Supporting Information

Light-induced autoxidation of aldehydes to peracids and carboxylic acids

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1. Supplementary Method 1:

General information

^{1}H-, and ^{13}C-NMR spectra were recorded with JEOL JMN ECS400 FT NMR or Bruker AVANCE II (^{1}H-NMR 400 MHz or 600 MHz, ^{13}C-NMR 101 MHz or 151 MHz). ^{1}H-NMR spectra are reported as follows: the chemical shift in ppm downfield of tetramethylsilane (TMS) and referenced to residual solvent peak ($CDCl_3$) at 7.26 ppm, (CD_3OD) at 3.31 ppm, or ($(CD_3)_2SO$) at 2.50 ppm, integration, multiplicities (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet), and coupling constants (Hz). ^{13}C-NMR spectra were reported in ppm relative to the central line of triplet for $CDCl_3$ at 77.16 ppm, or the central line of septet for ($(CD_3)_2SO$) at 39.52 ppm, or for (CD_3OD) at 49.00 ppm. ESI-MS spectra were obtained with JMS-T100LC (JEOL). FT-IR spectra were recorded on JASCO FT-IR system (FT/IR4100). Thin-layer chromatography (TLC) analysis of reaction mixtures was performed using Merck silica-gel 60 F254 TLC plates and visualized under UV Column chromatography on SiO_2 was performed with Kanto silica-gel 60 (63-210 μm). UV light irradiation experiments included in the optimization and substrate scope screening were performed with LED lamp (PER-AMP, Techno Sigma Co., Ltd.). Large scale synthesis experiments were performed using LED lamps (PR160L-390 nm, Kessil) and (EvoluChem 405 nm, HepatoChem Inc.). The stir plate/water bath/LED's are surrounded by a cardboard box covered with aluminum foil for increased light reflection (**Figure S1a – S1c**). Commercially available organic and inorganic compounds were used without further purification.

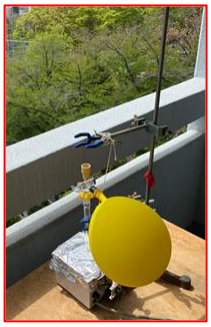
Fig. S1a. Reaction setting with LED lamp Techno Sigma

Fig. S1b. Reaction setting with LED PR160L-390 nm

Fig. S1c. Reaction setting with EvoluChem 405 nm

2. Supplementary Method 2:

a) General procedure for the aerobic oxidation of aldehydes to peracids under sunlight



To a dry 15 mL tube, aldehyde **1** (0.25 mmol) and *i*-PrOAc (1.25 mL) were added under oxygen atmosphere (using Schlenk Line). The mixture was stirred (150 rpm) under sunlight at 25 – 33 °C. In order to control reaction temperature under sunlight, we rigorously maintain them between the hours of 11:00 am. and 15:00 pm. During this timeframe, the temperature remains relatively constant, exhibiting minimal fluctuation throughout the course of the reaction. Additionally, we avoided conducting reactions during rainy or cloudy days to overcome unwanted temperature variations. The progress of the reaction was monitored by No-D NMR. After reaching the plateau (most of aldehydes are fully consumed and the yield of peracids **2** showed no improvement), the reaction was stopped and directly concentrated in *vacuo* (avoid any heating or high speed rotation during the concentration as this affects negatively on the yield). The yields of obtained peracids **2** were evaluated by ^{1}H-NMR. Further purification using 7 pH phosphate buffer was performed, then the mixture was extracted with ethyl acetate, dried over anhydrous sodium sulfate, and evaporated to get the final compound **2** (with ~10 – 20% acid impurities **3**). We avoided further purification, primarily due to safety and stability concerns. Peracids are highly shock-sensitive and pure samples can be flammable and potentially explosive upon thermal or mechanical stresses.

b) General procedure for the aerobic oxidation of aldehydes to peracids using UV-LED

To a dry 15 mL tube, aldehyde **1** (0.25 mmol) and *i*-PrOAc (1.25 mL) were added under oxygen atmosphere (using Schlenk Line). The mixture was stirred (150 rpm) with the irradiation of light (LEDs, 395 nm or 405 nm) at room temperature. We further ensure temperature control by submerging our reaction vessel in a water bath, effectively preventing any temperature increase due to the UV-vis light source. The progress of the reaction was monitored by No-D NMR. After reaching the plateau, the reaction was stopped and directly concentrated in *vacuo* (avoid any heating or high speed rotation). The yields of obtained peracids **2** were evaluated by ^{1}H-NMR. Further purification using 7 pH phosphate buffer was performed, then the mixture was extracted with ethyl acetate, dried over anhydrous sodium sulfate, and evaporated to obtain the final compound **2** (with ~10 – 20% acid impurities **3**). We avoided further purification, primarily due to safety and stability concerns. Peracids are highly shock-sensitive and pure samples can be flammable and potentially explosive upon thermal or mechanical stresses.

c) General procedure for the aerobic oxidation of aldehydes to carboxylic acids under sunlight

To a 15 mL reaction vessel, aldehyde **1** (0.0625 mmol) and H_2O/*iso*-propanol (1.25 mL, 50% v/v) (for some aldehydes, *i*-PrOAc was used) were added. The reaction mixture was stirred vigorously (500 rpm) under sunlight at 25 – 32 °C. The progress of the reaction was monitored by TLC. After the completion, the reaction was transferred indoors and directly concentrated in *vacuo*. The yields of obtained carboxylic acids **3** were evaluated by ^{1}H-NMR. The pH of crude mixture was adjusted to 12 with (1N NaOH) and washed with EtOAc. The basic aqueous layer was acidified with (1N HCl), extracted with EtOAc, dried over anhydrous sodium sulfate, and evaporated to obtain the final carboxylic acid **3**.

d) General procedure for the aerobic oxidation of aldehydes to carboxylic acids using UV-LED

To a dry 15 mL reaction vessel, aldehyde **1** (0.25 mmol) and *i*-PrOAc (1.25 mL) were added and the mixture was stirred vigorously (500 rpm) with the irradiation of light (365 nm LED) at room temperature. We further ensure temperature control by submerging our reaction vessel in a water bath, effectively preventing any temperature increase due to the UV-vis light source. The progress of the reaction was monitored by TLC. After the completion, the reaction was stopped and concentrated in *vacuo*. The pH of crude mixture was adjusted to 12 with (1N NaOH) and washed with EtOAc. The basic aqueous layer was acidified with (1N HCl), extracted with EtOAc, dried over anhydrous sodium sulfate, and evaporated to obtain the final carboxylic acid **3**.

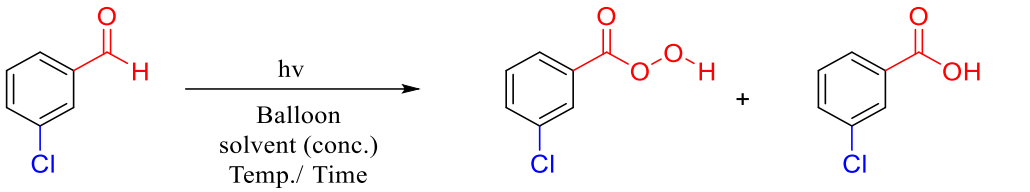
e) Semi-gram scale synthesis of *meta*-chloroperoxybenzoic acid (mCPBA) using LED PR160L-390 nm

To a dry 100 mL two-neck round-bottom flask, *meta*-chlorobenzaldehyde **1a** (5 mmol) and *i*-PrOAc (25 mL) were added under oxygen atmosphere (using Schlenk Line). The mixture was stirred (using 20mm magnet, 200 rpm) with the irradiation of light (390 nm LED). The stir plate/water bath/LED's are surrounded by a cardboard box covered with aluminum foil for increased light reflection at room temperature. The progress of the reaction was monitored by No-D NMR. After 3 h, the reaction was stopped, and directly concentrated in *vacuo* (avoid any heating or high speed rotation). Obtained compounds were washed with 7 pH phosphate buffer (2 × 10 mL), extracted with ethyl acetate, dried over anhydrous sodium sulfate, and evaporated to obtain the final compound mCPBA **2a** at 62.6% isolated yield (584 mg with 9% acid impurities). After calculating the yield, we kept the purity level below 77% and saved it in the refrigerator. We avoided further purification, primarily due to safety and stability concerns. Peracids are highly shock-sensitive and pure samples can be flammable and potentially explosive upon thermal or mechanical stresses.

f) Gram-scale synthesis of *meta*-chloroperoxybenzoic acid (mCPBA) using EvoluChem 405 nm

To a dry 100 mL two-neck round-bottom flask, *meta*-chlorobenzaldehyde **1a** (12.5 mmol) and *i*-PrOAc (50 mL) were added under oxygen atmosphere (using Schlenk Line). The mixture was stirred (using 20mm magnet, 300 rpm) with the irradiation of light (405 nm LED). The stir plate/water bath/LED's are surrounded by a cardboard box covered with aluminum foil for increased light reflection at room temperature. The progress of the reaction was monitored by No-D NMR. After 2.5 h, the reaction was stopped, and directly concentrated in *vacuo* (avoid any heating or high speed rotation). Obtained compounds were washed with 7 pH phosphate buffer (2 × 10 mL), extracted with ethyl acetate, dried over anhydrous sodium sulfate, and evaporated to obtain the final compound mCPBA **2a** at 51% isolated yield (1.24 g with 12% acid impurities). After calculating the yield, we kept the purity level below 75% and saved it in the refrigerator. We avoided further purification, primarily due to safety and stability concerns. Peracids are highly shock-sensitive and pure samples can be flammable and potentially explosive upon thermal or mechanical stresses.

3. Supplementary Method 3: *optimization of reaction conditions.*



Ald. **1a** peracid **2a** Carboxylic acid **3a**

Table S1: Optimization of wavelength.

Entry	hν	Solvent (conc.)	Atmosphere	Avg. T (°C)	Time	Conv. (%)	**2a** (%)	**3a** (%)	**2a/3a** ratio
1	room light	*i*-PrOAc (0.2 M)	O_2	r.t.	4 h	43.5	0	43.5	-
2	sunlight	*i*-PrOAc (0.2 M)	O_2	~28 °C	4 h	98.1	63.1	35	1.8
3	sunlight	*i*-PrOAc (0.2 M)	O_2	~28 °C	4 h	98.1	65.5	32.6	2[a]
4	sunlight	*i*-PrOAc (0.2 M)	Open-air	~28 °C	4 h	96.9	47.2	49.7	0.95
5	sunlight	*i*-PrOAc (0.2 M)	Air balloon	~28 °C	4 h	83.2	55.9	27.3	2.05
6	sunlight	*i*-PrOAc (0.2 M)	O_2	Hot bath	4 h	100	39.4	60.6	0.65
7	sunlight	*i*-PrOAc (0.2 M)	O_2	Cold bath	4 h	100	51	49	1.04
8	280 nm	*i*-PrOAc (0.2 M)	O_2	r.t.	3 h	83.4	43.4	40	1.09
9	340 nm	*i*-PrOAc (0.2 M)	O_2	r.t.	3 h	100	38.6	61.4	0.63
10	365 nm	*i*-PrOAc (0.2 M)	O_2	r.t.	2 h	100	40.2	59.8	0.67
11	395 nm	*i*-PrOAc (0.2 M)	O_2	r.t.	3 h	100	57.5	42.5	1.35
12	395 nm	*i*-PrOAc (0.2 M)	O_2	r.t.	4 h	100	58.1	41.9	1.39
13	405 nm	*i*-PrOAc (0.2 M)	O_2	r.t.	4 h	96.9	63.4	33.5	1.89
14	448 nm	*i*-PrOAc (0.2 M)	O_2	r.t.	4 h	97	44.5	52.5	0.85
15	470 nm	*i*-PrOAc (0.2 M)	O_2	r.t.	4 h	82.5	21.2	61.3	0.35
16	521 nm	*i*-PrOAc (0.2 M)	O_2	r.t.	4 h	24.2	0	24.2	0
17	631 nm	*i*-PrOAc (0.2 M)	O_2	r.t.	4 h	10.7	0	10.7	0

[a] Reproducibility. All ratios between **1a**, **2a** and **3a** were determined by ^{1}H-NMR. The stirring rate of these experiments was around 300 rpm.

Table S2: Optimization of atmosphere.

Entry	hν	Solvent (conc.)	Atmosphere	T (°C)	Time	Conv. (%)	**2a** (%)	**3a** (%)	**2a/3a** ratio
1	sunlight	*i*-PrOAc (0.2 M)	O_2 balloon	~28 °C	4 h	98.1	65.5	32.6	2.0

2	sunlight	*i*-PrOAc (0.2 M)	Air balloon	~28 °C	4 h	83.2	55.9	27.3	2.05
3	sunlight	*i*-PrOAc (0.2 M)	Open-air	~28 °C	4 h	96.9	47.2	49.7	0.95
4	385 nm	*i*-PrOAc (0.2 M)	Air balloon	r.t.	2 h	100	54.6	45.4	1.2
5	385 nm	*i*-PrOAc (0.2 M)	Open air	r.t.	2 h	100	60.2	39.8	1.51
6	395 nm	*i*-PrOAc (0.2 M)	O_2 balloon	r.t.	4 h	100	58.1	41.9	1.39
7	395 nm	*i*-PrOAc (0.2 M)	Air balloon	r.t.	4 h	98.6	55.6	43	1.29
8	395 nm	*i*-PrOAc (0.2 M)	Open air	r.t.	4 h	100	54	45	1.20
9	405 nm	*i*-PrOAc (0.2 M)	O_2 balloon	r.t.	4 h	96.9	63.4	33.5	1.89
10	405 nm	*i*-PrOAc (0.2 M)	Air balloon	r.t.	4 h	100	50.5	49.5	1.02
11	405 nm	*i*-PrOAc (0.2 M)	Open air	r.t.	4 h	98.3	47.2	51.1	0.92
12	405 nm	*i*-PrOAc (0.2 M)	N_2	r.t.	4 h	9	0	9	0

All ratios between **1a**, **2a** and **3a** were determined by ^{1}H-NMR. The stirring rate of these experiments was around 300 rpm.

Table S3: Optimization of stirring rate.

Entry	Wavelength	Solvent (conc.)	Balloon	T (°C)	Time	Stir. (rpm)	Conv. (%)	**2a** (%)	**3a** (%)	**2a/3a** ratio
1	sunlight	*i*-PrOAc (0.2 M)	O_2	~28 °C	4 h	without	100	37.5	62.5	0.6
2	sunlight	*i*-PrOAc (0.2 M)	O_2	~28 °C	4 h	150	92.8	72.1	20.7	3.48
3	sunlight	*i*-PrOAc (0.2 M)	O_2	~28 °C	3 h	400	96	67.5	28.5	2.37
4	sunlight	*i*-PrOAc (0.2 M)	O_2	~29 °C	3 h	600	93.4	63.4	30	2.11
5	395 nm	*i*-PrOAc (0.2 M)	O_2	r.t.	4 h	150	100	79.4	20.6	3.85
6	395 nm	*i*-PrOAc (0.2 M)	O_2	r.t.	4 h	400	98.6	67.8	30.8	2.2
7	395 nm	*i*-PrOAc (0.2 M)	O_2	r.t.	4 h	600	98	49.8	48.2	1.03
8	405 nm	*i*-PrOAc (0.2 M)	O_2	r.t.	4 h	50	95	61.2	33.8	1.81
9	405 nm	*i*-PrOAc (0.2 M)	O_2	r.t.	4 h	150	97.6	71.7	25.9	2.77
10	405 nm	*i*-PrOAc (0.2 M)	O_2	r.t.	4 h	200	97.9	67	30.9	2.17
11	405 nm	*i*-PrOAc (0.2 M)	O_2	r.t.	4 h	400	91.6	61.8	29.8	2.07
12	405 nm	*i*-PrOAc (0.2 M)	O_2	r.t.	4 h	600	97	63.1	33.8	1.87

All ratios between **1a**, **2a** and **3a** were determined by ^{1}H-NMR.

Table S4: Optimization of reaction temperature under LEDs (395 and 405 nm).

Entry	Wavelength	Solvent (conc.)	Balloon	T (°C)	Time	Stir. (rpm)	Conv. (%)	**2a** (%)	**3a** (%)	**2a**/**3a** ratio
1	395 nm	*i*-PrOAc (0.2 M)	O_2	r.t.	4 h	150	100	79.4	20.6	3.85
2	395 nm	*i*-PrOAc (0.2 M)	O_2	10	4 h	150	100	60.6	39.4	1.53
3	395 nm	*i*-PrOAc (0.2 M)	O_2	0	4 h	150	94.8	56	38.8	1.44
4	395 nm	*i*-PrOAc (0.2 M)	O_2	-10	4 h	150	89.4	64.4	35	2.58
5	395 nm	*i*-PrOAc (0.2 M)	O_2	-20	4h	150	94.6	51.6	43	1.2
6	405 nm	*i*-PrOAc (0.2 M)	O_2	35	4h	150	95.7	41.9	53.8	0.78
7	405 nm	*i*-PrOAc (0.2 M)	O_2	r.t.	4 h	150	97.6	71.7	25.9	2.77
8	405 nm	*i*-PrOAc (0.2 M)	O_2	10	4 h	150	93.9	63.9	30	2.13
9	405 nm	*i*-PrOAc (0.2 M)	O_2	0	4 h	150	92.1	55.5	36.6	1.5
10	405 nm	*i*-PrOAc (0.2 M)	O_2	-10	4 h	150	78.4	22.9	55.5	0.41

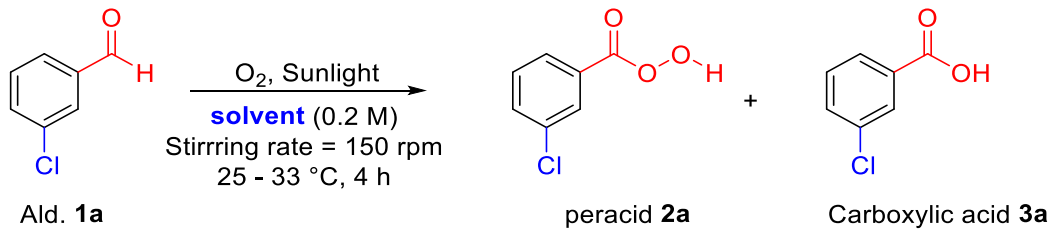
All ratios between **1a**, **2a** and **3a** were determined by ^{1}H-NMR.

Table S5: Optimization of concentration under sunlight.

Entry	Wavelength	Solvent (conc.)	Balloon	Time	Stir. (rpm)	Conv. (%)	**2a** (%)	**3a** (%)	**2a**/**3a** ratio
1	sunlight	*i*-PrOAc (0.6 M)	O_2	4 h	150	100	54.9	45.1	1.22
2	sunlight	*i*-PrOAc (0.4 M)	O_2	4 h	150	98.8	68.5	30.3	2.26
3	sunlight	*i*-PrOAc (0.2 M)	O_2	4 h	150	92.8	72.1	20.7	3.48
4	sunlight	*i*-PrOAc (0.1 M)	O_2	4 h	150	97.8	53.4	44.4	1.2
5	sunlight	*i*-PrOAc (0.05 M)	O_2	4 h	150	70.6	8.8	69.7	0.12

All ratios between **1a**, **2a** and **3a** were determined by ^{1}H-NMR. Temperature of these experiments were 27 – 32 °C.

Table S6: Solvent screening under sunlight.



Ald. **1a** peracid **2a** Carboxylic acid **3a**

Entry	Solvent	Conv. (%)	**2a** (%)	**3a** (%)	**2a**/**3a** ratio
1	DCM[a]	97.5	0.5	97	0.01

2	Acetone	97.7	30.5	67.2	0.45
3	THF	7.1	0.0	7.1	0.00
4	DMF[b]	1.7	0.0	1.7	0.00
5	DMSO	5.8	3.0	2.8	1.07
6	Toluene	4.3	0.0	4.3	0.00
7	Chloroform[b]	99.2	0.0	99.2	0.00
8	MeCN	97.6	50.6	47.0	1.08
9	Water	93.8	0.1	93.7	0.00
10	HFIP	0.0	0.0	0.0	--
11	DCE	95.2	31.6	63.6	0.50
12	1,4-dioxane	16.5	0	16.4	0.00
13	MeOH	47.8	0.1	47.7	0.00
14	EtOH	10.6	0.1	10.5	0.01
15	IPA	14.0	0.0	14.0	0.00
16	CCl_4	99.1	0.0	99.0	0.00
17	*i*-PrOAc	92.8	72.1	20.7	3.48
18	EtOAc	85.2	61.6	23.6	2.61
19	Hexane	80.7	0.0	80.7	0.00
20	Octane	69.3	0.0	69.3	0.00
21	MTBE	46.5	4.5	42.0	0.11
22	Hexanol	17.5	1.4	16.1	0.09
23	Solvent free	96.1	0.3	95.7	0.00
24	cyclohexane	37.3	0.0	37.3	0.00

[a] Reaction time = 3 h. [b] Reaction time = 5 h. All ratios between **1a**, **2a** and **3a** were determined by ^{1}H-NMR.

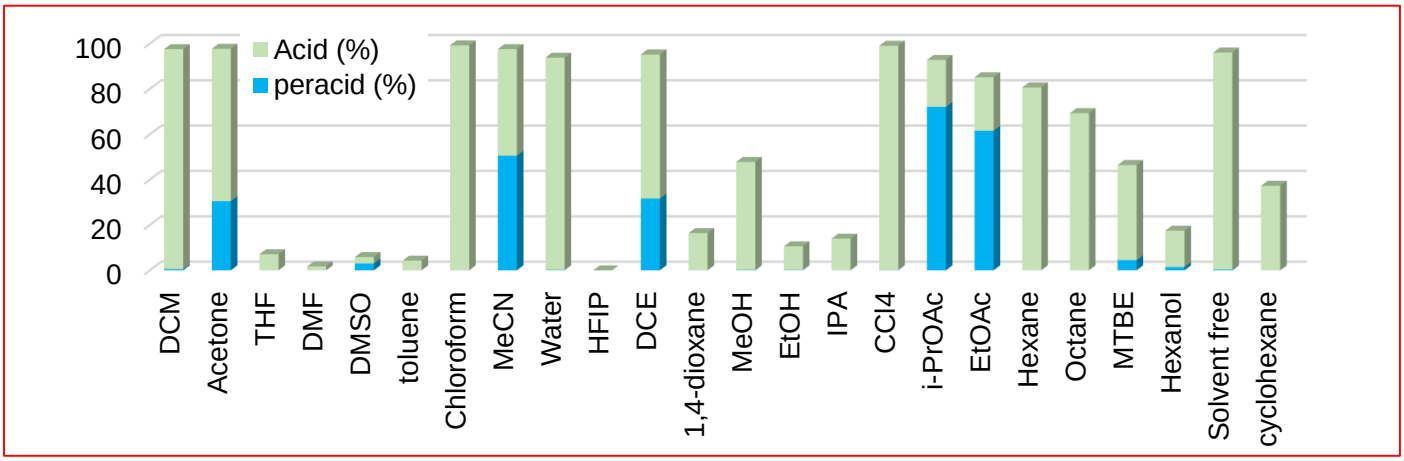
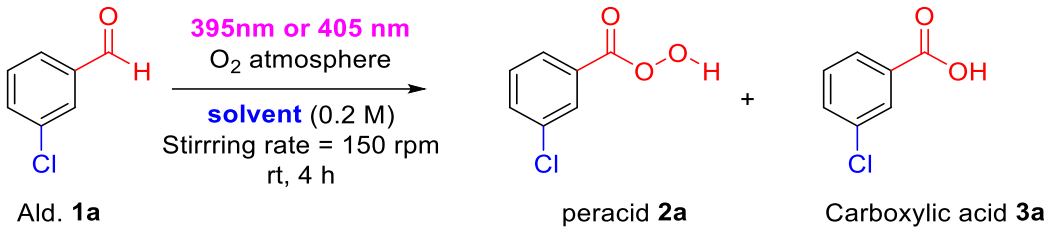


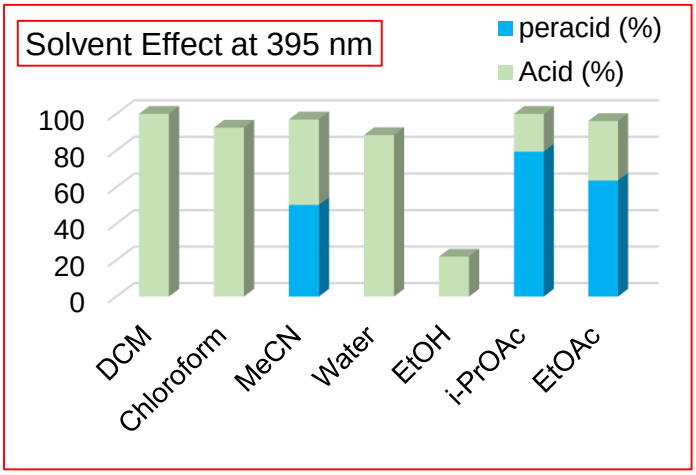
Table S7: Solvent screening under 395 nm and 405 nm.



Ald. **1a** peracid **2a** Carboxylic acid **3a**

Entry	Wavelength	Solvent	Time	Conv. (%)	**2a** (%)	**3a** (%)	**2a**/**3a** ratio
1	395 nm	*i*-PrOAc	4h	100	79.4	20.6	3.85
2	395 nm	DCM	3h	100	0	100	0
3	395 nm	EtOAc	5h	96.1	63.6	32.5	1.96
4	395 nm	$CHCl_3$	4h	92.5	0	92.5	0
5	395 nm	Water	4h	88.4	0	88.4	0
6	395 nm	EtOH	4h	21.9	0	21.9	0
7	395 nm	MeCN	4h	96.9	46.6	50.3	0.93
8	405 nm	*i*-PrOAc	4h	97.6	71.7	25.9	2.77
9	405 nm	DCM	3h	84.4	19.6	64.8	0.30
10	405 nm	EtOAc	5h	96.4	60.4	36	1.68
11	405 nm	$CHCl_3$	4h	98.9	0	98.9	0
12	405 nm	Water	4h	90.6	0	90.6	0
13	405 nm	EtOH	4h	15.3	0	15.3	0
14	405 nm	MeCN	4h	97.8	36.9	60.9	0.61

All ratios between **1a**, **2a** and **3a** were determined by ^{1}H-NMR.



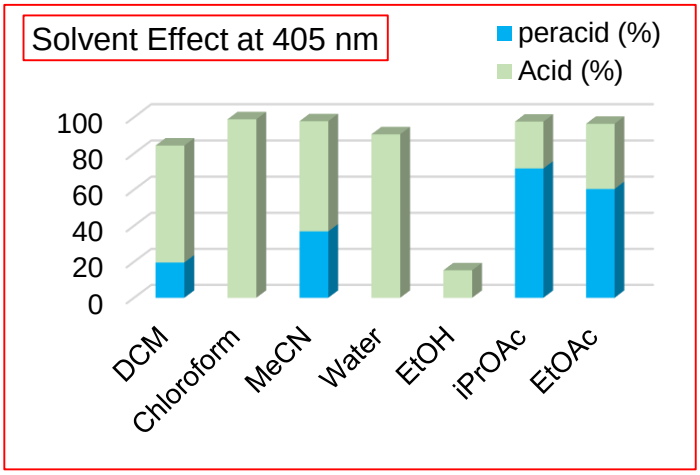
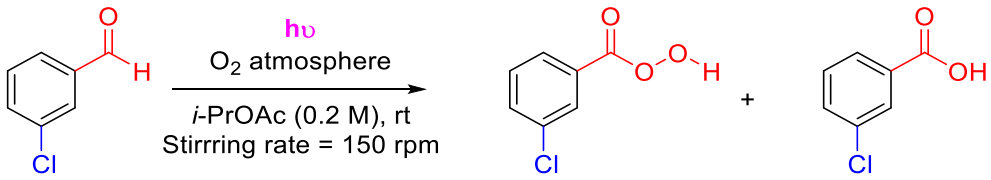


Table S8: Screening of different wavelengths under optimized conditions.

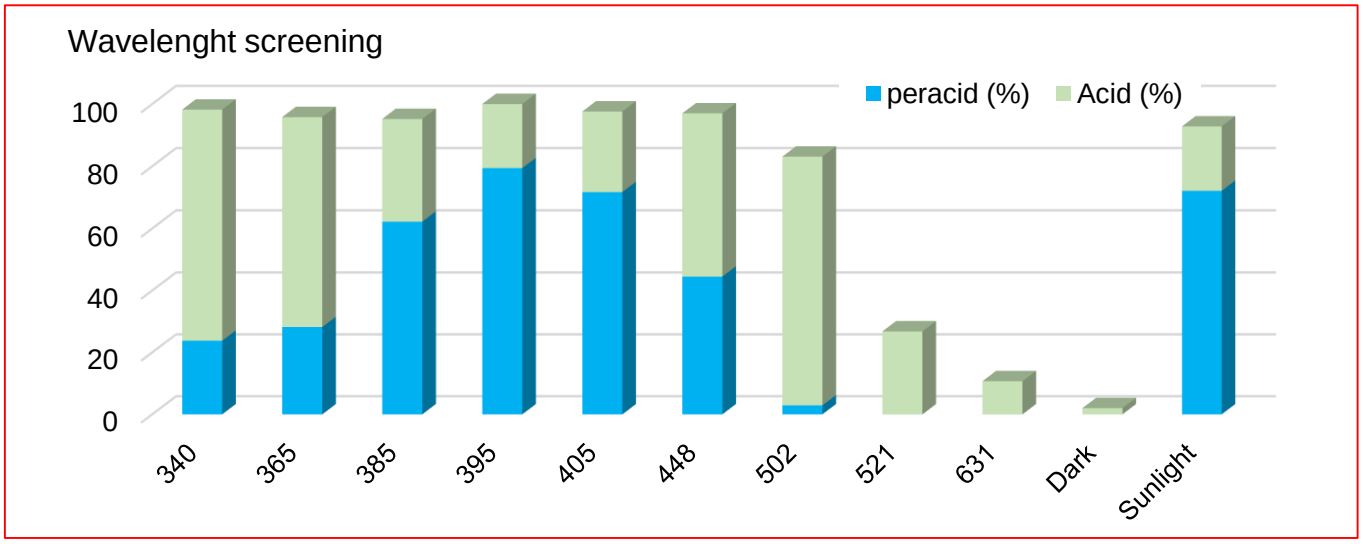


Ald. **1a** peracid **2a** Carboxylic acid **3a**

Entry	Light	Time	Conv. (%)	**2a** (%)	**3a** (%)	**2a**/**3a** ratio
1	340	2 h	98.2	23.8	74.4	0.32
2	365	2 h	95.8	28.2	67.6	0.42
3	385	2 h	95.2	62.2	33	1.88
4	395	4 h	100	79.4	20.6	3.85
5	405	4 h	97.6	71.7	25.9	2.77
6	448	4 h	97	44.5	52.5	0.85
7	502	4 h	83.1	2.9	80.2	0
8	521	4 h	26.8	0	26.8	0
9	631	5 h	10.7	0	10.7	0
10	Dark	4 h	2	0	2	0
11	Sunlight	3 h	92.8	72.1	20.7	3.48[a]
12	Sunlight	3 h	93	71	22	3.23[b]

[a] Date (27/04/2023); weather (fair); outdoor temperature (20–22 °C); time (13:00 pm–16:00 pm); humidity (43–49%).

[b] Date (25/09/2023); weather (sunny); outdoor temperature (29–31 °C); time (12:00 am–15:00 pm); humidity (43–45%).



4. Supplementary Note 1: *Kinetic study.*

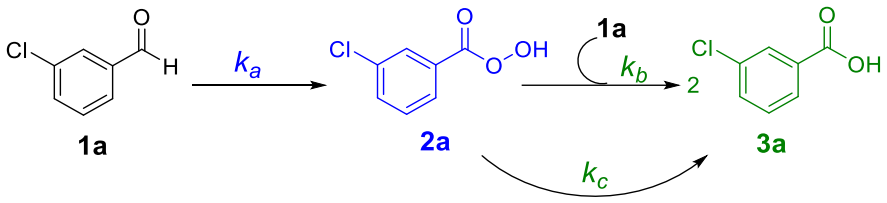
Our system can be defined by three ordinary differential equations (ODEs) as follow:

$$\frac{d[\mathbf{1a}]}{dt} = -ka[\mathbf{1a}] - kb[\mathbf{1a}][\mathbf{2a}] \qquad (1)$$

$$\frac{d[\mathbf{2a}]}{dt} = ka[\mathbf{1a}] - kc[\mathbf{2a}] - kb[\mathbf{1a}][\mathbf{2a}] \qquad (2)$$

$$\frac{d[\mathbf{3a}]}{dt} = kc[\mathbf{2a}] + 2\ kb[\mathbf{1a}][\mathbf{2a}] \qquad (3)$$

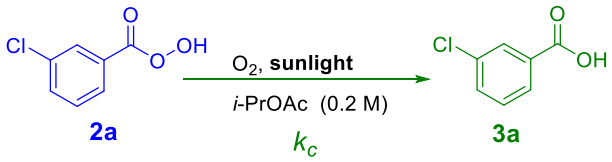
Using these equations, we were able to define some variables to represent the concentration of aldehyde **1a**, peracid **2a**, and carboxylic acid **3a** at any given time.



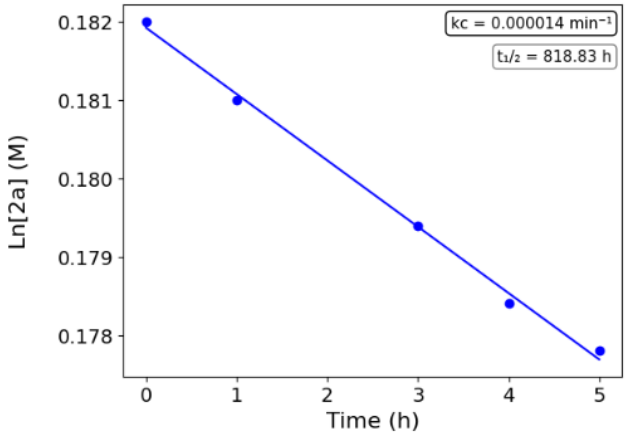
A. Using ***i*-PrOAc** as solvent under **sunlight irradiation**

To solve these equations numerically and define the values of *ka*, *kb*, and *kc*, we need to use experimental data from the reaction system. Specifically, we need to measure the concentrations of **1a**, **2a**, and **3a** as a function of time under specific reaction conditions. Hence, we can fit the experimental results to the differential equations using non-linear regression analysis *via* Python's Scipy library.

- **Calculation of *kc* value**



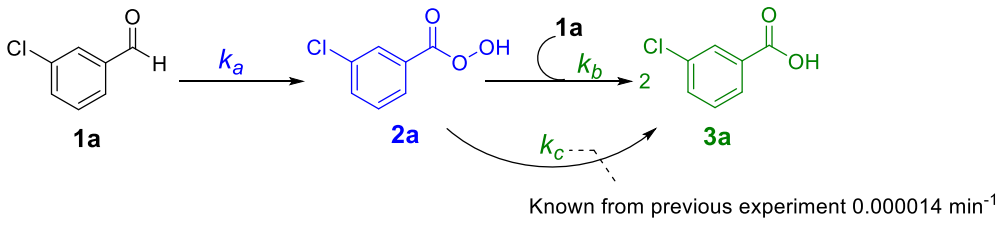
Using the commercially available mCPBA **2a**, we evaluated the rate of its decomposition to the corresponding carboxylic acid **3a** by monitoring the progress of the decomposition shown in the following figure:



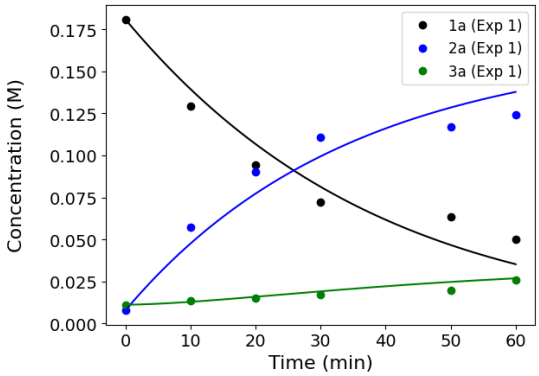
```python
import numpy as np
from scipy.stats import linregress
import matplotlib.pyplot as plt

# Define the experimental data for [B] vs. time
time = [0, 1, 3, 4, 5]
conc_B = [0.1820, 0.181, 0.1794, 0.1784, 0.1778]

# Convert time to a numpy array
time = np.array(time)

# Fit a line to the data
slope, intercept, r_value, p_value, std_err = linregress(time, conc_B)

# Calculate kc from the slope of the line (remember to take the negative)
kc = -slope / 60  # Divide by 60 to get kc in minute^-1 units

# Calculate t1/2 from kc
t_half = np.log(2) / kc

# Convert to hours
t_half_hours = t_half / 60

# Round kc and t1/2 to 6 decimal points
kc_rounded = round(kc, 6)
t_half_rounded = round(t_half_hours, 2)

# Add label for kc value on the plot in the upper right corner
kc_box = dict(boxstyle='round', facecolor='white', edgecolor='black')
plt.annotate("kc = {:.6f} min⁻¹".format(kc_rounded), xy=(0.98, 0.97), xycoords='axes fraction',
             fontsize=11, ha='right', va='top', bbox=kc_box)

# Add label for t1/2 value on the plot in the upper right corner
t_half_box = dict(boxstyle='round', facecolor='white', alpha=0.5)
plt.annotate("t₁/₂ = {} h".format(t_half_rounded), xy=(0.98, 0.88), xycoords='axes fraction',
             fontsize=11, ha='right', va='top', bbox=t_half_box)

# Plot the data and line of best fit
plt.plot(time, conc_B, 'bo', label='B -> C')  # Change label to 'B -> C'
plt.plot(time, slope * time + intercept, 'b-')
plt.xlabel('Time (h)', fontsize=16)  # Increase X-axis label font size
plt.ylabel('Ln[2a] (M)', fontsize=16, labelpad=20)  # Increase Y-axis label font size and adjust labelpad
plt.xticks(fontsize=14)  # Increase X-axis tick label font size
plt.yticks(fontsize=14)  # Increase Y-axis tick label font size
plt.show()
```

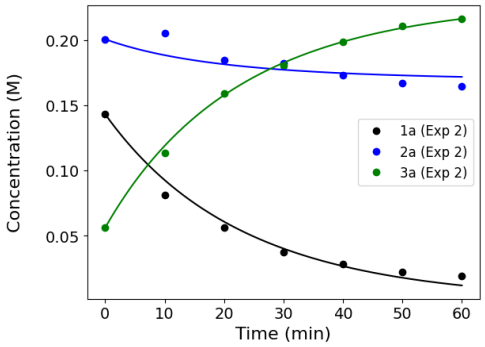
- **Calculation of *ka* and *kb* values**

It's very difficult to neglect the effect of ***kb*** when trying to calculate ***ka*** and vice versa. Then, we decided to use two scenarios to perform non-linear regression where the model is fitted to the data to find the best values of ***ka*** and ***kb*** that minimize the error between the model predictions and the actual data.



First experiment	Second experiment
O_2, **sunlight** *i*-PrOAc **1a** —k_a→ **2a** —k_c→ **3a** **1a** —k_b→ **3a + 3a** *Initial conditions:* *[**1a**] = 0.20 M* *[**2a**] = 0.00 M* *[**3a**] = 0.00 M*	O_2, **sunlight** *i*-PrOAc **1a** + **2a** —k_b→ **3a + 3a** **1a** —k_a→ **2a** **2a** —k_c→ **3a** *Initial conditions:* *[**1a**] = 0.14 M* *[**2a**] = 0.20 M* *[**3a**] = 0.06 M*





General solution: k_a = 0.031194 min^{-1} k_b = 0.052150 min^{-1}

```python
import numpy as np
from scipy.integrate import odeint
import matplotlib.pyplot as plt
from scipy.optimize import least_squares

# Define the system of differential equations
def model(y, t, ka, kc, kb):
    A, B, C = y
    dydt = [-ka*A - kb*A*B,
            ka*A - kc*B - kb*A*B,
            kc*B + 2*kb*A*B]
    return dydt

# First part: Individual fit for data_exp1
data_exp1 = np.array([[0, 0.1808, 0.0080, 0.0112],
                      [10, 0.1294, 0.0571, 0.0135],
                      [20, 0.0943, 0.0904, 0.0154],
                      [30, 0.0721, 0.1107, 0.0172],
                      [50, 0.0634, 0.1169, 0.0197],
                      [60, 0.0501, 0.1241, 0.0258]])

t_exp1 = data_exp1[:, 0]
A_exp1 = data_exp1[:, 1]
B_exp1 = data_exp1[:, 2]
C_exp1 = data_exp1[:, 3]

y0_exp1 = [A_exp1[0], B_exp1[0], C_exp1[0]]
kc_exp1 = 0.000014
p0_exp1 = [0.0001, 0.0001]

def residuals_exp1(p, t, y):
    ka, kb = p
    y_pred = odeint(model, y0_exp1, t, args=(ka, kc_exp1, kb))
    res = np.concatenate((y_pred[:, 0] - y[:, 0], y_pred[:, 1] - y[:, 1], y_pred[:, 2] - y[:, 2]))
    return res

fit_exp1 = least_squares(residuals_exp1, p0_exp1, args=(t_exp1, np.column_stack((A_exp1, B_exp1, C_exp1))))
ka_exp1 = fit_exp1.x[0]
kb_exp1 = fit_exp1.x[1]

t_fit = np.linspace(0, 60, 1000)
y_fit_exp1 = odeint(model, y0_exp1, t_fit, args=(ka_exp1, kc_exp1, kb_exp1))

plt.plot(t_exp1, A_exp1, 'ko', label='1a (Exp 1)')
plt.plot(t_exp1, B_exp1, 'bo', label='2a (Exp 1)')
plt.plot(t_exp1, C_exp1, 'go', label='3a (Exp 1)')
plt.plot(t_fit, y_fit_exp1[:, 0], 'black')
plt.plot(t_fit, y_fit_exp1[:, 1], 'b-')
plt.plot(t_fit, y_fit_exp1[:, 2], 'g-')
plt.legend(fontsize=12)
plt.xlabel('Time (min)', fontsize=16)
plt.ylabel('Concentration (M)', fontsize=16, labelpad=20)
plt.xticks(fontsize=14)
plt.yticks(fontsize=14)
plt.show()
```

```

# Second part: Individual fit for data_exp2
data_exp2 = np.array([[0, 0.1432, 0.2007, 0.0561],
                      [10, 0.0811, 0.2053, 0.1136],
                      [20, 0.0564, 0.1844, 0.1592],
                      [30, 0.0371, 0.1822, 0.1807],
                      [40, 0.0283, 0.1733, 0.1984],
                      [50, 0.0220, 0.1671, 0.2109],
                      [60, 0.0193, 0.1643, 0.2164]])

t_exp2 = data_exp2[:, 0]
A_exp2 = data_exp2[:, 1]
B_exp2 = data_exp2[:, 2]
C_exp2 = data_exp2[:, 3]

y0_exp2 = [A_exp2[0], B_exp2[0], C_exp2[0]]
kc_exp2 = 0.000014
p0_exp2 = [0.0001, 0.0001]

def residuals_exp2(p, t, y):
    ka, kb = p
    y_pred = odeint(model, y0_exp2, t, args=(ka, kc_exp2, kb))
    res = np.concatenate((y_pred[:, 0] - y[:, 0], y_pred[:, 1] - y[:, 1], y_pred[:, 2] - y[:, 2]))
    return res

fit_exp2 = least_squares(residuals_exp2, p0_exp2, args=(t_exp2, np.column_stack((A_exp2, B_exp2, C_exp2))))
ka_exp2 = fit_exp2.x[0]
kb_exp2 = fit_exp2.x[1]

y_fit_exp2 = odeint(model, y0_exp2, t_fit, args=(ka_exp2, kc_exp2, kb_exp2))

plt.plot(t_exp2, A_exp2, 'ko', label='1a (Exp 2)')
plt.plot(t_exp2, B_exp2, 'bo', label='2a (Exp 2)')
plt.plot(t_exp2, C_exp2, 'go', label='3a (Exp 2)')
plt.plot(t_fit, y_fit_exp2[:, 0], 'black')
plt.plot(t_fit, y_fit_exp2[:, 1], 'b-')
plt.plot(t_fit, y_fit_exp2[:, 2], 'g-')
plt.legend(fontsize=12)
plt.xlabel('Time (min)', fontsize=16)
plt.ylabel('Concentration (M)', fontsize=16, labelpad=20)
plt.xticks(fontsize=14)
plt.yticks(fontsize=14)
plt.show()

```

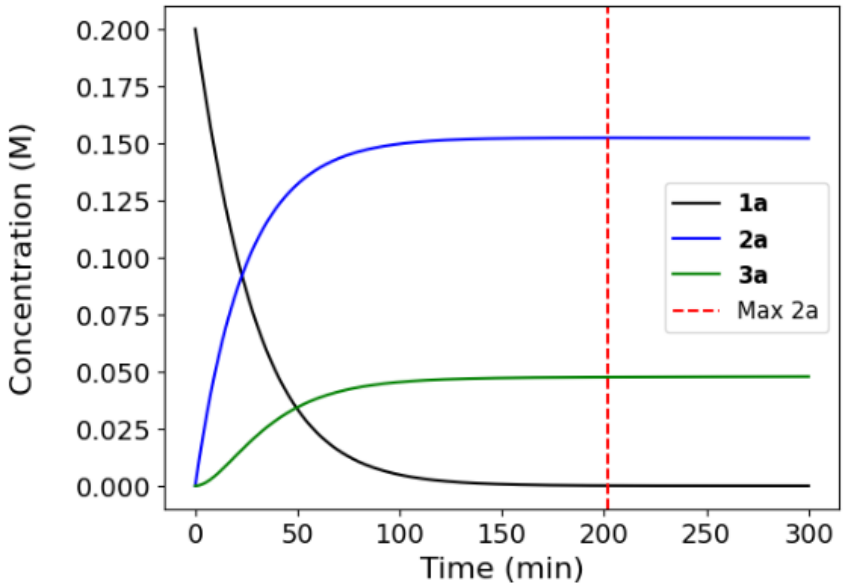
```

# Select only the first three points from exp1 and the last three points from exp2
  # to ignore the effect of time during measurment
data_exp1 = data_exp1[:3, :]
data_exp2 = data_exp2[-3:, :]

t_exp1 = data_exp1[:, 0]
A_exp1 = data_exp1[:, 1]
B_exp1 = data_exp1[:, 2]
C_exp1 = data_exp1[:, 3]

t_exp2 = data_exp2[:, 0]
A_exp2 = data_exp2[:, 1]
B_exp2 = data_exp2[:, 2]
C_exp2 = data_exp2[:, 3]

# Define the initial concentrations and parameters to be fit
y0_exp1 = [A_exp1[0], B_exp1[0], C_exp1[0]]
y0_exp2 = [A_exp2[0], B_exp2[0], C_exp2[0]]
kc_exp1 = 0.000014
kc_exp2 = 0.000014

```

```python
# Third part: Combined fit for both experiments
t_combined = np.concatenate((t_exp1, t_exp2))
A_combined = np.concatenate((A_exp1, A_exp2))
B_combined = np.concatenate((B_exp1, B_exp2))
C_combined = np.concatenate((C_exp1, C_exp2))

y0_combined_exp1 = [A_exp1[0], B_exp1[0], C_exp1[0]]
y0_combined_exp2 = [A_exp2[0], B_exp2[0], C_exp2[0]]
kc_combined_exp1 = 0.000014
kc_combined_exp2 = 0.000014
p0_combined = [0.03, 0.04]

def residuals_combined(p, t, y):
    res_exp1 = residuals_exp1(p, t[:len(t_exp1)], y[:len(t_exp1)])
    res_exp2 = residuals_exp2(p, t[len(t_exp1):], y[len(t_exp1):])
    return np.concatenate((res_exp1, res_exp2))

fit_combined = least_squares(residuals_combined, p0_combined,
                             args=(t_combined, np.column_stack((A_combined, B_combined, C_combined))))
ka_combined = fit_combined.x[0]
kb_combined = fit_combined.x[1]

print("\nGeneral solution:")
print("ka =", ka_combined)
print("kb =", kb_combined)
```

- **Modeling the chemical reaction**

After getting the values of k_a, k_b, and k_c, we could model the chemical reaction *via* solving the differential equations numerically that describe the reaction kinetics and plot the concentrations of **1a**, **2a**, and **3a** over time. Additionally, it calculates and displays the yield of product **2a** at specific time points and show the time at which 2a reaches the maximum hence we can decide the best time to stop the reaction.

```
Yield of peracid (product B) after 2 hours: 75.62%
Yield of peracid (product B) after 3 hours: 76.15%
Yield of peracid (product B) after 4 hours: 76.15%
Yield of peracid (product B) after 5 hours: 76.09%
```



```python
import numpy as np
from scipy.integrate import odeint
import matplotlib.pyplot as plt

def reaction_rates(concentrations, t, ka, kc, kb):
    A = concentrations[0]
    B = concentrations[1]
    C = concentrations[2]
    dAdt = -ka*A - kb*A*B
    dBdt = ka*A - kc*B - kb*A*B
    dCdt = kc*B + 2*kb*A*B
    return [dAdt, dBdt, dCdt]

# Initial concentrations (in M)
A0 = 0.2
B0 = 0.0
C0 = 0.0
concentrations0 = [A0, B0, C0]

# Reaction rate constants
ka = 0.031194
kc = 0.000014
kb = 0.052150
constants = [ka, kc, kb]

# Reaction volume (in liters)
V_reaction = 1.0

# Time points to evaluate the solution
hours = [2, 3, 4, 5] # in hours
t_list = [h*60 for h in hours] # in minutes
t_max = max(t_list)
dt = 0.1  # time step size in minutes
t = np.arange(0, t_max+dt, dt)

# Solve the system of differential equations numerically
solution = odeint(reaction_rates, concentrations0, t, args=tuple(constants))

# Find the time at which product B is at its maximum
t_max_B = t[np.argmax(solution[:, 1])]
```

```python

# Calculate initial and final amounts of A
initial_A = A0 * V_reaction

# Calculate amount of product B formed at each time point
B_amounts = [solution[(np.abs(t - t_list[i])).argmin(), 1] for i in range(len(t_list))]
product_B_formed = [B_amounts[i] * V_reaction for i in range(len(B_amounts))]

# Calculate yield of product B at each time point
yield_product_B = [product_B_formed[i] / initial_A * 100 for i in range(len(product_B_formed))]

# Print results
for i in range(len(hours)):
    print(f"Yield of peracid (product B) after {hours[i]} hours: {yield_product_B[i]:.2f}%")

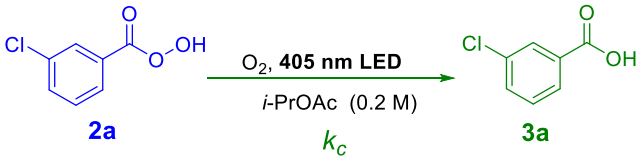
# Plot the results
plt.plot(t, solution[:, 0],'k-', label=r'$\mathbf{1a}$')
plt.plot(t, solution[:, 1],'b-',label=r'$\mathbf{2a}$')
plt.plot(t, solution[:, 2],'g-',label=r'$\mathbf{3a}$')
plt.xlabel('Time (min)', fontsize=16)
plt.ylabel('Concentration (M)', fontsize=16, labelpad=20)
plt.xticks(fontsize=14)
plt.yticks(fontsize=14)

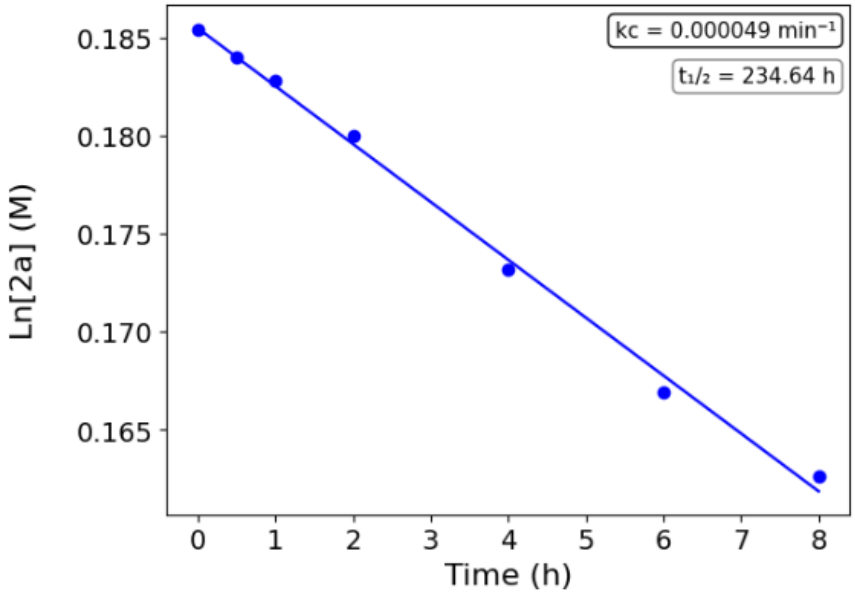
# Add a vertical line at the time of maximum B with a label showing the time
plt.axvline(x=t_max_B, color='r', linestyle='--', label='Max 2a')
plt.legend(fontsize=12)
plt.show()

```

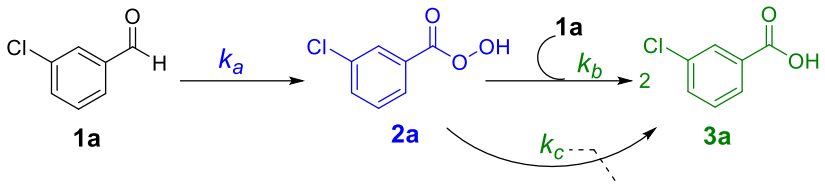
B. Using ***i*-PrOAc** as solvent under **405 nm** LED

- **Calculation of *kc* value**



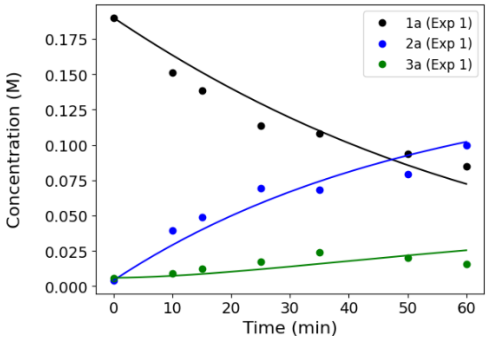


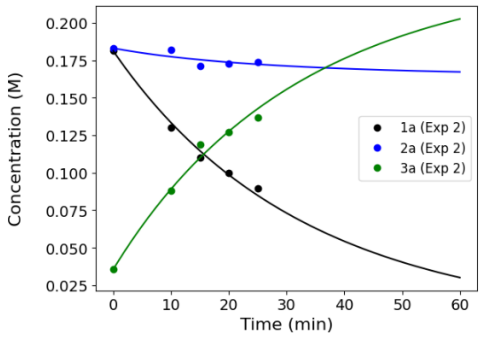
- **Calculation of *ka* and *kb* values**



Known from previous experiment 0.000049 min^{-1}

First experiment	Second experiment
O_2, **405 nm** *i*-PrOAc **1a** —k_a→ **2a** —k_c→ **3a** **1a** —k_b→ **3a + 3a** *Initial conditions:* ***[1a]*** *= 0.19 M* ***[2a]*** *= 0.00 M* ***[3a]*** *= 0.00 M*	O_2, **405 nm** *i*-PrOAc **1a** + **2a** —k_b→ **3a + 3a** **1a** —k_a→ **2a** **2a** —k_c→ **3a** *Initial conditions:* ***[1a]*** *= 0.18 M* ***[2a]*** *= 0.18 M* ***[3a]*** *= 0.03 M*

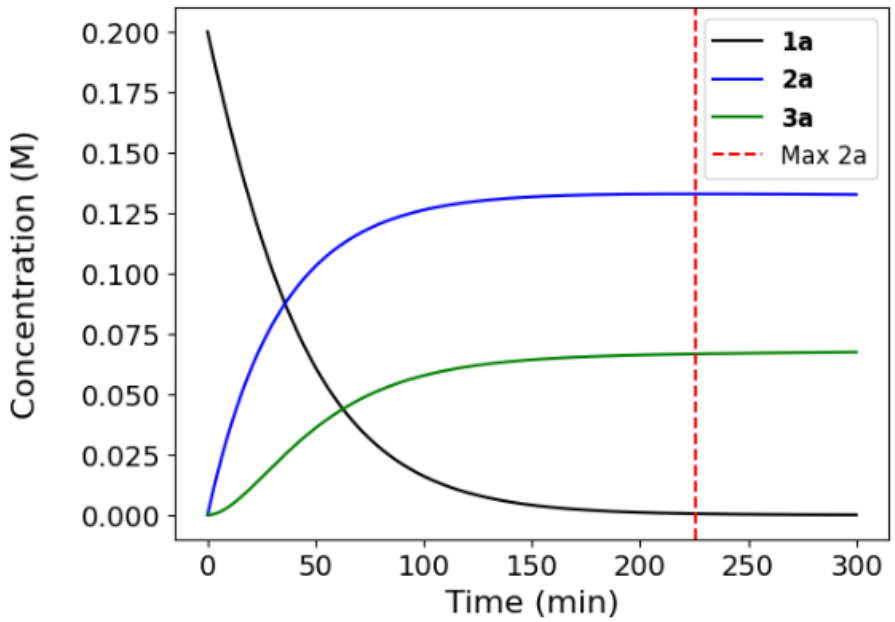




General solution:

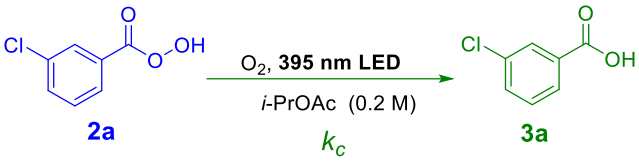
k_a = 0.020228 min^{-1} k_b = 0.0551017 min^{-1}

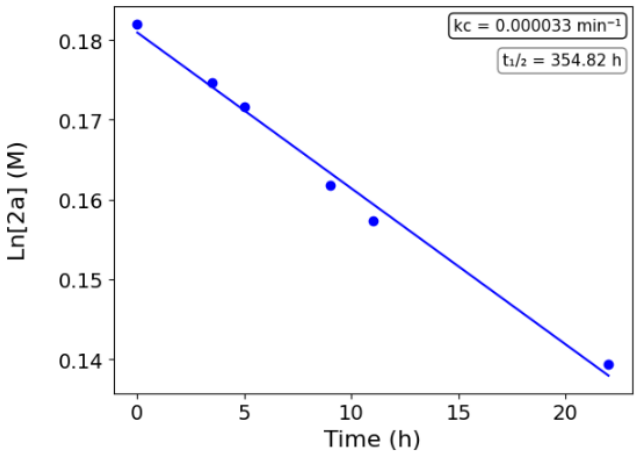
- **Modeling the chemical reaction**



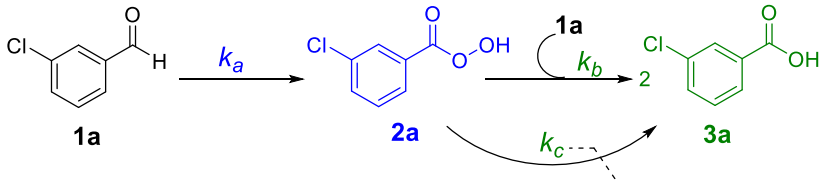
C. Using ***i*-PrOAc** as solvent under **395 nm** LED

- **Calculation of *kc* value**

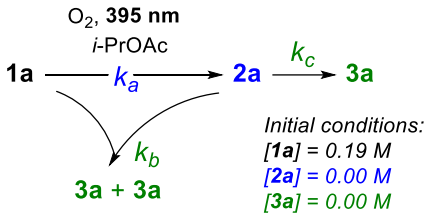
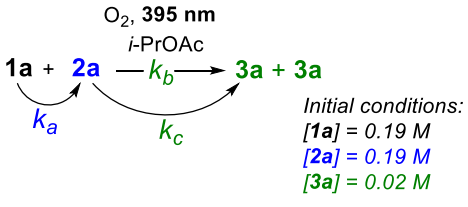


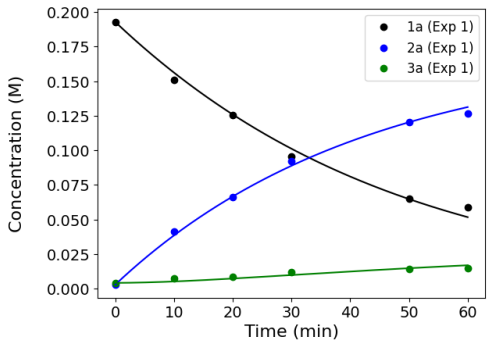


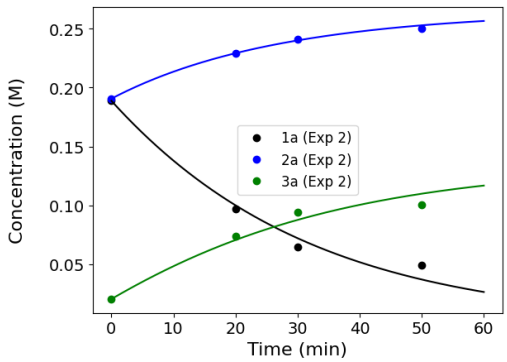
- **Calculation of *ka* and *kb* values**



Known from previous experiment 0.000033 min^{-1}

First experiment	Second experiment
	



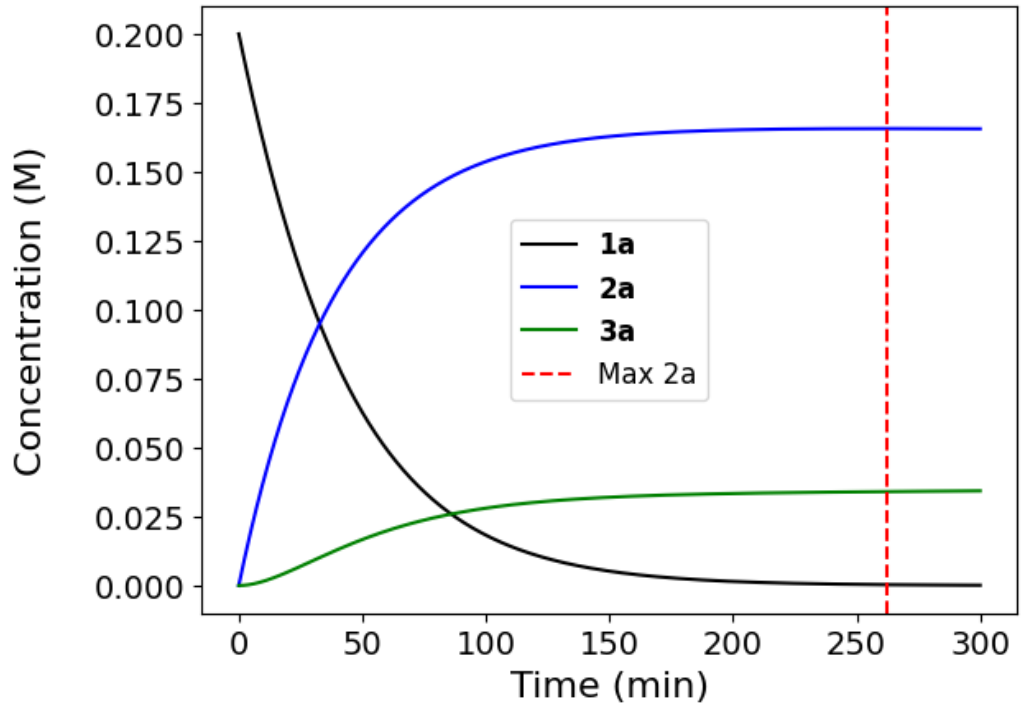


General solution:

k_a = 0.02154141 min^{-1} k_b = 0.02243828 min^{-1}

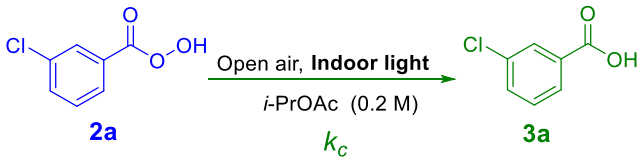
- **Modeling the chemical reaction**

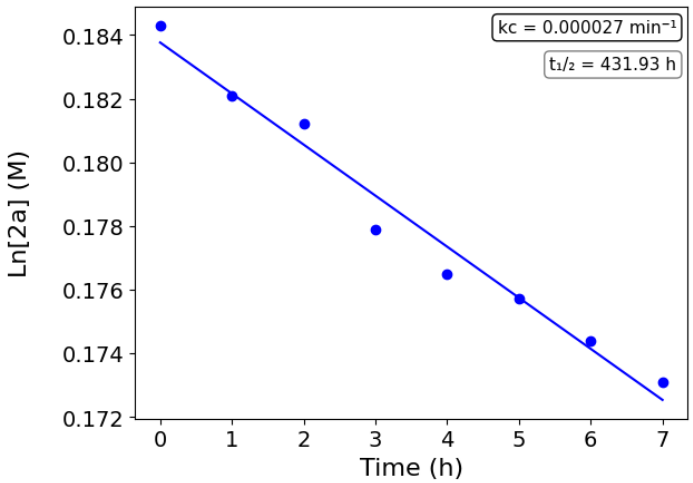
```
Yield of peracid (product B) after 2 hours: 79.39%
Yield of peracid (product B) after 3 hours: 82.29%
Yield of peracid (product B) after 4 hours: 82.80%
Yield of peracid (product B) after 5 hours: 82.78%
```



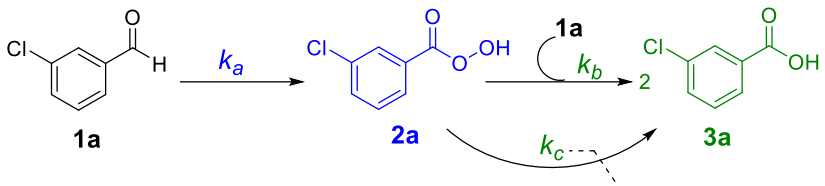
D. Using ***i*-PrOAc** as solvent under **Indoor light**

- **Calculation of *kc* value**



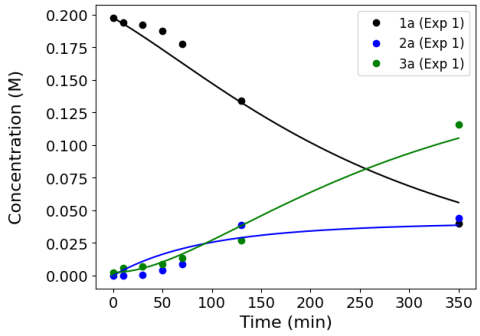


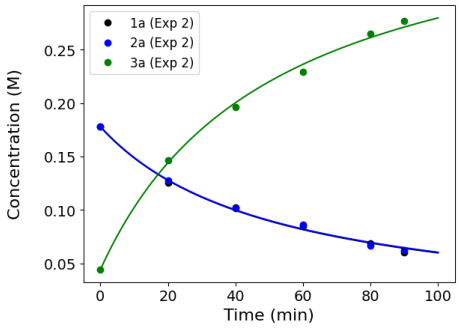
- **Calculation of *ka* and *kb* values**



Known from previous experiment 0.000027 min^{-1}

First experiment	Second experiment
air, **Indoor light** *i*-PrOAc **1a** —k_a→ **2a** —k_c→ **3a** k_b **3a + 3a** *Initial conditions:* *[**1a**] = 0.198 M* *[**2a**] = 0.000 M* *[**3a**] = 0.002 M*	air, **Indoor light** *i*-PrOAc **1a** + **2a** —k_b→ **3a + 3a** k_a k_c *Initial conditions:* *[**1a**] = 0.178 M* *[**2a**] = 0.178 M* *[**3a**] = 0.044 M*



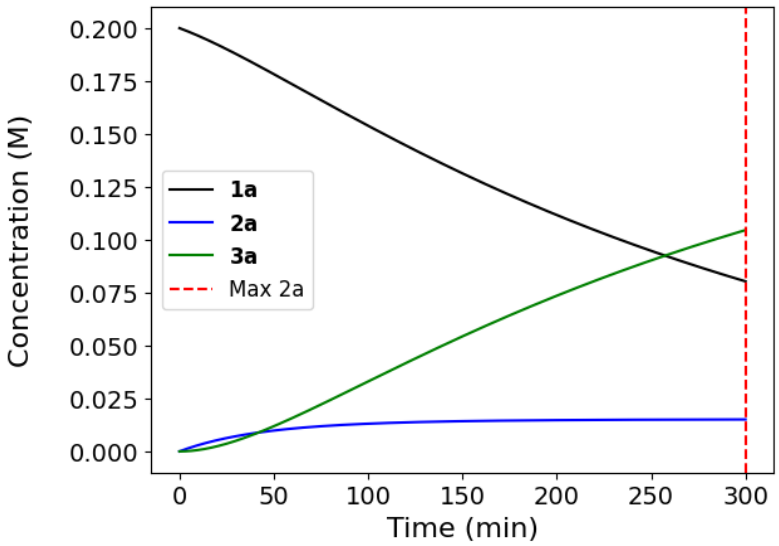


General solution:

k_a = 0.0016652 min^{-1} k_b = 0.1087275 min^{-1}

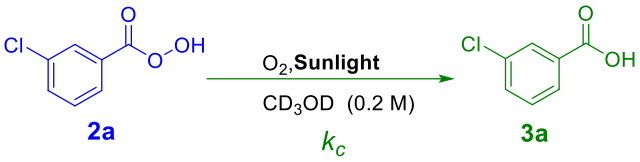
The reaction rate k_a is very slow here which can explain why the first experiment was slow at the beginning until the peracid **2a** started to accumulate push the BVO forward k_b

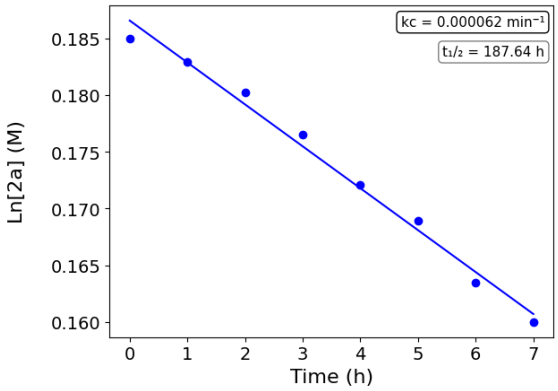
- **Modeling the chemical reaction**



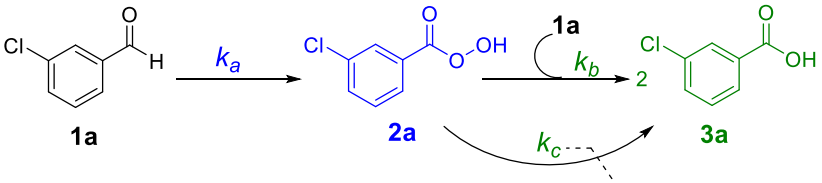
E. Using **Methanol-d$_4$** as solvent under **Sunlight**

- **Calculation of *kc* value**



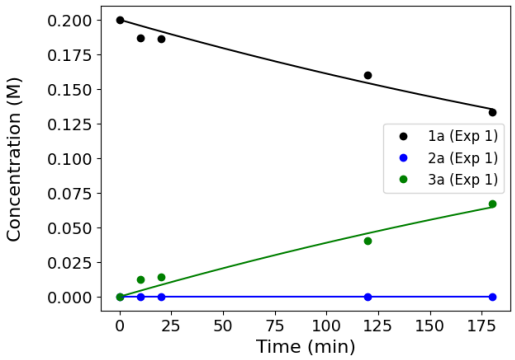


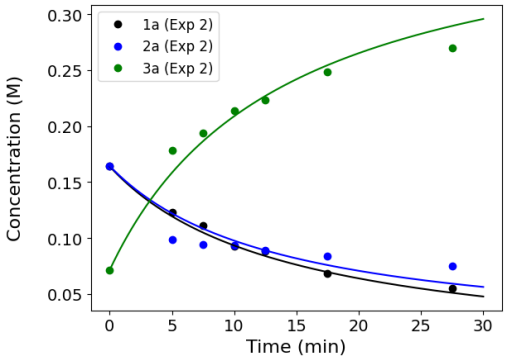
- **Calculation of *ka* and *kb* values**



Known from previous experiment 0.000062 min^{-1}

First experiment	Second experiment
O$_2$, **Sunlight** Methanol-d$_4$ **1a** —k_a→ **2a** —k_c→ **3a** **2a** —k_b→ **3a + 3a** *Initial conditions:* *[**1a**] = 0.20 M* *[**2a**] = 0.00 M* *[**3a**] = 0.00 M*	O$_2$, **Sunlight** Methanol-d$_4$ **1a** + **2a** —k_b→ **3a + 3a** **1a** —k_a→ **2a** **2a** —k_c→ **3a** *Initial conditions:* *[**1a**] = 0.164 M* *[**2a**] = 0.164 M* *[**3a**] = 0.071 M*

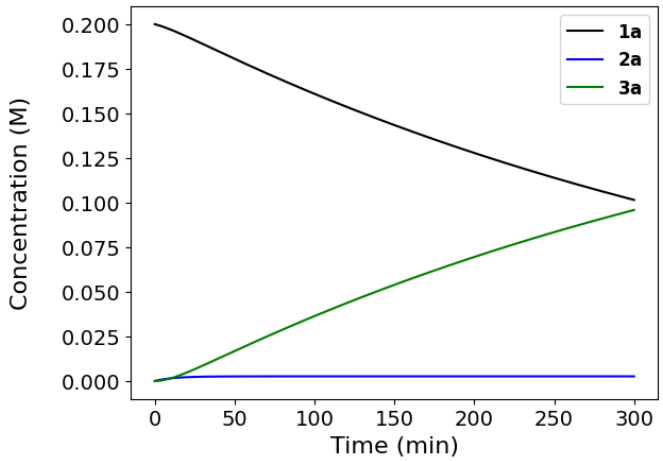




General solution: k_a = 0.001153242 min^{-1} k_b = 0.438607012 min^{-1}

The reaction rate k_a is very slow here while k_b is very fast which can explain why under these conditions the peracid **2a** can't be isolated or even observed.

- **Modeling the chemical reaction**



5. Supplementary Note 2: *Comparison between the isolated yields of various conditions*

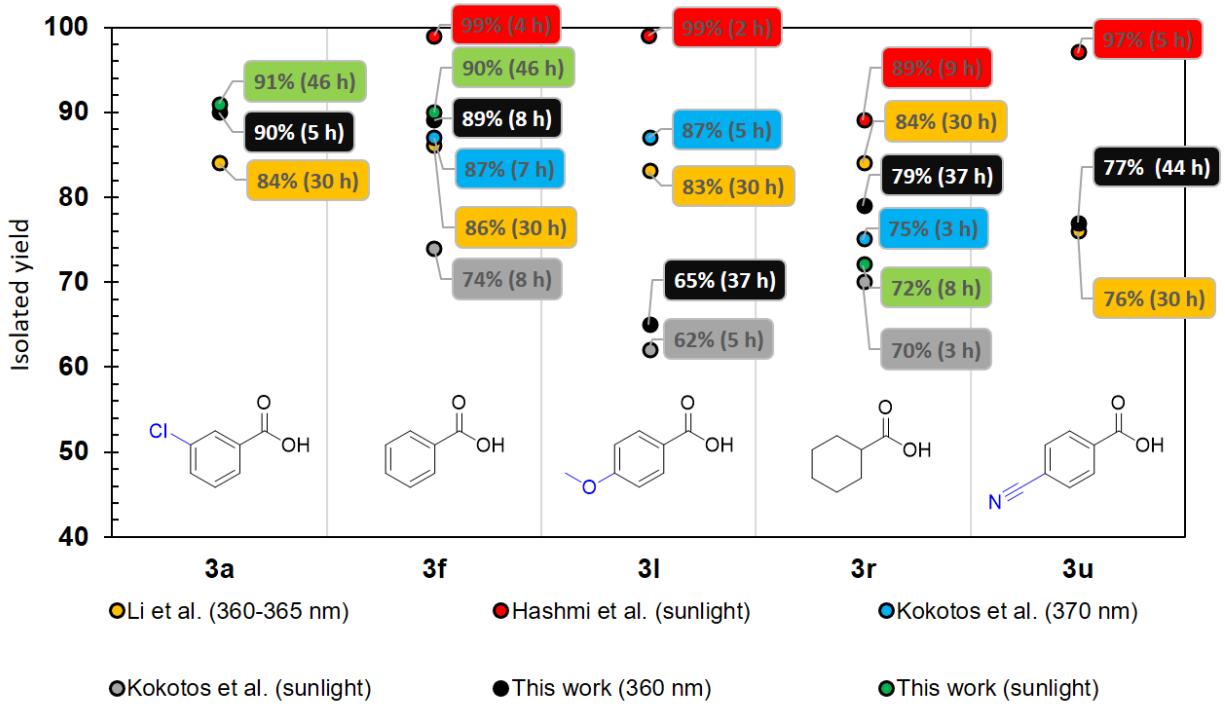


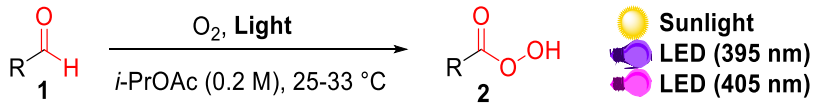
Fig. S2. Isolated yields of autoxidation of aldehydes to carboxylic acids

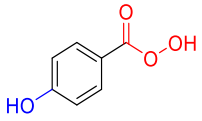
Li *et al.*	Under 360-365 nm irradiation, water (0.25 M), oxygen atmosphere, at r.t.	[***Ref 13e***]
Hashmi *et al.*	Under sunlight irradiation, acetone (1.0 M), open air, at r.t.	[***Ref 13f***]
Kokotos *et al.*	Under 370 nm irradiation, acetone/water 10/1 (0.3 M), open air, at r.t.	[***Ref 13g***]
	Under sunlight irradiation, acetone/water 10/1 (0.3 M), open air, at r.t.	
This work	Under 365 nm irradiation, *i*-PrOAc (0.2 M), open air (stirring rate = 500 rpm) at r.t.	
	Under sunlight, IPA/water 50% v/v (0.2 M), open air (stirring rate = 500 rpm) at r.t.	

*** Variations of reaction times can be attributed to the different reaction scales*

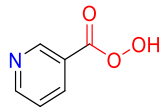
6. Supplementary Note 3: *Extended substrate scope for peracids and carboxylic acids.*

Scheme S1: *Unsuccessful and suboptimal substrates (peracids)*



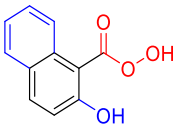


2aa
Sunlight, 37% (4 h)
395 nm, 12% (1.5 h)
405 nm, 26% (4 h)

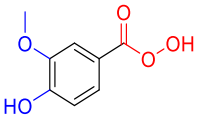


2ab
Sunlight, 0% (4 h)
395 nm, 0% (4 h)
405 nm, 0% (4 h)

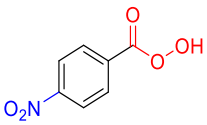
2ac
Sunlight, 6% (4 h)
395 nm, 0% (3 h)
405 nm, 0% (3 h)



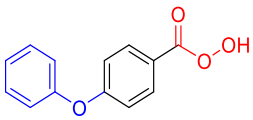
2ae
Sunlight, 0% (4 h)
395 nm, 0% (2 h)
405 nm, 0% (2 h)



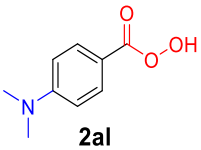
2ai
395 nm, 0% (4 h)
405 nm, 0% (4 h)



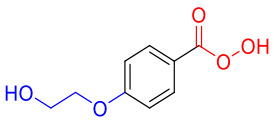
2aj
Sunlight, 0% (4 h)
395 nm, 0% (4 h)



2ak
Sunlight,15% (1.5 h)
395 nm, 11% (1 h)
405 nm, 8% (1 h)

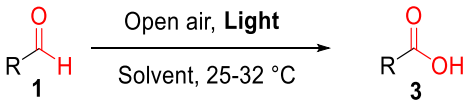


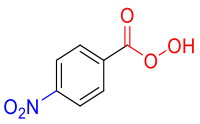
2al
395 nm, 0% (4 h)
405 nm, 0% (4 h)



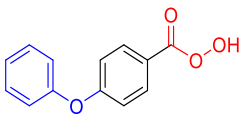
2am
Sunlight, 13% (8 h)
395 nm, 19% (4 h)
405 nm, 3% (10 h)

Scheme S2: *Unsuccessful and suboptimal substrates (carboxylic acids)*

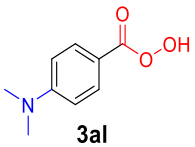




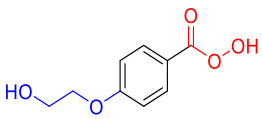
3aj
Sunlight, 0% (9 h)[a]
365 nm, 0% (37 h)



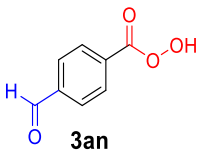
3ak
Sunlight, 0% (5 h)[a]
Sunlight, 83% (8 h)[b]
365 nm, 79% (46 h)



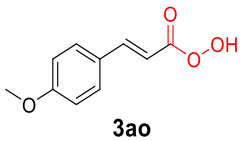
3al
Sunlight, 0% (5 h)[a]



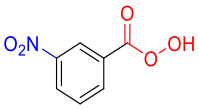
3am
Sunlight, 0% (5 h)[a]
Sunlight, 76% (8 h)[b]
365 nm, 67% (40 h)



3an
Sunlight, 0% (9 h)[a]
365 nm, 66% (40 h)



3ao
Sunlight, 0% (6 h)[a]

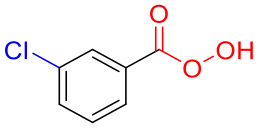


3ap
Sunlight, 0% (4 h)[a]
365 nm,80% (37 h)

[a]Solvent is water/IPA (50% v/v)
[b]Solvent is *i*-PrOAc

7. Supplementary Note 4: *Characterization data*

3-Chlorobenzoperoxoic acid (**2a**)[1]

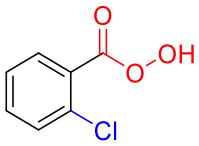


White solid

^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.58 (s, 1H), 7.99 (t, J = 1.8 Hz, 1H), 7.89 (dt, J = 7.8, 1.4 Hz, 1H), 7.63 (ddd, J = 8.0, 2.3, 1.8 Hz, 1H), 7.46 (t, J = 8.0 Hz, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.00, 135.28, 134.59, 130.38, 129.50, 127.51, 127.16.

2-Chlorobenzoperoxoic acid (**2b**)[2]

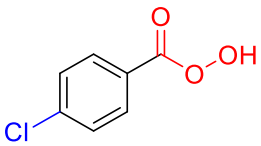


White solid

^{1}H-NMR (400 MHz, $CDCl_3$) δ 12.91-10.66 (1H), 7.81 (d, J = 7.6 Hz, 1H), 7.49-7.53 (m, 2H), 7.38 (d, J = 7.6 Hz, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.25, 134.28, 133.62, 132.55, 131.58, 127.07, 126.85.

4-Chlorobenzoperoxoic acid (**2c**)[3]

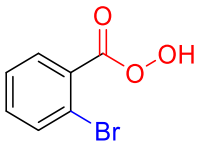


White solid

^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.59 (s, 1H), 7.94 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.40, 141.25, 130.79, 129.49, 123.75.

2-Bromobenzoperoxoic acid (**2d**)[2]

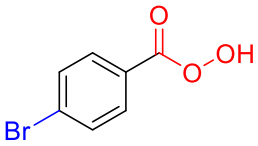


White solid

^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.59 (s, 1H), 7.72-7.78 (m, 2H), 7.42-7.47 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 170.30, 134.85, 134.22, 133.82, 133.63, 131.53, 127.60.

4-Bromobenzoperoxoic acid (**2e**)



White solid

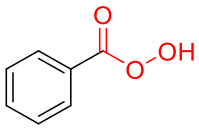
^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.64 (s, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.52, 132.48, 130.84, 129.94, 124.21.

HRMS (ESI): calcd for $C_7H_4BrO_3$: *m/z* 214.9349 $[M - H]^-$, found 214.9352.

IR (KBr): 3230, 3093, 1724, 1588, 1069, 745 cm^{-1}.

Benzoperoxoic acid (**2f**)[4]

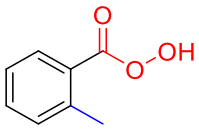


White solid

^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.67 (s, 1H), 8.00 (dd, J = 8.4, 1.5 Hz, 2H), 7.65 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.25, 134.53, 129.45, 129.02, 125.36.

2-Methylbenzoperoxoic acid (**2g**)[2]

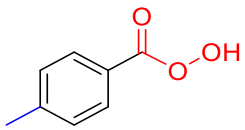


White solid

^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.72 (s, 1H), 7.84 (dd, J = 6.9, 2.3 Hz, 1H), 7.46-7.49 (m, 1H), 7.25-7.34 (m, 2H), 2.59 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 169.09, 140.64, 133.51, 132.03, 130.31, 126.15, 124.79, 21.41.

4-Methylbenzoperoxoic acid (**2h**)[2]

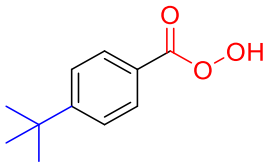


White solid

^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.61 (s, 1H), 7.89 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 2.44 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 169.53, 145.65, 129.75, 129.47, 122.45, 22.00.

4-(*tert*-Butyl)benzoperoxoic acid (**2i**)[2]

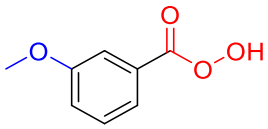


White solid

^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.60 (s, 1H), 7.92 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 1.34 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.25, 158.46, 129.32, 125.99, 122.46, 35.40, 31.10.

3-Methoxybenzoperoxoic acid (**2j**)[5]

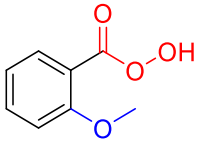


White solid

^{1}H-NMR (400 MHz, CD_3OD) δ 7.49 (dt, J = 7.6, 1.1 Hz, 1H), 7.43 (t, J = 2.1 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 7.16-7.19 (m, 1H), 3.82 (s, 3H).

^{13}C-NMR (101 MHz, CD_3OD) δ 167.30, 161.16, 130.93, 129.63, 122.17, 120.64, 114.84, 55.88.

2-Methoxybenzoperoxoic acid (**2k**)[2]

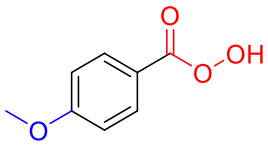


White solid

^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.78 (s, 1H), 7.82 (dd, J = 8.0, 1.9 Hz, 1H), 7.57 (t, J = 8.8 Hz, 1H), 6.99-7.09 (m, 2H), 3.93 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.34, 159.57, 135.52, 131.97, 122.42, 120.61, 112.28, 56.18.

4-Methoxybenzoperoxoic acid (**2l**)[5]

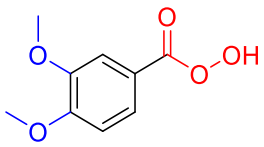


White solid

^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.64 (s, 1H), 7.95 (d, J = 9.2 Hz, 2H), 6.96 (d, J = 9.2 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.03, 164.58, 131.61, 117.34, 114.37, 55.71.

3,4-Dimethoxybenzoperoxoic acid (**2m**)



White solid

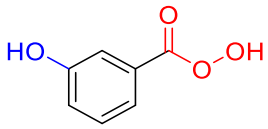
^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.63 (s, 1H), 7.65 (dd, J = 8.8, 1.9 Hz, 1H), 7.45 (d, J = 1.5 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 3.95 (s, 3H), 3.93 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.01, 154.29, 149.14, 123.86, 117.37, 111.47, 110.78, 56.25, 56.21.

HRMS (ESI): calcd for $C_9H_9O_5$: *m/z* 197.0456 $[M - H]^-$, found 197.0446.

IR (KBr): 3256, 2839, 1746, 1680, 1026, 764 cm^{-1}.

3-Hydroxybenzoperoxoic acid (**2p**)



White solid

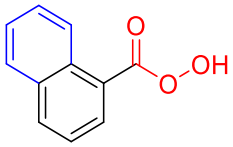
^{1}H-NMR (400 MHz, $(CD_3)_2SO$) δ 9.95 (s, 1H), 9.91 (s, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.35 (d, J = 7.6 Hz, 1H), 7.24 (t, J = 1.4 Hz, 1H), 7.08-7.11 (m, 1H).

^{13}C-NMR (101 MHz, $(CD_3)_2SO$) δ 193.14, 158.02, 137.69, 130.34, 121.84, 121.12, 114.68.

HRMS (ESI): calcd for $C_7H_5O_4$: *m/z* 153.0193 $[M - H]^-$, found 153.0187.

IR (KBr): 3247, 3010, 1751, 1624, 1078, 812 cm^{-1}.

Naphthalene-1-carboperoxoic acid (**2q**)[6]

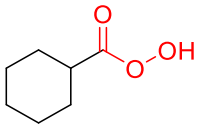


White solid

^{1}H-NMR (400 MHz, CD_3OD) δ 8.56 (d, J = 9.2 Hz, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.99 (dd, J = 7.3, 0.9 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.85-7.87 (m, 2H), 7.60-7.65 (m, 1H).

^{13}C-NMR (101 MHz, CD_3OD) δ 168.55, 135.18, 134.72, 131.96, 130.32, 129.76, 128.96, 127.67, 126.02, 125.85, 125.61.

Cyclohexanecarboperoxoic acid (**2r**)[5]

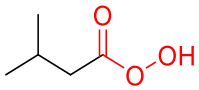


Colorless liquid

^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.38 (s, 1H), 2.48 (tt, J = 11.4, 3.7 Hz, 1H), 1.90-1.96 (m, 2H), 1.75-1.83 (m, 2H), 1.49-1.69 (m, 3H), 1.22-1.34 (m, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 176.93, 40.31, 28.71, 25.48, 25.22.

3-Methylbutaneperoxoic acid (**2s**)



Colorless liquid

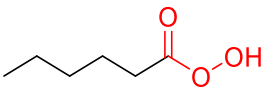
^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.23 (d, J = 6.9 Hz, 2H), 2.06-2.15 (m, 1H), 0.99 (d, J = 6.1 Hz, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 179.02, 43.16, 25.64, 22.51.

HRMS (ESI): calcd for $C_5H_9O_3$: *m/z* 117.0557 [M - H]$^-$, found 117.0542.

IR (KBr): 3255, 2963, 2874, 1751, 1712, 1210 cm^{-1}.

Hexaneperoxoic acid (**2t**)[3]

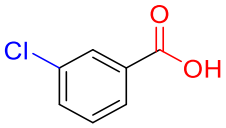


Colorless liquid

^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.35 (s, 1H), 2.41 (t, J = 7.6 Hz, 2H), 1.66-1.74 (m, 2H), 1.26-1.35 (m, 4H), 0.86-0.91 (m, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 174.82, 31.74, 30.53, 24.45, 22.79, 14.26.

3-Chlorobenzoic acid (**3a**)[7]

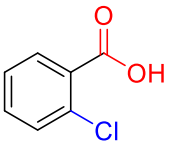


White solid, m.p. 154-155 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.57 (s, 1H), 8.10 (s, 1H), 8.01 (d, J = 8.3 Hz, 1H), 7.60 (d, J = 7.3 Hz, 1H), 7.43 (t, J = 7.8 Hz, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 171.23, 134.87, 134.08, 131.09, 130.42, 130.00, 128.48.

2-Chlorobenzoic acid (**3b**)[8]

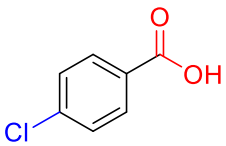


White solid, m.p. 128-129 °C.

^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 13.40 (s, 1H), 7.78 (dd, J = 7.3, 1.8 Hz, 1H), 7.50-7.53 (m, 2H), 7.39-7.43 (m, 1H).

^{13}C-NMR (101 MHz, $(CD_3)_2SO$) δ 166.85, 132.64, 131.71, 131.57, 130.90, 130.71, 127.30.

4-Chlorobenzoic acid (**3c**)[8]

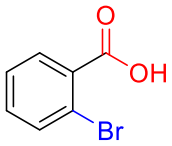


White solid, m.p. 207-208 °C.

^{1}H-NMR (400 MHz, $(CD_3)_2SO$) δ 12.80 (s, 1H), 7.93 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 7.3 Hz, 2H).

^{13}C-NMR (101 MHz, $(CD_3)_2SO$) δ 166.57, 137.90, 131.23, 129.70, 128.83.

2-Bromobenzoic acid (**3d**)[9]

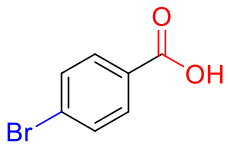


White solid, m.p. 138-139 °C.

^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 13.37 (s, 1H), 7.69-7.75 (m, 2H), 7.39-7.48 (m, 2H).

^{13}C-NMR (101 MHz, $(CD_3)_2SO$) δ 167.41, 133.79, 132.54, 130.62, 127.73, 119.98 (one carbon overlapped).

4-Bromobenzoic acid (**3e**)[8]

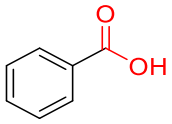


White solid, m.p. 226-227 °C.

^{1}H-NMR (400 MHz, $(CD_3)_2SO$) δ 13.17 (s, 1H), 7.86 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H).

^{13}C-NMR (101 MHz, $(CD_3)_2SO$) δ 166.63, 131.71, 131.31, 130.02, 126.90.

Benzoic acid (**3f**)[8]

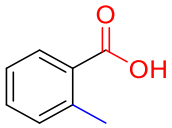


White solid, m.p. 114-115 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 12.15 (s, 1H), 8.14 (dd, J = 7.6, 2.3 Hz, 2H), 7.63 (t, J = 7.3 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 172.81, 133.96, 130.35, 129.47, 128.61.

2-Methylbenzoic acid (**3g**)[9]

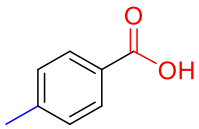


White solid, m.p. 94-95 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 12.58 (s, 1H), 8.09 (dd, J = 7.3, 1.8 Hz, 1H), 7.47 (t, J = 7.8 Hz, 1H), 7.28-7.32 (m, 2H), 2.68 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 173.79, 141.54, 133.12, 132.08, 131.76, 128.47, 126.01, 22.29.

4-Methylbenzoic acid (**3h**)[9]

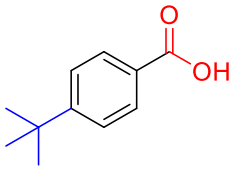


White solid, m.p. 185-186 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.50 (s, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 7.6 Hz, 2H), 2.44 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 172.40, 144.80, 130.41, 129.36, 126.72, 21.91.

4-(*tert*-Butyl)benzoic acid (**3i**)[8]

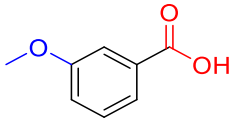


White solid, m.p. 161-162 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 12.67 (s, 1H), 8.07 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 8.3 Hz, 2H), 1.37 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 172.80, 157.75, 130.29, 126.75, 125.62, 35.33, 31.23.

3-Methoxybenzoic acid (**3j**)[7]

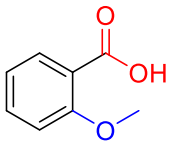


White solid, m.p. 97-98 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 12.01 (s, 1H), 7.73 (d, J = 7.3 Hz, 1H), 7.64 (t, J = 2.3 Hz, 1H), 7.39 (t, J = 7.8 Hz, 1H), 7.17 (dd, J = 8.3, 2.8 Hz, 1H), 3.88 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 172.40, 159.74, 130.70, 129.68, 122.84, 120.65, 114.52, 55.60.

2-Methoxybenzoic acid (**3k**)[9]

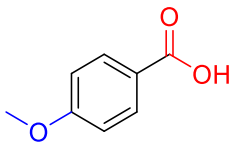


White solid, m.p. 88-89 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.82 (s, 1H), 8.18 (dd, J = 8.3, 1.8 Hz, 1H), 7.58 (ddd, J = 8.3, 7.3, 1.8 Hz, 1H), 7.14 (t, J = 7.8 Hz, 1H), 7.06 (d, J = 8.3 Hz, 1H), 4.08 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 165.66, 158.18, 135.22, 133.86, 122.27, 117.66, 111.77, 56.78.

4-Methoxybenzoic acid (**3l**)[8]

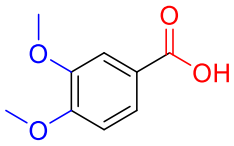


White solid, m.p. 177-178 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 12.13 (s, 1H), 8.08 (d, J = 8.3 Hz, 2H), 6.95 (d, J = 9.2 Hz, 2H), 3.88 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 171.70, 164.19, 132.51, 121.75, 113.90, 55.64.

3,4-Dimethoxybenzoic acid (**3m**)[10]

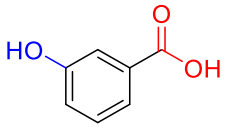


White solid, m.p. 180-181 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.39 (s, 1H), 7.76 (dd, J = 8.7, 1.8 Hz, 1H), 7.58 (d, J = 1.8 Hz, 1H), 6.90 (d, J = 8.7 Hz, 1H), 3.94 (s, 3H), 3.93 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 172.18, 153.85, 148.76, 124.71, 121.79, 112.40, 110.43, 56.16, 56.09.

3-Hydroxybenzoic acid (**3p**)[11]

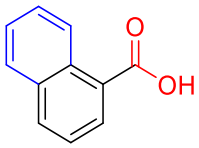


Off-white solid, m.p. 196-197 °C.

^{1}H-NMR (400 MHz, $(CD_3)_2SO$) δ 12.81 (s, 1H), 9.73 (s, 1H), 7.37 (d, J = 7.3 Hz, 1H), 7.33 (d, J = 1.8 Hz, 1H), 7.28 (t, J = 7.8 Hz, 1H), 6.99 (dd, J = 7.8, 2.3 Hz, 1H).

^{13}C-NMR (101 MHz, $(CD_3)_2SO$) δ 167.40, 157.46, 132.09, 129.65, 120.05, 119.92, 115.87.

1-Naphthoic acid (**3q**)[12]

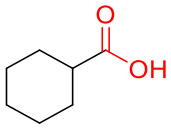


White solid, m.p. 154-155 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 12.50 (s, 1H), 9.12 (d, J = 8.3 Hz, 1H), 8.44 (d, J = 7.3 Hz, 1H), 8.11 (d, J = 7.3 Hz, 1H), 7.93 (d, J = 8.3 Hz, 1H), 7.68 (ddd, J = 8.3, 7.3, 1.8 Hz, 1H), 7.55-7.60 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 173.60, 134.83, 134.07, 132.05, 131.78, 128.87, 128.27, 126.48, 126.06, 125.72, 124.69.

Cyclohexanecarboxylic acid (**3r**)[12]

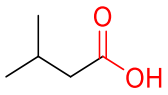


Colorless solid (at low temperature), m.p. 28-29 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.17 (s, 1H), 2.33 (tt, J = 11.2, 3.7 Hz, 1H), 1.91-1.97 (m, 2H), 1.63-1.79 (m, 3H), 1.41-1.51 (m, 2H), 1.20-1.35 (m, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 182.98, 43.07, 28.89, 25.82, 25.45.

3-Methylbutanoic acid (**3s**)[13]

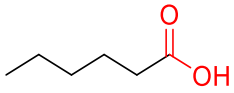


Colorless liquid

^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.23 (s, 1H), 2.23 (d, J = 7.3 Hz, 2H), 2.06-2.16 (m, 1H), 0.98 (d, J = 6.4 Hz, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 180.09, 43.32, 25.62, 22.48.

Hexanoic acid (**3t**)[14]

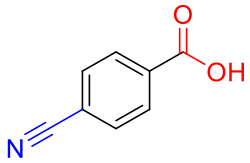


Colorless liquid

^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.39 (s, 1H), 2.34 (t, J = 7.6 Hz, 2H), 1.59-1.67 (m, 2H), 1.28-1.36 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 180.72, 34.23, 31.35, 24.50, 22.43, 14.00.

4-Cyanobenzoic acid (**3u**)[8]

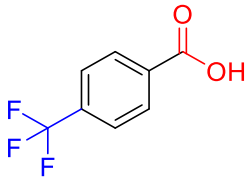


White solid, m.p. 222-223 °C.

^{1}H-NMR (400 MHz, $(CD_3)_2SO$) δ 13.61 (s, 1H), 8.07 (d, J = 8.3 Hz, 2H), 7.97 (d, J = 9.2 Hz, 2H).

^{13}C-NMR (101 MHz, $(CD_3)_2SO$) δ 166.09, 134.87, 132.71, 129.96, 118.22, 115.10.

4-(Trifluoromethyl)benzoic acid (**3v**)[8]

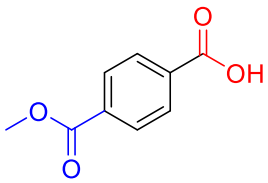


White solid, m.p. 182-183 °C.

^{1}H-NMR (400 MHz, $(CD_3)_2SO$) δ 13.44 (s, 1H), 8.11 (d, J = 8.3 Hz, 2H), 7.82 (d, J = 8.3 Hz, 2H).

^{13}C-NMR (101 MHz, $(CD_3)_2SO$) δ 166.28, 134.67, 132.60 (q, $J_{C\text{-}F}$ = 32.1 Hz), 130.14, 125.57 (q, $J_{C\text{-}F}$ = 2.9 Hz), 123.86 (q, $J_{C\text{-}F}$ = 272.7 Hz).

4-(Methoxycarbonyl)benzoic acid (**3w**)[12]

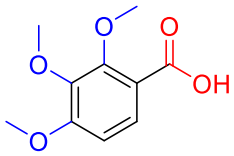


White solid, m.p. 219-220 °C.

^{1}H-NMR (400 MHz, $(CD_3)_2SO$) δ 13.35 (s, 1H), 8.01-8.06 (m, 4H), 3.87 (s, 3H).

^{13}C-NMR (101 MHz, $(CD_3)_2SO$) δ 166.61, 165.64, 134.84, 133.18, 129.61, 129.36, 52.48.

2,3,4-Trimethoxybenzoic acid (**3x**)[15]

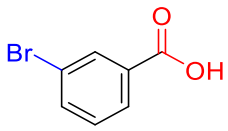


White solid, m.p. 87-88 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.12 (s, 1H), 7.90 (d, J = 9.2 Hz, 1H), 6.81 (d, J = 8.4 Hz, 1H), 4.14 (s, 3H), 3.94 (s, 3H), 3.88 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 165.22, 158.39, 153.03, 141.36, 128.53, 114.47, 108.17, 62.69, 61.20, 56.37.

3-Bromobenzoic acid (**3y**)[10]

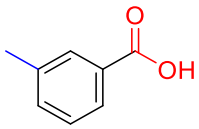


White solid, m.p. 149-150 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.52 (s, 1H), 8.26 (s, 1H), 8.05 (dd, J = 7.3, 1.8 Hz, 1H), 7.75 (dd, J = 8.3, 1.8 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 171.14, 137.00, 133.36, 131.28, 130.25, 128.93, 122.74.

3-Methylbenzoic acid (**3z**)[9]

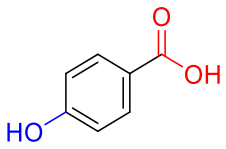


White solid, m.p. 100-102 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 12.38 (s, 1H), 7.93-7.96 (m, 2H), 7.44 (d, J = 8.3 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 2.43 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 172.89, 138.45, 134.75, 130.85, 129.38, 128.52, 127.52, 21.39.

4-Hydroxybenzoic acid (**3aa**)[10]

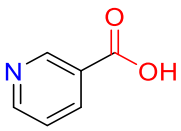


White solid, m.p. 204-205 °C.

^{1}H-NMR (400 MHz, $(CD_3)_2SO$) δ 12.42 (s, 1H), 10.21 (s, 1H), 7.80 (d, J = 8.3 Hz, 2H), 6.82 (d, J = 9.2 Hz, 2H).

^{13}C-NMR (101 MHz, $(CD_3)_2SO$) δ 167.31, 161.72, 131.66, 121.47, 115.23.

Nicotinic acid (**3ab**)[12]

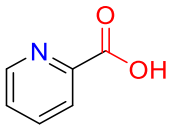


White solid, m.p. 205-206 °C.

^{1}H-NMR (400 MHz, $(CD_3)_2SO$) δ 13.46 (s, 1H), 9.07 (d, J = 1.8 Hz, 1H), 8.79 (dd, J = 4.6, 1.8 Hz, 1H), 8.25-8.28 (m, 1H), 7.55 (dd, J = 8.3, 4.6 Hz, 1H).

^{13}C-NMR (101 MHz, $(CD_3)_2SO$) δ 166.32, 153.32, 150.26, 137.00, 126.61, 123.84.

Picolinic acid (**3ac**)[16]

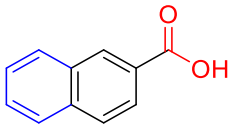


White solid, m.p. 128-129 °C.

^{1}H-NMR (400 MHz, $(CD_3)_2SO$) δ 12.96 (s, 1H), 8.70 (d, J = 4.6 Hz, 1H), 8.04 (d, J = 7.3 Hz, 1H), 7.96-8.00 (m, 1H), 7.62 (dd, J = 7.3, 5.5 Hz, 1H).

^{13}C-NMR (101 MHz, $(CD_3)_2SO$) δ 166.25, 149.48, 148.40, 137.58, 127.15, 124.74.

2-Naphthoic acid (**3ad**)[17]

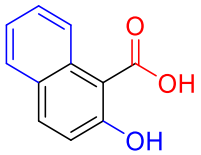


Buff solid, m.p. 176-177 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.69 (s, 1H), 8.74 (s, 1H), 8.14 (dd, J = 8.3, 1.8 Hz, 1H), 8.00 (d, J = 8.3 Hz, 1H), 7.92 (t, J = 7.8 Hz, 2H), 7.56-7.65 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 172.45, 136.13, 132.59, 132.34, 129.71, 128.84, 128.49, 127.98, 126.94, 126.65, 125.54.

2-Hydroxy-1-naphthoic acid (**3ae**)[18]

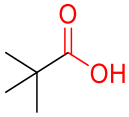


Off-white solid, m.p. 183-184 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 12.07 (s, 1H), 8.93 (d, J = 8.3 Hz, 1H), 7.98 (d, J = 9.2 Hz, 1H), 7.79 (d, J = 7.3 Hz, 1H), 7.63 (t, J = 7.8 Hz, 1H), 7.42 (t, J = 7.3 Hz, 1H), 7.20 (d, J = 9.2 Hz, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 176.55, 166.04, 138.55, 132.31, 129.35, 129.19, 128.86, 125.61, 124.20, 119.44, 103.38.

Pivalic acid (**3af**)[19]

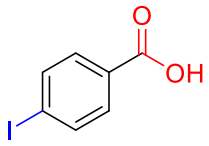


Colorless solid (at low temperature), m.p. 33-34 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.99 (s, 1H), 1.23 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 185.84, 38.74, 27.10.

4-Iodobenzoic acid (**3ag**)[20]

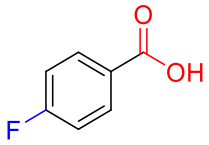


White solid, m.p. 207-208 °C.

^{1}H-NMR (400 MHz, $(CD_3)_2SO$) δ 13.20 (s, 1H), 7.88 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 8.3 Hz, 2H).

^{13}C-NMR (101 MHz, $(CD_3)_2SO$) δ 166.98, 137.63, 131.12, 130.31, 101.25.

4-Fluorobenzoic acid (**3ah**)[8]

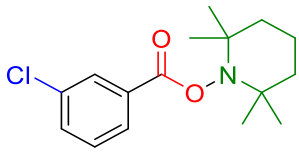


White solid, m.p. 127-128 °C.

^{1}H-NMR (400 MHz, $(CD_3)_2SO$) δ 13.05 (s, 1H), 8.00 (dd, J = 8.7, 6.0 Hz, 2H), 7.31 (t, J = 8.7 Hz, 2H).

^{13}C-NMR (101 MHz, $(CD_3)_2SO$) δ 166.42, 164.95 (d, $J_{C\text{-}F}$ = 250.2 Hz), 132.14 (d, $J_{C\text{-}F}$ = 9.6 Hz), 127.39 (d, $J_{C\text{-}F}$ = 2.9 Hz), 115.65 (d, $J_{C\text{-}F}$ = 22.0 Hz).

2,2,6,6-tetramethylpiperidin-1-yl 3-chlorobenzoate (**5a**)[21]



Red-orange liquid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ δ 8.02 (t, J = 1.7 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.54-7.56 (m, 1H), 7.41 (t, J = 7.9 Hz, 1H), 1.68-1.79 (m, 3H), 1.45-1.49 (m, 3H), 1.27 (s, 6H), 1.11 (s, 6H).

^{13}C-NMR (151 MHz, $CDCl_3$) δ 165.40, 134.76, 133.09, 131.59, 129.95, 129.72, 127.85, 60.68, 39.21, 32.08, 21.03, 17.11.

HRMS (ESI): calcd for $C_{16}H_{22}ClNO_2Na$: *m/z* 318.1231 $[M + Na]^+$, found 318.1229.

IR (KBr): 2975, 2935, 1751, 1575, 1281, 1231 cm^{-1}.

8. Supplementary References:

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14. Tanemura, K. & Rohand, T. Activated charcoal as an effective additive for alkaline and acidic hydrolysis of esters in water. *Tetrahedron Lett.* **61**, 152467 (2020).

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18. Li, Z., Park, H. S., Qiao, J. X., Yeung, K.-S. & Yu, J.-Q. Ligand-enabled C–H hydroxylation with Aqueous H_2O_2 at room temperature. *J. Am. Chem. Soc.* **144**, 18109–18116 (2022).

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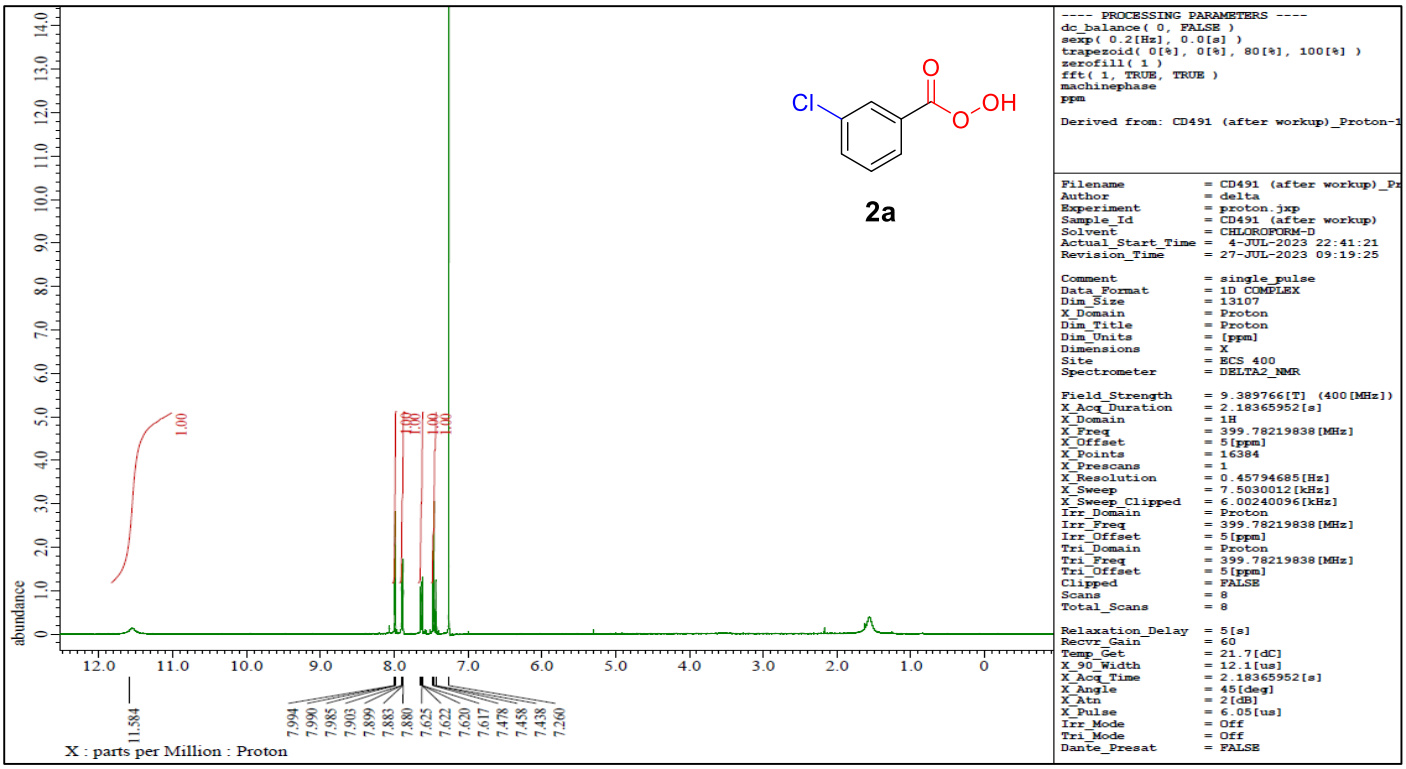
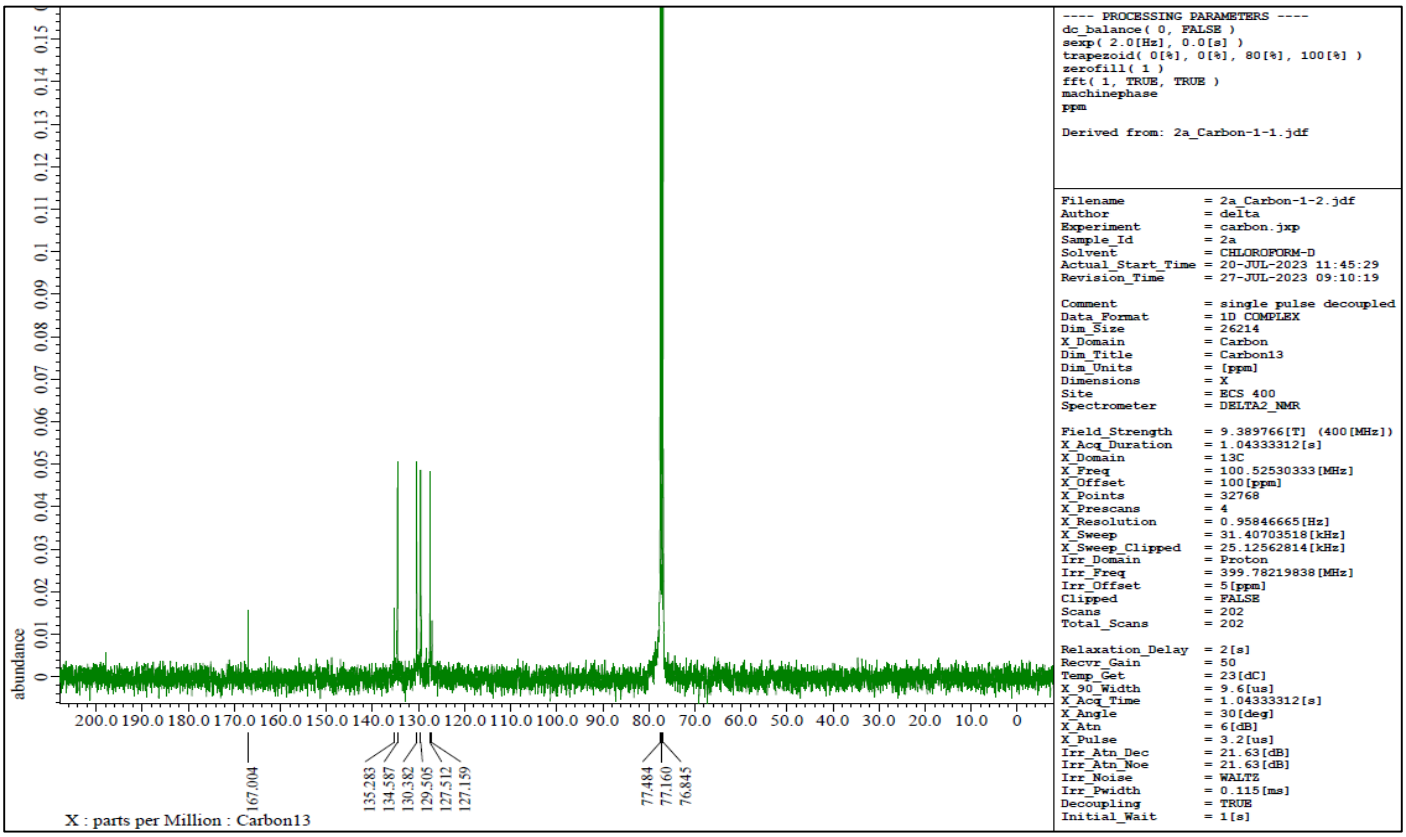
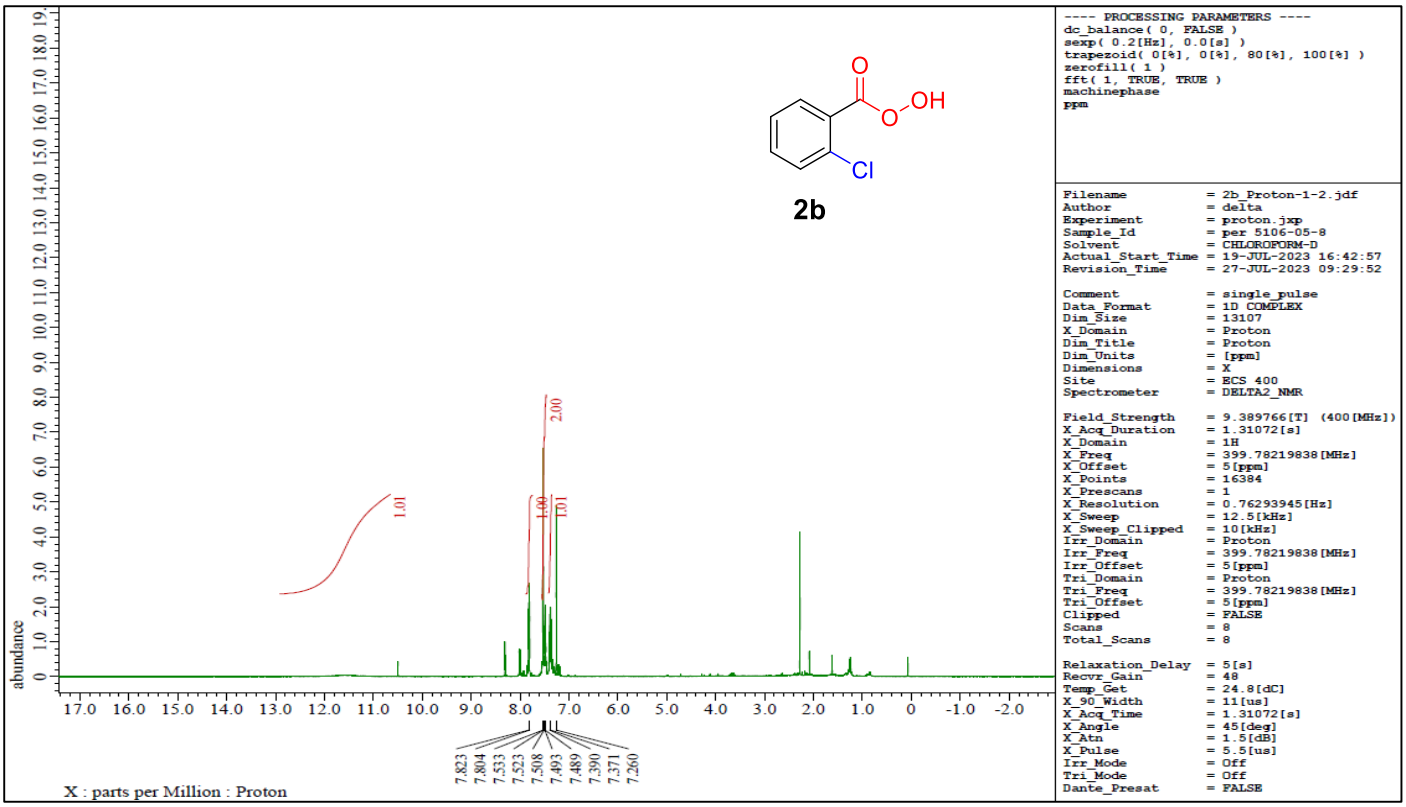
9. NMR Spectra



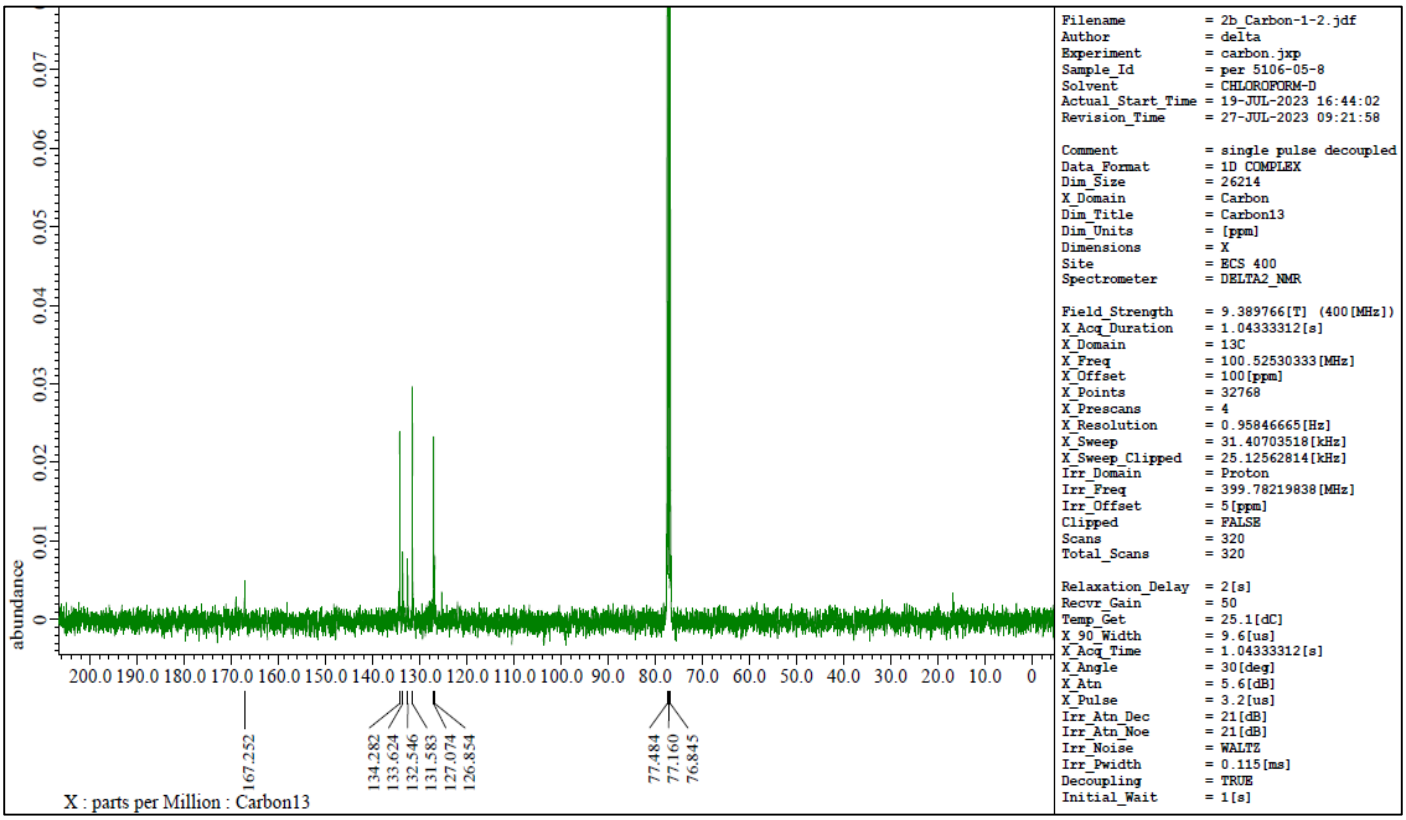
Compound **2a** (^{1}H NMR, 400 MHz, $CDCl_3$).



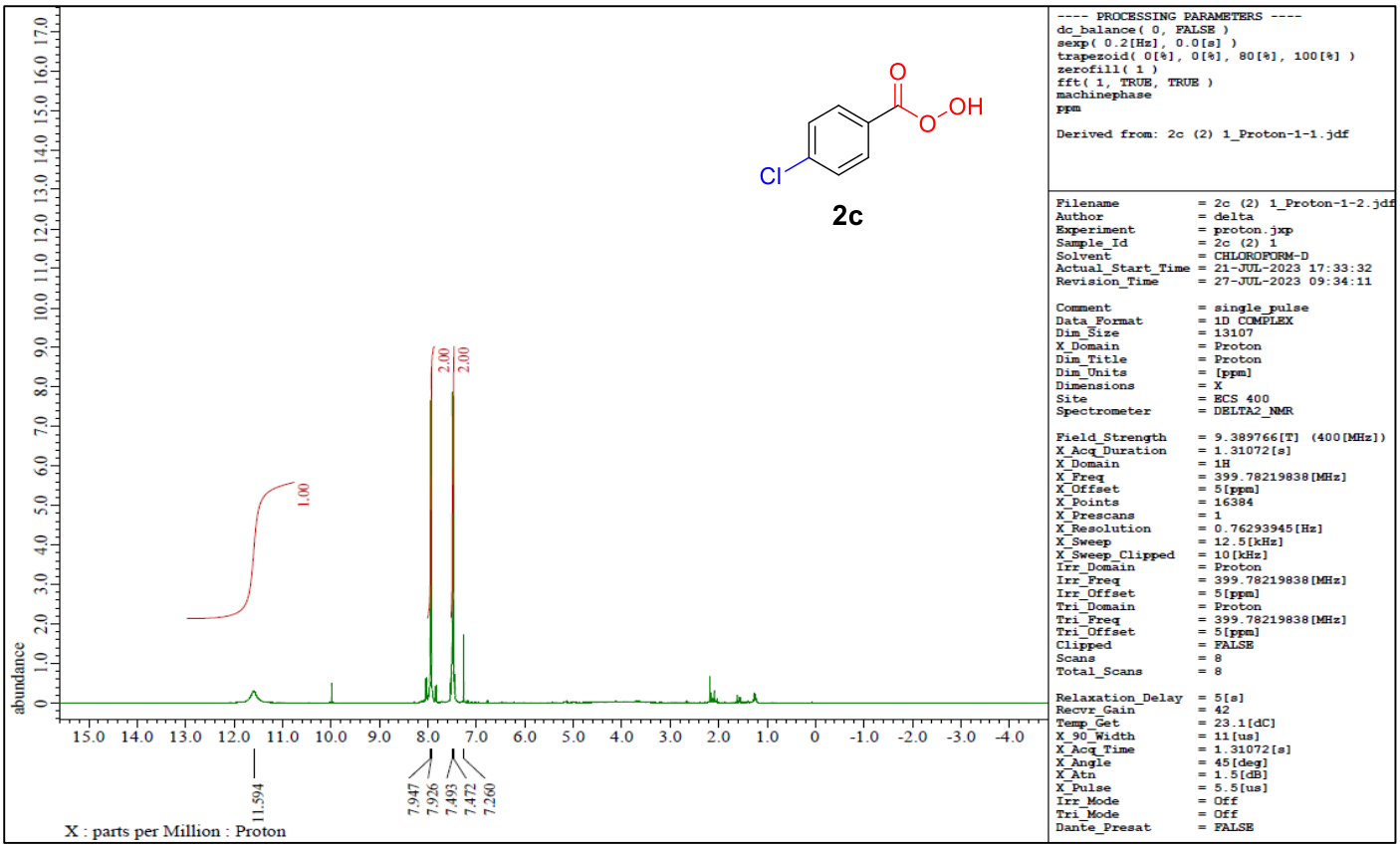
Compound **2a** (^{13}C NMR, 101 MHz, $CDCl_3$).



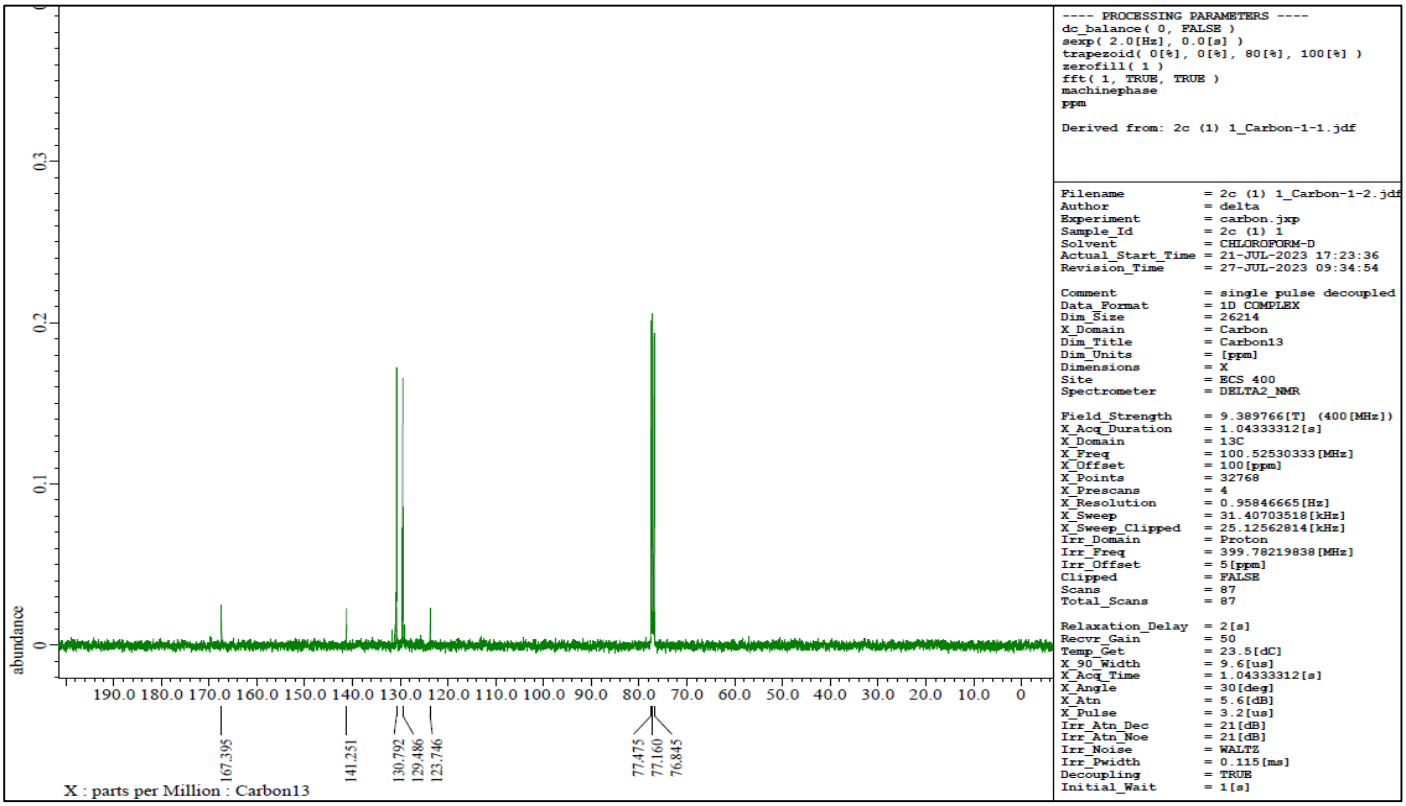
Compound **2b** (^{1}H NMR, 400 MHz, $CDCl_3$).



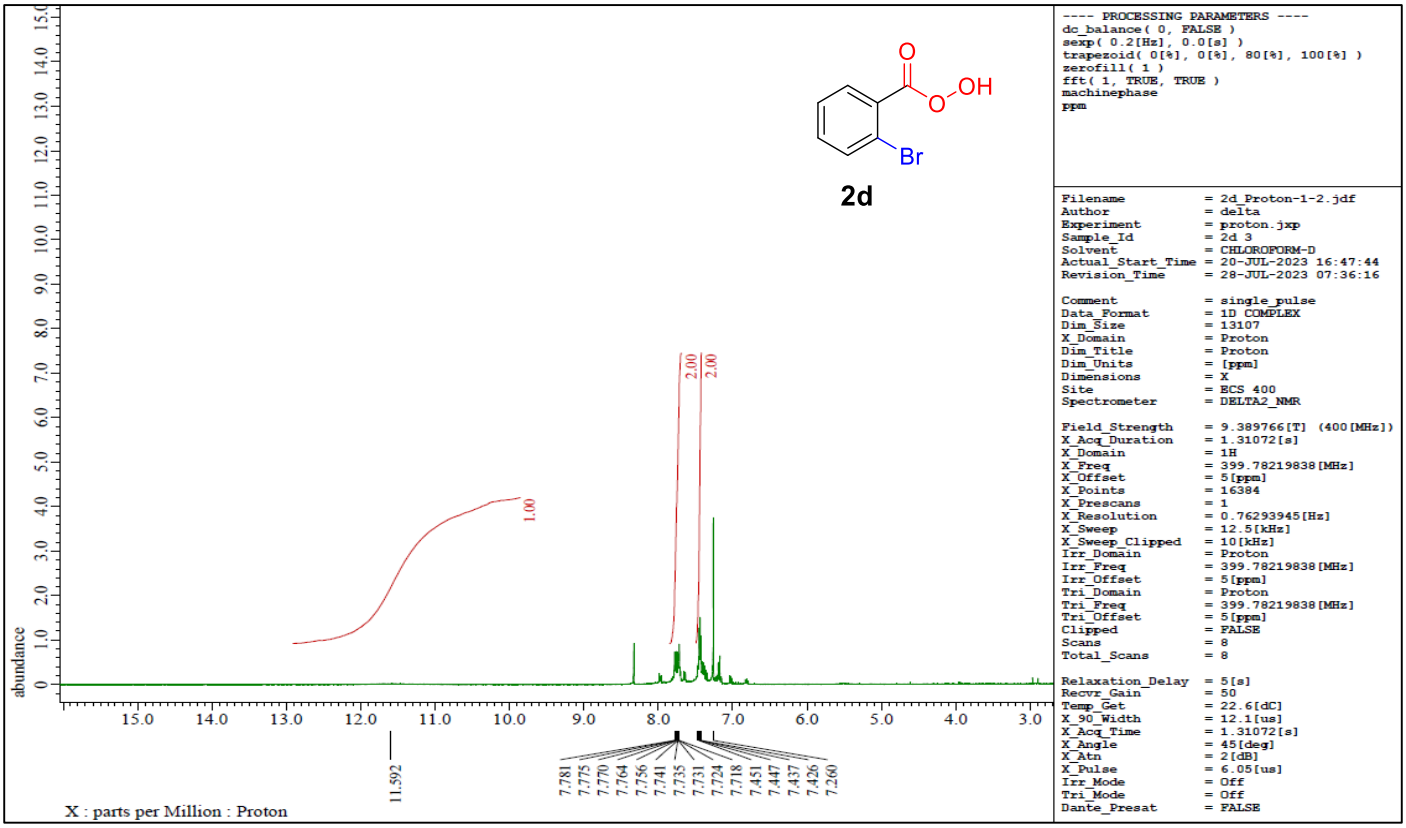
Compound **2b** (^{13}C NMR, 101 MHz, $CDCl_3$).



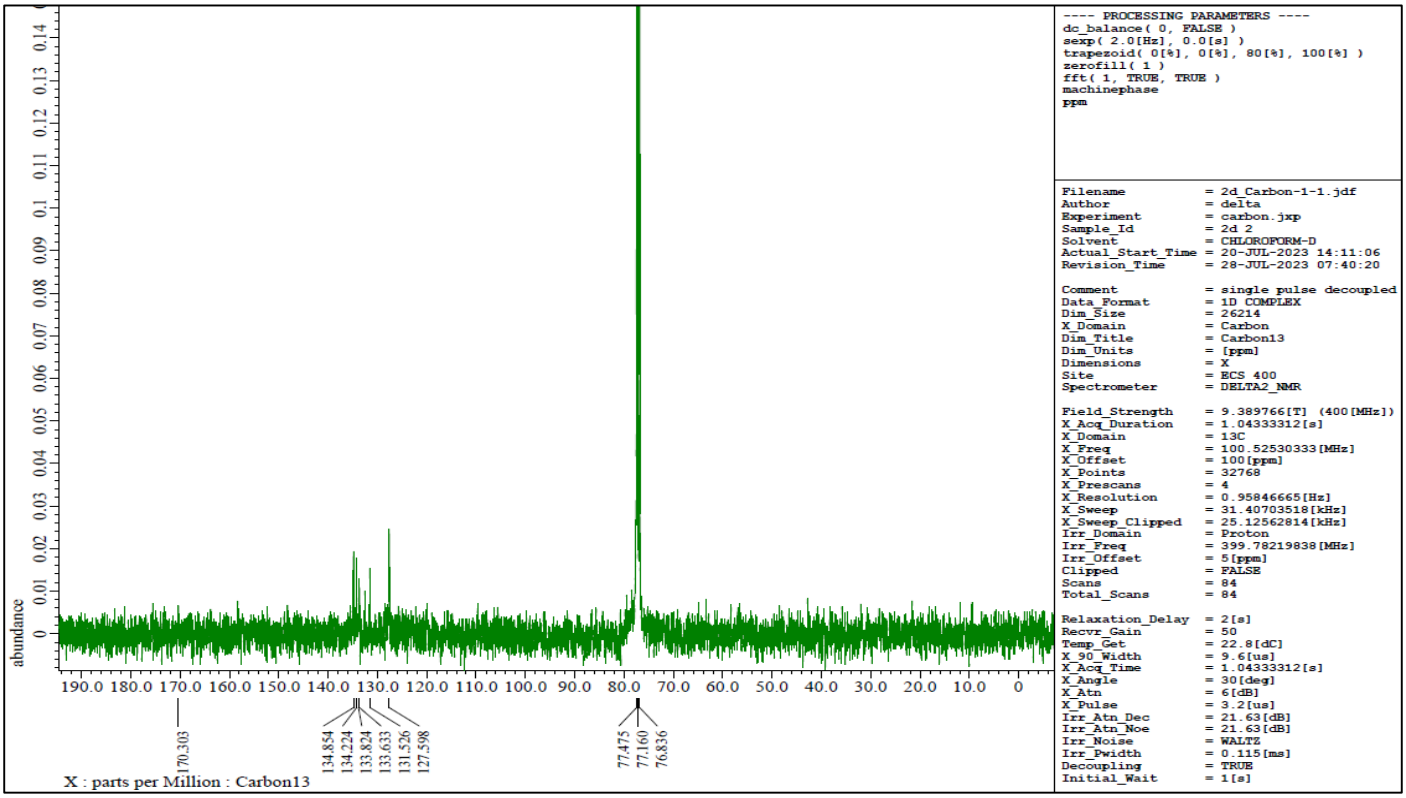
Compound **2c** (^{1}H NMR, 400 MHz, $CDCl_3$).



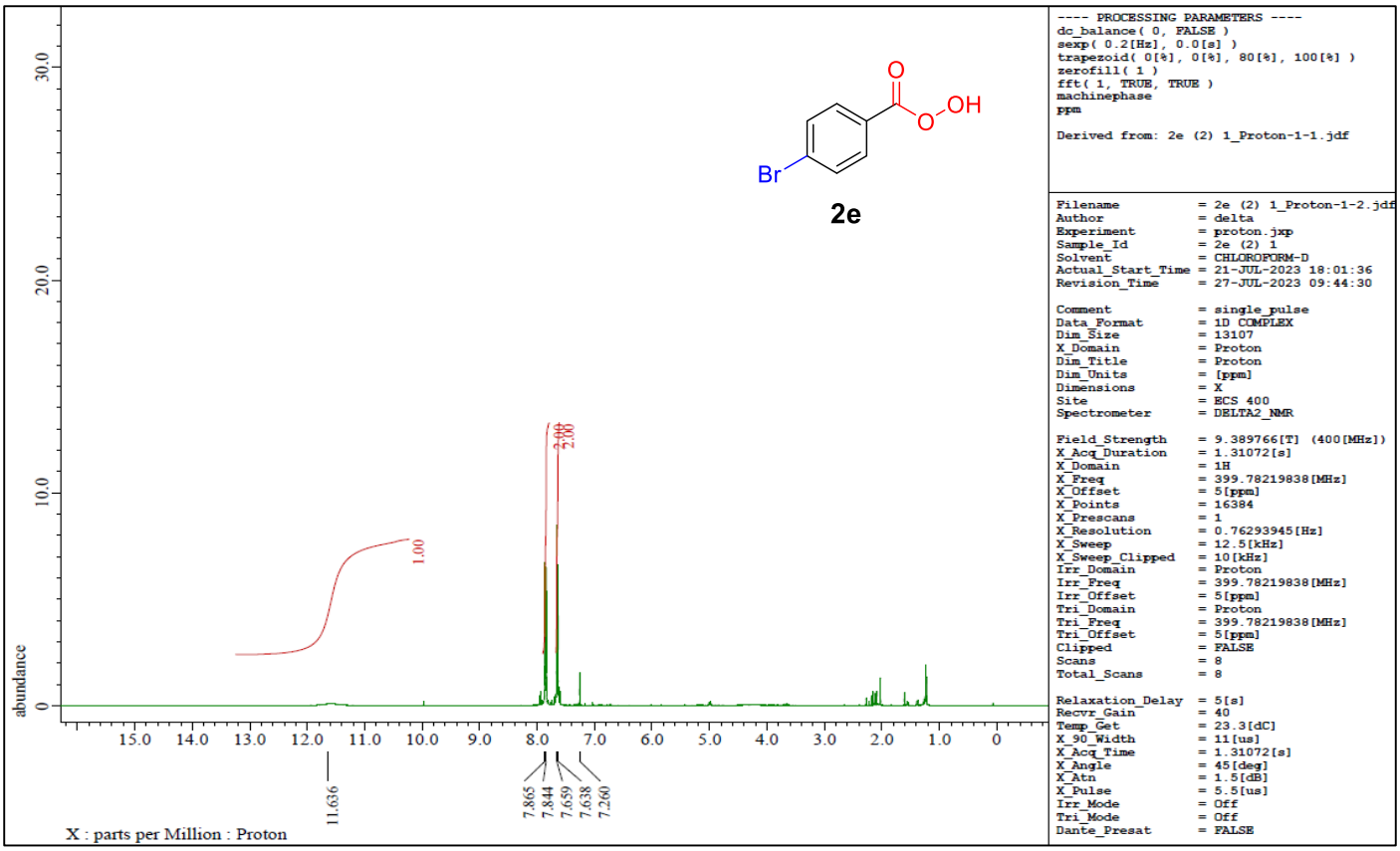
Compound 2**c** (^{13}C NMR, 101 MHz, $CDCl_3$).



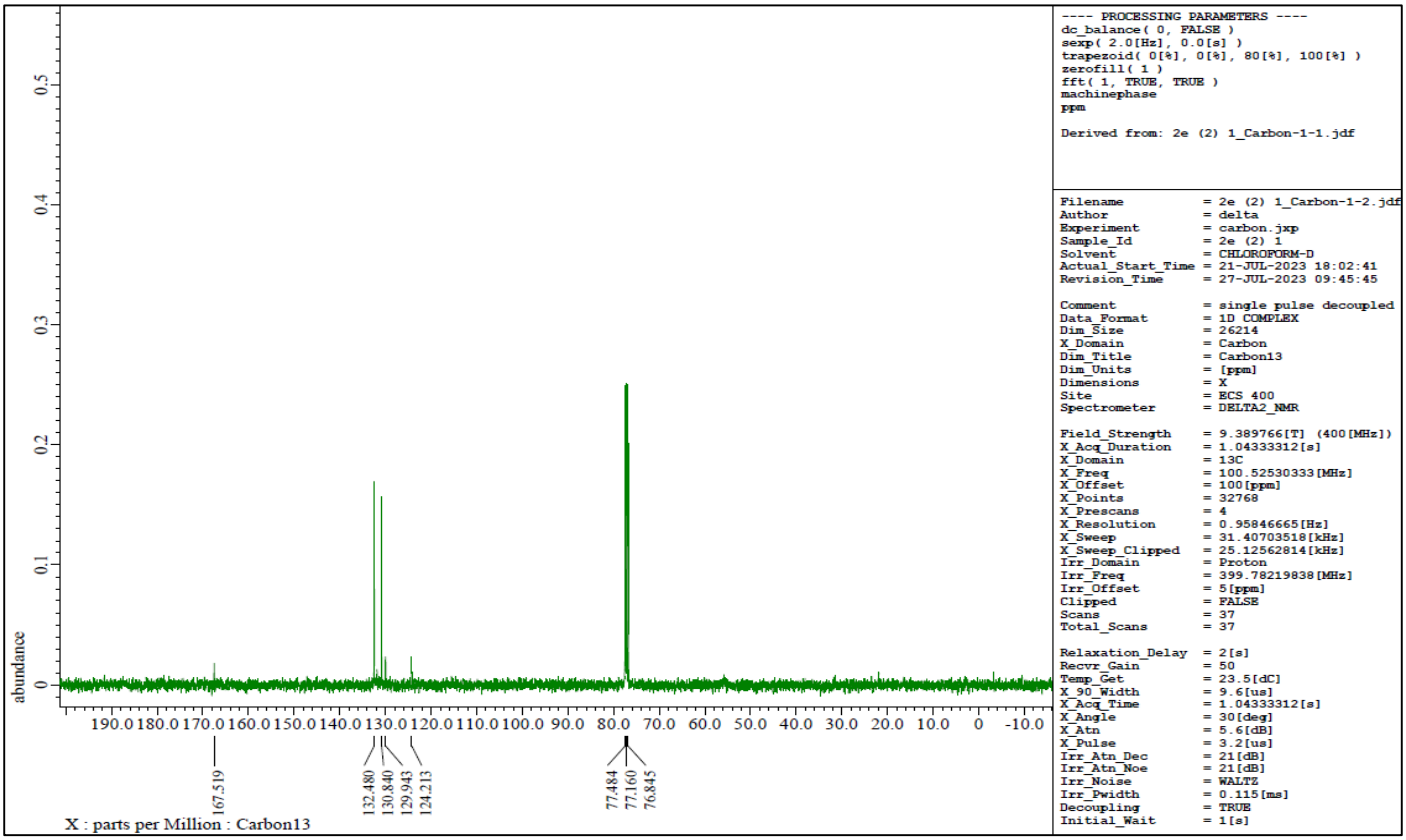
Compound **2d** (^{1}H NMR, 400 MHz, $CDCl_3$).



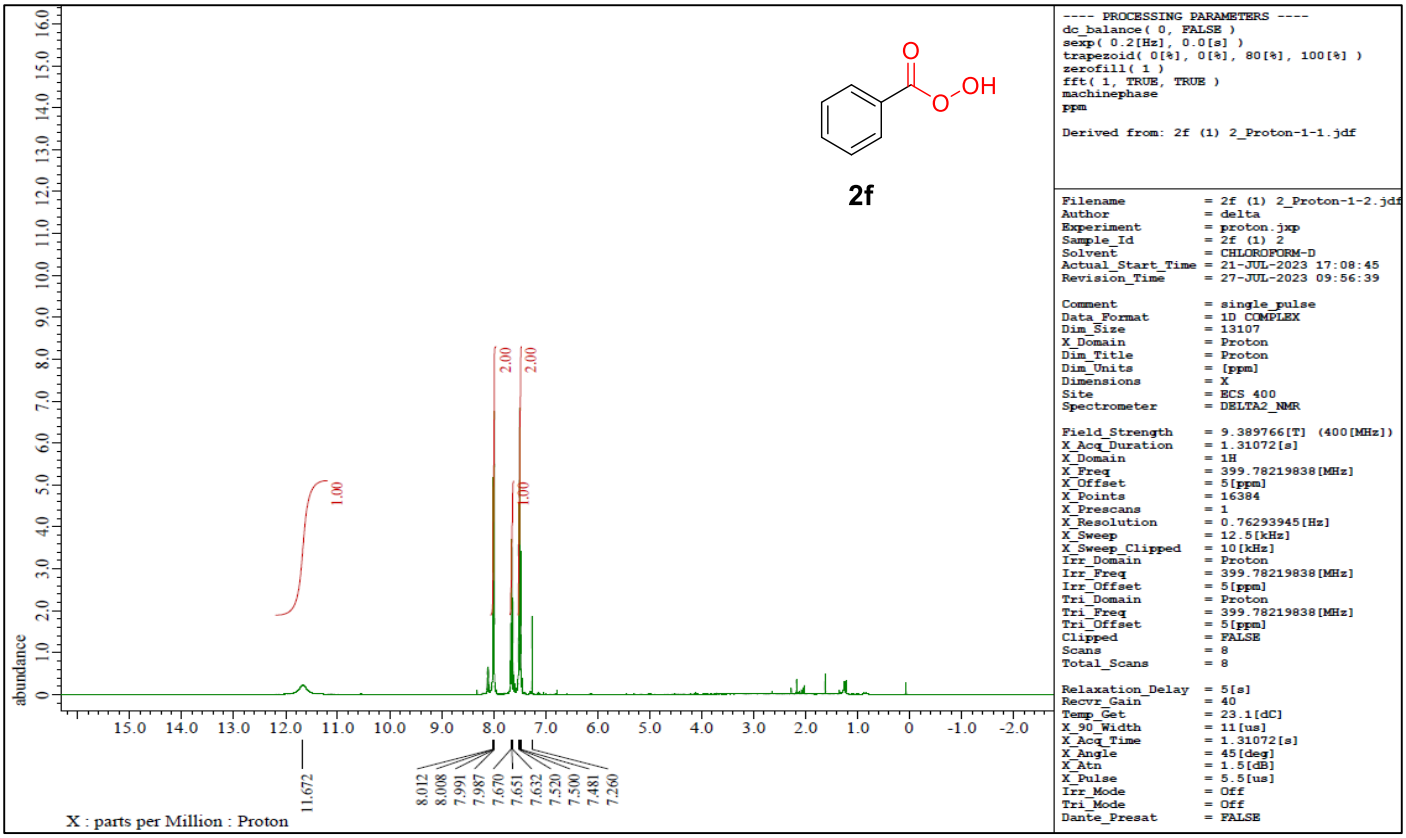
Compound **2d** (^{13}C NMR, 101 MHz, $CDCl_3$).



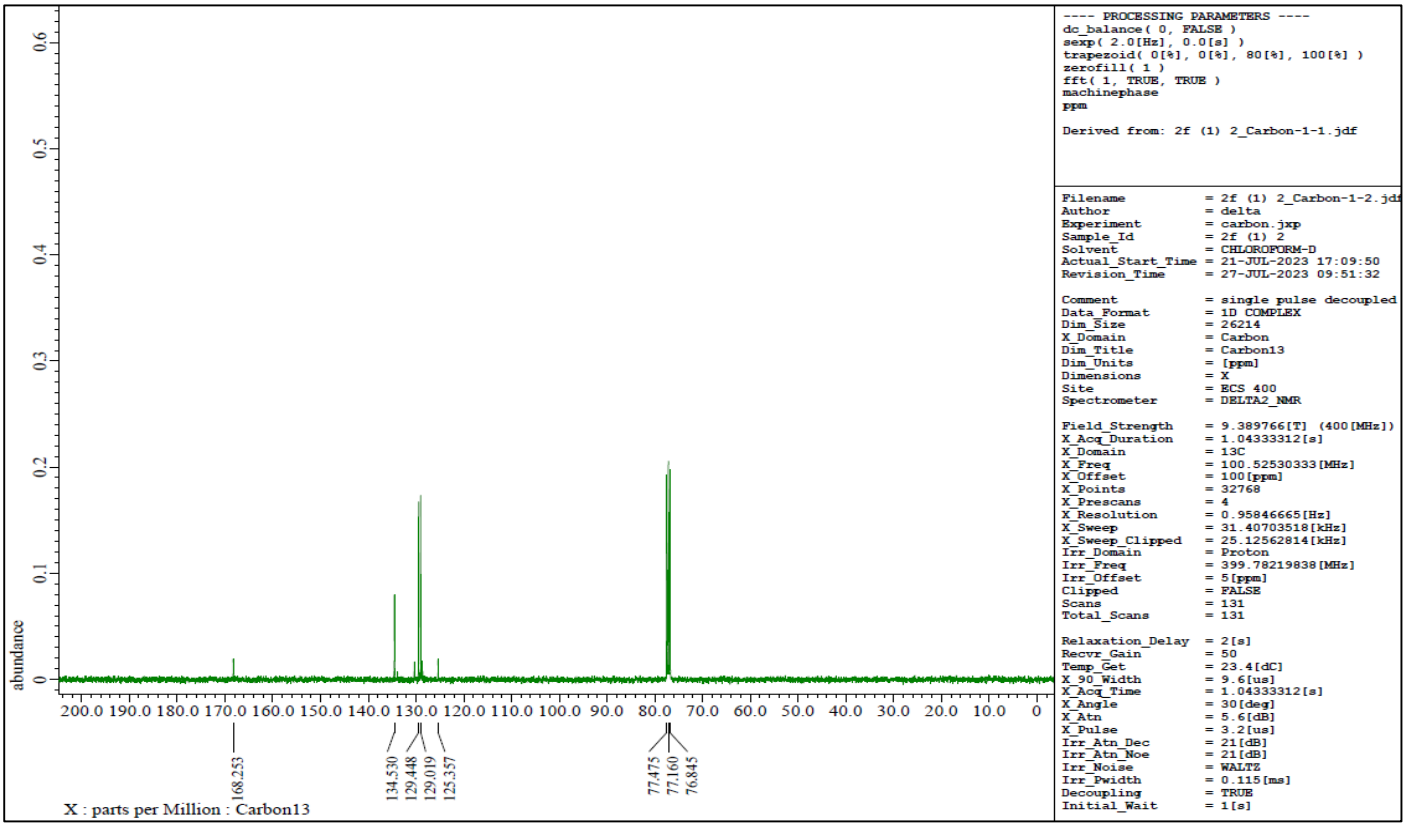
Compound **2e** (^{1}H NMR, 400 MHz, $CDCl_3$).



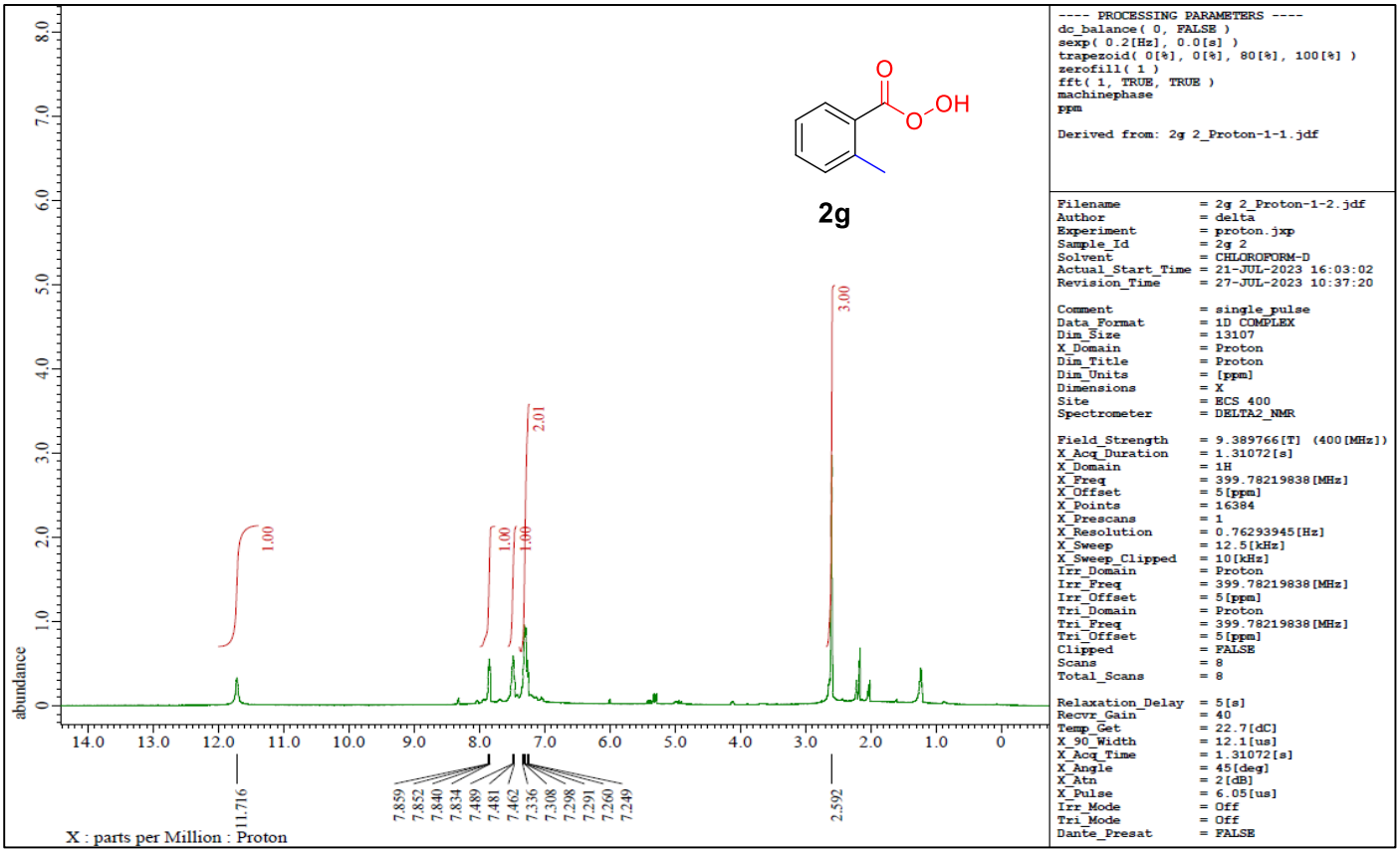
Compound **2e** (^{13}C NMR, 101 MHz, $CDCl_3$).



Compound **2f** (^{1}H NMR, 400 MHz, $CDCl_3$).



Compound **2f** (^{13}C NMR, 101 MHz, $CDCl_3$).




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: 2g 2_Proton-1-1.jdf

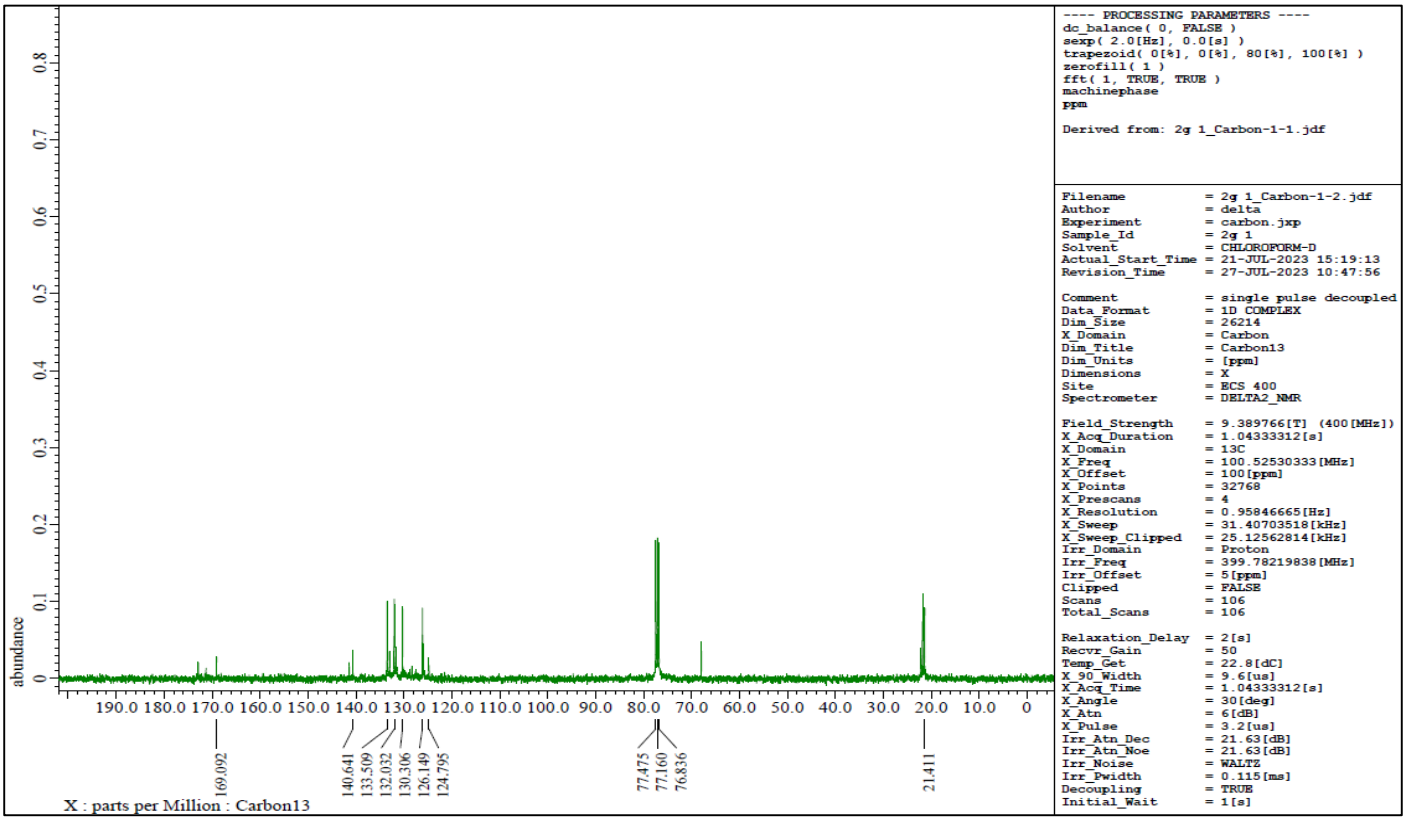
Filename            = 2g 2_Proton-1-2.jdf
Author              = delta
Experiment          = proton.jxp
Sample_Id           = 2g 2
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 21-JUL-2023 16:03:02
Revision_Time       = 27-JUL-2023 10:37:20

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = ECS 400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 1.31072[s]
X_Domain            = 1H
X_Freq              = 399.78219838[MHz]
X_Offset            = 5[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.76293945[Hz]
X_Sweep             = 12.5[kHz]
X_Sweep_Clipped     = 10[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 399.78219838[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 40
Temp_Get            = 22.7[dC]
X_90_Width          = 12.1[us]
X_Acq_Time          = 1.31072[s]
X_Angle             = 45[deg]
X_Atn               = 2[dB]
X_Pulse             = 6.05[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
```

Compound **2g** (^{1}H NMR, 400 MHz, $CDCl_3$).




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: 2g 1_Carbon-1-1.jdf

Filename            = 2g 1_Carbon-1-2.jdf
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = 2g 1
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 21-JUL-2023 15:19:13
Revision_Time       = 27-JUL-2023 10:47:56

Comment             = single pulse decoupled
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = ECS 400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 1.04333312[s]
X_Domain            = 13C
X_Freq              = 100.52530333[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 0.95846665[Hz]
X_Sweep             = 31.40703518[kHz]
X_Sweep_Clipped     = 25.12562814[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 106
Total_Scans         = 106

Relaxation_Delay    = 2[s]
Recvr_Gain          = 50
Temp_Get            = 22.8[dC]
X_90_Width          = 9.6[us]
X_Acq_Time          = 1.04333312[s]
X_Angle             = 30[deg]
X_Atn               = 6[dB]
X_Pulse             = 3.2[us]
Irr_Atn_Dec         = 21.63[dB]
Irr_Atn_Noe         = 21.63[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 0.115[ms]
Decoupling          = TRUE
Initial_Wait        = 1[s]
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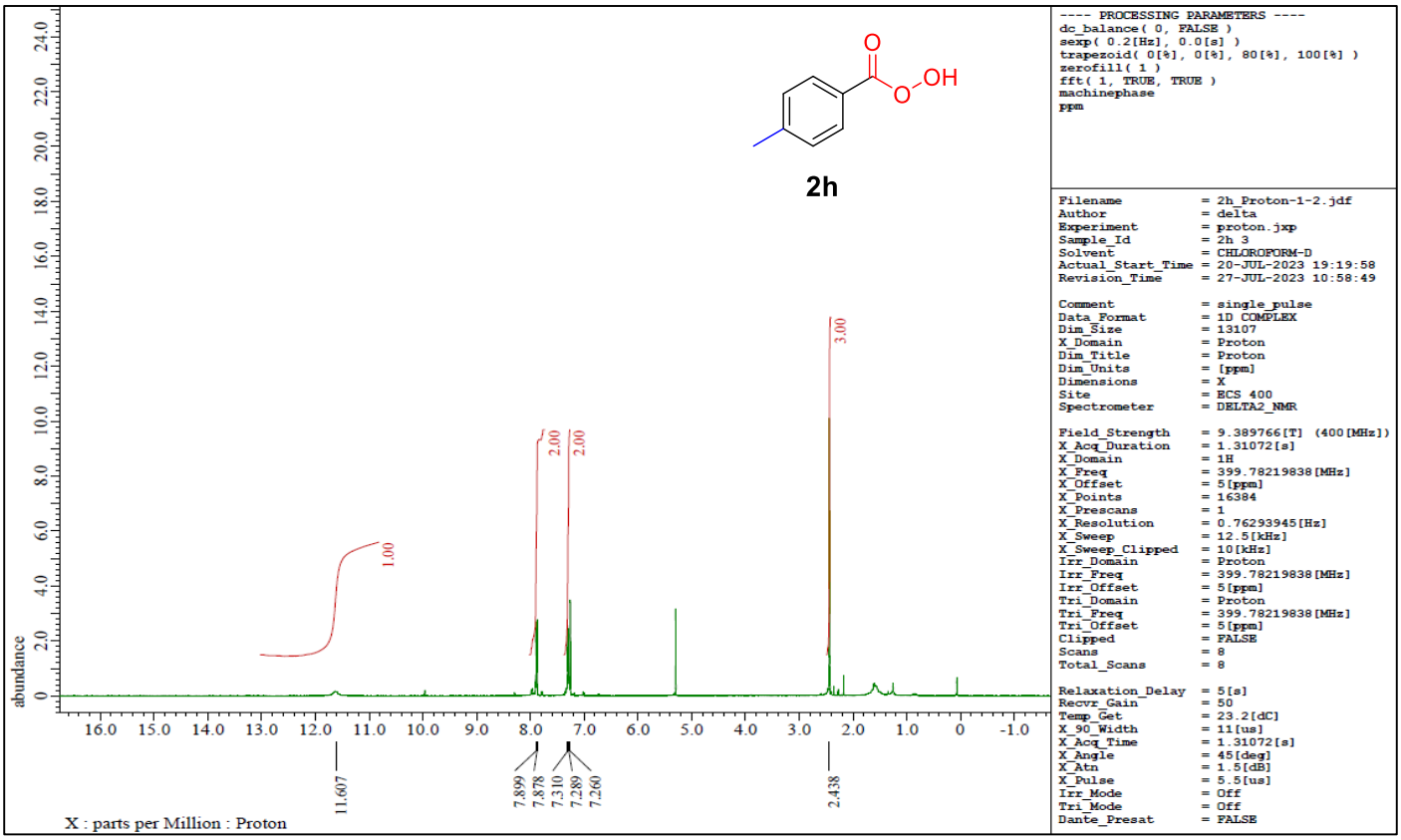
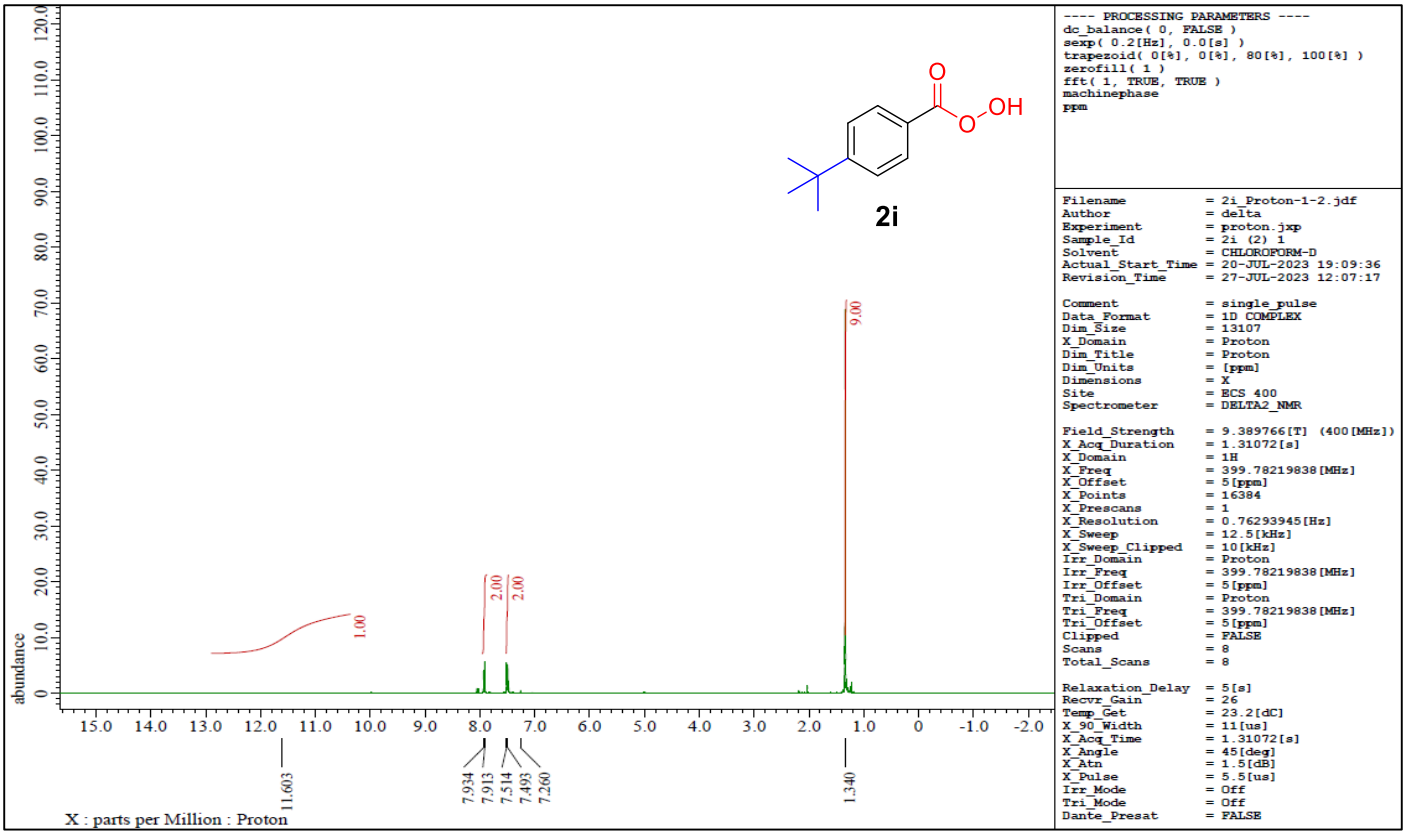
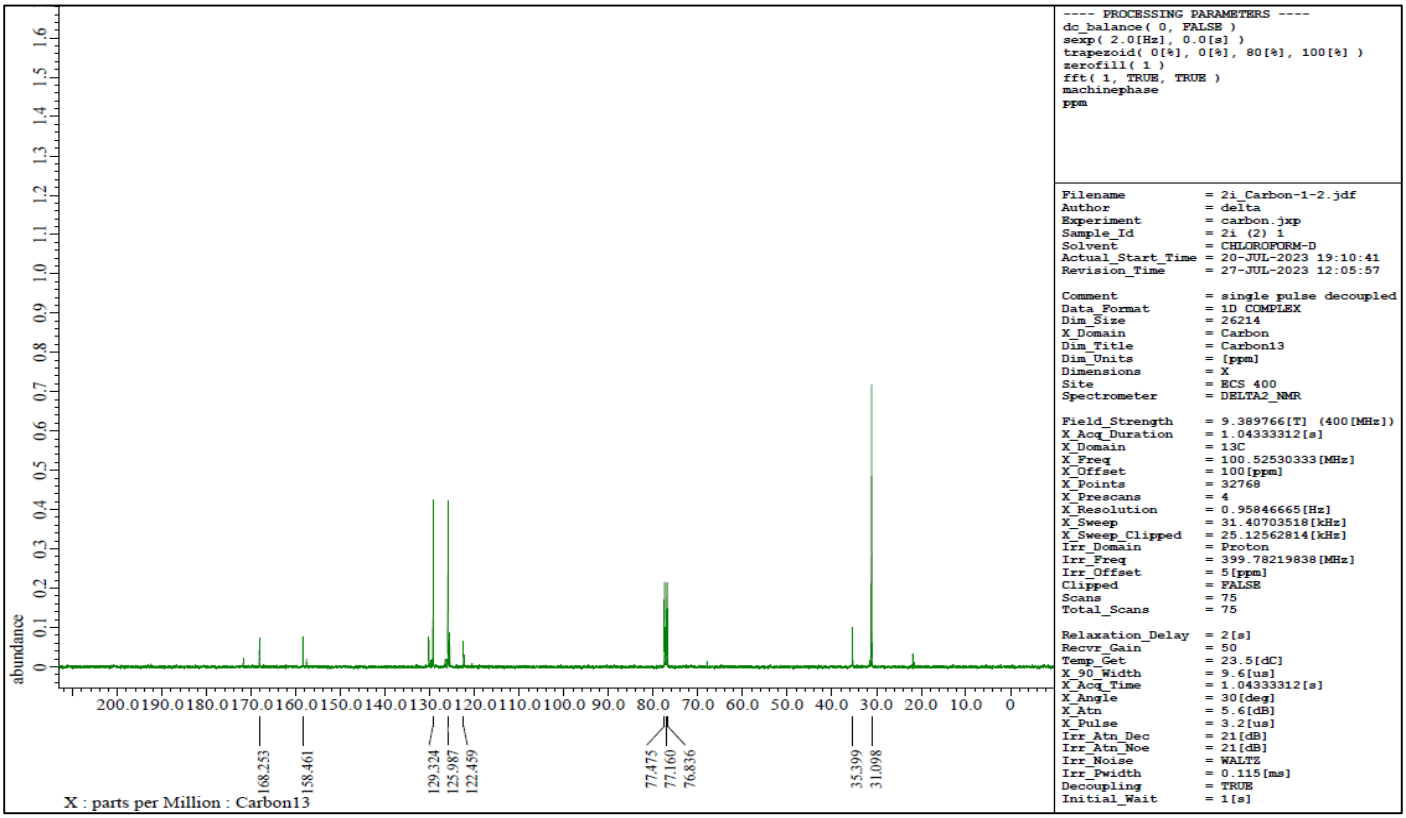
Compound **2g** (^{13}C NMR, 101 MHz, $CDCl_3$).



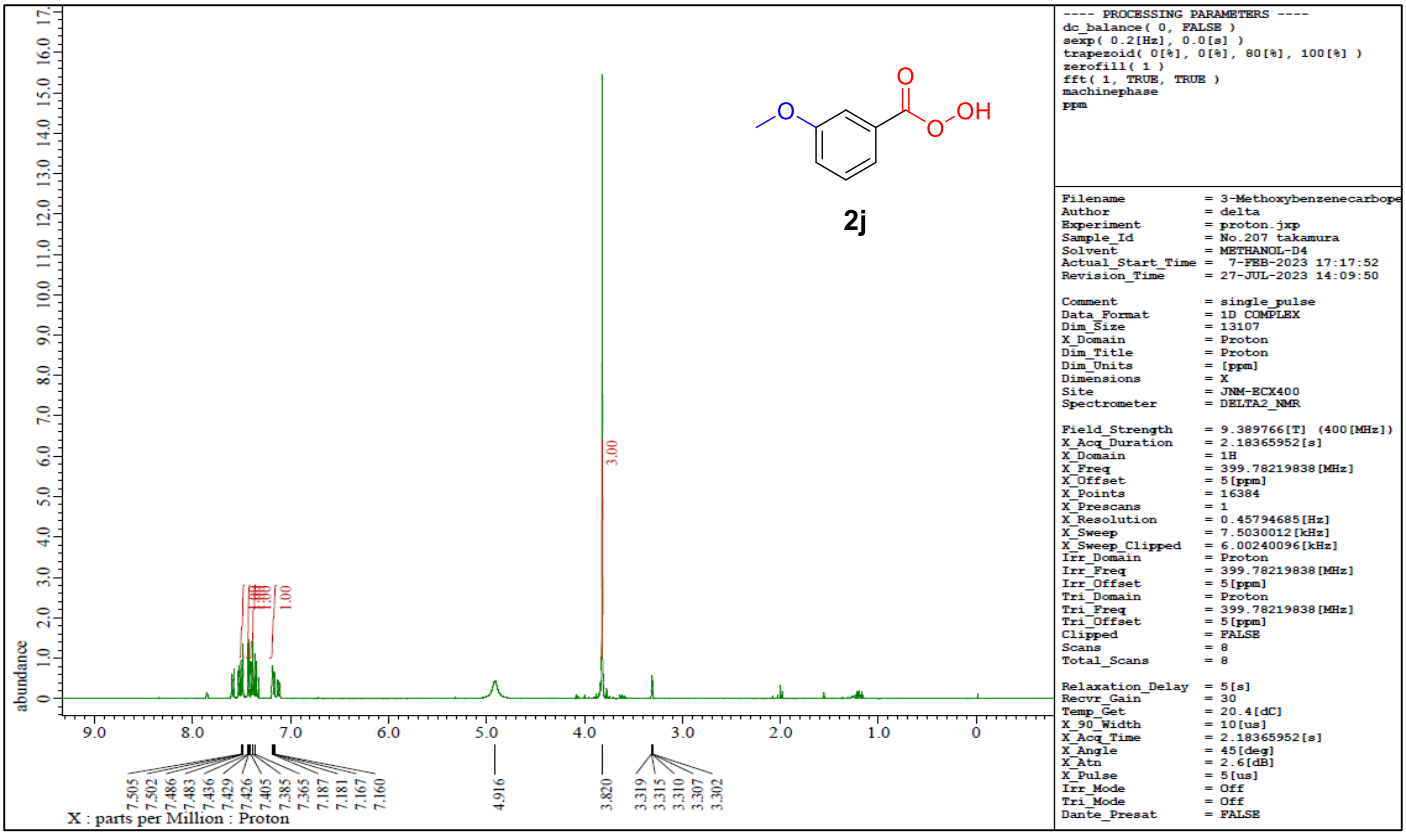
Compound **2h** (^{1}H NMR, 400 MHz, $CDCl_3$).



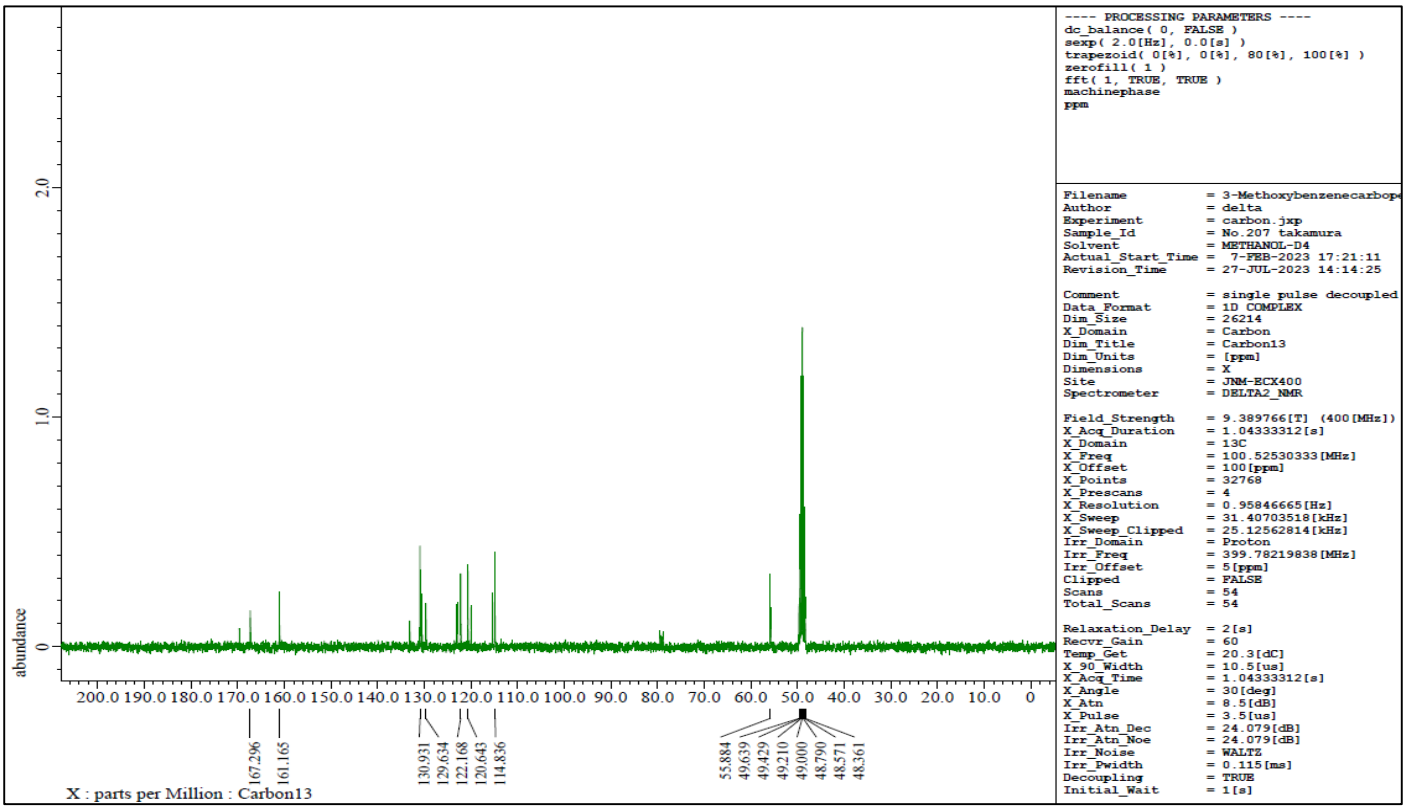
Compound **2i** (^{1}H NMR, 400 MHz, $CDCl_3$).



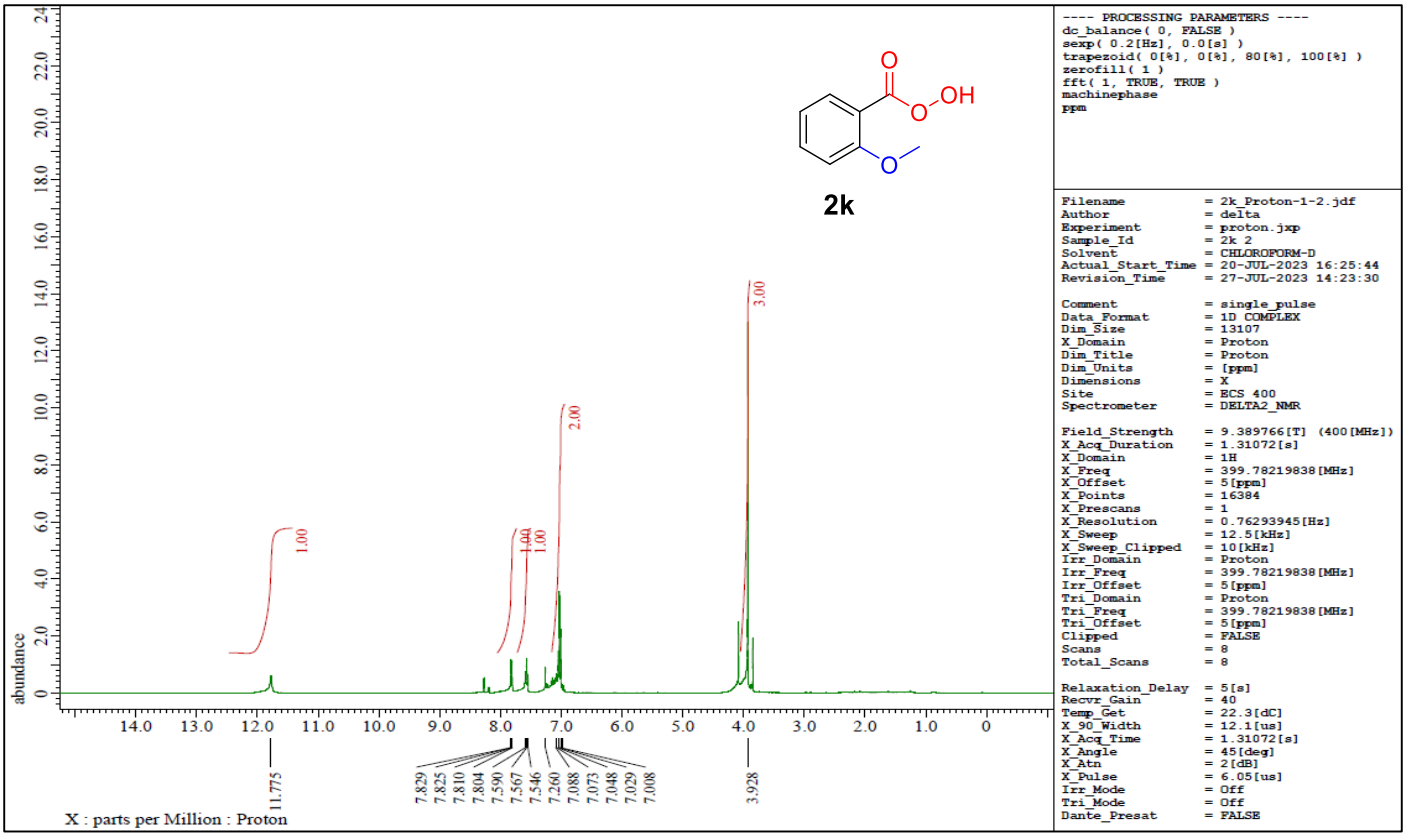
Compound **2i** (^{13}C NMR, 101 MHz, $CDCl_3$).



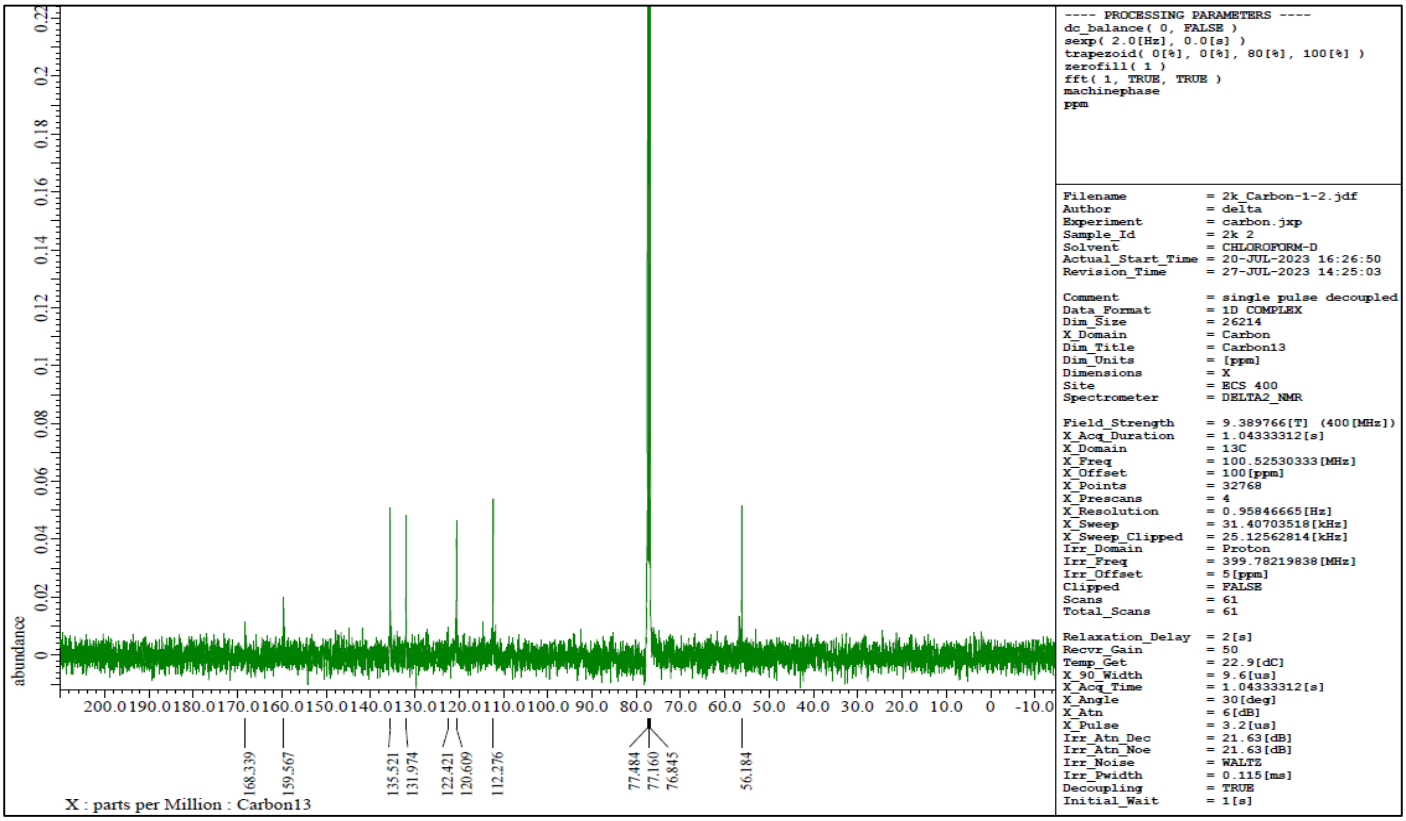
Compound **2j** (^{1}H NMR, 400 MHz, CD_3OD).



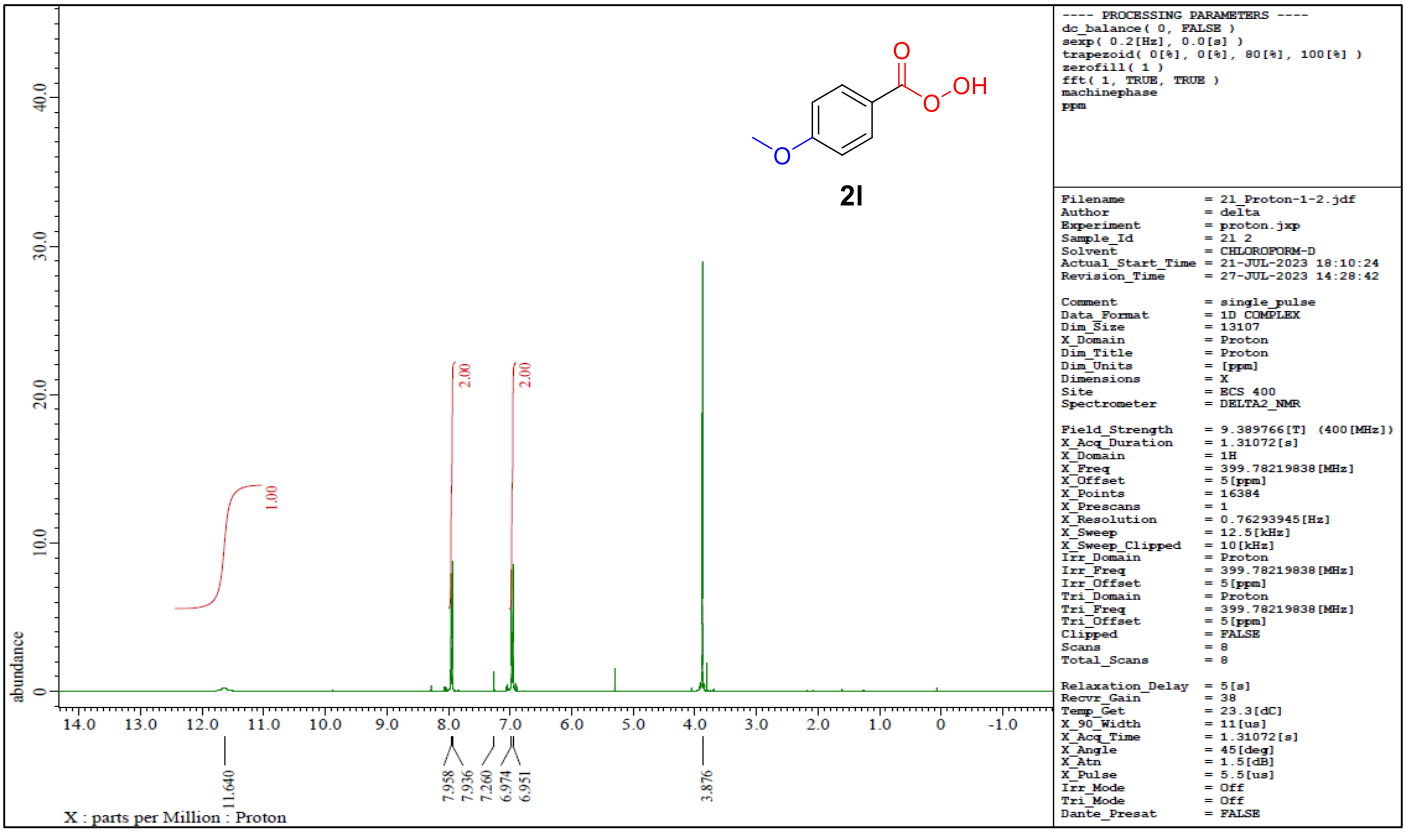
Compound **2j** (^{13}C NMR, 101 MHz, CD_3OD).



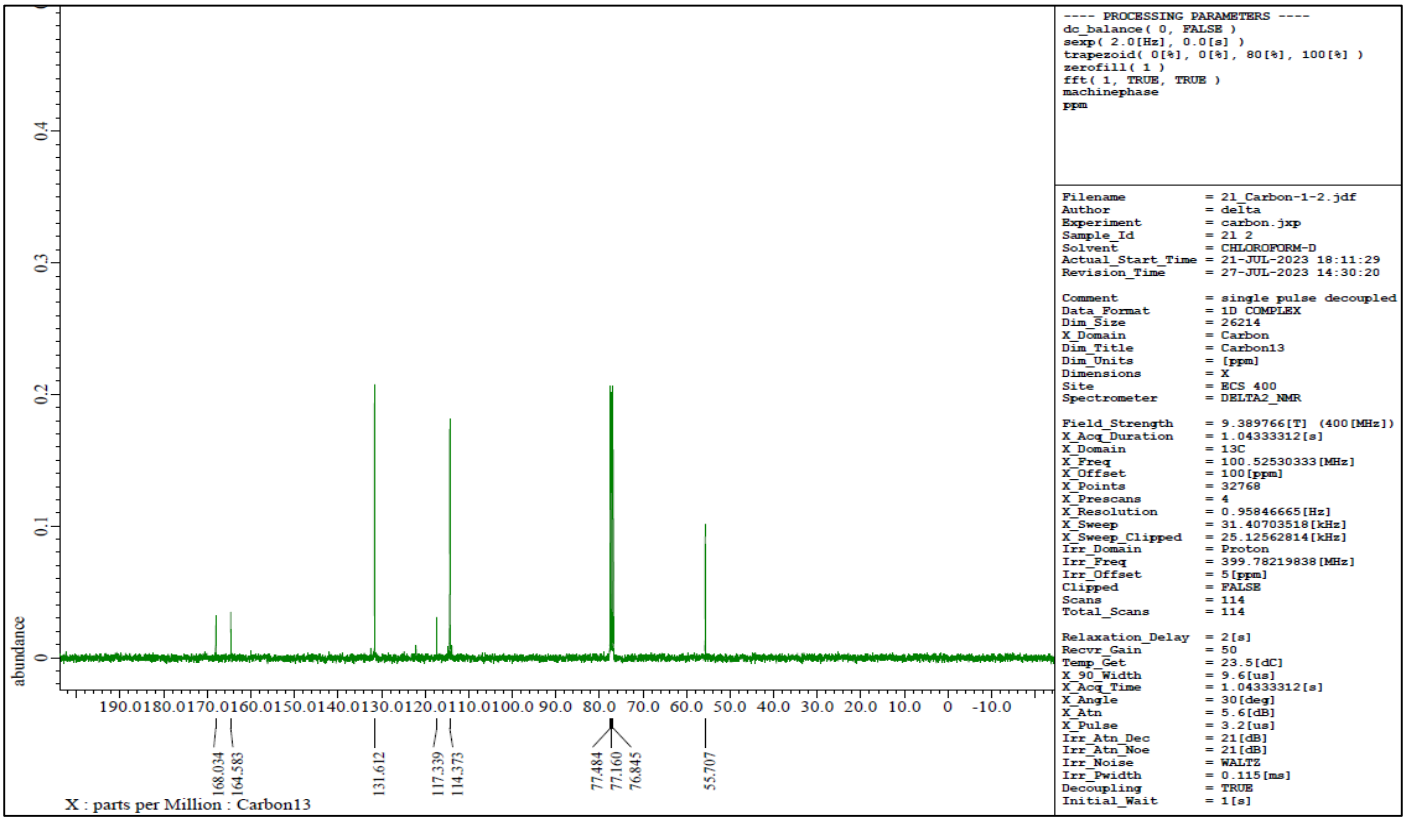
Compound **2k** (^{1}H NMR, 400 MHz, $CDCl_3$).



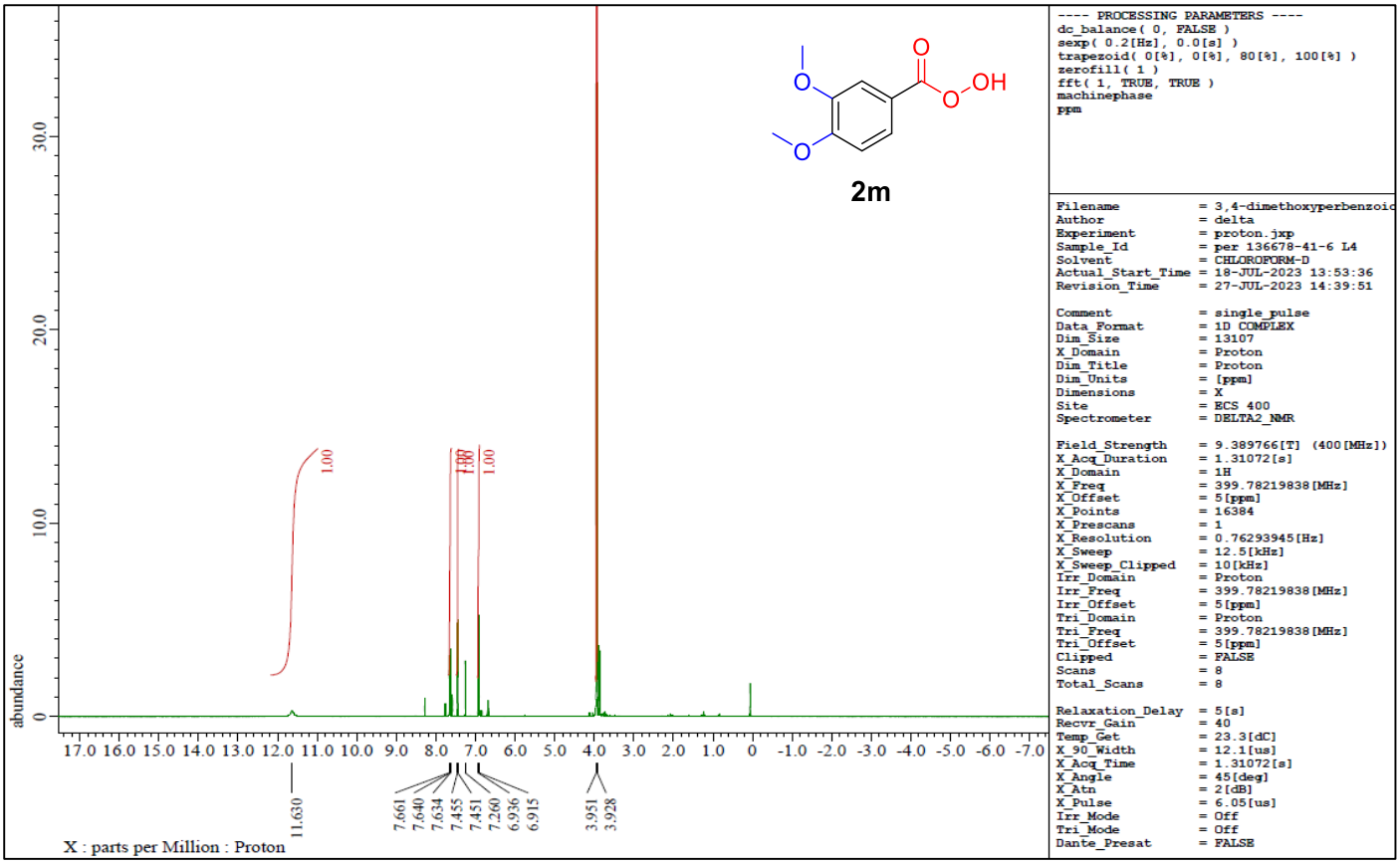
Compound **2k** (^{13}C NMR, 101 MHz, $CDCl_3$).



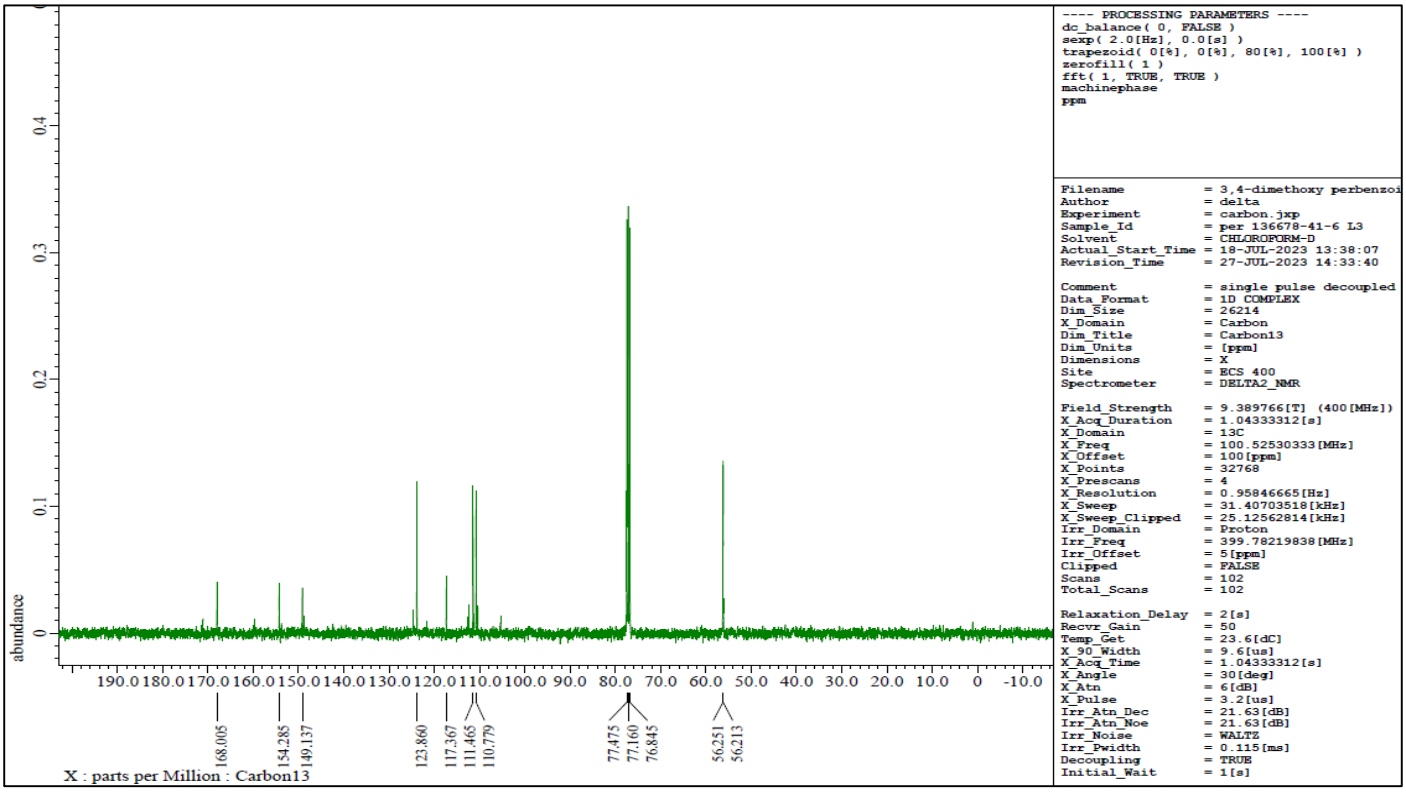
Compound **2l** (^{1}H NMR, 400 MHz, $CDCl_3$).



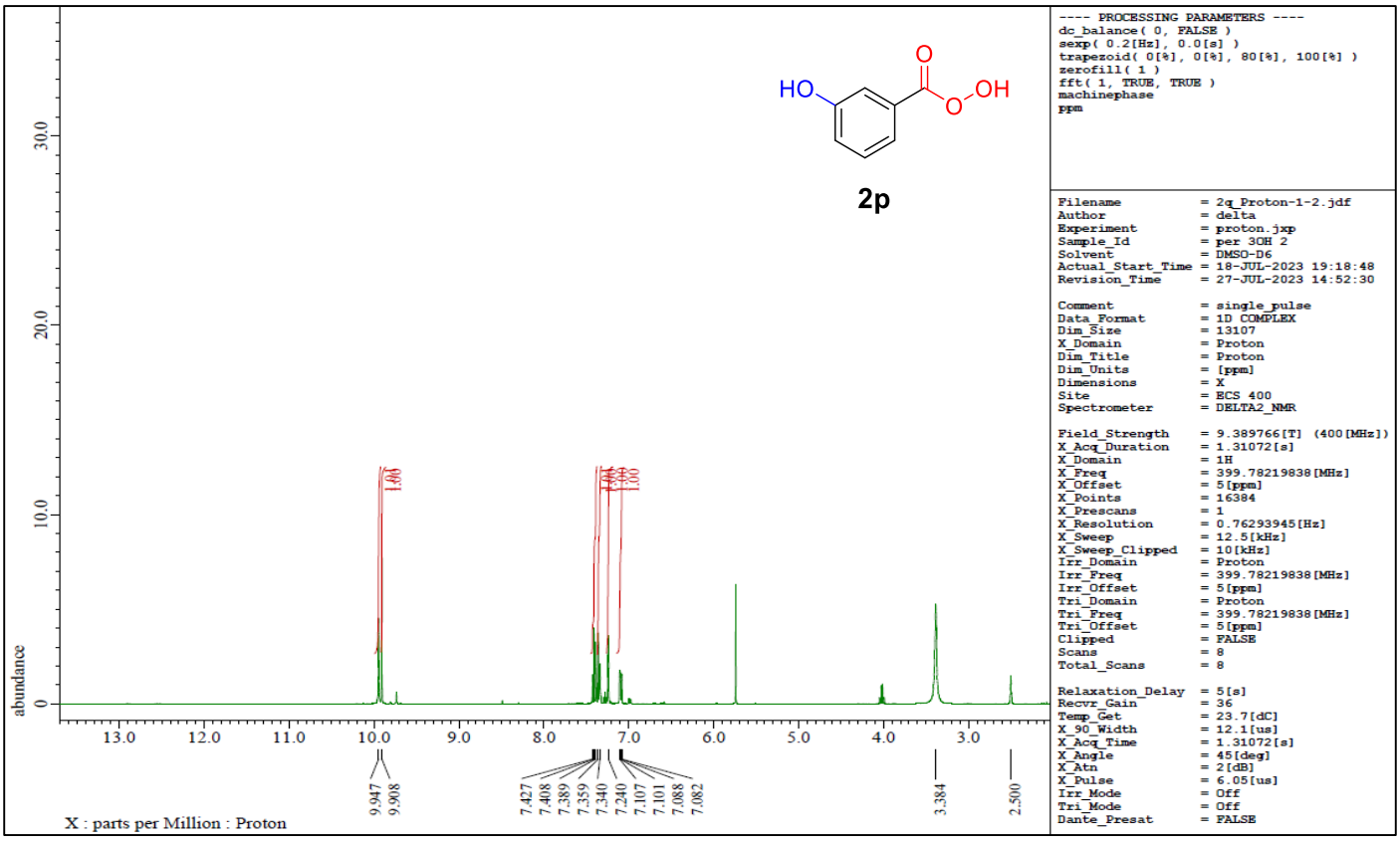
Compound **2l** (^{13}C NMR, 101 MHz, $CDCl_3$).



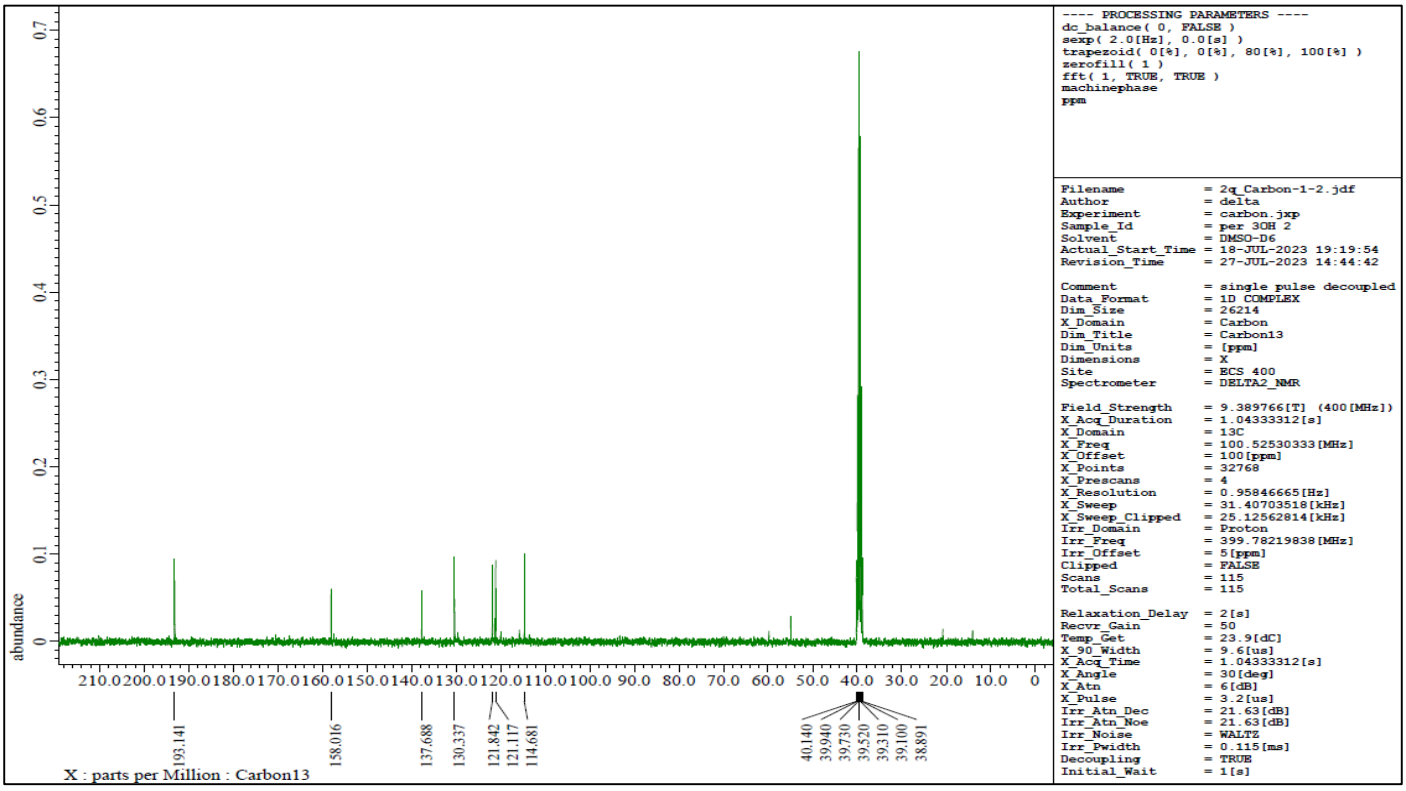
Compound **2m** (^{1}H NMR, 400 MHz, $CDCl_3$).



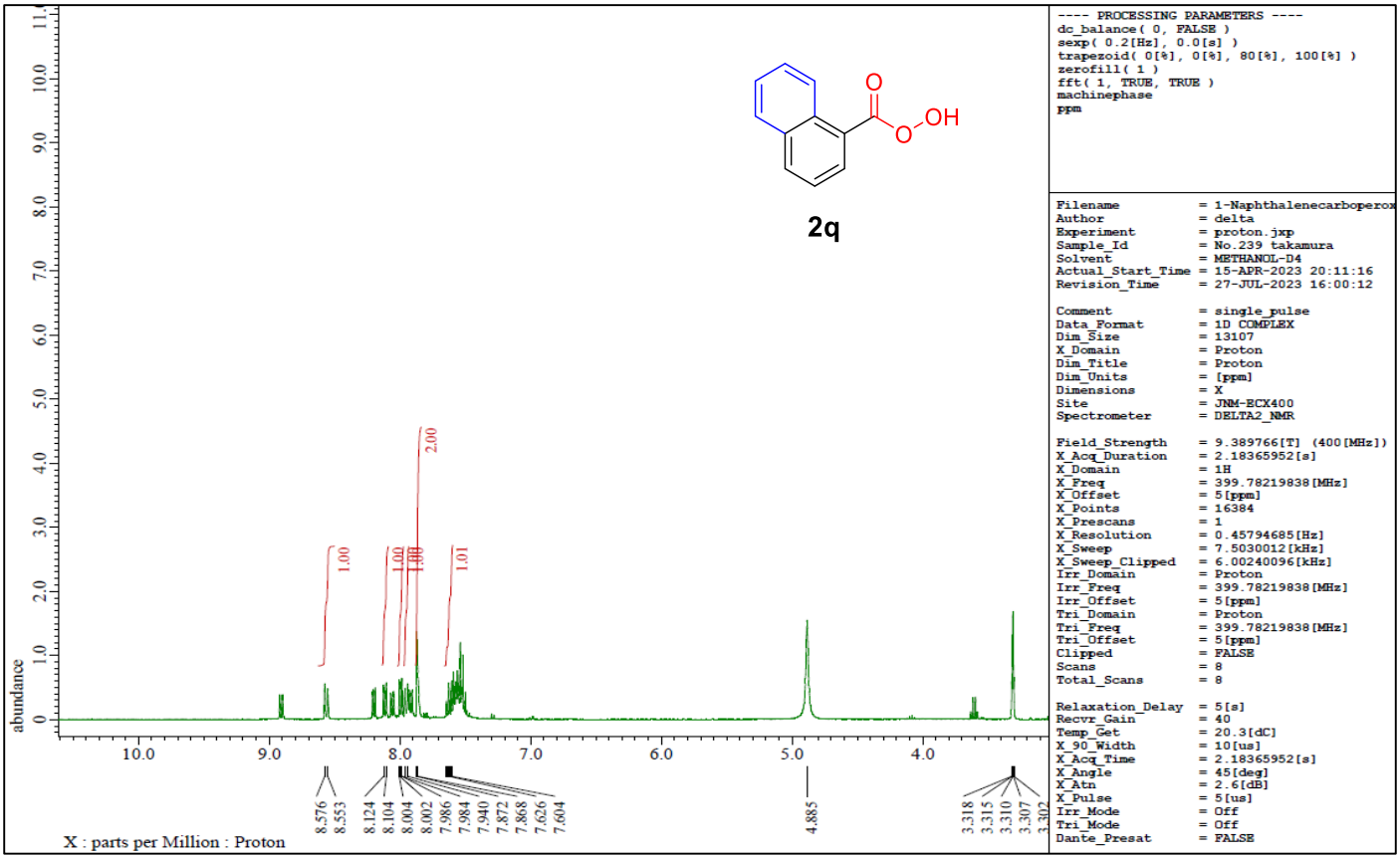
Compound **2m** (^{13}C NMR, 101 MHz, $CDCl_3$).



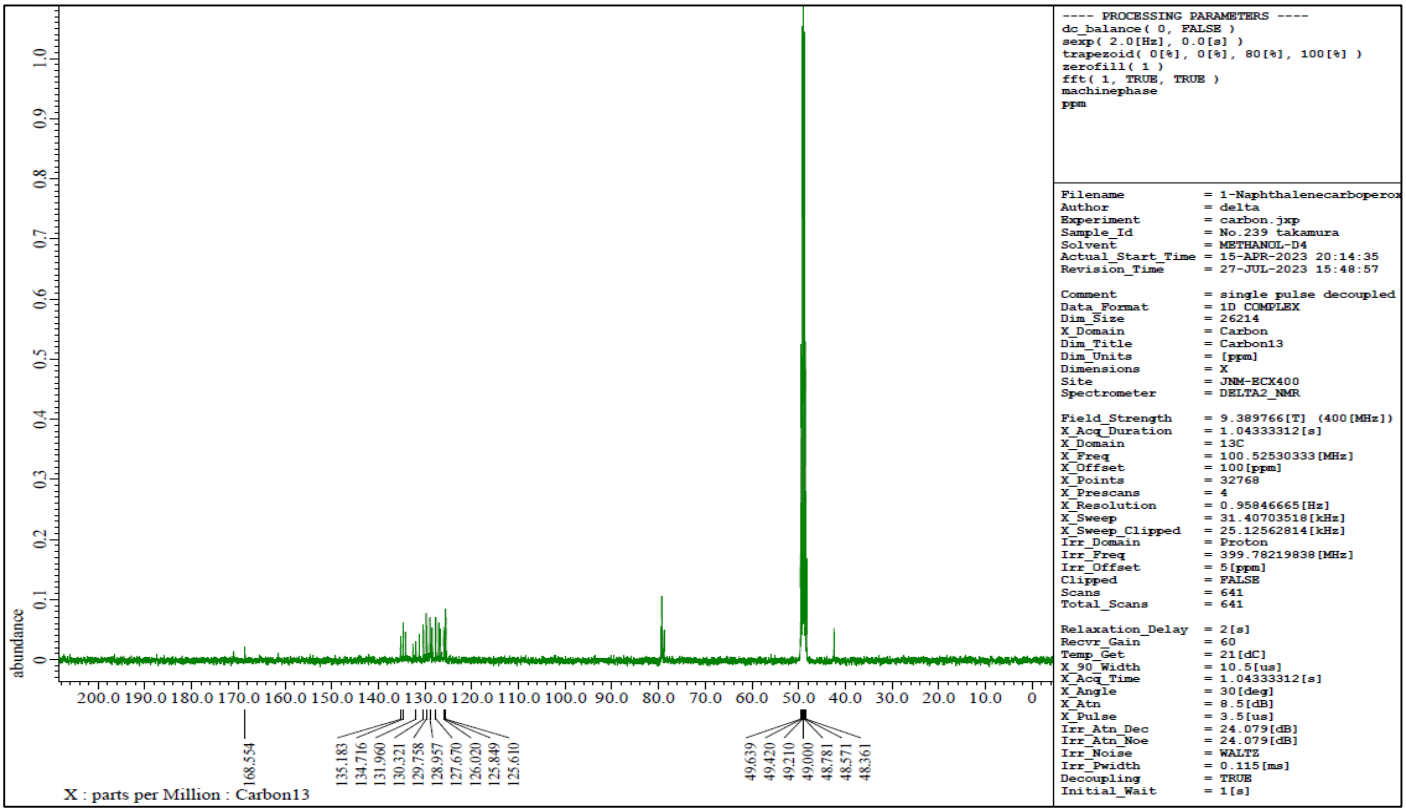
Compound **2p** (^{1}H NMR, 400 MHz, $(CD_3)_2SO$).



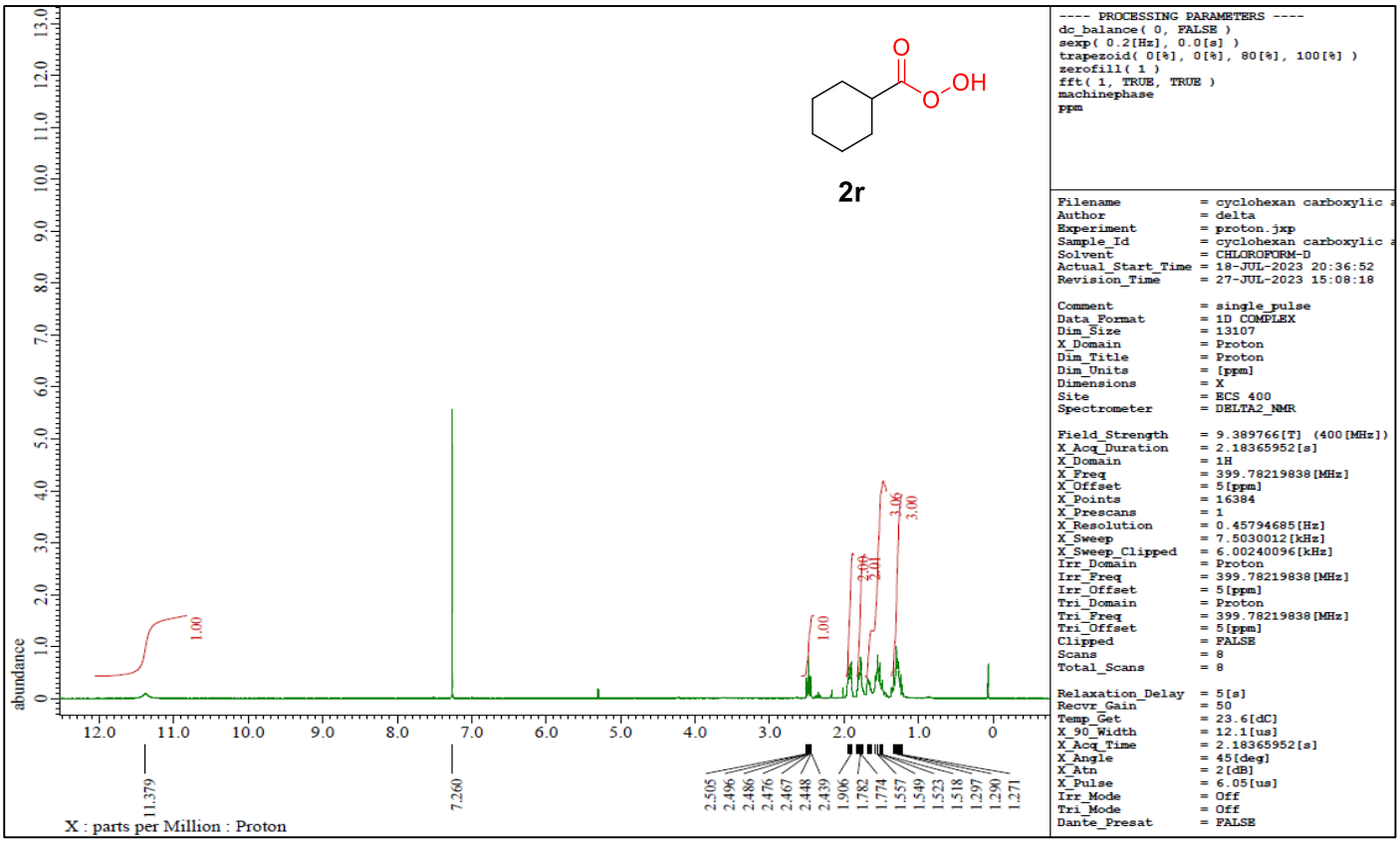
Compound **2p** (^{13}C NMR, 101 MHz, $(CD_3)_2SO$).



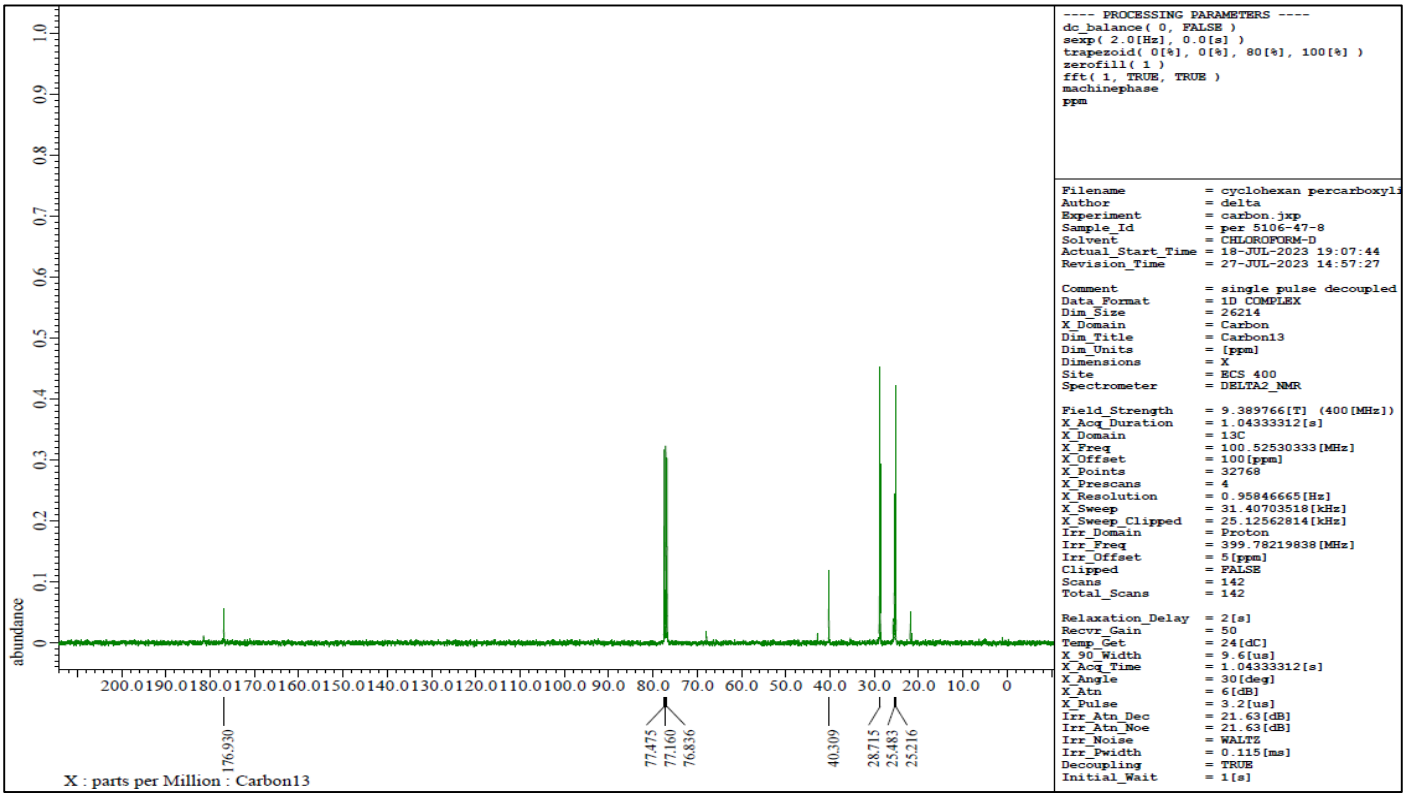
Compound **2q** (^{1}H NMR, 400 MHz, CD_3OD).



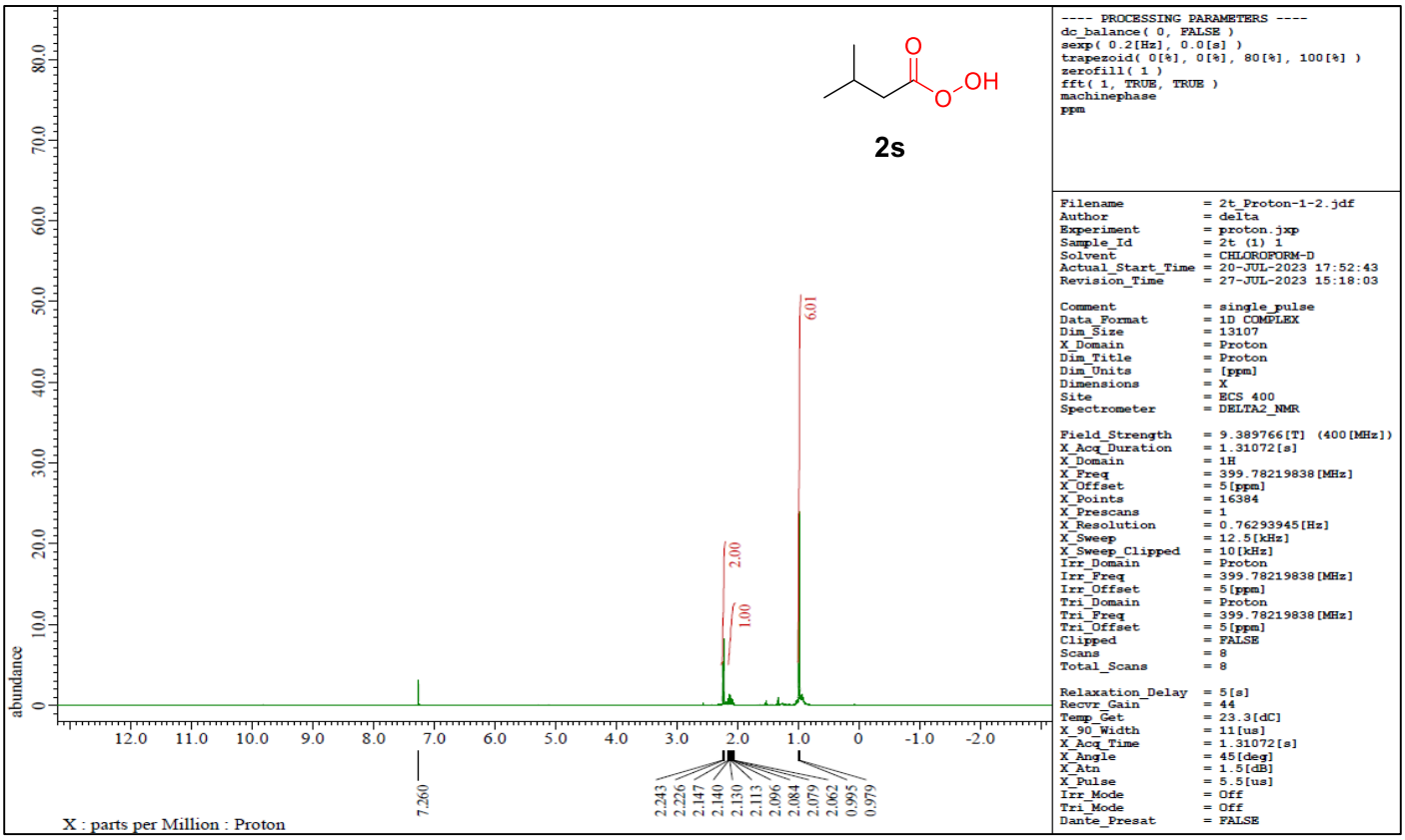
Compound **2q** (^{13}C NMR, 101 MHz, CD_3OD).



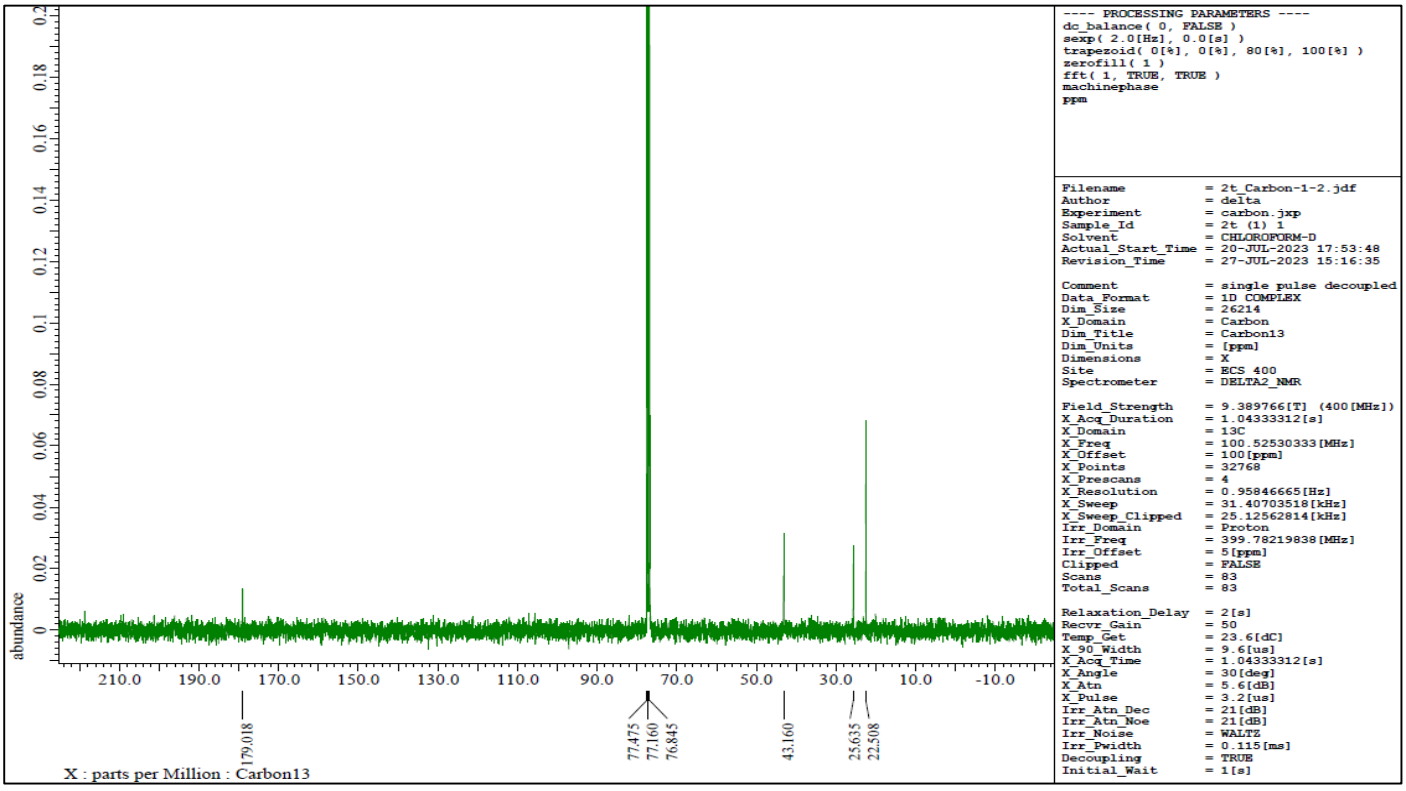
Compound **2r** (^{1}H NMR, 400 MHz, $CDCl_3$).



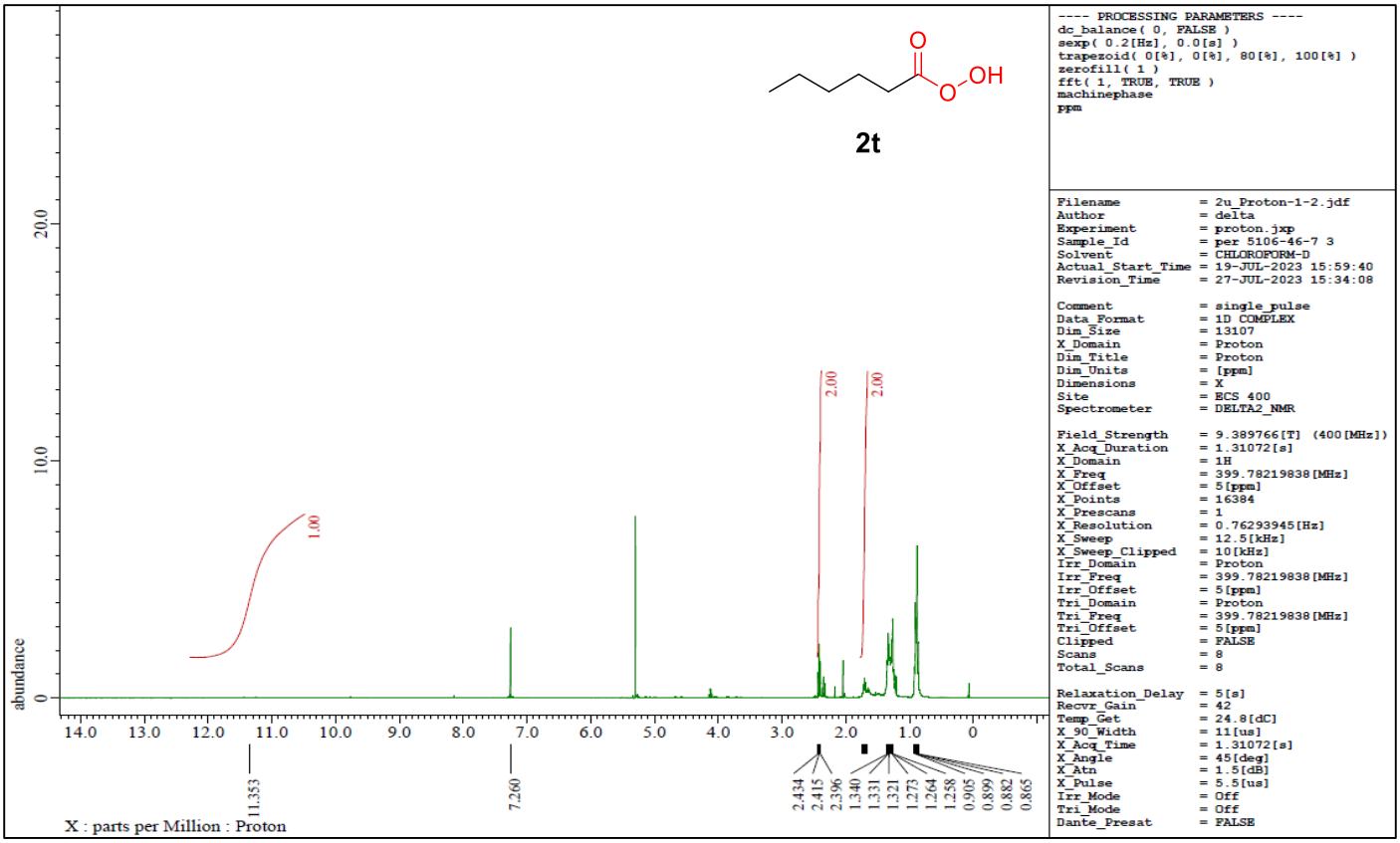
Compound **2r** (^{13}C NMR, 101 MHz, $CDCl_3$).



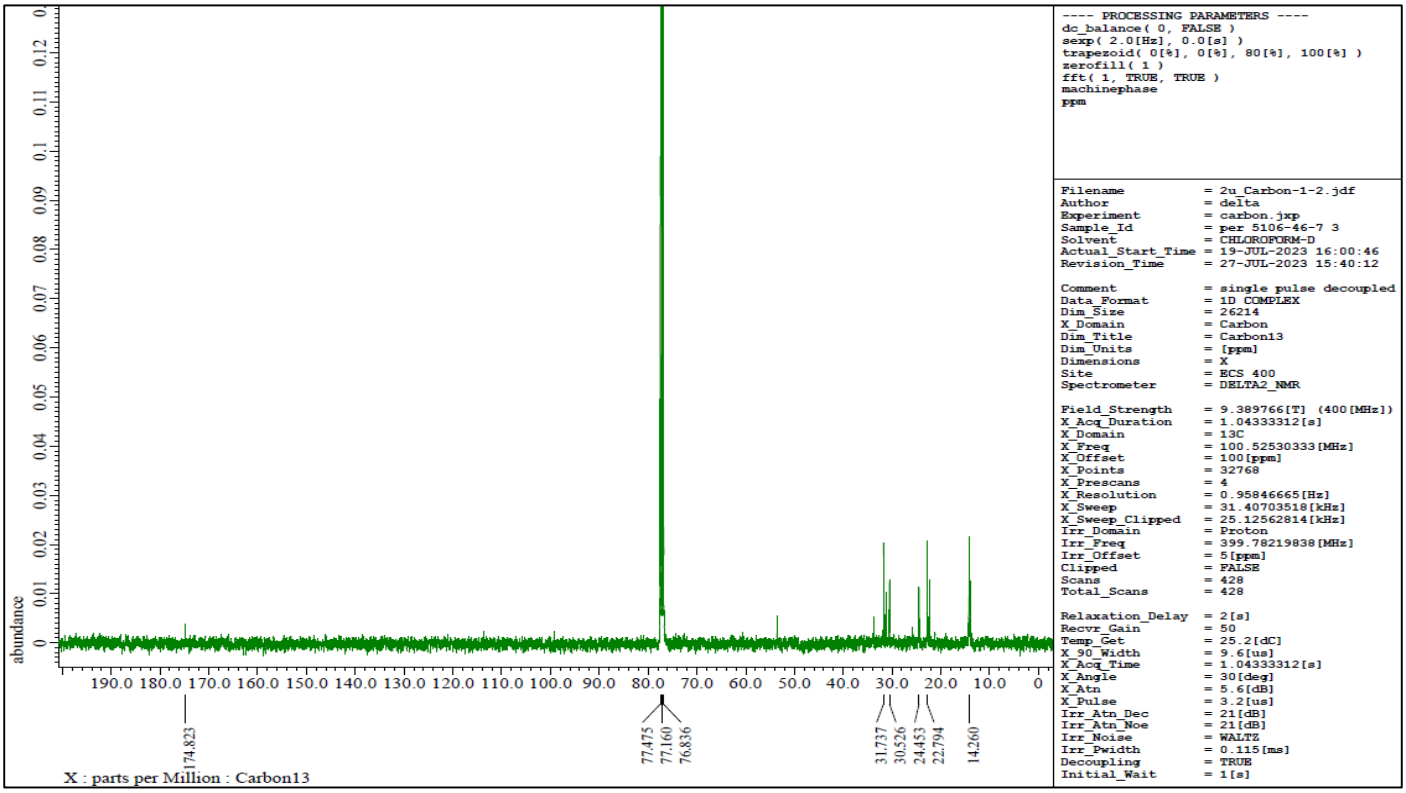
Compound **2s** (^{1}H NMR, 400 MHz, $CDCl_3$).



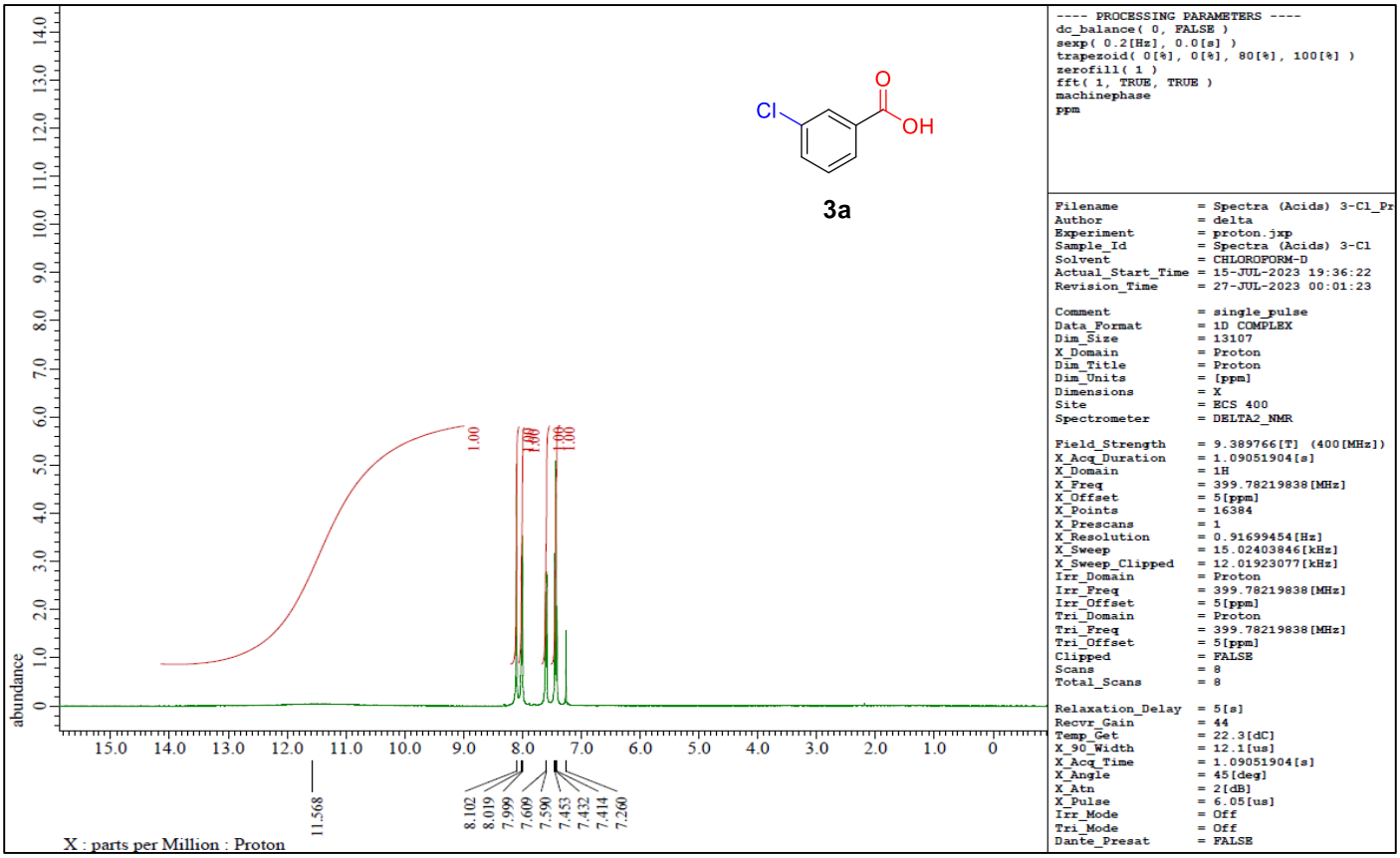
Compound **2s** (^{13}C NMR, 101 MHz, $CDCl_3$).



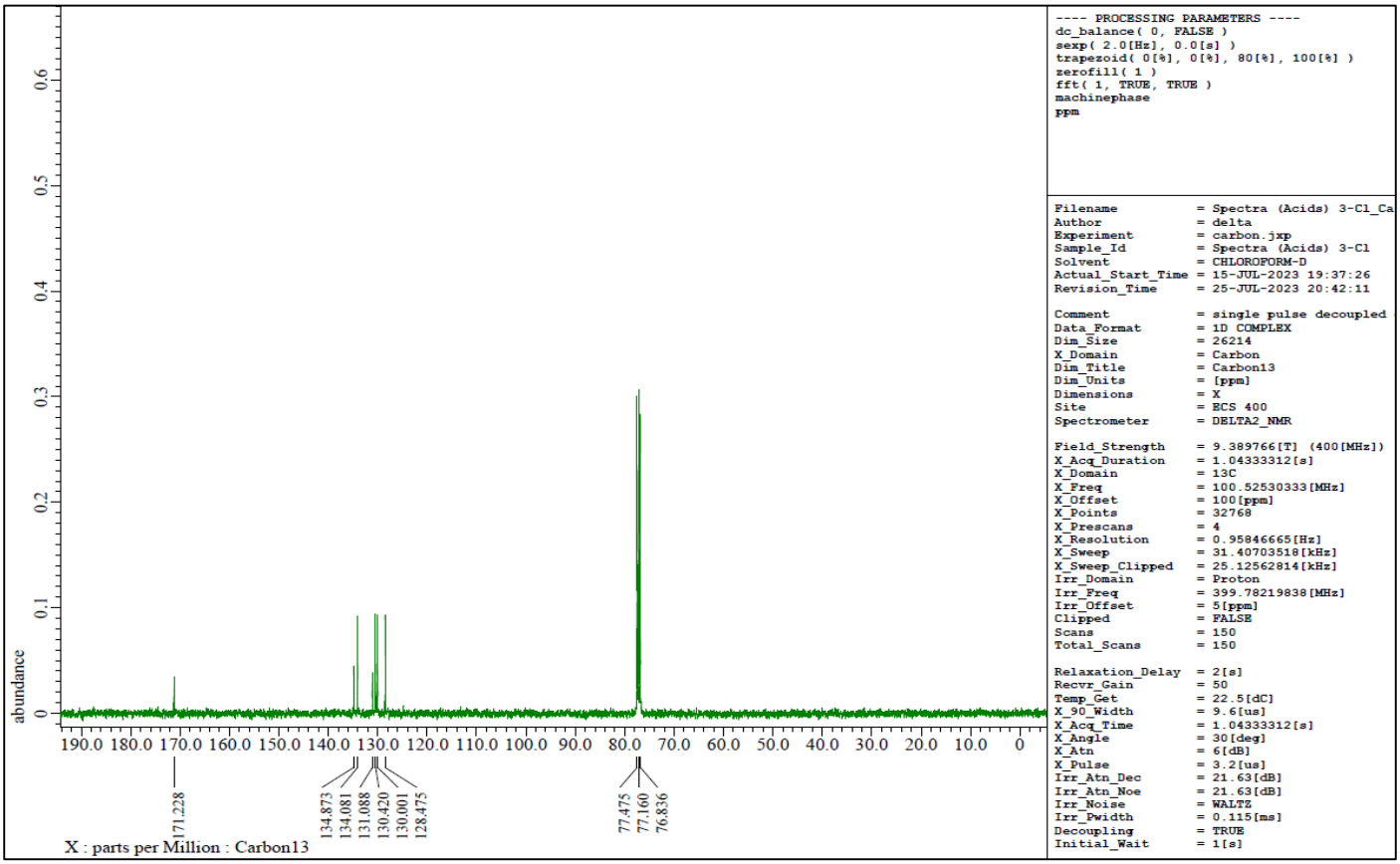
Compound **2t** (^{1}H NMR, 400 MHz, $CDCl_3$).



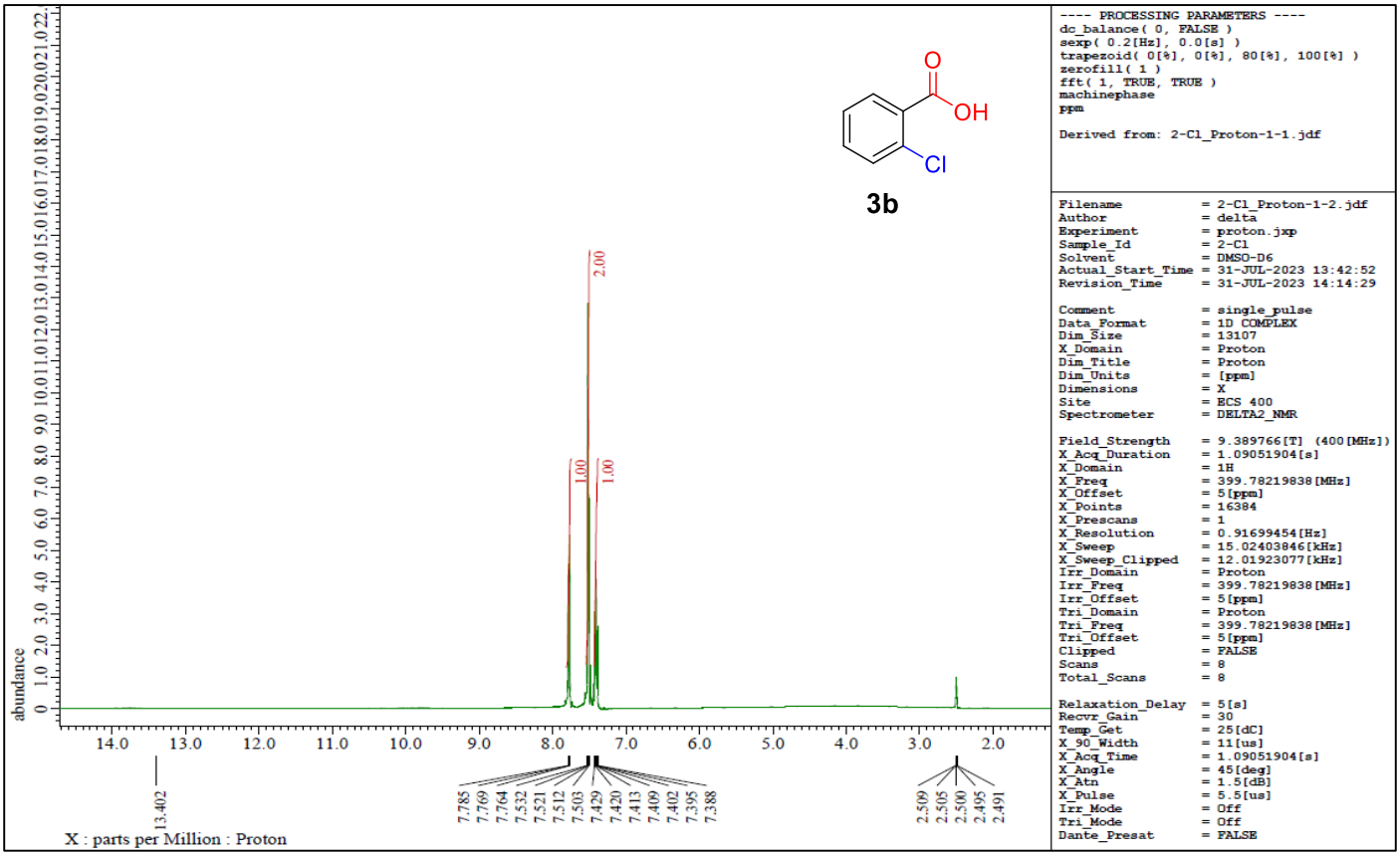
Compound **2t** (^{13}C NMR, 101 MHz, $CDCl_3$).



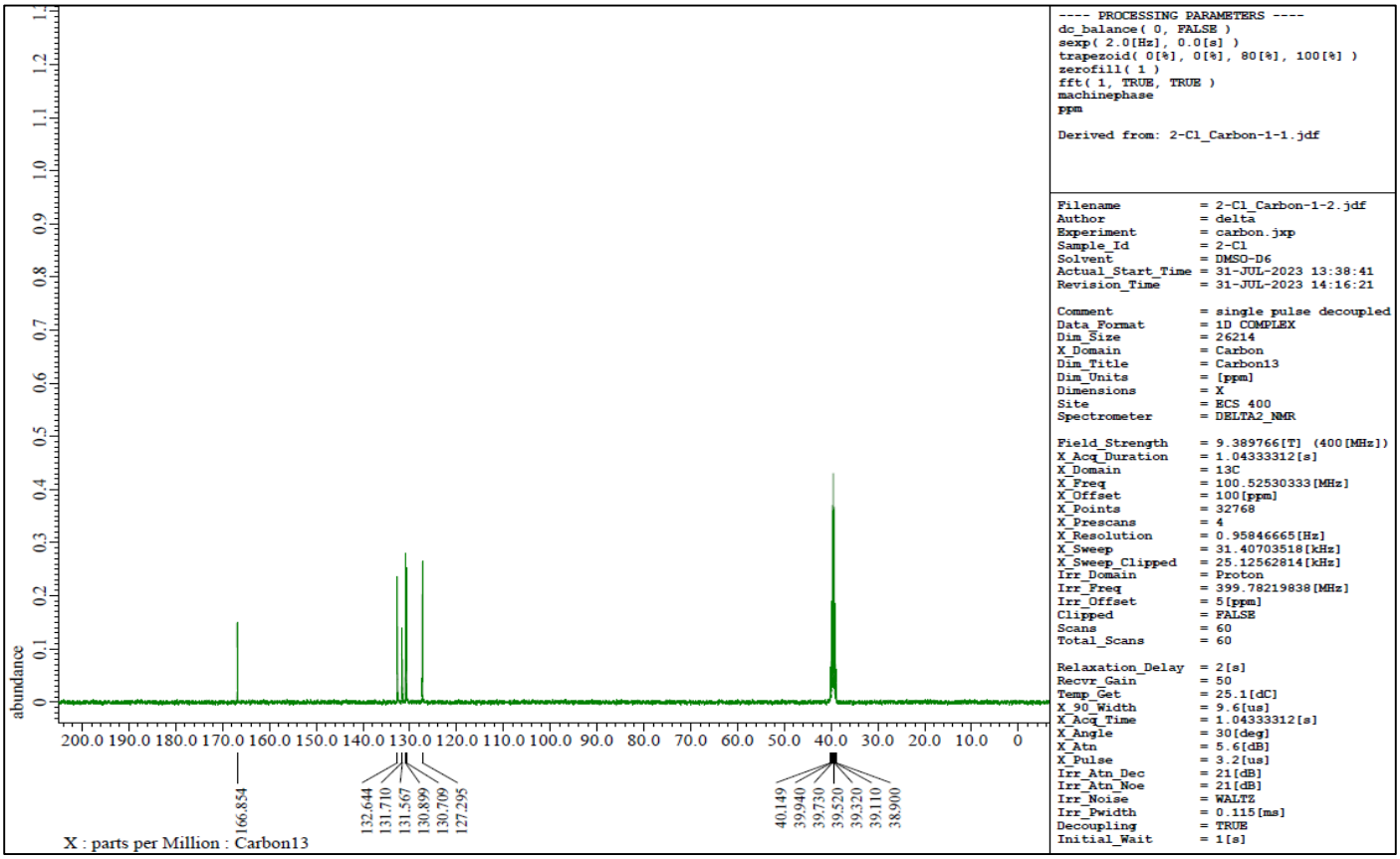
Compound **3a** (^{1}H NMR, 400 MHz, $CDCl_3$).



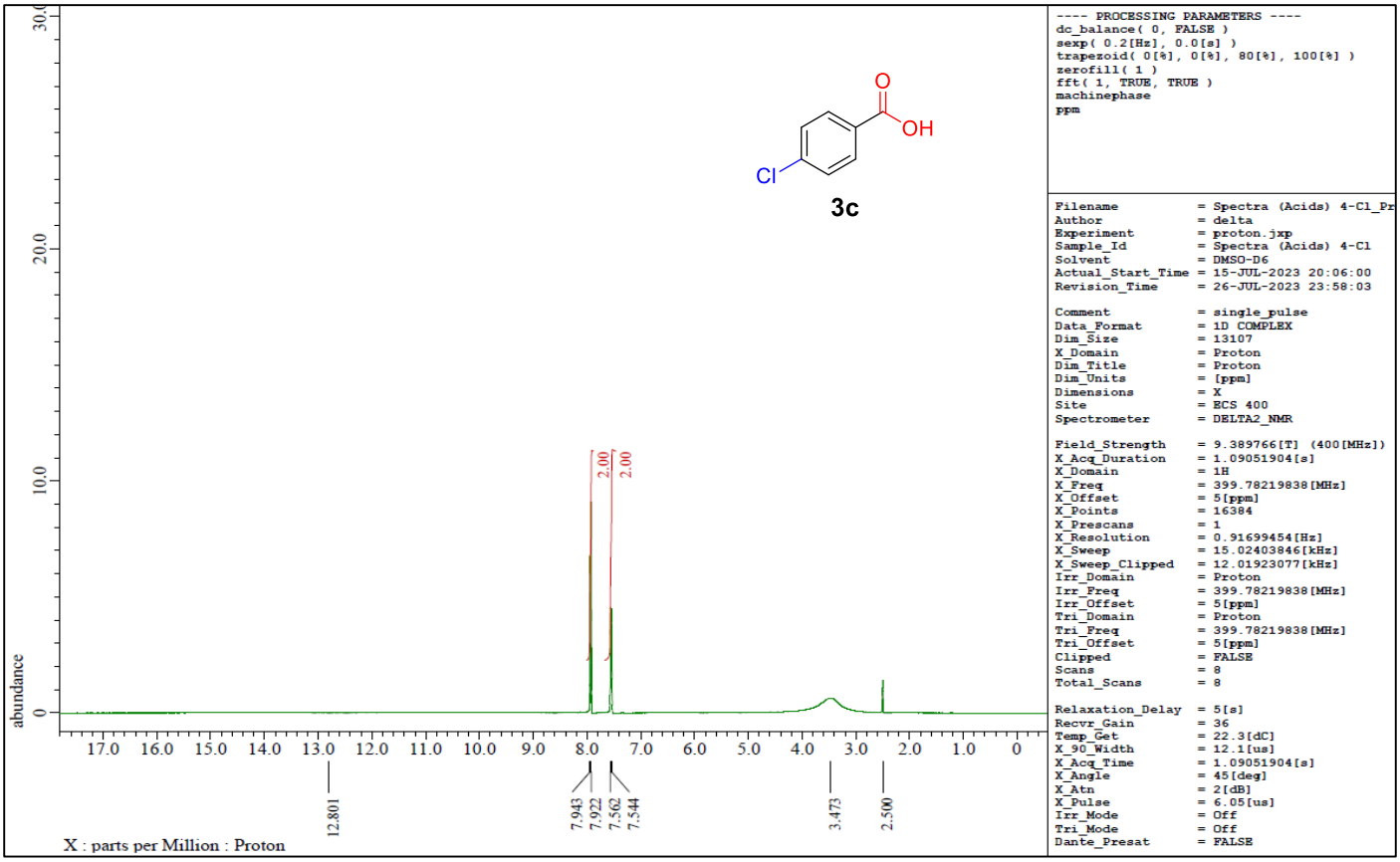
Compound **3a** (^{13}C NMR, 101 MHz, $CDCl_3$).



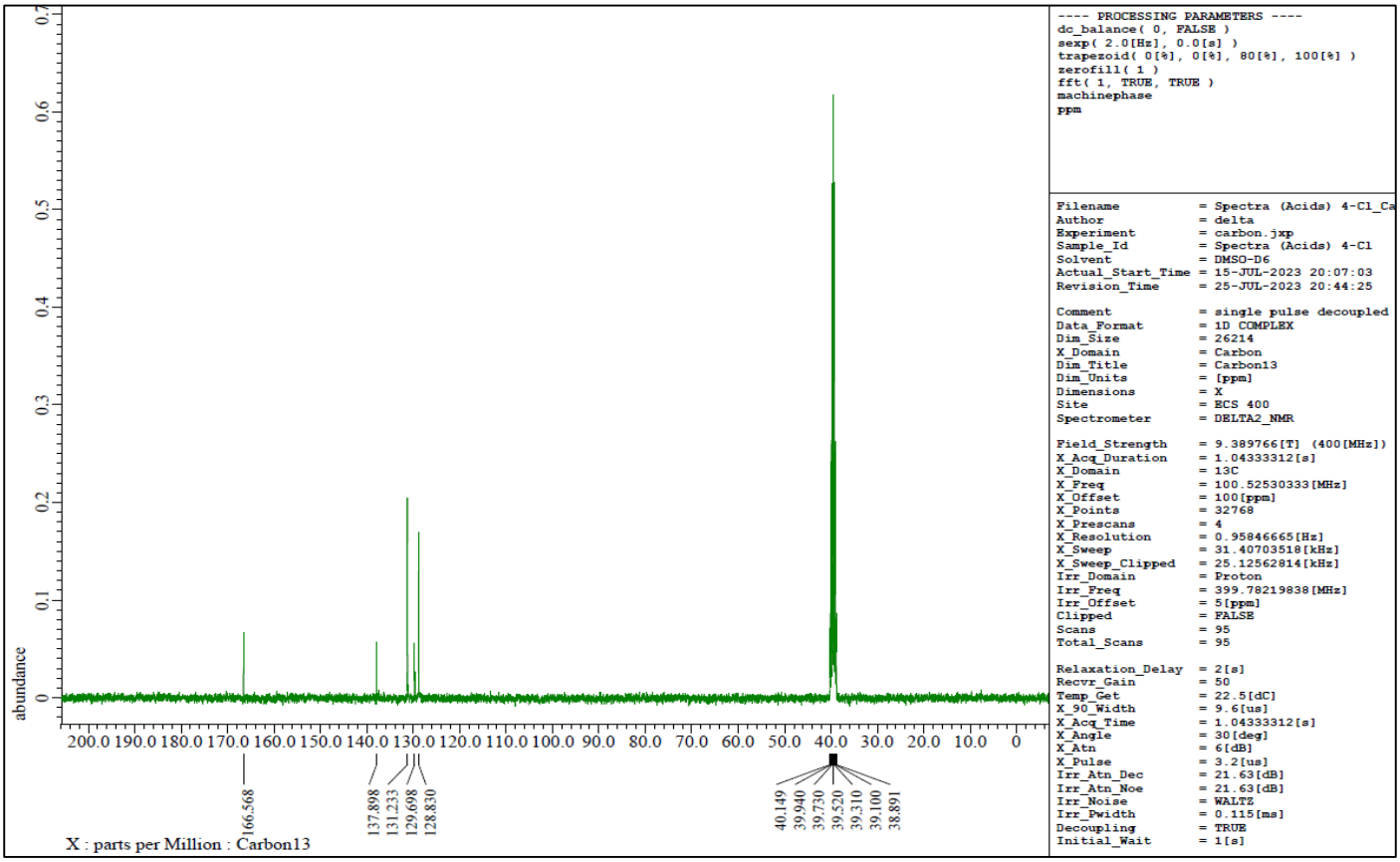
Compound **3b** (^{1}H NMR, 400 MHz, $(CD_3)_2SO$).



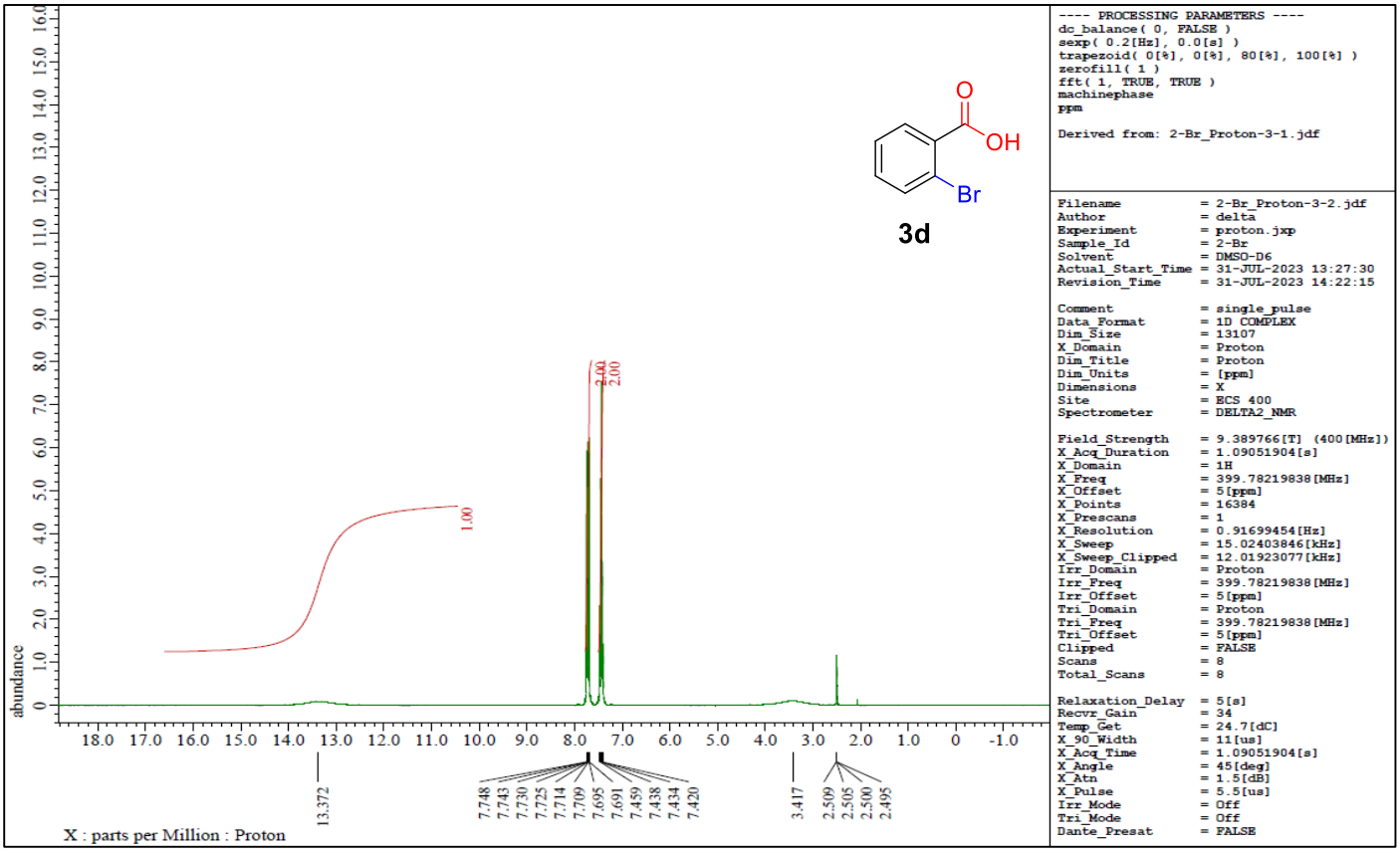
Compound **3b** (^{13}C NMR, 101 MHz, $(CD_3)_2SO$).



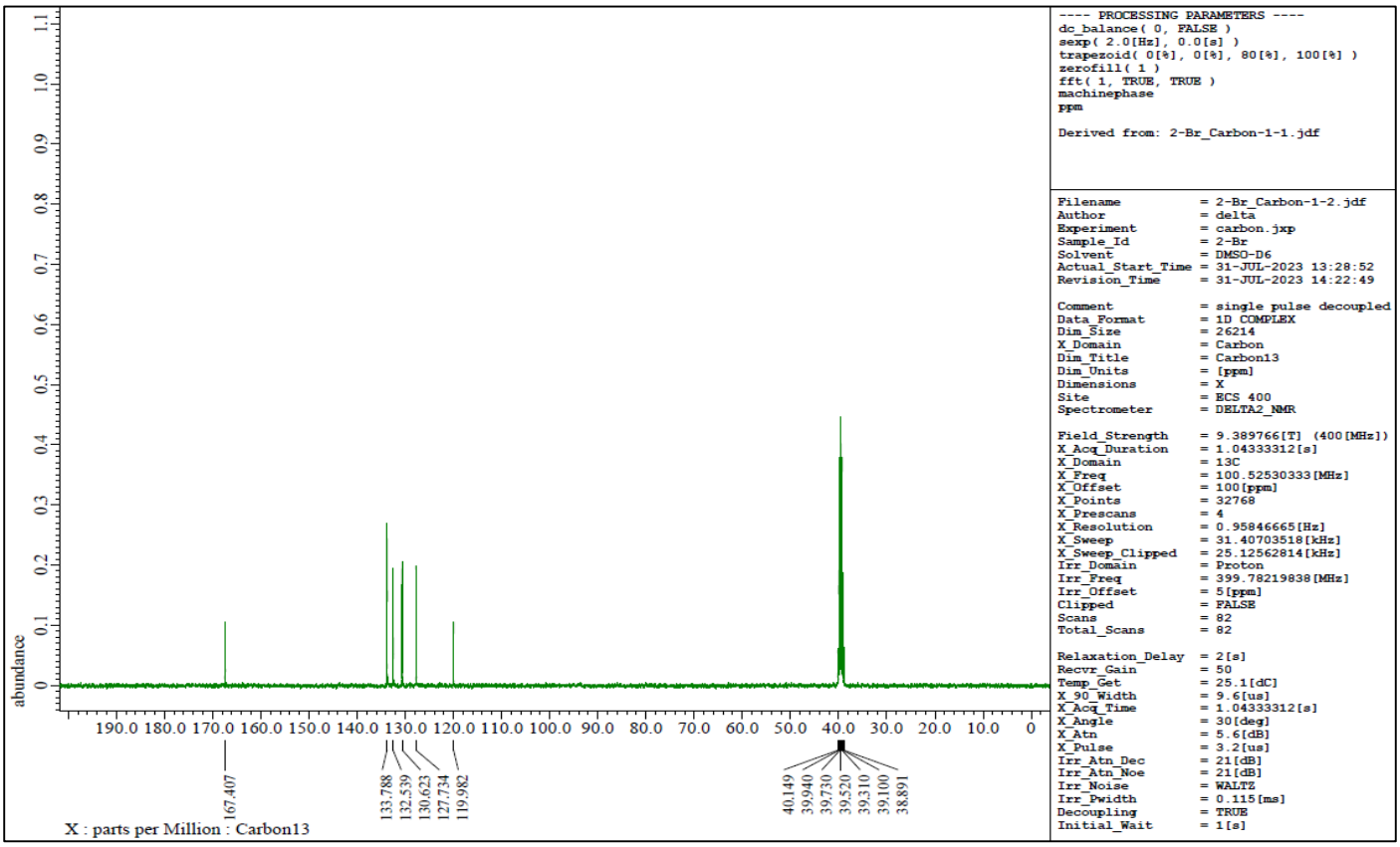
Compound **3c** (^{1}H NMR, 400 MHz, $(CD_3)_2SO$).



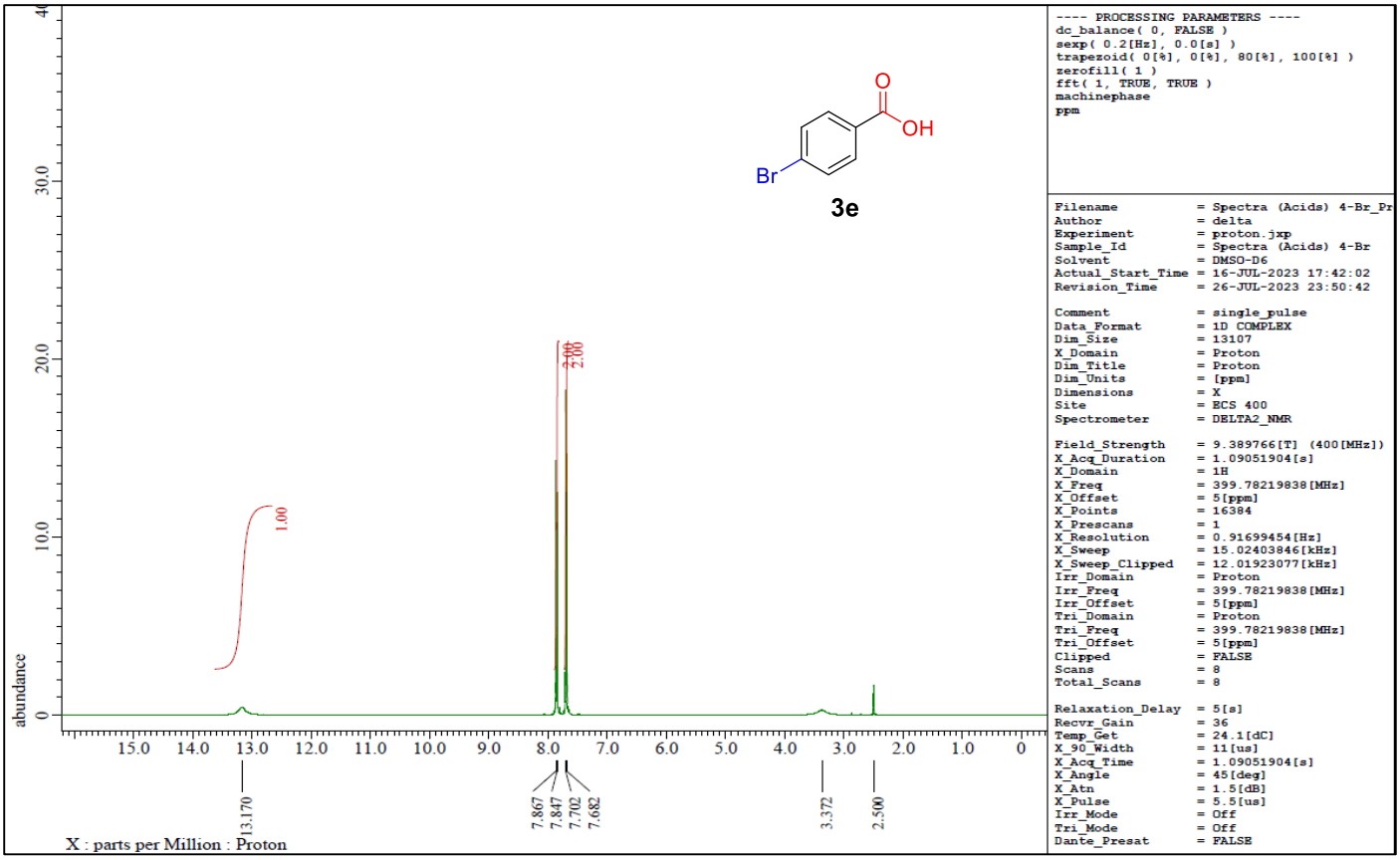
Compound **3c** (^{13}C NMR, 101 MHz, $(CD_3)_2SO$).



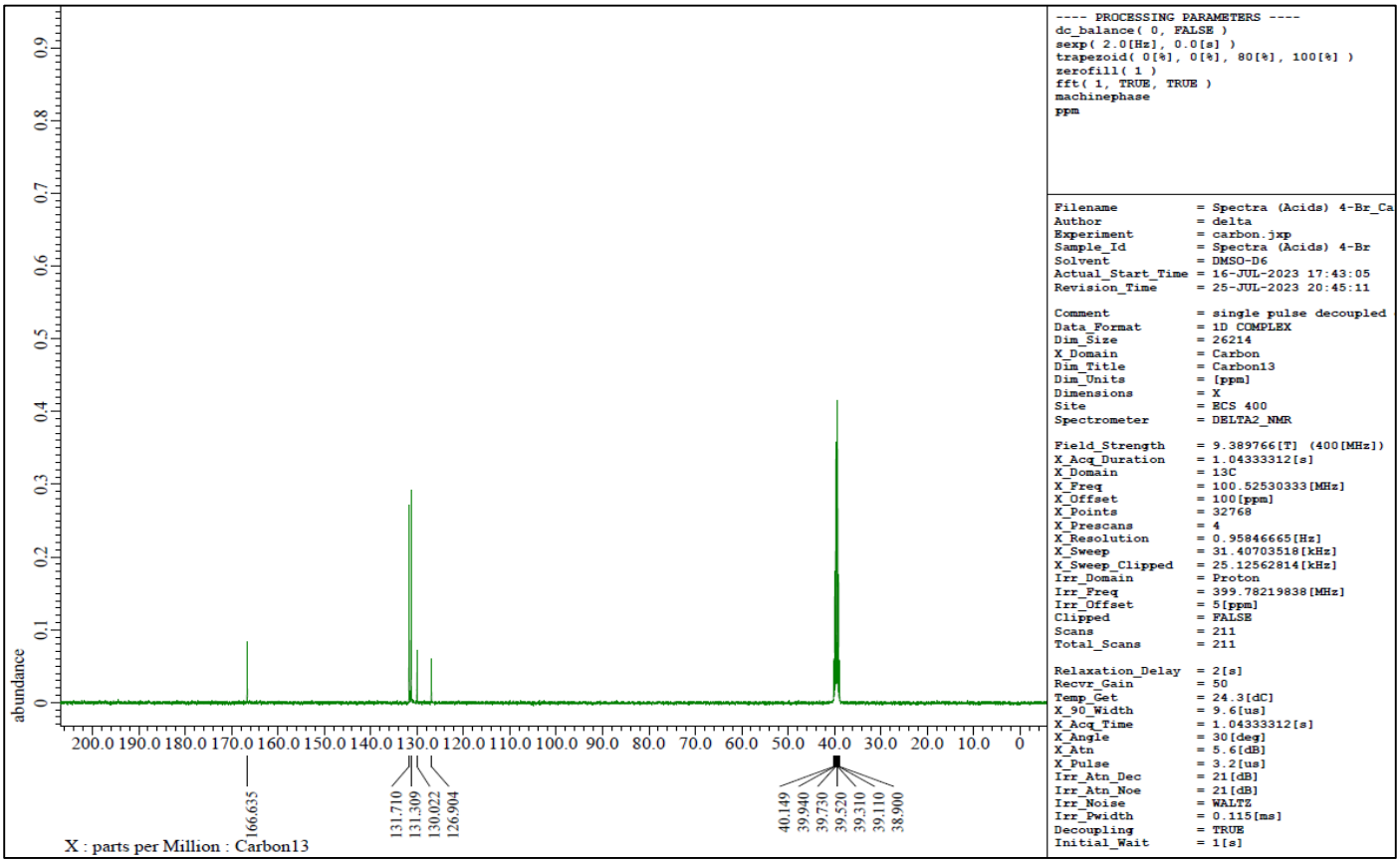
Compound **3d** (^{1}H NMR, 400 MHz, $(CD_3)_2SO$).



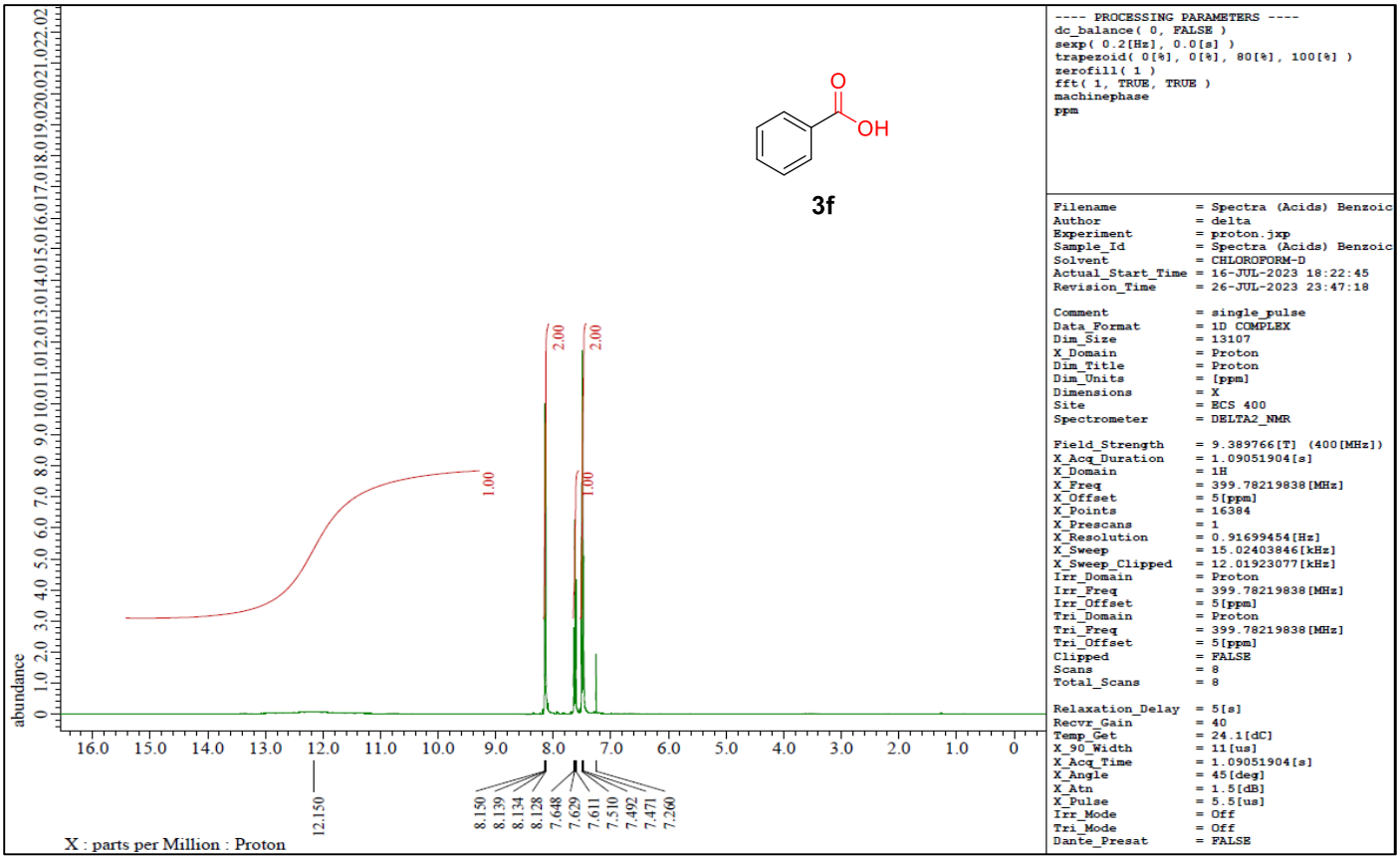
Compound **3d** (^{13}C NMR, 101 MHz, $(CD_3)_2SO$).



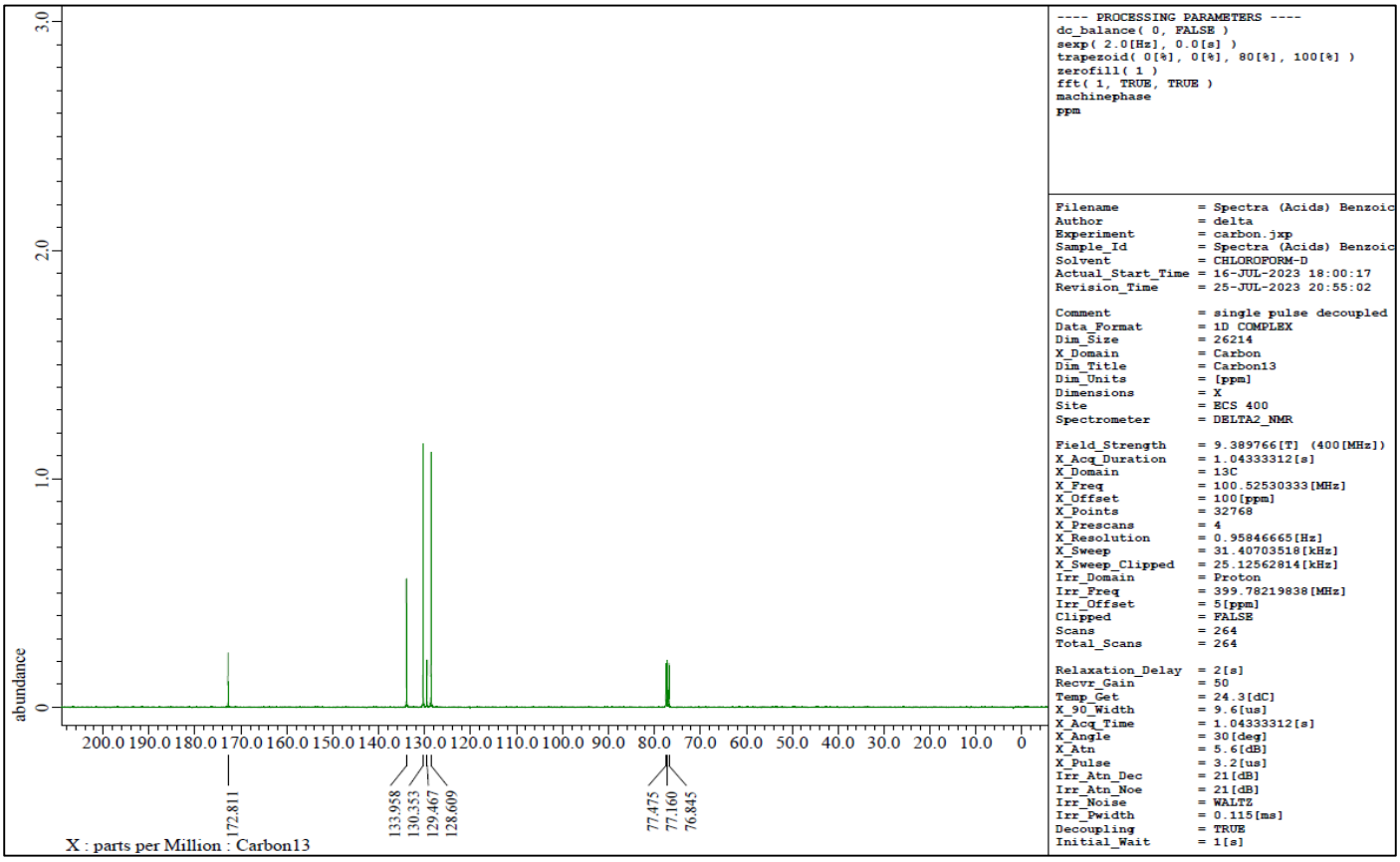
Compound **3e** (^{1}H NMR, 400 MHz, $(CD_3)_2SO$).



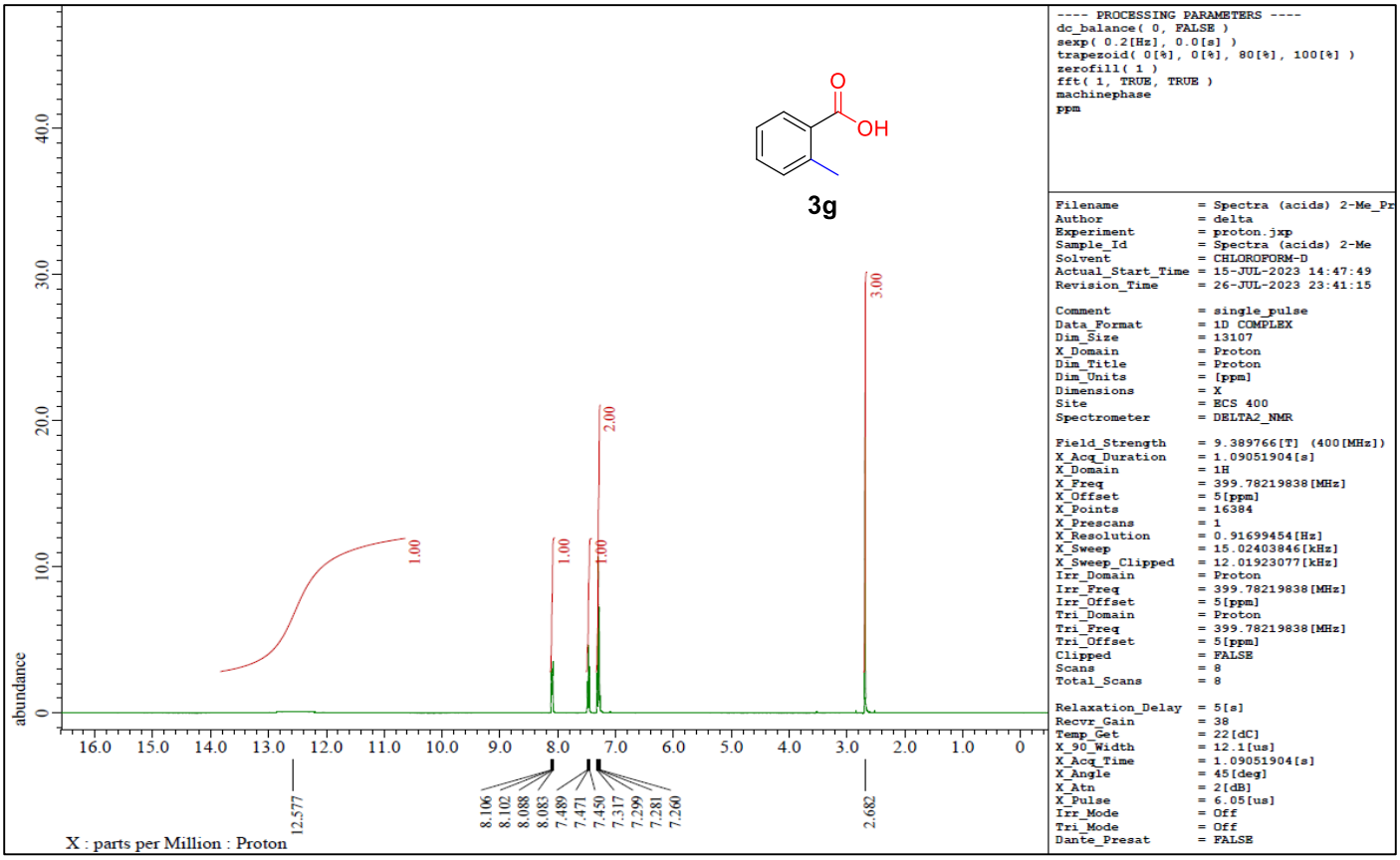
Compound **3e** (^{13}C NMR, 101 MHz, $(CD_3)_2SO$).



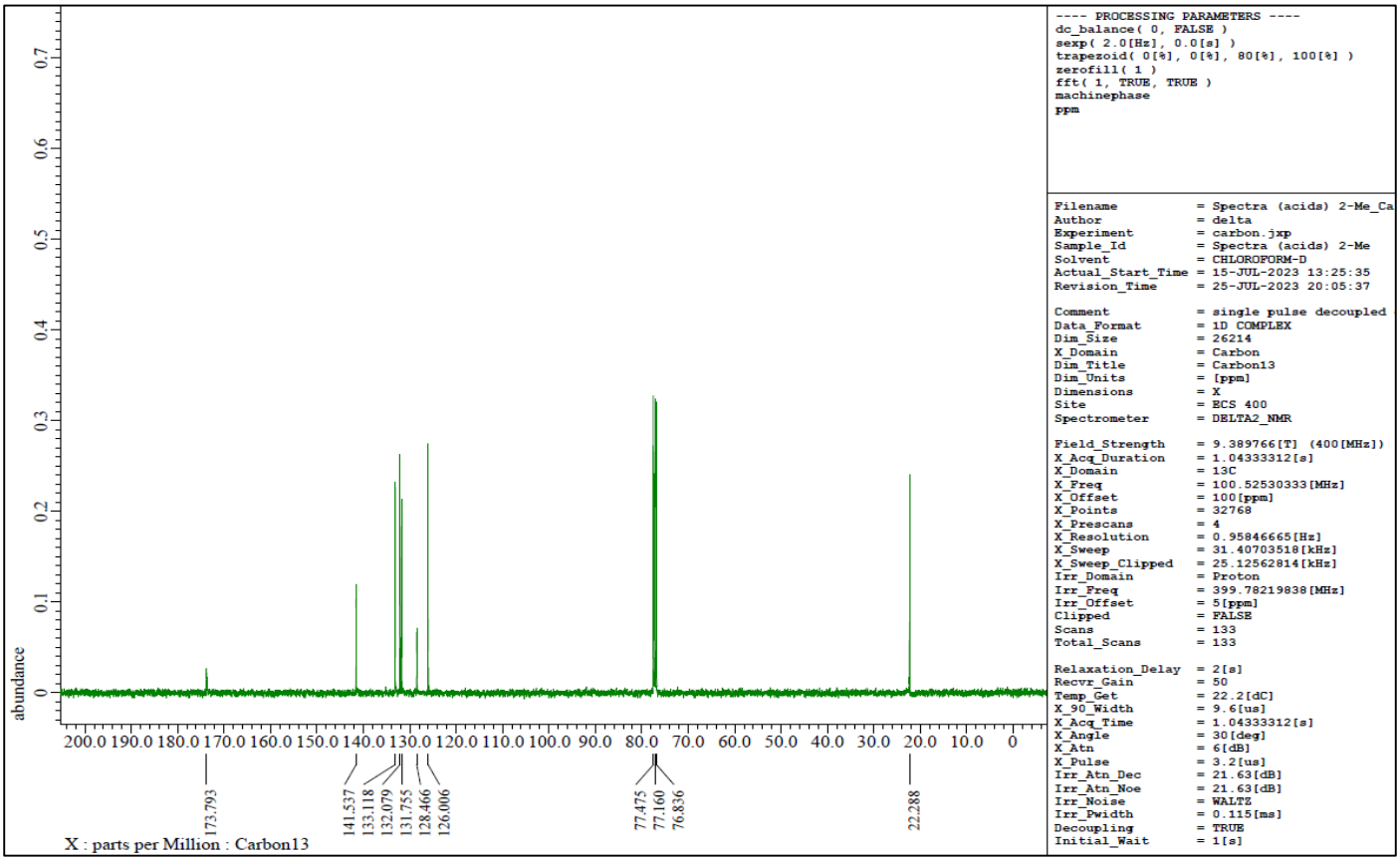
Compound **3f** (^{1}H NMR, 400 MHz, $CDCl_3$).



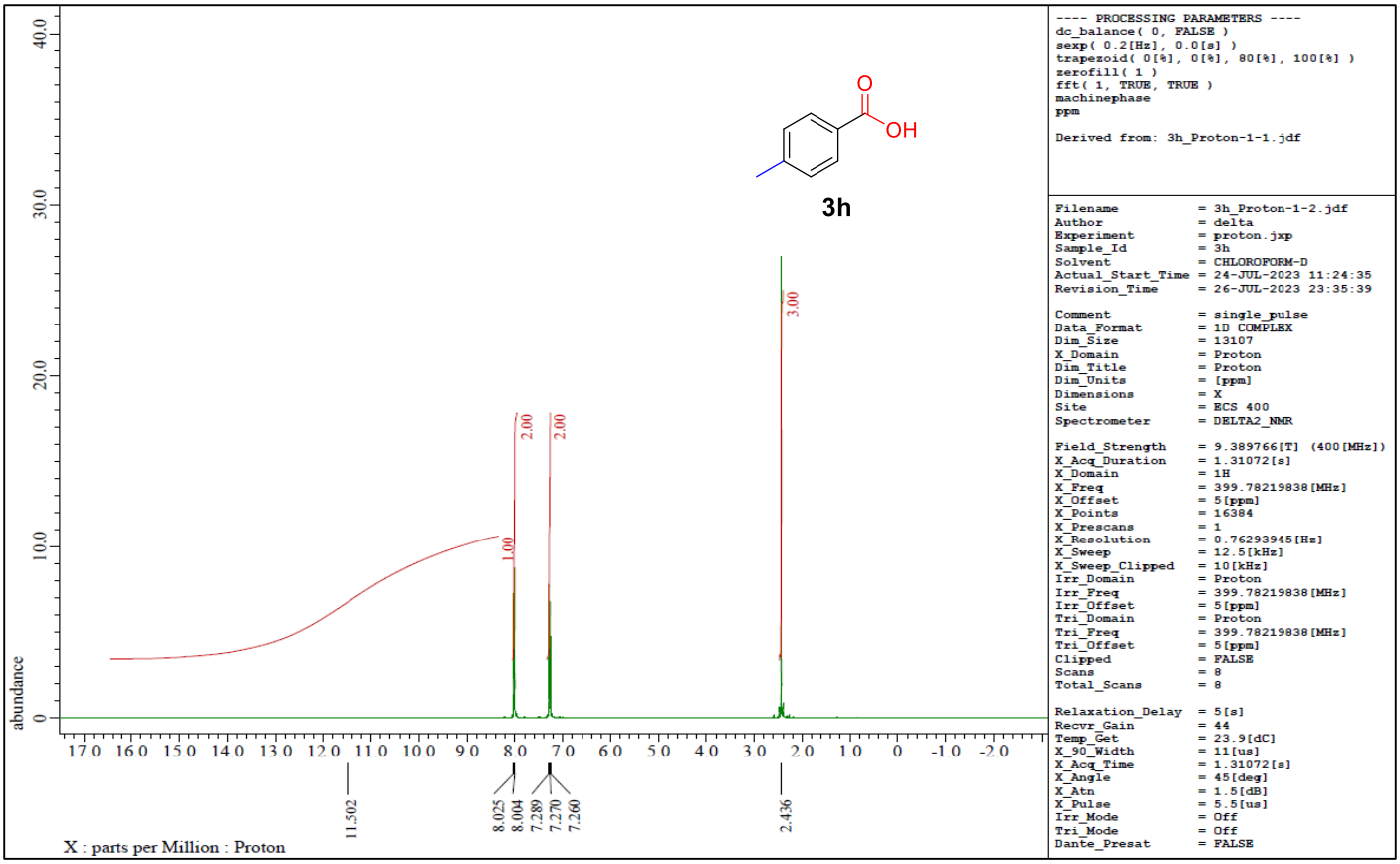
Compound **3f** (^{13}C NMR, 101 MHz, $CDCl_3$).



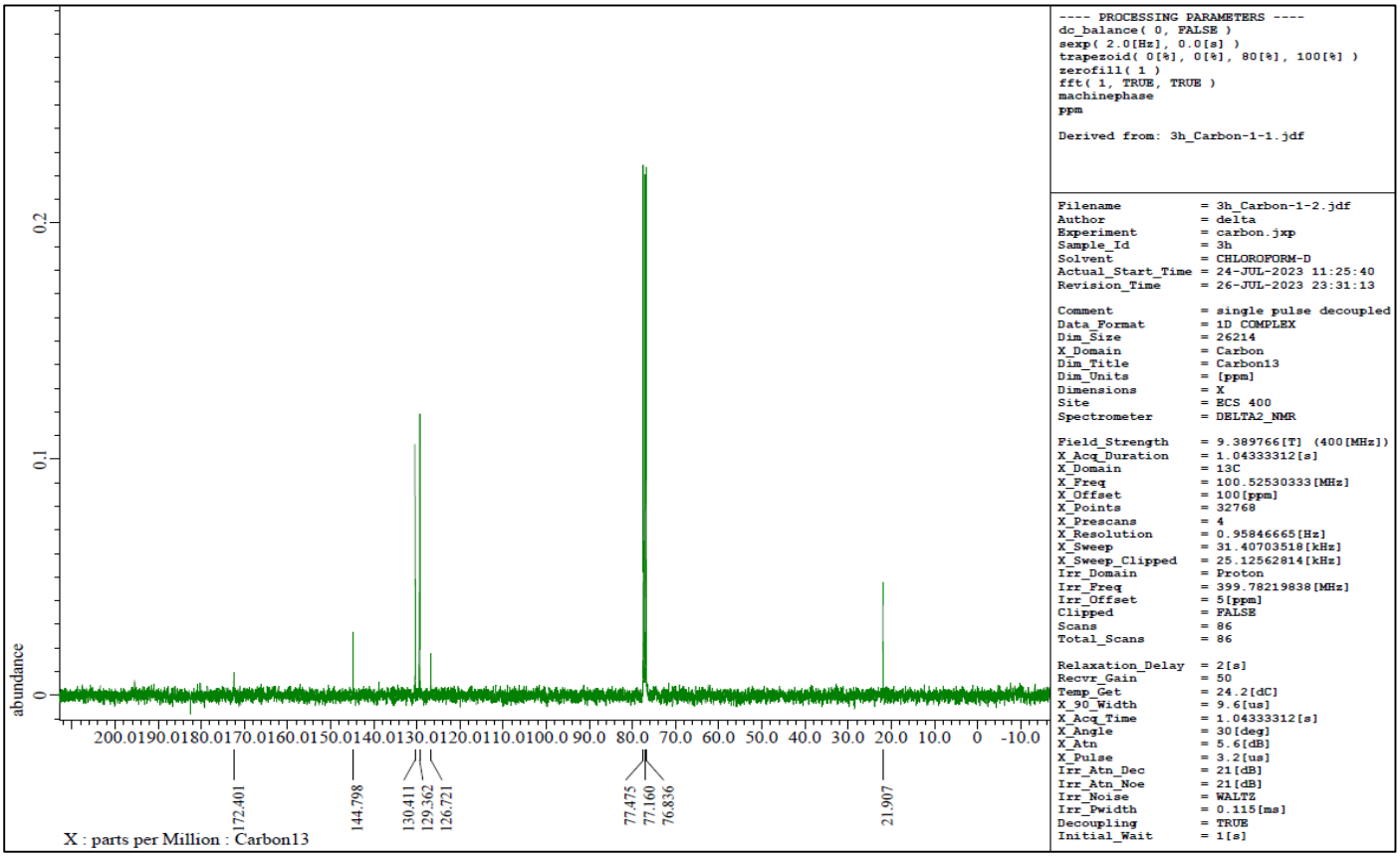
Compound **3g** (^{1}H NMR, 400 MHz, $CDCl_3$).



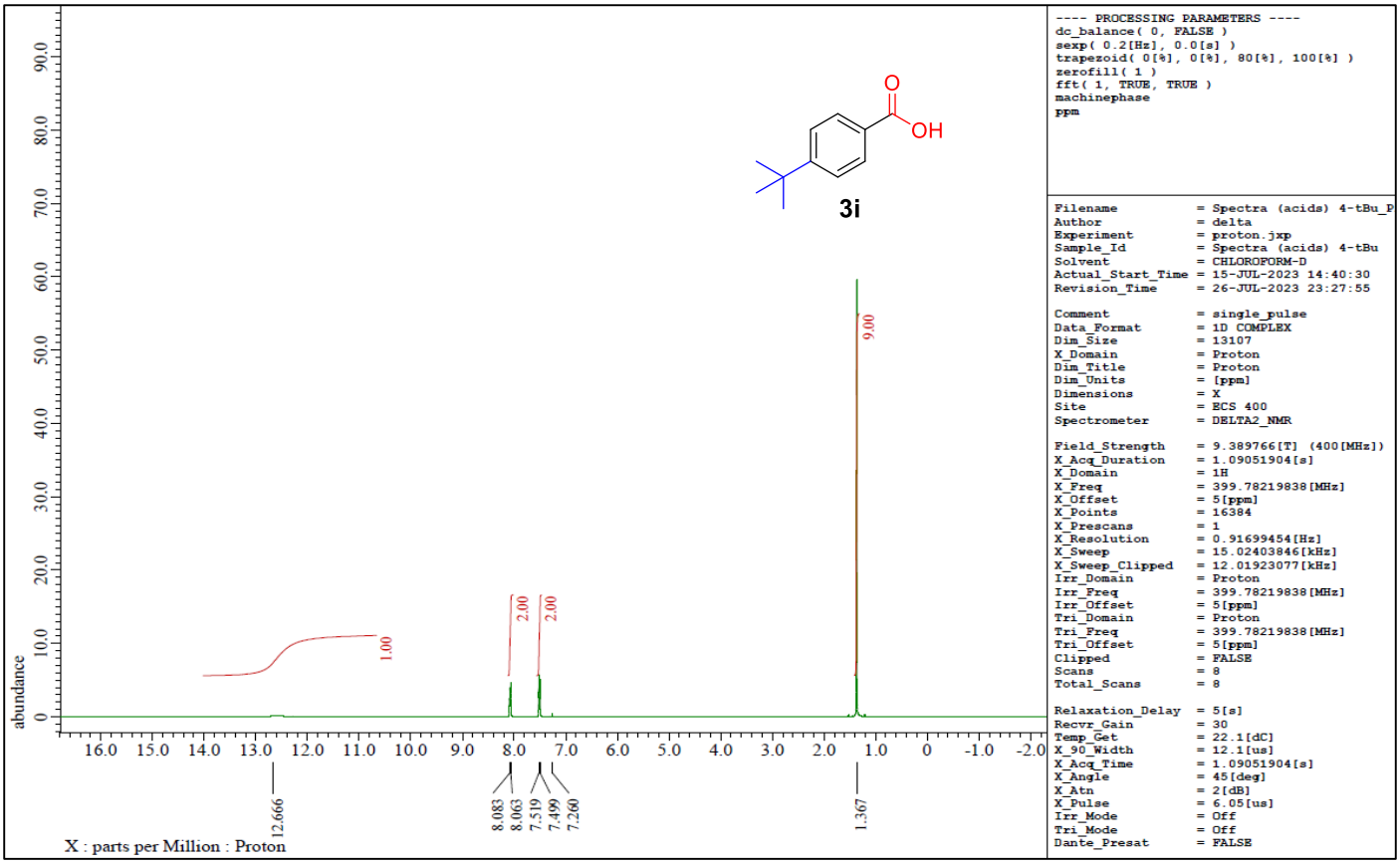
Compound **3g** (^{13}C NMR, 101 MHz, $CDCl_3$).



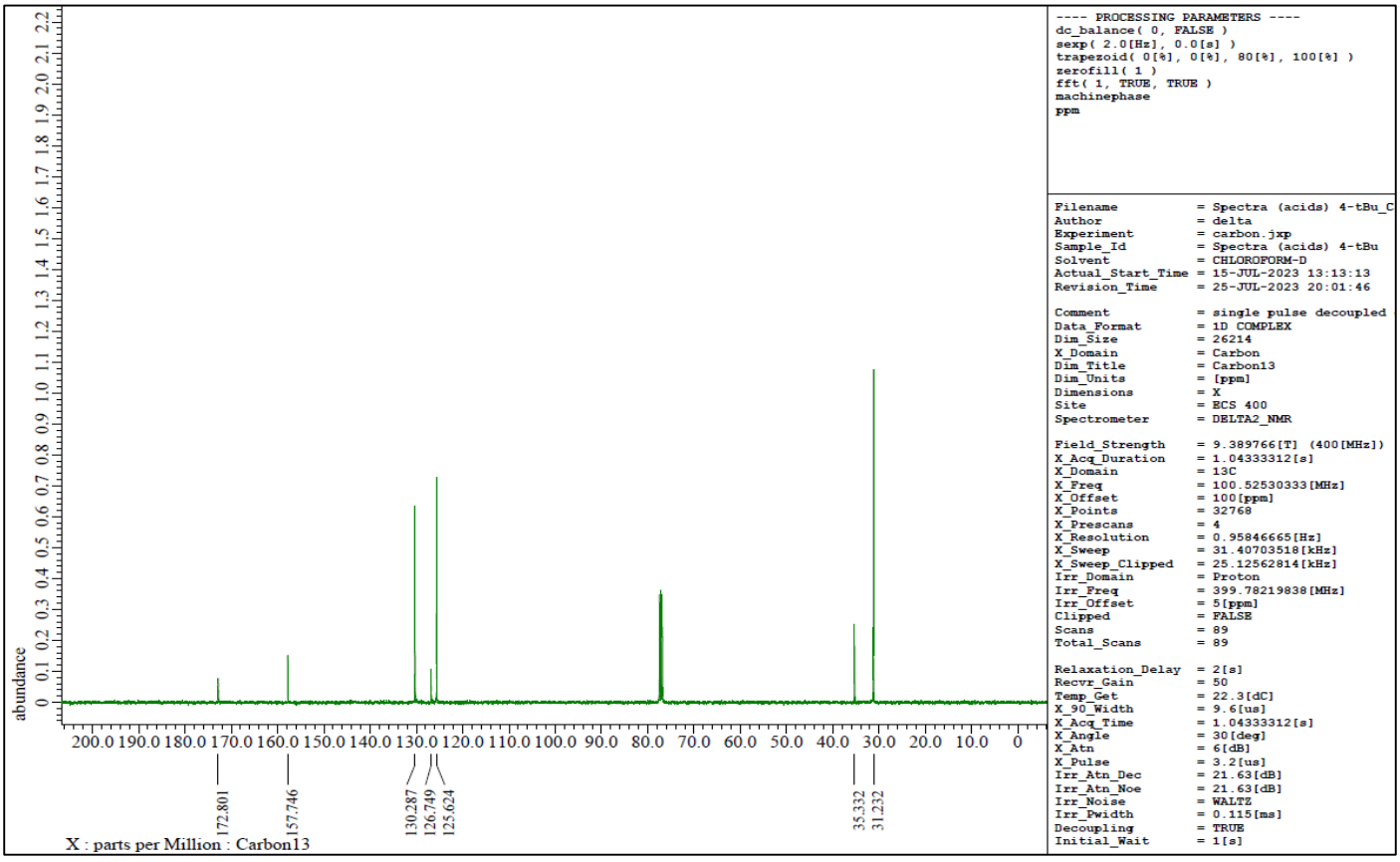
Compound **3h** (^{1}H NMR, 400 MHz, $CDCl_3$).



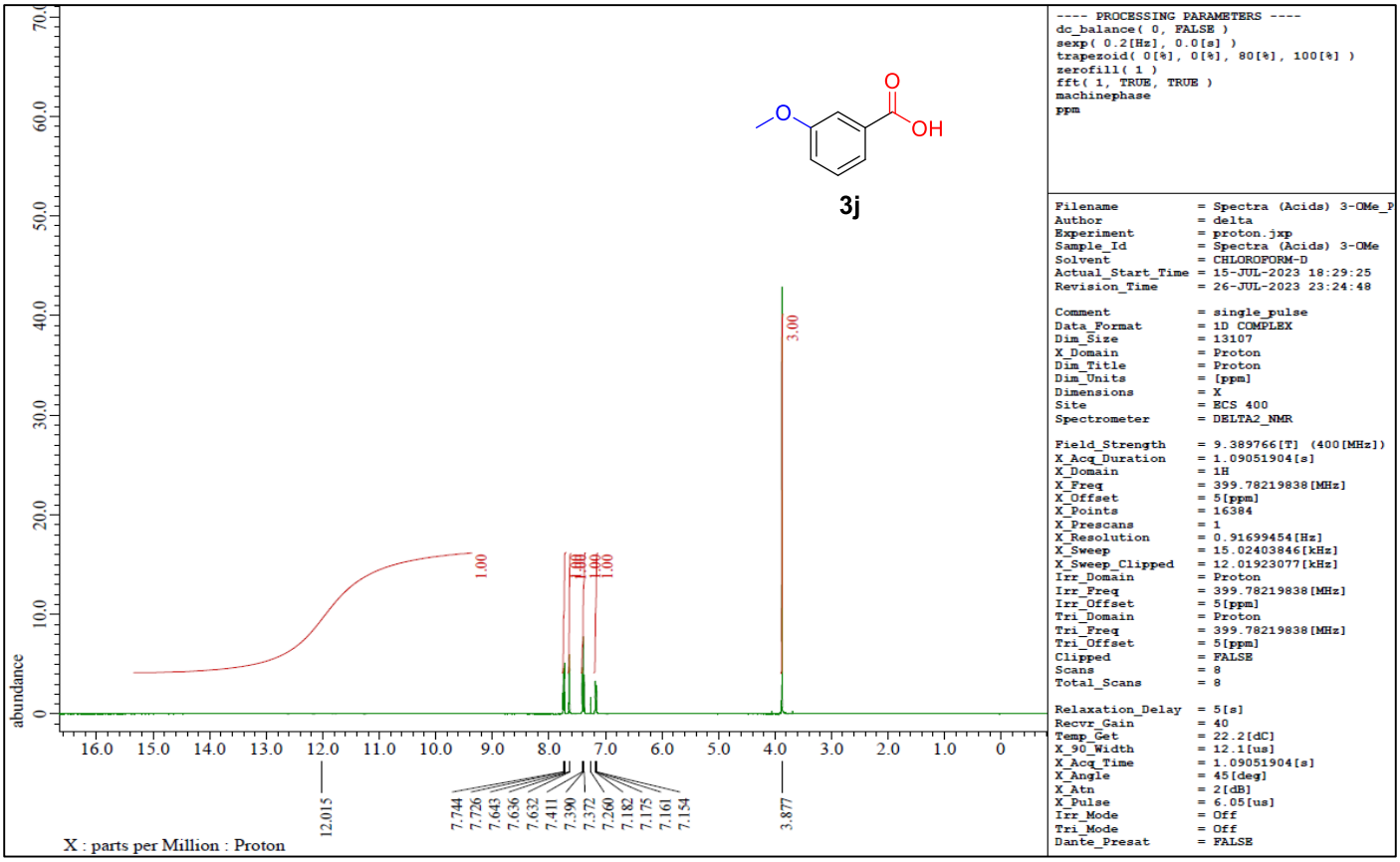
Compound **3h** (^{13}C NMR, 101 MHz, $CDCl_3$).



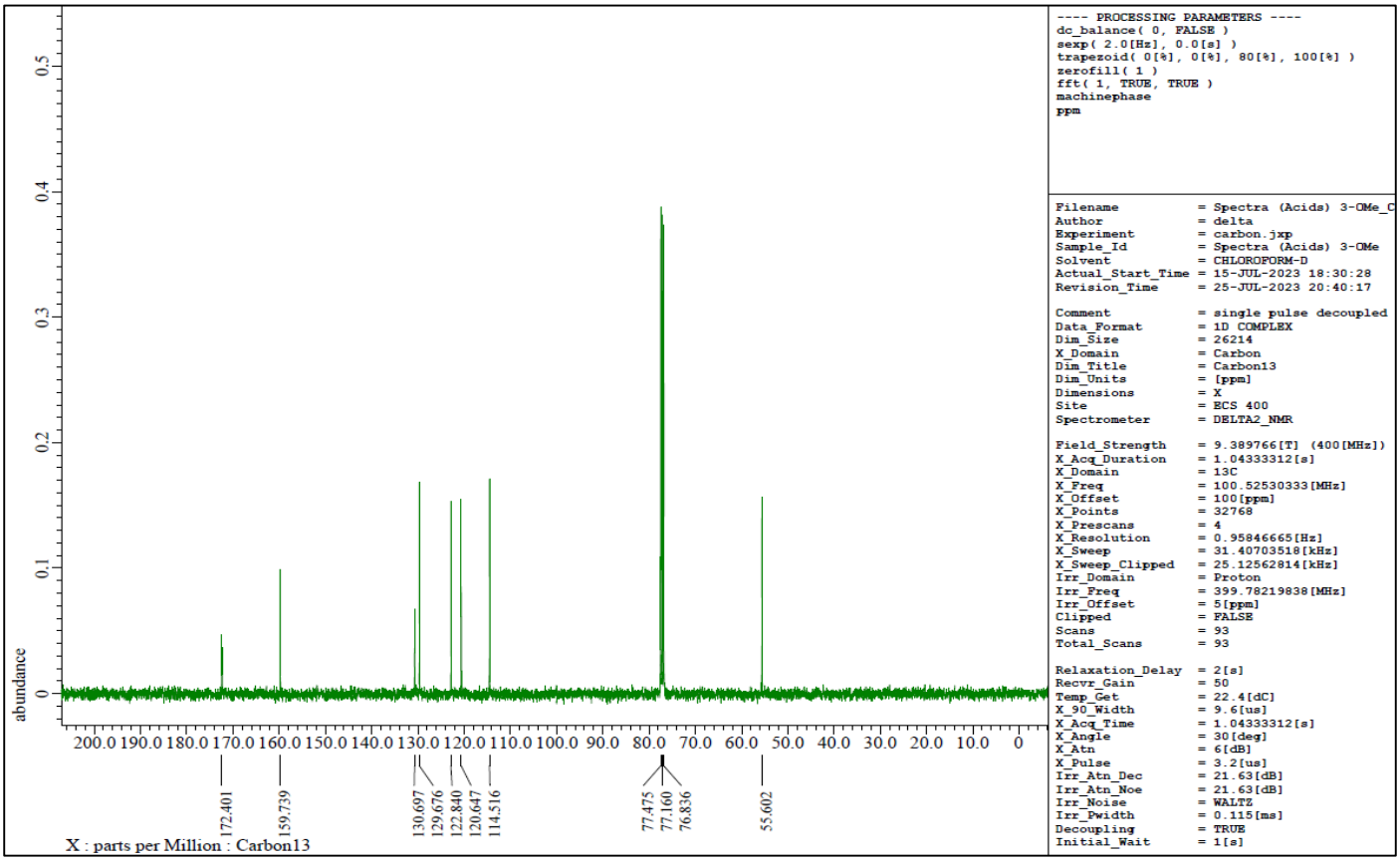
Compound **3i** (^{1}H NMR, 400 MHz, $CDCl_3$).



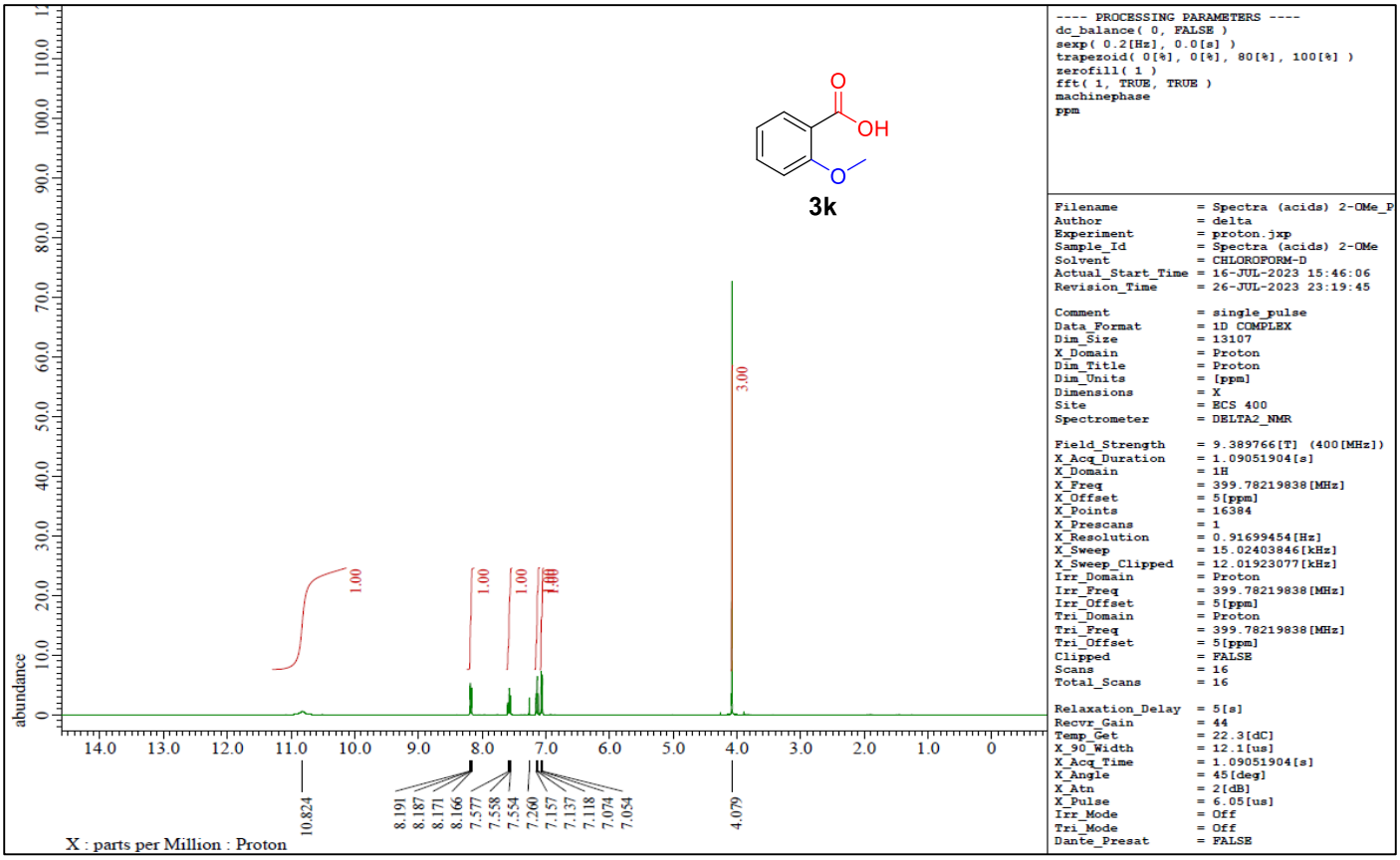
Compound **3i** (^{13}C NMR, 101 MHz, $CDCl_3$).



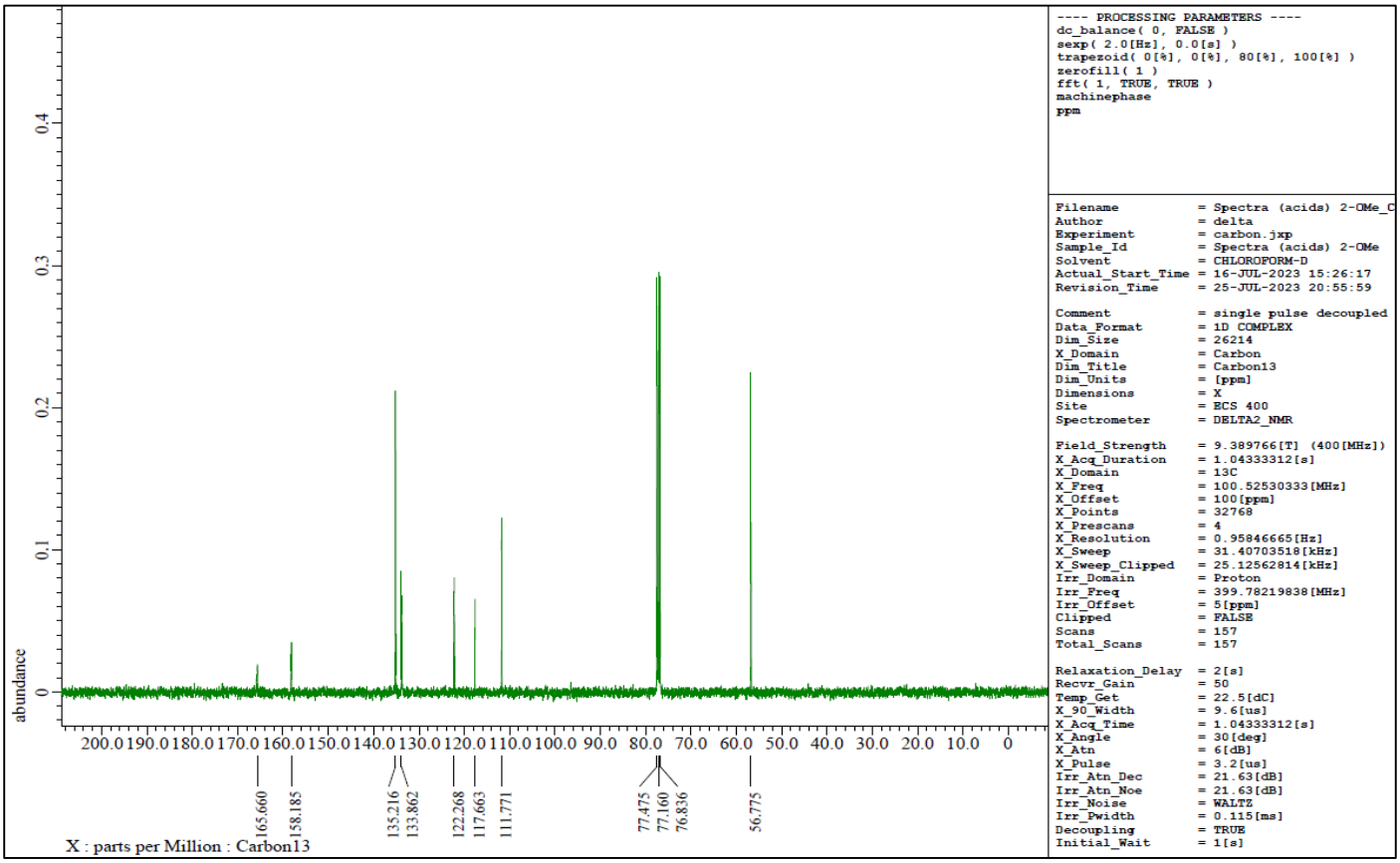
Compound **3j** (^{1}H NMR, 400 MHz, $CDCl_3$).



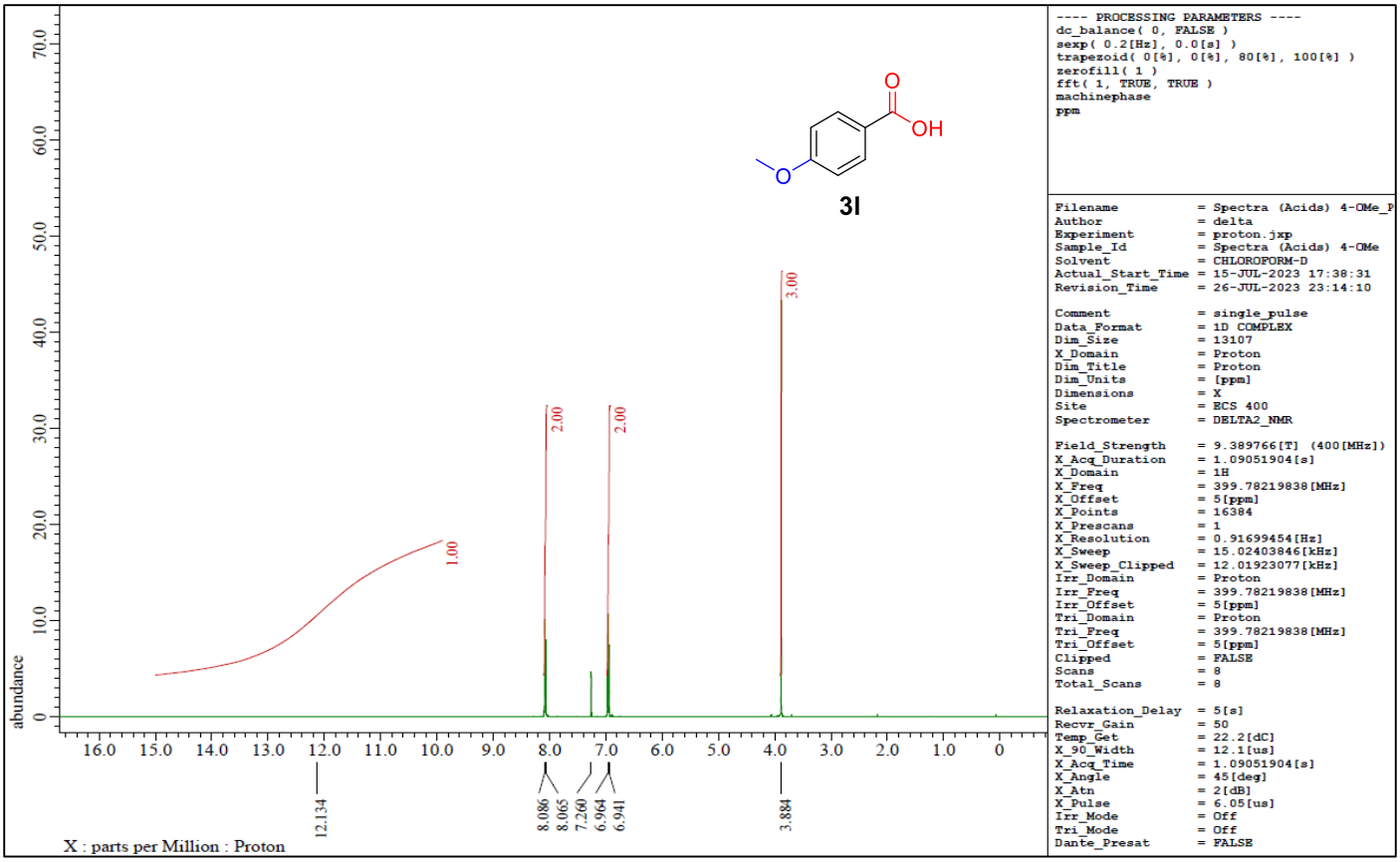
Compound **3j** (^{13}C NMR, 101 MHz, $CDCl_3$).



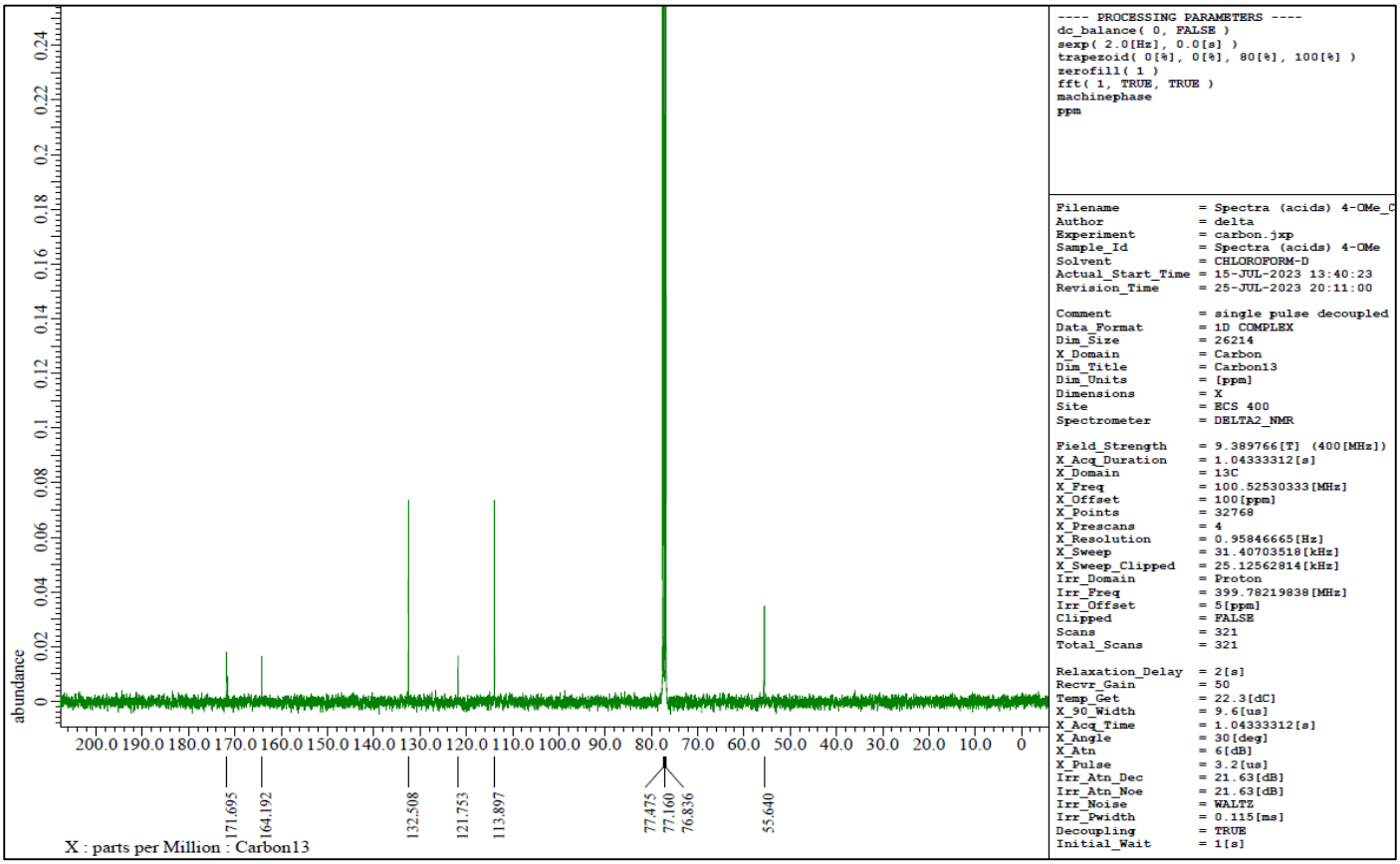
Compound **3k** (^{1}H NMR, 400 MHz, $CDCl_3$).



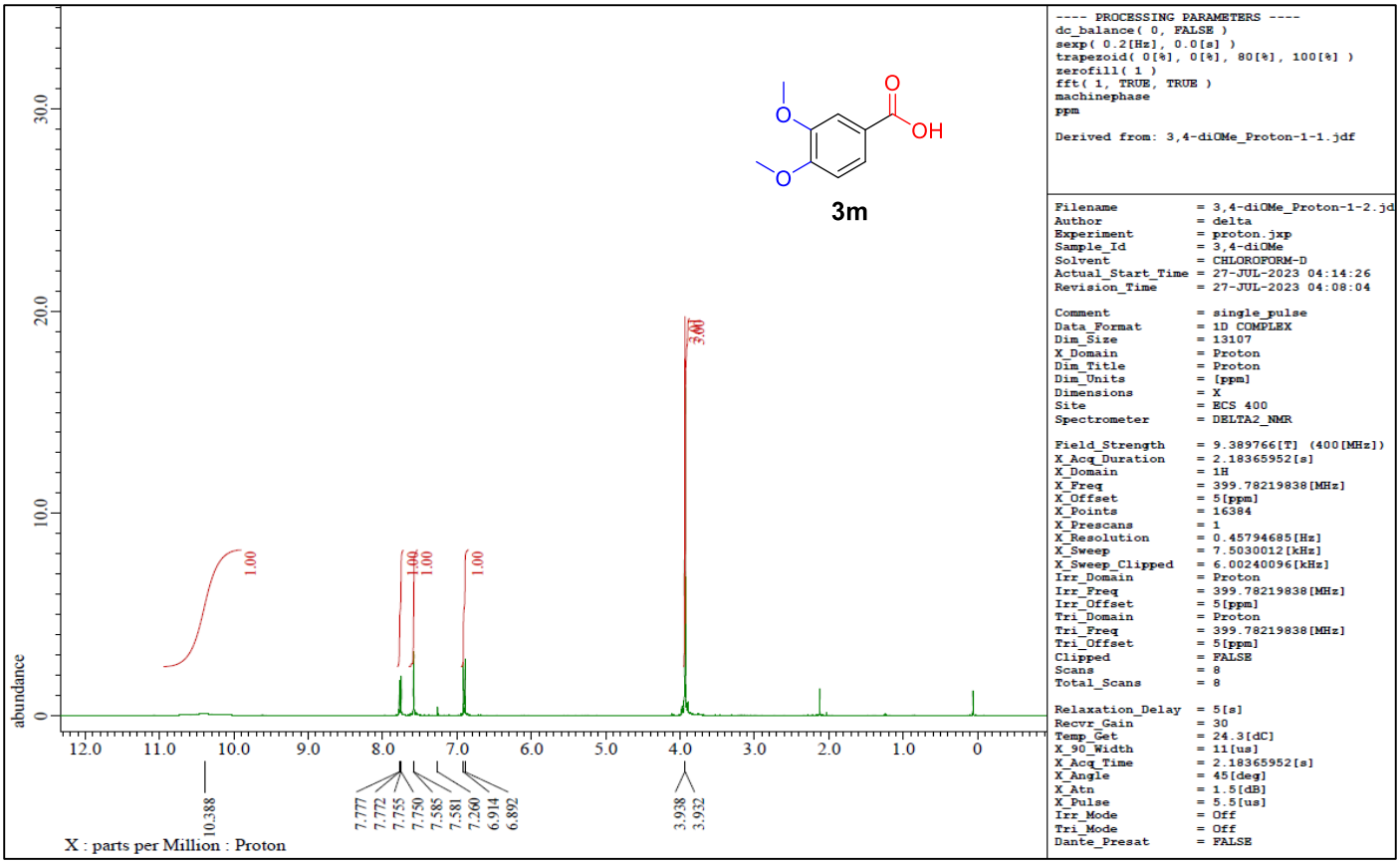
Compound **3k** (^{13}C NMR, 101 MHz, $CDCl_3$).



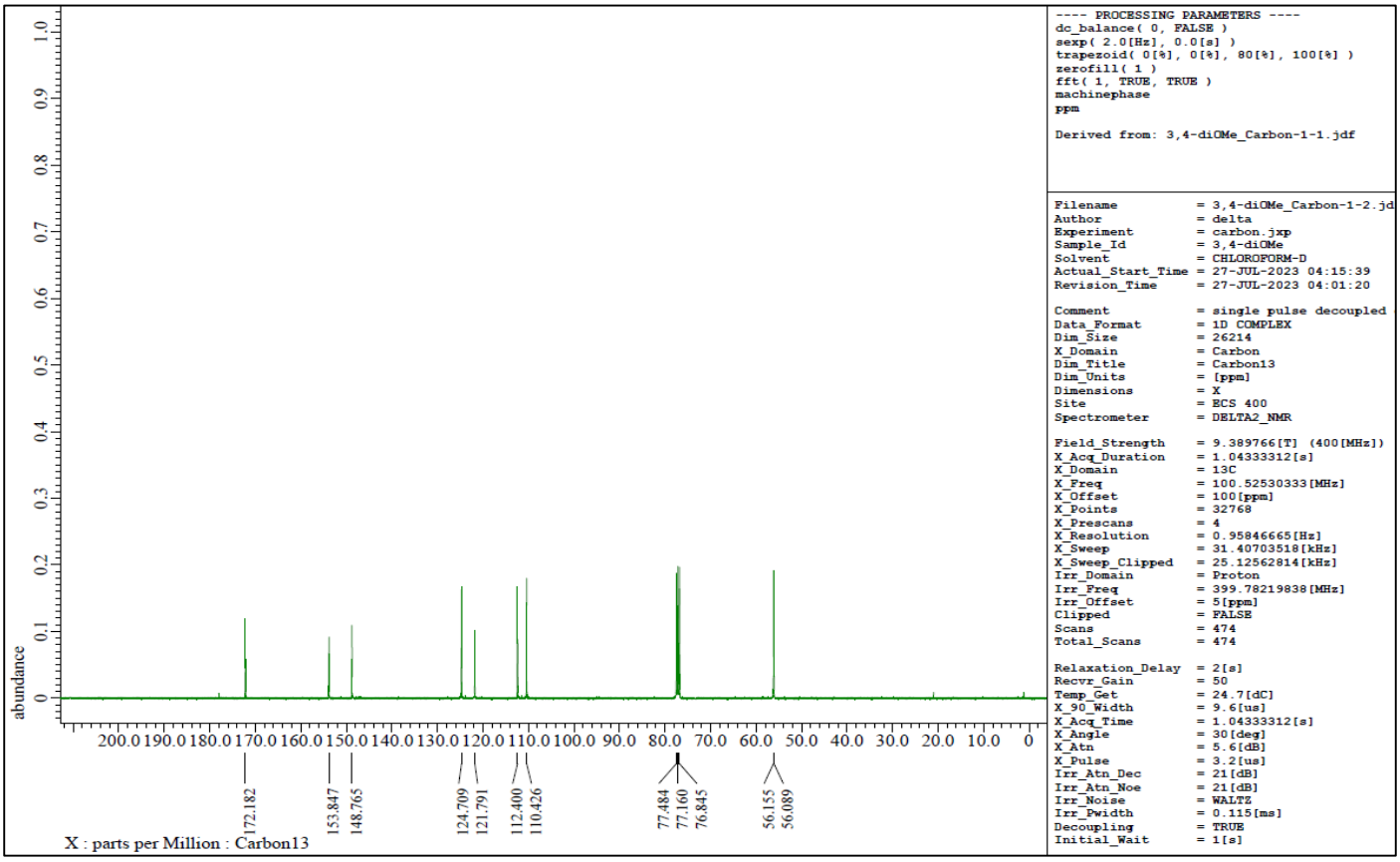
Compound **3l** (^{1}H NMR, 400 MHz, $CDCl_3$).



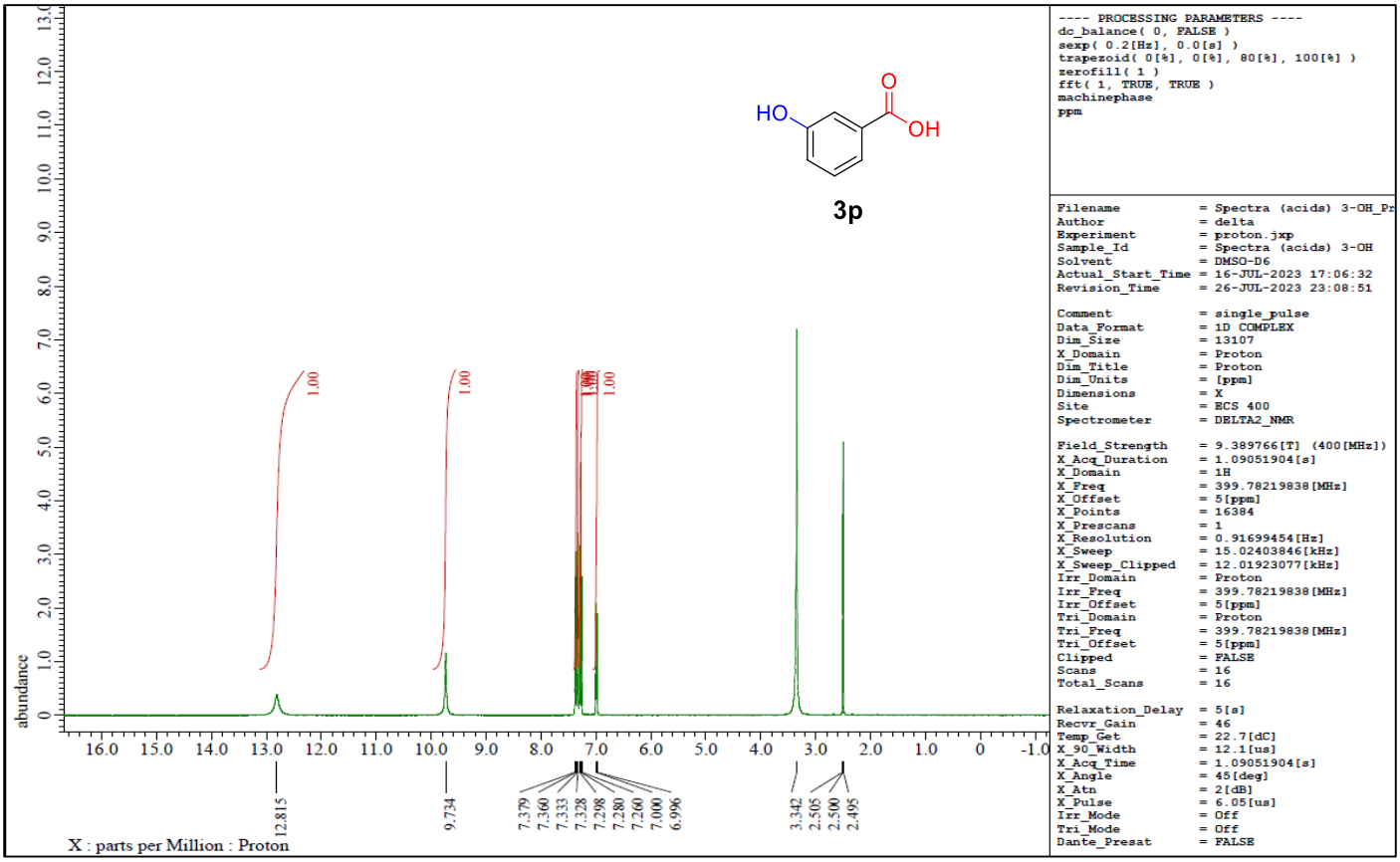
Compound **3l** (^{13}C NMR, 101 MHz, $CDCl_3$).



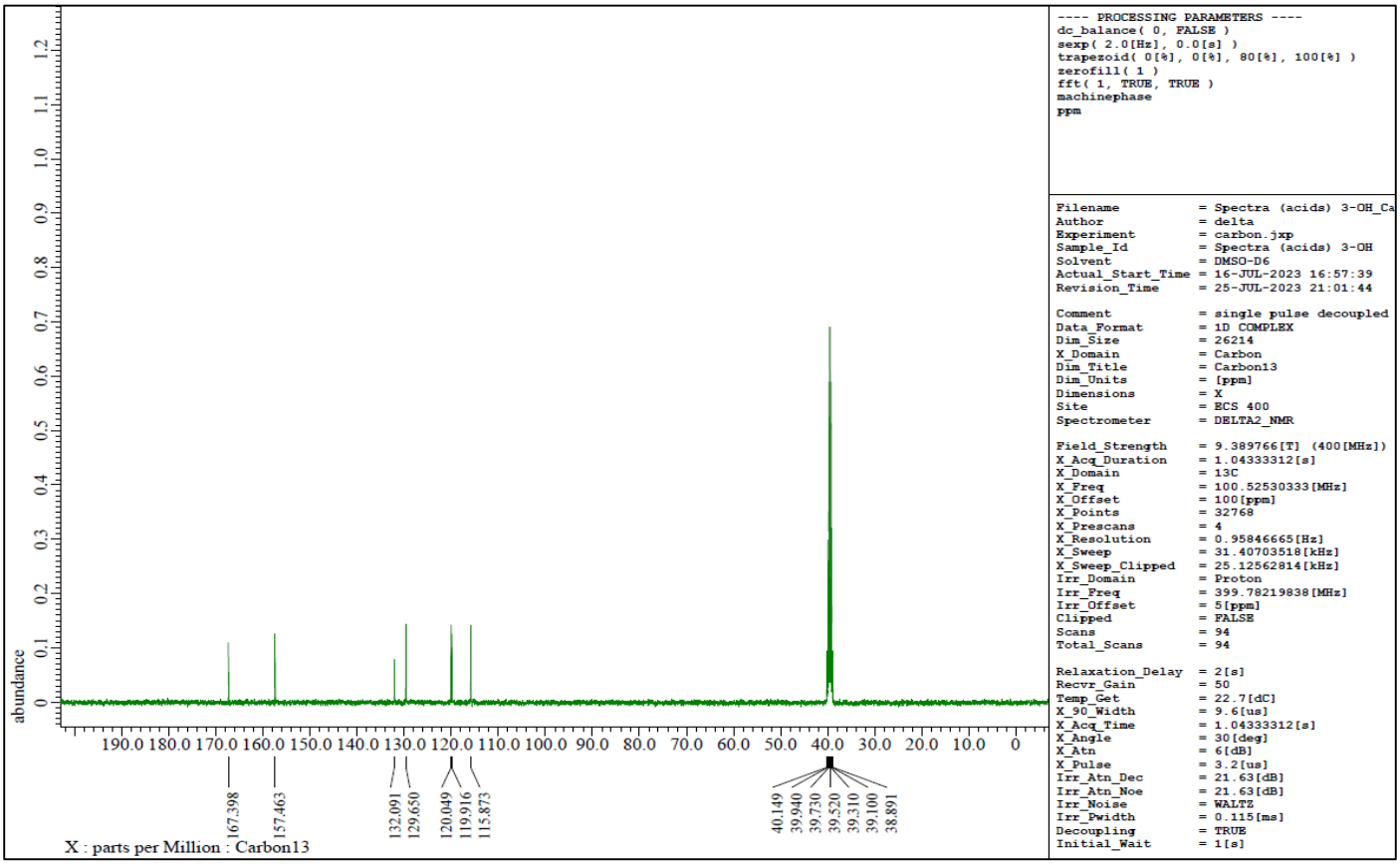
Compound **3m** (^{1}H NMR, 400 MHz, $CDCl_3$).



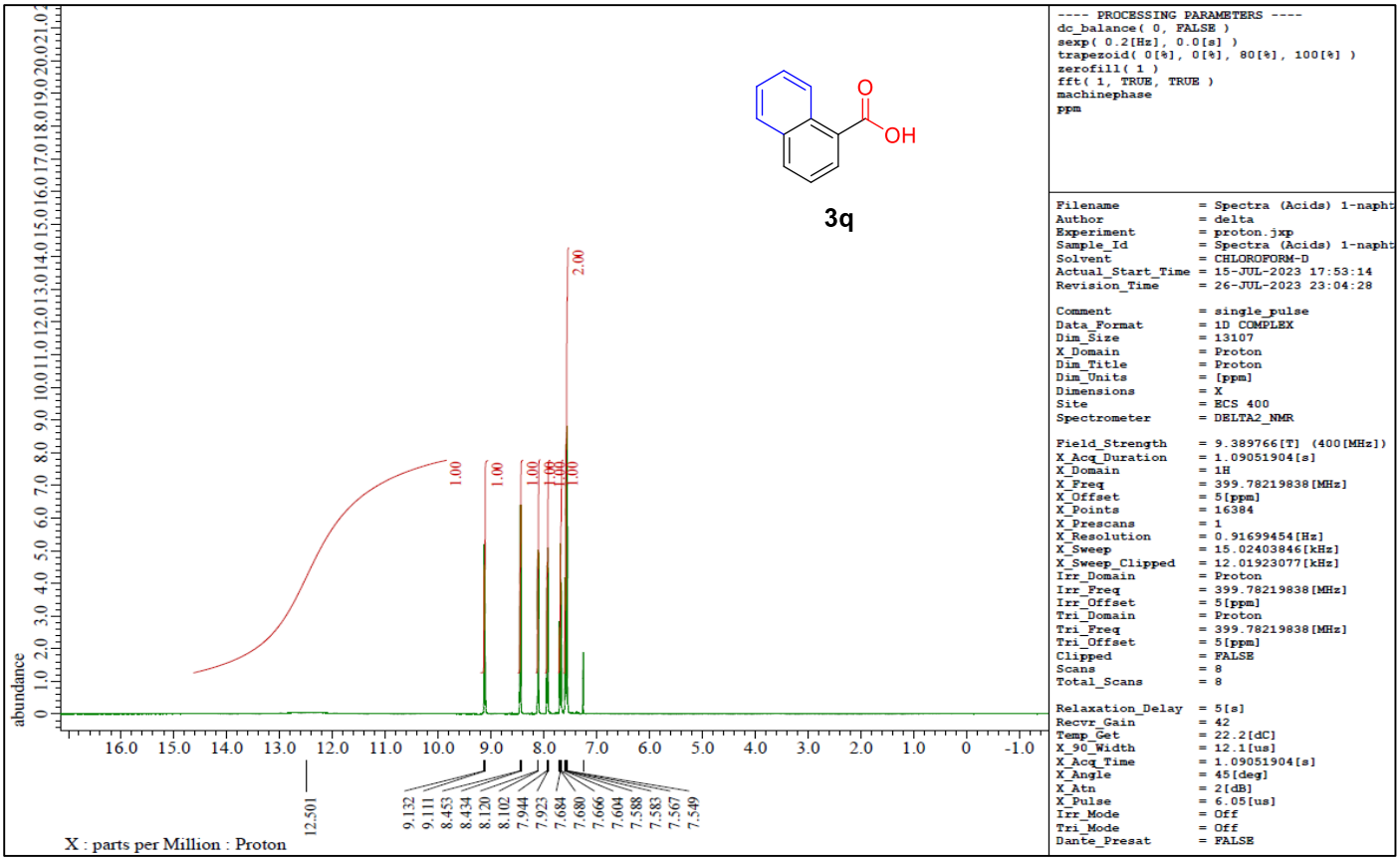
Compound **3m** (^{13}C NMR, 101 MHz, $CDCl_3$).



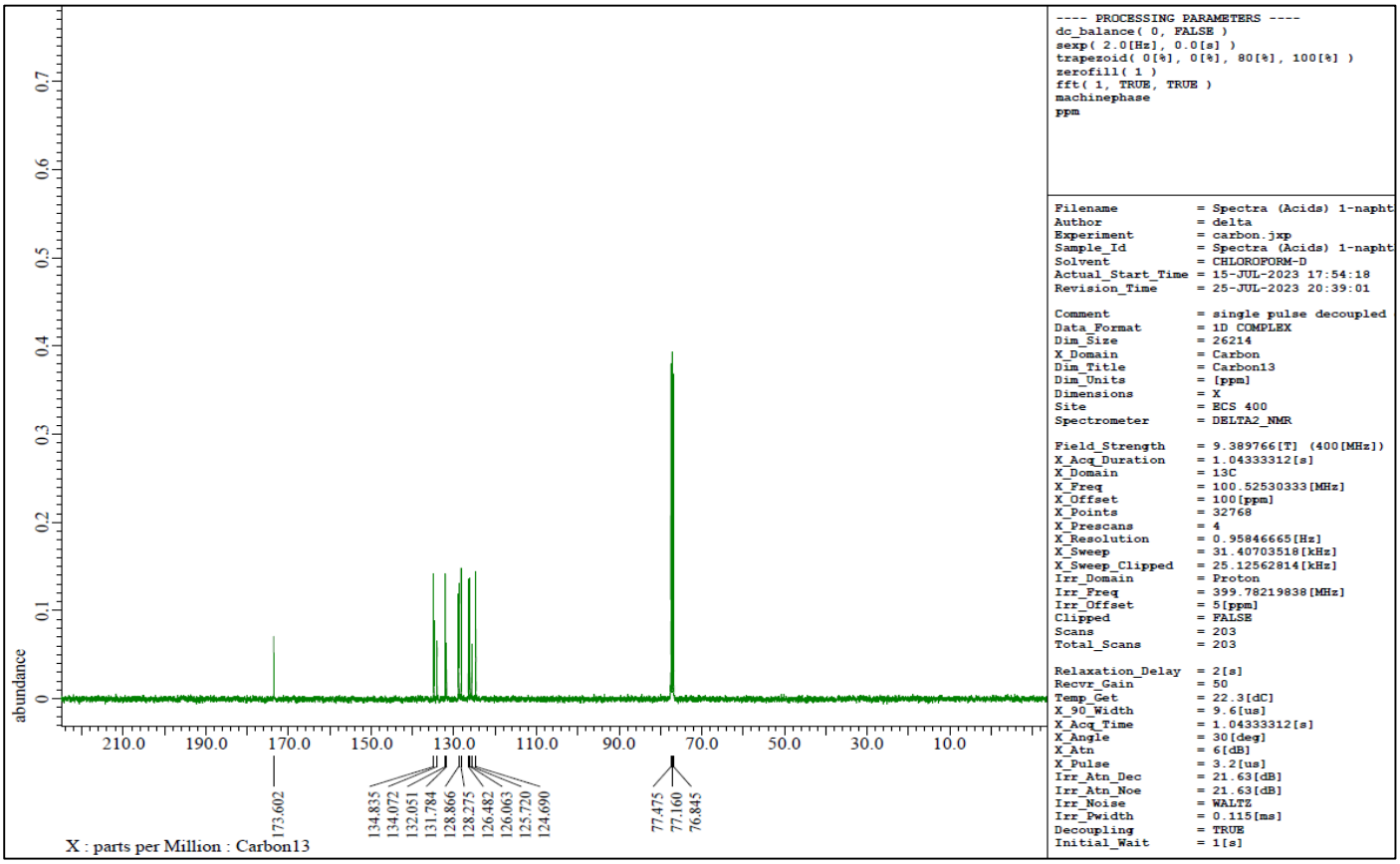
Compound **3p** (^{1}H NMR, 400 MHz, $(CD_3)_2SO$).



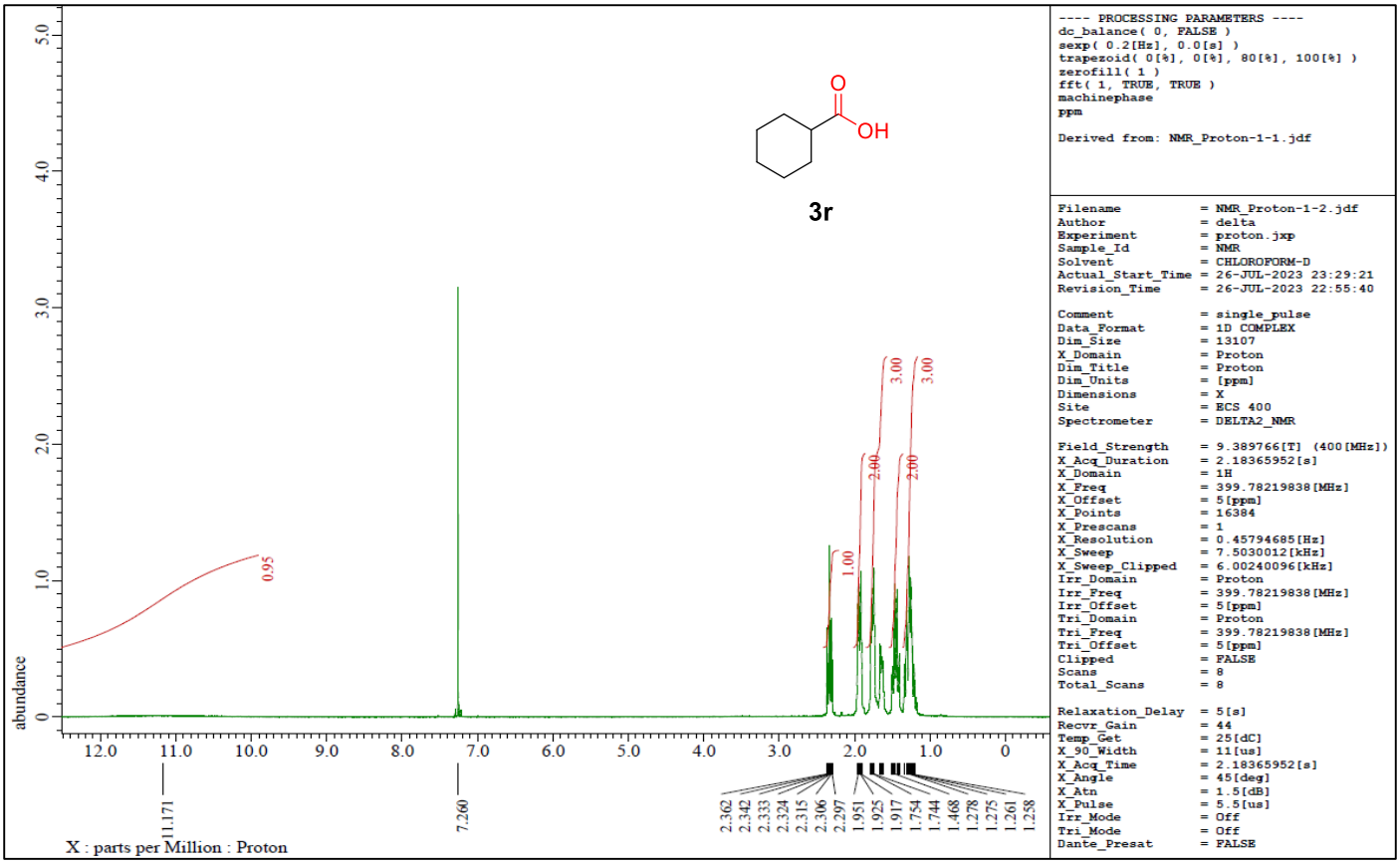
Compound **3p** (^{13}C NMR, 101 MHz, $(CD_3)_2SO$).



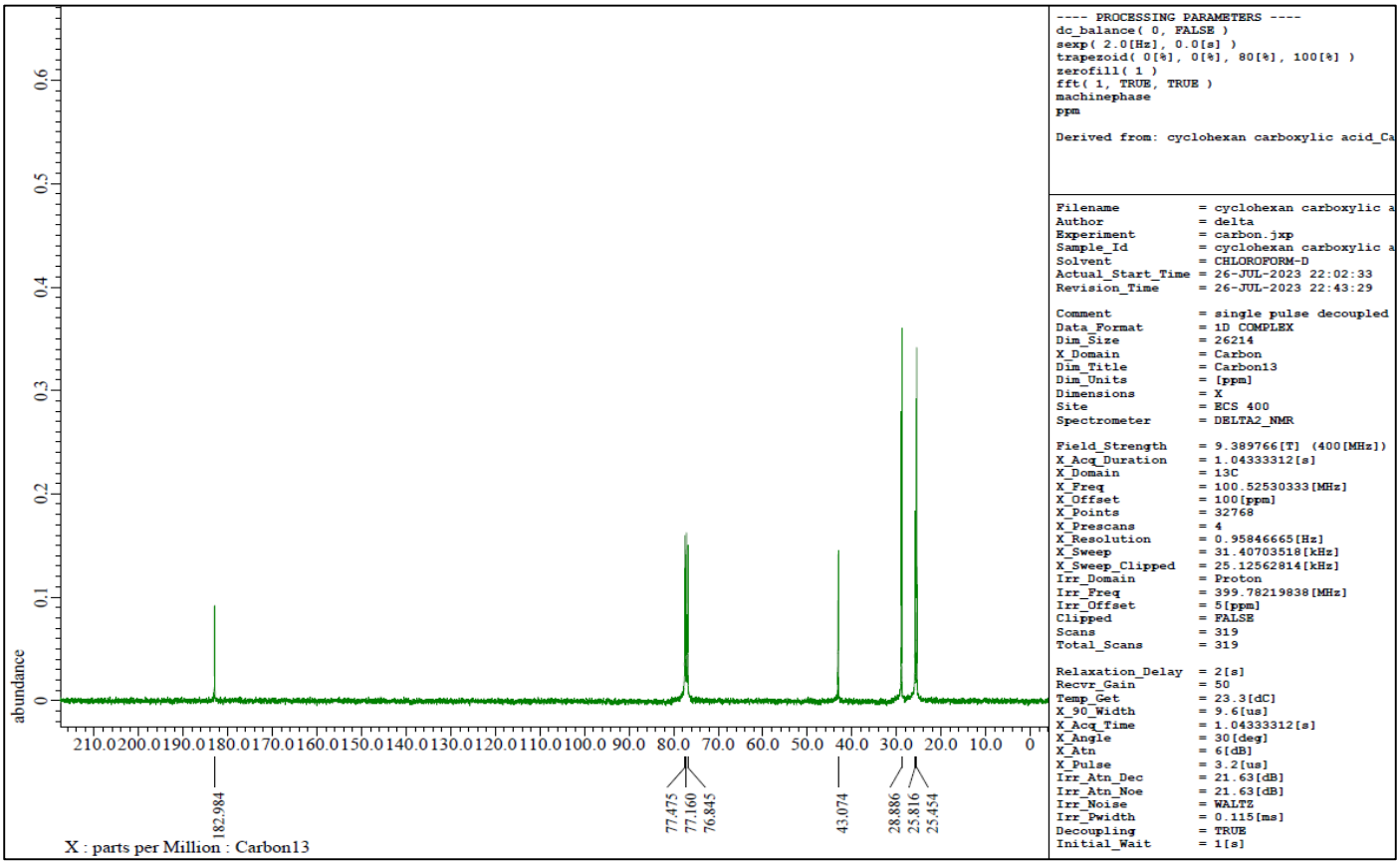
Compound **3q** (^{1}H NMR, 400 MHz, $CDCl_3$).



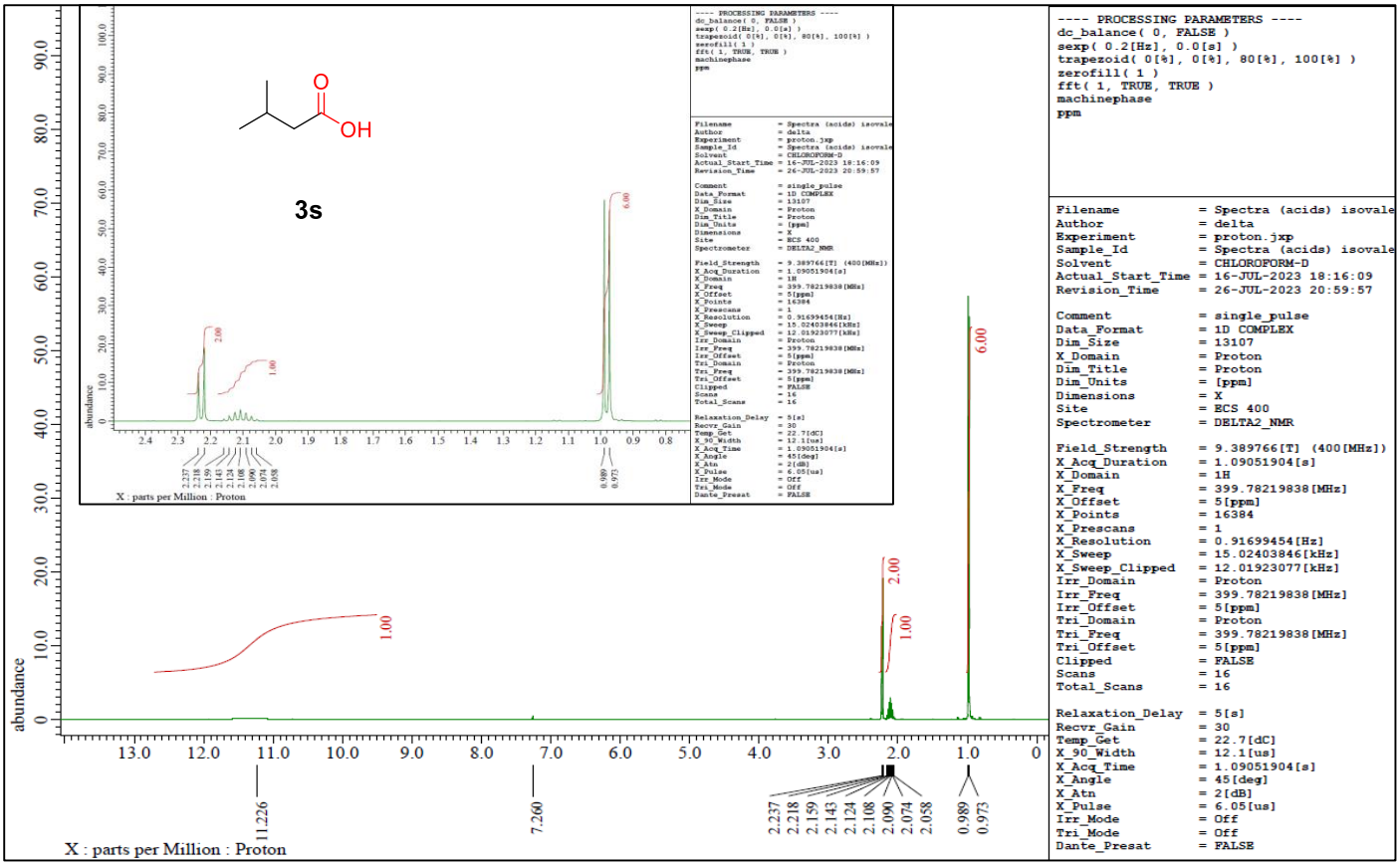
Compound **3q** (^{13}C NMR, 101 MHz, $CDCl_3$).



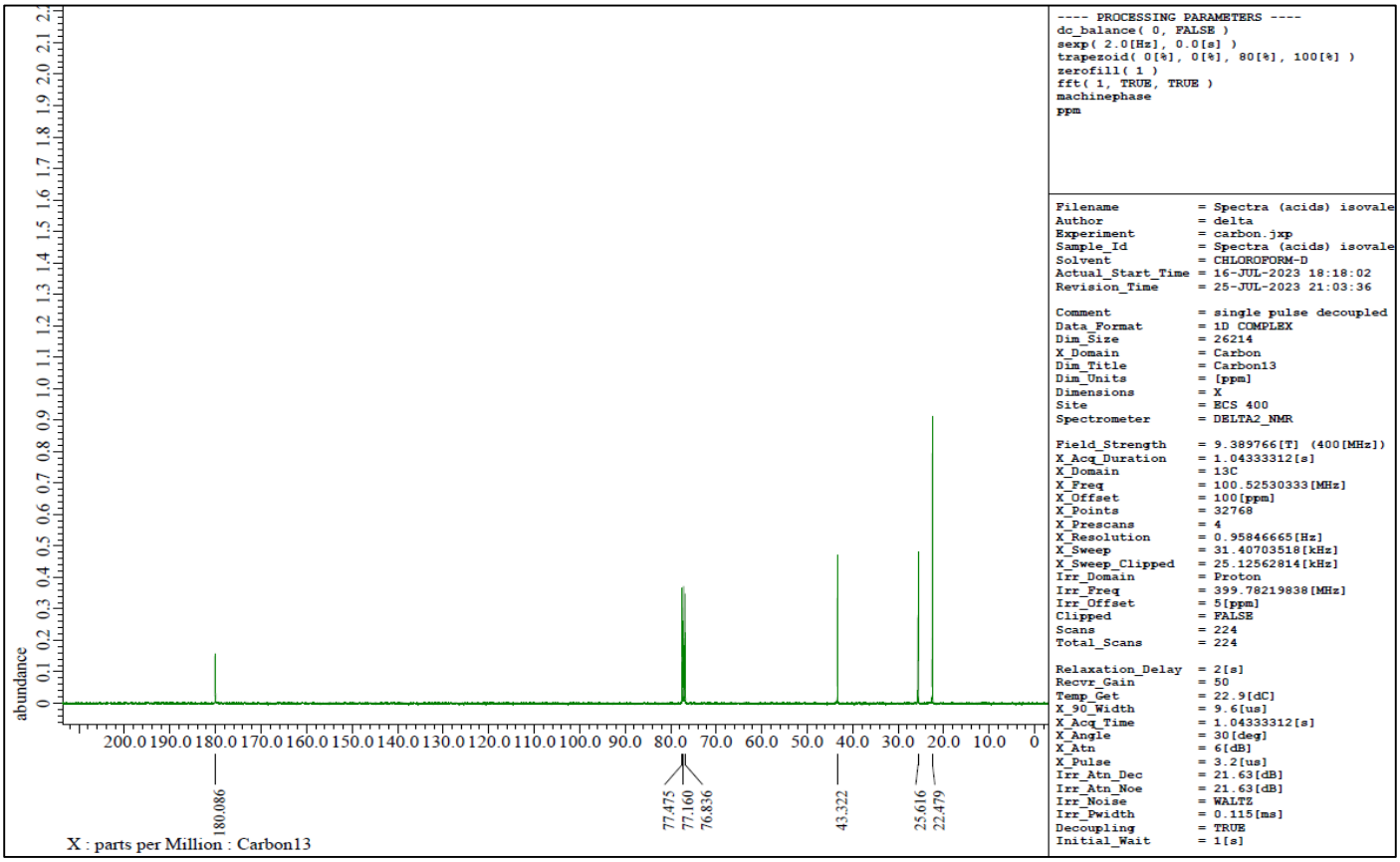
Compound **3r** (^{1}H NMR, 400 MHz, $CDCl_3$).



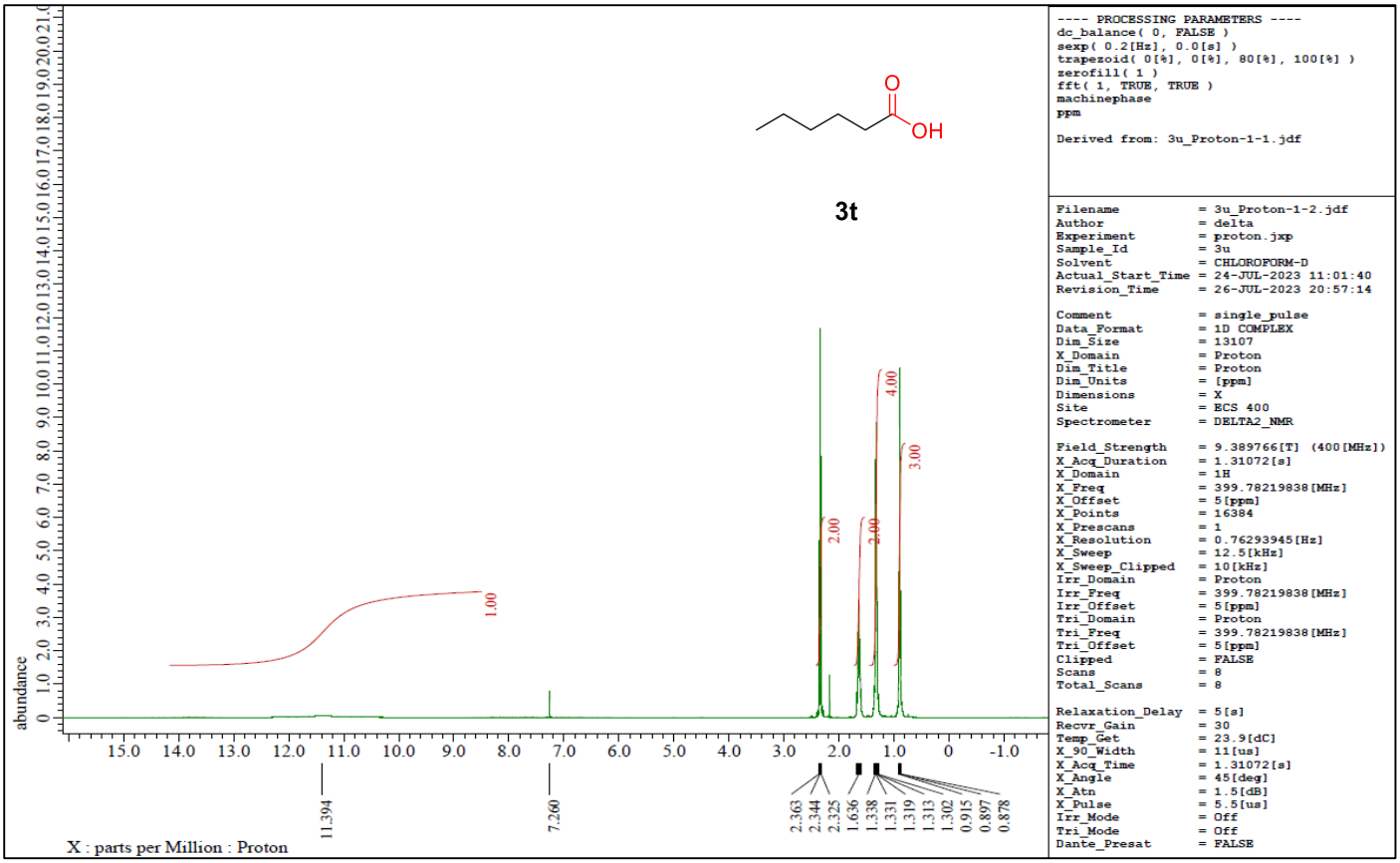
Compound **3r** (^{13}C NMR, 101 MHz, $CDCl_3$).



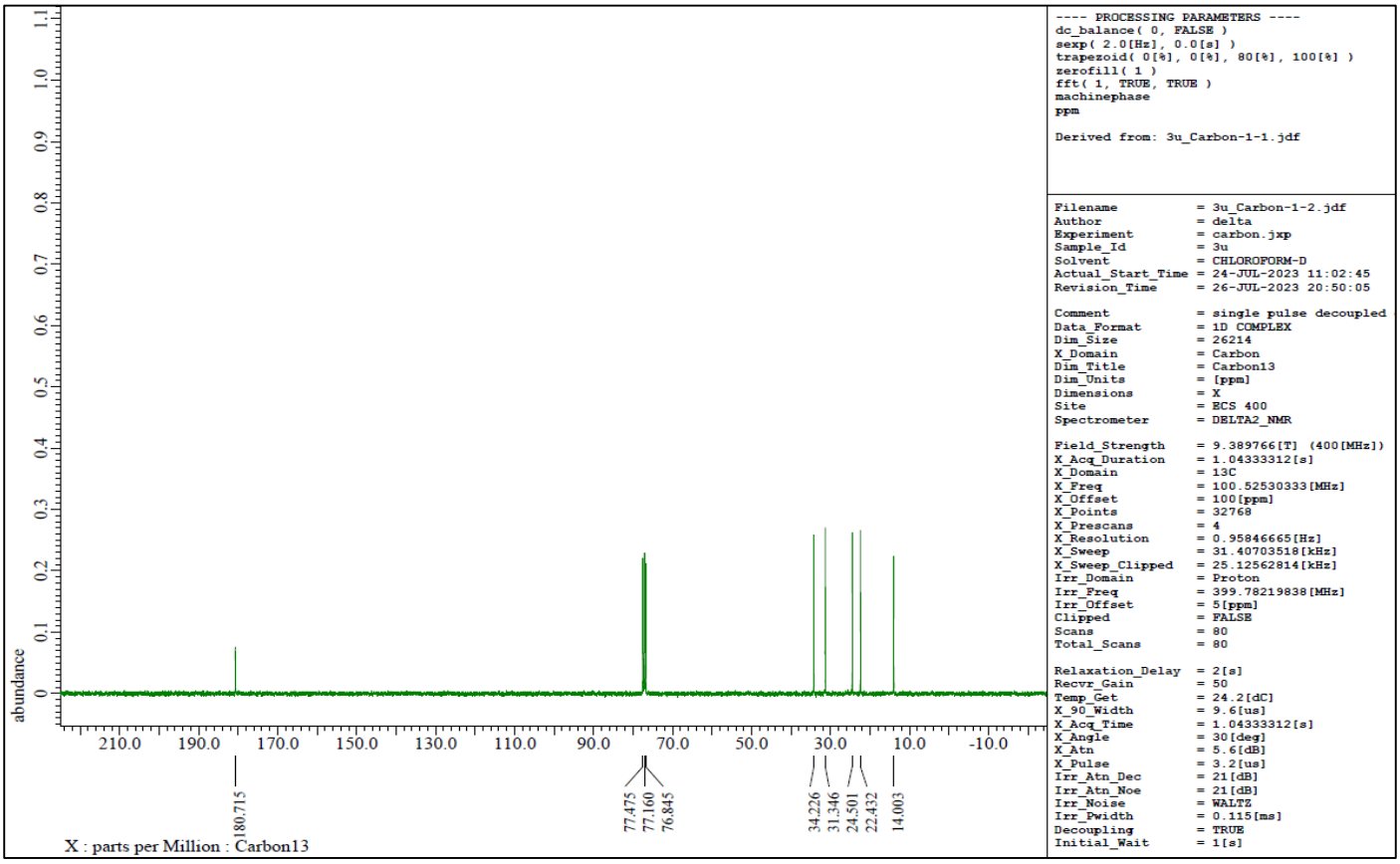
Compound **3s** (^{1}H NMR, 400 MHz, $CDCl_3$).



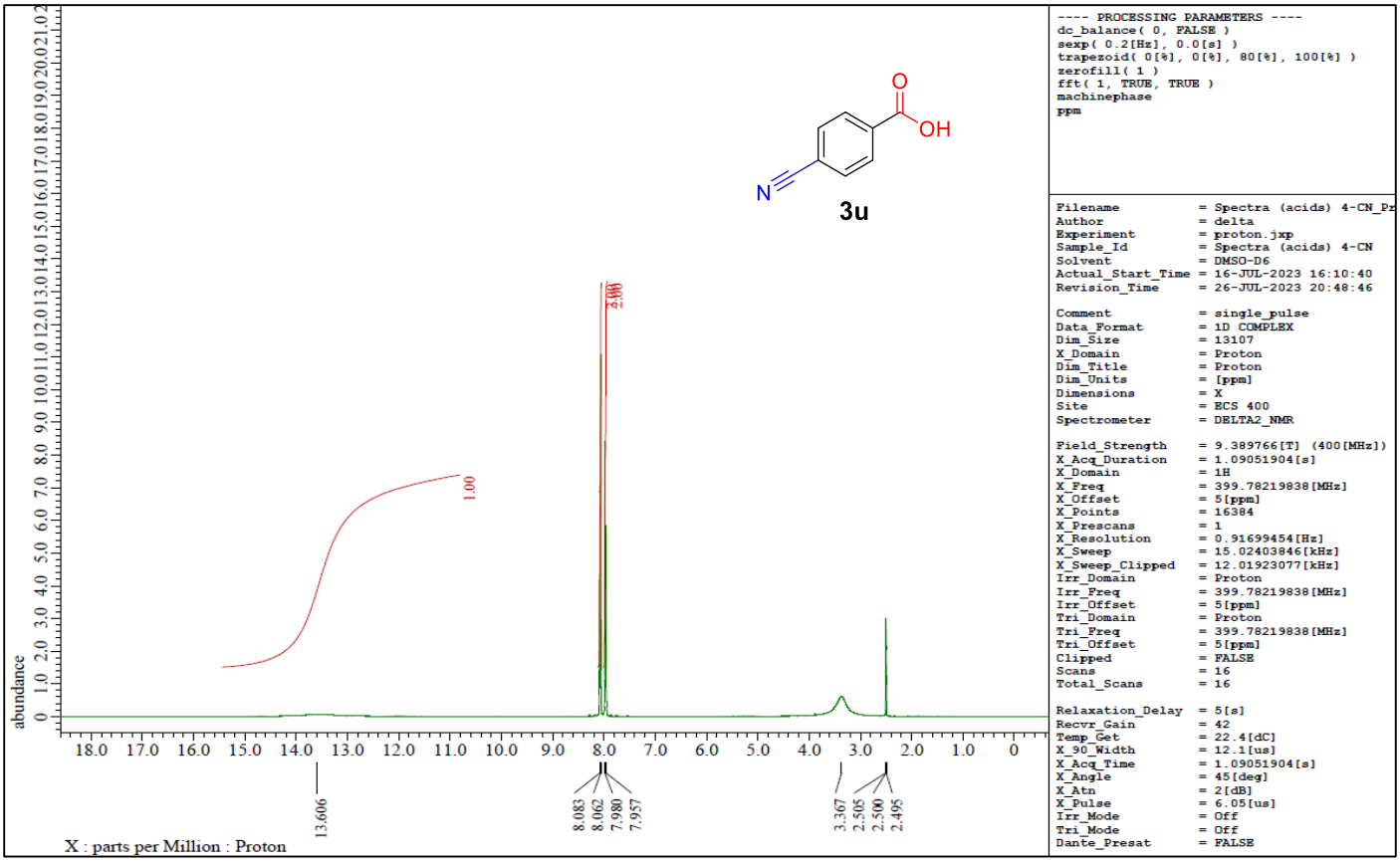
Compound **3s** (^{13}C NMR, 101 MHz, $CDCl_3$).



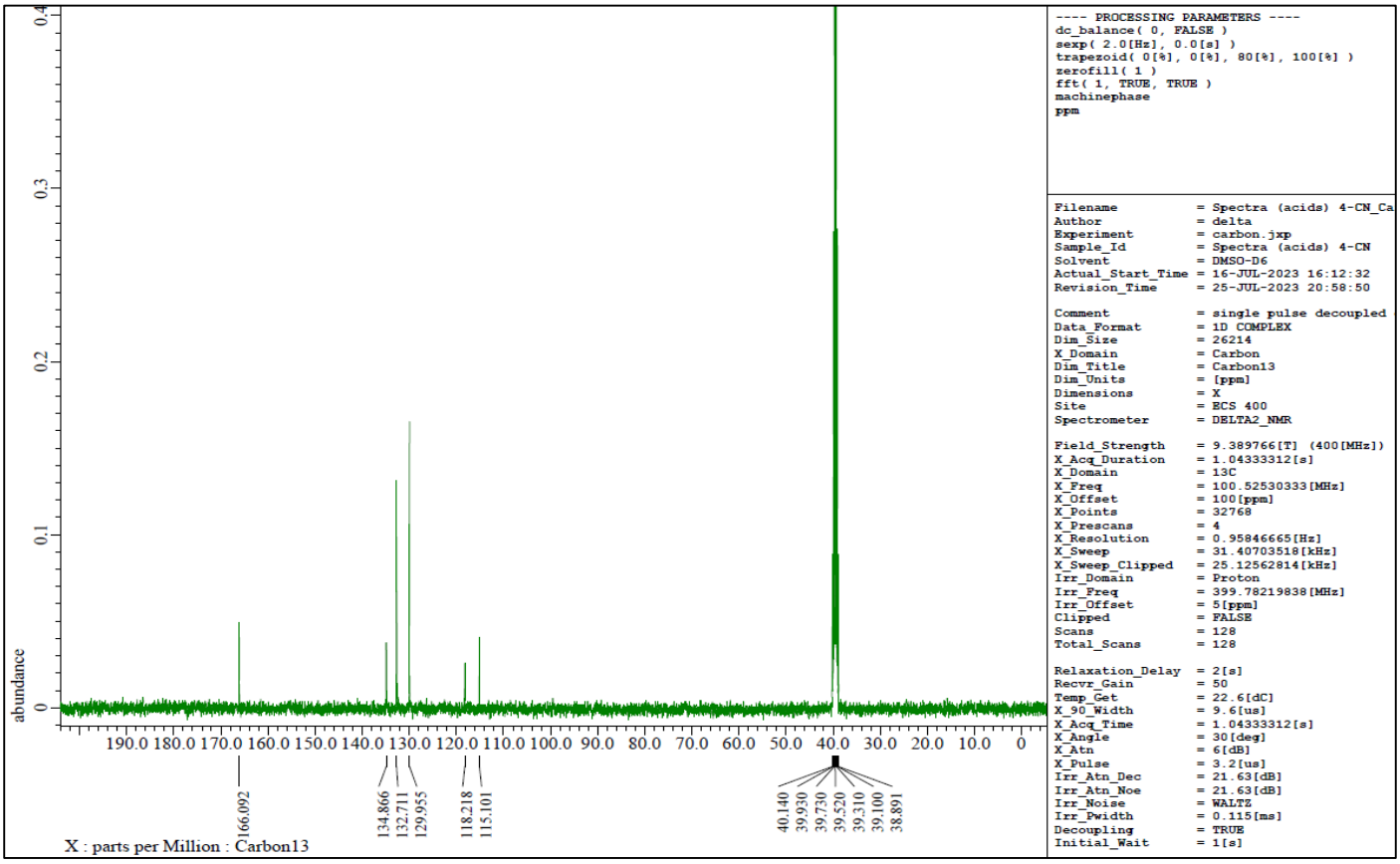
Compound **3t** (^{1}H NMR, 400 MHz, $CDCl_3$).



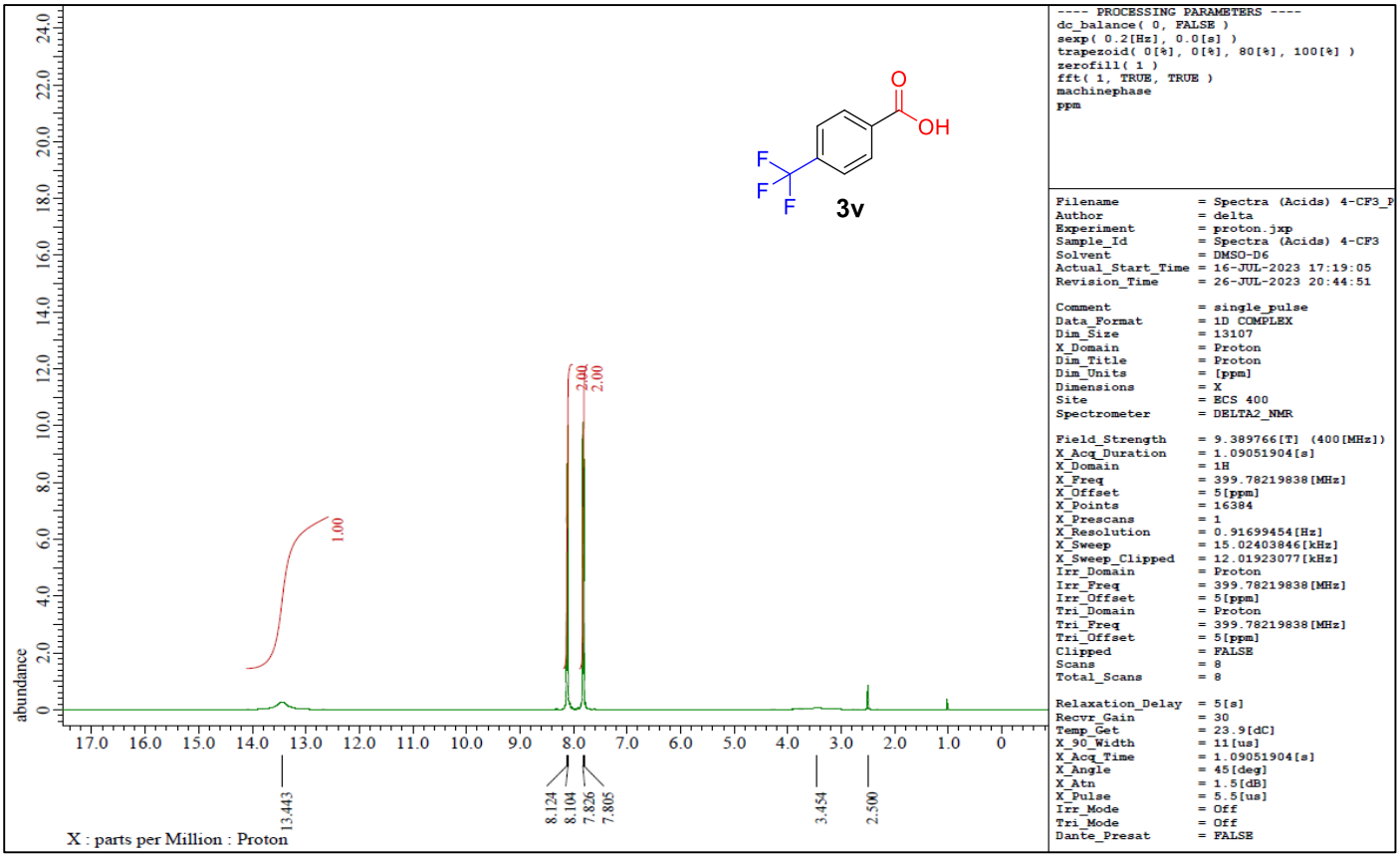
Compound **3t** (^{13}C NMR, 101 MHz, $CDCl_3$).



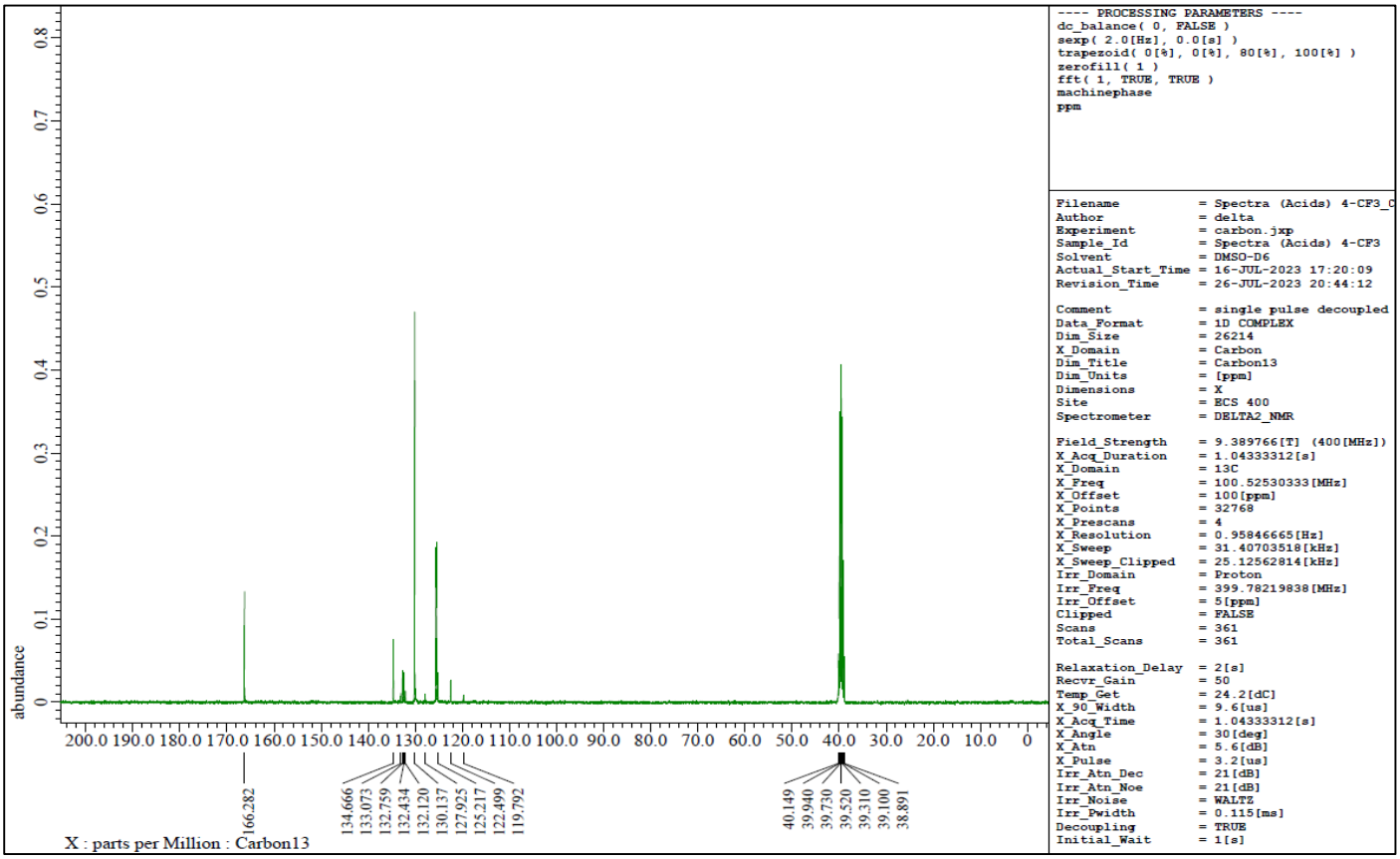
Compound **3u** (^{1}H NMR, 400 MHz, $(CD_3)_2SO$).



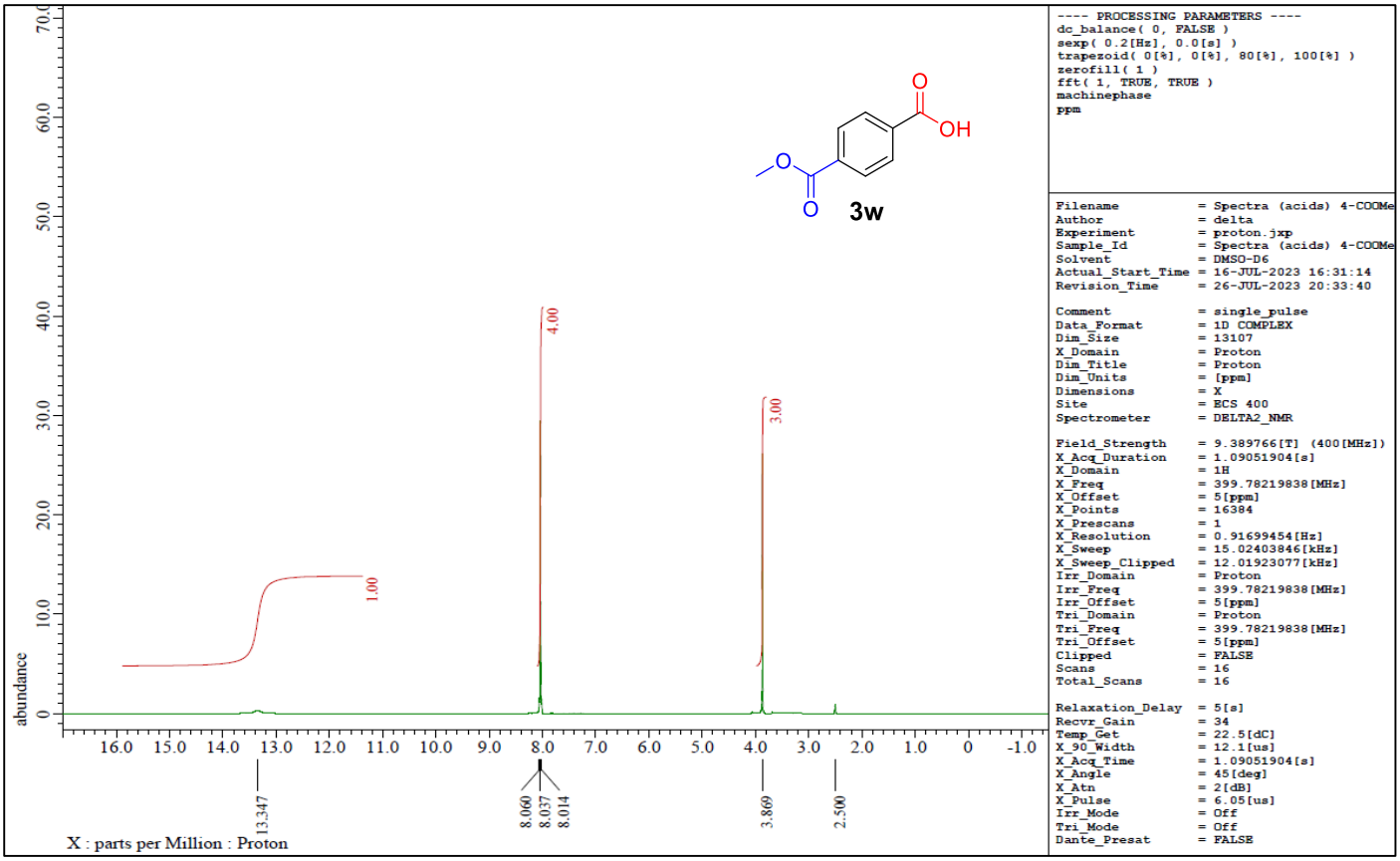
Compound **3u** (^{13}C NMR, 101 MHz, $(CD_3)_2SO$).



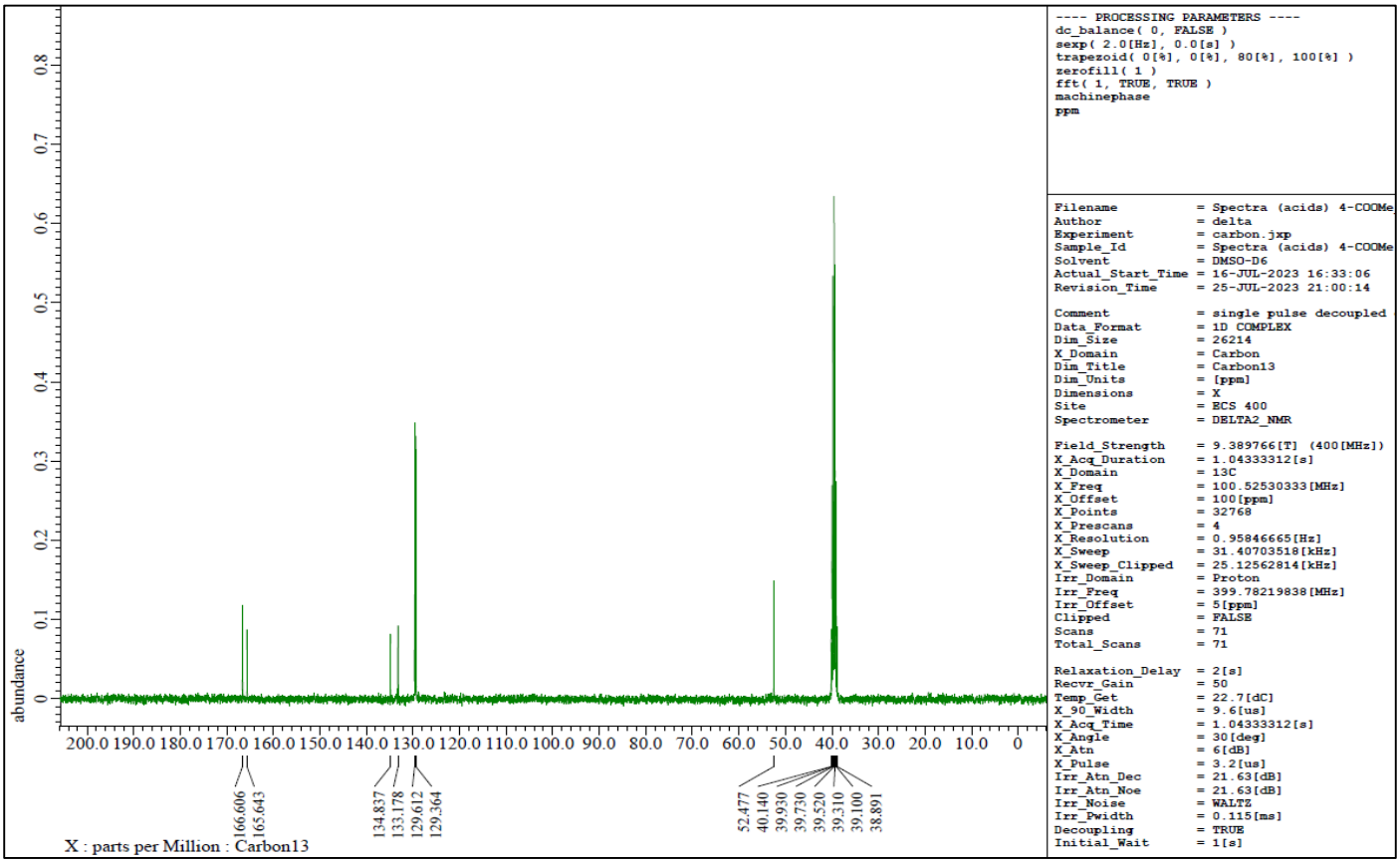
Compound **3v** (^{1}H NMR, 400 MHz, $(CD_3)_2SO$).



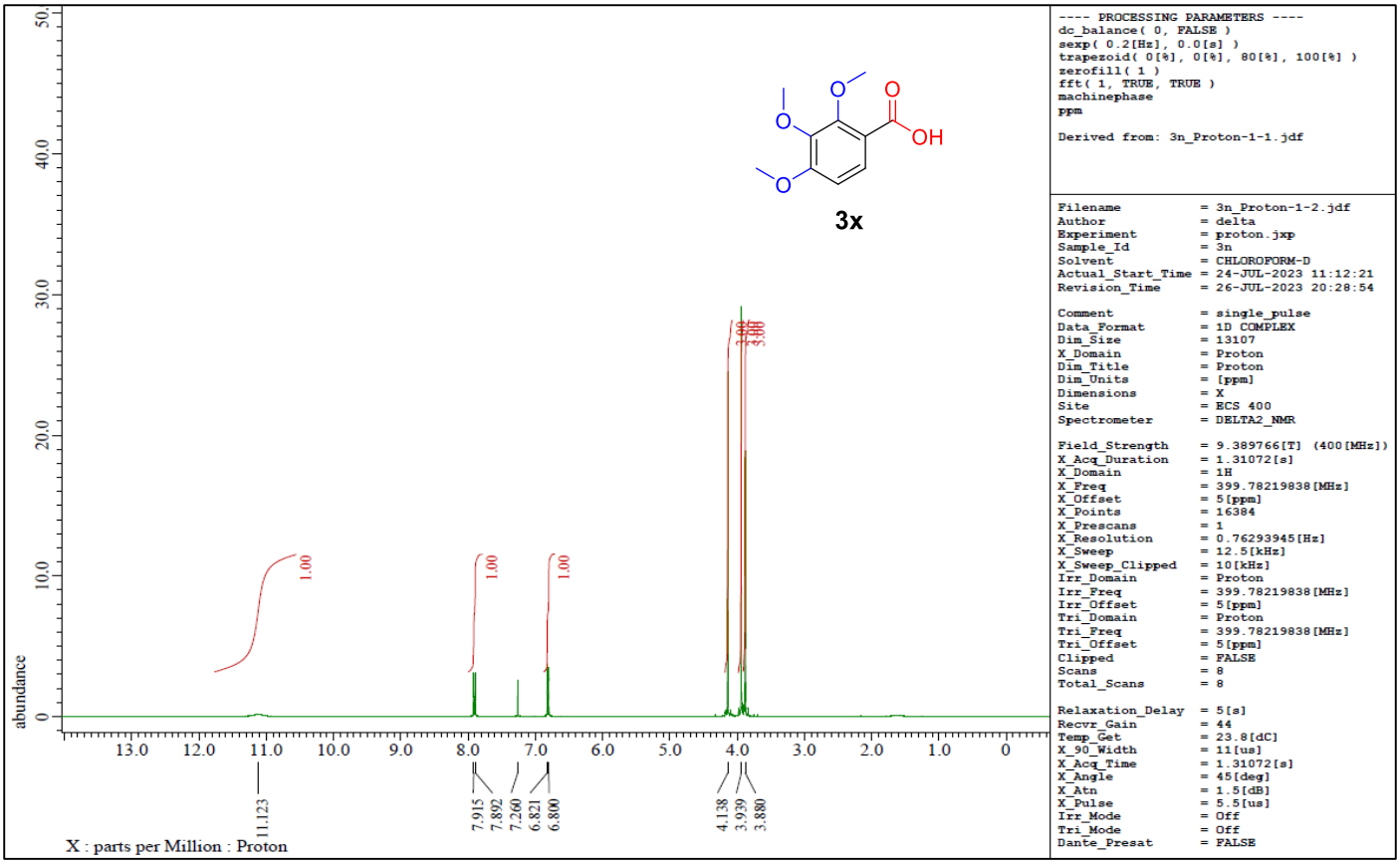
Compound **3v** (^{13}C NMR, 101 MHz, $(CD_3)_2SO$).



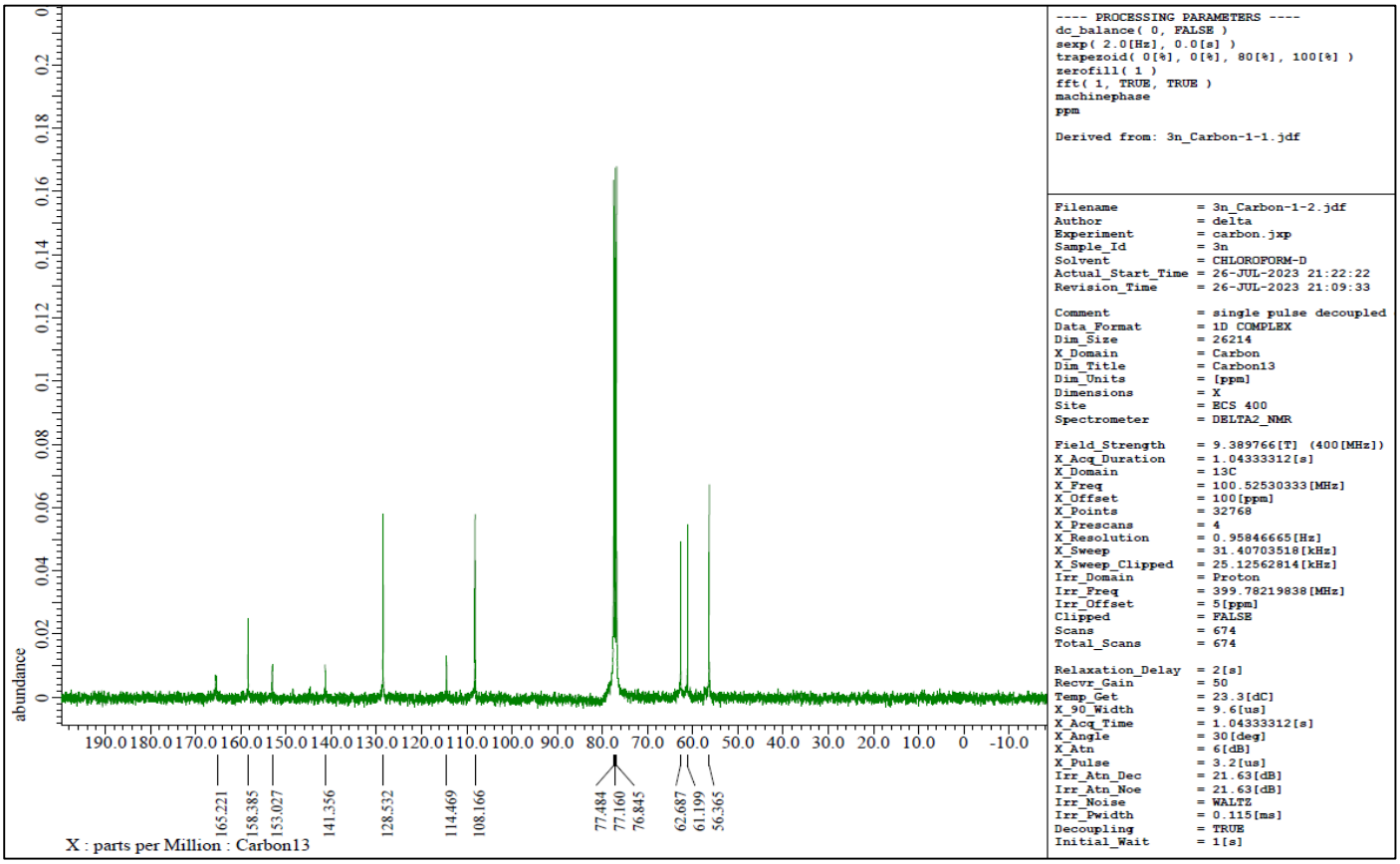
Compound **3w** (^{1}H NMR, 400 MHz, $(CD_3)_2SO$).



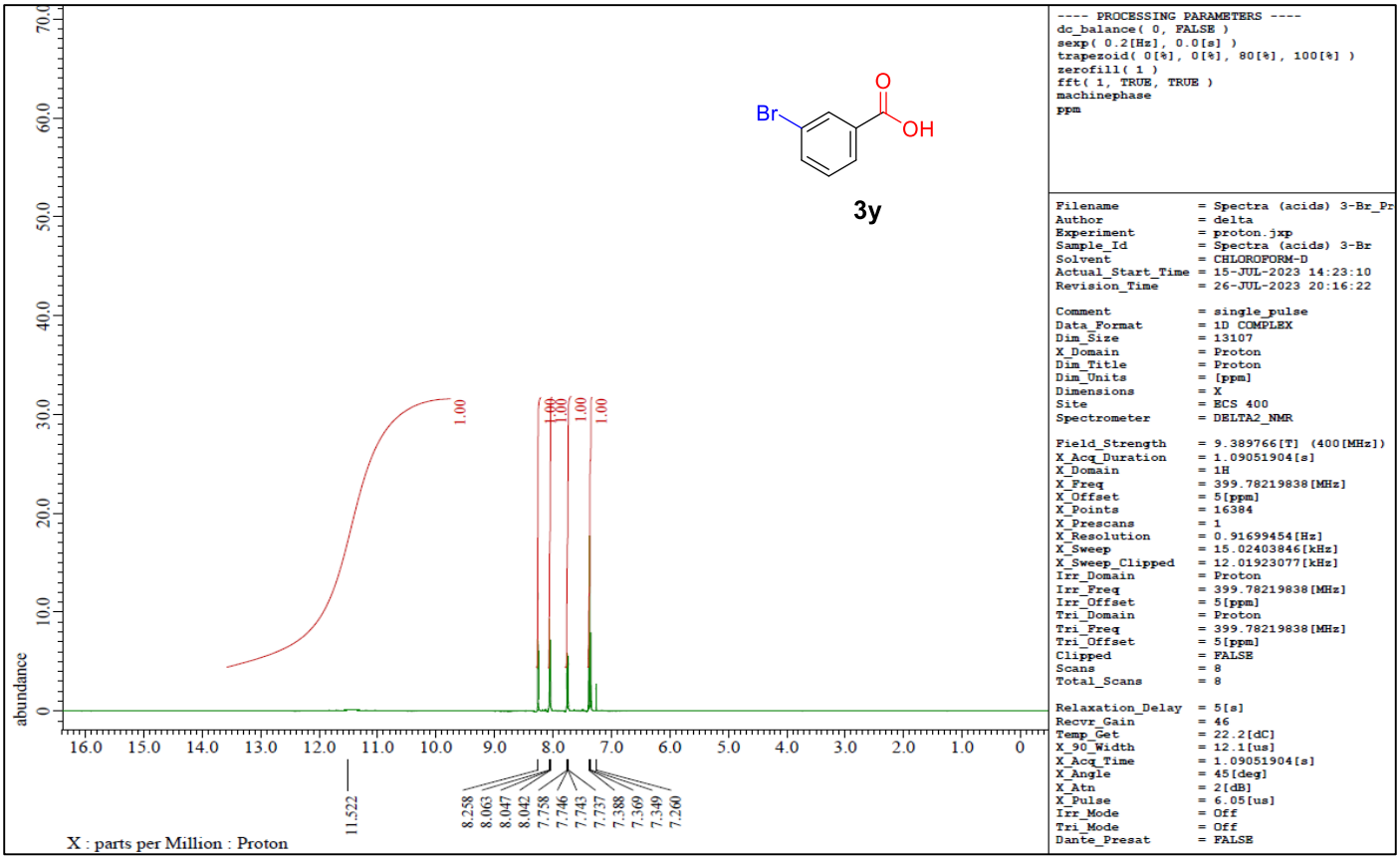
Compound **3w** (^{13}C NMR, 101 MHz, $(CD_3)_2SO$).



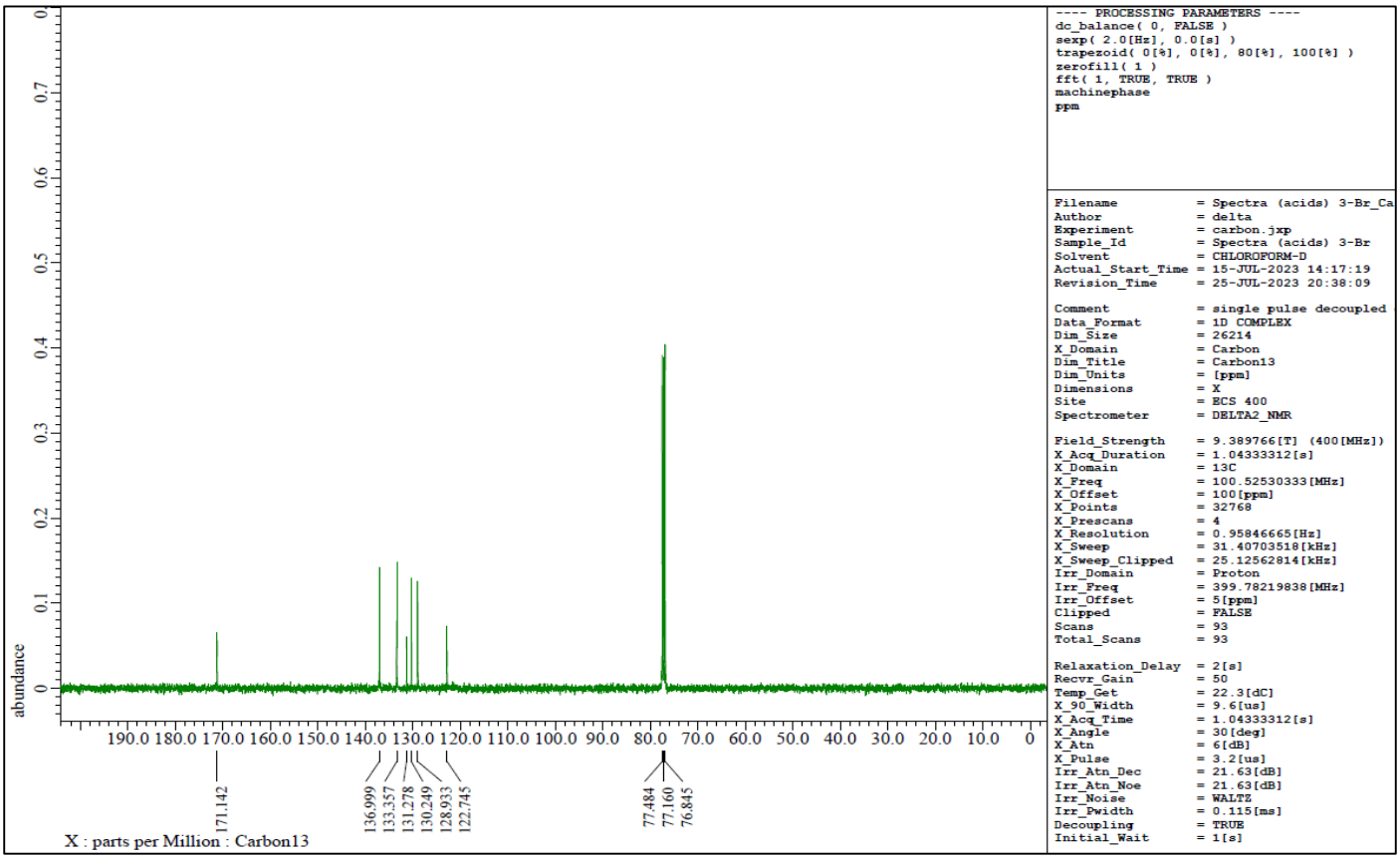
Compound **3x** (^{1}H NMR, 400 MHz, $CDCl_3$).



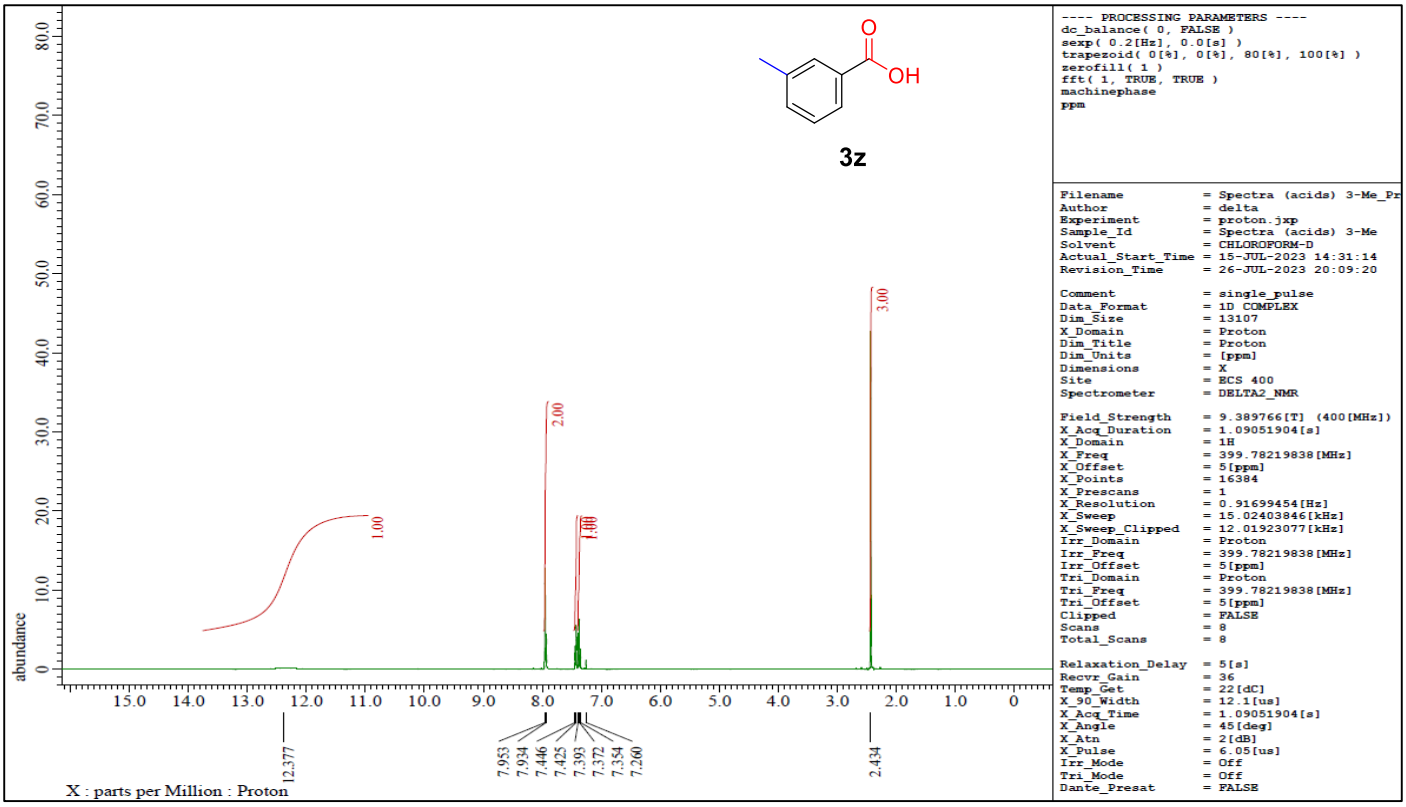
Compound **3x** (^{13}C NMR, 101 MHz, $CDCl_3$).



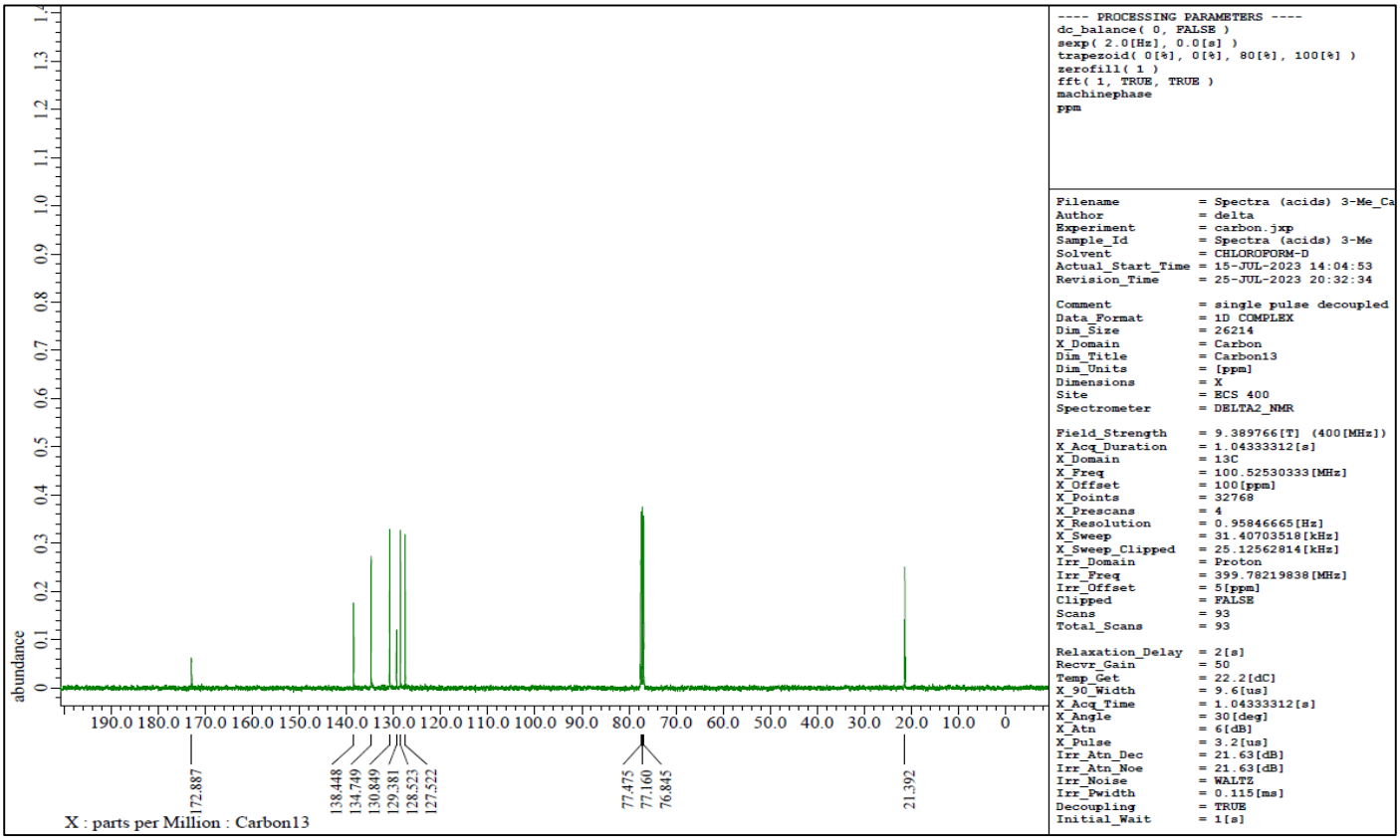
Compound **3y** (^{1}H NMR, 400 MHz, $CDCl_3$).



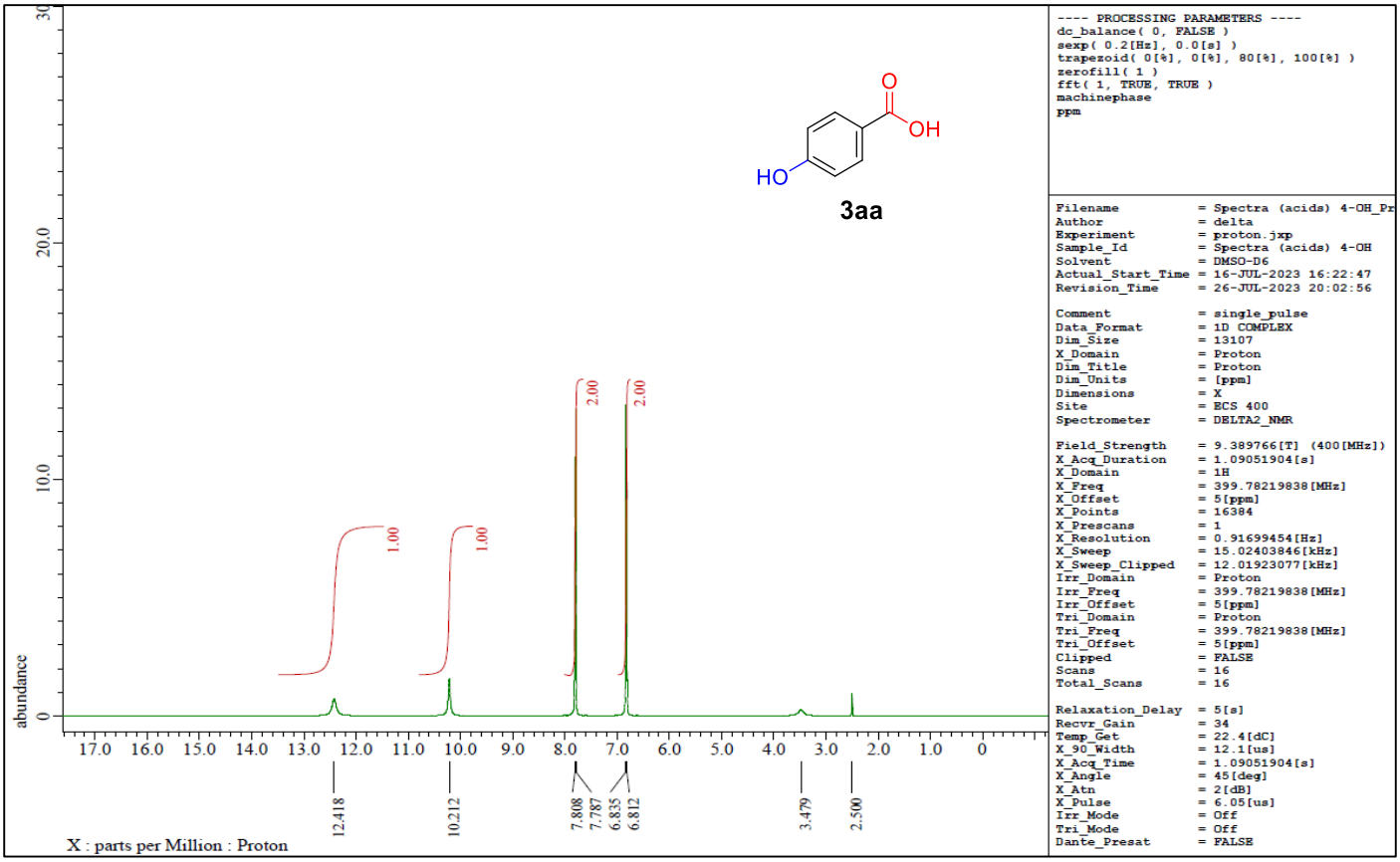
Compound **3y** (^{13}C NMR, 101 MHz, $CDCl_3$).



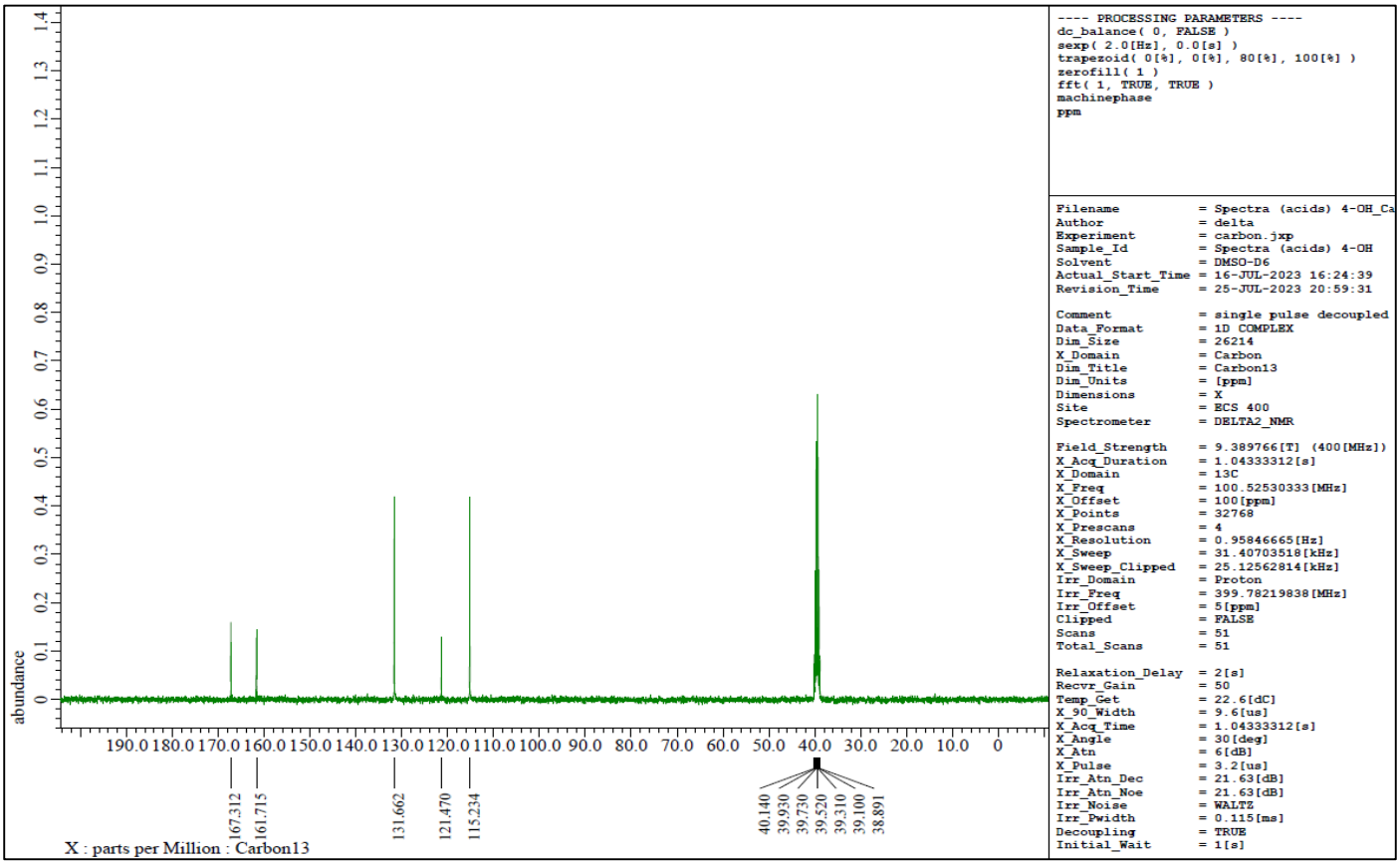
Compound **3z** (^{1}H NMR, 400 MHz, $CDCl_3$).



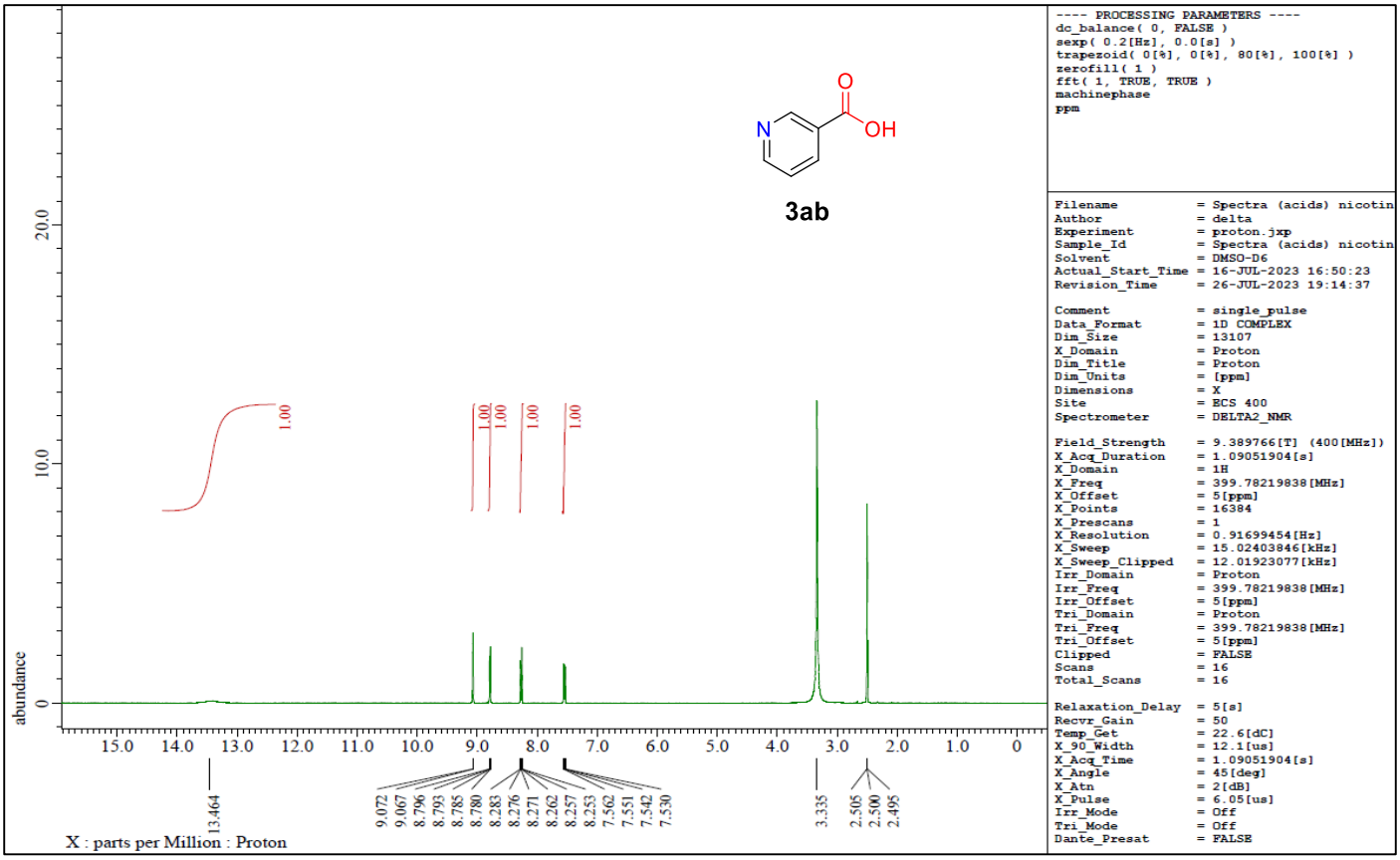
Compound **3z** (^{13}C NMR, 101 MHz, $CDCl_3$).



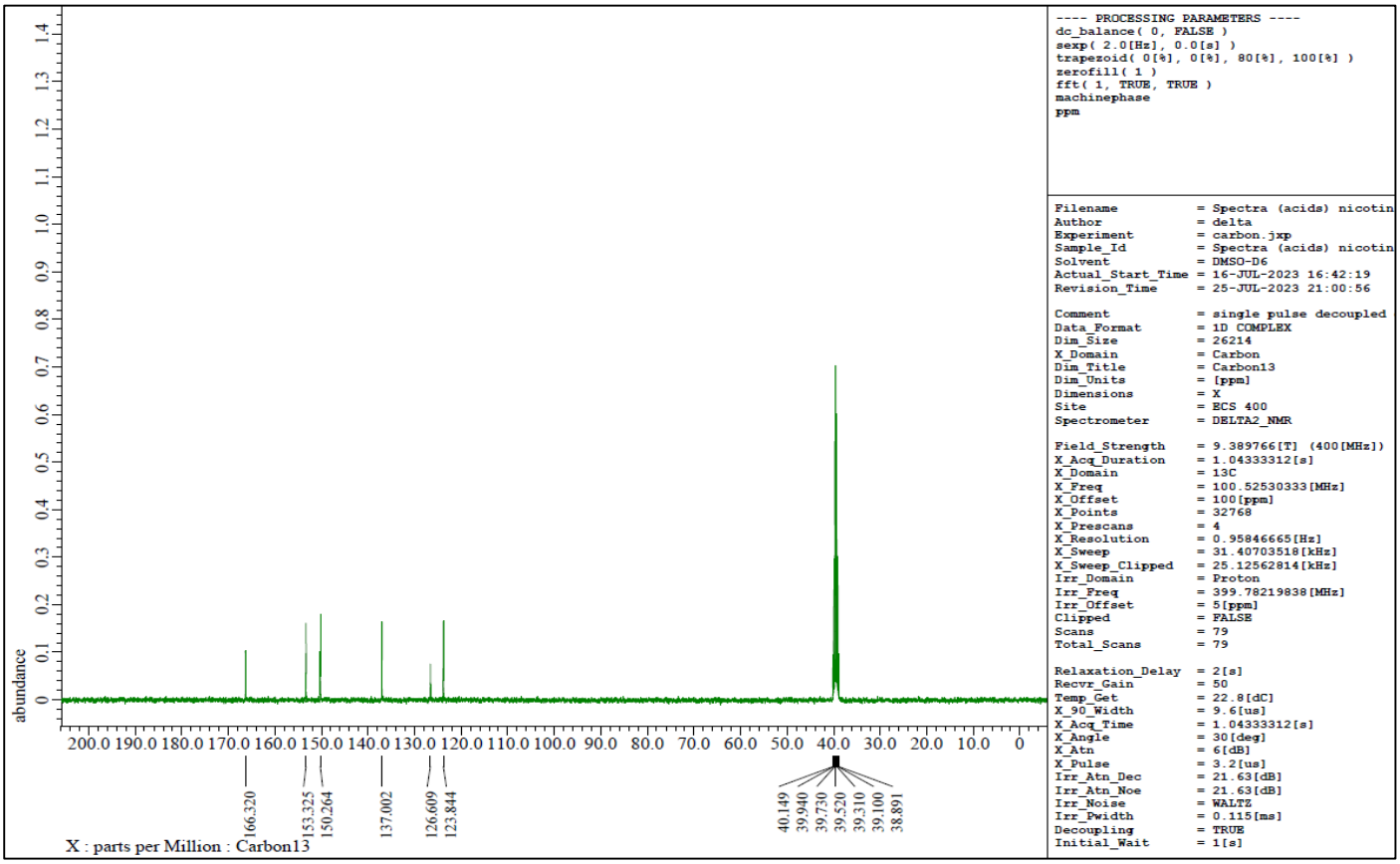
Compound **3aa** (^{1}H NMR, 400 MHz, $(CD_3)_2SO$).



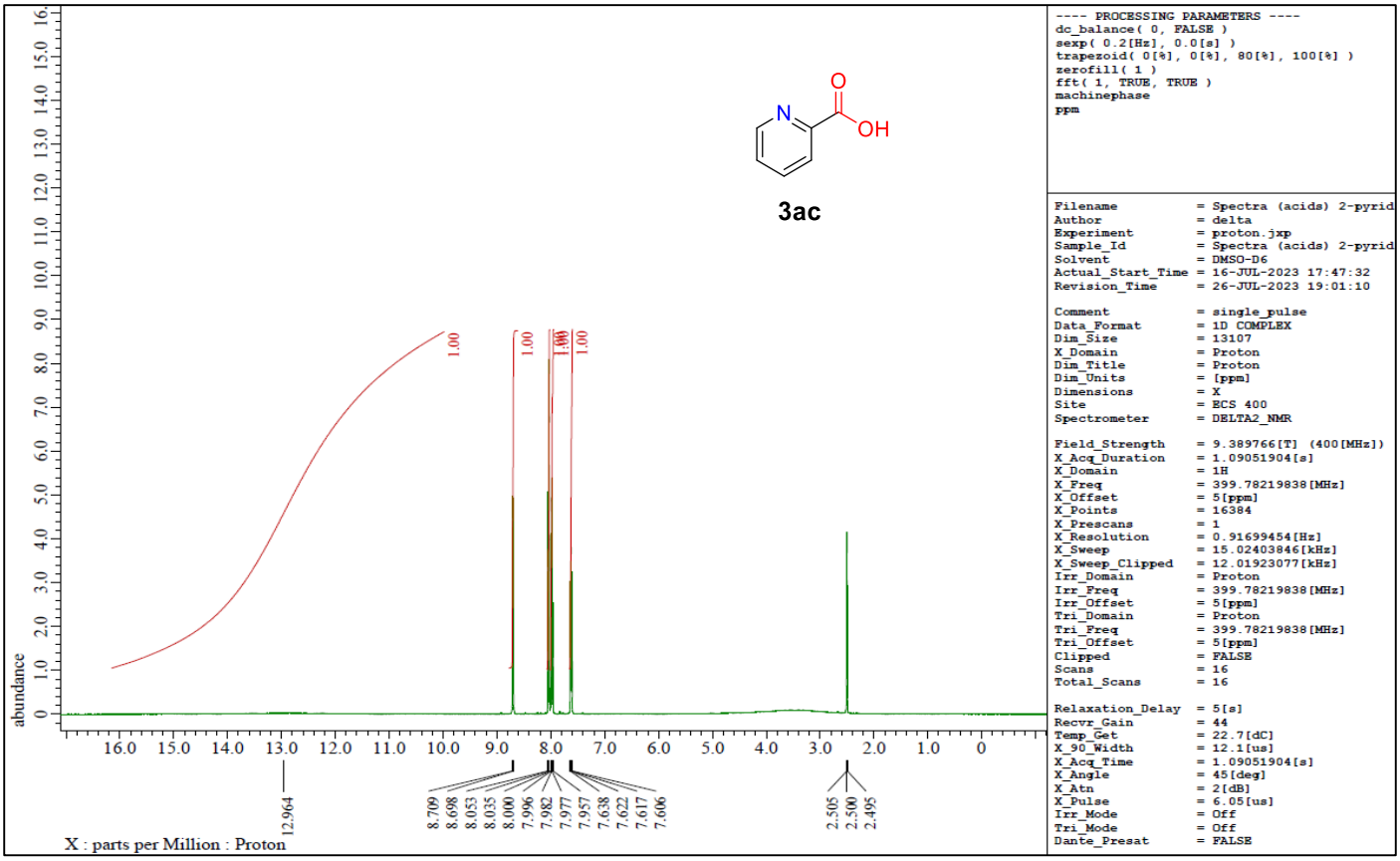
Compound **3aa** (^{13}C NMR, 101 MHz, $(CD_3)_2SO$).



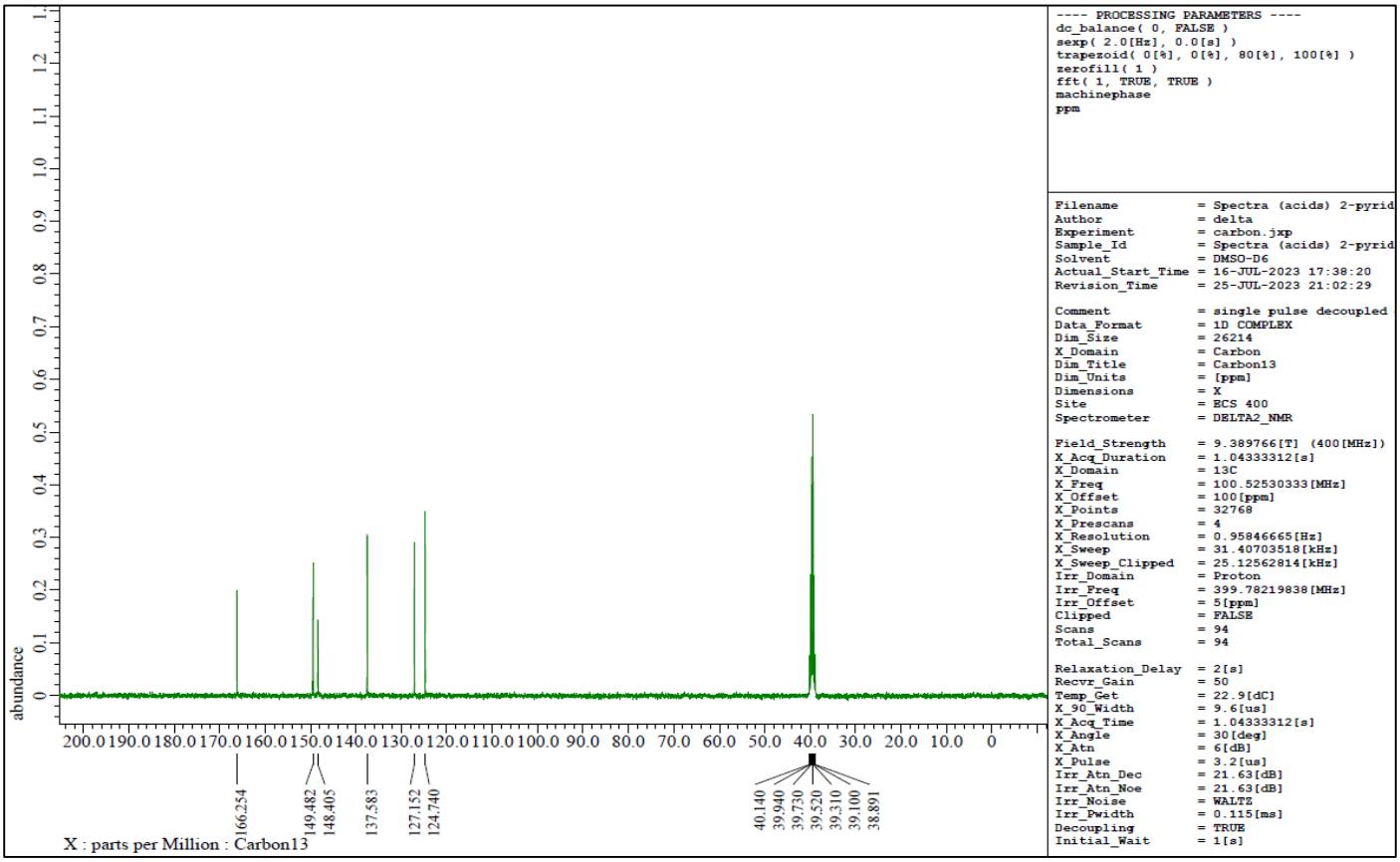
Compound **3ab** (^{1}H NMR, 400 MHz, $(CD_3)_2SO$).



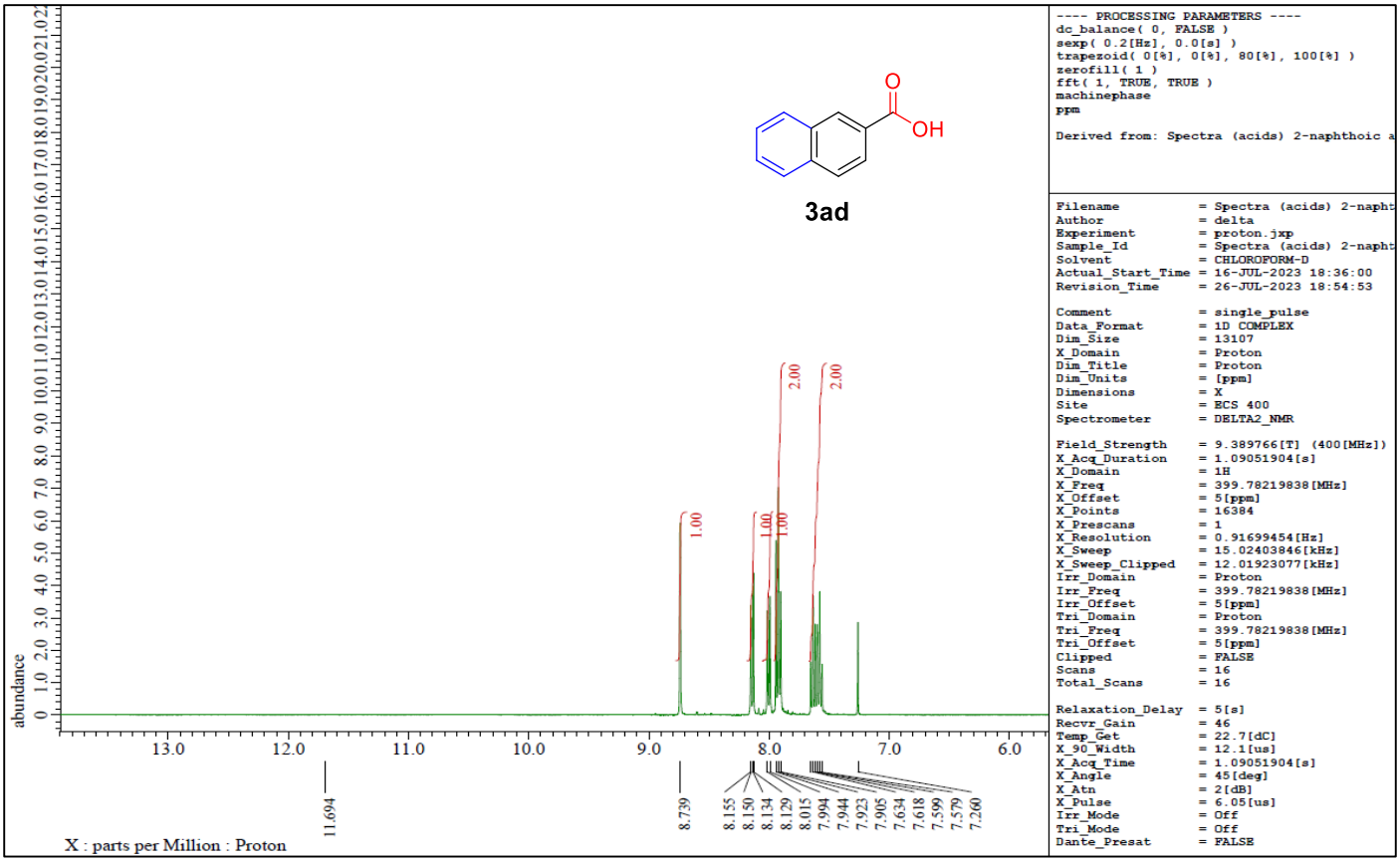
Compound **3ab** (^{13}C NMR, 101 MHz, $(CD_3)_2SO$).



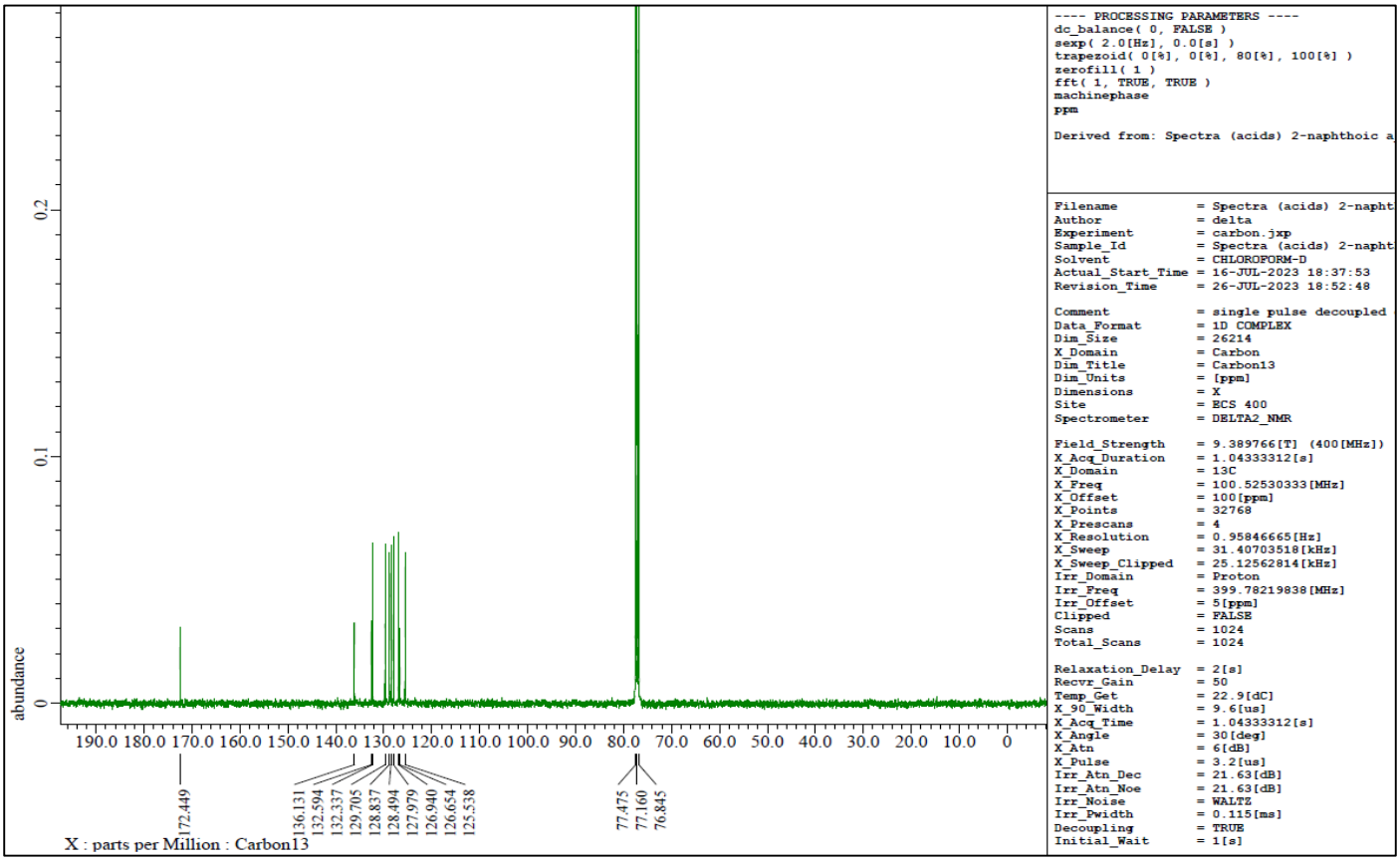
Compound **3ac** (^{1}H NMR, 400 MHz, $(CD_3)_2SO$).



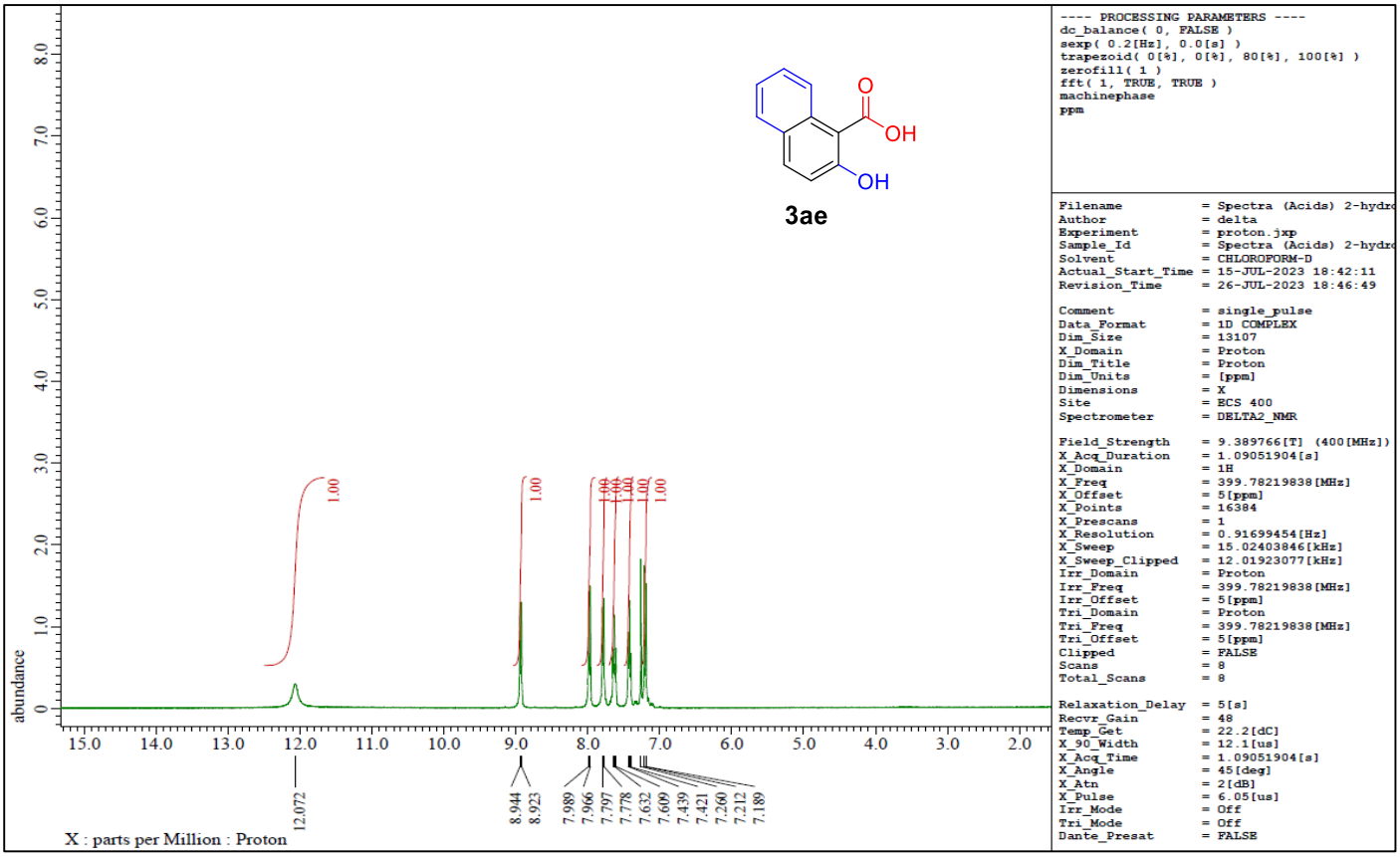
Compound **3ac** (^{13}C NMR, 101 MHz, $(CD_3)_2SO$).



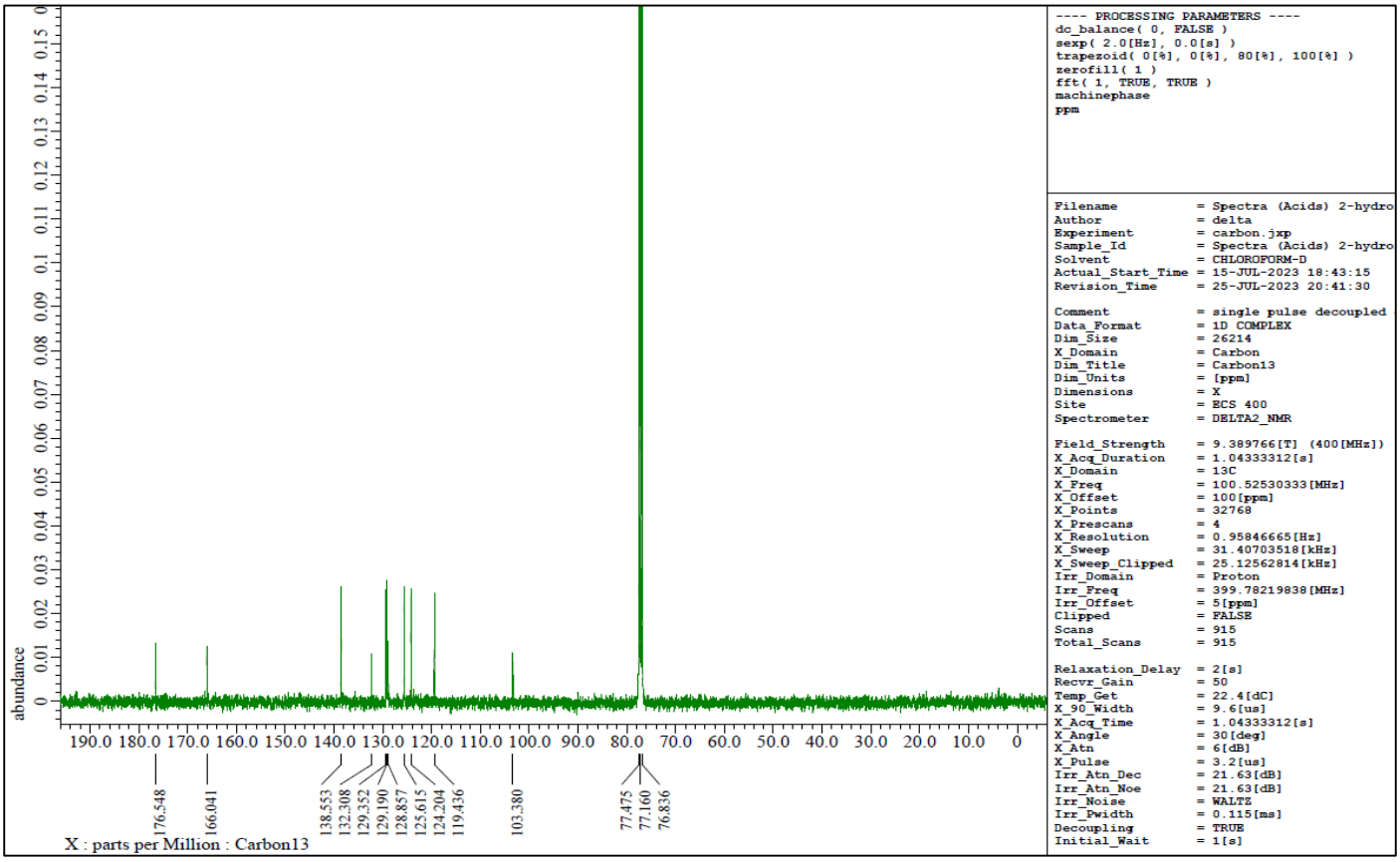
Compound **3ad** (^{1}H NMR, 400 MHz, $CDCl_3$).



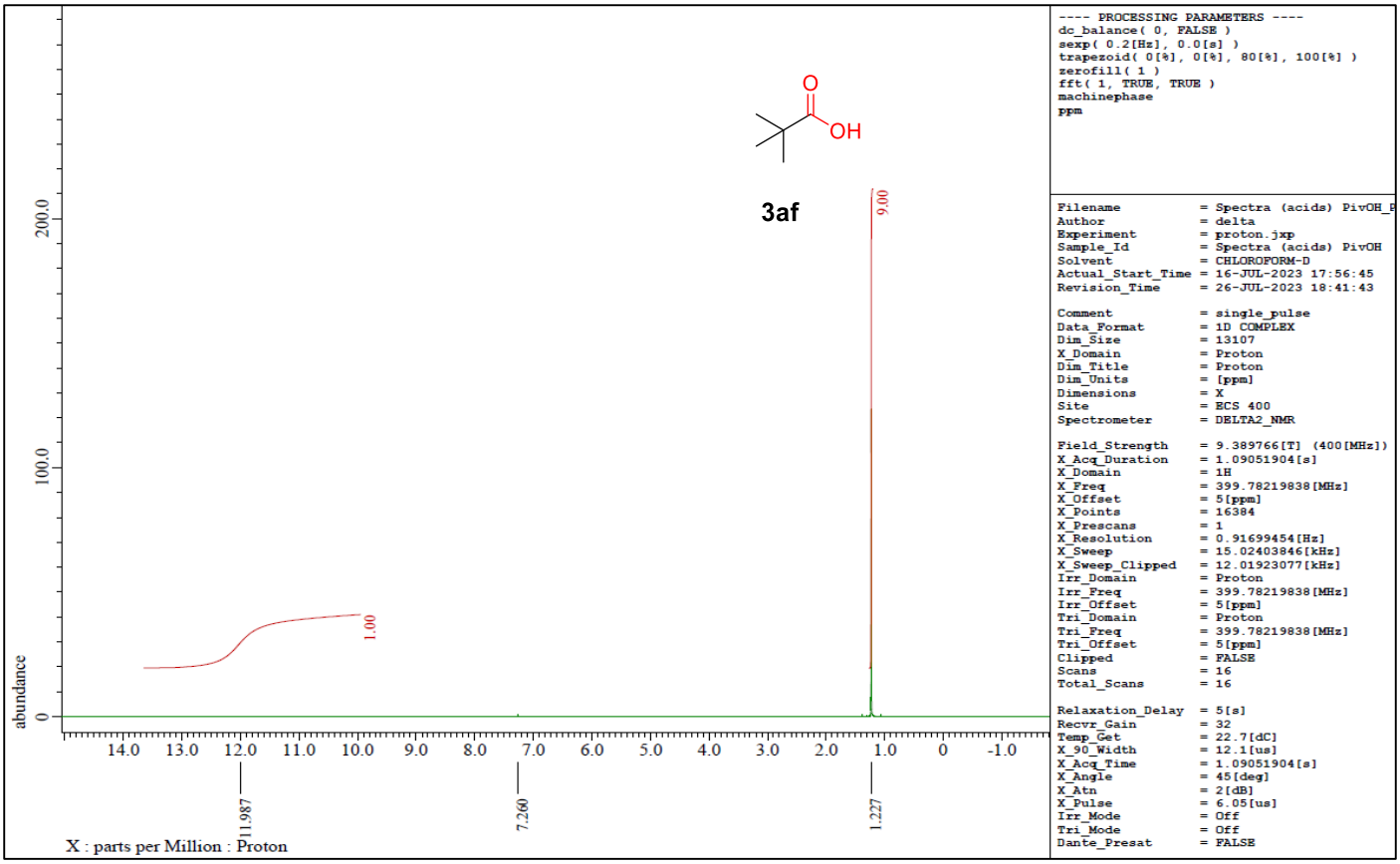
Compound **3ad** (^{13}C NMR, 101 MHz, $CDCl_3$).



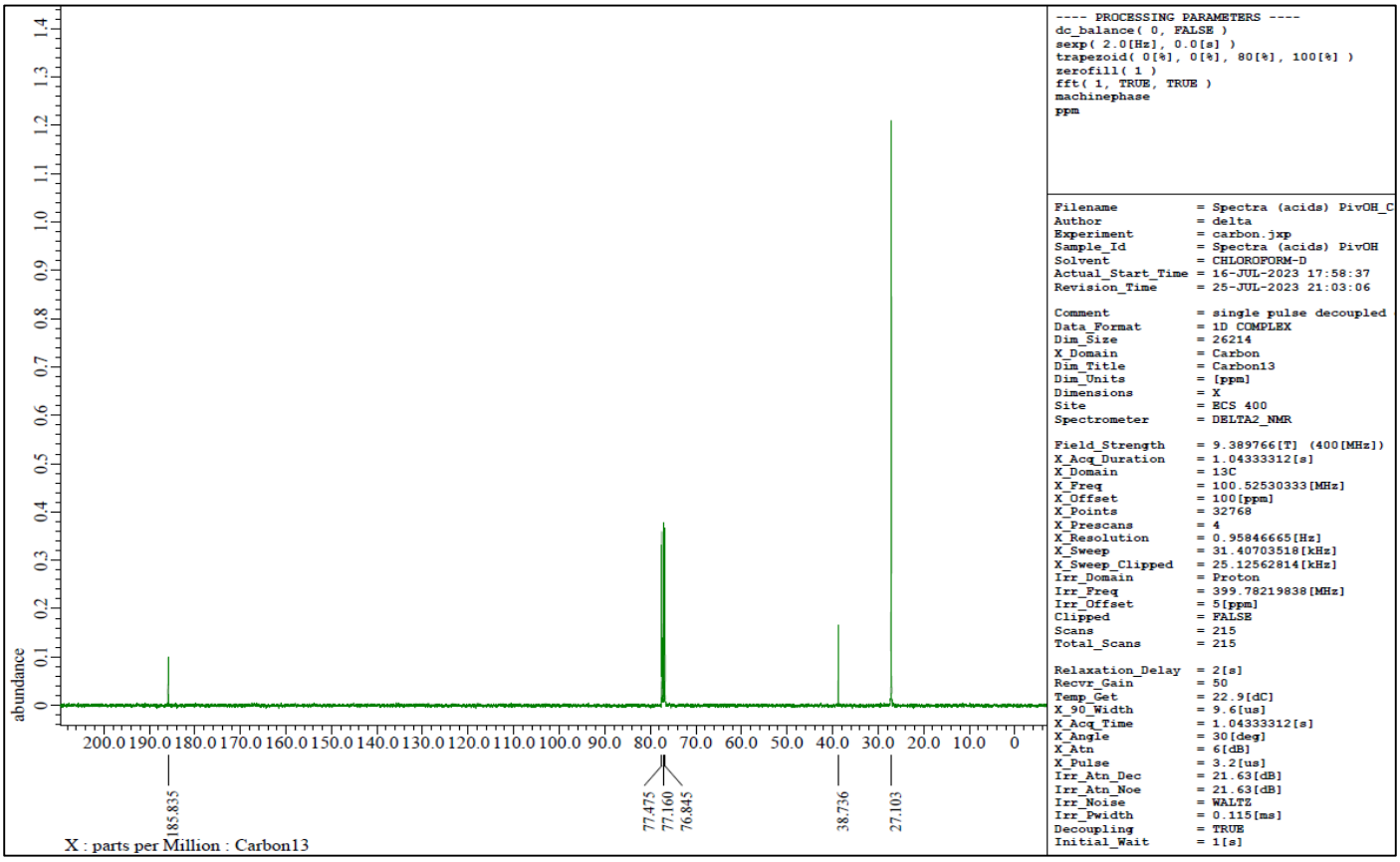
Compound **3ae** (^{1}H NMR, 400 MHz, $CDCl_3$).



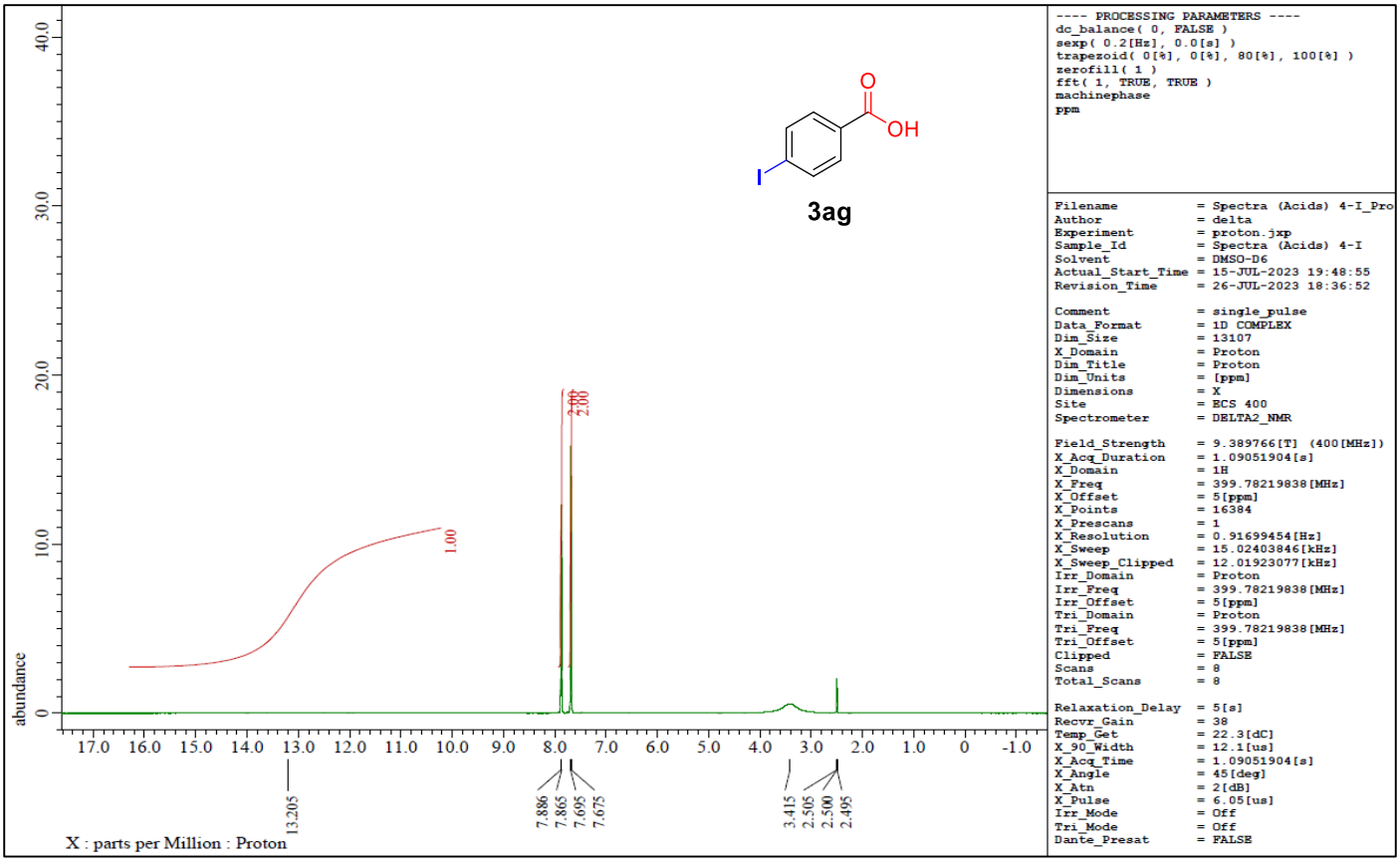
Compound **3ae** (^{13}C NMR, 101 MHz, $CDCl_3$).



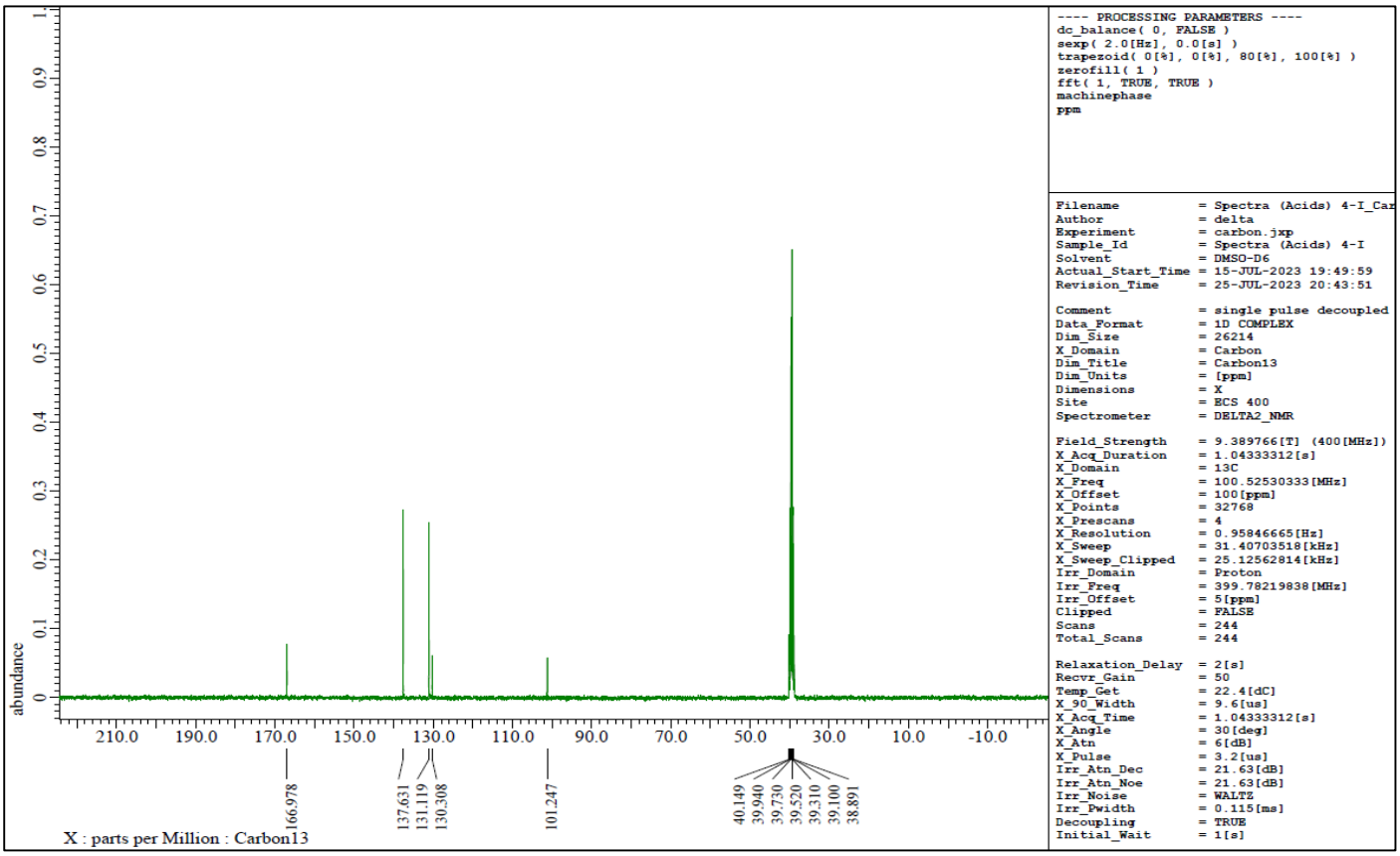
Compound **3af** (^{1}H NMR, 400 MHz, $CDCl_3$).



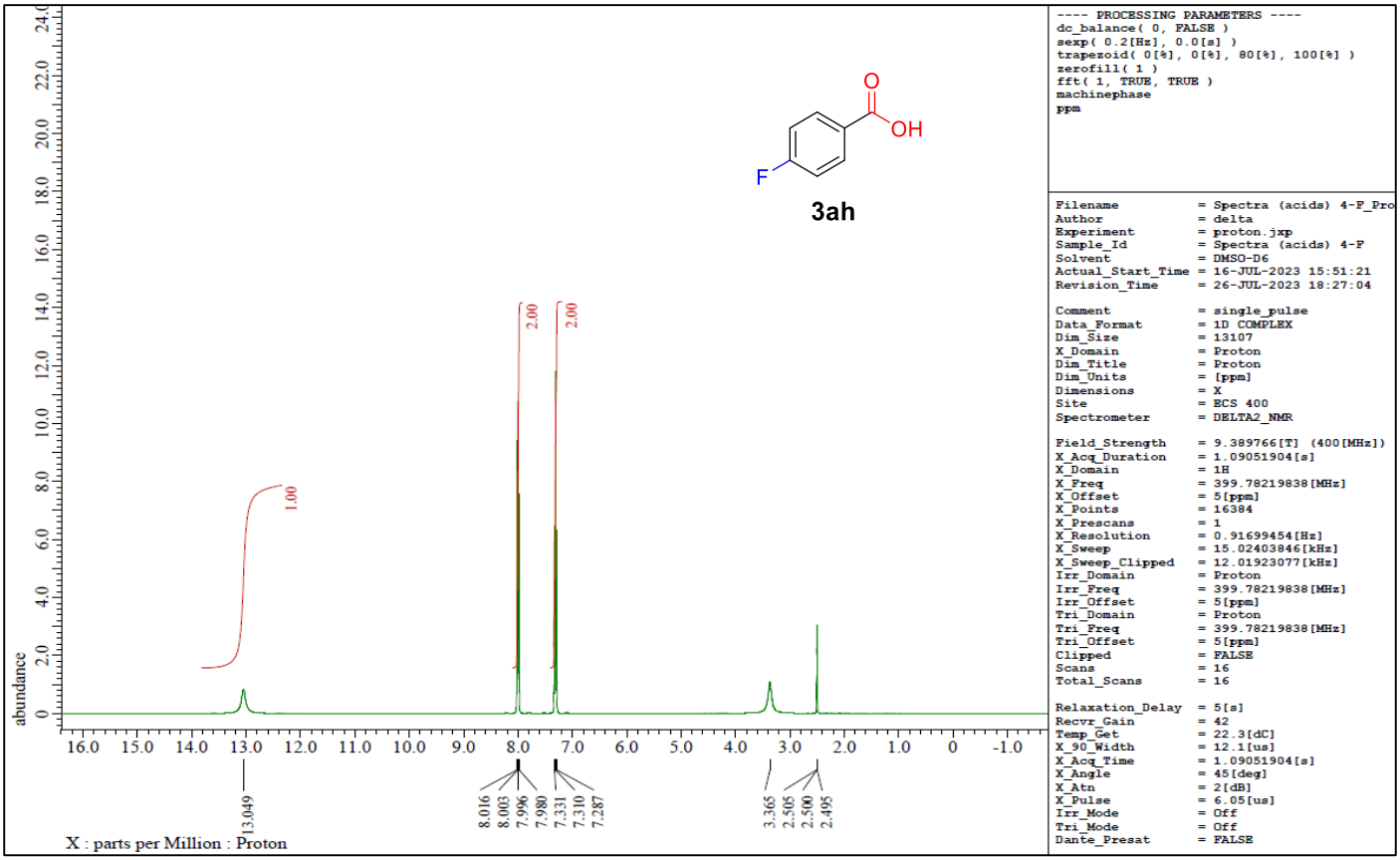
Compound **3af** (^{13}C NMR, 101 MHz, $CDCl_3$).



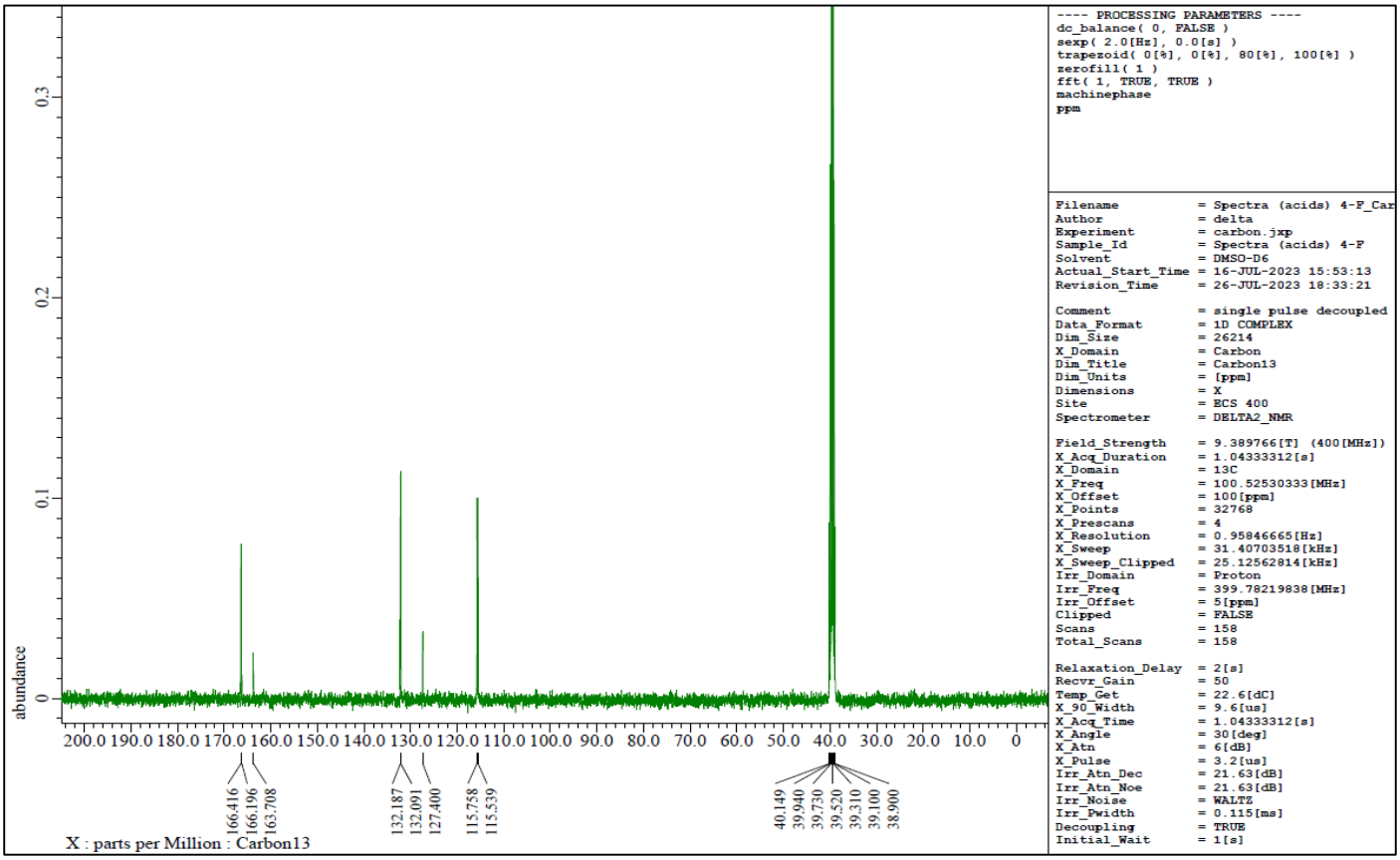
Compound **3ag** (^{1}H NMR, 400 MHz, $(CD_3)_2SO$).



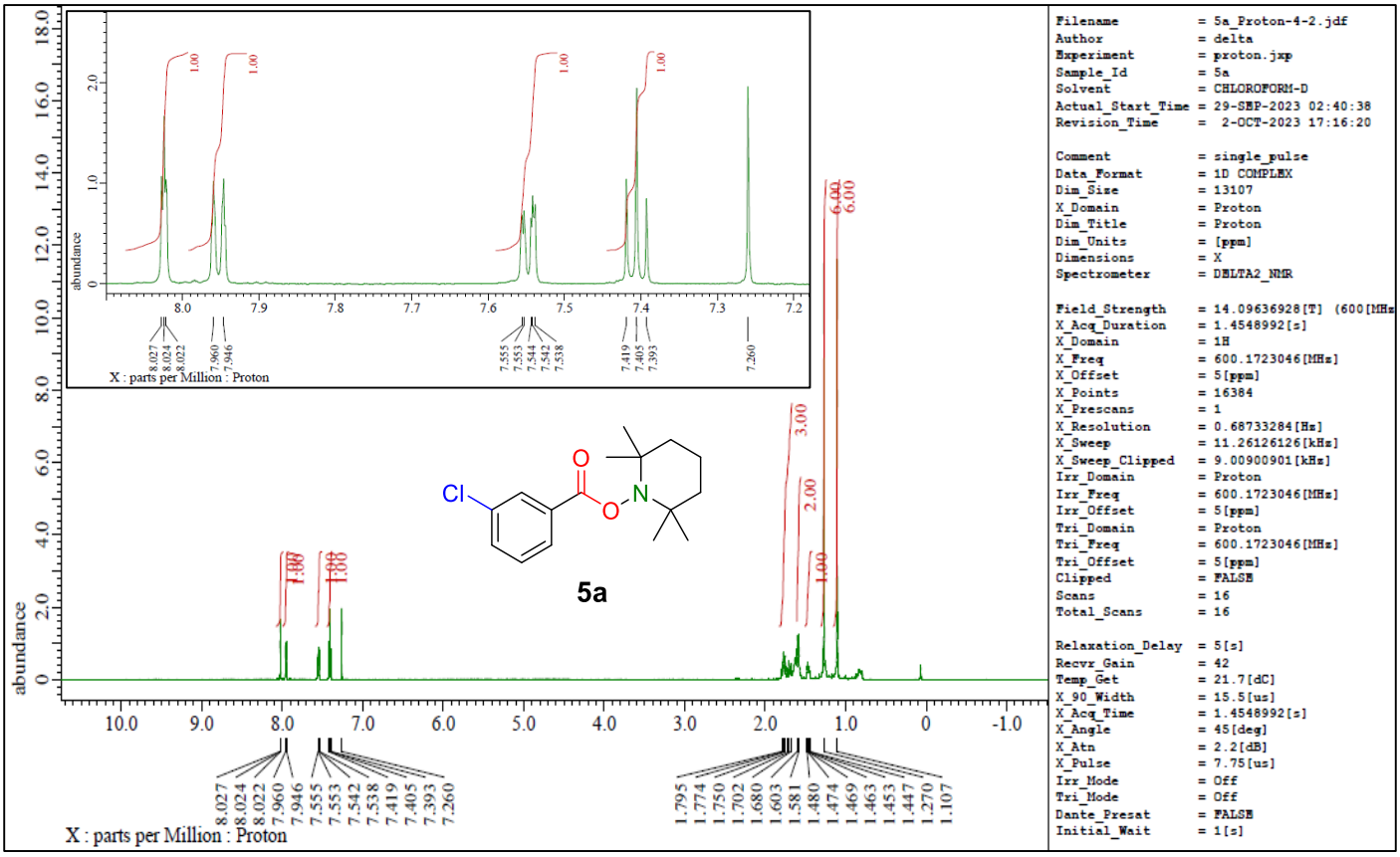
Compound **3ag** (^{13}C NMR, 101 MHz, $(CD_3)_2SO$).



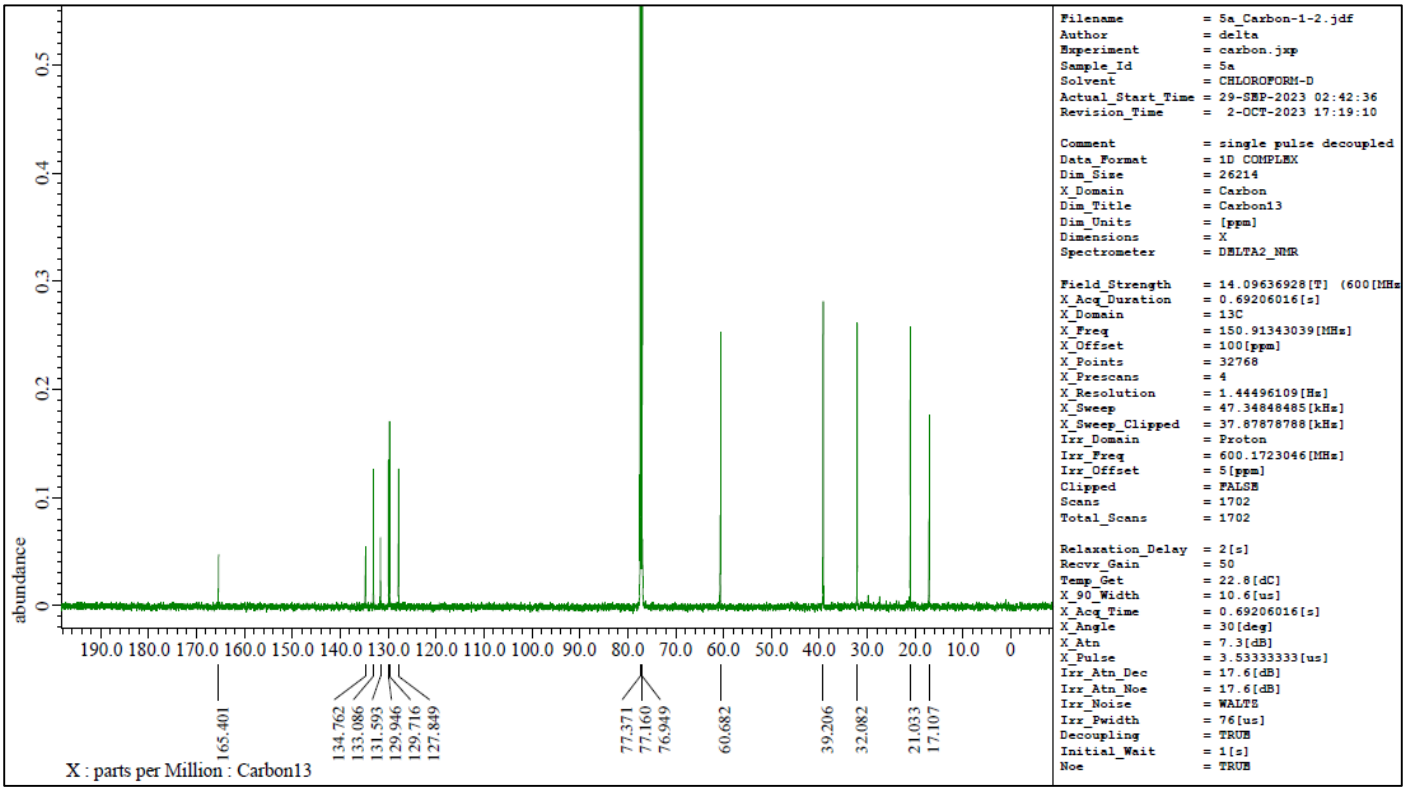
Compound **3ah** (^{1}H NMR, 400 MHz, $(CD_3)_2SO$).



Compound **3ah** (^{13}C NMR, 101 MHz, $(CD_3)_2SO$).



Compound **5a** (^{1}H NMR, 600 MHz, $CDCl_3$).



Compound **5a** (^{13}C NMR, 151 MHz, $CDCl_3$).