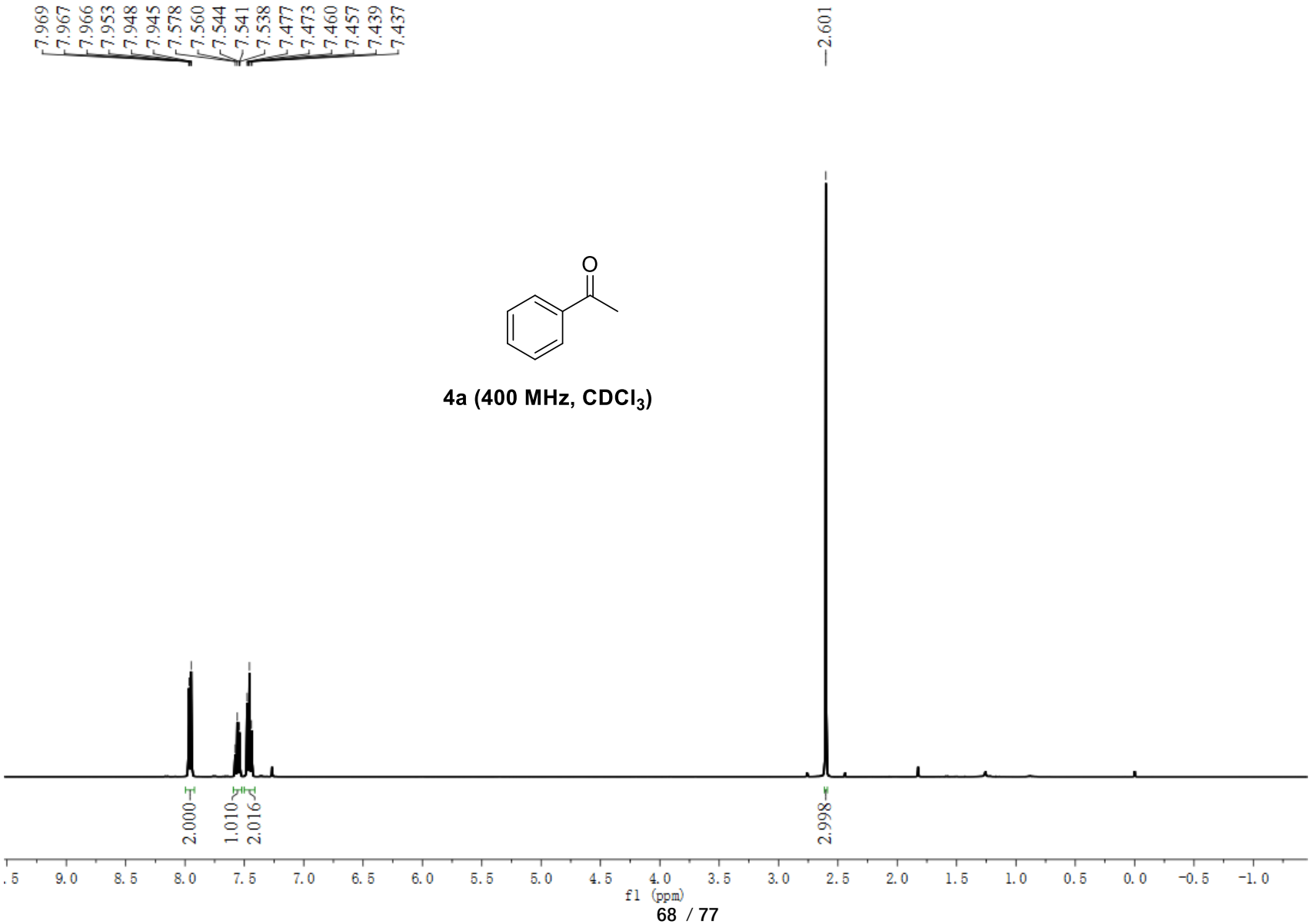
2v (101 MHz, $CDCl_3$)



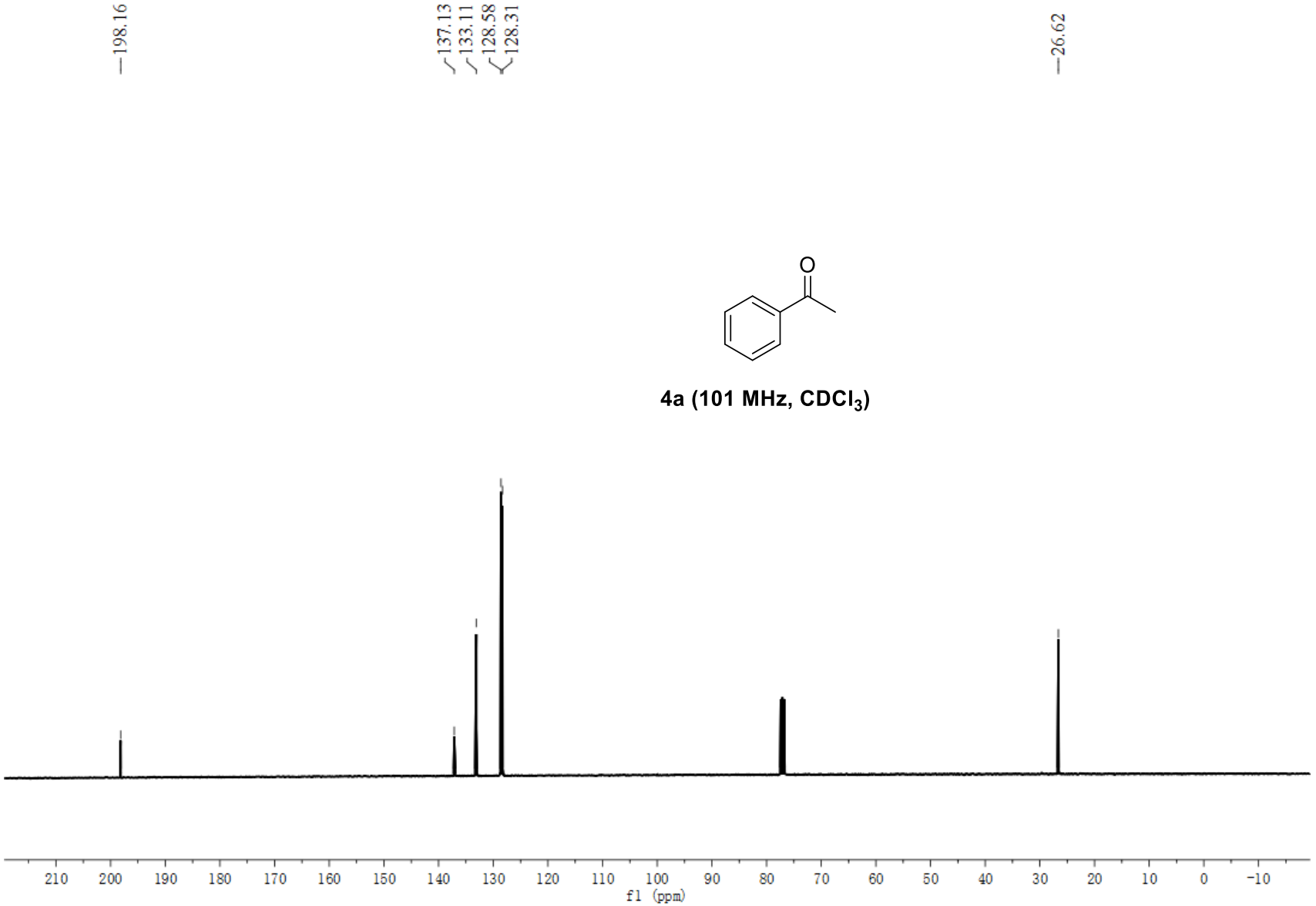
2w (400 MHz, $CDCl_3$)



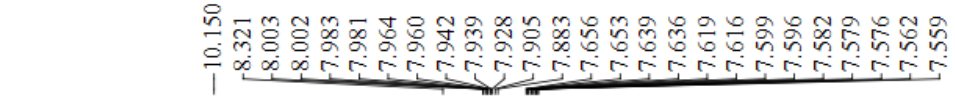
2w (101 MHz, $CDCl_3$)

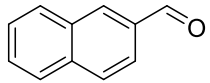


4a (400 MHz, $CDCl_3$)

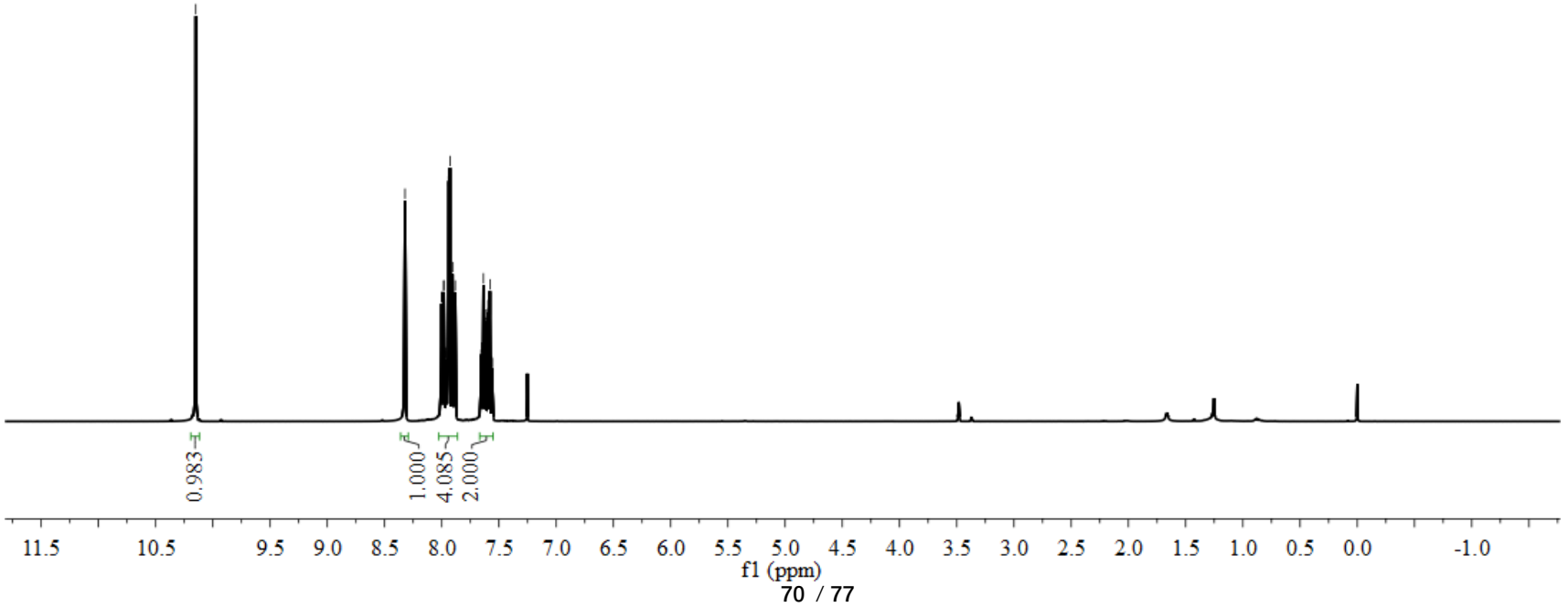


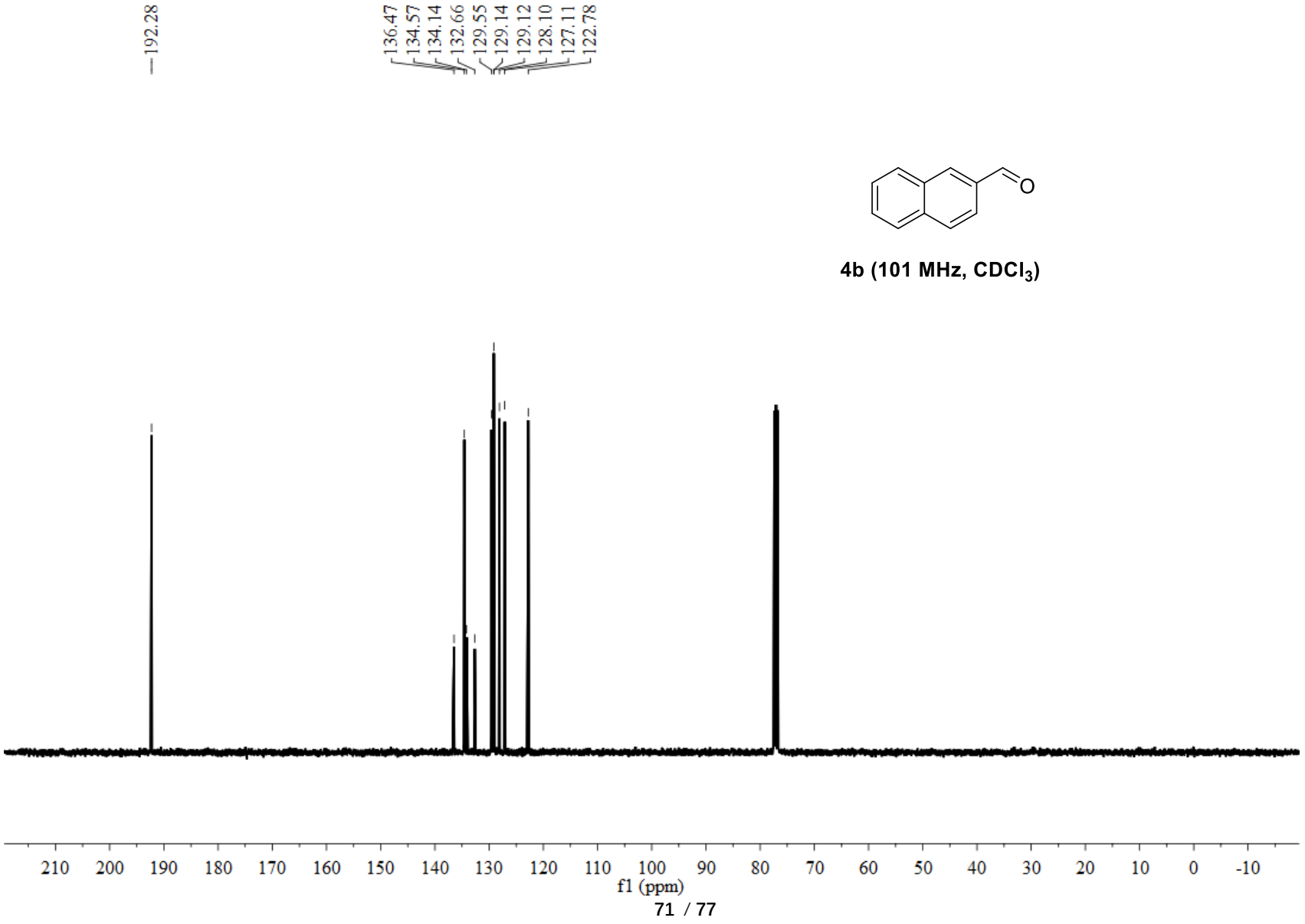
4a (101 MHz, $CDCl_3$)



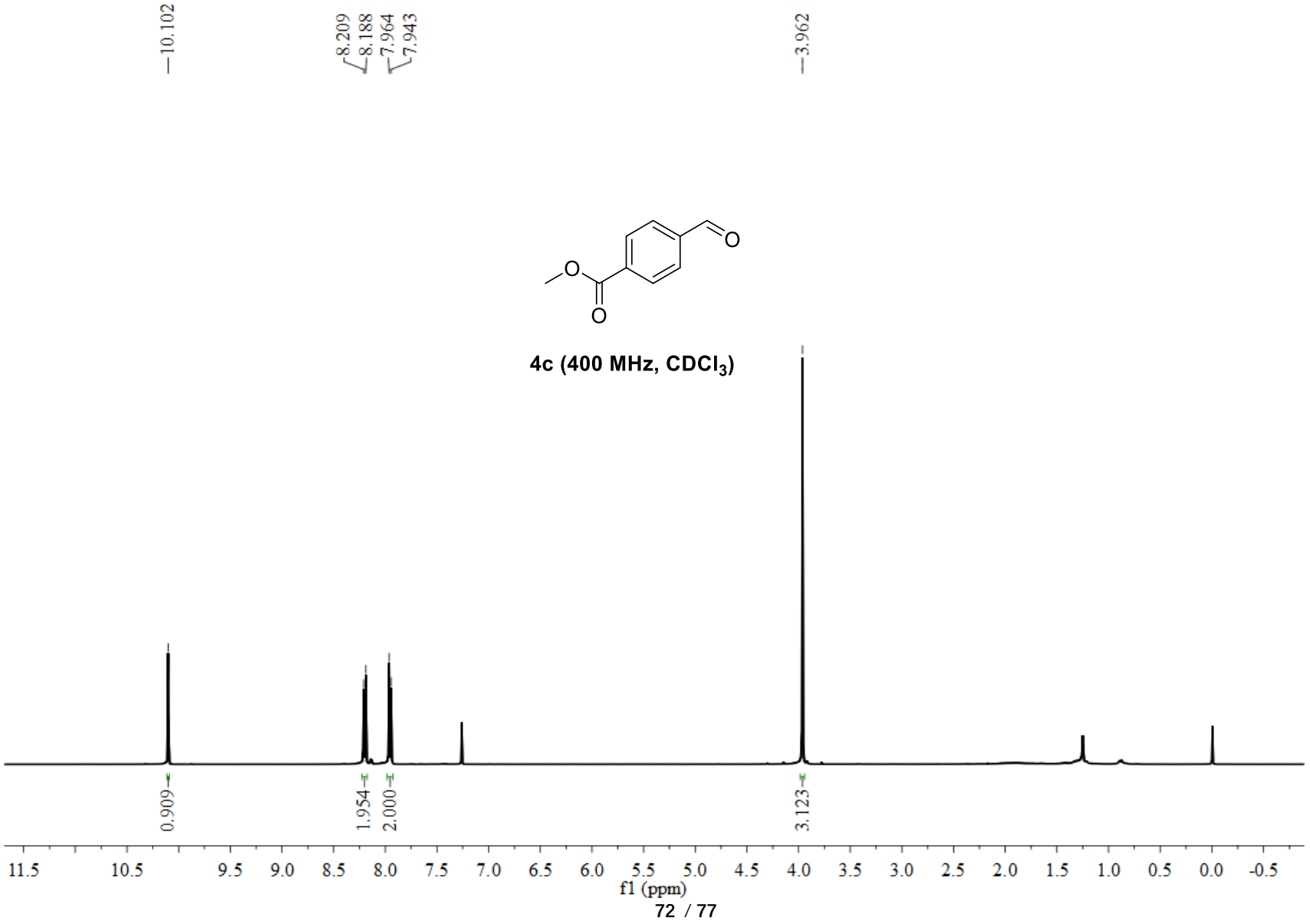


4b (400 MHz, $CDCl_3$)

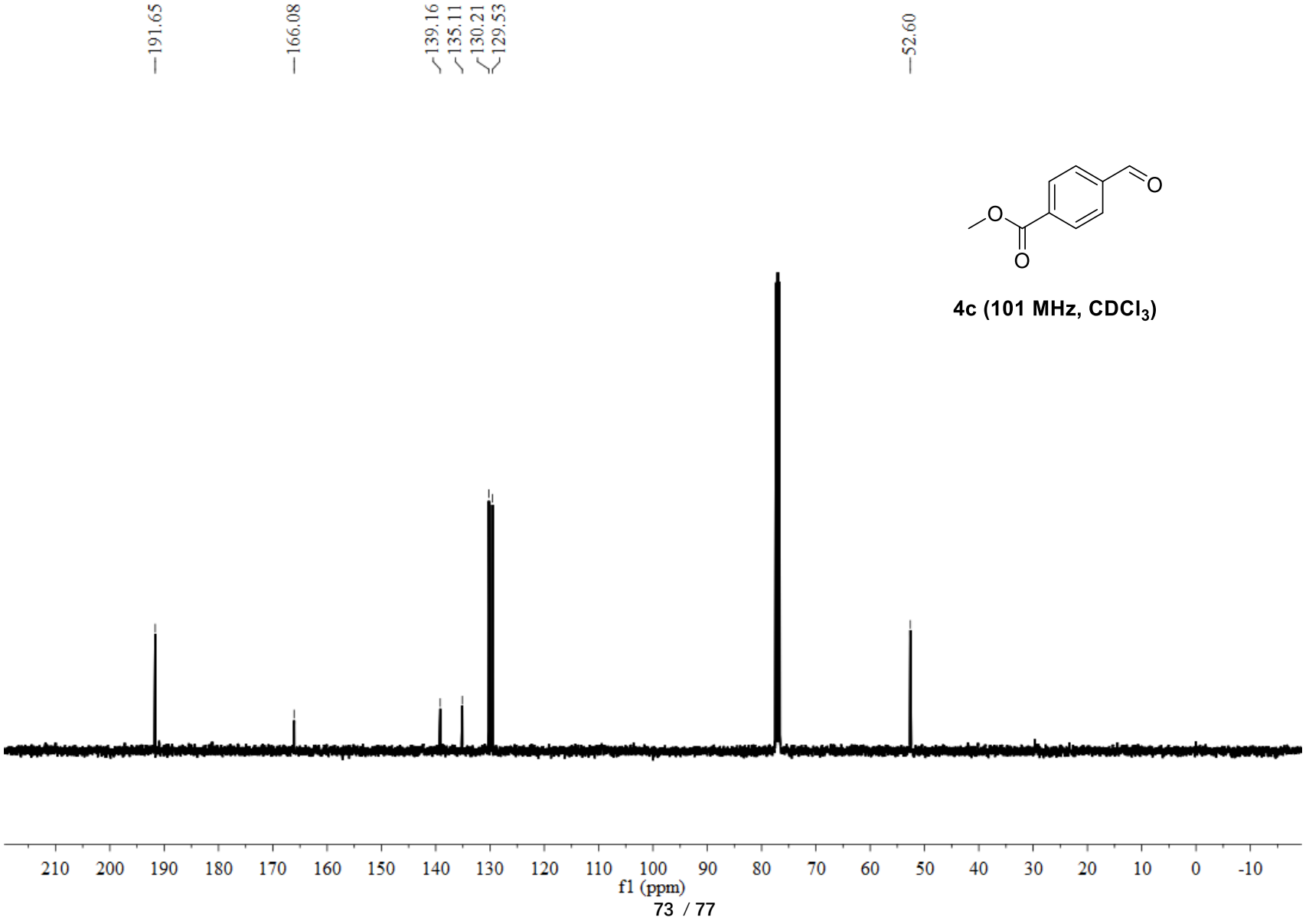


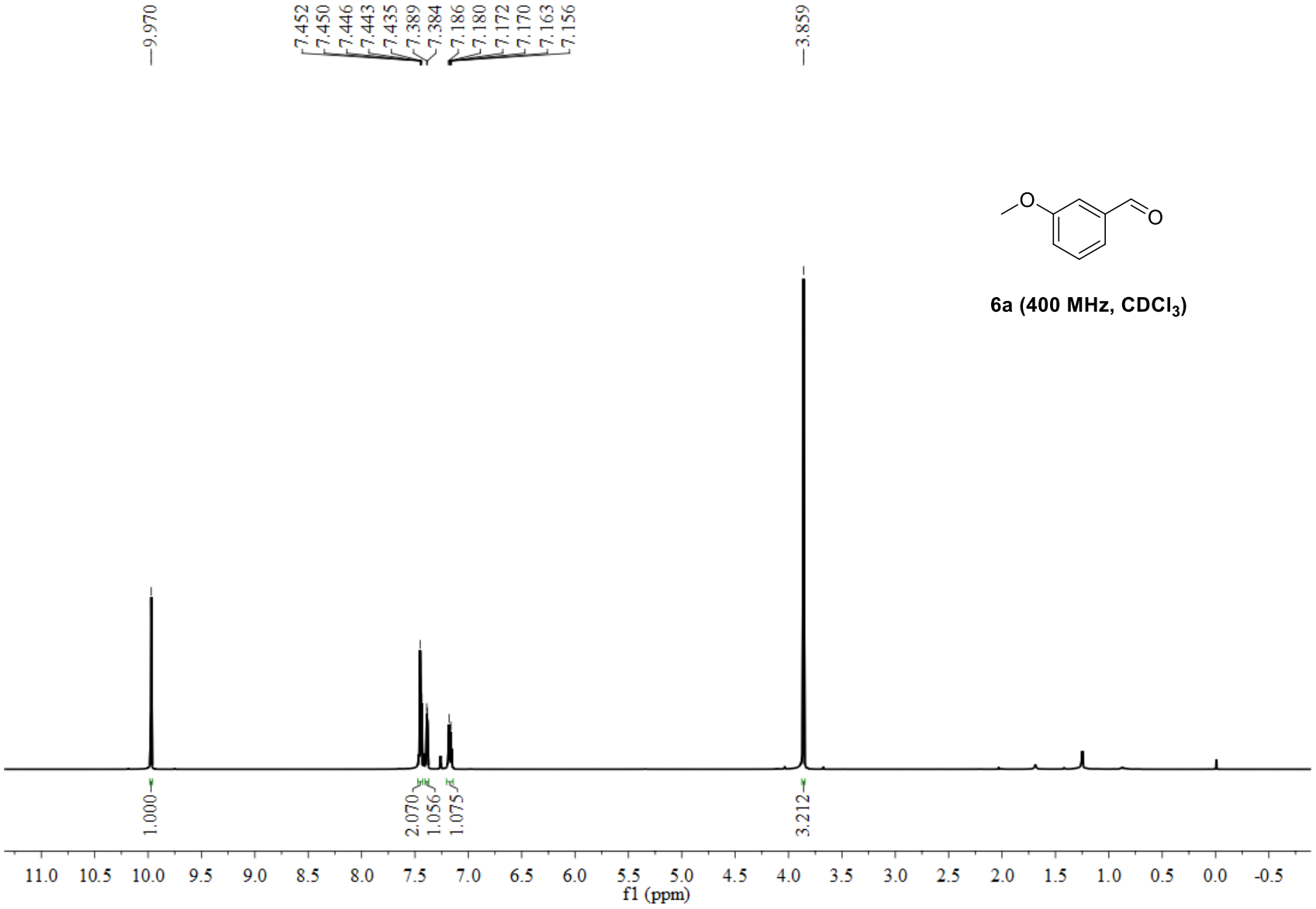


4b (101 MHz, $CDCl_3$)

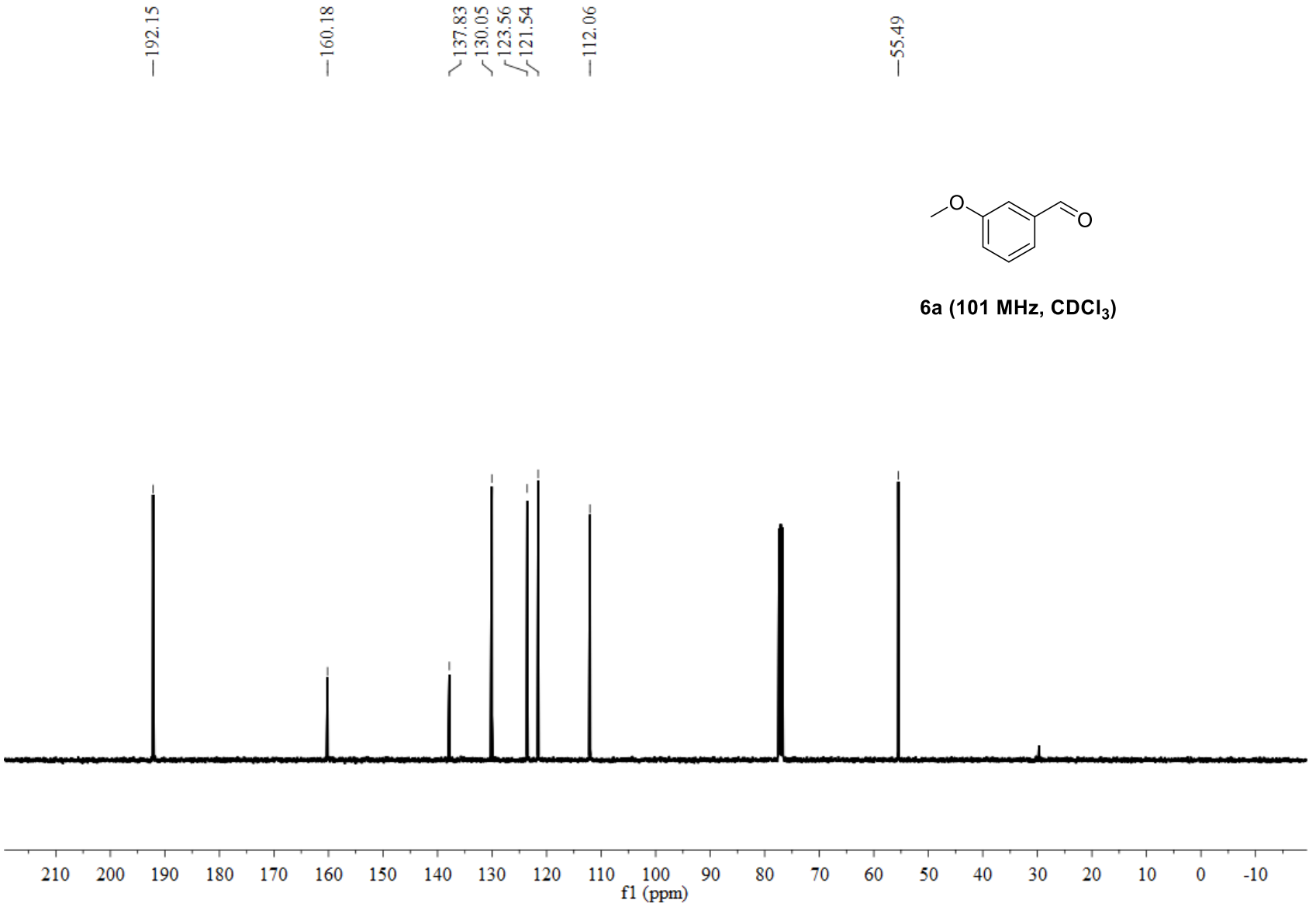


4c (400 MHz, $CDCl_3$)

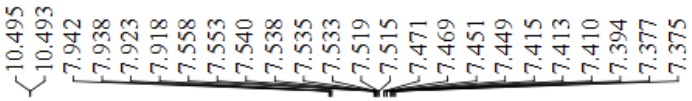

191.65
166.08
139.16
135.11
130.21
129.53
52.60
O
O
O
4c (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

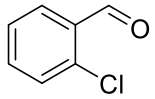


6a (400 MHz, $CDCl_3$)

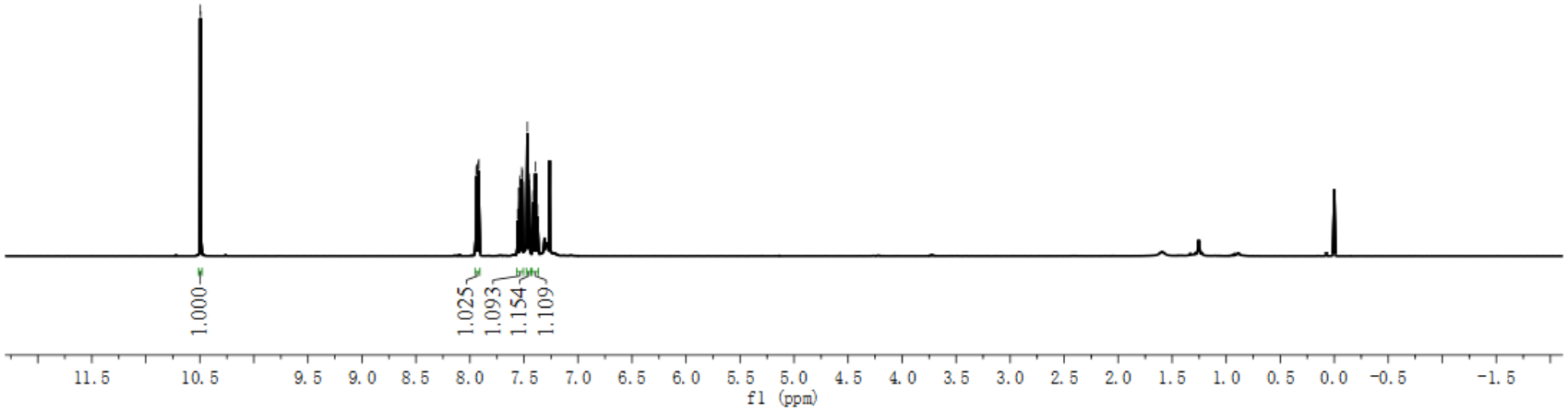


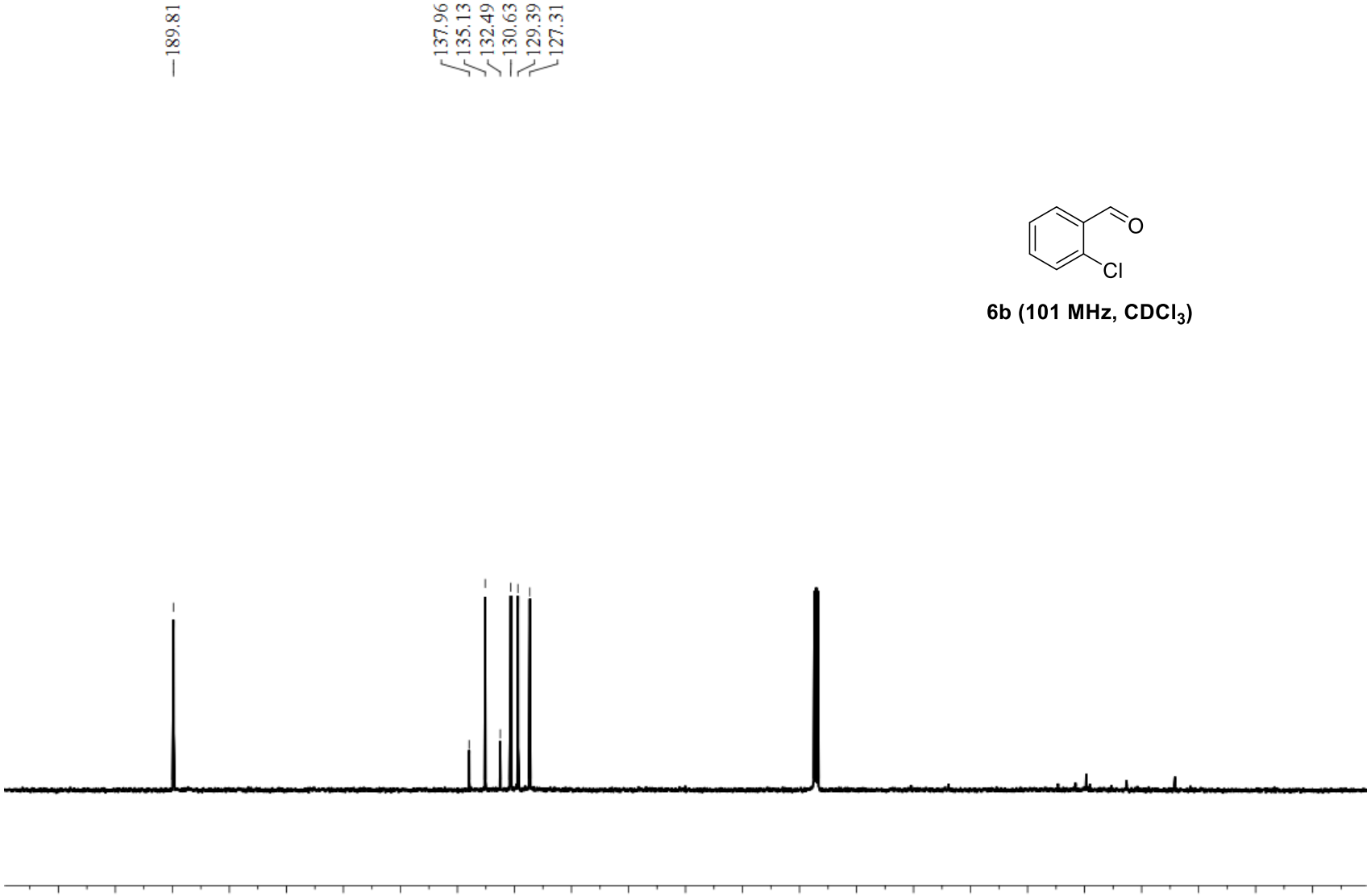
6a (101 MHz, $CDCl_3$)





6b (400 MHz, $CDCl_3$)





6b (101 MHz, $CDCl_3$)