Supporting Information

Stereoselective Epoxidation of Triterpenic Allylic Alcohols and Cytotoxicity Evaluation of Synthesized Compounds

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NMR and GC-MS spectra of synthesized compounds

**^{1}H NMR (3*S*)-3β-hydroxy-2-methyl-19β,28-epoxy-18α*H*-olean-1-ene (3)**
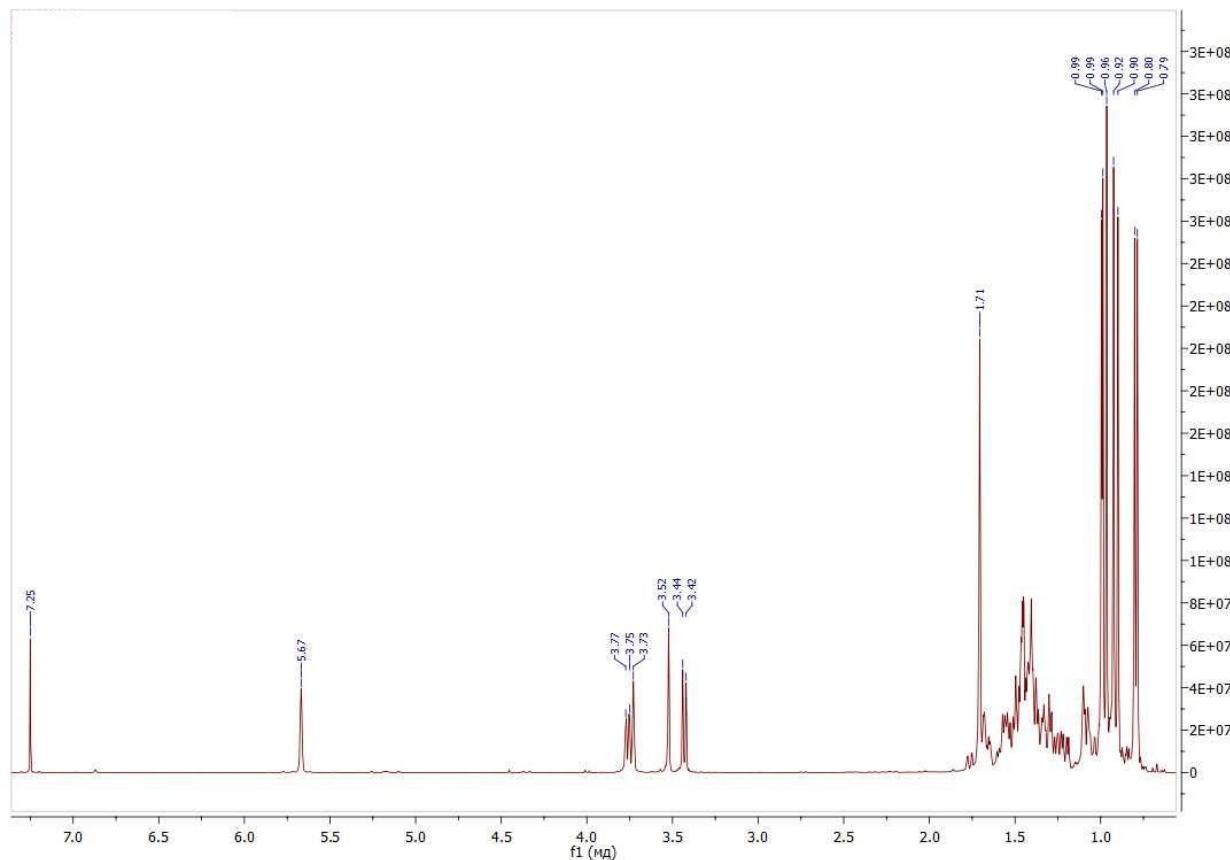
^{13}C NMR (CDCl₃) (3*S*)-3β-hydroxy-2-methyl-19β,28-epoxy-18α*H*-olean-1-ene (3)

**GC-MS (3*S*)-3β-hydroxy-2-methyl-19β,28-epoxy-18*αH*-olean-1-ene (3)**

Scan 600 (5.840 min): compound 3 D\data.ms (-590) (-654) (-)
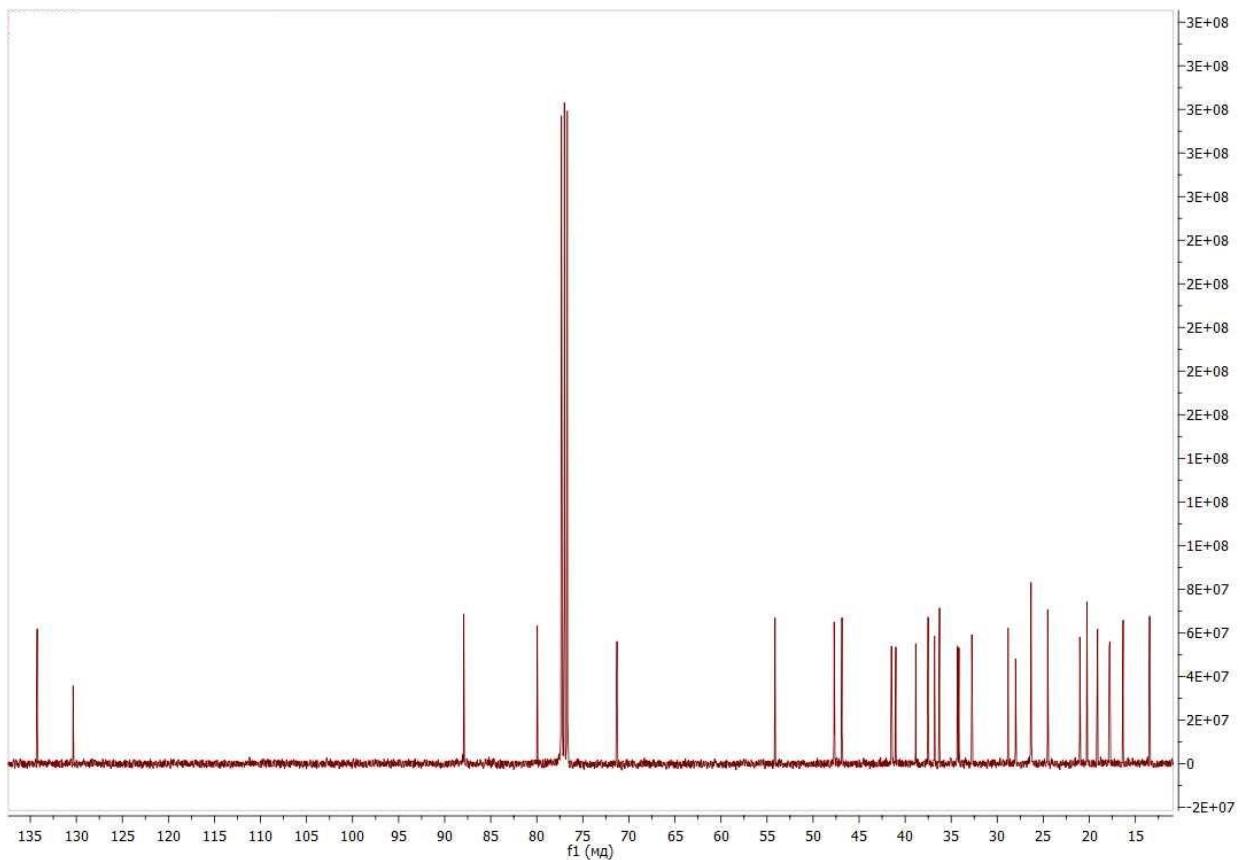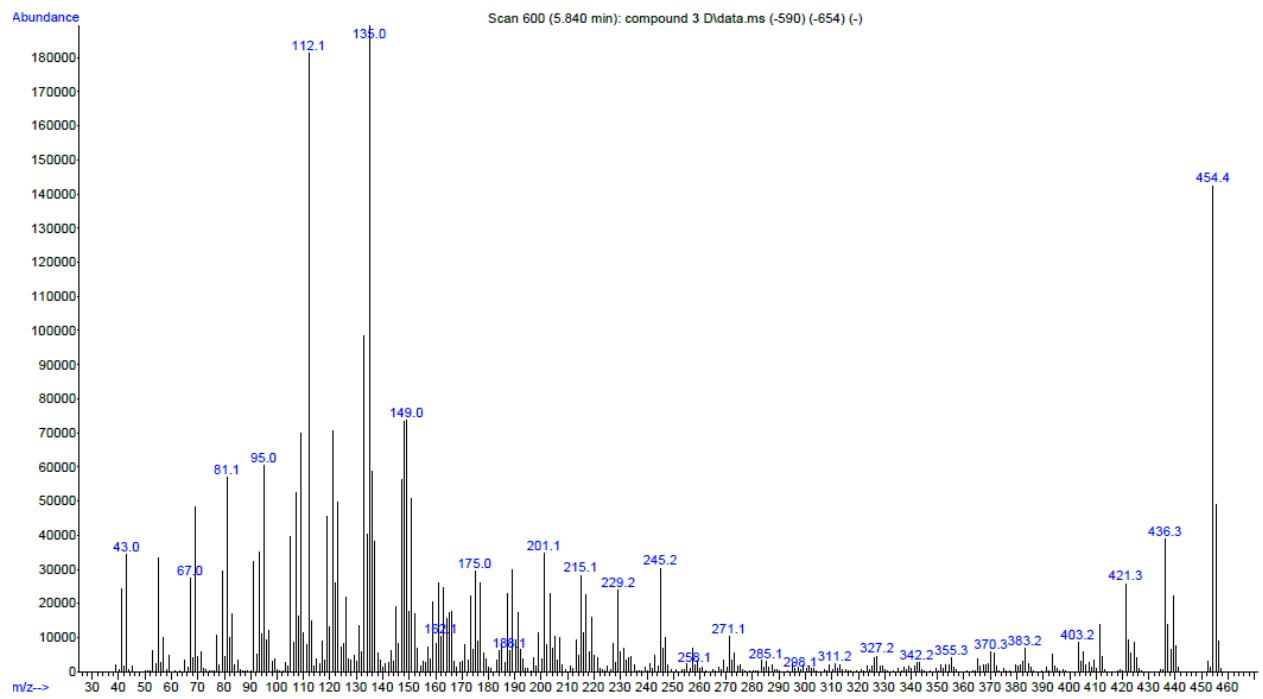
¹H NMR (1*R*,2*R*)-2-methyl-3-oxo-(1,2),(19β,28)-diepoxy-18*αH*-oleanane (4a)
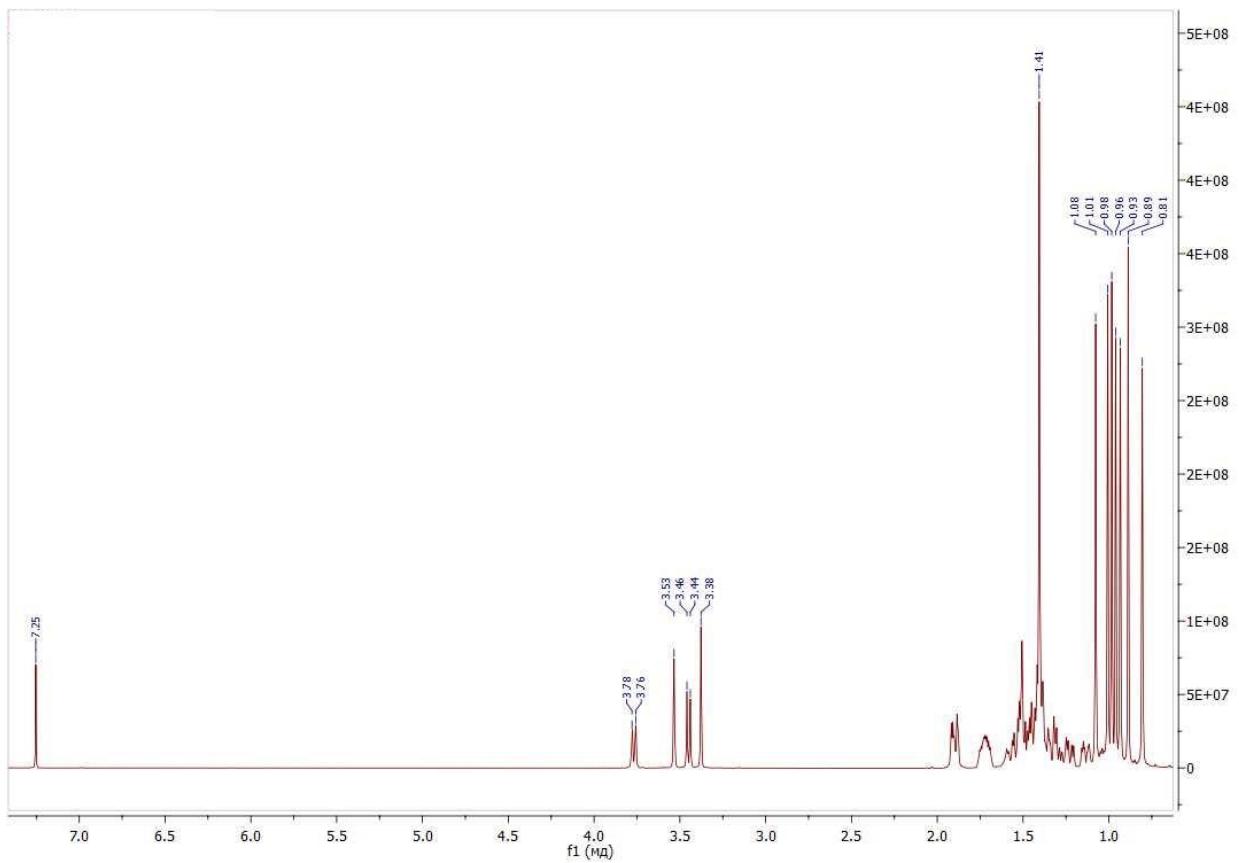
13C NMR (CDCl₃) (1R,2R)-2-methyl-3-oxo-(1,2),(19β,28)-diepoxy-18αH-oleanane (4a)
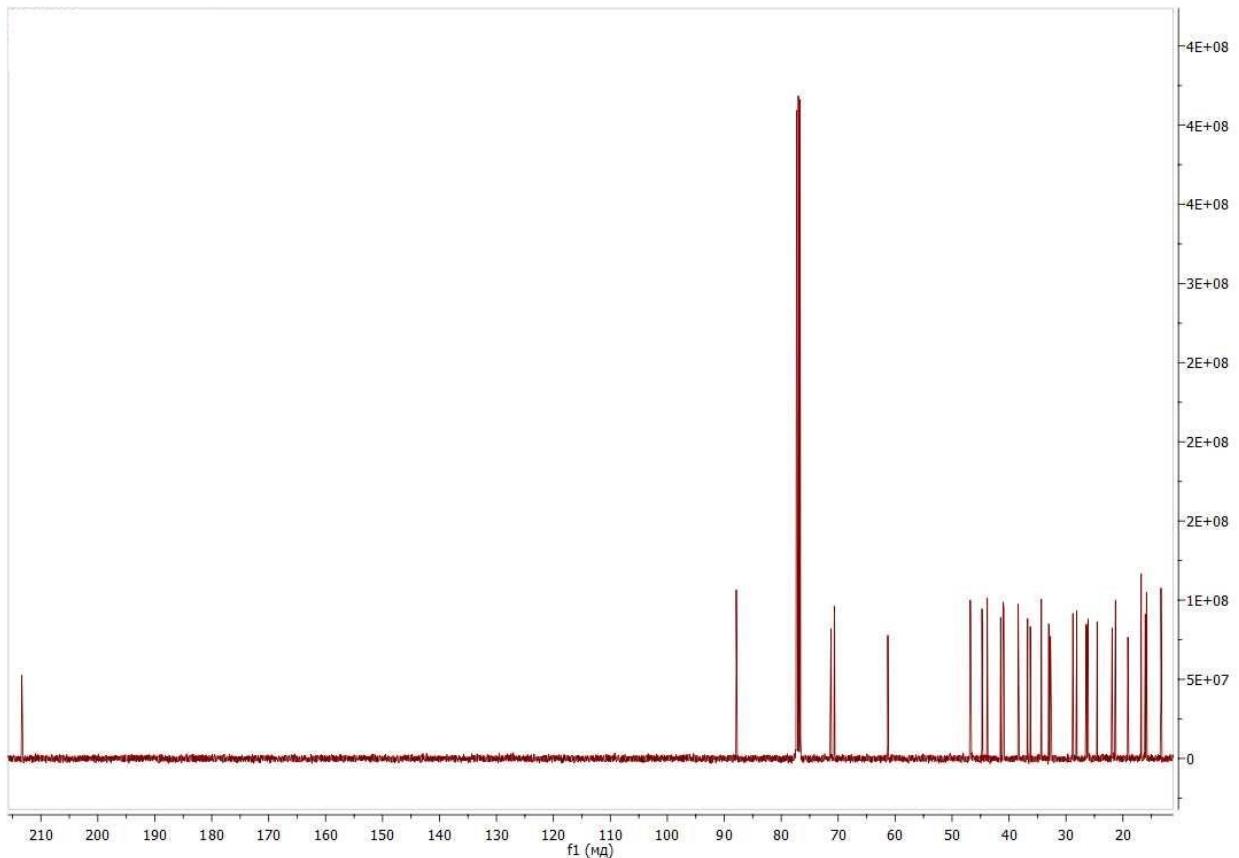
GC-MS (1R,2R)-2-methyl-3-oxo-(1,2),(19β,28)-diepoxy-18αH-oleanane (4a)

Scan 591 (5.784 min): compound 4a D\data.ms (-582) (-650) (-)
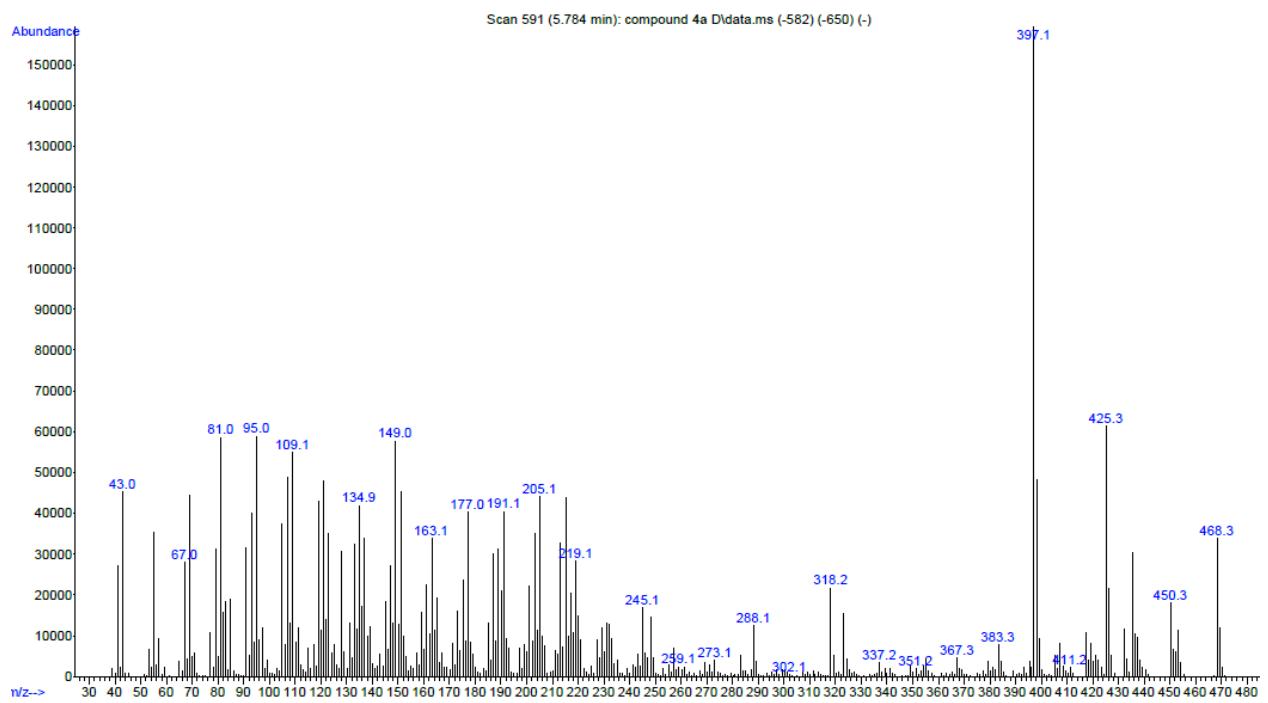
¹H NMR (1R,2S,3R)-3β-hydroxy-2-methyl-(1,2),(19β,28)-diepoxy-18αH-oleanane (5)
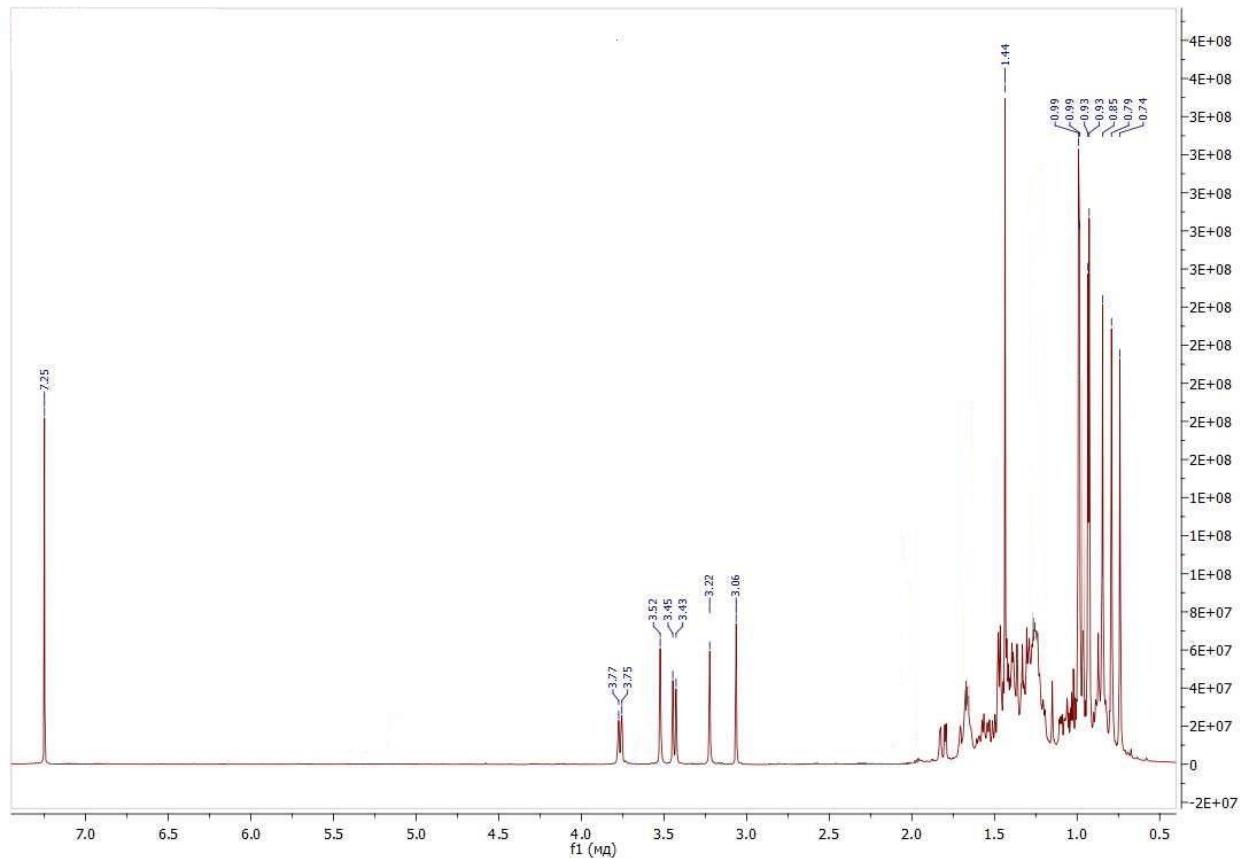
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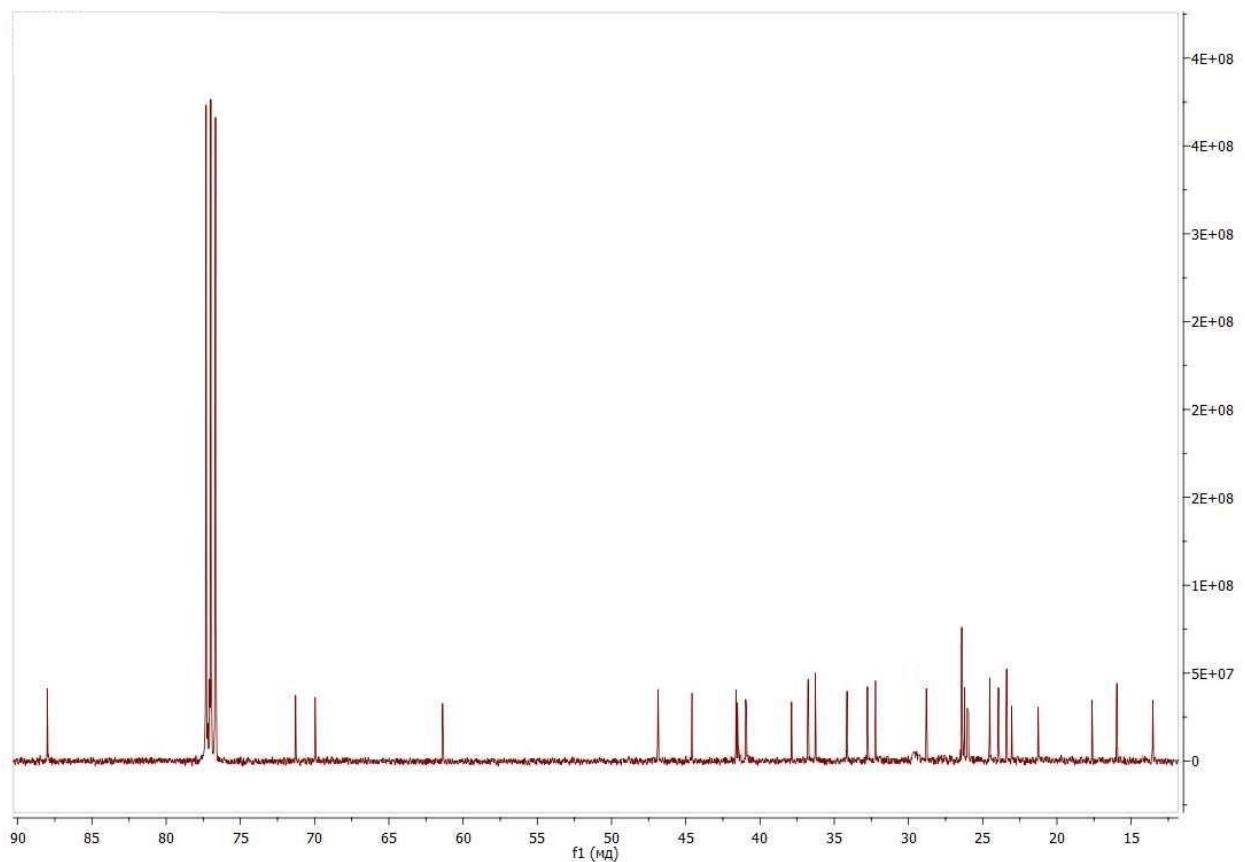
GC-MS (1*R*,2*S*,3*R*)-3β-hydroxy-2-methyl-(1,2),(19β,28)-diepoxy-18α*H*-oleanane (5)
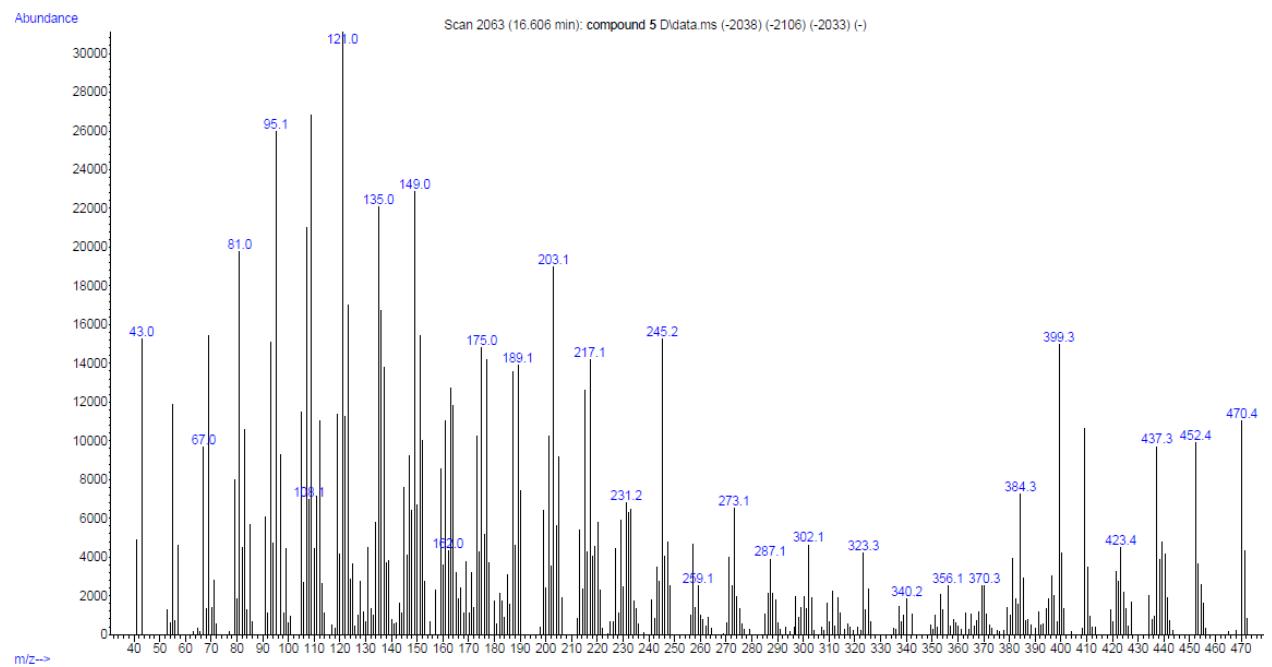
¹H NMR (1*S*,2*R*,3*R*)-3β-hydroxy-2-methyl-(1,2),(19β,28)-diepoxy-18α*H*-oleanane (6)
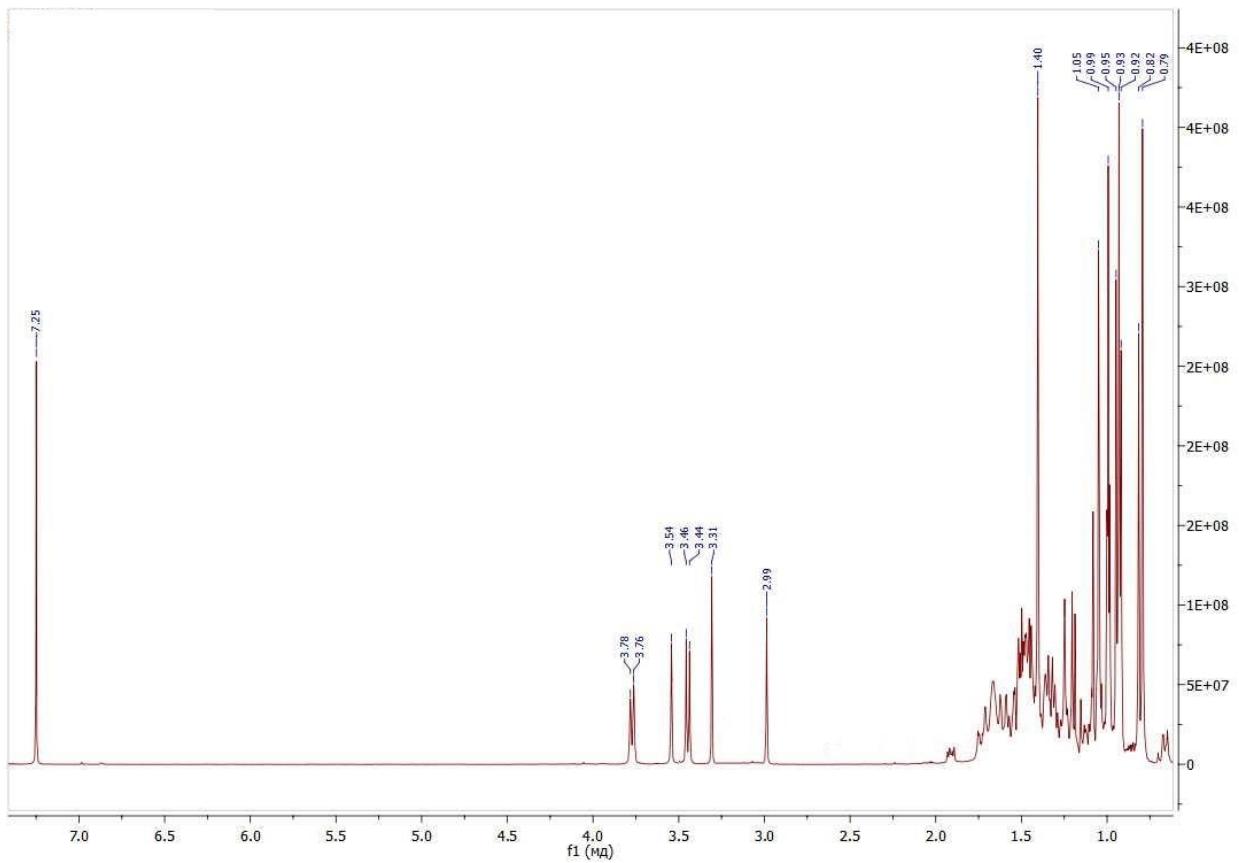

¹³C NMR (CDCl₃) (1*S*,2*R*,3*R*)-3β-hydroxy-2-methyl-(1,2),(19β,28)-diepoxy-18α*H*-oleanane (6)
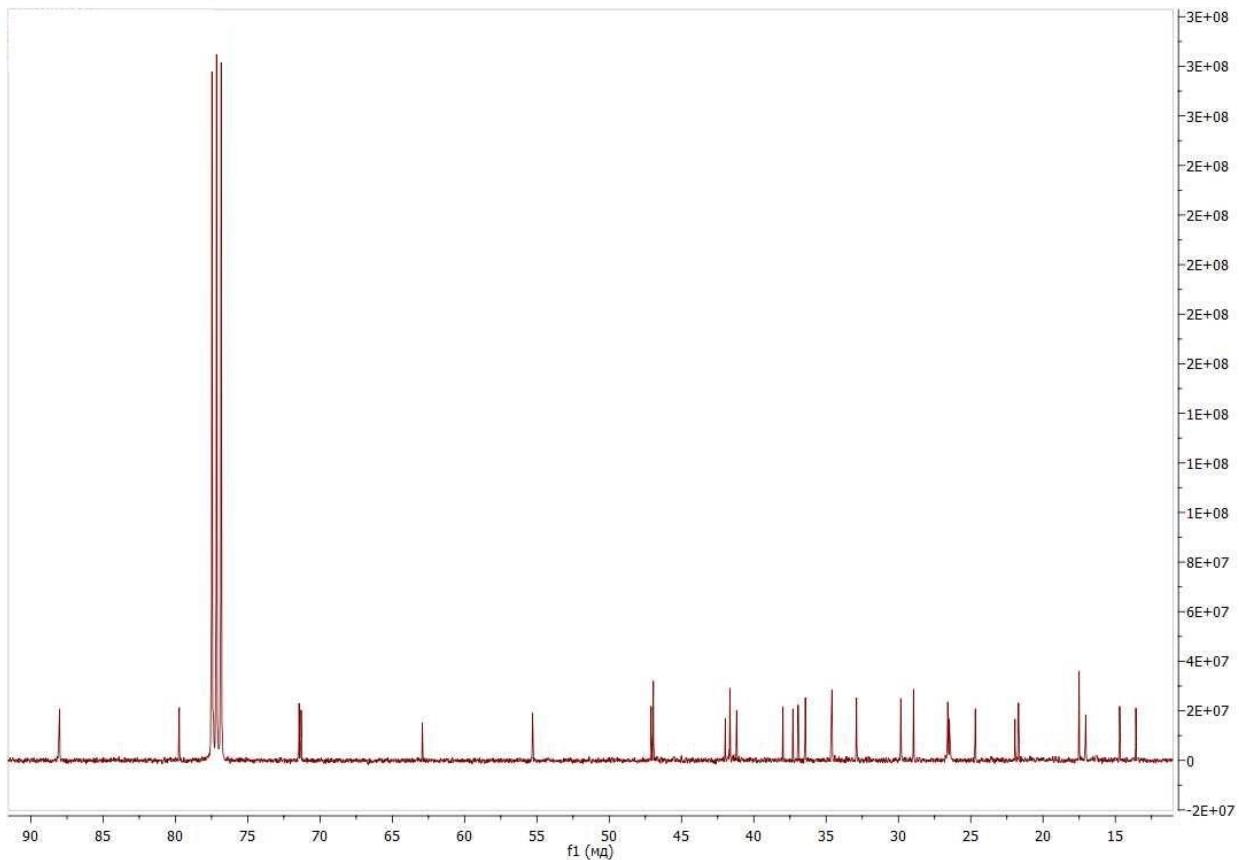
**GC-MS (1*S*,2*R*,3*R*)-3β-hydroxy-2-methyl-(1,2),(19β,28)-diepoxy-18α*H*-oleanane (6)**
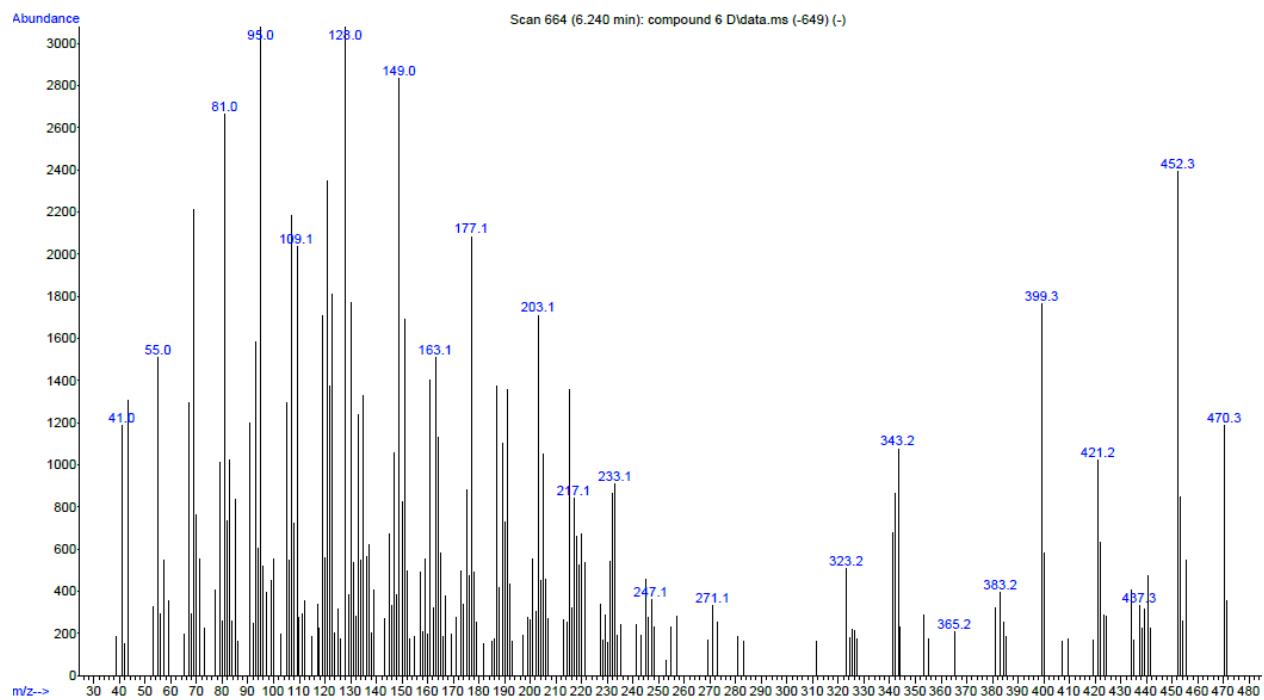
¹H NMR (3*S*)-3β-hydroxy-2,3-dimethyl-19β,28-epoxy-18α*H*-olean-1-ene (7)
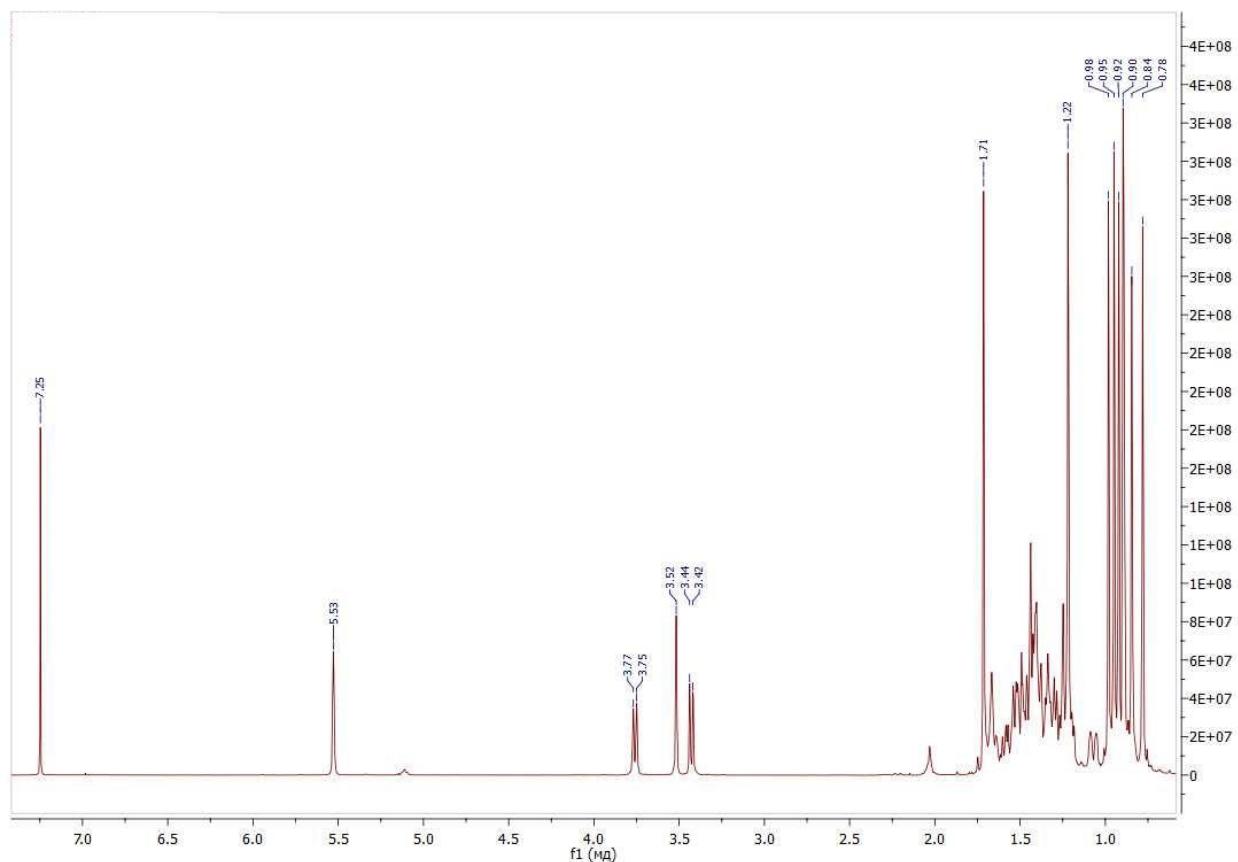
¹³C NMR (CDCl₃) (3*S*)-3β-hydroxy-2,3-dimethyl-19β,28-epoxy-18α*H*-olean-1-ene (7)
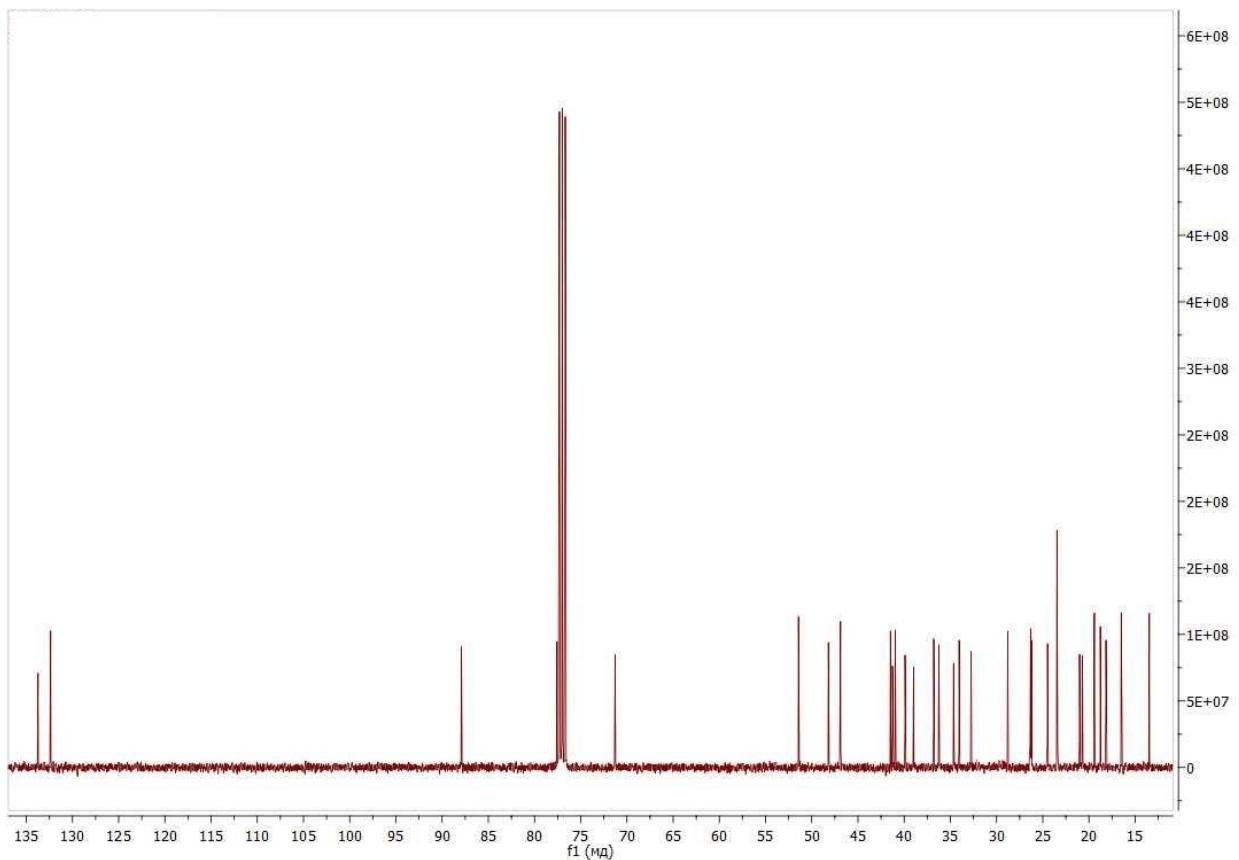
GC-MS (3*S*)-3β-hydroxy-2,3-dimethyl-19β,28-epoxy-18α*H*-olean-1-ene (7)
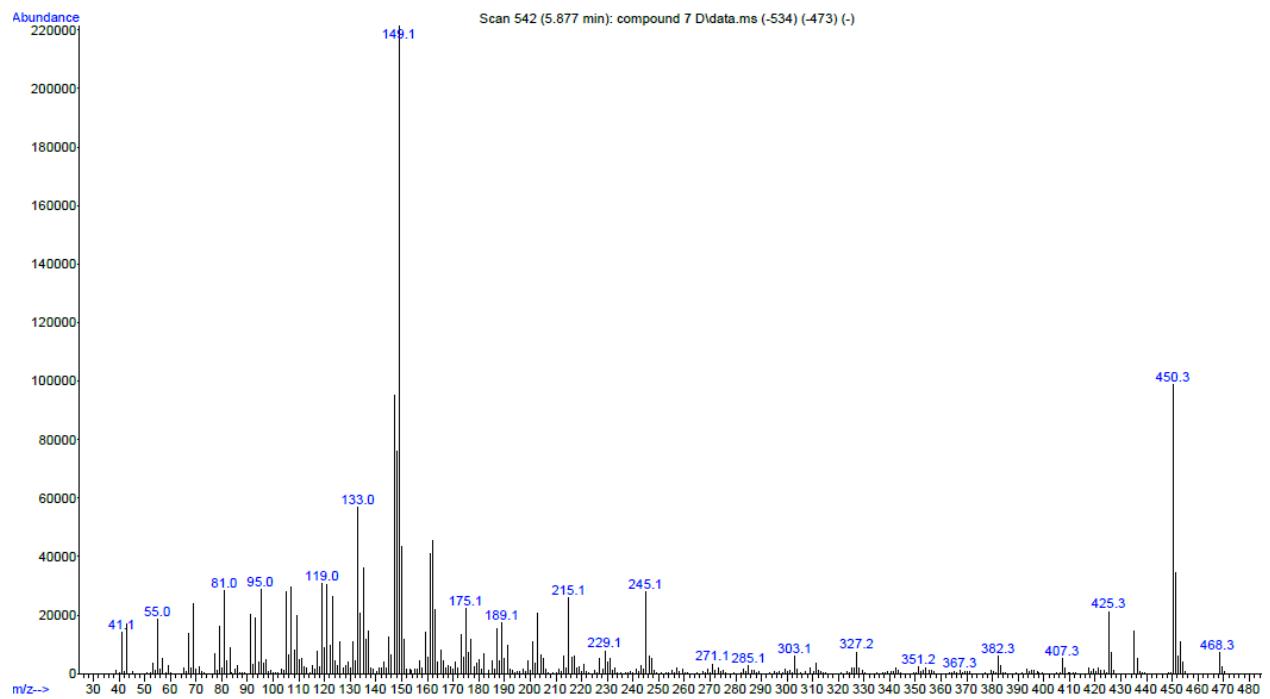
¹H NMR (3*S*)-3-ethyl-3β-hydroxy-2-methyl-19β,28-epoxy-18α*H*-olean-1-ene (8)
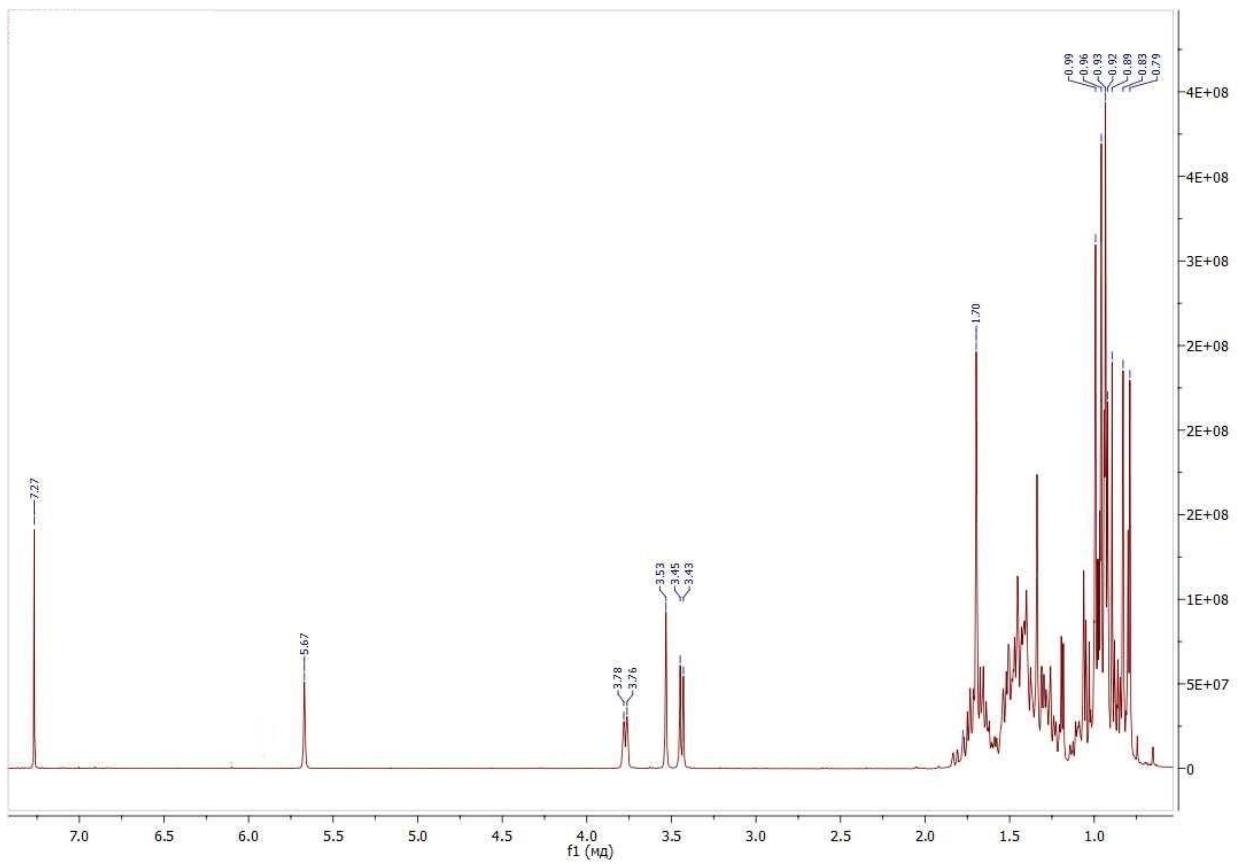
¹³C NMR (CDCl₃) (3*S*)-3-ethyl-3β-hydroxy-2-methyl-19β,28-epoxy-18α*H*-olean-1-ene (8)

GC-MS (3*S*)-3-ethyl-3β-hydroxy-2-methyl-19β,28-epoxy-18α*H*-olean-1-ene (8)

Scan 670 (6.278 min): compound 8 D\data.ms (-664) (-505) (-)
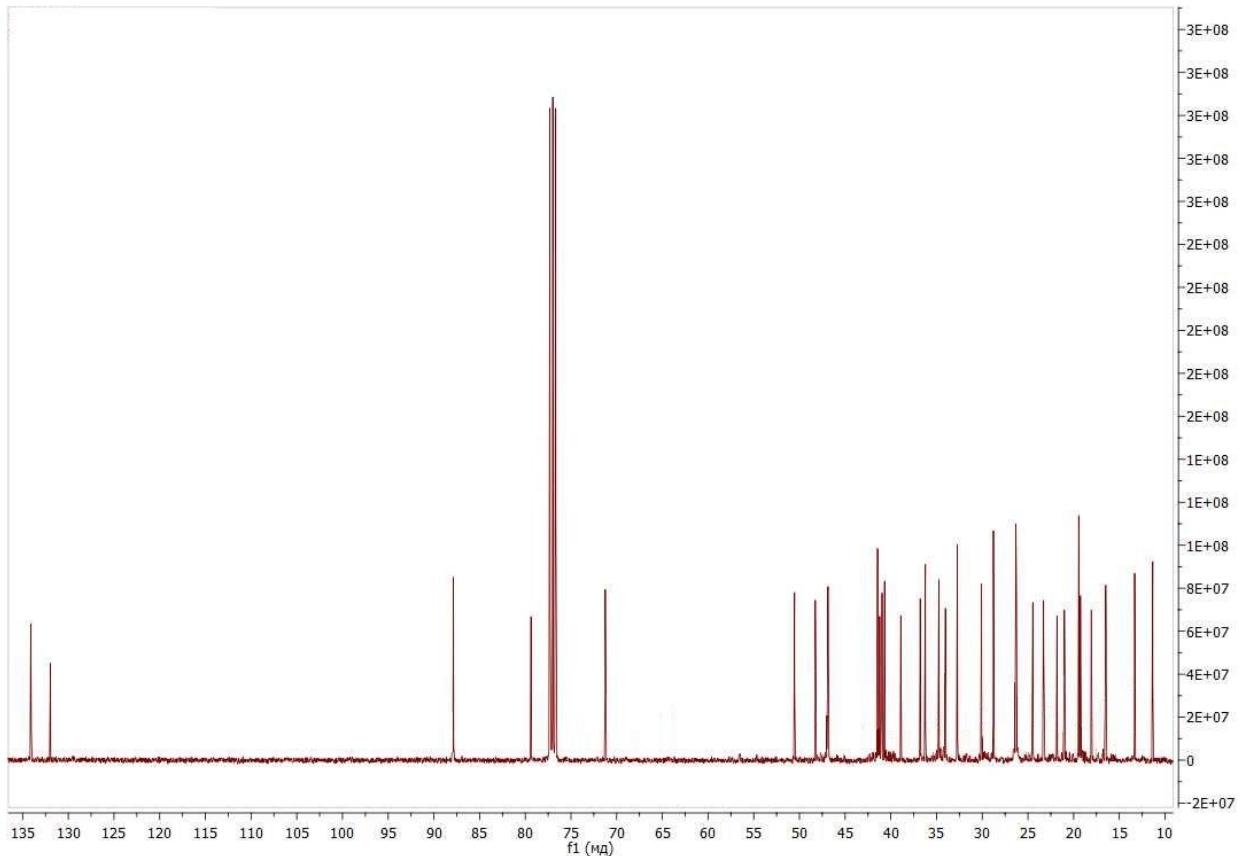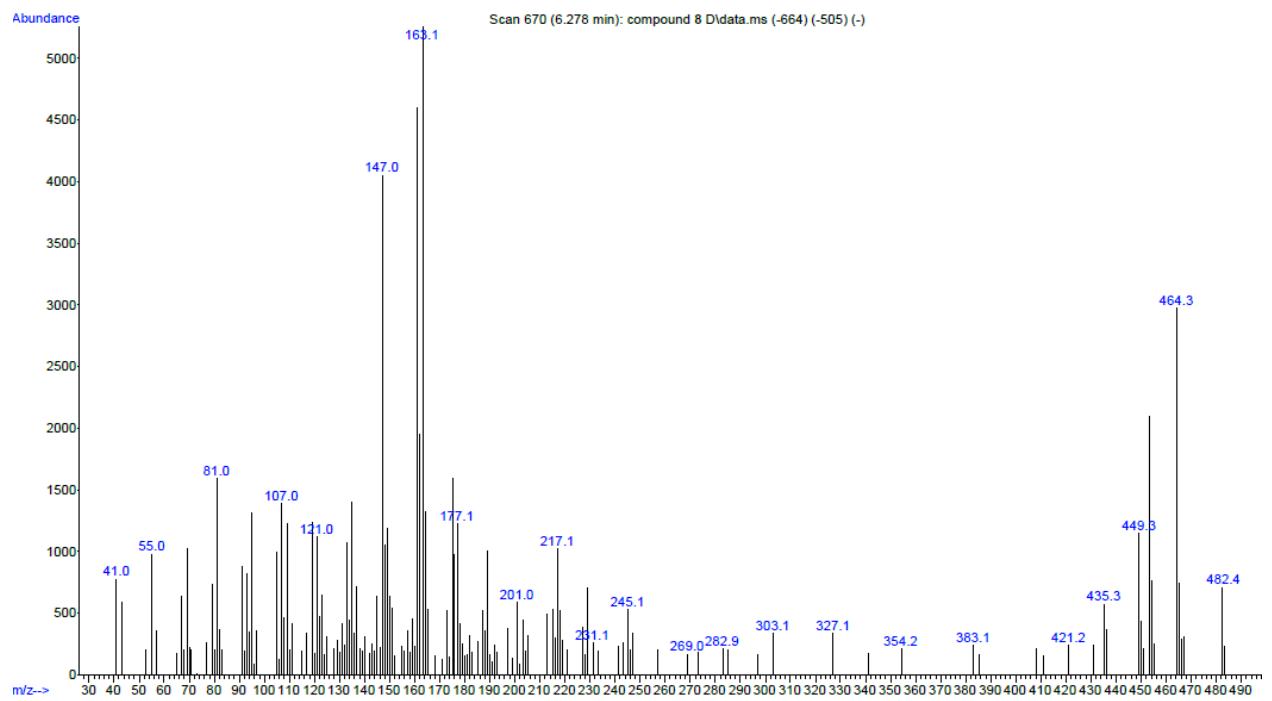
¹H NMR (3R)-3β-hydroxy-2-methyl-3-phenyl-19β,28-epoxy-18αH-olean-1-ene (9)
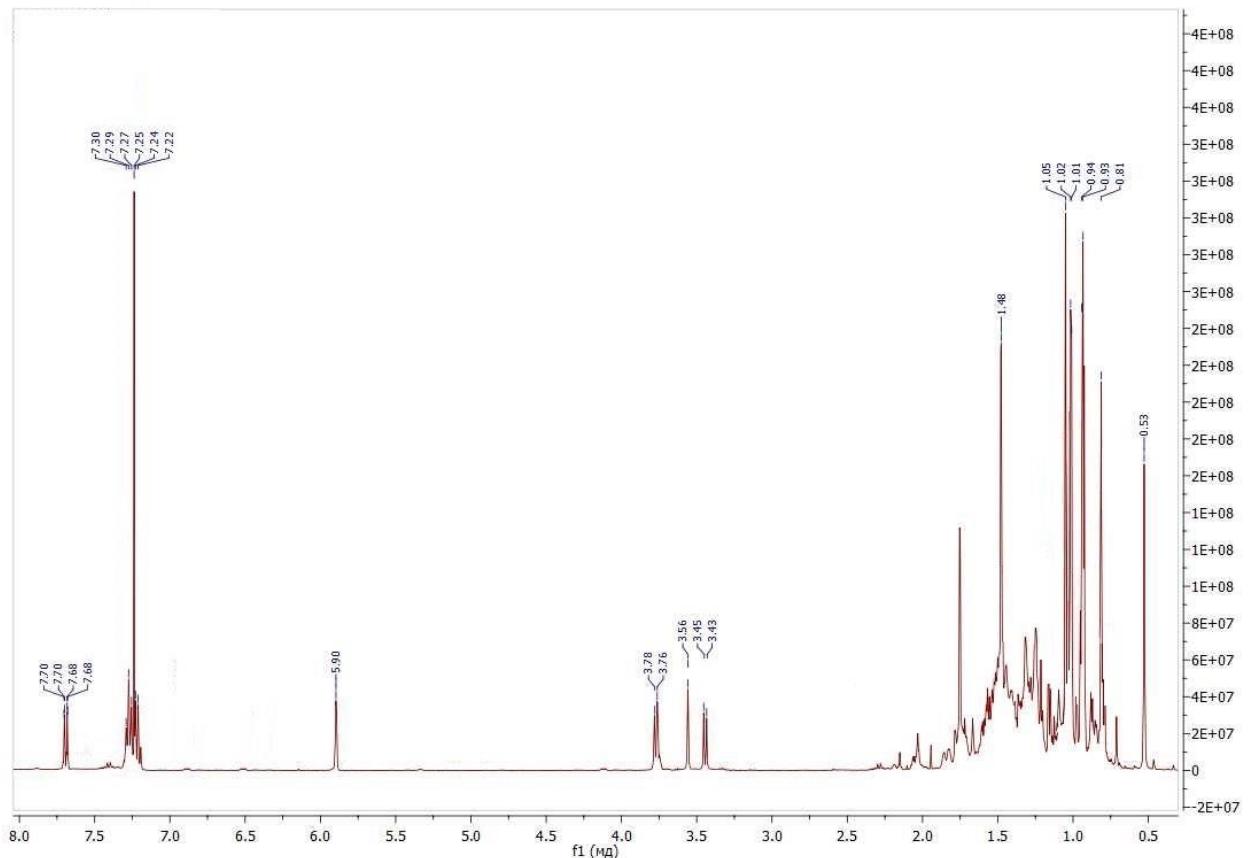
¹³C NMR (CDCl₃) (3R)-3β-hydroxy-2-methyl-3-phenyl-19β,28-epoxy-18αH-olean-1-ene (9)
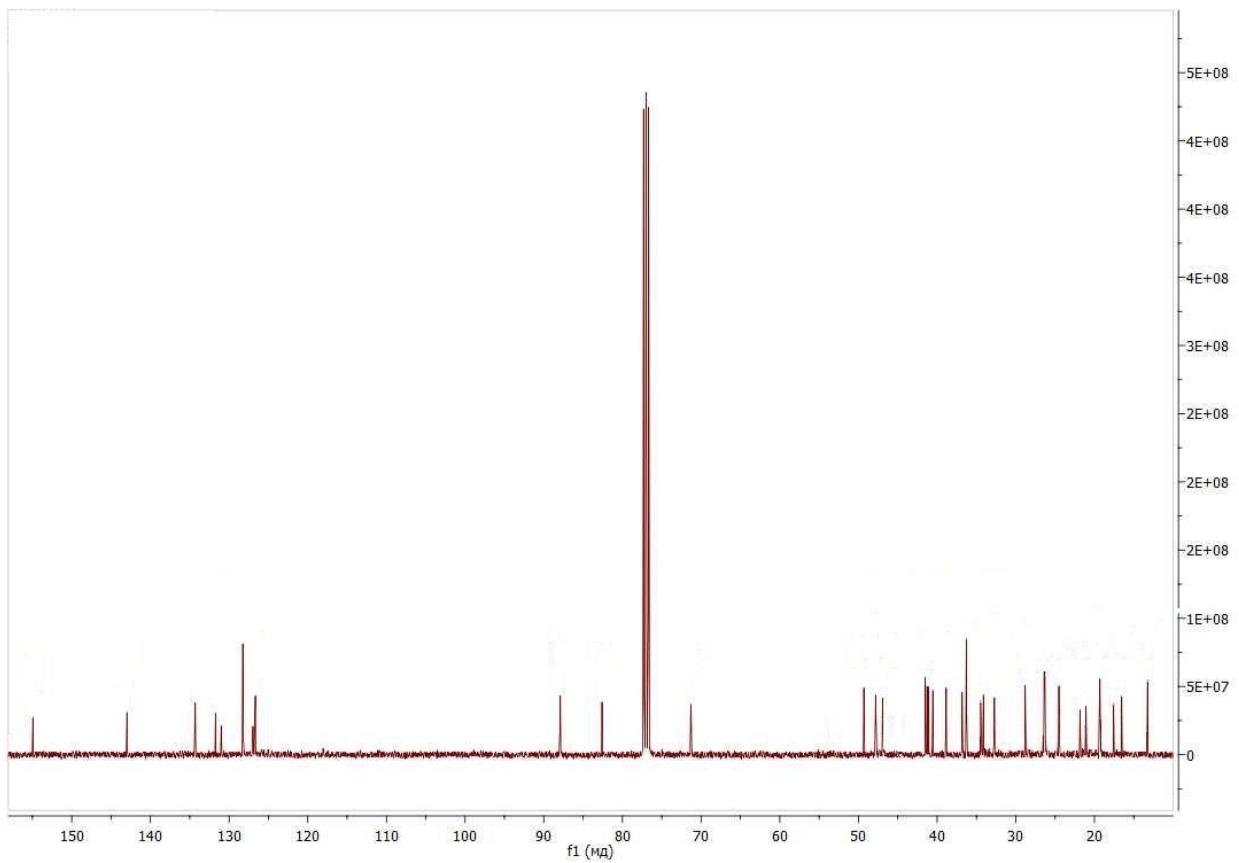
GC-MS (3*R*)-3β-hydroxy-2-methyl-3-phenyl-19β,28-epoxy-18α*H*-olean-1-ene (9)
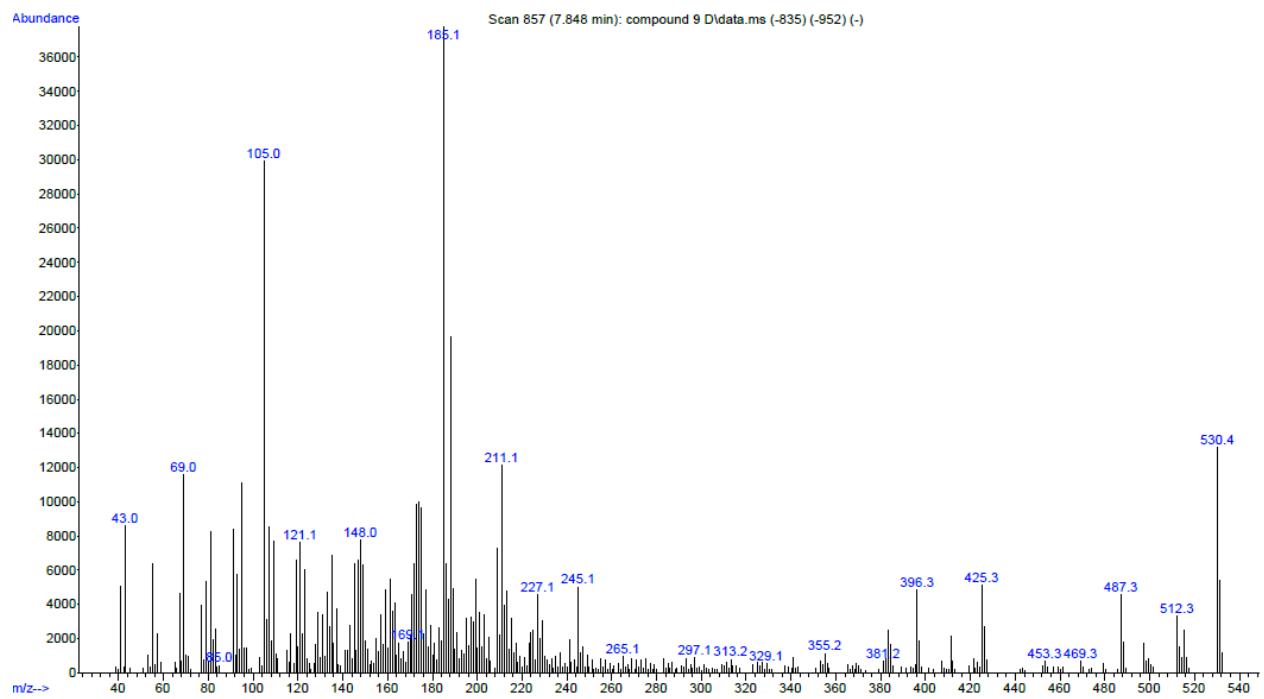
1H NMR (1S,2S,3R)-3β-hydroxy-2,3-dimethyl-(1,2),(19β,28)-diepoxy-18αH-oleanane (10)
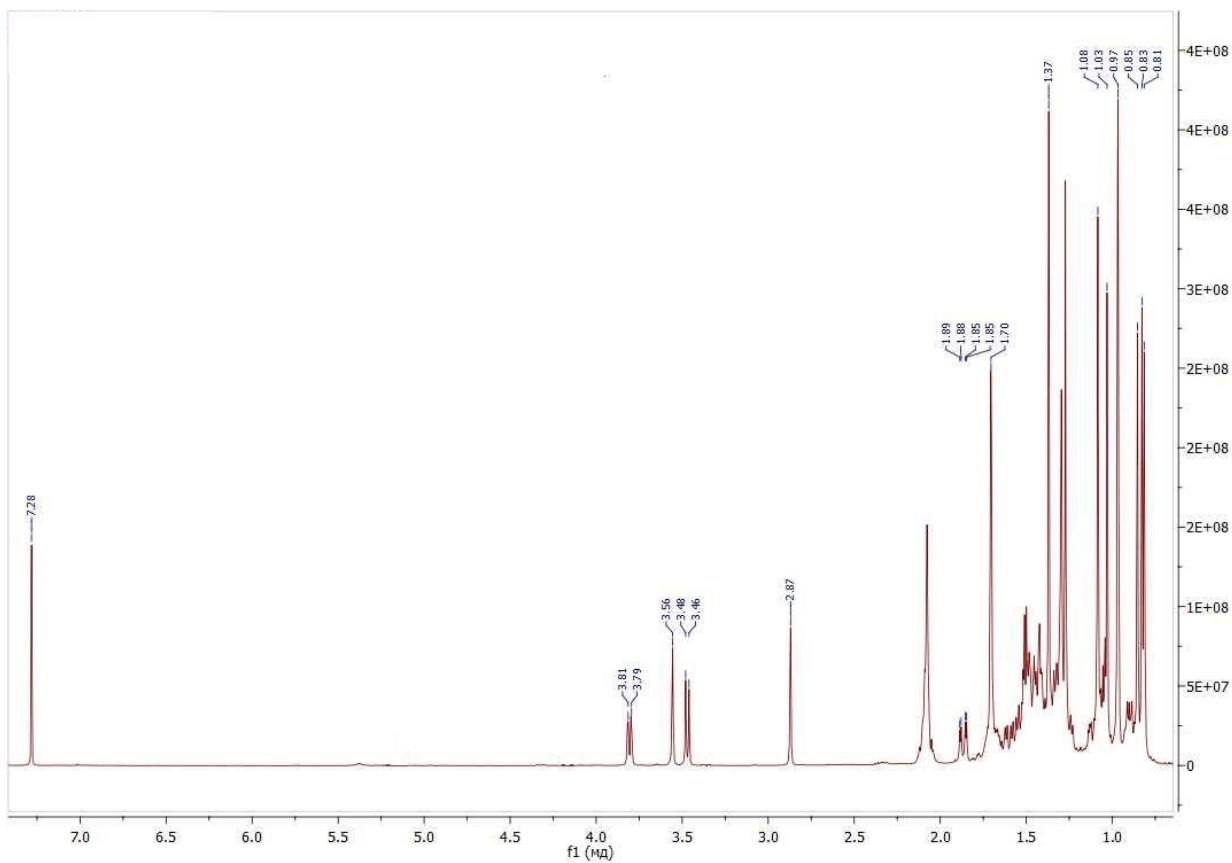
**13C NMR (CDCl₃) (1S,2S,3R)-3β-hydroxy-2,3-dimethyl-(1,2),(19β,28)-diepoxy-18αH-oleanane (10)**
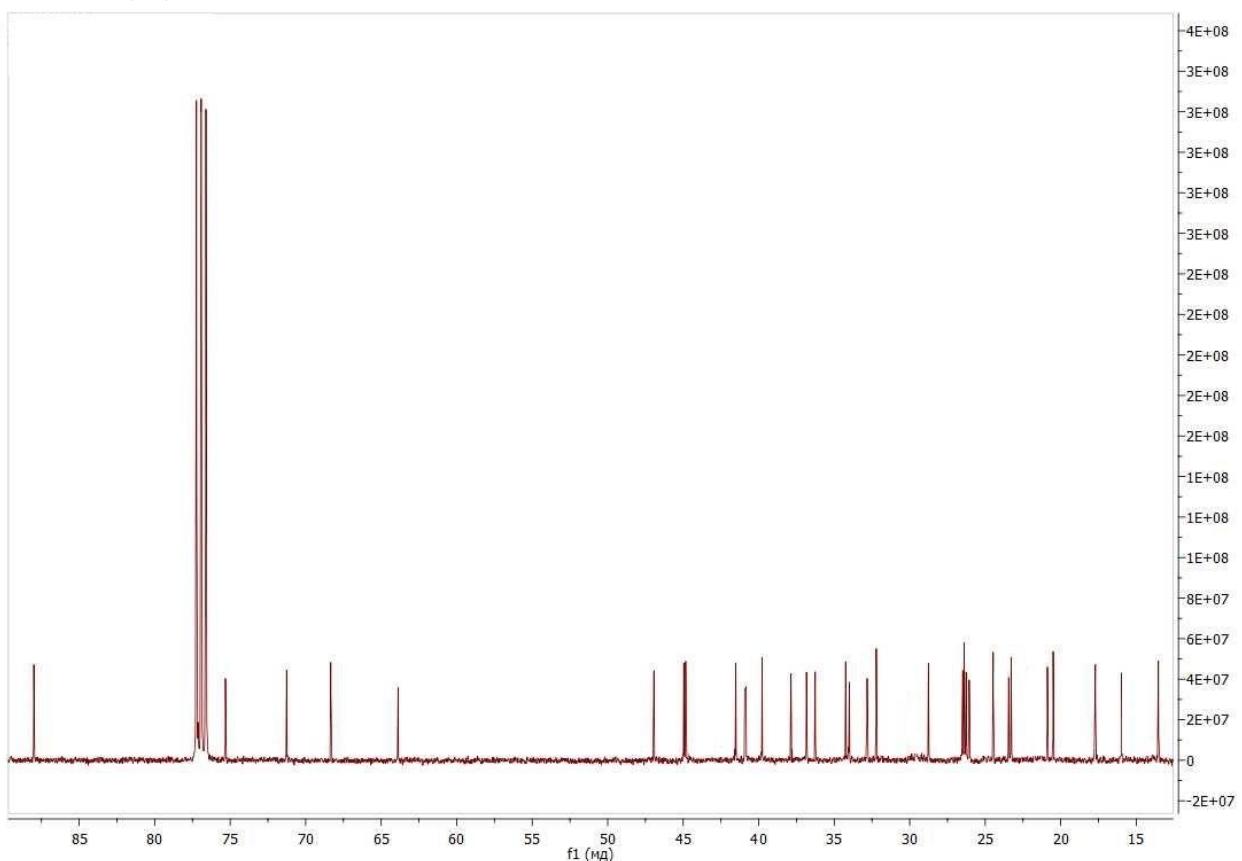
1H–1H COSY (CDCl₃) (1S,2S,3R)-3β-hydroxy-2,3-dimethyl-(1,2),(19β,28)-diepoxy-18αH-oleanane (10)
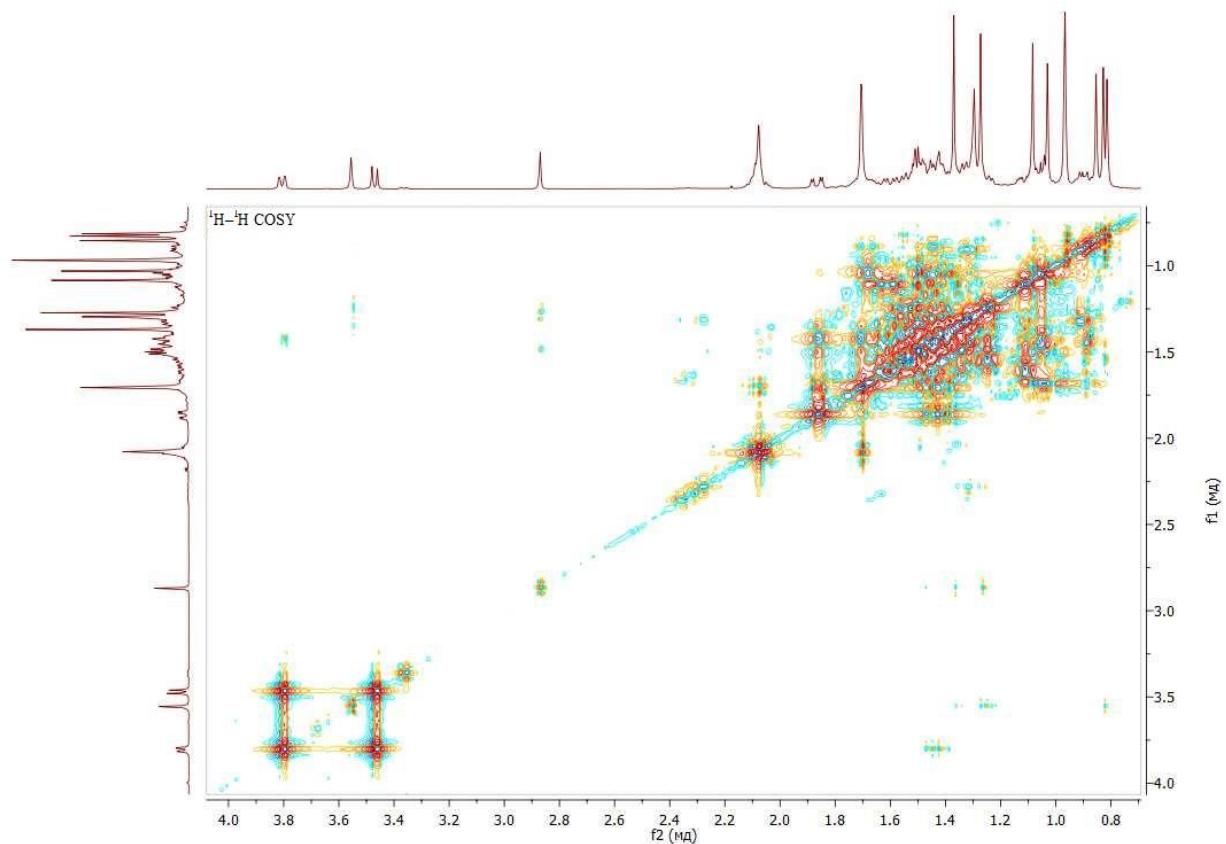
NOESY (CDCl₃) (1*S*,2*S*,3*R*)-3β-hydroxy-2,3-dimethyl-(1,2),(19β,28)-diepoxy-18*αH*-oleanane (10)
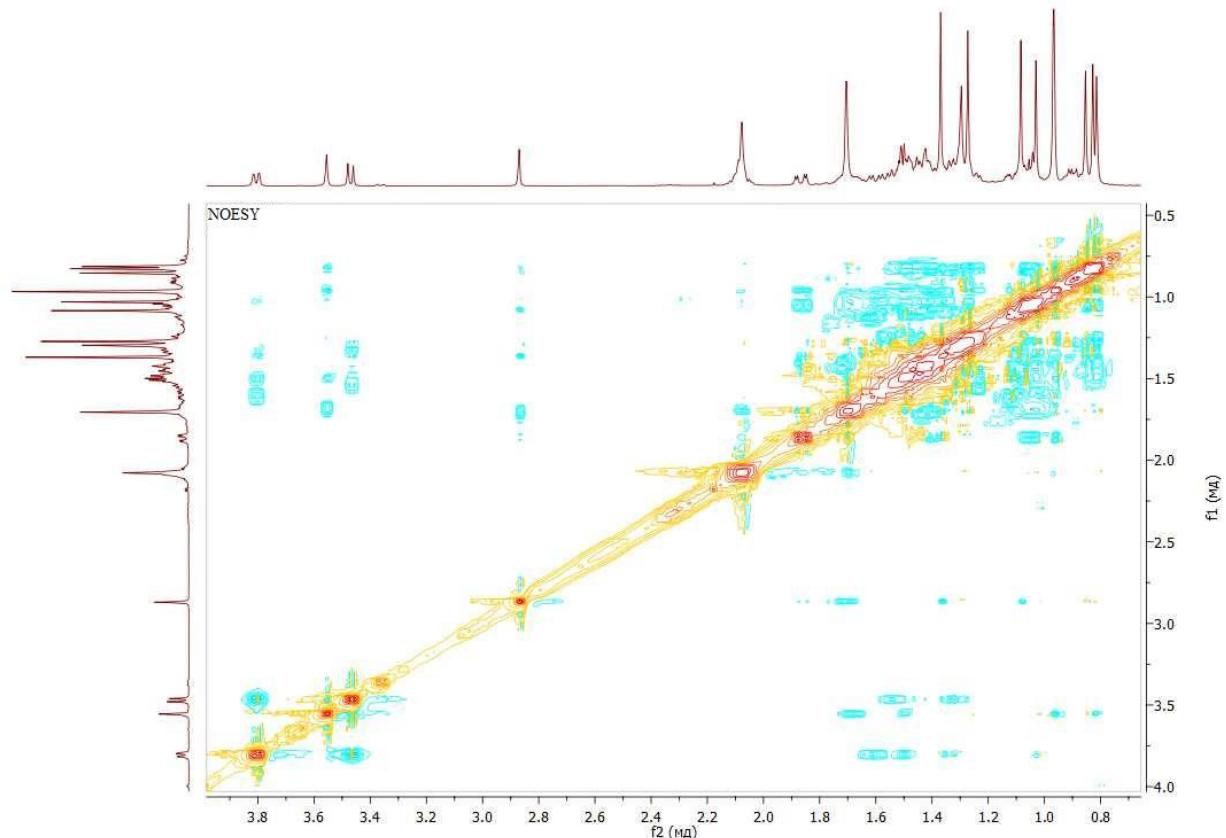
HMBC (CDCl₃) (1*S*,2*S*,3*R*)-3β-hydroxy-2,3-dimethyl-(1,2),(19β,28)-diepoxy-18*αH*-oleanane (10)
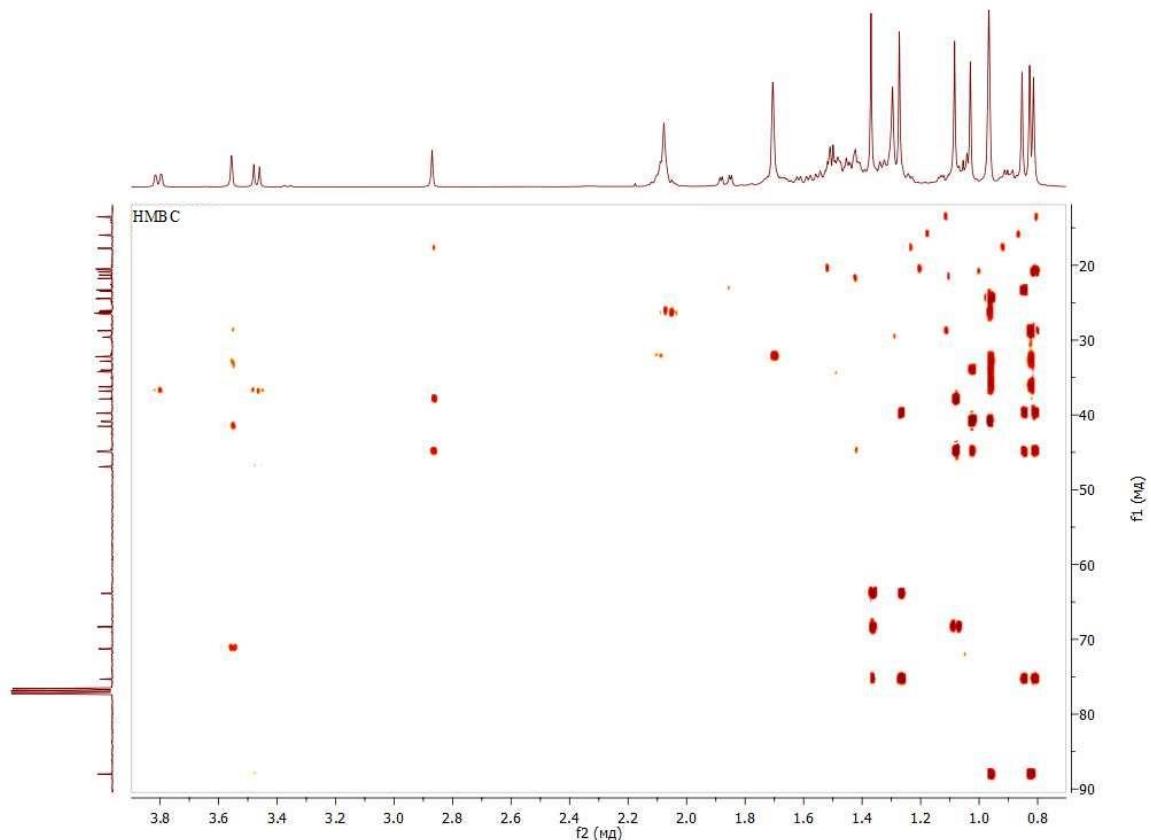
HSQC (CDCl₃) (1*S*,2*S*,3*R*)-3β-hydroxy-2,3-dimethyl-(1,2),(19β,28)-diepoxy-18α*H*-oleanane (10)

**GC-MS (1*S*,2*S*,3*R*)-3β-hydroxy-2,3-dimethyl-(1,2),(19β,28)-diepoxy-18α*H*-oleanane (10)**

Scan 1318 (11.834 min): compound 10 D\data.ms (-1306) (-)
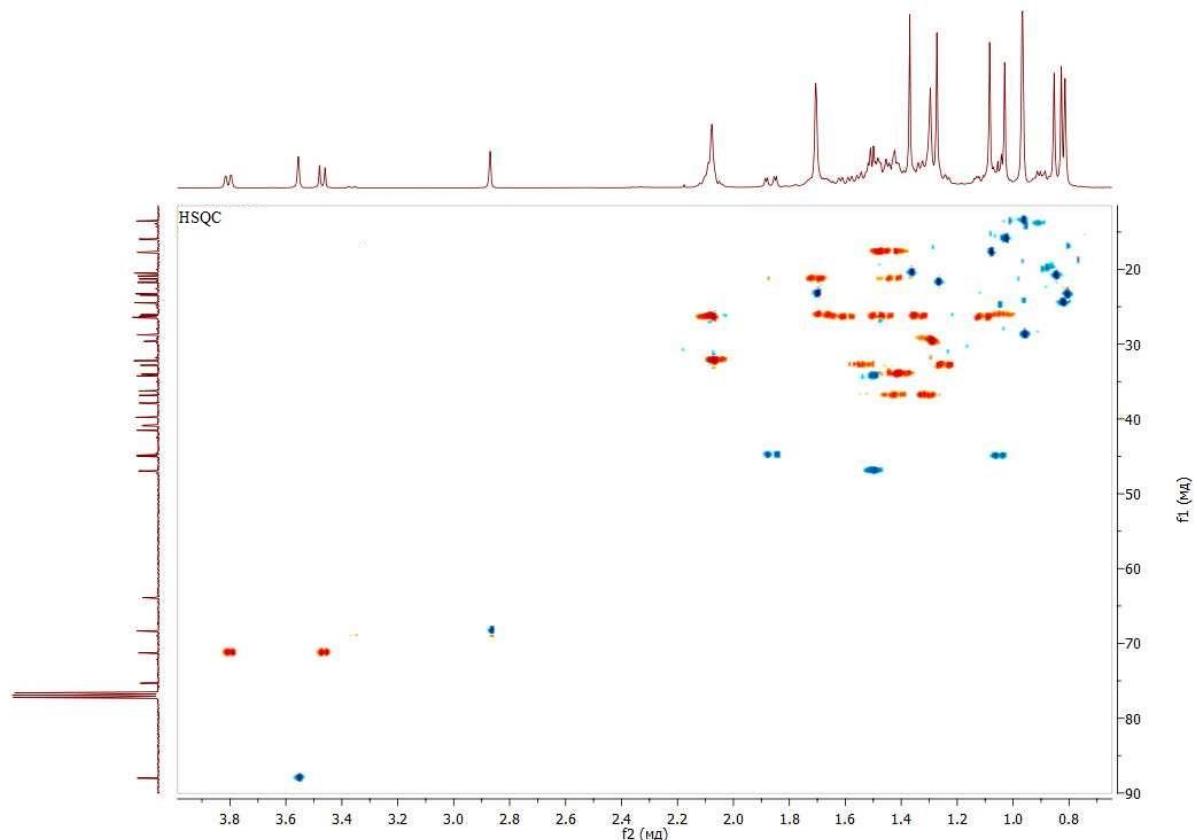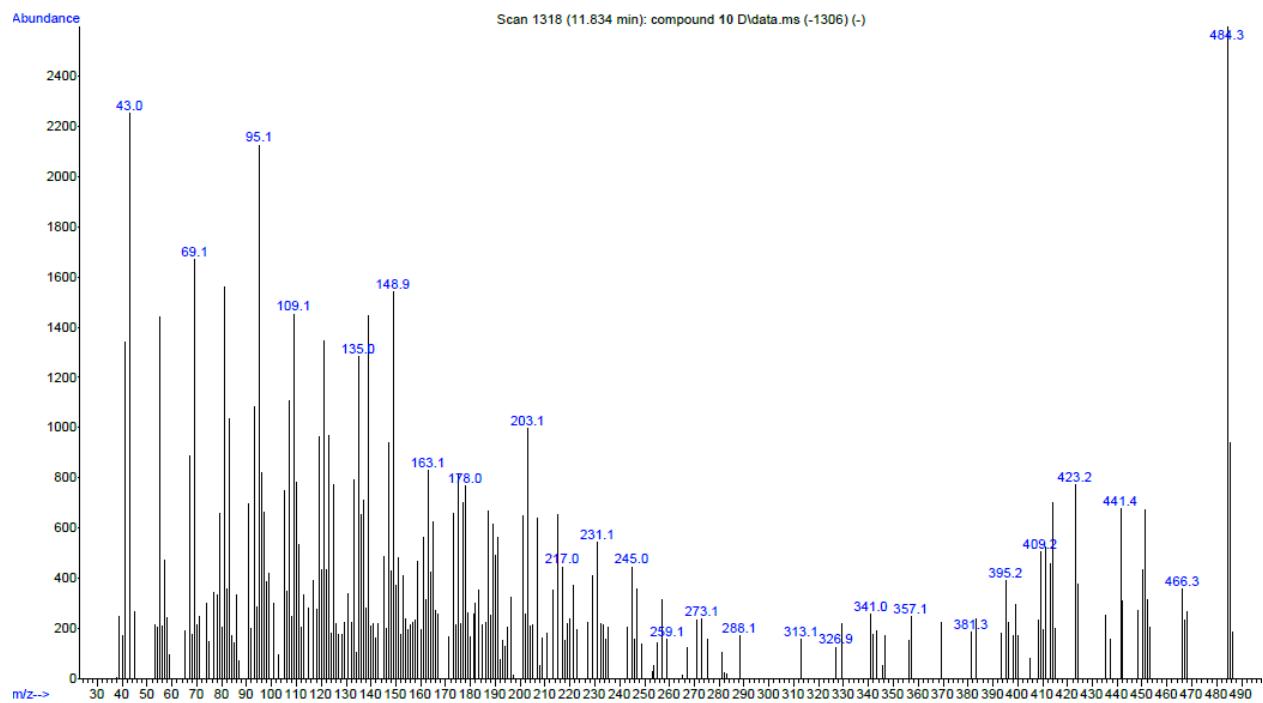
¹H NMR (1S,2S,3R)-3-ethyl-3β-hydroxy-2-methyl-(1,2),(19β,28)-diepoxy-18αH-oleanane (11)
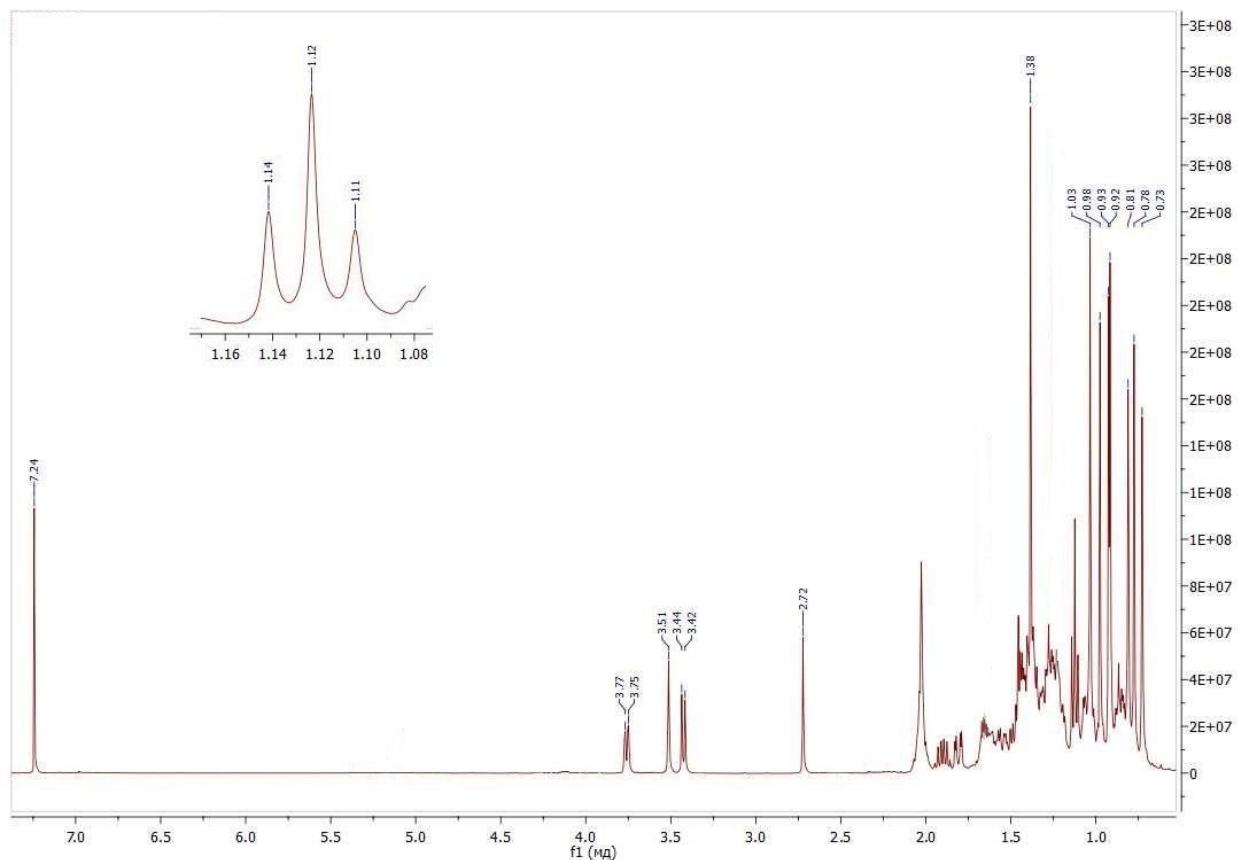
¹³C NMR (CDCl₃) (1S,2S,3R)-3-ethyl-3β-hydroxy-2-methyl-(1,2),(19β,28)-diepoxy-18αH-oleanane (11)
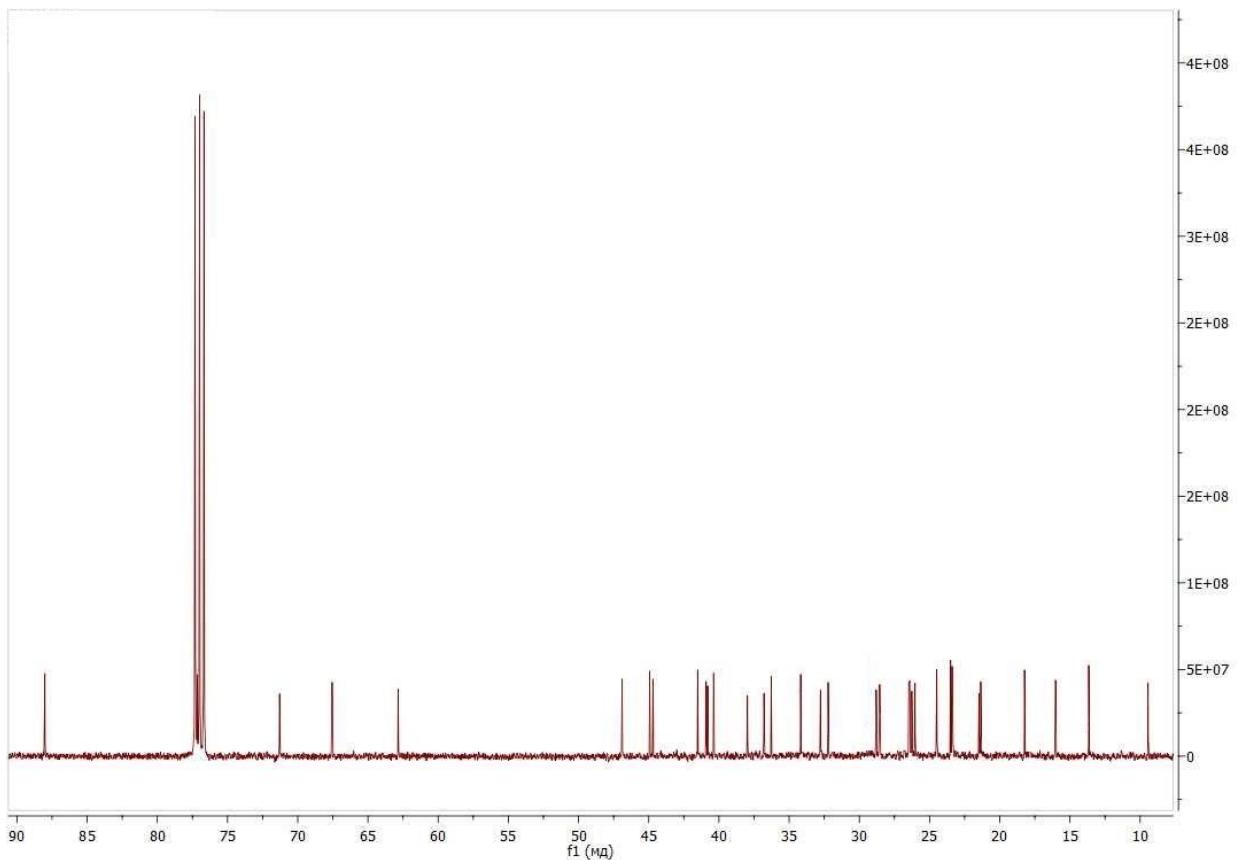
GC-MS (1*S*,2*S*,3*R*)-3-ethyl-3β-hydroxy-2-methyl-(1,2),(19β,28)-diepoxy-18α*H*-oleanane (11)
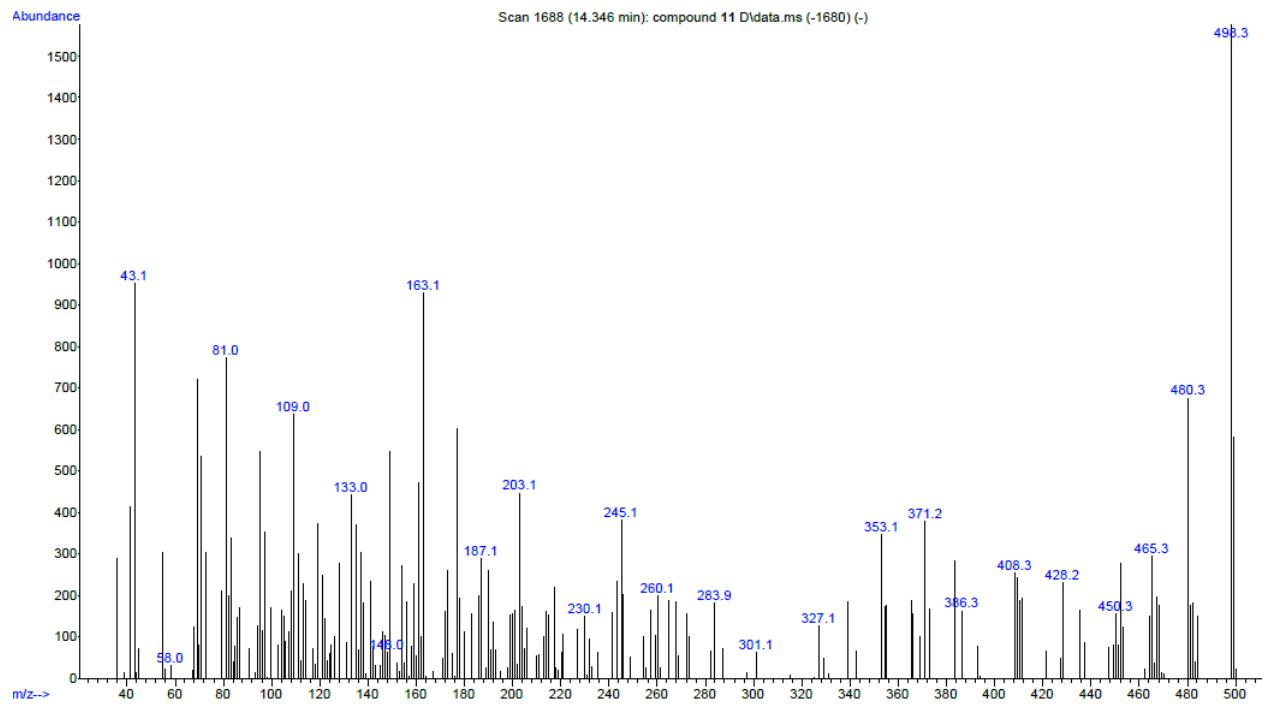
¹H NMR (1*S*,2*S*,3*R*)-3β-hydroxy-2-methyl-3-phenyl-(1,2),(19β,28)-diepoxy-18α*H*-oleanane (12)
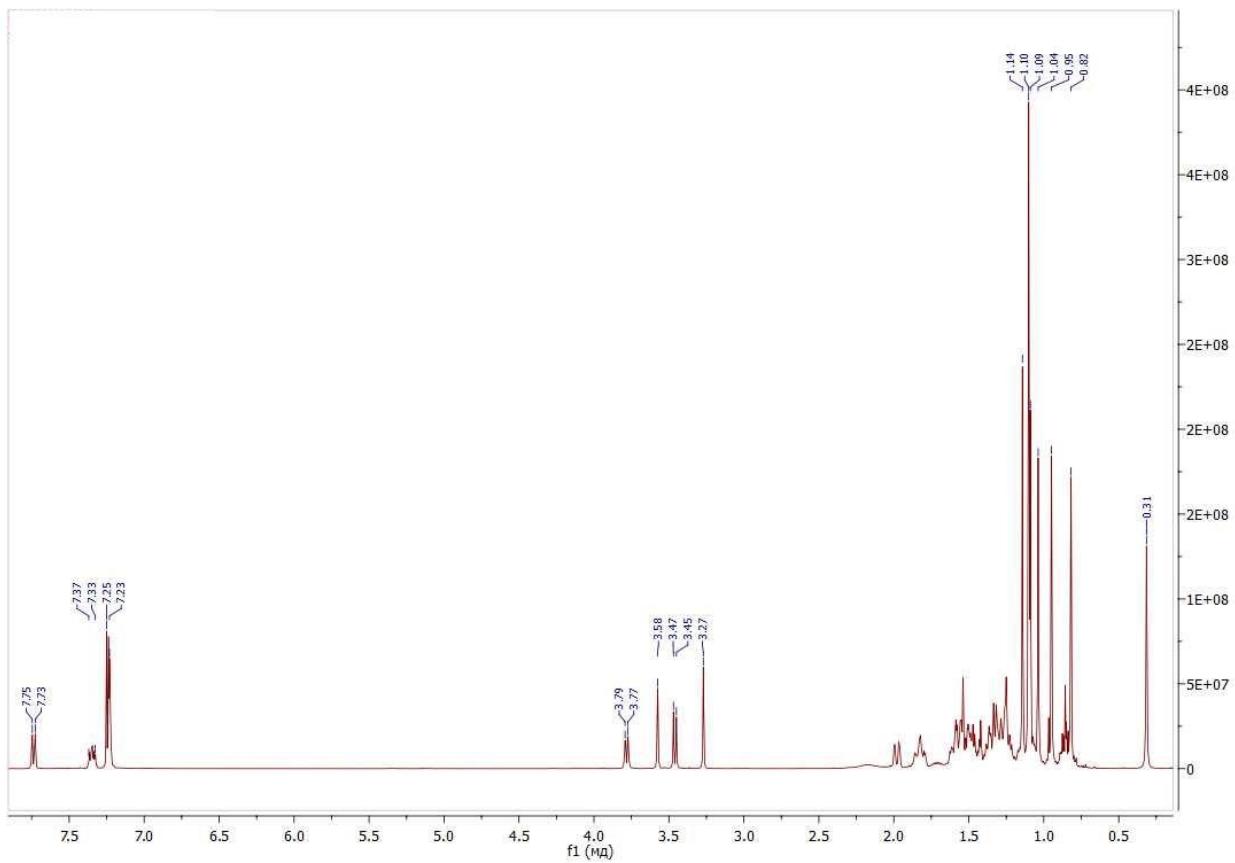
¹³C NMR (CDCl₃) (1*S*,2*S*,3*R*)-3β-hydroxy-2-methyl-3-phenyl-(1,2),(19β,28)-diepoxy-18*αH*-oleanane (12)
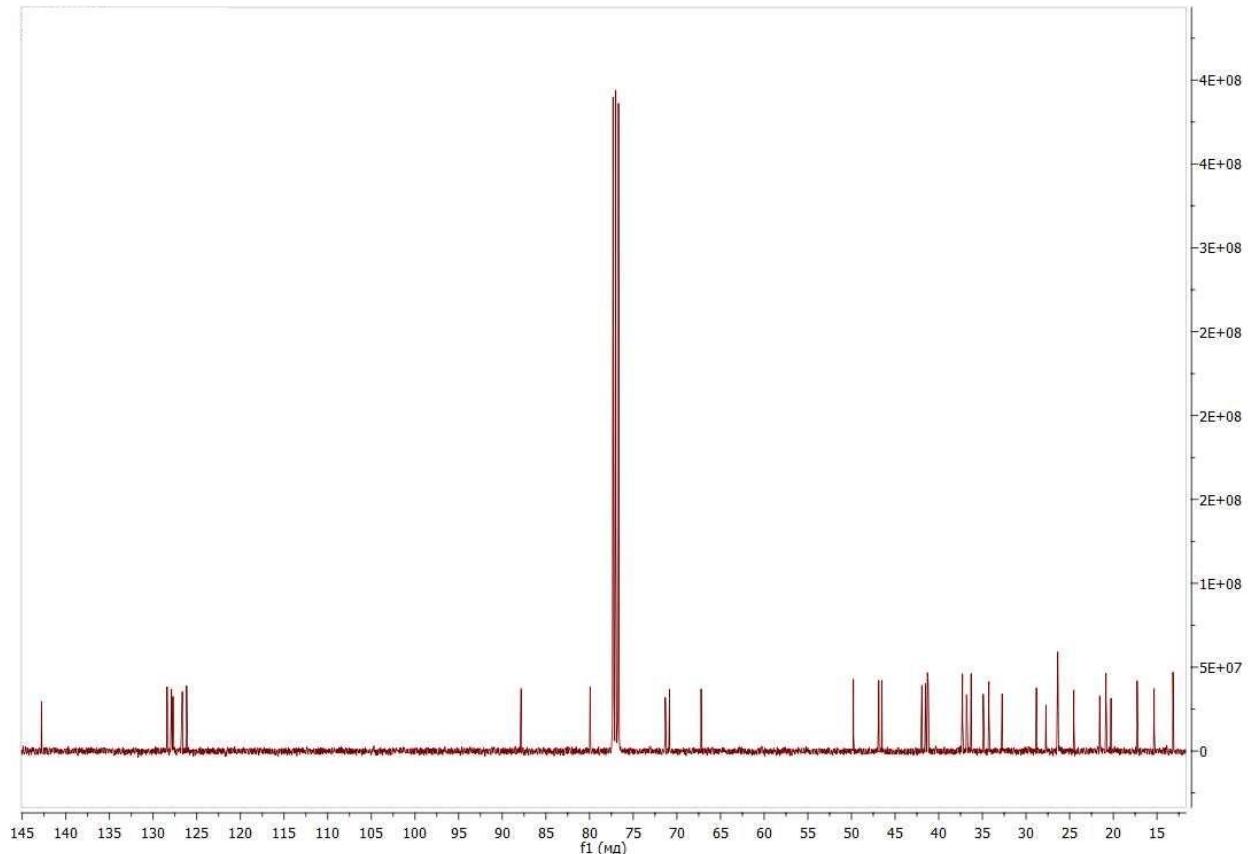
GC-MS (1*S*,2*S*,3*R*)-3β-hydroxy-2-methyl-3-phenyl-(1,2),(19β,28)-diepoxy-18*αH*-oleanane (12)
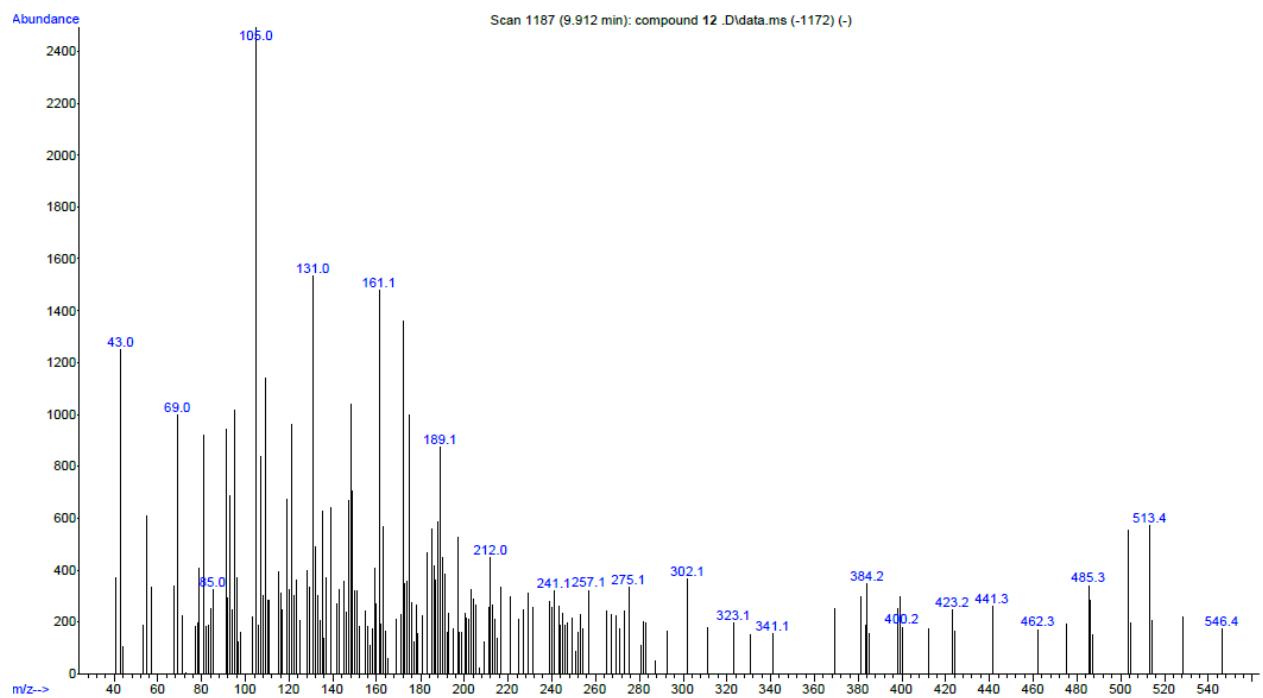
1H NMR (1S,2S)-1α-hydroxy-2-methyl-3-oxo-19β,28-epoxy-18αH-oleanane (13)
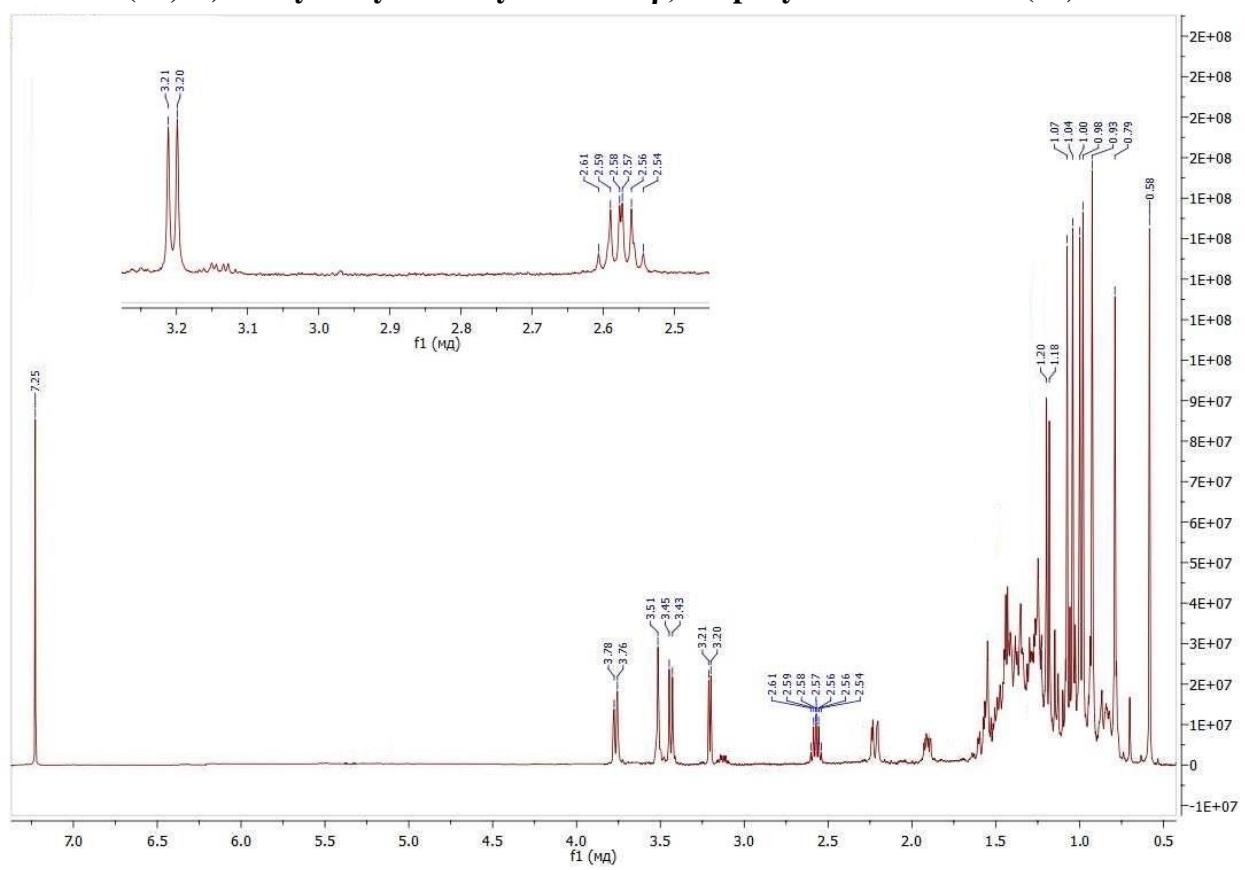
13C NMR (CDCl₃) (1S,2S)-1α-hydroxy-2-methyl-3-oxo-19β,28-epoxy-18αH-oleanane (13)
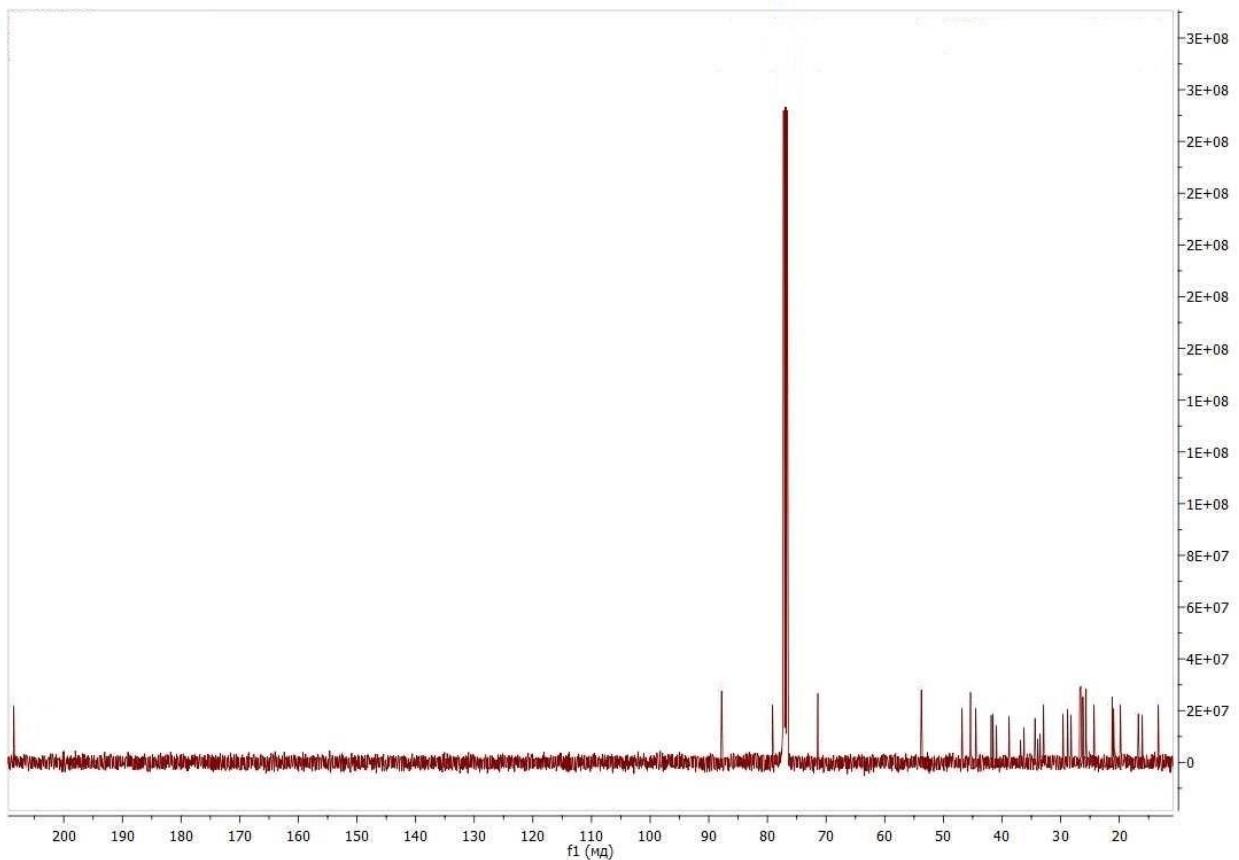
GC-MS (1*S*,2*S*)-1α-hydroxy-2-methyl-3-oxo-19β,28-epoxy-18α*H*-oleanane (13)
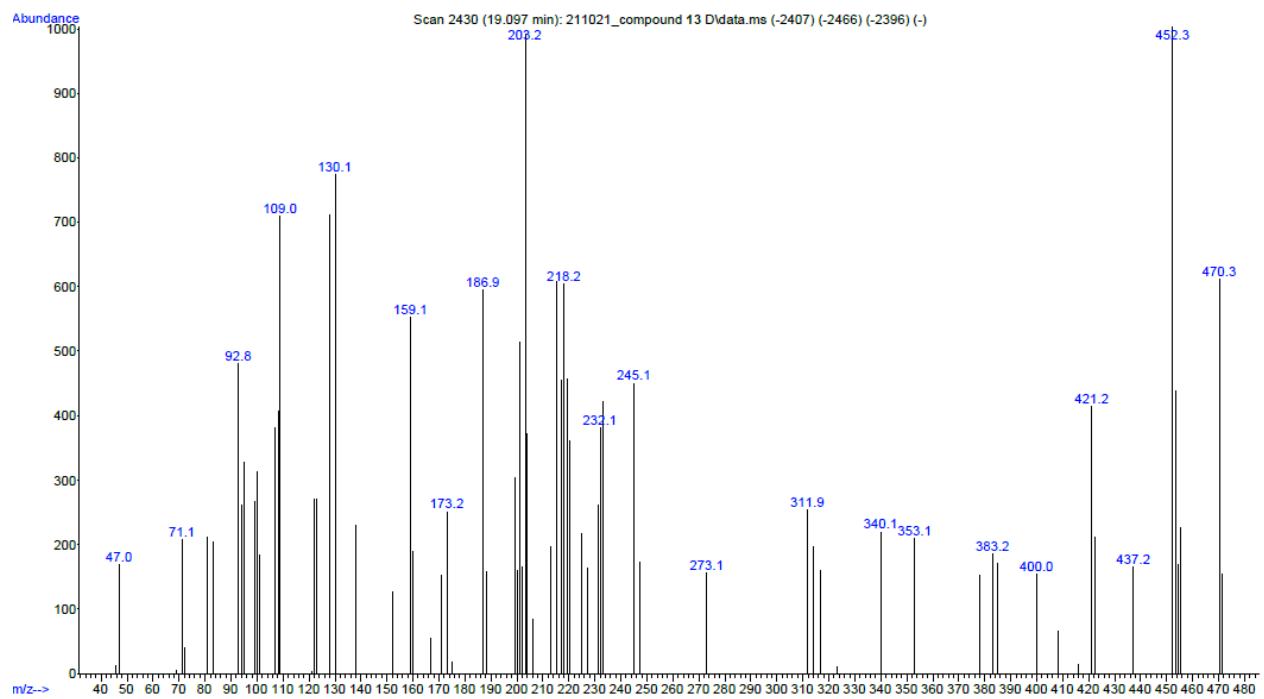
¹H NMR (1*S*,2*R*)-1α-hydroxy-2-methyl-3-oxo-19β,28-epoxy-18α*H*-olean-1-ene (14)
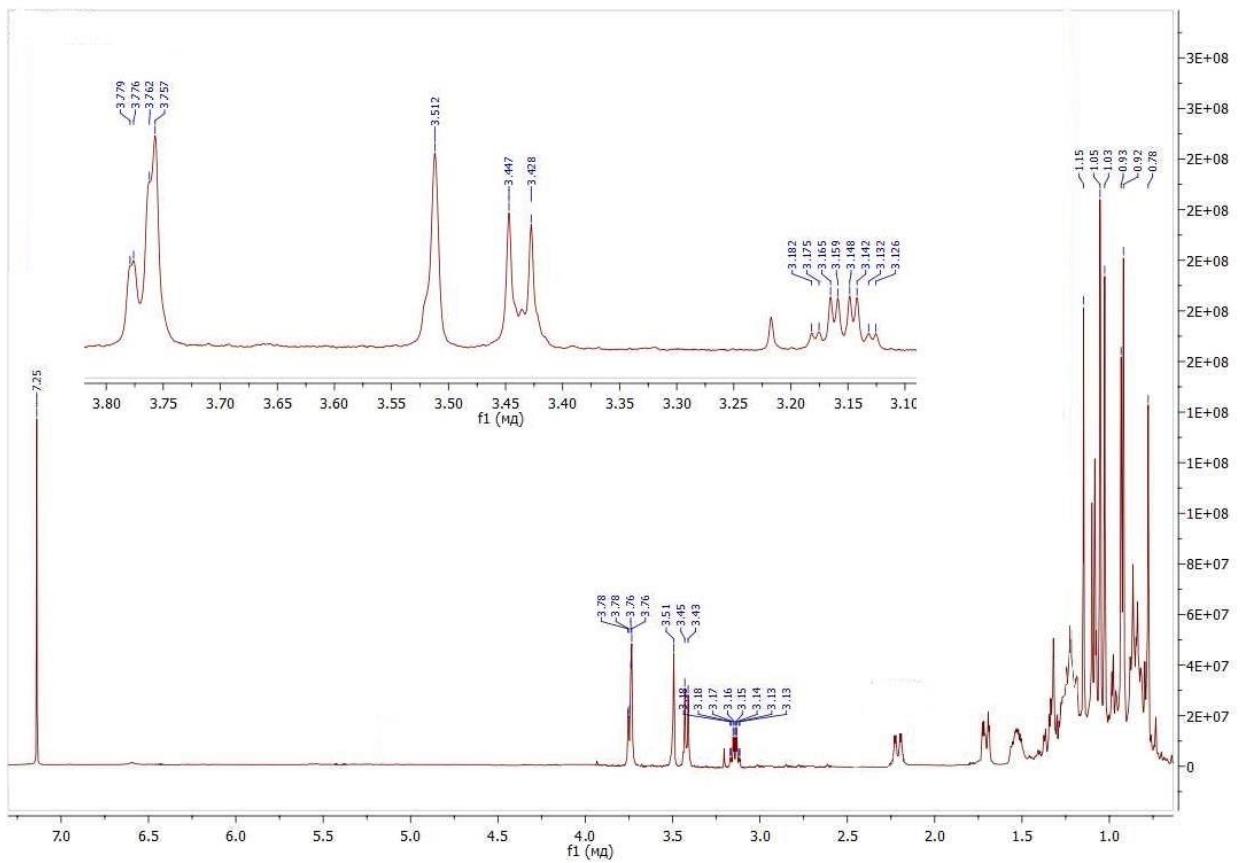
13C NMR (CDCl₃) (1S,2R)-1α-hydroxy-2-methyl-3-oxo-19β,28-epoxy-18αH-olean-1-ene (14)
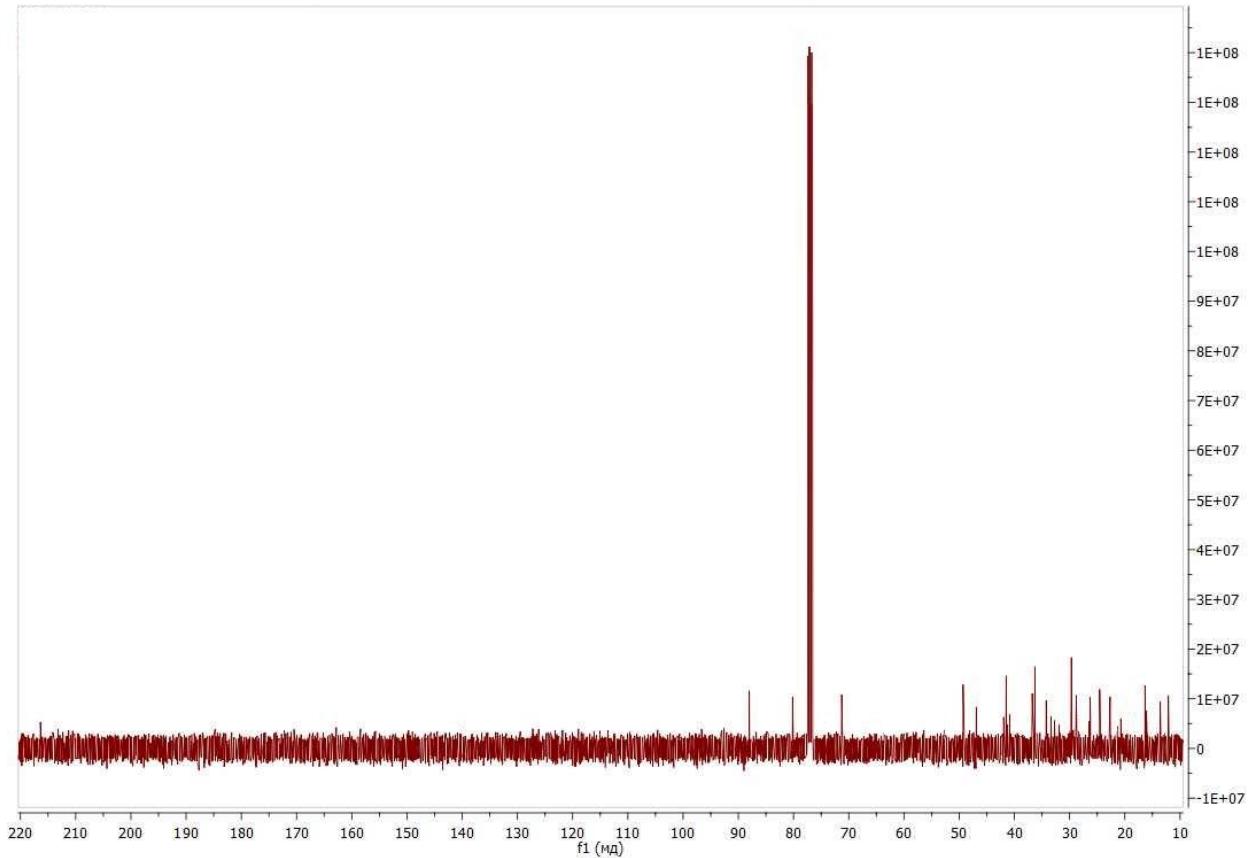
GC-MS (1S,2R)-1α-hydroxy-2-methyl-3-oxo-19β,28-epoxy-18αH-olean-1-ene (14)
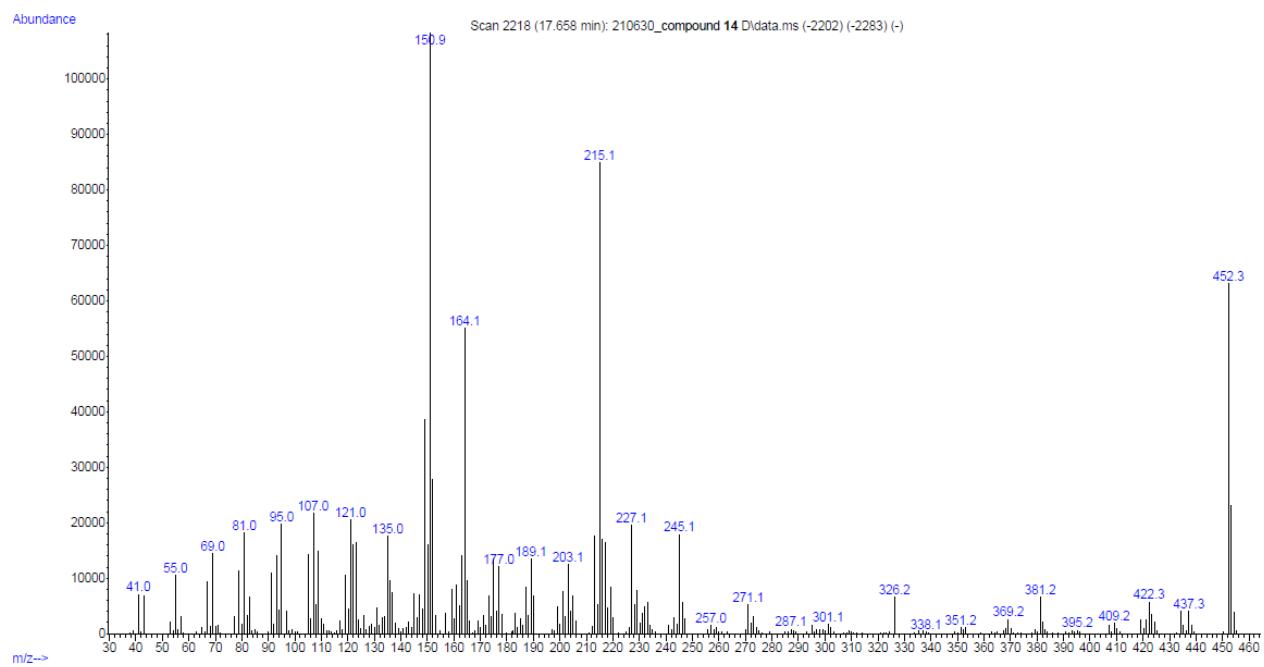
¹H NMR (1S,3S)-1α,3β-dihydroxy-3-ethyl-2-methylene-19β,28-epoxy-18αH-oleanane (15)
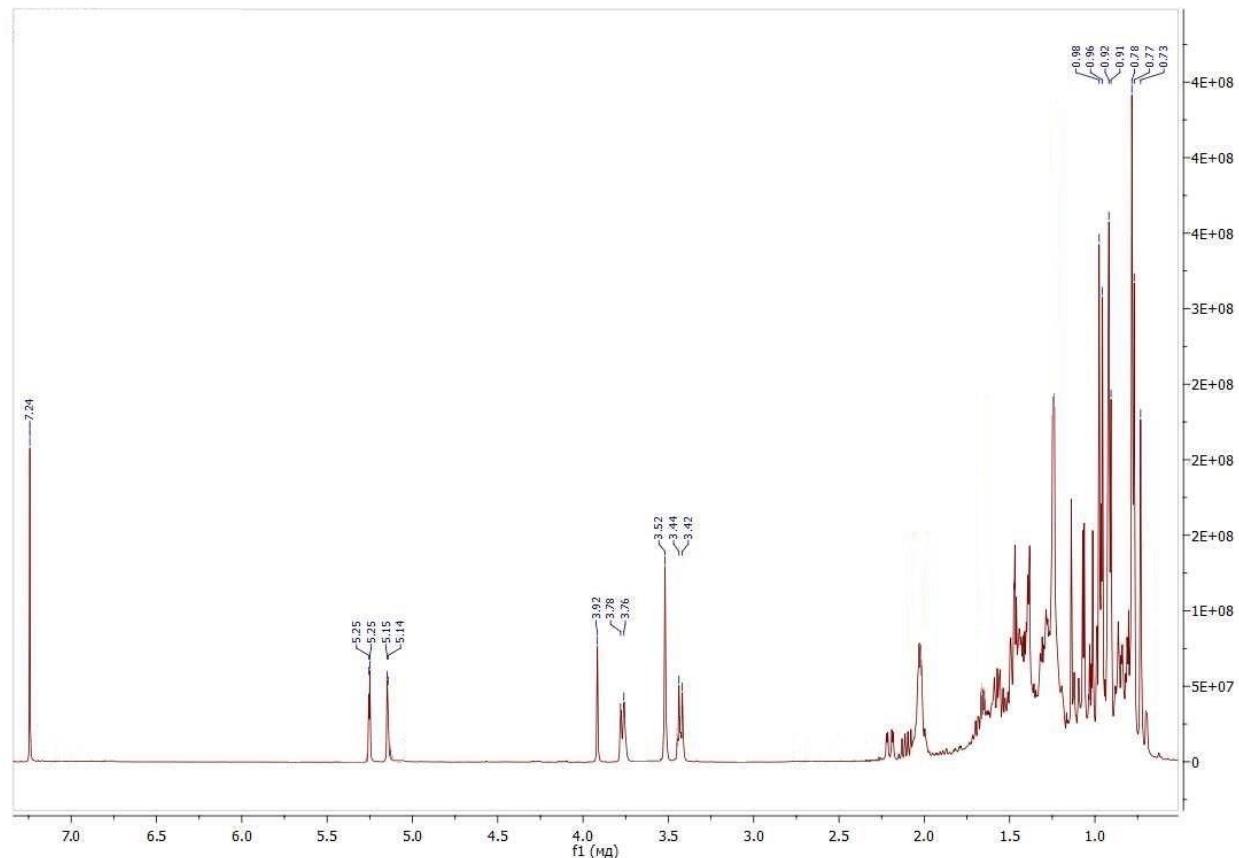
¹³C NMR (CDCl₃) (1S,3S)-1α,3β-dihydroxy-3-ethyl-2-methylene-19β,28-epoxy-18αH-oleanane (15)
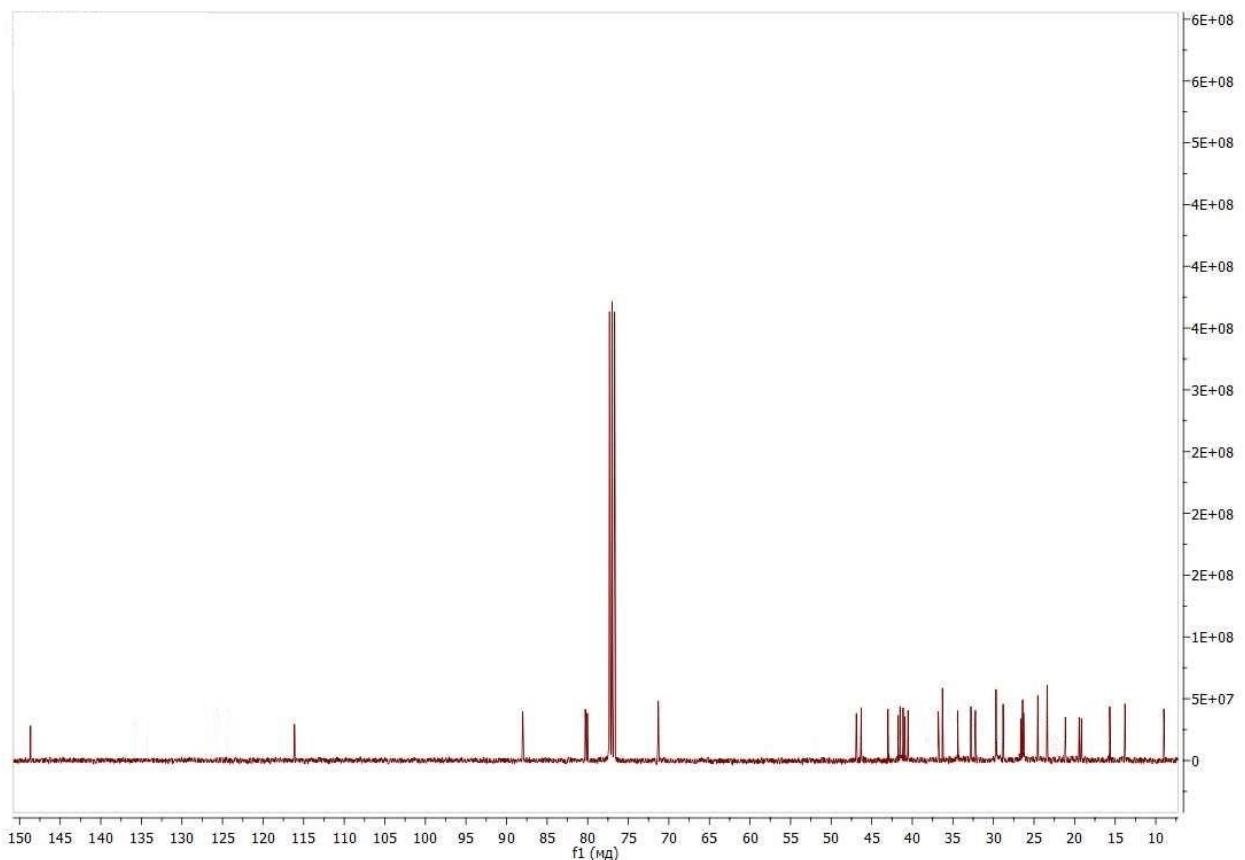
GC-MS (1*S*,3*S*)-1α,3β-dihydroxy-3-ethyl-2-methylene-19β,28-epoxy-18α*H*-oleanane (15)
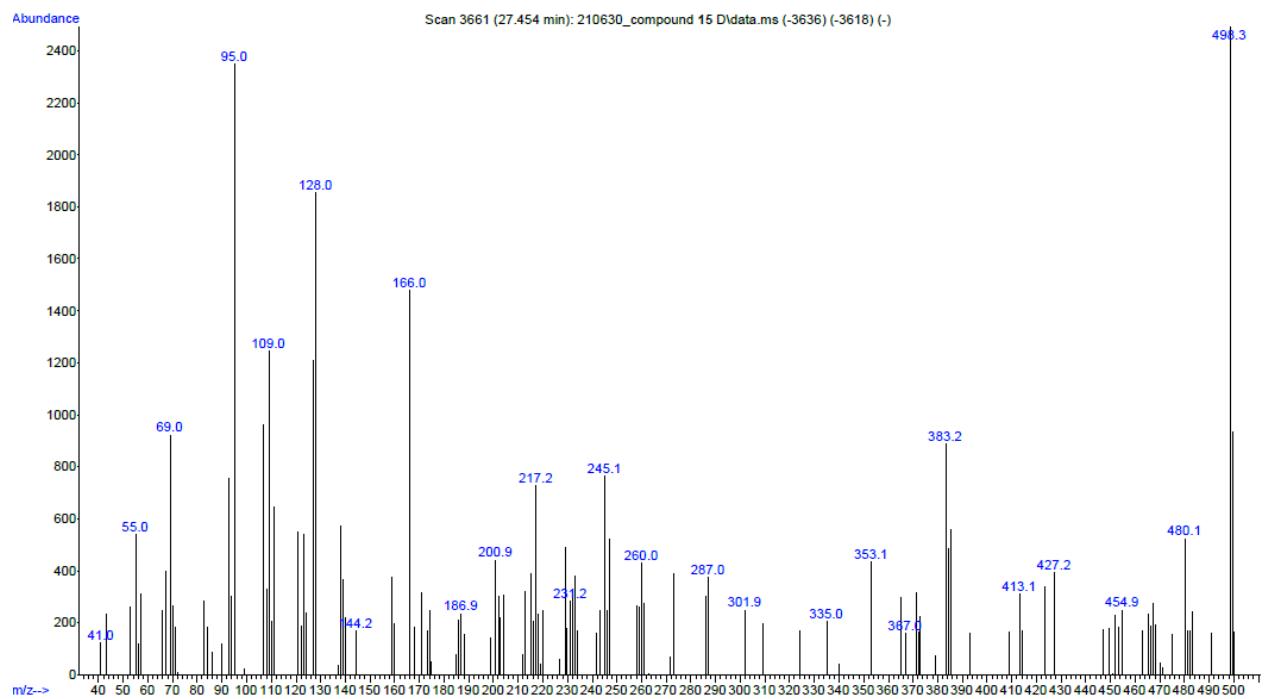
¹H NMR (2*S*,3*S*)-2,3-dimethyl-(2,3),(19β,28)-diepoxy-18α*H*-olean-1-one (16)
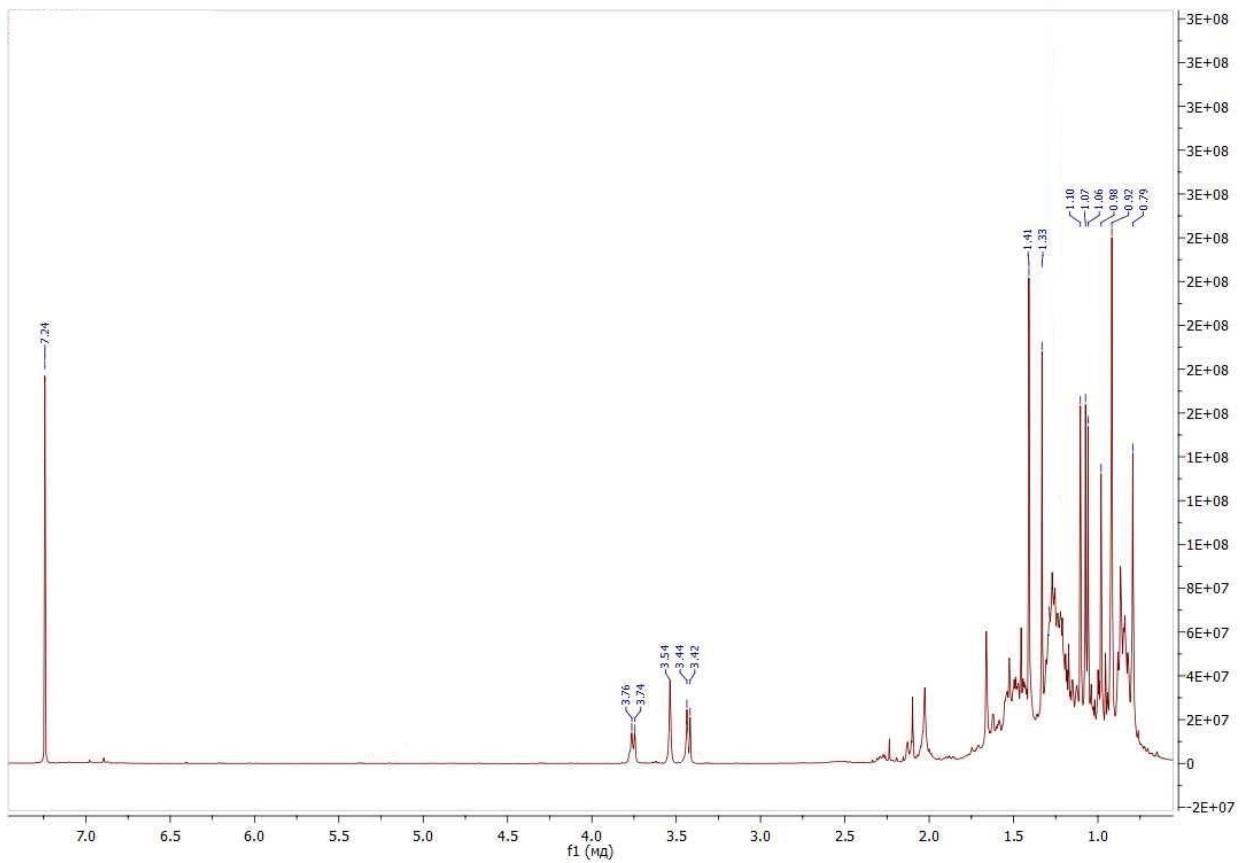
13C NMR (CDCl3) (2*S*,3*S*)-2,3-dimethyl-(2,3),(19β,28)-diepoxy-18α*H*-olean-1-one (16)
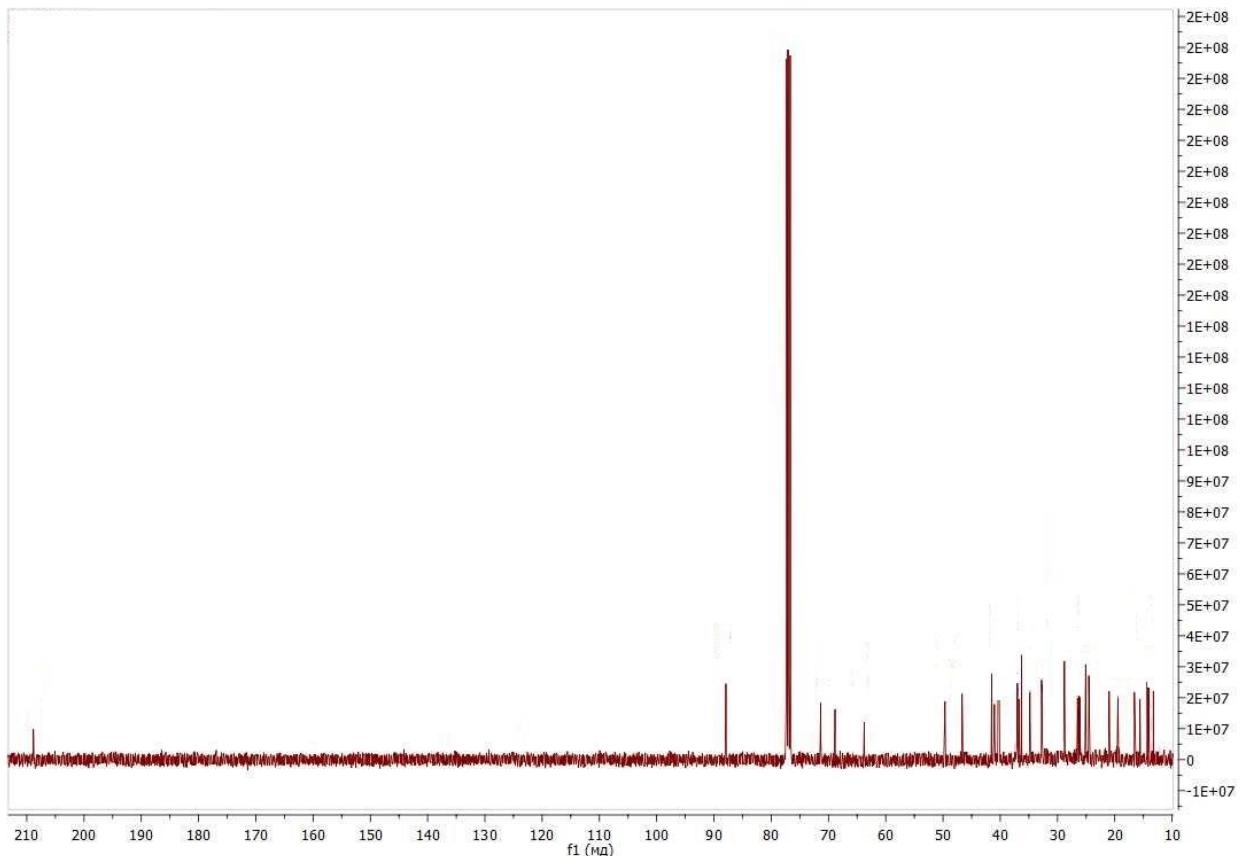
GC-MS (2*S*,3*S*)-2,3-dimethyl-(2,3),(19β,28)-diepoxy-18α*H*-olean-1-one (16)
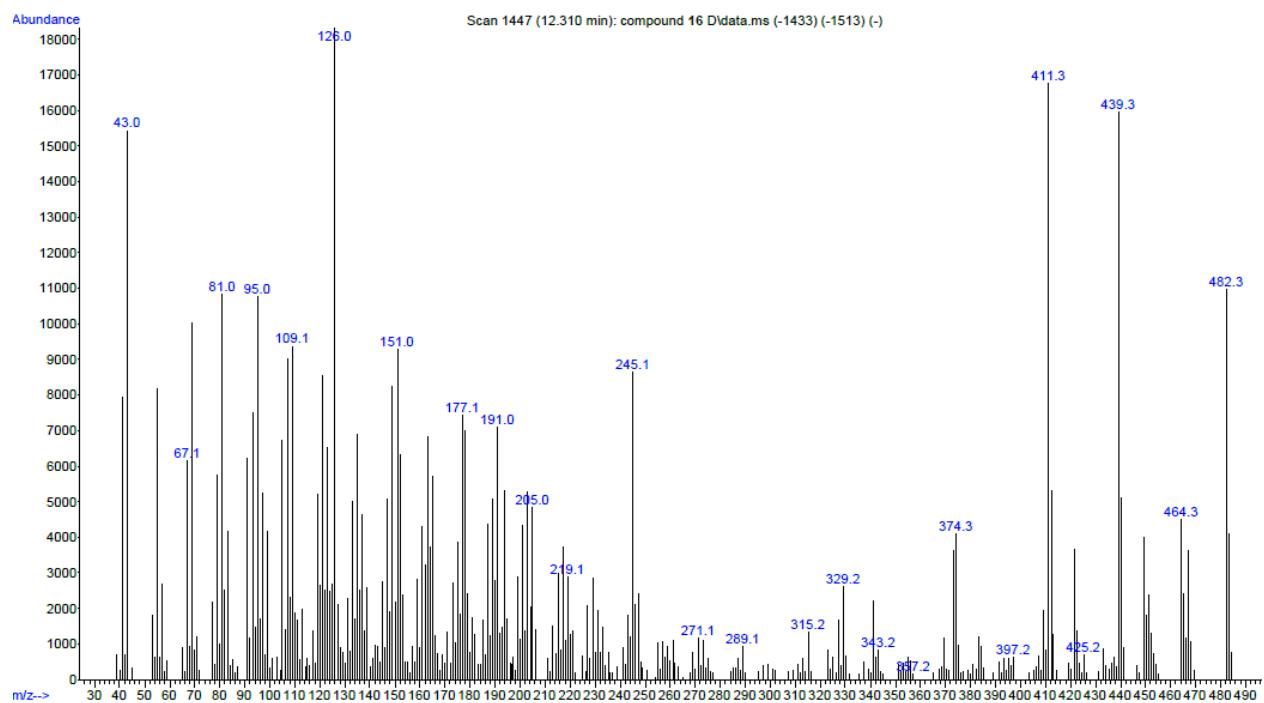
¹H NMR (2*S*,3*S*)-3-ethyl-2-methyl-(2,3),(19β,28)-diepoxy-18α*H*-olean-1-one (17)
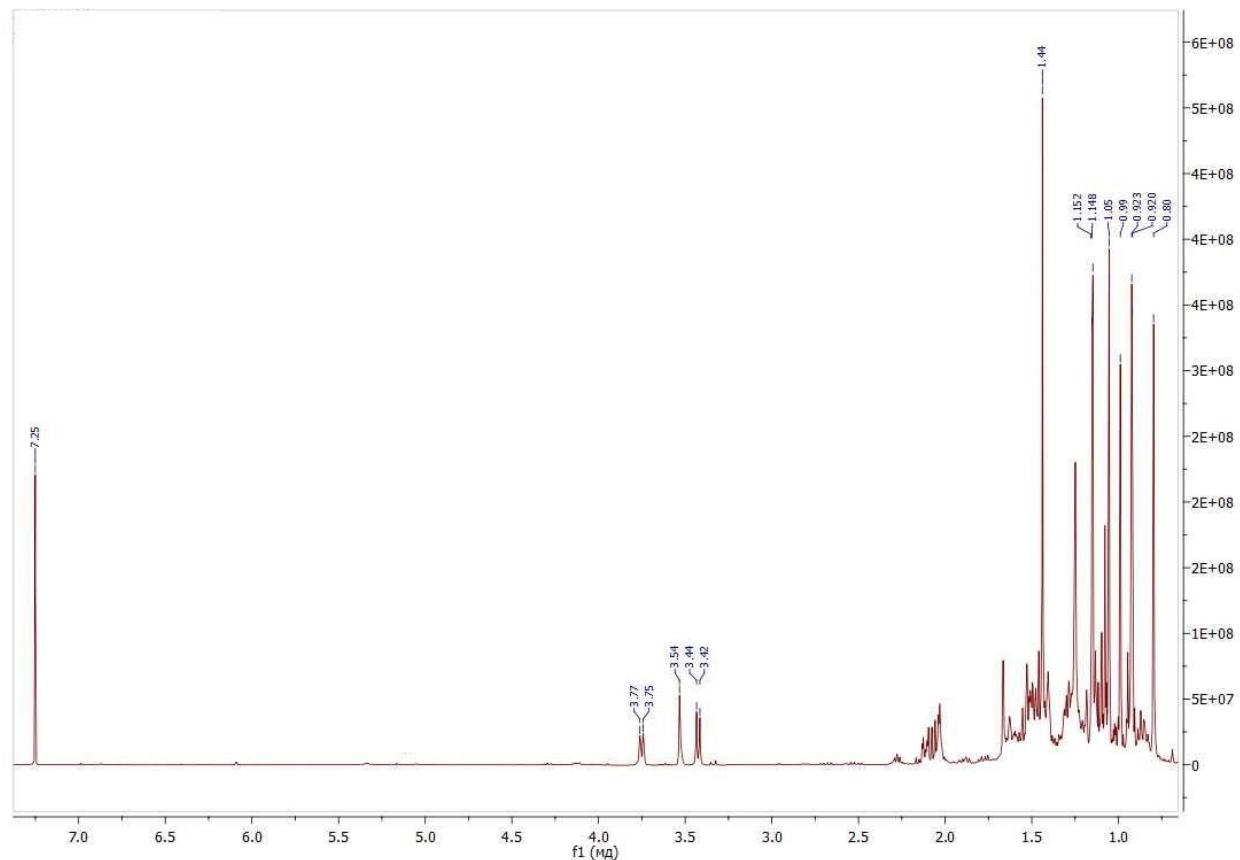
¹³C NMR (CDCl₃) (2*S*,3*S*)-3-ethyl-2-methyl-(2,3),(19β,28)-diepoxy-18α*H*-olean-1-one (17)
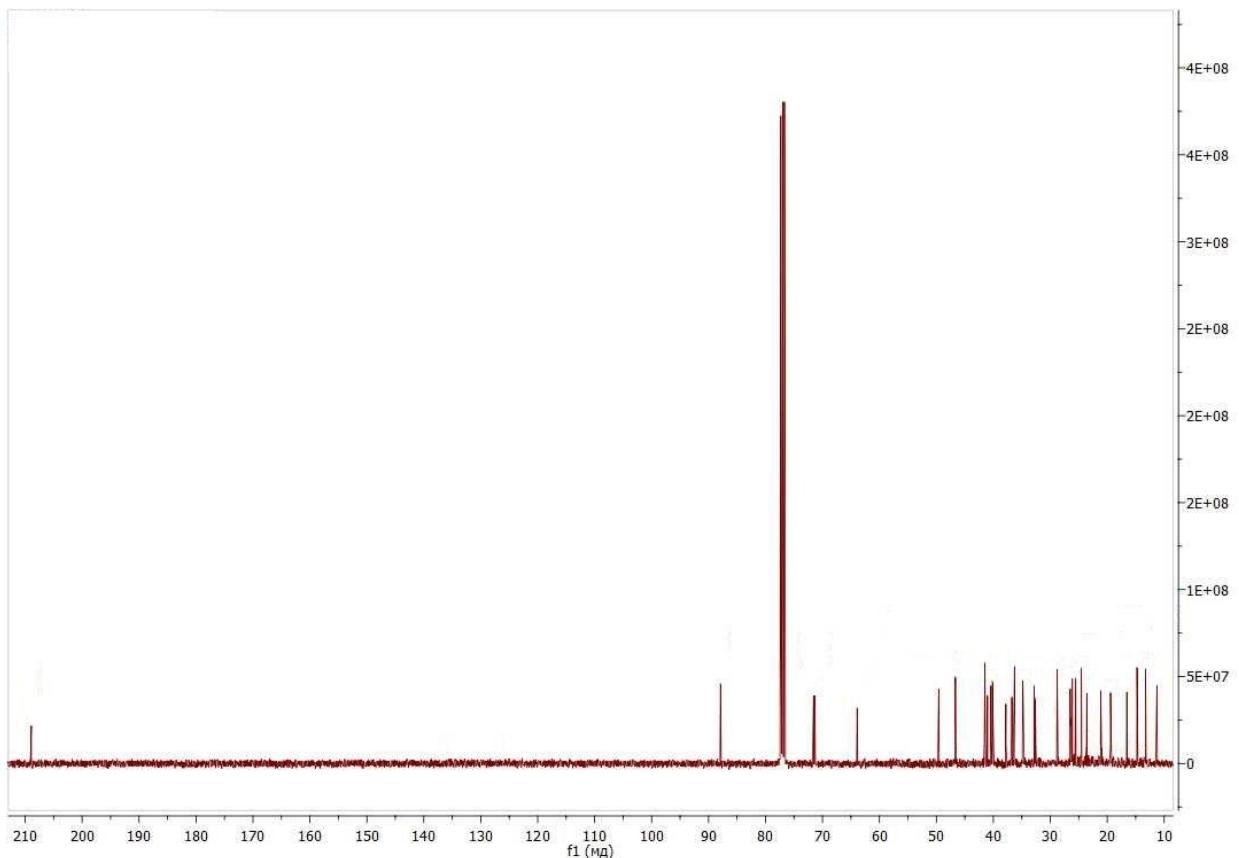
GC-MS (2*S*,3*S*)-3-ethyl-2-methyl-(2,3),(19β,28)-diepoxy-18α*H*-olean-1-one (17)
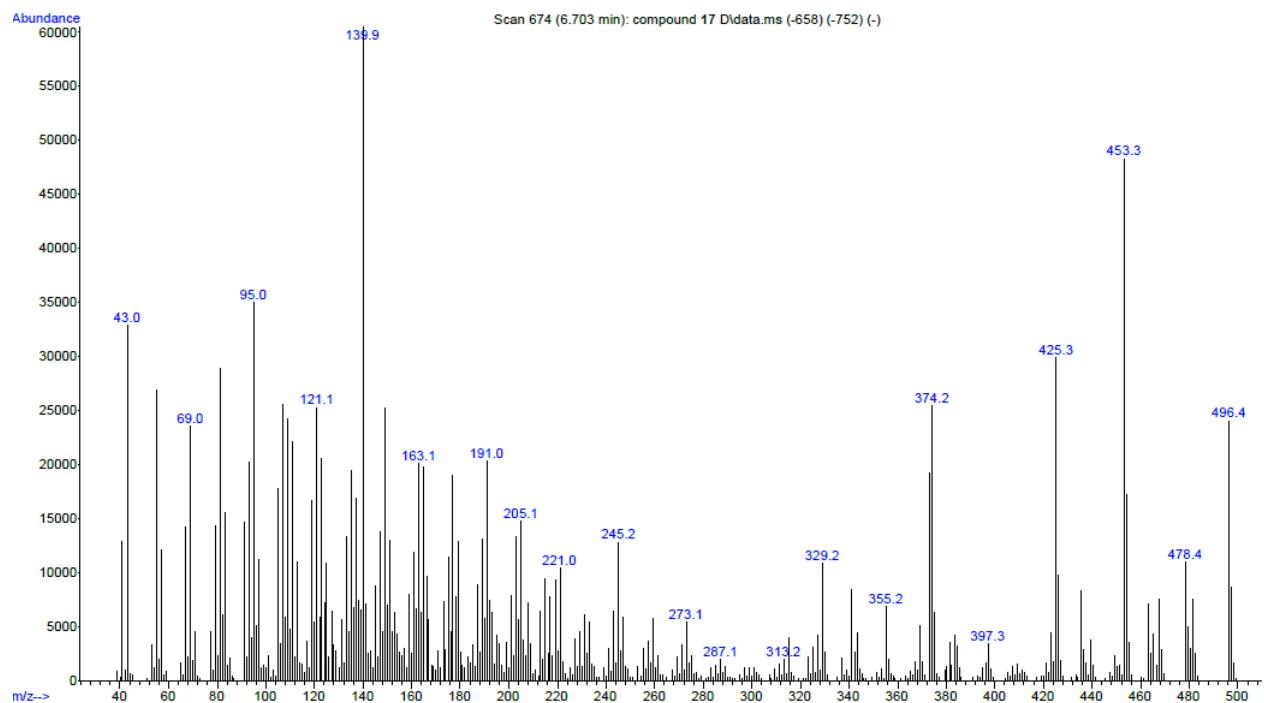
Single crystal X-ray crystallographic analysis

Table S1. Crystal data and structure refinement for **3**.

Empirical formula	$C_{31}H_{50}O_2$
Formula weight	454.71

Temperature, K	295.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a, Å	7.8661(9)
b, Å	18.674(2)
c, Å	36.982(6)
Volume, Å^3	5432.2(13)
Z	8
Density (calculated), g/cm^3	1.112
Absorption coefficient, mm^{-1}	0.067
F(000)	2016.0
Crystal size, mm^3	$0.5 \times 0.32 \times 0.15$
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection, °	5.924 to 58.69
Index ranges	-10 ≤ h ≤ 7, -21 ≤ k ≤ 25, -48 ≤ l ≤ 45
Reflections collected	35617
Independent reflections	13094 [R_{int} = 0.0458, R_{sigma} = 0.0720]
Data/restraints/parameters	13094/2/619
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0615, wR_2 = 0.1164
Final R indexes [all data]	R_1 = 0.1138, wR_2 = 0.1417
Largest diff. peak/hole, eÅ^{-3}	0.19/-0.18

Table S2. Crystal data and structure refinement for **4a**.

Empirical formula	$C_{31}H_{48}O_3$
Formula weight	468.69
Temperature, K	295.15
Crystal system	monoclinic
Space group	$P2_1$
a, Å	6.8715(19)
b, Å	12.581(3)
c, Å	15.706(4)
β, °	99.87(2)
Volume, Å^3	1337.7(6)
Z	2
Density (calculated), g/cm^3	1.164
Absorption coefficient, mm^{-1}	0.072
F(000)	516.0
Crystal size, mm^3	$0.48 \times 0.2 \times 0.12$
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection, °	6.018 to 58.694
Index ranges	-9 ≤ h ≤ 8, -16 ≤ k ≤ 17, -20 ≤ l ≤ 19
Reflections collected	11784
Independent reflections	6210 [R_{int} = 0.0344, R_{sigma} = 0.0488]
Data/restraints/parameters	6210/1/315
Goodness-of-fit on F^2	1.028

Final R indexes [I>=2σ (I)]	R$_1$ = 0.0545, wR$_2$ = 0.1188
Final R indexes [all data]	R$_1$ = 0.0746, wR$_2$ = 0.1347
Largest diff. peak/hole, eÅ^{-3}	0.14/-0.21

Table S3. Crystal data and structure refinement for **7**.

Empirical formula	C$_{32}$H$_{52}$O$_2$
Formula weight	468.73
Temperature, K	295.15
Crystal system	orthorhombic
Space group	P2$_1$2$_1$2$_1$
a, Å	12.059(3)
b, Å	13.264(3)
c, Å	17.403(3)
Volume, Å^3	2783.6(11)
Z	4
Density (calculated), g/cm^3	1.118
Absorption coefficient, mm^{-1}	0.067
F(000)	1040.0
Crystal size, mm^3	0.56 × 0.45 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection, °	6.144 to 58.632
Index ranges	-15 ≤ h ≤ 11, -15 ≤ k ≤ 17, -15 ≤ l ≤ 23
Reflections collected	10656
Independent reflections	6080 [R$_{int}$ = 0.0272, R$_{sigma}$ = 0.0513]
Data/restraints/parameters	6080/0/320
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R$_1$ = 0.0551, wR$_2$ = 0.1143
Final R indexes [all data]	R$_1$ = 0.0801, wR$_2$ = 0.1300
Largest diff. peak/hole, eÅ^{-3}	0.20/-0.16

Table S4. Crystal data and structure refinement for **8**.

Empirical formula	C$_{33}$H$_{54}$O$_2$
Formula weight	482.76
Temperature, K	295.15
Crystal system	orthorhombic
Space group	P2$_1$2$_1$2$_1$
a, Å	12.230(3)
b, Å	13.313(3)
c, Å	17.488(3)
Volume, Å^3	2847.5(11)
Z	4
Density (calculated), g/cm^3	1.126
Absorption coefficient, mm^{-1}	0.067
F(000)	1072.0
Crystal size, mm^3	0.5 × 0.35 × 0.22

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection, °	6.494 to 58.89
Index ranges	-14 ≤ h ≤ 15, -18 ≤ k ≤ 14, -23 ≤ l ≤ 22
Reflections collected	14727
Independent reflections	6740 [R_{int} = 0.0347, R_{sigma} = 0.0544]
Data/restraints/parameters	6740/1/329
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0623, wR_2 = 0.1413
Final R indexes [all data]	R_1 = 0.0884, wR_2 = 0.1603
Largest diff. peak/hole, $eÅ^{-3}$	0.40/-0.22

Table S5. Crystal data and structure refinement for **12**.

Empirical formula	$C_{37}H_{54}O_3$
Formula weight	546.80
Temperature, K	295.15
Crystal system	monoclinic
Space group	$P2_1$
a, Å	7.7161(12)
b, Å	20.087(3)
c, Å	23.884(4)
β, °	94.519(15)
Volume, $Å^3$	3690.5(10)
Z	4
Density (calculated), g/cm^3	0.984
Absorption coefficient, mm^{-1}	0.060
F(000)	1200.0
Crystal size, mm^3	0.46 × 0.28 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection, °	5.518 to 58.798
Index ranges	-9 ≤ h ≤ 10, -25 ≤ k ≤ 27, -30 ≤ l ≤ 32
Reflections collected	42332
Independent reflections	17443 [R_{int} = 0.0596, R_{sigma} = 0.0944]
Data/restraints/parameters	17443/3/745
Goodness-of-fit on F^2	0.933
Final R indexes [I>=2σ (I)]	R_1 = 0.0599, wR_2 = 0.1410
Final R indexes [all data]	R_1 = 0.1365, wR_2 = 0.1820
Largest diff. peak/hole, $eÅ^{-3}$	0.15/-0.15

Table S6. Crystal data and structure refinement for **13**.

Empirical formula	$C_{31}H_{50}O_3$
Formula weight	470.71
Temperature, K	295.15
Crystal system	monoclinic
Space group	$P2_1$
a, Å	7.102(2)

b, Å	12.082(5)
c, Å	15.784(7)
β, °	95.88(4)
Volume, Å^3	1347.2(9)
Z	2
Density (calculated), g/cm^3	1.160
Absorption coefficient, mm^{-1}	0.072
F(000)	520.0
Crystal size, mm^3	0.5 × 0.4 × 0.02
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection, °	6.076 to 58.776
Index ranges	-9 ≤ h ≤ 7, -16 ≤ k ≤ 10, -20 ≤ l ≤ 17
Reflections collected	6513
Independent reflections	4585 [R_{int} = 0.0587, R_{sigma} = 0.1026]
Data/restraints/parameters	4585/1/319
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0761, wR_2 = 0.1794
Final R indexes [all data]	R_1 = 0.1293, wR_2 = 0.2248
Largest diff. peak/hole, eÅ^{-3}	0.25/-0.26

Table S7. Crystal data and structure refinement for **14**.

Empirical formula	$C_{31}H_{50}O_3 \cdot 2CHCl_3$
Formula weight	709.44
Temperature, K	295.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a, Å	10.753(2)
b, Å	11.3197(17)
c, Å	29.710(7)
Volume, Å^3	3616.2(12)
Z	4
Density (calculated), g/cm^3	1.303
Absorption coefficient, mm^{-1}	0.506
F(000)	1504.0
Crystal size, mm^3	0.45 × 0.35 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection, °	5.902 to 58.562
Index ranges	-13 ≤ h ≤ 14, -15 ≤ k ≤ 9, -25 ≤ l ≤ 40
Reflections collected	17455
Independent reflections	8303 [R_{int} = 0.0429, R_{sigma} = 0.0778]
Data/restraints/parameters	8303/0/388
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0679, wR_2 = 0.1544
Final R indexes [all data]	R_1 = 0.1453, wR_2 = 0.1940
Largest diff. peak/hole, eÅ^{-3}	0.28/-0.28
Flack parameter	0.02(4)

Table S8. Crystal data and structure refinement for **15**.

Empirical formula	$C_{33}H_{54}O_3$
Formula weight	498.76
Temperature, K	295.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a, Å	7.2239(17)
b, Å	12.282(3)
c, Å	32.677(7)
Volume, Å^3	2899.1(12)
Z	4
Density (calculated), g/cm^3	1.143
Absorption coefficient, mm^{-1}	0.070
F(000)	1104.0
Crystal size, mm^3	$0.5 \times 0.15 \times 0.1$
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection, °	5.776 to 59.188
Index ranges	$-6 \leq h \leq 9$, $-16 \leq k \leq 10$, $-30 \leq l \leq 43$
Reflections collected	11280
Independent reflections	6564 [R_{int} = 0.0374, R_{sigma} = 0.0640]
Data/restraints/parameters	6564/0/338
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0701, wR_2 = 0.1667
Final R indexes [all data]	R_1 = 0.1005, wR_2 = 0.1948
Largest diff. peak/hole, eÅ^{-3}	0.44/-0.23

Table S9. Crystal data and structure refinement for **16**.

Empirical formula	$C_{32}H_{50}O_3$
Formula weight	482.72
Temperature, K	295.15
Crystal system	monoclinic
Space group	$P2_1$
a, Å	6.7002(16)
b, Å	15.587(3)
c, Å	13.665(4)
β, °	103.50(3)
Volume, Å^3	1387.7(6)
Z	2
Density (calculated), g/cm^3	1.155
Absorption coefficient, mm^{-1}	0.072
F(000)	532.0
Crystal size, mm^3	$0.55 \times 0.36 \times 0.24$
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection, °	6.06 to 58.75
Index ranges	$-8 \leq h \leq 9$, $-20 \leq k \leq 20$, $-18 \leq l \leq 11$

Reflections collected	7208
Independent reflections	5266 [R_{int} = 0.0391, R_{sigma} = 0.0549]
Data/restraints/parameters	5266/1/325
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0585, wR_2 = 0.1389
Final R indexes [all data]	R_1 = 0.0788, wR_2 = 0.1595
Largest diff. peak/hole, eÅ^{-3}	0.23/-0.22

Table S10. Crystal data and structure refinement for **17**.

Empirical formula	$C_{33}H_{52}O_3$
Formula weight	496.74
Temperature, K	295.15
Crystal system	monoclinic
Space group	$P2_1$
a, Å	8.011(3)
b, Å	15.691(4)
c, Å	11.978(4)
β, °	107.98(4)
Volume, Å^3	1432.1(8)
Z	2
Density (calculated), g/cm^3	1.152
Absorption coefficient, mm^{-1}	0.071
F(000)	548.0
Crystal size, mm^3	0.56 × 0.44 × 0.35
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection, °	5.944 to 58.522
Index ranges	-10 ≤ h ≤ 10, -20 ≤ k ≤ 21, -15 ≤ l ≤ 14
Reflections collected	7225
Independent reflections	5551 [R_{int} = 0.0463, R_{sigma} = 0.0757]
Data/restraints/parameters	5551/1/334
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0724, wR_2 = 0.1681
Final R indexes [all data]	R_1 = 0.1003, wR_2 = 0.2028
Largest diff. peak/hole, eÅ^{-3}	0.28/-0.26