The Synthesis of Di-carboxylate Esters using Continuous Flow Vortex Fluidics

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Supplementary information

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Experimental comments

Unless otherwise indicated, all reagents were commercially available and used directly from the supplier without further purification. ^{1}H and ^{13}C NMR were recorded at 20.6 °C using $CDCl_3$ (7.27 ppm) unless otherwise indicated. Chemical shift values are expressed in parts per million (ppm) and *J*-values in Hertz (Hz). Splitting patterns are indicated at s: singlet, d: doublet, t: triplet, q: quartet, quin: quintet, sex: sextet, sept: septet or combination br s: broad singlet or m: multiplet.

Water loss experiments

For this experiment the following procedure was followed. To a 20 mm external diameter VFD sample tube was added 2.00 mL of water. The tube was weighed and then loaded into a VFD at a 45° tilt angle relative to the horizontal position. The tube was then rotated about its axis for two-minute time periods and then weighed immediately to log water loss. The exact same experiment was performed in a 5 mL round bottom flask to give a direct comparison to traditional batch type techniques. All results were performed in triplicate and the error indicated is the maximum and minimum of the data set. Experiments were carried out at RT (23°C) standard pressure (Fig.S1).

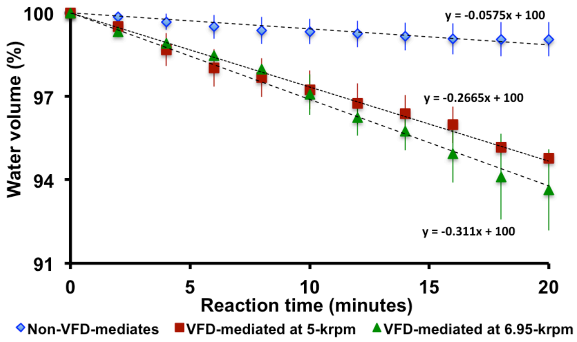


Fig. S1. The results for the experiment described above. Results show that in a non-VFD-mediated reaction, water is lost at 106 µmoles per second whilst at 5-krpm and 6.95-krpm water loss was 493 and 575 µmoles per second. This indicates that the VFD has greater water loss than batch processing. This is presumably prime cause for the enhancement in the position of equilibrium.

Catalyst optimization

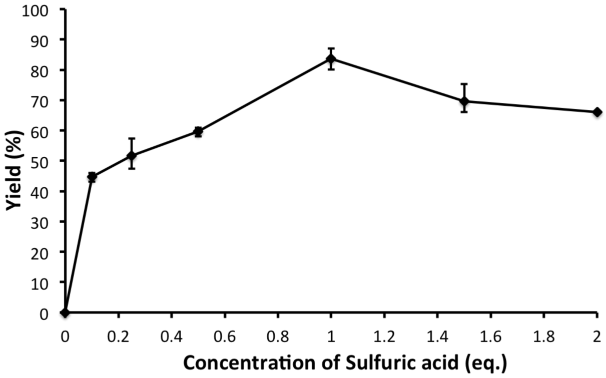


Fig. S2. The optimal concentration of acid catalyst used for the synthesis of di-methyladipate. A sample tube rotational speed of 5250 rpm was used at a 0.45 mL/min flow rate. The results indicate that 1.0 eq of sulfuric acid catalyst generates a response that can be further enhanced through flow rate and rotational speed optimization. The error shown is the maximum and minimum of the data set around the mean (n=3).

VFD operation

The VFD is a microfluidic processing platform that can be set up in under ten minutes to run a continuous flow reaction (Fig. S3).

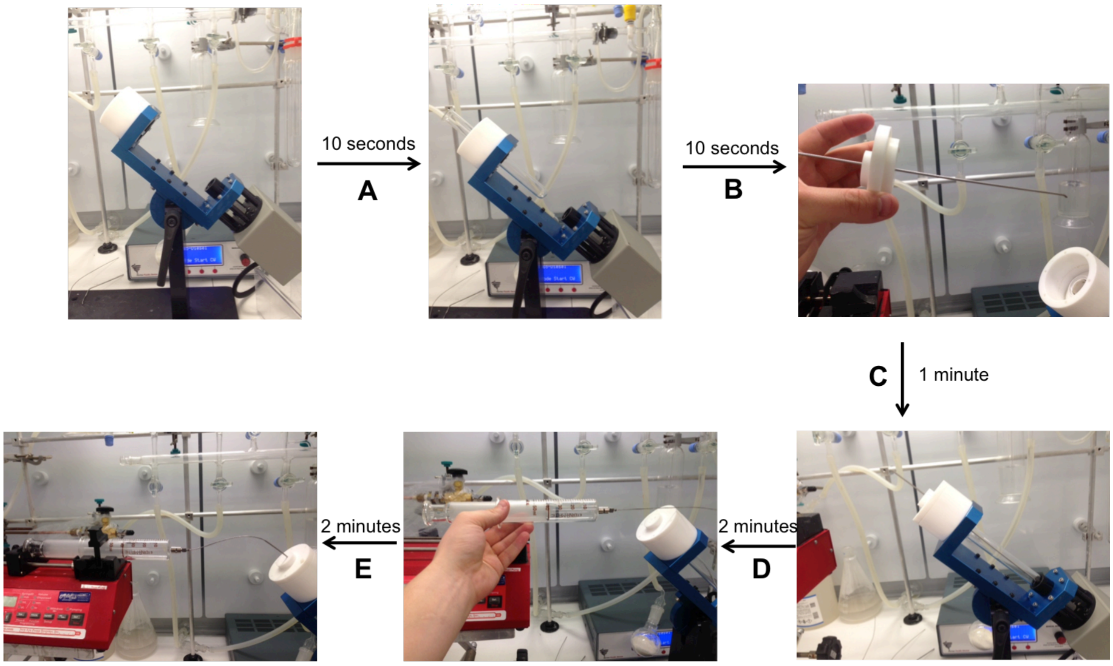
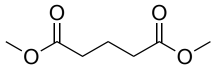


Fig. S3. Shown are the operational steps and the times needed to perform each step. (**A**) Insertion of the glass sample tube into the VFD after a small amount of lubrication is placed around the tube, (**B**) Placing the lid on the Teflon housing unit. The lid contains the jet feeds that deliver the fluid to the rapidly rotating tube, (**C**) Screwing down the lid with six nylon screws to secure the feed jets, (**D**) Loading the syringe pump with the fluid of choice (time is dependent on the volume of fluid used) and (**E**) Loading the syringe into the computer controlled syringe pump and placing the end of the syringe needed down the jet feed. If the solutions have been made up, the time it takes to go from a vacant VFD to an operating VFD is in the order of five minutes.

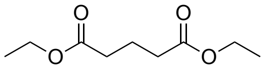
Compound assignment

[1] Di-methylglutarate



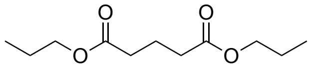
^{1}H NMR (600 MHz, $CDCl_3$): δ 3.65 (s, 6 H, CH_3), δ 2.36 (t, *J* = 6.0 Hz, 4 H, CH_2), δ 1.93 (quin, *J* = 6.0 Hz, 2 H, CH_2); ^{13}C (150 MHz, $CDCl_3$): 173.5, 51.7, 33.1 and 20.2.

[2] Di-ethylglutarate



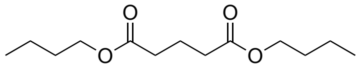
^{1}H NMR (600 MHz, $CDCl_3$): δ 4.10 (q, *J* = 6.0 Hz, 4 H, CH_2), δ 2.33 (t, *J* = 6.0 Hz, 4 H, CH_2), δ 1.92 (quin, *J* = 6.0 Hz, 2 H, CH_2), δ 1.22 (t, *J* = 12.0 Hz, 6 H, CH_3); ^{13}C (150 MHz, $CDCl_3$): 173.0, 60.4, 33.4, 20.3 and 14.3.

[3] Di-propylglutarate



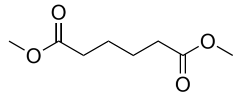
^{1}H NMR (600 MHz, $CDCl_3$): δ 4.00 (t, *J* = 6.0 Hz, 4 H, CH_2), δ 2.34 (t, *J* = 6.0 Hz, 4 H, CH_2), δ 1.92 (quin, *J* = 6.0 Hz, 2 H, CH_2), δ 1.62 (quin, *J* = 6.0 Hz, 4 H, CH_2), δ 0.91 (t, *J* = 6.0 Hz, 6 H, CH_3); ^{13}C (150 MHz, $CDCl_3$): 173.1, 66.1, 33.4, 22.0, 20.3 and 10.4.

[4] Di-butylglutarate



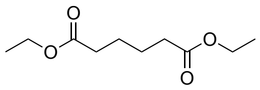
^{1}H NMR (600 MHz, $CDCl_3$): δ 4.02 (t, *J* = 6.0 Hz, 4 H, CH_2), δ 2.31 (t, *J* = 6.0 Hz, 4 H, CH_2), δ 1.89 (quin, *J* = 6.0 Hz, 2 H, CH_2), δ 1.55 (quin, *J* = 6.0 Hz, 4 H, CH_2), δ 1.33 (sex, *J* = 6.0 Hz, 4 H, CH_2), δ 0.88 (t, *J* = 7.3 Hz, 6 H, CH_3); ^{13}C (150 MHz, $CDCl_3$): 173.0, 64.3, 33.3, 30.7, 20.2, 19.1 and 13.7.

[5] Di-methyladipate



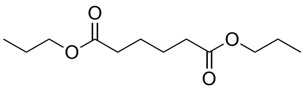
^{1}H NMR (600 MHz, $CDCl_3$): δ 3.65 (br.s, 6 H, CH_3), δ 2.32 (br.s, 4 H, CH_2), δ 1.65 (br.s, 4 H, CH_2); ^{13}C (150 MHz, $CDCl_3$): 173.8, 51.5, 33.7 and 24.4.

[6] Di-ethyladipate



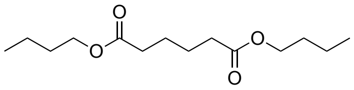
^{1}H NMR (600 MHz, $CDCl_3$): δ 4.07 (q, *J* = 6.0 Hz, 4 H, CH_2), δ 2.27 (t, *J* = 6.0 Hz, 4 H, CH_2), δ 1.62 (quin, *J* = 3.5 Hz, 4 H, CH_2), δ 1.21 (t, *J* = 7.1 Hz, 6 H, CH_3); ^{13}C (150 MHz, $CDCl_3$): 173.3, 60.3, 34.0, 24.5 and 14.3.

[7] Di-propyladipate



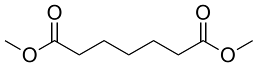
^{1}H NMR (600 MHz, $CDCl_3$): δ 4.02 (t, *J* = 6.0 Hz, 4 H, CH_2), δ 2.35-2.29 (m, 4 H, CH_2), δ 1.67-1.60 (m, 8 H, CH_2), δ 0.93 (t, *J* = 12.0 Hz, 6 H, CH_3); ^{13}C (150 MHz, $CDCl_3$): 173.5, 66.1, 34.1, 24.6, 22.1 and 10.5.

[8] Di-butyladipate



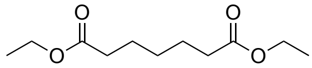
^{1}H NMR (600 MHz, CDCl$_3$): δ 4.03 (t, J = 6.0 Hz, 4 H, CH$_2$), δ 2.28 (t, J = 6.0 Hz, 4 H, CH$_2$), δ 1.62 (quin, J = 6.0 Hz, 4 H, CH$_2$), δ 1.56 (quin, J = 6.0 Hz, 4 H, CH$_2$), δ 1.34 (h, J = 6.0 Hz, 4 H, CH$_2$), δ 0.89 (t, J = 6.0 Hz, 6 H, CH$_3$); ^{13}C (150 MHz, CDCl$_3$): 173.4, 64.2, 34.0, 30.7, 24.5, 19.2 and 13.7.

[9] Di-methylpimelate



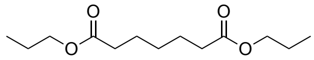
^{1}H NMR (600 MHz, CDCl$_3$): δ 3.63 (s, 6 H, CH$_3$), δ 2.28 (t, J = 6.0 Hz, 4 H, CH$_2$), δ 1.61 (q, J = 6.0 Hz, 4 H, CH$_2$), δ 1.32 (quin, J = 8.3 Hz, 2 H, CH$_2$); ^{13}C (150 MHz, CDCl$_3$): 174.0, 51.5, 33.9, 28.7 and 24.6.

[10] Di-ethylpimelate



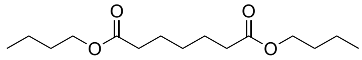
^{1}H NMR (600 MHz, CDCl$_3$): δ 4.09 (q, J = 6.0 Hz, 4 H, CH$_2$), δ 2.27 (t, J = 6.0 Hz, 4 H, CH$_2$), δ 1.61 (quin, J = 6.0 Hz, 4 H, CH$_2$), δ 1.33 (q, J = 6.0 Hz, 2 H, CH$_2$), δ 1.22 (t, J = 6.0 Hz, 6 H, CH$_3$); ^{13}C (150 MHz, CDCl$_3$): 173.7, 60.3, 34.2, 28.7, 24.7 and 14.3.

[11] Di-proylpimelate



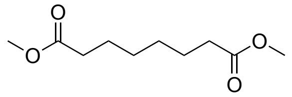
^{1}H NMR (600 MHz, CDCl$_3$): δ 3.99 (t, J = 6.0 Hz, 4H, CH$_2$), δ 2.28 (t, J = 6.0 Hz, 4 H, CH$_2$), δ 1.64 – 1.59 (m, 8 H, CH$_2$), δ 1.36 – 1.31 (m, 2 H, CH$_2$), δ 0.91 (t, J = 6.0 Hz, 6 H, CH$_2$); ^{13}C (150 MHz, CDCl$_3$): 173.8, 66.0, 34.2, 28.7, 24.7, 22.1 and 10.5.

[12] Di-butylpimelate



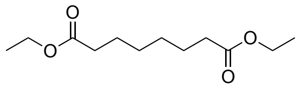
^{1}H NMR (600 MHz, CDCl$_3$): δ 4.02 (t, J = 6.0 Hz, 4 H, CH$_2$), δ 2.26 (t, J = 6.0 Hz, 4 H, CH$_2$), δ 1.62 – 1.53 (m, 8H, CH$_2$), 1.36 – 1.29 (m, 6 H, CH$_2$), 0.89 (t, J = 6.0 Hz, 6 H, CH$_3$) ^{13}C (150 MHz, CDCl$_3$): 173.7, 64.2, 34.2, 30.7, 28.7, 24.7,19.2 and 13.7.

[13] Di-methylsuberate



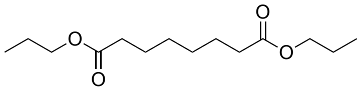
^{1}H NMR (600 MHz, CDCl$_3$): δ 3.51 (s, 6 H, CH$_3$), δ 2.15 (t, J = 6.0 Hz, 4 H, CH$_2$), δ 1.48 (quin, J = 6.0 Hz, 4 H, CH$_2$), δ 1.20 – 1.18 (m, 4 H, CH$_2$); ^{13}C (150 MHz, CDCl$_3$): 174.3, 51.6, 34.1, 28.9 and 24.8.

[14] Di-ethylsuberate



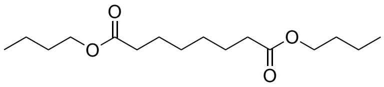
^{1}H NMR (600 MHz, CDCl$_3$): δ 4.10 (q, J = 6.0 Hz, 4 H, CH$_2$), δ 2.27 (t, J = 6.0 Hz, 4 H, CH$_2$), δ 1.61 (quin, J = 6.0 Hz, 4 H, CH$_2$), δ 1.33 (quin, J = 6.0 Hz, 2 H, CH$_2$), δ 1.22 (t, J = 7.12 Hz, 6 H, CH$_3$). ^{13}C (150 MHz, CDCl$_3$): 173.9, 60.3, 34.4, 28.9, 24.9 and 14.4.

[15] Di-propylsuberate



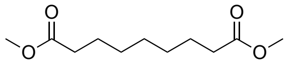
^{1}H NMR (600 MHz, CDCl$_3$): δ 3.99 (t, *J* = 6.0 Hz, 4 H, CH$_2$), δ 2.28 (t, *J* = 6.0 Hz, 4 H, CH$_2$), δ 1.62 (quin, *J* = 6.0 Hz, 8 H, CH$_2$), δ 1.36 – 1.31 (m, 2 H, CH$_2$), δ 0.91 (t, *J* = 6.0 Hz, 6 H, CH$_3$); ^{13}C (150 MHz, CDCl$_3$): 173.7, 66.0, 34.1, 28.7, 24.7, 22.1 and 10.5.

[16] Di-butylsuberate



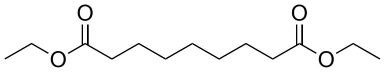
^{1}H NMR (600 MHz, CDCl$_3$): δ 4.06 (t, *J* = 6.0 Hz, 4 H, CH$_2$), δ 2.28 (t, *J* = 7.5 Hz, 4 H, CH$_2$), δ 1.66 – 1.57 (m, 8 H, CH$_2$), δ 1.40 – 1.32 (m, 8 H, CH$_2$), δ 0.93 (t, *J* = 6.0 Hz, 6 H, CH$_3$); ^{13}C (150 MHz, CDCl$_3$): 173.9, 64.3, 34.4, 30.8, 28.9, 24.9, 19.3 and 13.8.

[17] Di-methylazelate



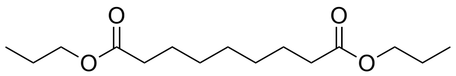
^{1}H NMR (600 MHz, CDCl$_3$): δ 3.64 (s, 6 H, CH$_3$), δ 2.28 (t, *J* = 6.0 Hz, 4 H, CH$_2$), δ 1.60 (quin, *J* = 6.0 Hz, 4 H, CH$_2$), δ 1.30 (br.s, 6H, CH$_2$); ^{13}C (150 MHz, CDCl$_3$): 174.3, 51.5, 34.1, 29.0(2) and 24.9.

[18] Di-ethylazelate



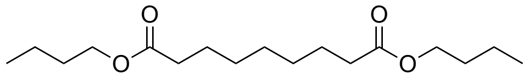
^{1}H NMR (600 MHz, CDCl$_3$): δ 4.11 (q, *J* = 6.0 Hz, 4 H, CH$_2$), δ 2.27 (t, *J* = 6.0 Hz, 4 H, CH$_2$), δ 1.60 (quin, *J* = 7.2 Hz, 4 H, CH$_2$), δ 1.30 (br.s, 6 H, CH$_2$), δ 1.24 (t, *J* = 6.0 Hz, 6 H, CH$_2$); ^{13}C (150 MHz, CDCl$_3$): 174.0, 60.3, 34.4, 29.0 (2), 25.0 and 14.4

[19] Di-propylazelate



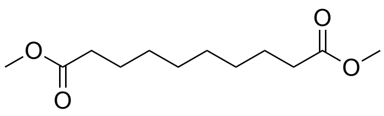
^{1}H NMR (600 MHz, CDCl$_3$): δ 4.01 (t, *J* = 6.0 Hz, 4 H, CH$_2$), δ 2.27 (t, *J* = 7.4 Hz, 4 H, CH$_2$), δ 1.66 - 1.58 (m, 8 H, CH$_2$), δ 1.30 (br.s, 6 H, CH$_2$), δ 0.92 (t, *J* = 7.4 Hz, 6 H, CH$_3$); ^{13}C (150 MHz, CDCl$_3$): 174.0, 65.9, 34.4, 29.1, 29.0, 25.0, 22.1 and 10.4.

[20] Di-butylazelate



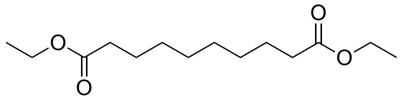
^{1}H NMR (600 MHz, CDCl$_3$): δ 4.03 (t, *J* = 6.0 Hz, 4 H, CH$_2$), δ 2.25 (t, *J* = 7.4 Hz, 4 H, CH$_2$), δ 1.60 - 1.54 (m, 8 H, CH$_2$), δ 1.37-1.28 (m, 10 H, CH$_2$), δ 0.90 (t, *J* = 6.0 Hz, 6 H, CH$_3$); ^{13}C (150 MHz, CDCl$_3$): 173.9, 64.1, 34.4, 30.8, 29.0, 28.95, 25.0, 19.2 and 13.8.

[21] Di-methylsebasate



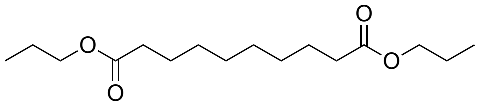
^{1}H NMR (600 MHz, CDCl$_3$): δ 3.62 (s, 6 H, CH$_3$), δ 2.25 (t, *J* = 6.0 Hz, 4 H, CH$_2$), δ 1.61 – 1.52 (m, 4 H, CH$_2$), δ 1.28 (br.s, 8 H, CH$_2$); ^{13}C (150 MHz, CDCl$_3$): 174.3, 51.5, 34.1, 29.1(2) and 24.9.

[22] Di-ethylsebasate



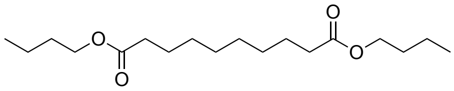
^{1}H NMR (600 MHz, $CDCl_3$): δ 4.06 (q, *J* = 6.0 Hz, 4 H, CH_2), δ 2.22 (t, *J* = 7.4 Hz, 4 H, CH_2), δ 1.59 – 1.51 (m, 4 H, CH_2), δ 1.24 (br.s, 8 H, CH_2), δ 1.19 (t, *J* = 7.1 Hz, 6 H, CH_3); ^{13}C (150 MHz, $CDCl_3$): 173.8, 60.1, 34.3, 29.1, 29.0, 24.9 and 14.2.

[23] Di-propylsebasate

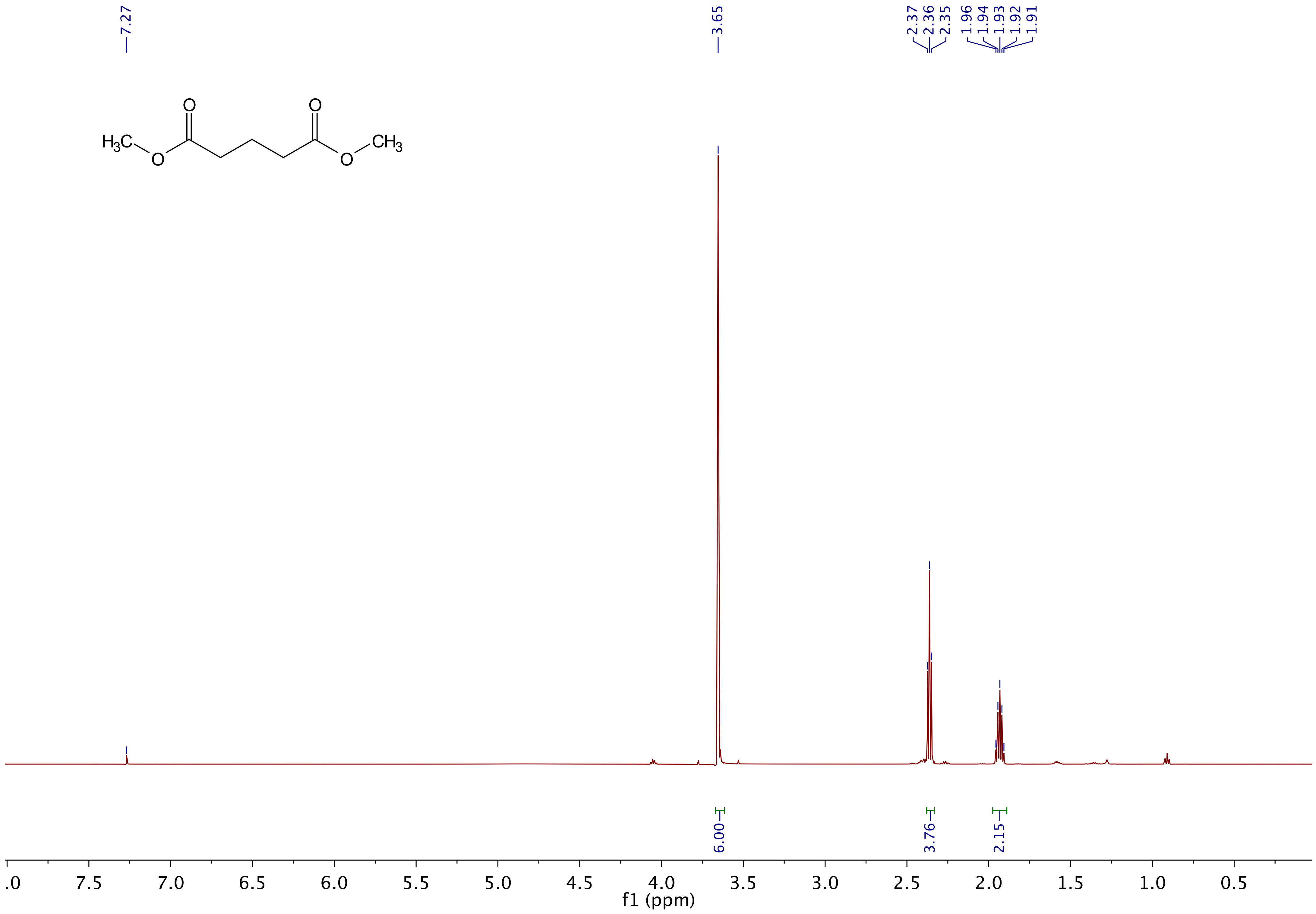


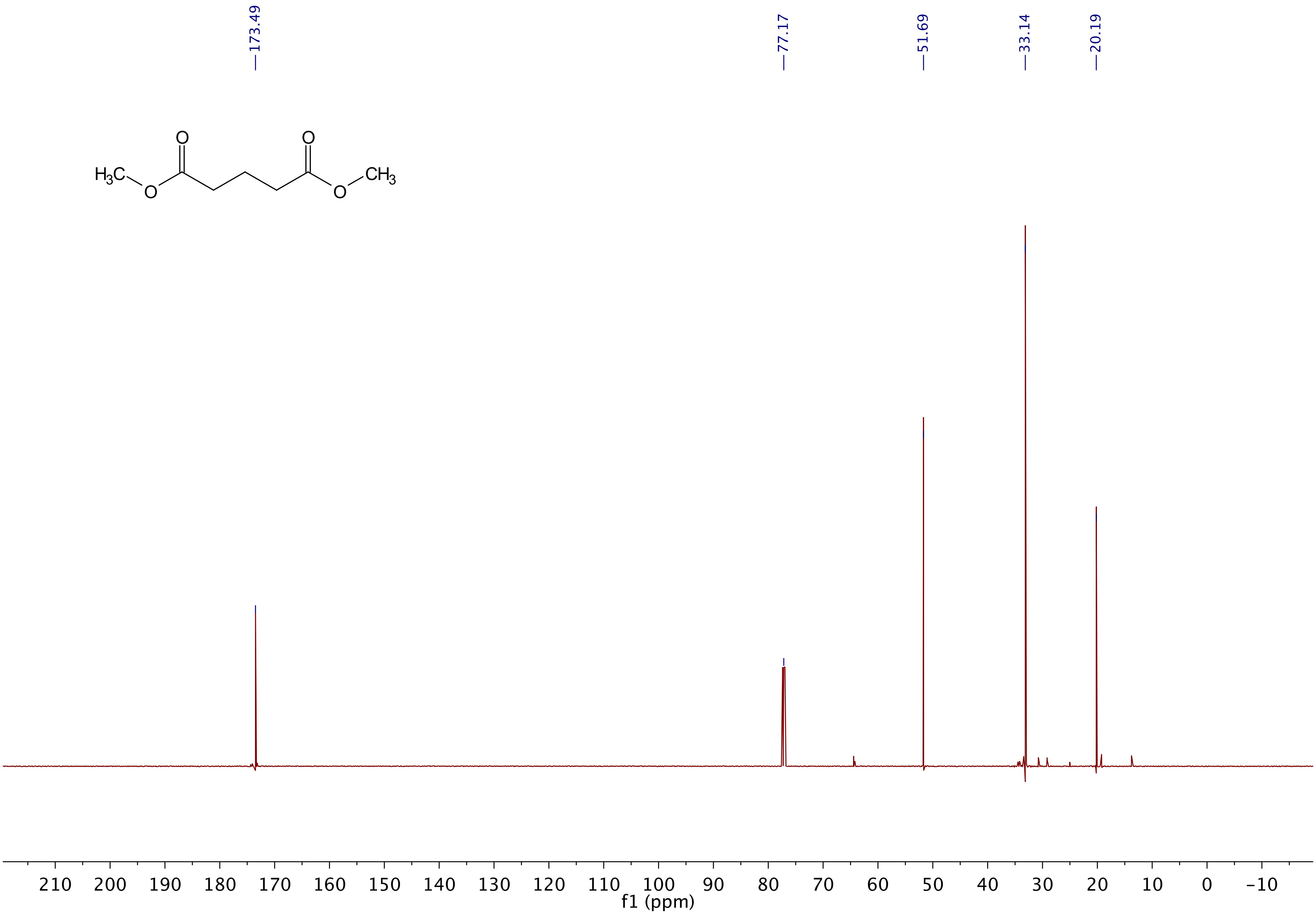
^{1}H NMR (600 MHz, $CDCl_3$): δ 3.93-3.89 (m, 4 H, CH_2), δ 2.22-2.12 (m, 4 H, CH_2), δ 1.57 - 1.45 (m, 8 H, CH_2), δ 1.20 (br.s, 8 H, CH_2), δ 0.86 - 0.78 (m, 6 H, CH_3); ^{13}C (150 MHz, $CDCl_3$): 173.6, 34.2, 28.9, 24.8, 21.9 and 10.2.

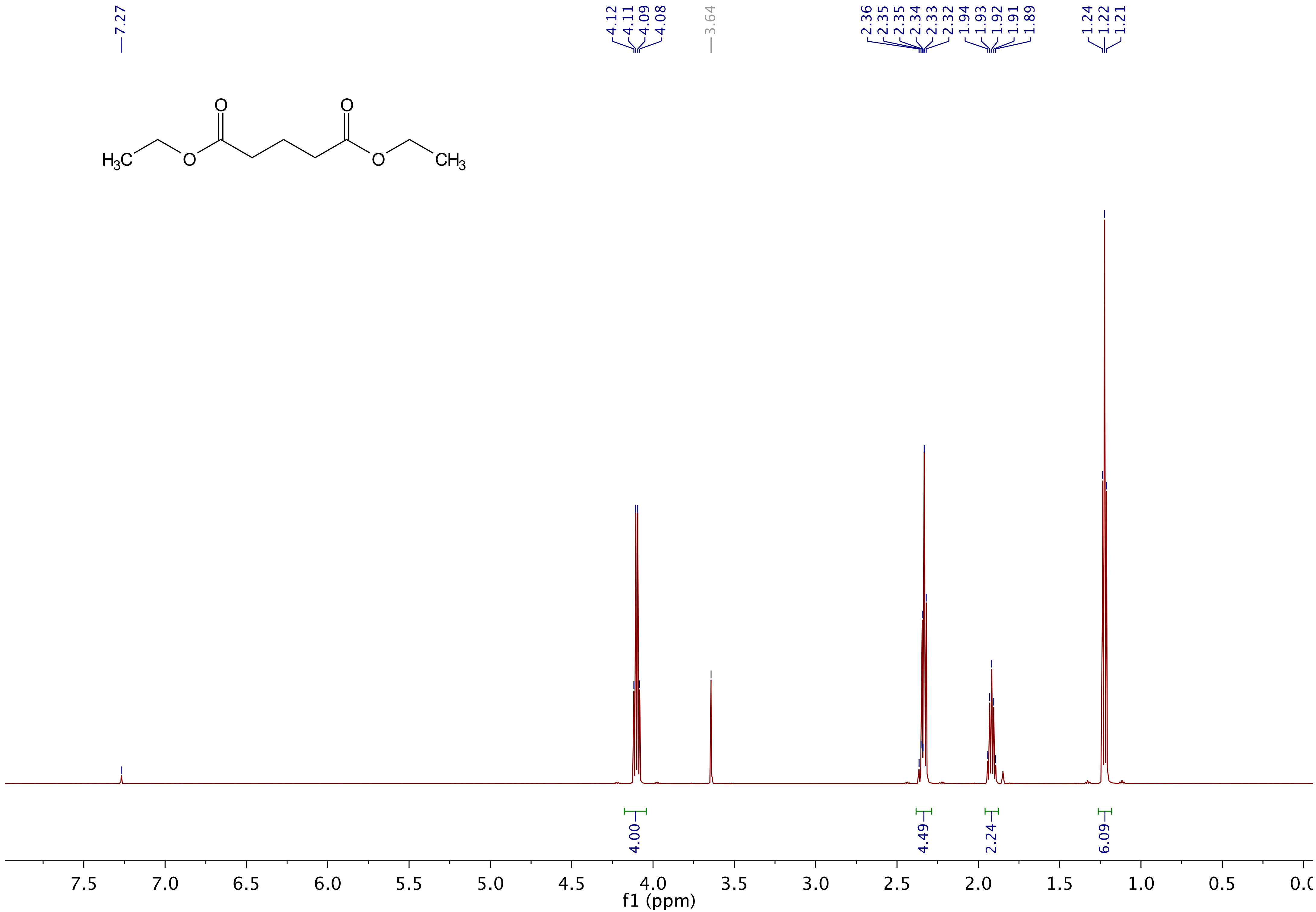
[24] Di-butylsebasate



^{1}H NMR (600 MHz, $CDCl_3$): δ 4.06 - 4.03 (m, 4 H, CH_2), δ 2.28 - 2.25 (m, 4 H, CH_2), δ 1.64 - 1.56 (m, 8 H, CH_2), δ 1.40 - 1.33 (m, 12 H, CH_2), δ 1.28 (br.s, 8 H, CH_2), δ 0.91 - 0.88 (m, 6 H, CH_3), ^{13}C (150 MHz, $CDCl_3$): 174.0, 64.1, 34.4, 30.8, 29.2, 25.1, 19.3 and 13.8.


7.27
3.65
2.37
2.36
2.35
1.96
1.94
1.93
1.92
1.91
O
O
H_3C
O
O
CH_3
6.00
3.76
2.15
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


173.49
77.17
51.69
33.14
20.19
H3C
O
O
O
O
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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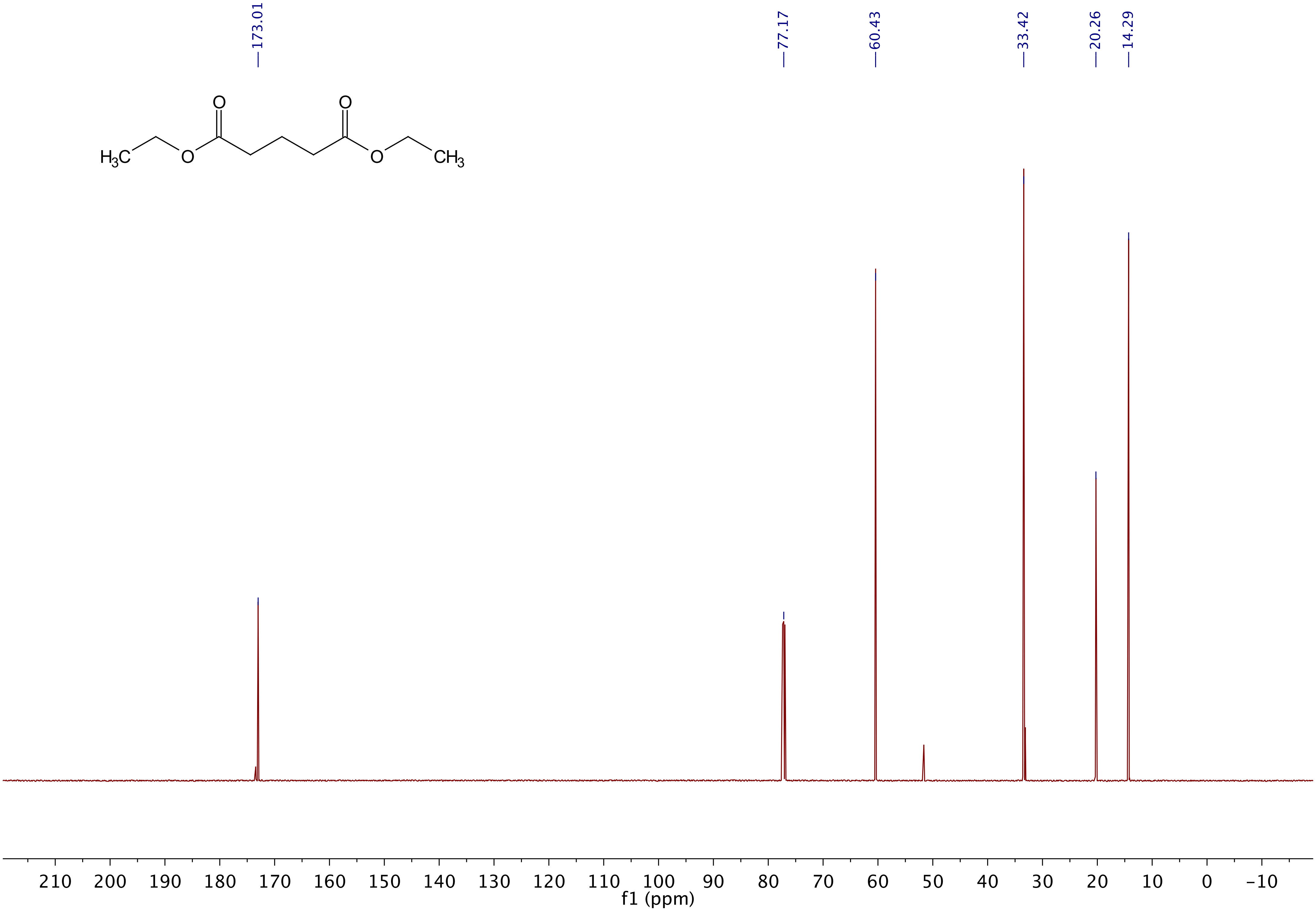
4.11
4.09
4.08
3.64
2.36
2.35
2.35
2.34
2.33
2.32
1.94
1.93
1.92
1.91
1.89
1.24
1.22
1.21
O
O
H3C
O
O
CH3
4.00
4.49
2.24
6.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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77.17
60.43
33.42
20.26
14.29
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H3C
O
O
CH3
210
200
190
180
170
160
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100
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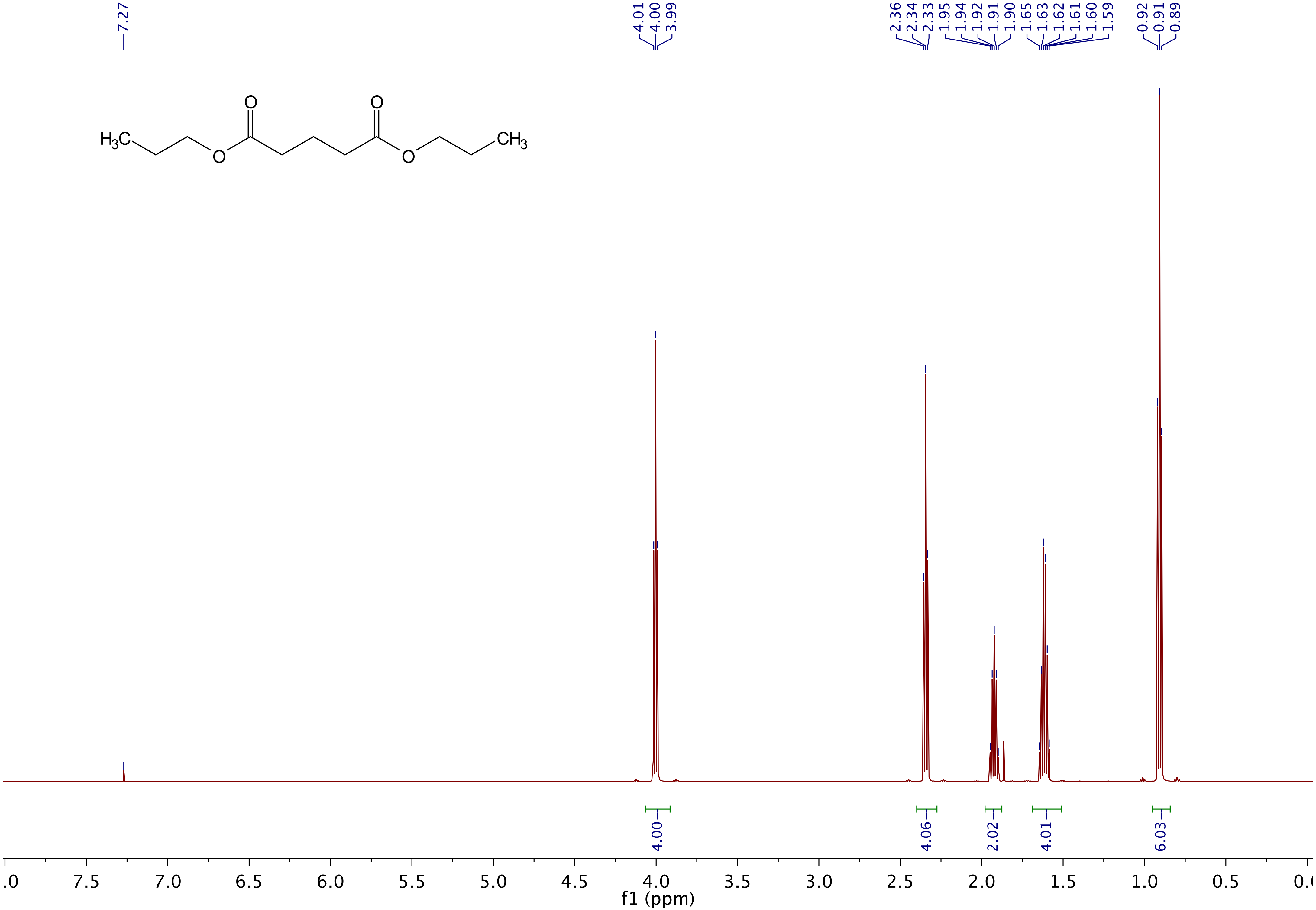
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)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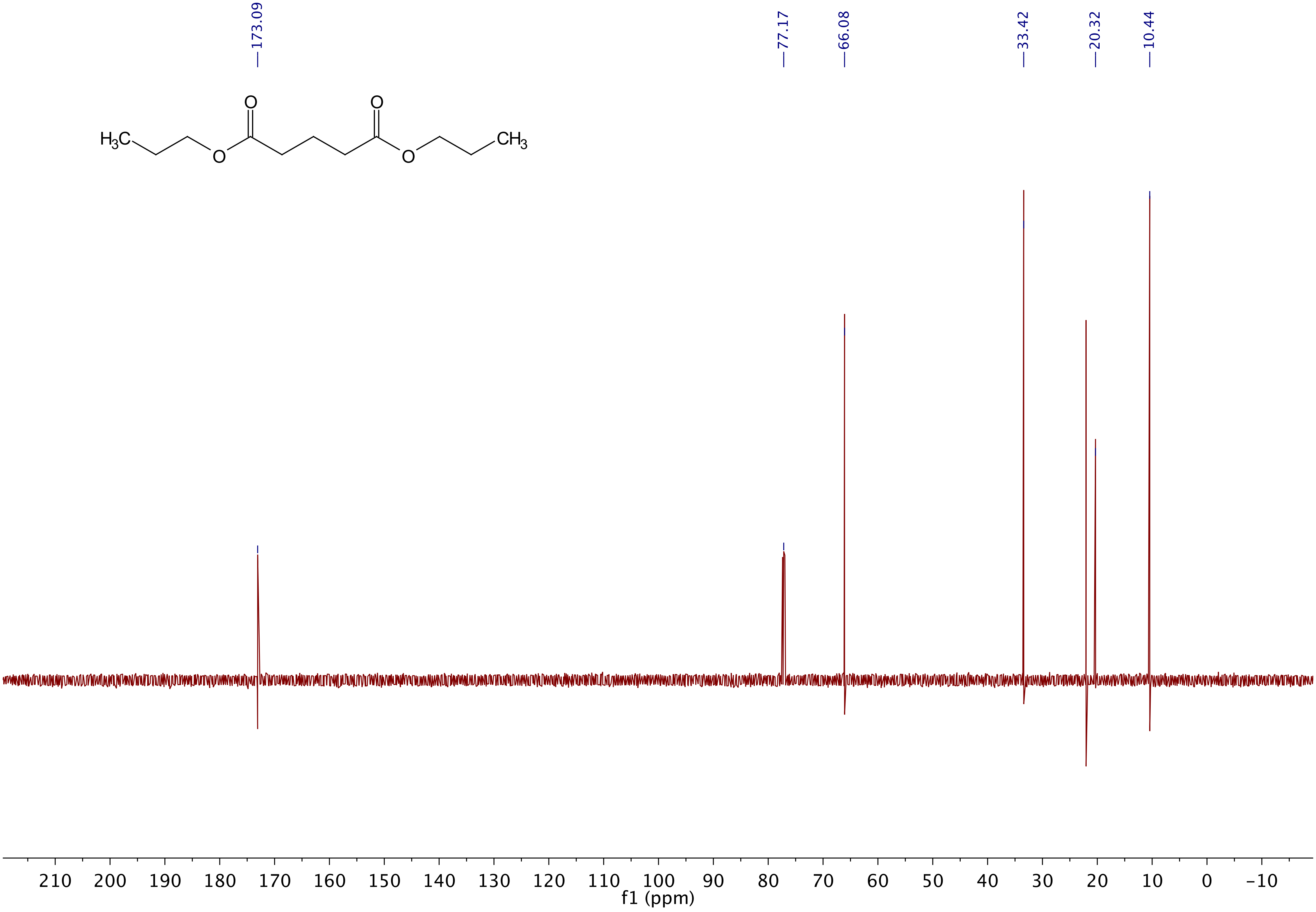
1.94
1.92
1.91
1.90
1.65
1.63
1.62
1.61
1.60
1.59
0.92
0.91
0.89
H3C
O
O
O
O
CH3
4.00
4.06
2.02
4.01
6.03
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.(
f1 (ppm)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10.44
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O
CH3
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200
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180
170
160
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140
130
120
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100
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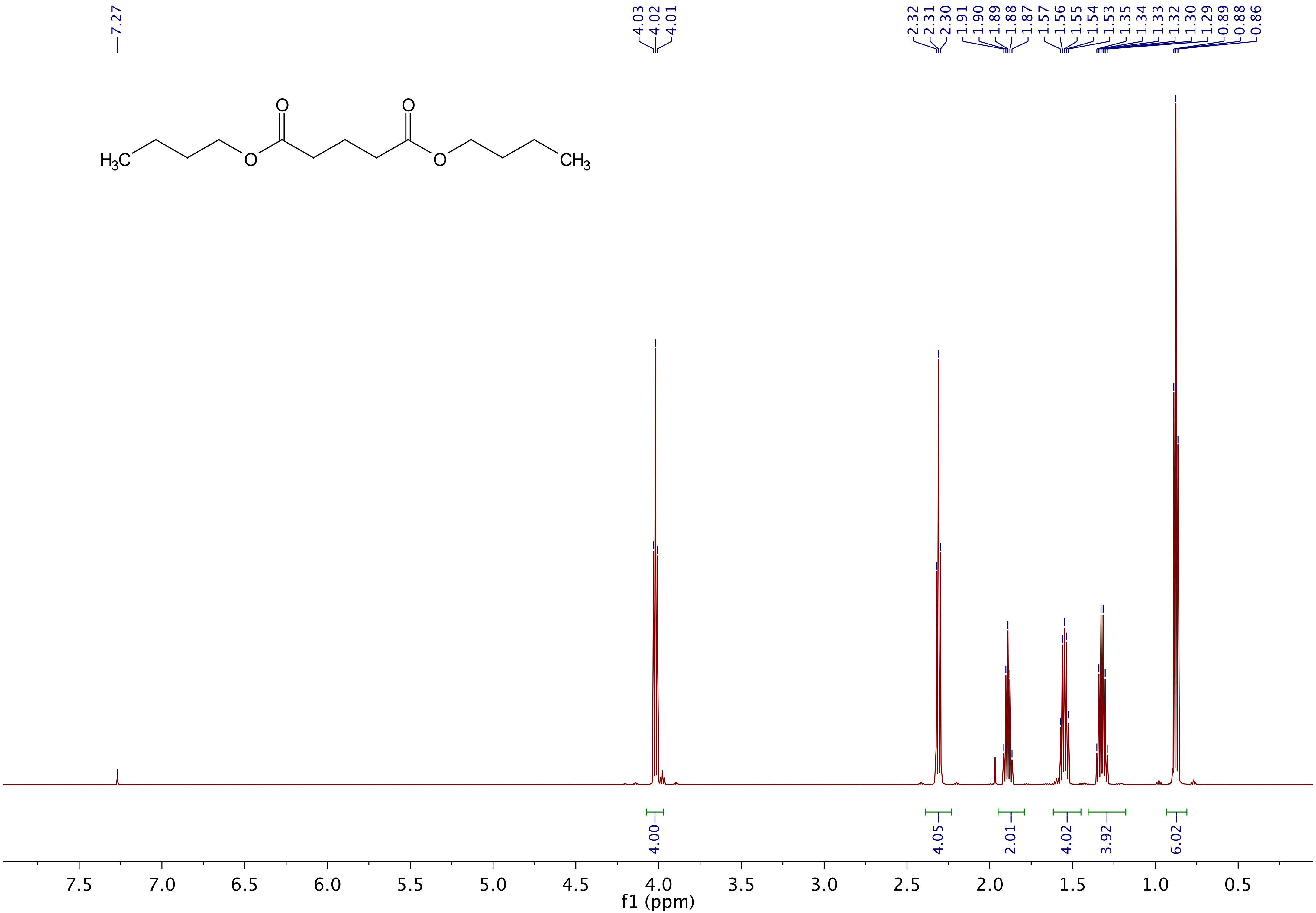
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)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4.01
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1.91
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1.89
1.88
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1.57
1.56
1.55
1.54
1.53
1.35
1.34
1.33
1.32
1.30
1.29
0.89
0.88
0.86
O
O
H_3C
O
O
CH_3
4.00
4.05
2.01
4.02
3.92
6.02
7.5
7.0
6.5
6.0
5.5
5.0
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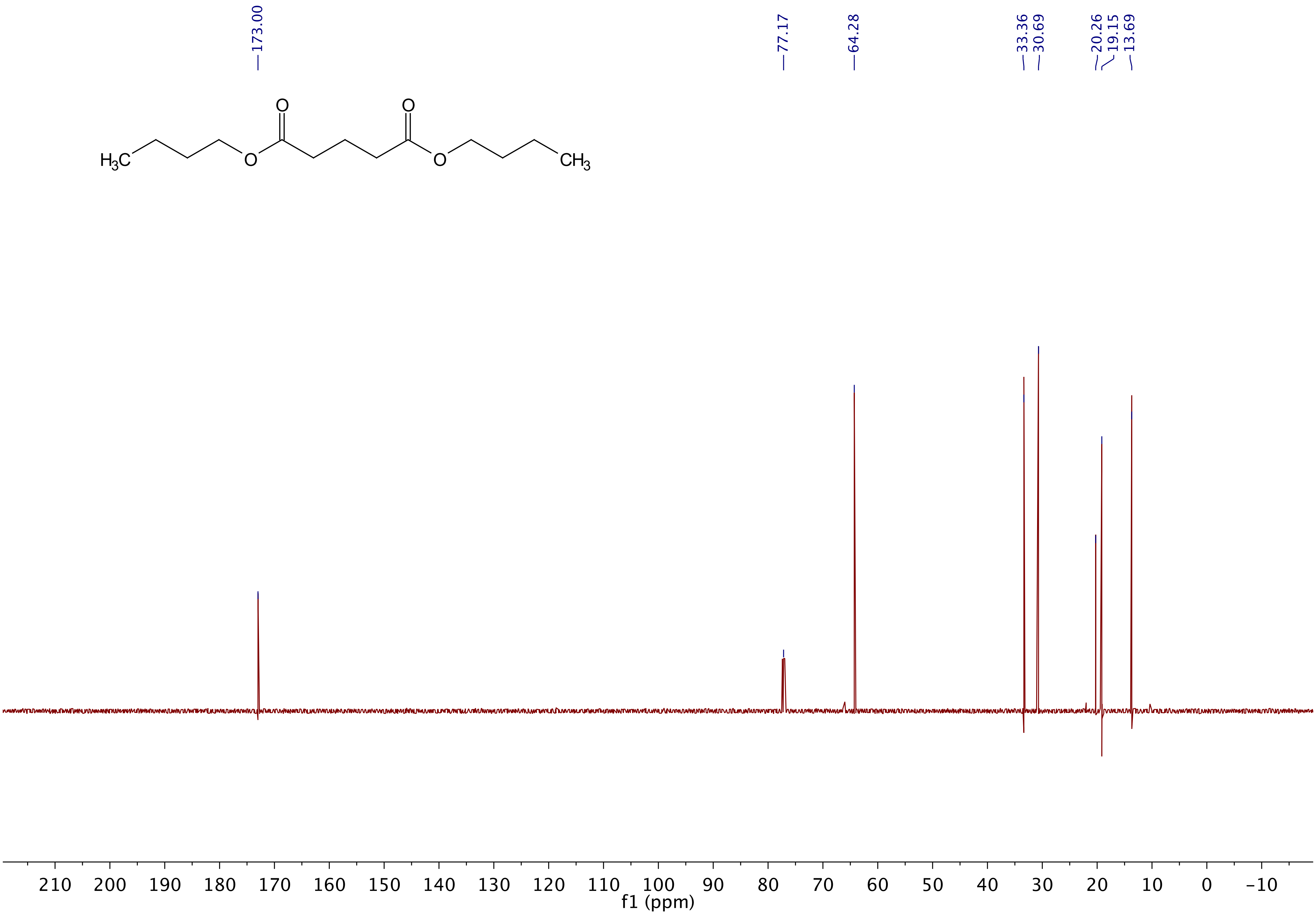
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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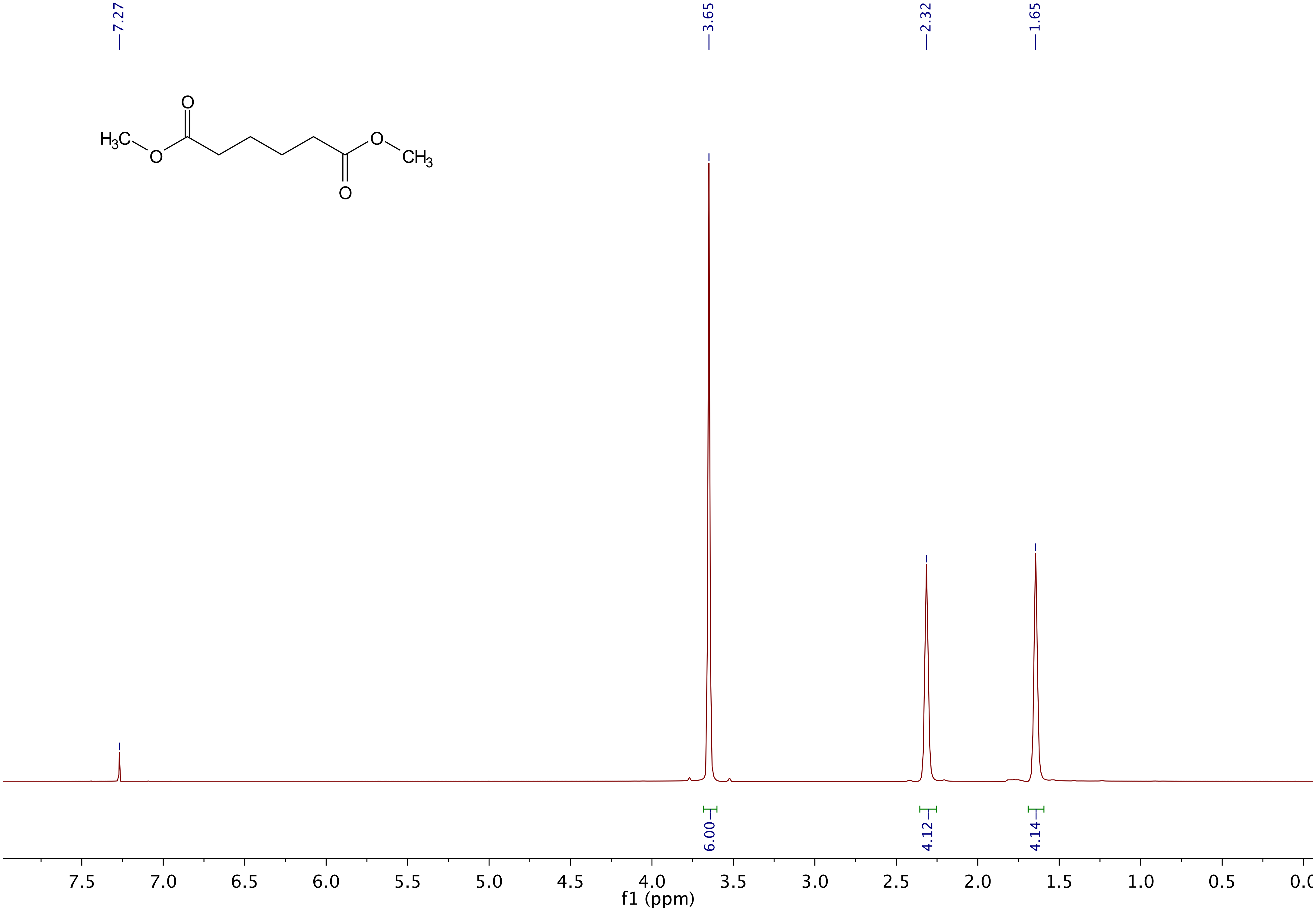
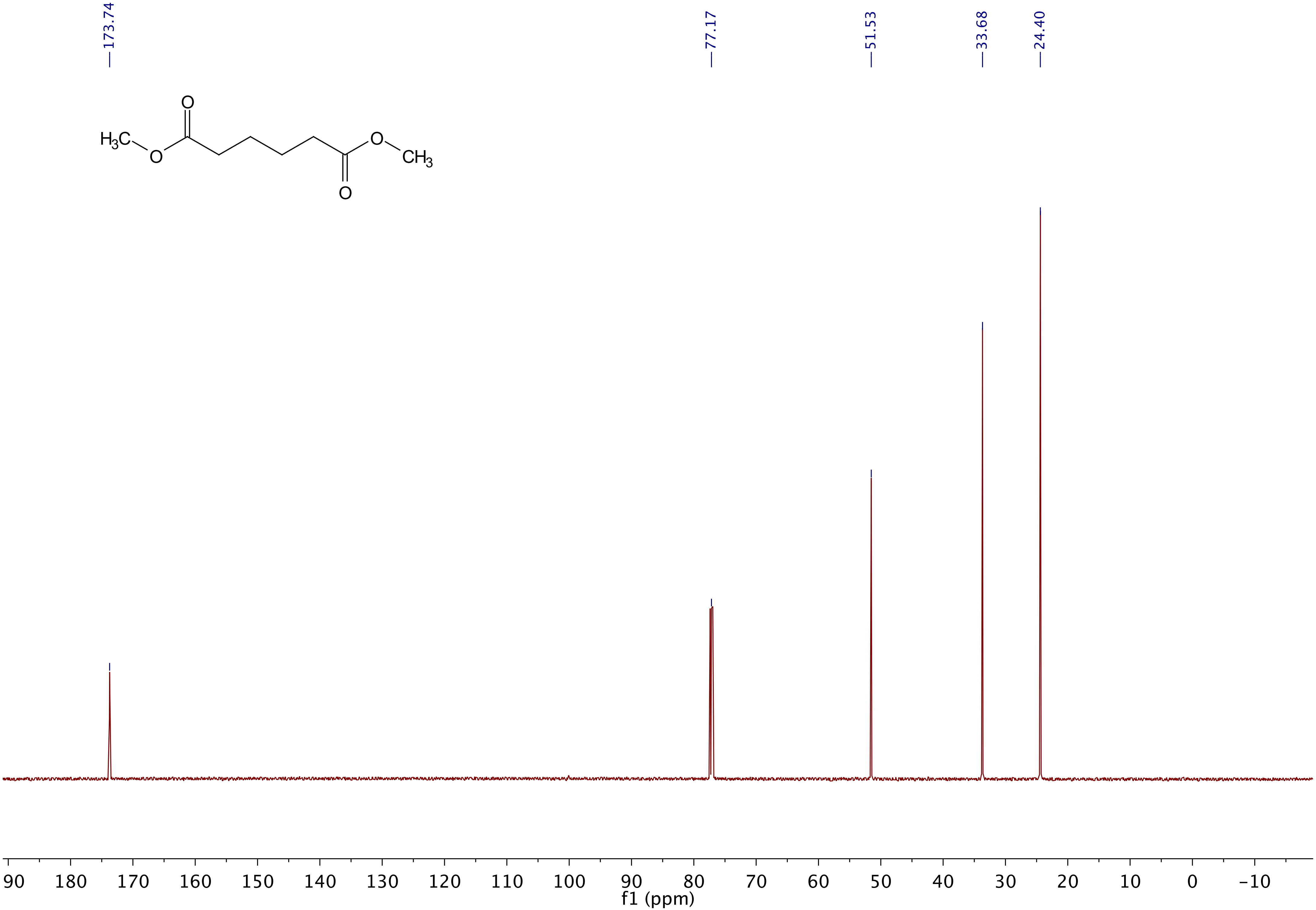
77.17
64.28
33.36
30.69
20.26
19.15
13.69
O
O
H_3C
O
O
CH_3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)



7.27
3.65
2.32
1.65
6.00
4.12
4.14
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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77.17
51.53
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24.40
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H3C
O
O
CH3
O
90
180
170
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140
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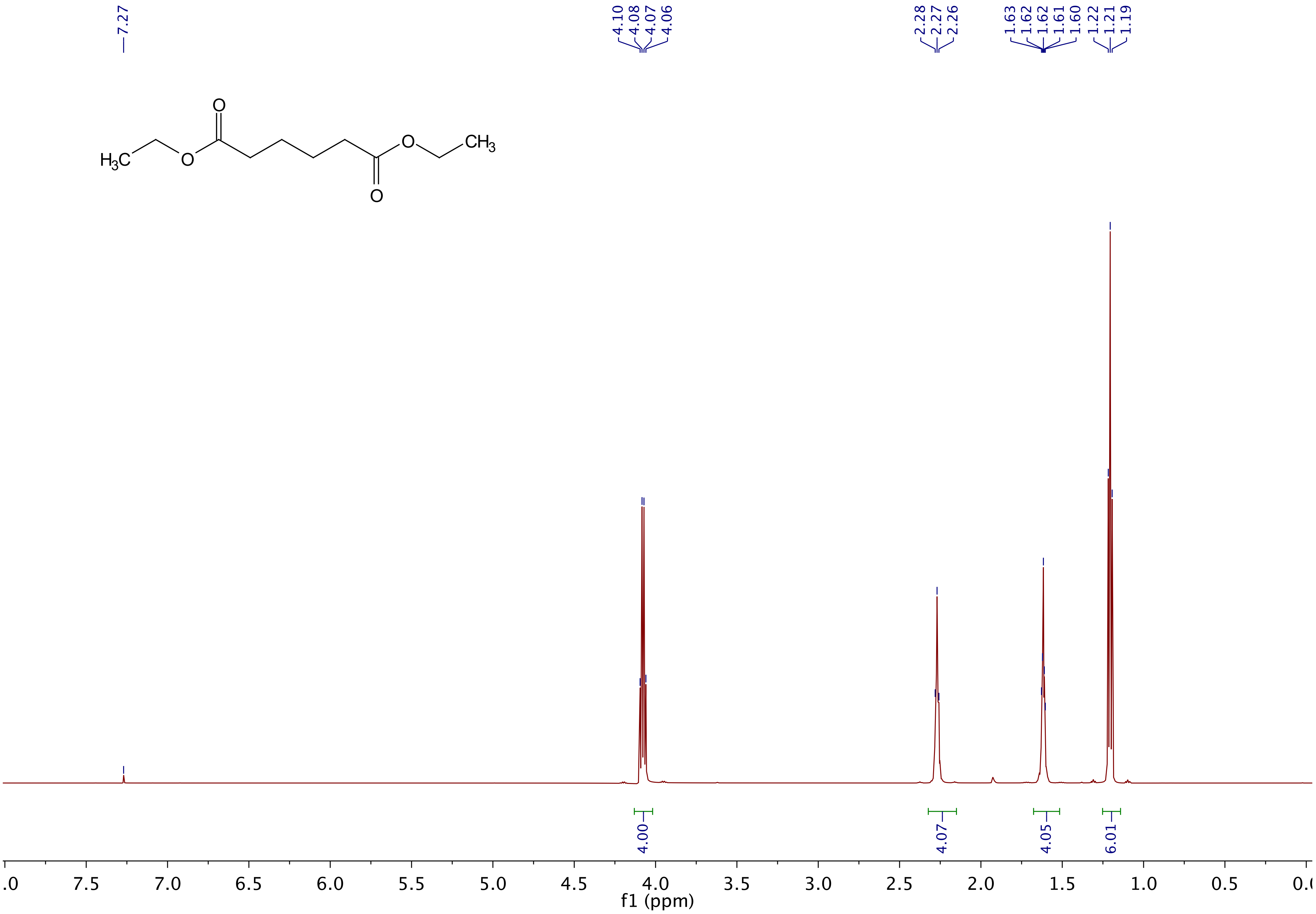
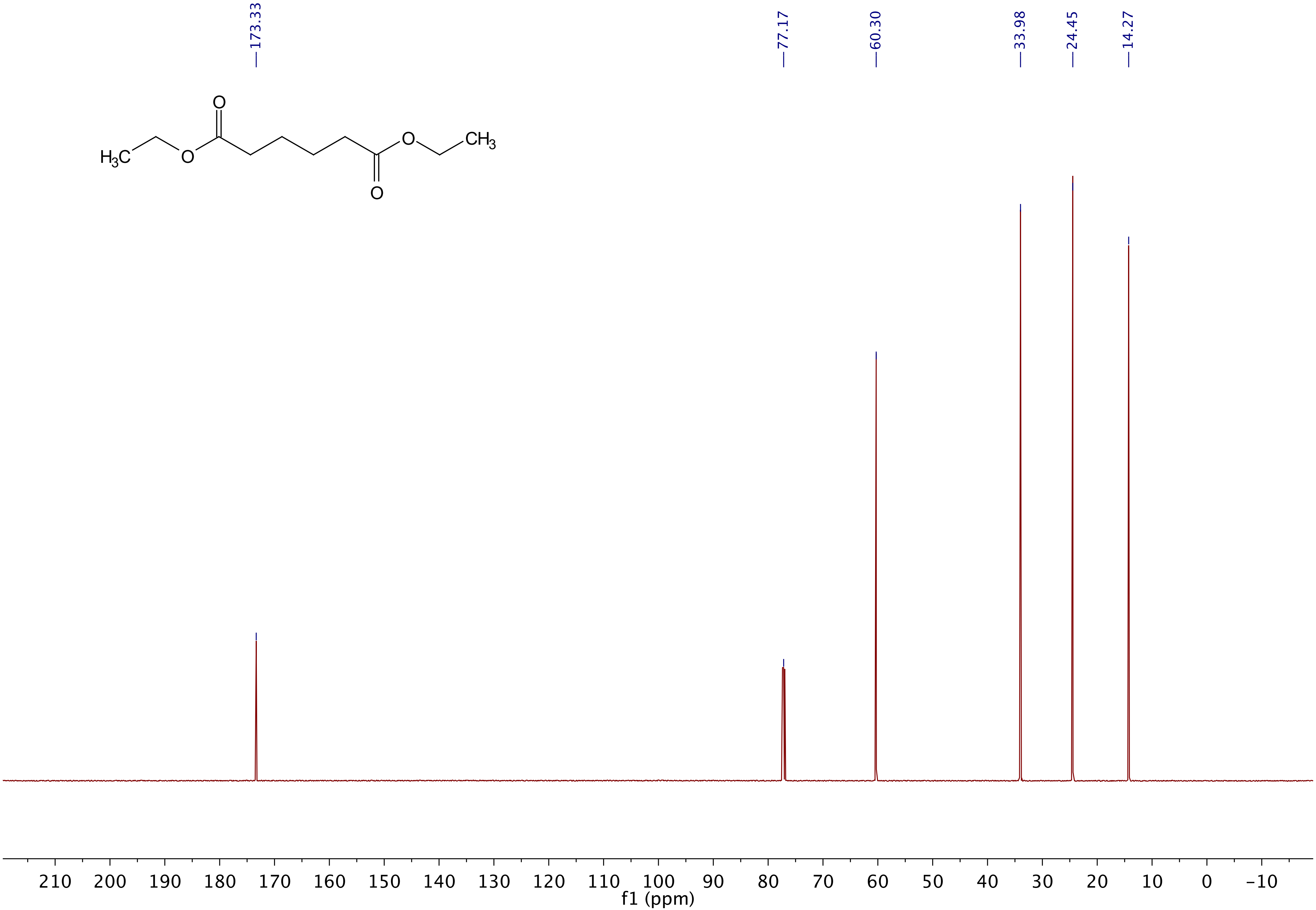
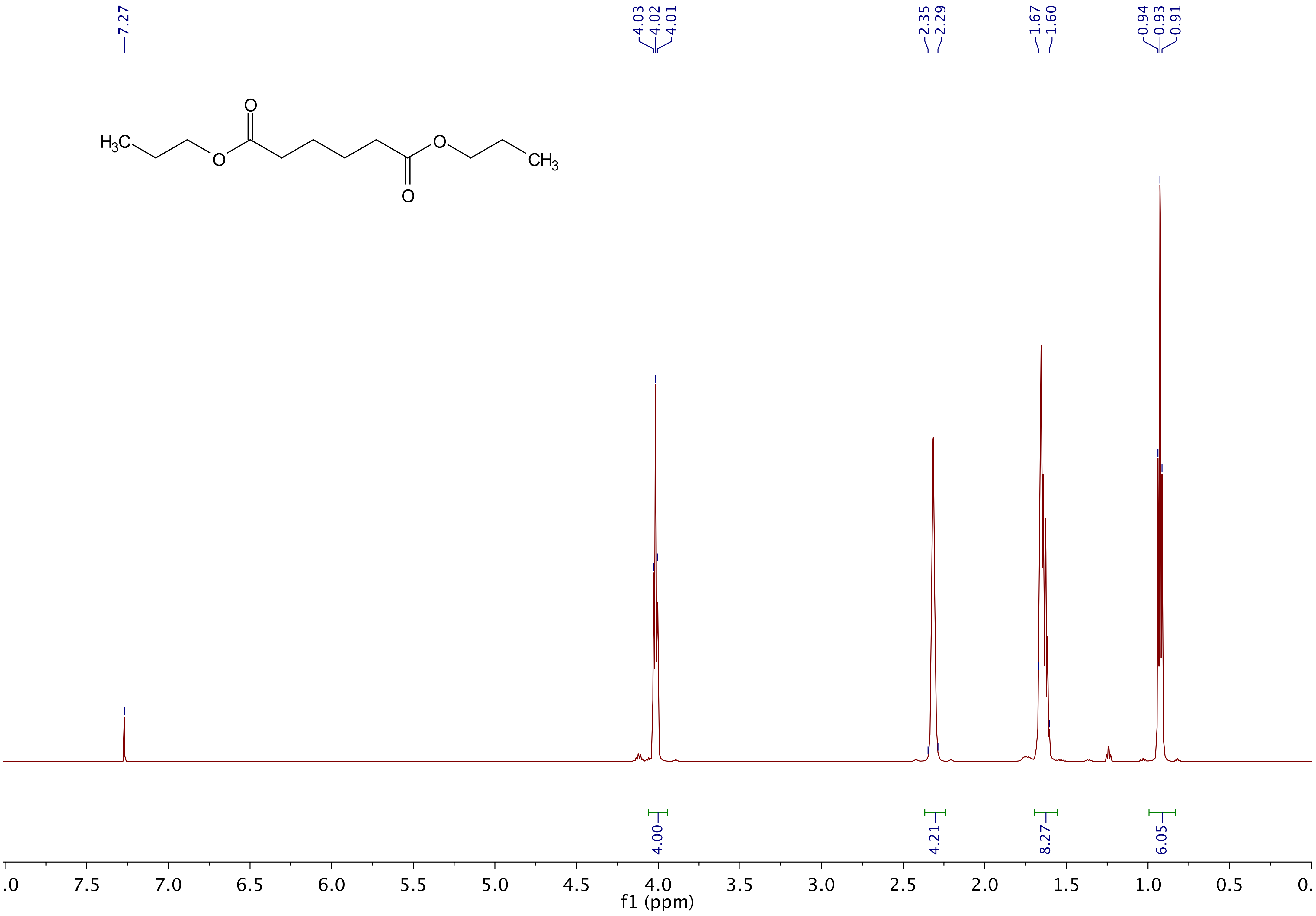
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.27
4.10
4.08
4.07
4.06
2.28
2.27
2.26
1.63
1.62
1.62
1.61
1.60
1.22
1.21
1.19
O
H3C
O
O
CH3
O
4.00
4.07
4.05
6.01
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


173.33
77.17
60.30
33.98
24.45
14.27
O
O
O
O
H_3C
CH_3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)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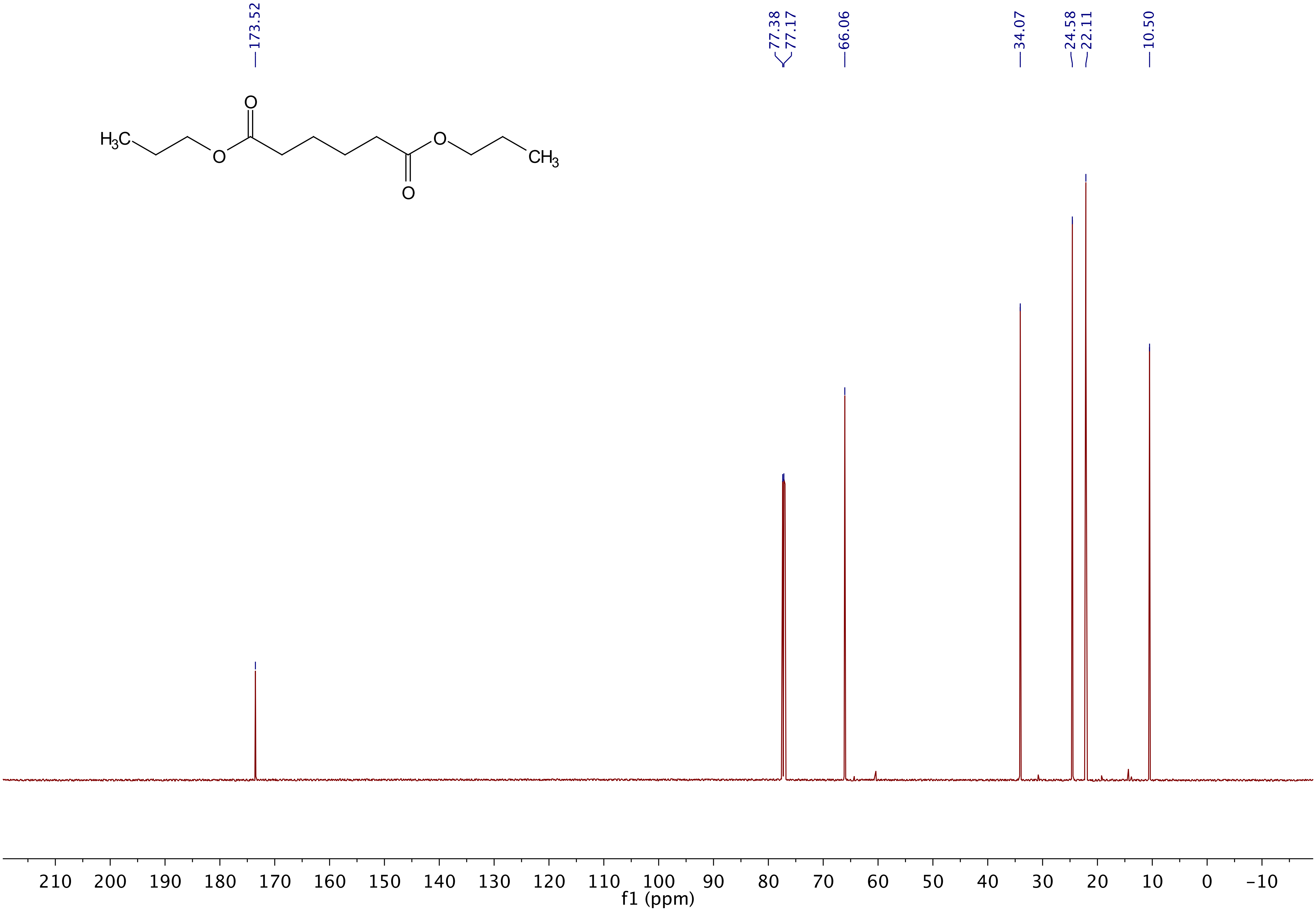
4.03
4.02
4.01
2.35
2.29
1.67
1.60
0.94
0.93
0.91
H3C
O
O
O
O
CH3
4.00
4.21
8.27
6.05
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)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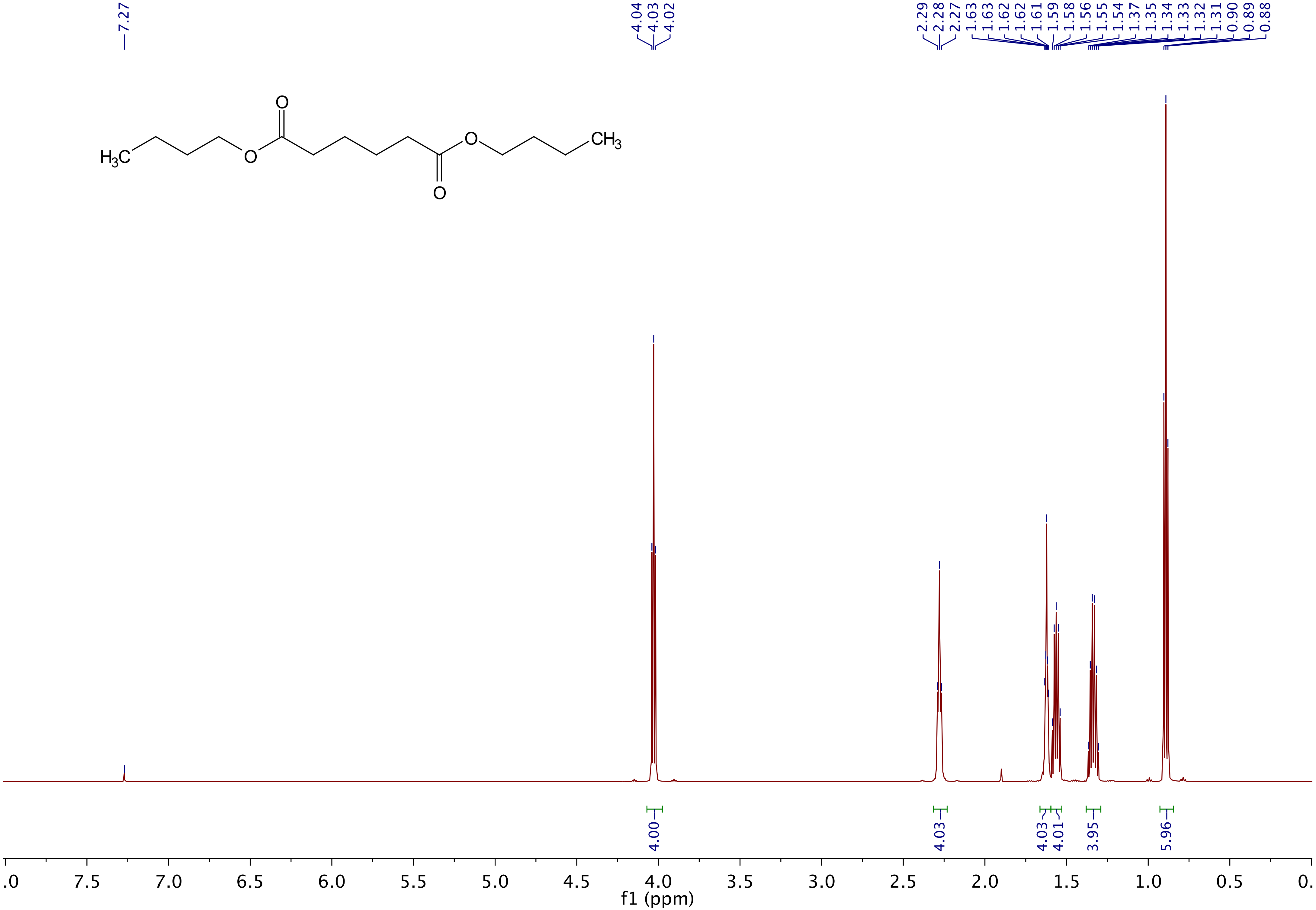
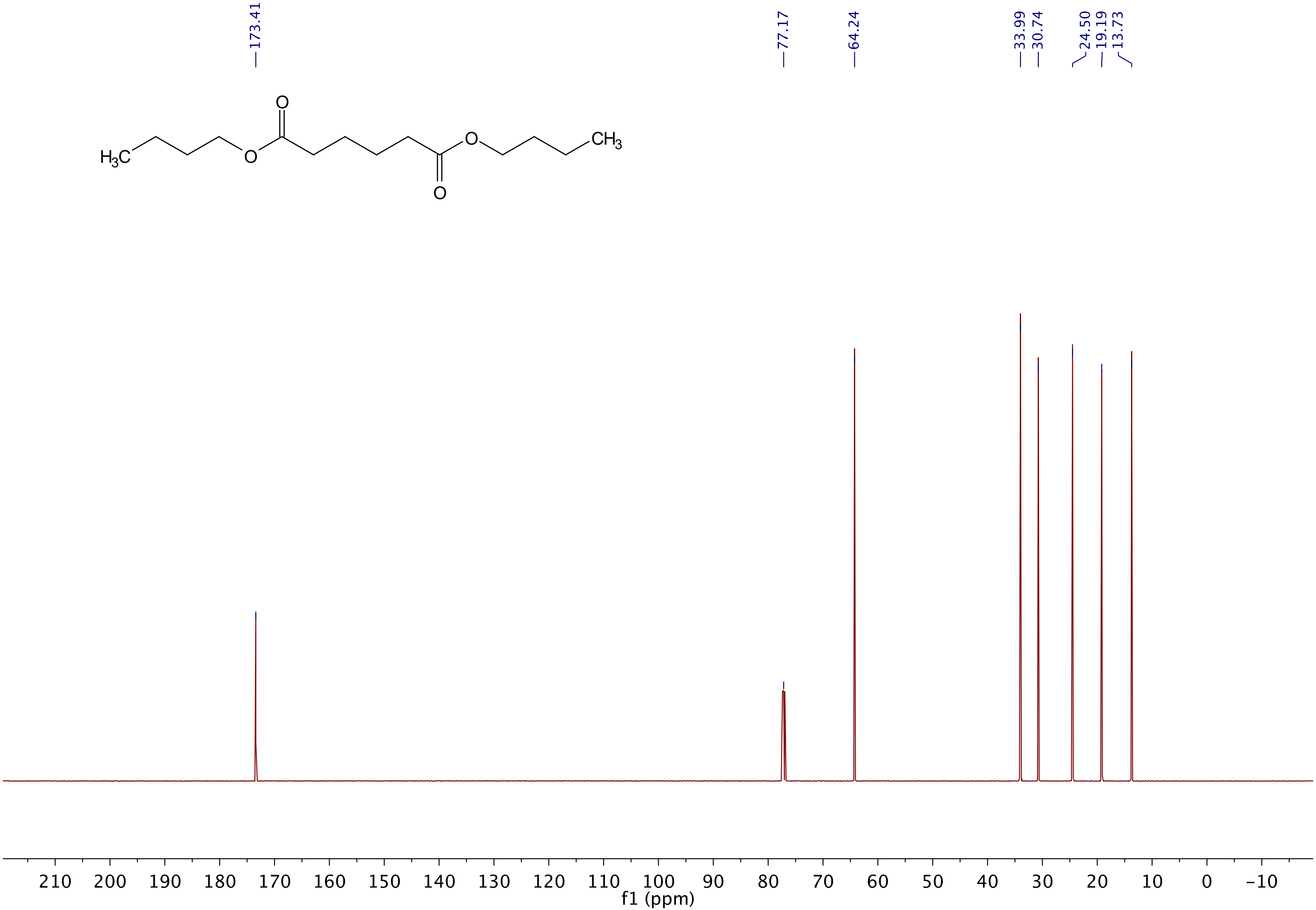
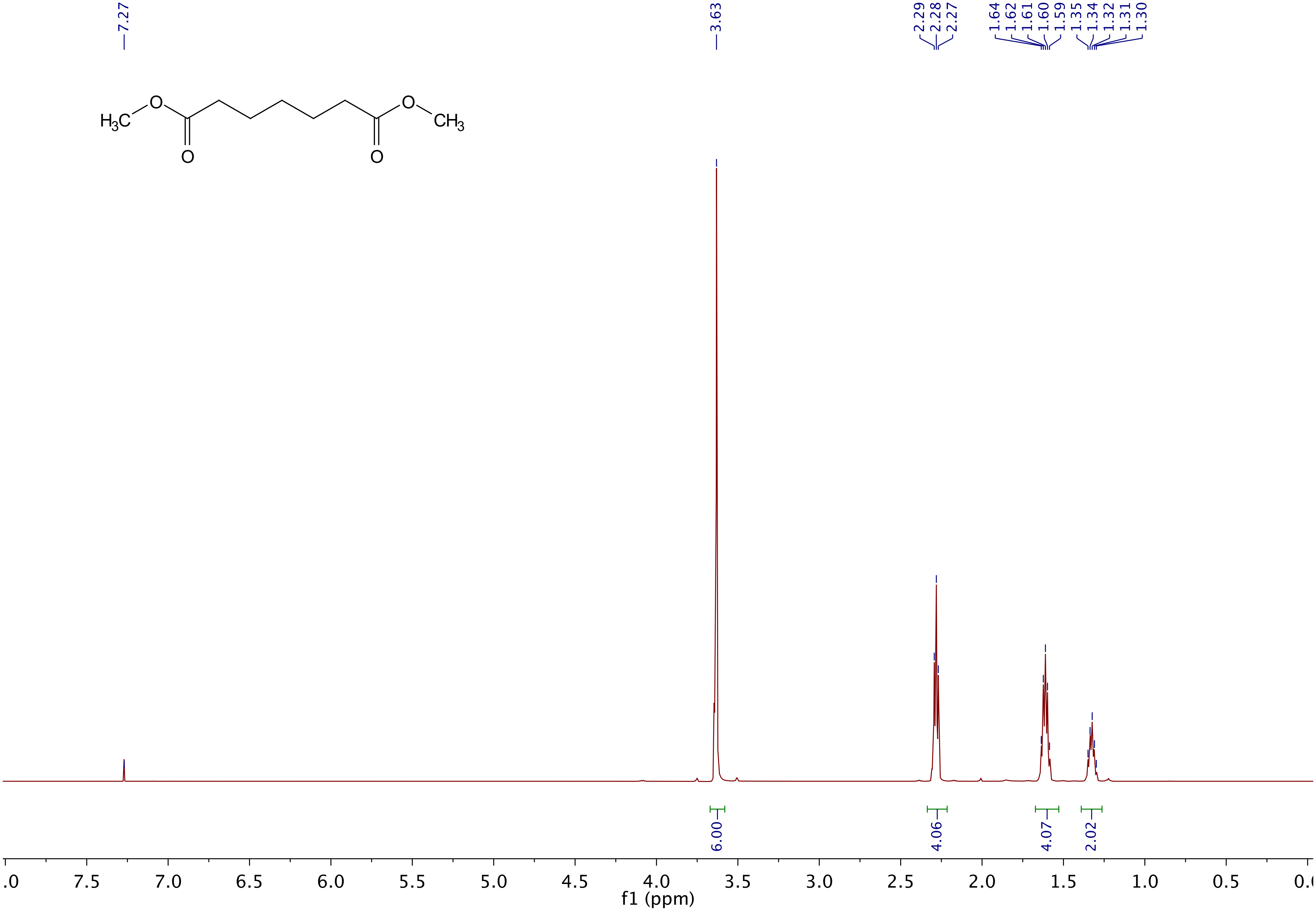
77.38
77.17
66.06
34.07
24.58
22.11
10.50
O
H3C
O
O
CH3
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)


7.27
4.04
4.03
4.02
2.29
2.28
2.27
1.63
1.63
1.62
1.62
1.61
1.59
1.58
1.56
1.55
1.54
1.37
1.35
1.34
1.33
1.32
1.31
0.90
0.89
0.88
O
H$_3$C
O
O
CH$_3$
O
4.00
4.03
4.03
4.01
3.95
5.96
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)



173.41
77.17
64.24
33.99
30.74
24.50
19.19
13.73
O
H_3C
O
O
O
CH_3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)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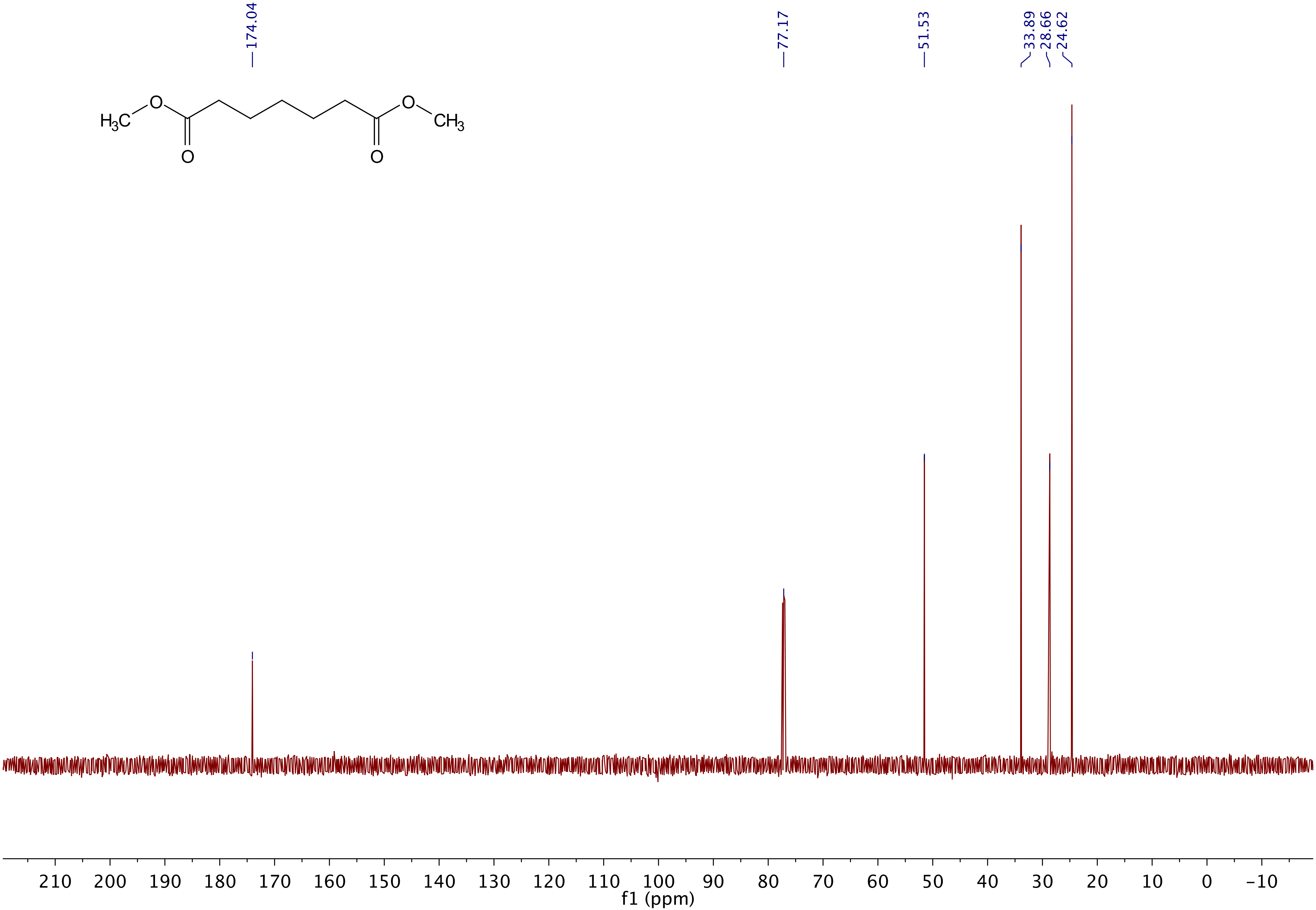
3.63
2.29
2.28
2.27
1.64
1.62
1.61
1.60
1.59
1.35
1.34
1.32
1.31
1.30
H3C
O
O
O
O
CH3
6.00
4.06
4.07
2.02
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.(
f1 (ppm)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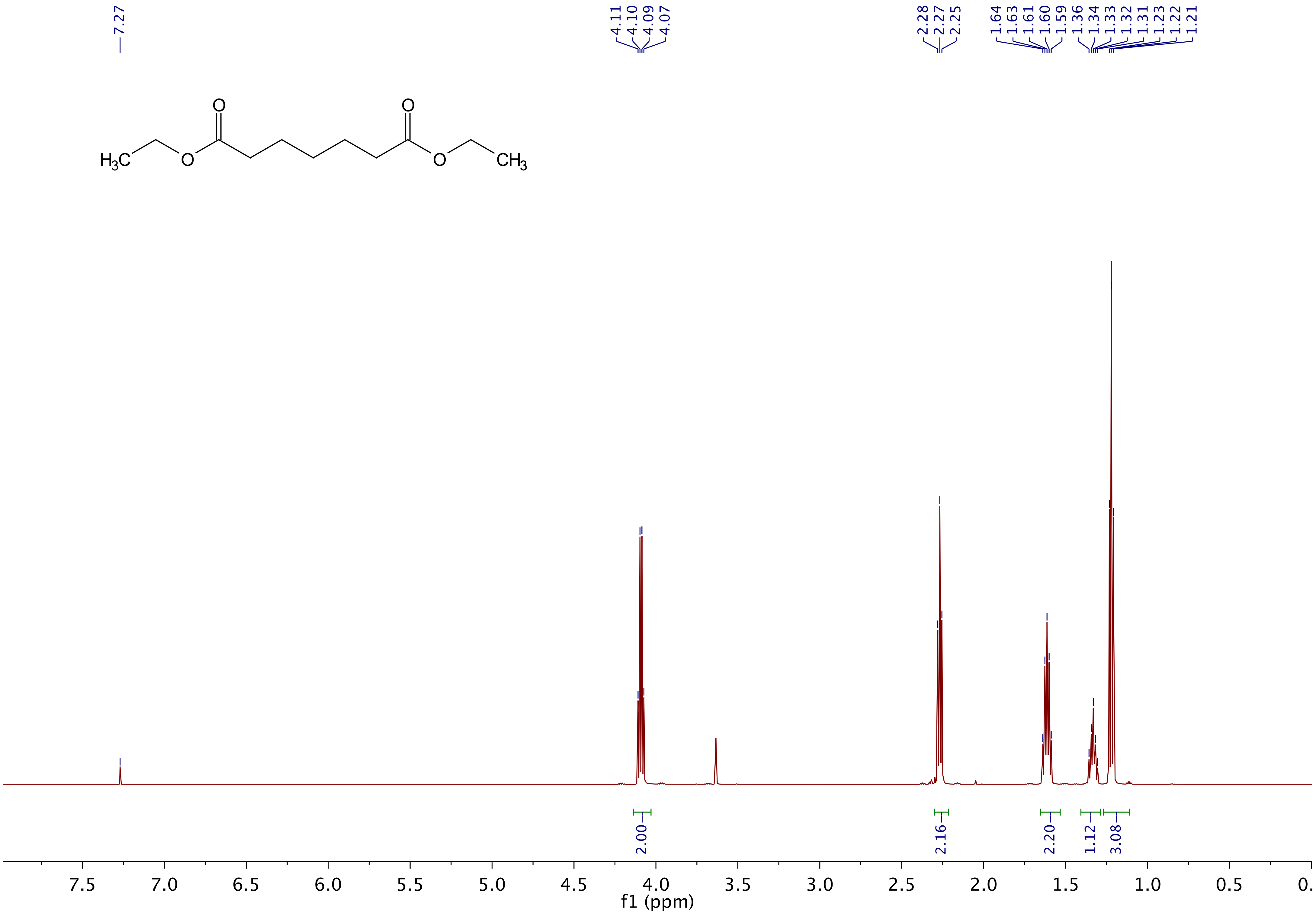
51.53
33.89
28.66
24.62
H3C
O
O
O
O
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)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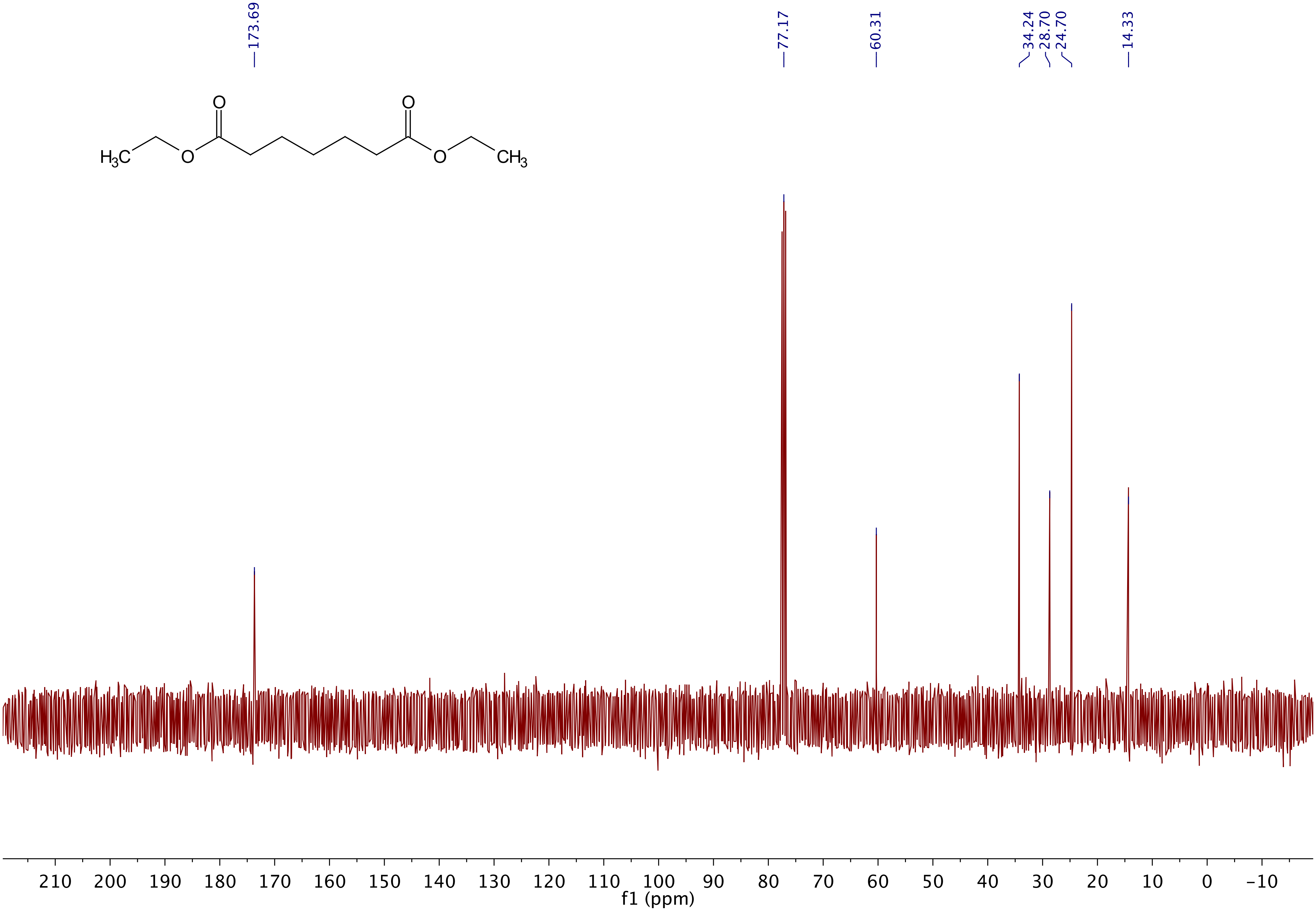
4.10
4.09
4.07
2.28
2.27
2.25
1.64
1.63
1.61
1.60
1.59
1.36
1.34
1.33
1.32
1.31
1.23
1.22
1.21
O
O
H_3C
O
O
CH_3
2.00
2.16
2.20
1.12
3.08
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)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77.17
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24.70
14.33
O
O
H_3C
O
O
CH_3
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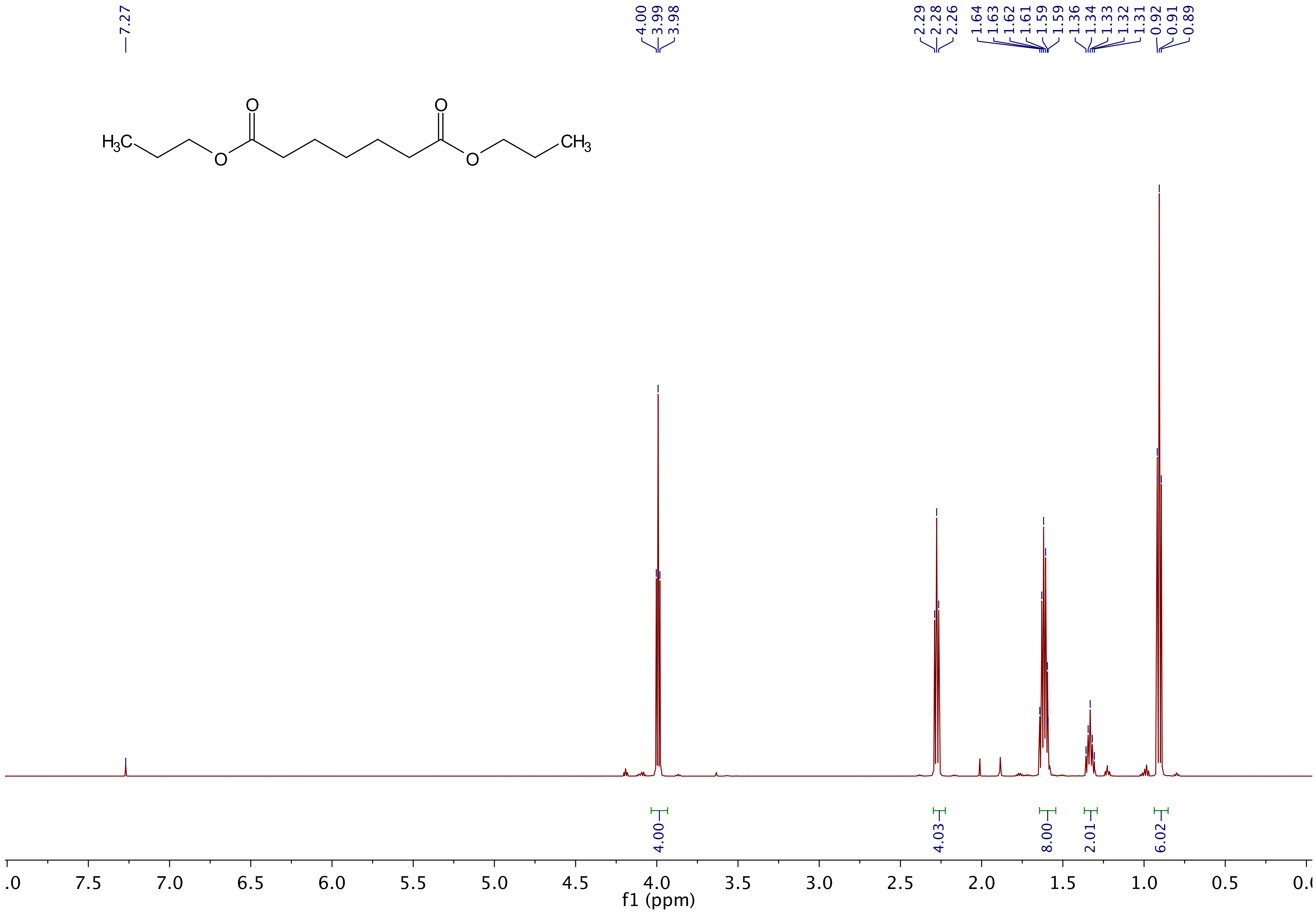
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)


7.27
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3.99
3.98
2.29
2.28
2.26
1.64
1.63
1.62
1.61
1.59
1.59
1.36
1.34
1.33
1.32
1.31
0.92
0.91
0.89
O
O
H3C
O
O
CH3
4.00
4.03
8.00
2.01
6.02
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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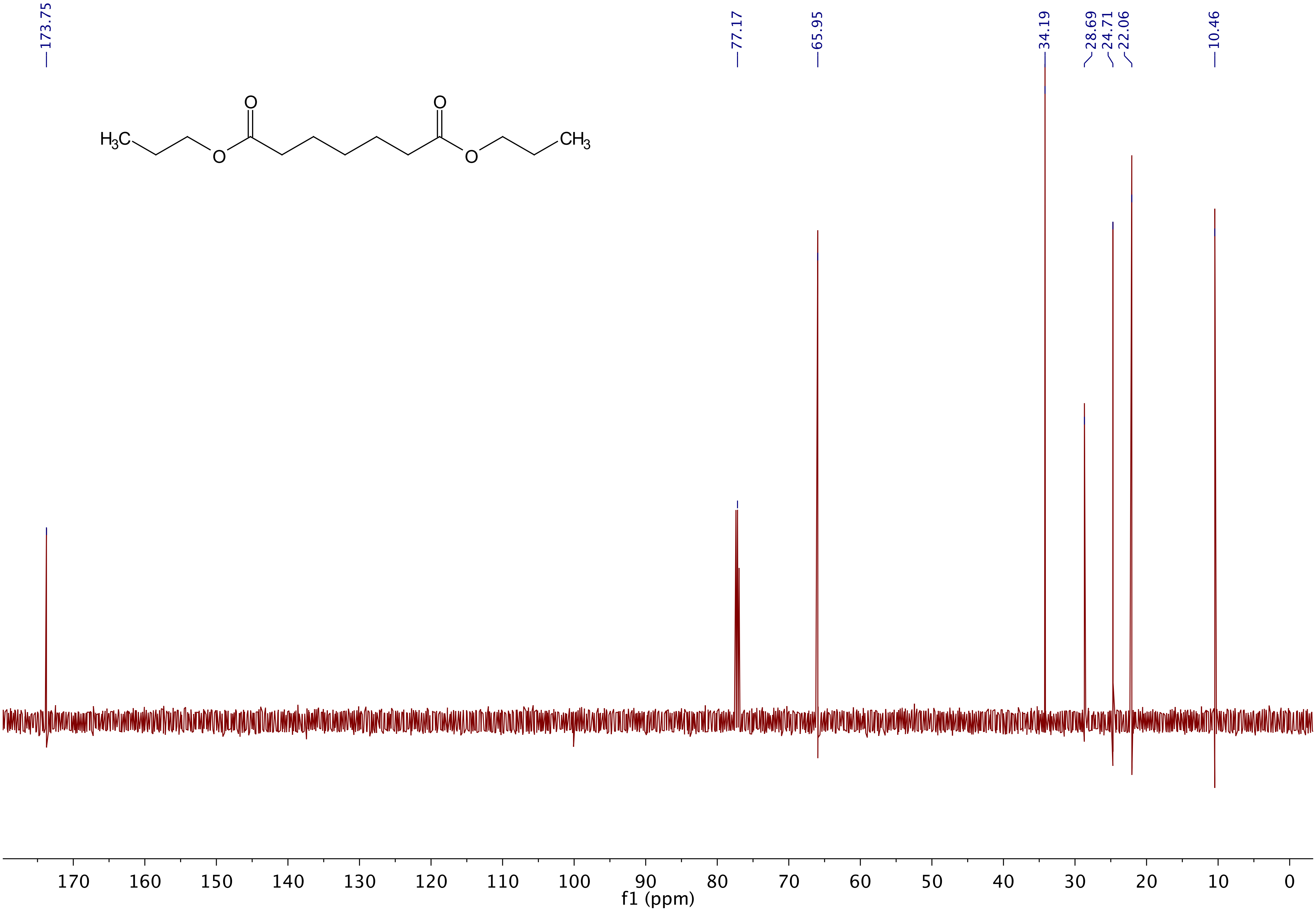
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)



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24.71
22.06
10.46
O
O
H3C
O
O
CH3
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130
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110
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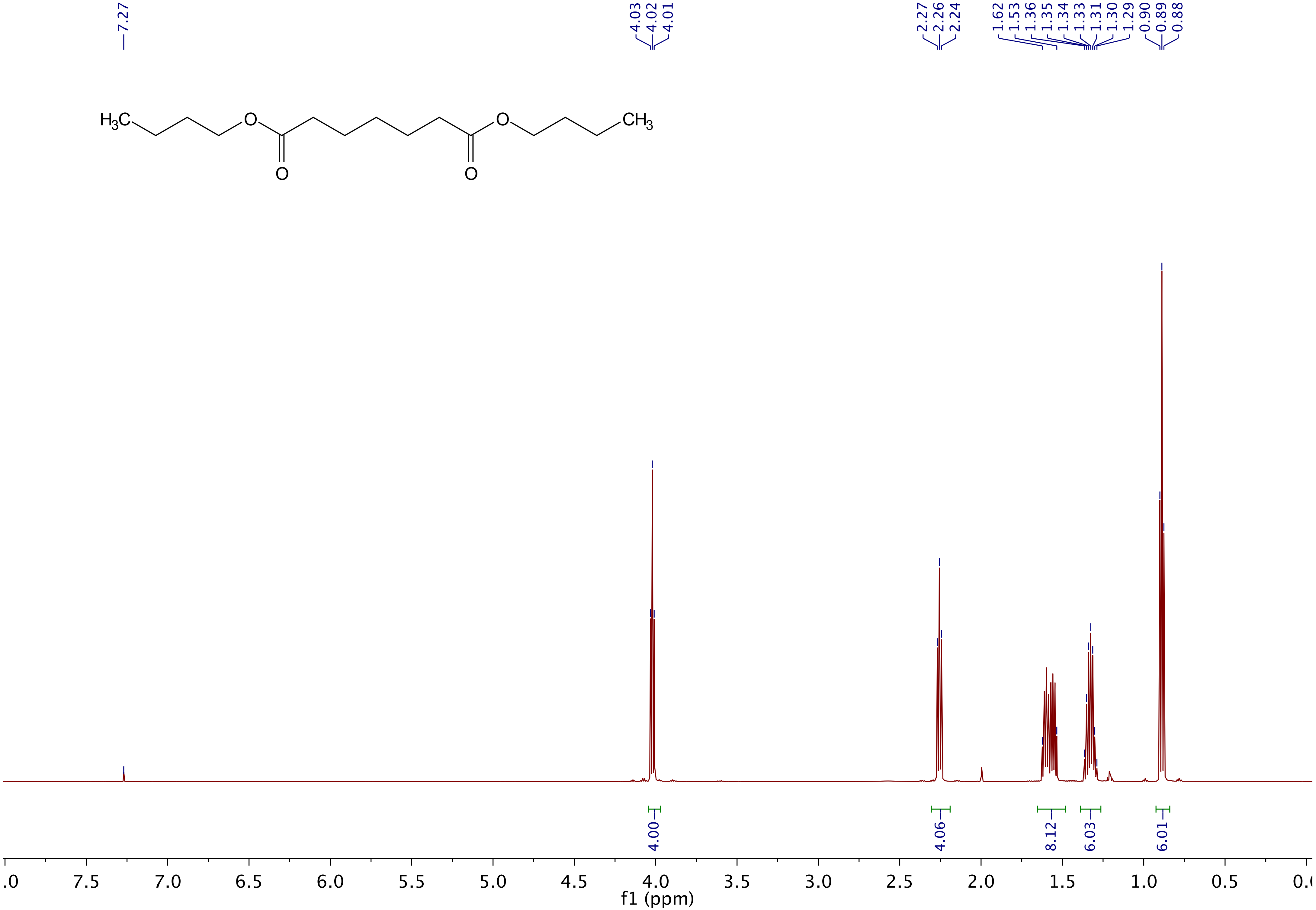
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.27
4.03
4.02
4.01
2.27
2.26
2.24
1.62
1.53
1.36
1.35
1.34
1.33
1.31
1.30
1.29
0.90
0.89
0.88
H3C
O
O
O
O
CH3
4.00
4.06
8.12
6.03
6.01
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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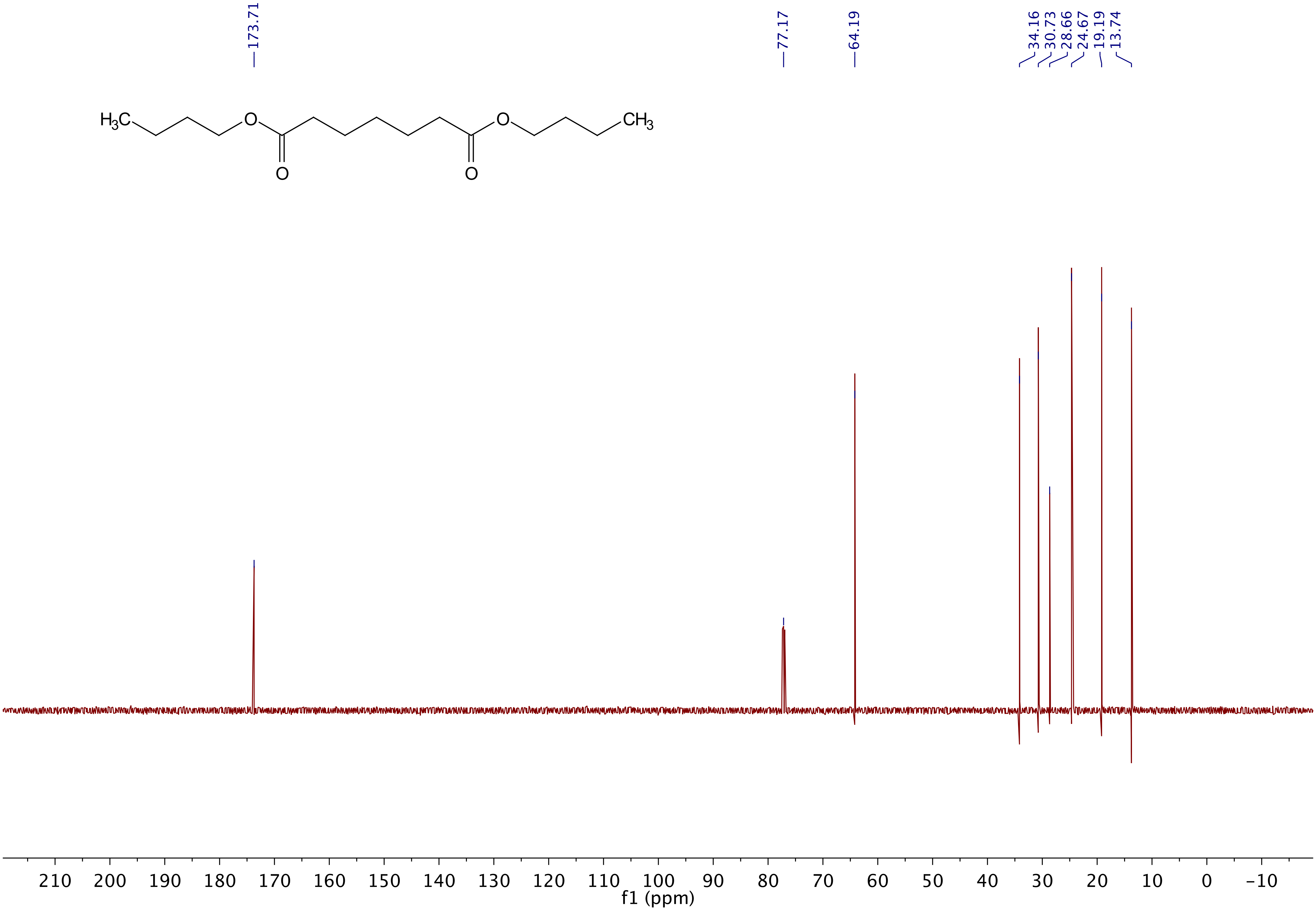
0.(
f1 (ppm)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13.74
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O
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O
CH3
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200
190
180
170
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140
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100
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80
70
60
50
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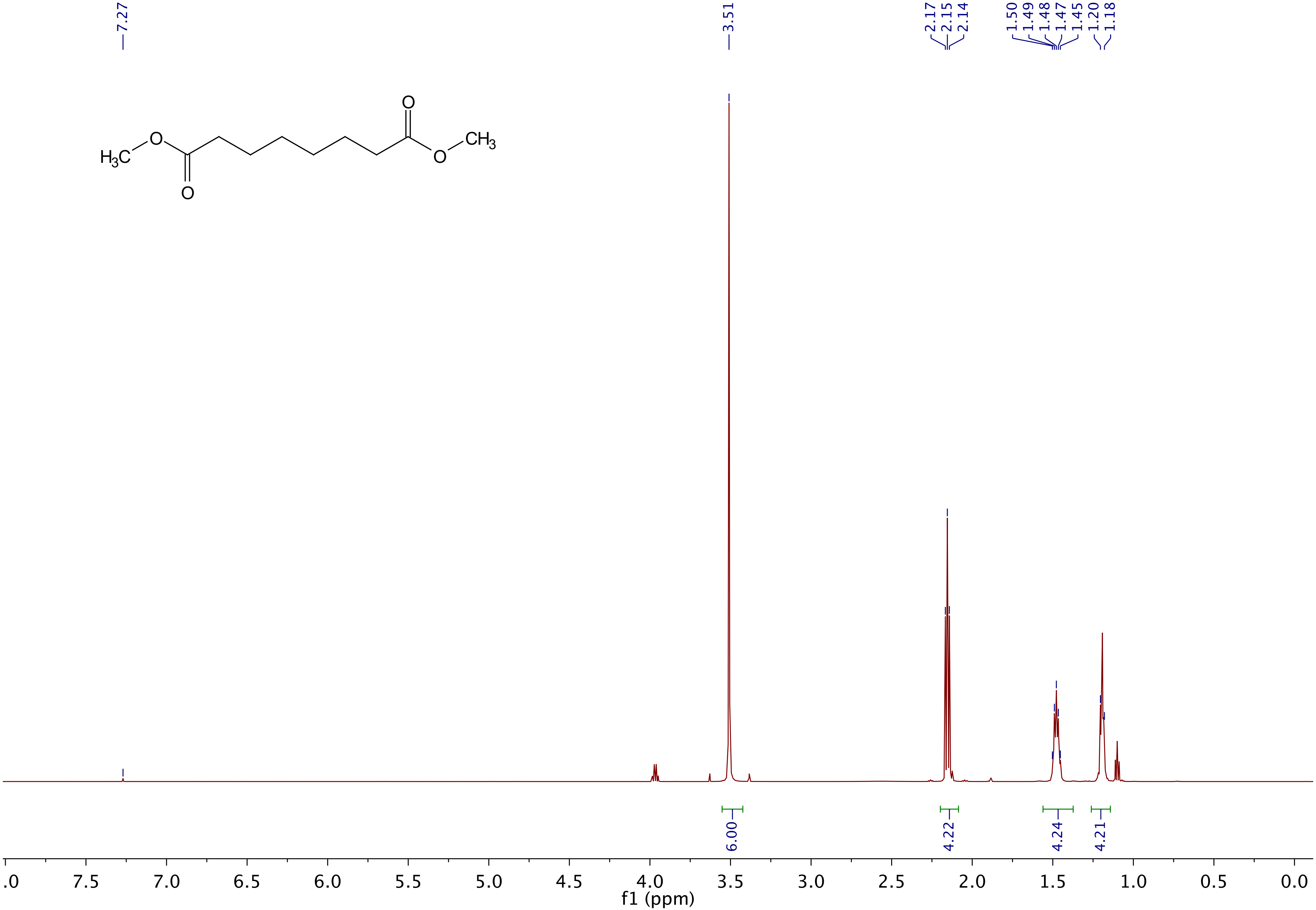
30
20
10
0
–10
f1 (ppm)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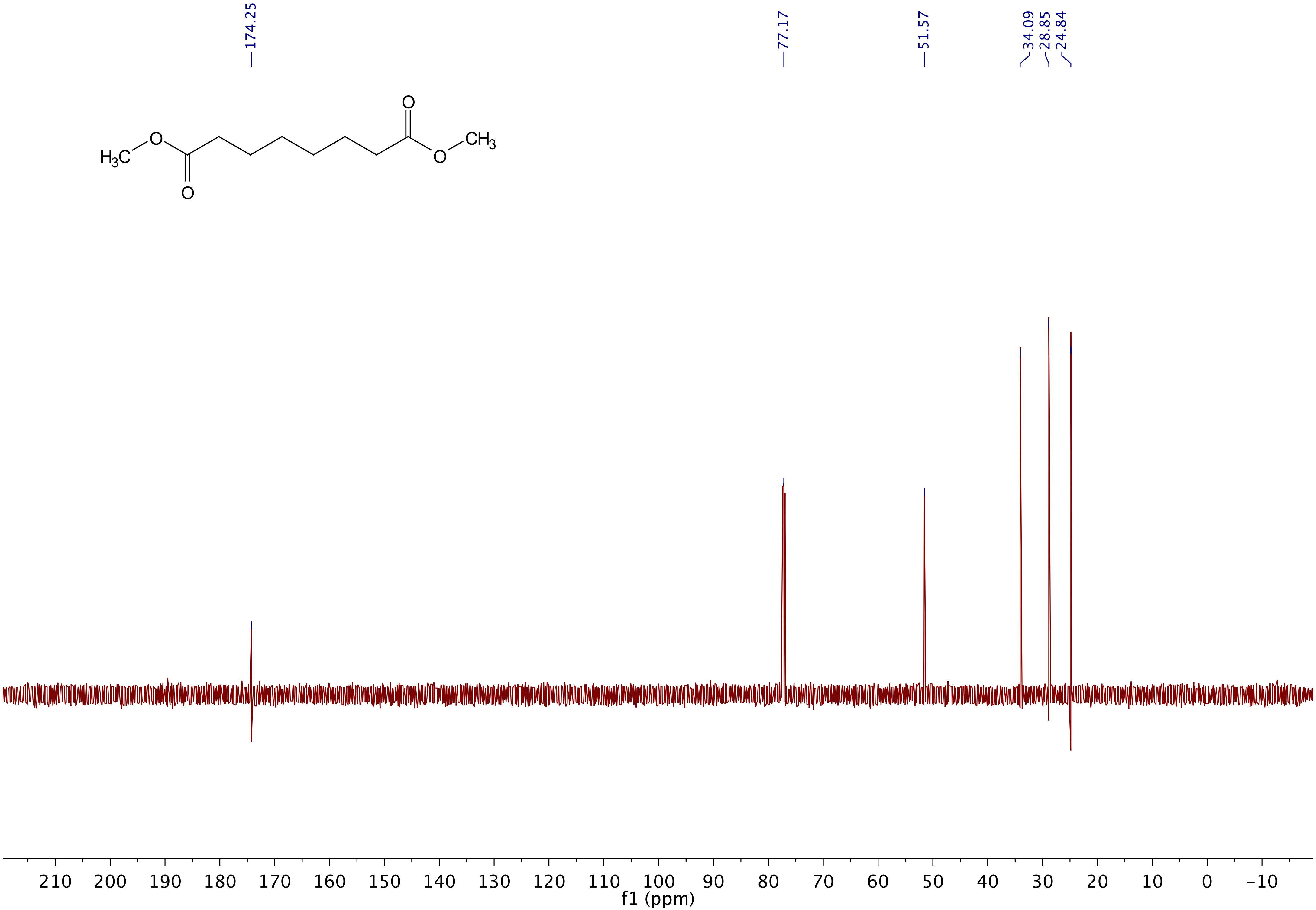
1.47
1.45
1.20
1.18
H_3C
O
O
O
O
CH_3
6.00
4.22
4.24
4.21
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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51.57
34.09
28.85
24.84
H_3C
O
O
O
O
CH_3
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200
190
180
170
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140
130
120
110
100
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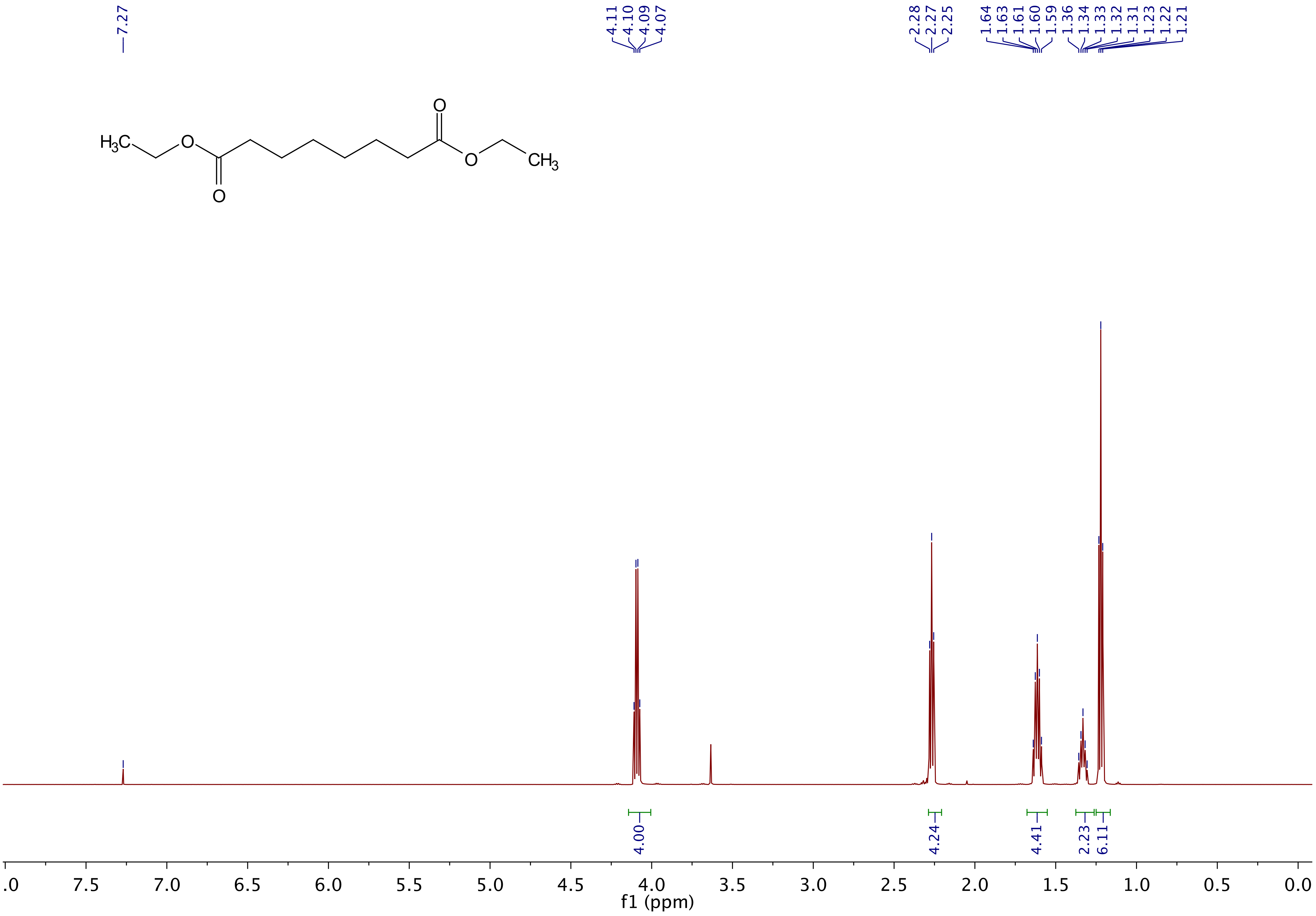
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)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4.10
4.09
4.07
2.28
2.27
2.25
1.64
1.63
1.61
1.60
1.59
1.36
1.34
1.33
1.32
1.31
1.23
1.22
1.21
H3C
O
O
O
O
CH3
4.00
4.24
4.41
2.23
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.0
7.5
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6.5
6.0
5.5
5.0
4.5
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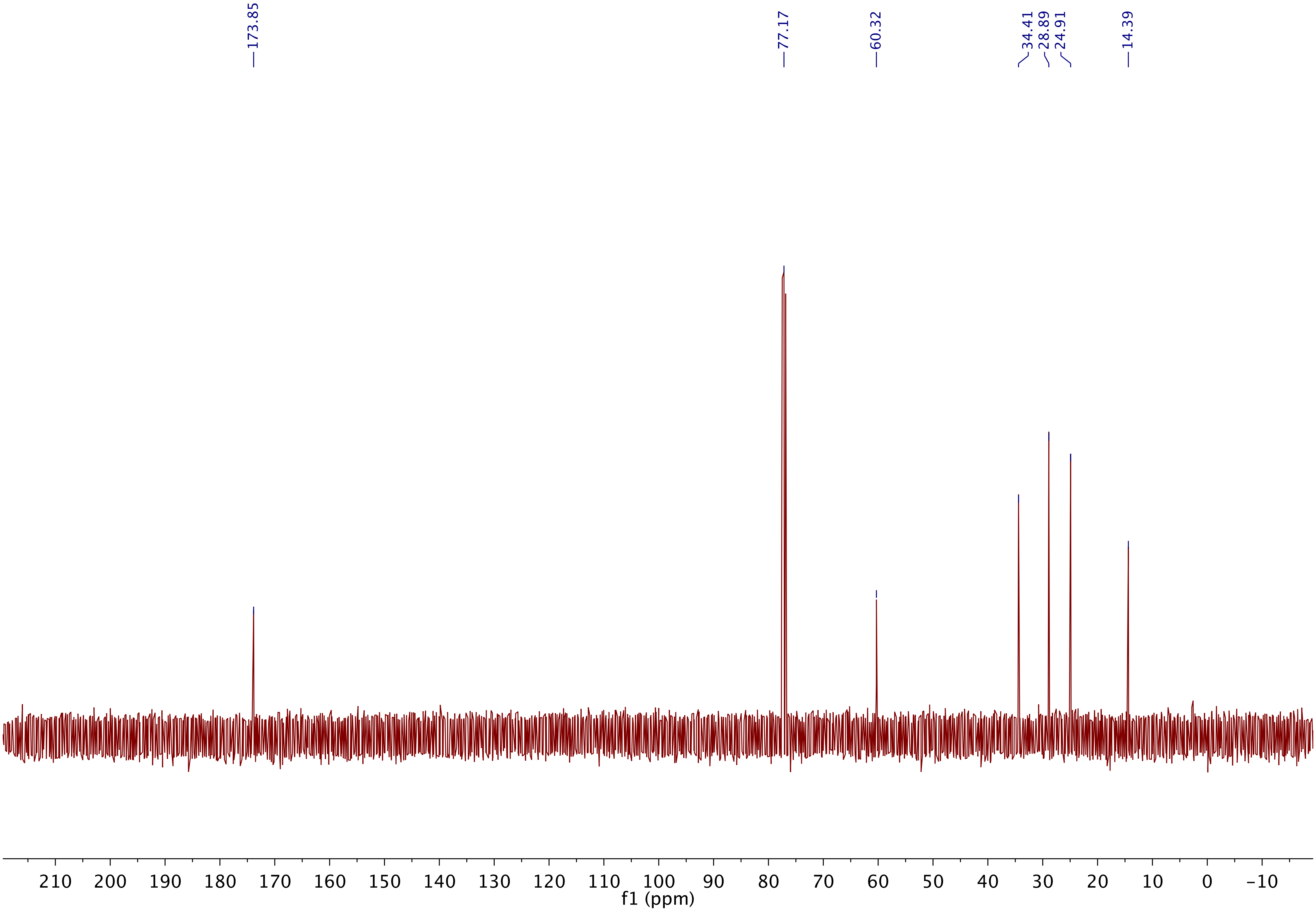
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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24.91
14.39
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200
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180
170
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140
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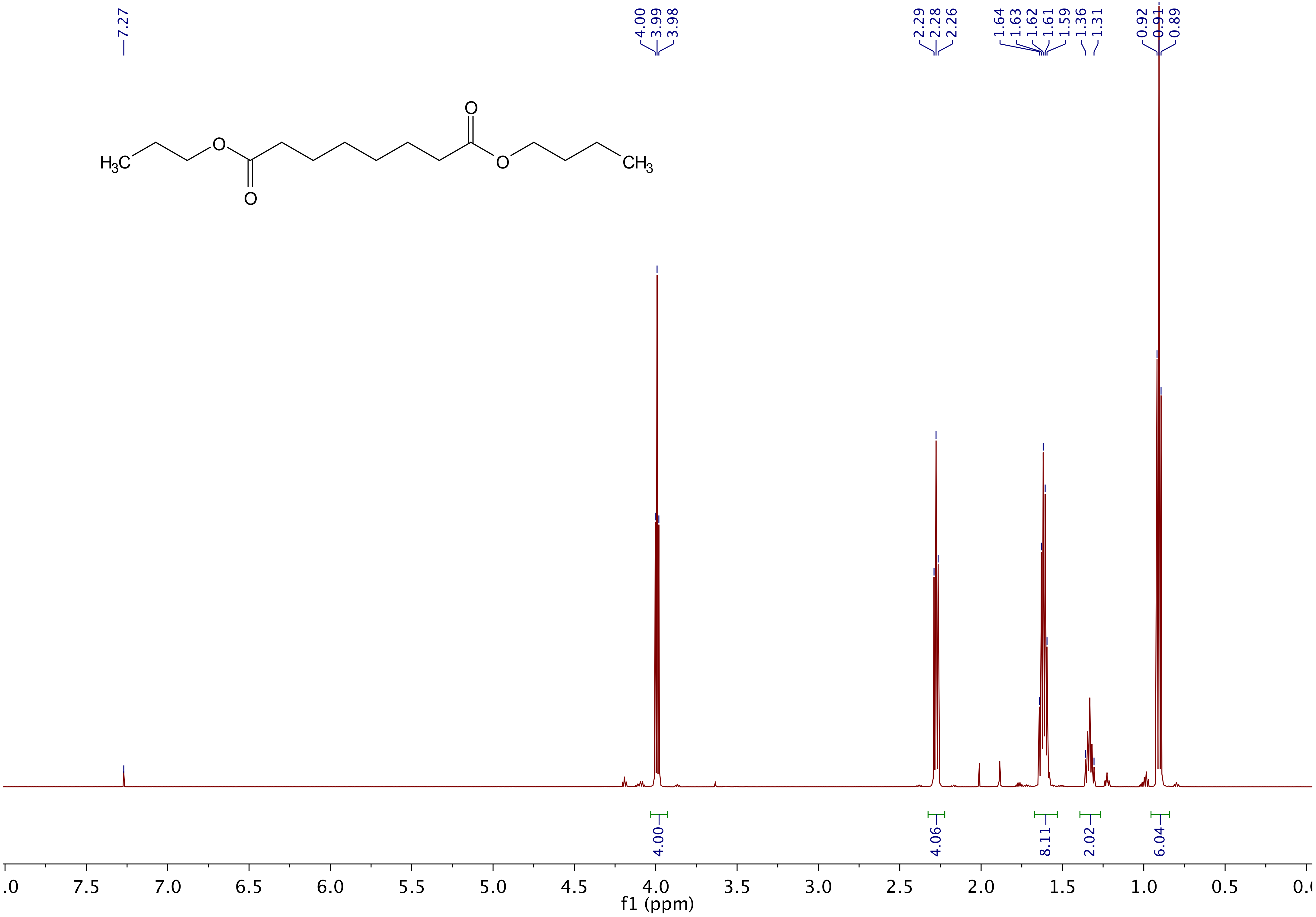
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)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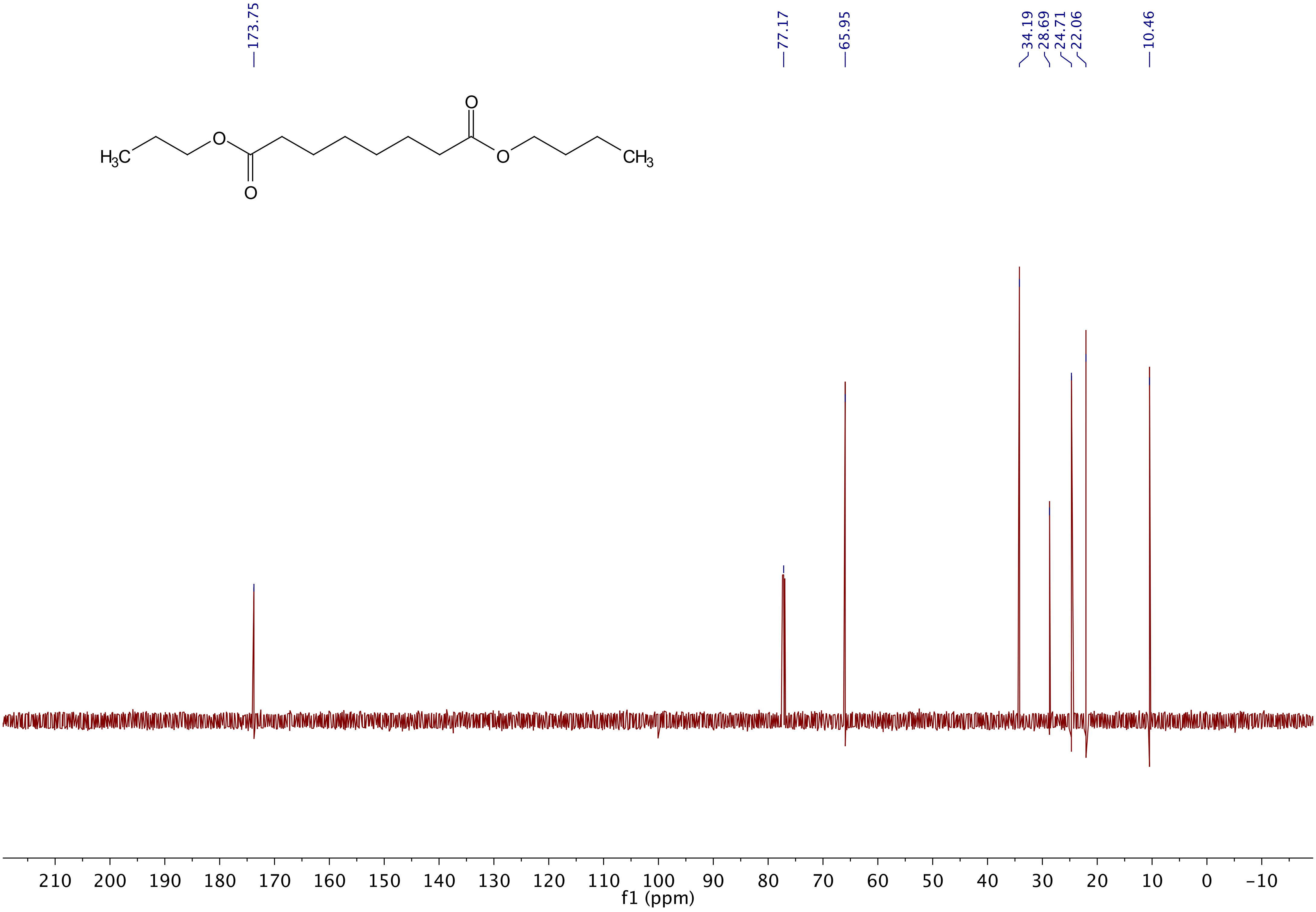
3.99
3.98
2.29
2.28
2.26
1.64
1.63
1.62
1.61
1.59
1.36
1.31
0.92
0.91
0.89
H3C
O
O
O
O
CH3
4.00
4.06
8.11
2.02
6.04
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)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65.95
34.19
28.69
24.71
22.06
10.46
H3C
O
O
O
O
CH3
210
200
190
180
170
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120
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100
90
80
70
60
50
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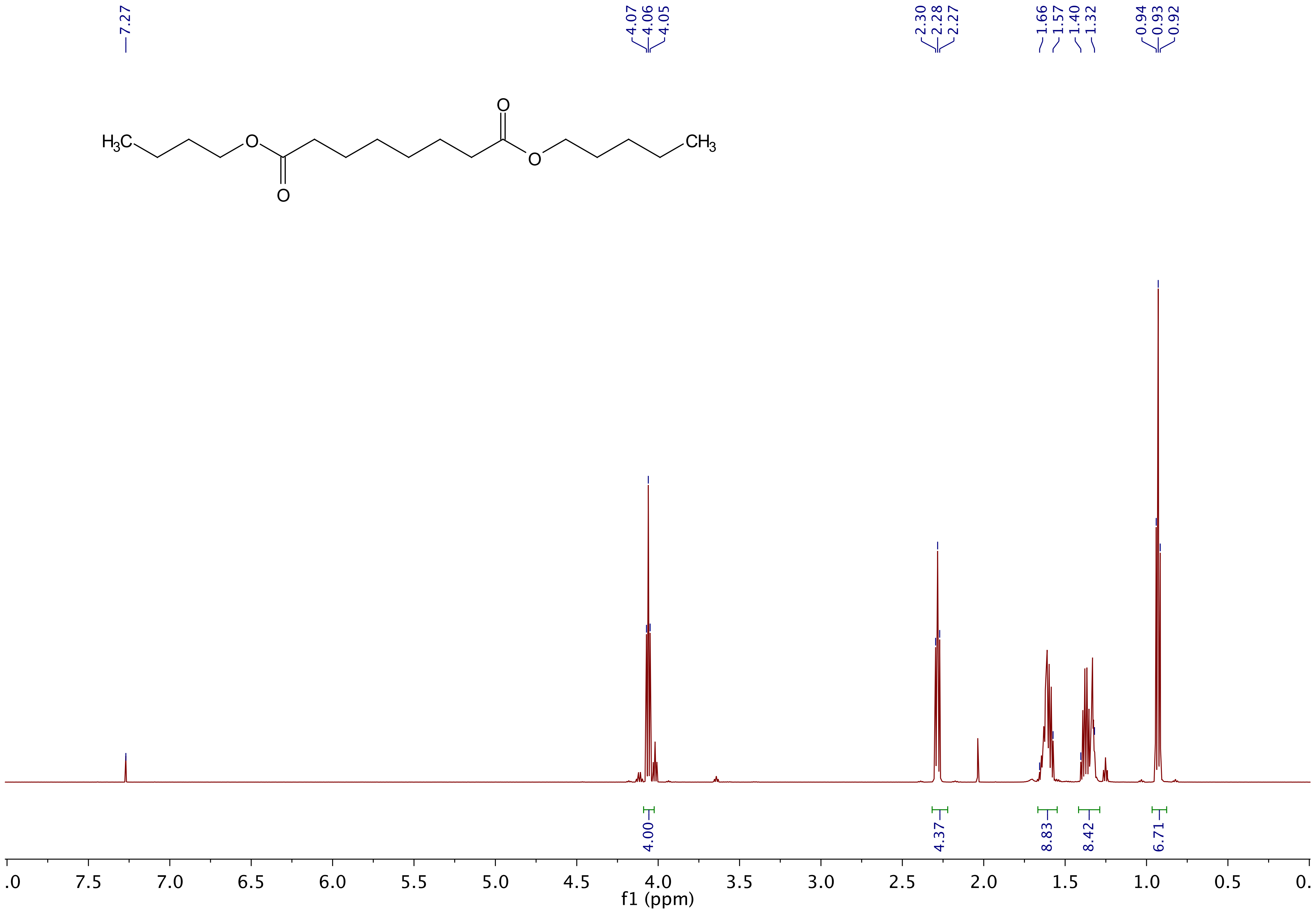
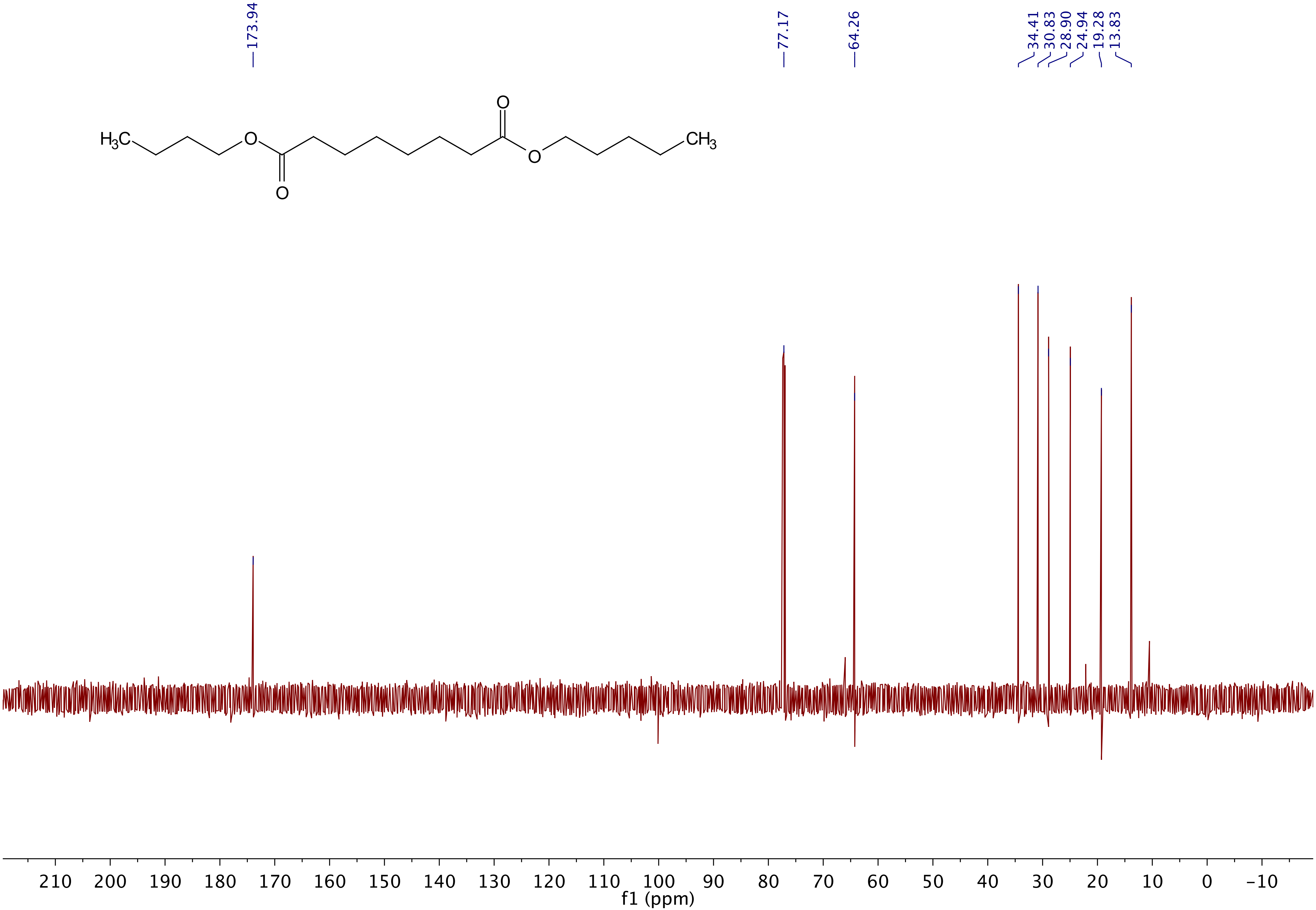
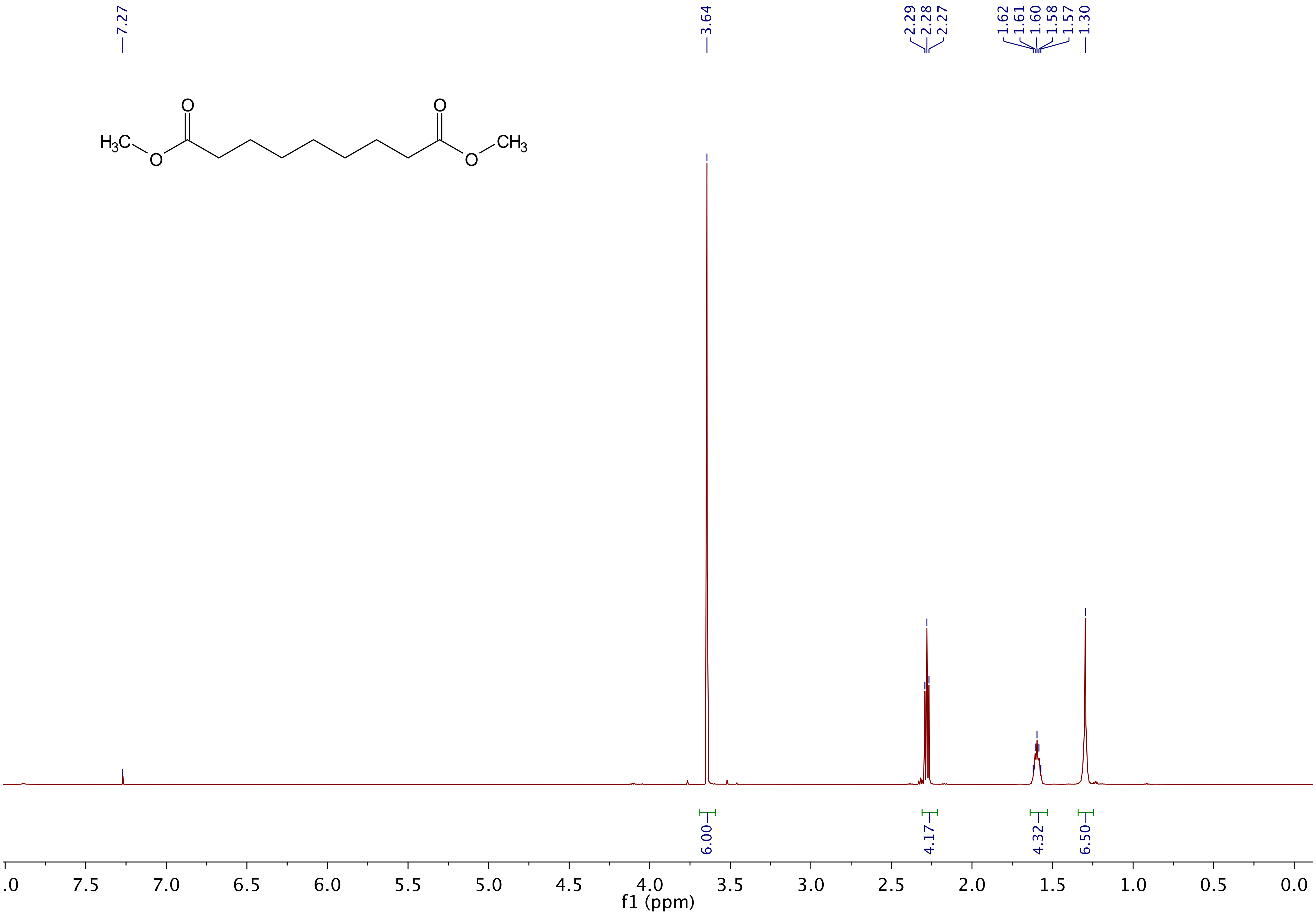
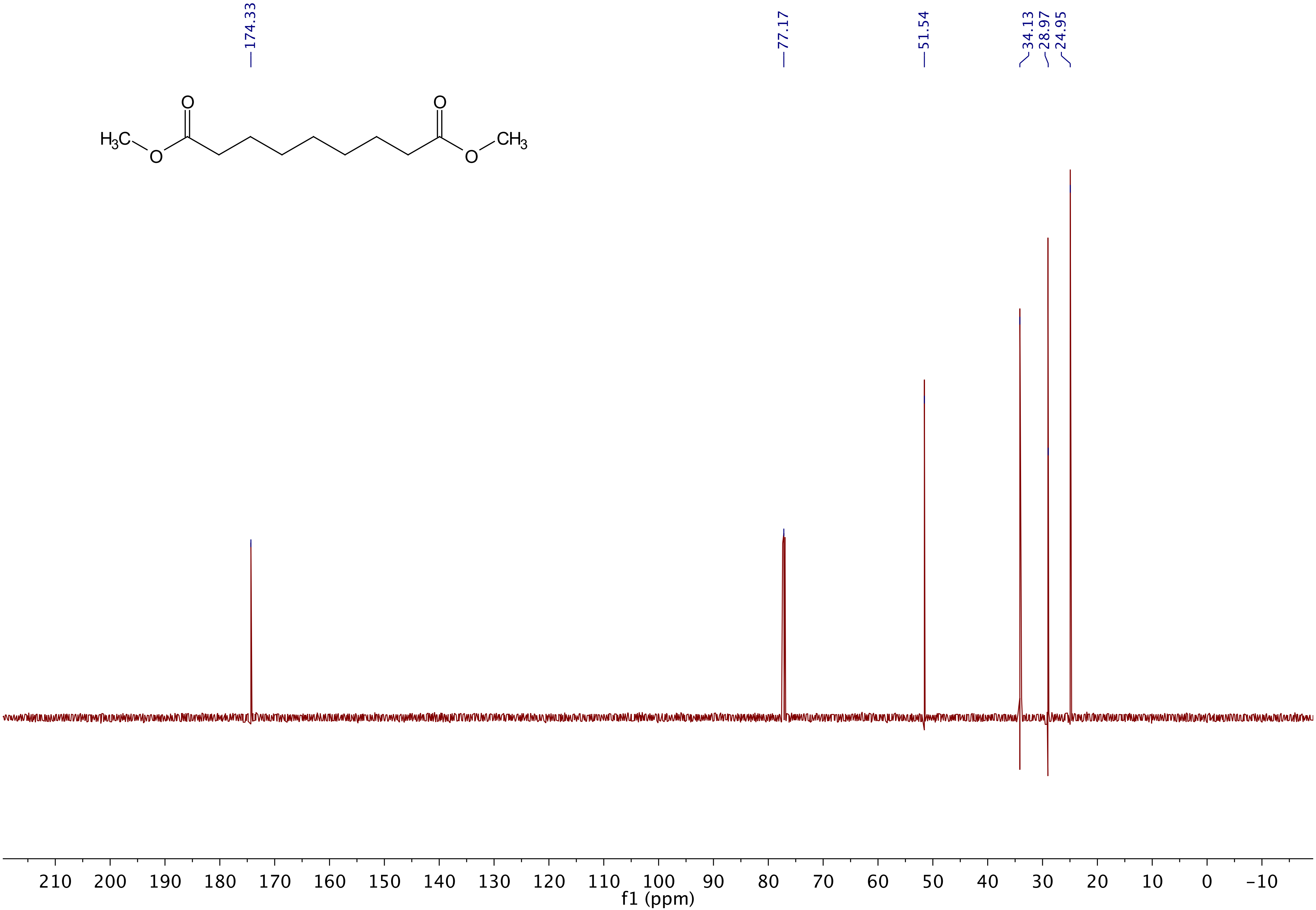
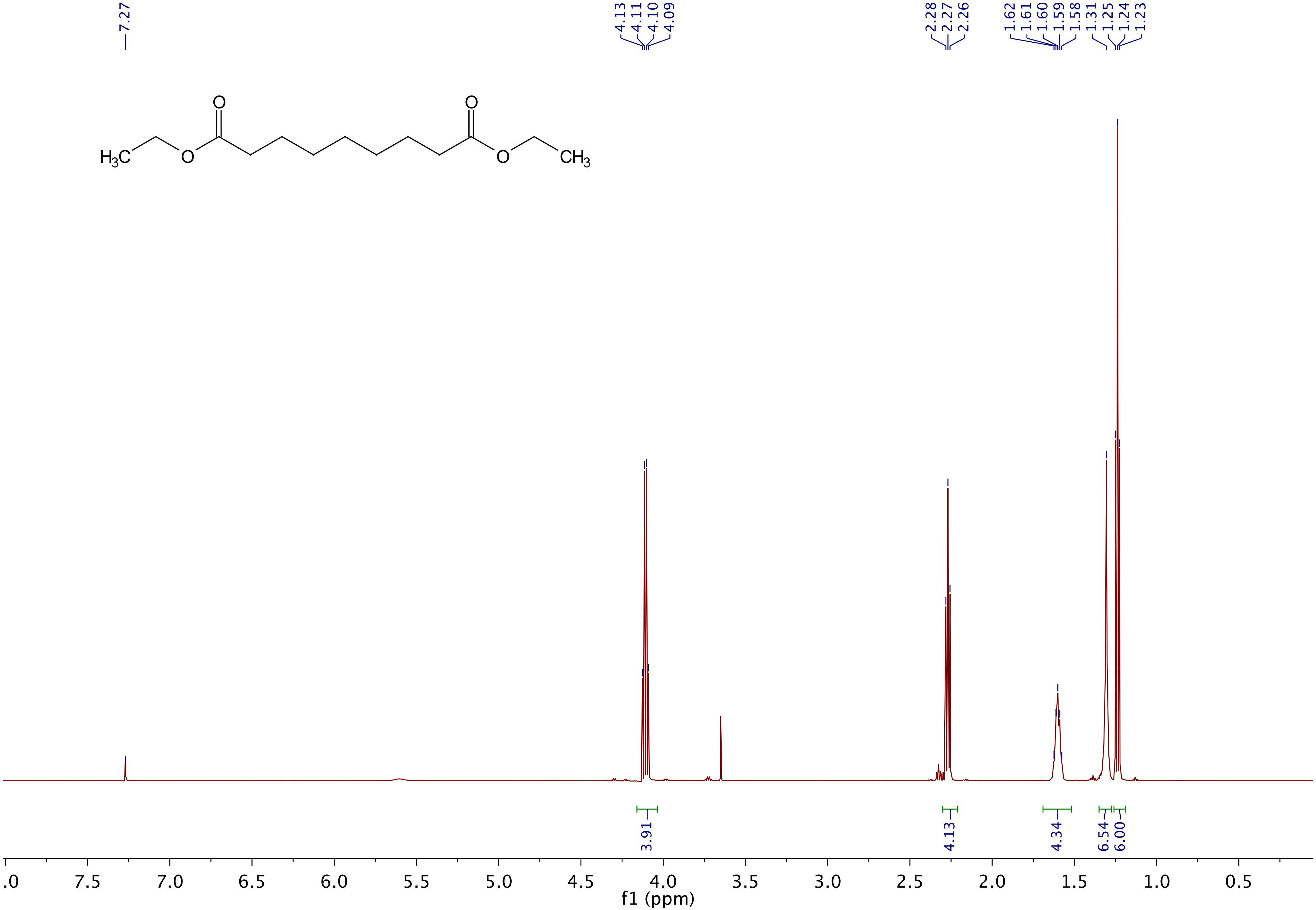
30
20
10
0
–10
f1 (ppm)

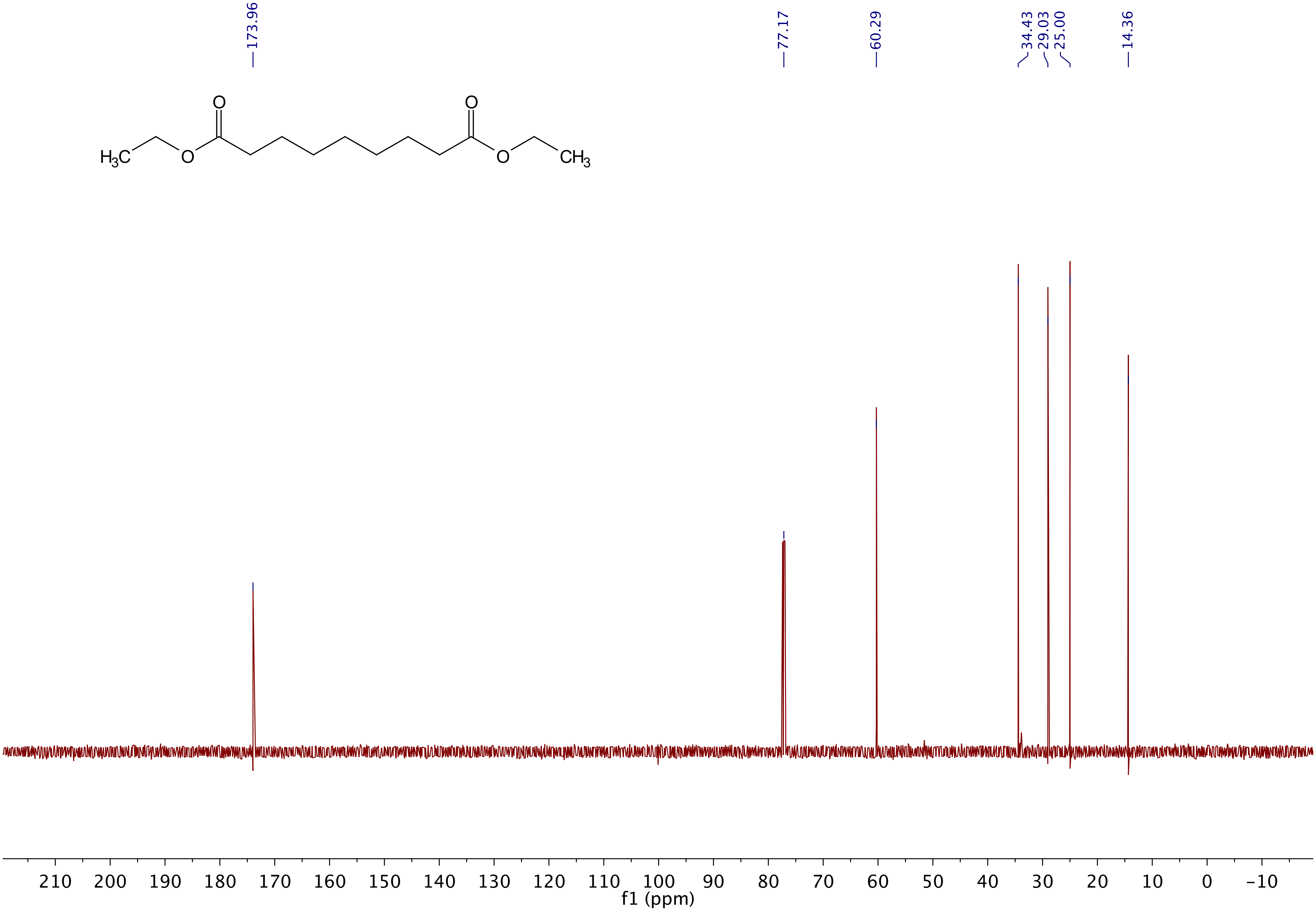

7.27
4.07
4.06
4.05
2.30
2.28
2.27
1.66
1.57
1.40
1.32
0.94
0.93
0.92
H3C
O
O
O
O
CH3
4.00
4.37
8.83
8.42
6.71
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

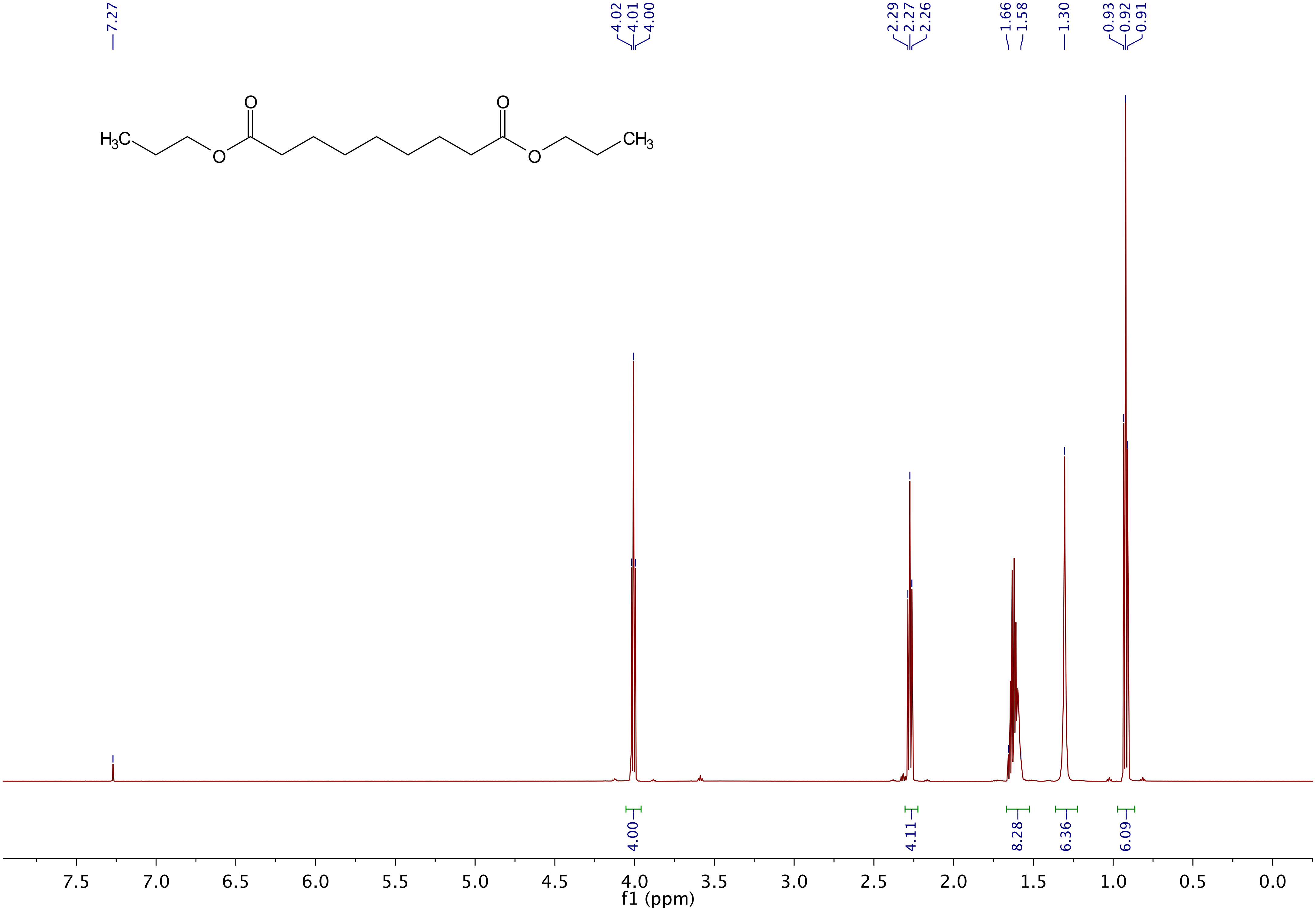

173.94
77.17
64.26
34.41
30.83
28.90
24.94
19.28
13.83
H3C
O
O
O
O
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)

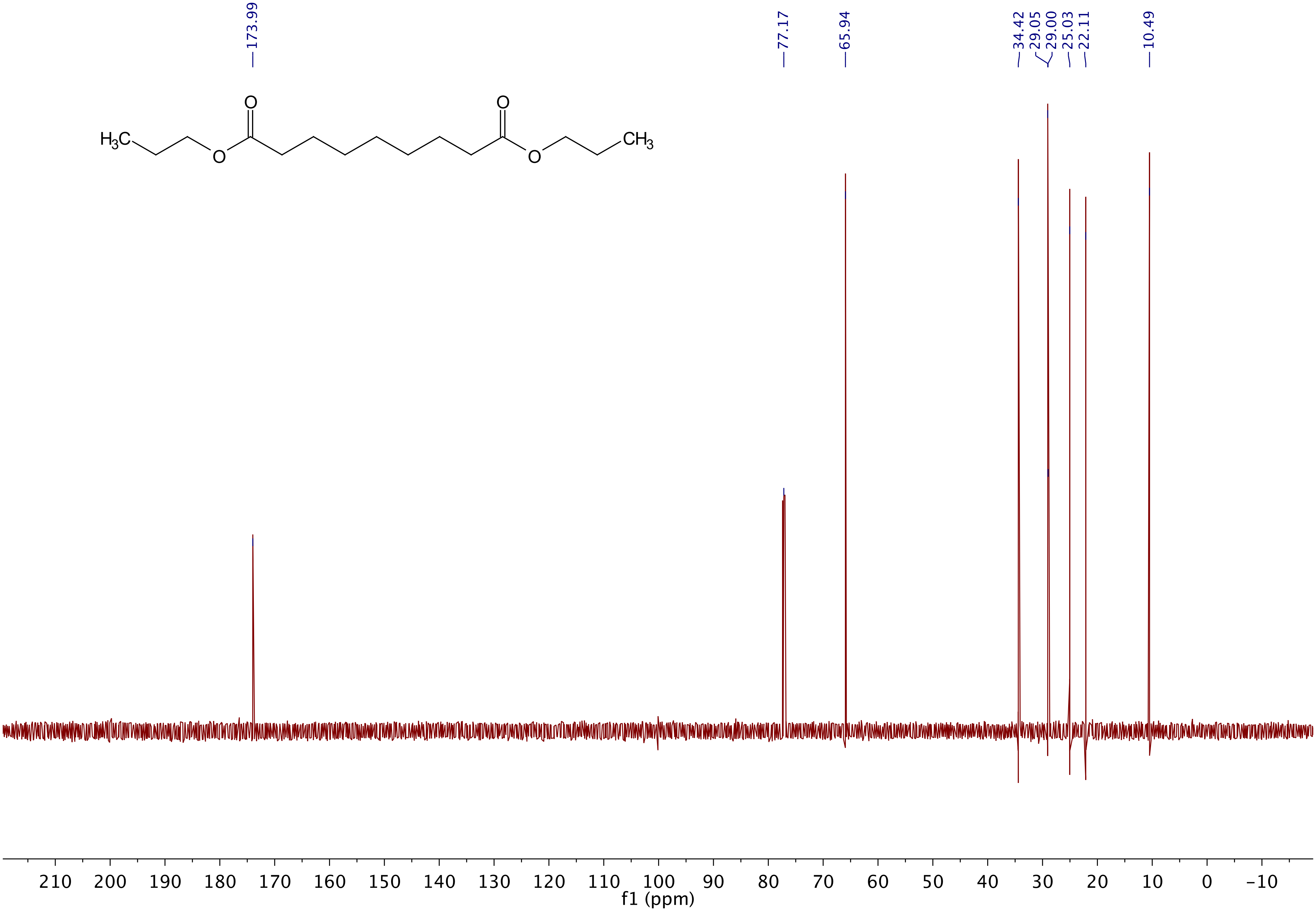

7.27
3.64
2.29
2.28
2.27
1.62
1.61
1.60
1.58
1.57
1.30
H3C
O
O
O
O
CH3
6.00
4.17
4.32
6.50
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


174.33
77.17
51.54
34.13
28.97
24.95
H3C
O
O
O
O
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)


7.27
4.13
4.11
4.10
4.09
2.28
2.27
2.26
1.62
1.61
1.60
1.59
1.58
1.31
1.25
1.24
1.23
O
O
H3C
O
O
CH3
3.91
4.13
4.34
6.54
6.00
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


173.96
77.17
60.29
34.43
29.03
25.00
14.36
O
O
H3C
O
O
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)


7.27
4.02
4.01
4.00
2.29
2.27
2.26
1.66
1.58
1.30
0.93
0.92
0.91
H3C
O
O
O
O
CH3
4.00
4.11
8.28
6.36
6.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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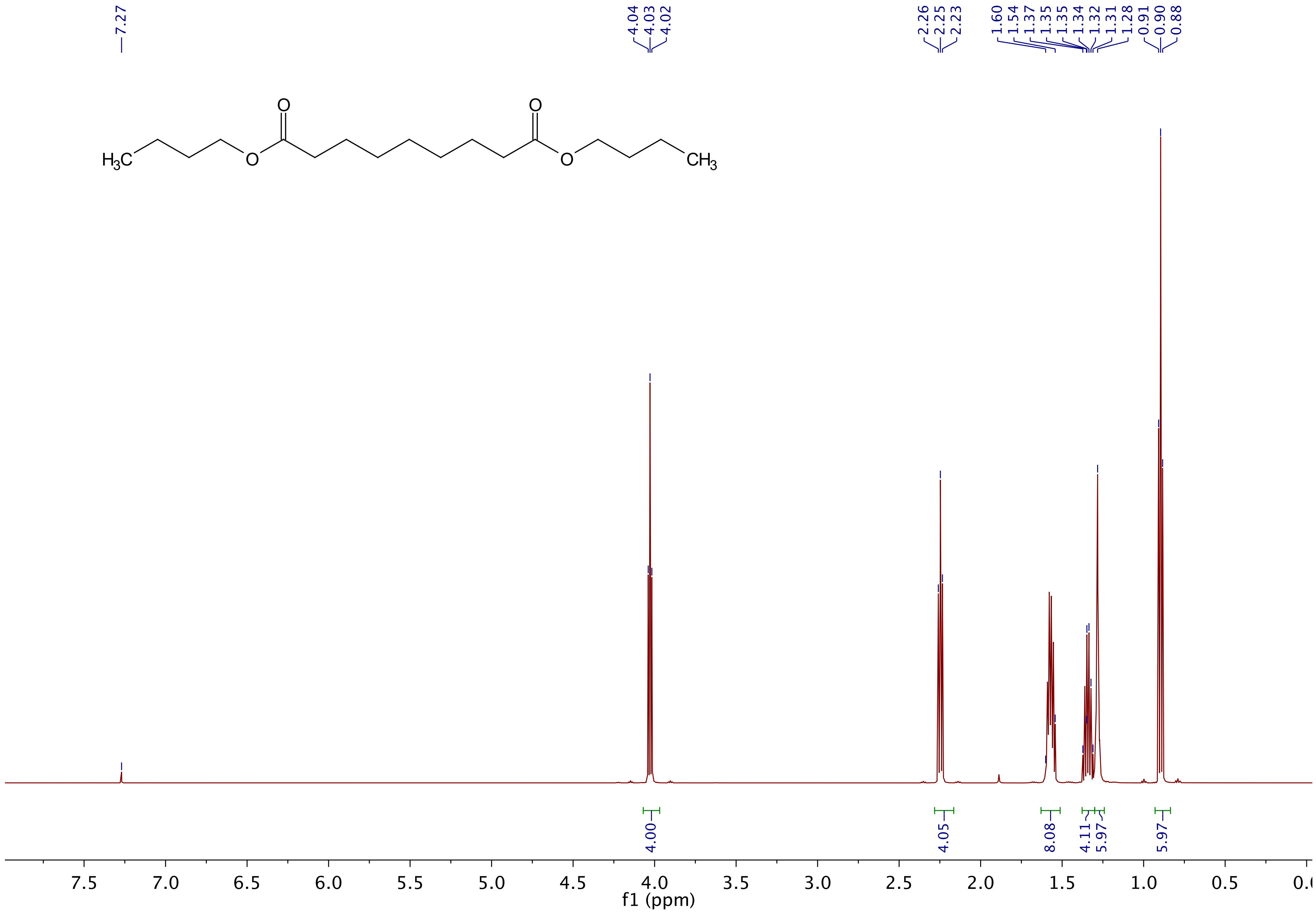
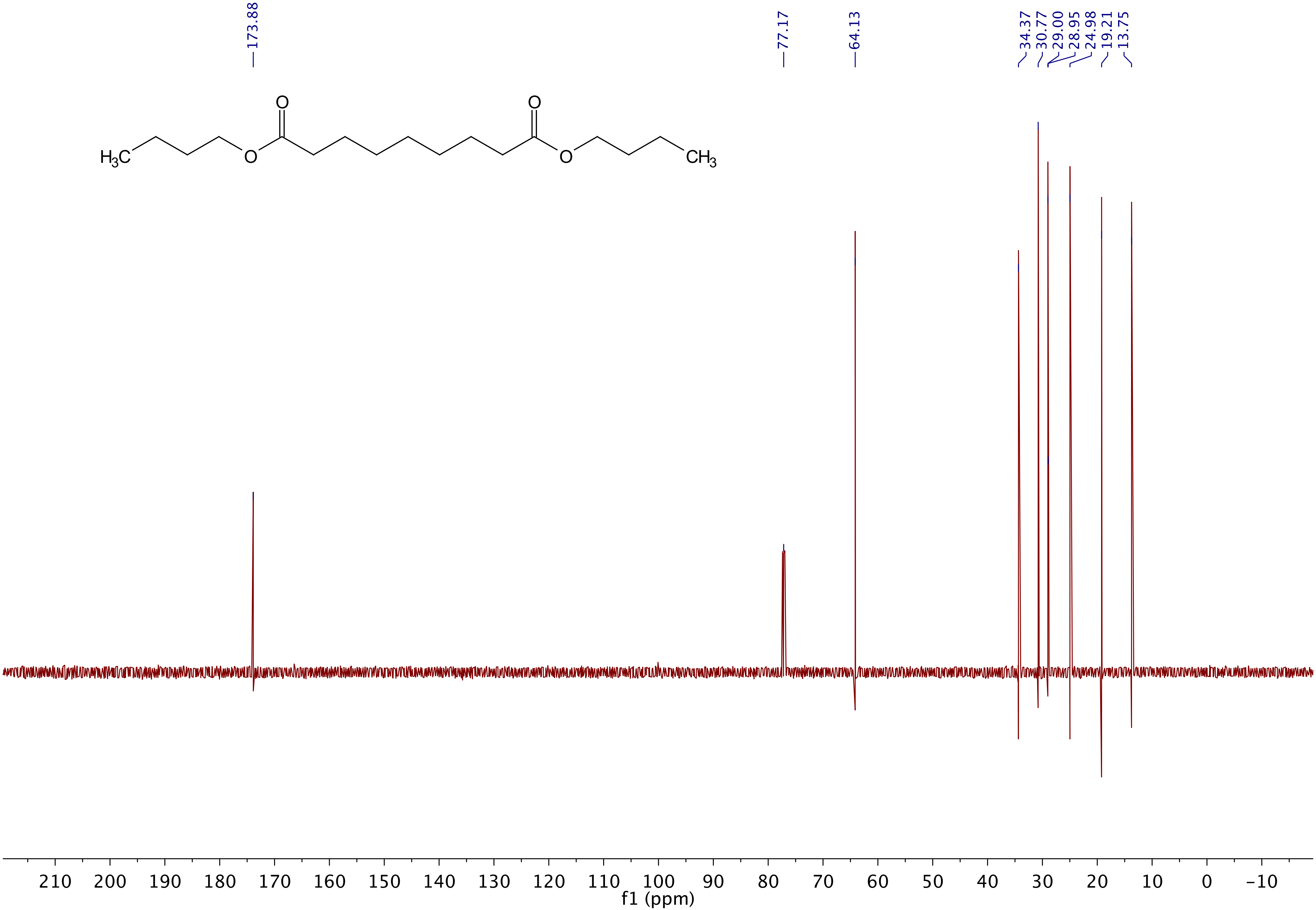
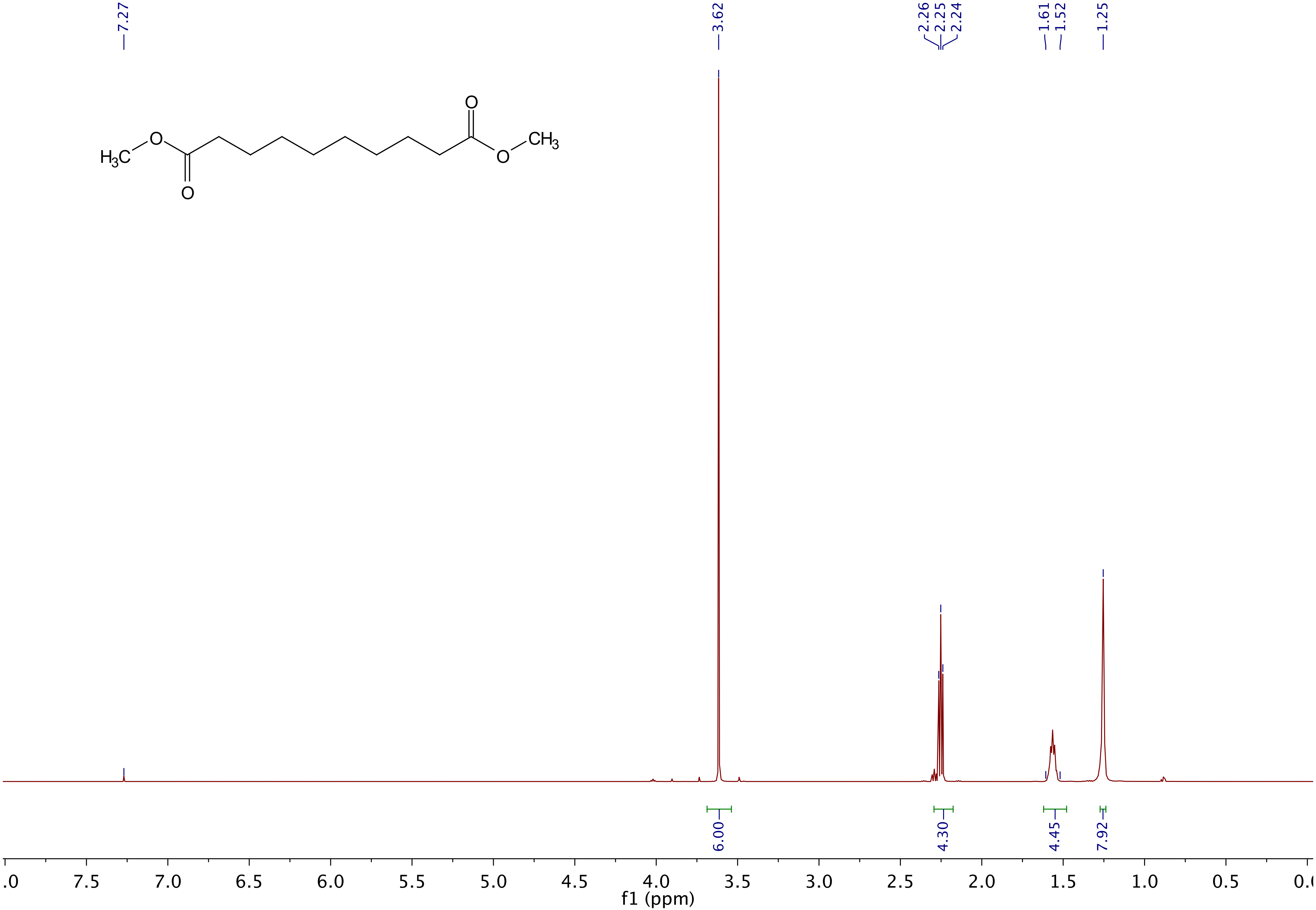
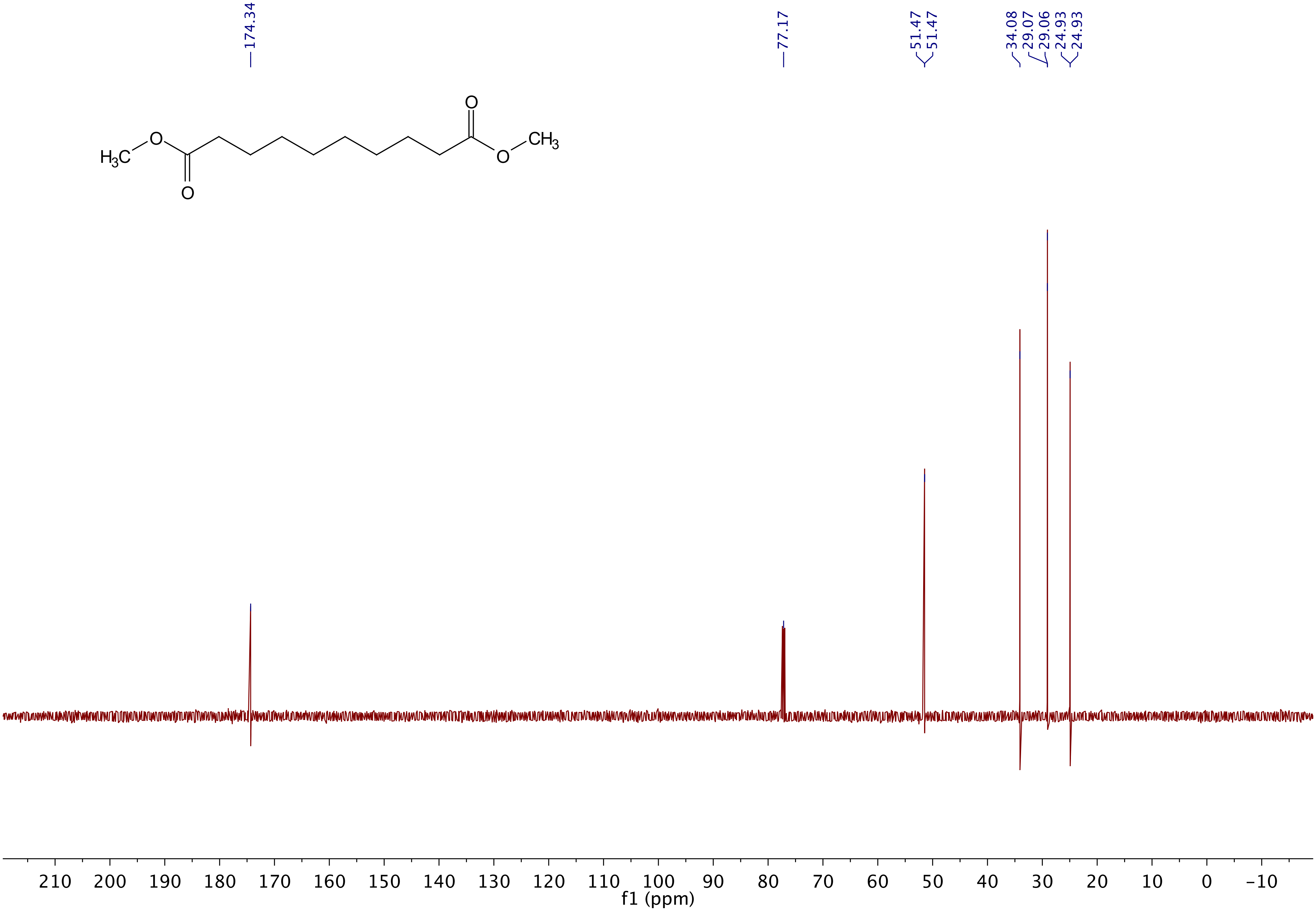
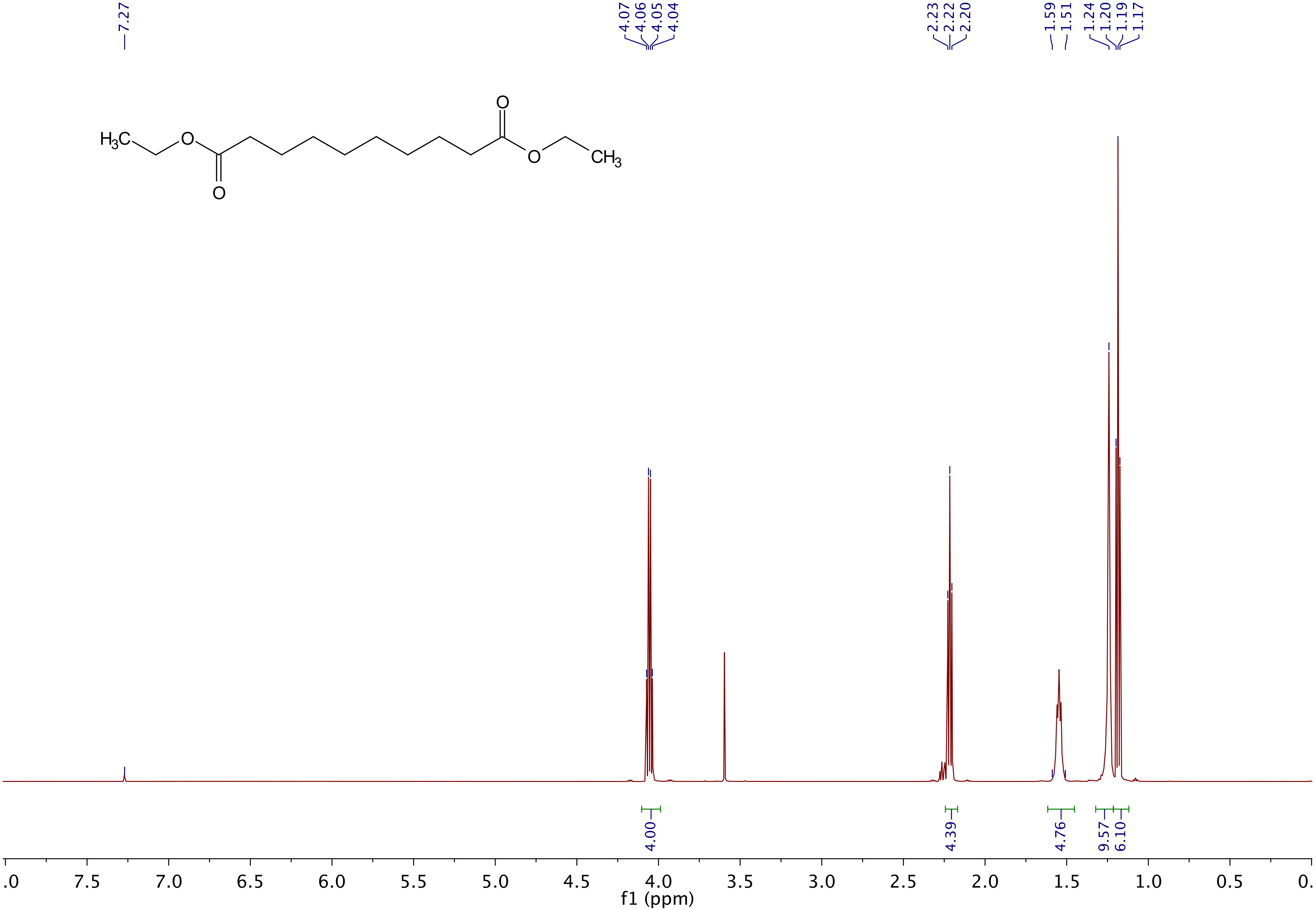
77.17
65.94
34.42
29.05
29.00
25.03
22.11
10.49
O
O
H3C
O
O
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)

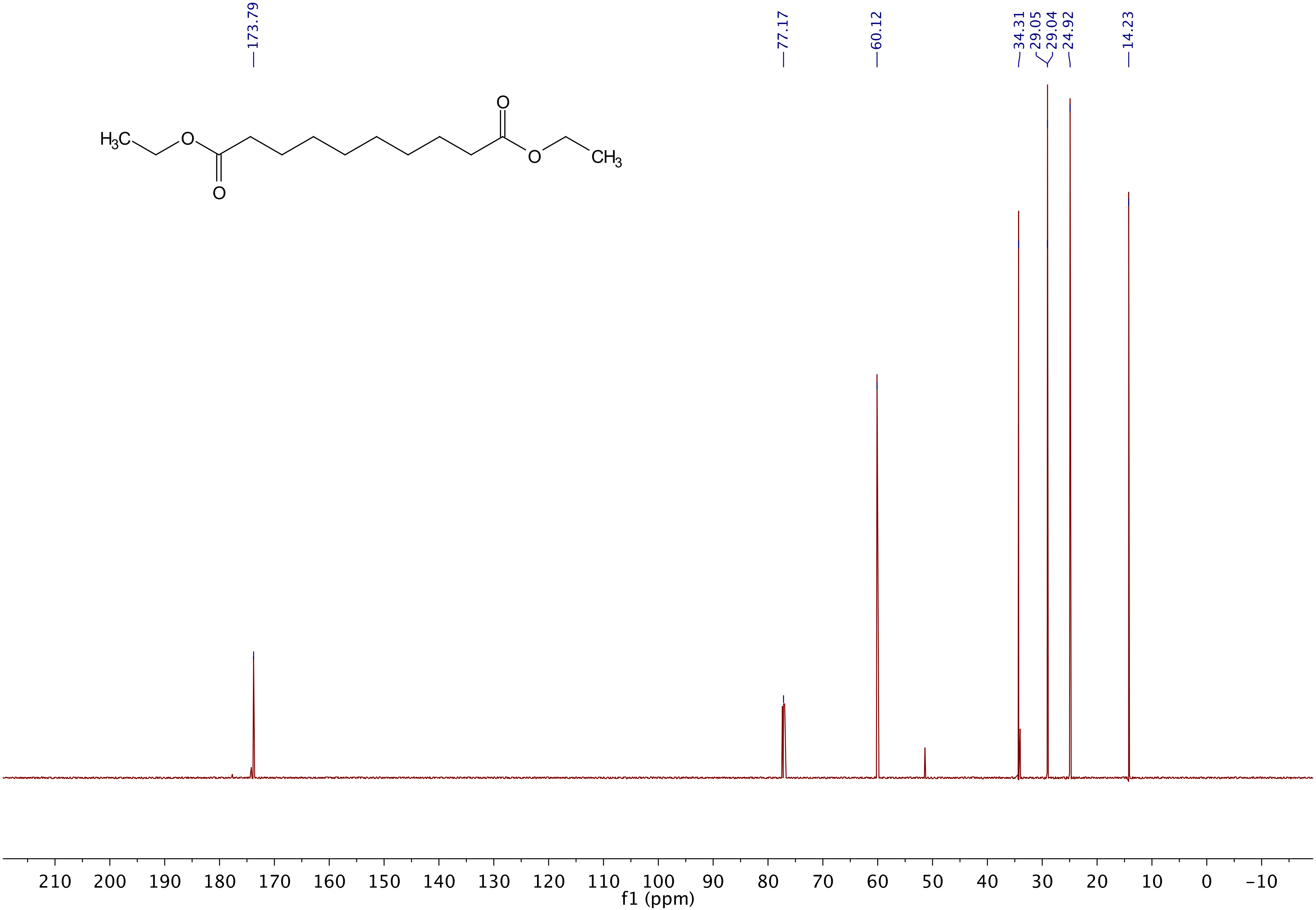

7.27
4.04
4.03
4.02
2.26
2.25
2.23
1.60
1.54
1.37
1.35
1.35
1.34
1.32
1.31
1.28
0.91
0.90
0.88
O
O
H_3C
O
O
CH_3
4.00
4.05
8.08
4.11
5.97
5.97
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

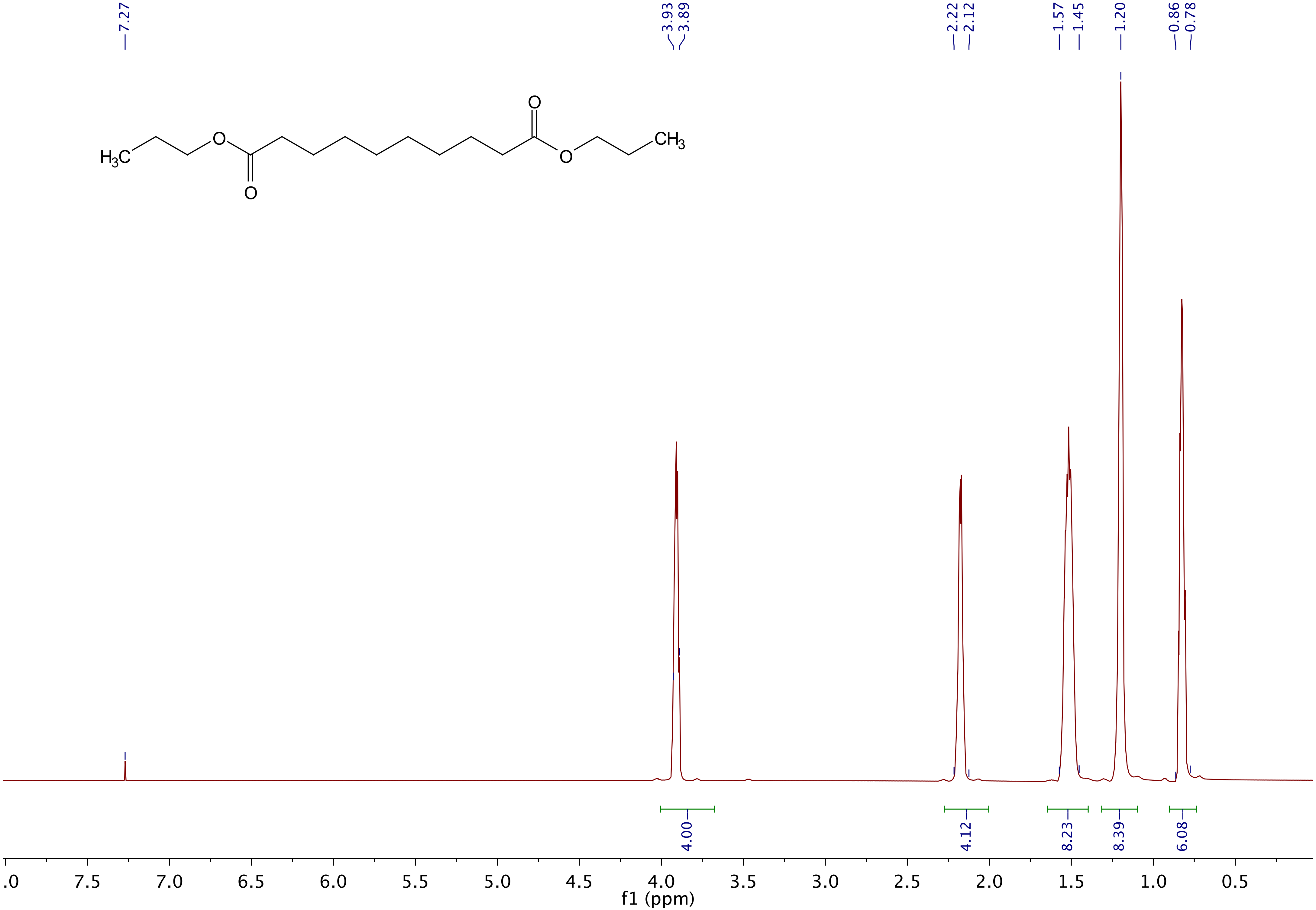

173.88
77.17
64.13
34.37
30.77
29.00
28.95
24.98
19.21
13.75
O
O
H_3C
O
O
CH_3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)

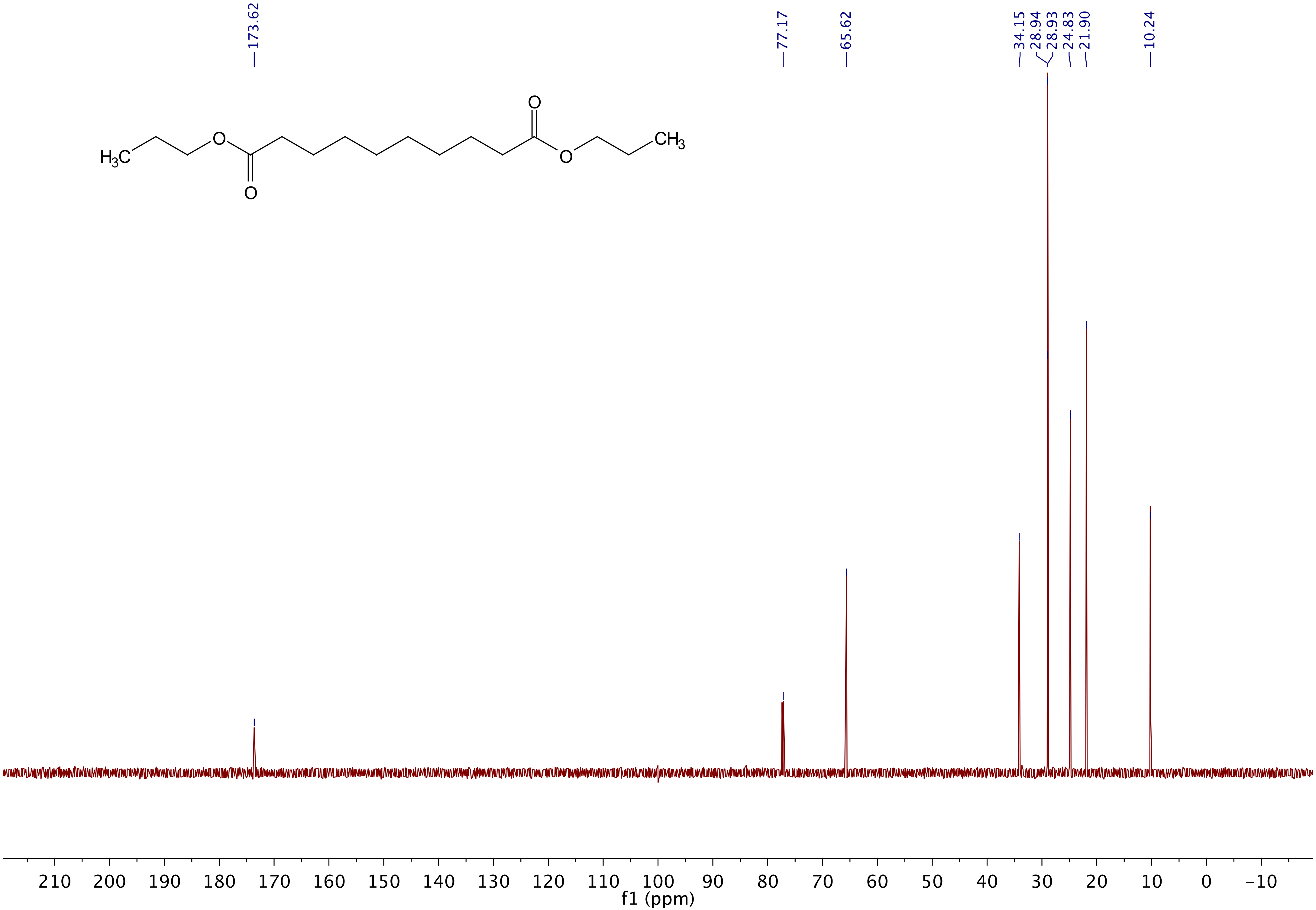

7.27
3.62
2.26
2.25
2.24
1.61
1.52
1.25
O
H$_3$C
O
O
O
CH$_3$
6.00
4.30
4.45
7.92
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


174.34
77.17
51.47
51.47
34.08
29.07
29.06
24.93
24.93
O
H3C
O
O
O
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)

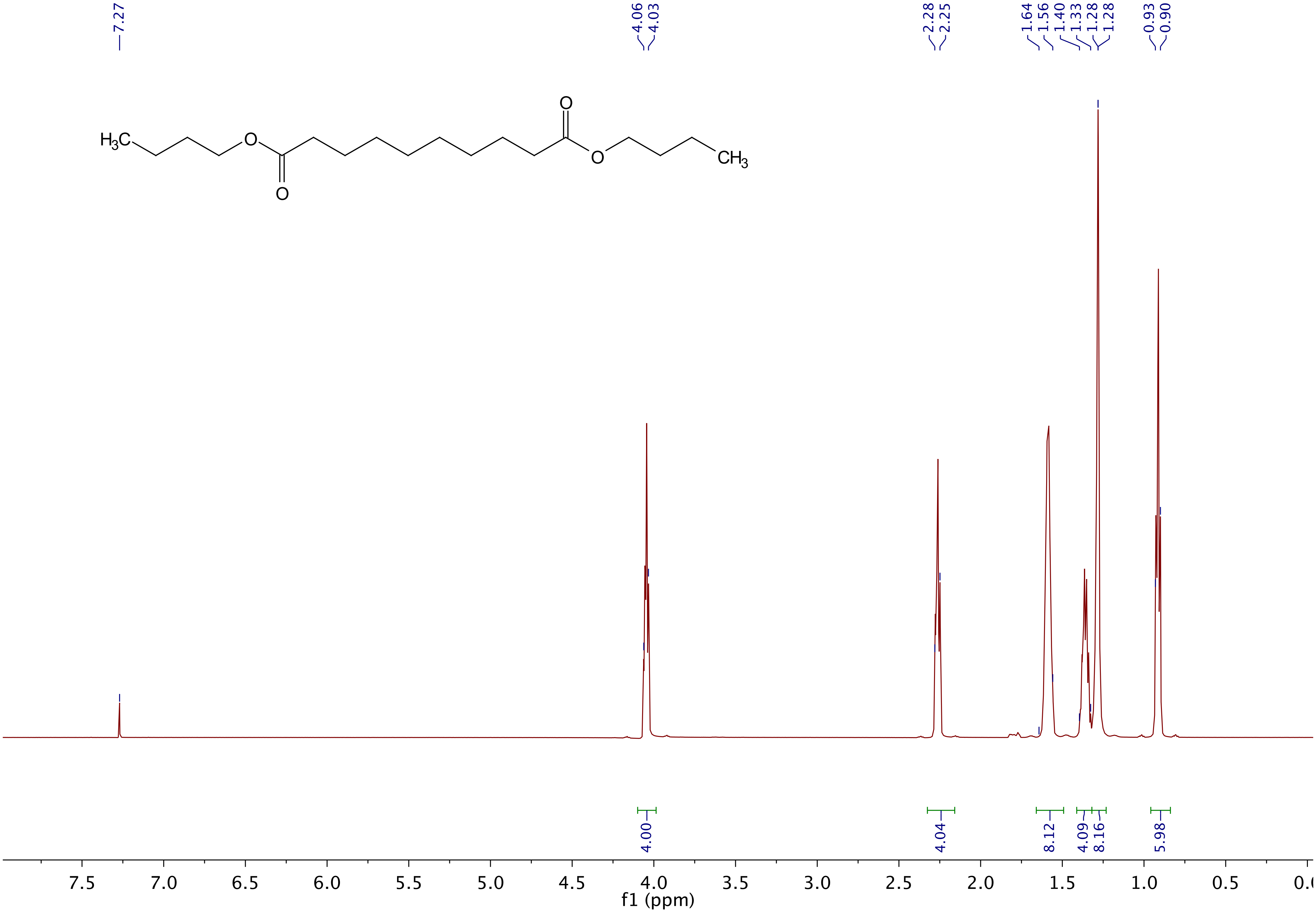

7.27
4.07
4.06
4.05
4.04
2.23
2.22
2.20
1.59
1.51
1.24
1.20
1.19
1.17
H3C
O
O
O
O
CH3
4.00
4.39
4.76
9.57
6.10
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

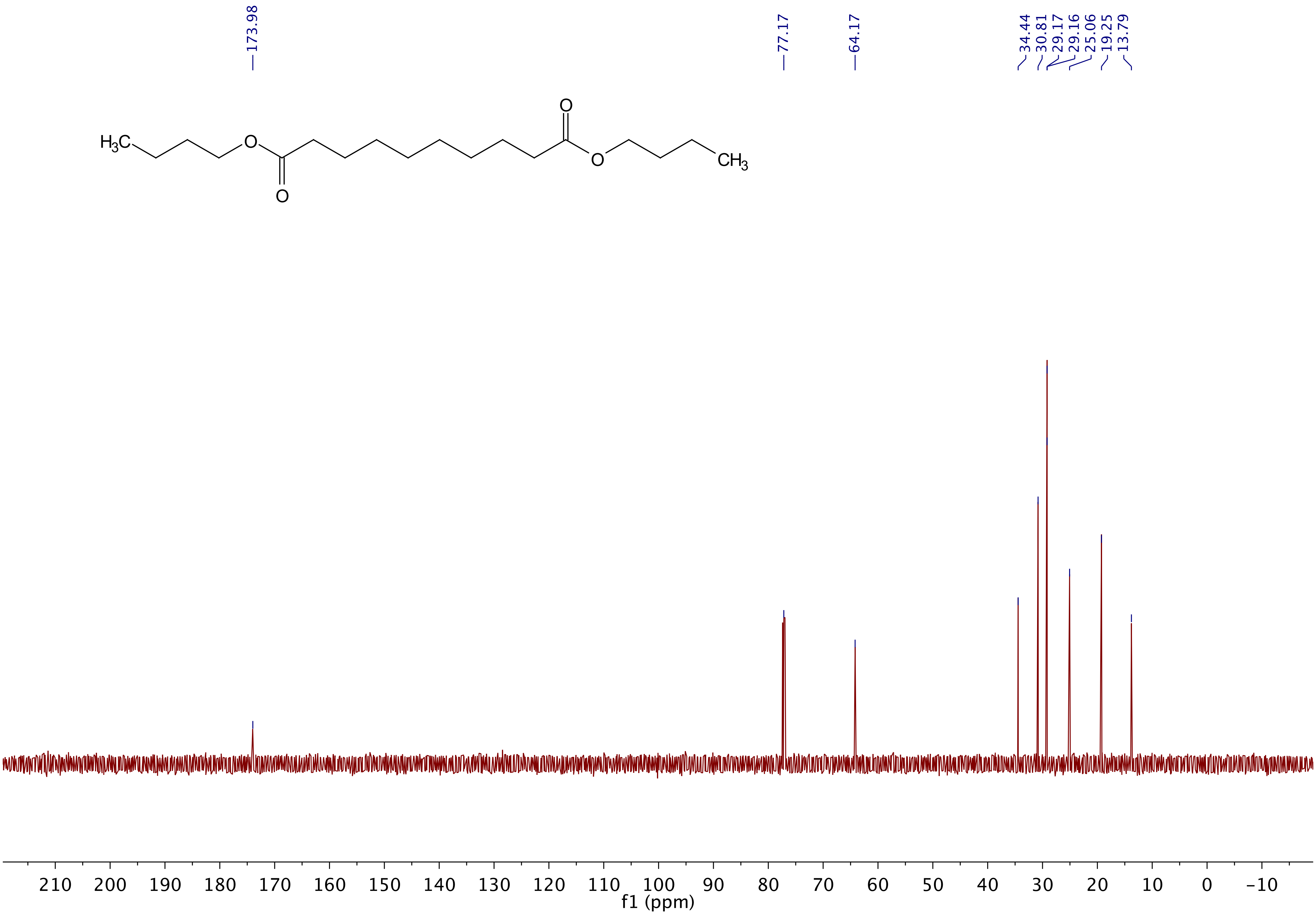

173.79
77.17
60.12
34.31
29.05
29.04
24.92
14.23
H3C
O
O
O
O
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)


7.27
3.93
3.89
2.22
2.12
1.57
1.45
1.20
0.86
0.78
H3C
O
O
O
O
CH3
4.00
4.12
8.23
8.39
6.08
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



173.62
77.17
65.62
34.15
28.94
28.93
24.83
21.90
10.24
H3C
O
O
O
O
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)


7.27
4.06
4.03
2.28
2.25
1.64
1.56
1.40
1.33
1.28
1.28
0.93
0.90
H3C
O
O
O
O
CH3
4.00
4.04
8.12
4.09
8.16
5.98
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


173.98
77.17
64.17
34.44
30.81
29.17
29.16
25.06
19.25
13.79
H3C
O
O
O
O
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)