Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Synthesis of benzoyl cyanide through aerobic photooxidation of benzyl cyanide using carbon tetrabromide as a catalyst

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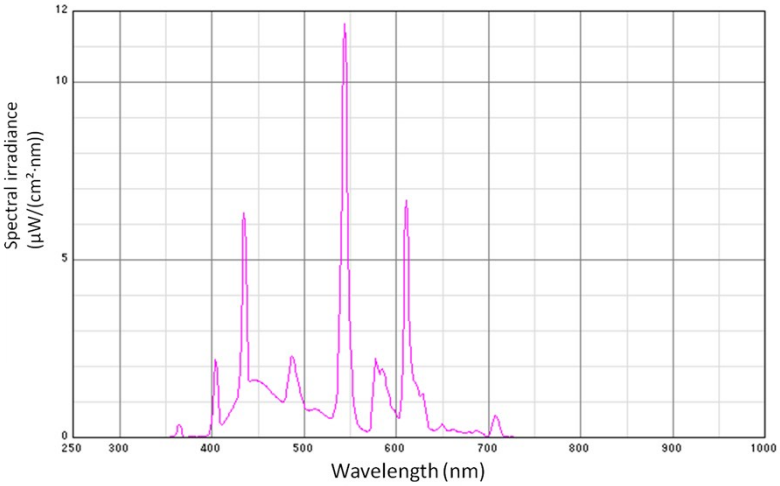
1. General Information

Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. The fluorescent lamps were EFR25ED 22W from Panasonic as shown detailed in the bellow.

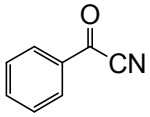


Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Merck silica gel 60 F_{254}) and preparative thin-layer chromatography (PTLC) was carried out using 0.50 mm commercial silica gel plates (Merck silica gel 60 F_{254}). ^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL ECA 500 spectrometer (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR) or a JEOL AL 400 spectrometer (400MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). Chemical shifts (δ) are expressed in parts per million and are internally referenced [0.00 ppm (tetramethylsilane) for ^{1}H NMR].

2. General Procedure

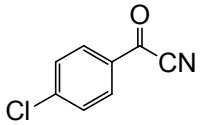
Synthesis of benzoyl cyanide (2a) and isolation (Table 1): A solution of benzyl cyanide (**1a**, 0.3 mmol), CBr_4 (0.2 equiv), and H_2O (1.5 equiv) in EtOAc (5 mL) was stirred and irradiated using fluorescent lamps under an O_2 atmosphere for 20 h. The solvent was removed by rotary evaporation, then we took ^{1}H NMR. After dryness by rotary evaporation again, it was added H_2O(140 mL) and conc. H_2SO_4 (150 mL). The mixture was stirred under reflux for 30 min. After that, the mixture was extracted by 10% NaOH and 2N HCL, and carboxylic acid (**3a**) was obtained. The yields of benzoyl cyanides (**2**) were determined by ^{1}H NMR with 1,1,2,2-tetrachloroethane as internal standard.

Benzoyl cyanide (2a)[S-1]



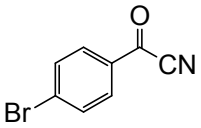
^{1}H-NMR yield: 74 %; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.16 (dd, J = 7.4, 1.1 Hz, 2H), 7.80 (t, J = 7.4 Hz, 1H), 7.62 (t, J = 7.7 Hz, 2H).

4-Chlorobenzoyl cyanide (2b) [S-1]



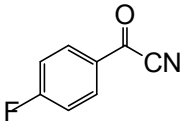
^{1}H-NMR yield: 73 %; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.10 (dd, J = 6.6, 2.0 Hz, 2H), 7.60 (t, J = 6.0, 1.7 Hz, 2H).

4-Bromobenzoyl cyanide (2c)[S-4]



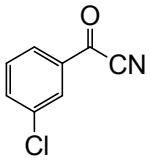
^{1}H-NMR yield: 88 %; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.00 (dd, *J* = 6.9, 2.3 Hz, 2H), 7.77 (dd, *J* = 7.7, 1.7 Hz, 2H).

4-Fluorobenzoyl cyanide (2d)[S-5]



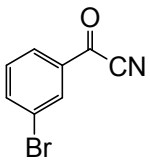
^{1}H-NMR yield: 45 %; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.23-8.20 (m, 2H), 7.33-7.29 (m, 2H).

3-Chlorobenzoyl cyanide (2e)[S-2]



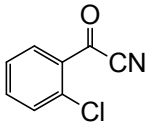
^{1}H-NMR yield: 68 %; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.08 (t, *J* = 7.5 Hz, 1H), 7.79-7.22 (m, 3H).

3-Bromobenzoyl cyanide (2f)[S-3]



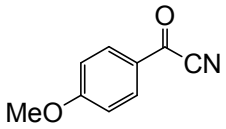
^{1}H-NMR yield: 64 %; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.25 (s, 1H), 8.11 (d, *J* = 7.2 Hz, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H).

2-Chlorobenzoyl cyanide (2g)[S-2]



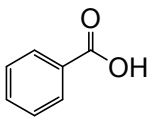
^{1}H-NMR yield: 53 %; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.15 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.64-7.23 (m, 3H).

4-Methoxybenzoyl cyanide (2k) [S-1]



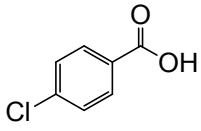
^{1}H-NMR yield: 37 %; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.06 (d, *J* = 9.1 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 3.80 (s, 3H).

Benzoic acid (3a)[S-6]



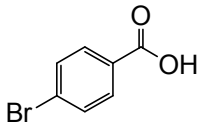
Prepared according to the general procedure. Isolated yield: 73 %; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.13 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.5, 1H), 7.49 (t, *J* = 7.5 Hz, 2H)**.** ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 134.0, 130.3, 129.4, 128.6.

4-Chlorobenzoic acid (3b)[S-6]



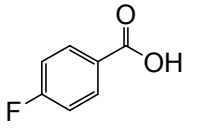
Prepared according to the general procedure. Isolated yield: 72 %; ^{1}H-NMR (500 MHz, DMSO): δ 7.90 (d, *J* = 7.4 Hz, 2H), 7.52 (d, *J* = 8.5, 2H). ^{13}C NMR (125 MHz, DMSO) δ 167.0, 138.3, 131.7, 130.1, 129.3.

4-Bromobenzoic acid (3c)[S-6]



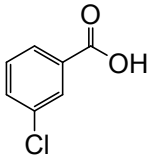
Prepared according to the general procedure. isolated yield: 71 %; ^{1}H-NMR (500 MHz, DMSO): δ 7.82 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.6, 2H). ^{13}C NMR (125 MHz, DMSO) δ 167.2, 132.2, 131.8, 130.5, 127.4.

4-Fluorobenzoic acid (3d)[S-6]



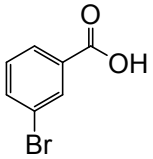
Prepared according to the general procedure. Isolated yield: 49 %; ^{1}H-NMR (400 MHz, DMSO): δ 7.98-7.95 (m, 2H), 7.31-7.26 (m, 2H). ^{13}C NMR (125 MHz, DMSO) δ 166.4, 166.0, 164.0, 132.2, 13.21, 127.4, 115.8, 115.6.

3-Chlorobenzoic acid (3e)[S-6]



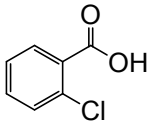
Prepared according to the general procedure. Isolated yield: 60 %; ^{1}H-NMR (400 MHz, DMSO): δ 7.92-7.91 (m, 2H), 7.73-7.70 (m, 1H), 7.58-7.54 (m, 1H). ^{13}C NMR (100 MHz, DMSO) δ 166.1, 133.4, 132.9, 132.7, 130.7, 128.9, 127.9.

3-Bromobenzoic acid (3f)[S-7]



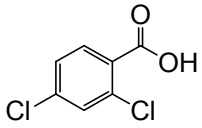
Prepared according to the general procedure. Isolated yield: 67 %; ^{1}H-NMR (400 MHz, DMSO): δ 8.06 (t, *J* = 1.7 Hz, 1H), 7.97-7.94 (m, 1H), 7.86-7.83 (m, 1H), 7.49 (t, *J* = 7.97 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ 166.0, 135.6, 133.1, 131.8, 130.9, 128.3, 121.8.

2-Chlorobenzoic acid (3g)[S-6]



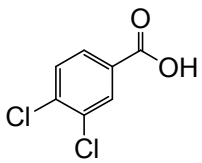
Prepared according to the general procedure. Isolated by preparative thin-layer chromatography (PTLC). Isolated yield: 46 %; ^{1}H-NMR (400 MHz, DMSO): δ 7.74 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.52-7.47 (m, 2H), 7.42-7.35 (m, 1H). ^{13}C NMR (125 MHz, DMSO) δ 166.8, 132.6, 131.6, 131.5, 130.8, 130.7, 127.3.

2,4-dichlorobenzoic acid (3h)[S-6]



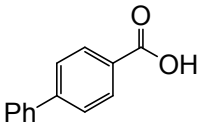
Prepared according to the general procedure. Isolated yield: 40 %; ^{1}H-NMR (400 MHz, DMSO): δ 7.83-7.80 (m, 1H), 7.72 (d, *J* = 1.9 Hz, 1H), 7.52-7.50 (m, 1H). ^{13}C NMR (100Hz, DMSO) δ 165.9, 136.6, 133.1, 132.4, 130.2, 130.1, 127.5.

3,4-dichlorobenzoic acid (3i)[S-6]



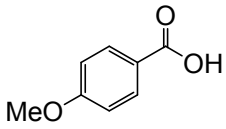
Prepared according to the general procedure. Isolated by preparative thin-layer chromatography (PTLC). Isolated yield: 19 %; ^{1}H-NMR (400 MHz, DMSO): δ 8.02 (d, *J* = 2.3 Hz, 1H), 7.84 (dd, *J* = 6.3, 2.0, 1H), 7.75 (d, *J* = 4.2, 1H). ^{13}C NMR (100Hz, DMSO) δ 165.5, 135.8, 131.5, 131.4, 131.1, 131.0, 129.3.

4-Phenylbenzoic acid (3j)[S-6]



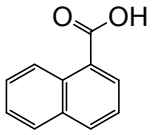
Prepared according to the general procedure. Isolated by preparative thin-layer chromatography (PTLC). Isolated yield: 21 %; ^{1}H-NMR (400 MHz, DMSO): δ 7.99 (d, *J* = 8.6 Hz, 2H), 7.77-7.66 (m, 2H), 7.50-7.44 (m, 2H), 7.40-7.33 (m, 2H). ^{13}C NMR (125 MHz, DMSO) δ 167.7, 144.8, 139.5, 130.5, 130.1, 129.6, 128.8, 127.5, 127.4.

4-Methoxybenzoic acid (3k) [S-6]



Prepared according to the general procedure. Isolated by preparative thin-layer chromatography (PTLC). Isolated yield: 34 %; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.65 (dd, *J* = 6.9, 2.3 Hz, 2H), 6.95 (d, *J* = 9.1, 2H), 3.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.7, 164.0, 132.3, 121.6, 113.7, 55.5.

1-Naphthoic acid (3l) [S-6]



Prepared according to the general procedure. Isolated by preparative thin-layer chromatography (PTLC). Isolated yield: 16 %; ^{1}H-NMR (400 MHz, DMSO): δ 8.85 (d, *J* = 8.7 Hz, 1H), 8.14 (t, *J* = 6.8, 2H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.63-7.56(m, 3H). ^{13}C NMR (125 MHz, DMSO) δ 173.2, 134.7, 133.9, 131.9, 131.6, 128.7, 128.1, 126.3, 125.9, 125.5, 124.5.

4. References

[S-1] C. Duplais, F. Bures, I. Sapountzis, T. J. Korn, G. Cahiez and P. Knochel, *Angew. Chem. Int. Ed.,* 2004, **43**(22), 2968.

[S-2] Z. Li, S. Shi and J. Yang, *Synlett*, 2006, **15**, 2495.

[S-3] A. J. Muller, K. Nishiyama, G. W. Griffin, K. Ishikawa and D. M. Gibson, *J. Org. Chem.,*1982, **47** (12), 2342.

[S-4] K. Sukata, *Bull. Chem. Soc. Jpn.,* 1987, **60**, 1085.

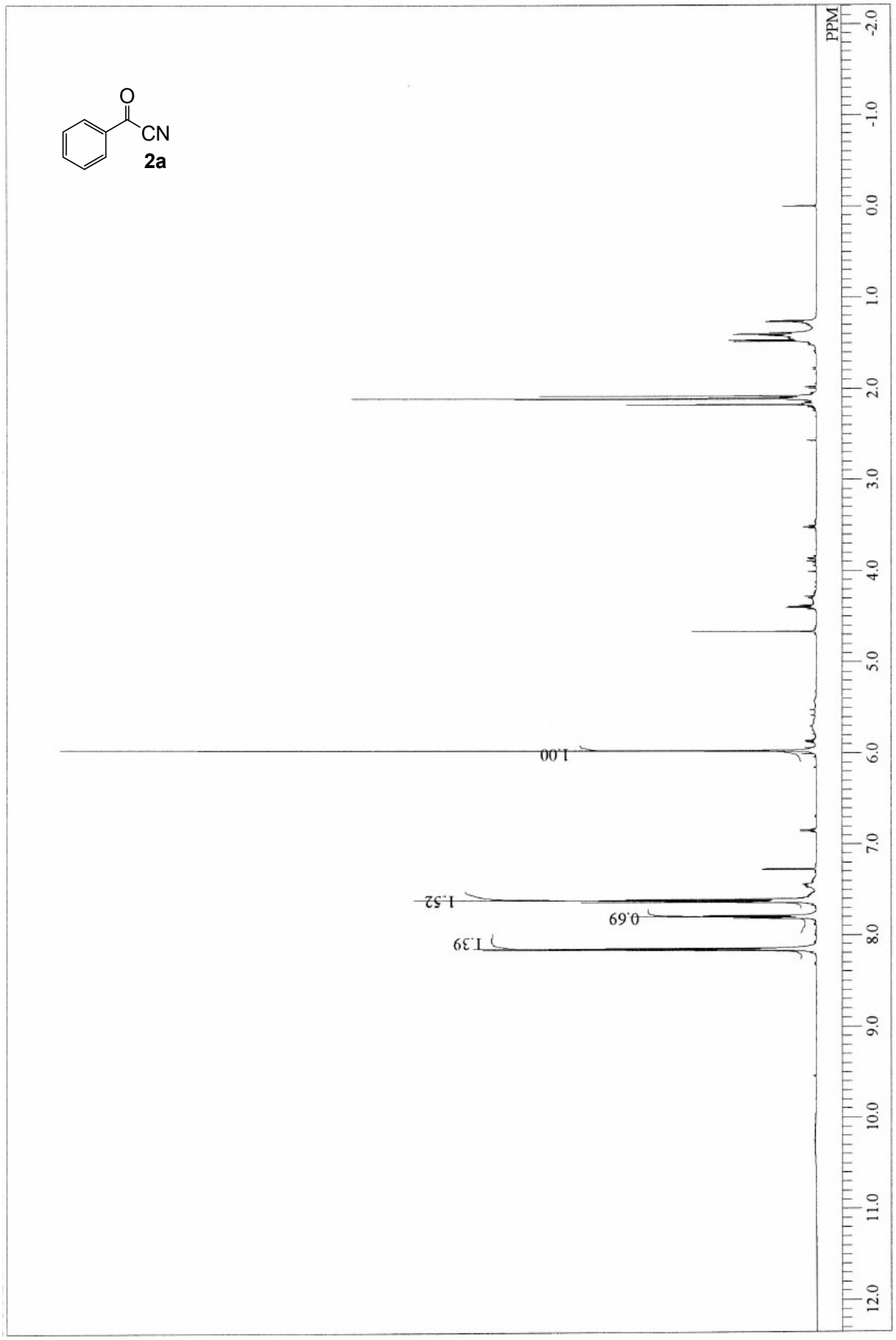
[S-5] H. Hoffmann, K. Haase, Z. Ismail, S. Preftitsi and A. Weberm, *Chemische Berichte,* 1982, **115**, 3880.

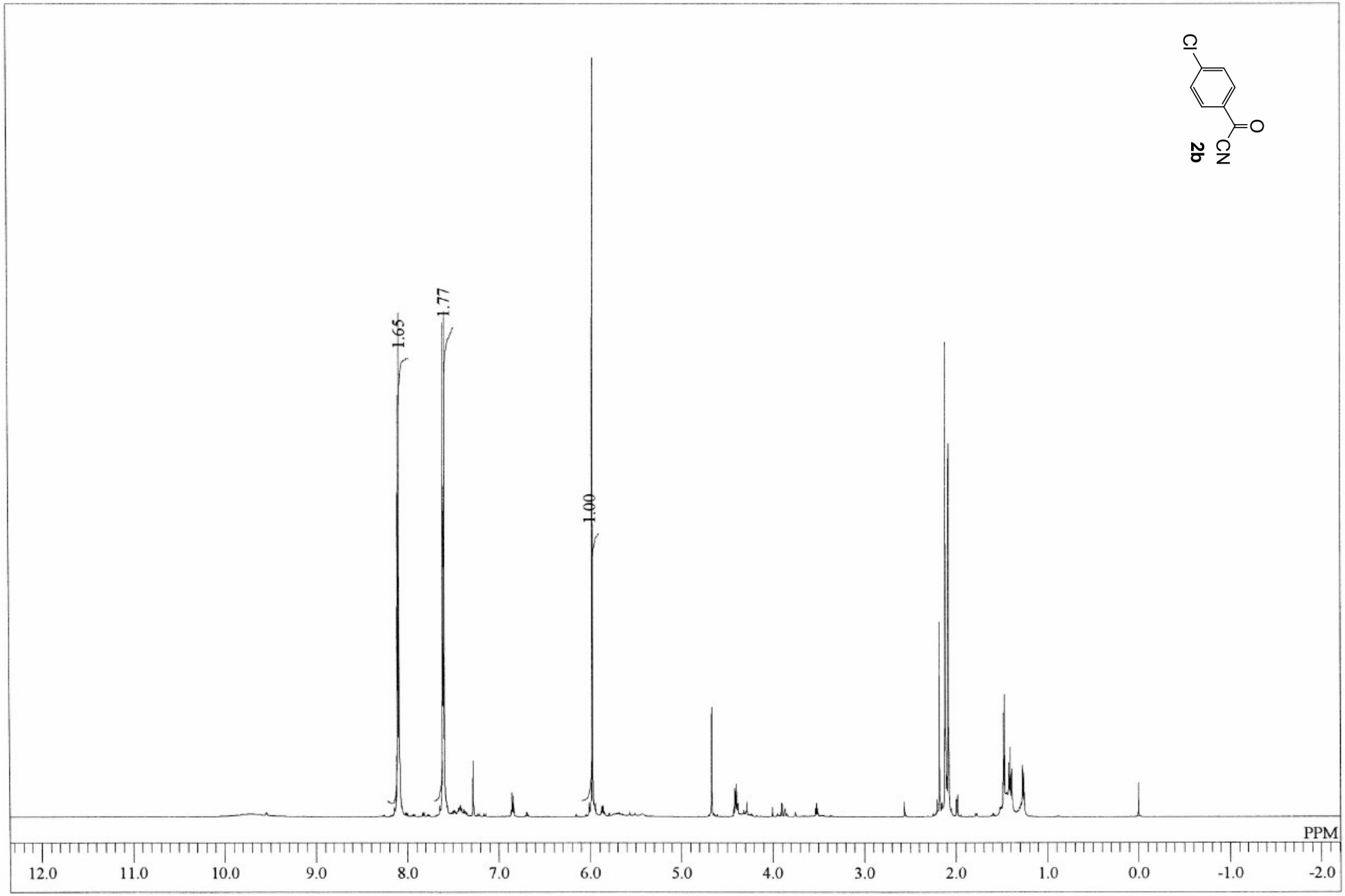
[S-6] AIST: Integrated Spectral Database System of Organic Compounds. (Data were obtained from the National Institute of Advanced Industrial Science and Technology (Japan))

[S-7] ACD-A: Sigma-Aldrich (Spectral data were obtained from Advanced Chemistry Development, Inc.)

Appendix: ^{1}H and ^{13}C spectra

As benzoyl cyanides are generally labile, they were characterized by ^{1}H NMR and isolated as the corresponding carboxylic acids. So the ^{1}H NMR spectra of benzoyl cyanides are not purified, it was crude.




Cl
O
CN
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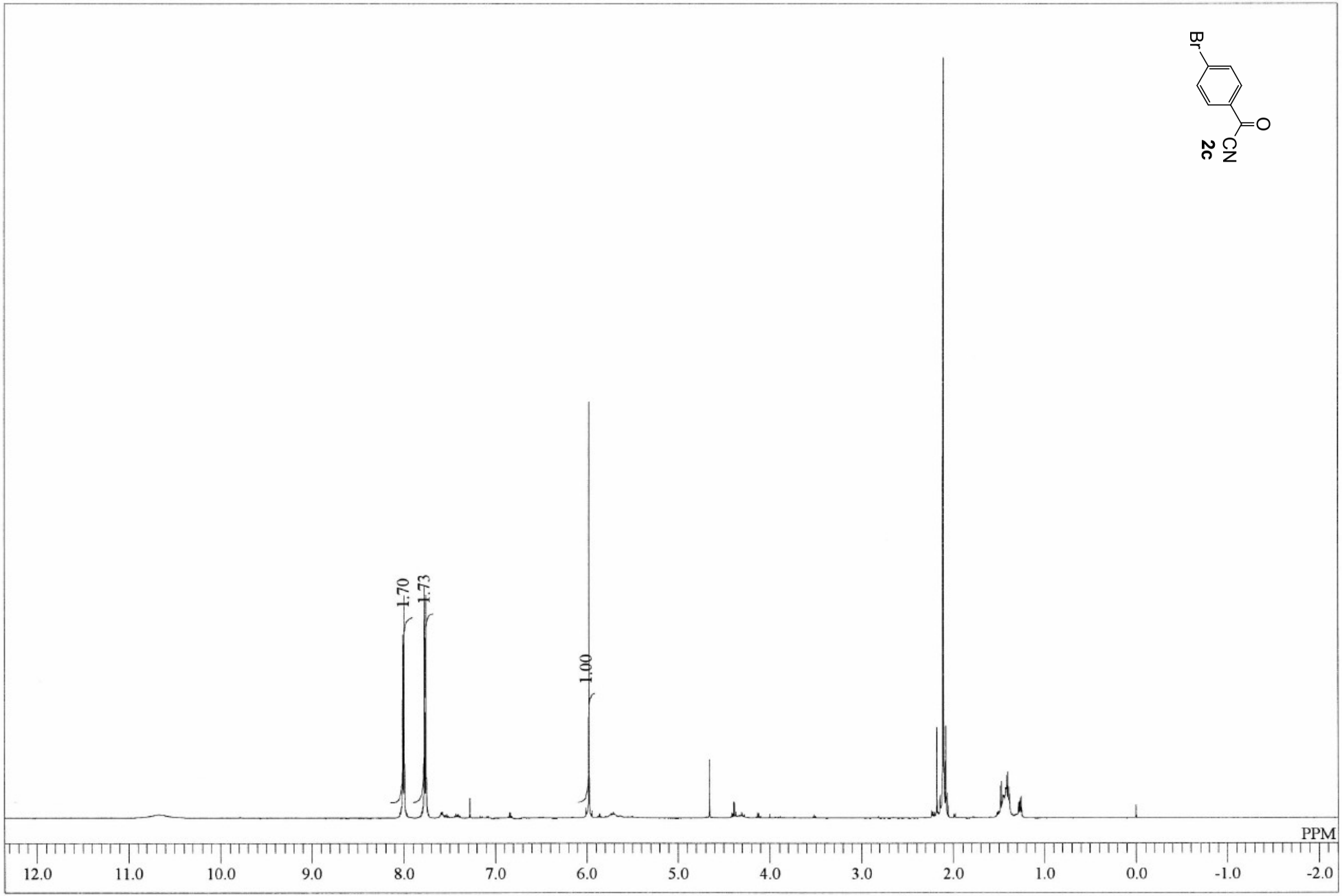
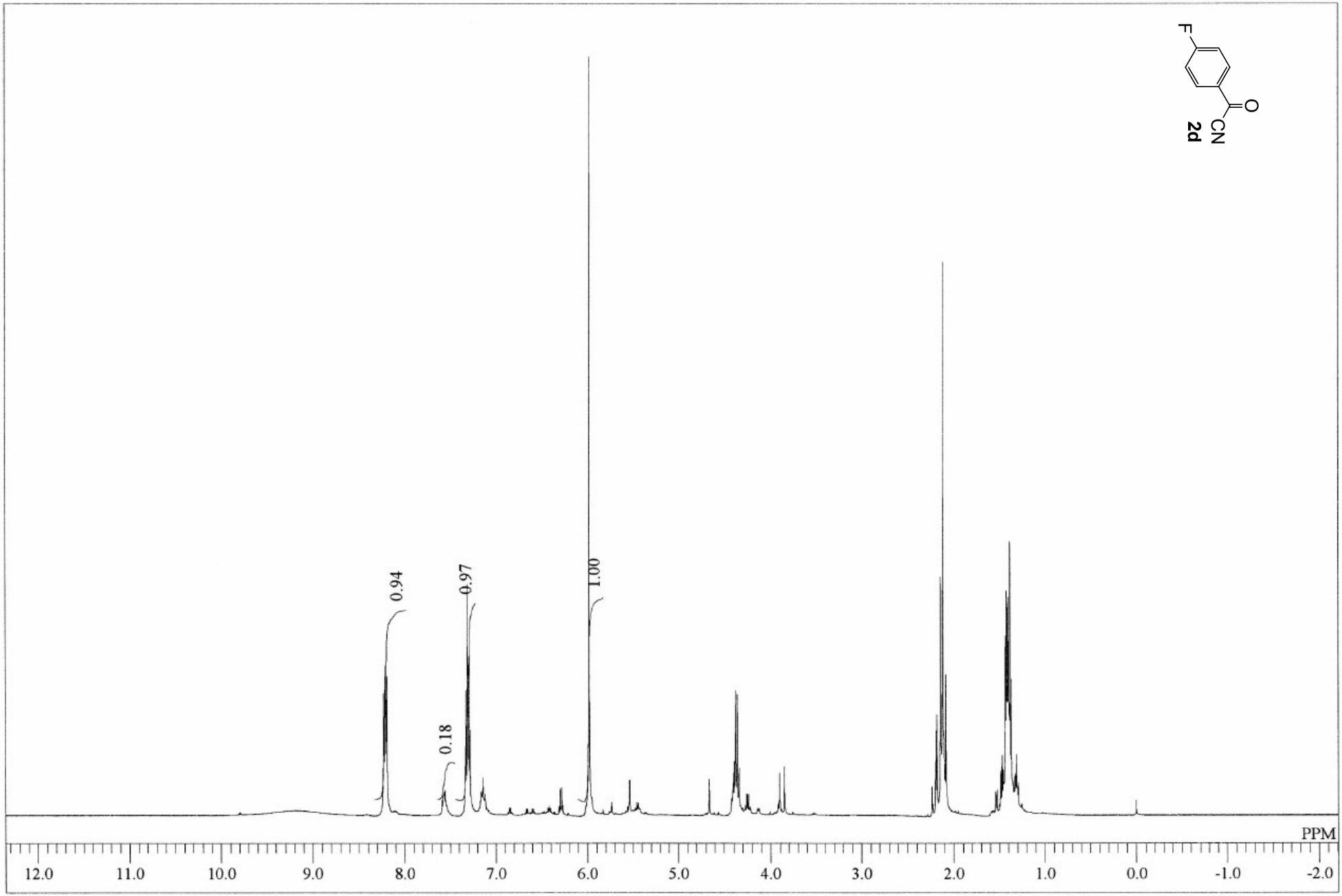
1.65
1.77
1.00
PPM
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0


Br
O
CN
2c
1.70
1.73
1.00
PPM
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0


F
O
CN
2d
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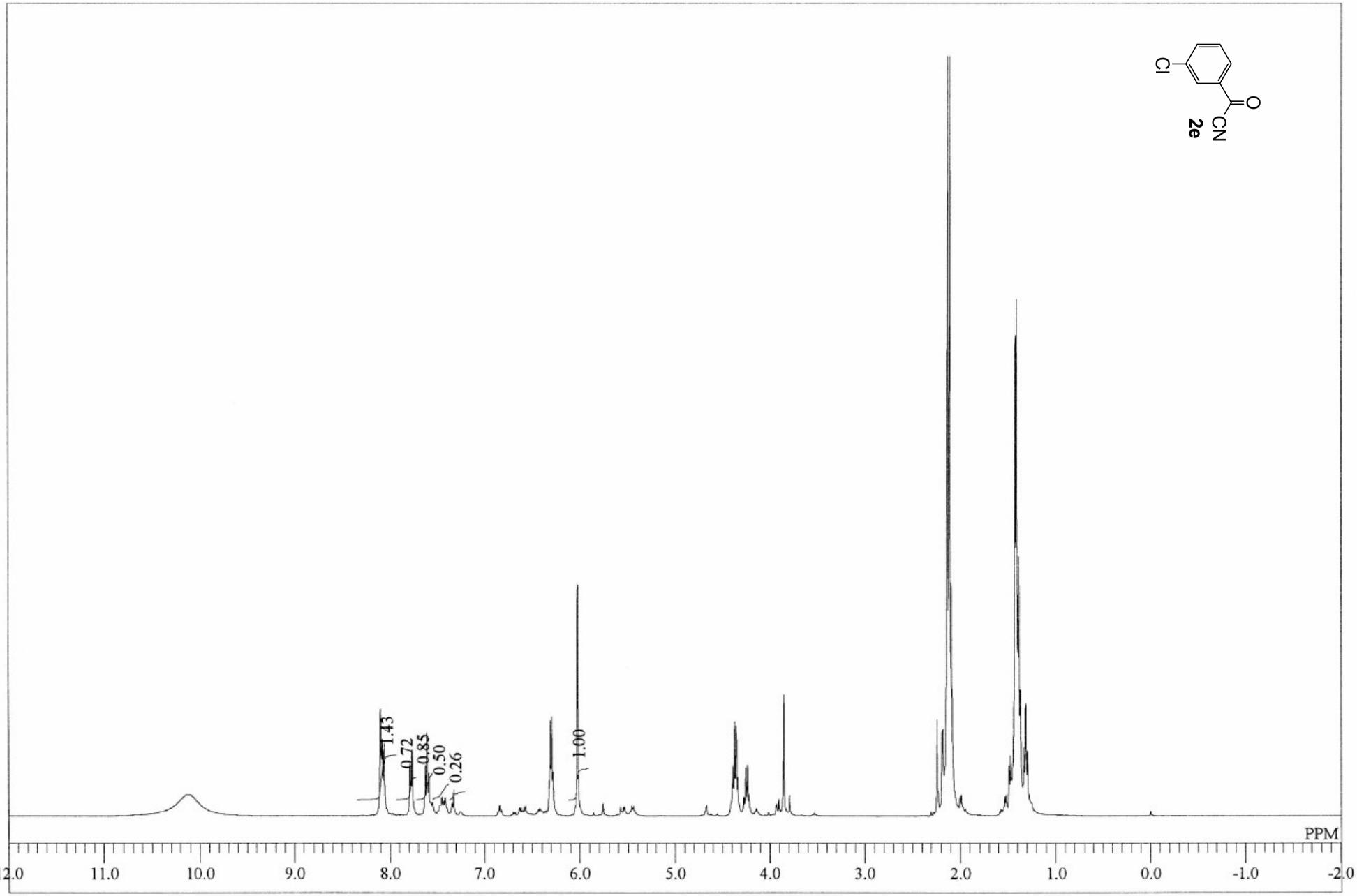
0.18
0.97
1.00
PPM
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0


Cl
O
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0.50
0.26
1.00
PPM
12.0
11.0
10.0
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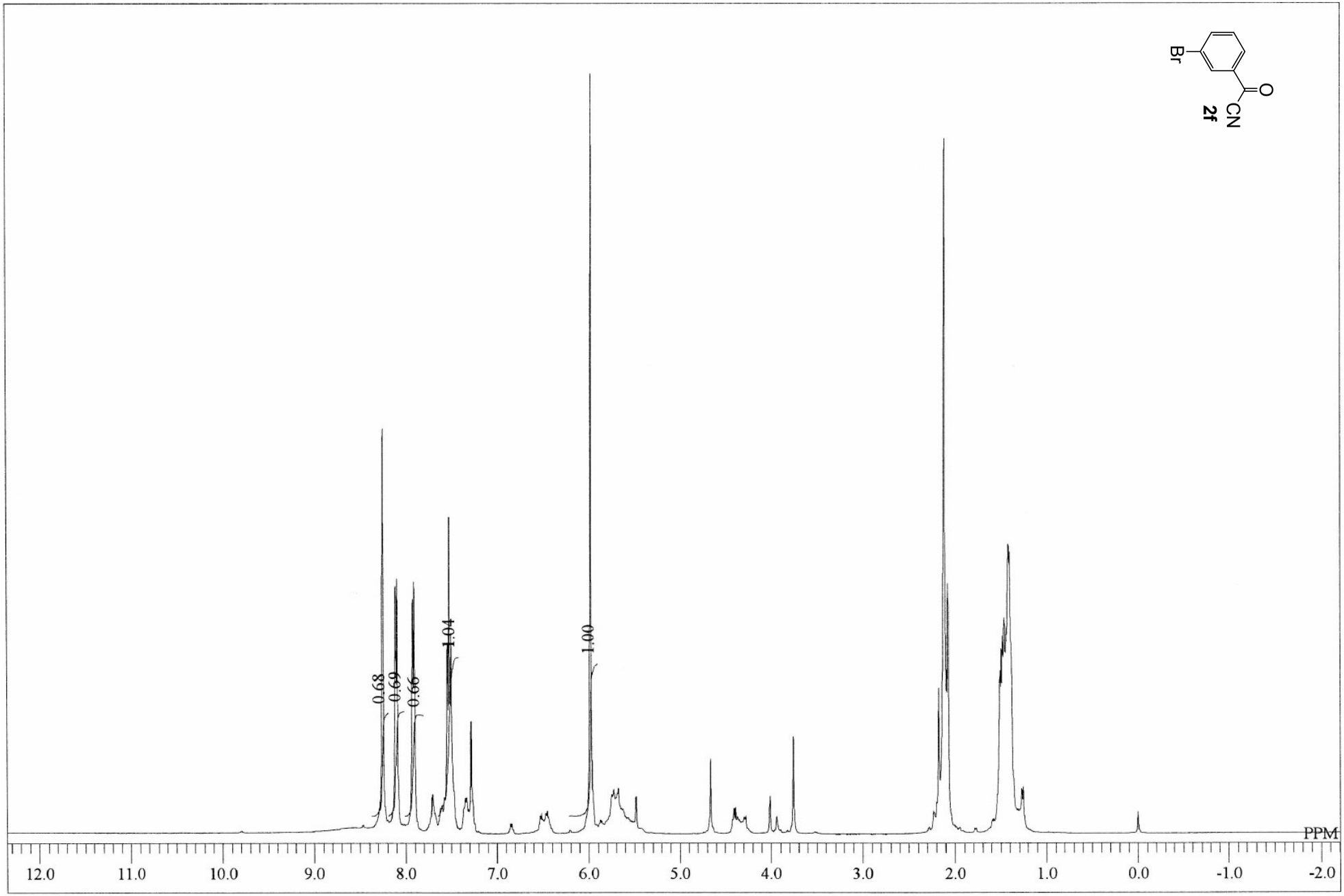
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0


Br
O
CN
2f
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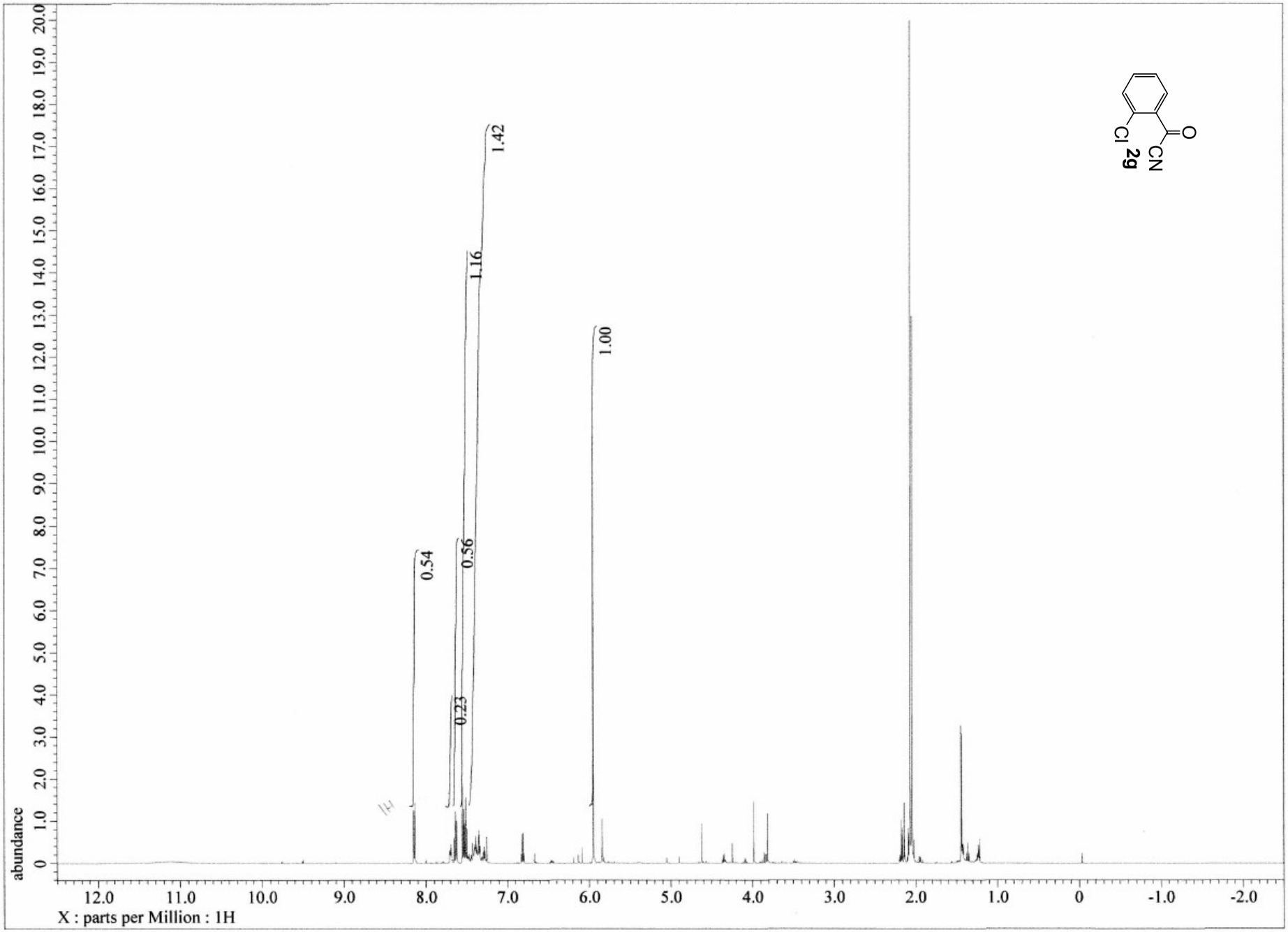
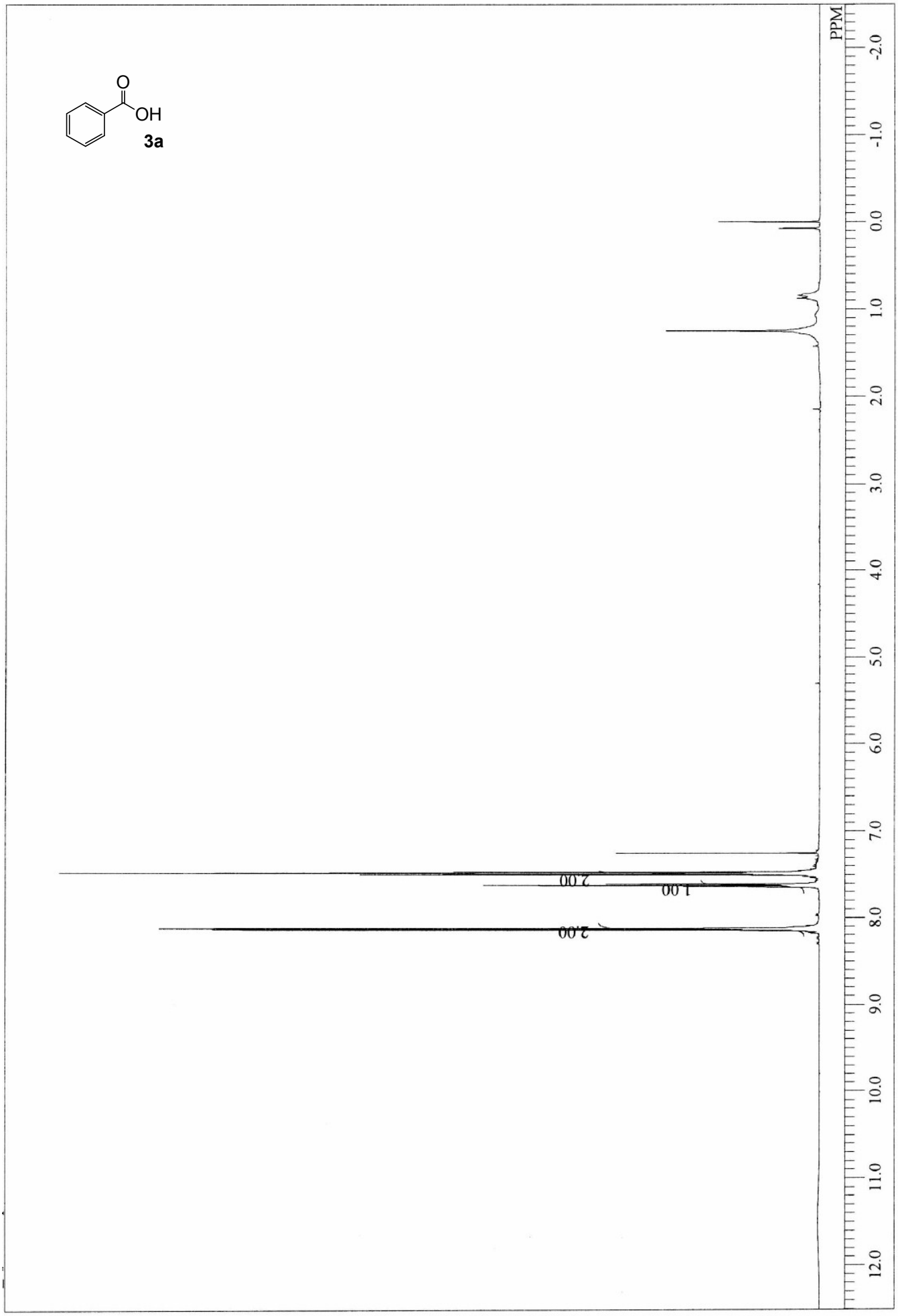
0.69
0.66
1.04
1.00
PPM
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0


abundance
X : parts per Million : 1H
0.54
0.23
0.56
1.16
1.42
1.00
Cl
O
CN
2g

O
CN
MeO
2k
1.82
1.00
1.02
0.79
0.95
0.79
abundance
X : parts per Million : 1H


O
OH
3a
PPM
-2.0
-1.0
0.0
1.0
2.0
3.0
4.0
5.0
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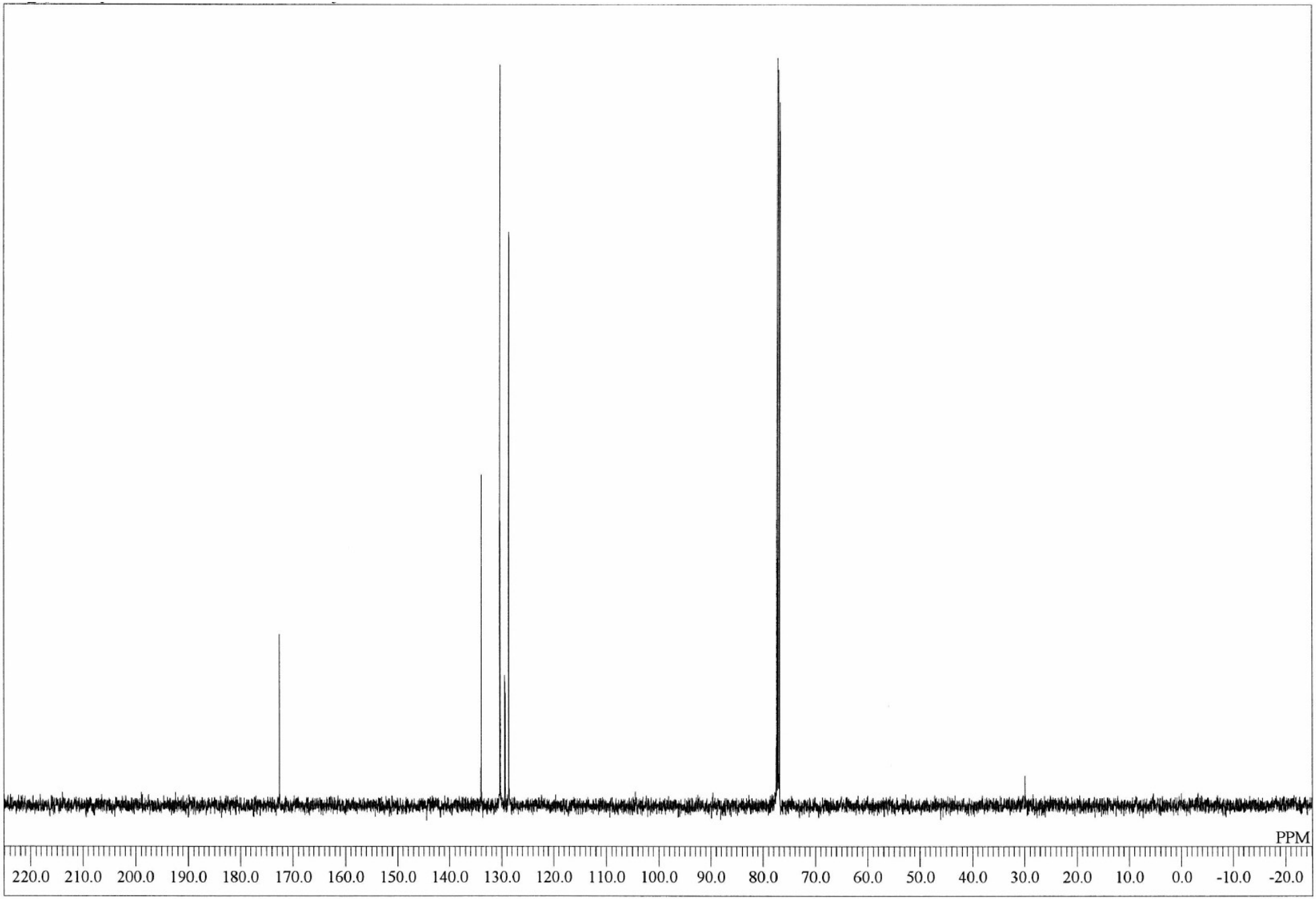
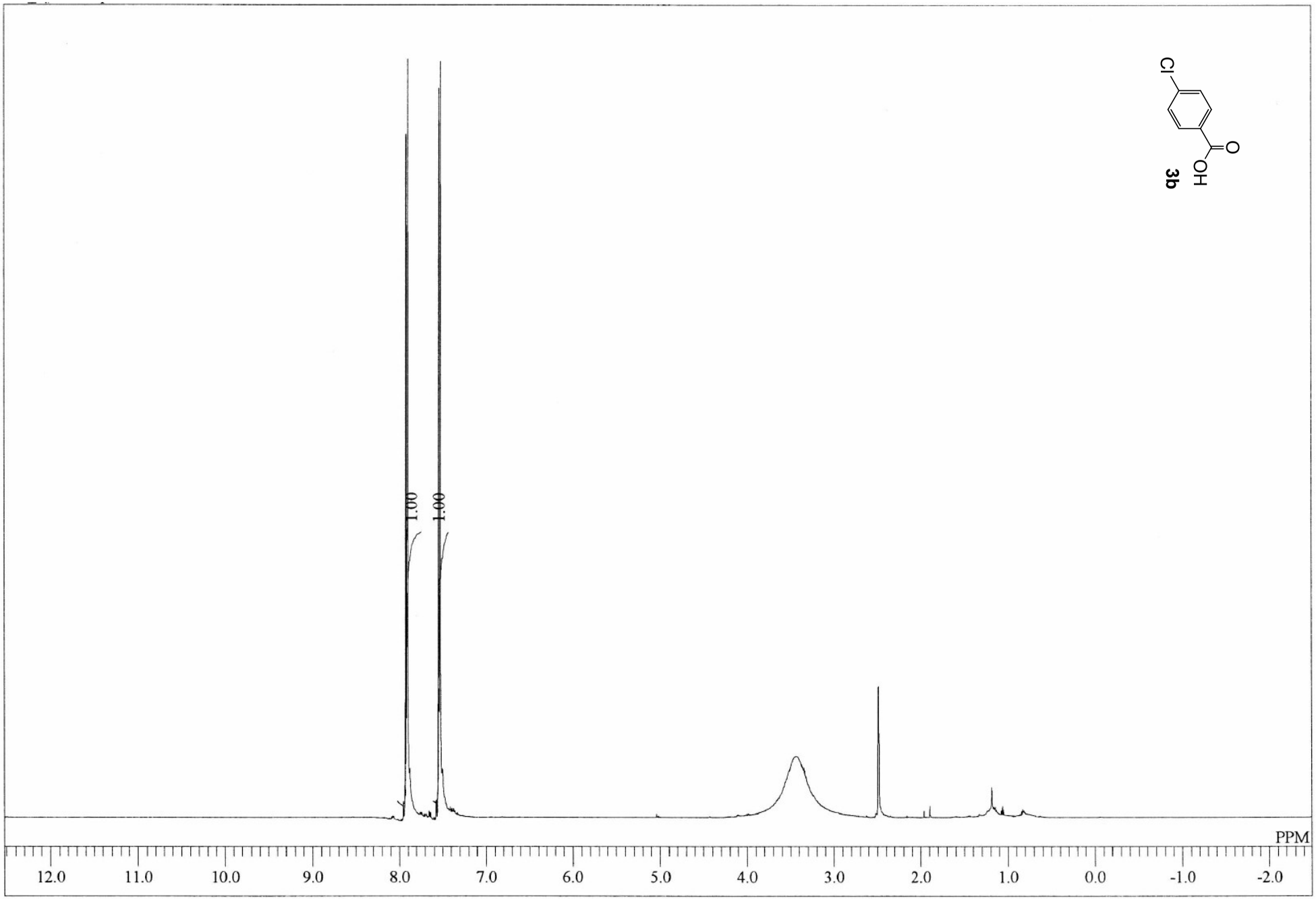
10.0
11.0
12.0
2.00
1.00
2.00


PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0 -20.0


Cl
O
OH
3b
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1.00
PPM
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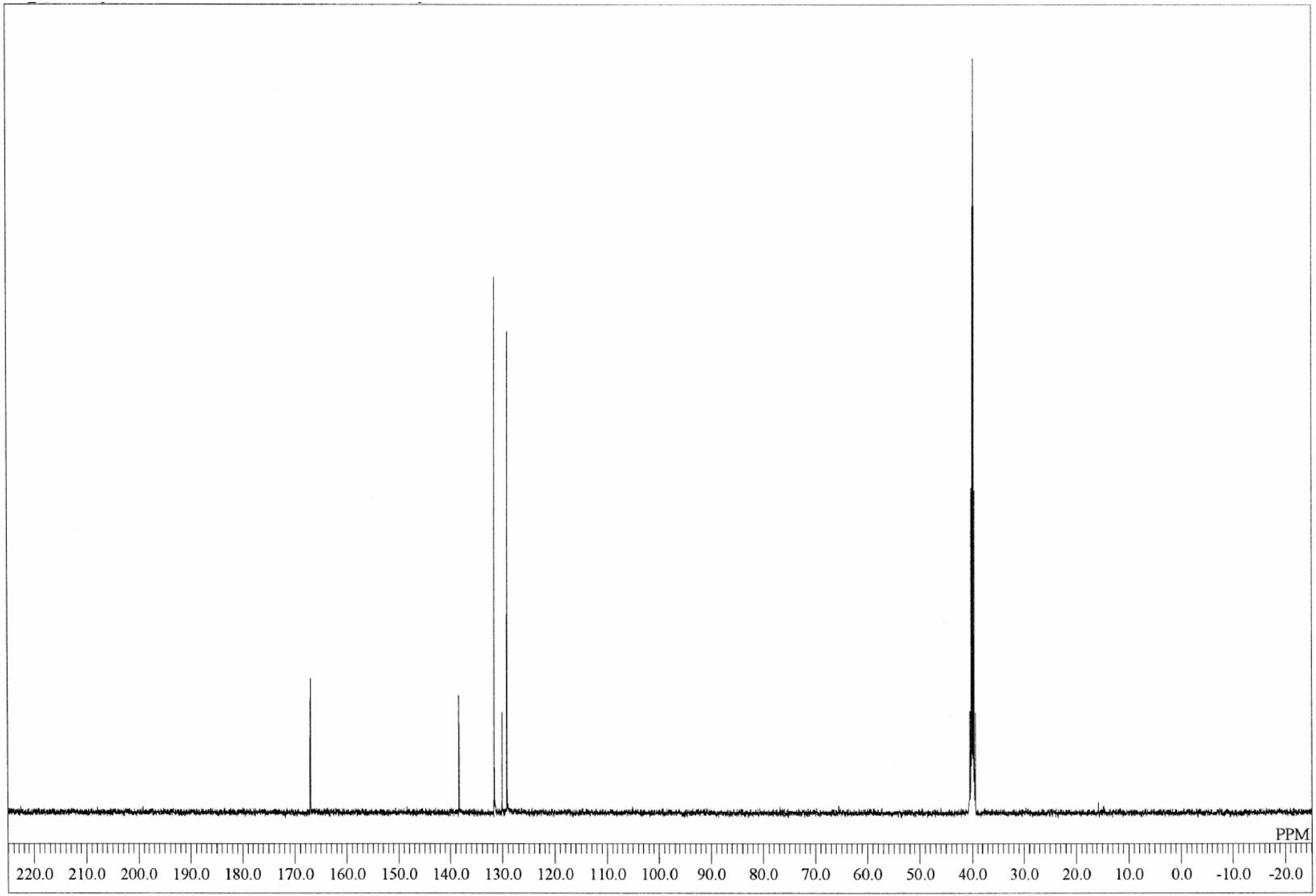
-2.0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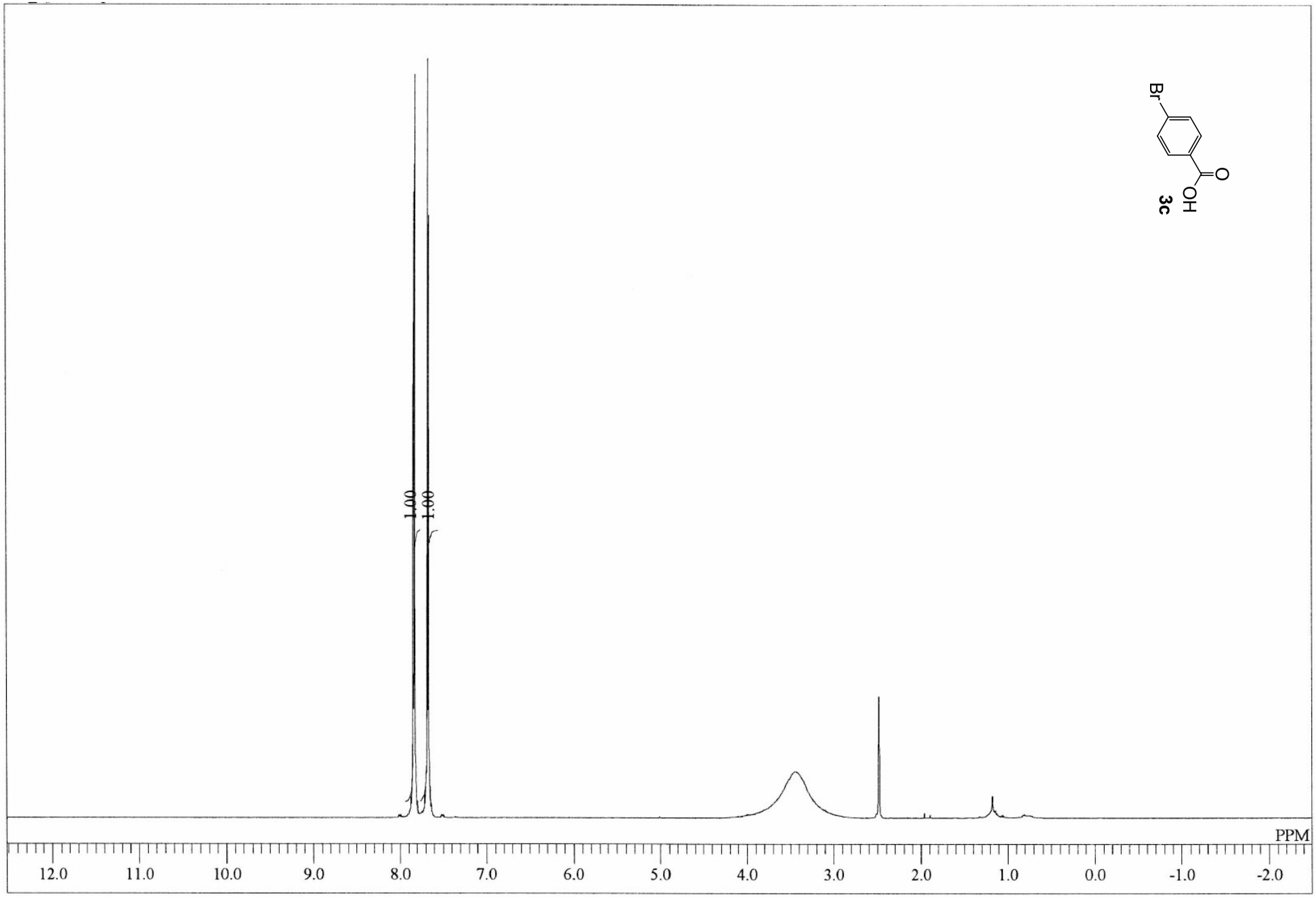
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O
OH
3c
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1.00
PPM
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10.0
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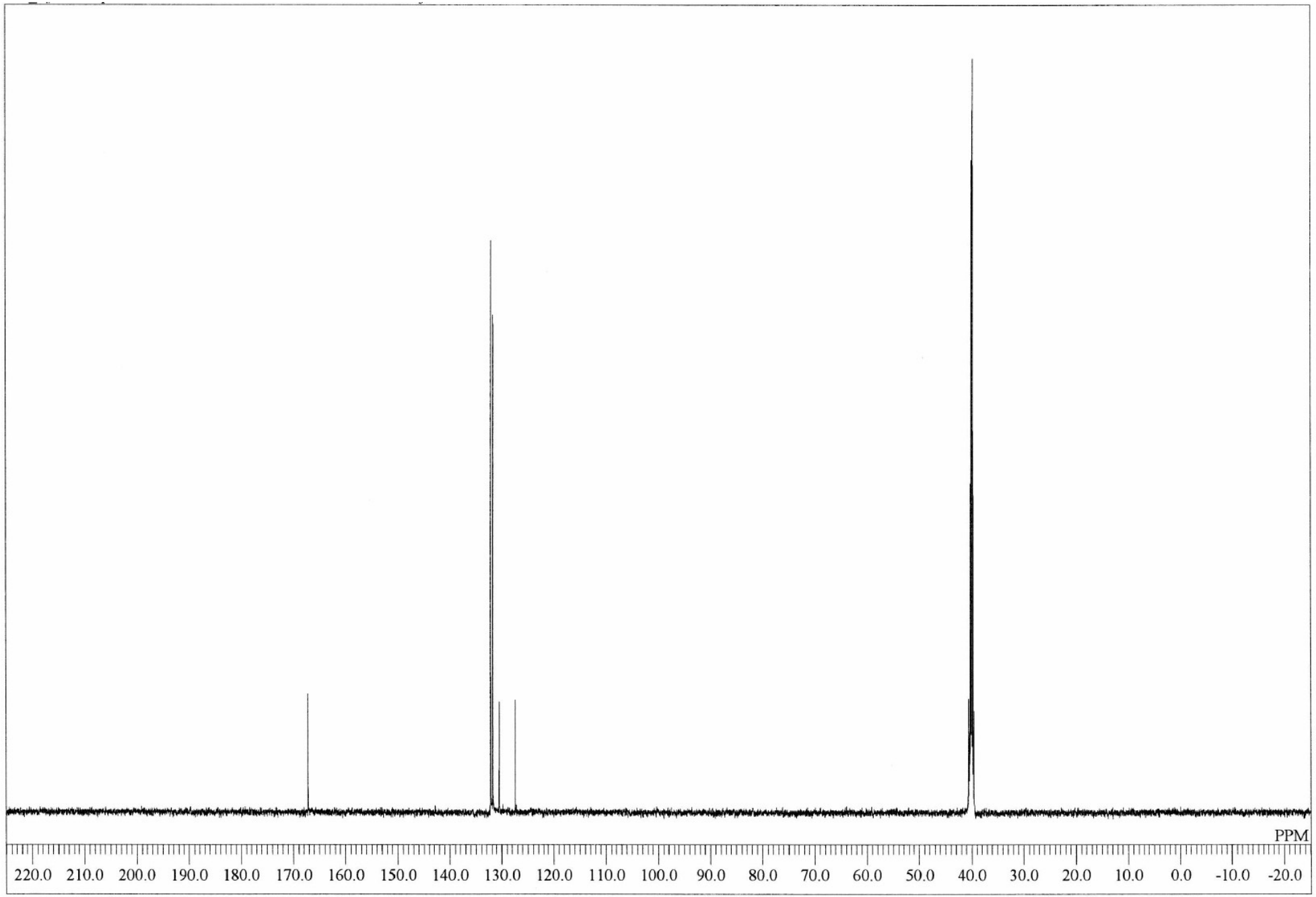
-2.0


PPM
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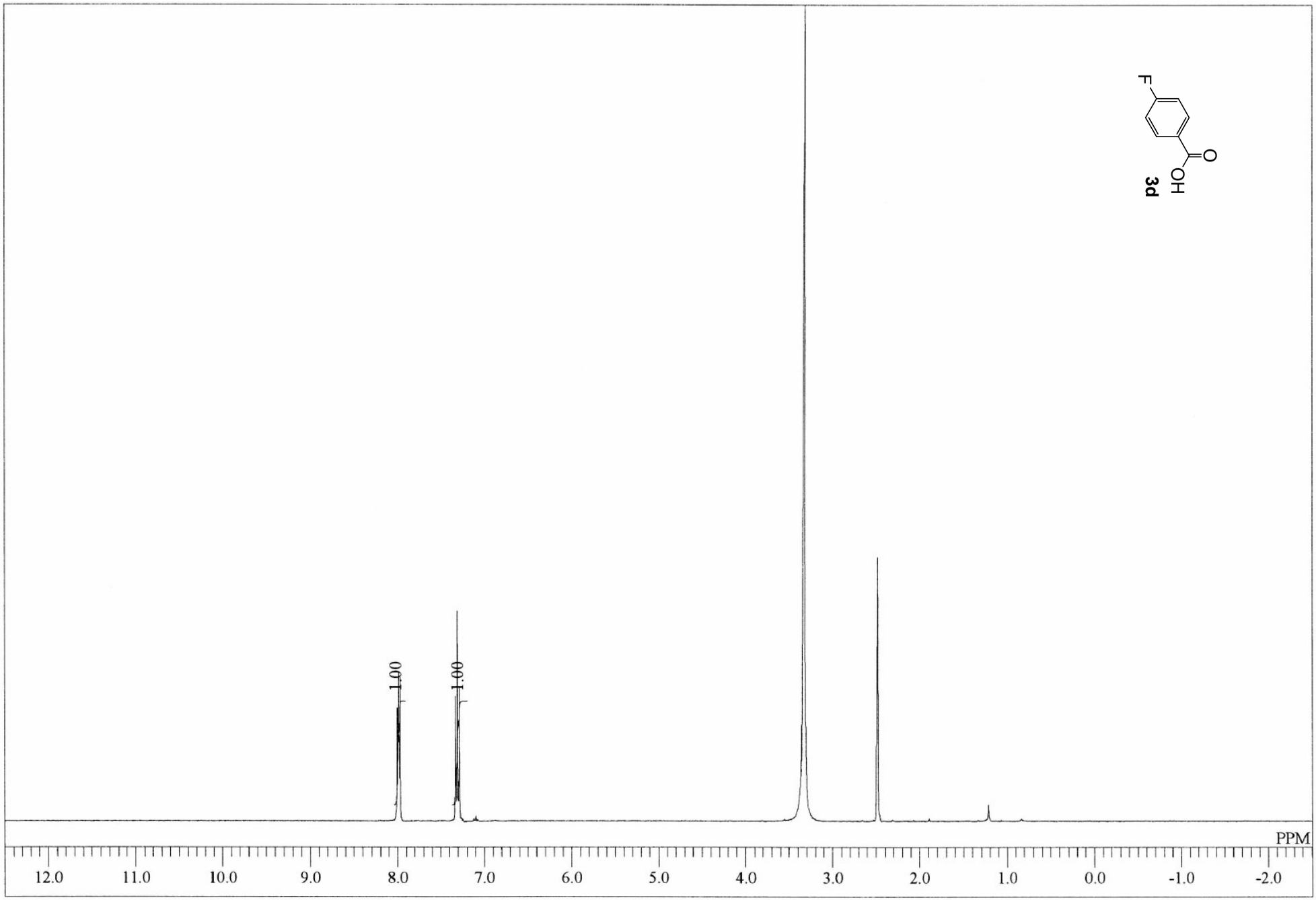
F
O
OH
3d
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1.00
PPM
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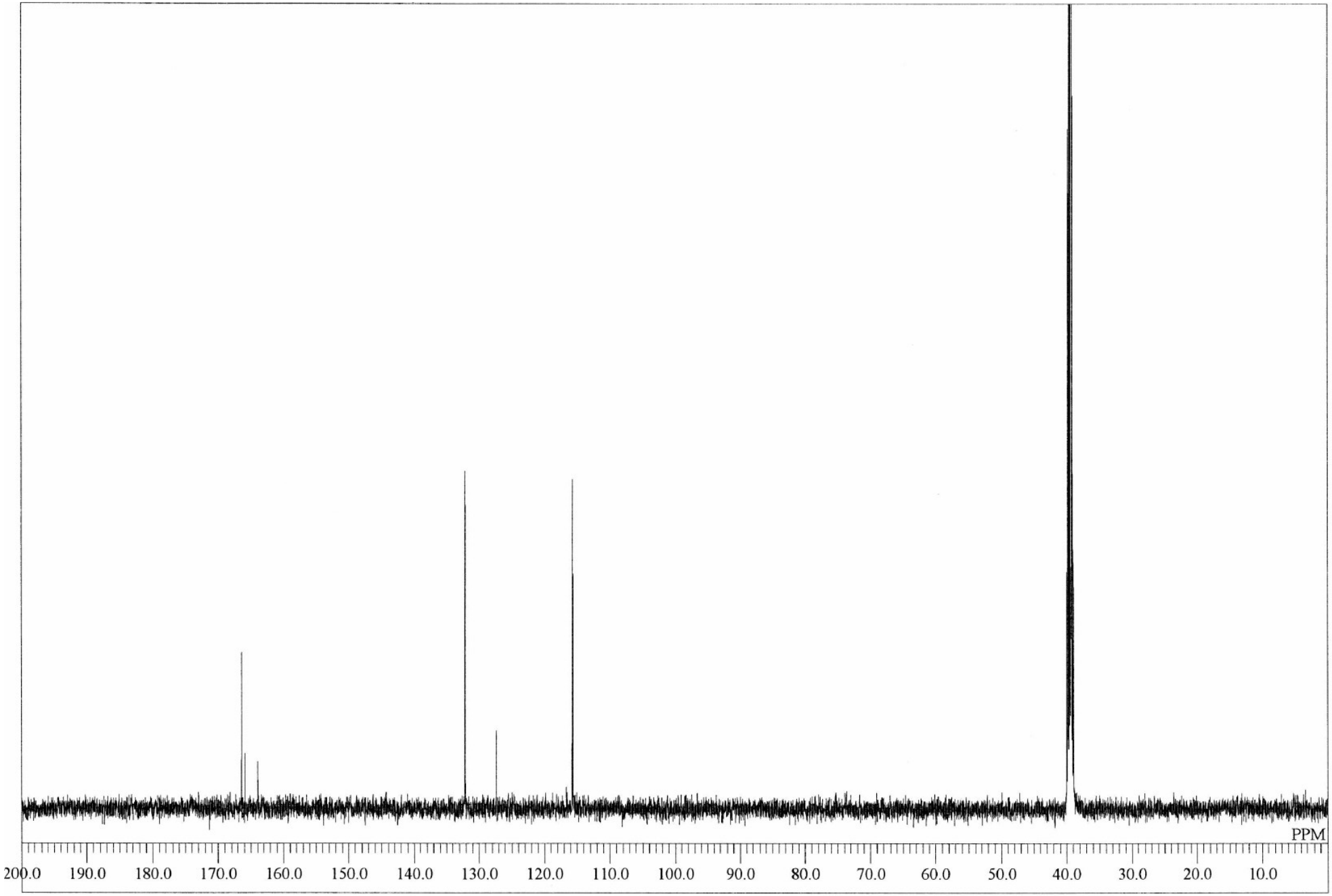
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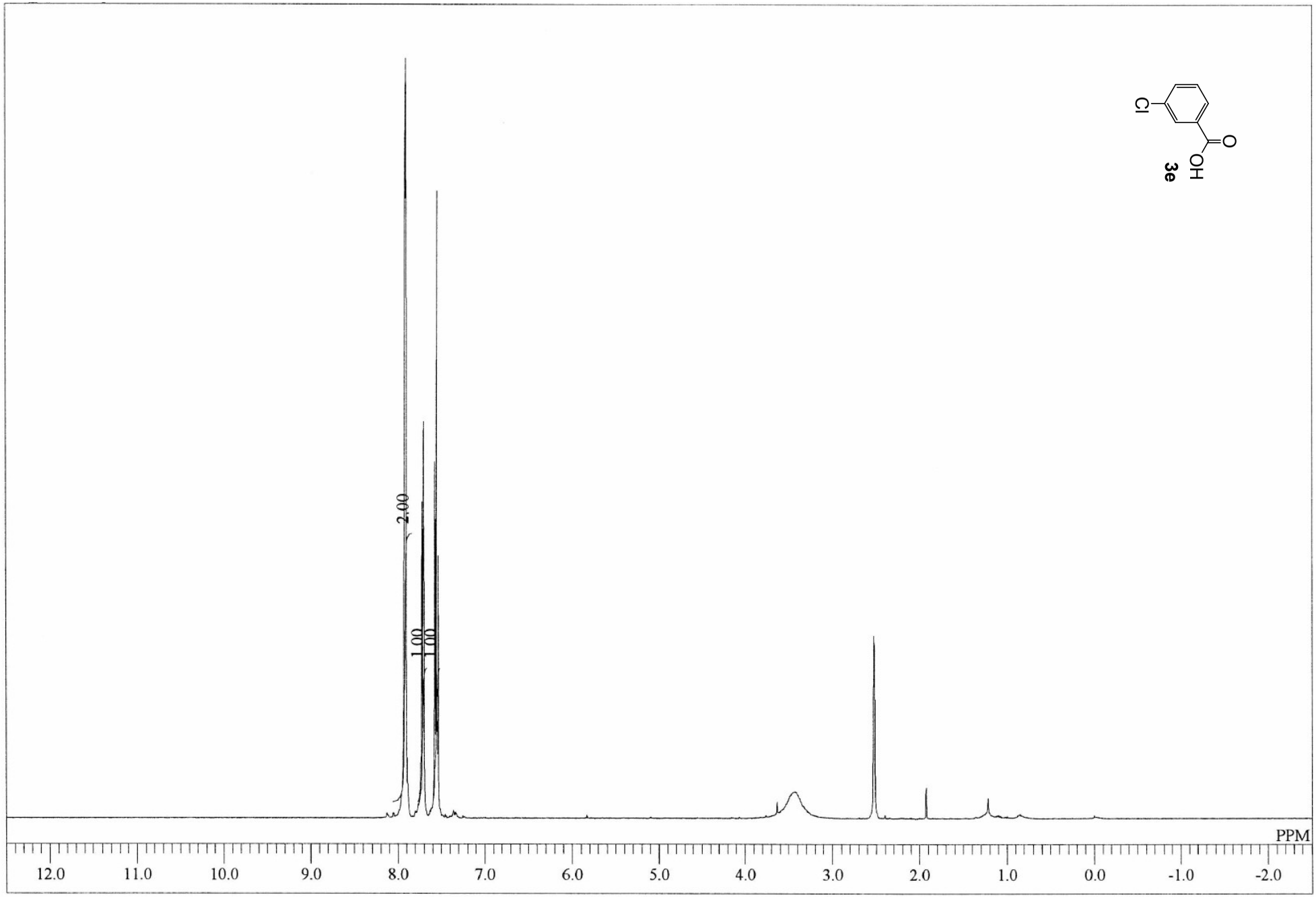
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OH
3e
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1.00
1.00
PPM
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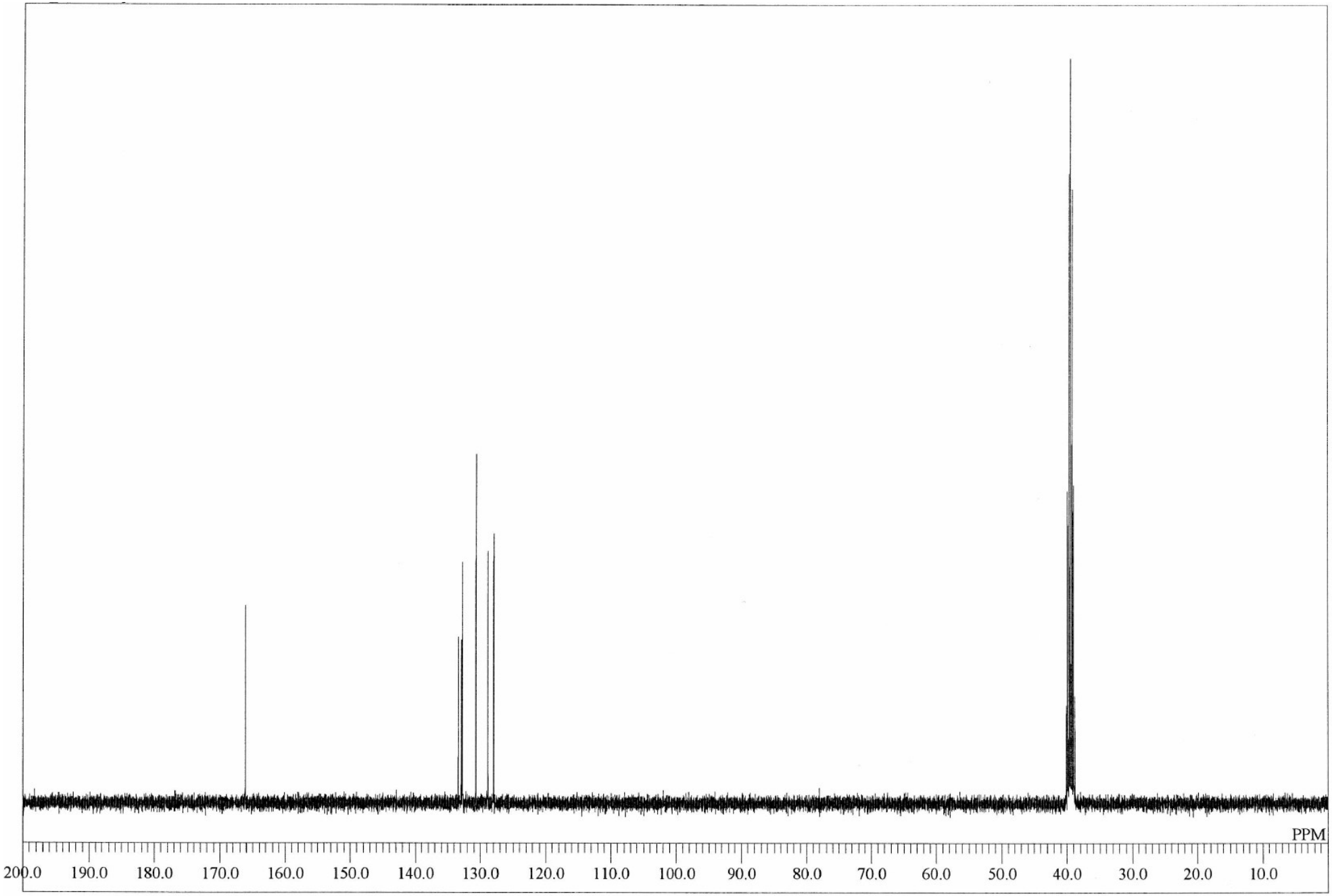
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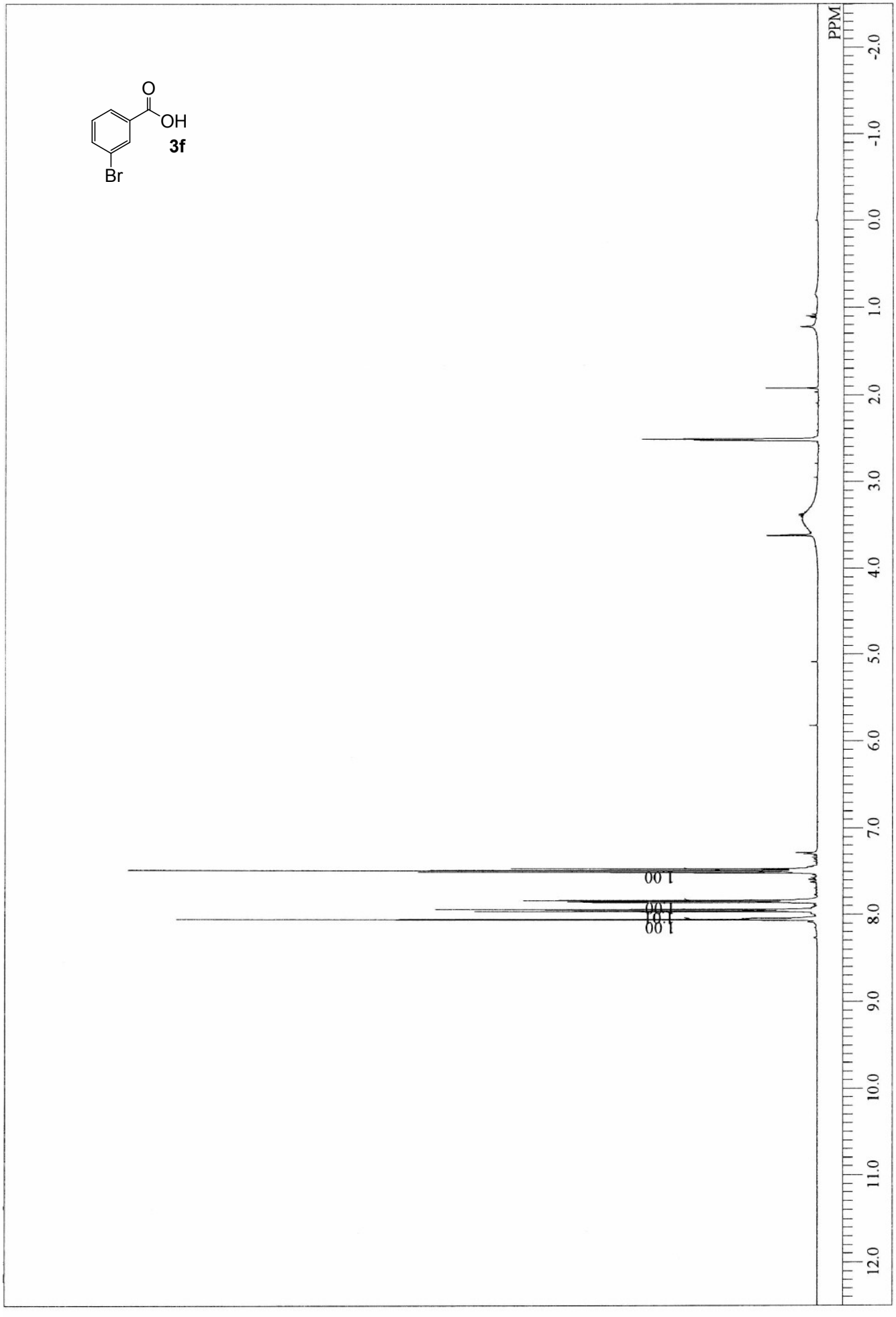
O
OH
Br
3f
PPM
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-1.0
0.0
1.0
2.0
3.0
4.0
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8.0
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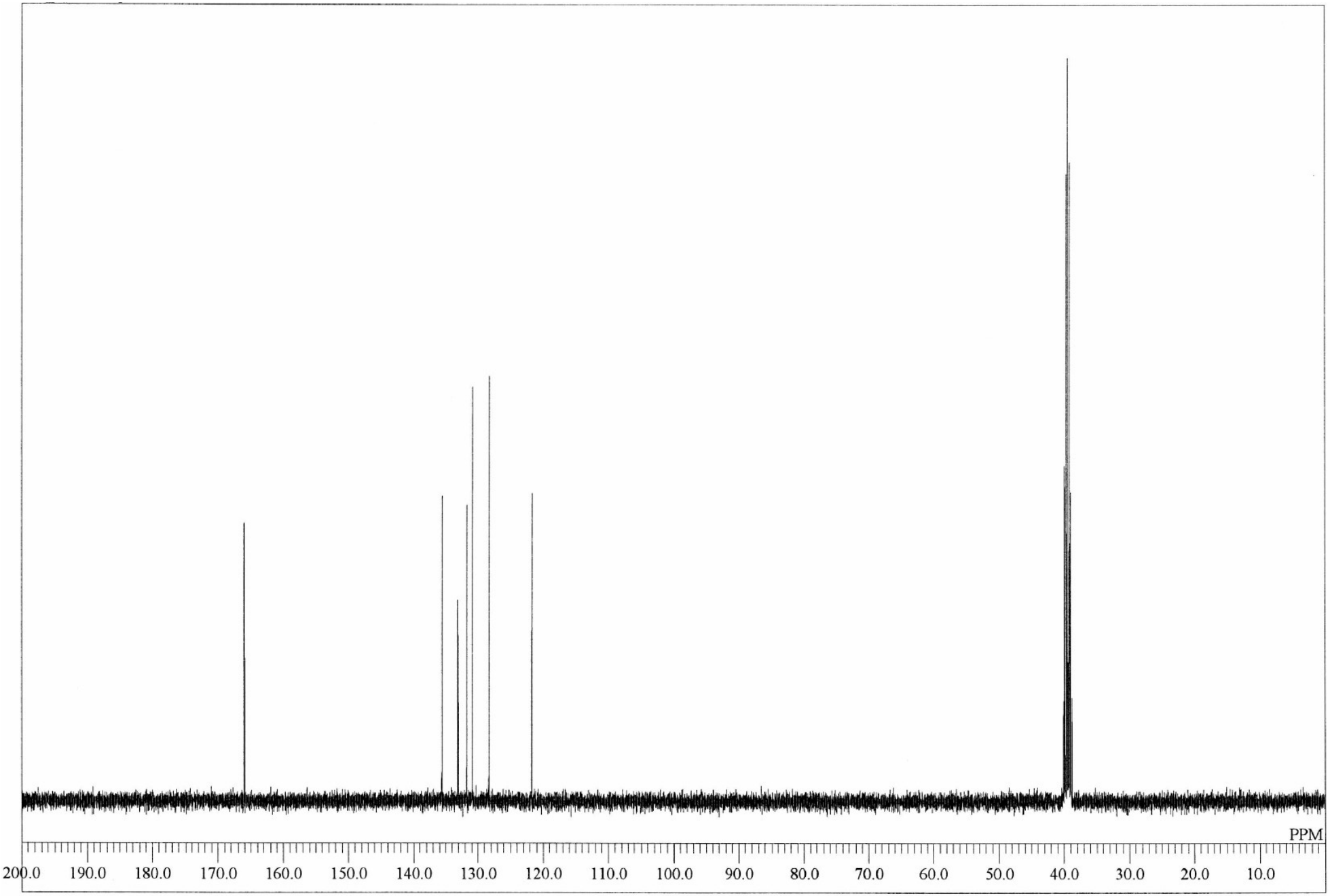
10.0
11.0
12.0
1.00
1.00
1.01
1.00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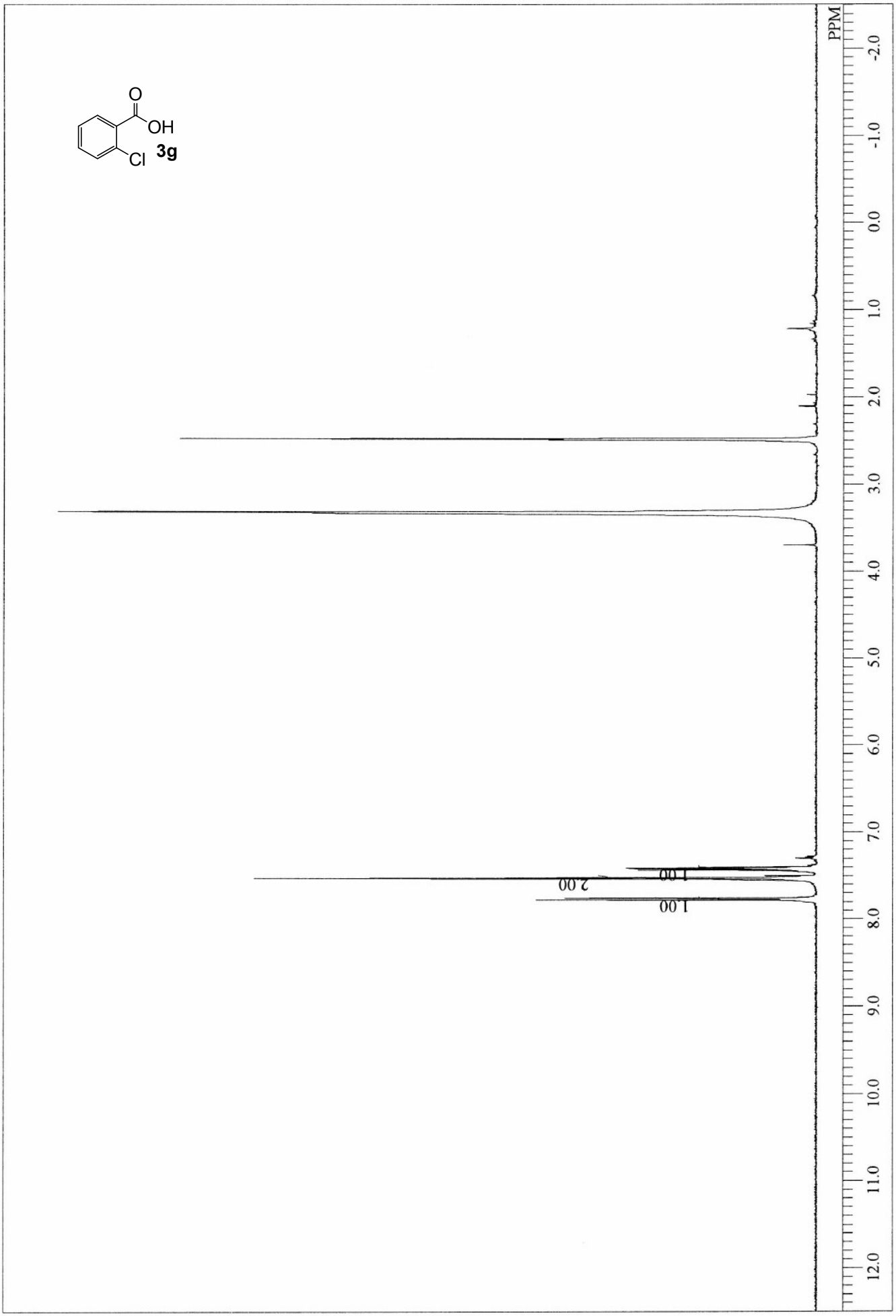
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OH
Cl
3g
PPM
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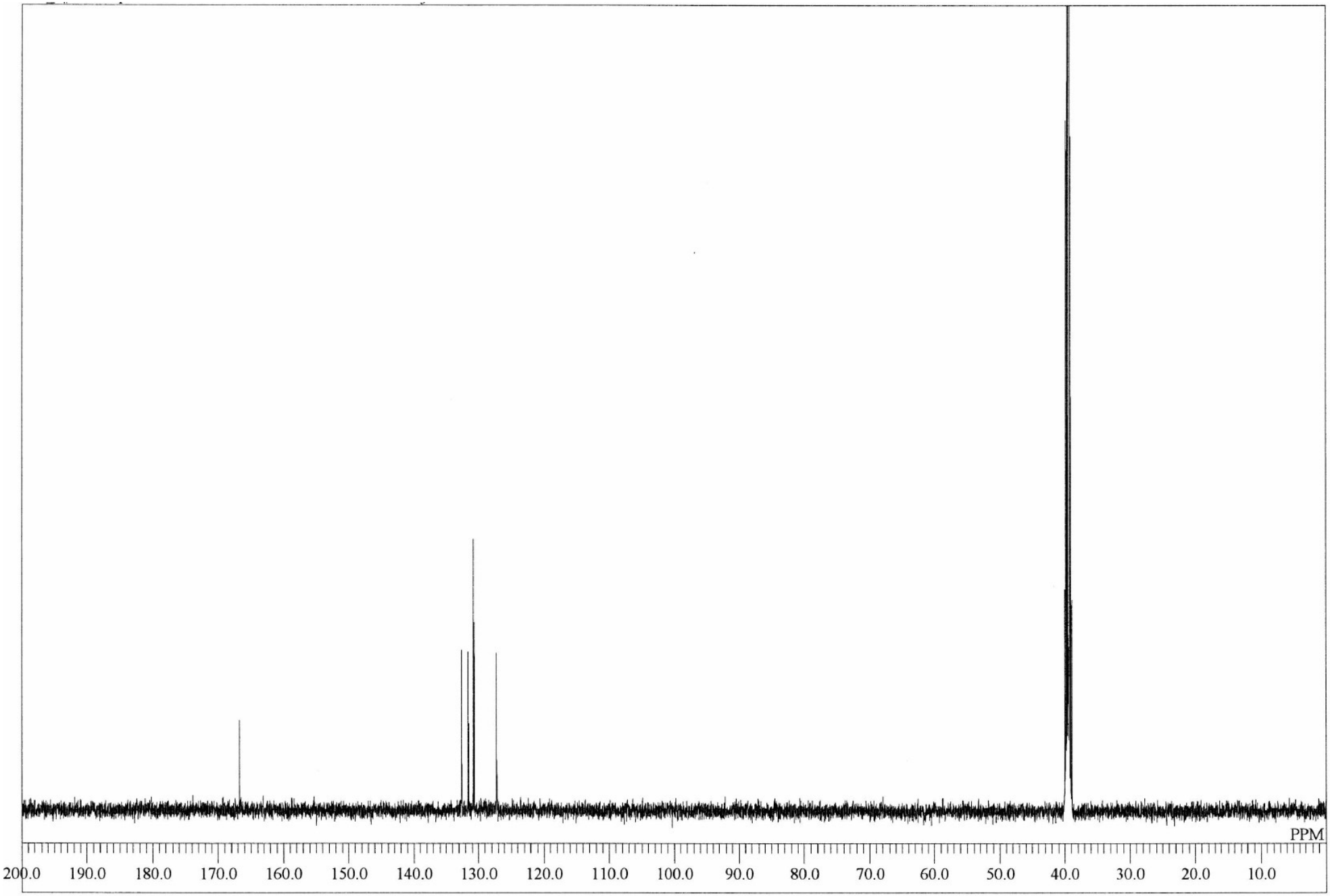
PPM
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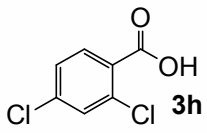
10.0


O
OH
Cl
Cl

3h

PPM
-2.0
-1.0
0.0
1.0
2.0
3.0
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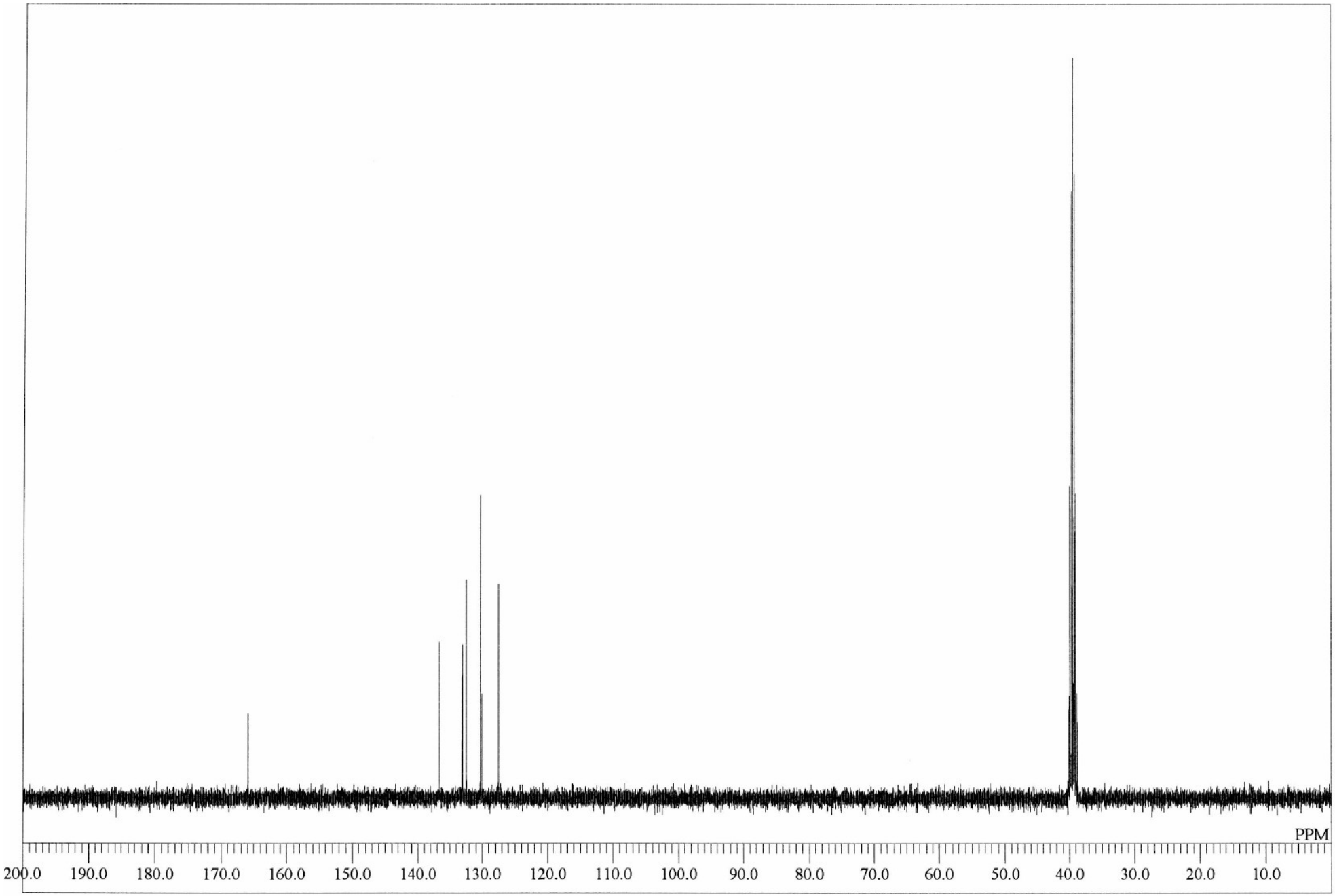
1.00


PPM
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140.0
130.0
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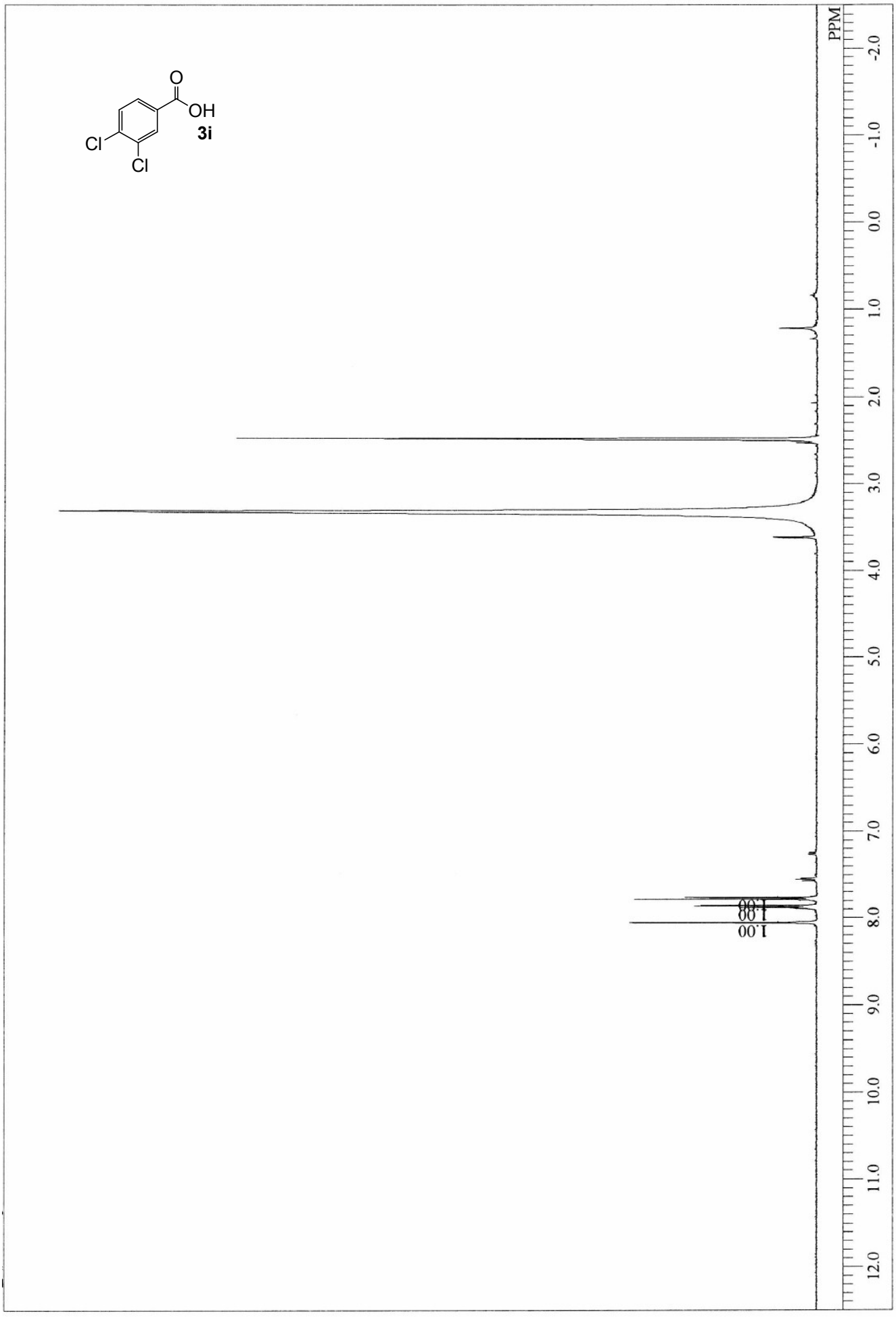
O
OH
Cl
Cl
3i
PPM
-2.0
-1.0
0.0
1.0
2.0
3.0
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11.0
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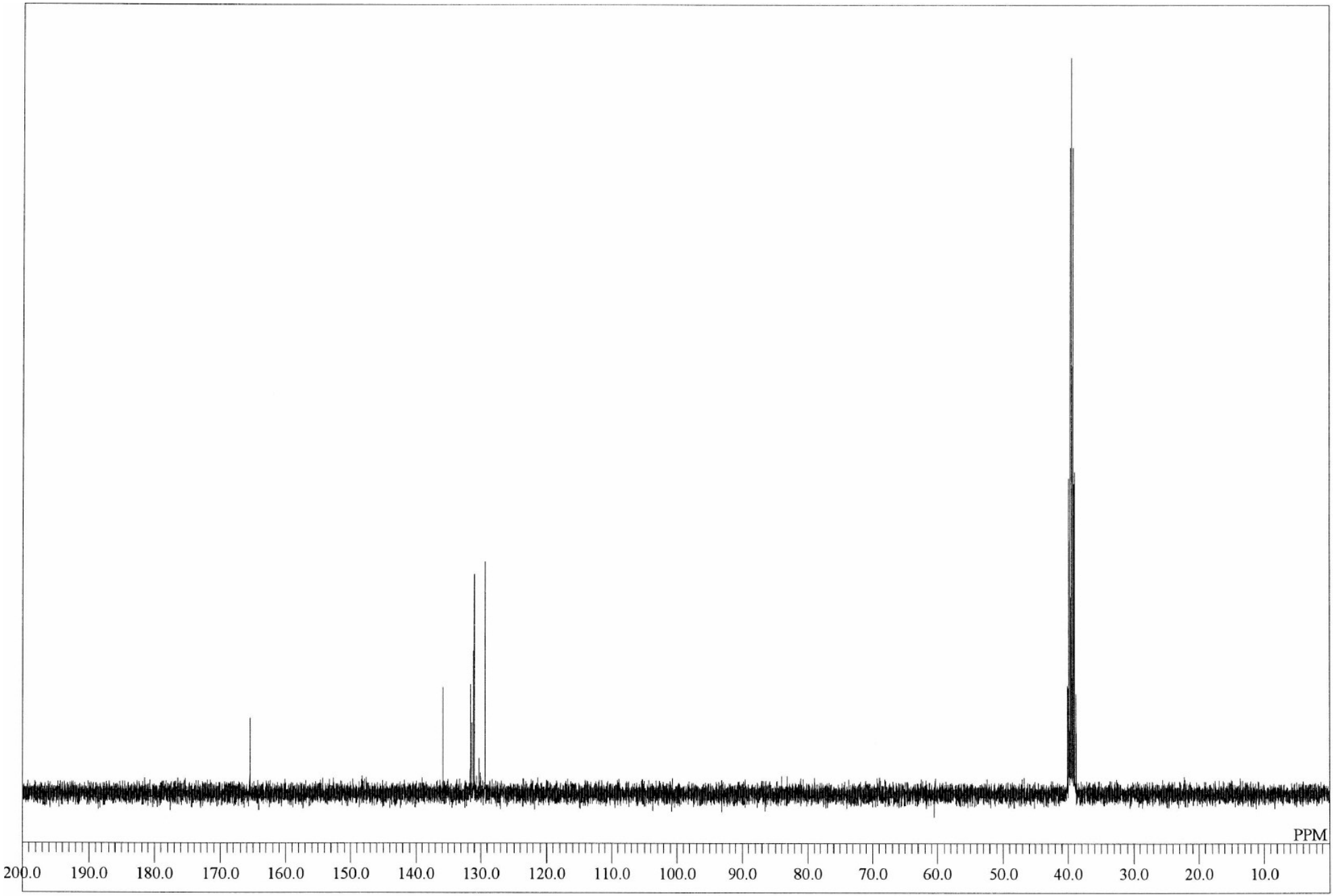
1.00


PPM
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140.0
130.0
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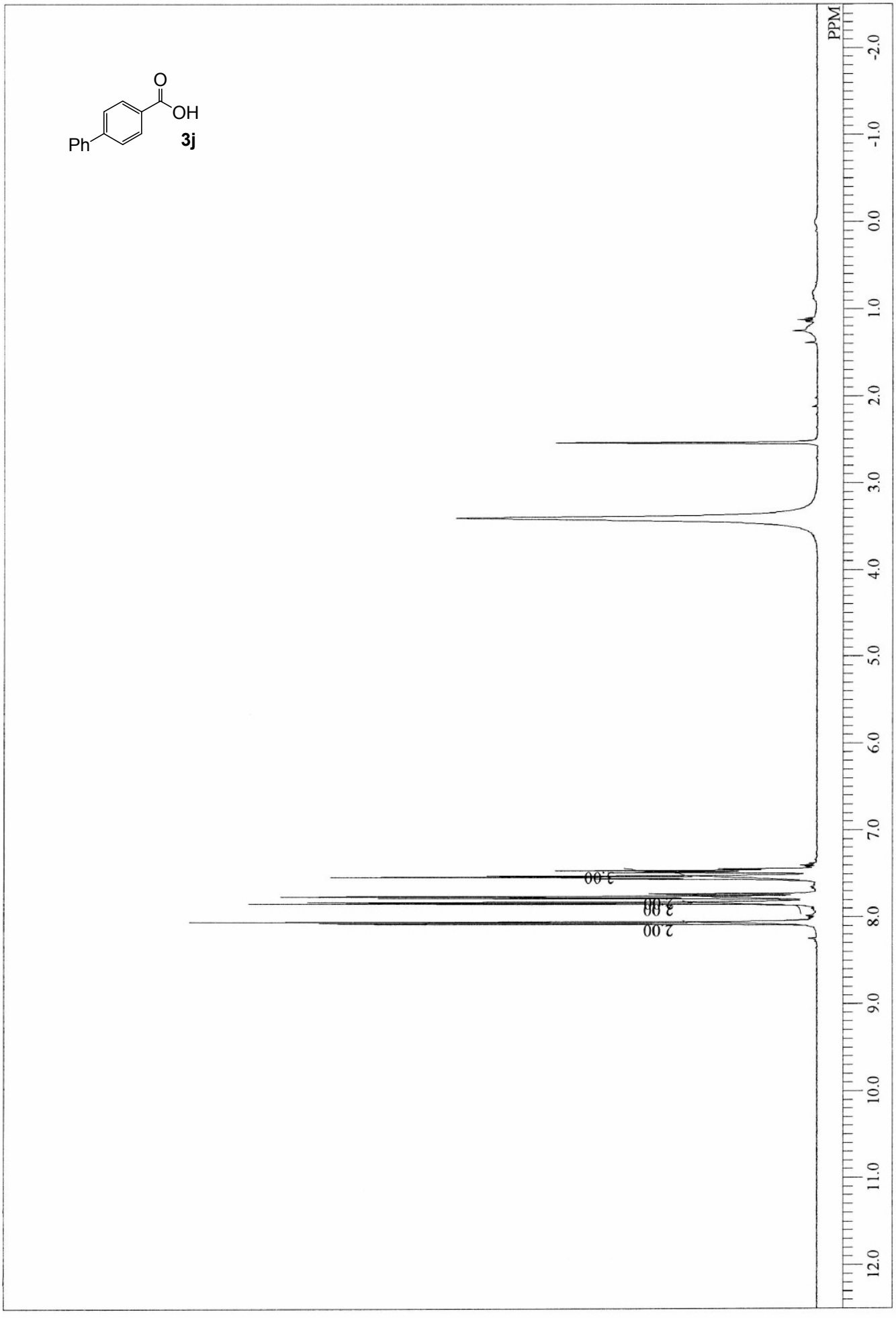
O
OH
Ph
3j
PPM
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-1.0
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1.0
2.0
3.0
4.0
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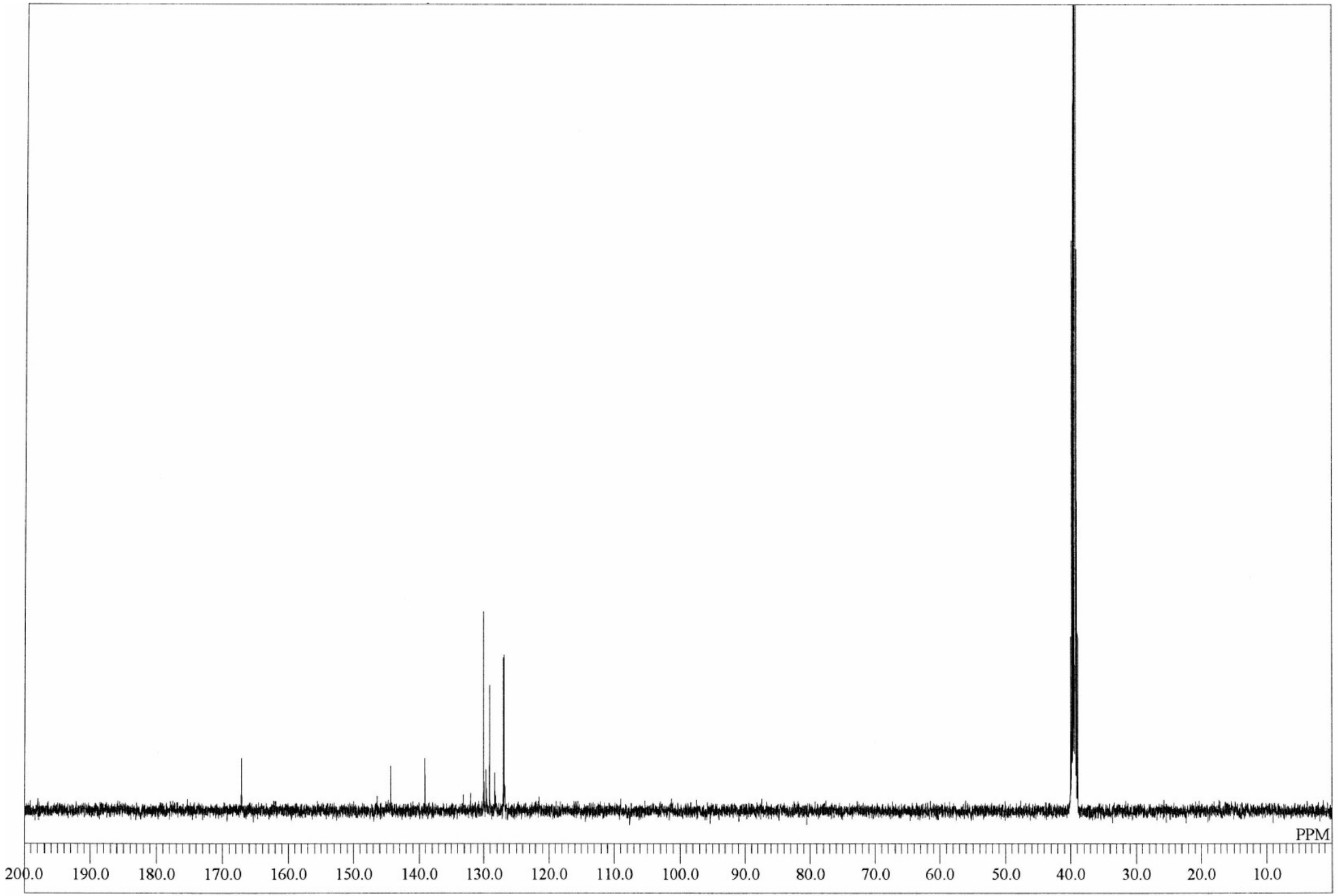
2.00


PPM
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130.0
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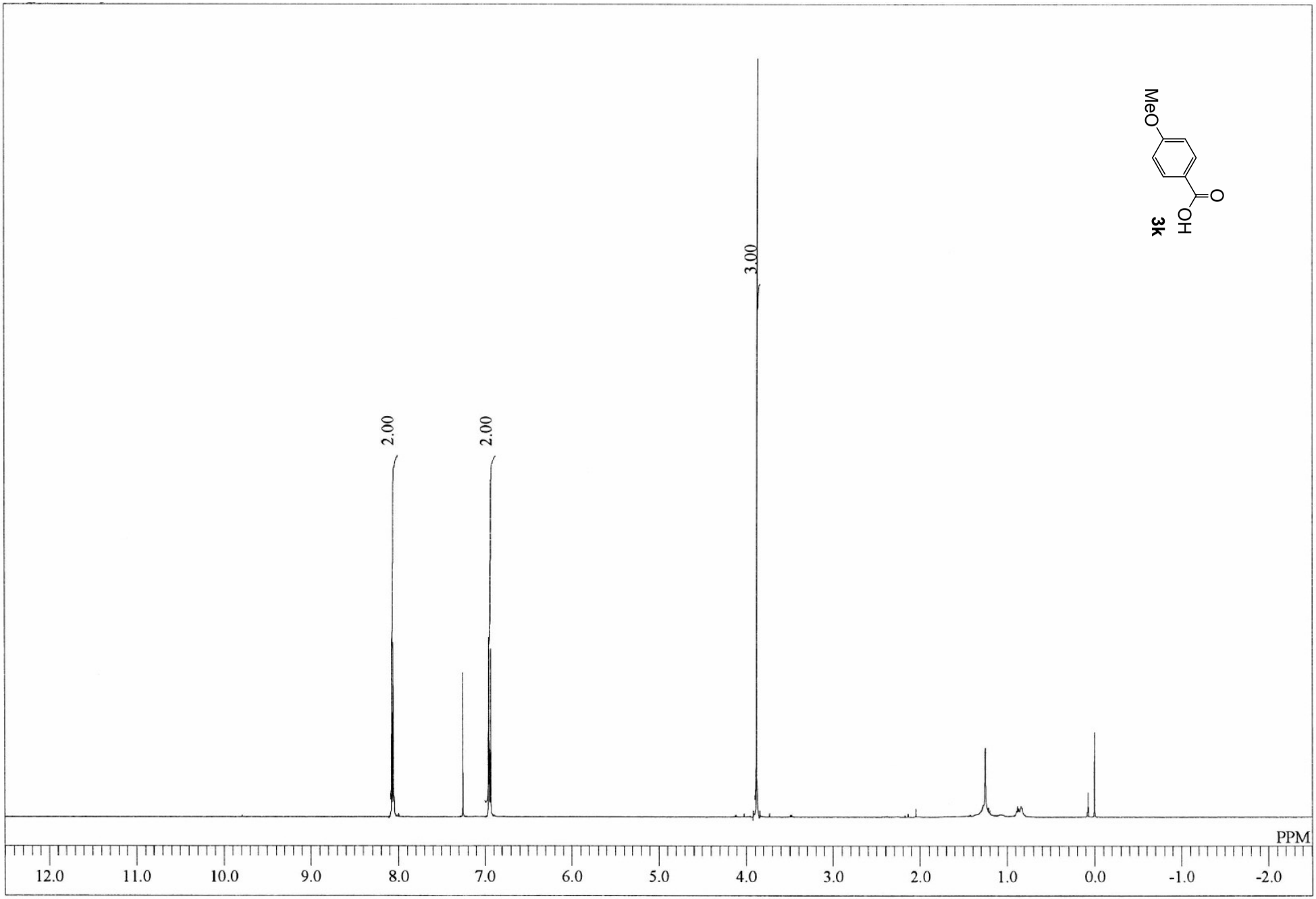
MeO
O
OH
3k
2.00
2.00
3.00
PPM
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11.0
10.0
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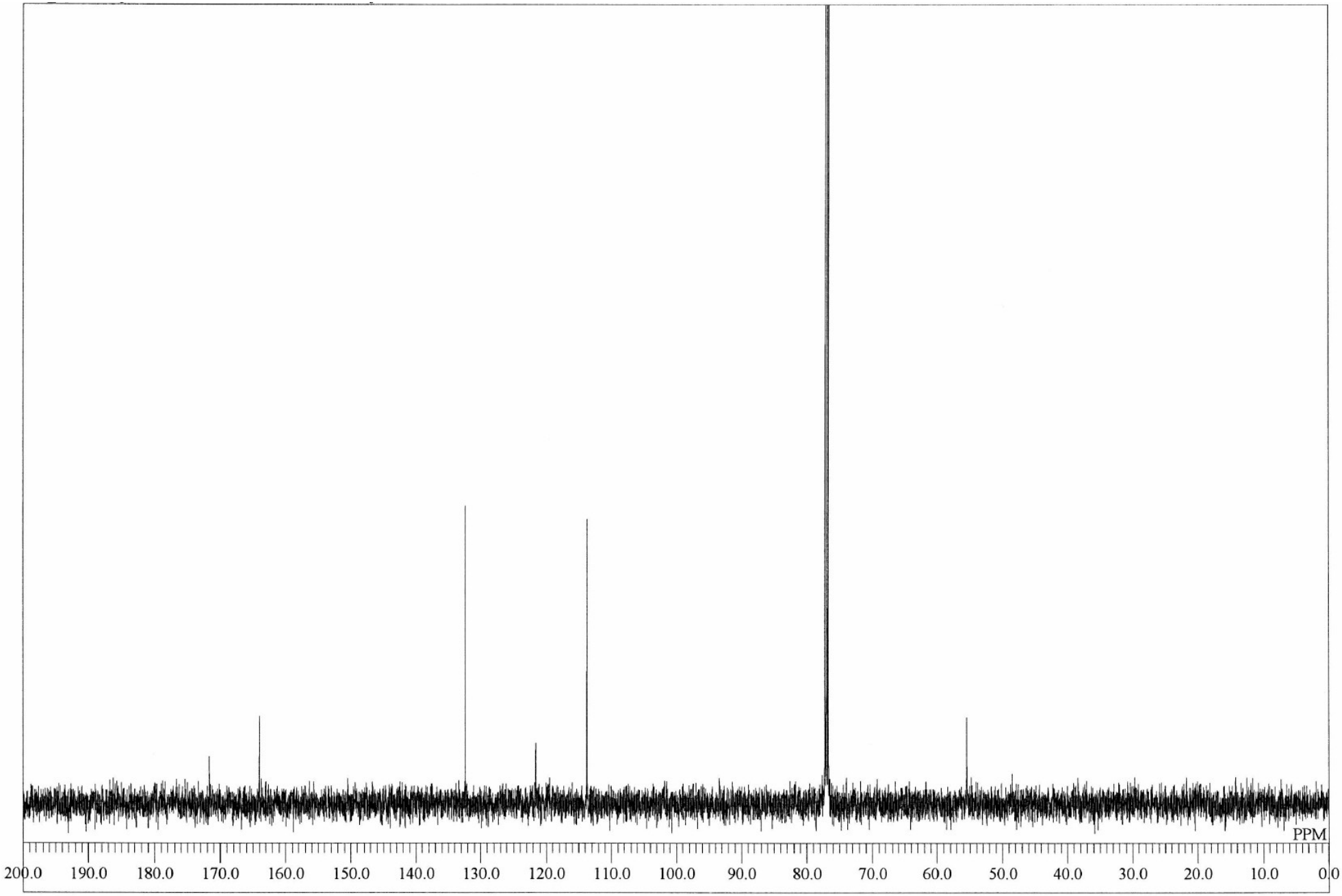
PPM
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130.0
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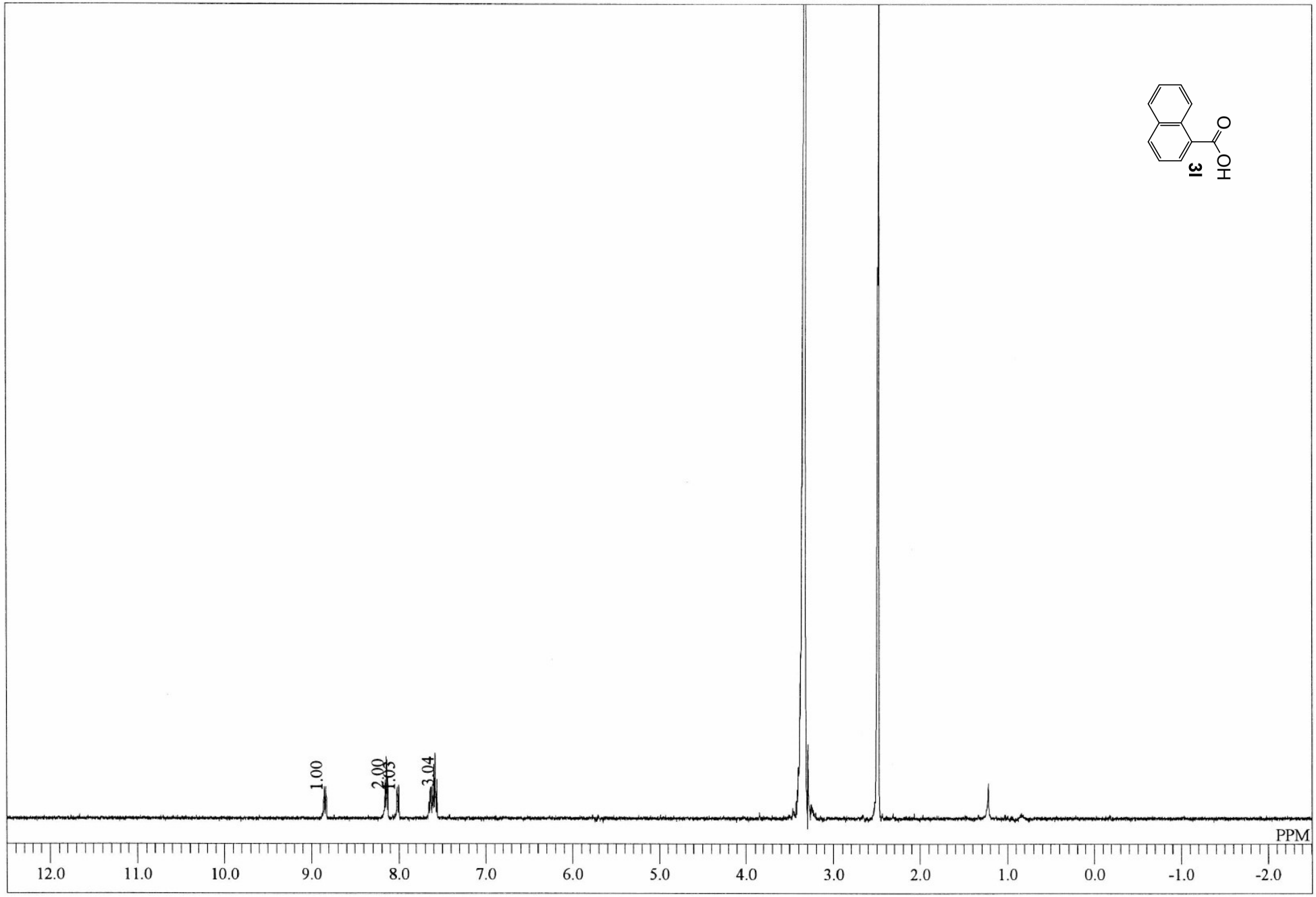
OH
O
31
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3.04
PPM
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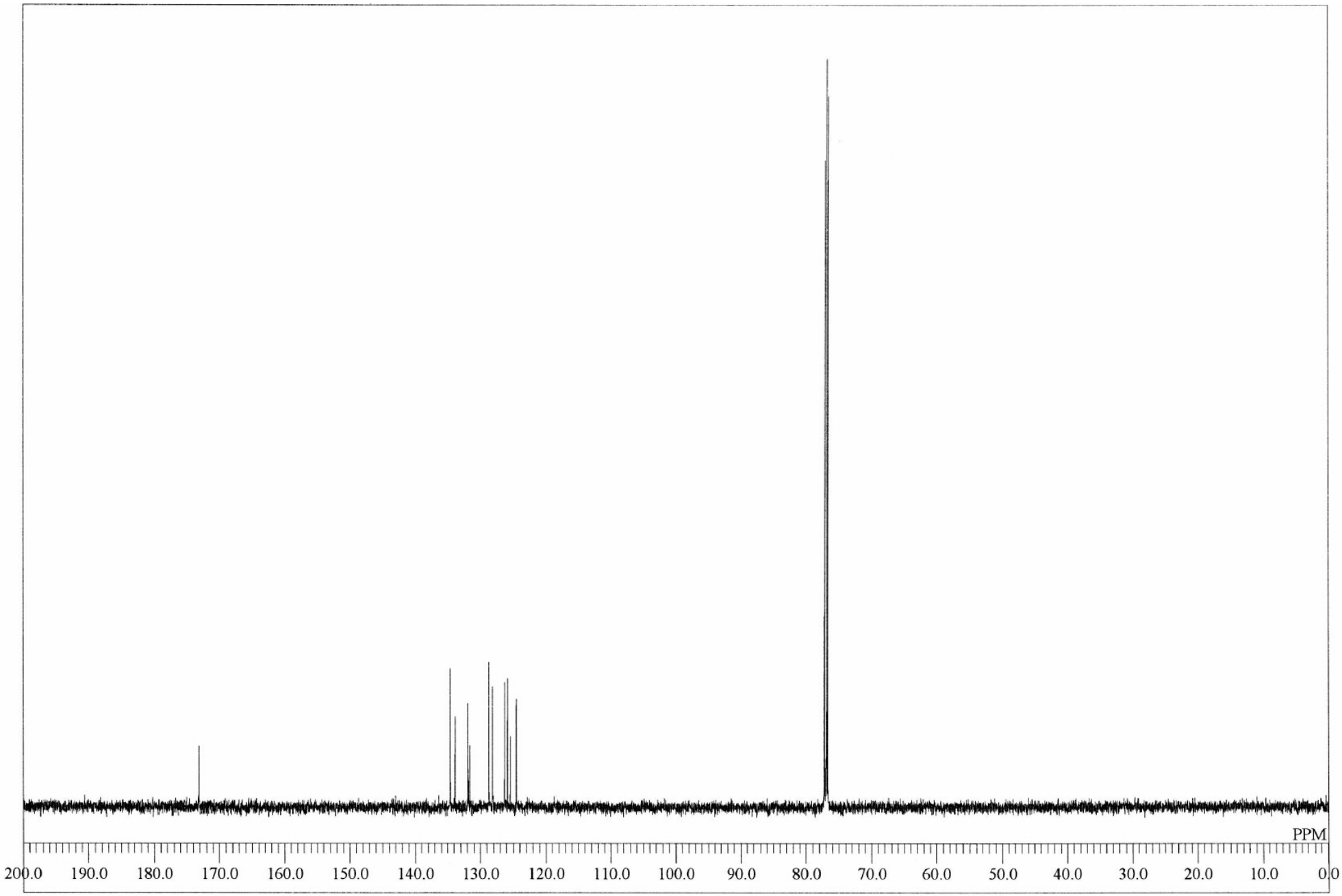
PPM
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60.0
50.0
40.0
30.0
20.0
10.0
0.0