The synthesis of α,β-unsaturated 18αH,19βH-ursane methyl ketones

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Table of Contents

1. X-ray studies of 3β,28-dibenzoyloxy-l8α,19βH-ursa-20(21)-ene-29-al (4)

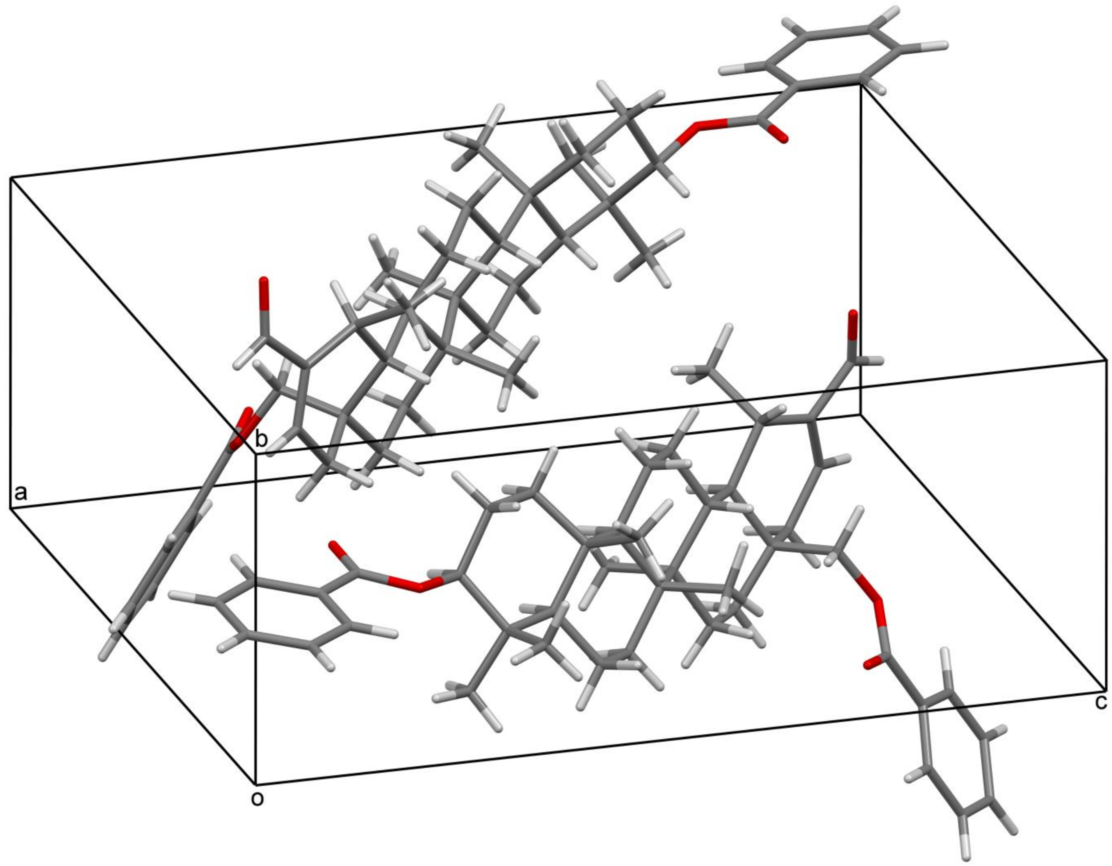


Figure S1. Packing of compound 3β,28-dibenzoyloxy-l8α,19βH-ursa-20(21)-ene-29-al **(4)** in crystalline lattice (CCDC 1914625).

Crystal structure determination

The unit cell parameters and the X-ray diffraction intensities were measured on the Xcalibur Ruby diffractometer. The empirical absorption correction was introduced by the multi-scan method using the SCALE3 ABSPACK algorithm[1]. Using the OLEX2[2], the structure was solved with the Superflip program[3] and refined by the full-matrix least-squares method in the anisotropic approximation for all non-hydrogen atoms using the SHELXL[4] program package. Positions of the hydrogen atoms were calculated from the Fourier synthesis of the electron density and refined using the "riding" model.

Crystal Data of 3β,28-dibenzoyloxy-l8α,19βH-ursa-20(21)-ene-29-al (4). $C_{44}H_{56}O_5$, M = 664.88, monoclinic, a = 13.786(3) Å, b = 7.5936(16) Å, c = 18.038(4) Å, β = 97.41(2)°, V = 1872.6(7) Å^3, T = 295(2), space group $P2_1$, Z = 2, μ(Mo Kα) = 0.075 mm^{-1}. The final refinement parameters: R_1 = 0.0635, wR_2 = 0.1442 [for observed 6068 reflections with $I > 2\sigma(I)$]; R_1 = 0.0937, wR_2 = 0.1686 (for all independent 8819 reflections, R_{int} = 0.0518), S = 1.022.

CCDC 1914625 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

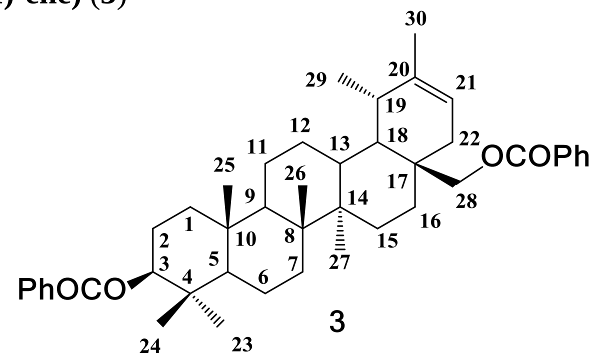
References

1. CrysAlisPro, Agilent Technologies, Version 1.171.37.33 (release 27-03-2014 CrysAlis171 .NET).

2. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339. http://dx.doi.org/10.1107/S0021889808042726
3. Palatinus, L.; Chapuis, G. *J. Appl. Cryst.* **2007**, *40*, 786. https://doi.org/10.1107/S0021889807029238
4. Sheldrick, G. M. *Acta Cryst*. **2015**, *C71*, 3. https://doi.org/10.1107/S2053229614024218

2. ^{1}H, ^{13}C NMR and 2D spectra

^{1}H NMR Dibenzoylheterobetulin (3β,28-dibenzoyloxy-l8αH,19βH-ursa-20(21)-ene) (3)



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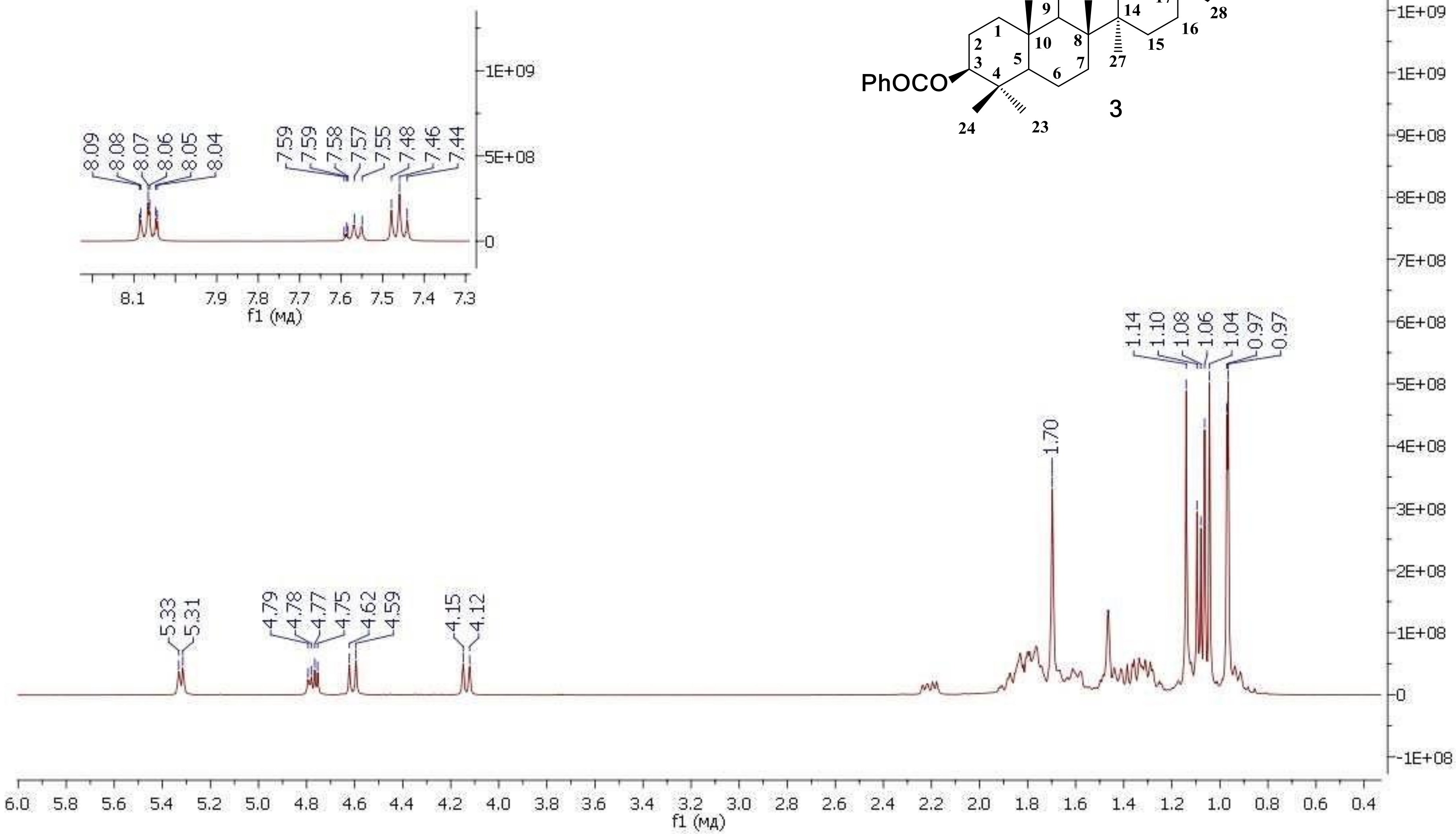

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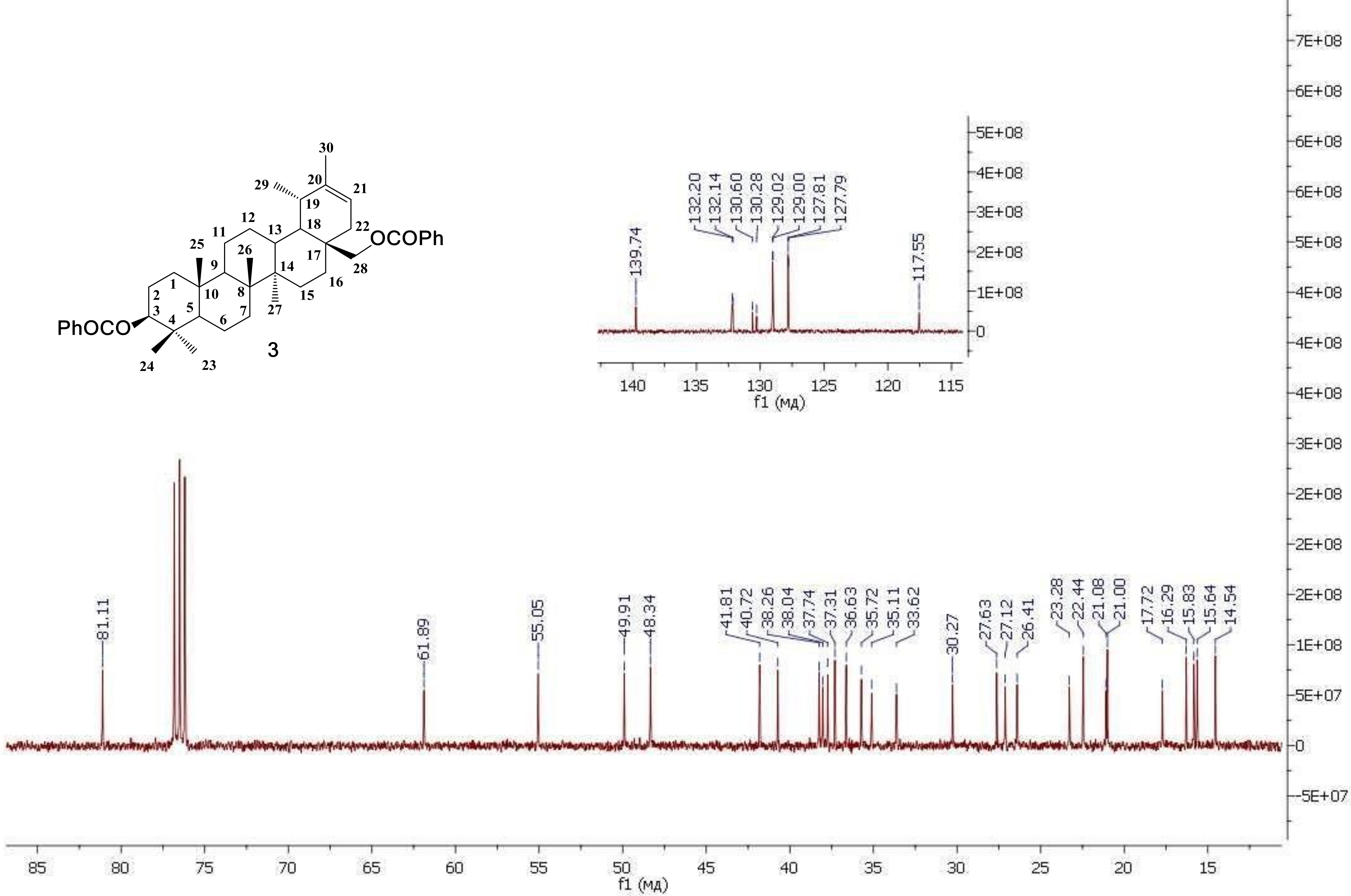

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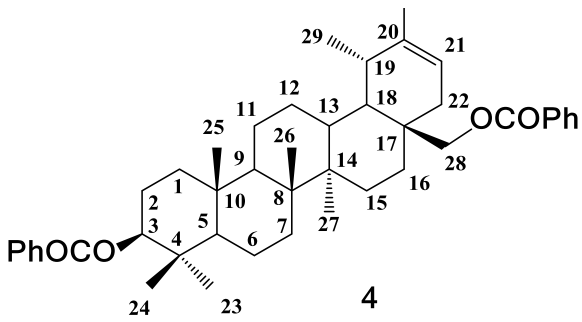

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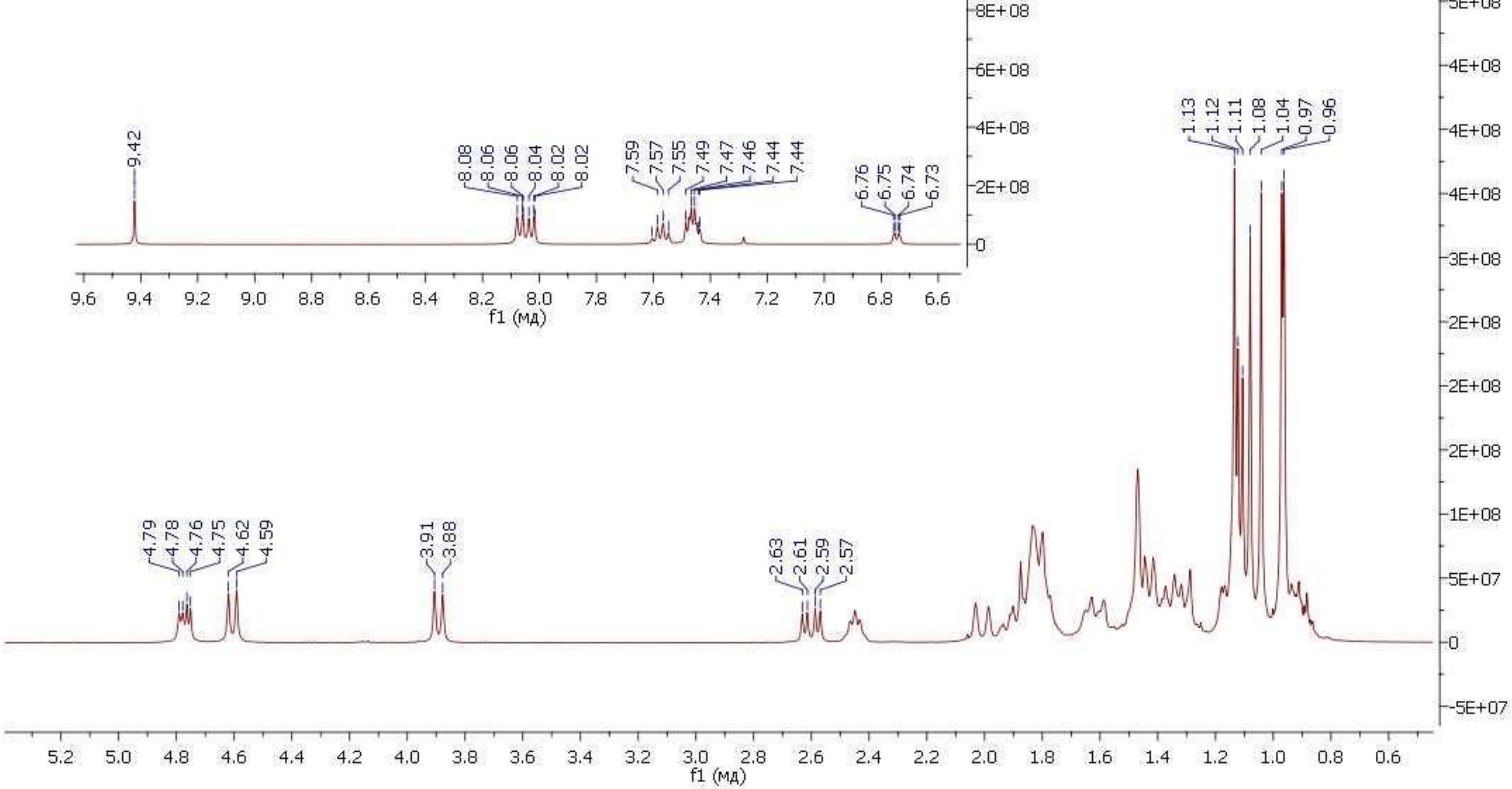

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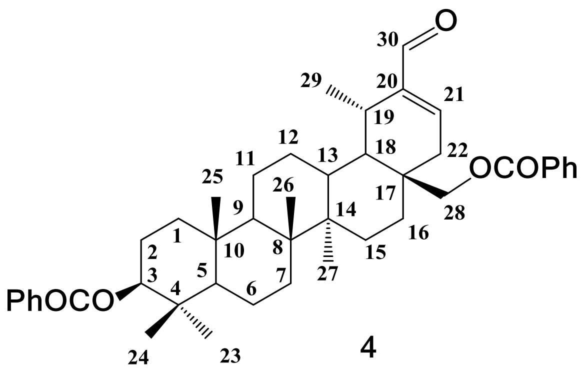

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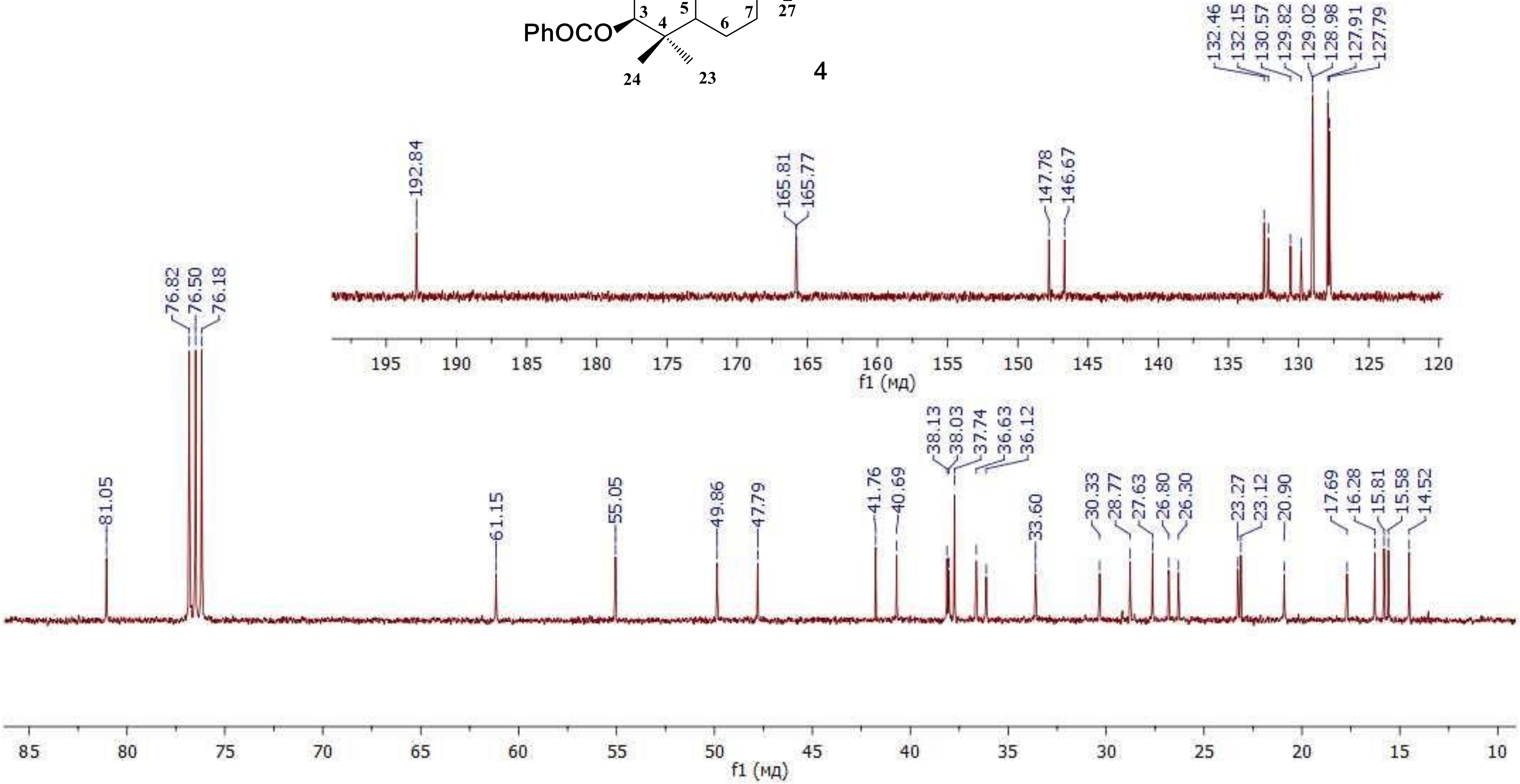

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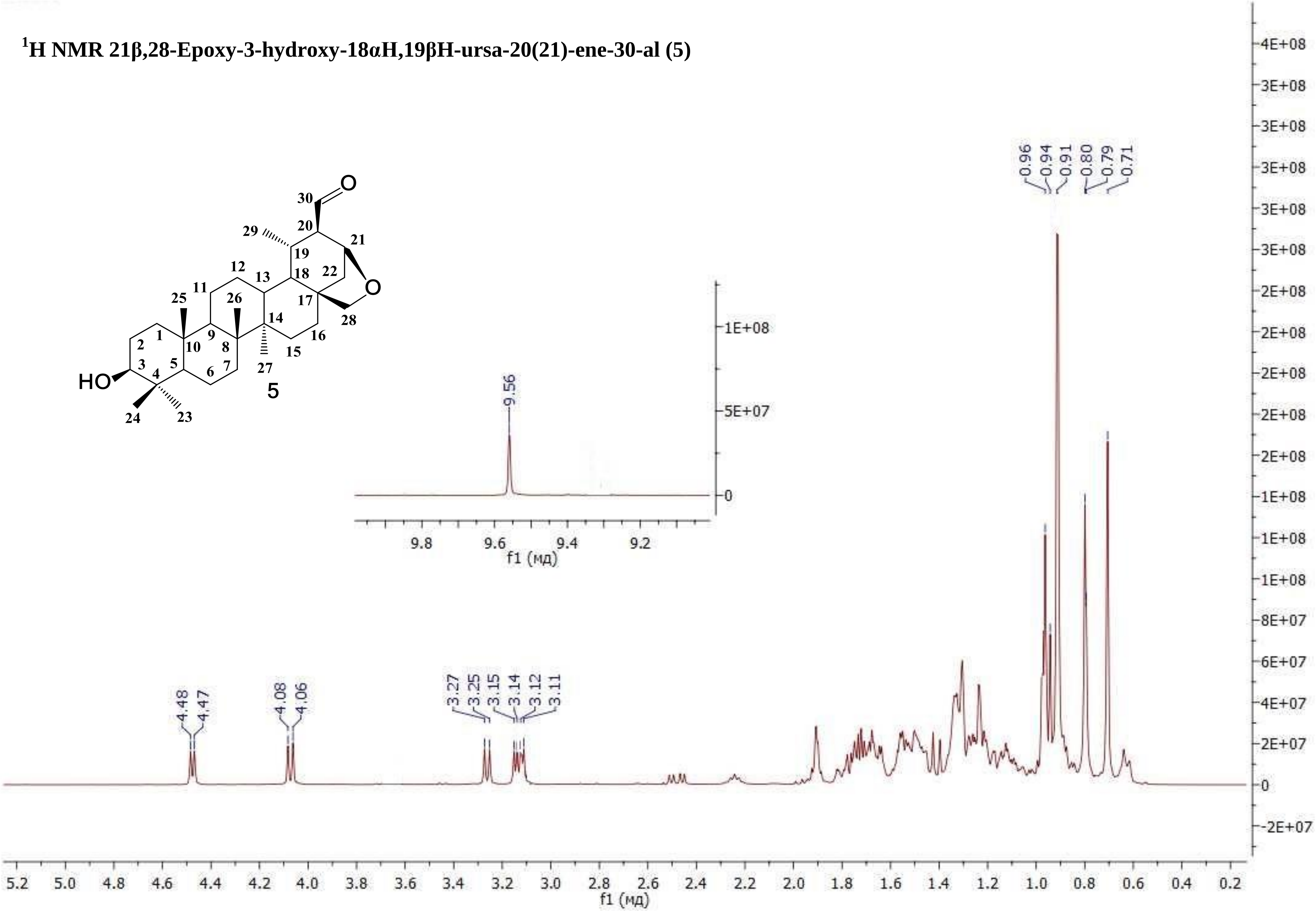

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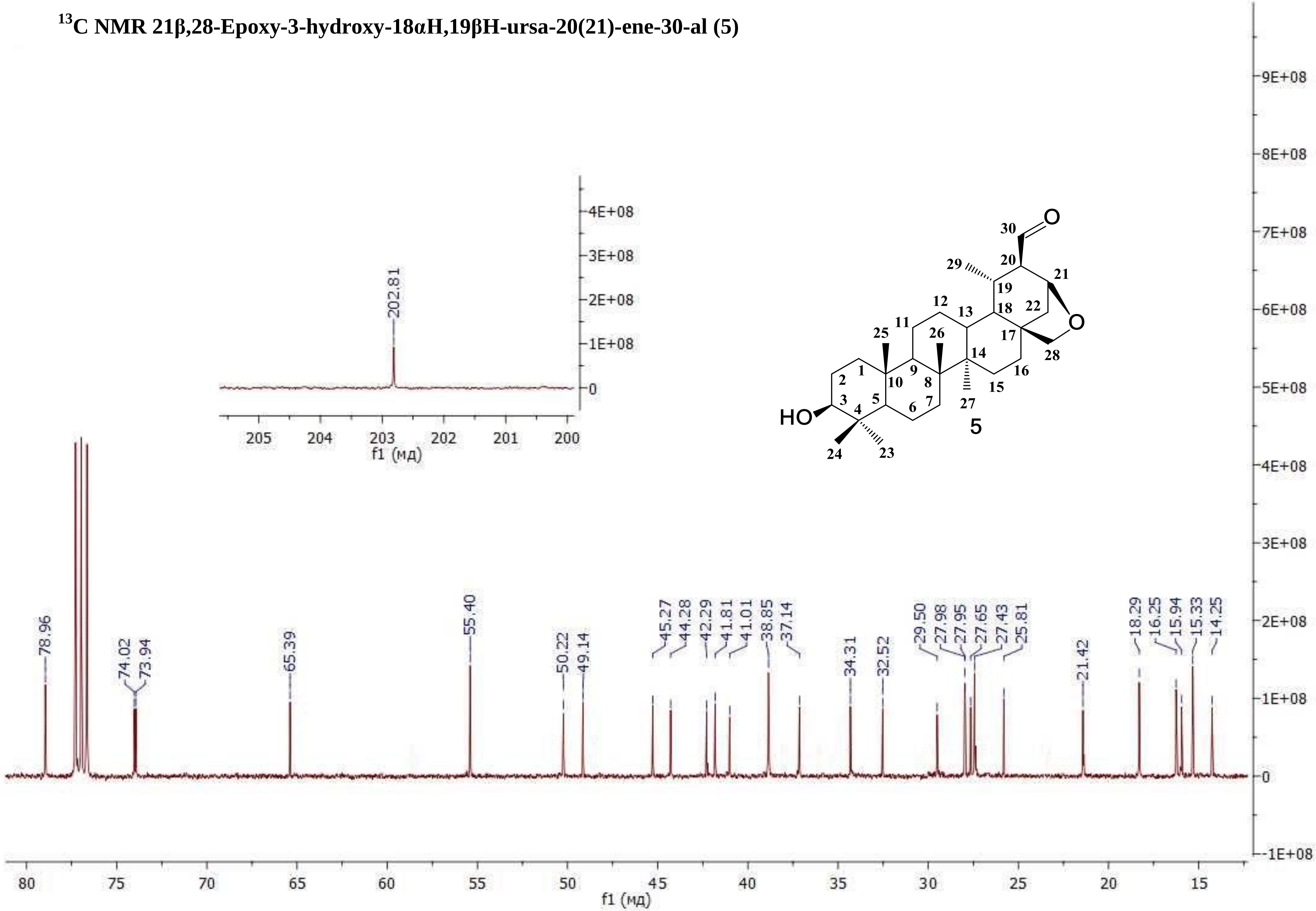

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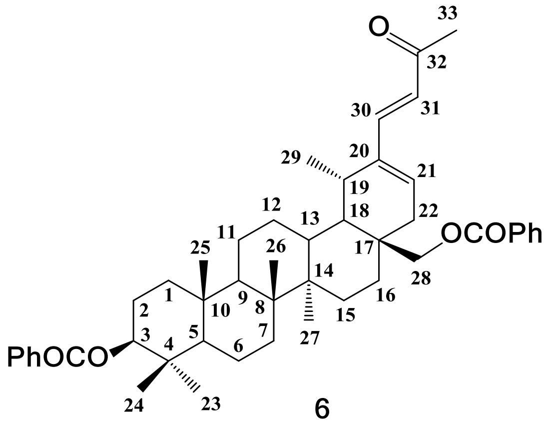

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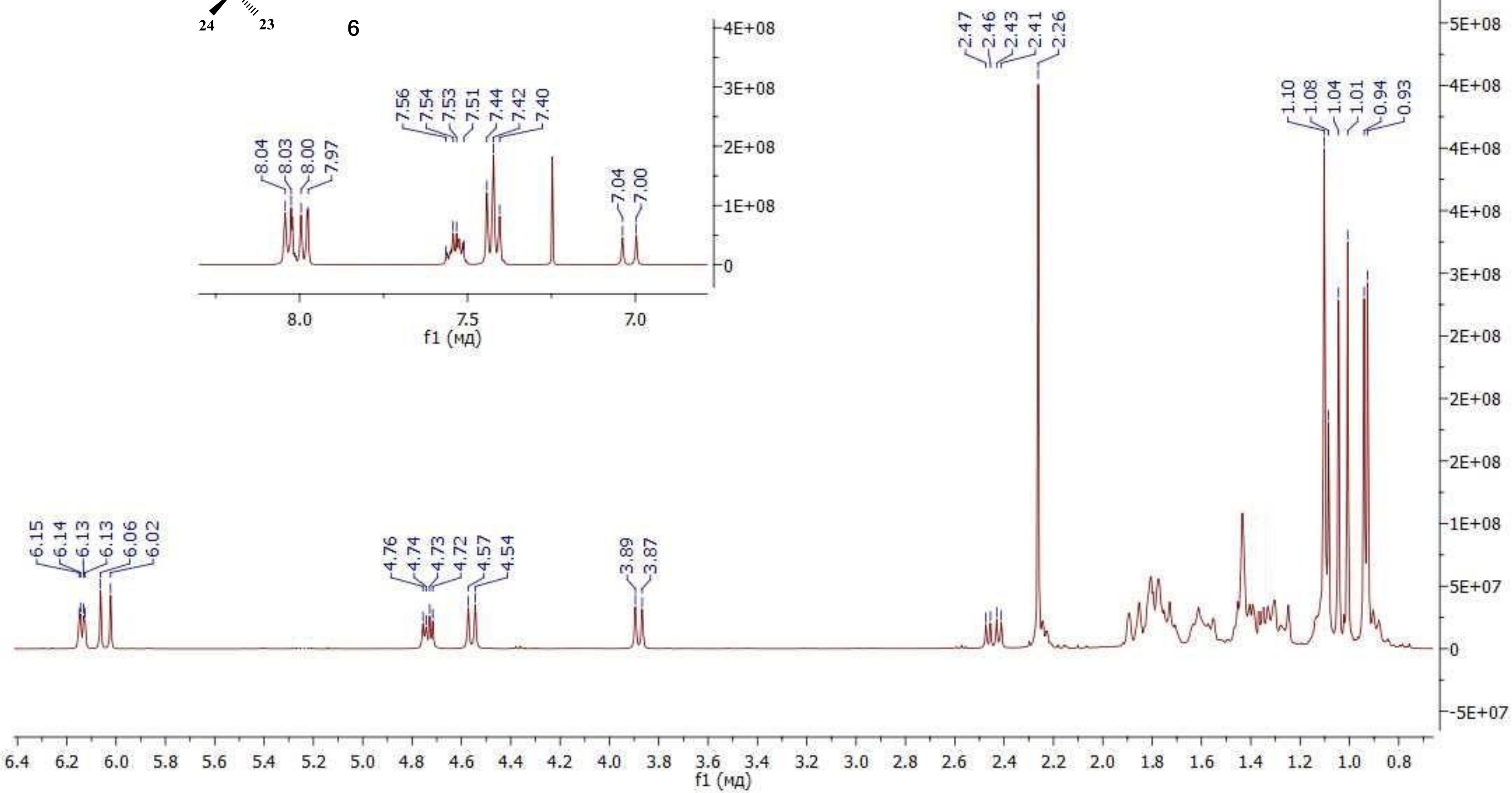

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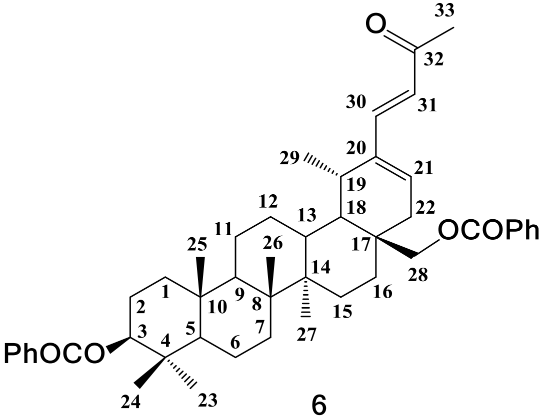

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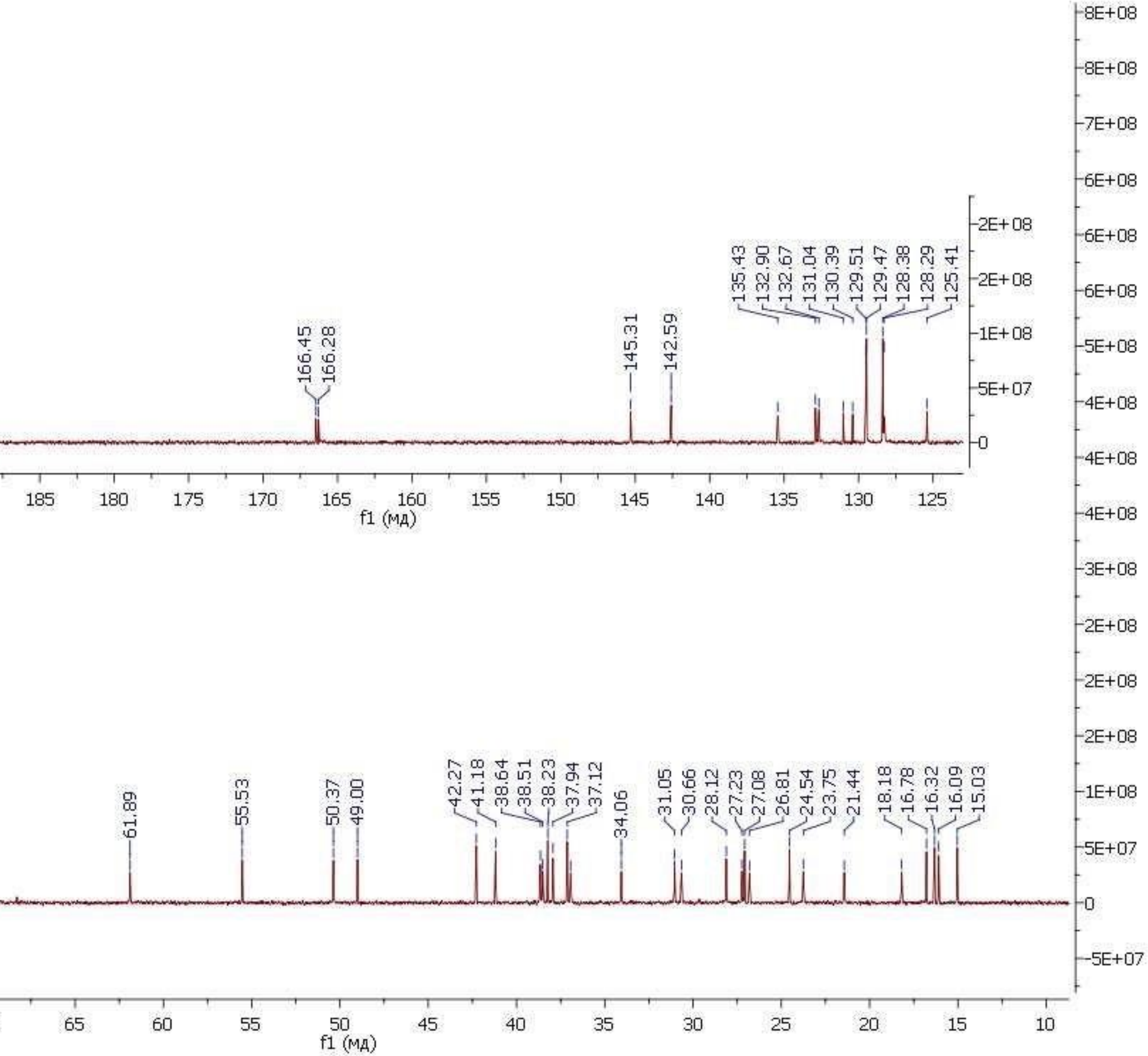

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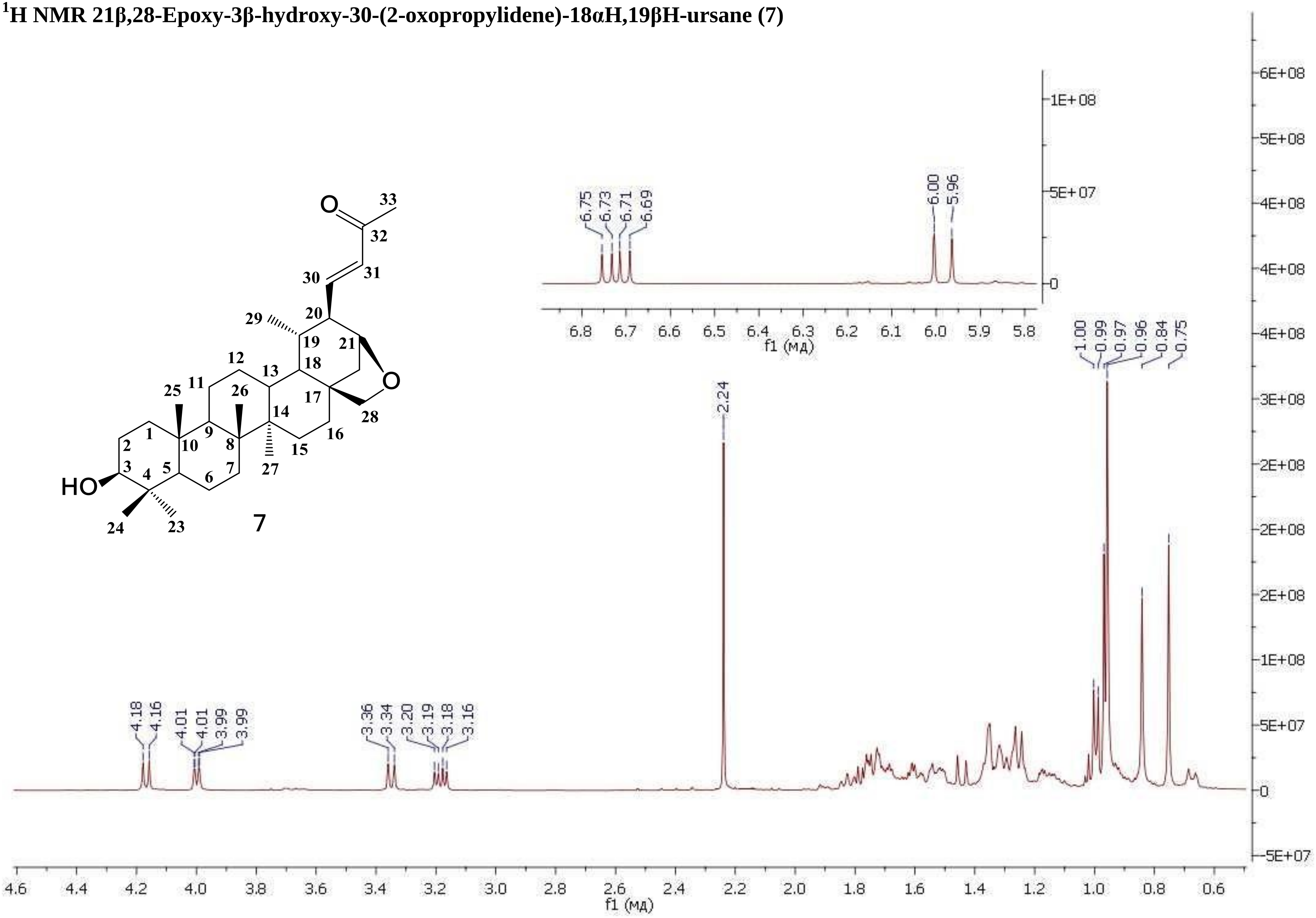

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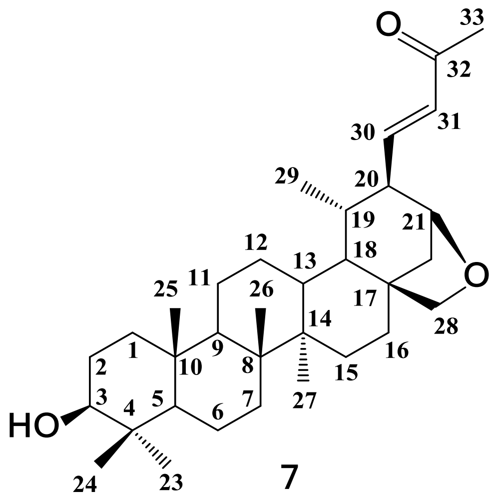

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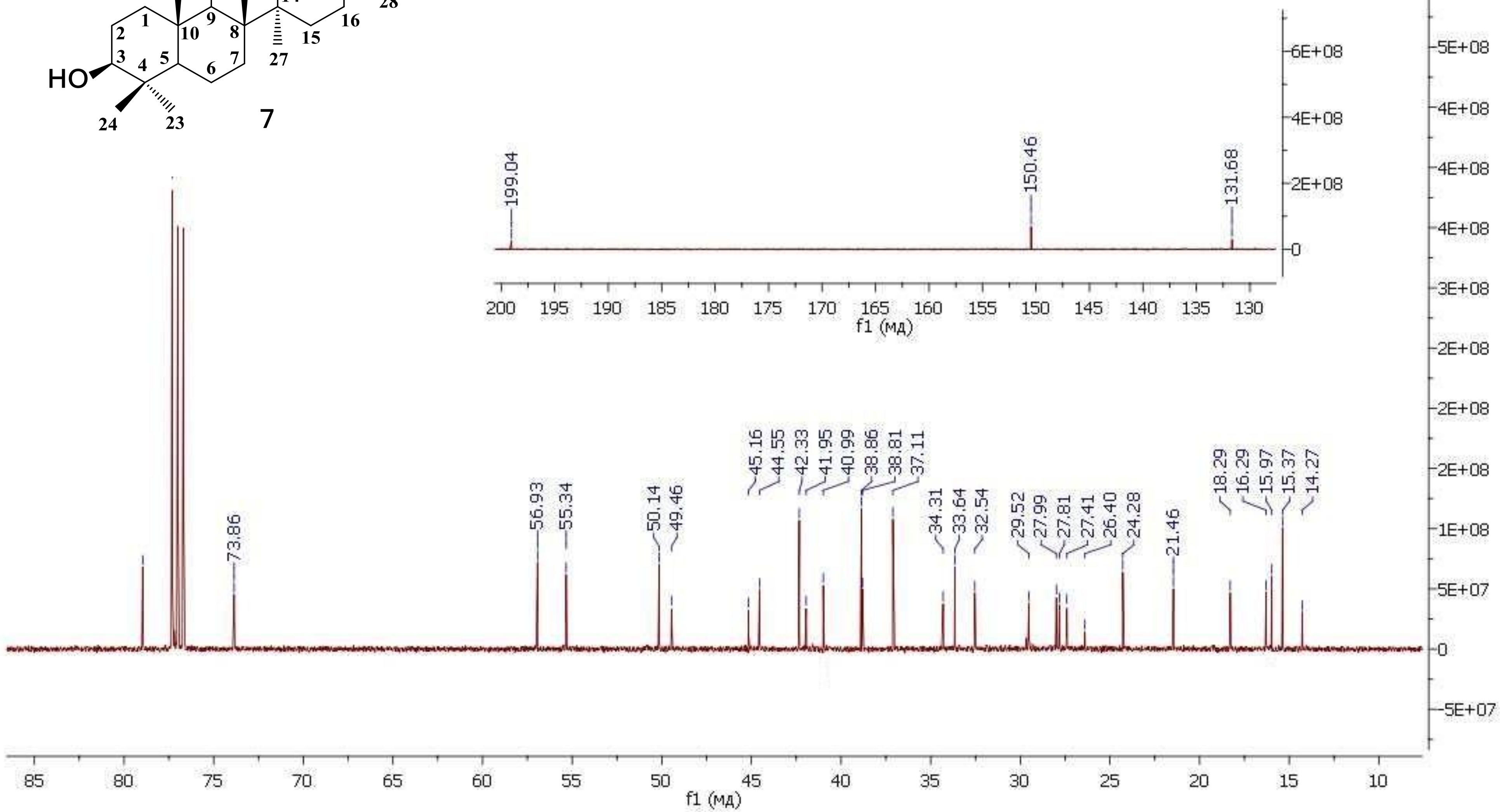
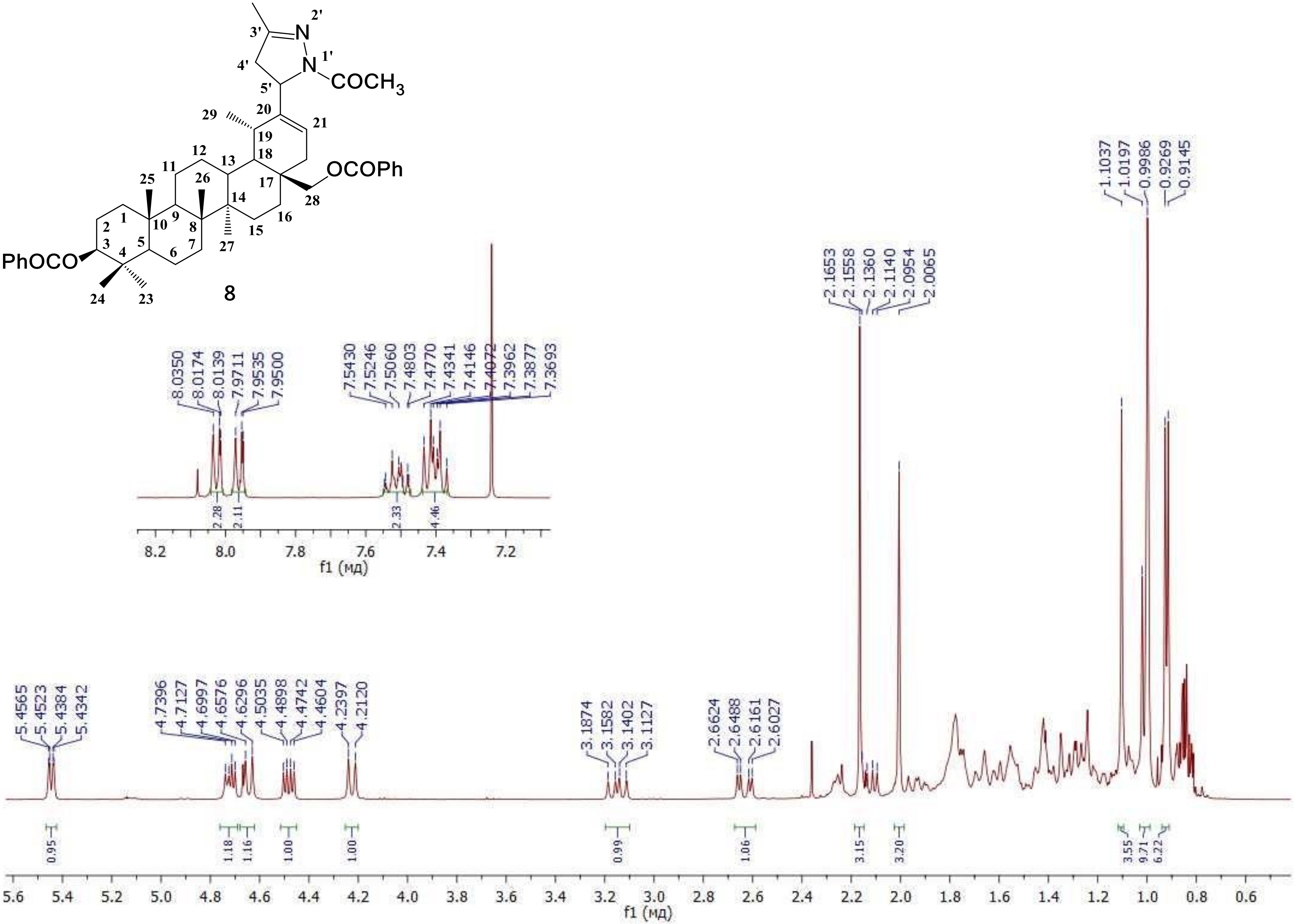
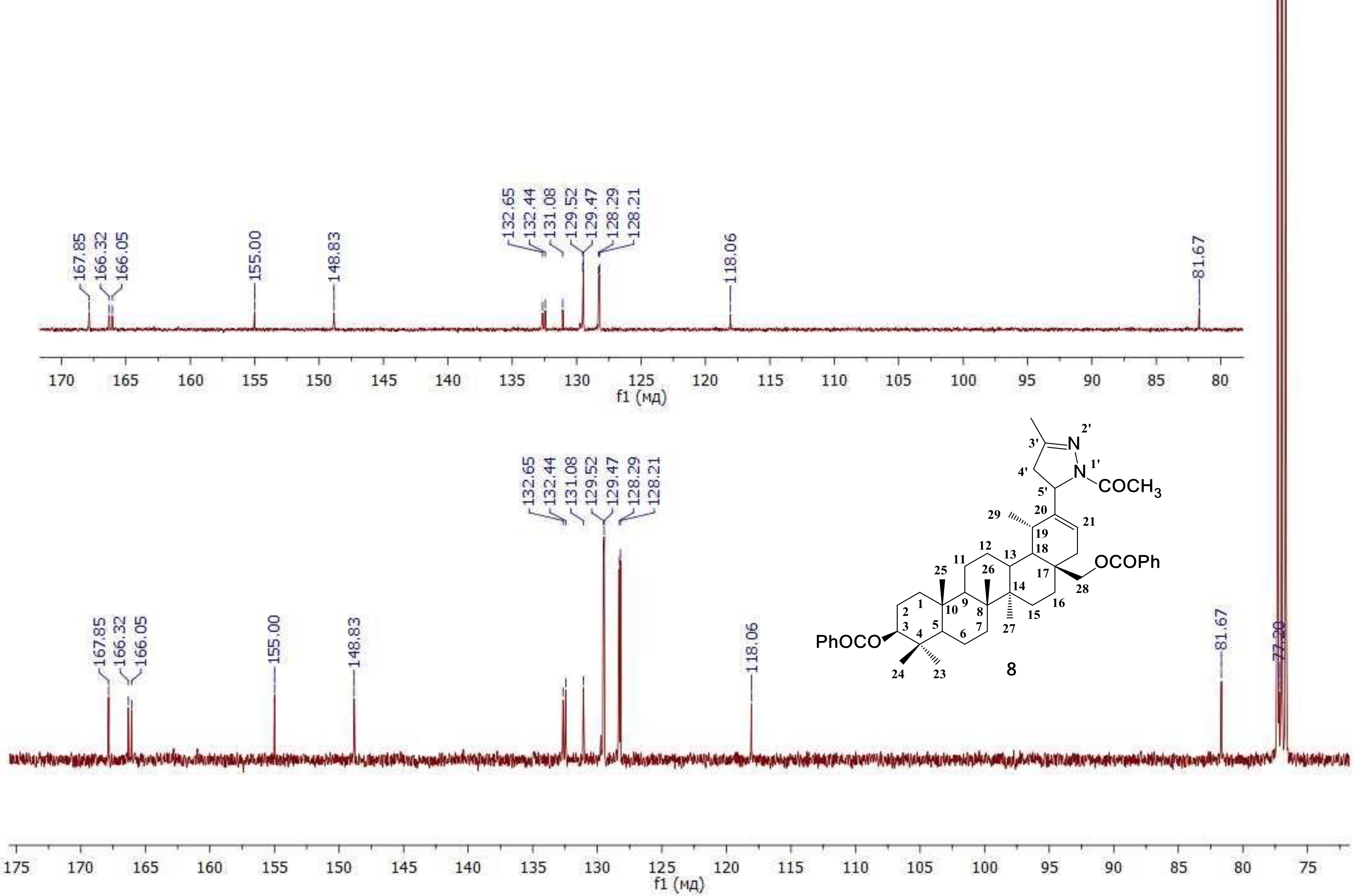
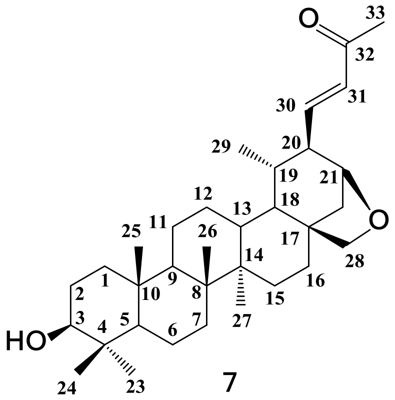


^{1}H NMR 20-(1´-Acetyl-3´-metyl-4´,5´-dihydro-1H-pyrazol-5´(*S*)-yl)-3β,28-dibenzoyloxy-30-nor-18αH,19βH-urs-20(21)-ene (8)



[13]C NMR 20-(1´-Acetyl-3´-metyl-4´,5´-dihydro-1H-pyrazol-5´(*S*)-yl)-3β,28-dibenzoyloxy-30-nor-18αH,19βH-urs-20(21)-ene (8)





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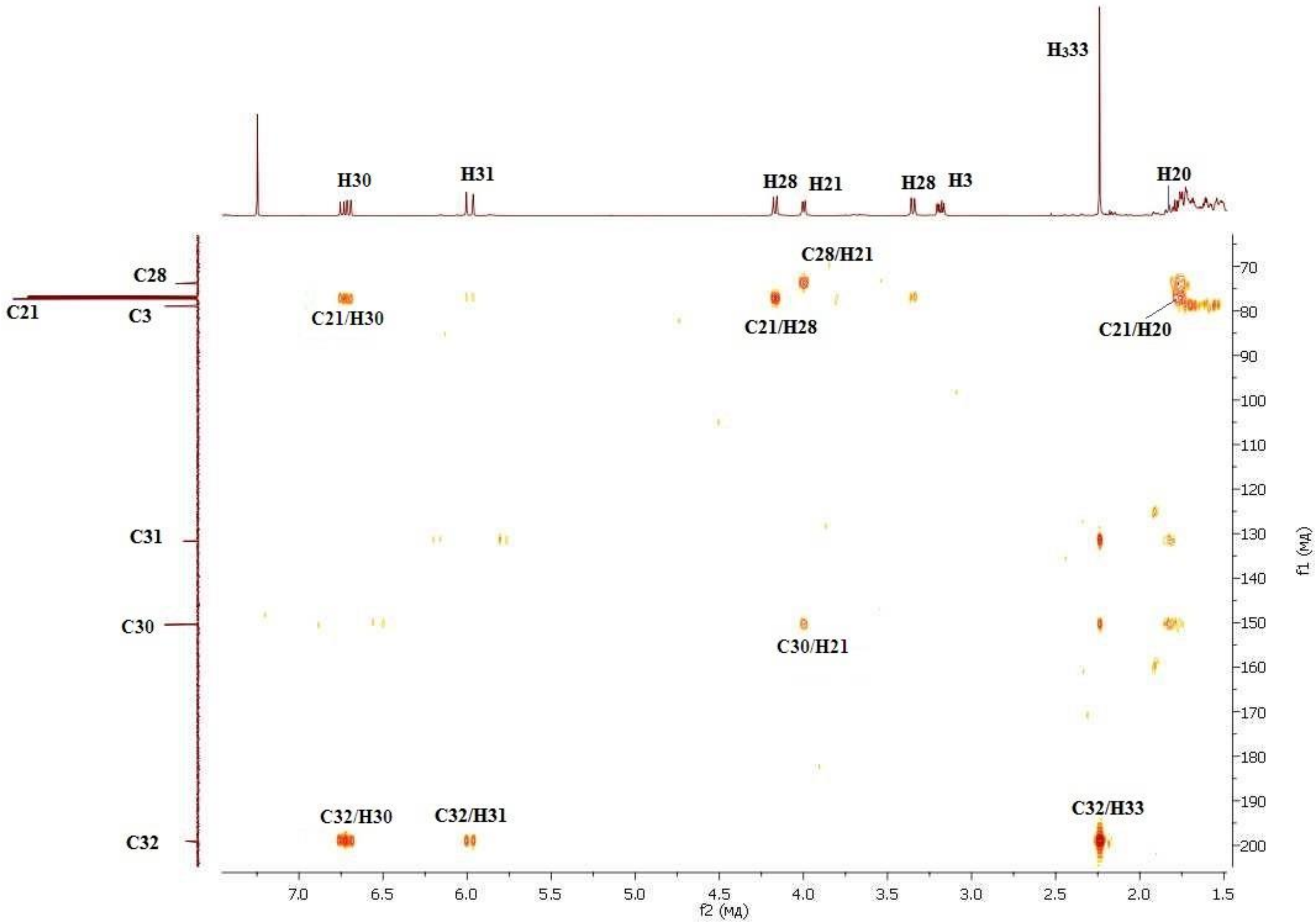
Fragment of HMBC

21β,28-Epoxy-3β-hydroxy-30-(2-oxopropylidene)-18αH,19βH-ursane (7)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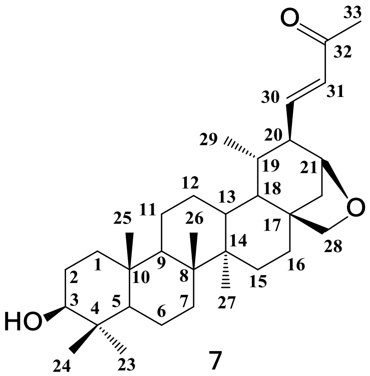
H31
H28
H21
H28
H3
H20
C28/H21
C28
C21
C3
C21/H30
C21/H28
C21/H20
C31
C30
C30/H21
C32/H30
C32/H31
C32/H33
C32
f1 (мд)
f2 (мд)



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Fragment 1 of NOESY

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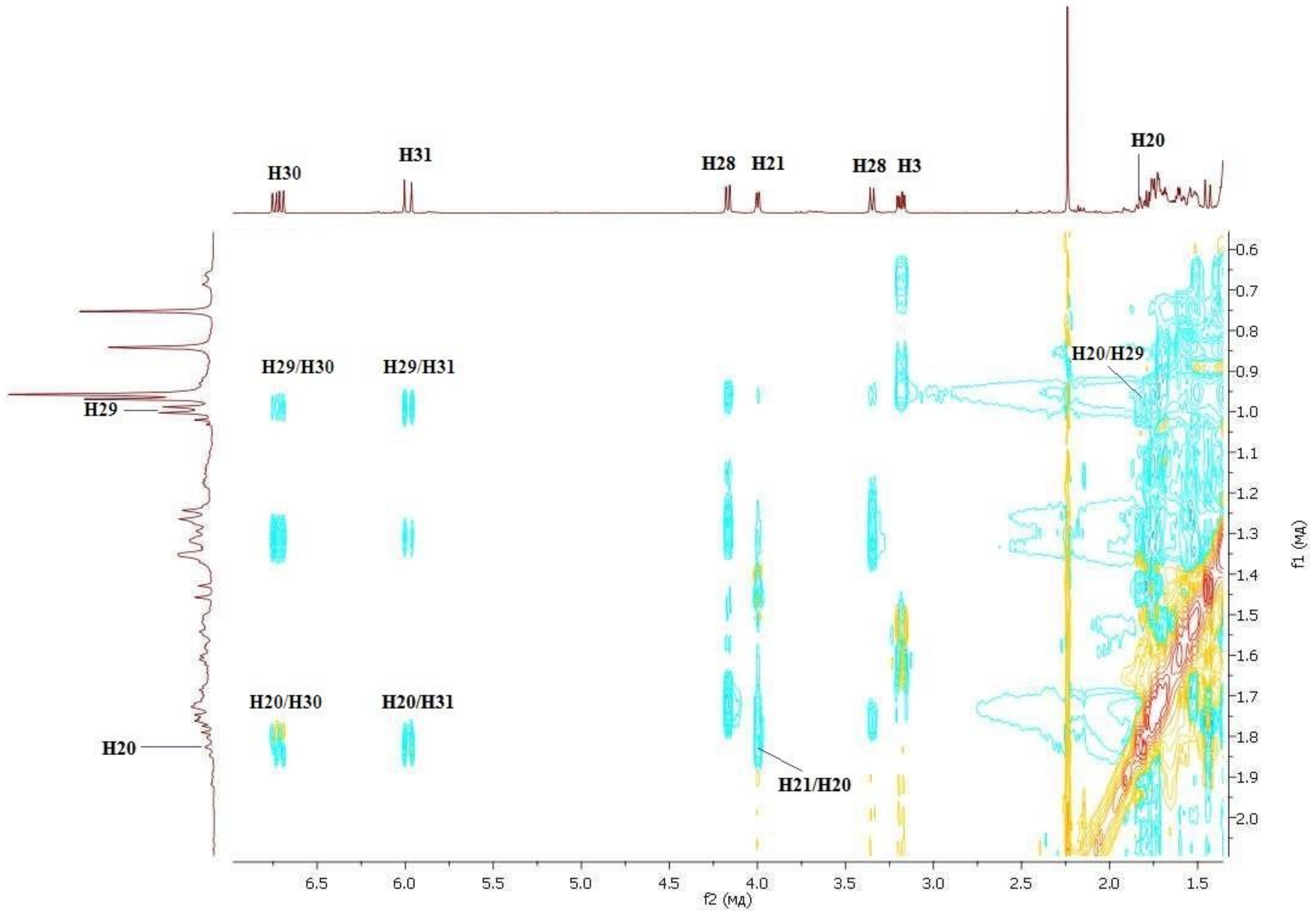
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H31
H28
H21
H28
H3
H20
H29/H30
H29/H31
H20/H29
H29
H20/H30
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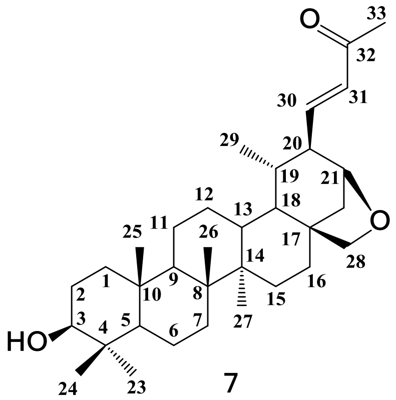
H21/H20
f2 (мд)
f1 (мд)



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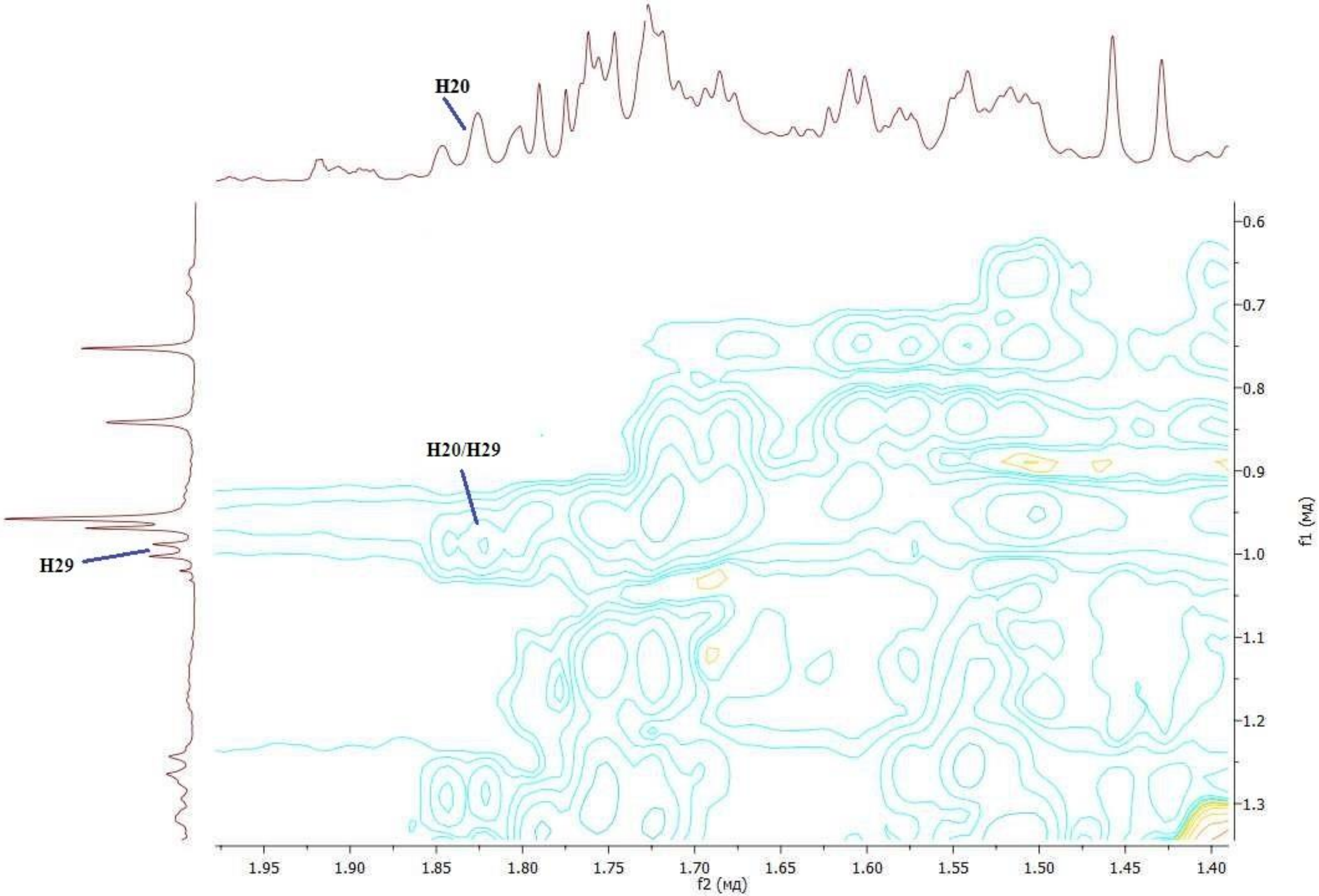
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H20/H29
H29
f2 (мд)
f1 (мд)
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1.80
1.75
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1.65
1.60
1.55
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0.9
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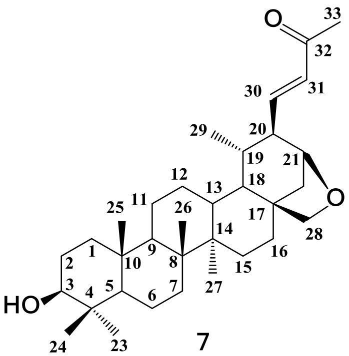
1.1
1.2
1.3



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Fragment 3 of NOESY
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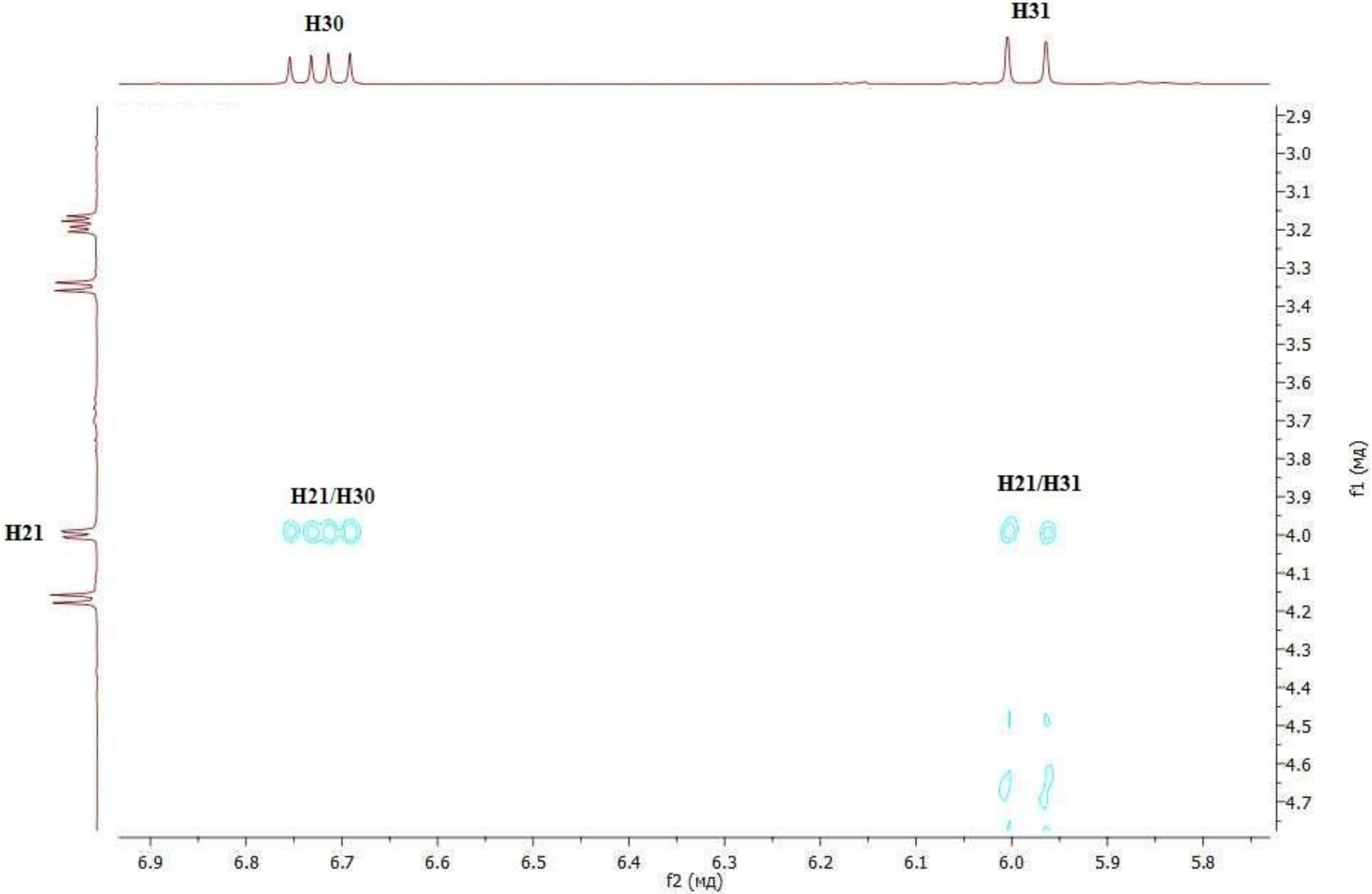

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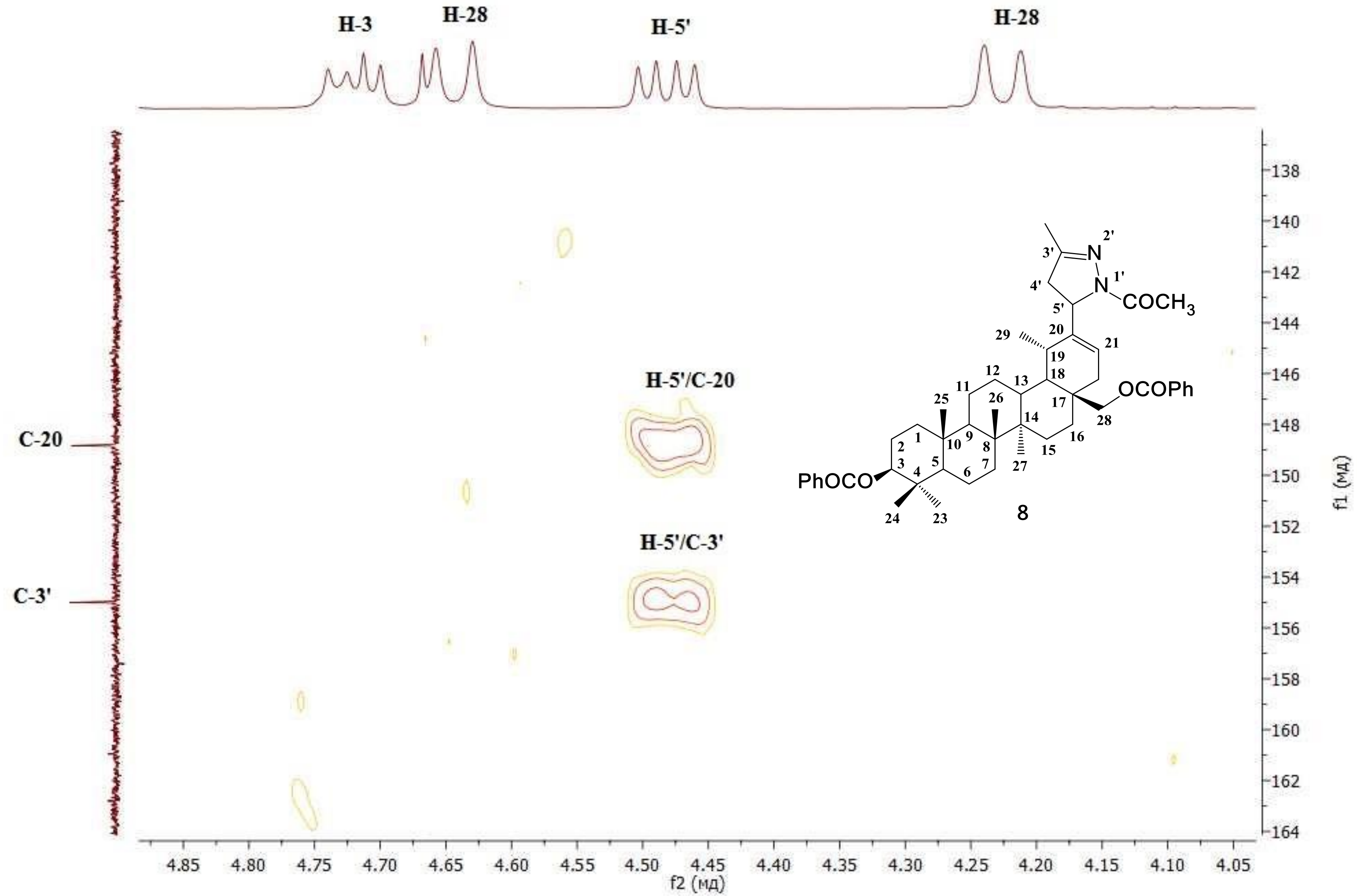
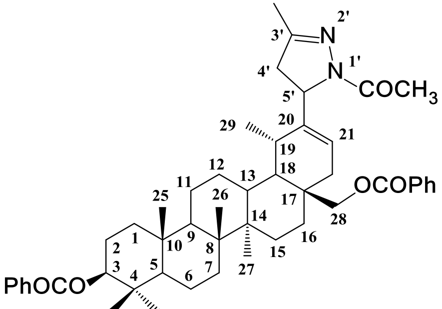
20-(1´-Acetyl-3´-methyl-4´,5´-dihydro-1H-pyrazol-5´(*S*)-yl)-3β,28-dibenzoyloxy-30-nor-18αH,19βH-urs-20(21)-ene (8)





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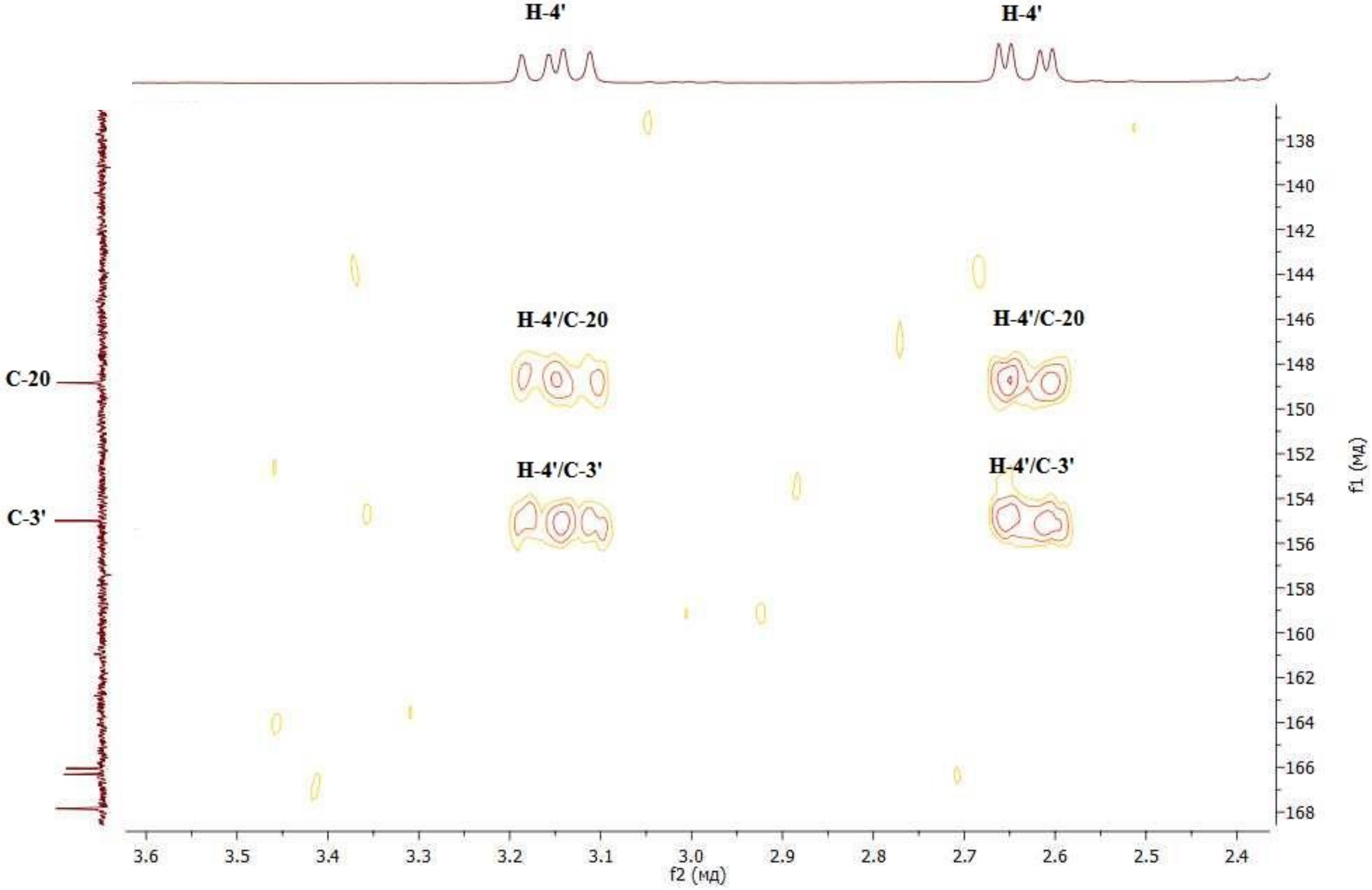

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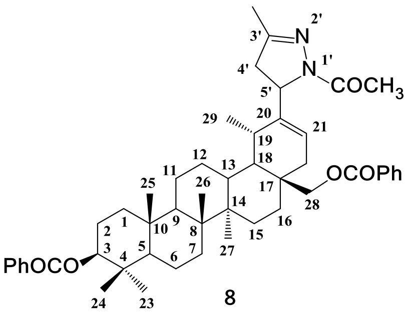

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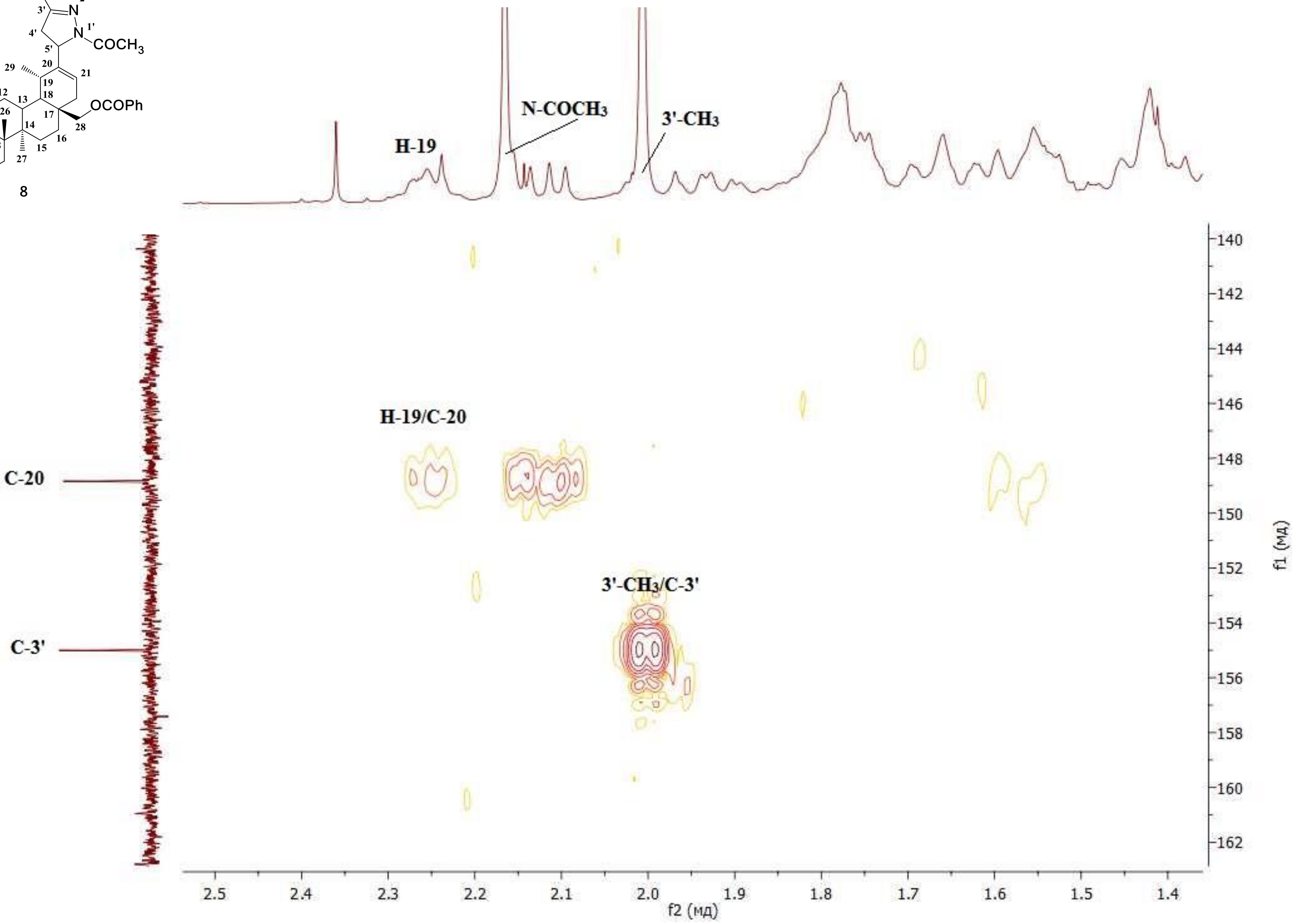

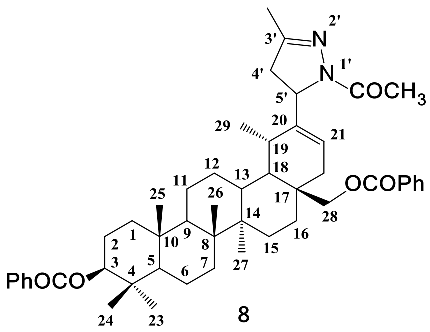

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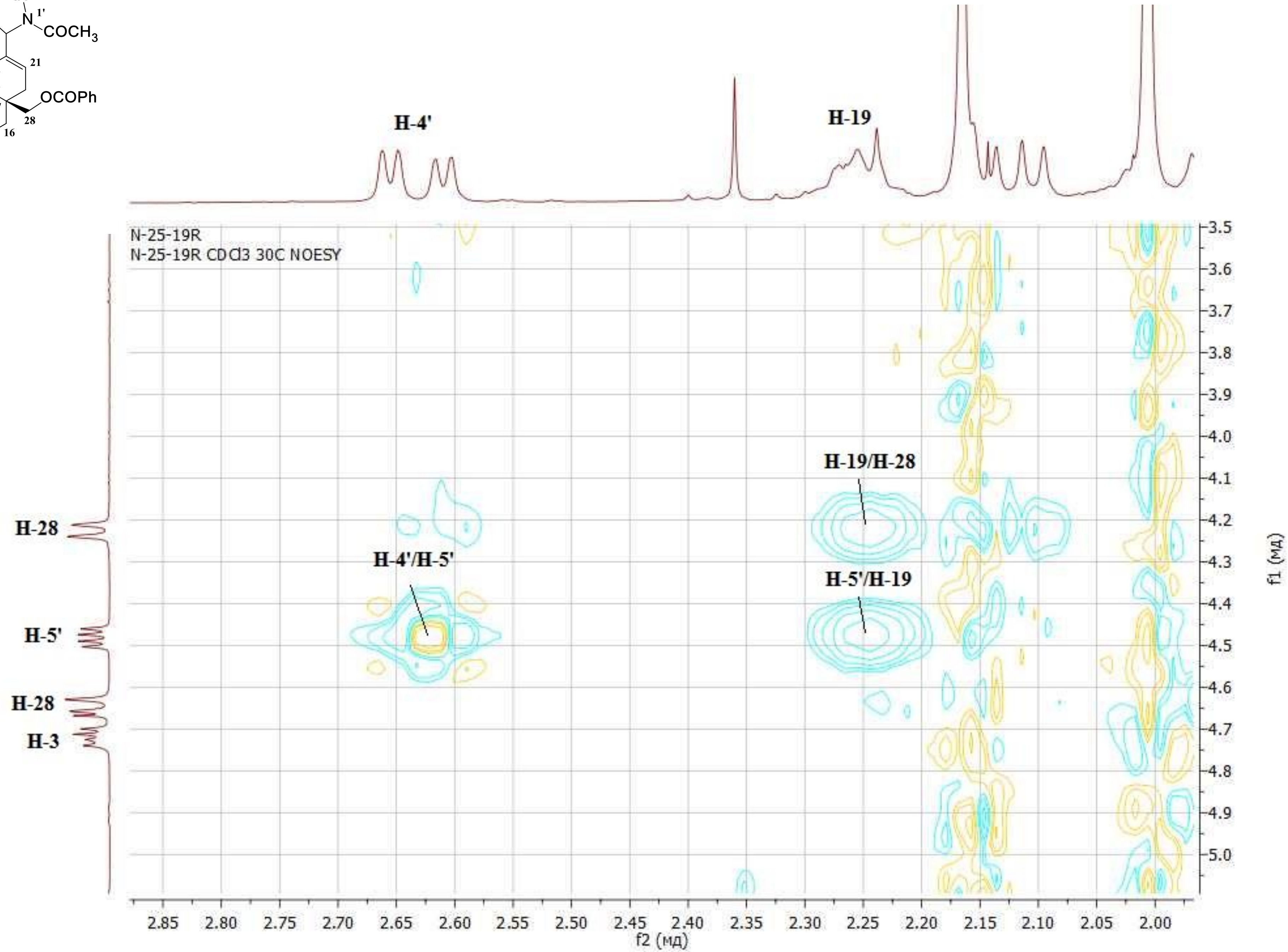

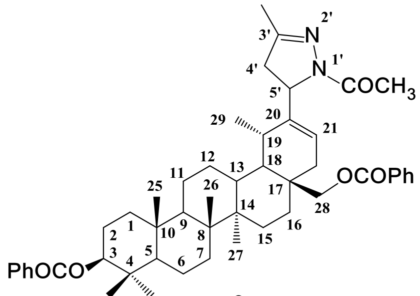

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