Palladium Catalyzed Synthesis of Benzannulated Steroid Spiroketals

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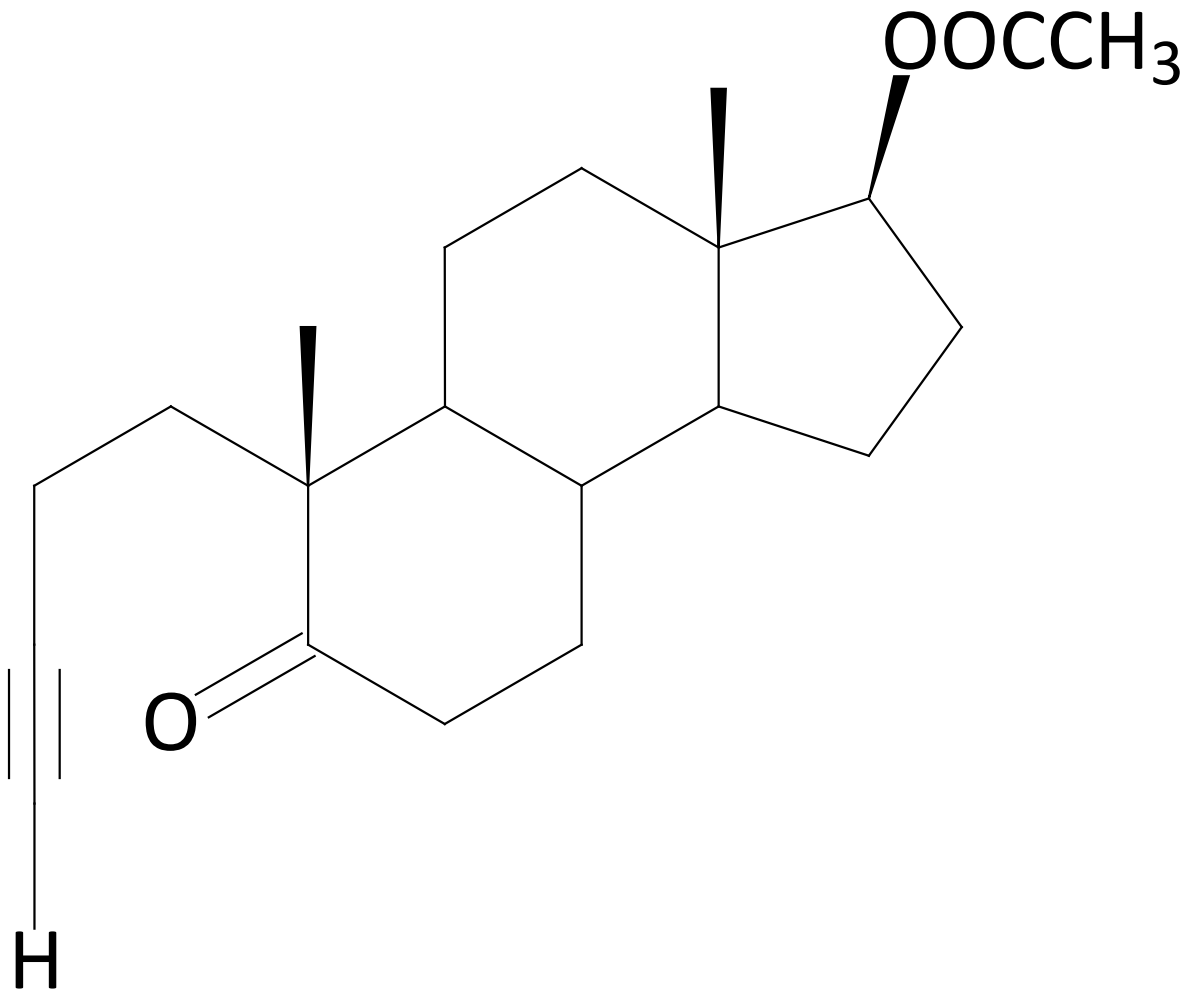
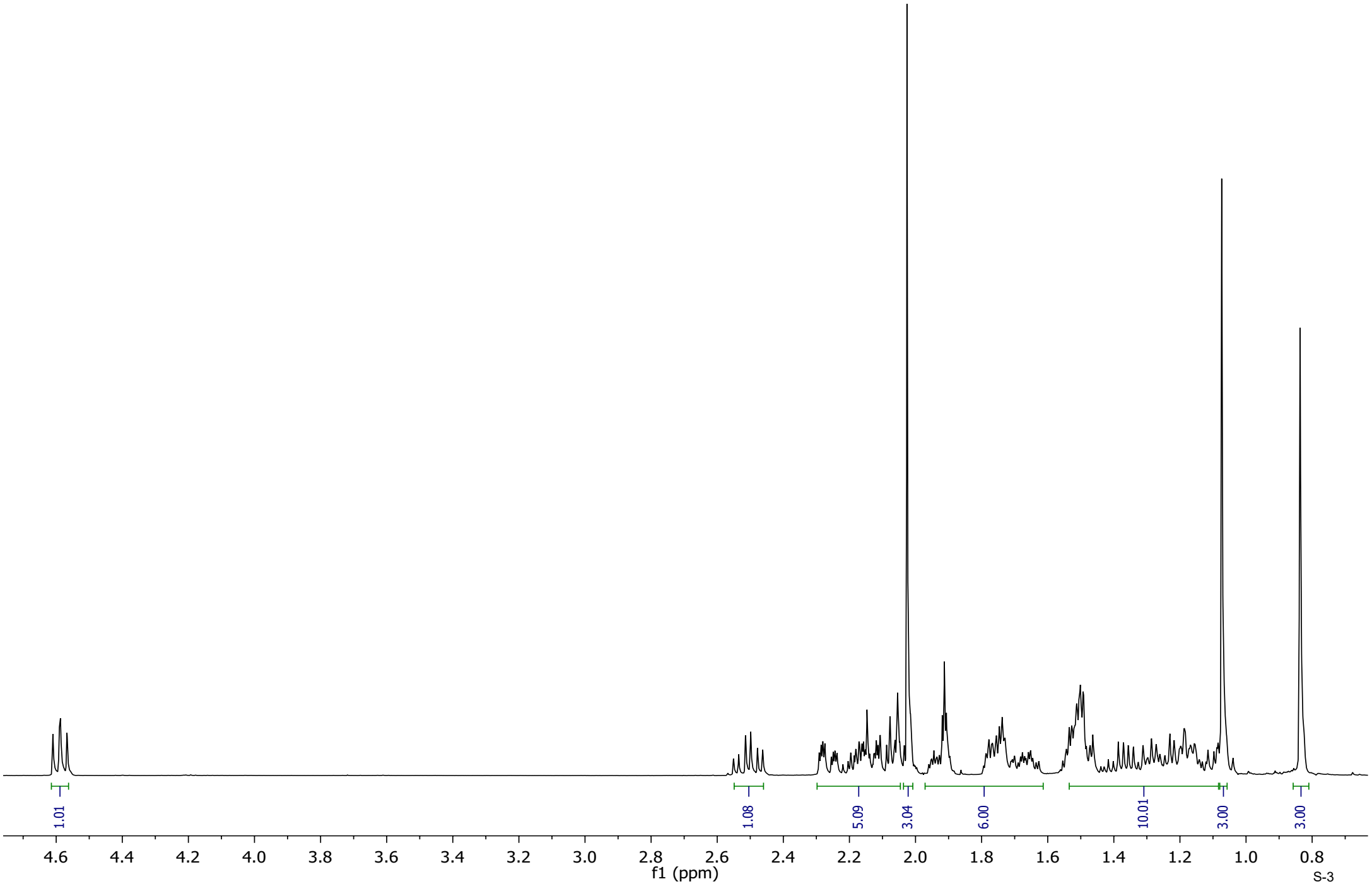
- **^{1}H and ^{13}C{^{1}H} NMR spectra**



17β-Acetoxy-4,5-secoandrost-3-yn-5-one **(11)**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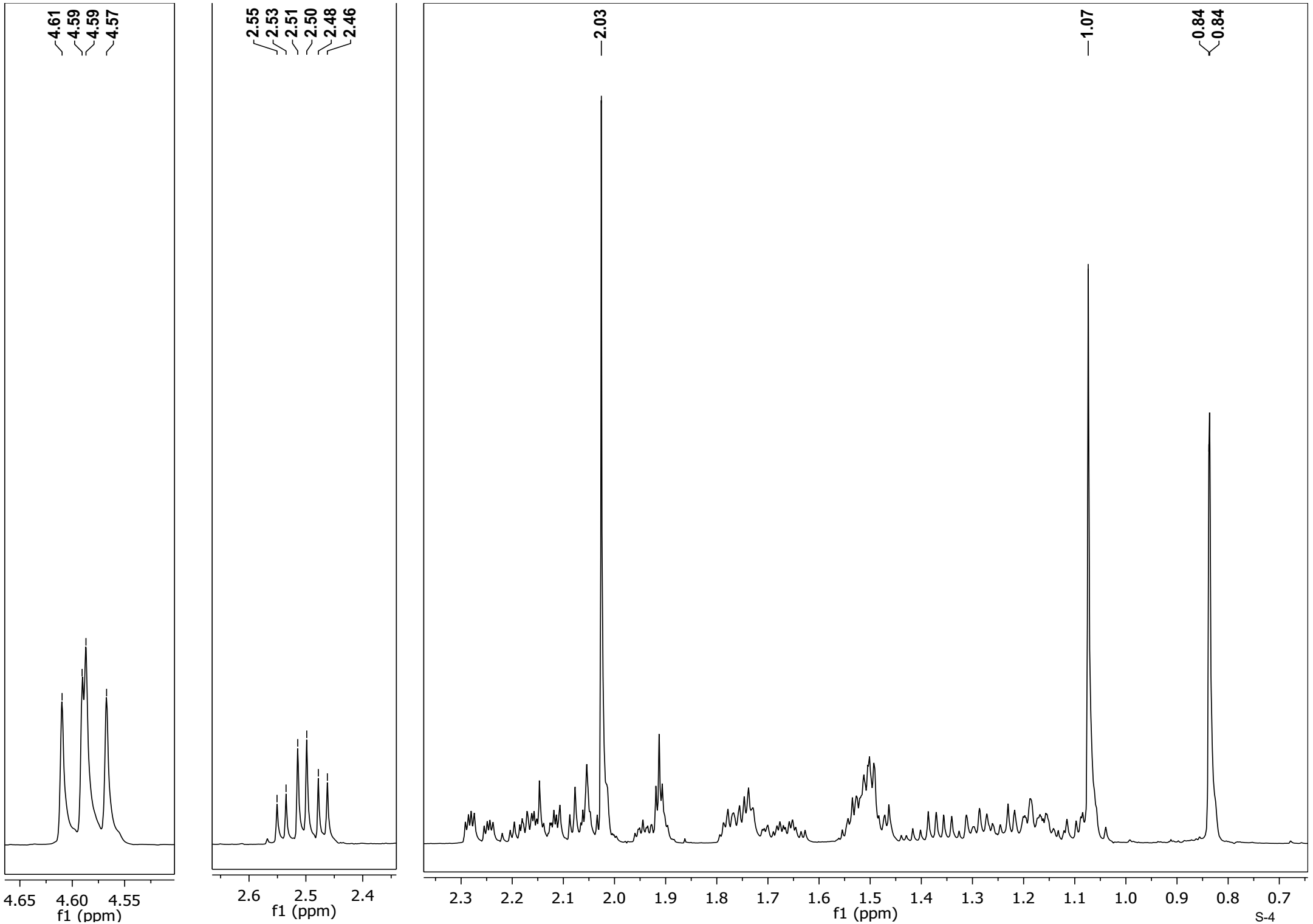
f1 (ppm)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2.4
f1 (ppm)
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2.2
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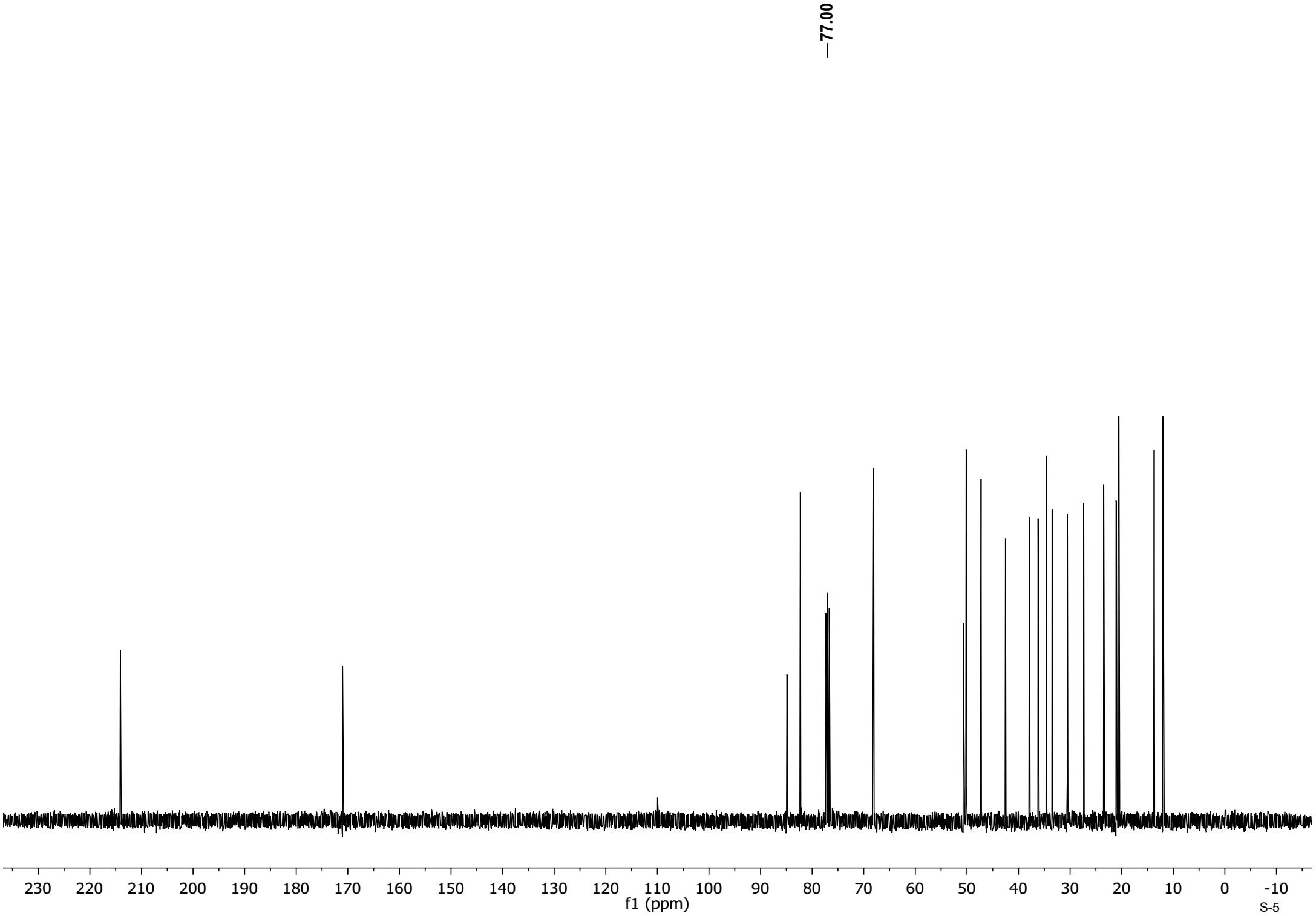
0.7
f1 (ppm)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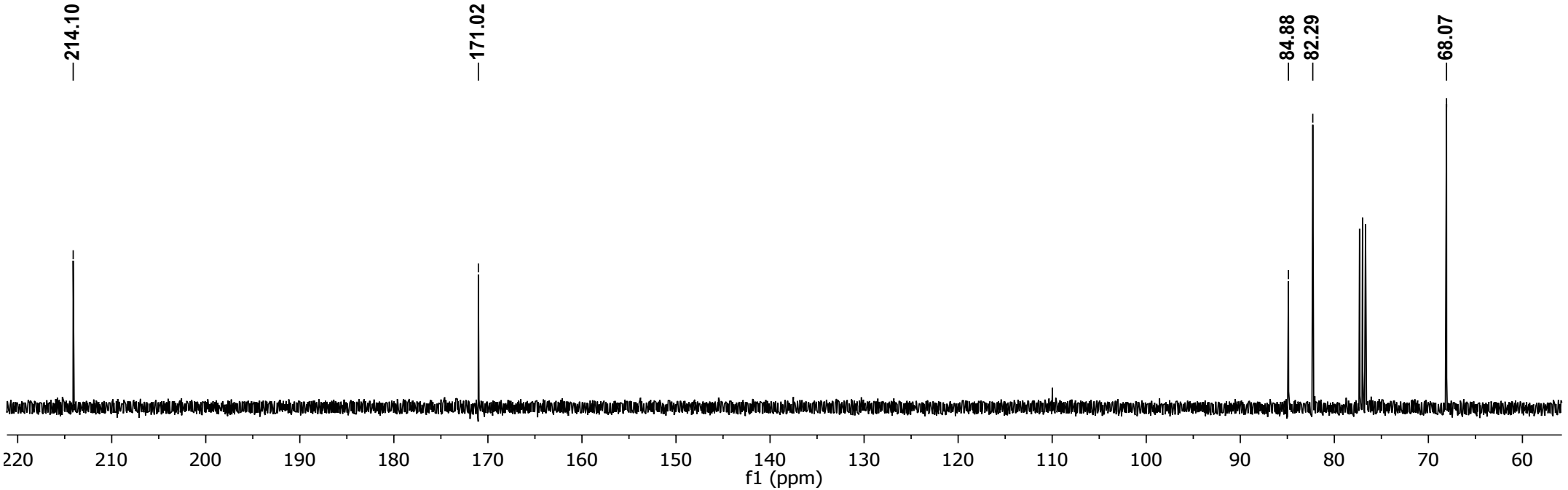
f1 (ppm)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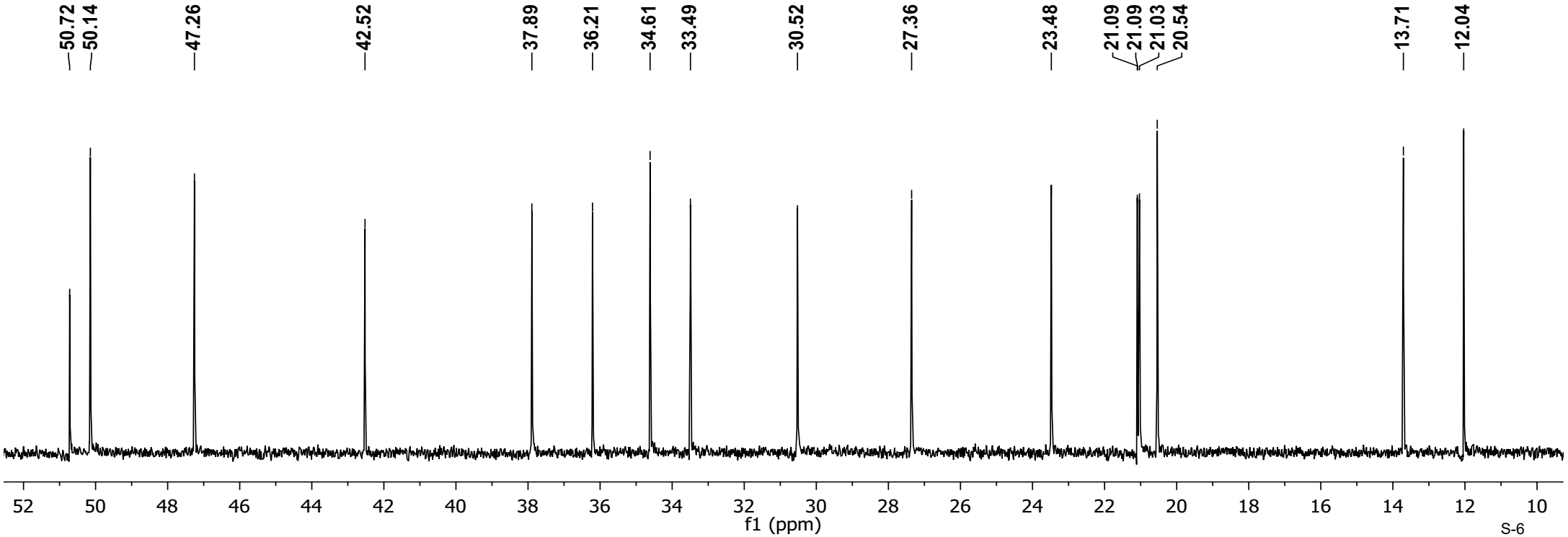
f1 (ppm)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20.54
13.71
12.04
52
50
48
46
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18
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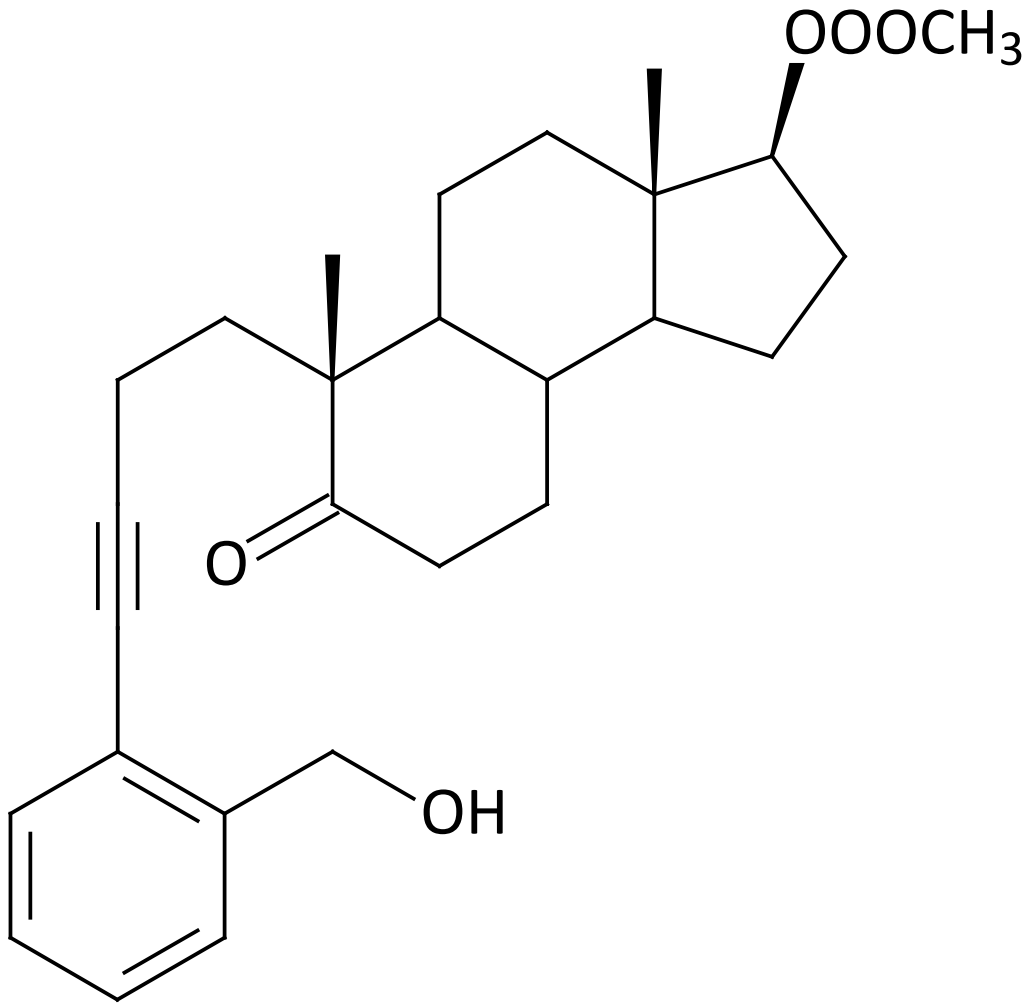
14
12
10
f1 (ppm)



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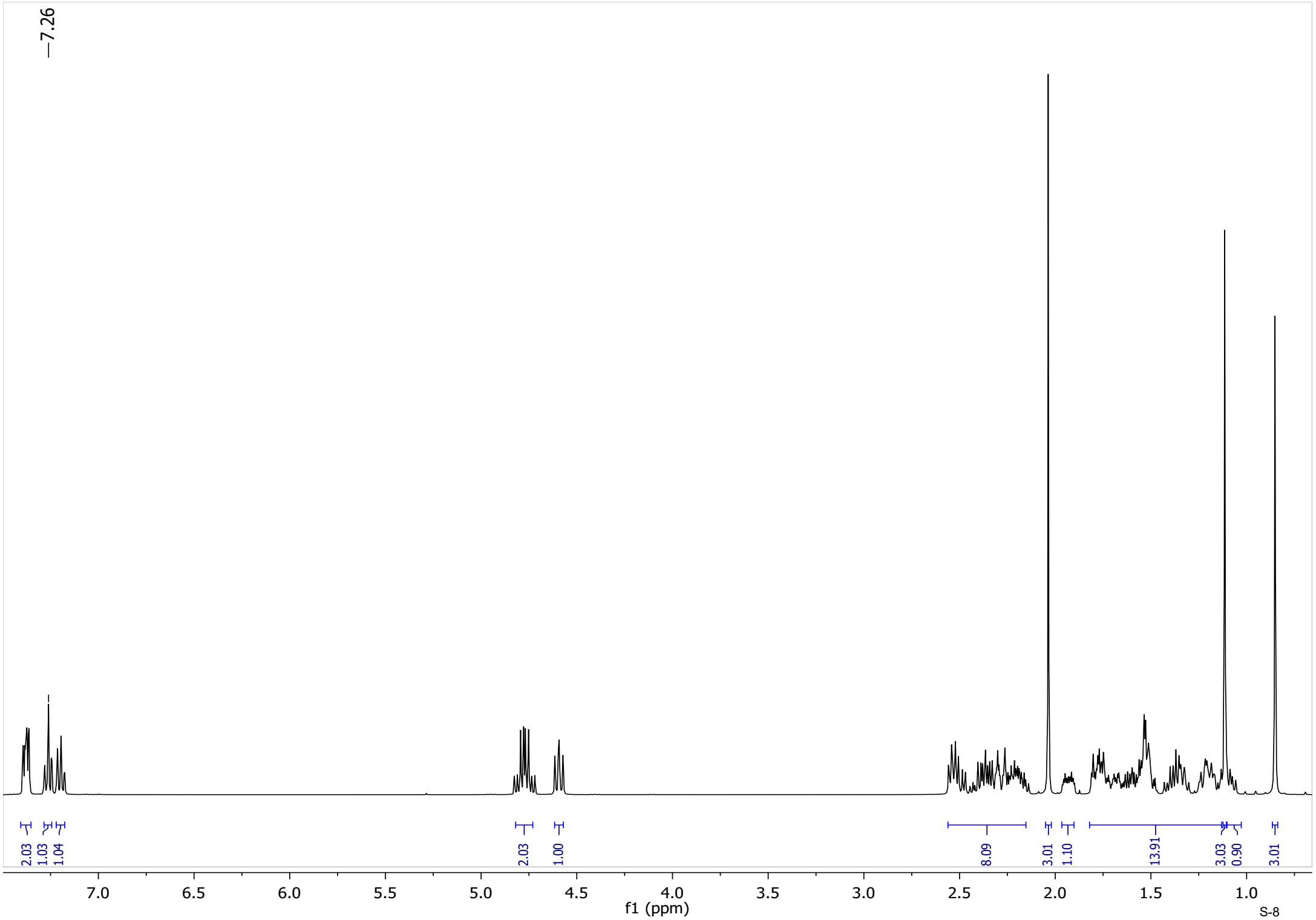
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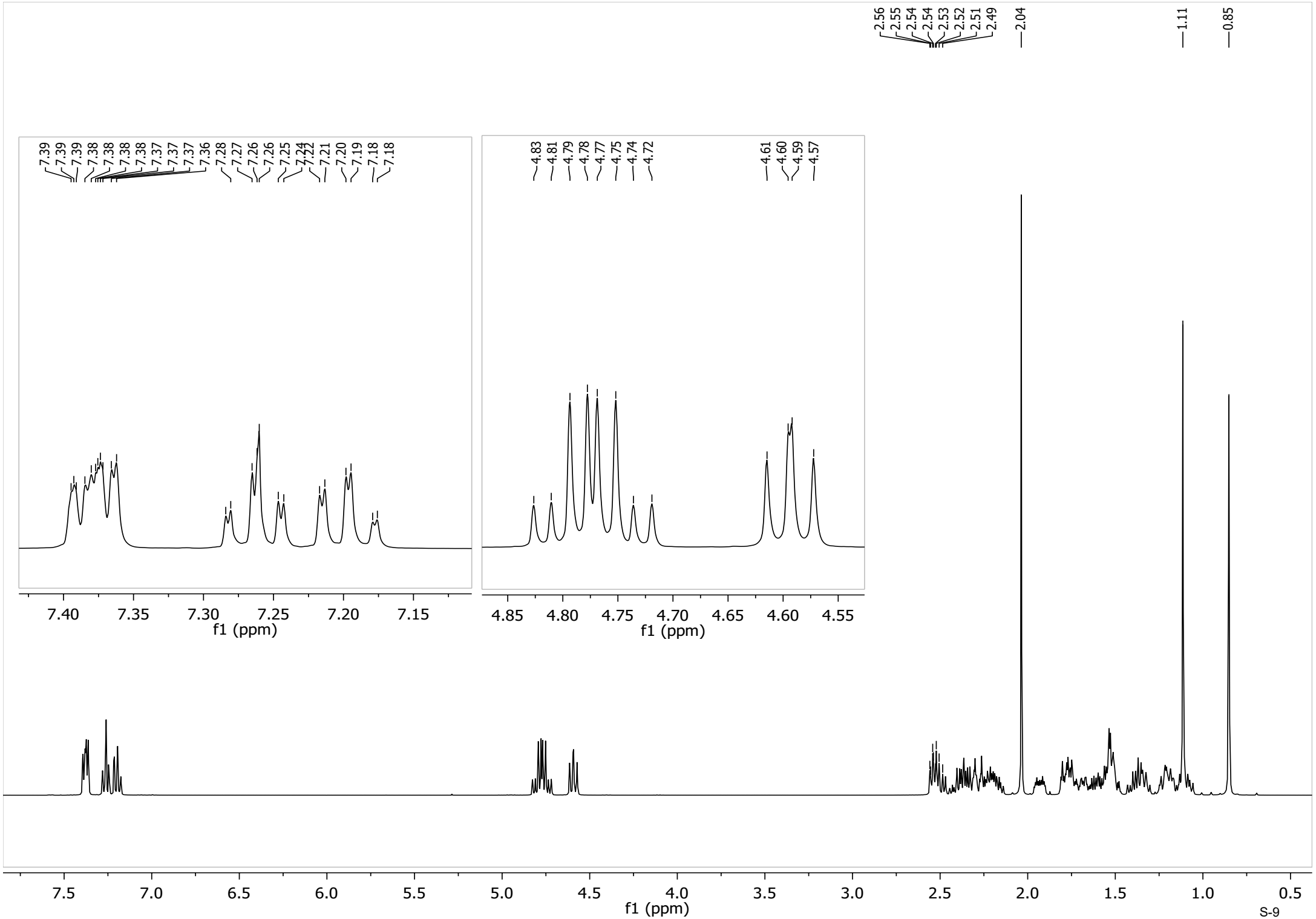
f1 (ppm)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7.38
7.38
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7.36
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7.27
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7.26
7.25
7.24
7.22
7.21
7.20
7.19
7.18
7.18
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4.79
4.78
4.77
4.75
4.74
4.72
4.61
4.60
4.59
4.57
7.40 7.35 7.30 7.25 7.20 7.15
f1 (ppm)
4.85 4.80 4.75 4.70 4.65 4.60 4.55
f1 (ppm)
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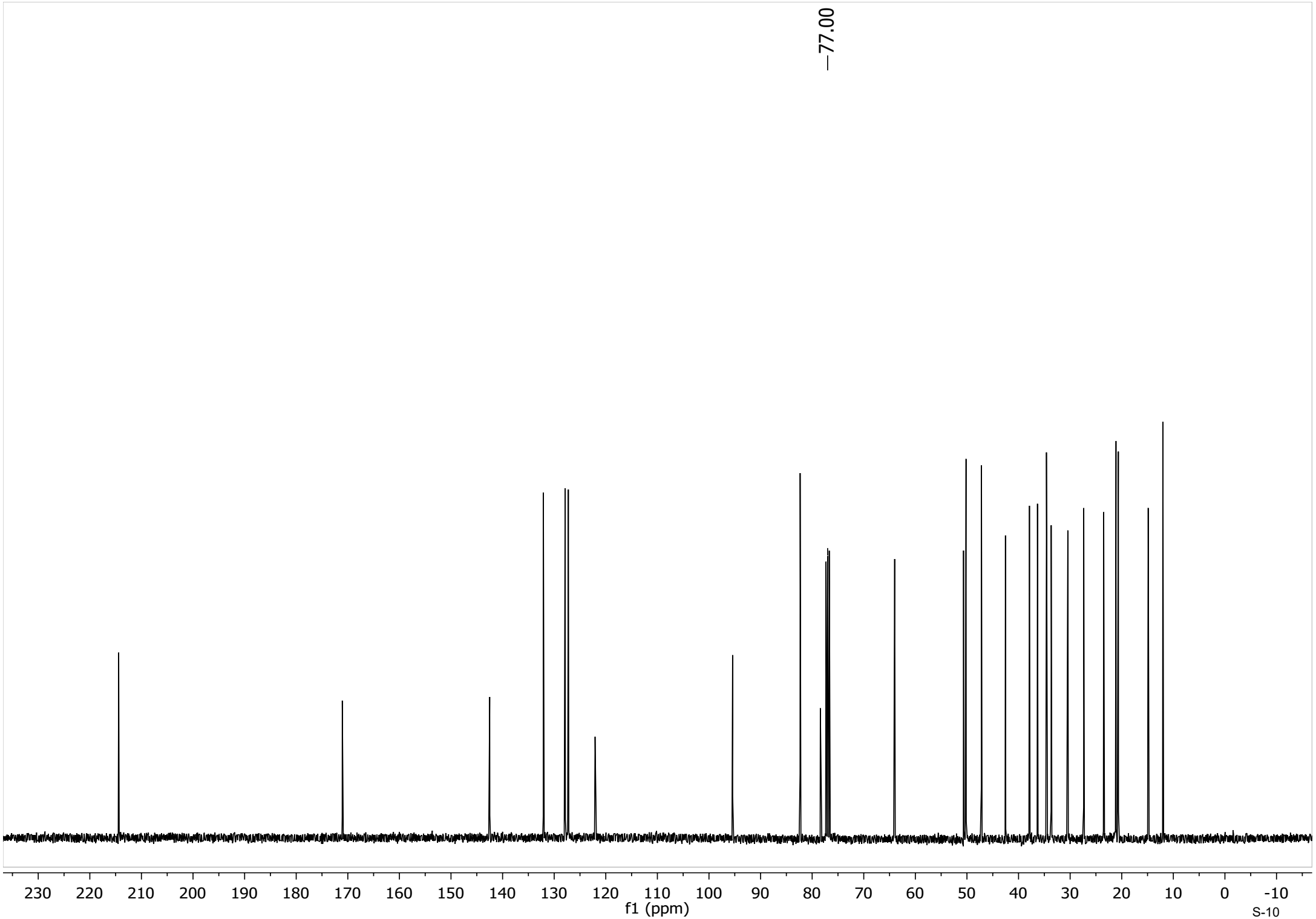
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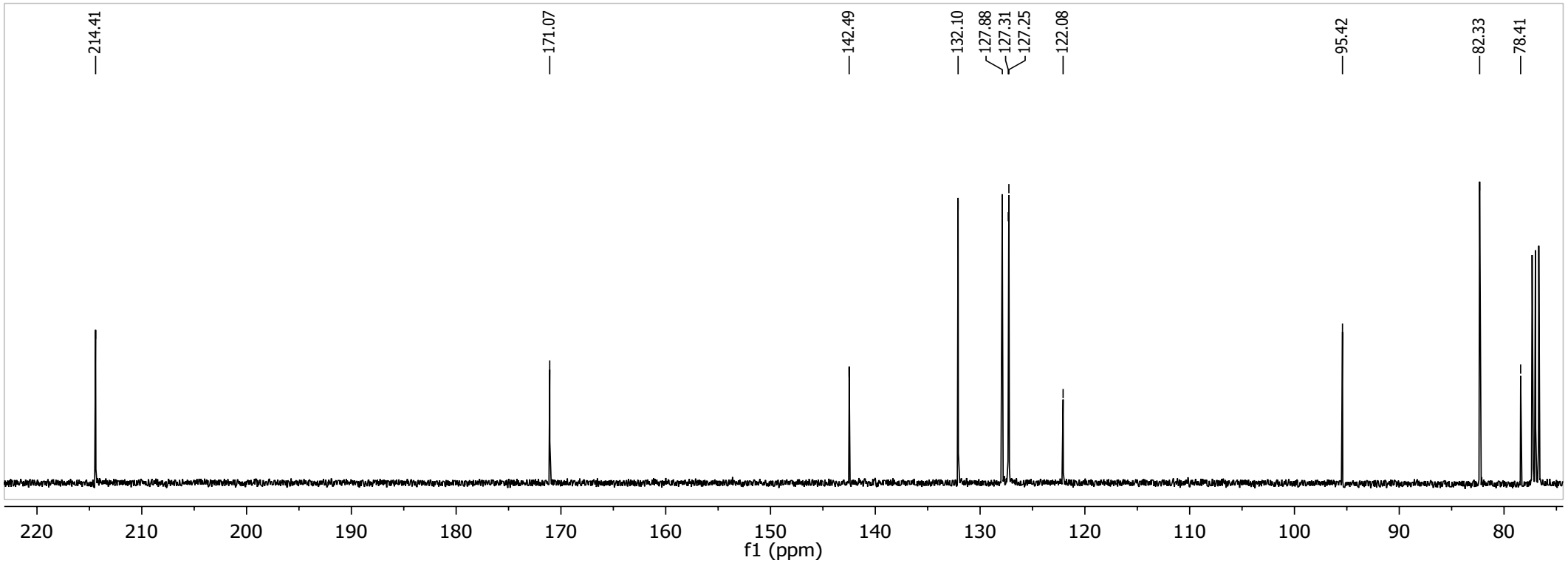
f1 (ppm)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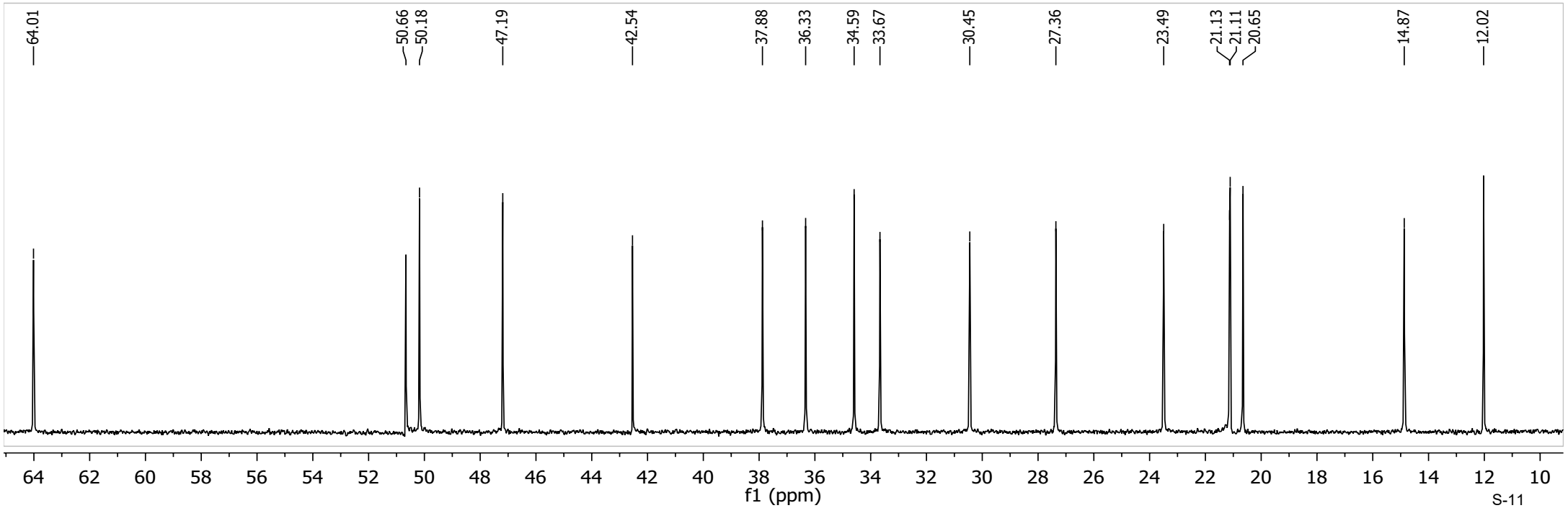
f1 (ppm)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60
58
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52
50
48
46
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12
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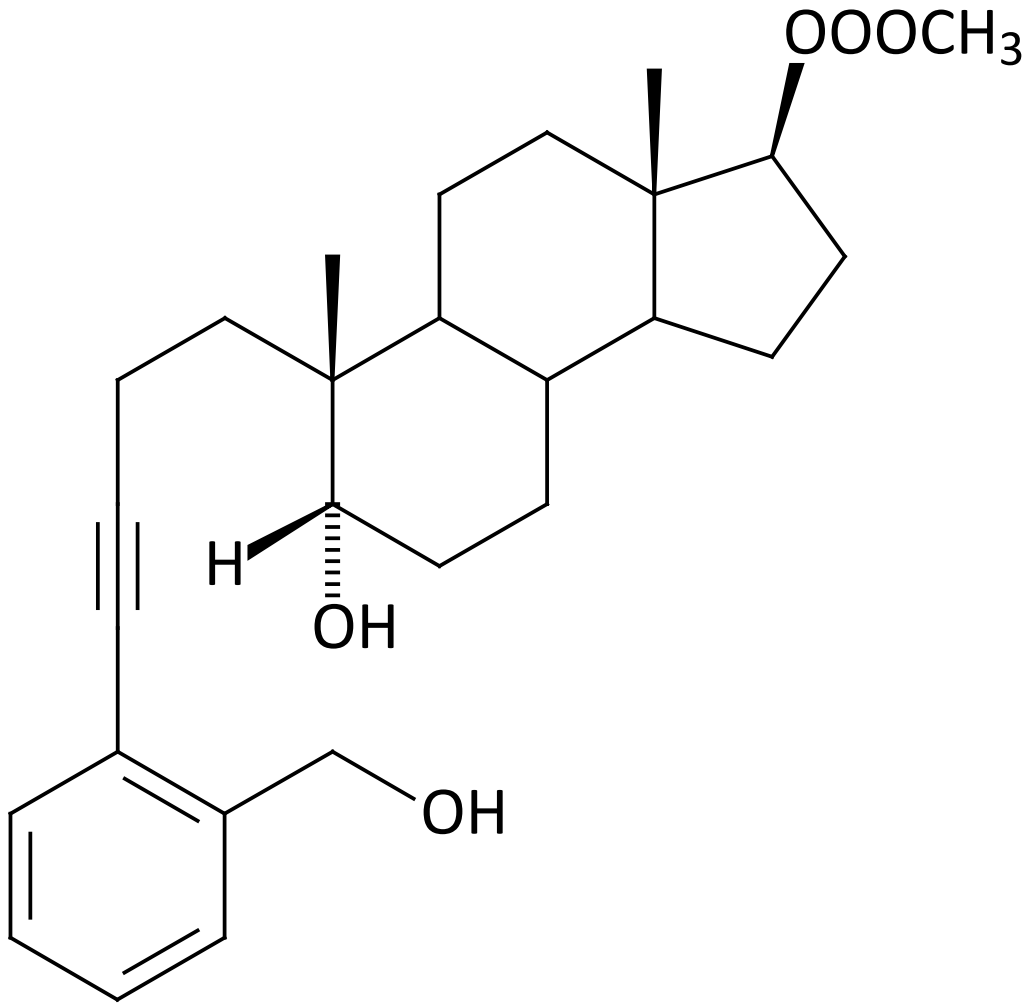
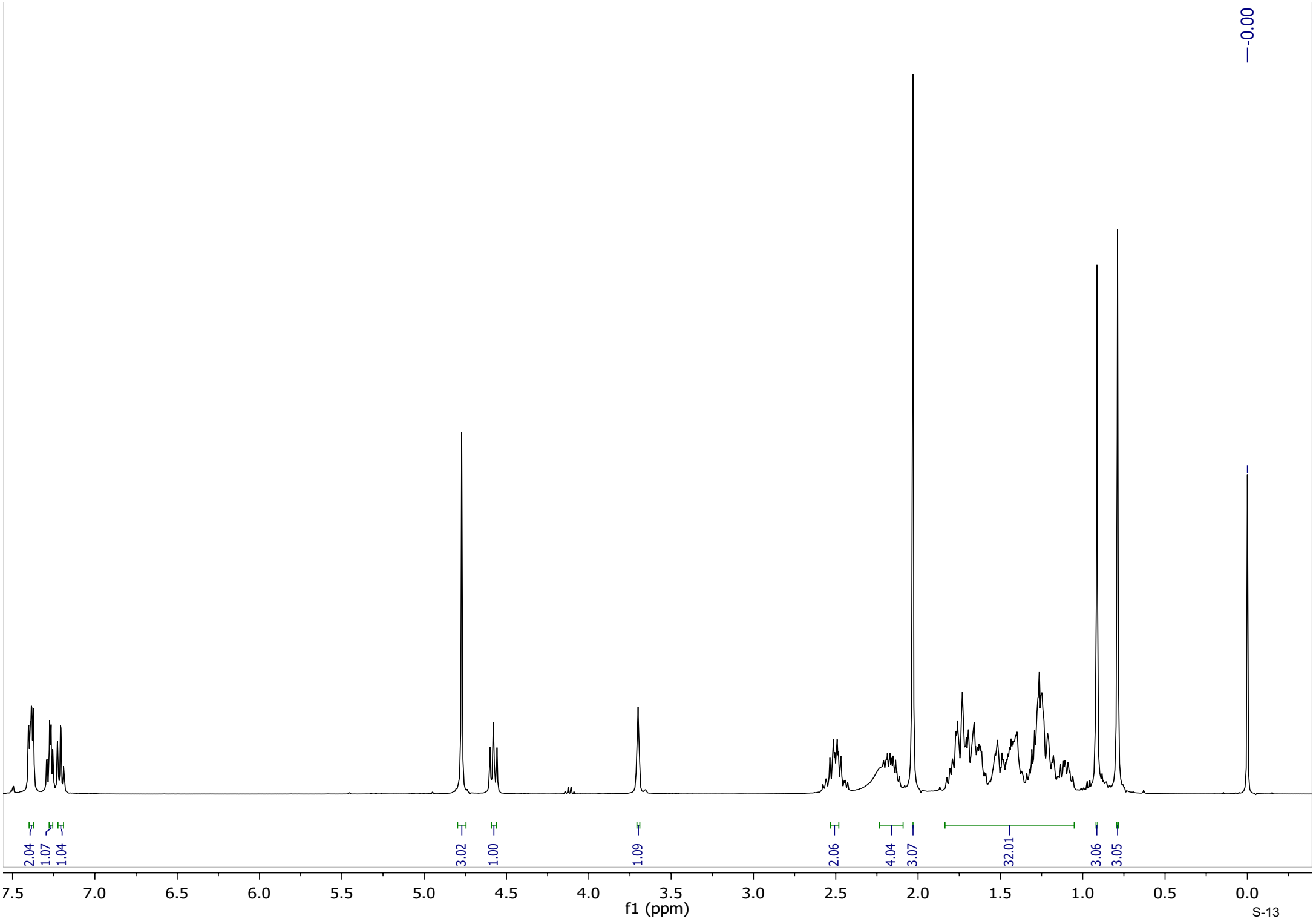
f1 (ppm)



4-(2´-(hydroxymethyl)phenyl)-4,5-secoandrost-3-yn-5α,17β-diol 17-monoacetate (13a)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6.5
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2.0
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1.0
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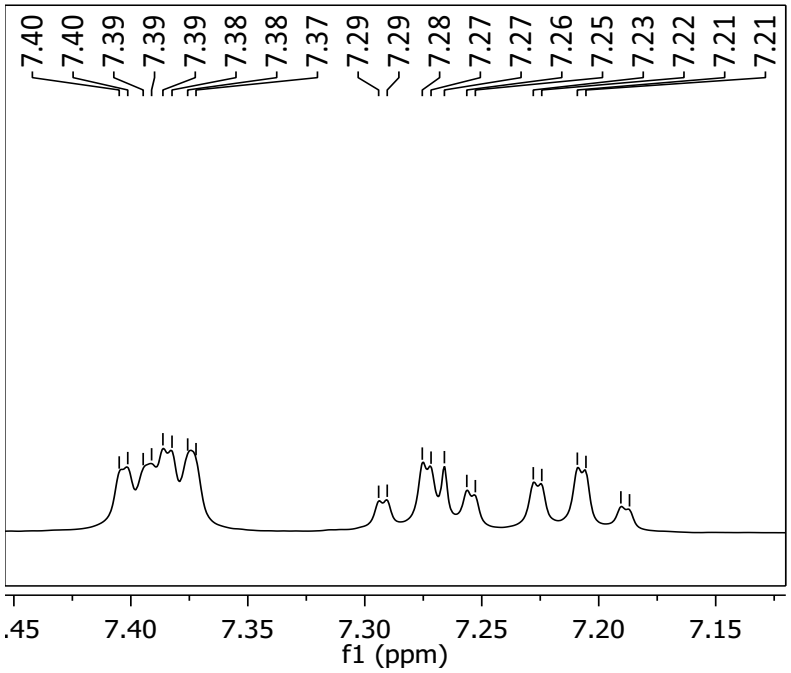
0.0
f1 (ppm)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7.27
7.26
7.25
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7.25
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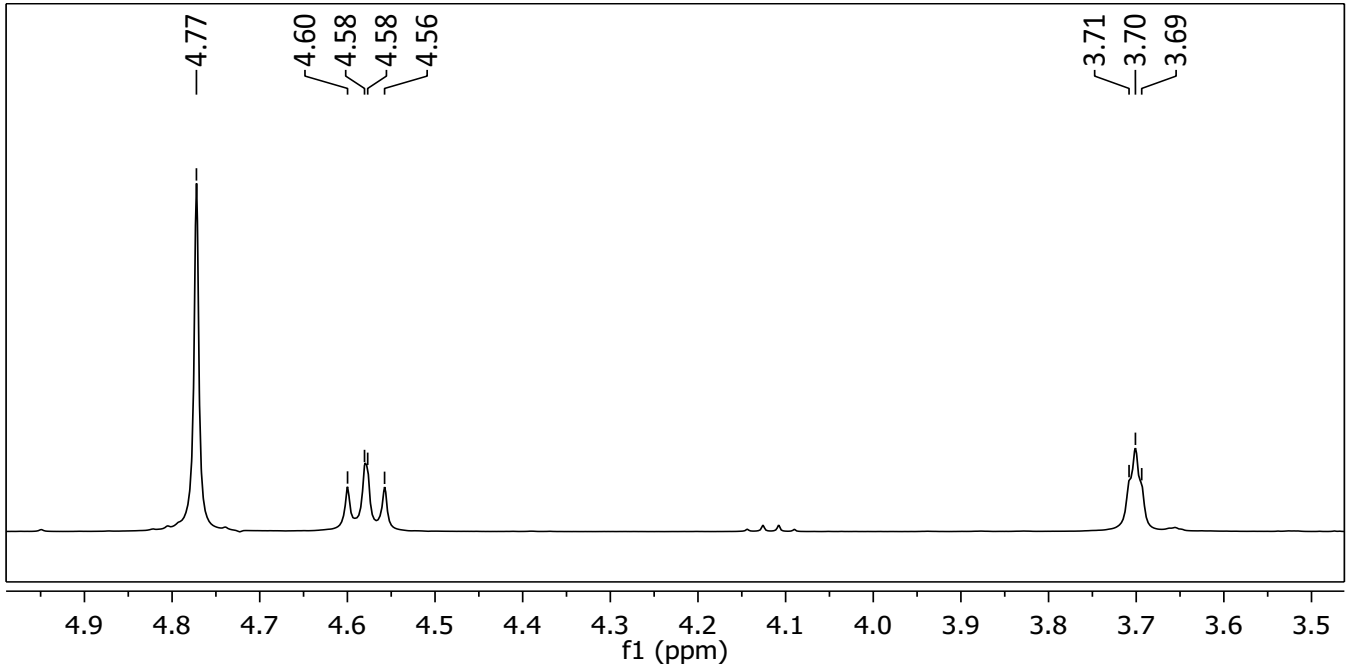
f1 (ppm)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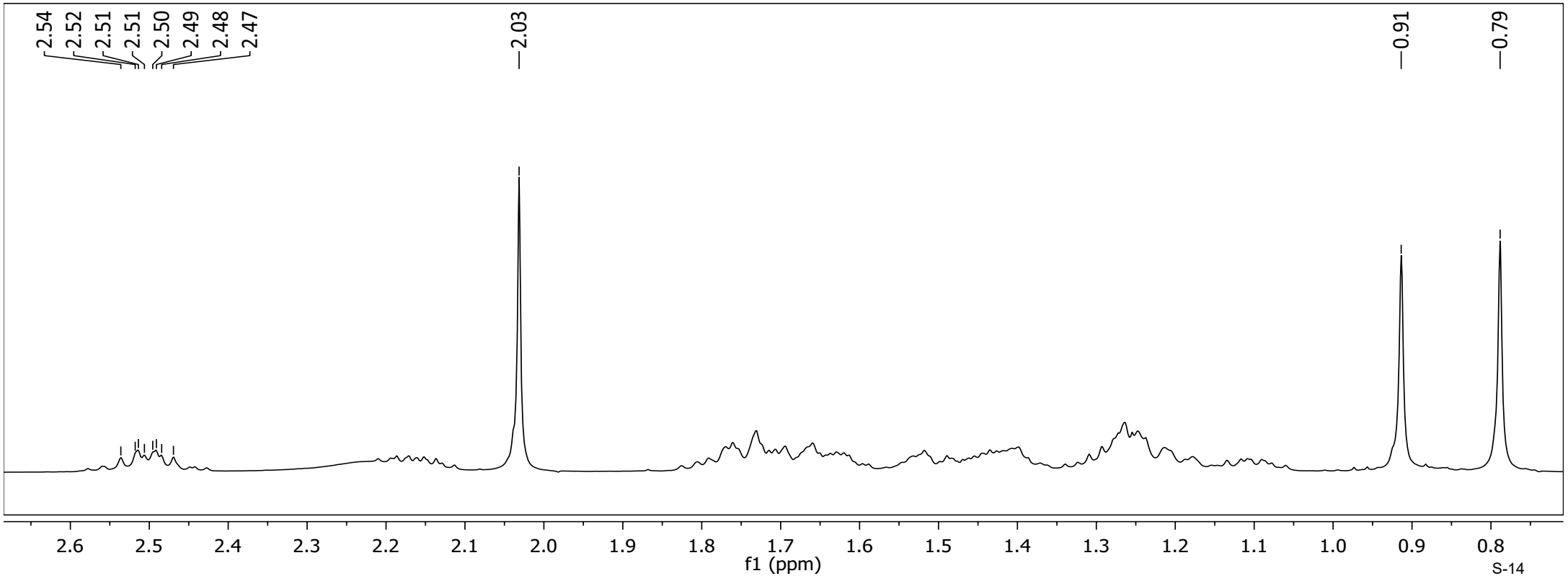
3.9
3.8
3.7
3.6
3.5
f1 (ppm)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2.4
2.3
2.2
2.1
2.0
1.9
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1.2
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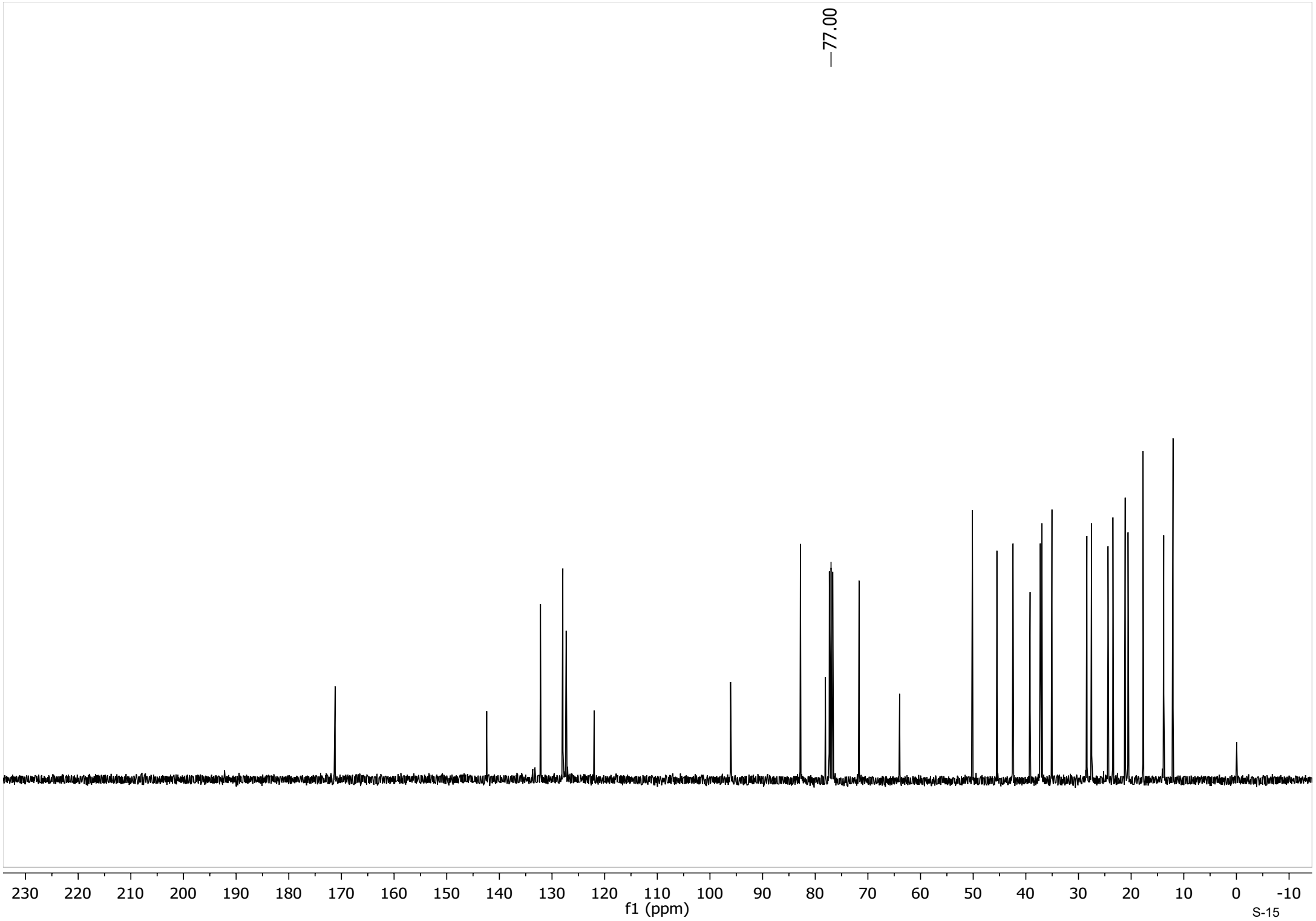
f1 (ppm)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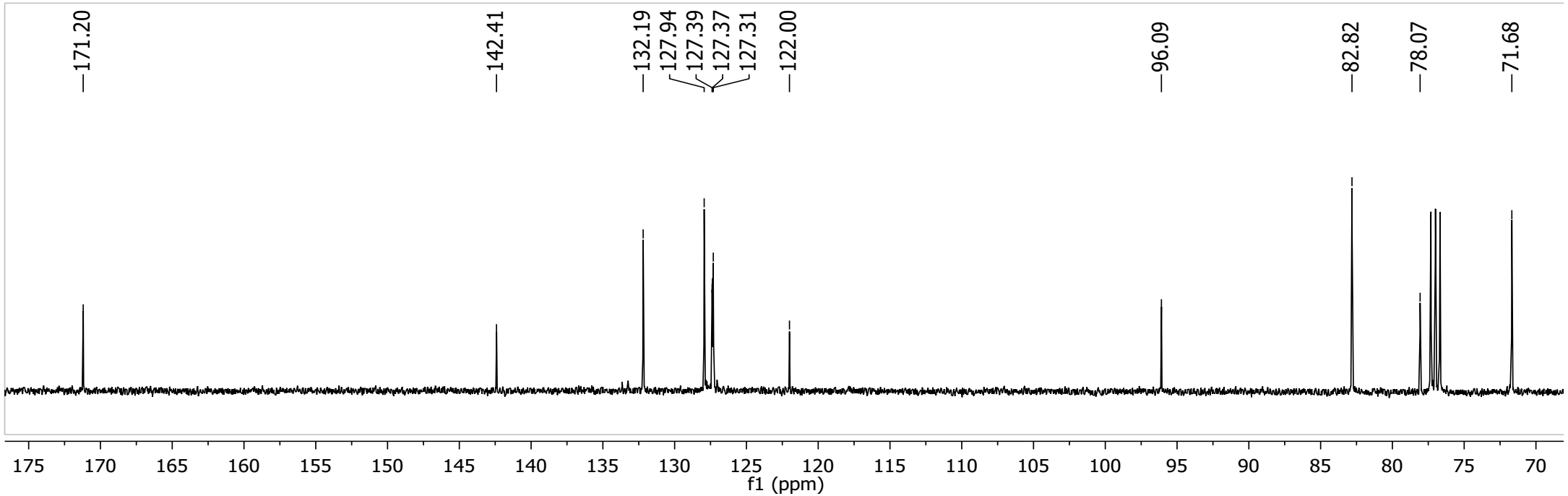
40
30
20
10
0
-10
f1 (ppm)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132.19
127.94
127.39
127.37
127.31
122.00
96.09
82.82
78.07
71.68
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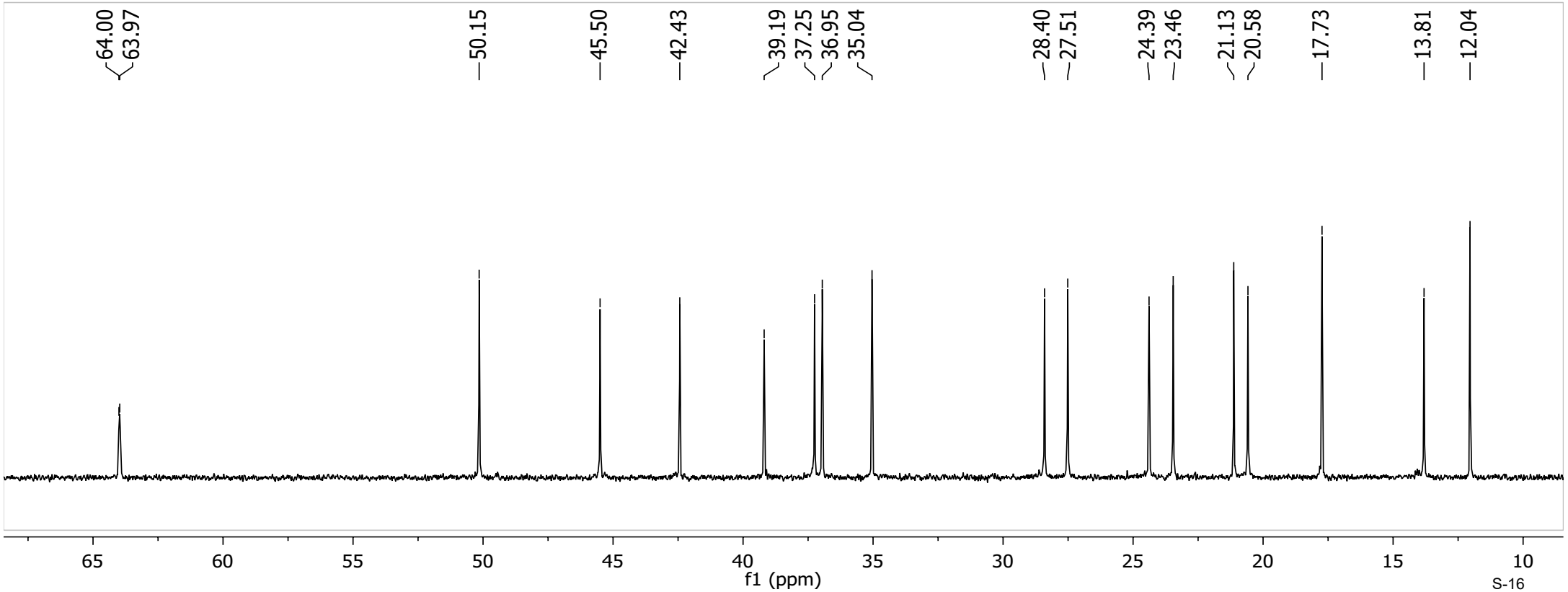
f1 (ppm)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12.04
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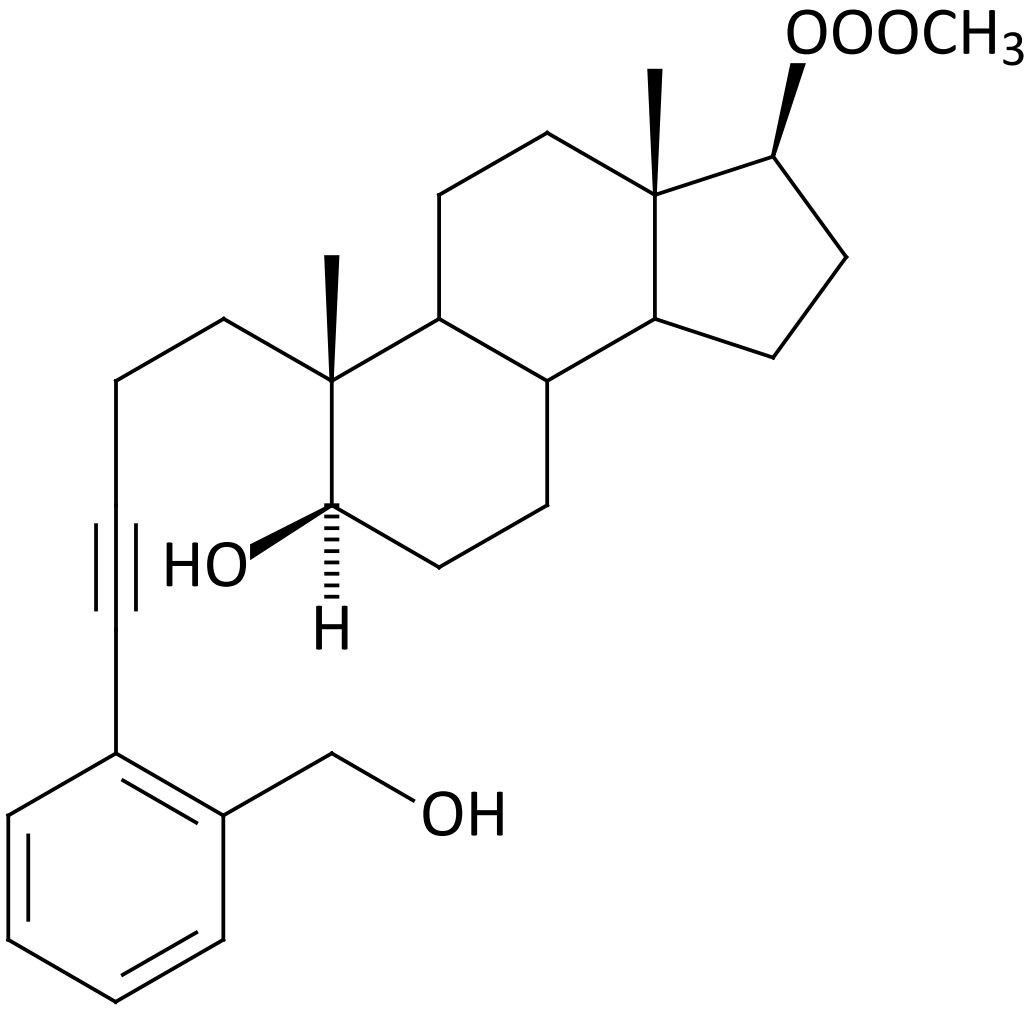
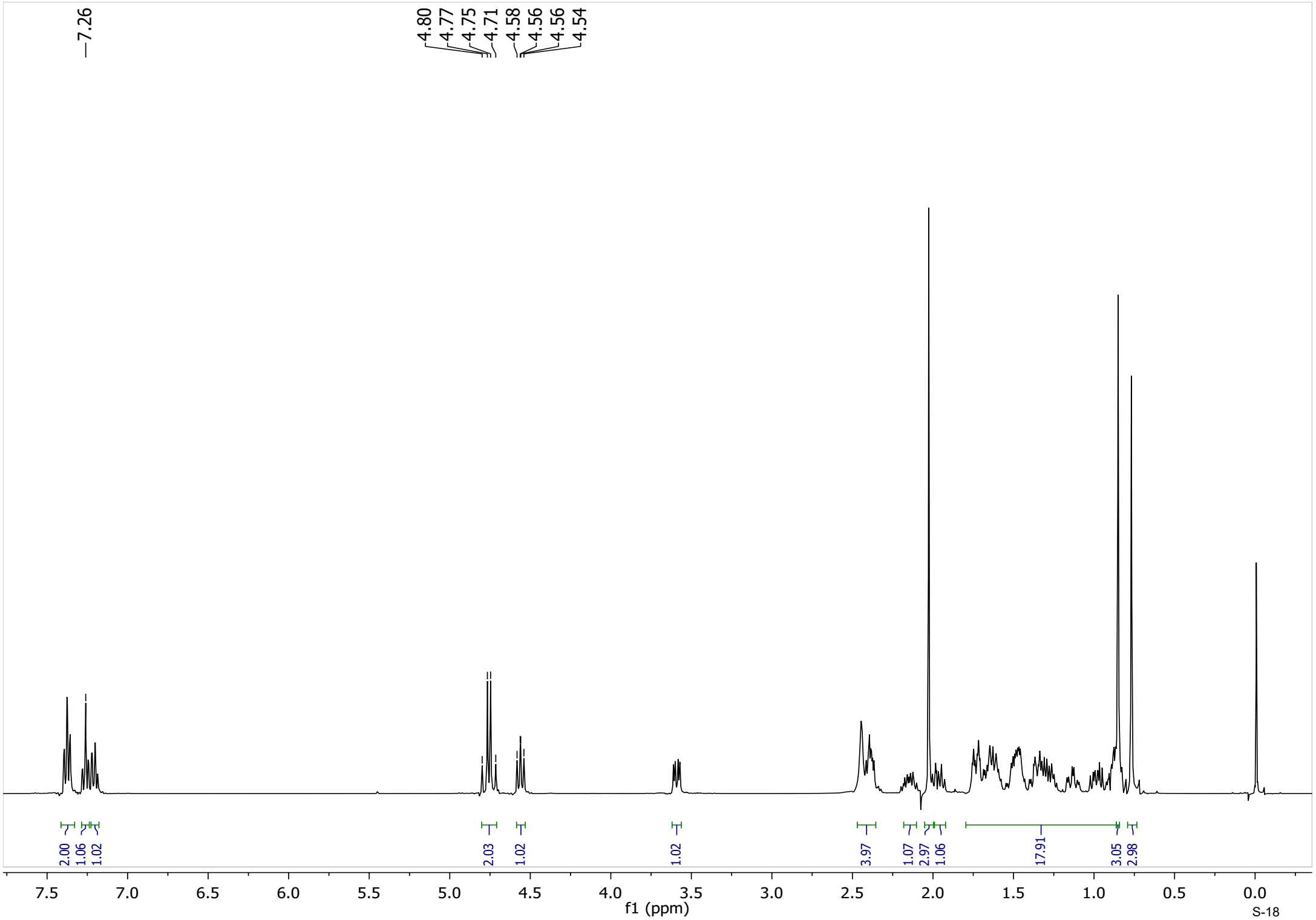


4-(2´-(hydroxymethyl)phenyl)-4,5-secoandrost-3-yn-5β,17β-diol 17-monoacetate (13b)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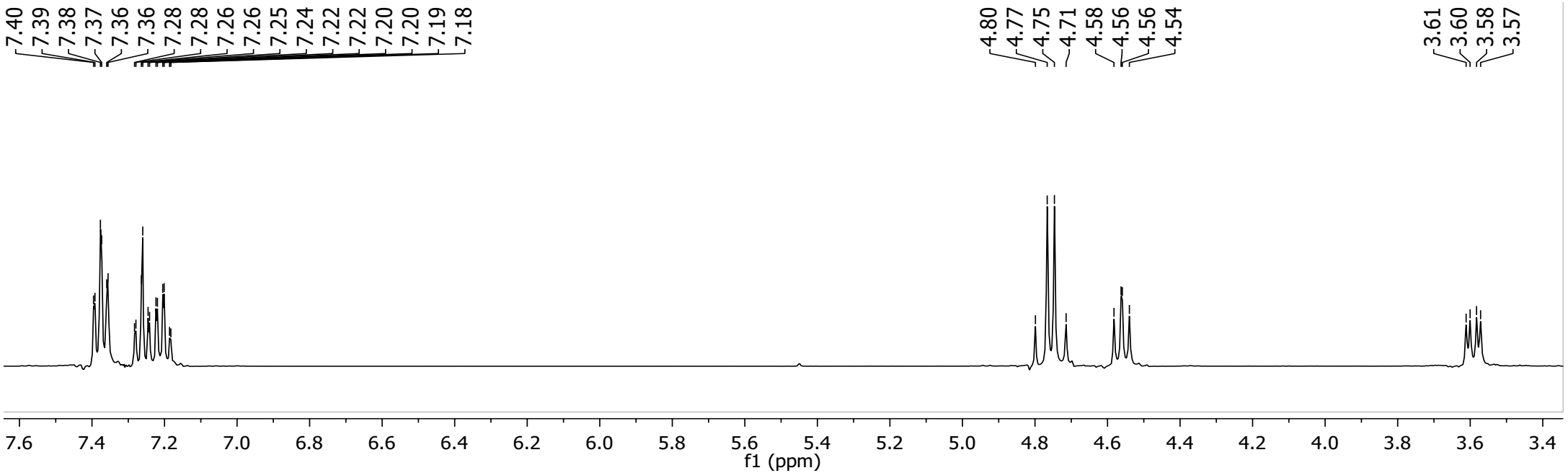
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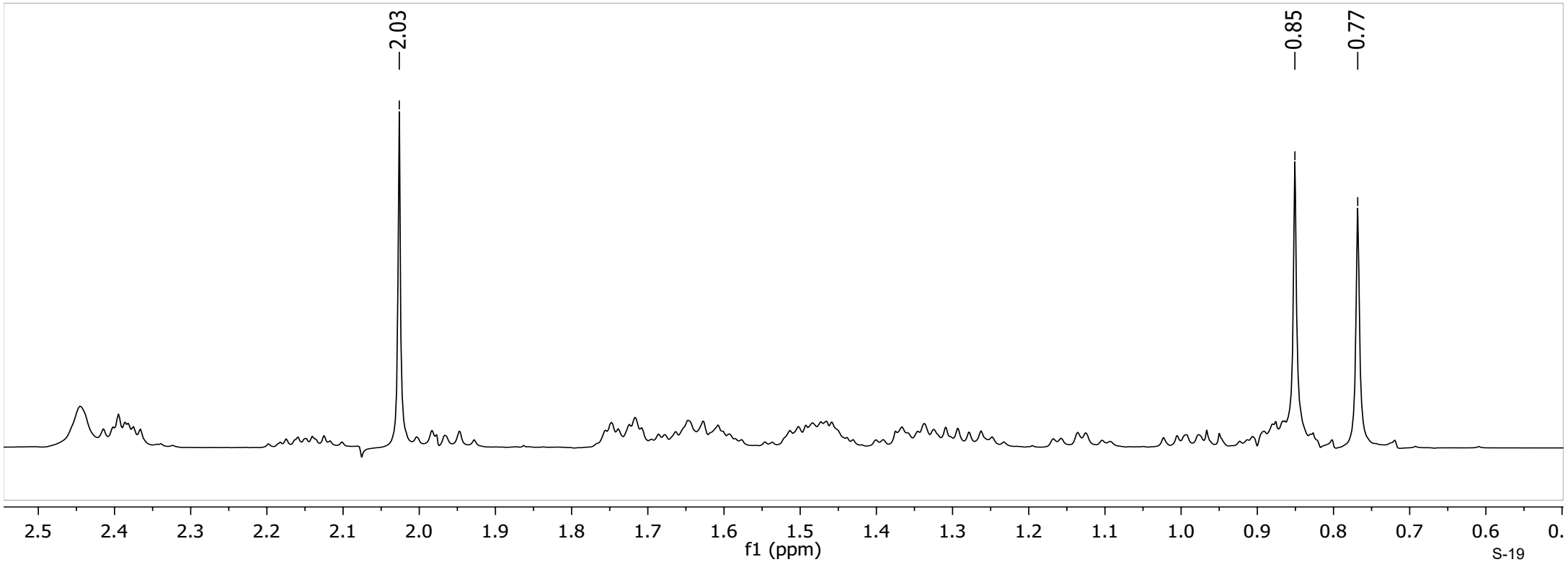
7.22
7.20
7.20
7.19
7.18
4.80
4.77
4.75
4.71
4.58
4.56
4.56
4.54
3.61
3.60
3.58
3.57
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4
f1 (ppm)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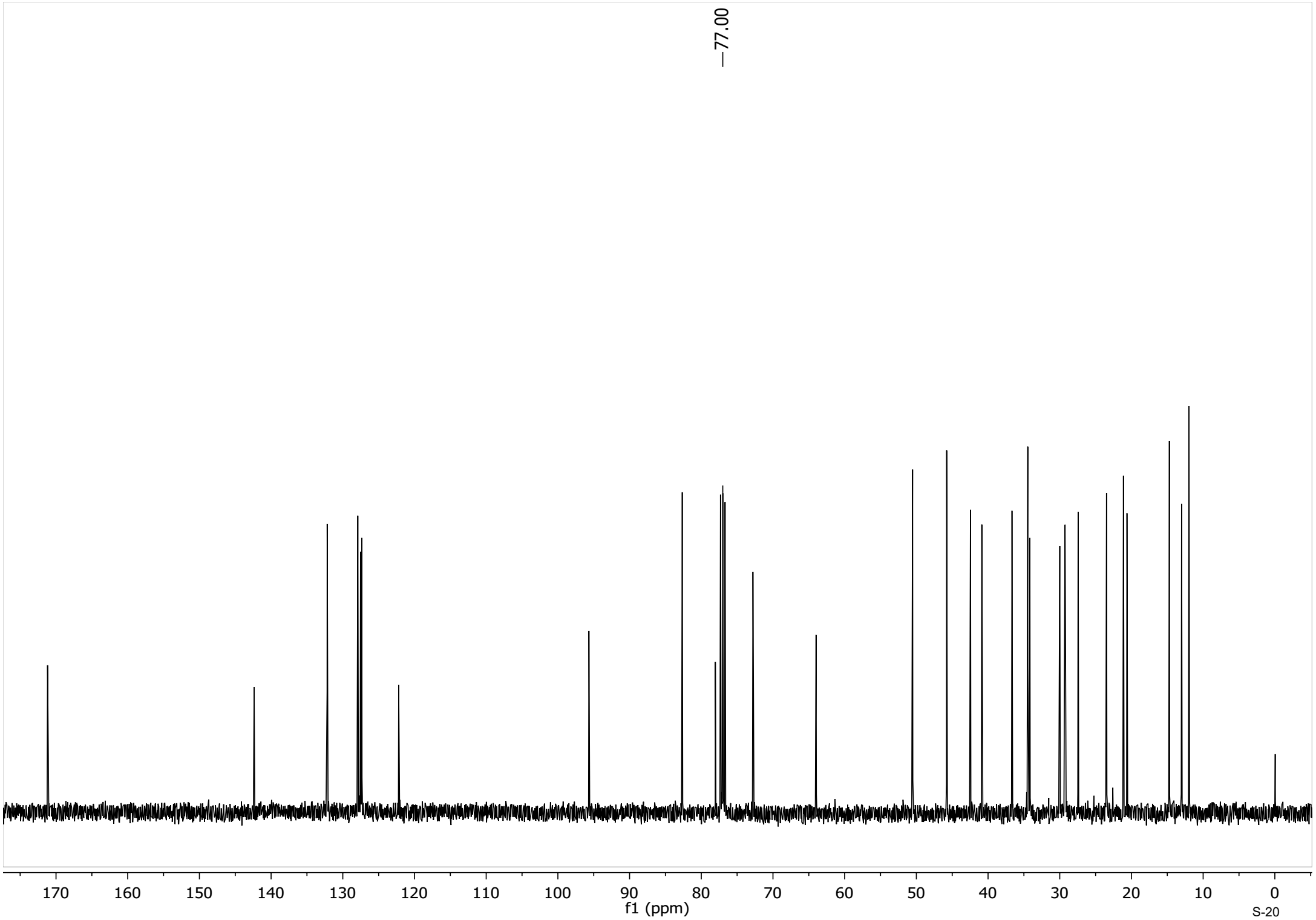
f1 (ppm)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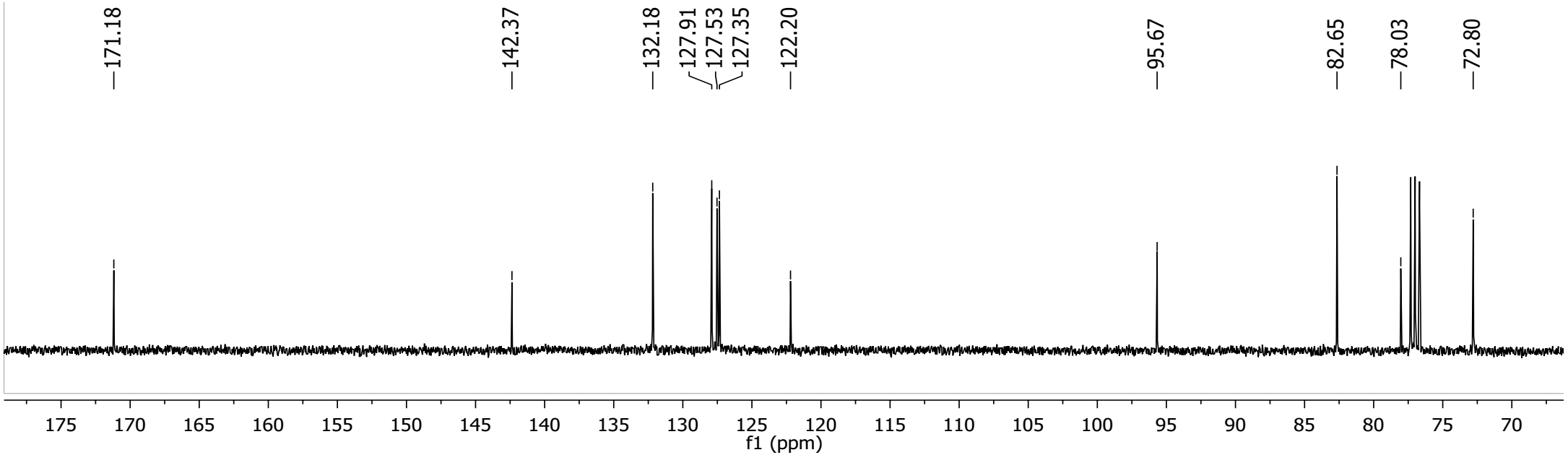
0
f1 (ppm)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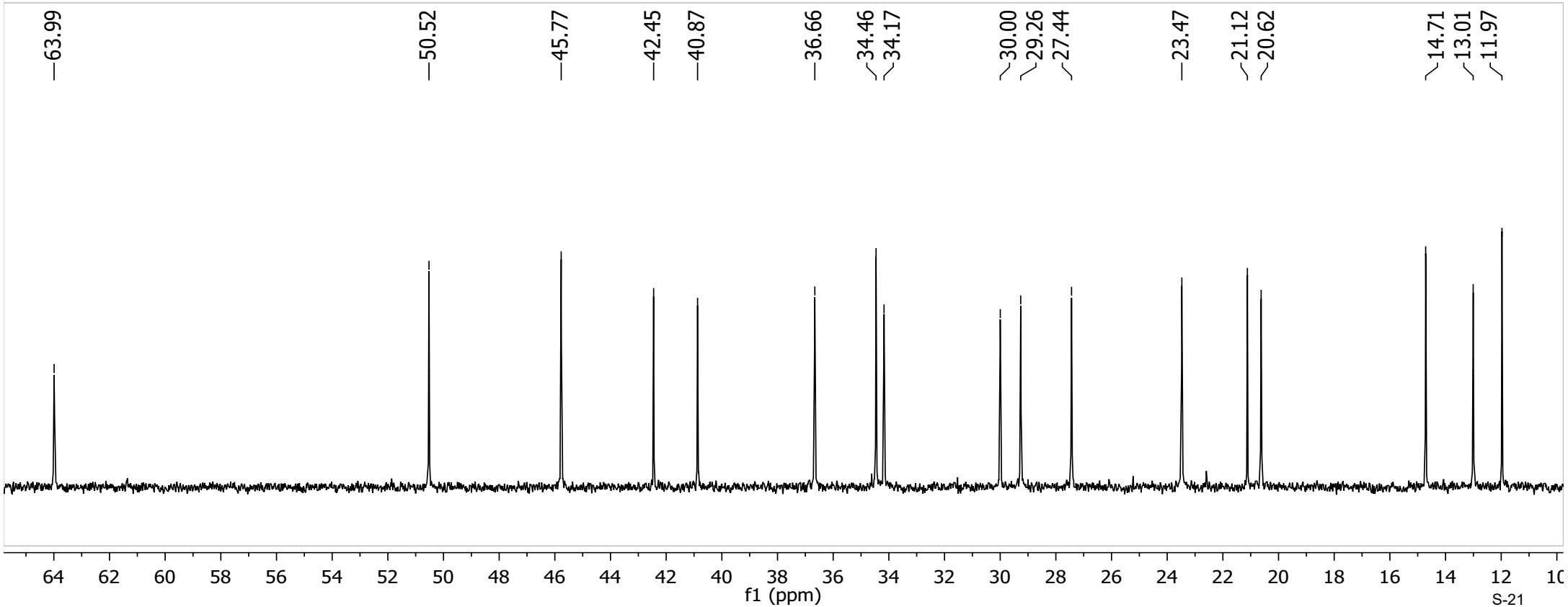
f1 (ppm)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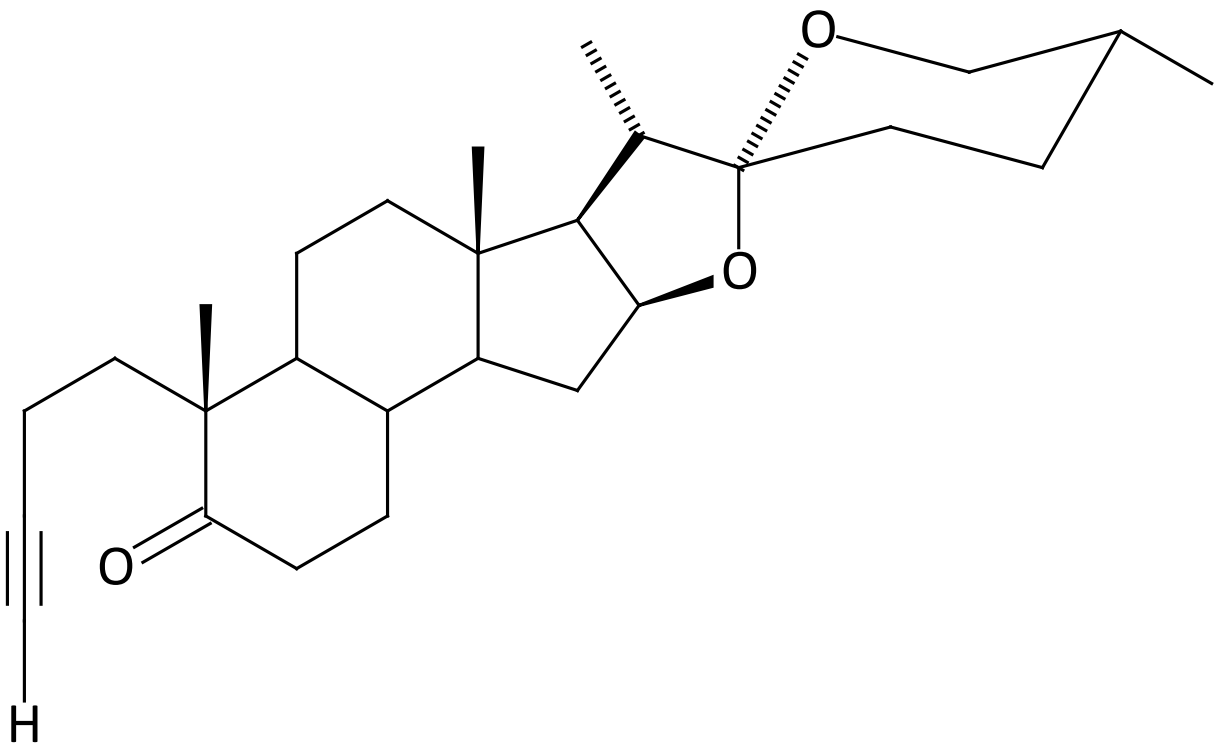
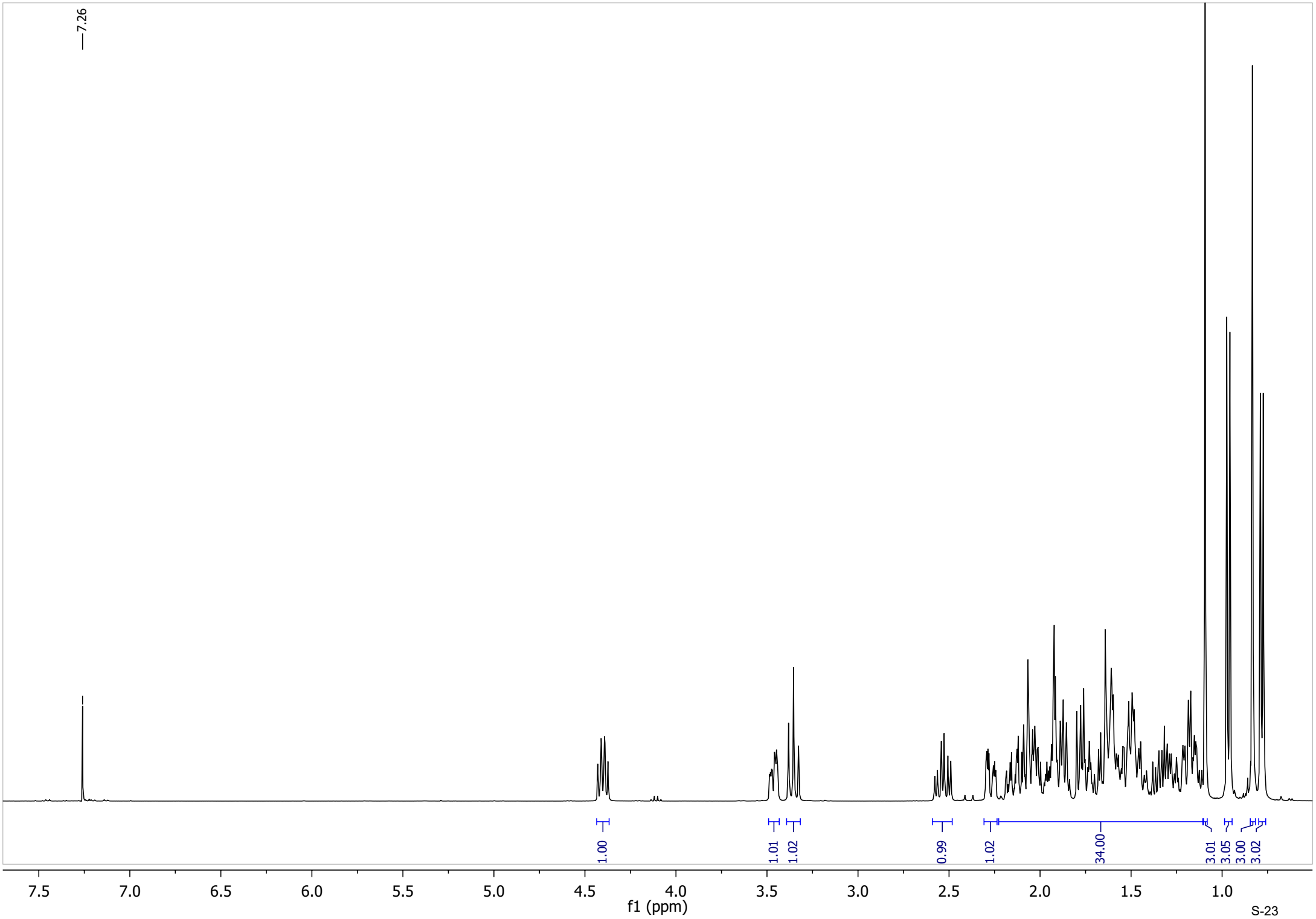


(25*R*)-4,5-secospiros-3-yn-5-one **(15)**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6.5
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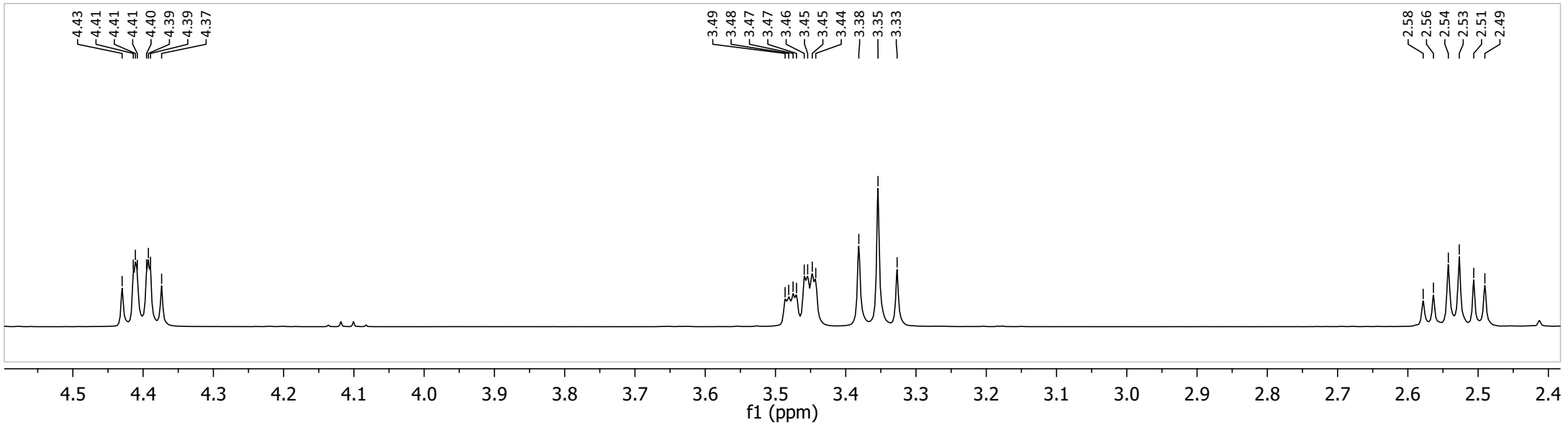
1.0
f1 (ppm)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2.6
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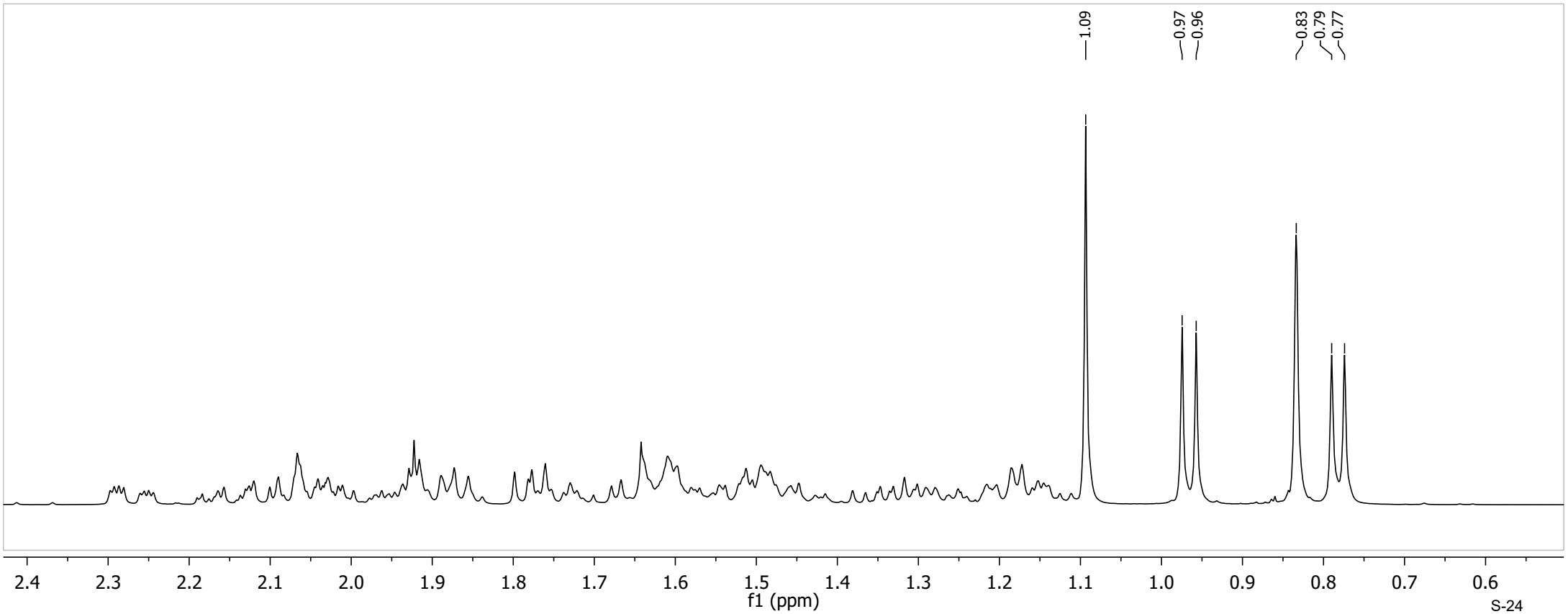
f1 (ppm)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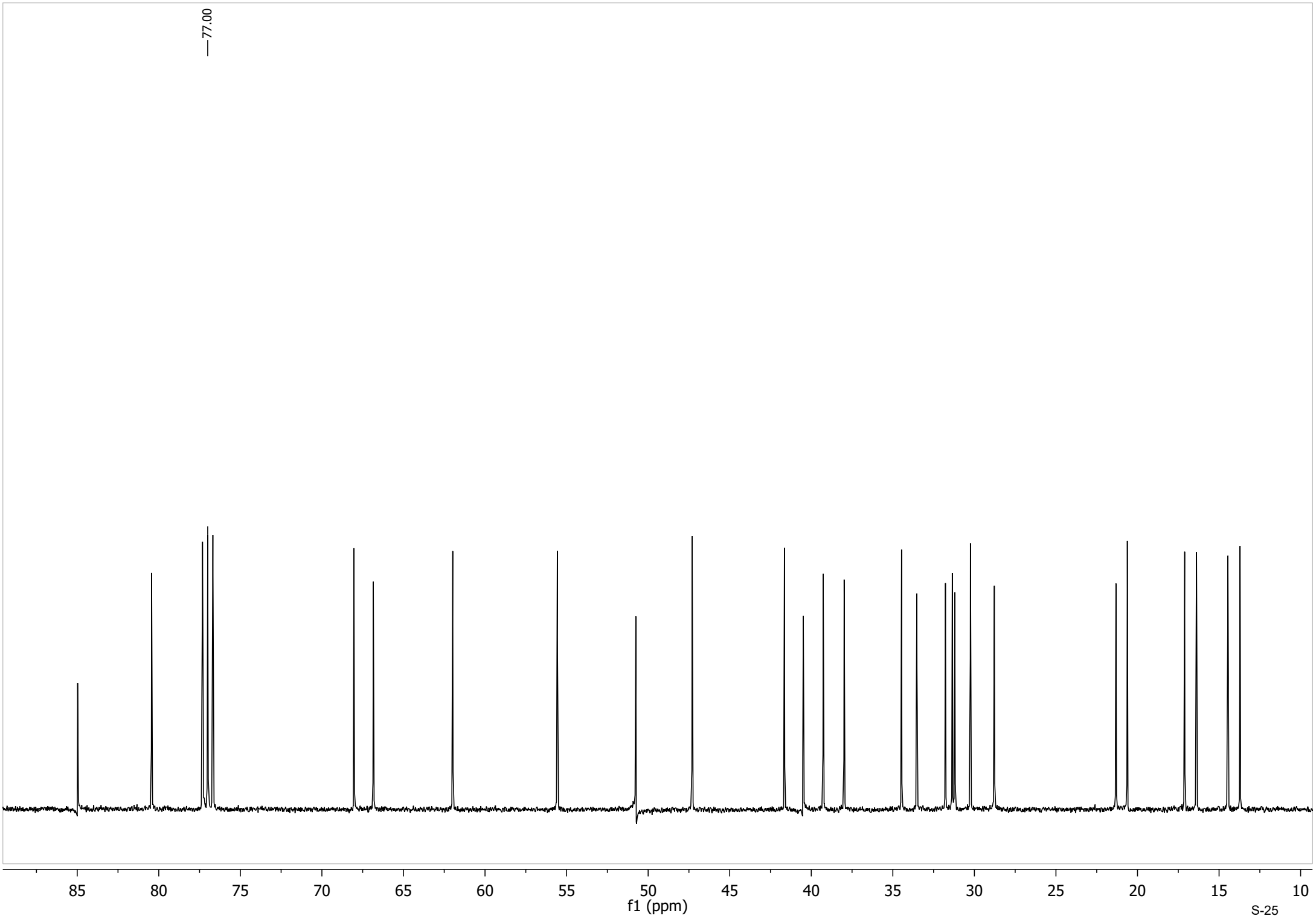
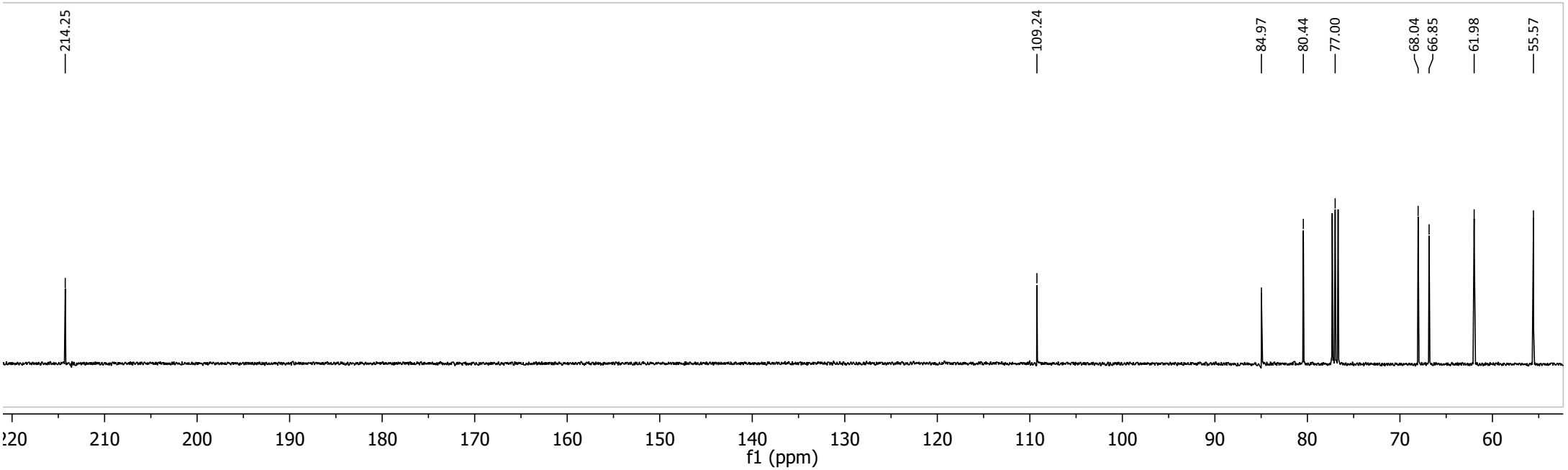
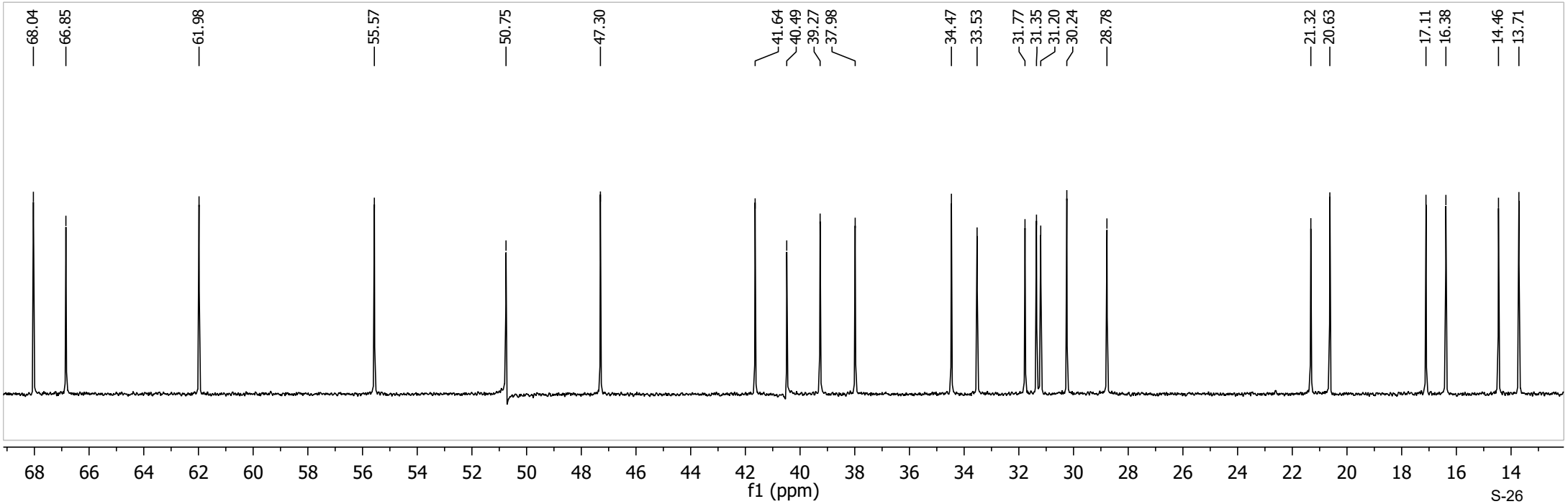
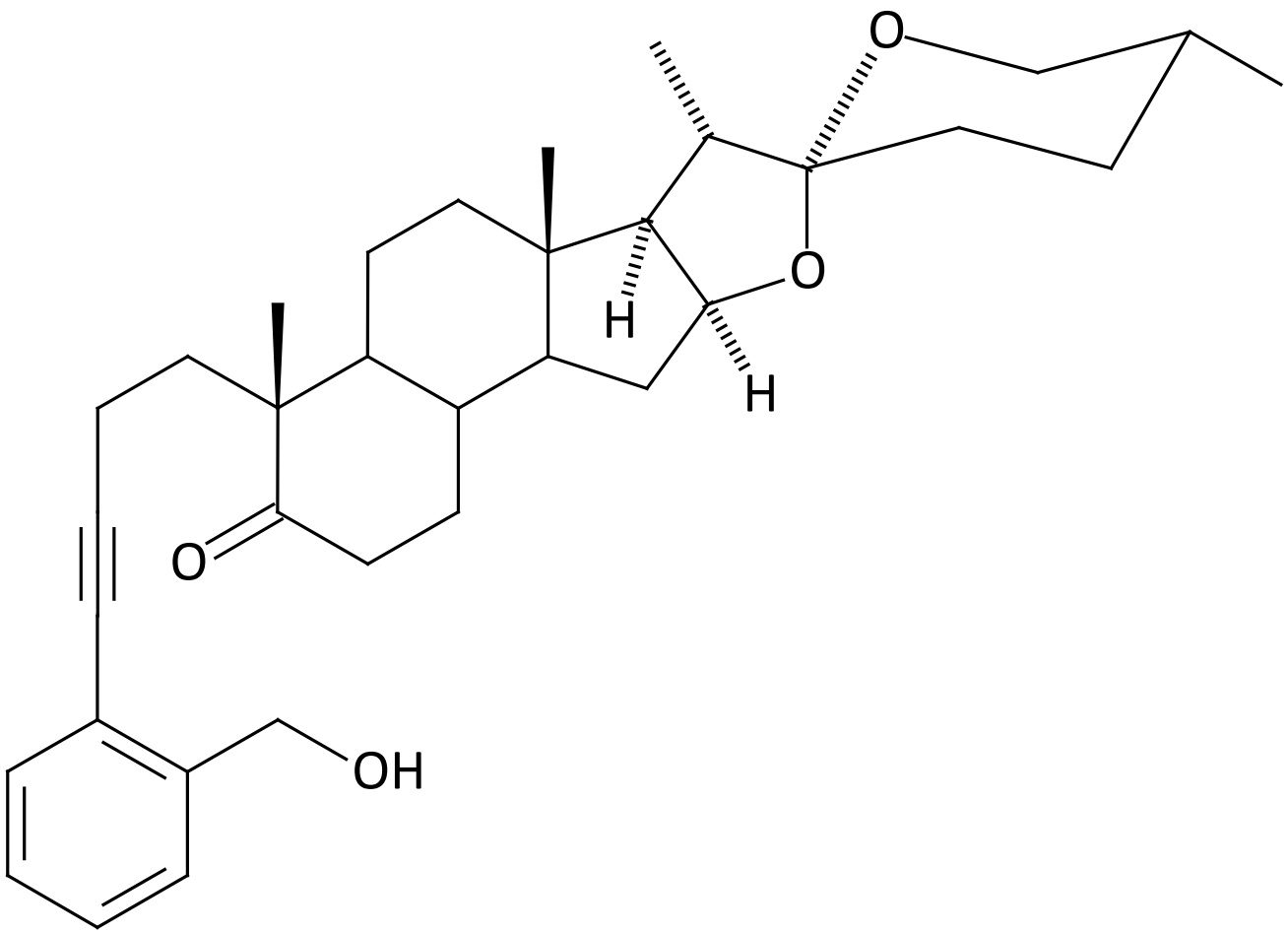
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
f1 (ppm)

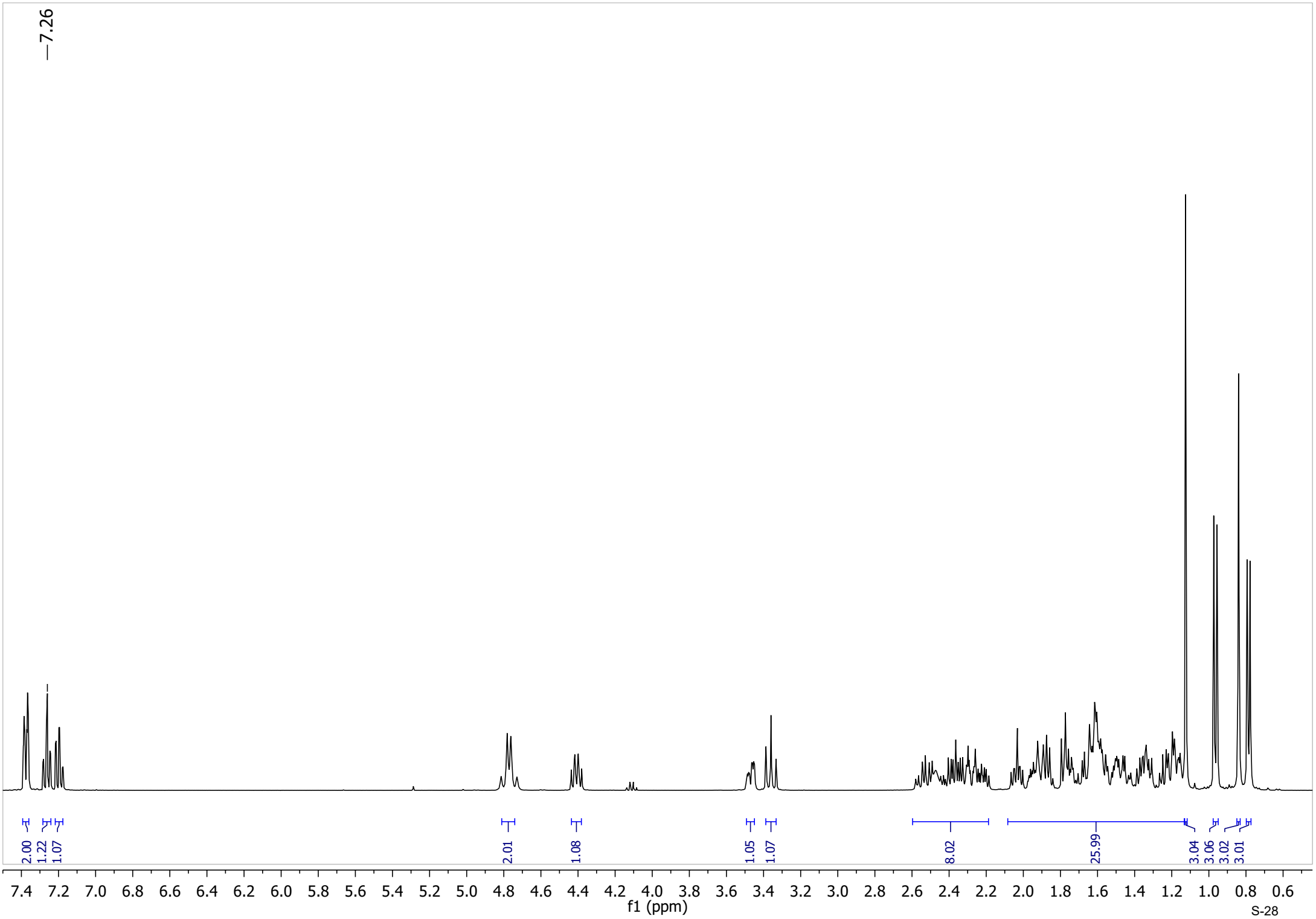

77.00
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

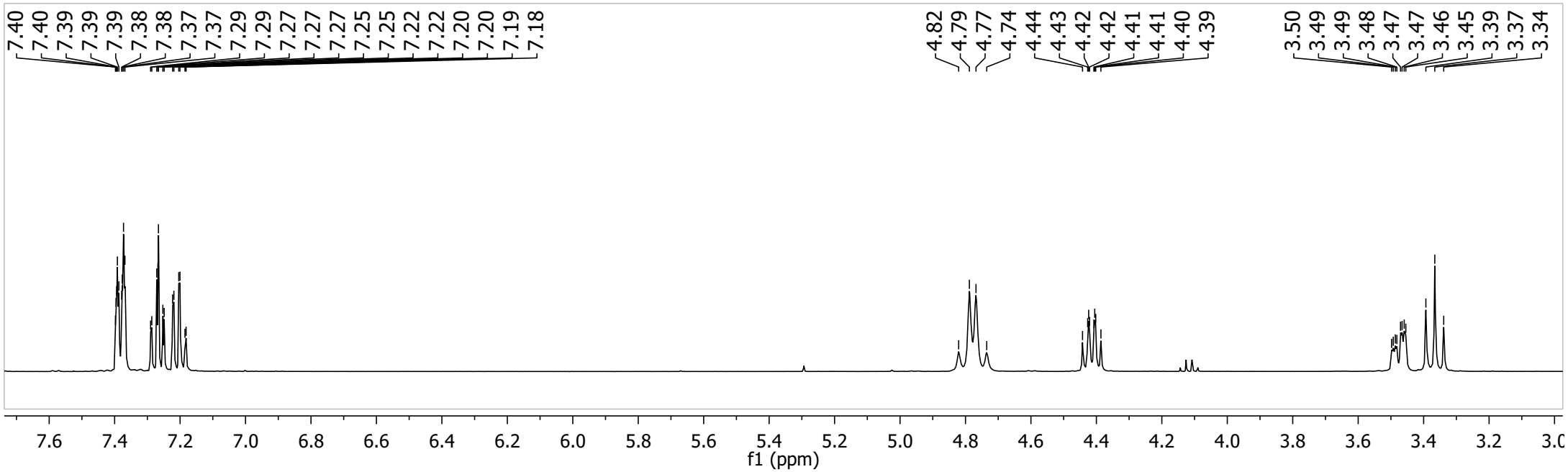

214.25
109.24
84.97
80.44
77.00
68.04
66.85
61.98
55.57
f1 (ppm)

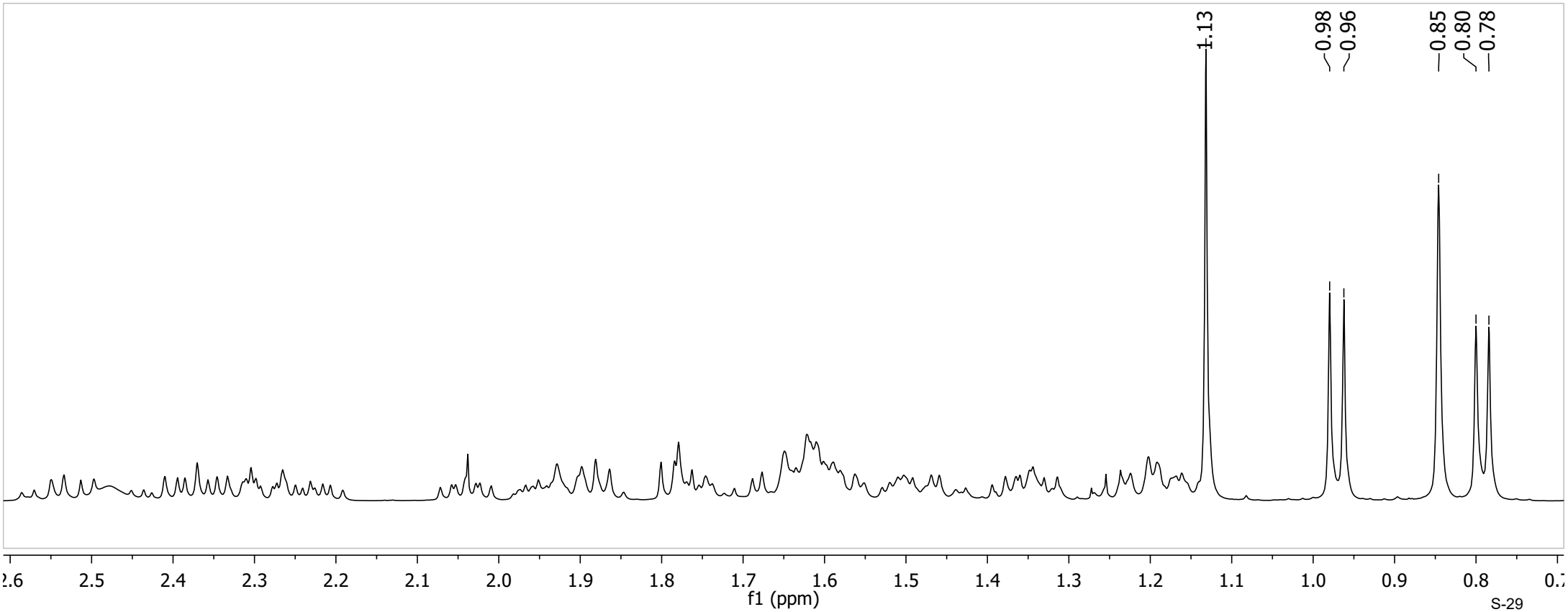

68.04
66.85
61.98
55.57
50.75
47.30
41.64
40.49
39.27
37.98
34.47
33.53
31.77
31.35
31.20
30.24
28.78
21.32
20.63
17.11
16.38
14.46
13.71
f1 (ppm)

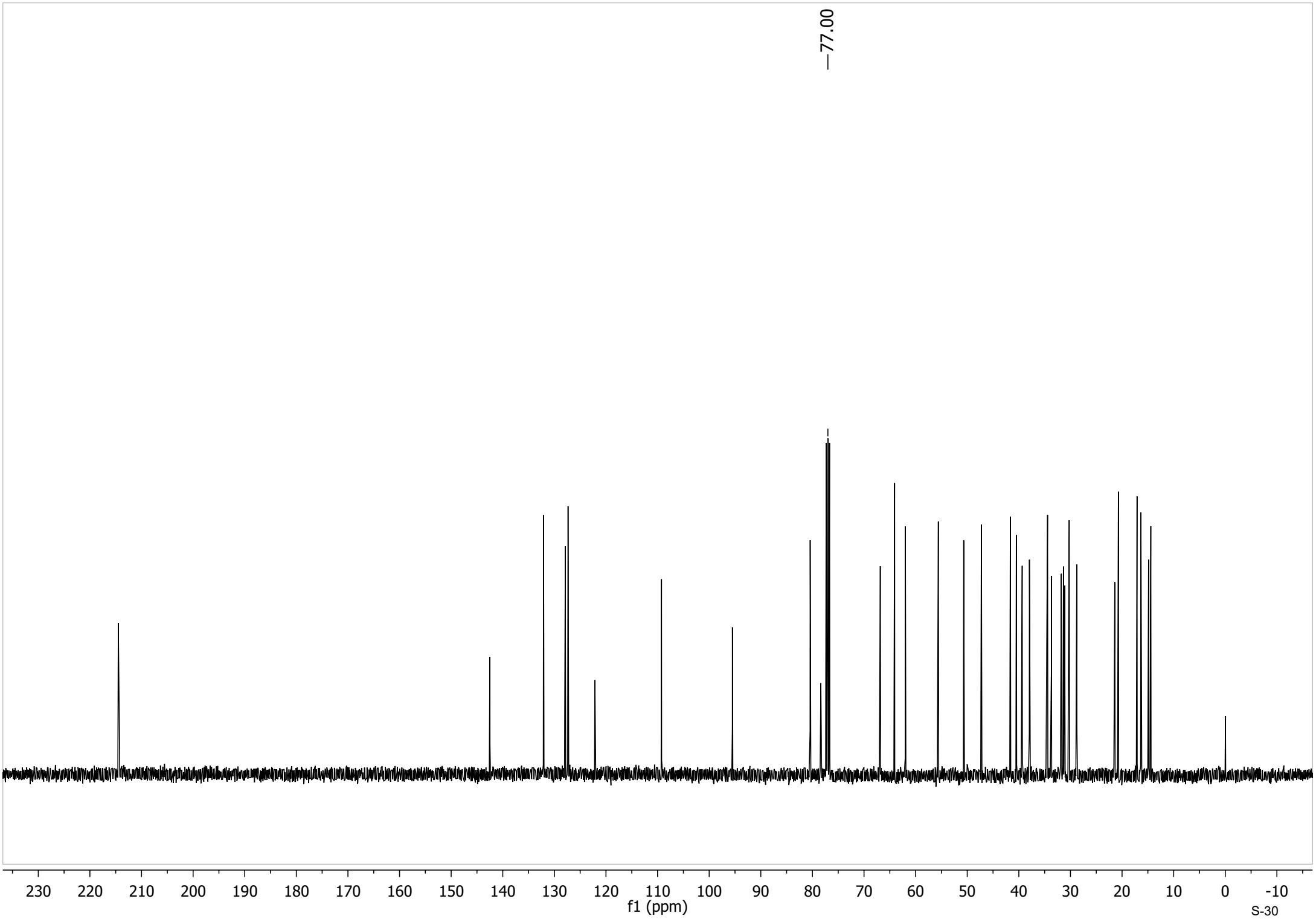


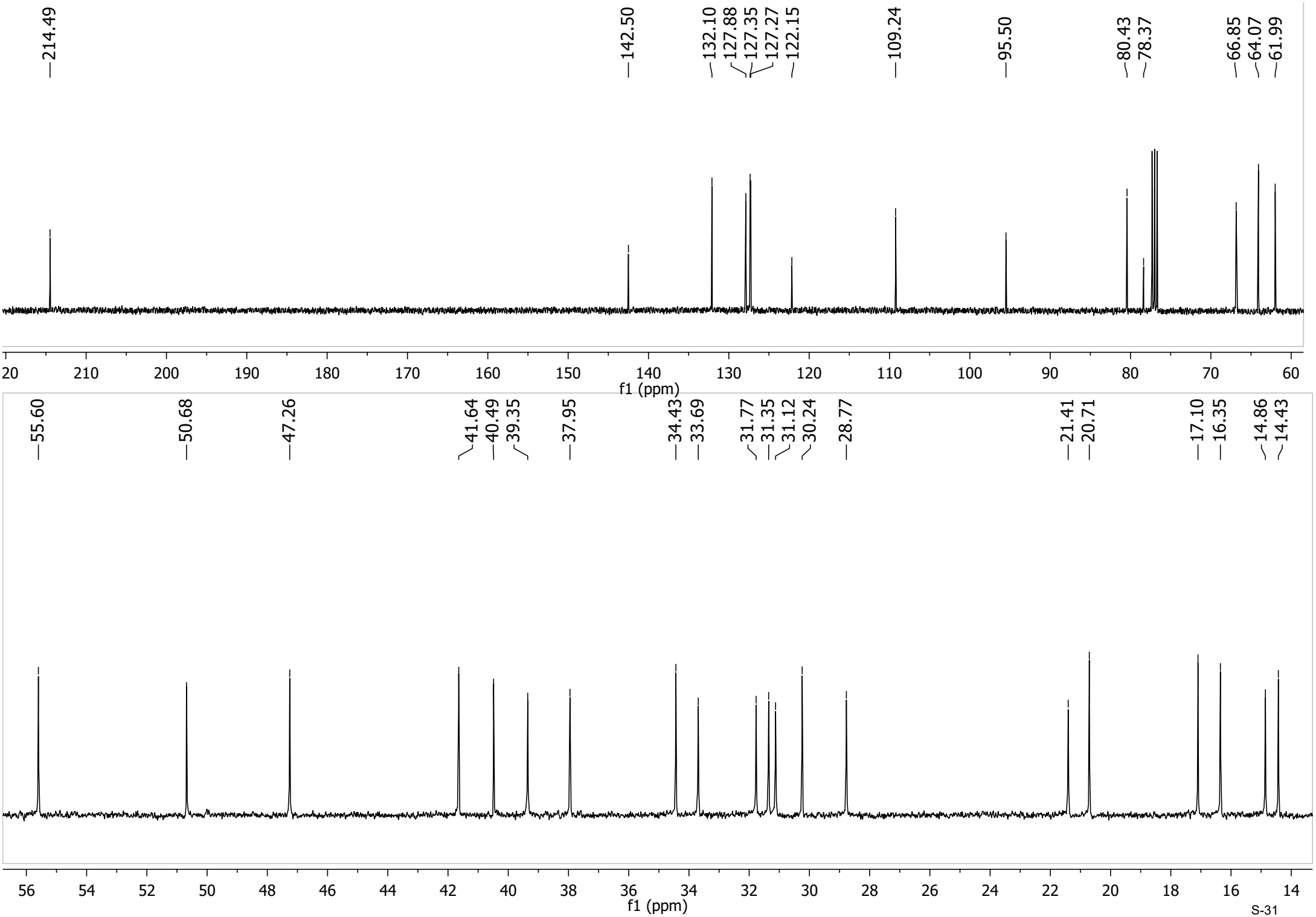
(25*R*)-4-(2´-(hydroxymethyl)phenyl)-4,5-secoespirost-3-yn-5-one (16)

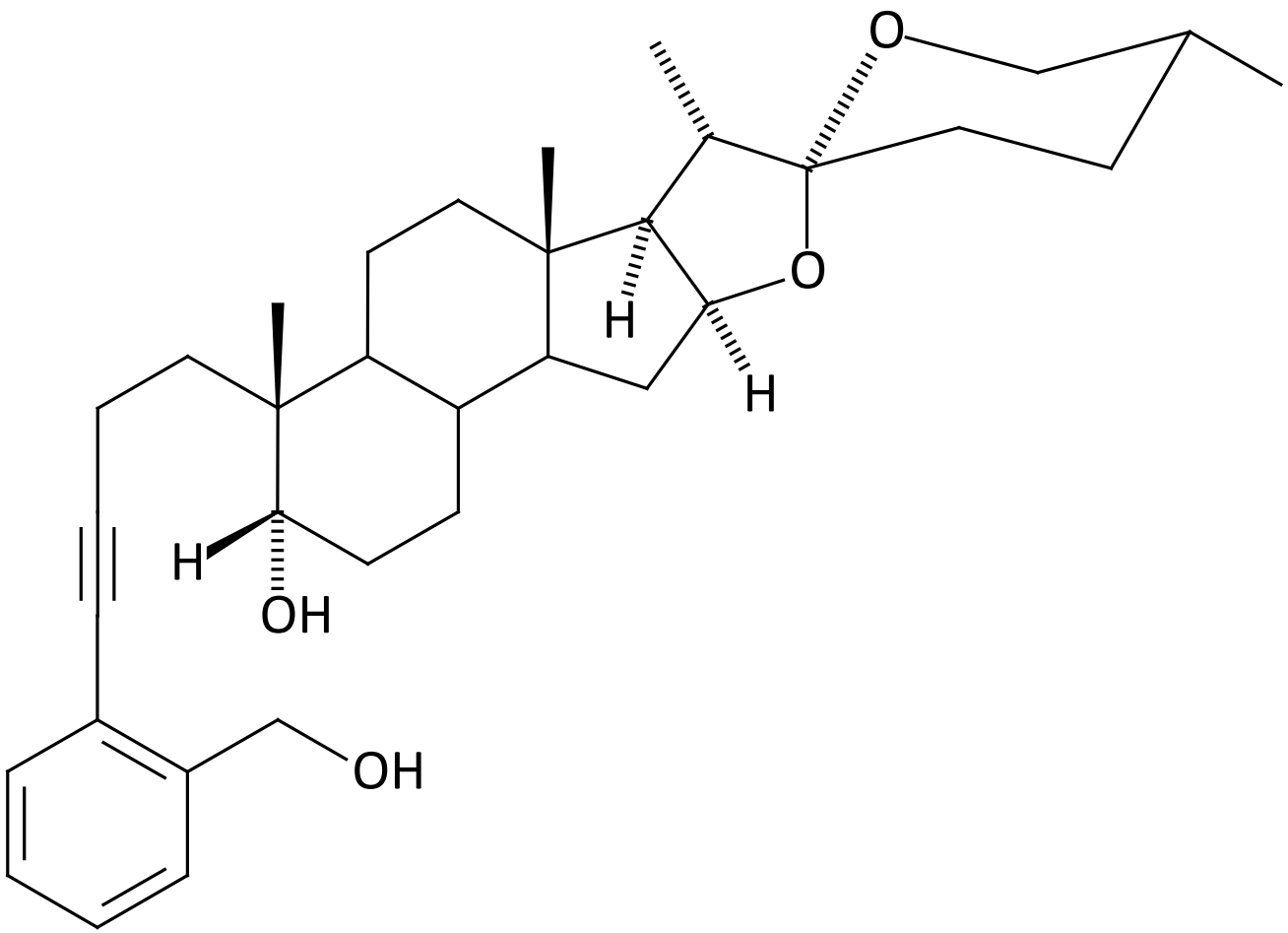

7.26
2.00
1.22
1.07
2.01
1.08
1.05
1.07
8.02
25.99
3.04
3.06
3.02
3.01
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
f1 (ppm)


7.40
7.40
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.29
7.29
7.27
7.27
7.27
7.25
7.25
7.22
7.22
7.20
7.20
7.19
7.18
4.82
4.79
4.77
4.74
4.44
4.43
4.42
4.42
4.41
4.41
4.40
4.39
3.50
3.49
3.49
3.48
3.47
3.47
3.46
3.45
3.39
3.37
3.34
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
f1 (ppm)

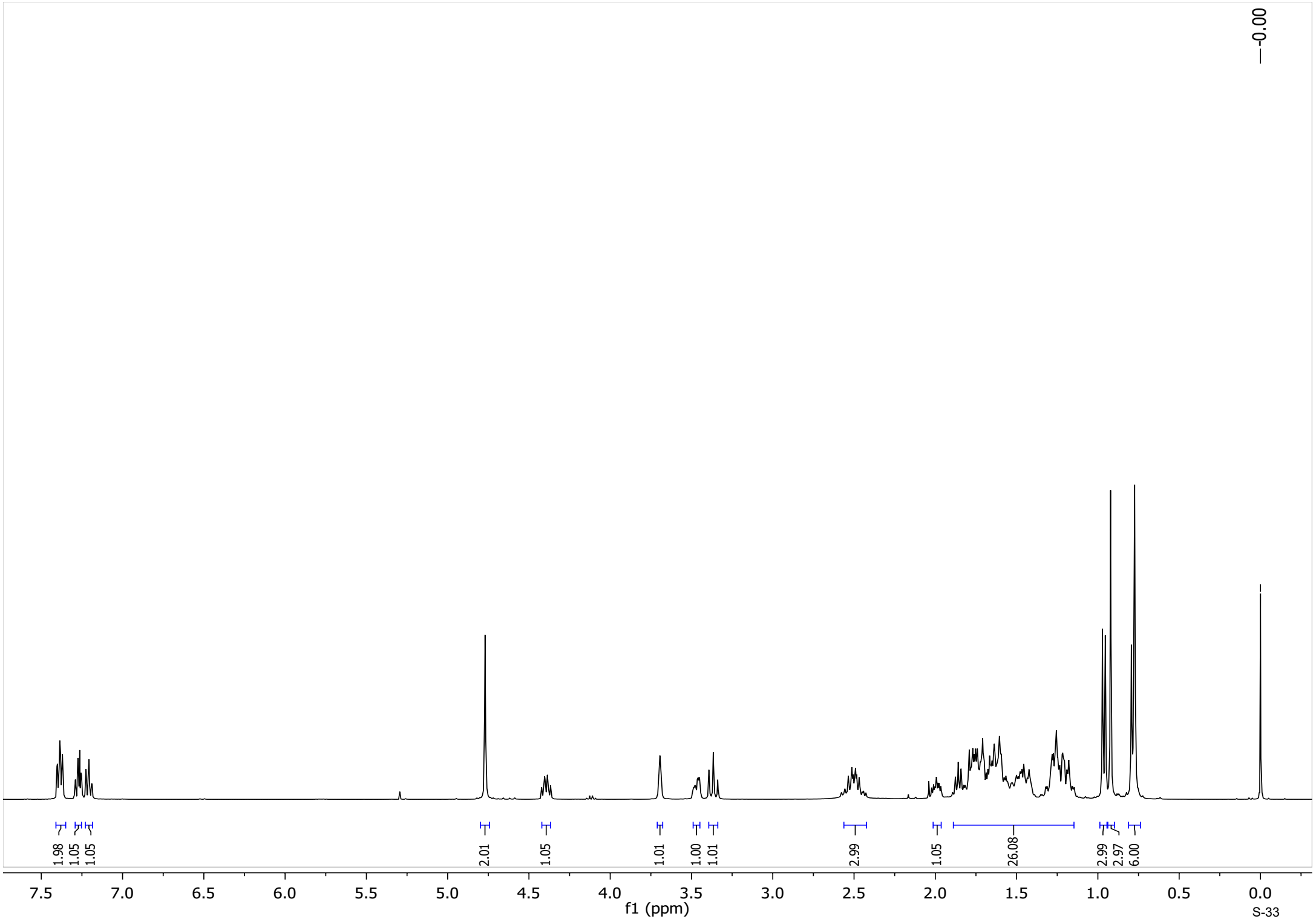

1.13
0.98
0.96
0.85
0.80
0.78
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
f1 (ppm)

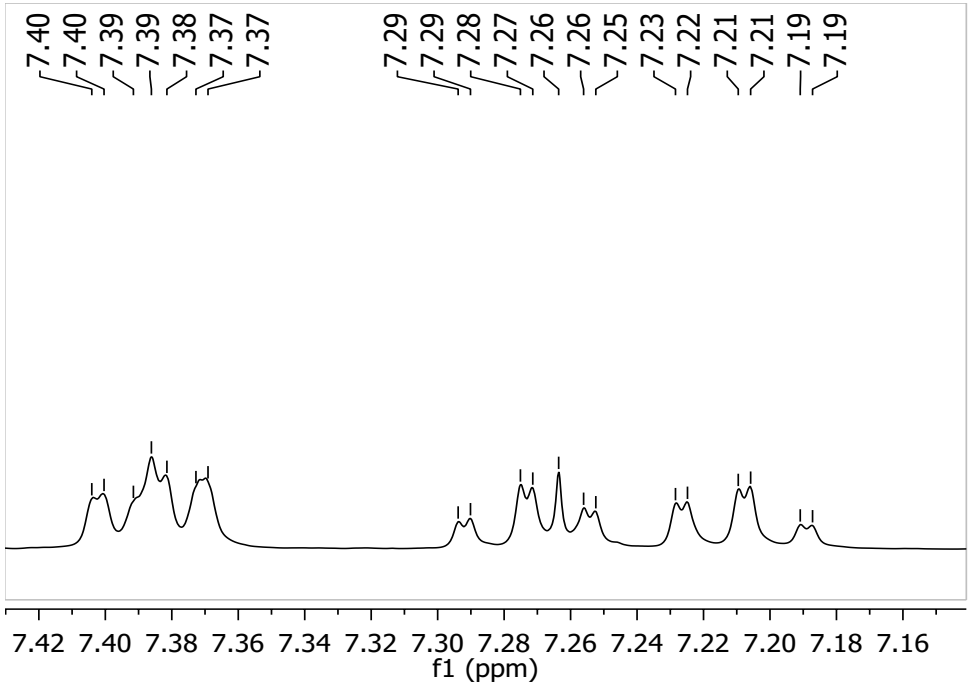

77.00
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

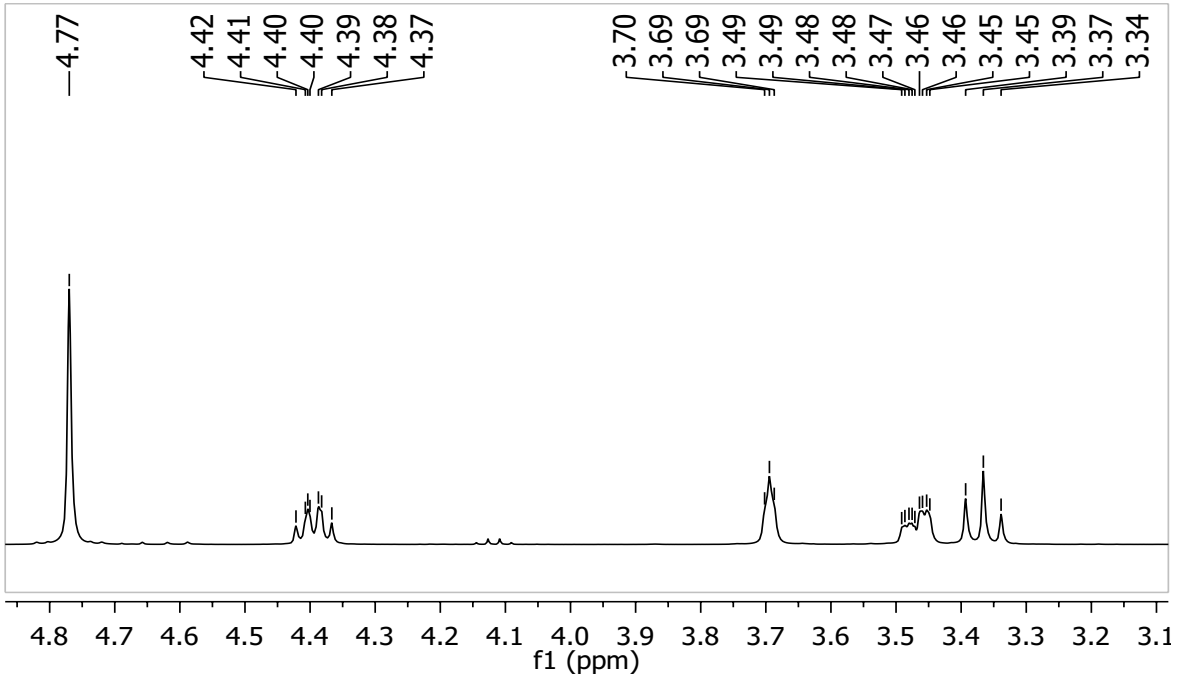

214.49
142.50
132.10
127.88
127.35
127.27
122.15
109.24
95.50
80.43
78.37
66.85
64.07
61.99
f1 (ppm)
55.60
50.68
47.26
41.64
40.49
39.35
37.95
34.43
33.69
31.77
31.35
31.12
30.24
28.77
21.41
20.71
17.10
16.35
14.86
14.43
f1 (ppm)

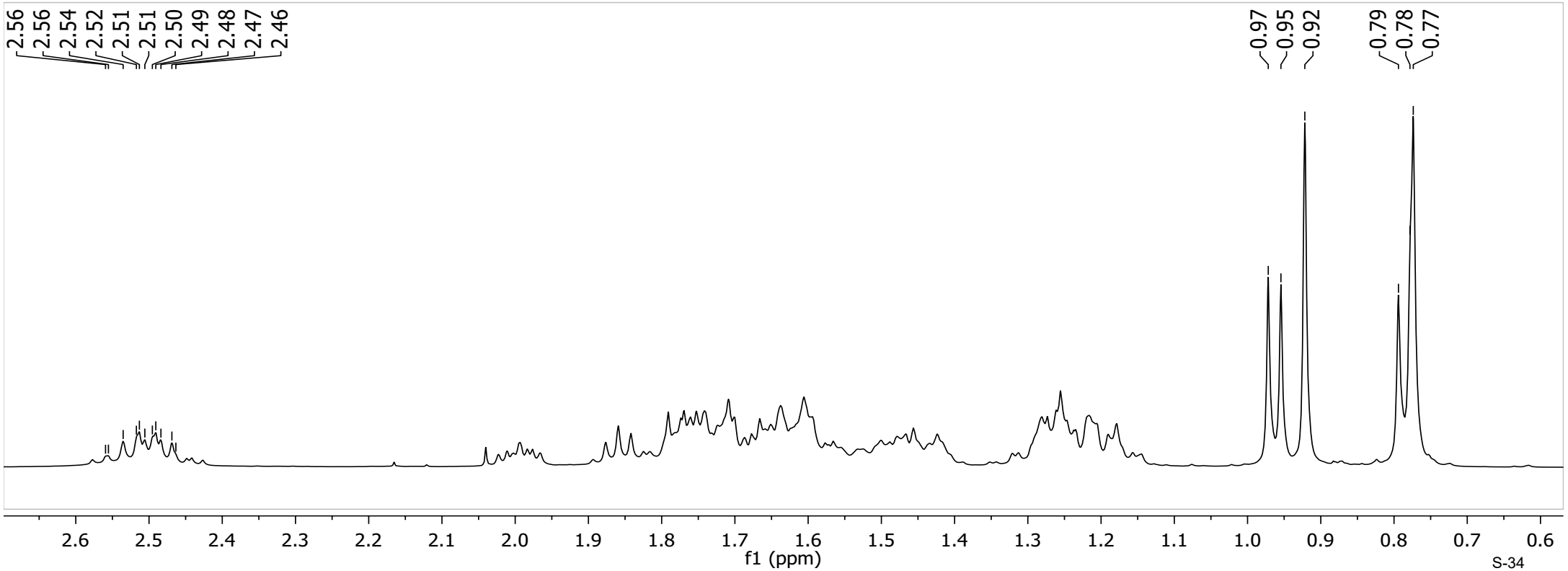


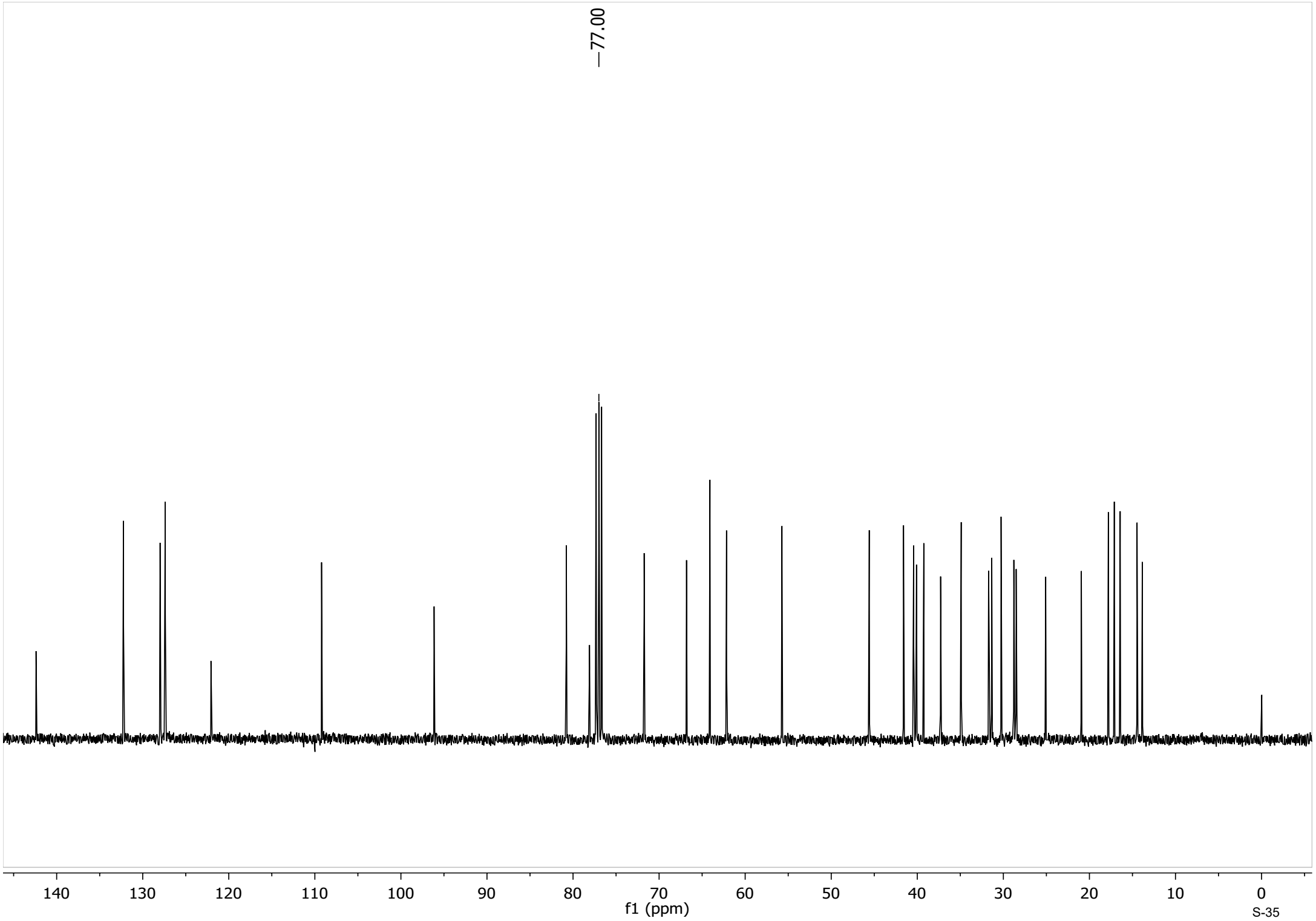
(25*R*)-4-(2´-(hydroxymethyl)phenyl)-4,5-secospirost-3-yn-5α-ol (17a)

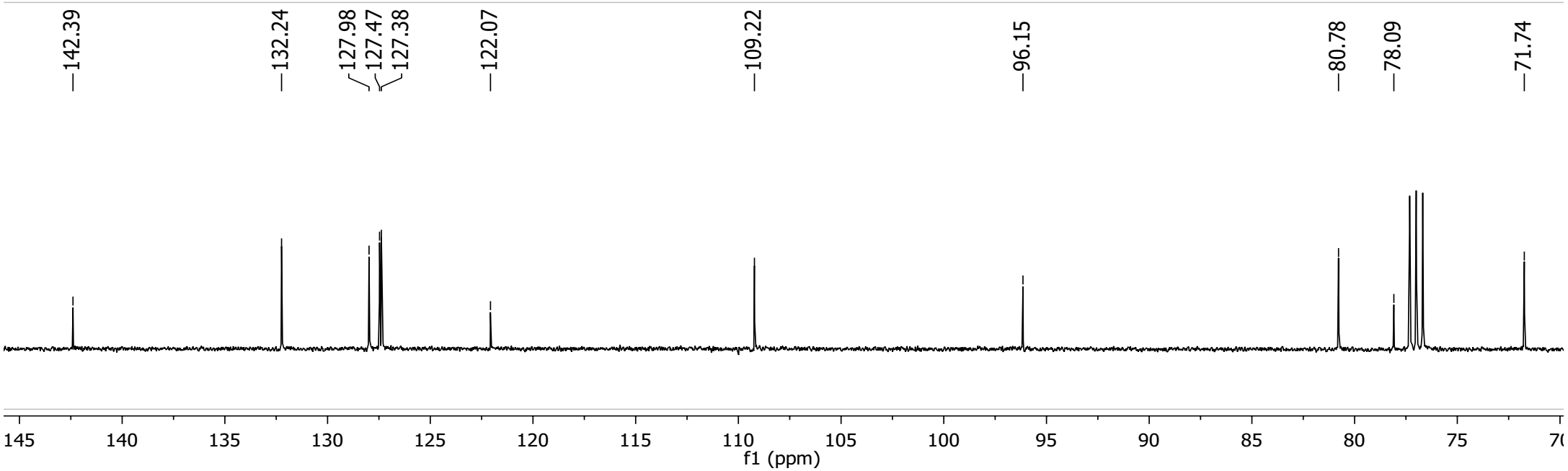

-0.00
1.98
1.05
1.05
2.01
1.05
1.01
1.00
1.01
2.99
1.05
26.08
2.99
2.97
6.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

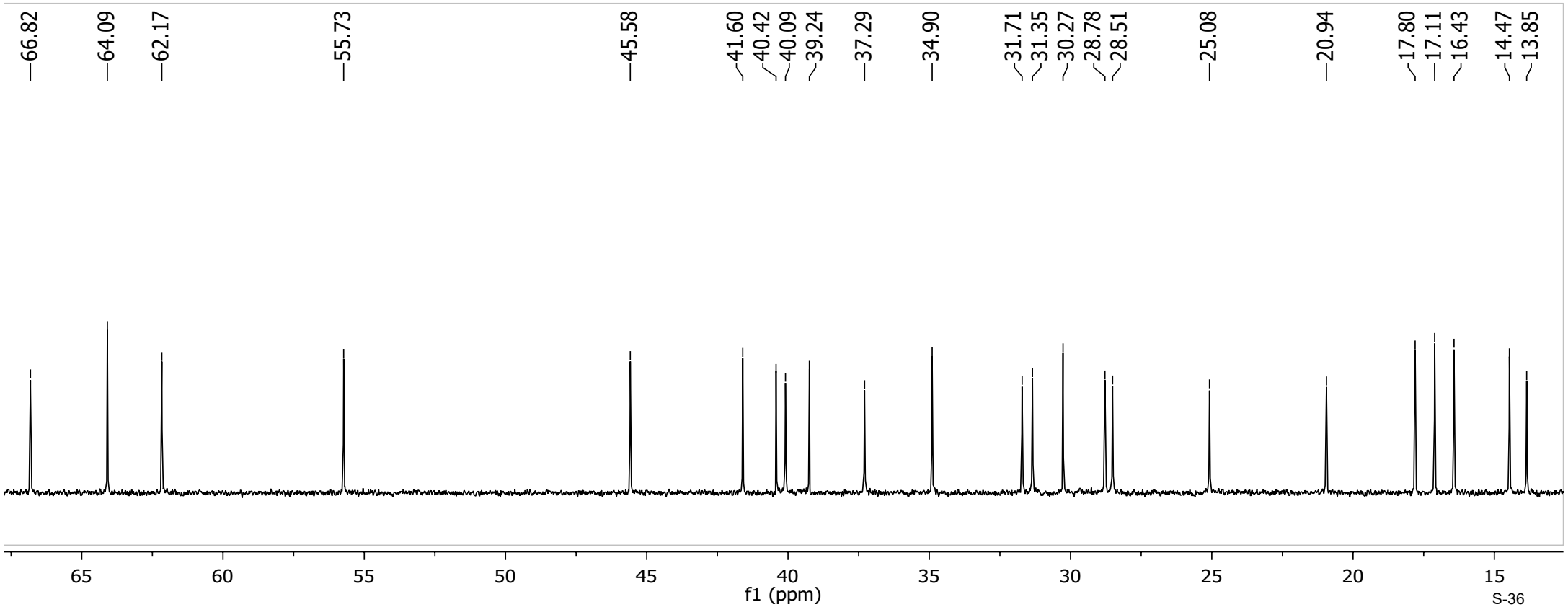

7.40
7.40
7.39
7.39
7.38
7.37
7.37
7.29
7.29
7.28
7.27
7.26
7.26
7.25
7.23
7.22
7.21
7.21
7.19
7.19
7.42 7.40 7.38 7.36 7.34 7.32 7.30 7.28 7.26 7.24 7.22 7.20 7.18 7.16
f1 (ppm)

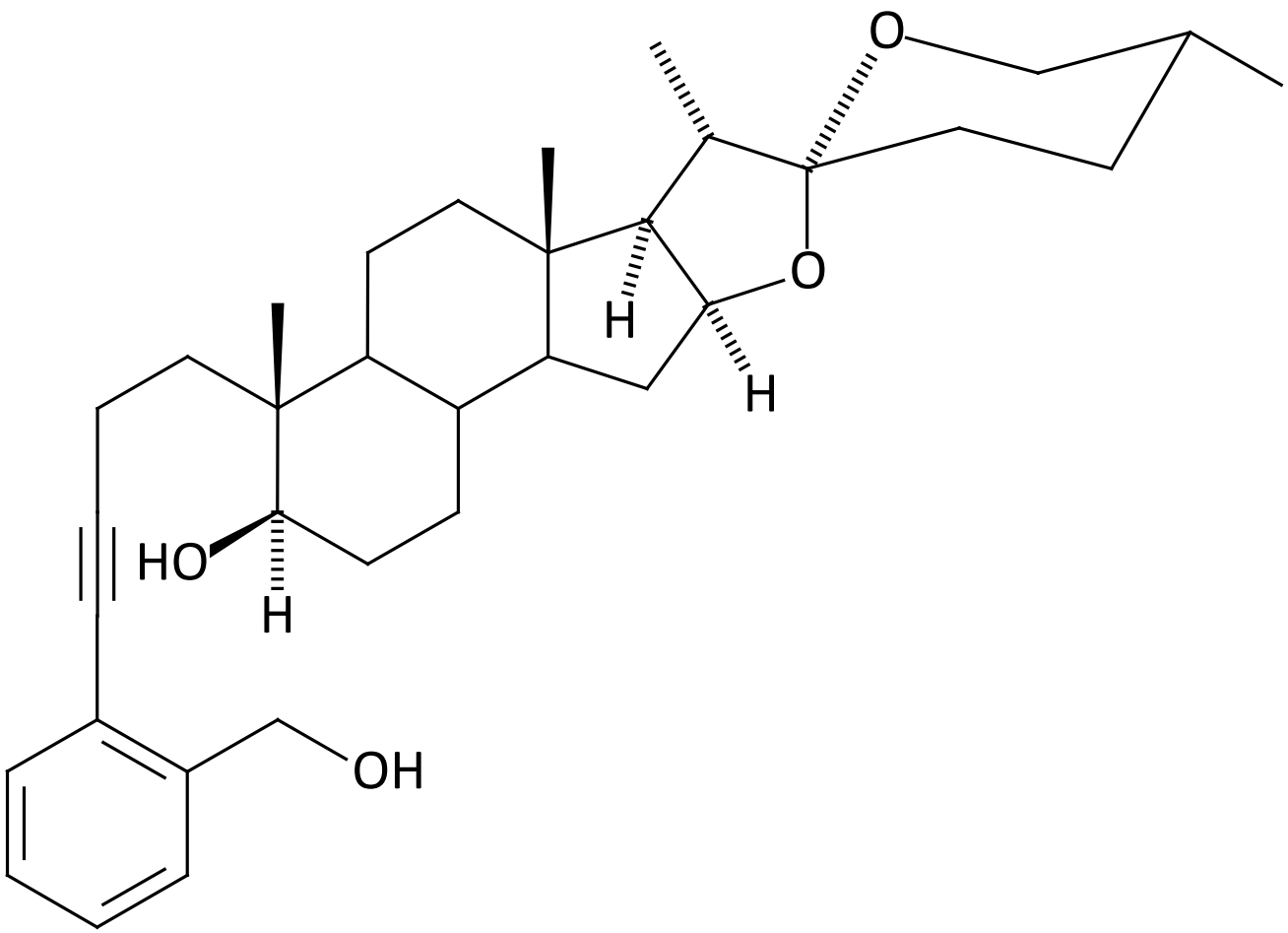

4.77
4.42
4.41
4.40
4.40
4.39
4.38
4.37
3.70
3.69
3.69
3.49
3.49
3.48
3.48
3.47
3.46
3.46
3.45
3.45
3.39
3.37
3.34
4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1
f1 (ppm)


2.56
2.56
2.54
2.52
2.51
2.51
2.50
2.49
2.48
2.47
2.46
0.97
0.95
0.92
0.79
0.78
0.77
2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6
f1 (ppm)

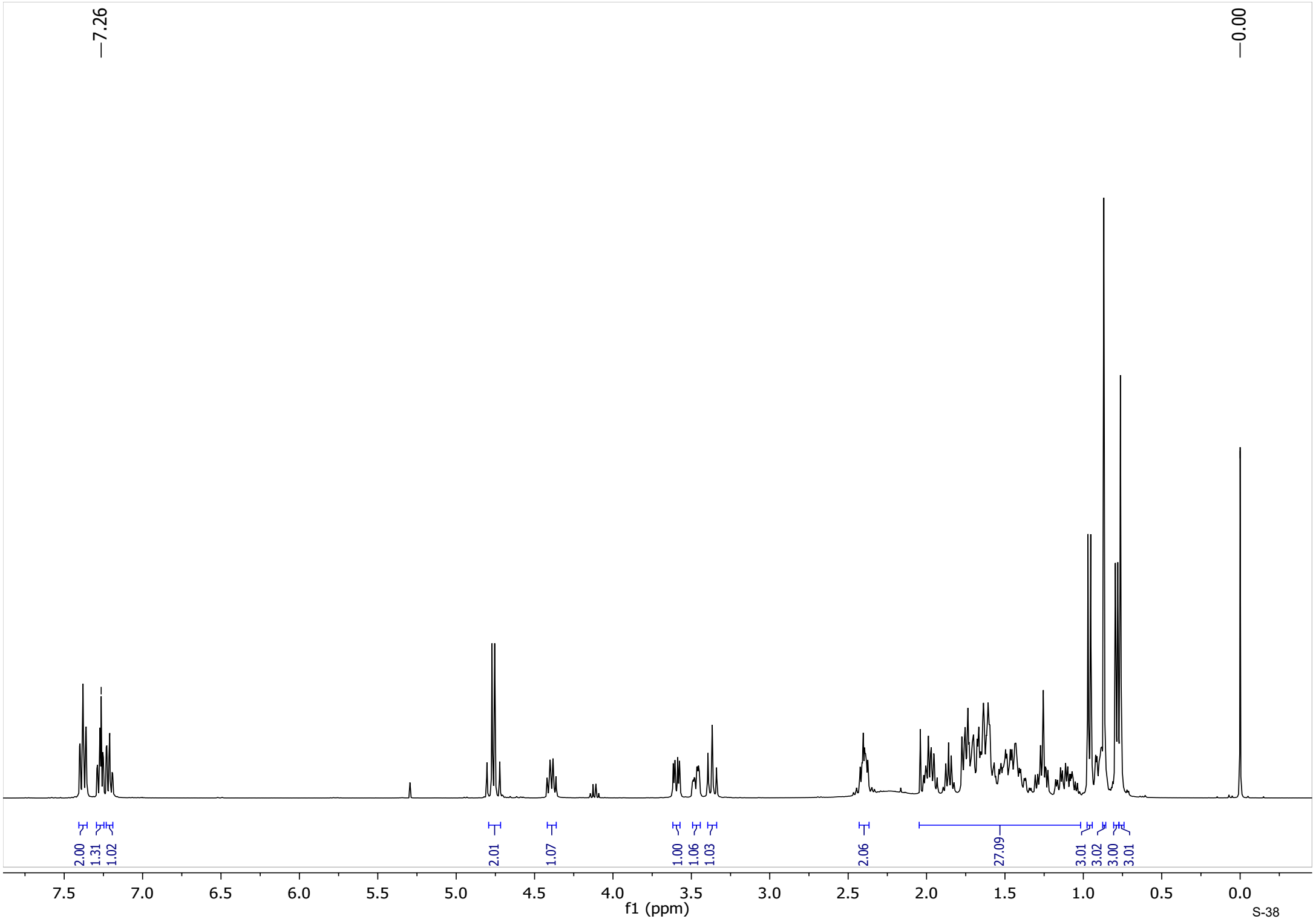

77.00
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

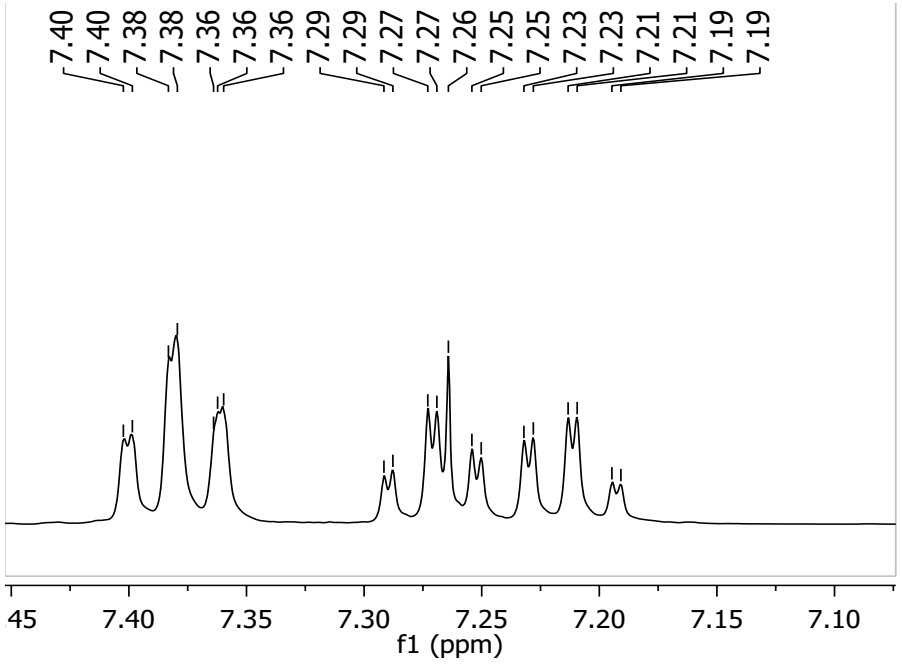

142.39
132.24
127.98
127.47
127.38
122.07
109.22
96.15
80.78
78.09
71.74
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
f1 (ppm)

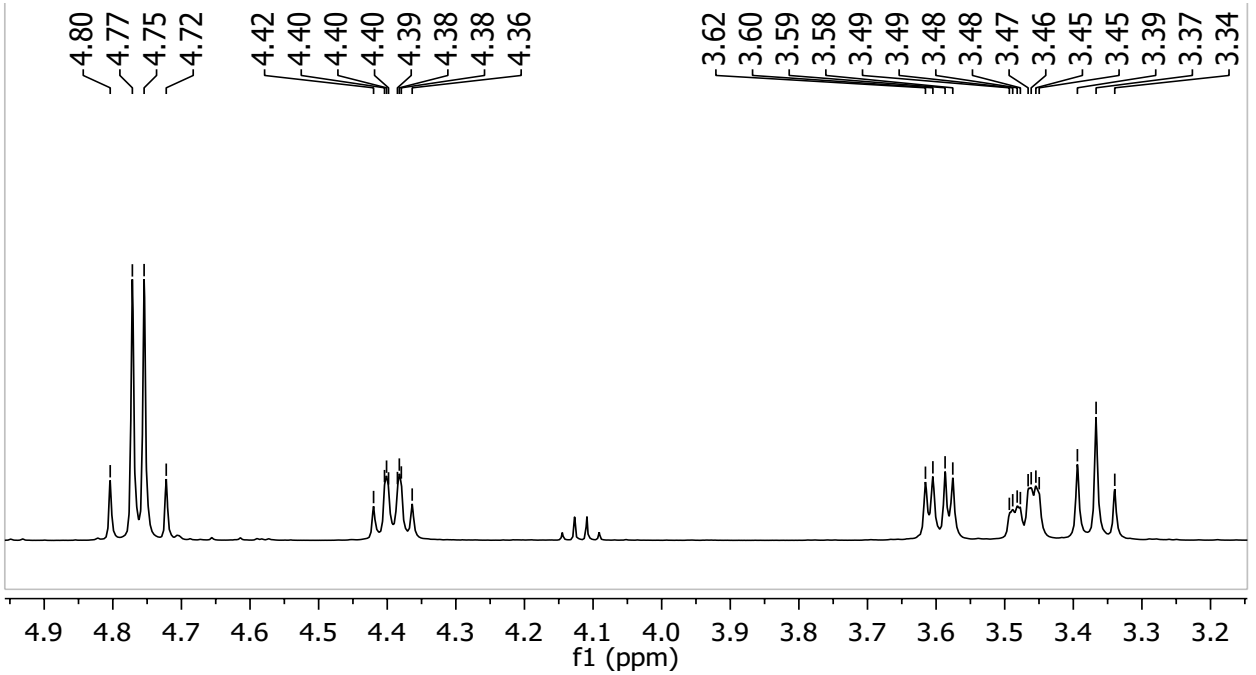

66.82
64.09
62.17
55.73
45.58
41.60
40.42
40.09
39.24
37.29
34.90
31.71
31.35
30.27
28.78
28.51
25.08
20.94
17.80
17.11
16.43
14.47
13.85
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)

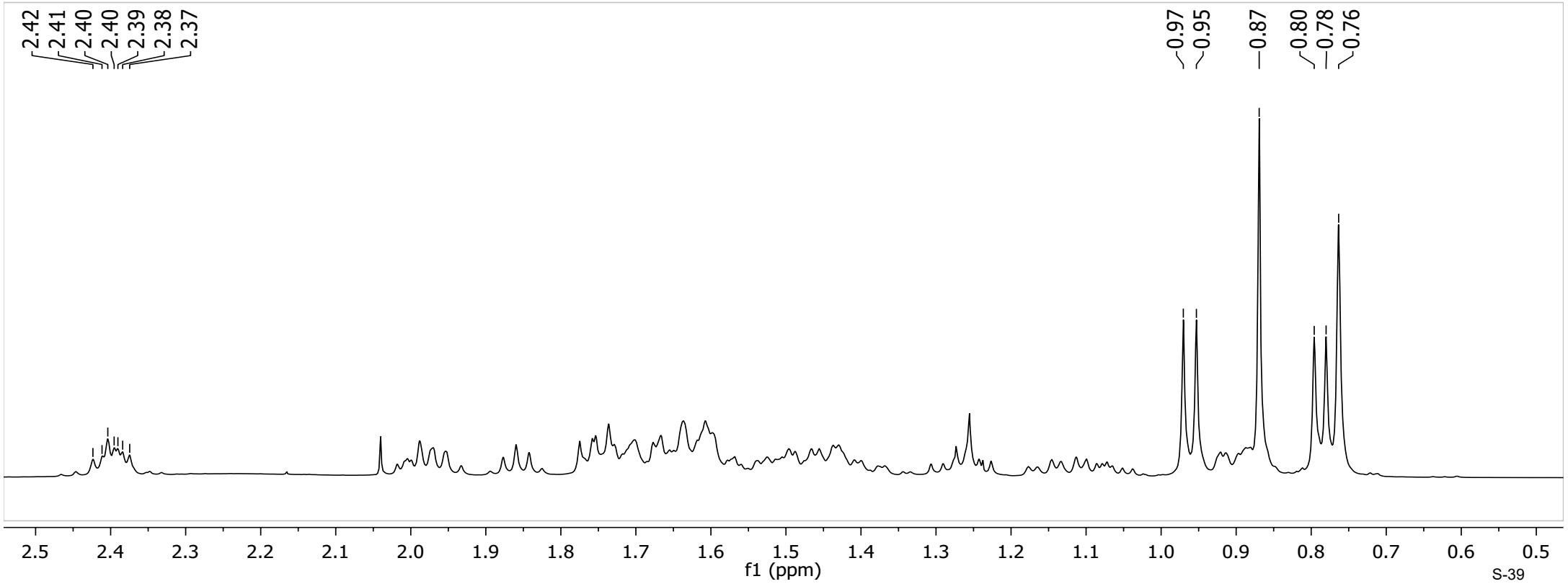


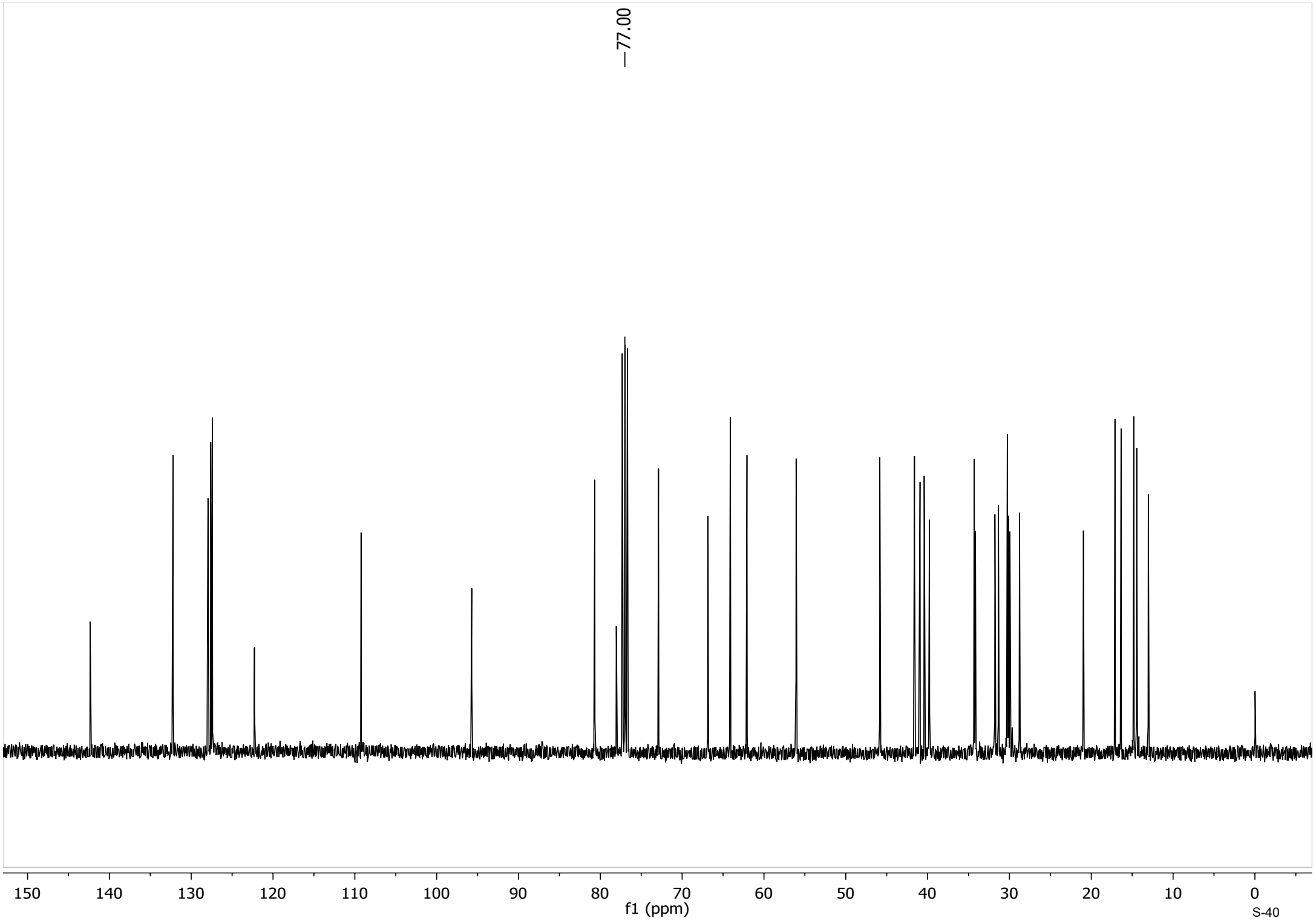
(25*R*)-4-(2´-(hydroxymethyl)phenyl)-4,5-secospirost-3-yn-5β-ol (17b)

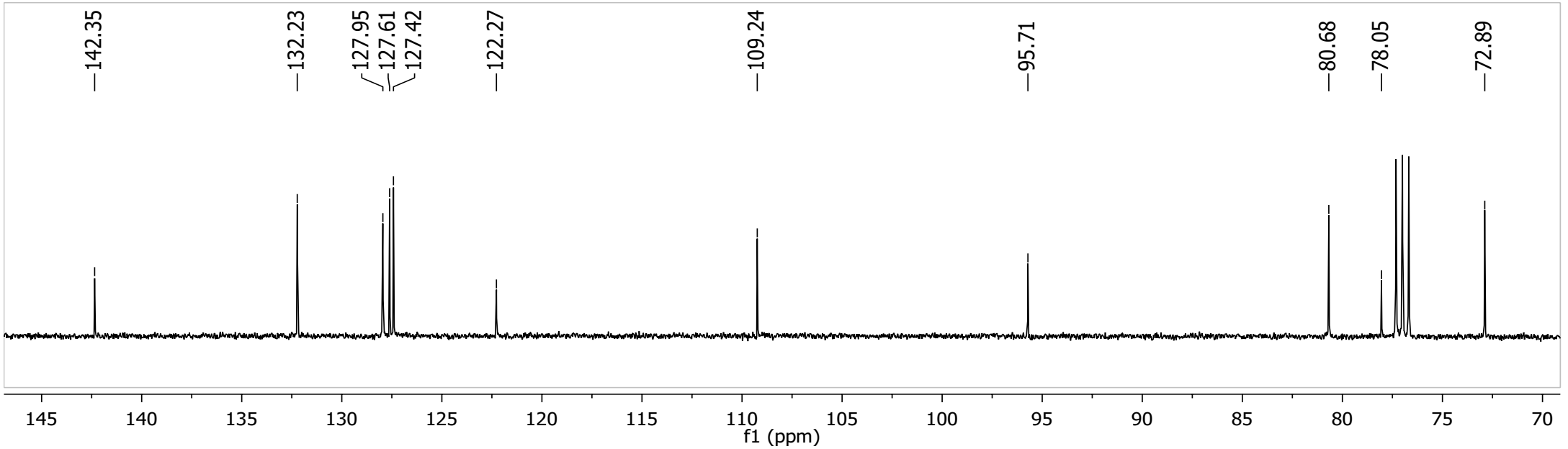

7.26
0.00
2.00
1.31
1.02
2.01
1.07
1.00
1.06
1.03
2.06
27.09
3.01
3.02
3.00
3.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

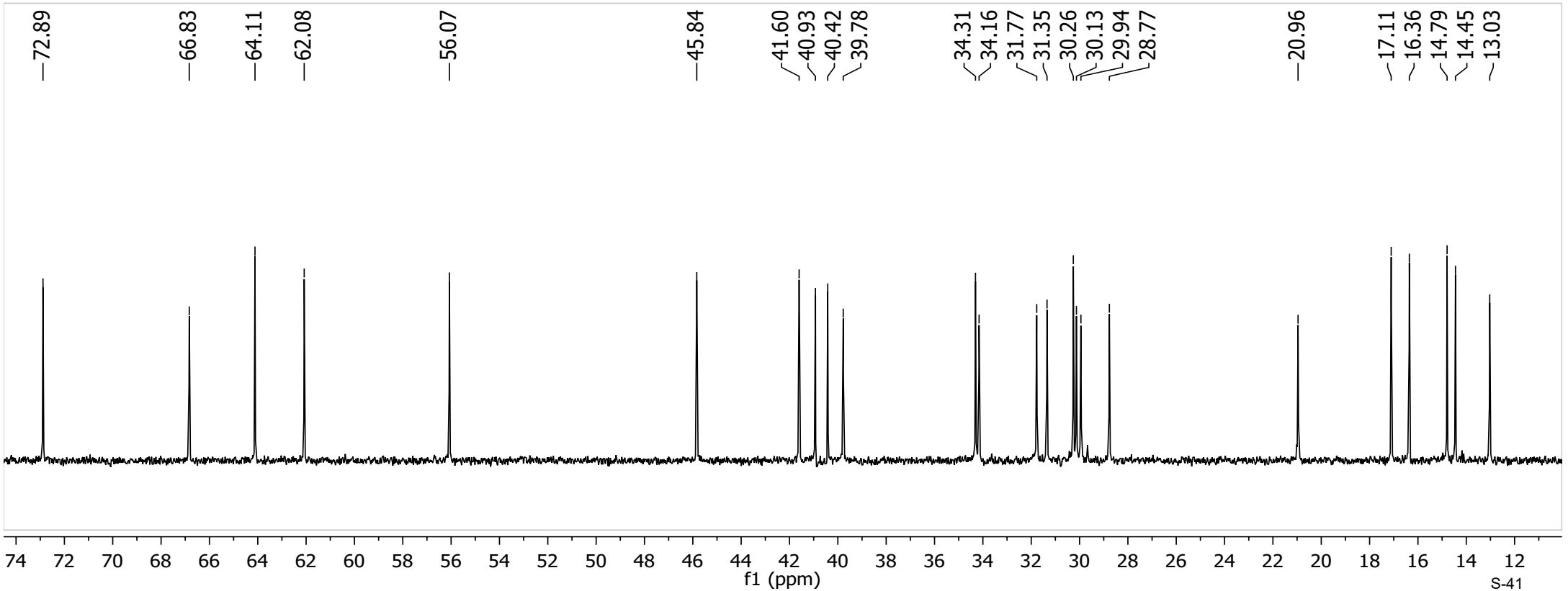

7.40
7.40
7.38
7.38
7.36
7.36
7.36
7.29
7.29
7.27
7.27
7.26
7.25
7.25
7.23
7.23
7.21
7.21
7.19
7.19
45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
f1 (ppm)

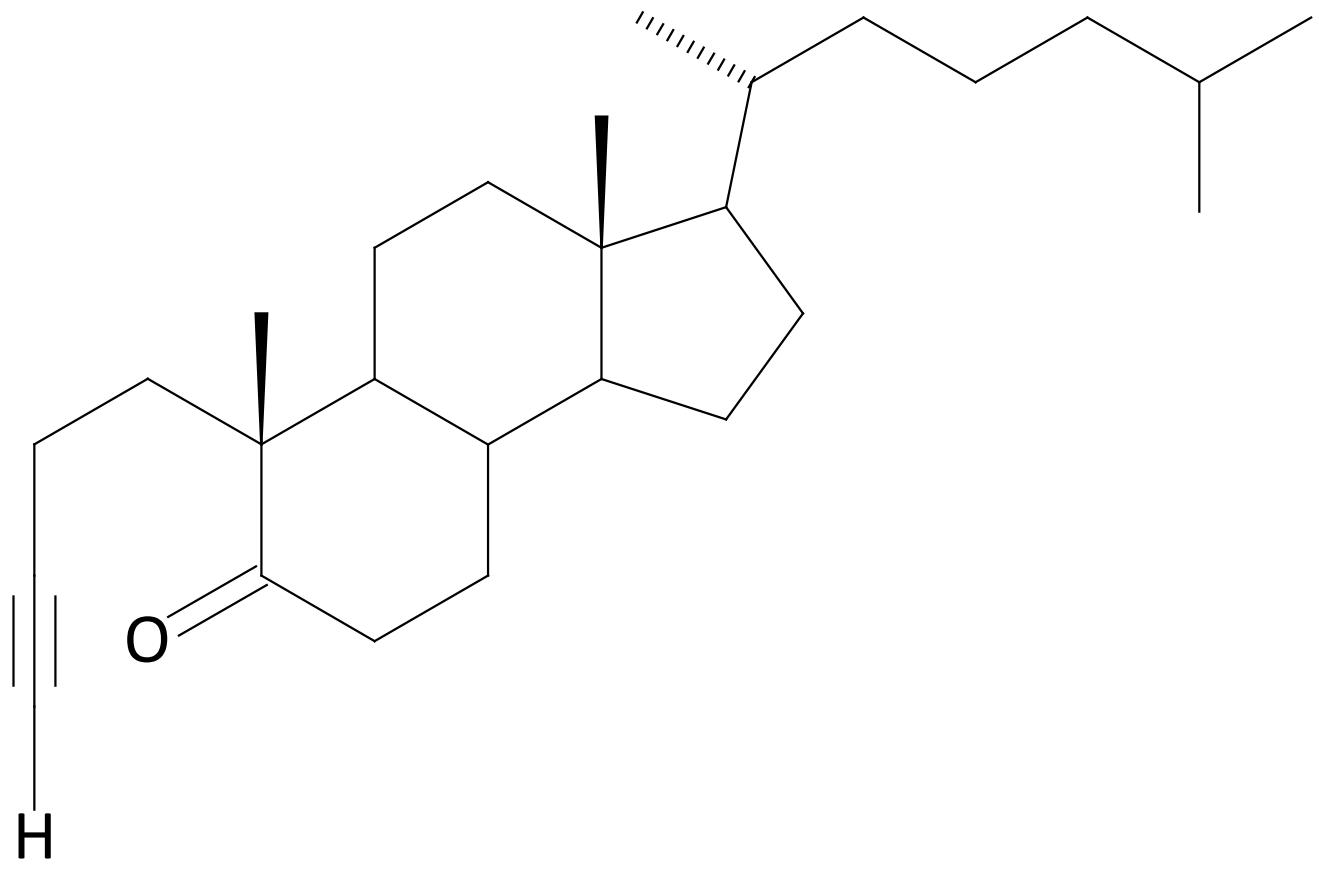

4.80
4.77
4.75
4.72
4.42
4.40
4.40
4.40
4.39
4.38
4.38
4.36
3.62
3.60
3.59
3.58
3.49
3.49
3.48
3.48
3.47
3.46
3.45
3.45
3.39
3.37
3.34
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
f1 (ppm)


2.42
2.41
2.40
2.40
2.39
2.38
2.37
0.97
0.95
0.87
0.80
0.78
0.76
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
f1 (ppm)

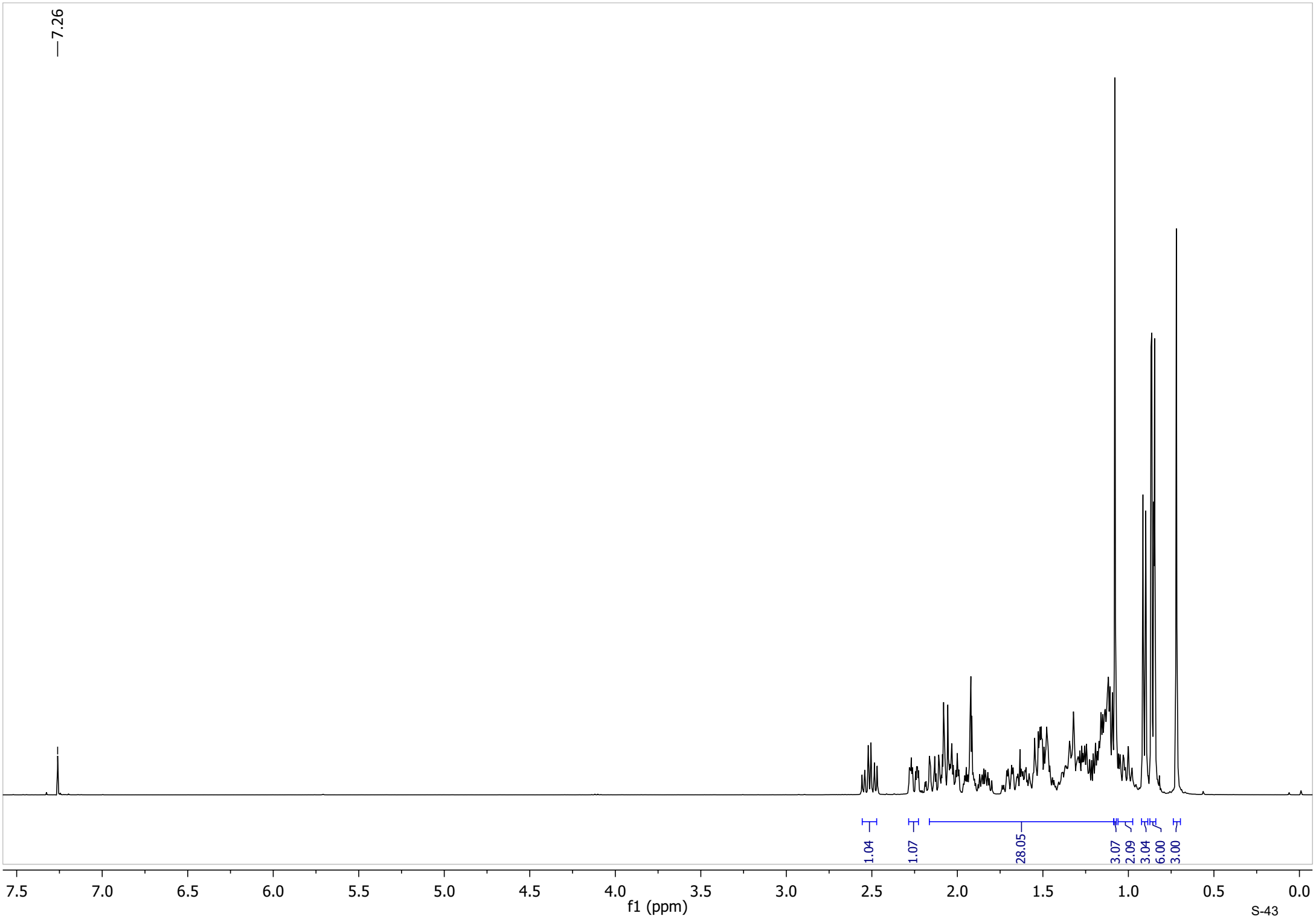

77.00
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

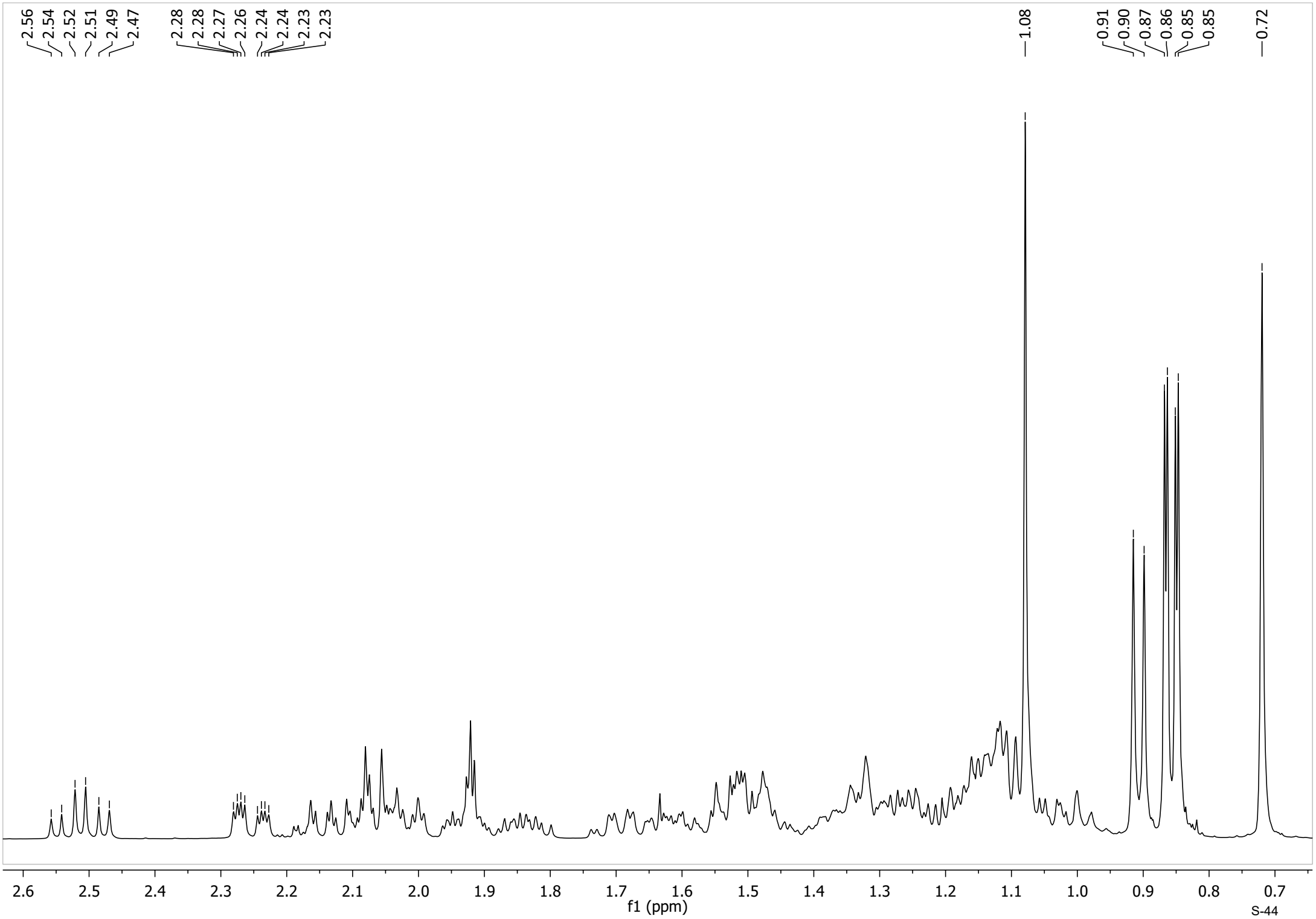

142.35
132.23
127.95
127.61
127.42
122.27
109.24
95.71
80.68
78.05
72.89
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
f1 (ppm)

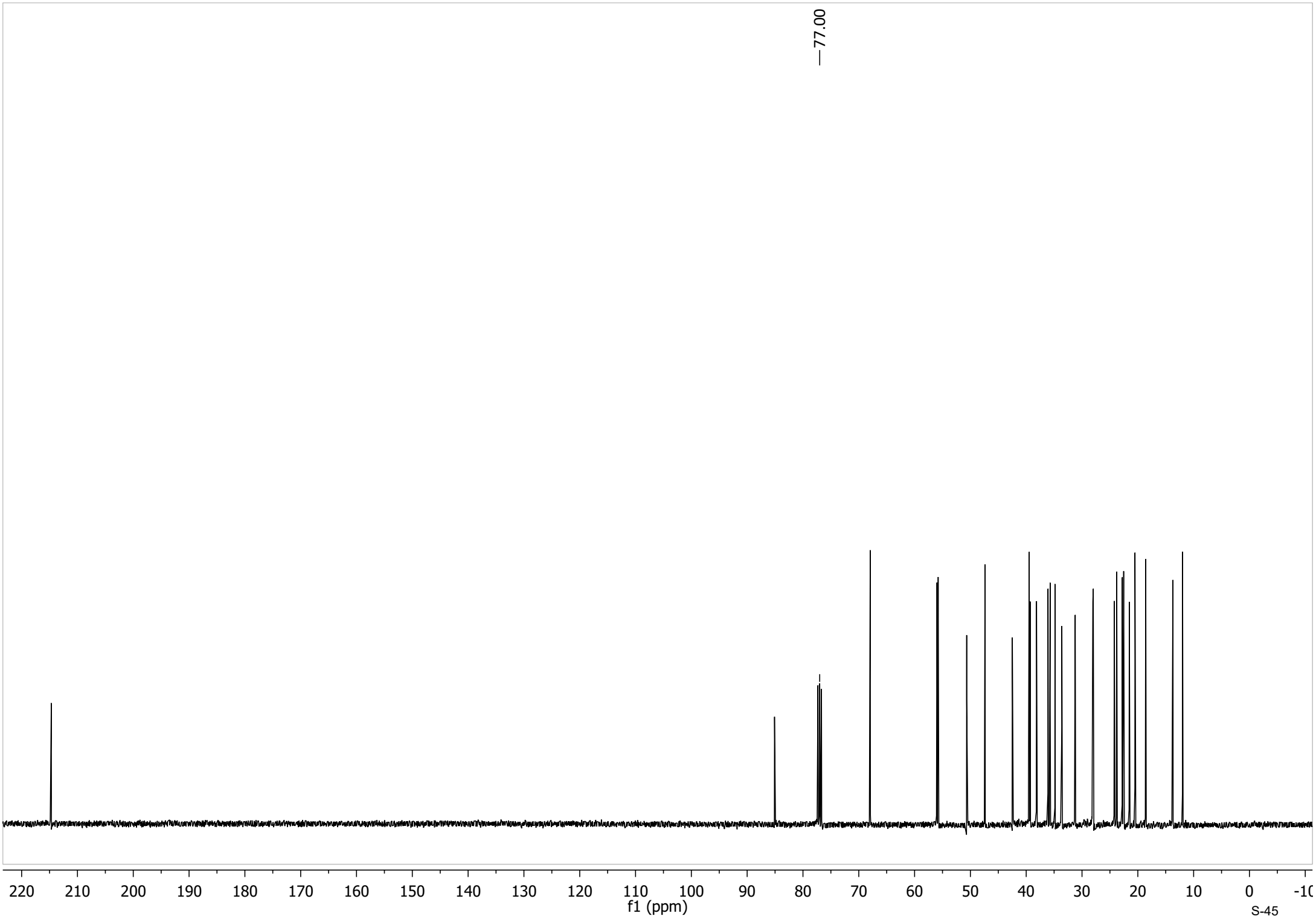

72.89
66.83
64.11
62.08
56.07
45.84
41.60
40.93
40.42
39.78
34.31
34.16
31.77
31.35
30.26
30.13
29.94
28.77
20.96
17.11
16.36
14.79
14.45
13.03
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
f1 (ppm)

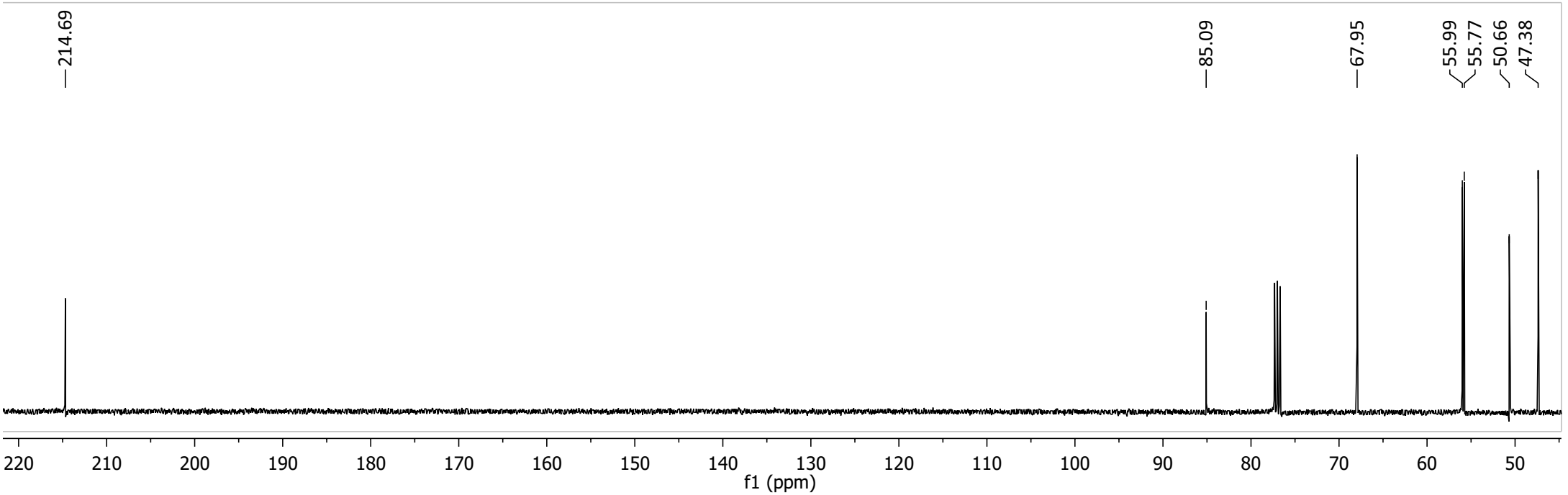


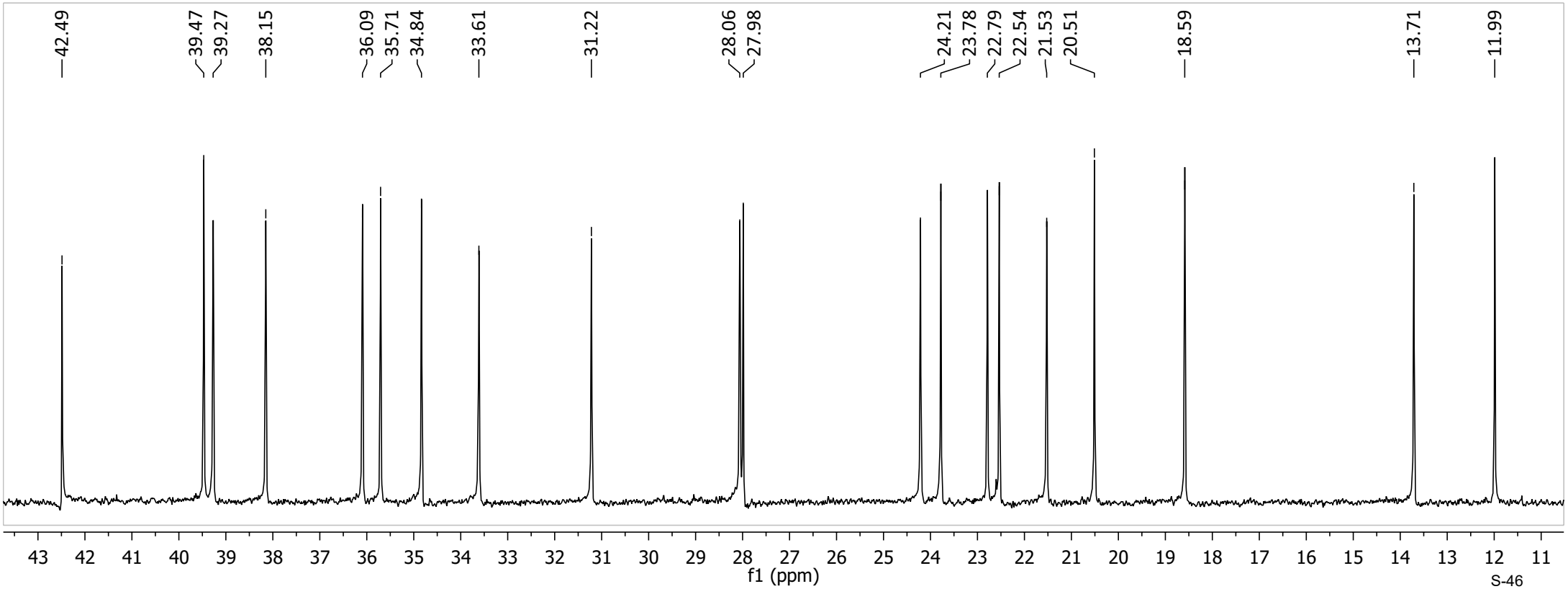
4,5-secocholest-3-yn-5-one **(19)**

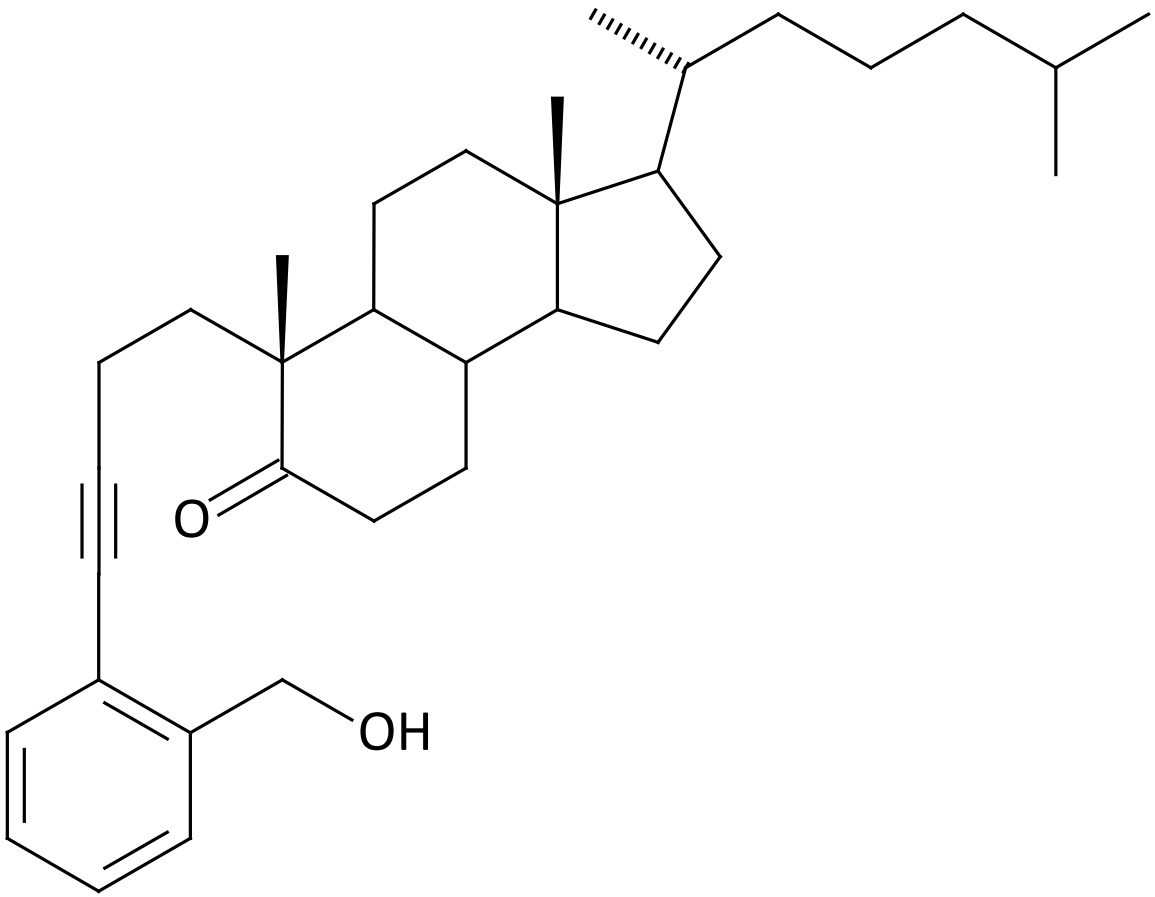

7.26
1.04
1.07
28.05
3.07
2.09
3.04
6.00
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


2.56
2.54
2.52
2.51
2.49
2.47
2.28
2.28
2.27
2.26
2.24
2.24
2.23
2.23
1.08
0.91
0.90
0.87
0.86
0.85
0.85
0.72
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
f1 (ppm)

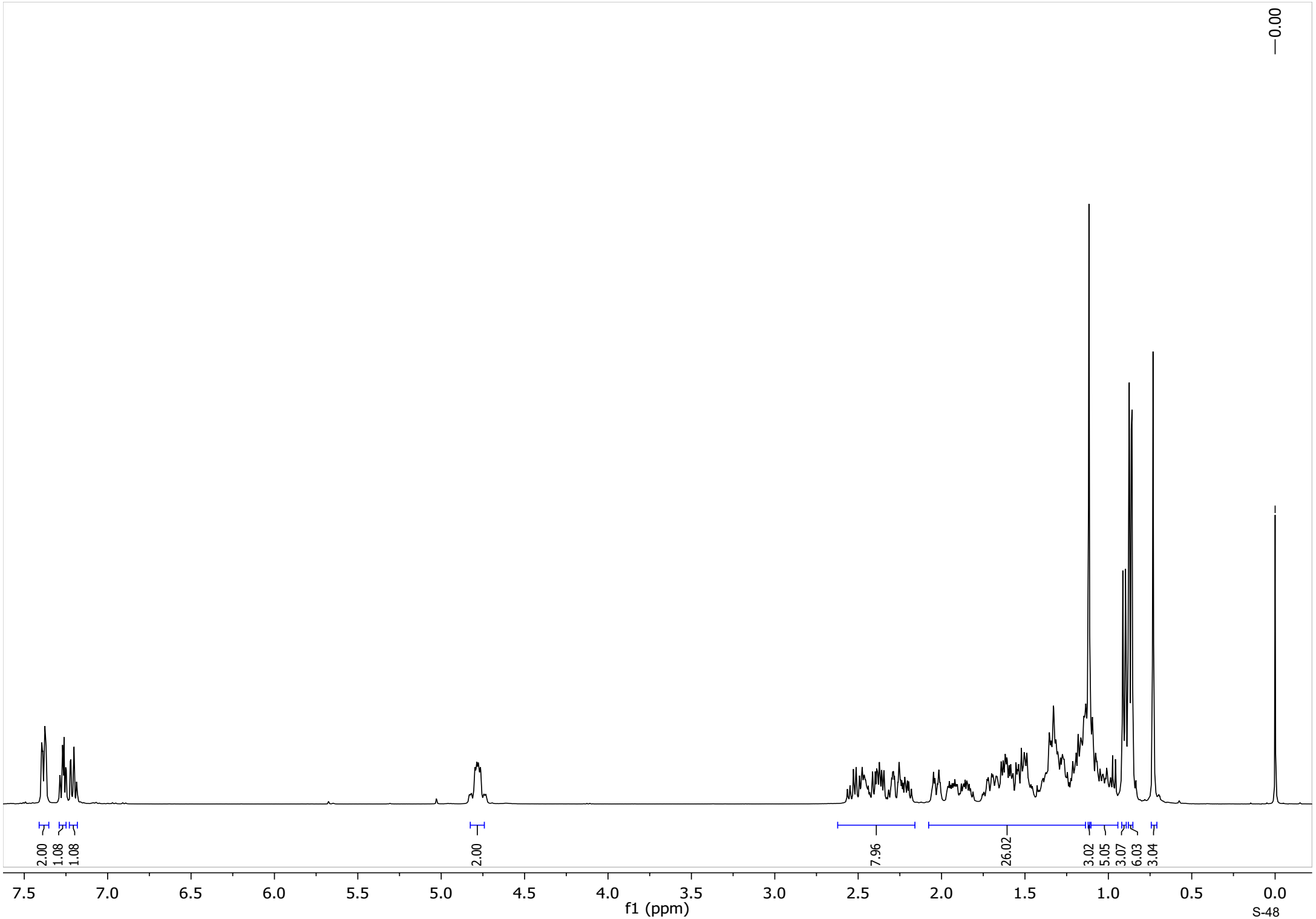

77.00
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

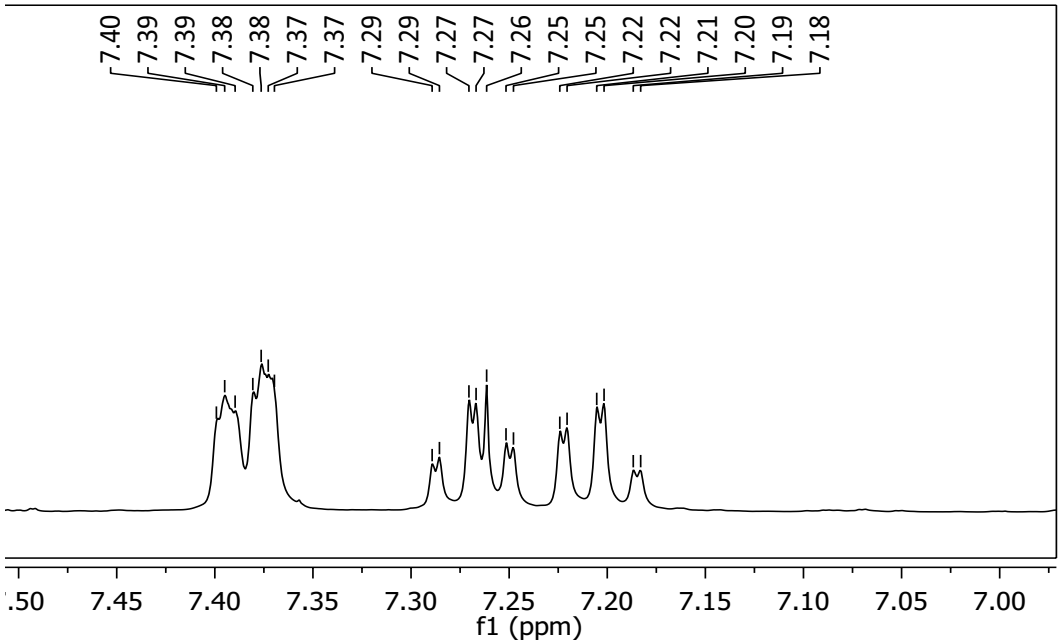

214.69
85.09
67.95
55.99
55.77
50.66
47.38
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
f1 (ppm)

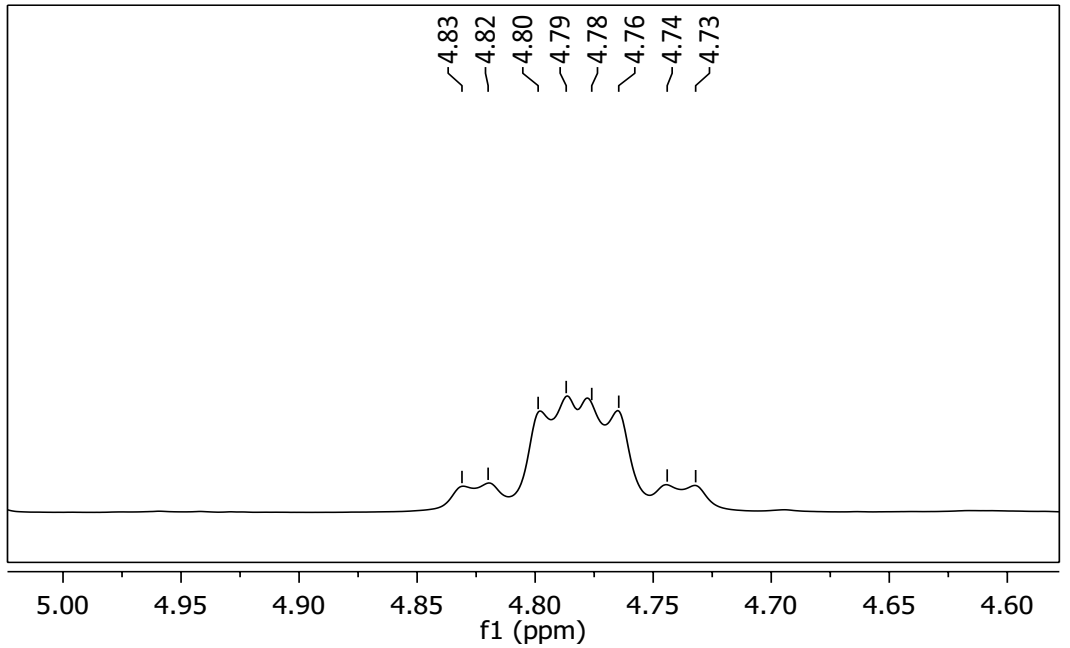

42.49
39.47
39.27
38.15
36.09
35.71
34.84
33.61
31.22
28.06
27.98
24.21
23.78
22.79
22.54
21.53
20.51
18.59
13.71
11.99
43
42
41
40
39
38
37
36
35
34
33
32
31
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
f1 (ppm)

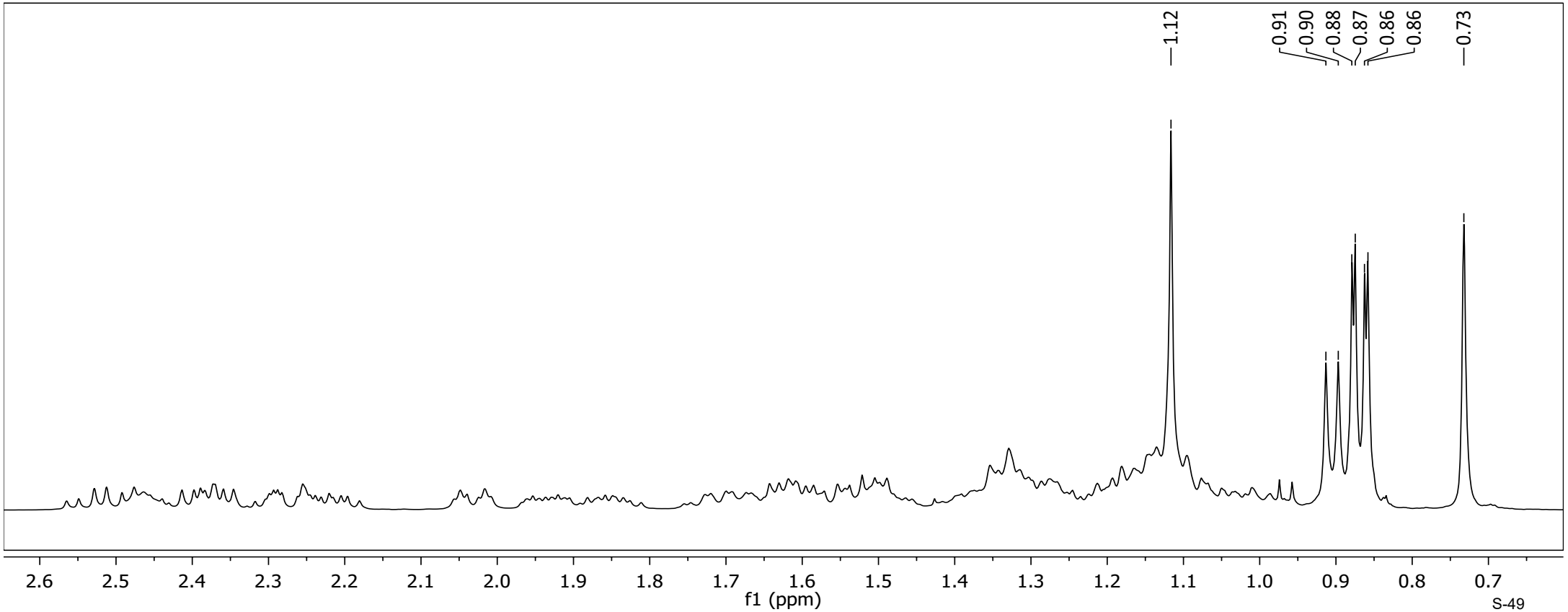


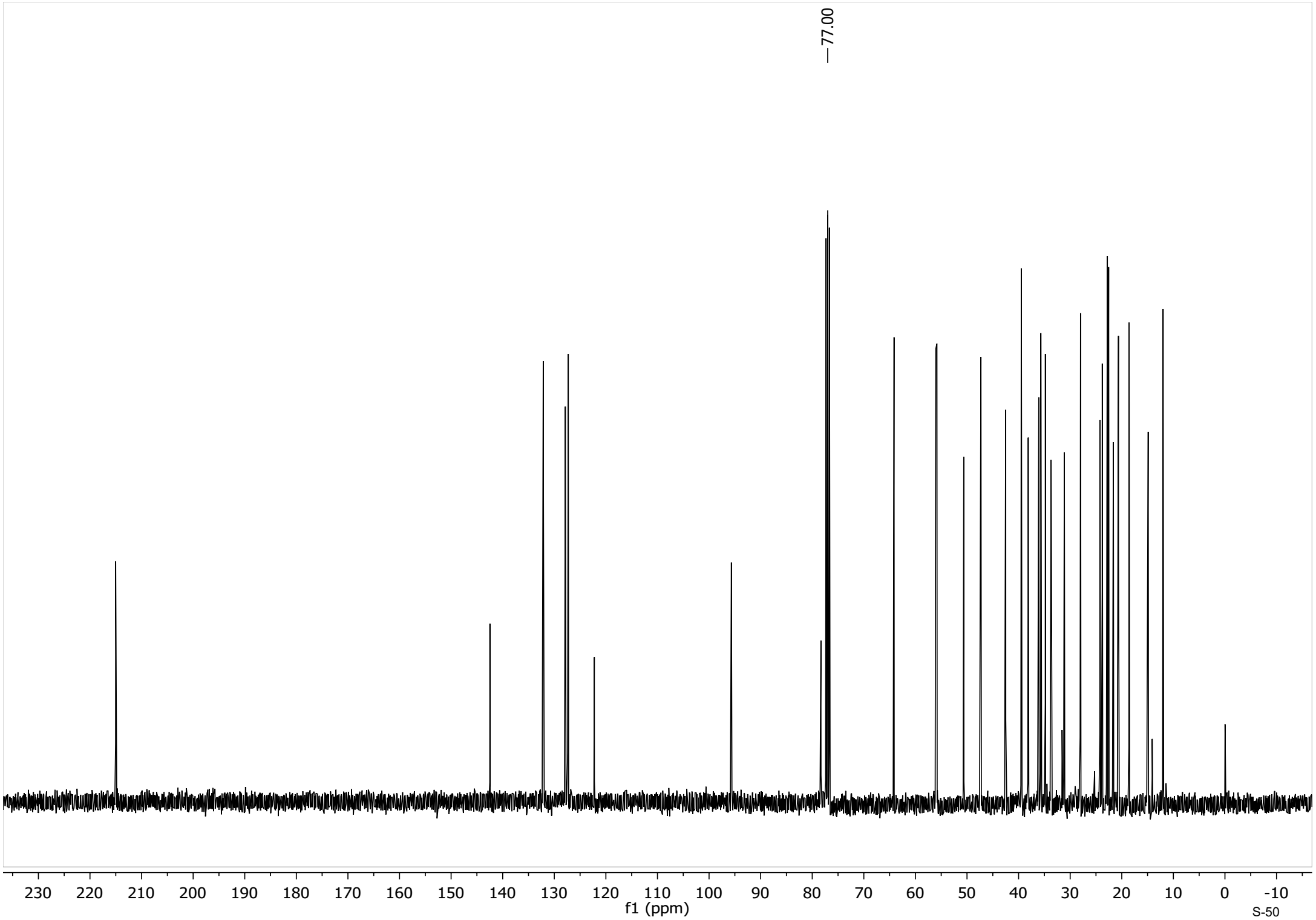
4-(2´-(hydroxymethyl)phenyl)-4,5-secocholest-3-yn-5-one (20)

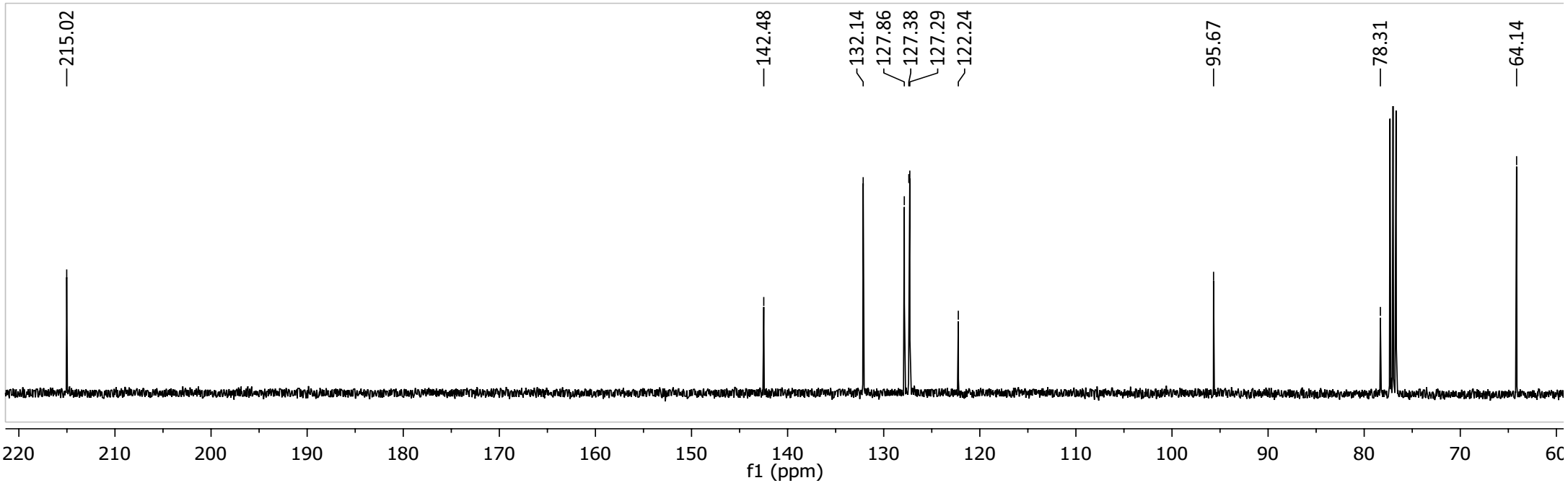

0.00
2.00
1.08
1.08
2.00
7.96
26.02
3.02
5.05
3.07
6.03
3.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

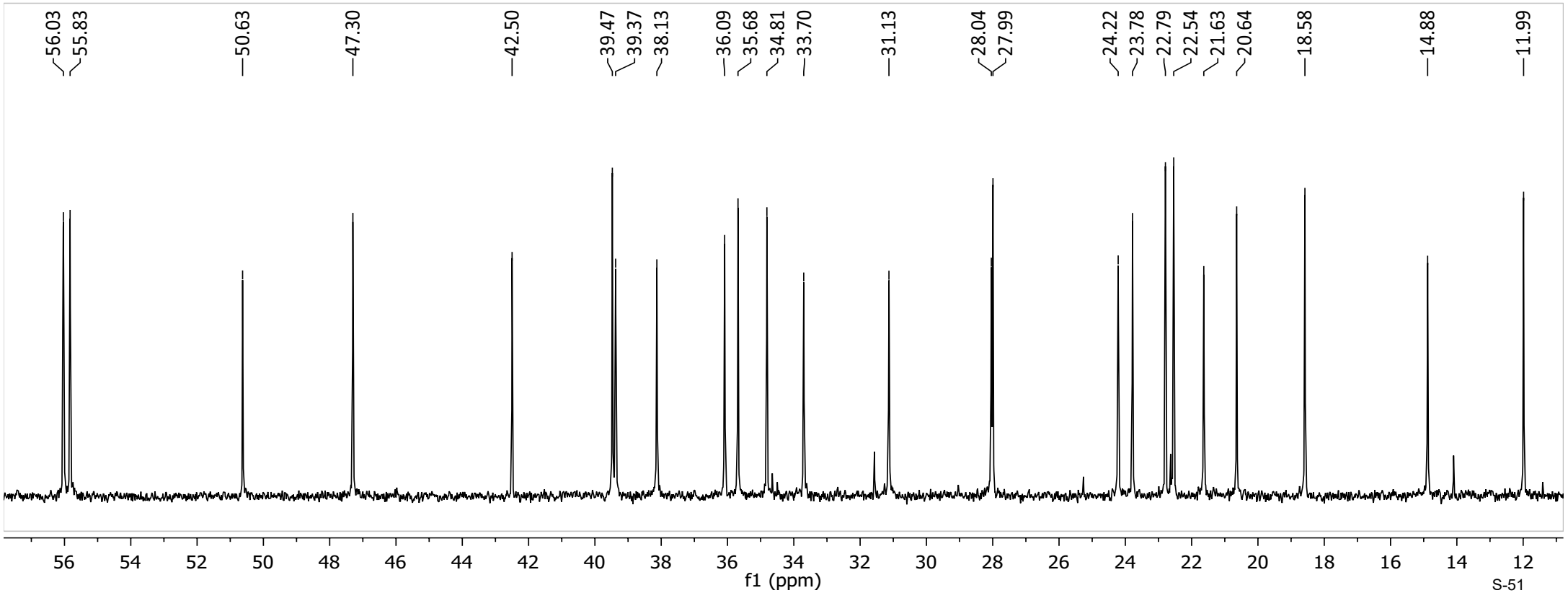

7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.29
7.29
7.27
7.27
7.26
7.25
7.25
7.22
7.22
7.21
7.20
7.19
7.18
.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
7.00
f1 (ppm)

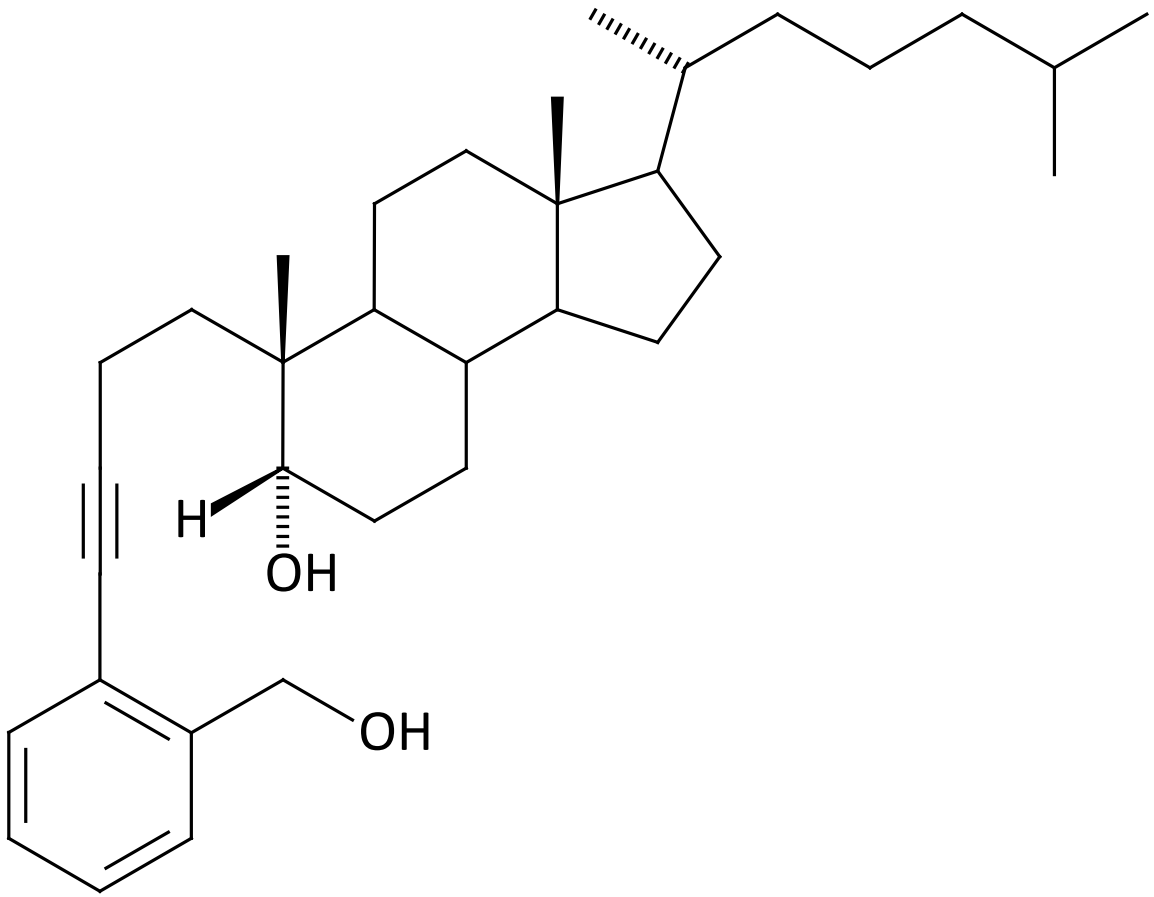

4.83
4.82
4.80
4.79
4.78
4.76
4.74
4.73
5.00
4.95
4.90
4.85
4.80
4.75
4.70
4.65
4.60
f1 (ppm)


1.12
0.91
0.90
0.88
0.87
0.86
0.86
0.73
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
f1 (ppm)

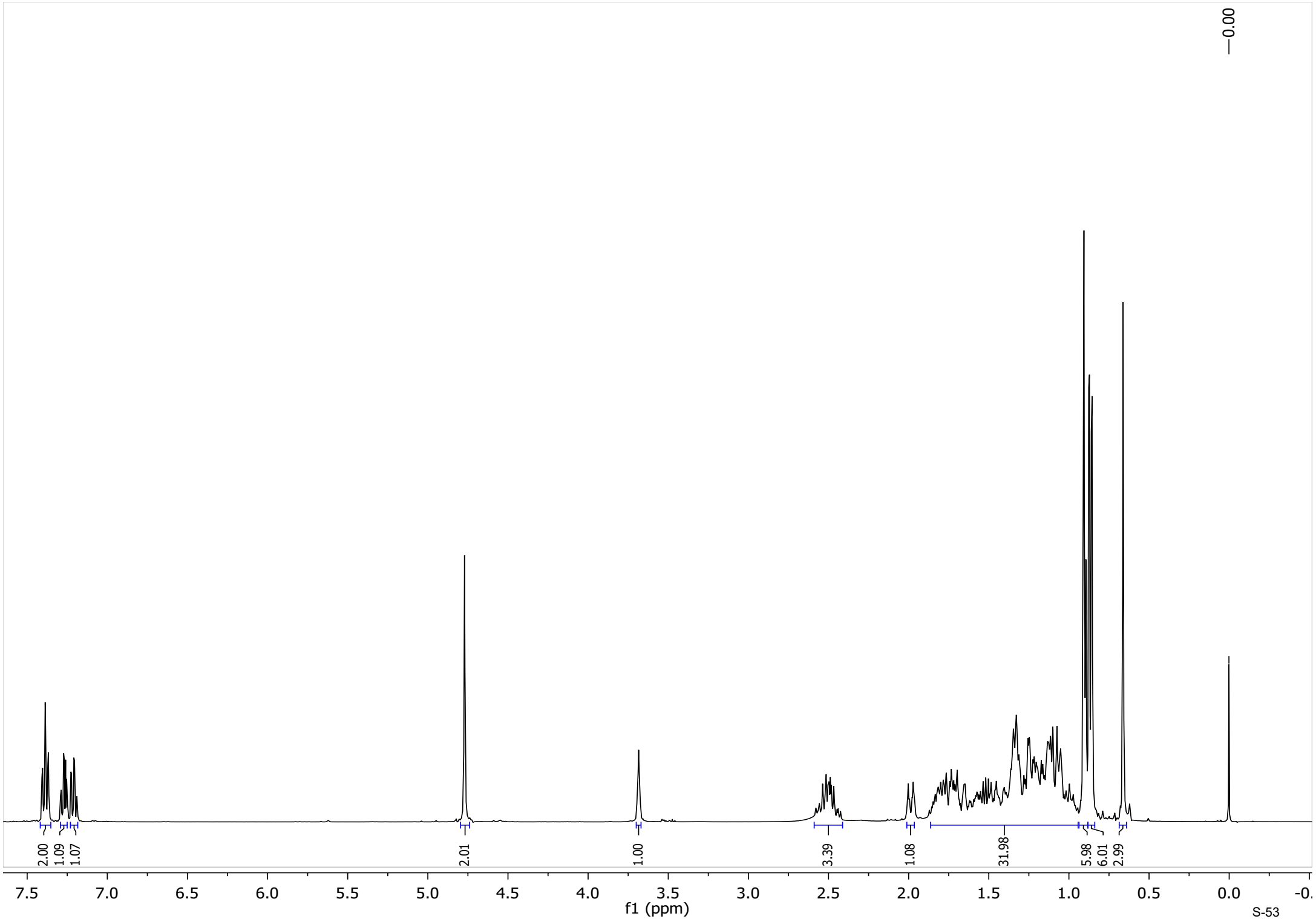

77.00
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

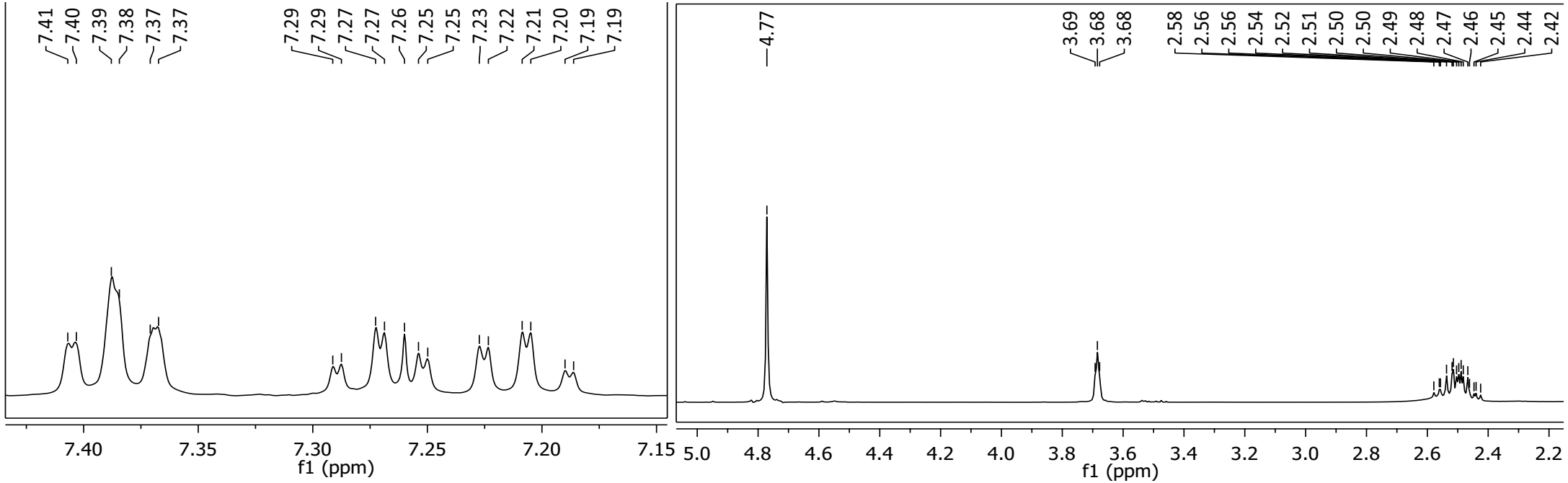

215.02
142.48
132.14
127.86
127.38
127.29
122.24
95.67
78.31
64.14
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
f1 (ppm)

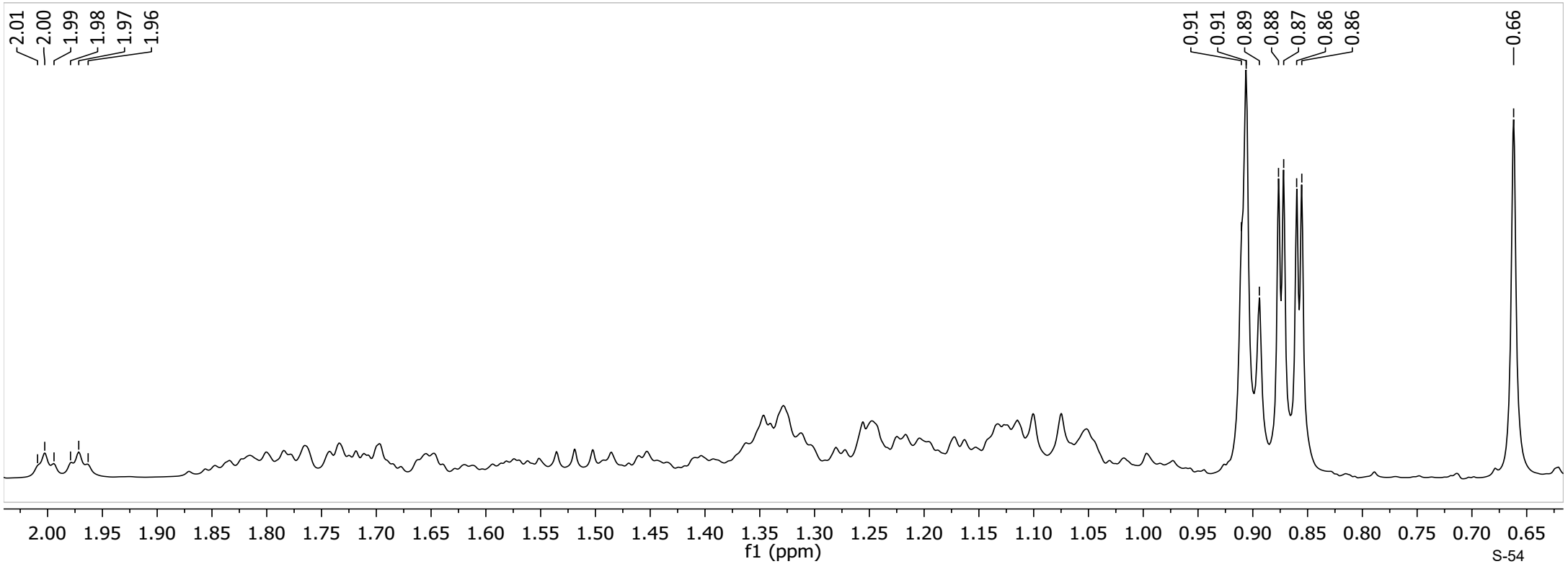

56.03
55.83
50.63
47.30
42.50
39.47
39.37
38.13
36.09
35.68
34.81
33.70
31.13
28.04
27.99
24.22
23.78
22.79
22.54
21.63
20.64
18.58
14.88
11.99
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
f1 (ppm)

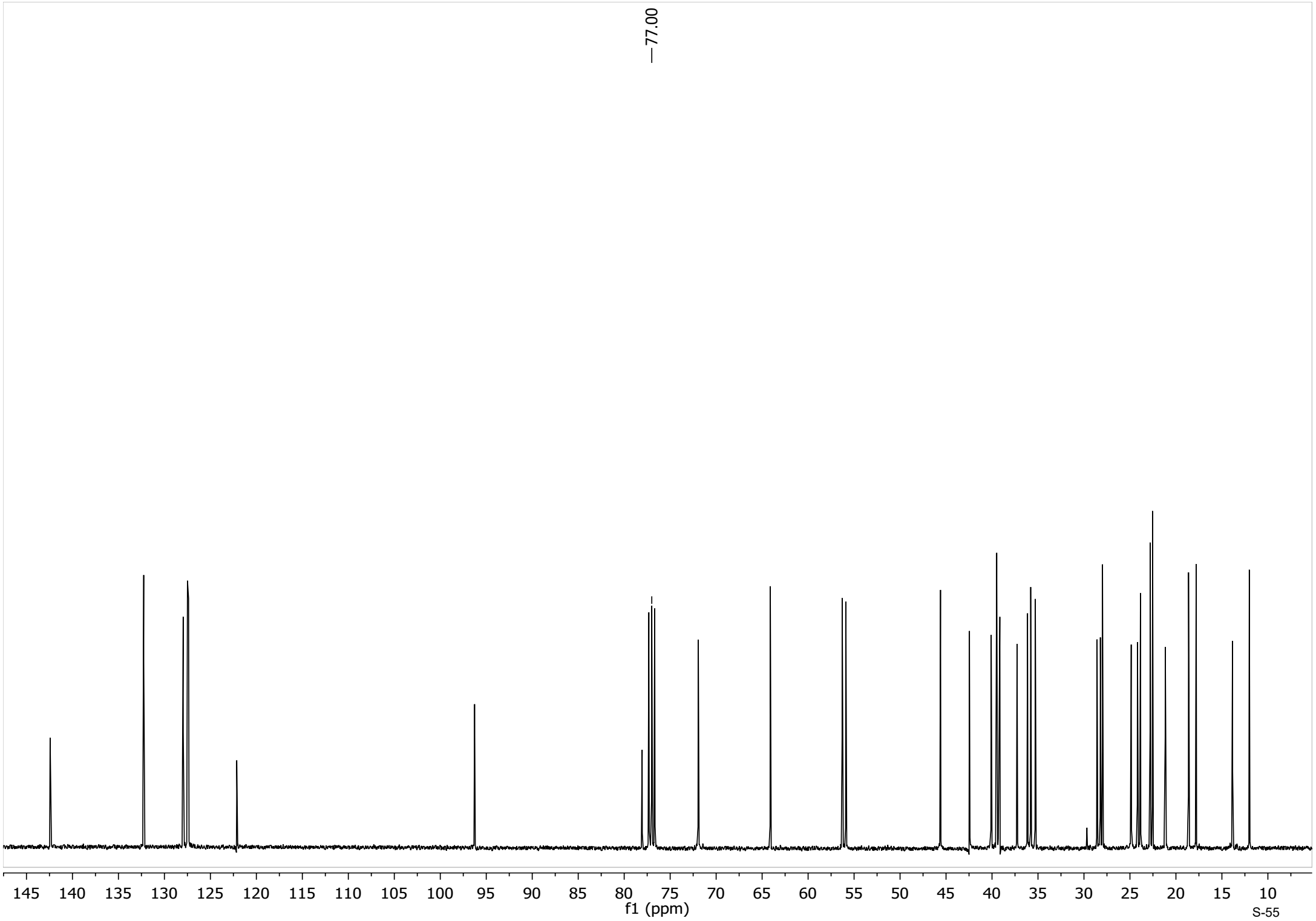


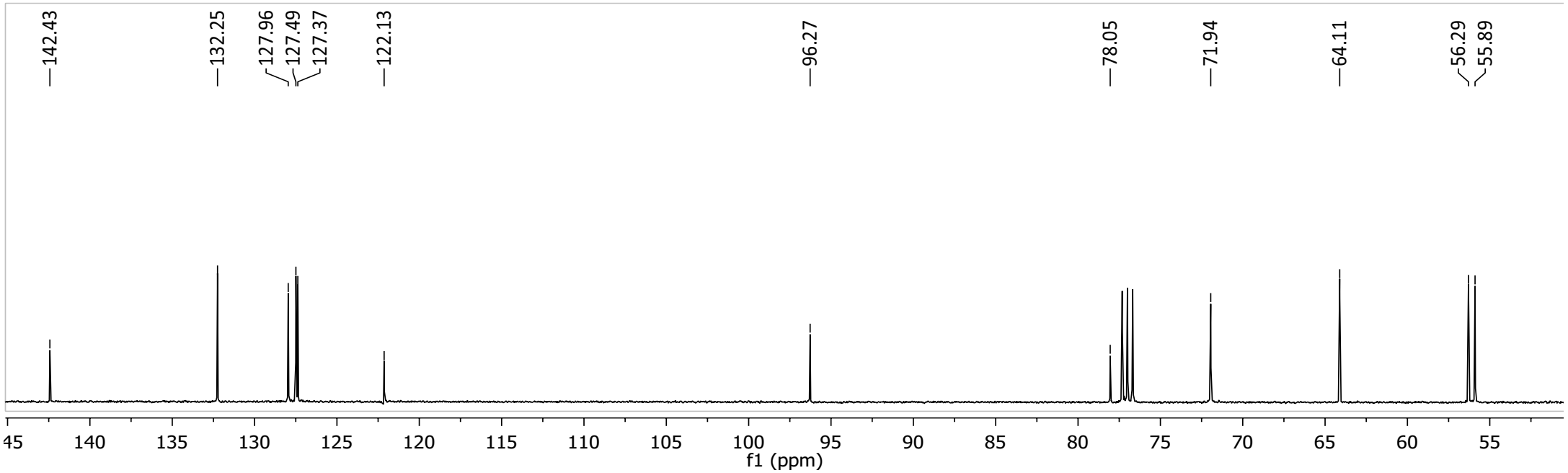
4-(2´-(hydroxymethyl)phenyl)-4,5-secocholest-3-yn-5α-ol (21a)

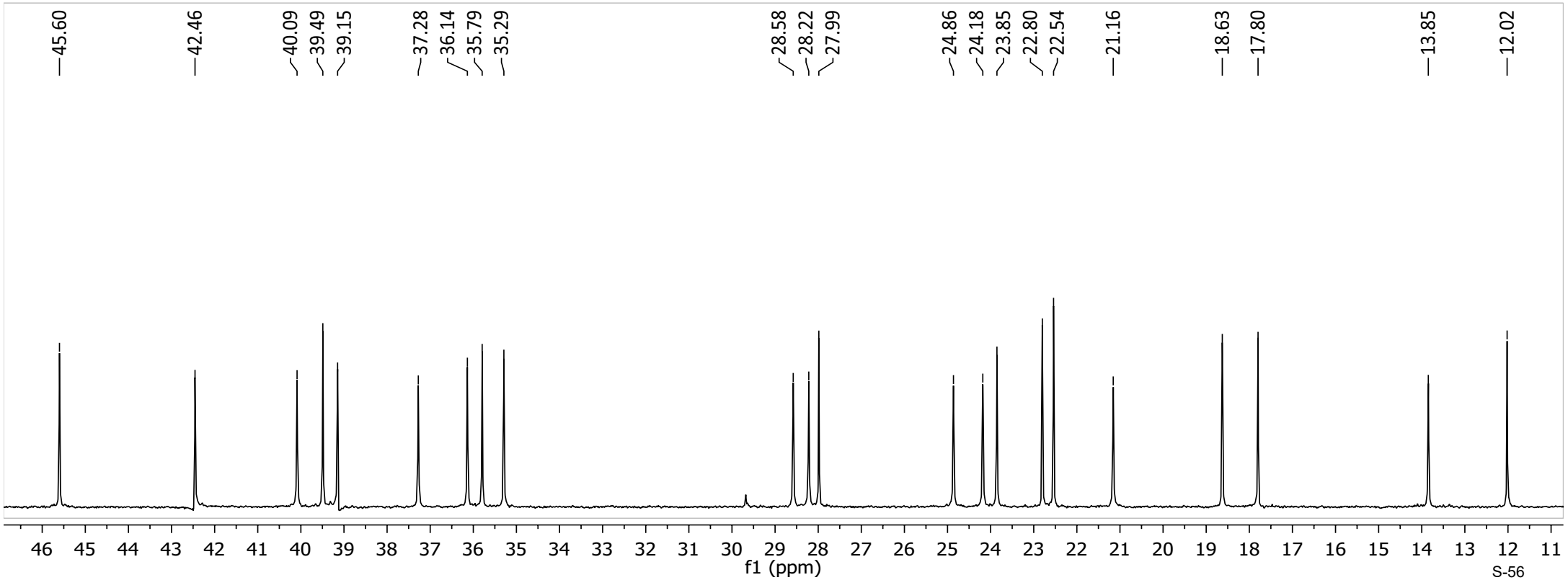

0.00
2.00
1.09
1.07
2.01
1.00
3.39
1.08
31.98
5.98
6.01
2.99
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

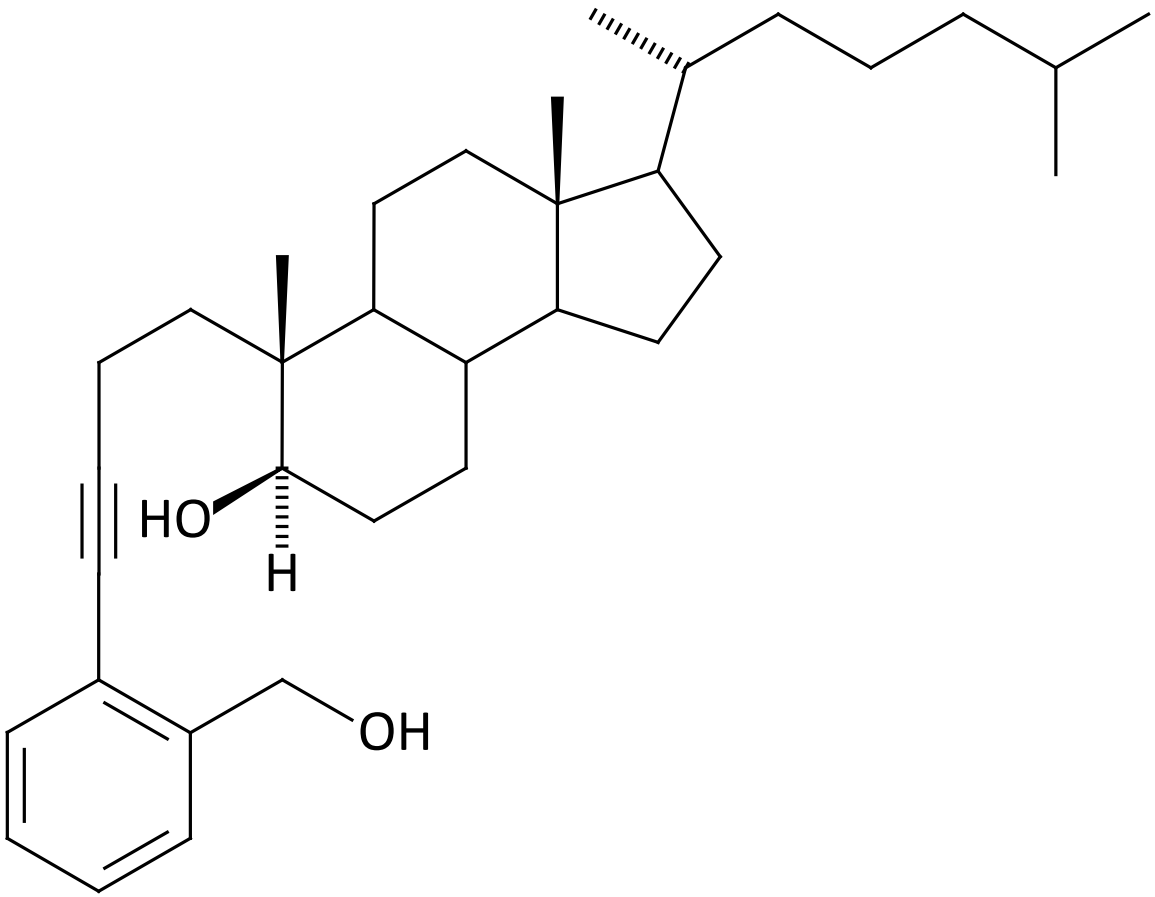

7.41
7.40
7.39
7.38
7.37
7.37
7.29
7.29
7.27
7.27
7.26
7.25
7.25
7.23
7.22
7.21
7.20
7.19
7.19
7.40
7.35
7.30
7.25
7.20
7.15
f1 (ppm)
4.77
3.69
3.68
3.68
2.58
2.56
2.56
2.54
2.52
2.51
2.50
2.50
2.49
2.48
2.47
2.46
2.45
2.44
2.42
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
f1 (ppm)


2.01
2.00
1.99
1.98
1.97
1.96
0.91
0.91
0.89
0.88
0.87
0.86
0.86
0.66
2.00
1.95
1.90
1.85
1.80
1.75
1.70
1.65
1.60
1.55
1.50
1.45
1.40
1.35
1.30
1.25
1.20
1.15
1.10
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
f1 (ppm)

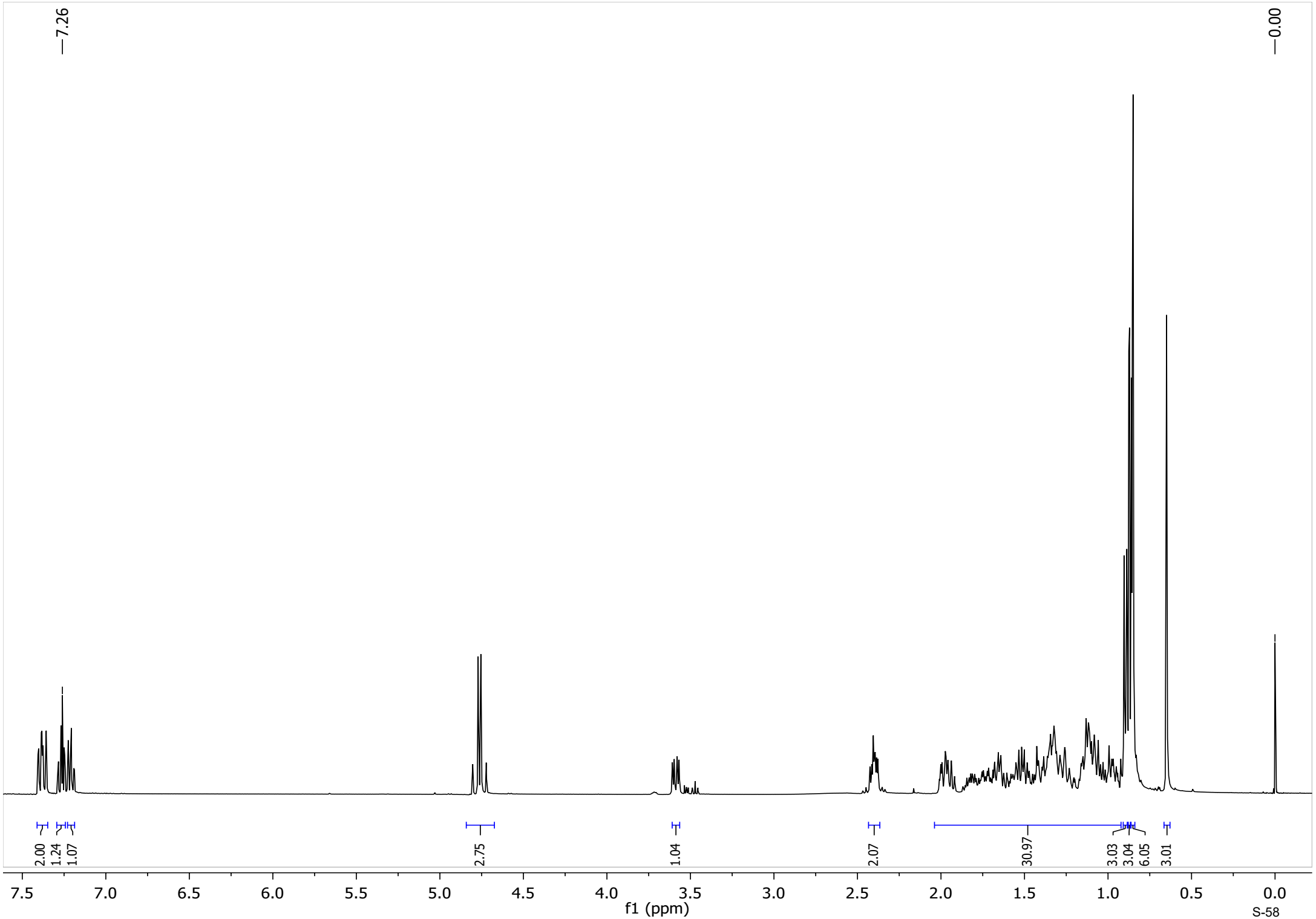

77.00
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

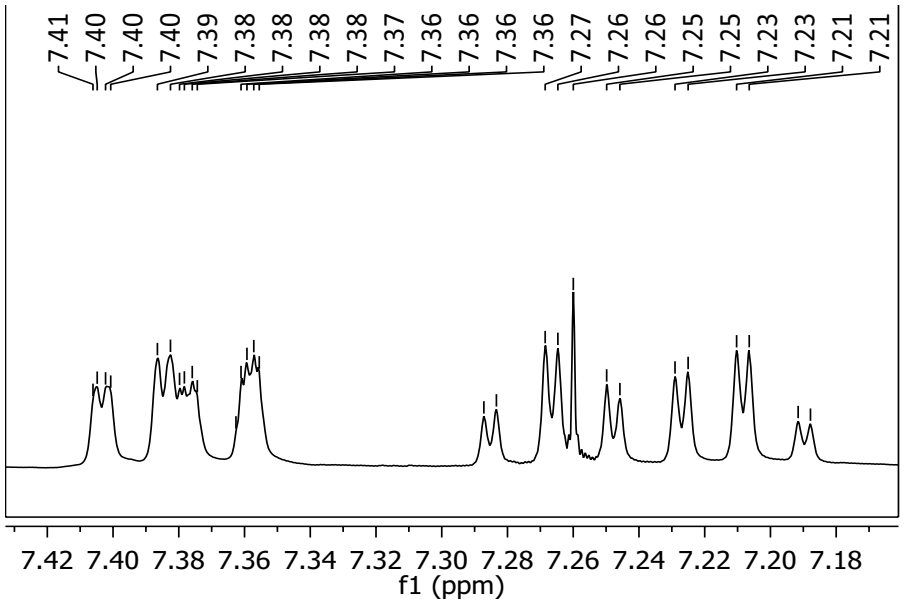

142.43
132.25
127.96
127.49
127.37
122.13
96.27
78.05
71.94
64.11
56.29
55.89
f1 (ppm)

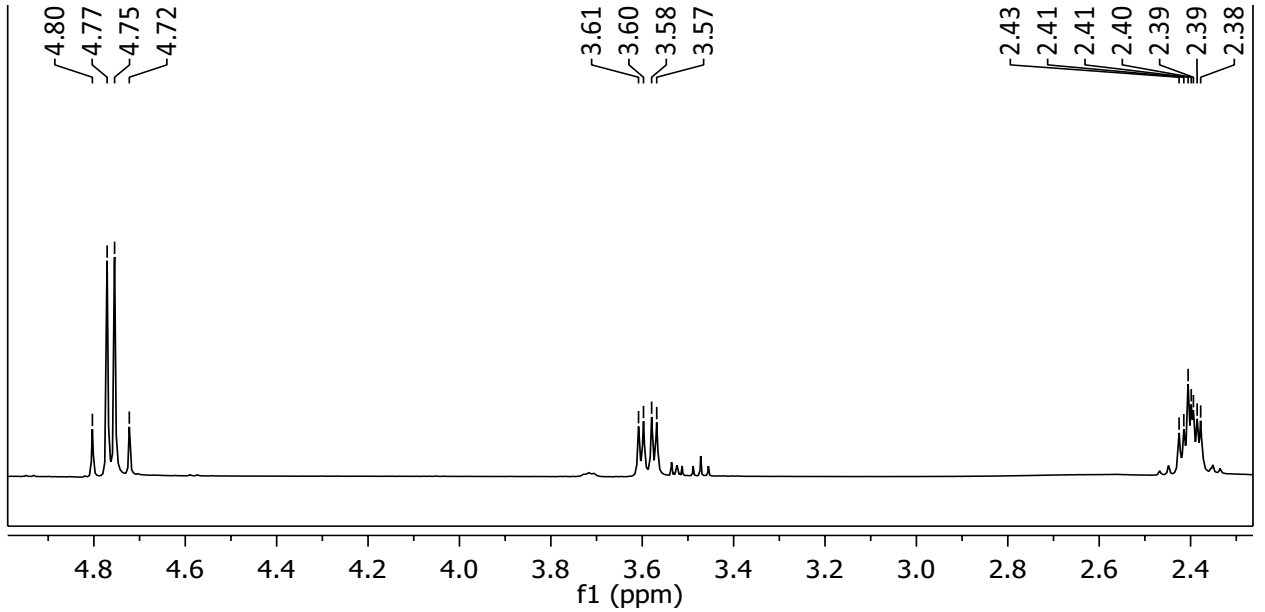

45.60
42.46
40.09
39.49
39.15
37.28
36.14
35.79
35.29
28.58
28.22
27.99
24.86
24.18
23.85
22.80
22.54
21.16
18.63
17.80
13.85
12.02
f1 (ppm)

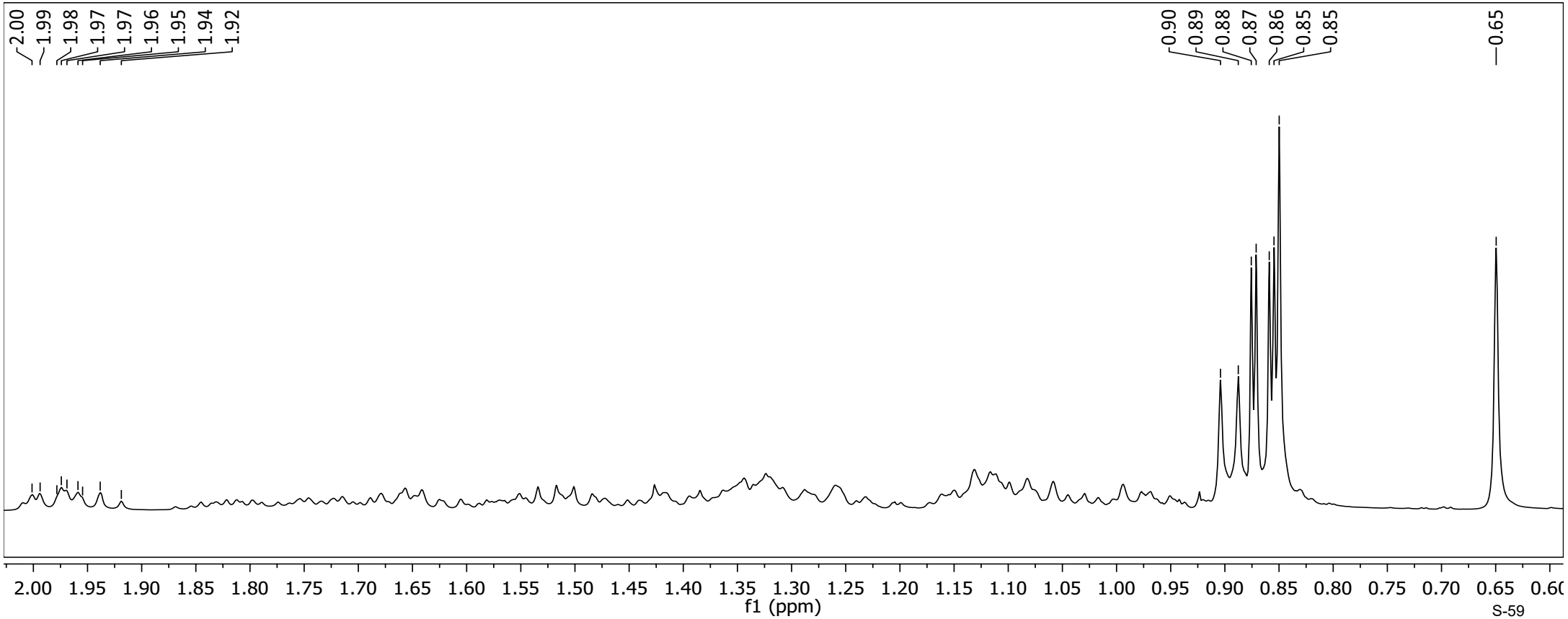


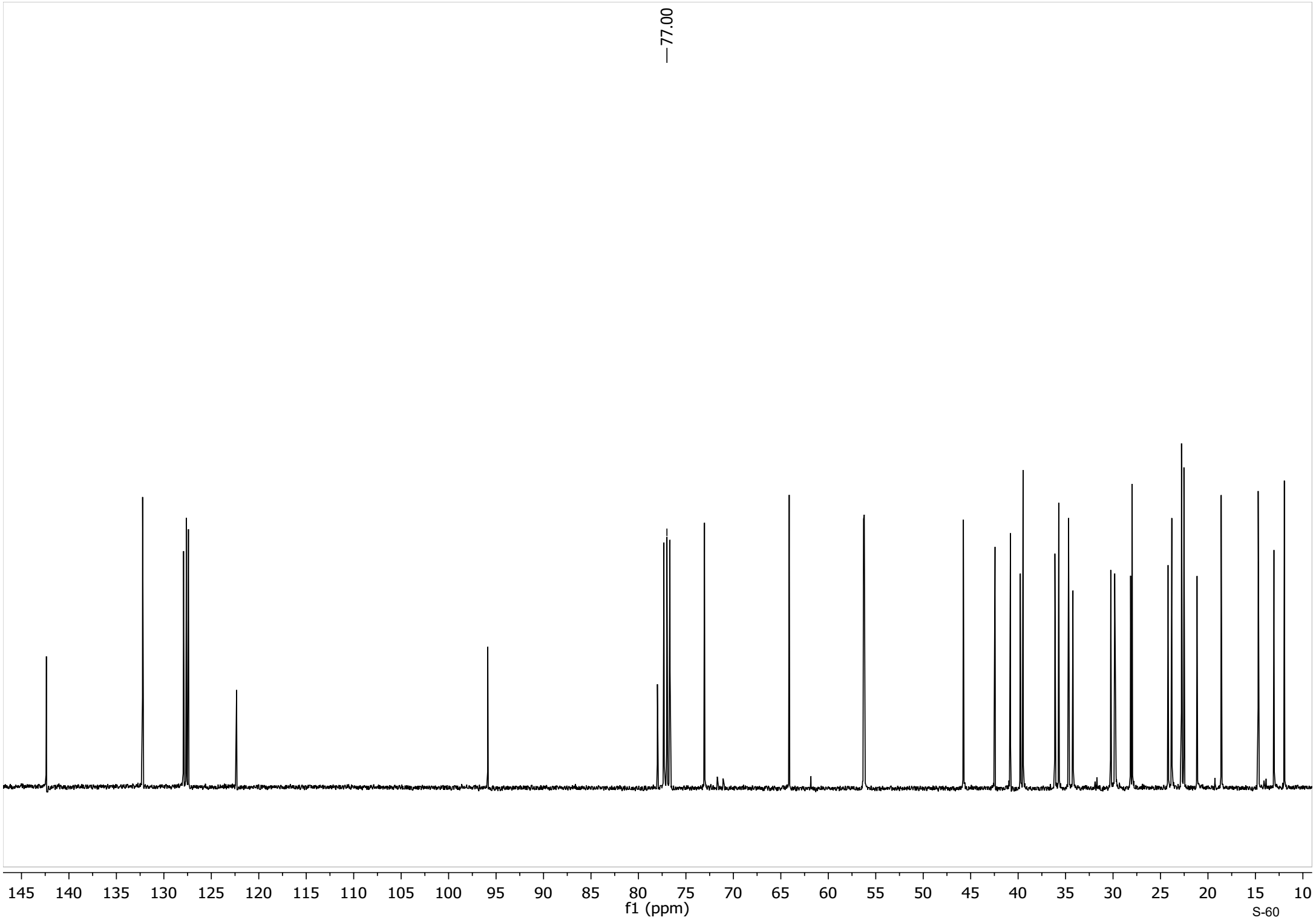
4-(2´-(hydroxymethyl)phenyl)-4,5-secocholest-3-yn-5β-ol (21b)

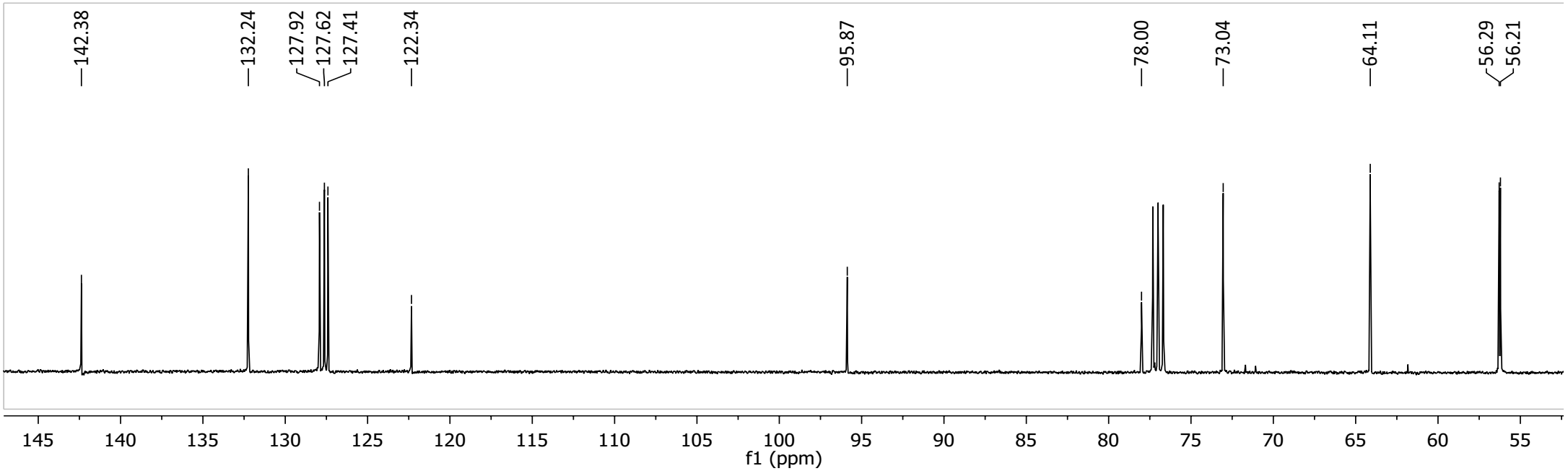

7.26
0.00
2.00
1.24
1.07
2.75
1.04
2.07
30.97
3.03
3.04
6.05
3.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

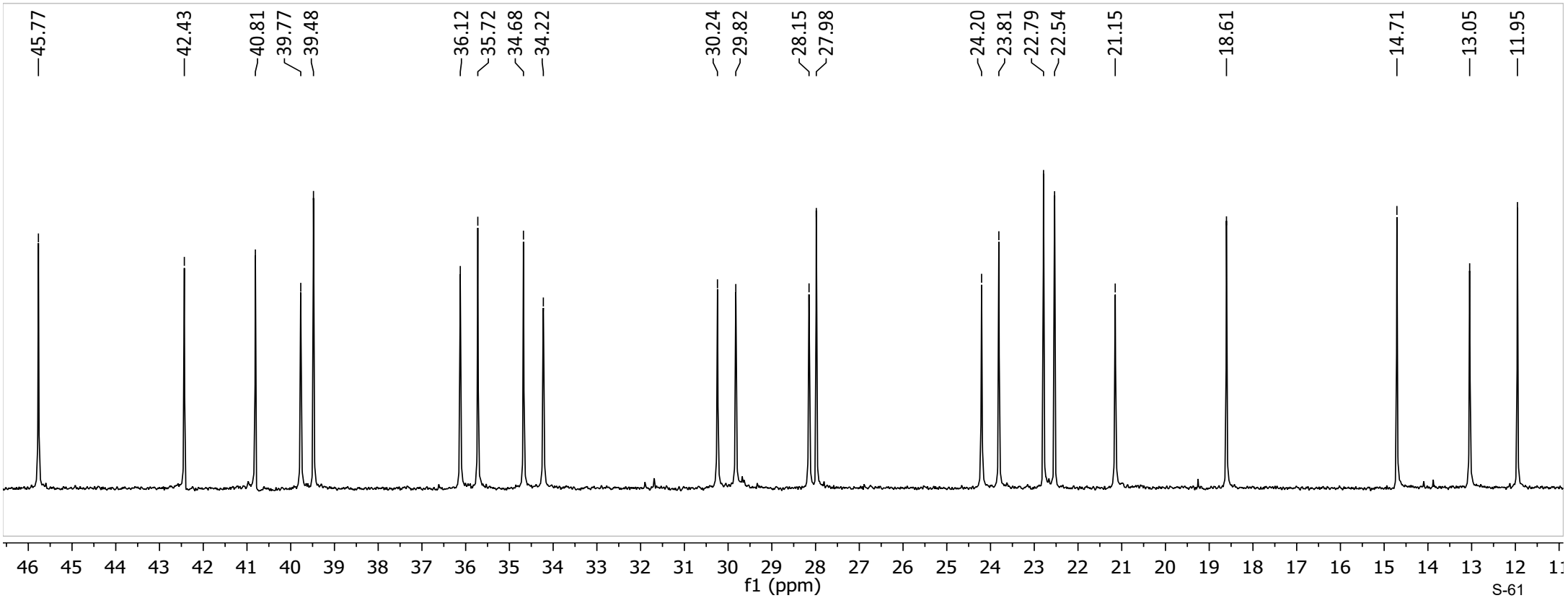

7.41
7.40
7.40
7.40
7.39
7.38
7.38
7.38
7.38
7.37
7.36
7.36
7.36
7.36
7.27
7.26
7.26
7.25
7.25
7.23
7.23
7.21
7.21
7.42 7.40 7.38 7.36 7.34 7.32 7.30 7.28 7.26 7.24 7.22 7.20 7.18
f1 (ppm)

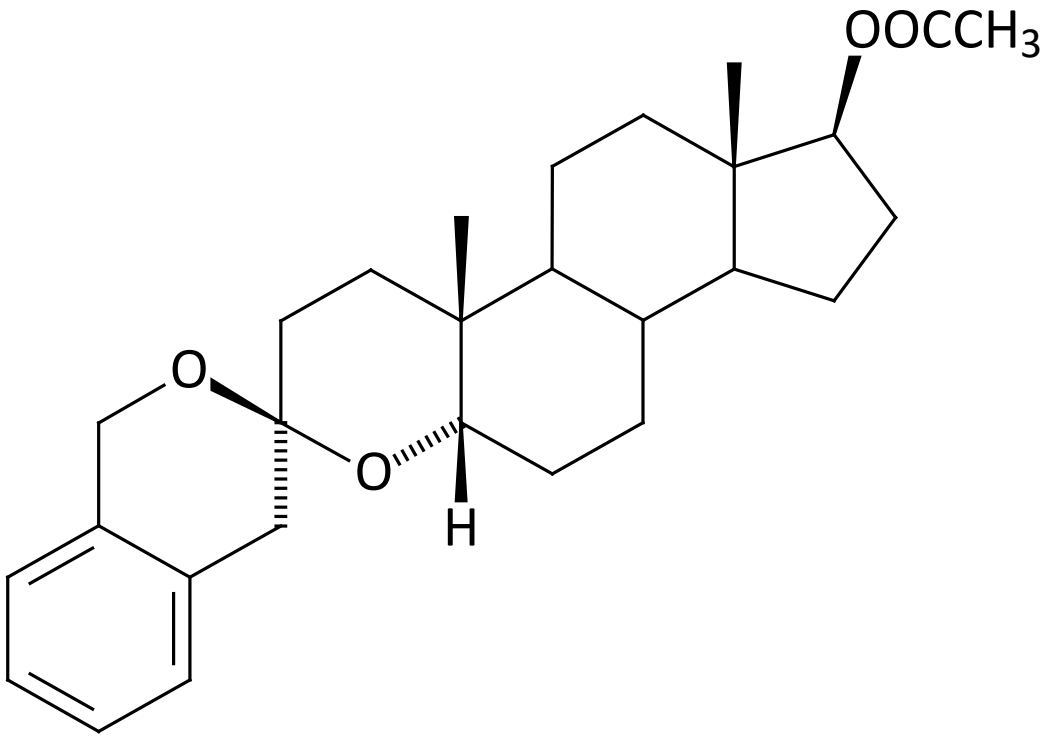

4.80
4.77
4.75
4.72
3.61
3.60
3.58
3.57
2.43
2.41
2.41
2.40
2.39
2.39
2.38
4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4
f1 (ppm)


2.00
1.99
1.98
1.97
1.97
1.96
1.95
1.94
1.92
0.90
0.89
0.88
0.87
0.86
0.85
0.85
0.65
2.00 1.95 1.90 1.85 1.80 1.75 1.70 1.65 1.60 1.55 1.50 1.45 1.40 1.35 1.30 1.25 1.20 1.15 1.10 1.05 1.00 0.95 0.90 0.85 0.80 0.75 0.70 0.65 0.60
f1 (ppm)

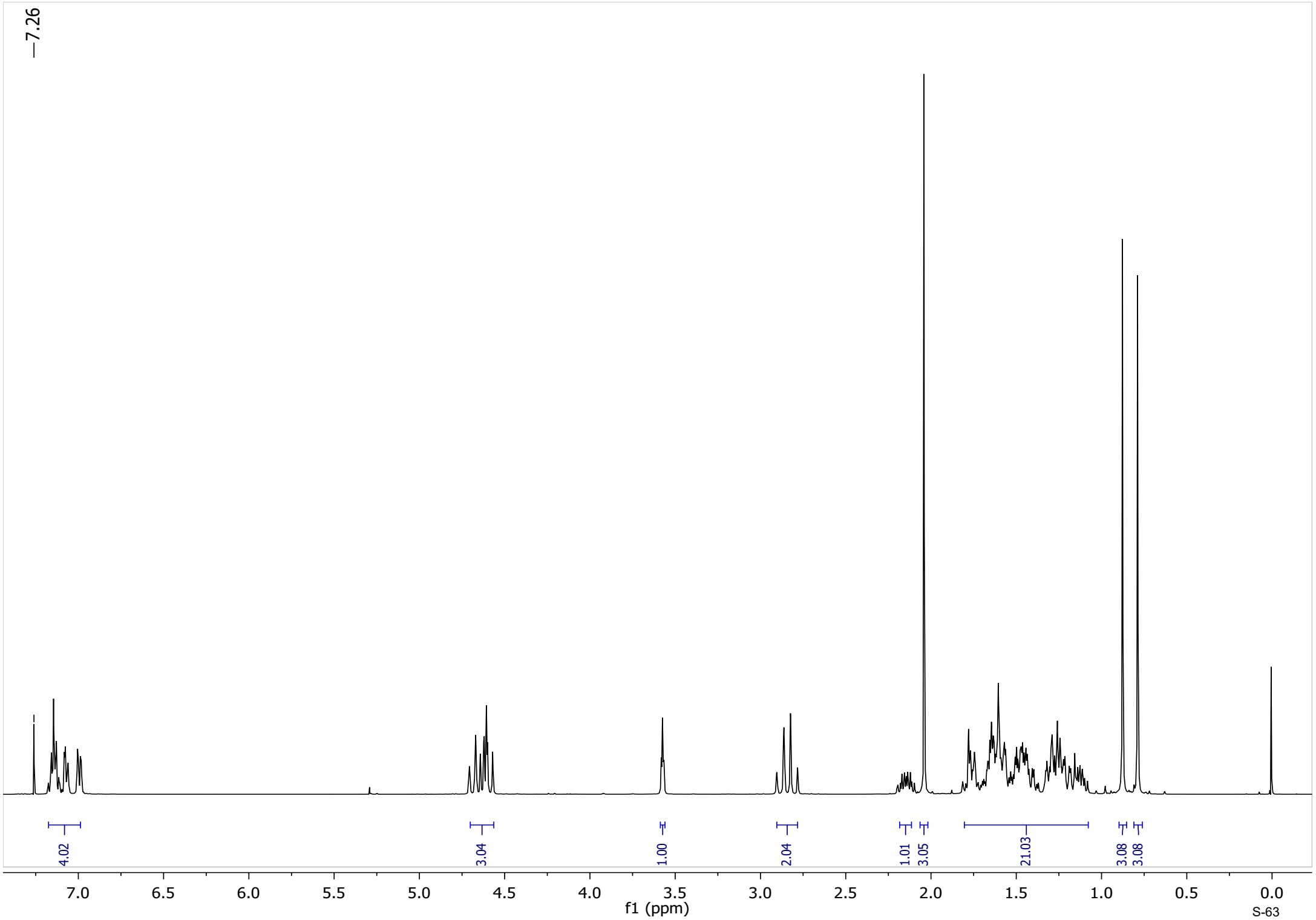

77.00
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

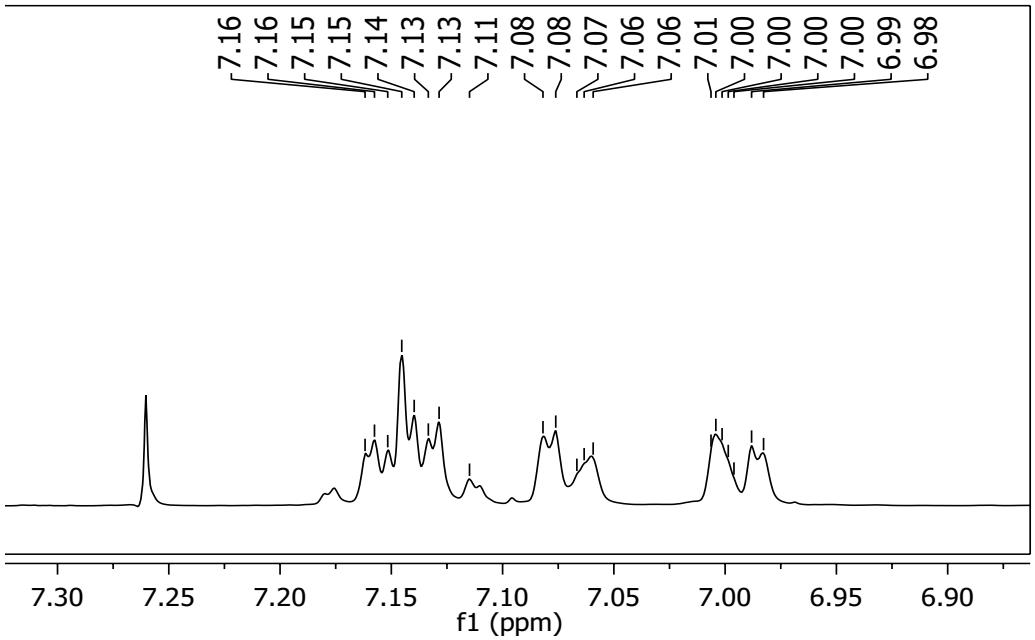

142.38
132.24
127.92
127.62
127.41
122.34
95.87
78.00
73.04
64.11
56.29
56.21
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55
f1 (ppm)

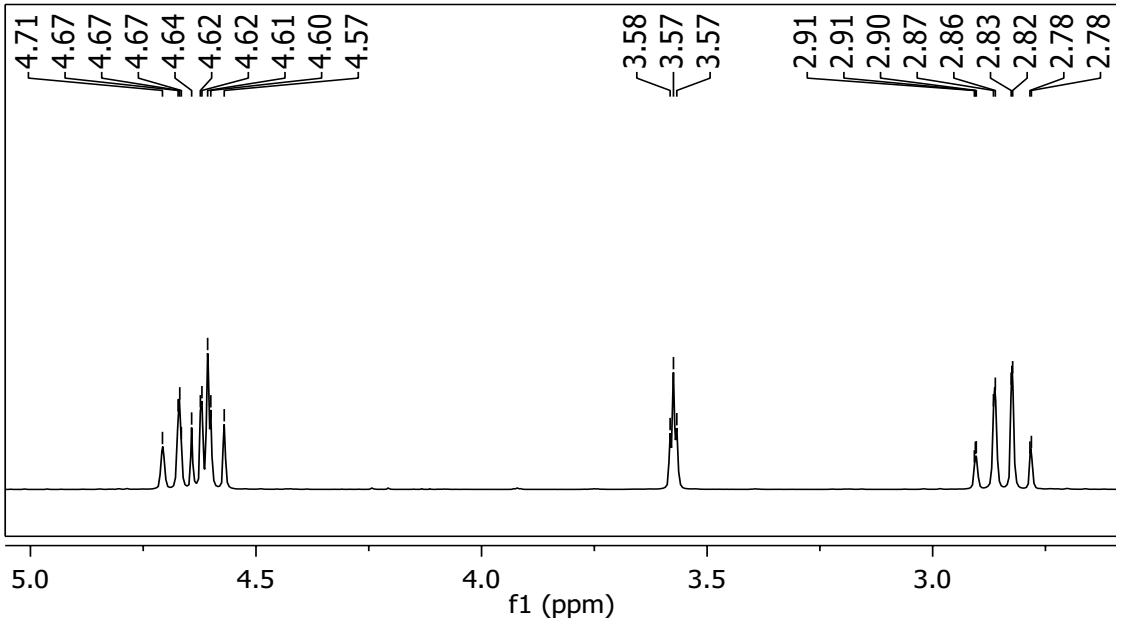

45.77
42.43
40.81
39.77
39.48
36.12
35.72
34.68
34.22
30.24
29.82
28.15
27.98
24.20
23.81
22.79
22.54
21.15
18.61
14.71
13.05
11.95
46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12
f1 (ppm)

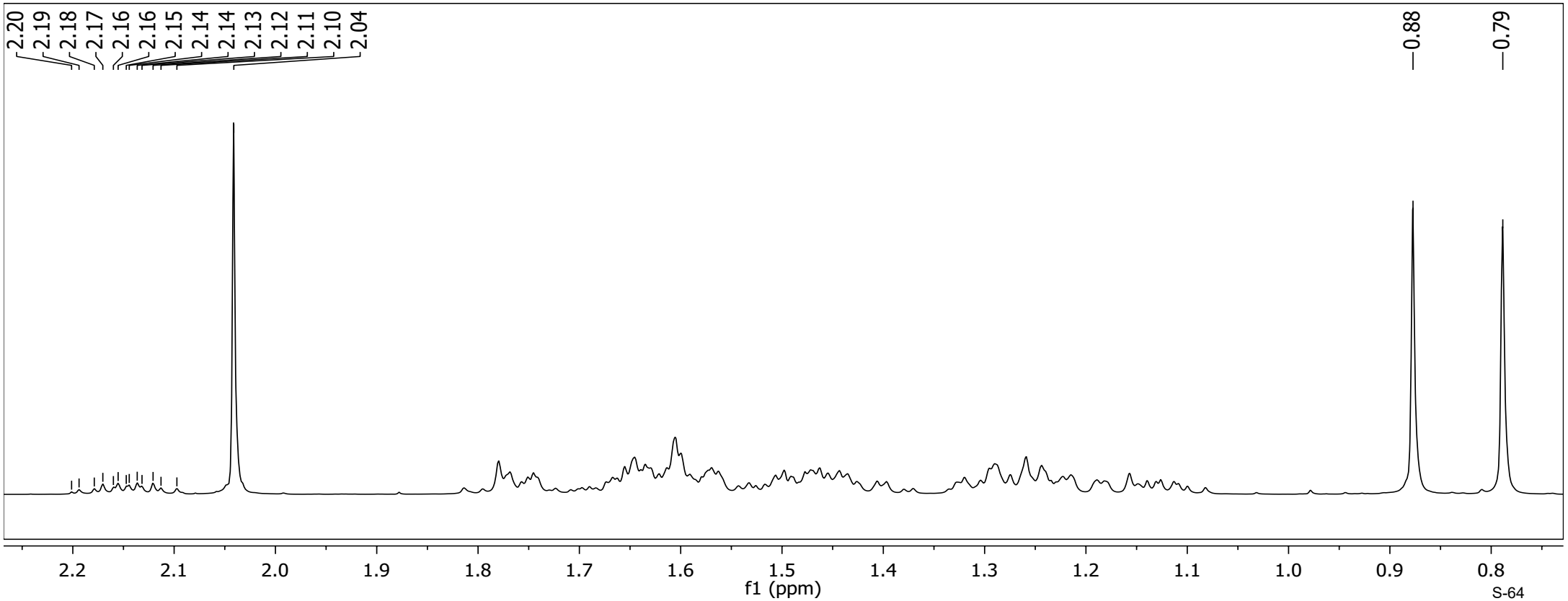


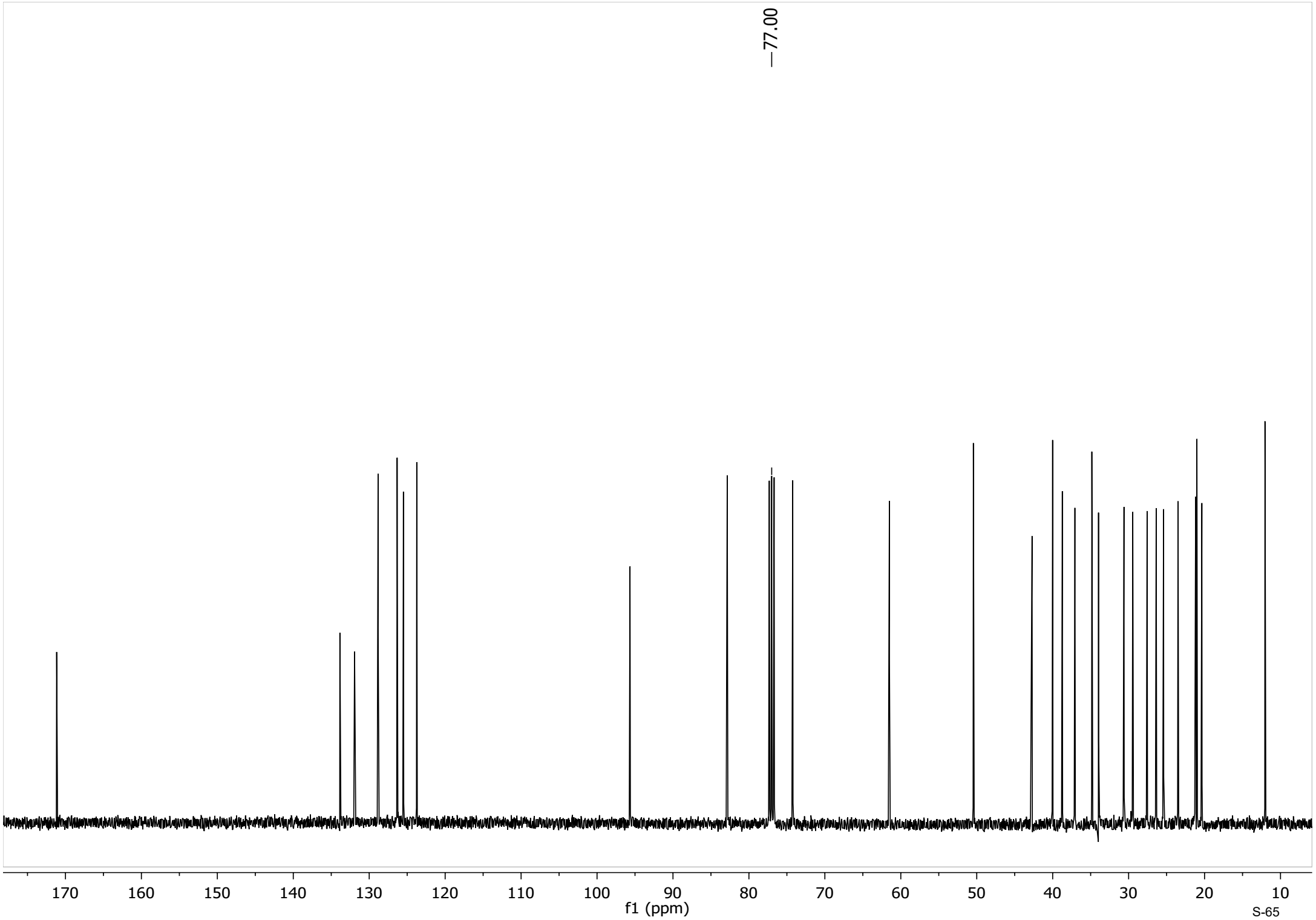
(3*S*)-Spiro-17β-acetoxy-4-oxa-5β-androstan-3,3´-isochromane **(22)**

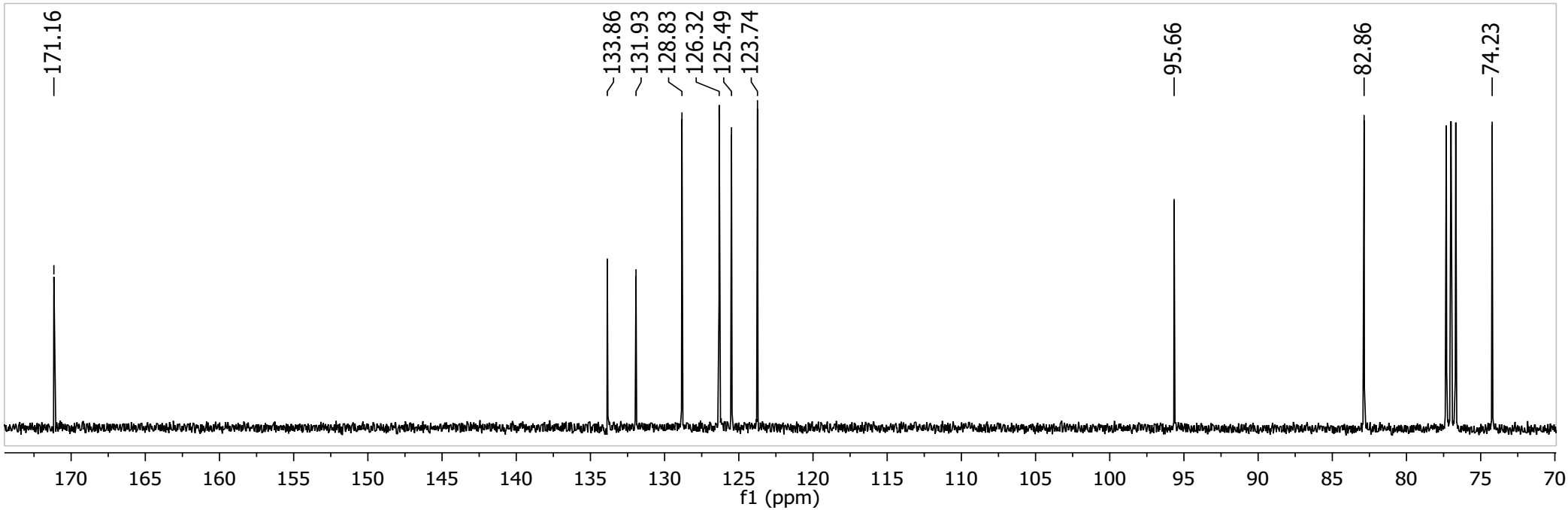

7.26
4.02
3.04
1.00
2.04
1.01
3.05
21.03
3.08
3.08
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

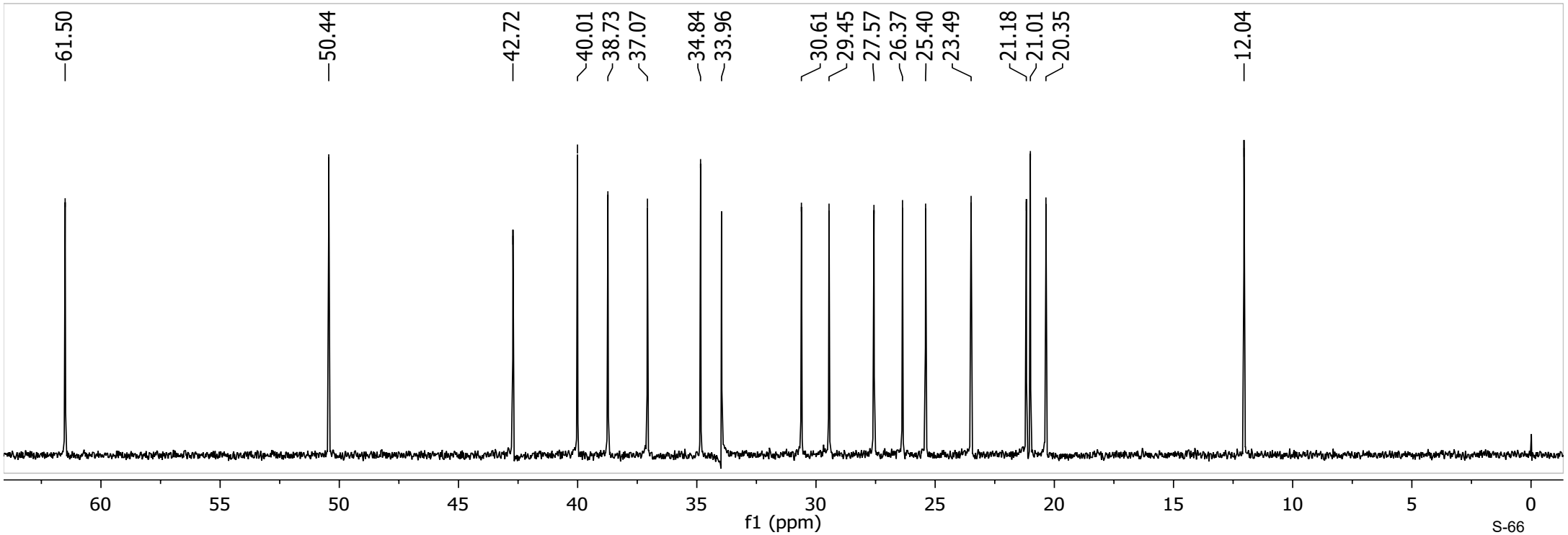

7.16
7.16
7.15
7.15
7.14
7.13
7.13
7.11
7.08
7.08
7.07
7.06
7.06
7.01
7.00
7.00
7.00
7.00
6.99
6.98
7.30
7.25
7.20
7.15
7.10
7.05
7.00
6.95
6.90
f1 (ppm)

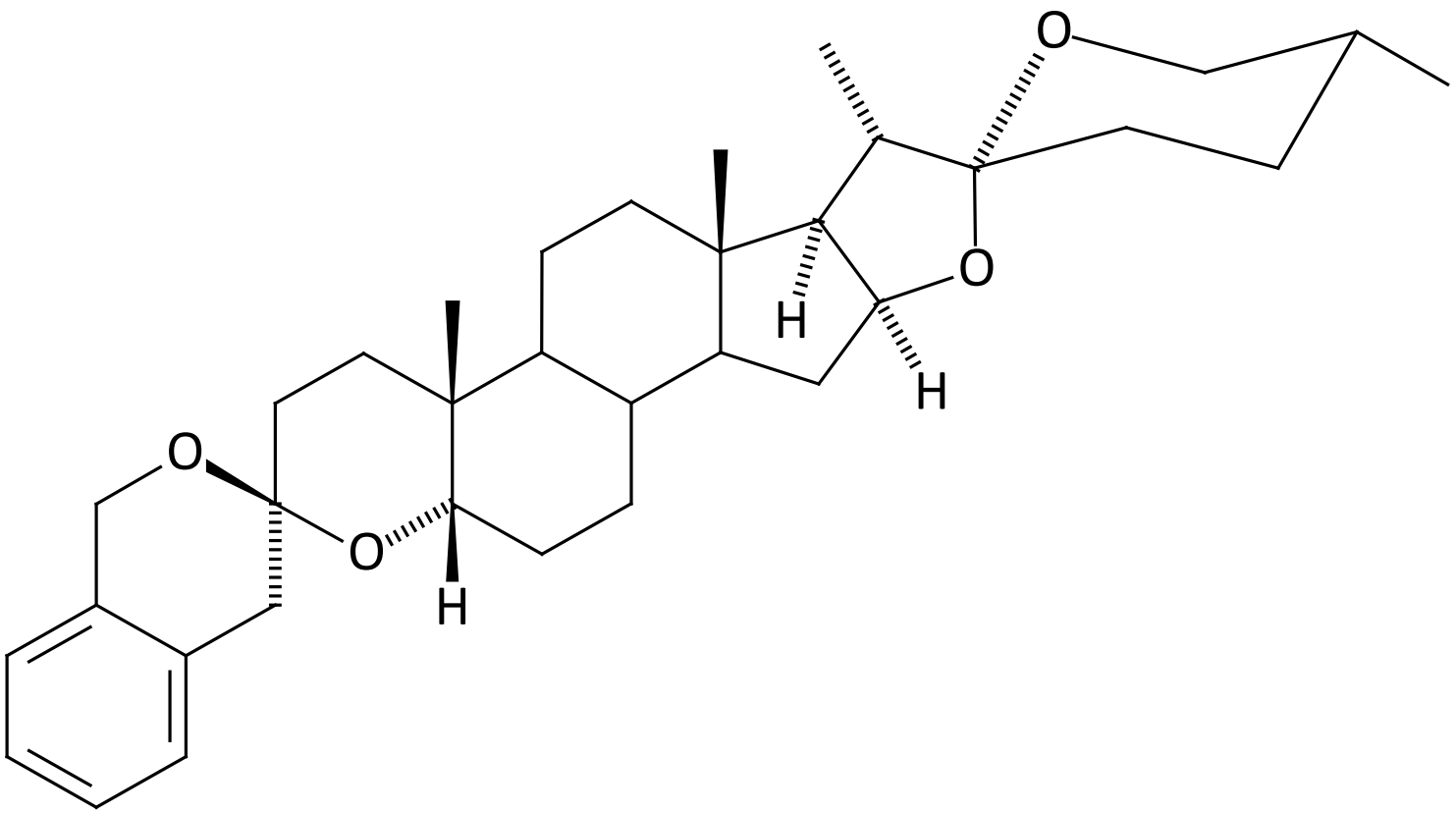

4.71
4.67
4.67
4.67
4.64
4.62
4.62
4.61
4.60
4.57
3.58
3.57
3.57
2.91
2.91
2.90
2.87
2.86
2.83
2.82
2.78
2.78
5.0
4.5
4.0
3.5
3.0
f1 (ppm)


2.20
2.19
2.18
2.17
2.16
2.16
2.15
2.14
2.14
2.13
2.12
2.11
2.10
2.04
0.88
0.79
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
f1 (ppm)

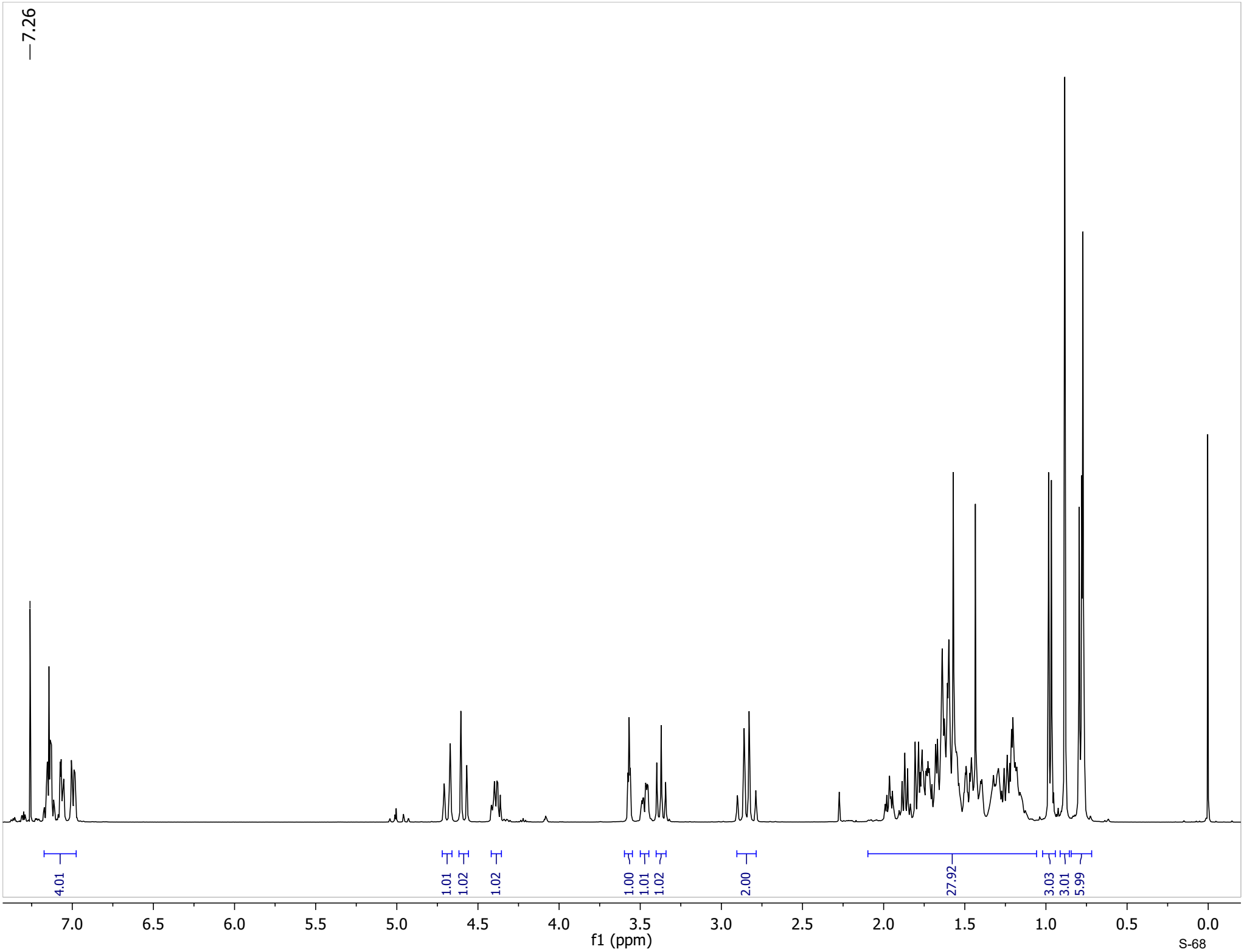

77.00
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

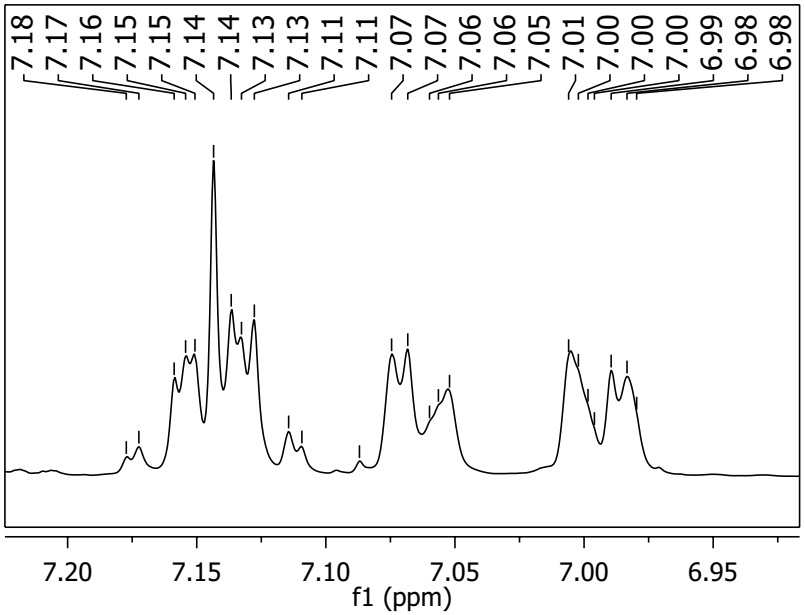

171.16
133.86
131.93
128.83
126.32
125.49
123.74
95.66
82.86
74.23
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70
f1 (ppm)

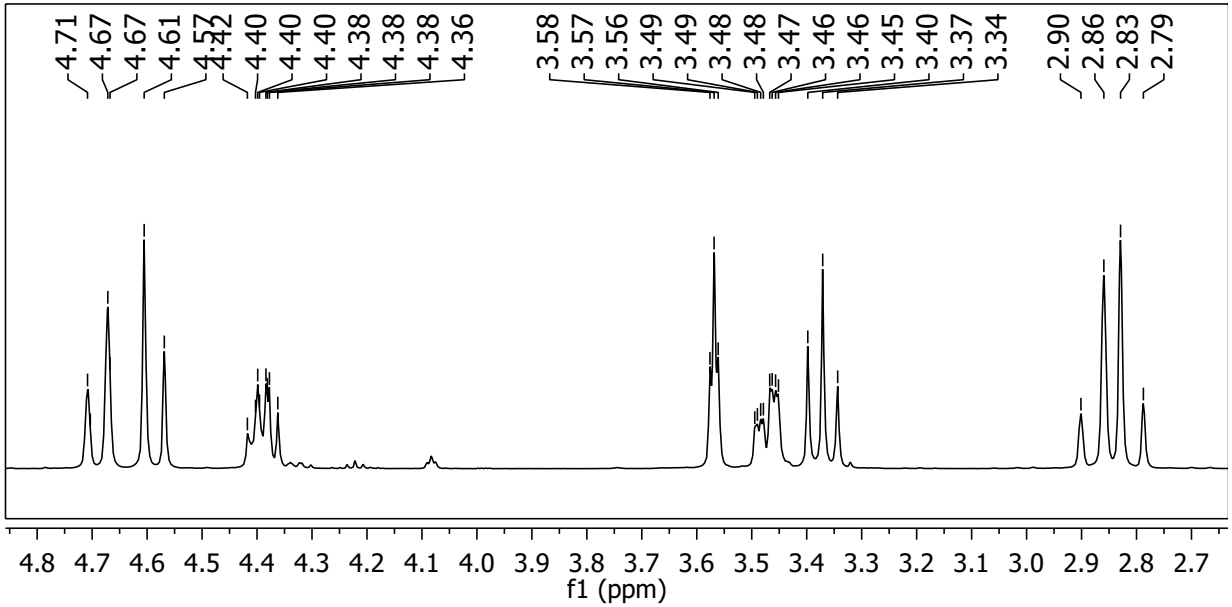

61.50
50.44
42.72
40.01
38.73
37.07
34.84
33.96
30.61
29.45
27.57
26.37
25.40
23.49
21.18
21.01
20.35
12.04
60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

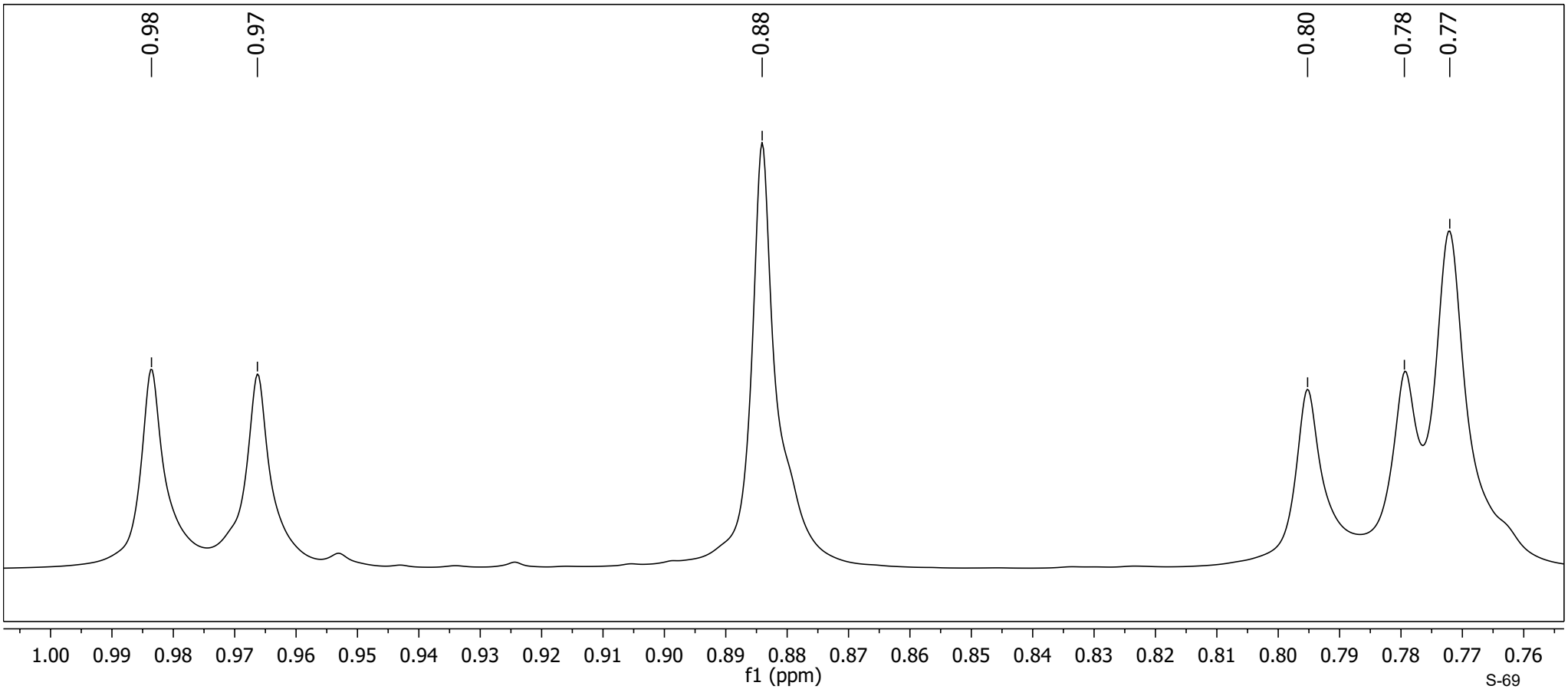


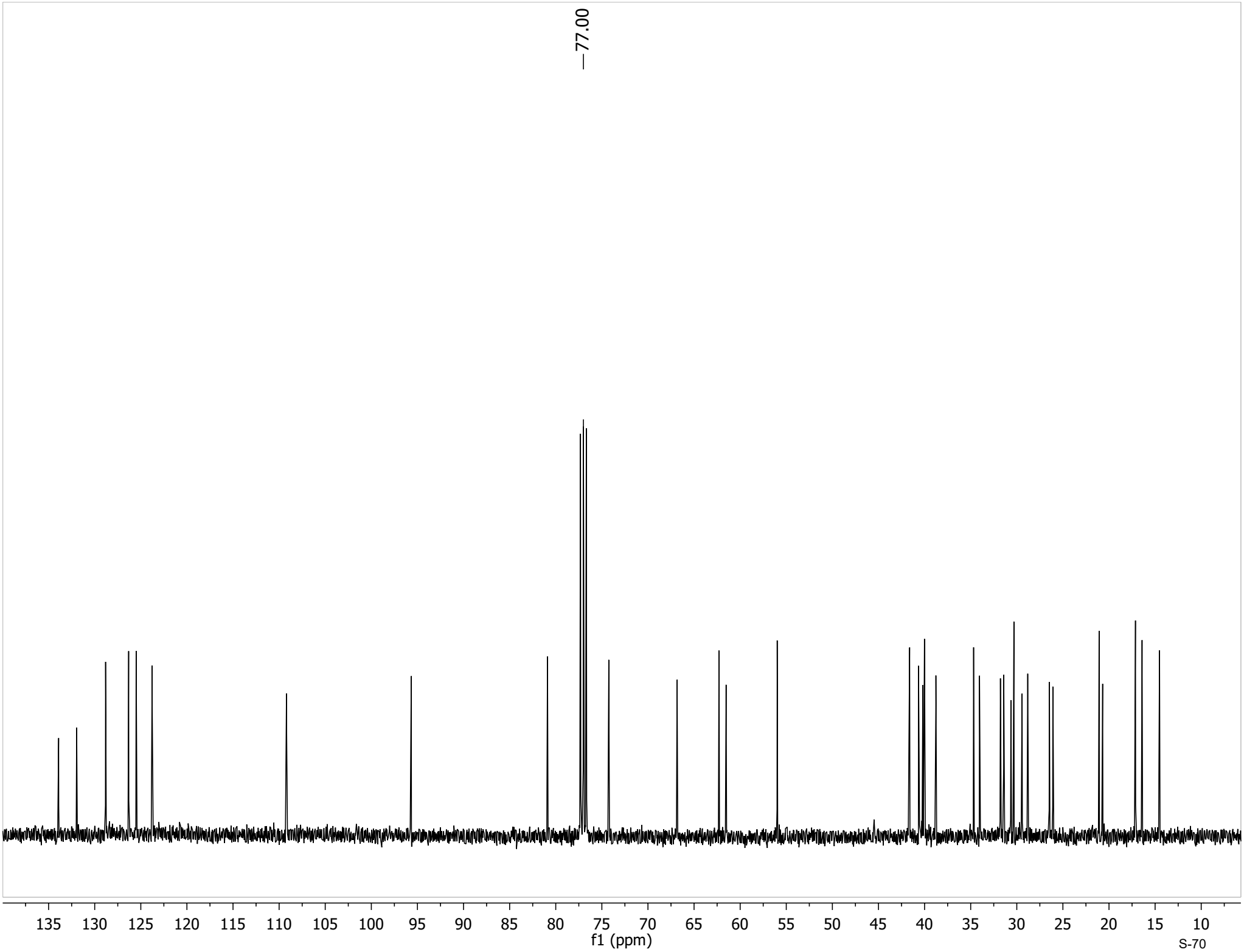
(3*S*)-Spiro-4-oxa-5β-spirostan-3,3´-isochromane **(23)**

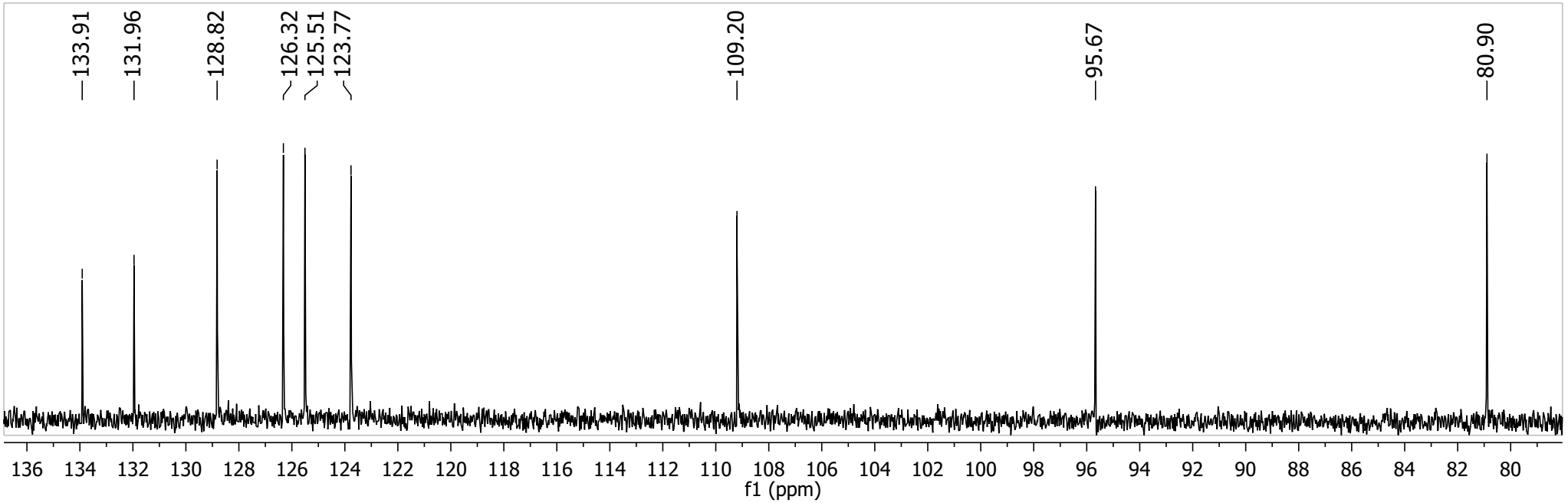

7.26
4.01
1.01
1.02
1.02
1.00
1.01
1.02
2.00
27.92
3.03
3.01
5.99
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

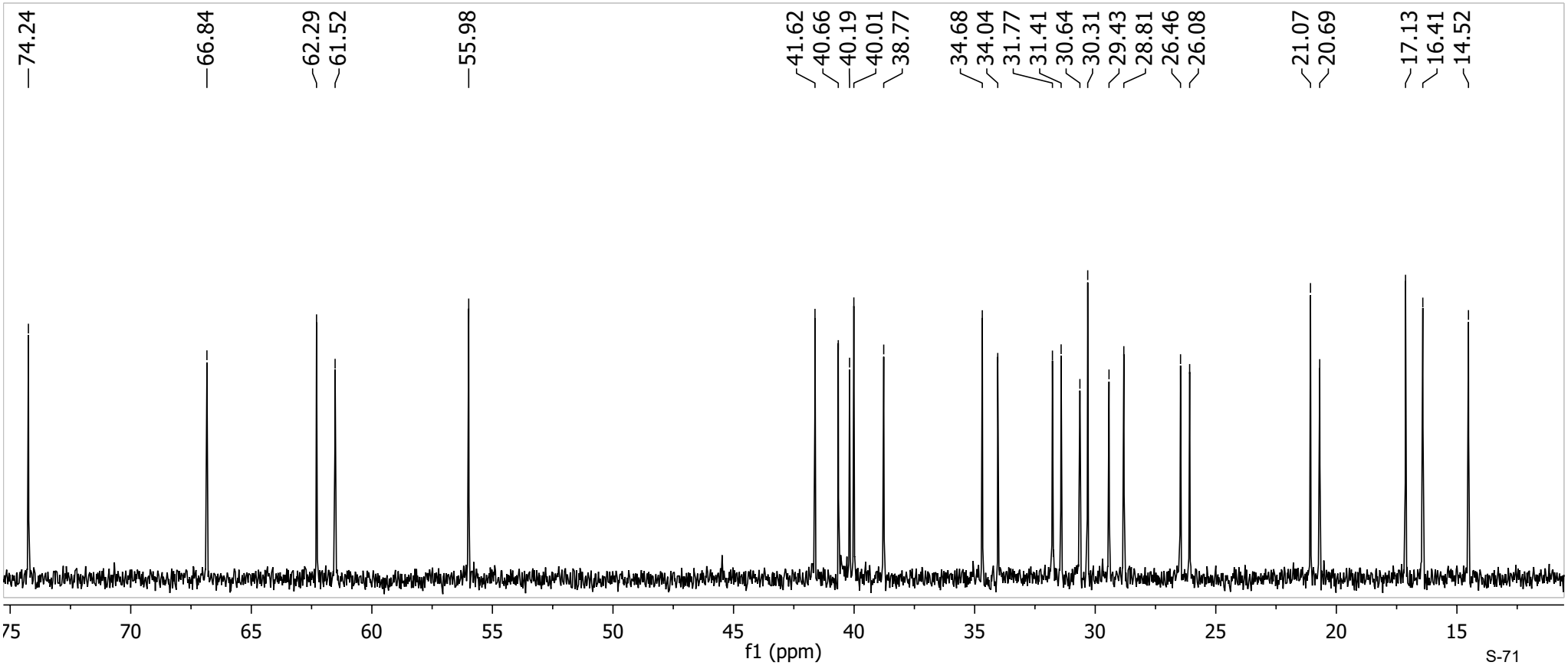

7.18
7.17
7.16
7.15
7.15
7.14
7.14
7.13
7.13
7.11
7.11
7.07
7.07
7.06
7.06
7.05
7.01
7.00
7.00
7.00
6.99
6.98
6.98
7.20
7.15
7.10
7.05
7.00
6.95
f1 (ppm)

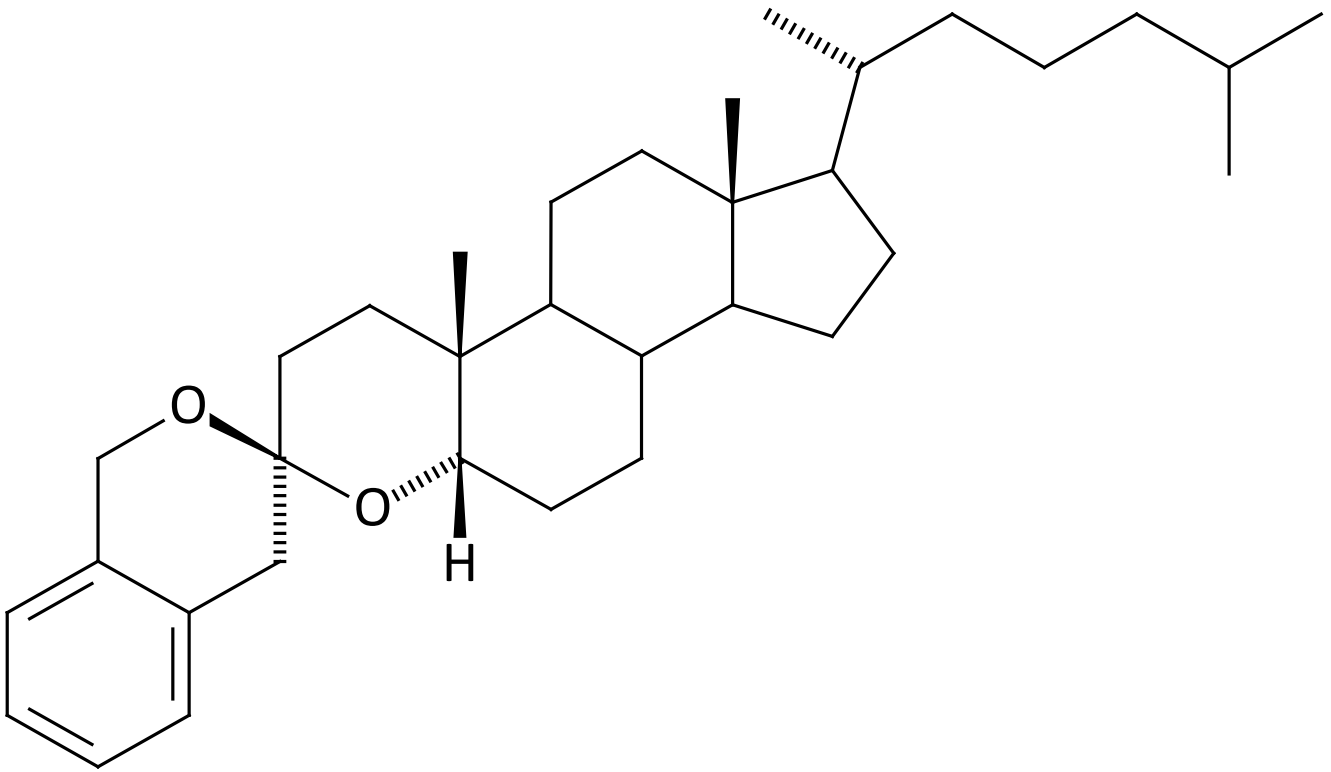

4.71
4.67
4.67
4.61
4.57
4.42
4.40
4.40
4.40
4.38
4.38
4.38
4.36
3.58
3.57
3.56
3.49
3.49
3.48
3.48
3.47
3.46
3.46
3.45
3.40
3.37
3.34
2.90
2.86
2.83
2.79
4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7
f1 (ppm)


0.98
0.97
0.88
0.80
0.78
0.77
1.00 0.99 0.98 0.97 0.96 0.95 0.94 0.93 0.92 0.91 0.90 0.89 0.88 0.87 0.86 0.85 0.84 0.83 0.82 0.81 0.80 0.79 0.78 0.77 0.76
f1 (ppm)

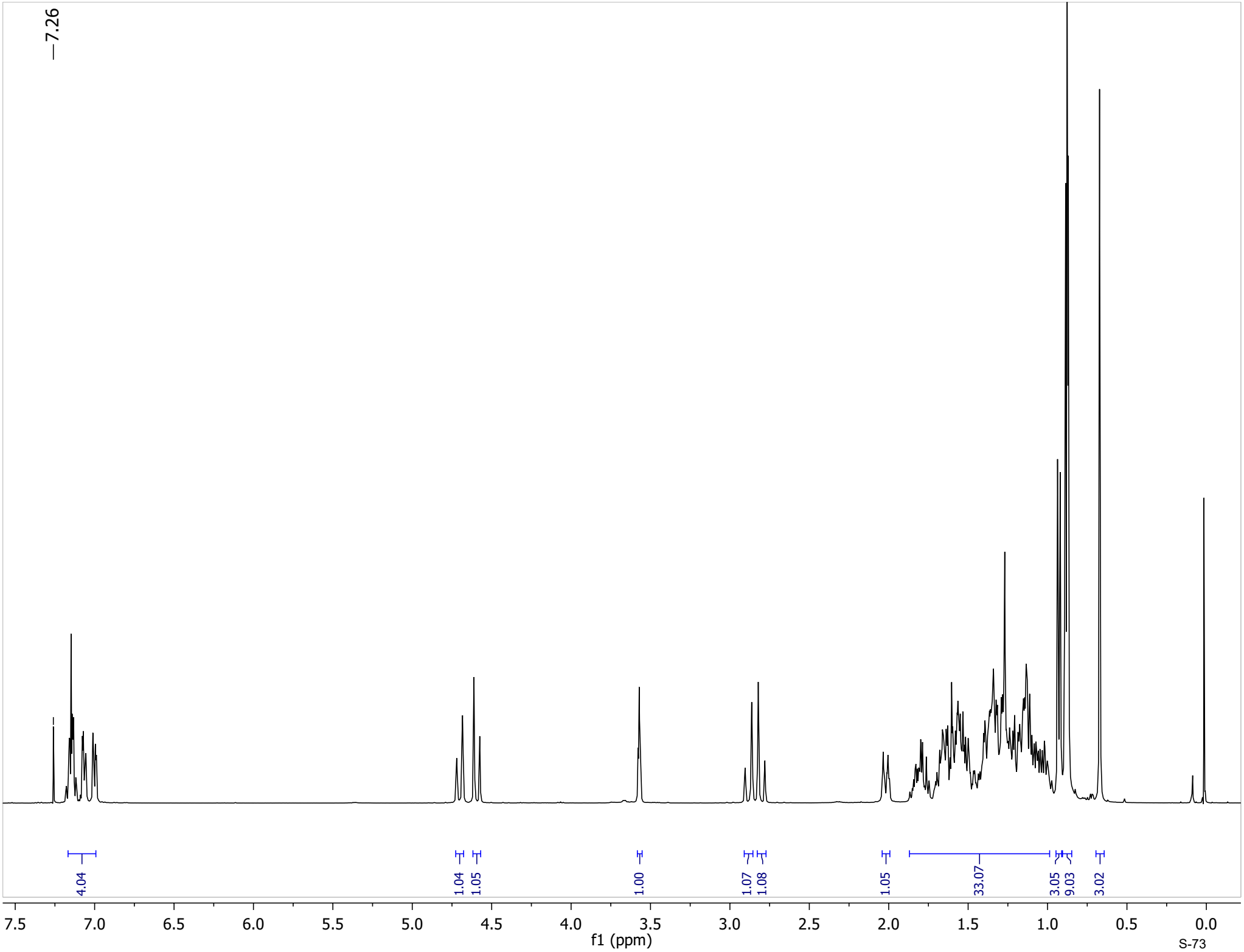

77.00
135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

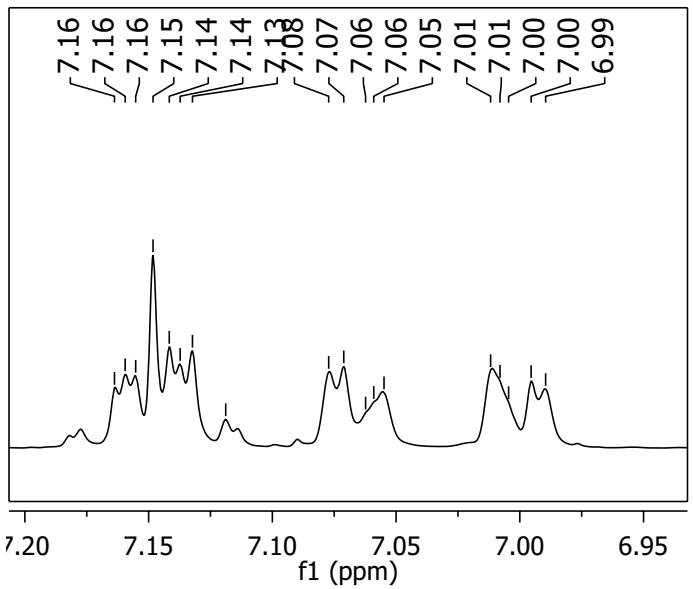

133.91
131.96
128.82
126.32
125.51
123.77
109.20
95.67
80.90
136 134 132 130 128 126 124 122 120 118 116 114 112 110 108 106 104 102 100 98 96 94 92 90 88 86 84 82 80
f1 (ppm)

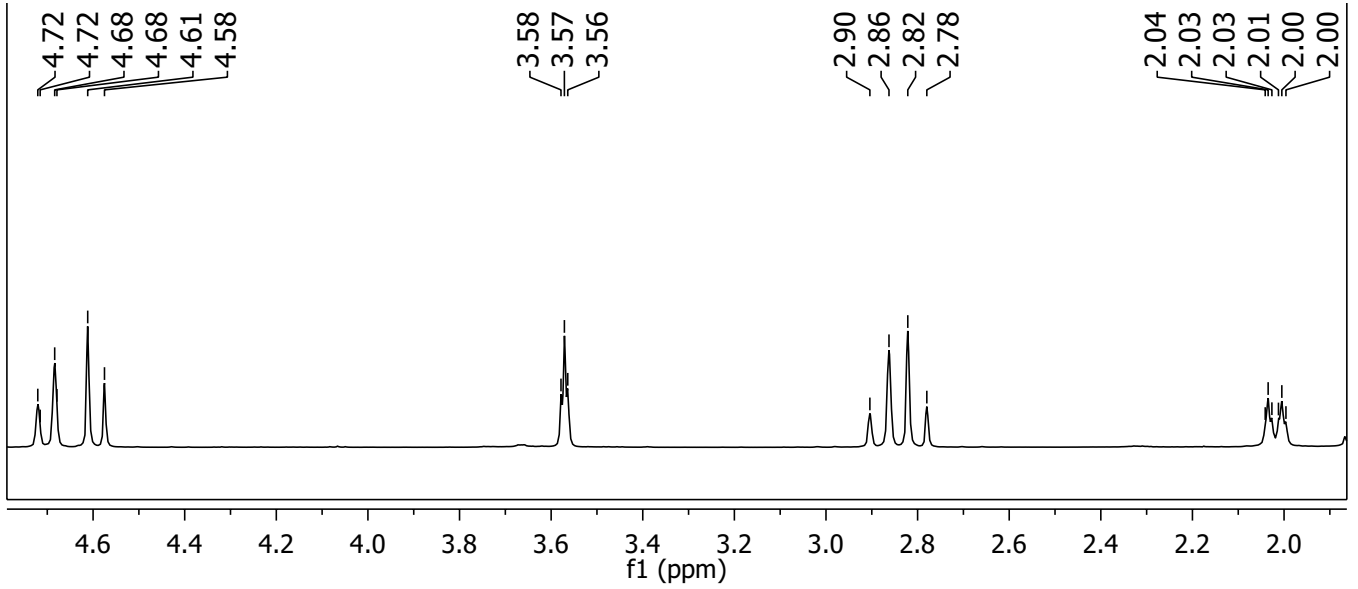

74.24
66.84
62.29
61.52
55.98
41.62
40.66
40.19
40.01
38.77
34.68
34.04
31.77
31.41
30.64
30.31
29.43
28.81
26.46
26.08
21.07
20.69
17.13
16.41
14.52
75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)

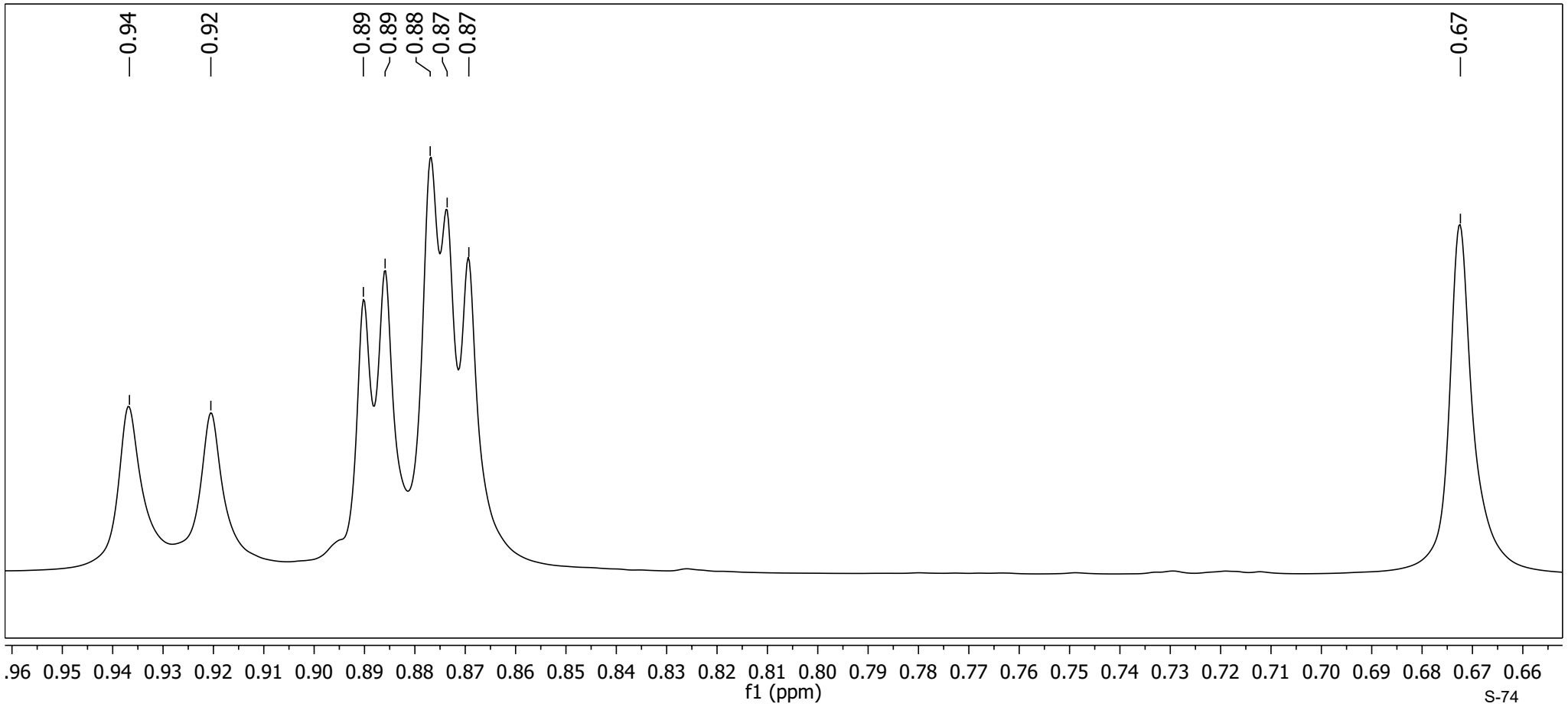


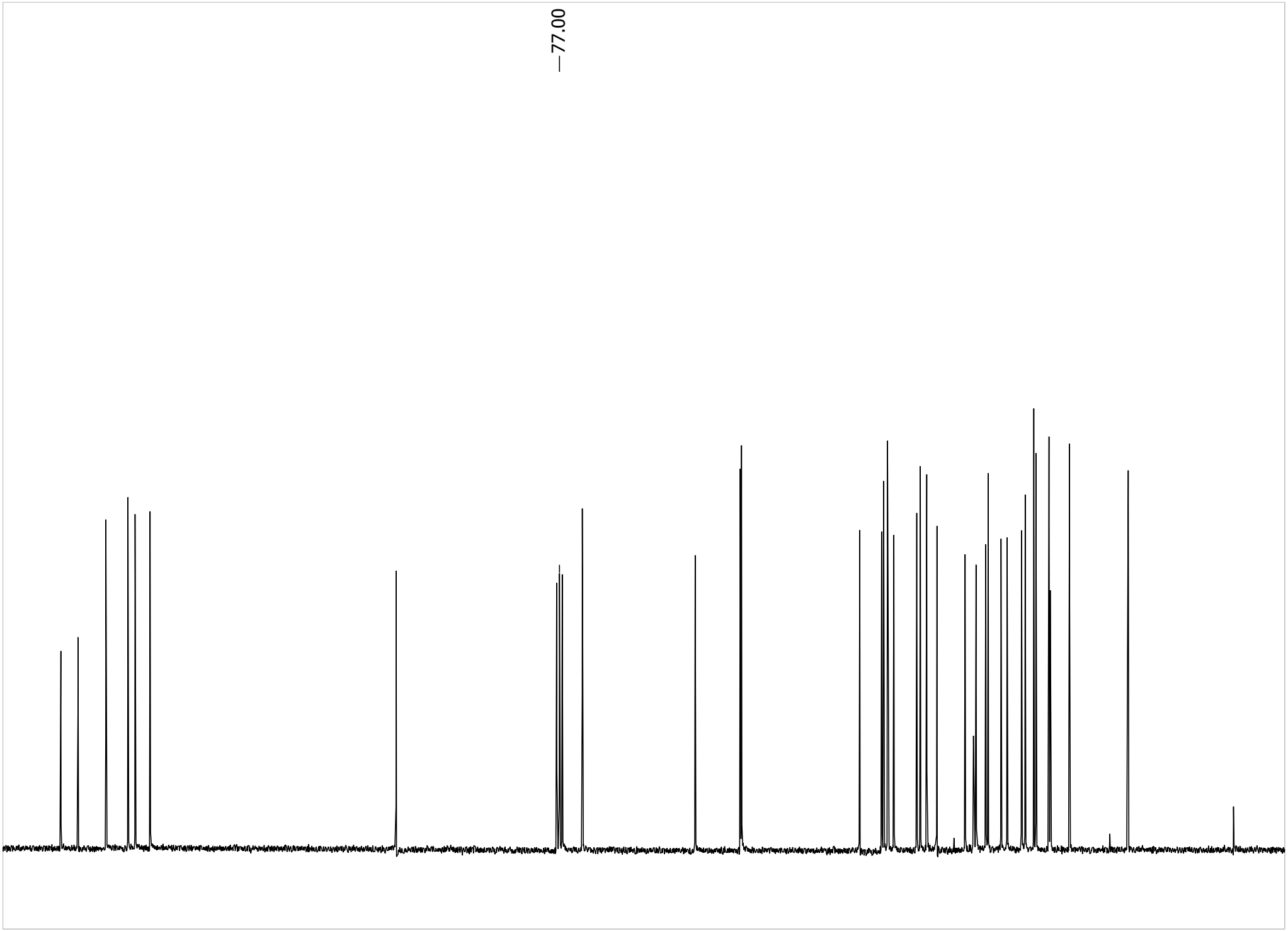
(3*S*)-Spiro-4-oxa-5β-cholestan-3,3´-isochromane (24)

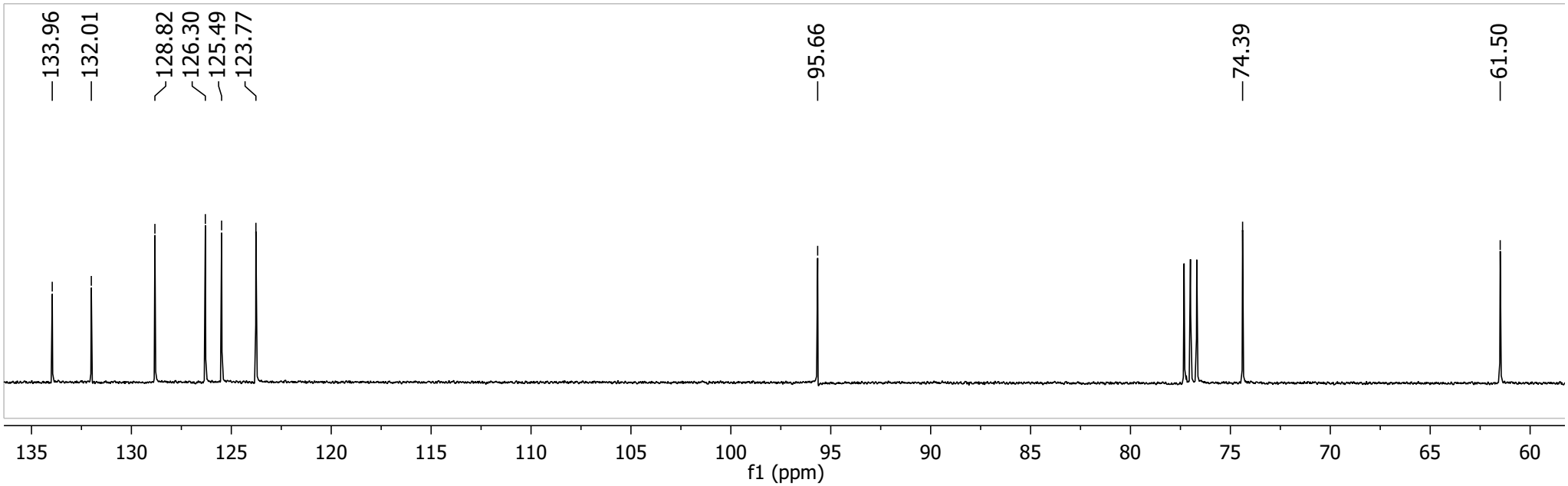

7.26
4.04
1.04
1.05
1.00
1.07
1.08
1.05
33.07
3.05
9.03
3.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

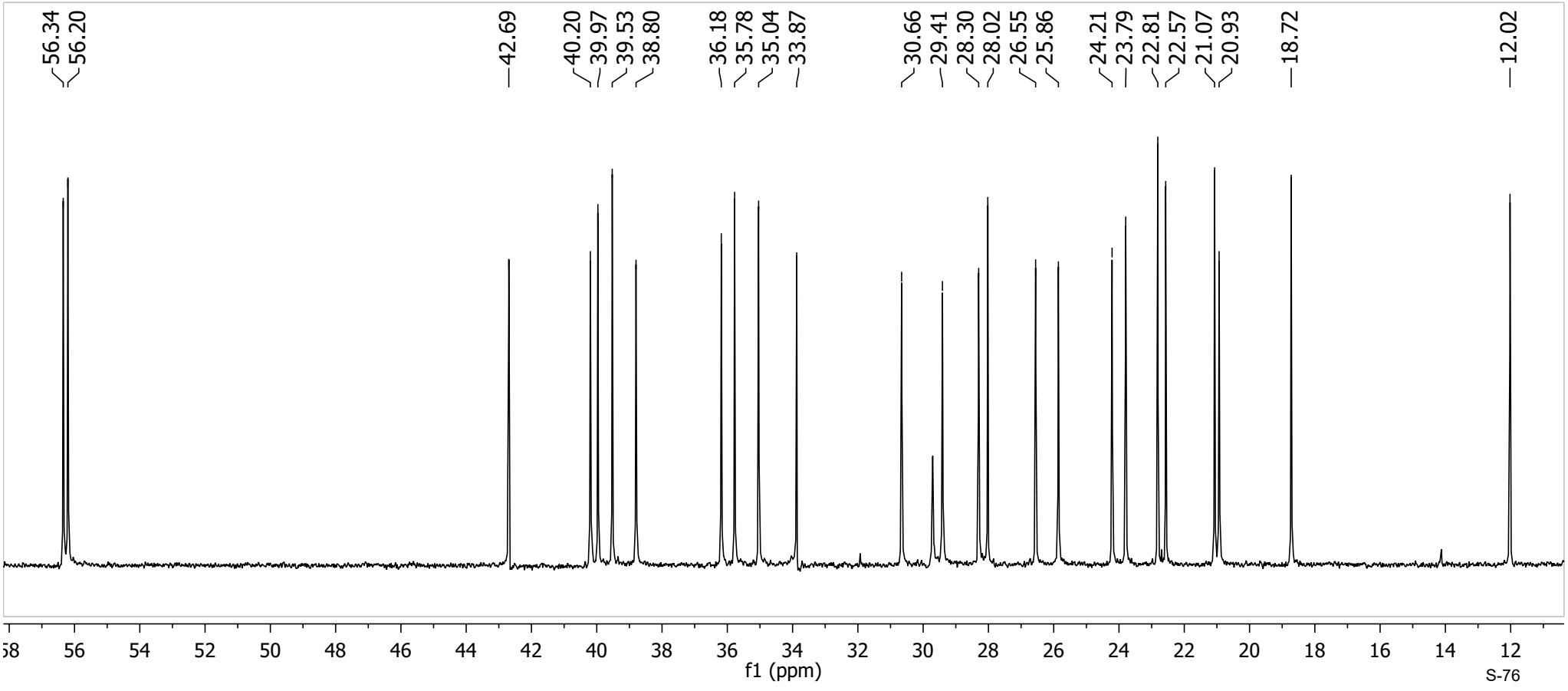

7.16
7.16
7.16
7.15
7.14
7.14
7.13
7.08
7.07
7.06
7.06
7.05
7.01
7.01
7.00
7.00
6.99
7.20
7.15
7.10
7.05
7.00
6.95
f1 (ppm)

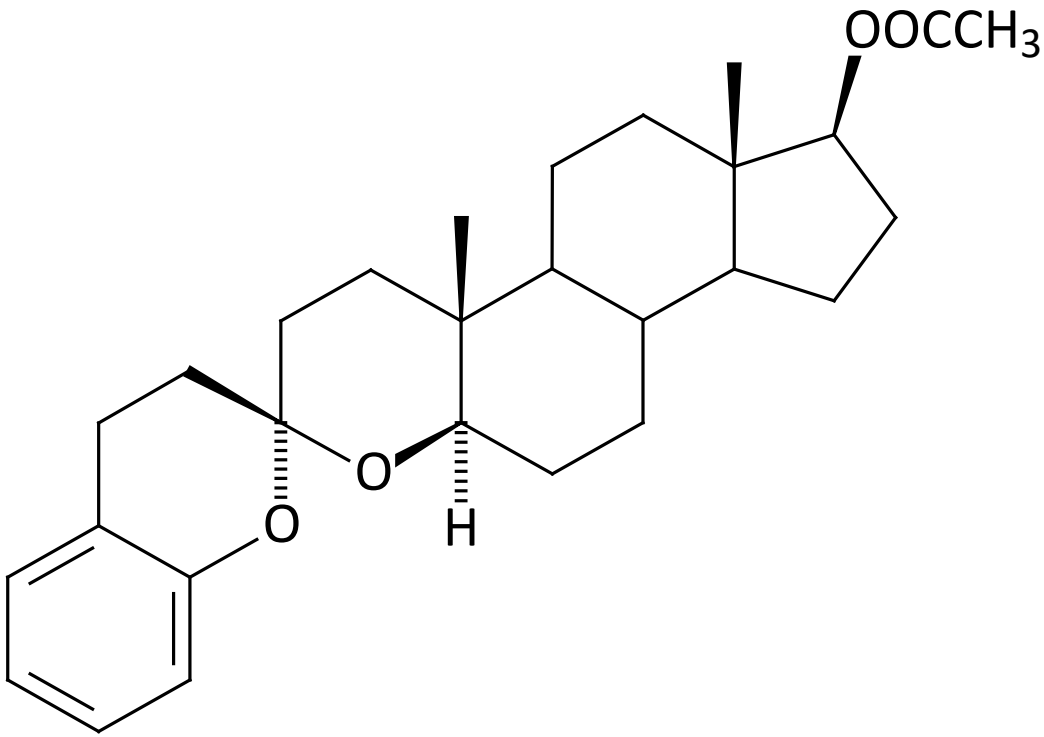

4.72
4.72
4.68
4.68
4.61
4.58
3.58
3.57
3.56
2.90
2.86
2.82
2.78
2.04
2.03
2.03
2.01
2.00
2.00
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
f1 (ppm)


0.94
0.92
0.89
0.89
0.88
0.87
0.87
0.67
.96 0.95 0.94 0.93 0.92 0.91 0.90 0.89 0.88 0.87 0.86 0.85 0.84 0.83 0.82 0.81 0.80 0.79 0.78 0.77 0.76 0.75 0.74 0.73 0.72 0.71 0.70 0.69 0.68 0.67 0.66
f1 (ppm)

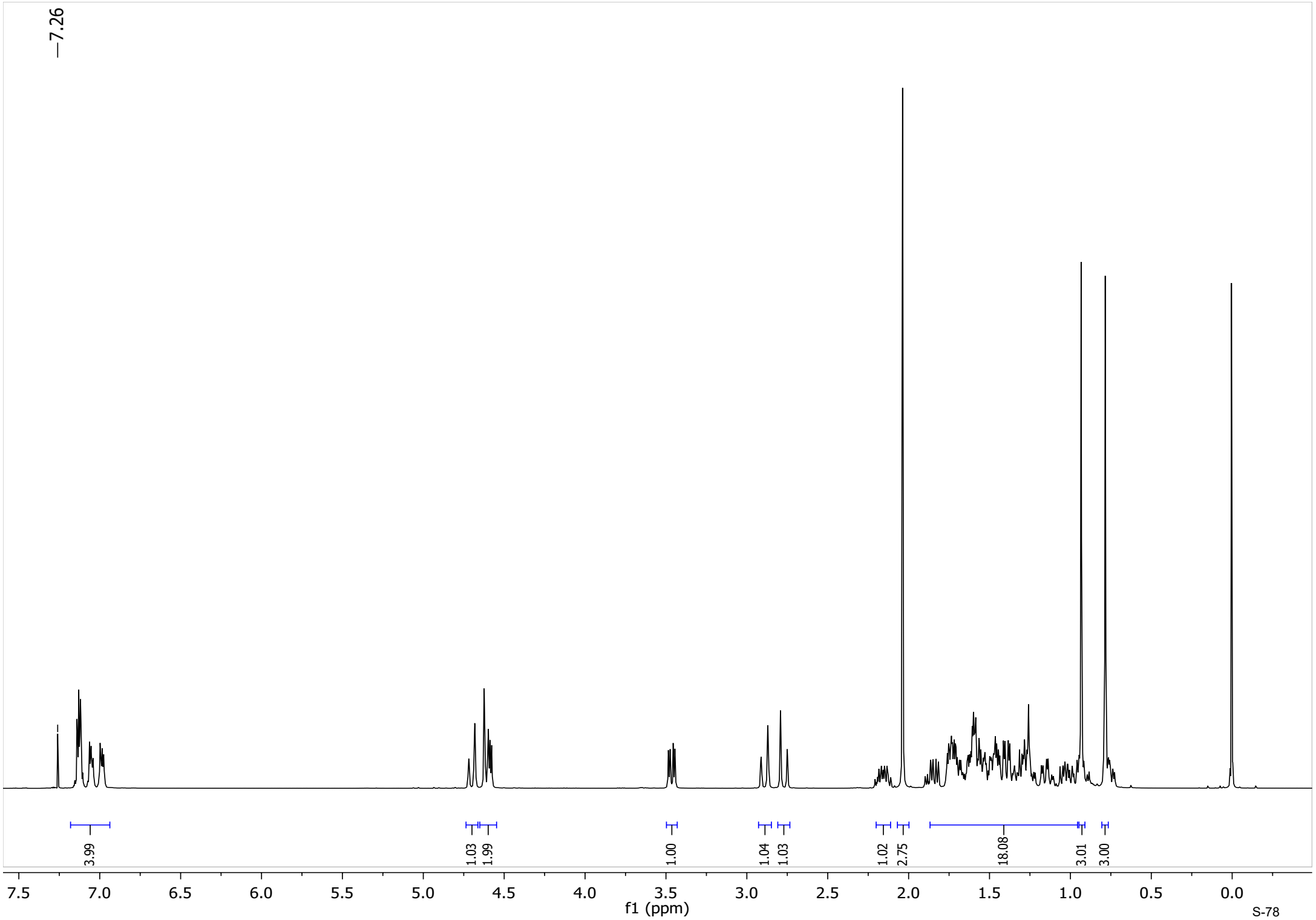

77.00
40
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

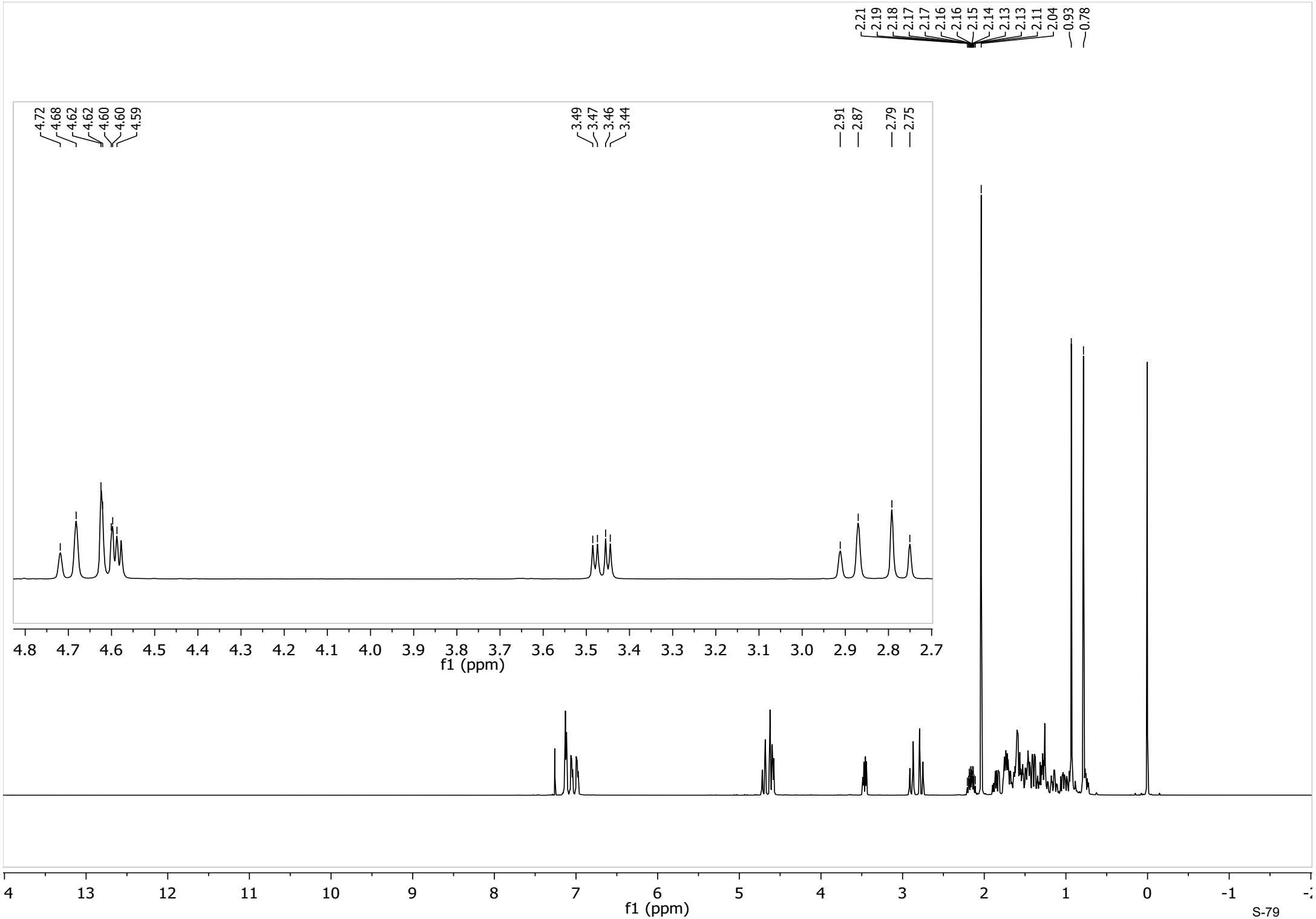

133.96
132.01
128.82
126.30
125.49
123.77
95.66
74.39
61.50
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
f1 (ppm)

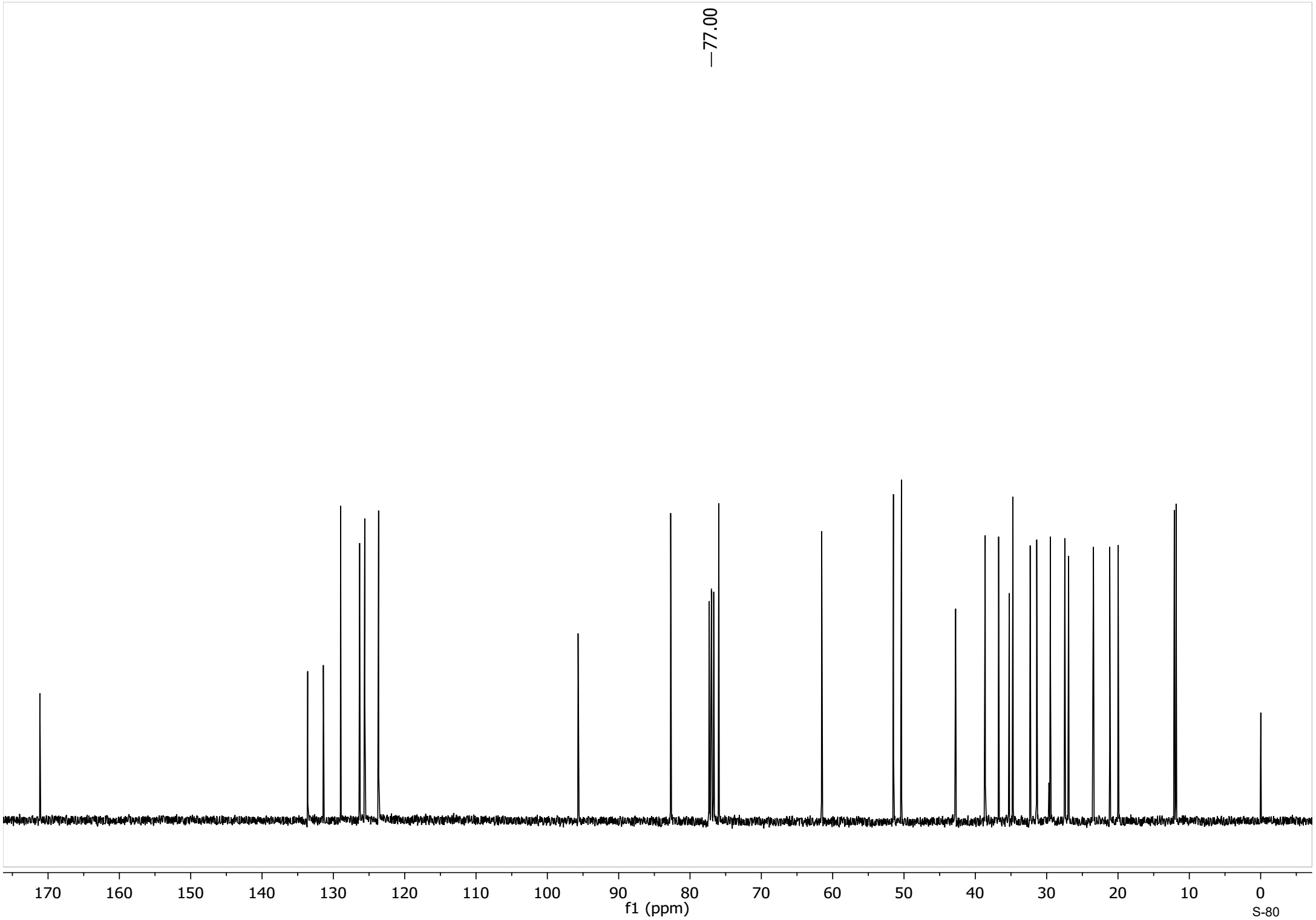

56.34
56.20
42.69
40.20
39.97
39.53
38.80
36.18
35.78
35.04
33.87
30.66
29.41
28.30
28.02
26.55
25.86
24.21
23.79
22.81
22.57
21.07
20.93
18.72
12.02
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
f1 (ppm)

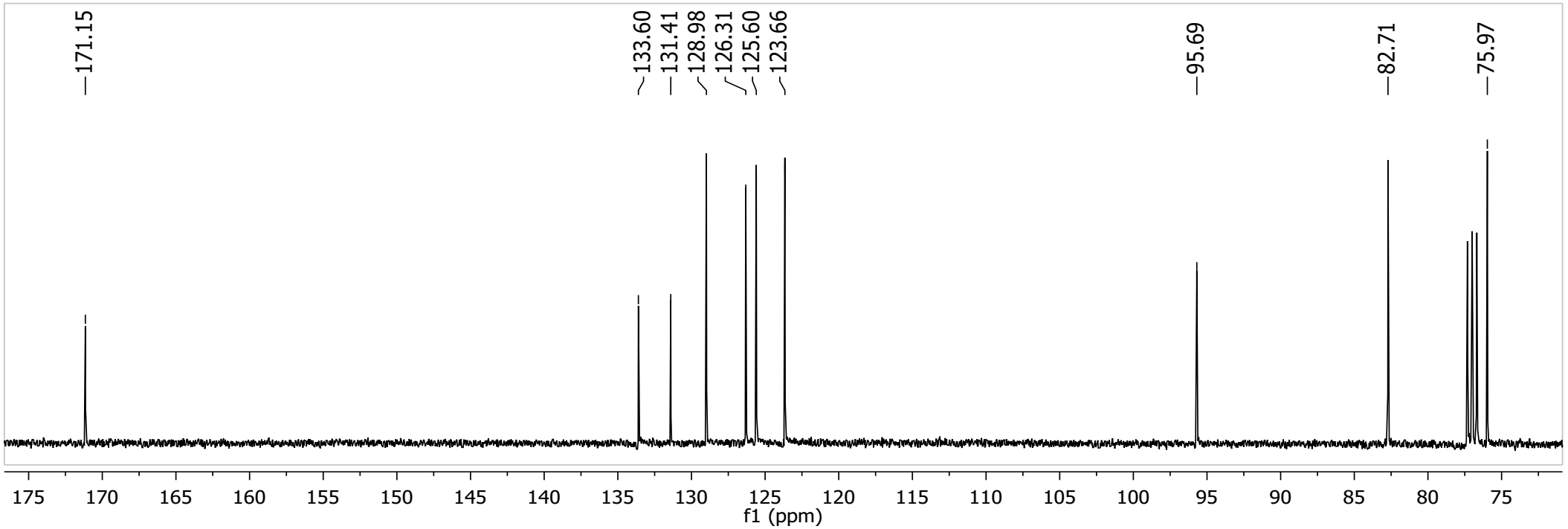


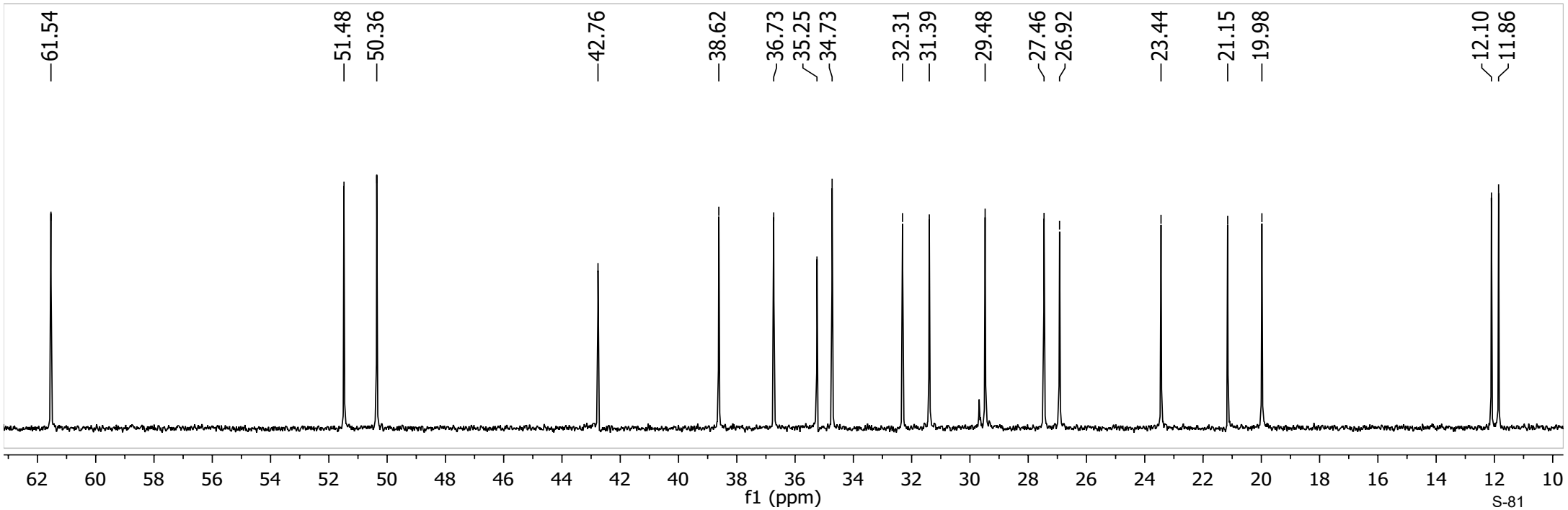
(3*R*)-Spiro-17β-acetoxy-4-oxa-5α-androstan-3,3´-isochromane **(25)**

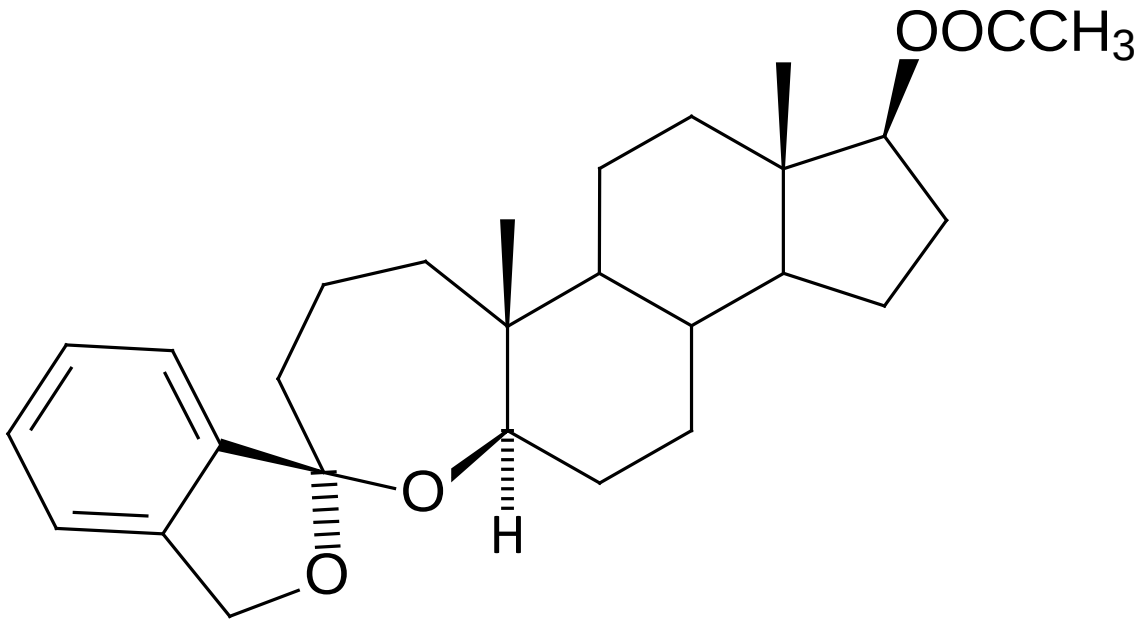

7.26
3.99
1.03
1.99
1.00
1.04
1.03
1.02
2.75
18.08
3.01
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


2.21
2.19
2.18
2.17
2.17
2.16
2.16
2.15
2.14
2.13
2.13
2.11
2.04
0.93
0.78
4.72
4.68
4.62
4.62
4.60
4.60
4.59
3.49
3.47
3.46
3.44
2.91
2.87
2.79
2.75
4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7
f1 (ppm)
4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

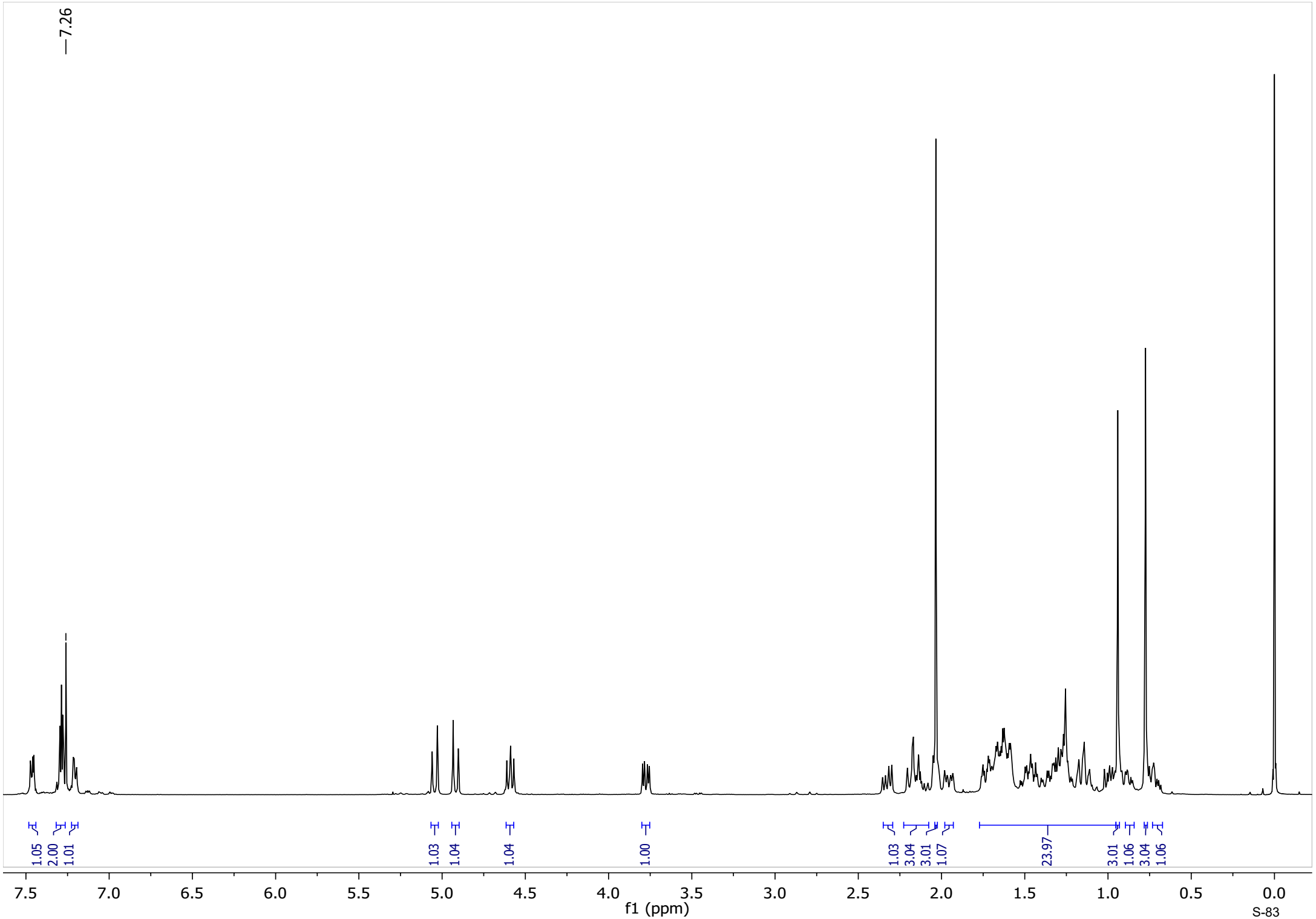

77.00
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

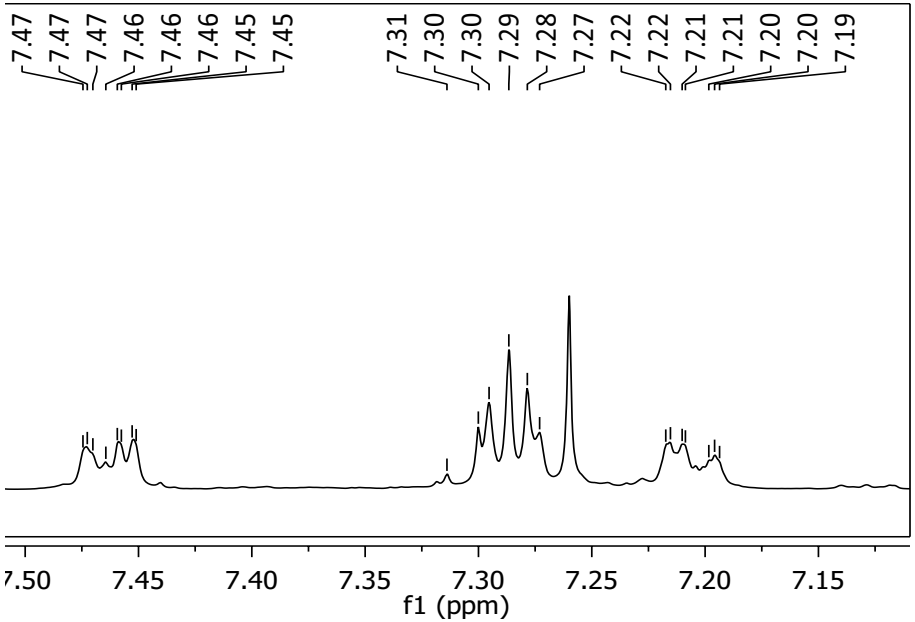

171.15
133.60
131.41
128.98
126.31
125.60
123.66
95.69
82.71
75.97
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75
f1 (ppm)

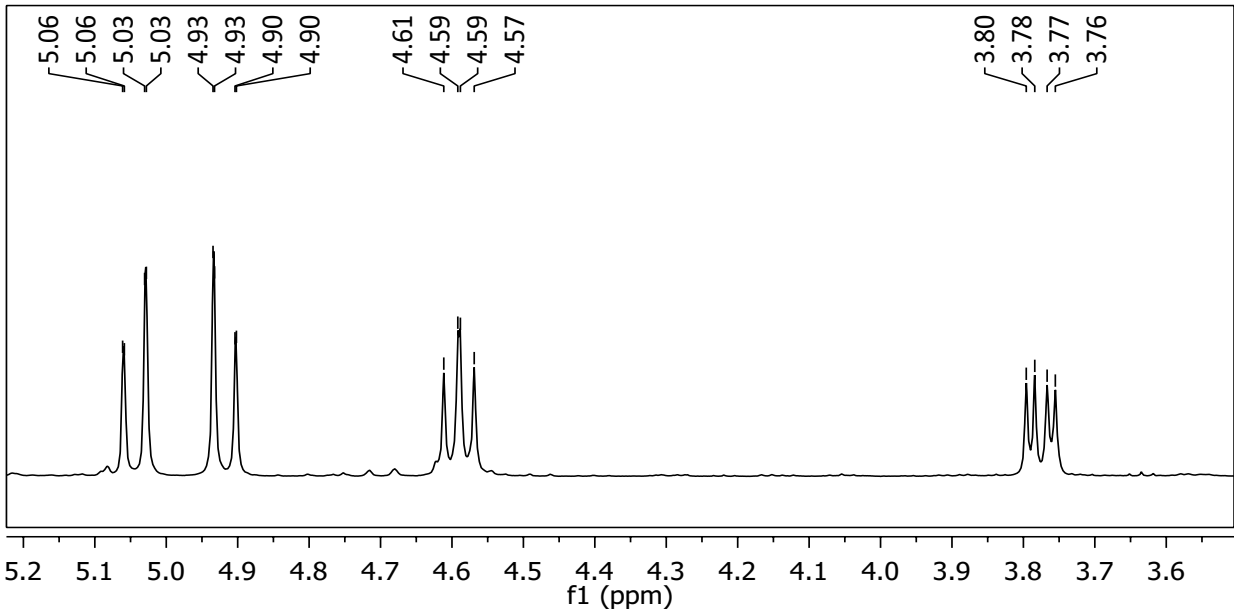

61.54
51.48
50.36
42.76
38.62
36.73
35.25
34.73
32.31
31.39
29.48
27.46
26.92
23.44
21.15
19.98
12.10
11.86
62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10
f1 (ppm)

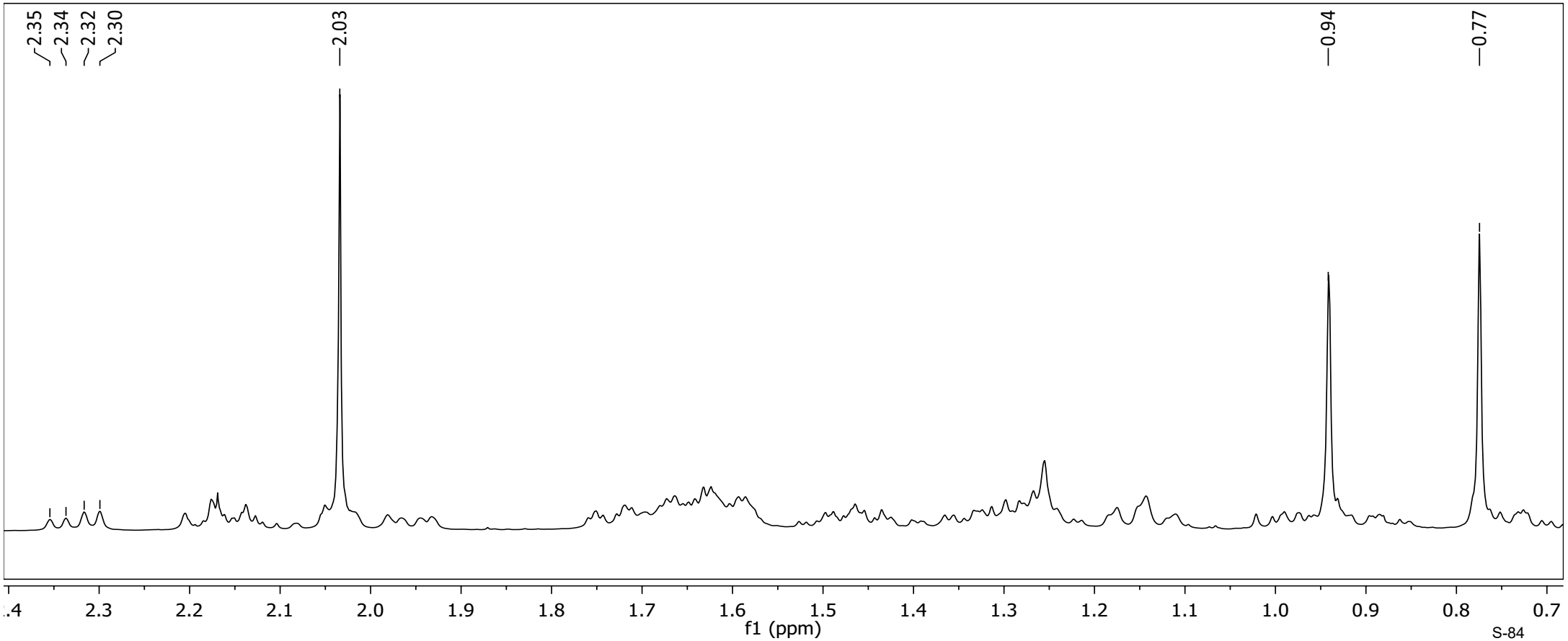


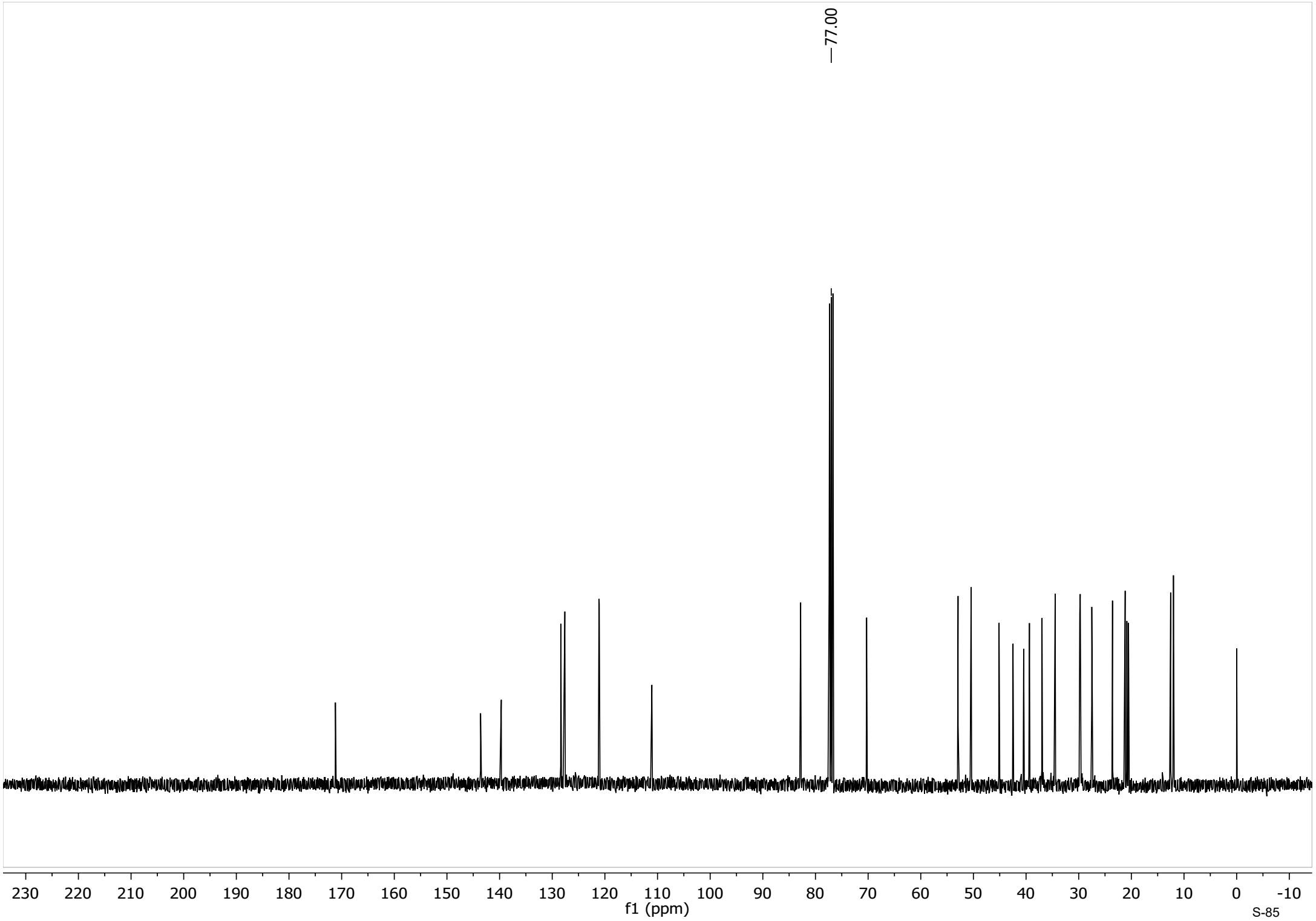
(4*S*)-Spiro-[isobenzofuran-1,2´-(17β-acetoxy-A-homo-4a-oxa-5α-androstan)-oxepane] **(26)**

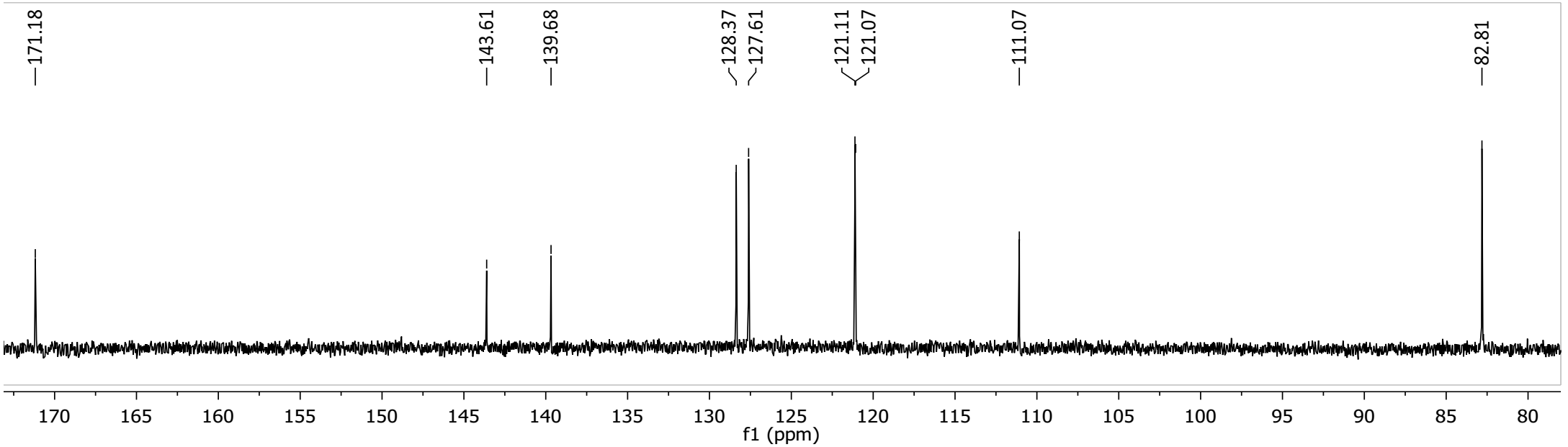

7.26
1.05
2.00
1.01
1.03
1.04
1.04
1.00
1.03
3.04
3.01
1.07
23.97
3.01
1.06
3.04
1.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

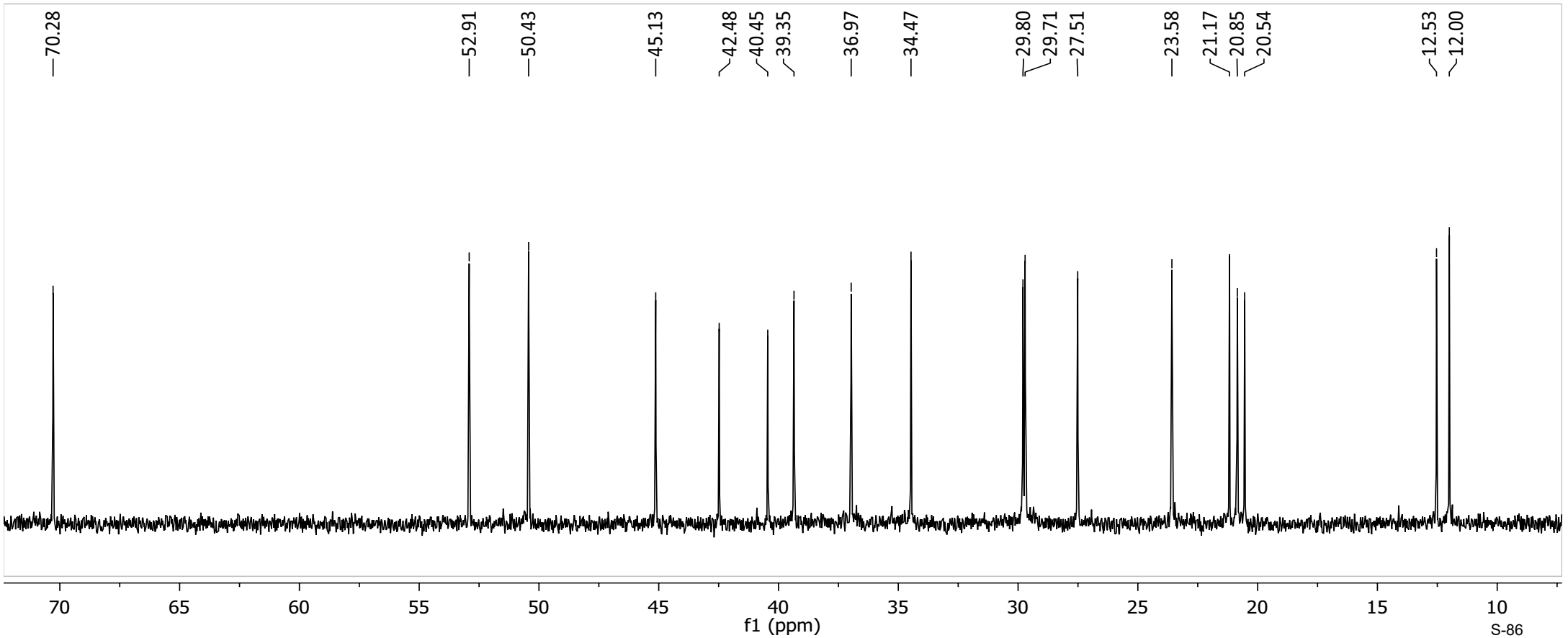

7.47
7.47
7.47
7.46
7.46
7.46
7.45
7.45
7.31
7.30
7.30
7.29
7.28
7.27
7.22
7.22
7.21
7.21
7.20
7.20
7.19
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
f1 (ppm)

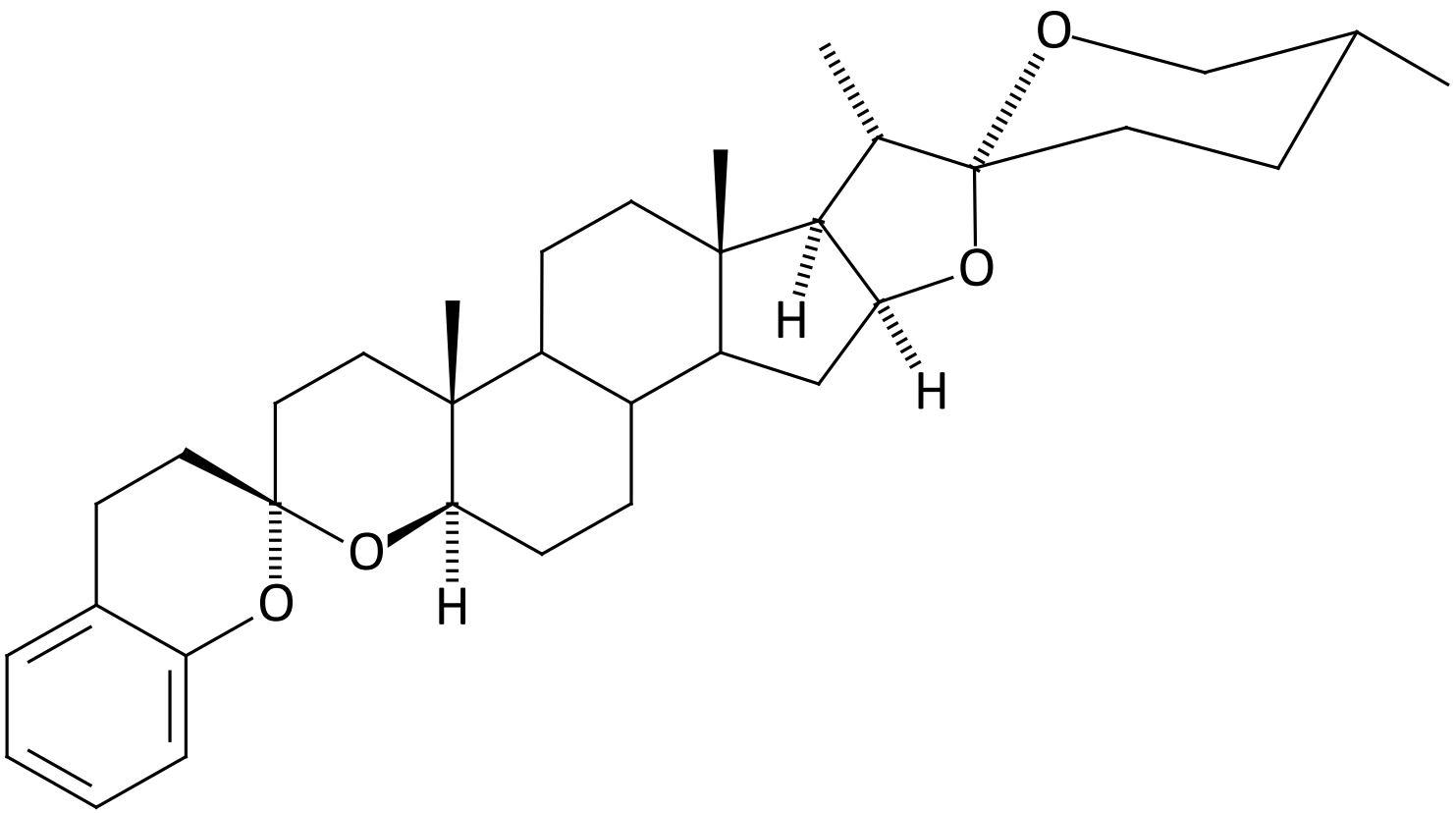

5.06
5.06
5.03
5.03
4.93
4.93
4.90
4.90
4.61
4.59
4.59
4.57
3.80
3.78
3.77
3.76
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
f1 (ppm)


2.35
2.34
2.32
2.30
2.03
0.94
0.77
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
f1 (ppm)

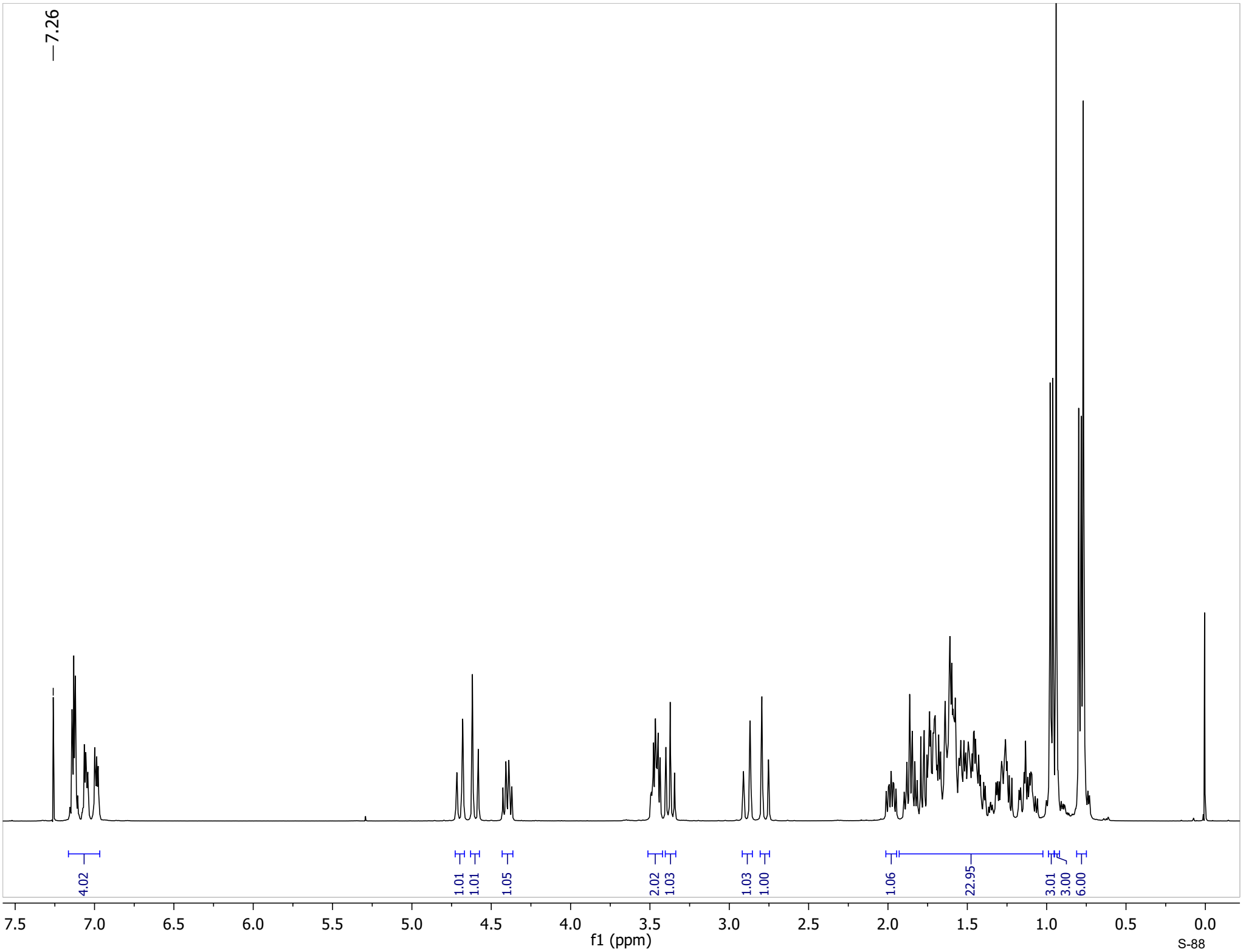

77.00
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

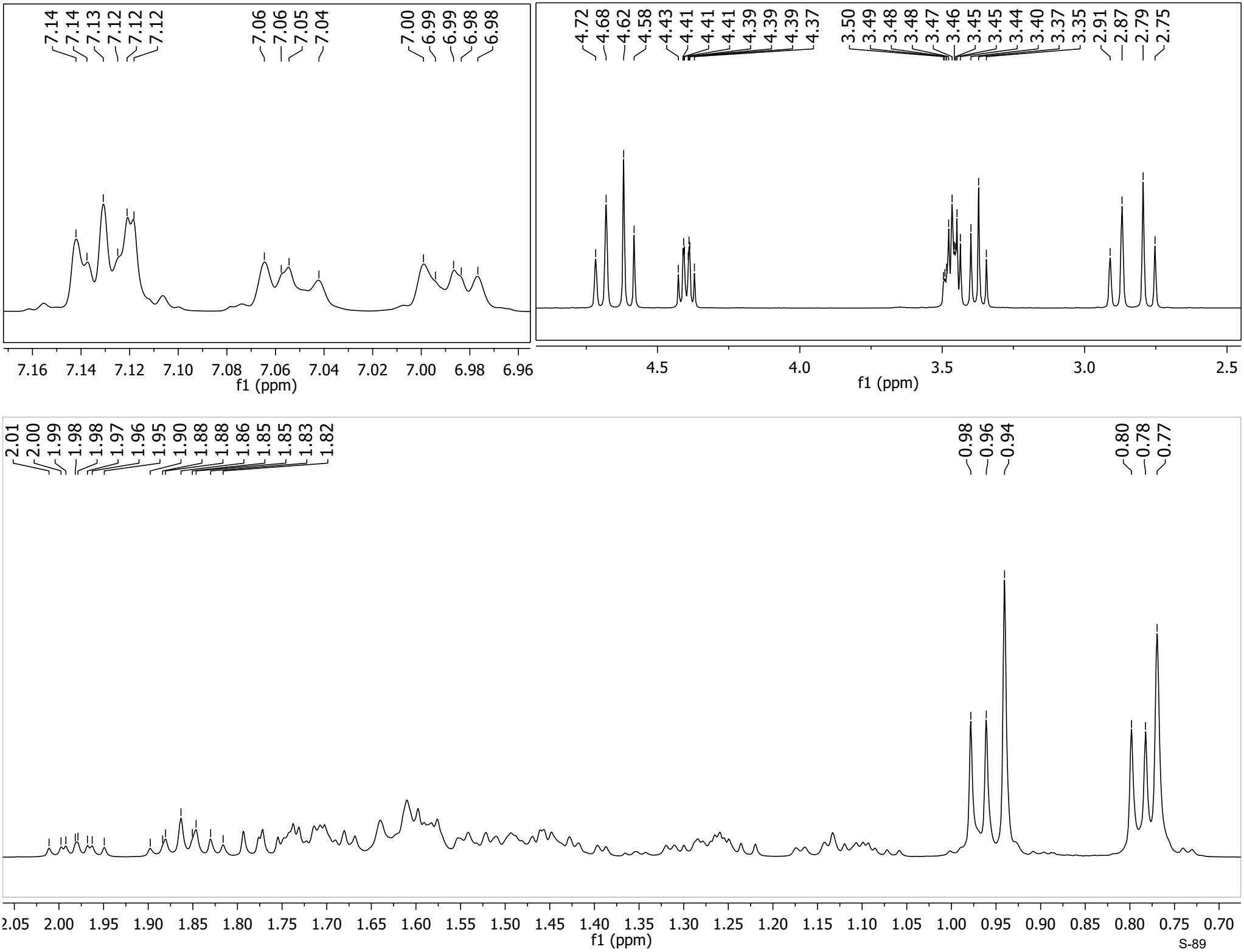

171.18
143.61
139.68
128.37
127.61
121.11
121.07
111.07
82.81
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
f1 (ppm)

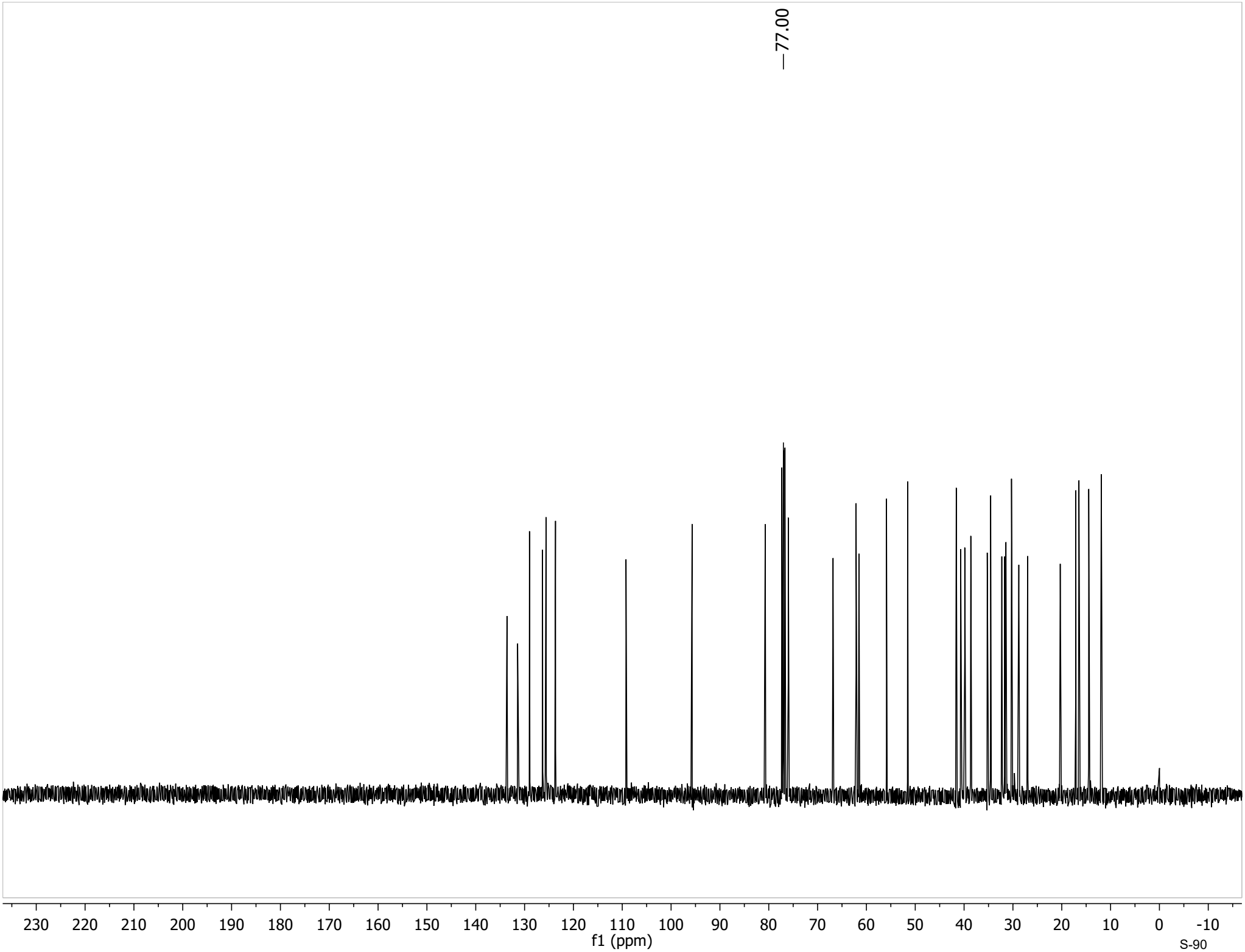

70.28
52.91
50.43
45.13
42.48
40.45
39.35
36.97
34.47
29.80
29.71
27.51
23.58
21.17
20.85
20.54
12.53
12.00
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

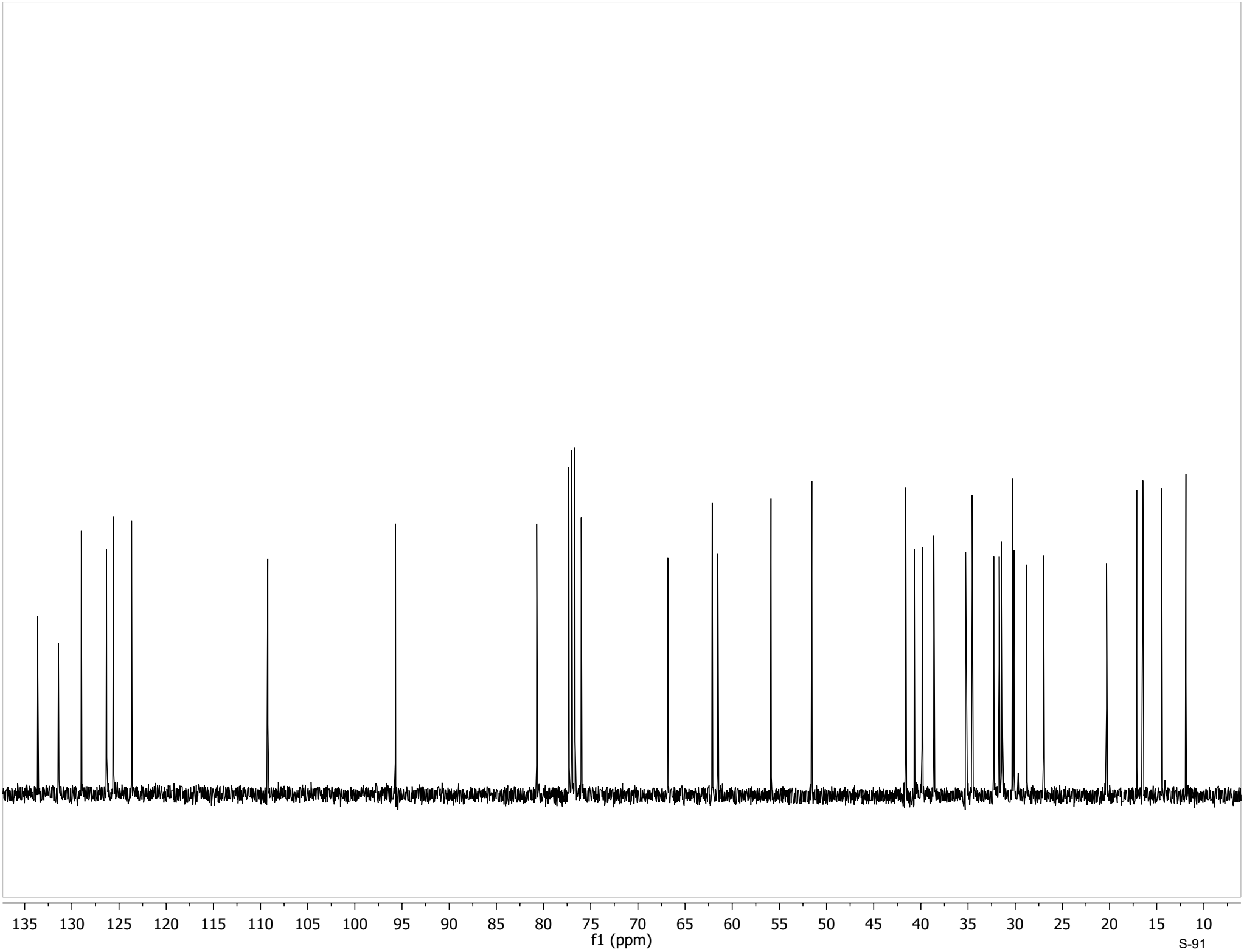


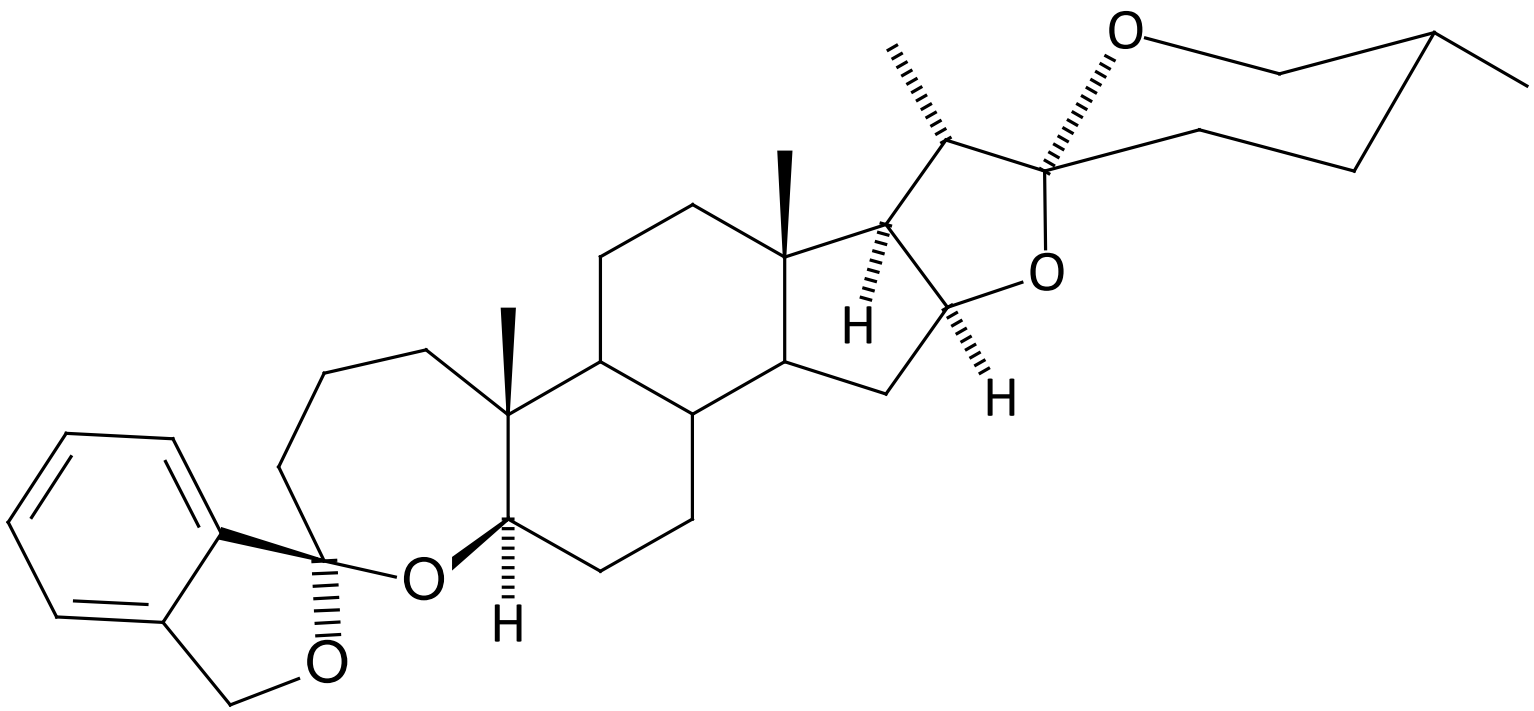
(3*R*,25*R*)-Spiro-4-oxa-5α-spirostan-3,3´-isochromane **(27)**


7.26
4.02
1.01
1.01
1.05
2.02
1.03
1.03
1.00
1.06
22.95
3.01
3.00
6.00
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)

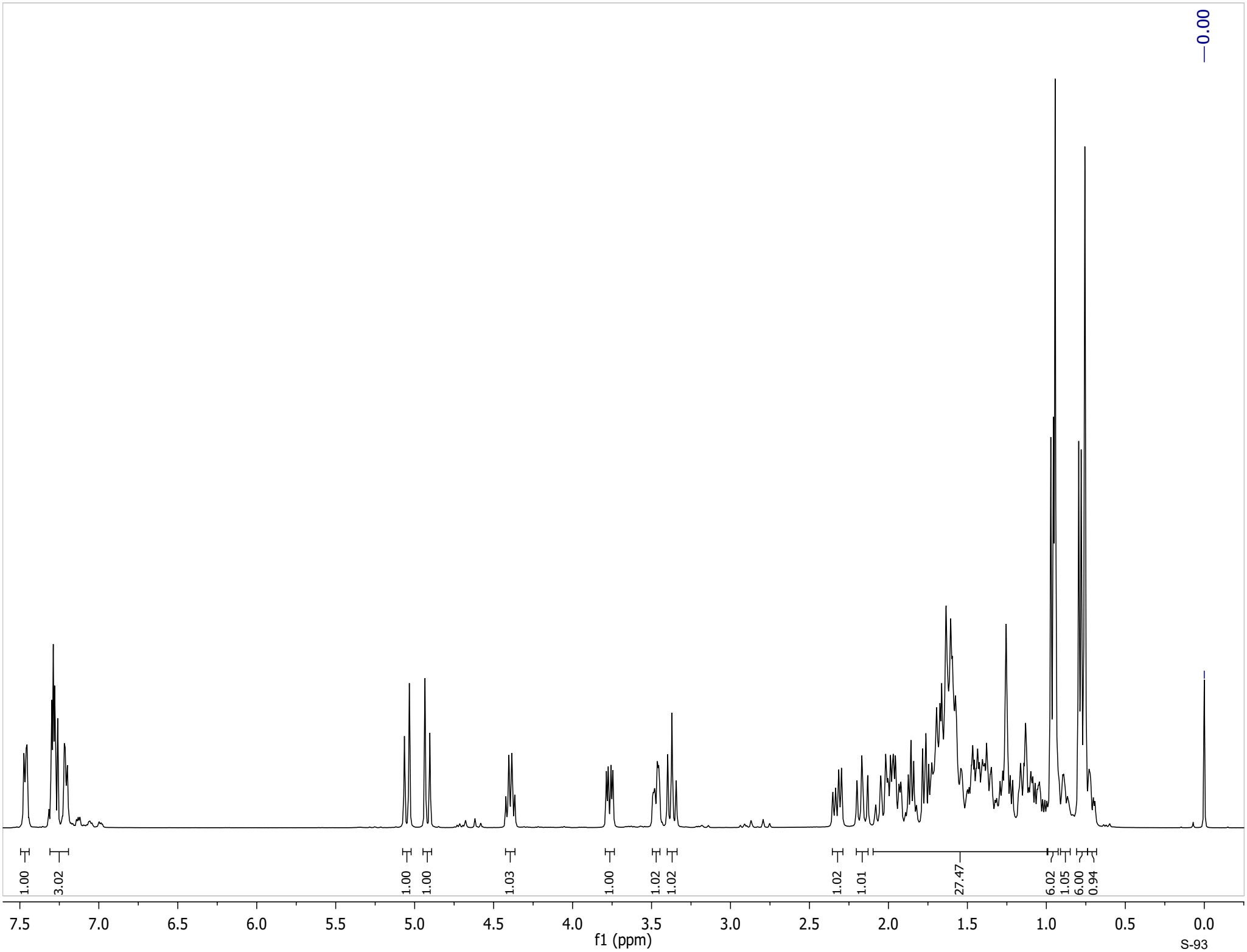

7.14
7.14
7.13
7.12
7.12
7.12
7.06
7.06
7.05
7.04
7.00
6.99
6.99
6.98
6.98
7.16 7.14 7.12 7.10 7.08 7.06 7.04 7.02 7.00 6.98 6.96
f1 (ppm)
4.72
4.68
4.62
4.58
4.43
4.41
4.41
4.41
4.39
4.39
4.39
4.37
3.50
3.49
3.48
3.48
3.47
3.46
3.45
3.45
3.44
3.40
3.37
3.35
2.91
2.87
2.79
2.75
4.5 4.0 3.5 3.0 2.5
f1 (ppm)
2.01
2.00
1.99
1.98
1.98
1.97
1.96
1.95
1.90
1.88
1.88
1.86
1.85
1.85
1.83
1.82
0.98
0.96
0.94
0.80
0.78
0.77
2.05 2.00 1.95 1.90 1.85 1.80 1.75 1.70 1.65 1.60 1.55 1.50 1.45 1.40 1.35 1.30 1.25 1.20 1.15 1.10 1.05 1.00 0.95 0.90 0.85 0.80 0.75 0.70
f1 (ppm)

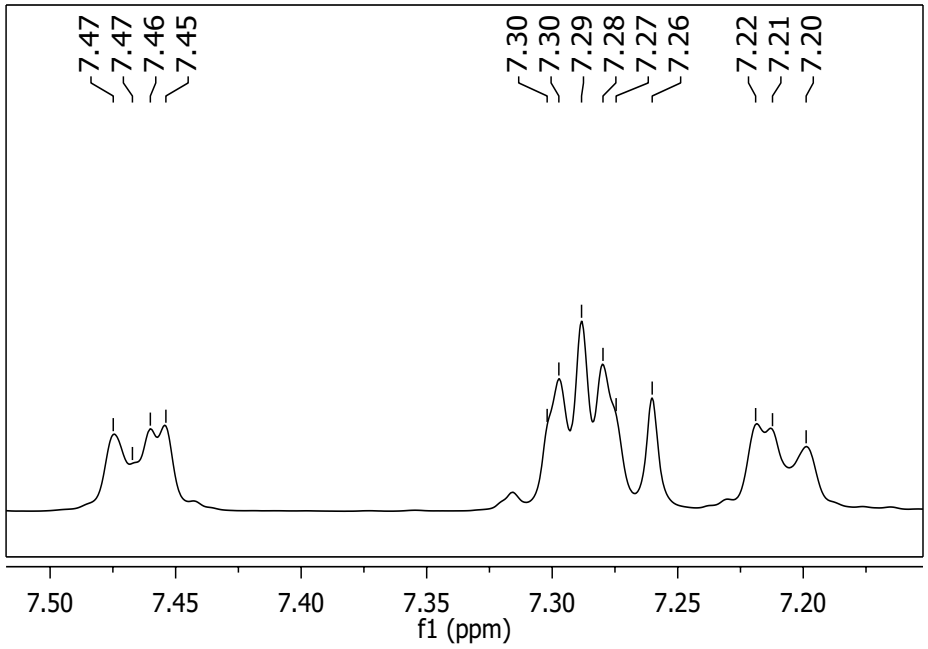

77.00
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

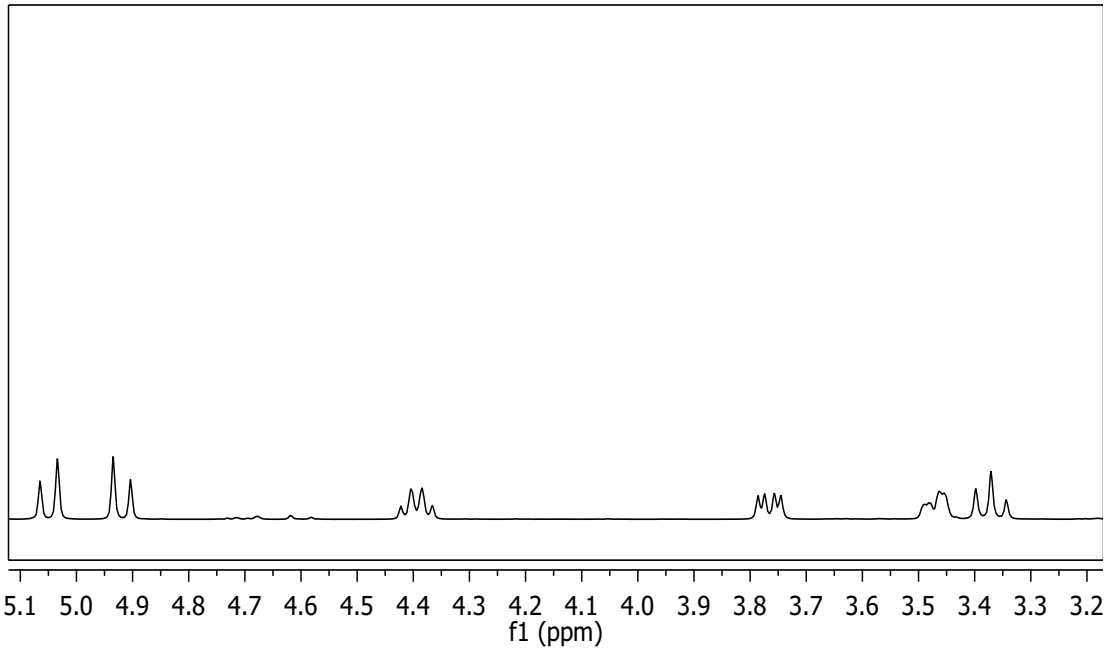

135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

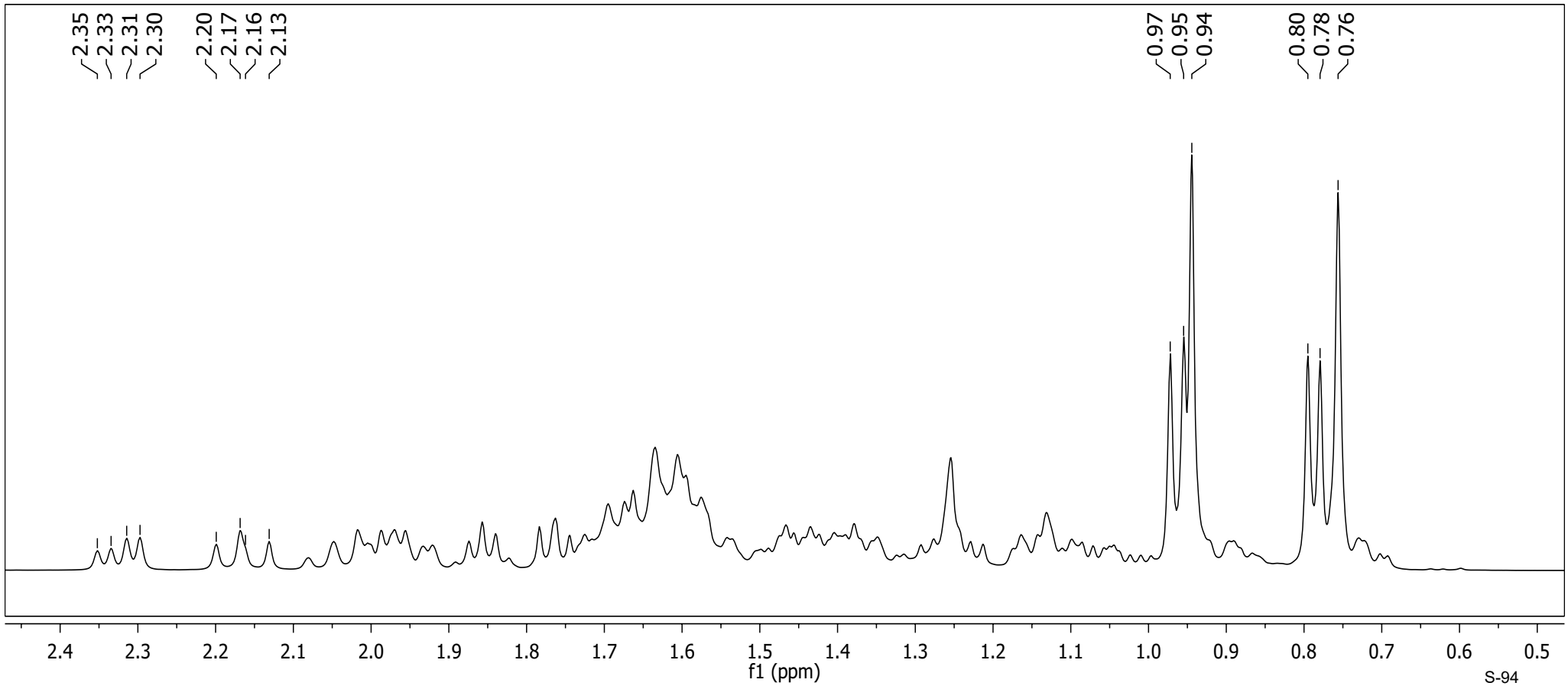


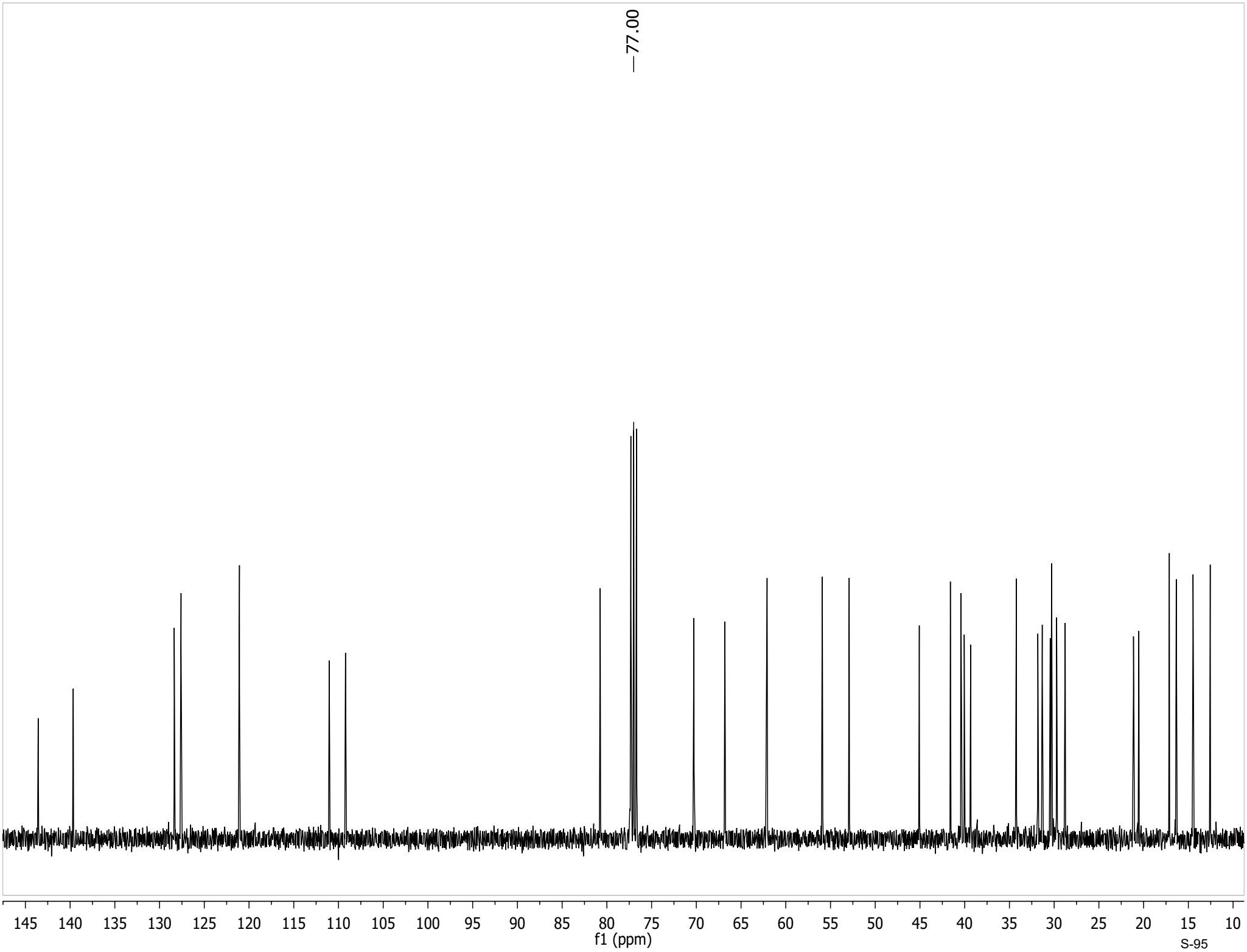
(4*S*,25*R*)-Spiro-[isobenzofuran-1,2´-(A-homo-4a-oxa-5α-spirostan)-oxepane] **(28)**

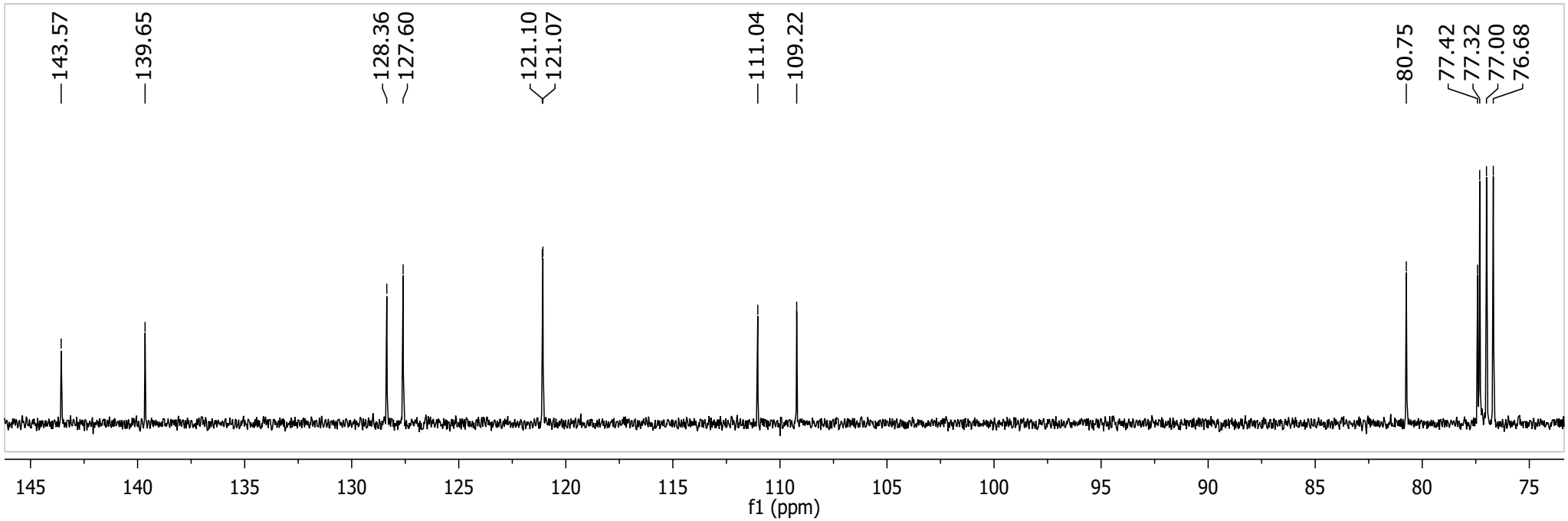

0.00
1.00
3.02
1.00
1.00
1.03
1.00
1.02
1.02
1.02
1.01
27.47
6.02
1.05
6.00
0.94
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


7.47
7.47
7.46
7.45
7.30
7.30
7.29
7.28
7.27
7.26
7.22
7.21
7.20
7.50
7.45
7.40
7.35
7.30
7.25
7.20
f1 (ppm)


5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2
f1 (ppm)


2.35
2.33
2.31
2.30
2.20
2.17
2.16
2.13
0.97
0.95
0.94
0.80
0.78
0.76
2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5
f1 (ppm)


77.00
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)


143.57
139.65
128.36
127.60
121.10
121.07
111.04
109.22
80.75
77.42
77.32
77.00
76.68
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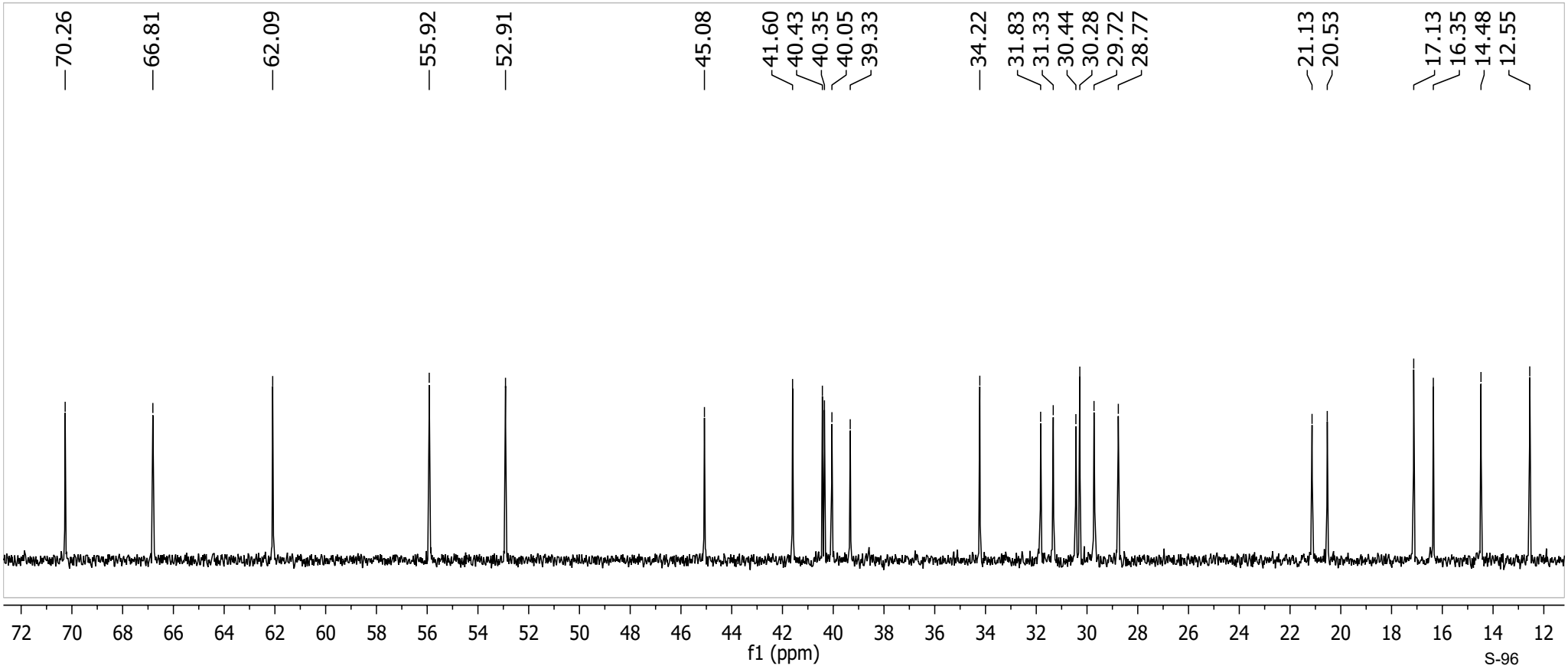
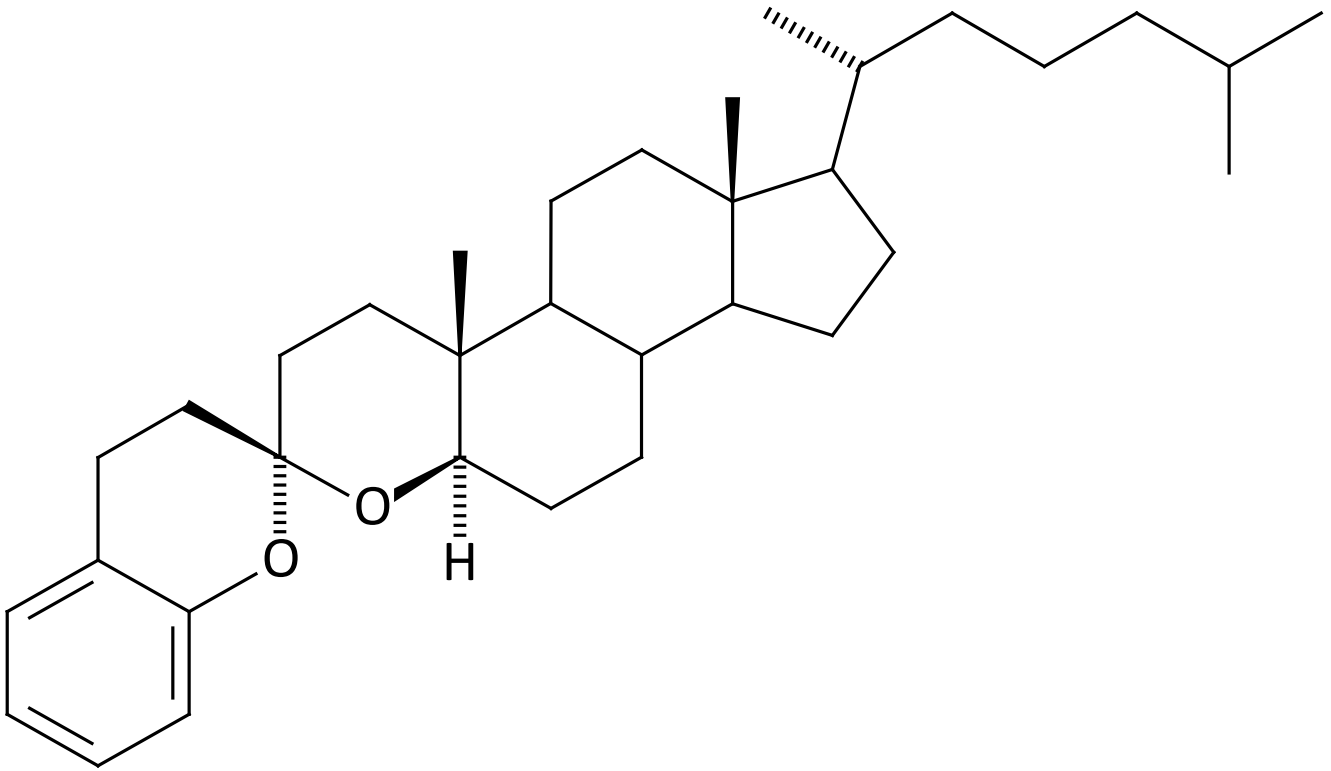
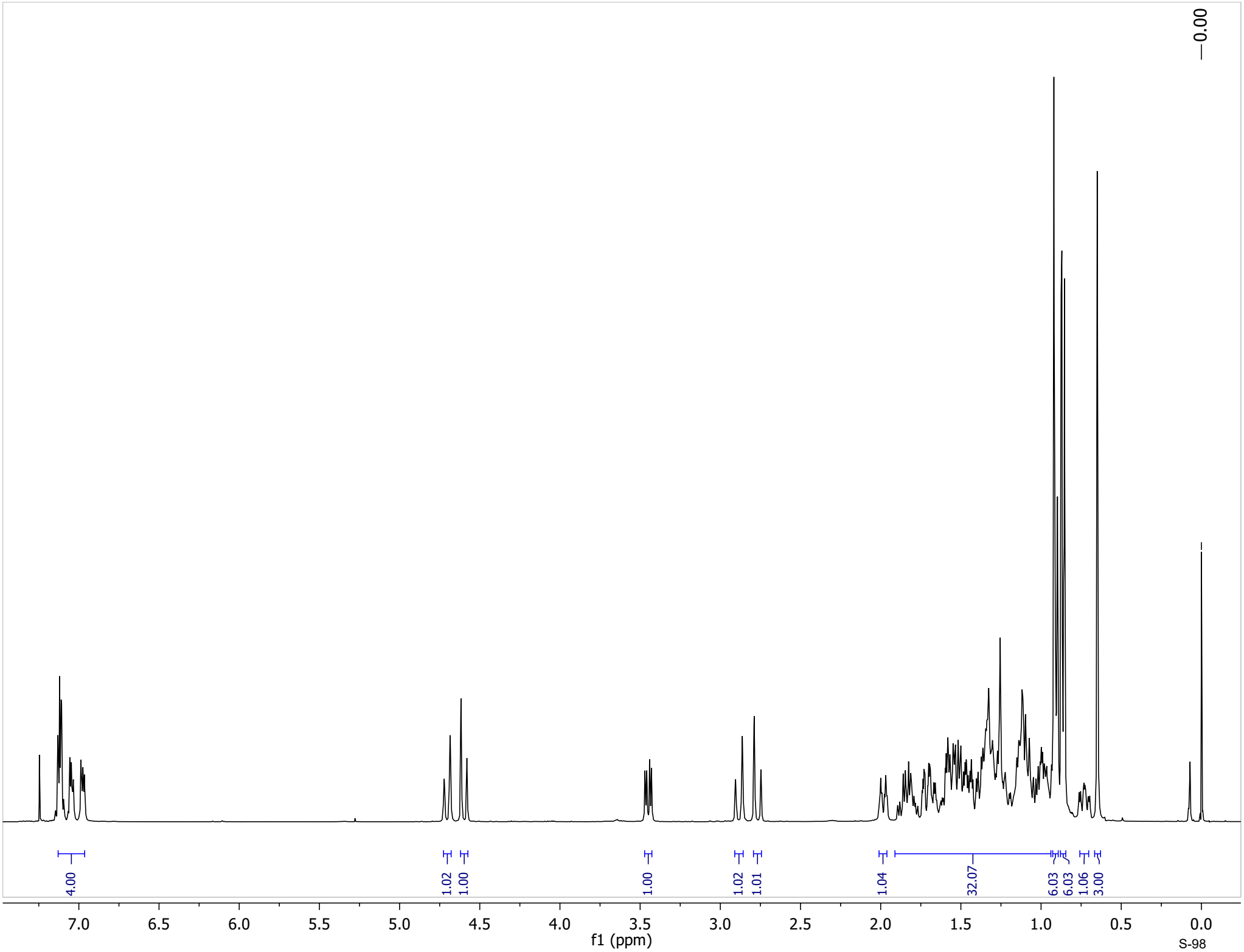
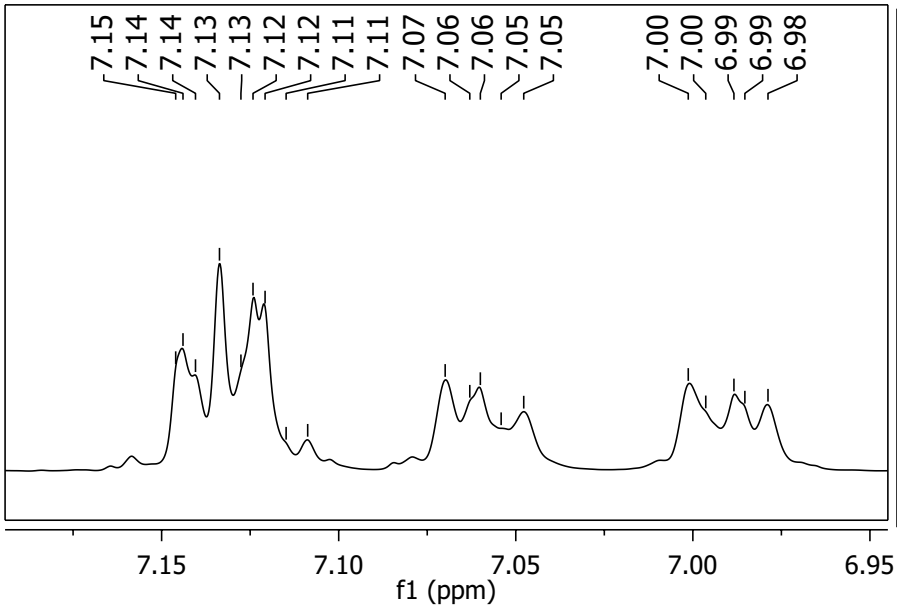
140
135
130
125
120
115
110
105
100
95
90
85
80
75
f1 (ppm)


70.26
66.81
62.09
55.92
52.91
45.08
41.60
40.43
40.35
40.05
39.33
34.22
31.83
31.33
30.44
30.28
29.72
28.77
21.13
20.53
17.13
16.35
14.48
12.55
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
f1 (ppm)



(3*S*)-Spiro-4-oxa-5α-cholestan-3,3´-isochromane (29)


0.00
4.00
1.02
1.00
1.00
1.02
1.01
1.04
32.07
6.03
6.03
1.06
3.00
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)


7.15
7.14
7.14
7.13
7.13
7.12
7.12
7.11
7.11
7.07
7.06
7.06
7.05
7.05
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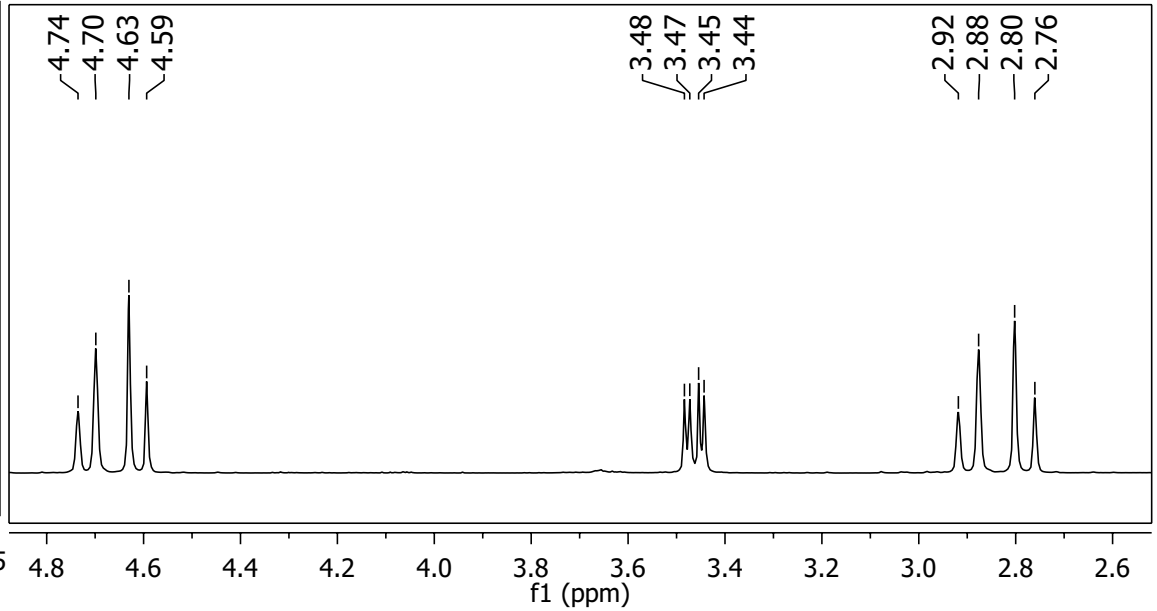
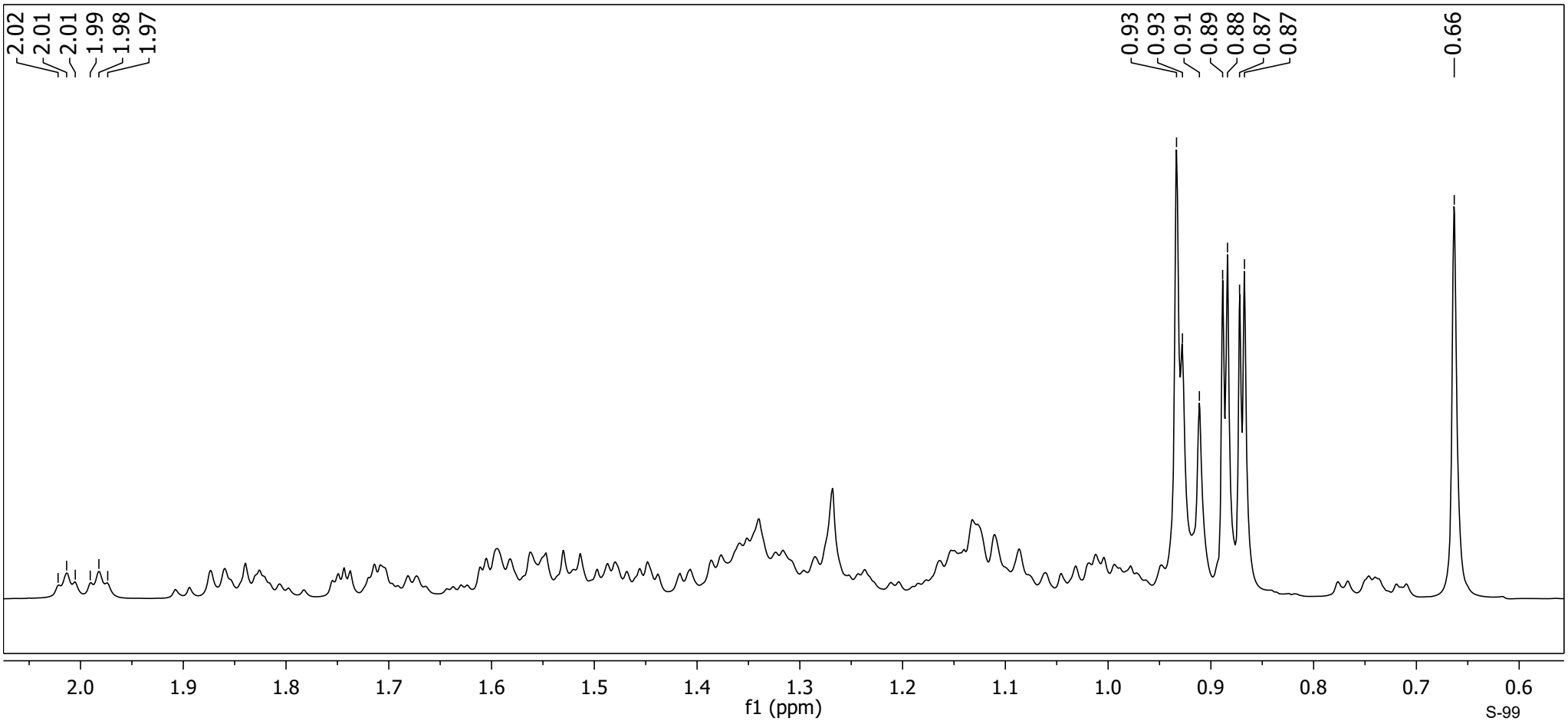
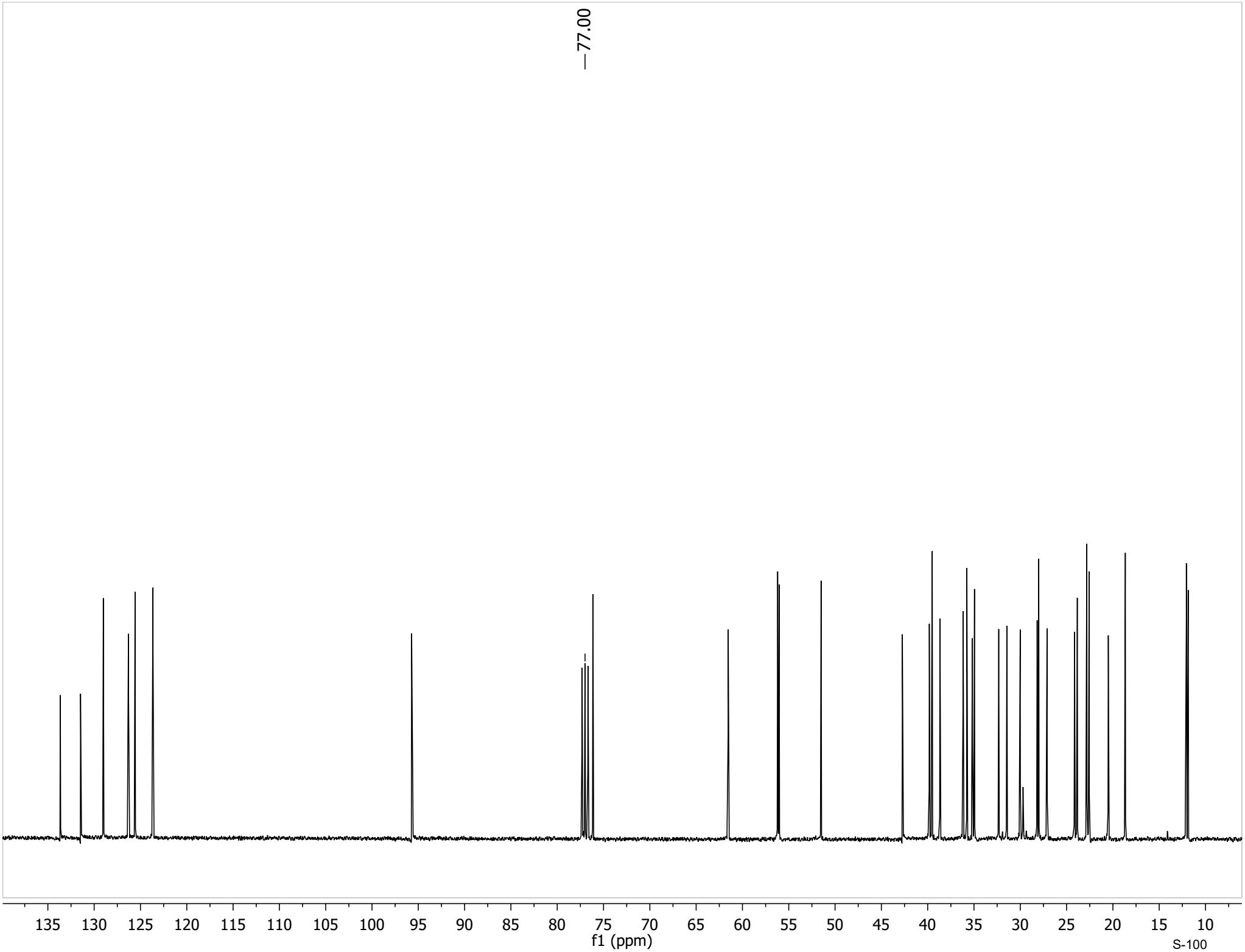
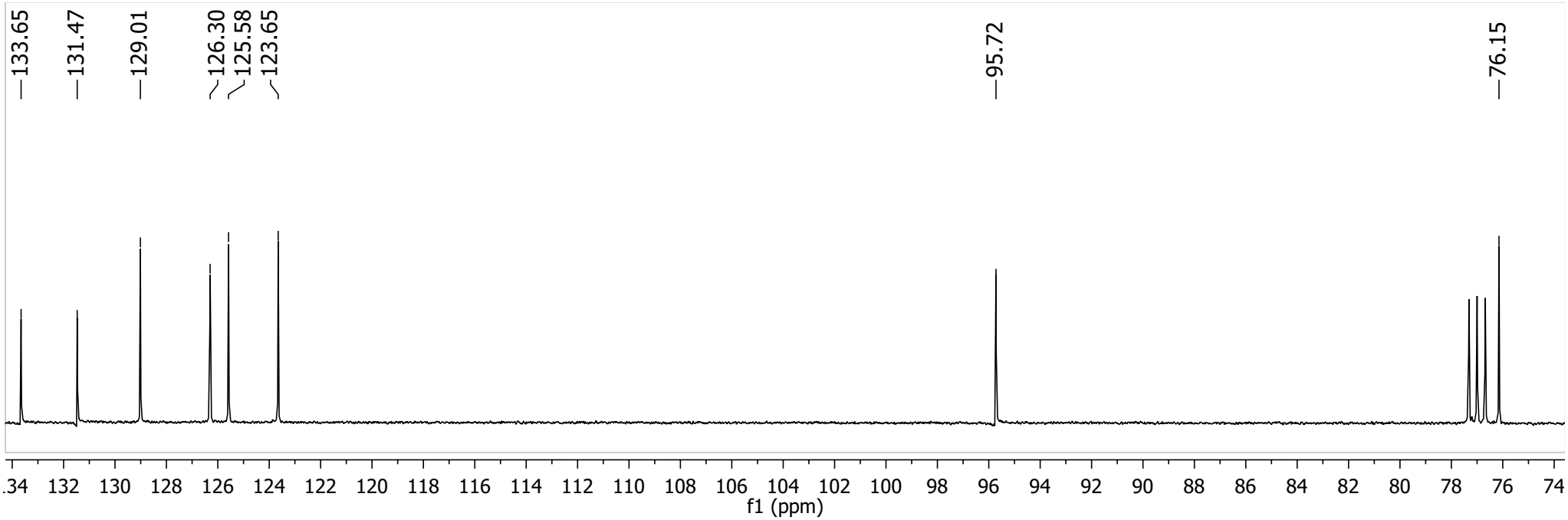
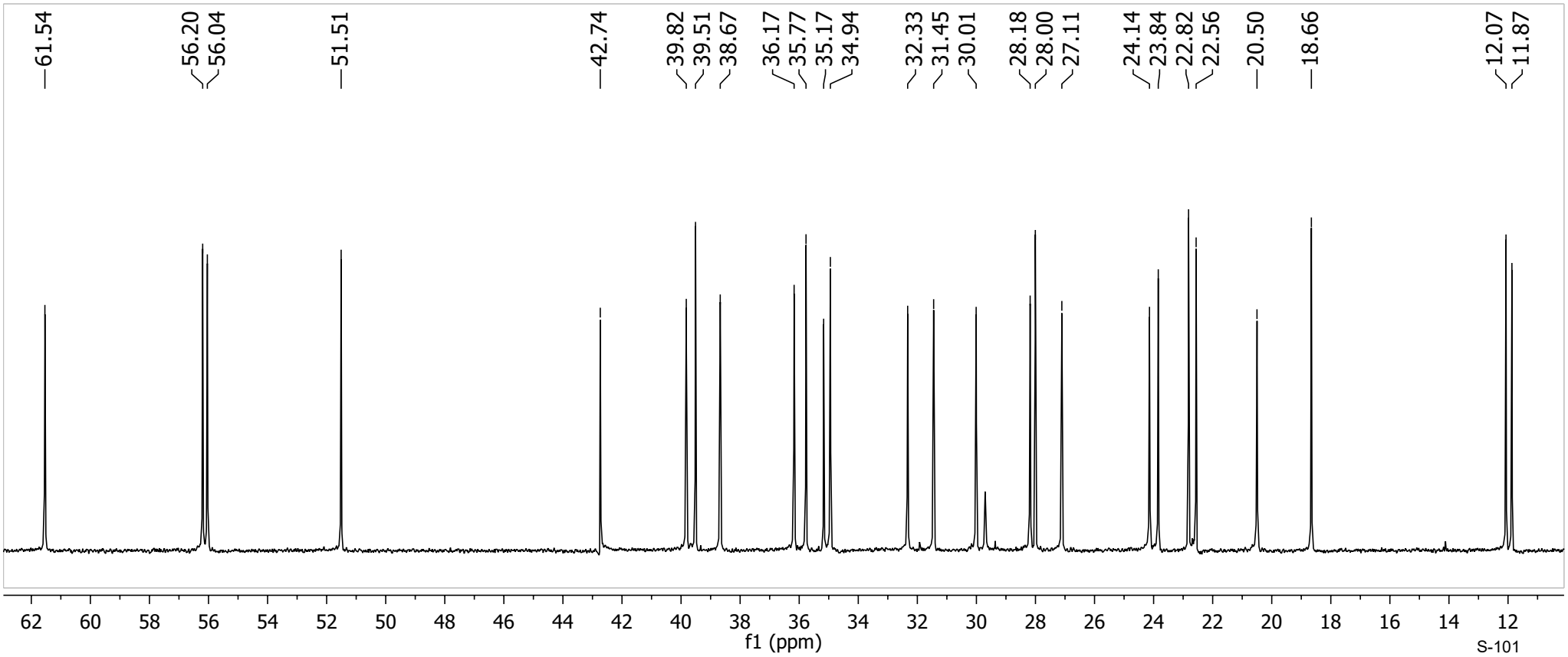
6.99
6.98
7.15
7.10
7.05
7.00
6.95
f1 (ppm)

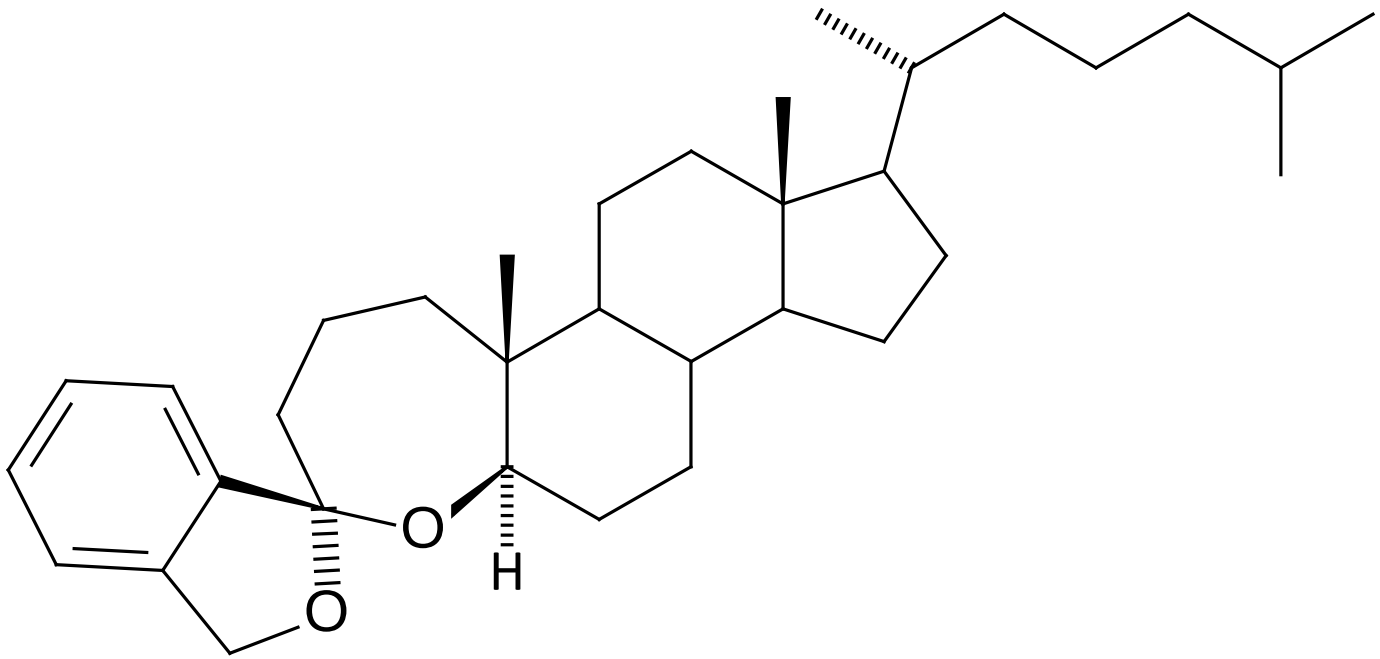

4.74
4.70
4.63
4.59
3.48
3.47
3.45
3.44
2.92
2.88
2.80
2.76
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
f1 (ppm)


2.02
2.01
2.01
1.99
1.98
1.97
0.93
0.93
0.91
0.89
0.88
0.87
0.87
0.66
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
f1 (ppm)

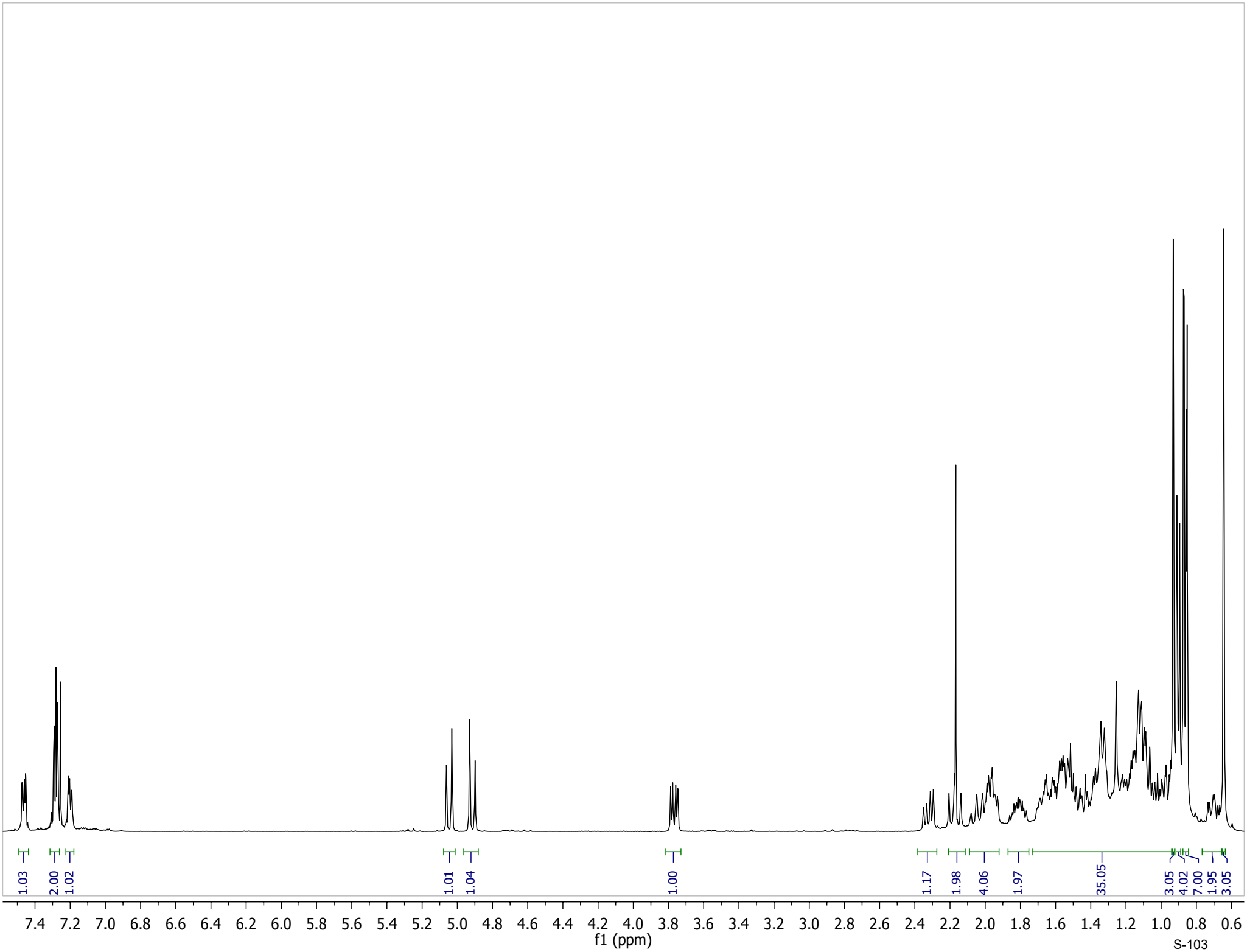

77.00
135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

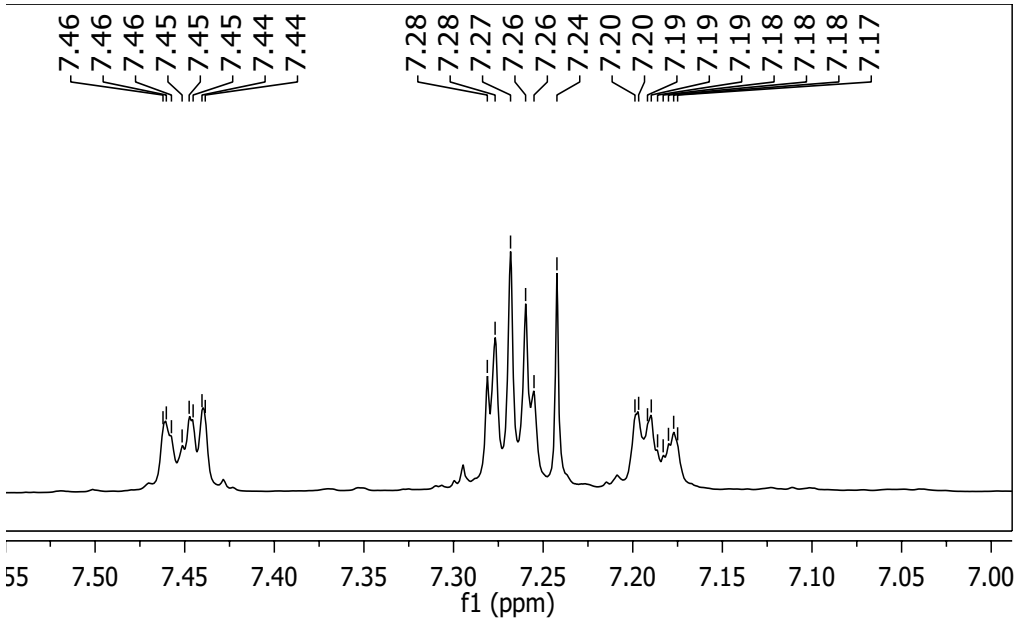

133.65
131.47
129.01
126.30
125.58
123.65
95.72
76.15
f1 (ppm)

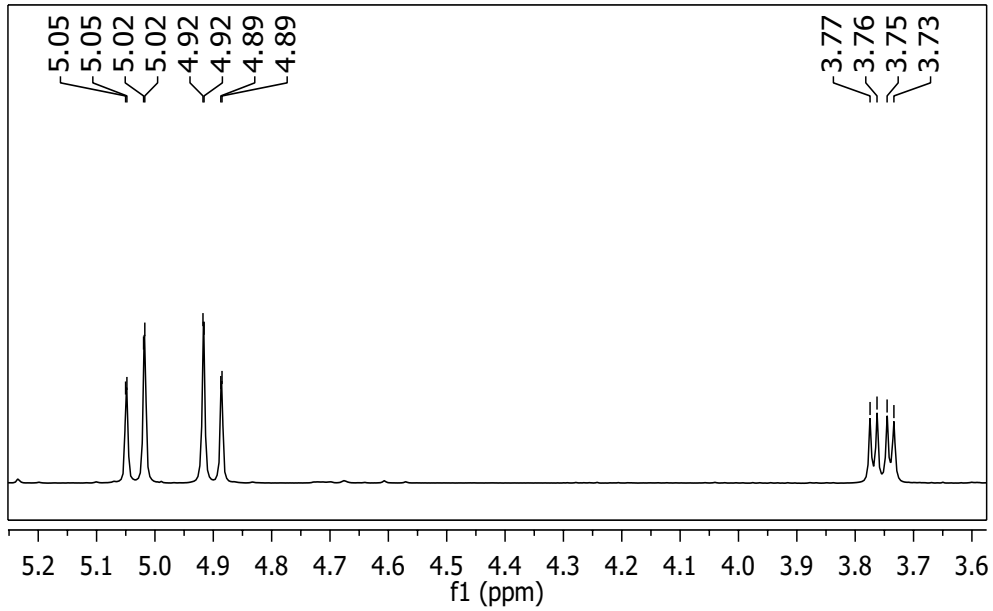

61.54
56.20
56.04
51.51
42.74
39.82
39.51
38.67
36.17
35.77
35.17
34.94
32.33
31.45
30.01
28.18
28.00
27.11
24.14
23.84
22.82
22.56
20.50
18.66
12.07
11.87
f1 (ppm)

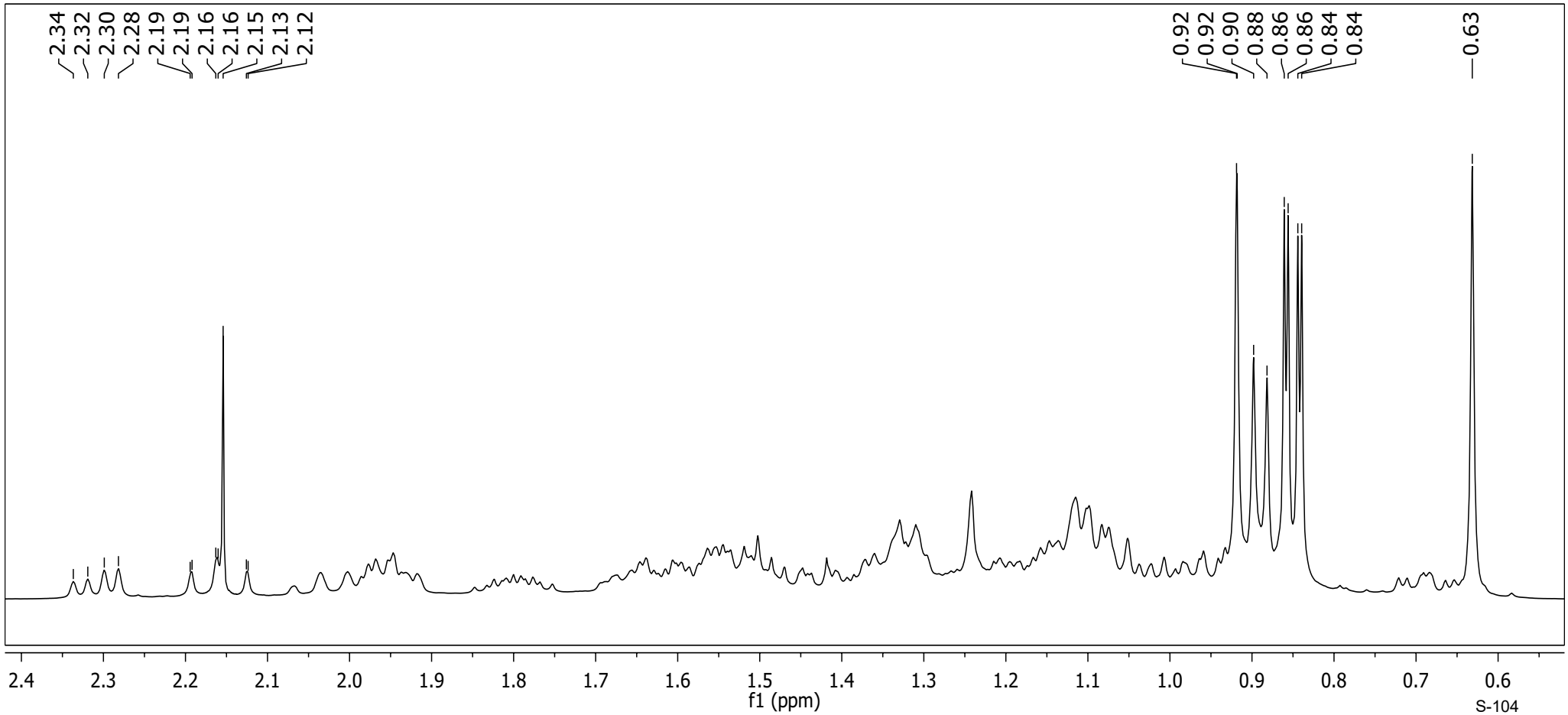


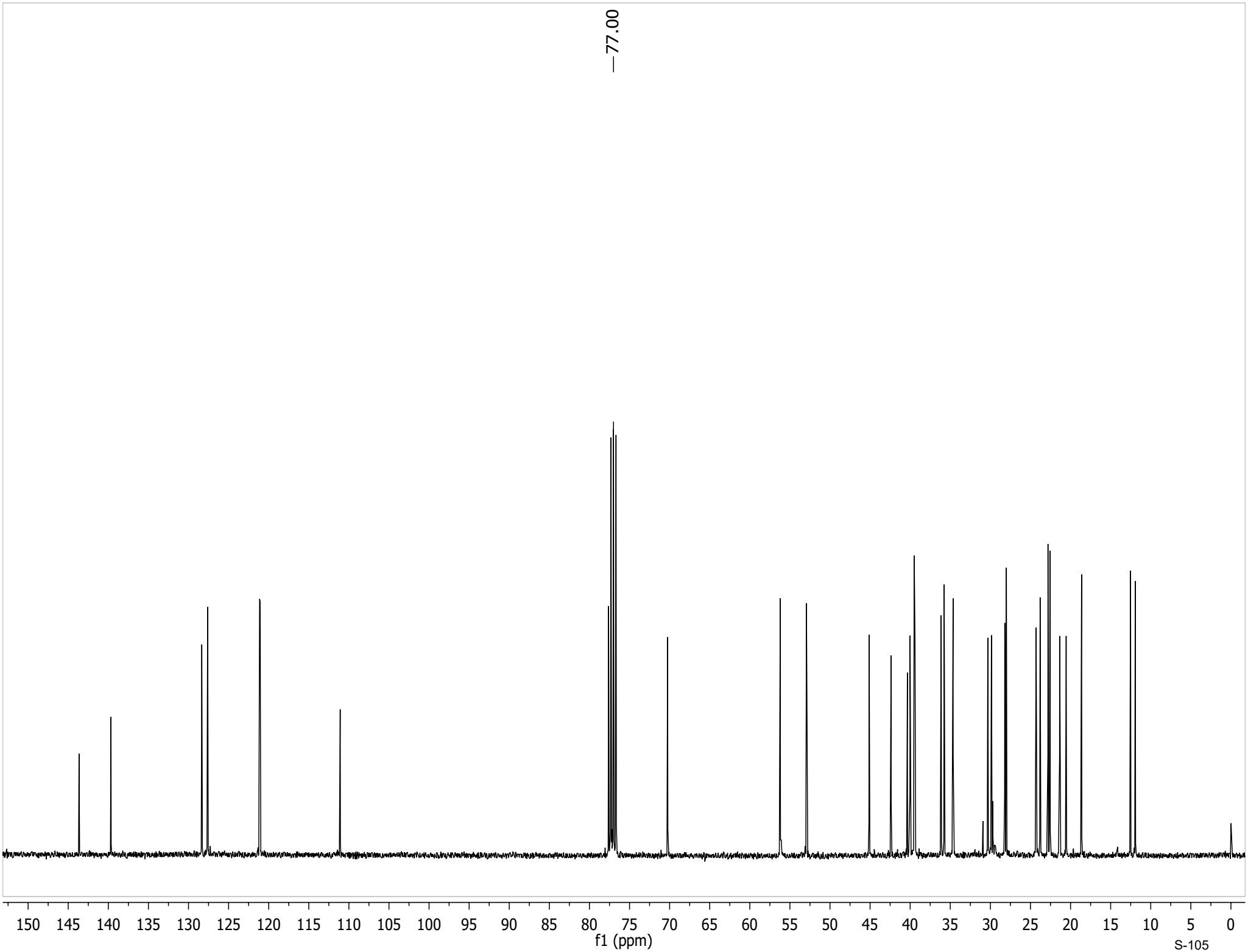
(4*S*)-Spiro-[isobenzofuran-1,2´-(A-homo-4a-oxa-5α-cholestan)-oxepane] **(30)**

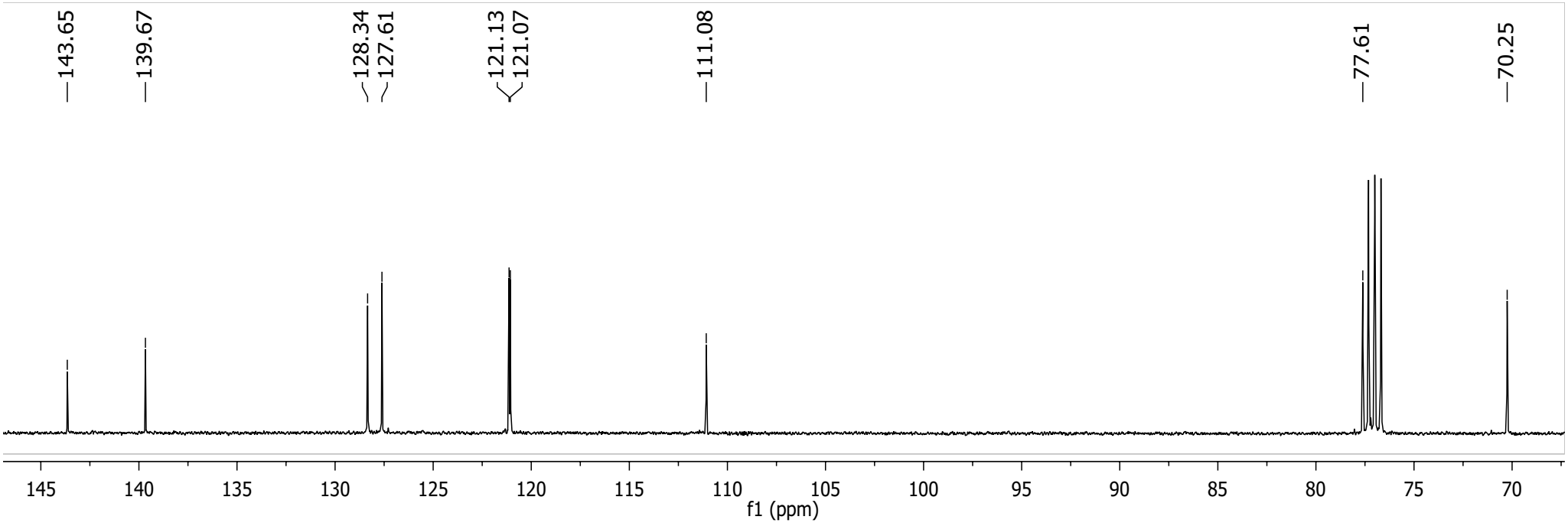

1.03
2.00
1.02
1.01
1.04
1.00
1.17
1.98
4.06
1.97
35.05
3.05
4.02
7.00
1.95
3.05
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
f1 (ppm)


7.46
7.46
7.46
7.45
7.45
7.45
7.44
7.44
7.28
7.28
7.27
7.26
7.26
7.24
7.20
7.20
7.19
7.19
7.19
7.18
7.18
7.18
7.17
55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
f1 (ppm)


5.05
5.05
5.02
5.02
4.92
4.92
4.89
4.89
3.77
3.76
3.75
3.73
5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6
f1 (ppm)


2.34
2.32
2.30
2.28
2.19
2.19
2.16
2.16
2.15
2.13
2.12
0.92
0.92
0.90
0.88
0.86
0.86
0.84
0.84
0.63
2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6
f1 (ppm)


77.00
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


143.65
139.67
128.34
127.61
121.13
121.07
111.08
77.61
70.25
145
140
135
130
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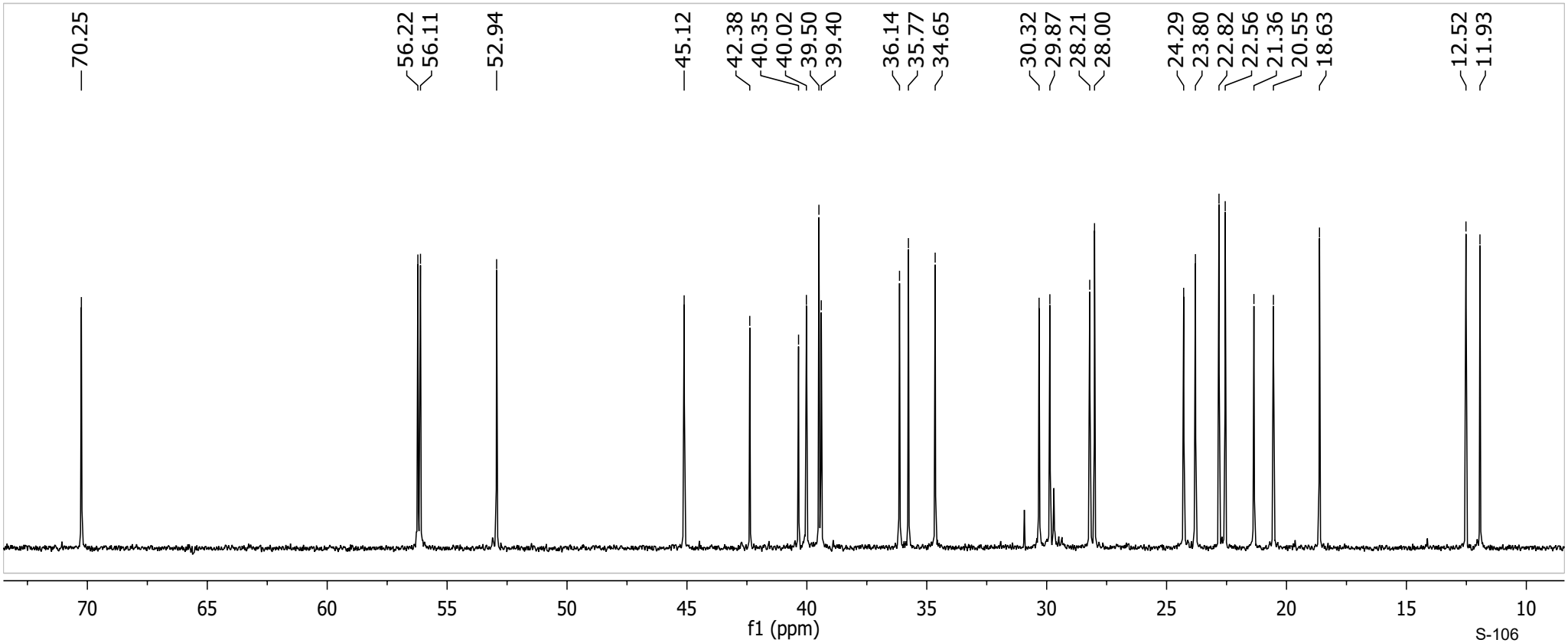
115
110
105
100
95
90
85
80
75
70
f1 (ppm)


70.25
56.22
56.11
52.94
45.12
42.38
40.35
40.02
39.50
39.40
36.14
35.77
34.65
30.32
29.87
28.21
28.00
24.29
23.80
22.82
22.56
21.36
20.55
18.63
12.52
11.93
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

X-ray crystallography

Suitable single crystals grown by slow evaporation of solutions of compounds **12** (CH_2Cl_2/ethyl acetate/hexane), **23** (acetone/hexane), **24** (CH_2Cl_2/acetone), **27** (ethyl acetate), **28** (CH_2Cl_2/acetone) and **29** (CH_2Cl_2/hexane) were mounted on a glass fiber and crystallographic data were collected with an Oxford Diffraction Gemini "A" diffractometer with a CCD area detector ($\lambda_{CuK\alpha}$ = 1.54184 Å, monochromator: graphite) at 130 K. Unit cell parameters were determined with a set of three runs of 15 frames (1° in ω). The double pass method of scanning was used to exclude any noise. The collected frames were integrated by using an orientation matrix determined from the narrow frame scans. CrysAlisPro and CrysAlis RED software packages[1] were used for data collection and integration. Analysis of the integrated data did not reveal any decay. Final cell parameters were determined by a global refinement of 6388, 2604, 1396, 9964, 2195, 2126, 4338 and 2293 reflections ($3.519 < \theta < 73.581$ °) for compounds **12, 23, 24, 27, 28** and **29** respectively. Collected data were corrected for absorption effects by using an Analytical numeric absorption correction[2] using a multifaceted crystal model based on expressions upon the Laue symmetry using equivalent reflections. Structure solution and refinement were carried with the programs SHELXS-2014[3] and SHELXL-2014[4] respectively. WinGX v2014.1 and Ortep[5] software were used to prepare material for publication. Full-matrix least-squares refinement was carried out by minimizing $(Fo^2 - Fc^2)^2$. All nonhydrogen atoms were refined anisotropically. For H atom of the hydroxy group was located in a difference map and refined isotropically with Uiso(H) = 1.5 for H–O. Hydrogen atoms attached to carbon atoms were placed in geometrically idealized positions and refined as riding on their parent atoms, with C—H = 0.98 – 1.00 Å with Uiso (H) = 1.2Ueq(C) for aromatic, methylene and methyne groups, and Uiso (H) = 1.5 Ueq(C) for methyl group. For **28** attempts made to model the solvent molecule were not successful; the SQUEEZE[6] option in PLATON indicated there was a large solvent cavity of 202 $Å^3$. In the final cycles of refinement, this contribution of 50 electrons to the electron density was removed from the observed data. For the electron density, F(000) value in the molecular weight and the formula are given without taking into account the results obtained with SQUEEZE.

Crystal data and experimental details of the structure determination are listed in Tables S1 and S2. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary material numbers CCDC 1953054 **(12)**, CCDC 1953055 **(23)**, CCDC 1953056 **(24)**, CCDC 1953057 **(27)**, CCDC 1953058 **(28)** and CCDC 1953059 **(29)**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. E-mail:deposit@ccdc.cam.ac.uk.

Table S1. Crystal data and structure refinement for compounds **12** and **23-24**

Parameter	**12**	**23**	**24**
Empirical formula	$C_{28}H_{36}O_4$	$C_{34}H_{47}O_4$	$C_{34}H_{52}O_2$
Formula weight	436.57	519.71	492.75
Temperature	130(2) K	130(2) K	130(2) K
Wavelength	1.54184 Å	1.54184 Å	1.54184 Å
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P\,2_1\,2_1\,2_1$	$C\,2$	$P\,2_1$
Unit cell dimensions	a = 7.7797(3) Å	a = 13.1096(16) Å	a = 8.4637(4) Å
	b = 13.9645(7) Å	b = 6.5478(7) Å	b = 7.4511(3) Å
	c = 21.3823(10) Å	c = 34.244(4) Å	c = 47.1253(17) Å
		β= 95.486(11)°.	β= 90.048(4)°.
Volume	2322.96(18) $Å^3$	2926.0(6) $Å^3$	2971.9(2) $Å^3$
Z	4	4	4
Density (calculated)	1.248 Mg/m^3	1.180 Mg/m^3	1.101 Mg/m^3
Absorption coefficient	0.647 mm^{-1}	0.588 mm^{-1}	0.498 mm^{-1}
F(000)	944	1132	1088
Crystal size (mm^3)	0.560 x 0.380 x 0.350	0.600 x 0.400 x 0.080	0.480 x 0.250 x 0.110
Theta range for data collection	3.781 to 73.807°.	3.890 to 73.596°.	3.752 to 74.025°.
Index ranges	-9<=h<=6, -17<=k<=17, -26<=l<=26	-15<=h<=15, -7<=k<=5, -42<=l<=28	-10<=h<=10, -8<=k<=8, -58<=l<=57
Reflections collected	14520	6246	65679
Independent reflections	4554 [R(int) = 0.0254]	4169 [R(int) = 0.0270]	11470 [R(int) = 0.0632]
Completeness to theta = 67.684°	100.0 %	99.7 %	99.9 %
Absorption correction	Analytical	Analytical	Analytical
Max. and min. transmission	0.826 and 0.750	0.952 and 0.773	0.948 and 0.840
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4554 / 1 / 296	4169 / 1 / 347	11470 / 1 / 659
Goodness-of-fit on F^2	1.046	1.045	1.053
Final R indices [I>2sigma(I)]	R1 = 0.0367, wR2 = 0.0913	R1 = 0.0539, wR2 = 0.1275	R1 = 0.0492, wR2 = 0.1042
R indices (all data)	R1 = 0.0402, wR2 = 0.0941	R1 = 0.0741, wR2 = 0.1398	R1 = 0.0675, wR2 = 0.1143
Absolute structure parameter	-0.03(9)	0.2(2)	-0.14(11)
Largest diff. peak and hole	0.238 and -0.233 e.$Å^{-3}$	0.423 and -0.255 e.$Å^{-3}$	0.249 and -0.229 e.$Å^{-3}$

Table S2. Crystal data and structure refinement for compounds **27** to **29**

Parameter	**27**	**28**	**29**
Empirical formula	$C_{34}H_{48}O_4$	$C_{34}H_{48}O_4$	$C_{34}H_{52}O_2$
Formula weight	520.72	520.72	492.75
Temperature	298(2) K	130(2) K	130(2) K
Wavelength	1.54184 Å	1.54184 Å	1.54184 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C* 2	*P* 2_1	*P* 2_1
Unit cell dimensions	a = 21.7423(15) Å	a = 11.3526(7) Å	a = 7.4753(5) Å
	b = 7.1223(5) Å	b = 7.2237(3) Å	b = 8.3777(7) Å
	c = 19.5816(14) Å	c = 19.7666(12) Å	c = 23.7615(17) Å
	β= 101.416(7)°.	β= 104.982(6)°.	β= 97.224(6)°.
Volume	2972.3(4) $Å^3$	1565.91(16) $Å^3$	1476.27(19) $Å^3$
Z	4	2	2
Density (calculated)	1.164 Mg/m^3	1.104 Mg/m^3	1.109 Mg/m^3
Absorption coefficient	0.579 mm^{-1}	0.550 mm^{-1}	0.501 mm^{-1}
F(000)	1136	568	544
Crystal size (mm^3)	0.400 x 0.280 x 0.060	0.420 x 0.080 x 0.050	0.540 x 0.180 x 0.090
Theta range for data collection	4.149 to 73.558°.	4.031 to 74.106°.	3.750 to 73.391°.
Index ranges	-26<=h<=25, -6<=k<=8, -24<=l<=23	-14<=h<=14, -8<=k<=6, -22<=l<=24	-5<=h<=9, -10<=k<=10, -29<=l<=26
Reflections collected	9202	14649	7536
Independent reflections	4812 [R(int) = 0.0376]	4727 [R(int) = 0.0439]	4662 [R(int) = 0.0360]
Completeness to theta = 67.684°	99.9 %	99.9 %	99.8 %
Absorption correction	Analytical	Analytical	Analytical
Max. and min. transmission	0.962 and 0.853	0.975 and 0.879	0.959 and 0.853
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4812 / 1 / 347	4727 / 1 / 347	4662 / 1 / 330
Goodness-of-fit on F^2	1.098	1.038	1.057
Final R indices [I>2sigma(I)]	R1 = 0.0556, wR2 = 0.1165	R1 = 0.0417, wR2 = 0.0957	R1 = 0.0527, wR2 = 0.1152
R indices (all data)	R1 = 0.0746, wR2 = 0.1380	R1 = 0.0513, wR2 = 0.1028	R1 = 0.0736, wR2 = 0.1417
Absolute structure parameter	0.6(3)	0.3(2)	-0.2(3)
Largest diff. peak and hole	0.132 and -0.196 e.$Å^{-3}$	0.146 and -0.235 e.$Å^{-3}$	0.201 and -0.242 e.$Å^{-3}$

References X-ray crystallography

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2. Clark, R. C.; Reid, J. S. The analytical calculation of absorption in multifaceted crystals. *Acta Cryst.* **1995**, A51, 887-897.
3. Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination; *Acta Cryst.* **2015**, A71, 3-8
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5. Farrugia L.J. WinGX and ORTEP for Windows: an update. *J. Appl. Cryst*. **2012**, 45, 849-854
6. Spek, A.L. PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Cryst.* **2015**, C71, 9-18

Additional Cytotoxicity Data

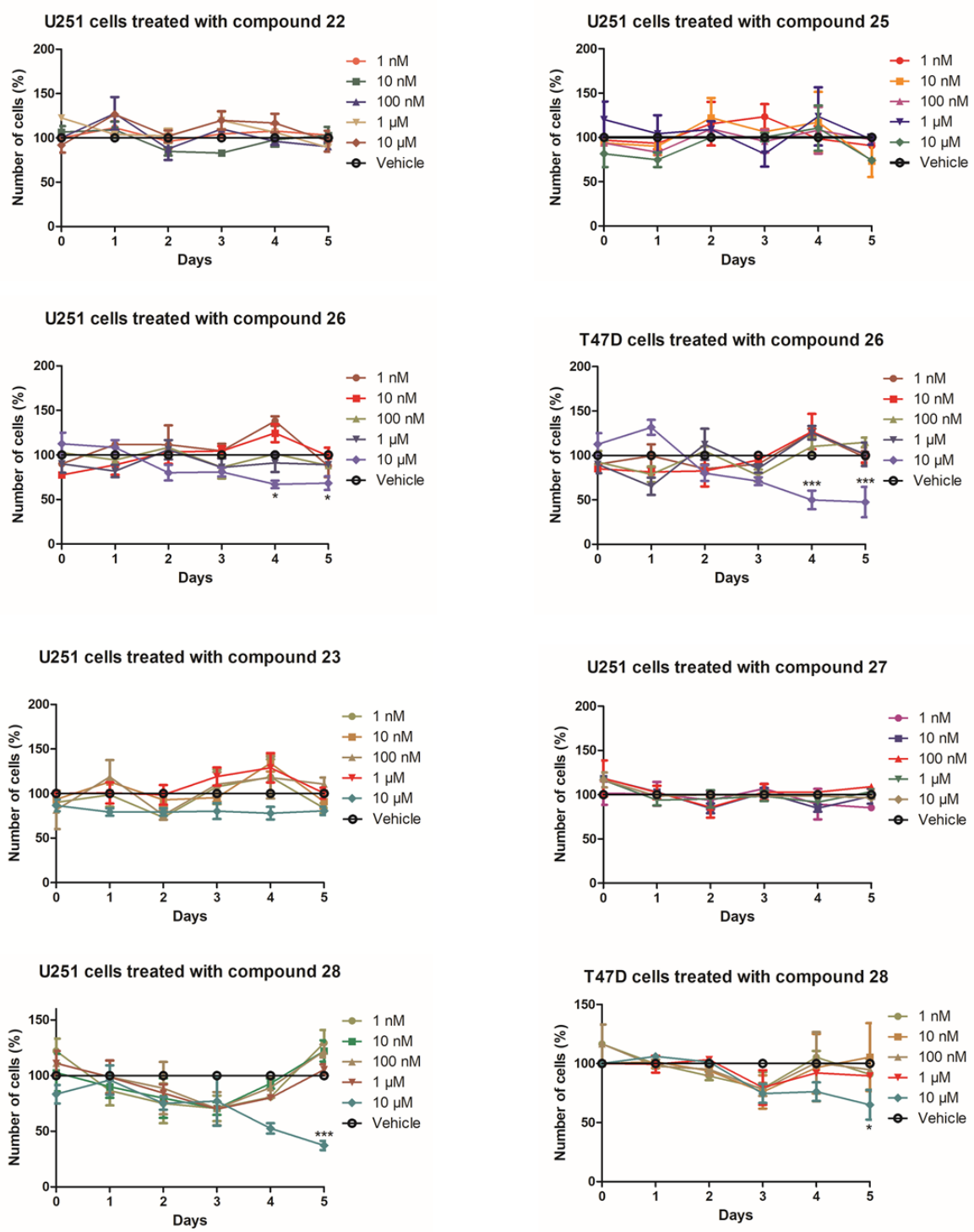

Figure S1. Cytotoxic effects of the synthetized BSS compounds. Cells derived from human tumors were treated with the compounds 22, 25, 26, 23, 27 and 28 (1 nM, 10 nM, 100 nM, 1 µM and 10 µM), and vehicle as control (1% DMSO) for five days. The figure shows the percentage of the number of cells after the treatment with the compounds. The number of cells was determined each day using the trypan blue dye exclusion assay and is represented as percentage considering the number of cells counted in the vehicle as 100%. The results are expressed as the mean ± S.E.M., n=3; *p<0.05 *vs.* Vehicle, ***p<0.005 *vs.* Vehicle.

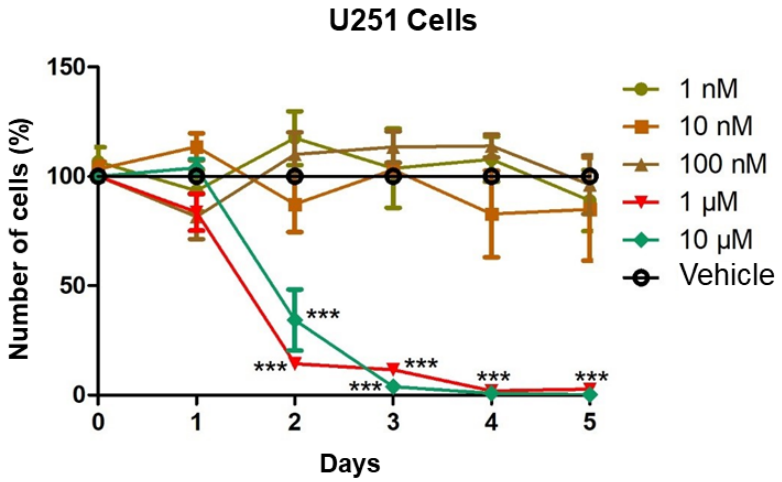

Figure S2. The potent antitumoral drug Ara-C decreases the number of U251 cells. Cells were treated with Ara-C (1 nM, 10 nM, 100 nM, 1 µM and 10 µM), and vehicle (1% DMSO) for five days. The figure shows the percentage of the number of cells in U251 line after treatment with Ara-C. The number of cells was determined each day using the trypan blue dye exclusion assay and is represented as percentage considering the number of cells counted in the vehicle as 100%. IC50 value calculated after two days of treatment: 0.748 µM. The results are expressed as the mean ± S.E.M., n=3; ***p<0.001 *vs.* Vehicle.