Electronic supplementary materials *Mendeleev Commun.*, 2018, **28**, 644–645

Pentafluoroperbenzoic acid as the efficient reagent for Baeyer–Villiger oxidation of cyclic ketones

Ravil I. Khusnutdinov, Tatyana M. Egorova, Rishat I. Aminov and Usein M. Dzhemilev

Methods and Materials

^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance-III 400 Ascend instrument (400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C in $CDCl_3$). Mass spectra were run on a Shimadzu GCMS-QP2010Plus mass spectrometer (SPB-5 capillary column, 30 m ×0.25 mm, helium as the carrier gas, temperature programming from 40 to 300ºC at 8 °C/min, evaporation temperature of 280ºC, ion source temperature of 200ºC, and ionization energy of 70 eV). The course of the reaction and the purity of the products were monitored by gas liquid chromatography on a CristalLux 4000M, instrument [2 m ×3 mm column, SE-30 silicone (5%) on Chromaton N-AW-HMDS as the stationary phase, temperature programming from 50 to 270ºC at 8 °C/min, helium as the carrier gas (47 mL/min)].

Oxo–peroxo molibdenum complexe $MoO(O_2)_2 \cdot 2QOH$ was synthesized as reported [S1].

Preparation of pentafluoroperbenzoic acid (PFPBA) [S2,S3]. A solution of pentafluorobenzaldehyde (3 g, 0.015 mol) in CCl_4 (40 ml) was placed in a 100 ml conical flask equipped with a bubbler. An oxygen-ozone mixture was passed on stirring within 3 h. The solution was flushed with argon and kept at -18°C for 10-12 hours. The resulting white crystals were filtered off, washed with CCl_4 and dried at 20-25 °C. The mother liquor after cooling was evaporated by 2/3 at room temperature *in vacuo*, the crystals formed were filtered off, washed with CCl_4, dried and combined with the first crop. The yield of PFPBA was 2.6 g (80%), mp 57.5-58.5°C.

General procedure for the oxidation of cyclic ketones with pentafluoroperbenzoic acid. A mixture of cyclic ketone **1**,**3,5,7a-e,9,11** (0.05 g) (**1**: 0.33 mmol, **3**: 0.25 mmol, **5**: 0.30 mmol, **7a**: 0.59 mmol, **7b**: 0.51 mmol, **7c**: 0.44 mmol, **7d**: 0.40 mmol, **7e**: 0.27 mmol, **9**: 0.45 mmol, **11**: 0.33 mmol) and [Mo] catalyst [in case of compounds **5** (0.015 mmol) or **9** (0.023 mmol)] in DCE (2 ml) at 20-50 °C was subjected to dropwise (for 1 h) addition of solution of PFPBA (0.37-0.68

mmol for ketones **1**,**3**,**5**,**9** and 0.54-1.18 mmol for ketones **7a-e**,**11**) in CH_2Cl_2 (2 ml). The mixture was then stirred for more 5 h (or 19 h in case of **11**). The mixture was then treated with 10% Na_2CO_3 solution (aq.) and stirred for 5 min. The organic layer was decanted and filtered through a pad of Al_2O_3 (eluent – CH_2Cl_2-DCE), the aqueous one was extracted with $CHCl_3$. The combined extracts were concentrated, the products were isolated by column chromatography on silica gel (60-200 μm, 60Å), the eluent was ethyl acetate.

4-Oxahomoadamantan-5-one 2 [S4]. Yield 98%, white crystals, m.p. 285-288ºC (Ref. 286-289ºC [5]) . ^{1}H NMR (400.13 MHz, $CDCl_3$): 1.65-1.72 (m, 4H), 1.75-1.81 (m, 4H), 1.86-2.06 (m, 9H), 3.01 (t, 1H, CHCO, *J* 5.6 Hz), 4.43 (s, 1H, CHOCO). ^{13}C NMR (100.62 MHz, $CDCl_3$): 25.79 ($C^{1,8}$), 30.92 ($C^{7,10}$), 33.73 (C^9), 35.73 ($C^{2,11}$), 41.22 (C^6), 73.18 (C^3), 178.98 (C^5). MS (EI, 70eV), *m/z* 166(1) $[M]^+$,122(13), 107(4), 93(16), 80(100), 67 (11), 53(9), 41(15).

11-Oxahomodiamantan-10-one 4a and 10-oxahomodiamantan-11-one 4b [S6]. Total yield 98%, white crystal. ^{1}H NMR (400.13 MHz, $CDCl_3$): 1.67-2.14 (m, 32H), 3.01 (t, 1H, CHCO, *J* 6.0 Hz, **4a**), 3.08 (s, 1H, CHCO, **4b**), 4.30 (s, 1H, CHCO, **4a**), 4.45 (s, 1H, CHCO, **4b**). ^{13}C NMR (100.62 MHz, $CDCl_3$), **4a**: 25.69 (C^4), 31.58 ($C^{6,14}$), 35.13 (C^2), 35.89 (C^1), 35.96 (C^7), 37.52 ($C^{6,13}$), 38.02 ($C^{5,15}$), 38.14 (C^3), 39.84 (C^9), 83.09 (C^{12}), 180.60 (C^{10}). MS (EI, 70eV) **4a**, *m/z* 218(2) $[M]^+$, 202 (1), 175(15), 174(100), 159(4), 145(9), 131(17), 117(29), 105(15), 96(50), 91(52), 79(50), 67(13), 55(11), 41(17). ^{13}C NMR (100.62 MHz, $CDCl_3$), **4b**: 26.02 (C^4), 33.02 ($C^{6,13}$), 34.79 (C^2), 35.96 ($C^{1,7}$), 36.82 ($C^{8,14}$), 38.02 (C^3), 38.24($C^{5,15}$), 53.49 (C^{12}), 72.59 (C^9), 179.61 (C^{11}). MS (EI, 70eV) **4b**, *m/z*, 218(5) $[M]^+$, 202 (1), 175(14), 174(100), 159(3), 145(8), 131(14), 117(23), 105(15), 96(40), 91(42), 79(46), 67(11), 55(8), 41(14).

1-Hydroxy-4-oxahomoadamantan-5-one 6 [S7]. Yield 81%, R_f 0.34 (EtOAc), white crystal, m.p. 335-336ºC (CH_2Cl_2) (Ref. 337ºC). ^{1}H NMR (400.13 Hz, $CDCl_3$): 1.21-2.08 (m, 10H), 2.43 (s, 1H, OH), 3.18 (t, 1H, CH, *J* 6.0 Hz), 3.68, 3.70 (q, 1H, CHCO, *J* 10.6 Hz, *J* 7.2 Hz), 4.63 (s,1H, CHOCO). ^{13}C NMR (100.62 MHz, $CDCl_3$): 29.98 (C^8), 30.52(C^7), 34.81 (C^6), 39.05 (C^{11}), 41.63 (C^{10}), 42.36 (C^2), 43.89 (C^9), 66.93 (C^3), 74.45 (C^1), 177.84 (C^5). MS (EI, 70eV), *m/z* 182(1) $[M]^+$,167(1), 138(2), 123(4), 109(3), 95(100), 82(24), 67 (10), 55(11), 41(15).

5-Pentanolide 8a and 5-hydroxypentanoic acid [S4]. Total yield 100%, R_f 0.32 (EtOAc) colourless oil. Compound **8a**. Yield 50%. ^{1}H NMR (400.13 Hz, $CDCl_3$): 1.85-1.96 (m, 4H), 2.59 (t, 2H, CH_2CO, *J* 6.8 Hz), 4.36-4.38 (m, 2H, CH_2OCO). ^{13}C NMR (100.62 MHz, $CDCl_3$): 18.97 (C^3), 22.29 (C^4), 29.86 (C^2), 70.16 (C^5), 174.75 (C^1). MS (EI, 70eV), *m/z* 100(30) $[M]^+$, 70(13), 56 (58), 55(22), 42(100), 40(77). **5-hydroxypentanoic acid**. Yield 50%. ^{1}H NMR

(400.13 Hz, $CDCl_3$): 1.65-1.69 м (2H, CH_2), 1.94-1.97 м (2H, CH_2), 2.19-2.22 м (2H, CH_2COOH), 2.32-2.38 м (2H, CH_2COH), 5.27 с (2H, 2OH). ^{13}C NMR (100.62 MHz, $CDCl_3$): 21.46 (C^3), 28.07 (C^4), 33.81 (C^2), 64.32 (C^5), 174.13 (C^1). MS (EI, 70eV), *m/z* 118(13) $[M]^+$,117(16), 99(100), 70(13), 56 (60), 44(76), 42(92).

6-Hexanolide 8b [S4]. Yield 93%, R_f 0.35 (EtOAc), colourless oil. ^1H NMR (400.13 Hz, $CDCl_3$): 1.68-1.82 (m, 6H), 2.59-2.61 (m, 2H, CH_2CO), 4.19 (t, 2H, CH_2OCO, *J* 4.8 Hz). ^{13}C NMR (100.62 MHz, $CDCl_3$): 22.97 (C^3), 28.98(C^5), 29.32 (C^4), 34.59 (C^2), 69.36 (C^6), 176.32 (C^1). MS (EI, 70eV), *m/z* 114(14) $[M]^+$, 84(28), 70(15), 56 (37), 55(100), 42(94), 41(48).

7-Heptanolide 8c [S8] . Yield 53%, R_f 0.51 (EtOAc), colourless oil. ^1H NMR (400.13 Hz, $CDCl_3$): 1.59-1.87 (m, 8H), 2.55 (t, 2H, CH_2CO, *J* 6.4 Hz), 4.35 (t, 2H, CH_2OCO, *J* 5.6 Hz). ^{13}C NMR (100.62 MHz, $CDCl_3$): 24.06 (C^3), 25.95 (C^4), 28.50 (C^5), 31.05 (C^6), 31.42 (C^2), 68.03 (C^7), 175.57 (C^1). MS (EI, 70eV), *m/z* 128(1) $[M]^+$, 112(6), 98(26), 84(10), 70(24), 69 (41), 55(100), 41(56), 40(68).

8-Octanolide 8d [S8]. Yield 60%, R_f 0.43 (EtOAc), colourless oil. ^1H NMR (400.13 Hz, $CDCl_3$): 1.30-1.87 (m, 12H), 2.24 (t, 2H, CH_2CO, *J* 6.4 Hz), 4.25 (t, 2H, CH_2OCO, *J* 5.6 Hz). ^{13}C NMR (100.62 MHz, $CDCl_3$): 22.88 (C^3), 24.05 (C^4), 25.05 (C^5), 27.71 (C^6), 29.44 (C^7), 35.54 (C^2), 64.47 (C^8), 175.79 (C^1). MS (EI, 70eV), *m/z* 142(1) $[M]^+$, 126(11), 112(6), 98(74), 83(41), 72(1), 70(25), 55(100), 41(60).

12-Dodecanolide 8e [S9]. Yield 50%, R_f 0.47 (EtOAc), colourless oil. ^1H NMR (400.13 Hz, $CDCl_3$): 1.28-1.42 (m, 14H), 1.61-1.71 (m, 4H), 2.32-2.35 (m, 2H, CH_2CO), 4.14 (t, 2H, CH_2OCO, *J* 5.2 Hz). ^{13}C NMR (100.62 MHz, $CDCl_3$): 24.30 (C^3), 24.61 (C^7), 25.04 (C^{10}), 25.45 (C^4), 25.49 (C^{11}), 26.50 ($C^{5,9}$), 26.71 (C^6), 27.52 (C^8), 34.77 (C^2), 64.68 (C^{12}), 174.27 (C^1). MS (EI, 70eV), *m/z* 198(2) $[M]^+$,180(4), 162(5), 151(5), 138(14), 112(16), 98(66), 96(52), 83(59), 69 (52), 55(100), 41(56).

2-Oxabicyclo[3.2.1]octan-3-one 10a [S10]. Yield 94%, R_f 0.59 (EtOAc), colorless. ^1H NMR (400.13 Hz, $CDCl_3$): 1.68-2.16 (m, 6H), 2.46-2.75 (m, 3H, CH, CH_2CO), 4.86 (s, 1H, CHOCO). ^{13}C NMR (100.62 MHz, $CDCl_3$): 29.24 (C^6), 31.67 (C^7), 32.47 (C^4), 35.72 (C^5), 40.59 (C^8), 81.68 (C^1), 172.72 (C^3). MS (EI, 70eV), *m/z* 126(10) $[M]^+$, 98(18), 97(13), 82(100), 67 (90), 55(58), 43(18).

1,8,8-Trimethyl-2-oxabicyclo[3.2.1]octan-3-one 12a and 1,8,8-trimethyl-3-oxabicyclo[3.2.1]octan-2-one 12b (1:2.5 mixture) [S11]. Yield 40%, white crystals, R_f 0.14 (EtOAc). ^{1}H NMR (400.13 Hz, $CDCl_3$): 0.91 (s, 3H, CH_3, **12b**), 0.97 (s, 3H, CH_3, **12a**), 1.00 (s, 3H, CH_3, **12b**), 1.05 (s, 3H, CH_3, **12a**), 1.09 (s, 3H, CH_3, **12b**), 1.16 (s, 3H, CH_3, **12a**), 1.31-2.20 (m, 10H), 2.39-2.49 (m, 3H, CH, CH_2CO, **12b**), 4.12 (d, 1H, CH_2OCO, *J* 10.8 Hz, **12a**), 4.47-4.50 (m, 1H, CH_2OCO, **12a**). ^{13}C NMR (100.62 MHz, $CDCl_3$), **12a**: 14.21 (C^9), 19.95 (C^{11}), 22.46 (C^{10}), 27.90 (C^6), 36.29 (C^7), 38.59 (C^8), 44.60 (C^5), 47.18 (C^1), 74.73 (C^4), 175.46 (C^2). MS (EI, 70eV) **12a**, *m/z* 168(4) $[M]^+$, 140(12), 126(33), 109(100), 95(16), 83(47), 67(36), 55(52), 41(36). ^{13}C NMR (100.62 MHz, $CDCl_3$), **12b**: 17.52 (C^9), 18.22 (C^{11}), 23.89 (C^{10}), 30.06 (C^6), 37.12 (C^7), 38.11 (C^8), 38.59 (C^5), 42.30 (C^1), 94.09 (C^4), 171.40 (C^3). MS (EI, 70eV) **12b**, *m/z* 168(4) $[M]^+$, 140(1), 126(1), 109(100), 95(15), 83(14), 67(26), 55(15), 41(17).

References

[S1] R. Bandyopadhyay, S. Biswas, S. Guha, A. K. Mukherjee and R. Bhattacharyya, *Chem. Commun*., 1999, 1627.

[S2] U. M. Dzhemilev, N. S.Vostrikov, A. M.Moiseenkov and G. A. Tolstikov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1979, **28**, 857 (*Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 913).

[S3] U. M. Dzhemilev, N. S. Vostrikov, A. M. Moiseenkov and G. A. Tolstikov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 1051 (*Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1320)

[S4] T. Bradley, A. Dragan and N. Tomkinson, *Tetrahedron*, 2015, **41**, 8155.

[S5] W. Ando, R. Sato, H. Sonobe and T. Akasaka, *Tetrahedron Lett.*, 1984, **25**, 853.

[S6] J. Ondráček, J. Jankú, J. Novotný and L.Vodička, *Collect. Czech. Chem. Commun.*, 1989, **54**, 3260.

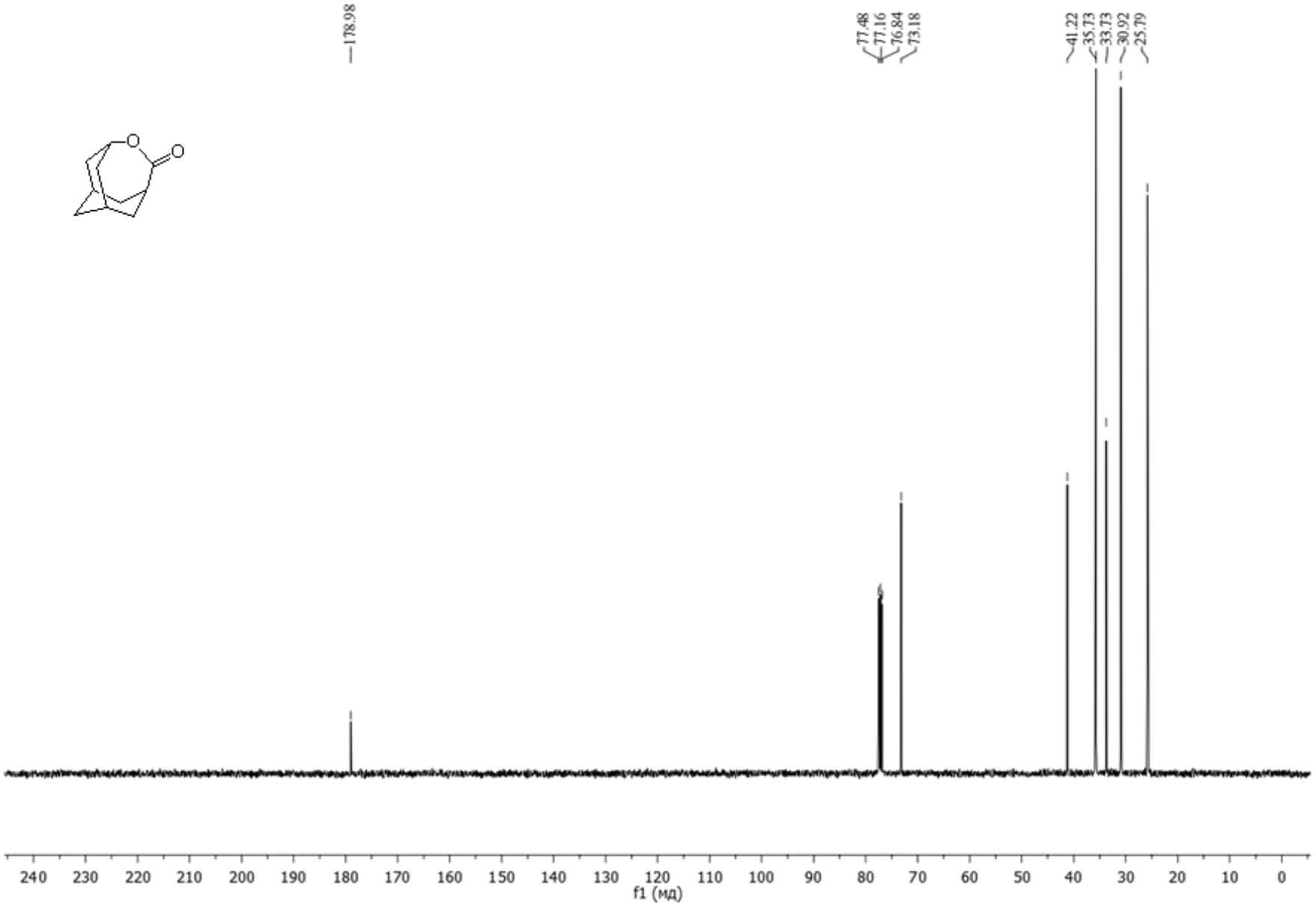
[S7] J. Hlavaty, L. Vodicka and J. Triska, *Sb. Vys. Sk. Chem.-Technol. Praze, Technol. Paliv*., 1984, **49**, 205.

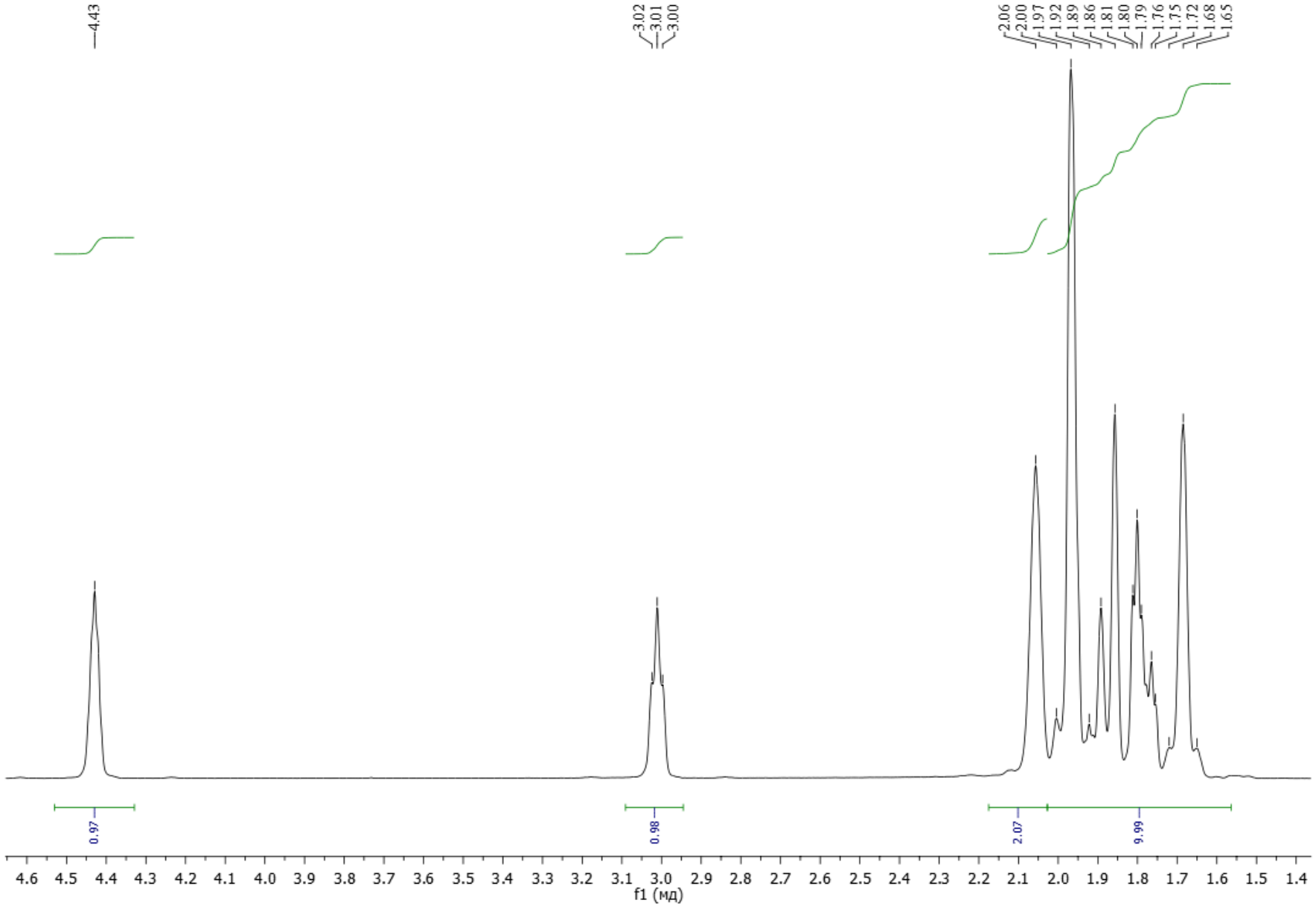
[S8] M. Rajabi, M. Lanfranchi, F. Campo and L. Panza, *Synth. Commun.*, 2014, **44**, 1149.

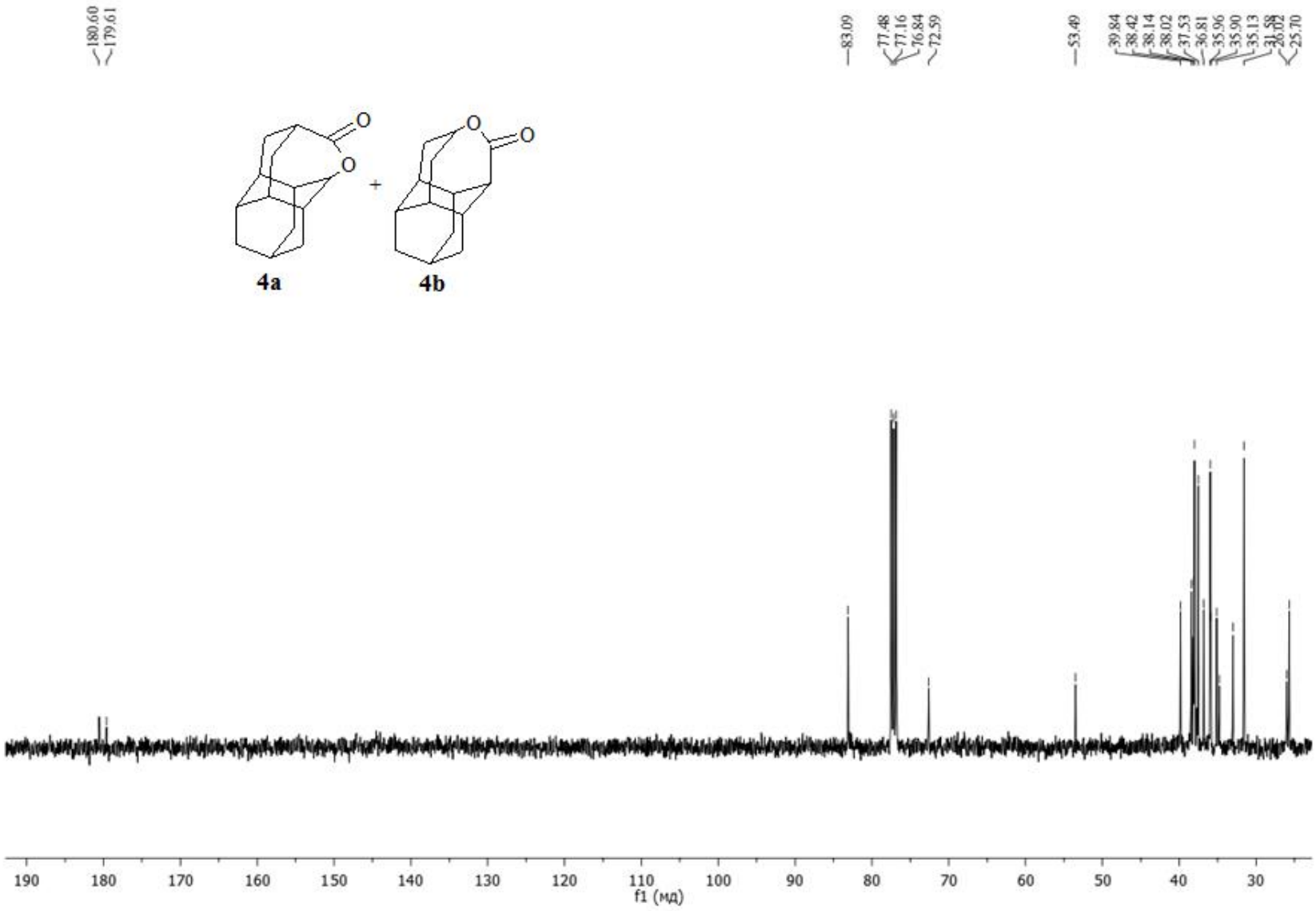
[S9] S. Matsubara, K. Takai and N. Hitosi, *Bull. Chem. Soc. Jpn*., 1983, **56**, 2029.

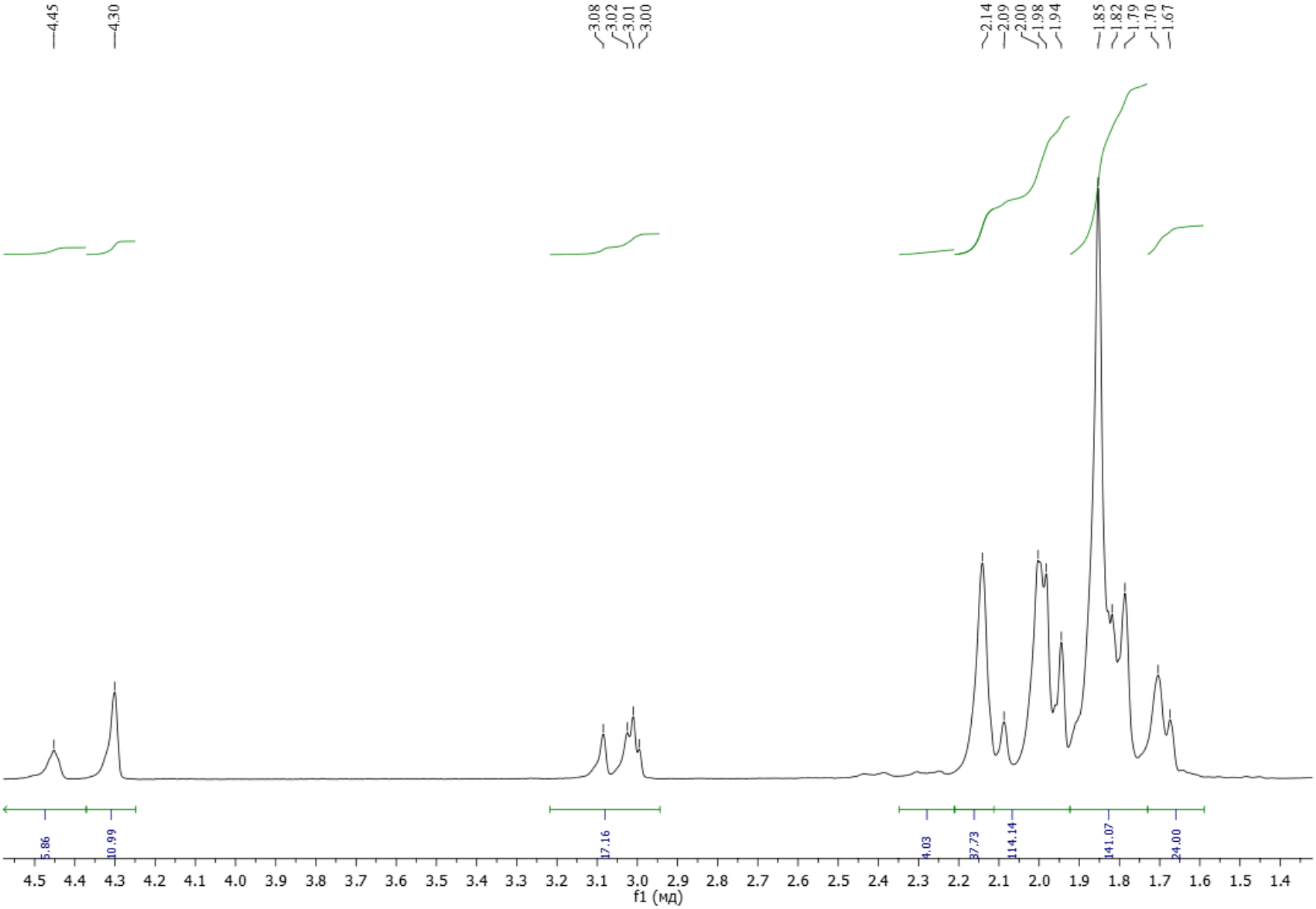
[S10] G. A. Olah, Q. Wang, N. J. Trivedi and G. K. S. Prakash, *Synthesis*, 1991, 739.

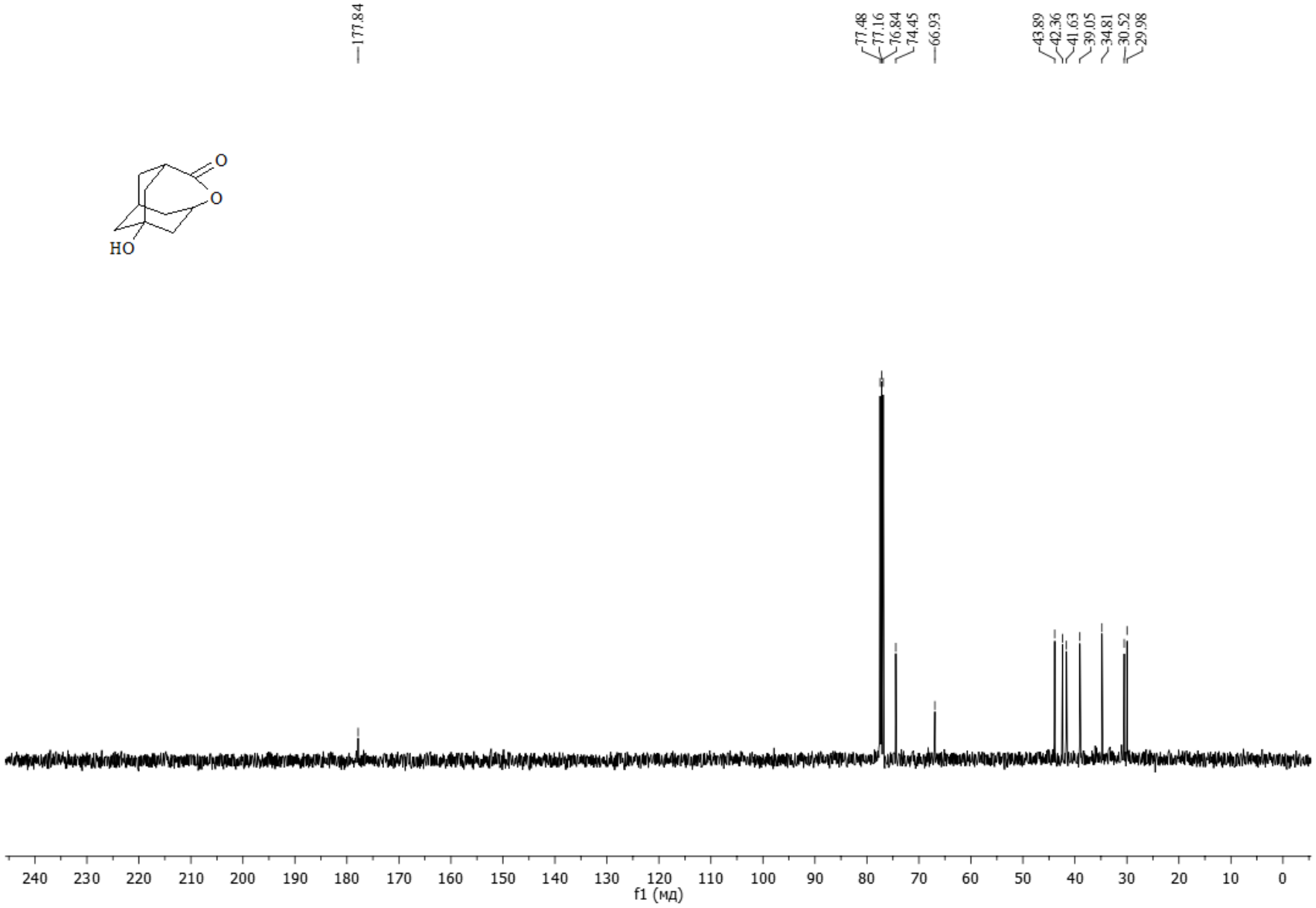
[S11] M. Zarraga, V. Salas, A. Miranda, P. Arroyo and C. Paz, *Tetrahedron: Asymmetry*, 2008, **19**, 796.

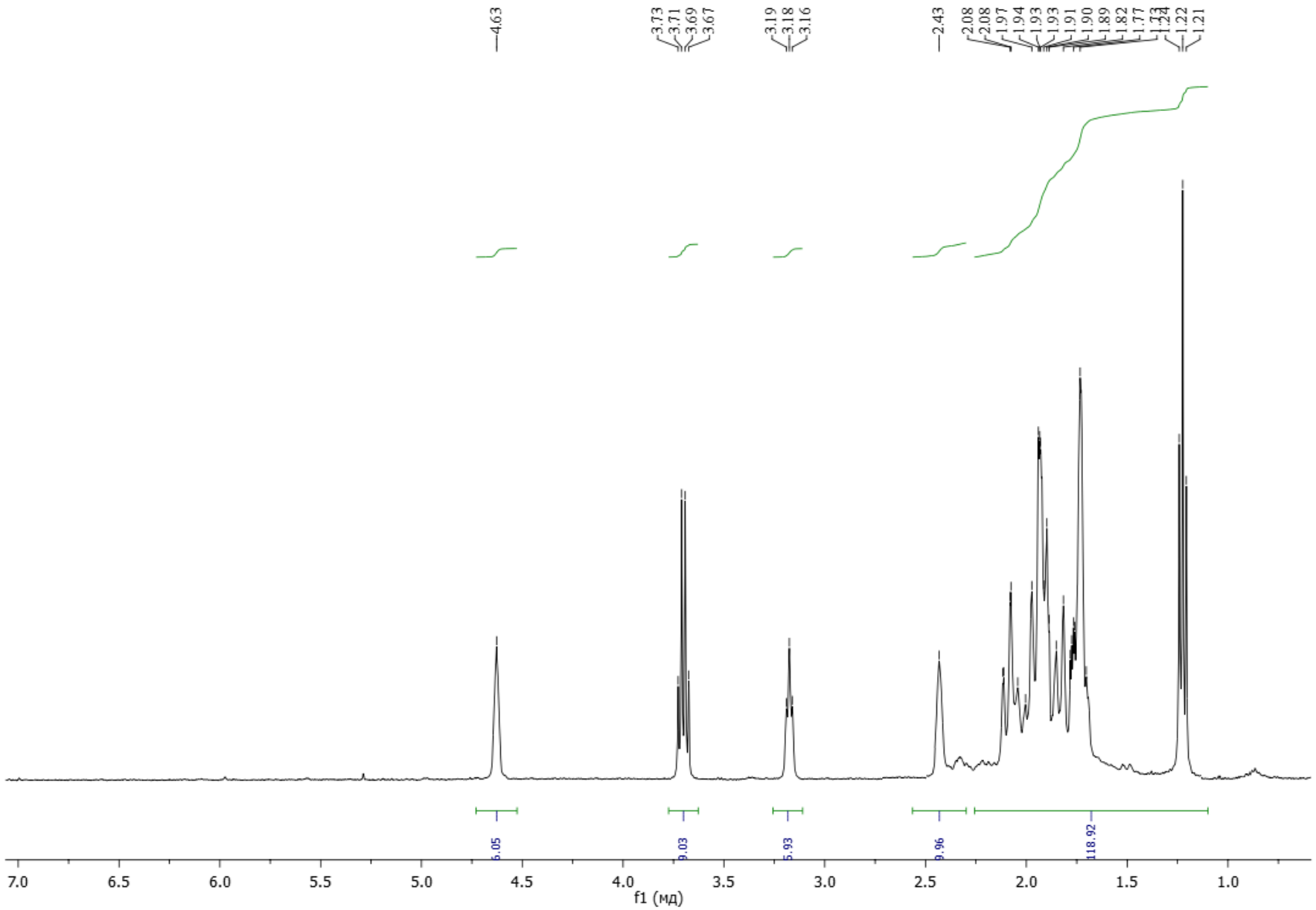

178.98
77.48
77.16
76.84
73.18
41.22
35.73
33.73
30.92
25.79
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (мд)

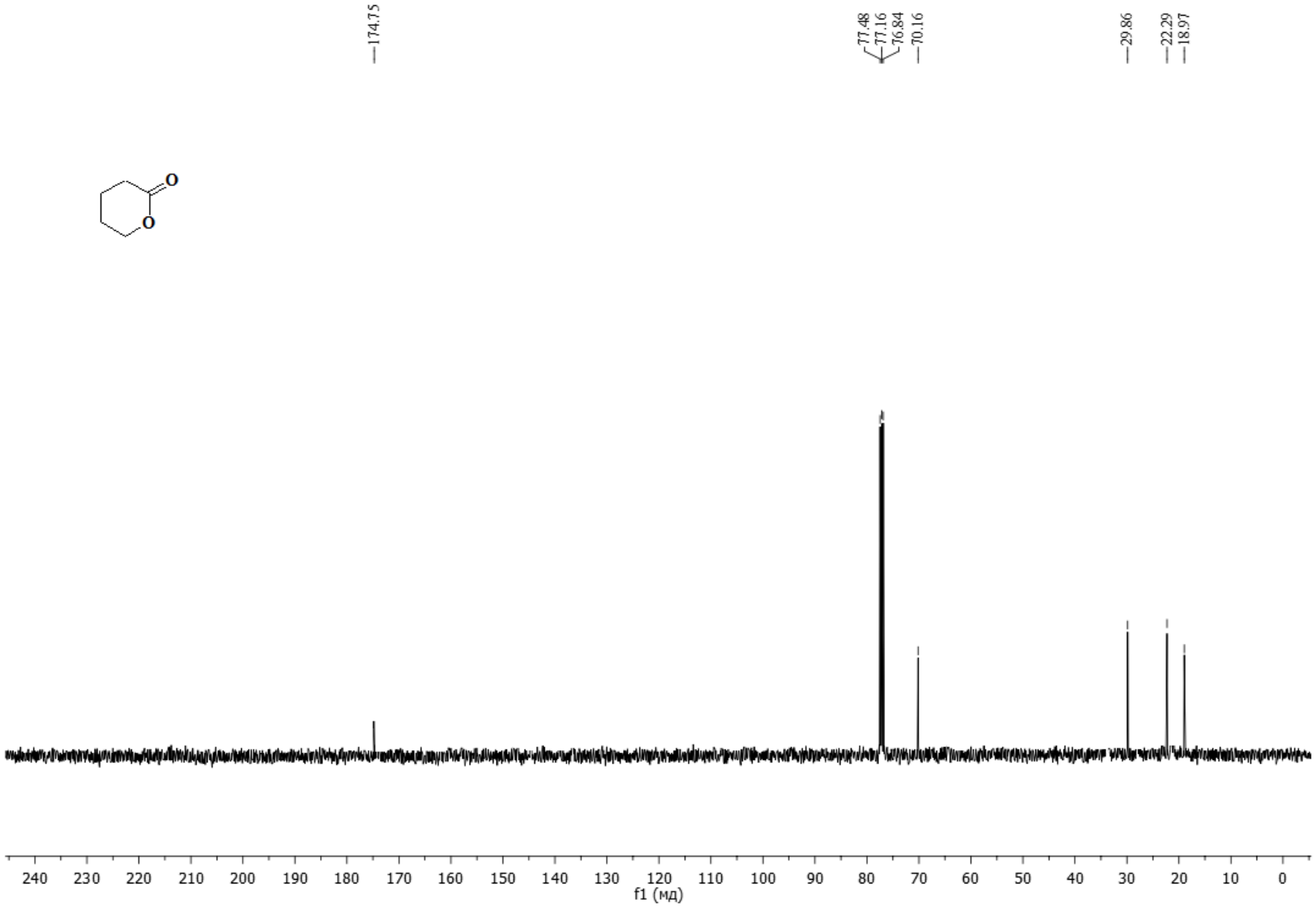

4.43
3.02
3.01
3.00
2.06
2.00
1.97
1.92
1.89
1.86
1.81
1.80
1.79
1.76
1.75
1.72
1.68
1.65
0.97
0.98
2.07
9.99
4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4
f1 (мд)

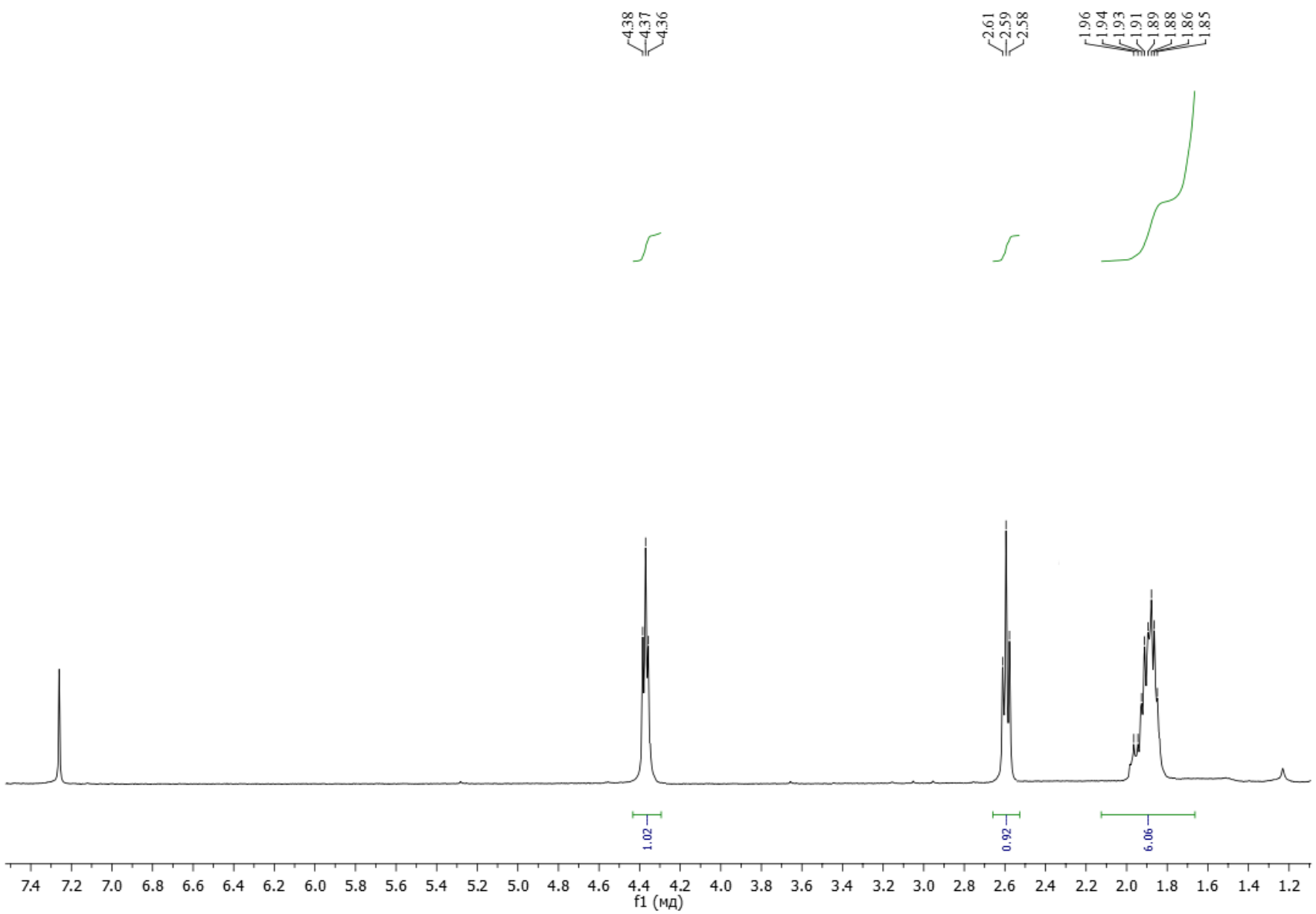

180.60
179.61
83.09
77.48
77.16
76.84
72.59
53.49
39.84
38.42
38.14
38.02
37.53
36.81
35.96
35.90
35.13
31.58
26.02
25.70
4a
4b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (мд)

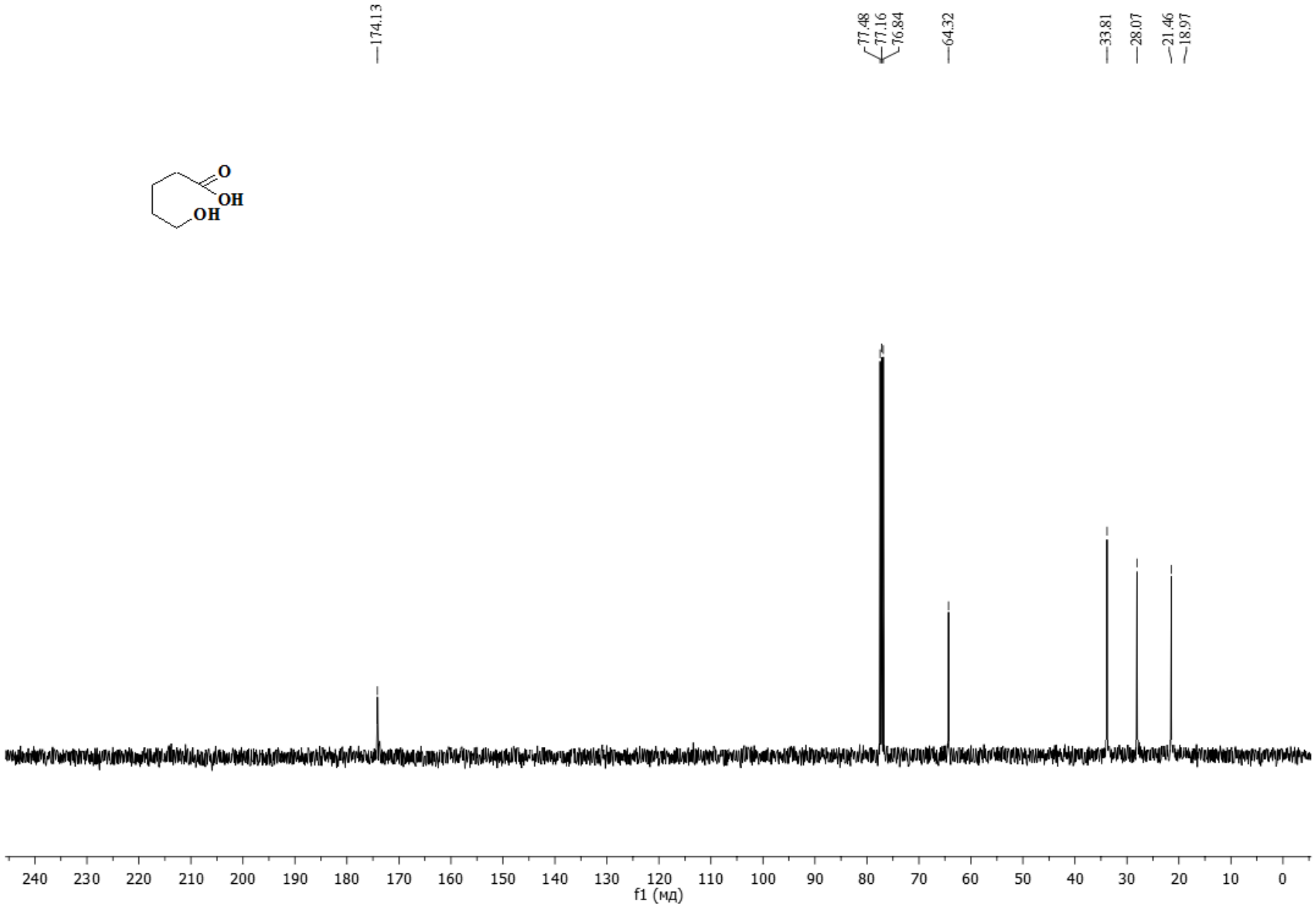

4.45
4.30
3.08
3.02
3.01
3.00
2.14
2.09
2.00
1.98
1.94
1.85
1.82
1.79
1.70
1.67
5.86
10.99
17.16
4.03
37.73
114.14
141.07
24.00
4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4
f1 (мд)

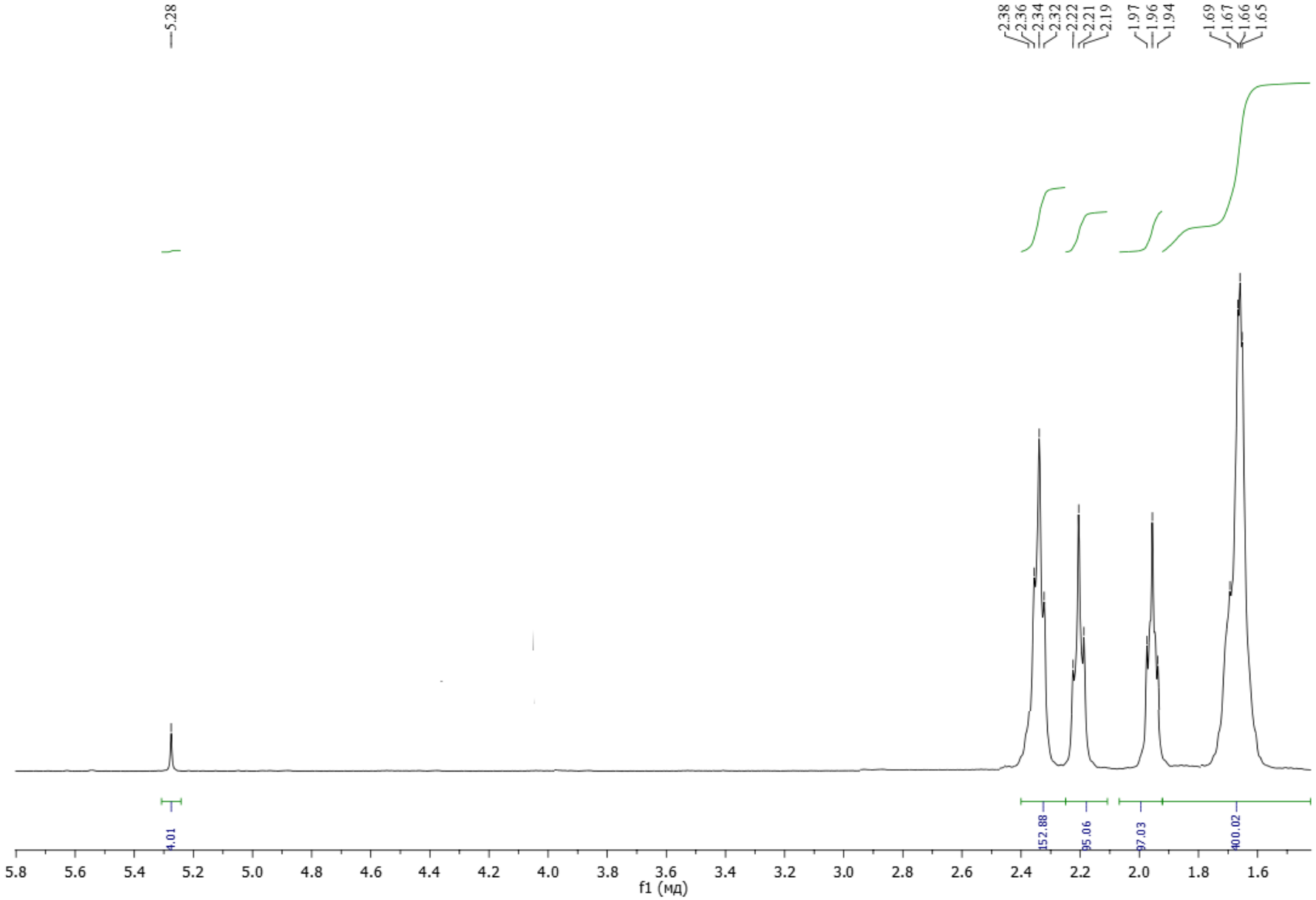

177.84
77.48
77.16
76.84
74.45
66.93
43.89
42.36
41.63
39.05
34.81
30.52
29.98
O
O
HO
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (мд)

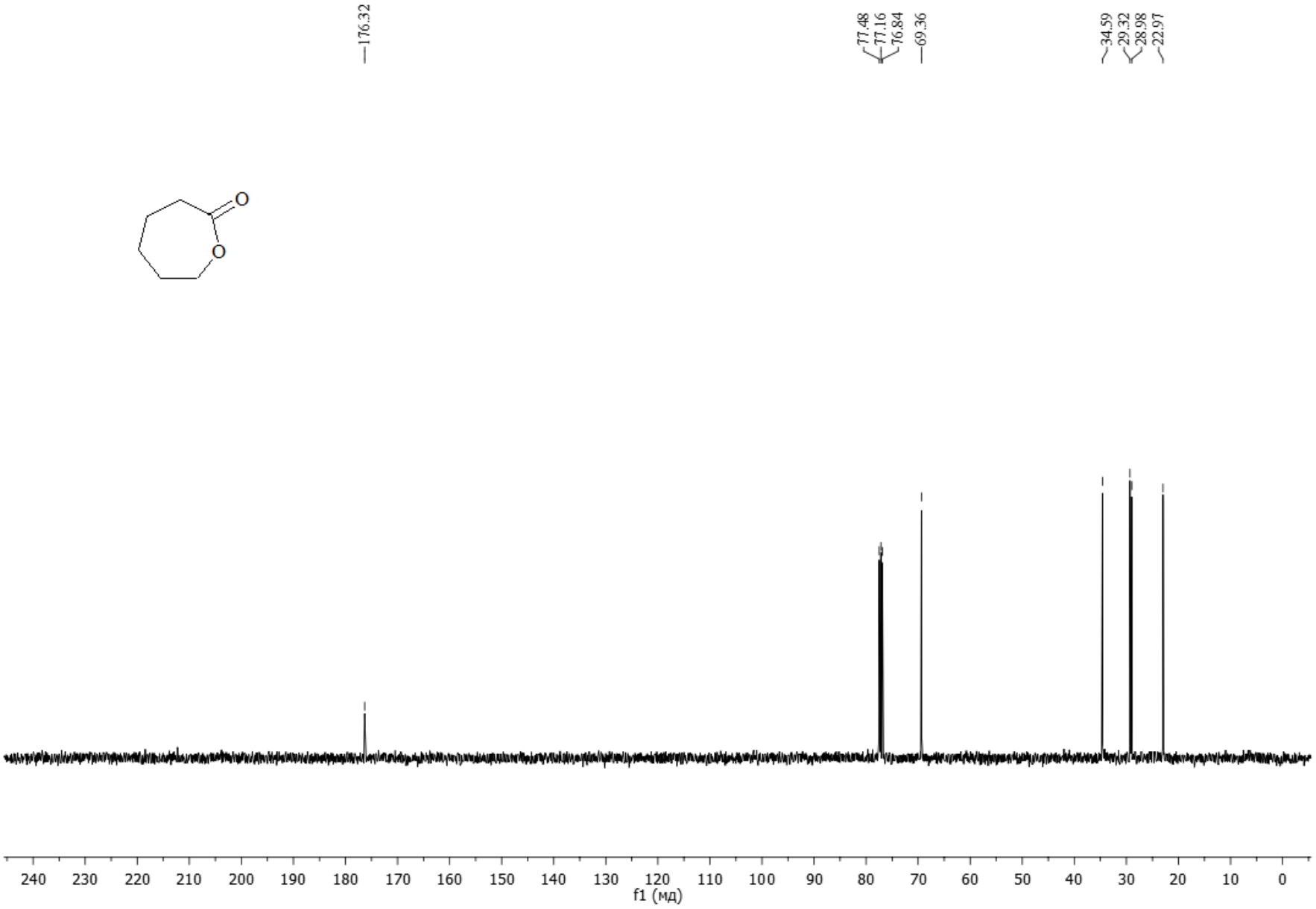

4.63
3.73
3.71
3.69
3.67
3.19
3.18
3.16
2.43
2.08
2.08
1.97
1.94
1.93
1.93
1.91
1.90
1.89
1.82
1.77
1.24
1.22
1.21
6.05
9.03
5.93
9.96
118.92
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (мд)

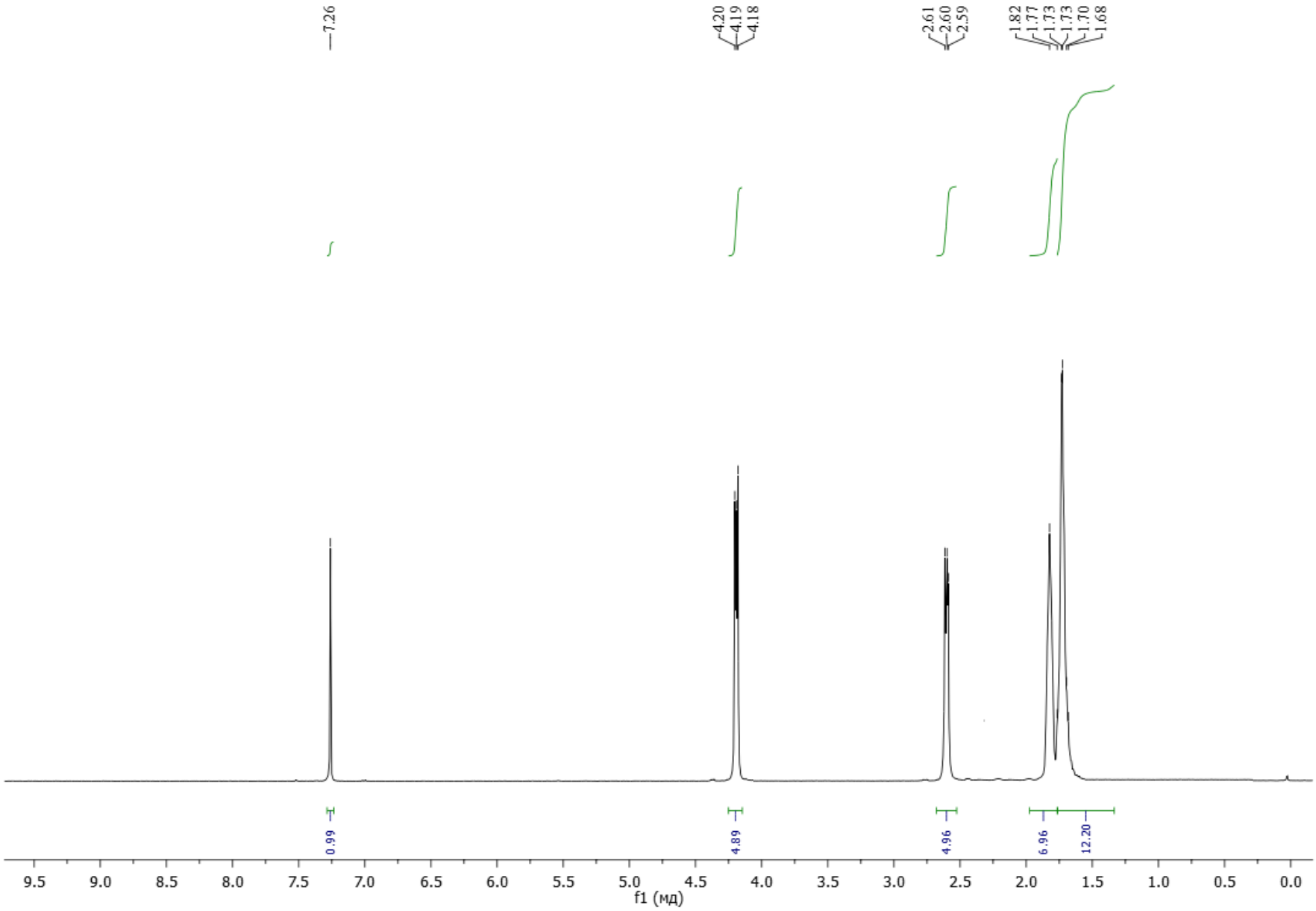

174.75
77.48
77.16
76.84
70.16
29.86
22.29
18.97
O
O
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (мд)

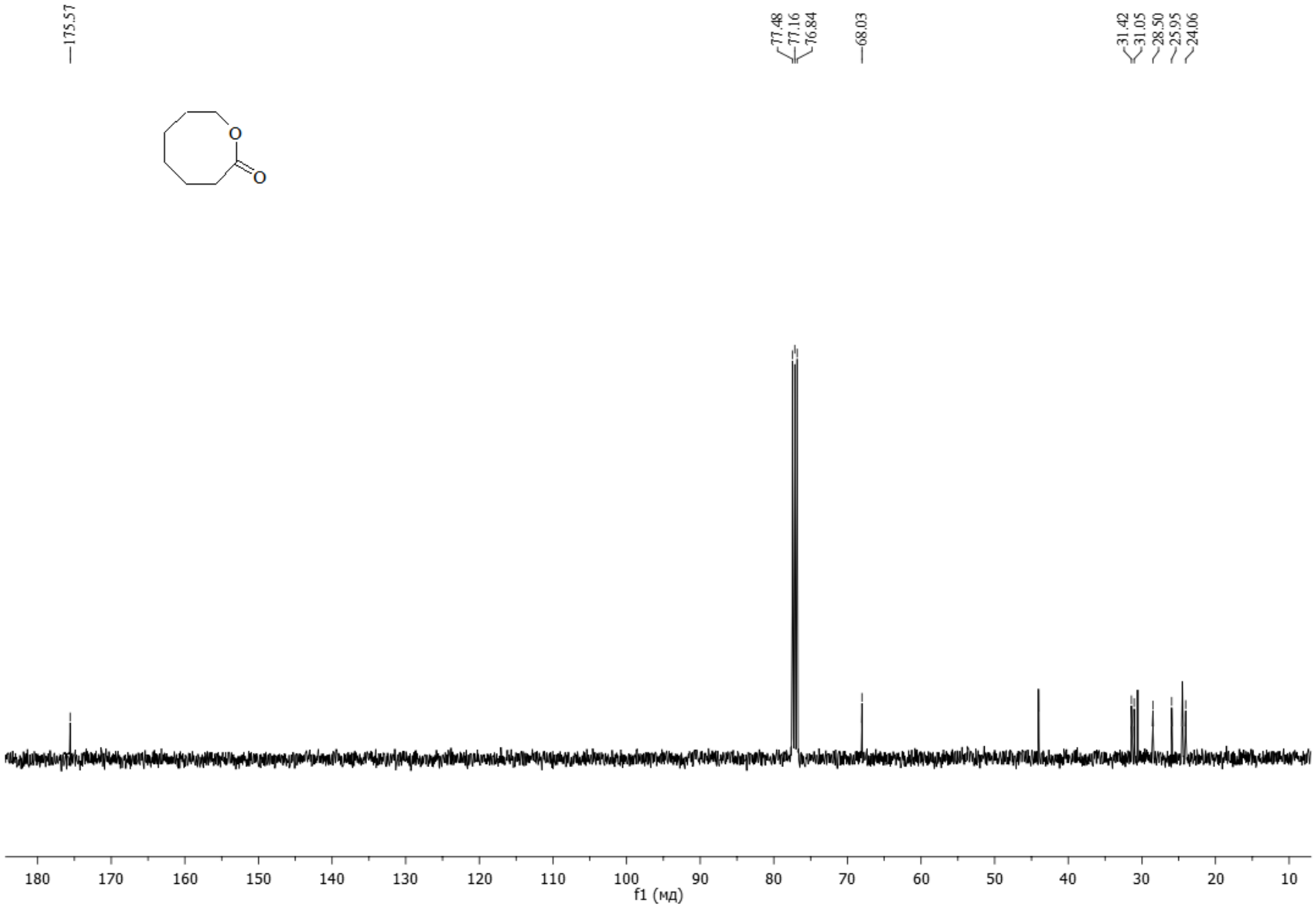

4.38
4.37
4.36
2.61
2.59
2.58
1.96
1.94
1.93
1.91
1.89
1.88
1.86
1.85
1.02
0.92
6.06
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f1 (мд)

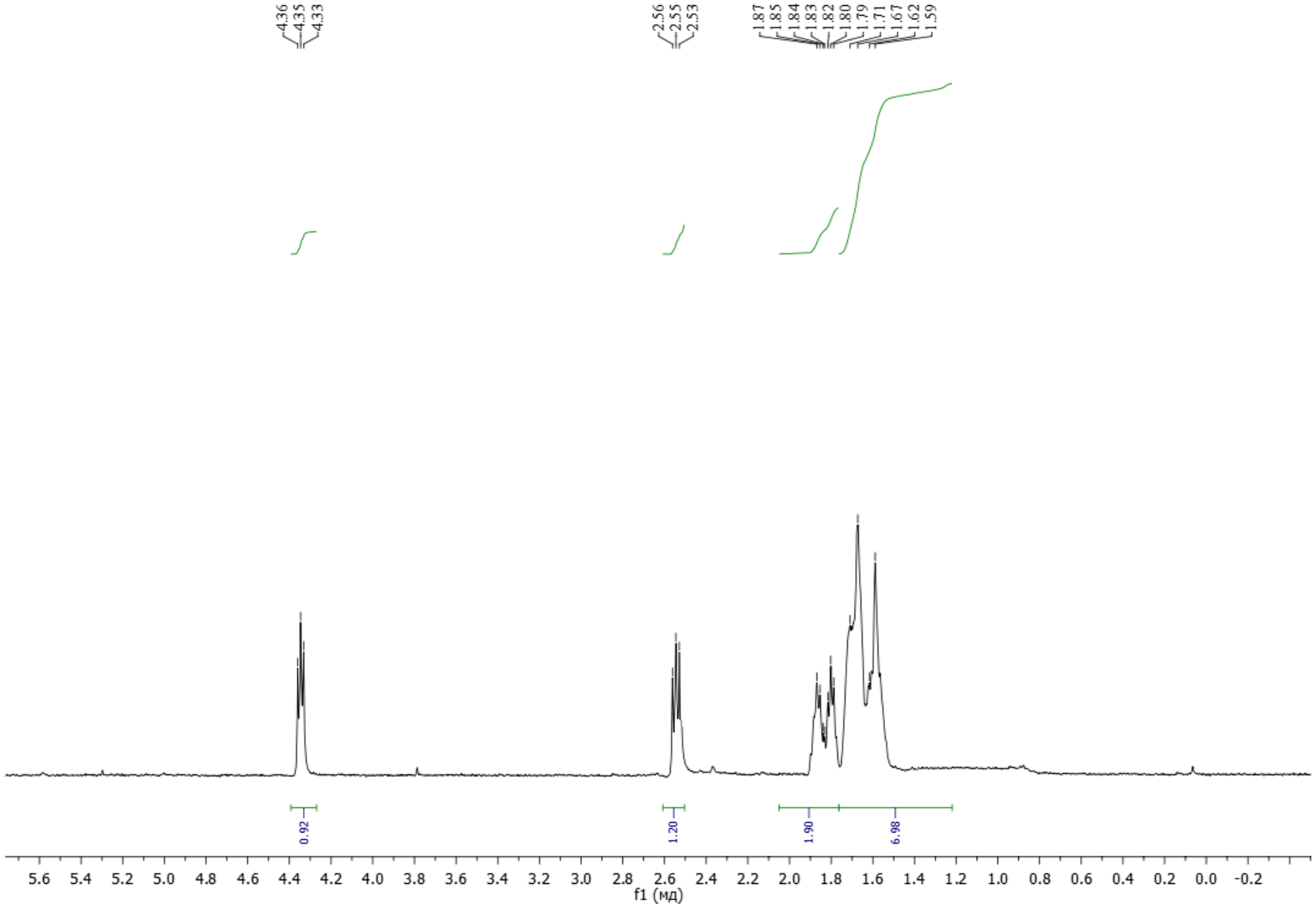

174.13
77.48
77.16
76.84
64.32
33.81
28.07
21.46
18.97
O
OH
OH
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (мд)

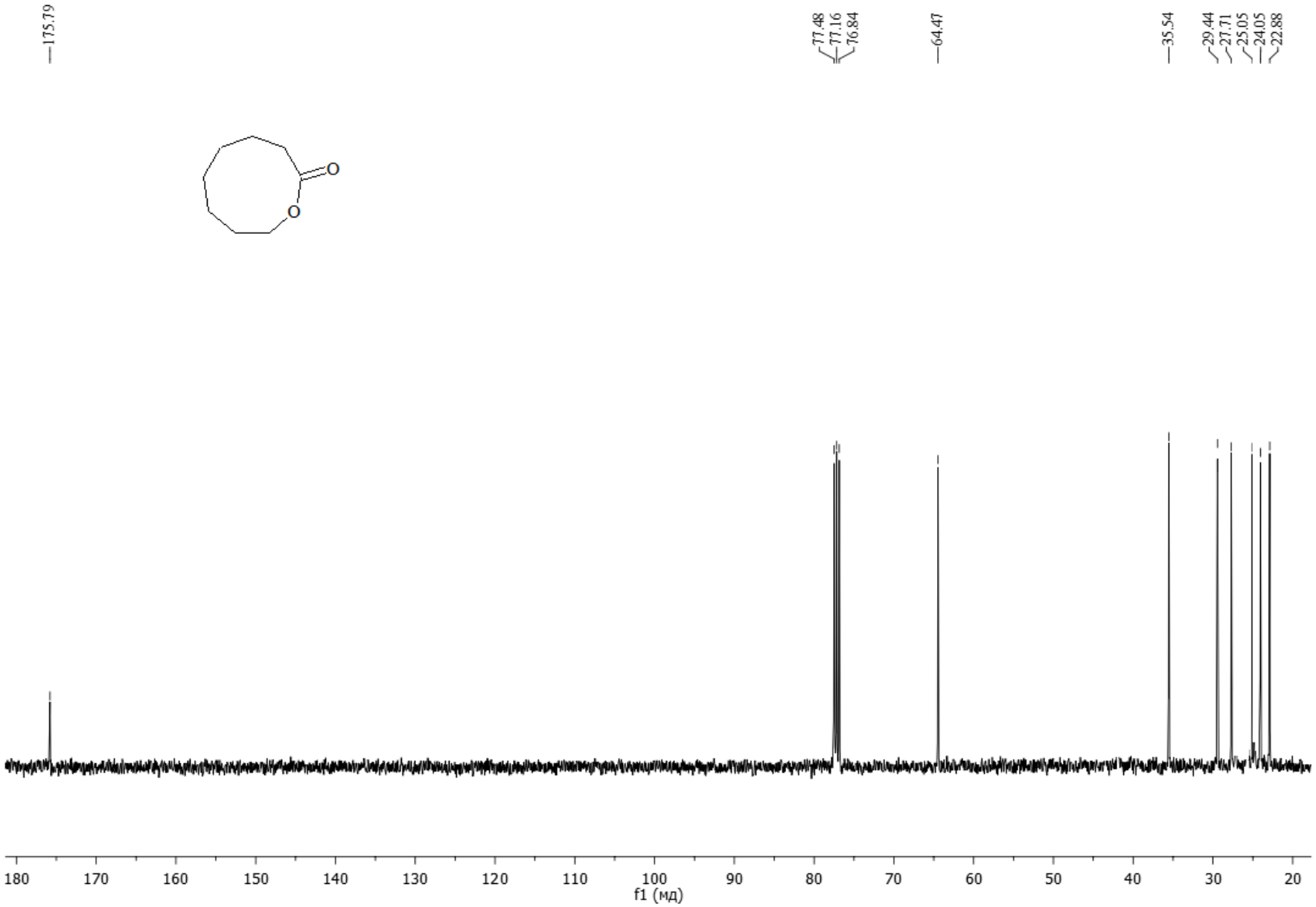

5.28
2.38
2.36
2.34
2.32
2.22
2.21
2.19
1.97
1.96
1.94
1.69
1.67
1.66
1.65
4.01
152.88
95.06
97.03
400.02
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f1 (мд)

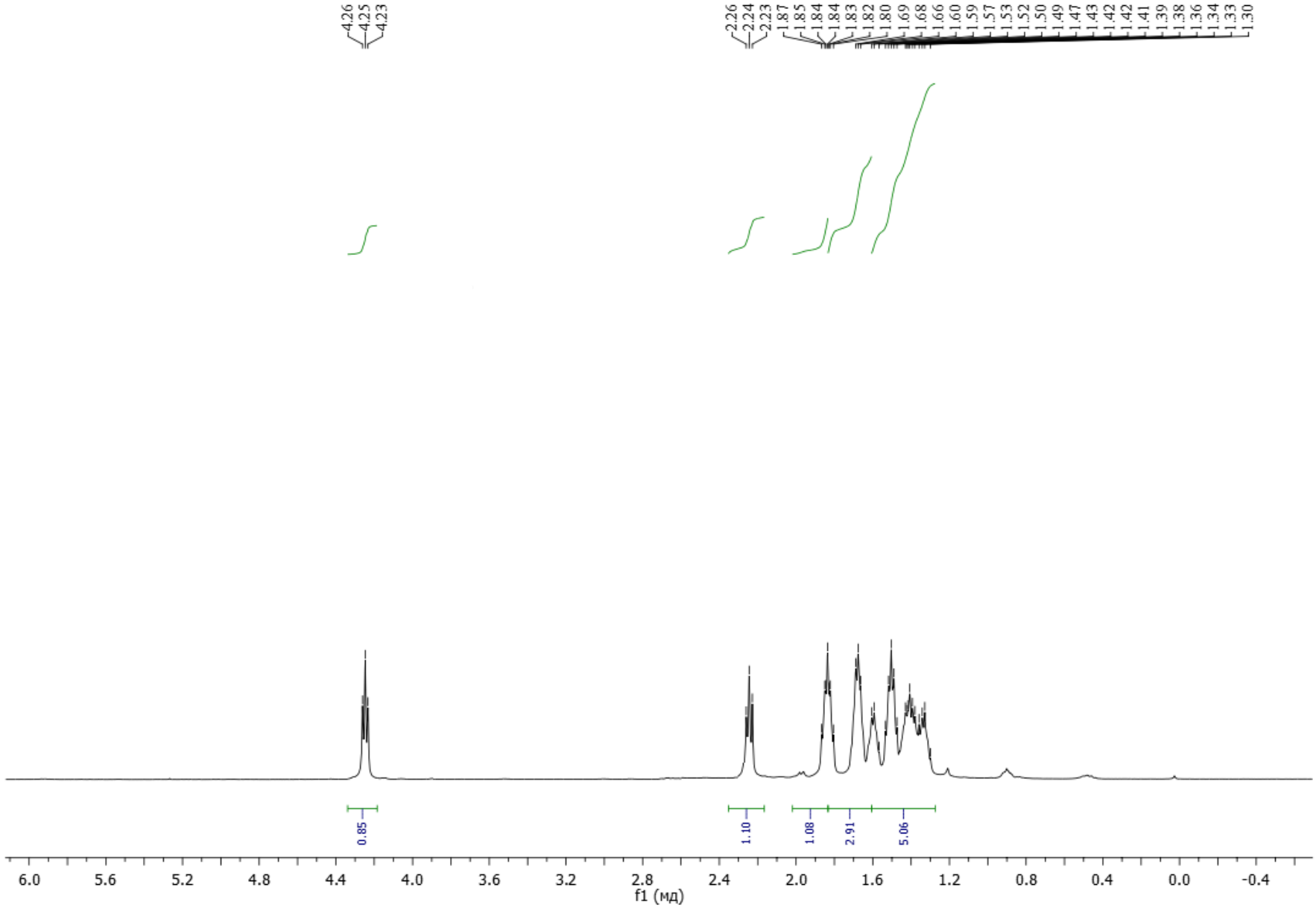

176.32
77.48
77.16
76.84
69.36
34.59
29.32
28.98
22.97
O
O
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (мд)

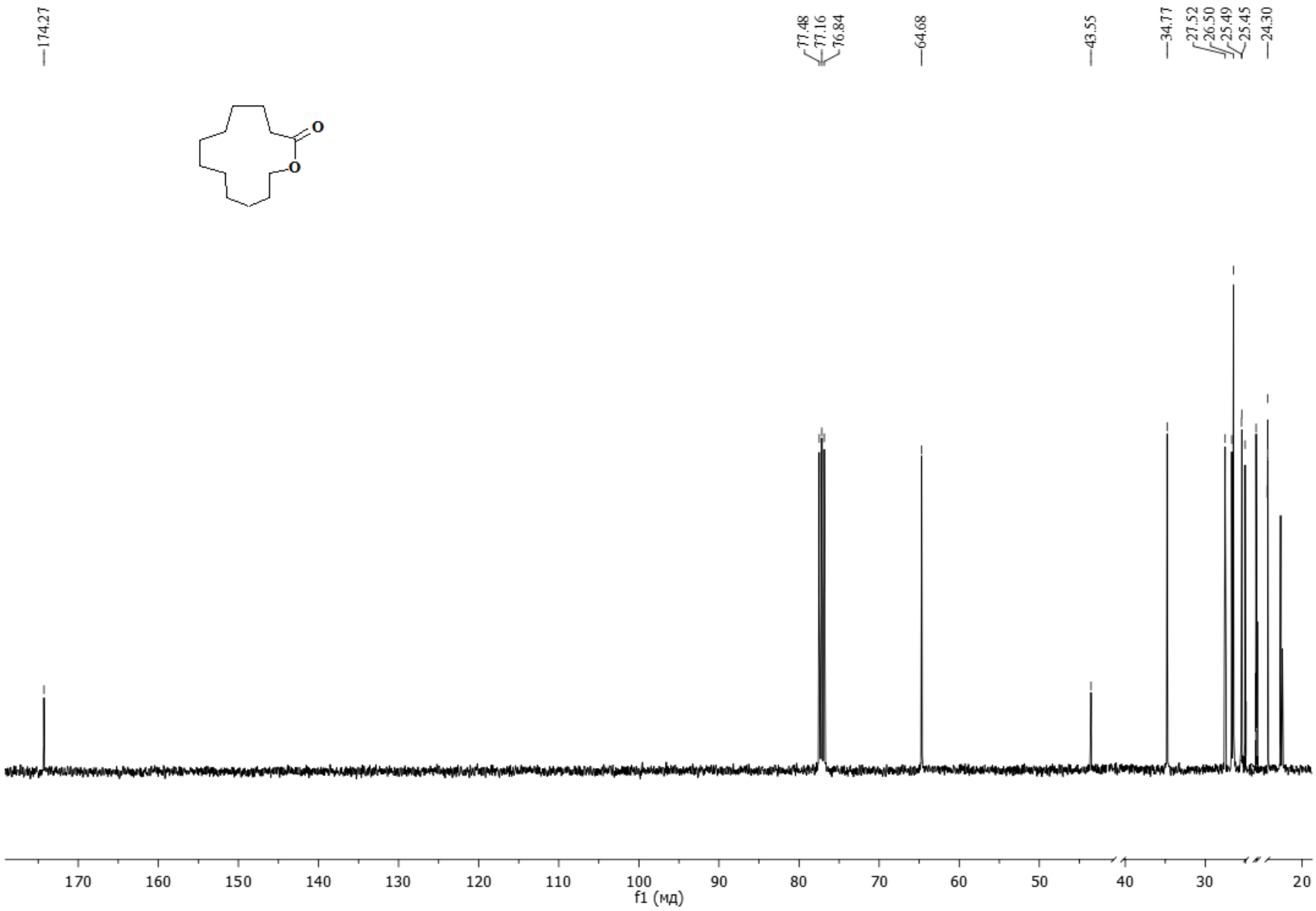

7.26
4.20
4.19
4.18
2.61
2.60
2.59
1.82
1.77
1.73
1.73
1.70
1.68
0.99
4.89
4.96
6.96
12.20
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (мд)

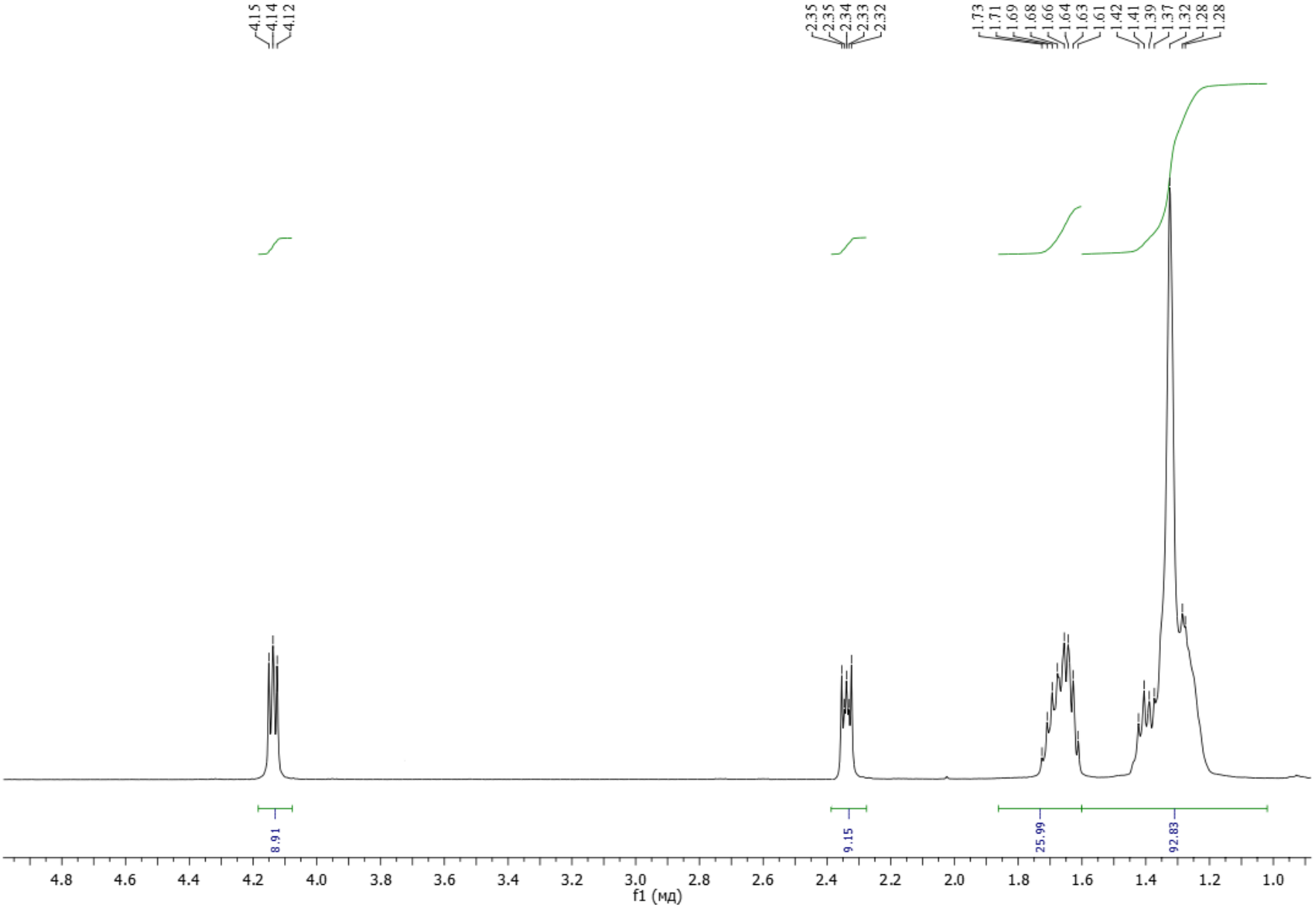

175.57
77.48
77.16
76.84
68.03
31.42
31.05
28.50
25.95
24.06
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (мд)

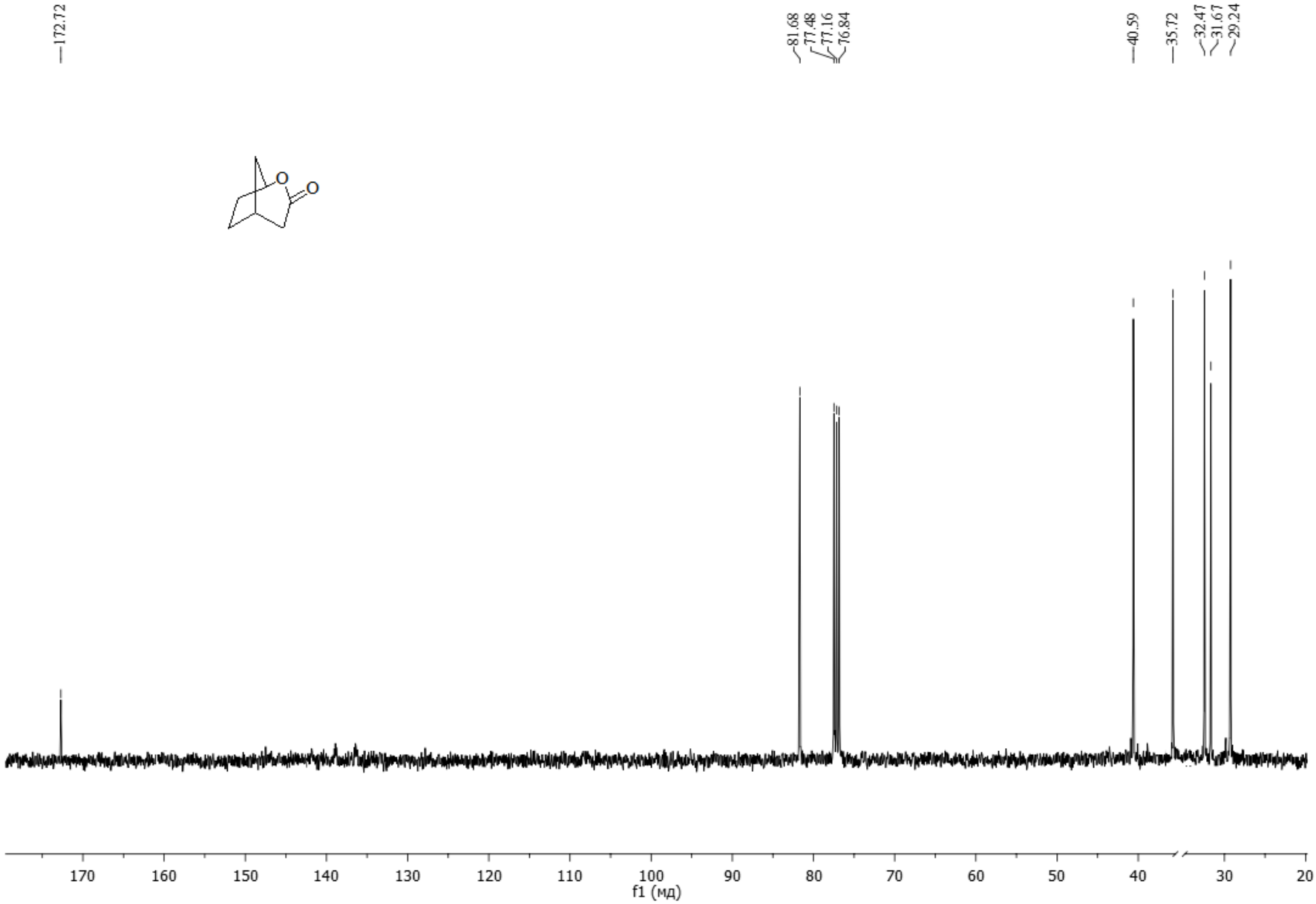

4.36
4.35
4.33
2.56
2.55
2.53
1.87
1.85
1.84
1.83
1.82
1.80
1.79
1.71
1.67
1.62
1.59
0.92
1.20
1.90
6.98
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0 -0.2
f1 (мд)

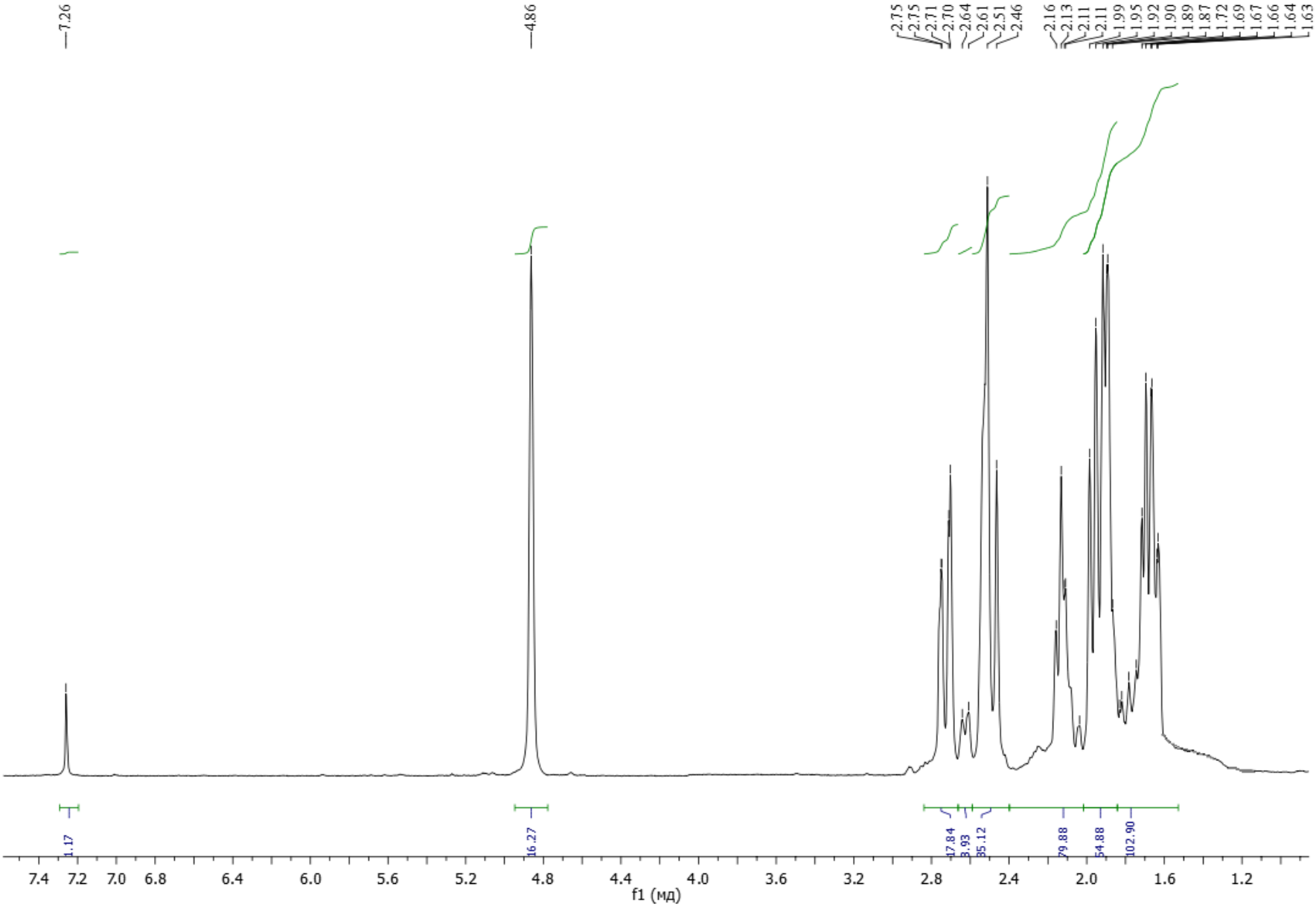

175.79
77.48
77.16
76.84
64.47
35.54
29.44
27.71
25.05
24.05
22.88
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (мд)

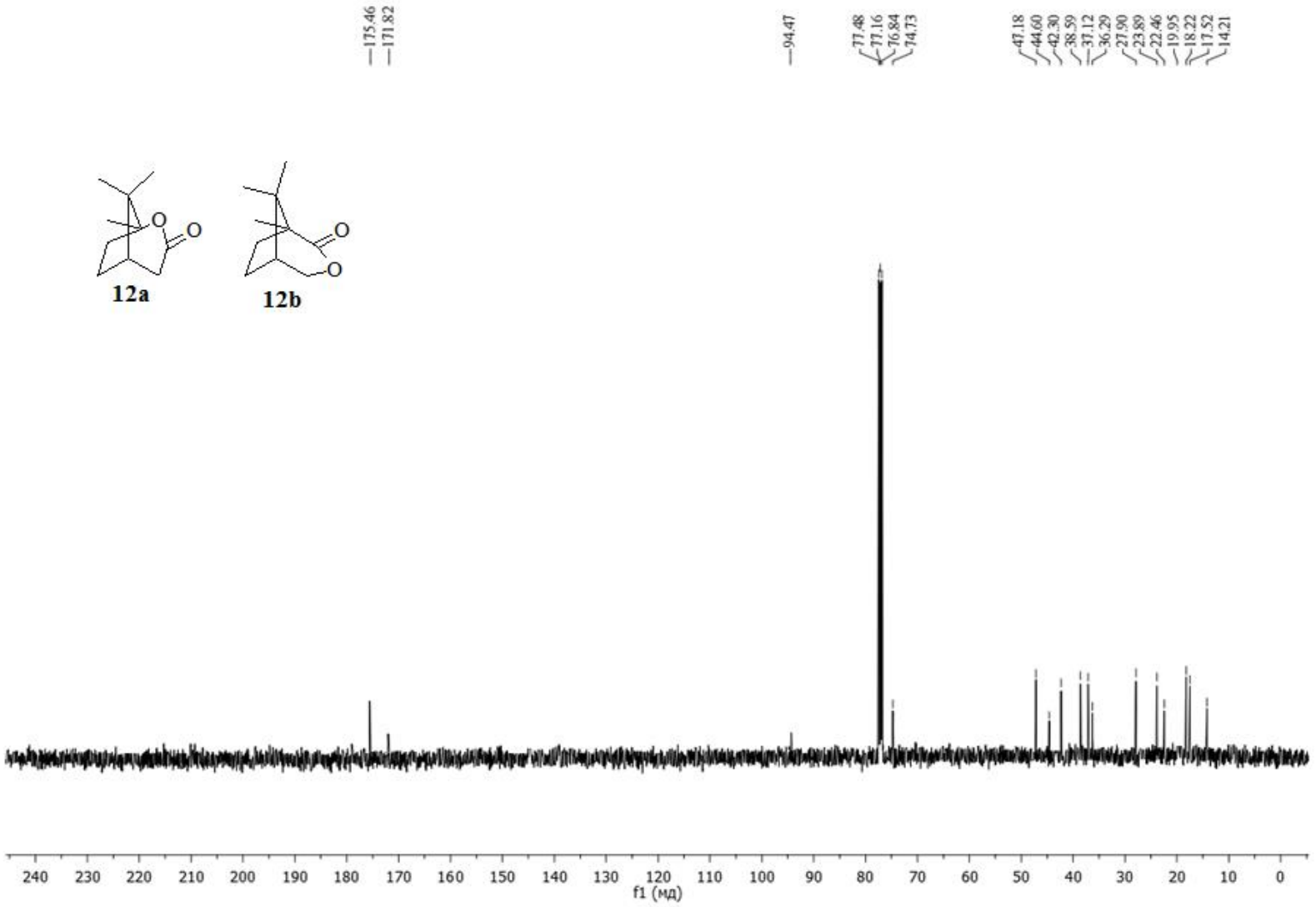

4.26
4.25
4.23
2.26
2.24
2.23
1.87
1.85
1.84
1.84
1.83
1.82
1.80
1.69
1.68
1.66
1.60
1.59
1.57
1.53
1.52
1.50
1.49
1.47
1.43
1.42
1.42
1.41
1.39
1.38
1.36
1.34
1.33
1.30
0.85
1.10
1.08
2.91
5.06
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
f1 (мд)

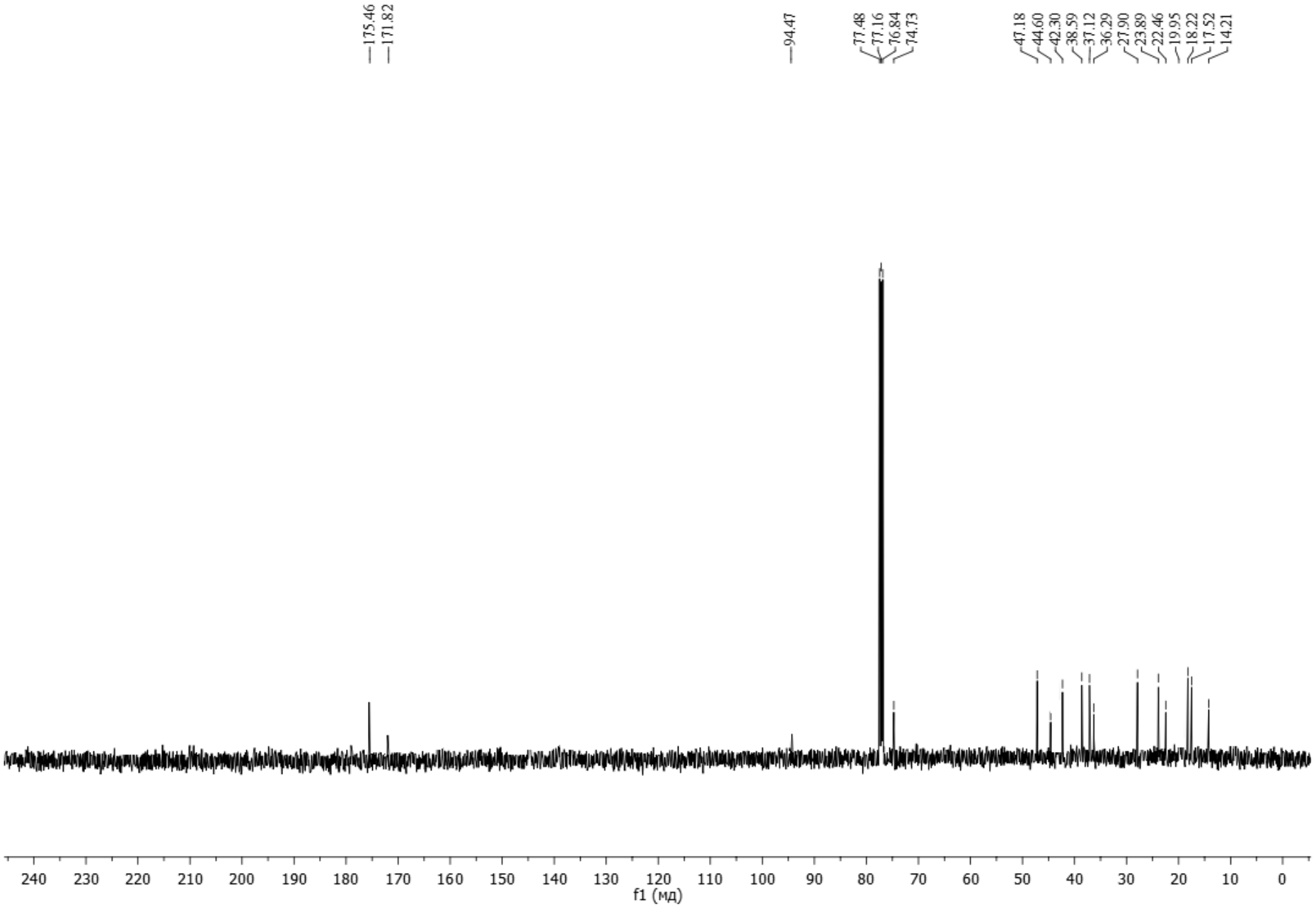

174.27
77.48
77.16
76.84
64.68
43.55
34.77
27.52
26.50
25.49
25.45
24.30
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (мд)

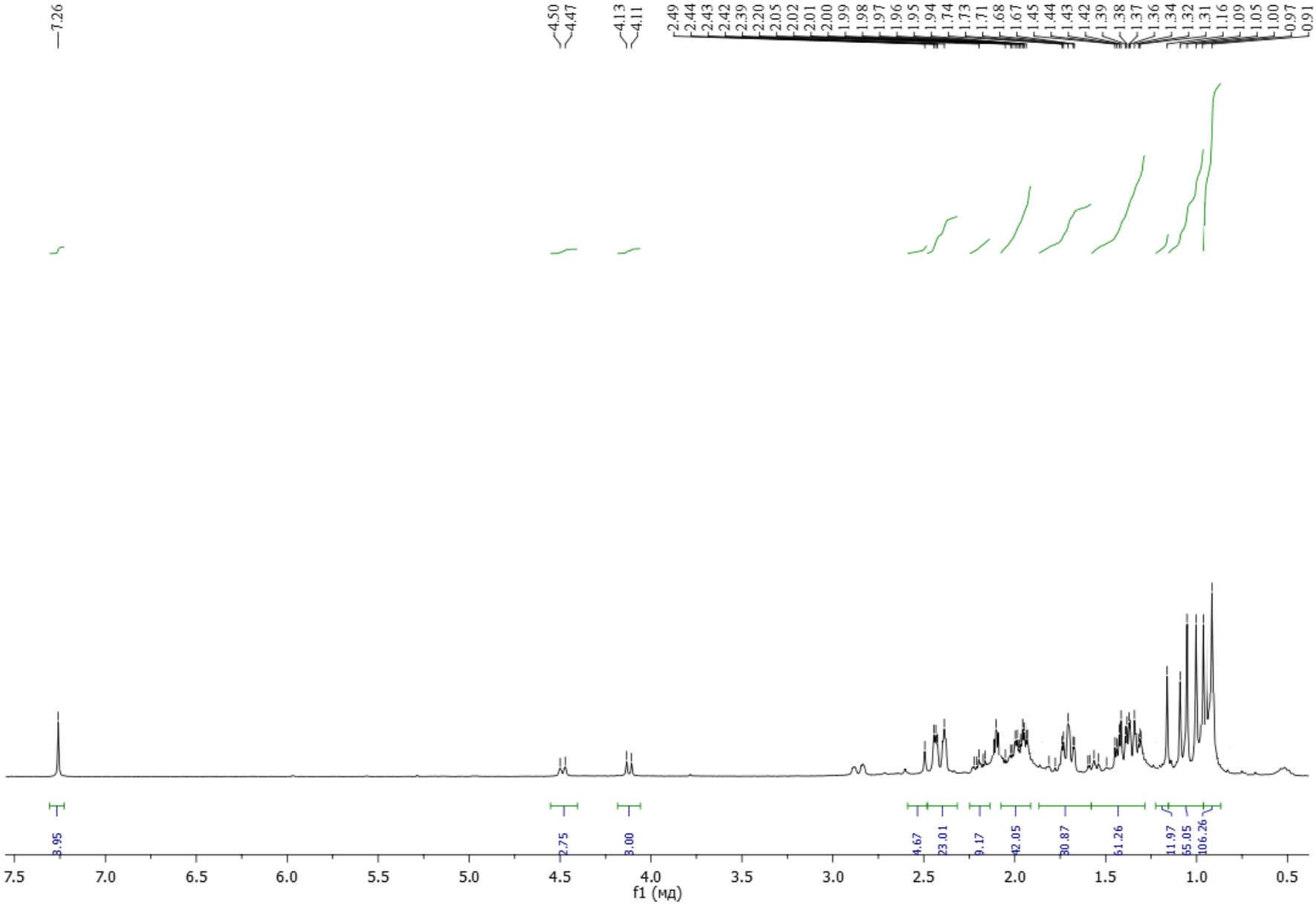

4.15
4.14
4.12
2.35
2.35
2.34
2.33
2.32
1.73
1.71
1.69
1.68
1.66
1.64
1.63
1.61
1.42
1.41
1.39
1.37
1.32
1.28
1.28
8.91
9.15
25.99
92.83
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
f1 (мд)


172.72
81.68
77.48
77.16
76.84
40.59
35.72
32.47
31.67
29.24
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (мд)


7.26
4.86
2.75
2.75
2.71
2.70
2.64
2.61
2.51
2.46
2.16
2.13
2.11
2.11
1.99
1.95
1.92
1.90
1.89
1.87
1.72
1.69
1.67
1.66
1.64
1.63
1.17
16.27
17.84
3.93
35.12
79.88
54.88
102.90
7.4
7.2
7.0
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
f1 (мд)


175.46
171.82
94.47
77.48
77.16
76.84
74.73
47.18
44.60
42.30
38.59
37.12
36.29
27.90
23.89
22.46
19.95
18.22
17.52
14.21
12a
12b
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (мд)


175.46
171.82
94.47
77.48
77.16
76.84
74.73
47.18
44.60
42.30
38.59
37.12
36.29
27.90
23.89
22.46
19.95
18.22
17.52
14.21
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (мд)


7.26
4.50
4.47
4.13
4.11
2.49
2.44
2.43
2.42
2.39
2.20
2.05
2.02
2.01
2.00
1.99
1.98
1.97
1.96
1.95
1.94
1.74
1.73
1.71
1.68
1.67
1.45
1.44
1.43
1.42
1.39
1.38
1.37
1.36
1.34
1.32
1.31
1.16
1.09
1.05
1.00
0.97
0.91
3.95
2.75
3.00
4.67
23.01
9.17
42.05
30.87
61.26
11.97
65.05
106.26
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 (мд)