Supporting Information

Total Syntheses of Angelicoin A, Hericenone J and Hericenol A via Migratory Prenyl- and Geranylation-Aromatization Sequences

Jens Cordes, Frederick Calo, Katie Anderson, Toni Pfaffeneder,

Sylvain Laclef, Andrew J. P. White, and Anthony G. M. Barrett*

Department of Chemistry, Imperial College, London, SW7 2AZ, England.

agm.barrett@imperial.ac.uk

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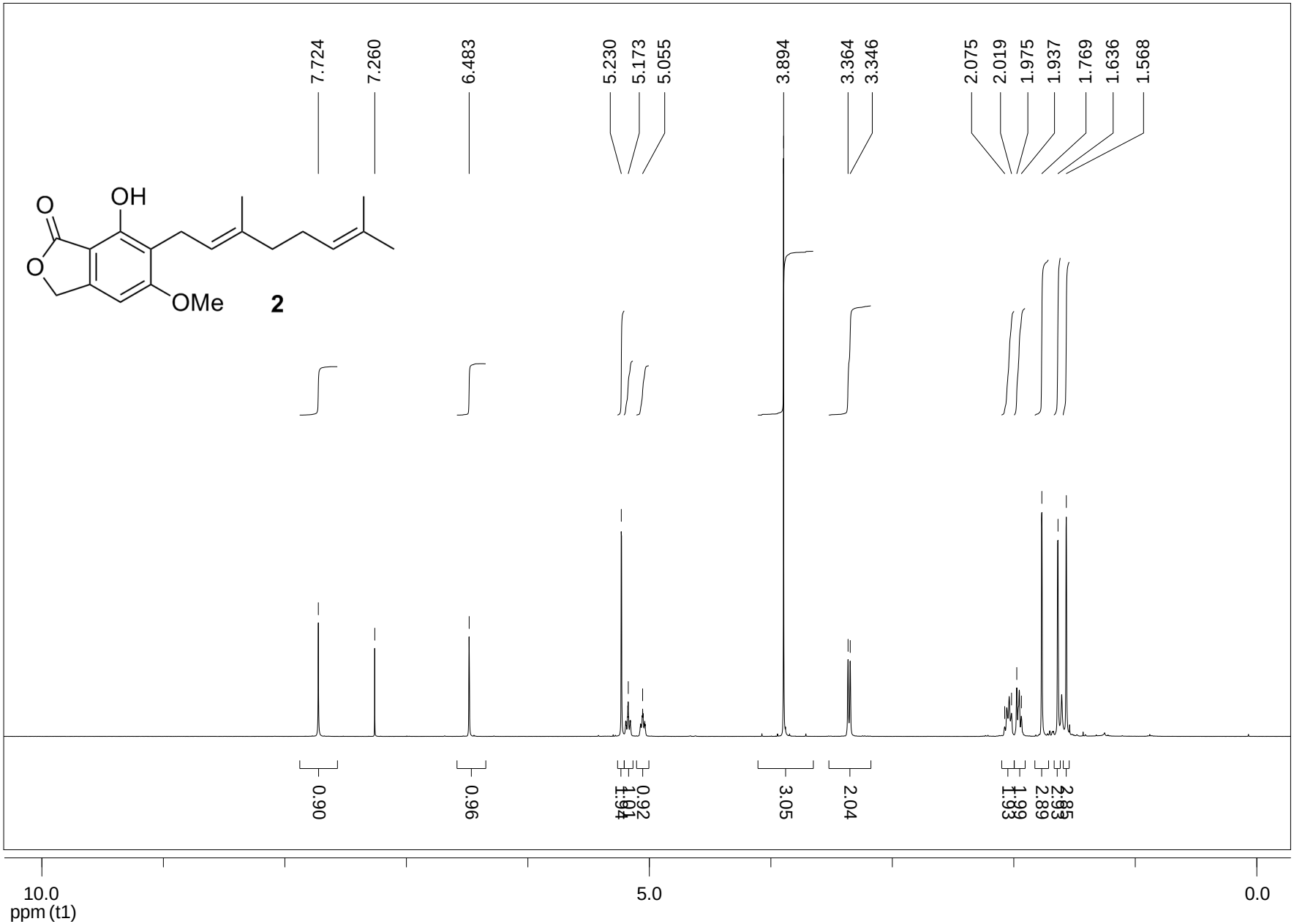
1. ^{1}H and ^{13}C spectra ($CDCl_3$, respectively 400 MHz and 100 MHz)

2. Crystallographic data

Hericenone J ((*E*)-6-(3,7-dimethylocta-2,6-dienyl)-7-hydroxy-5-methoxyisobenzofuran-1(3*H*)-one, 2)



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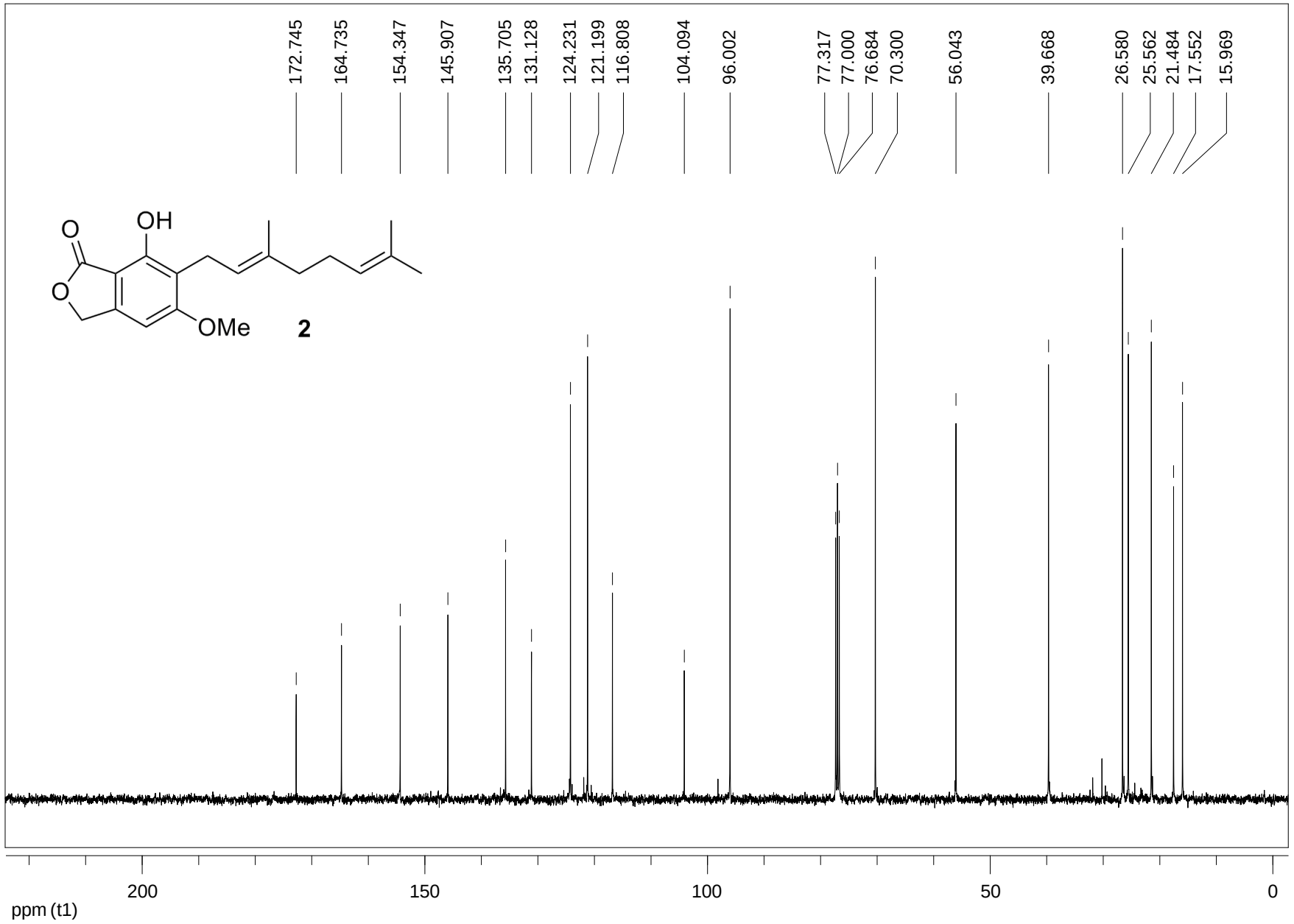
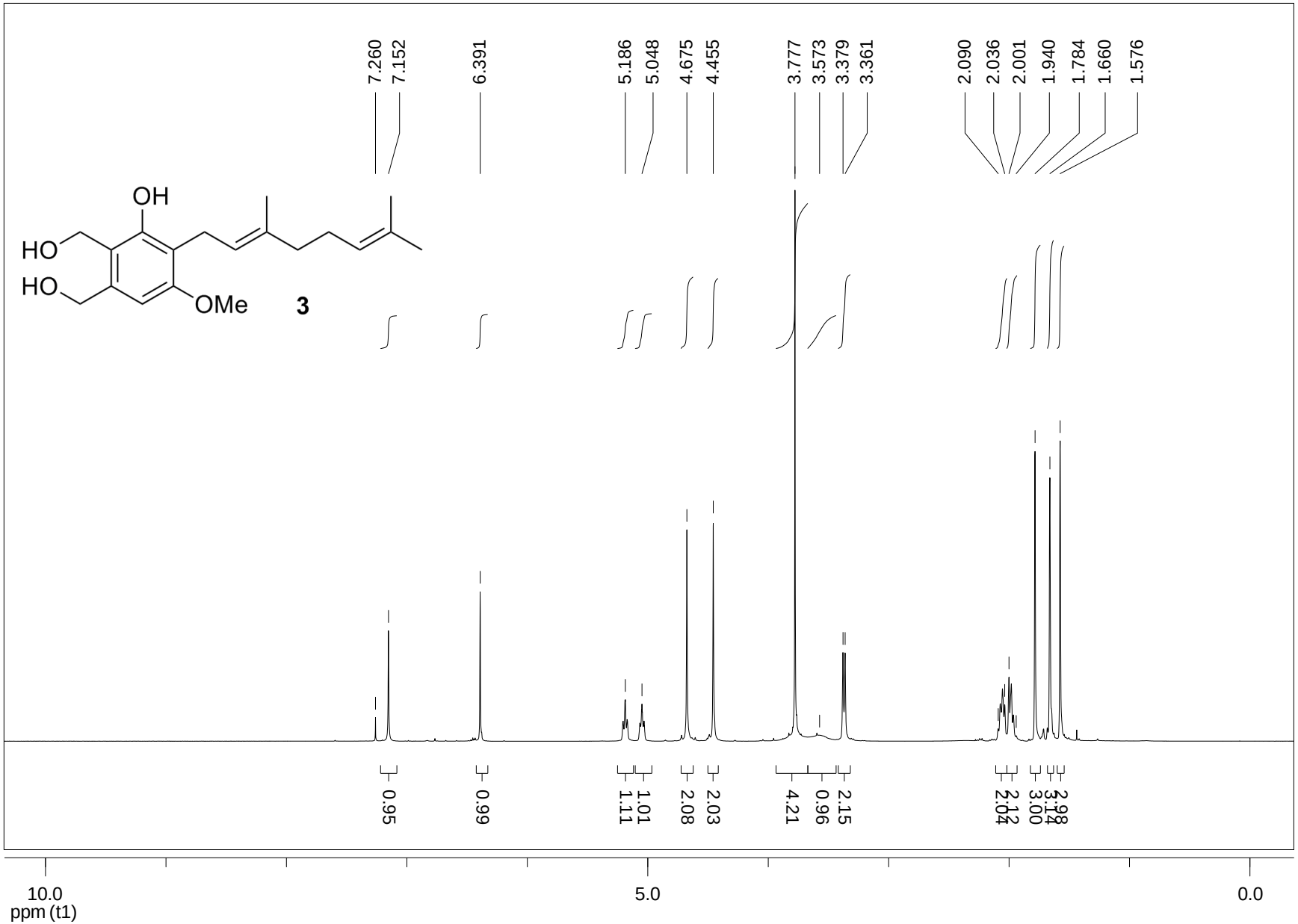


Hericenol A ((*E*)-(4-(3,7-dimethylocta-2,6-dienyl)-3-hydroxy-5-methoxy-1,2-phenylene)-dimethanol, 3)



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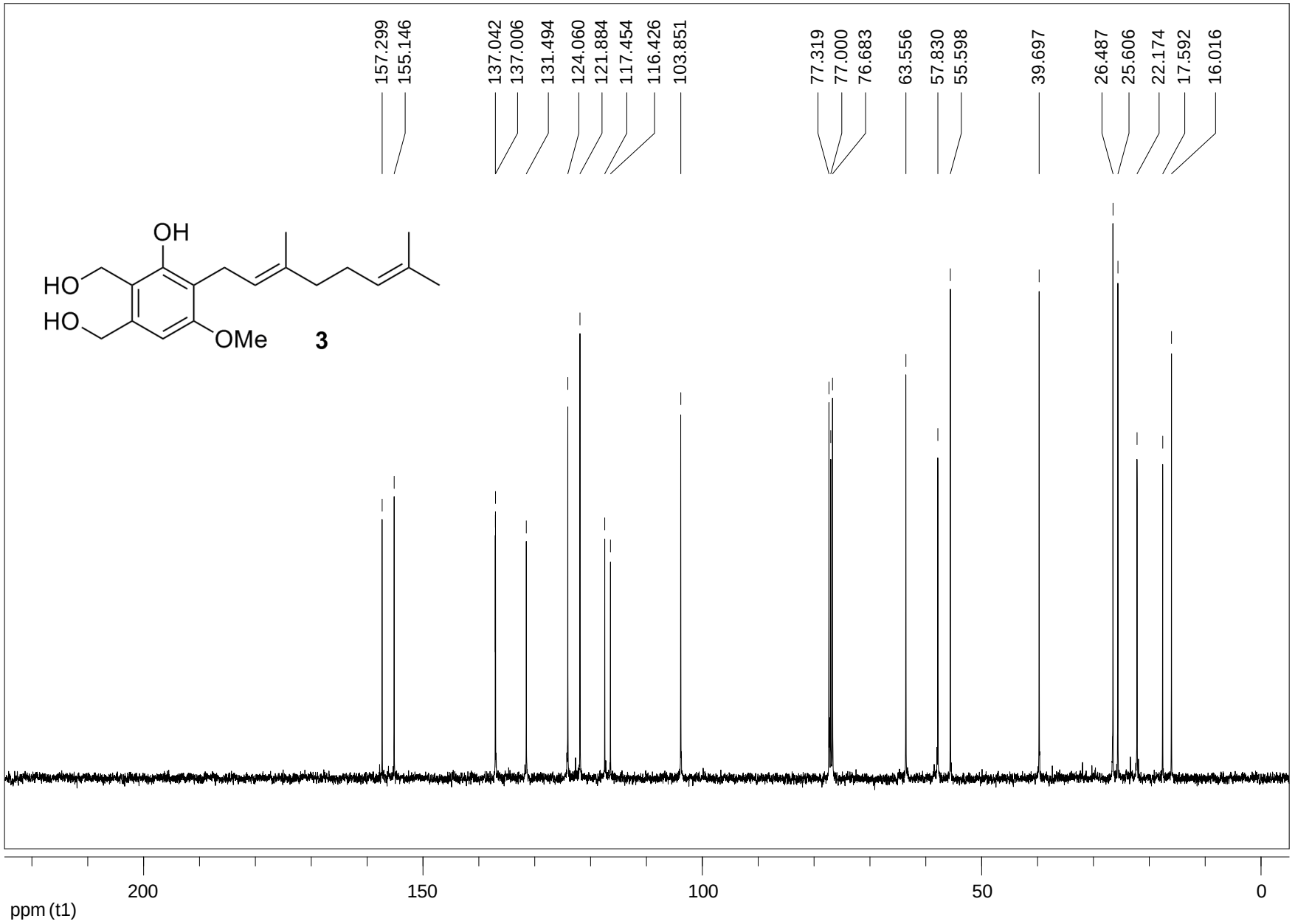
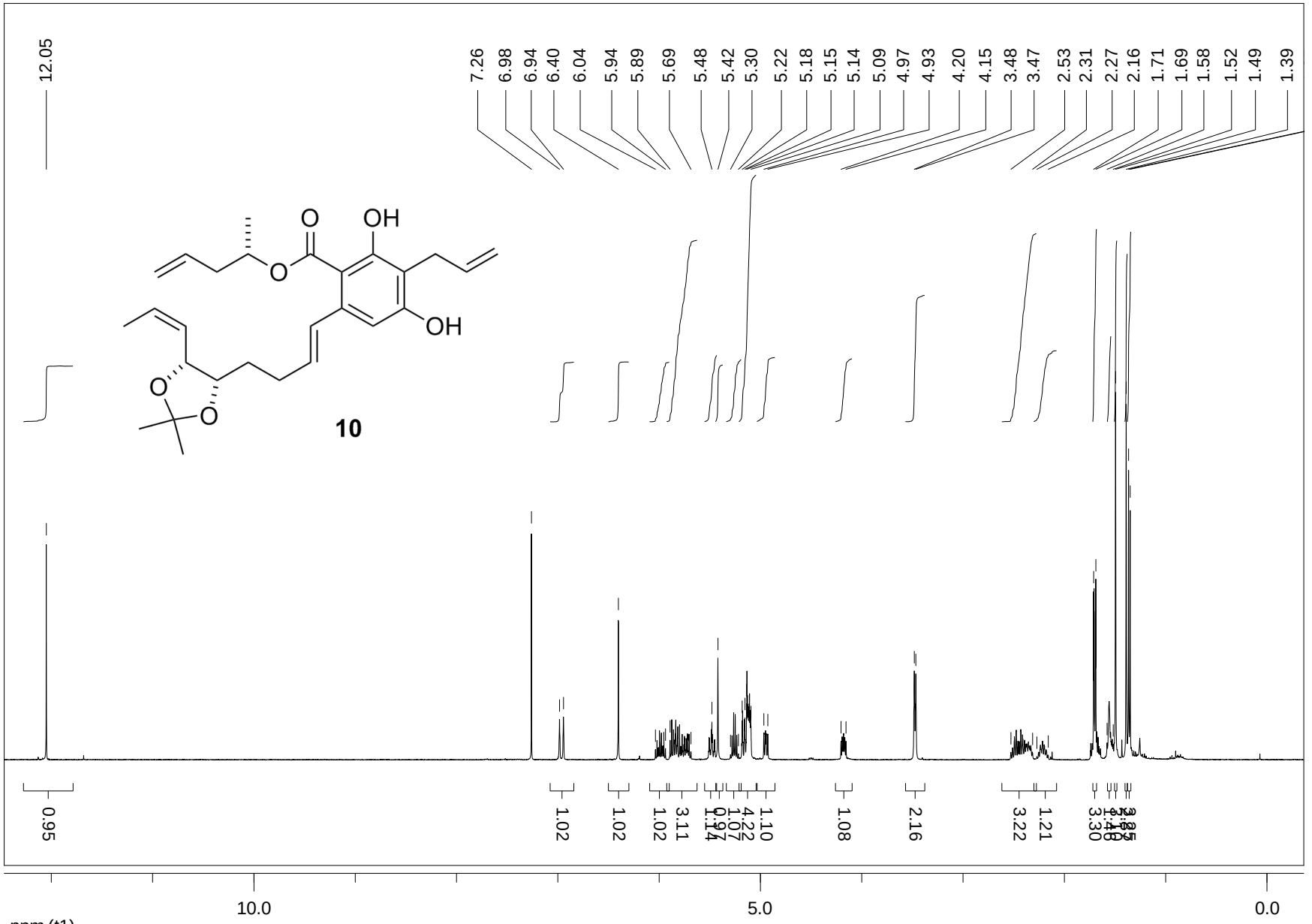


(*S*)-Pent-4-en-2-yl 3-allyl-6-((*E*)-4-((4*S*,5*S*)-2,2-dimethyl-5-((*Z*)-prop-1-enyl)-1,3-diox-olan-4-yl)but-1-enyl)-2,4-dihydroxybenzoate (10)



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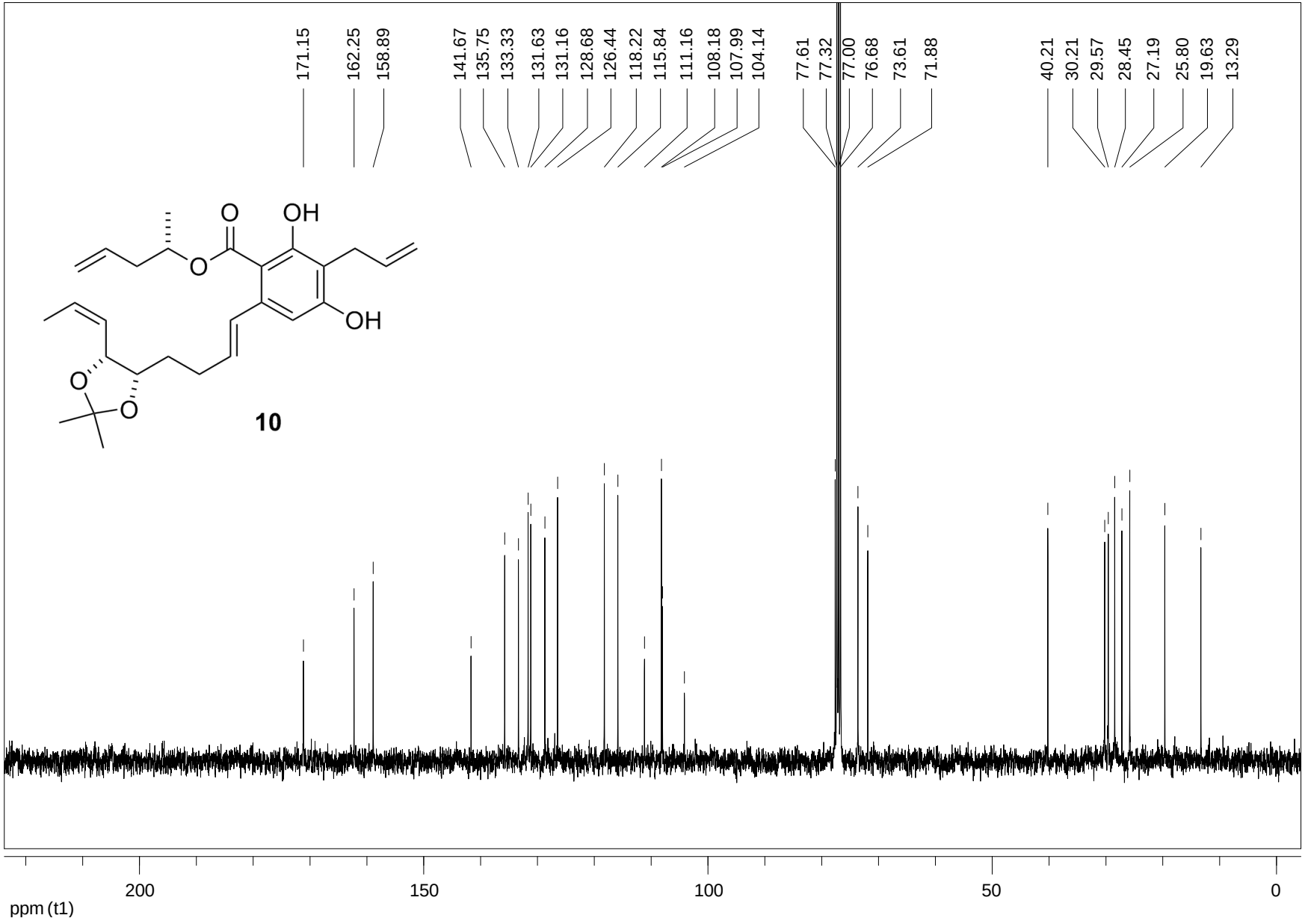
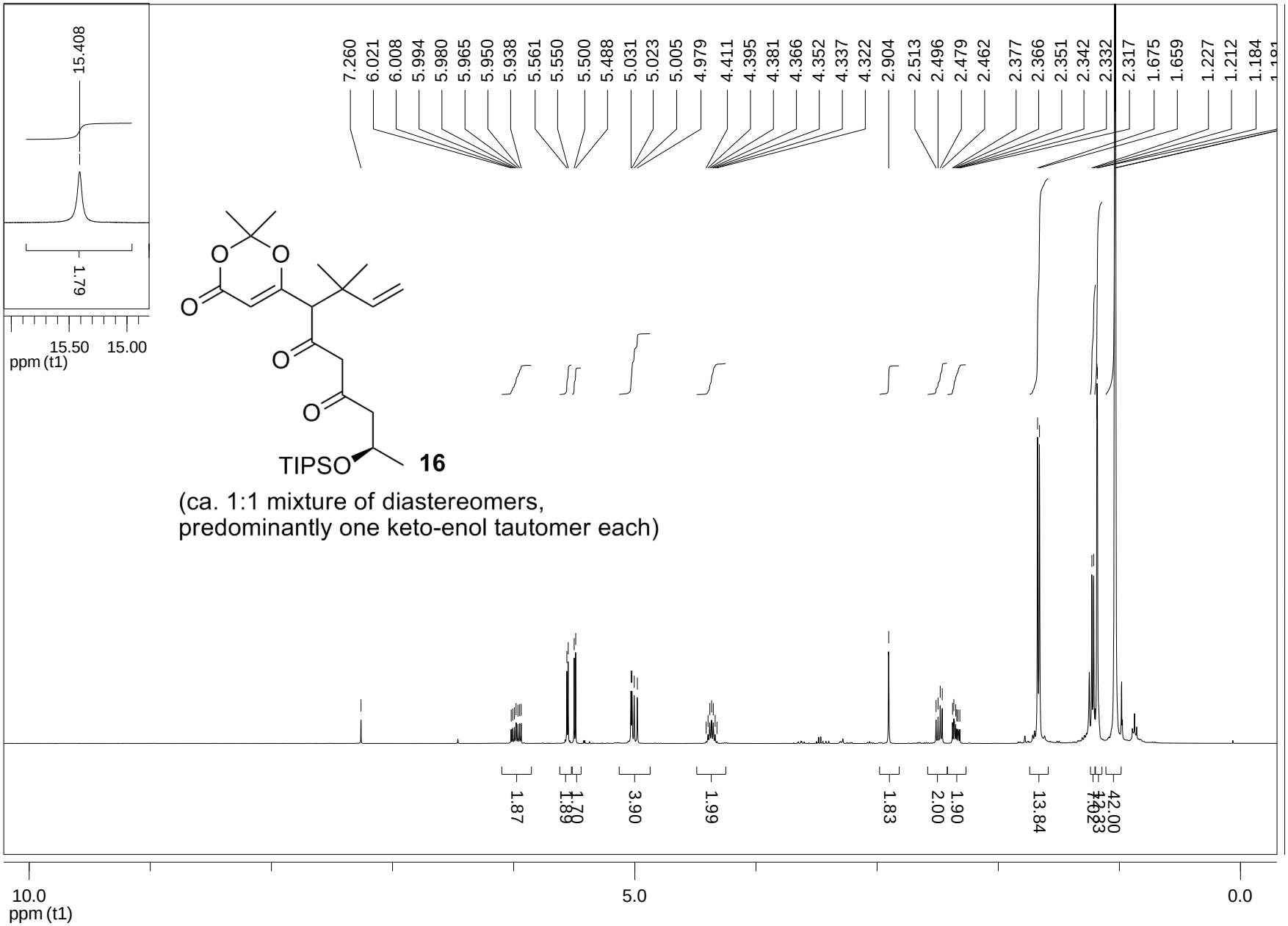


(2*R*)-7-(2,2-Dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)-8,8-dimethyl-2-(tri-isopropylsilyloxy)-dec-9-ene-4,6-dione (16)



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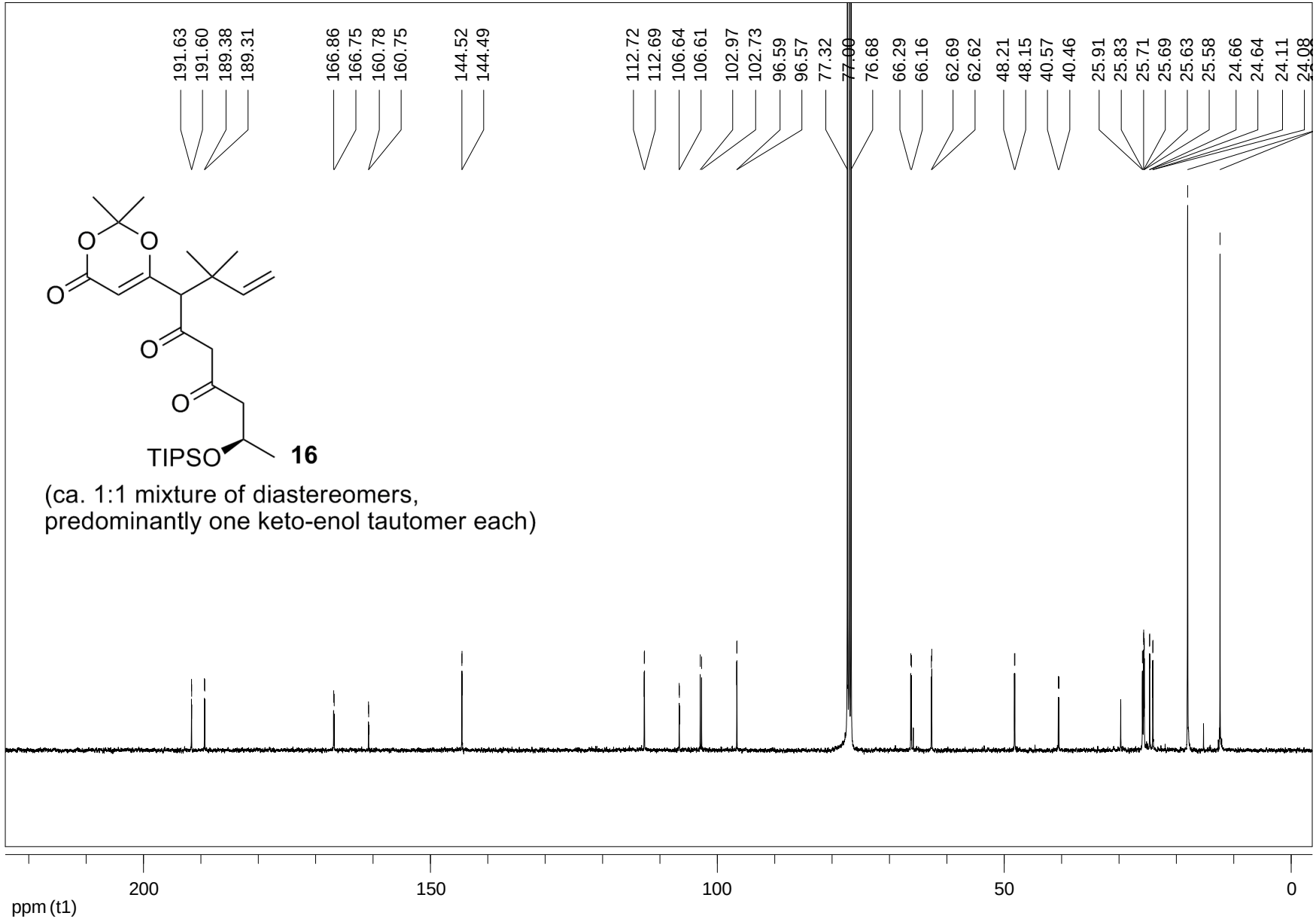
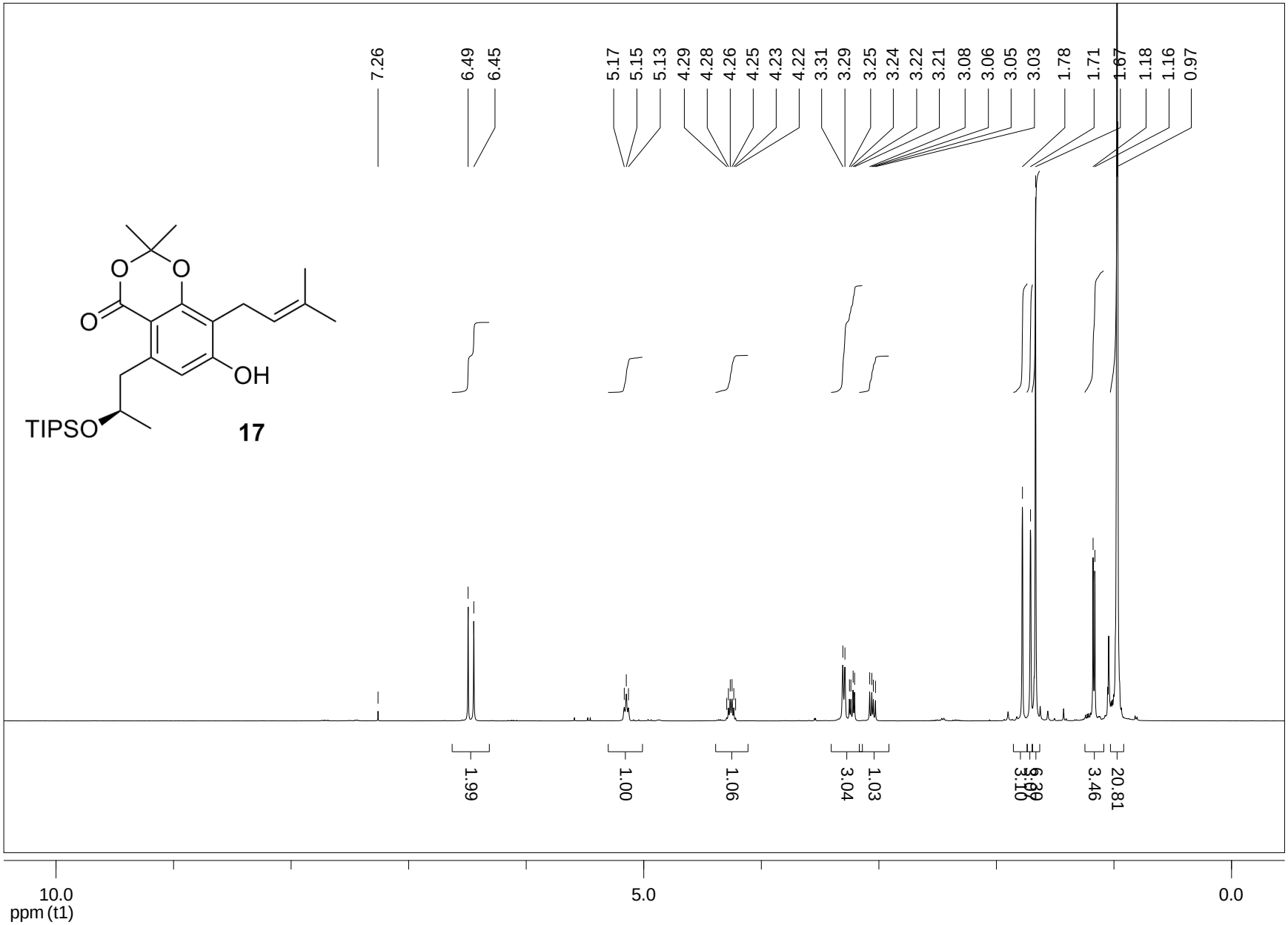


(*R*)-7-Hydroxy-2,2-dimethyl-8-(3-methylbut-2-enyl)-5-(2-(triisopropylsilyloxy)-propyl)-4*H*-benzo[*d*][1,3]dioxin-4-one (17)



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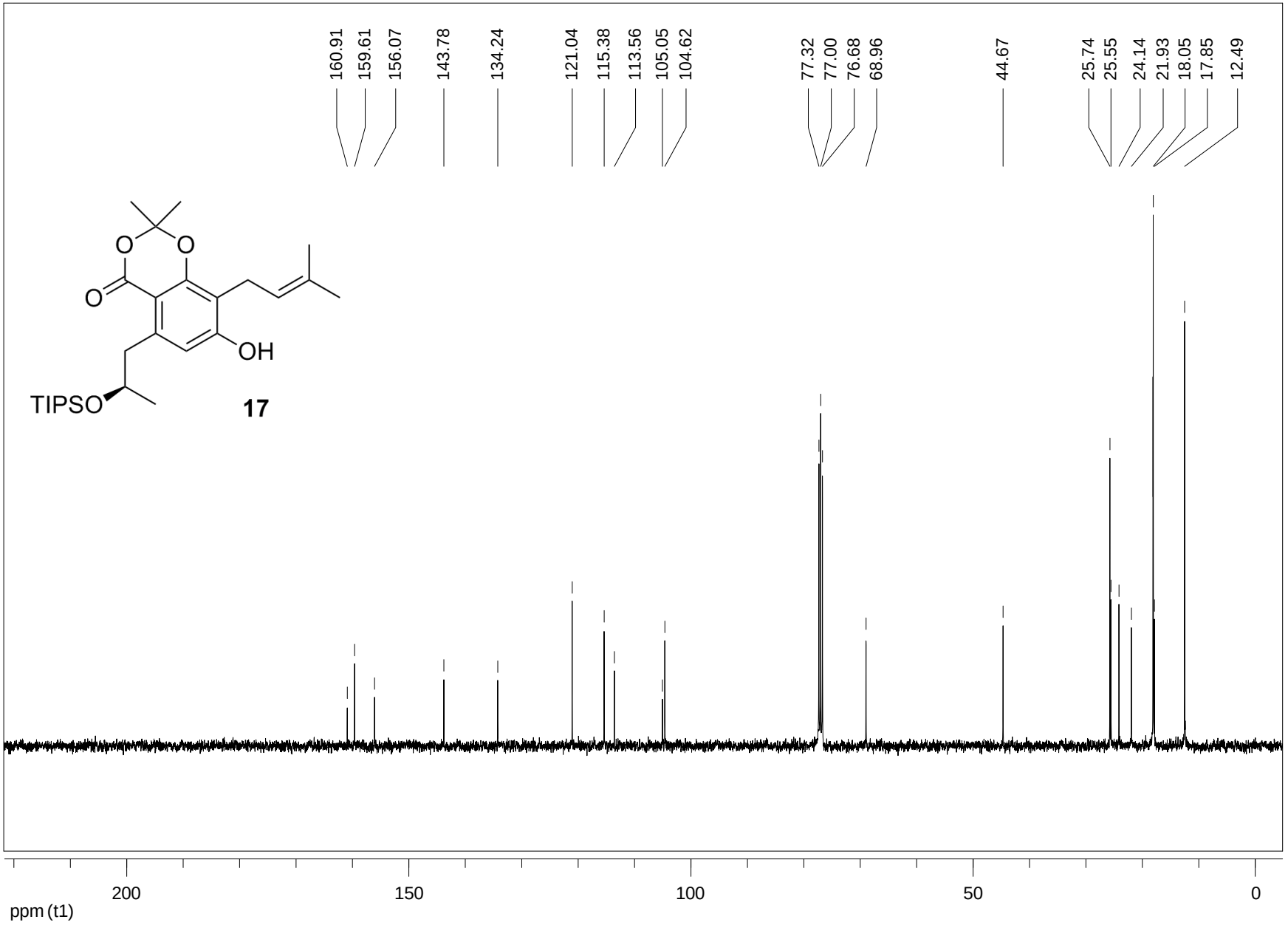
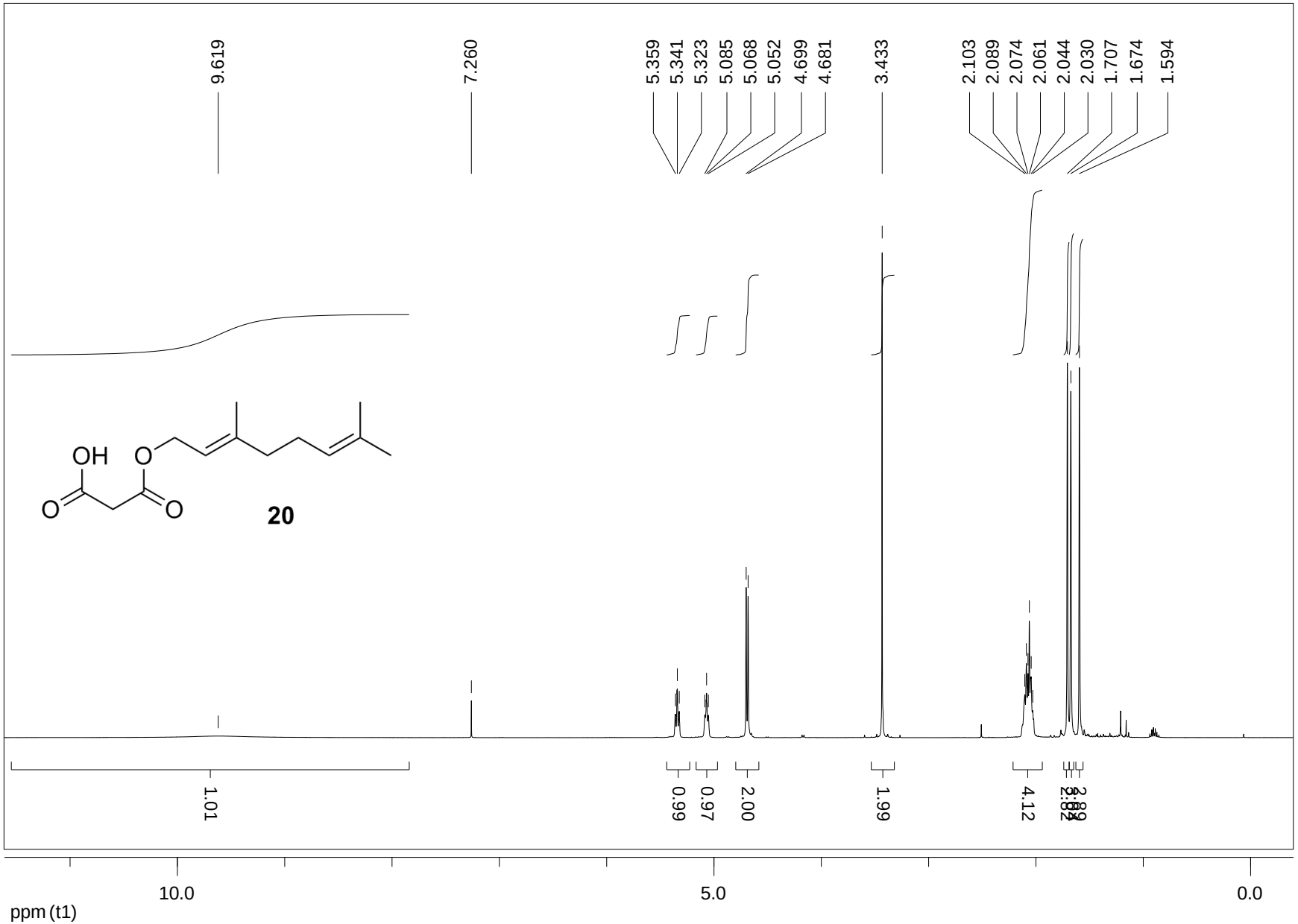
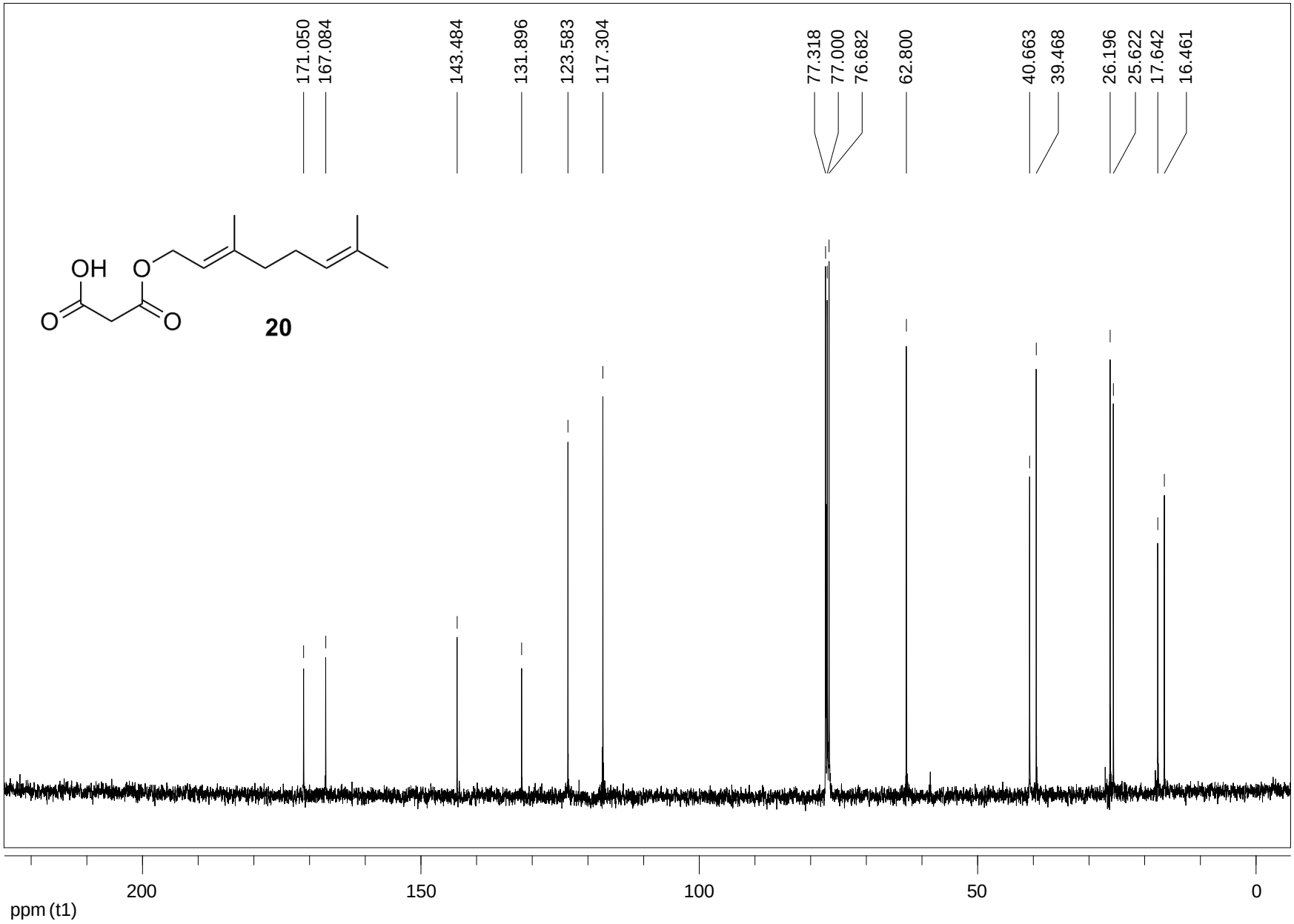


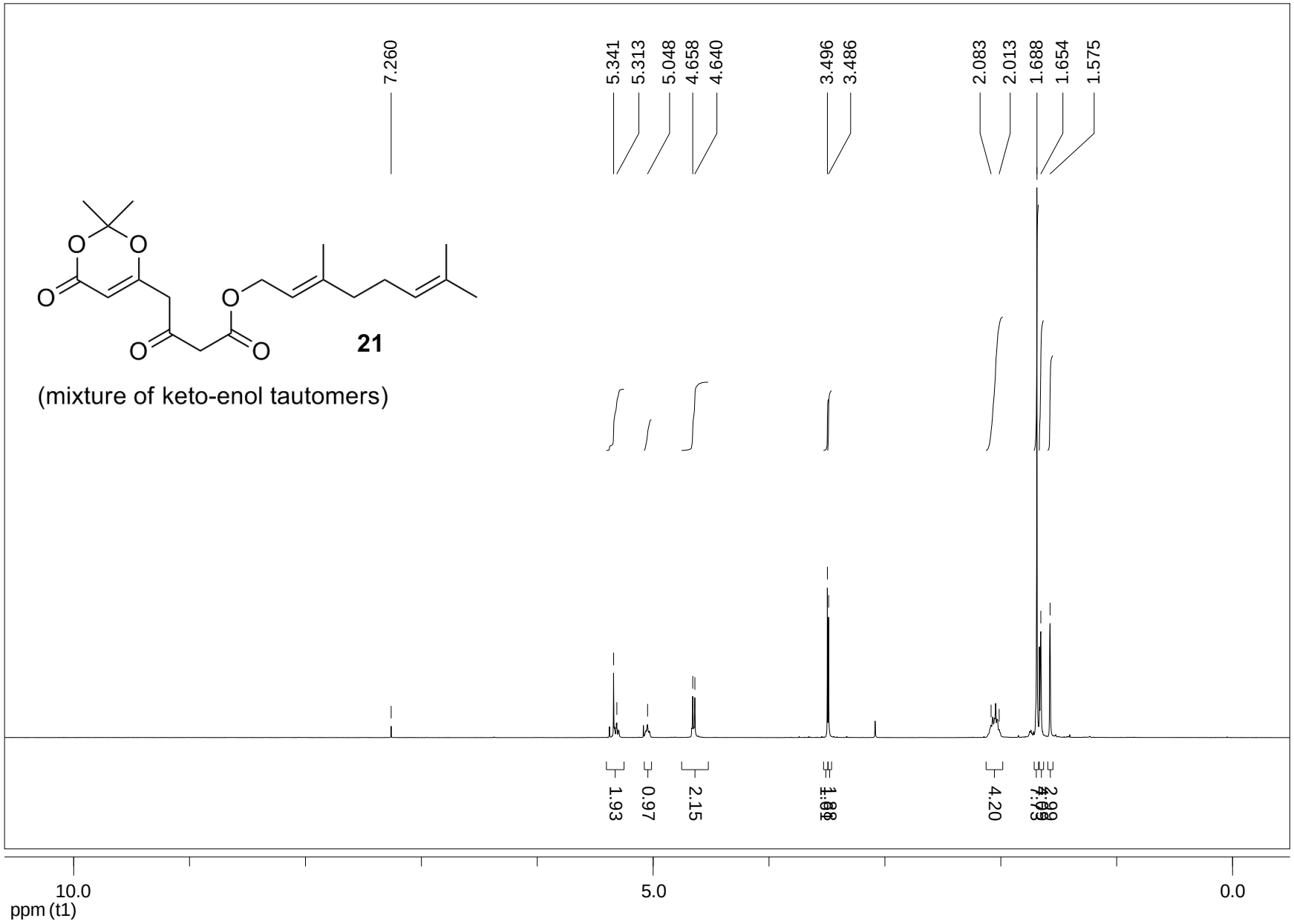
(*E*)-3-(3,7-Dimethyl-2,6-octadienyl-1-oxy)-3-oxopropanoic acid (20)



(*E*)-3-(3,7-Dimethyl-2,6-octadienyl-1-oxy)-3-oxopropanoic acid (20)



(*E*)-3,7-Dimethyl-2,6-octadien-1-yl 4-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)-3-oxobutanoate (21)



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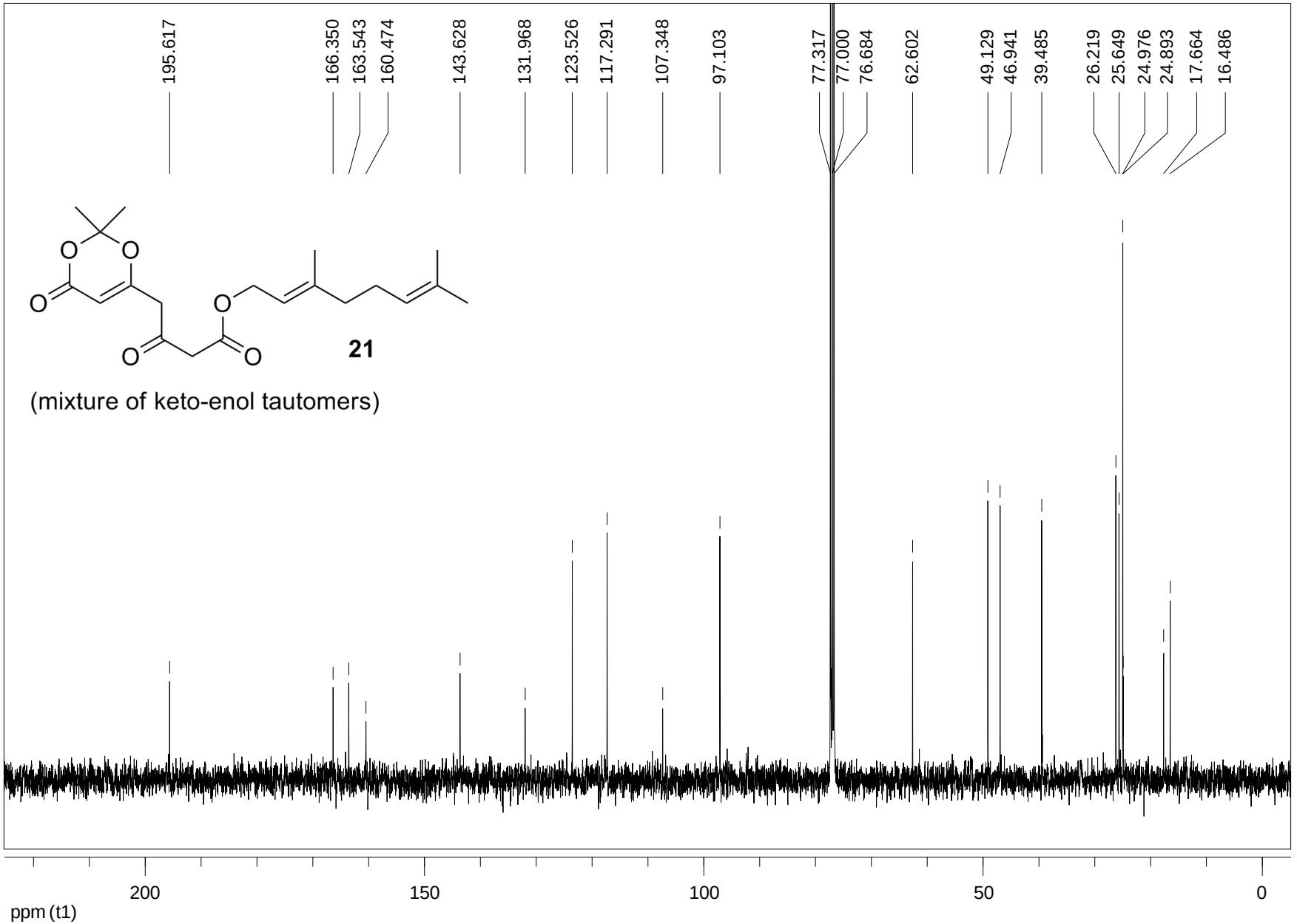
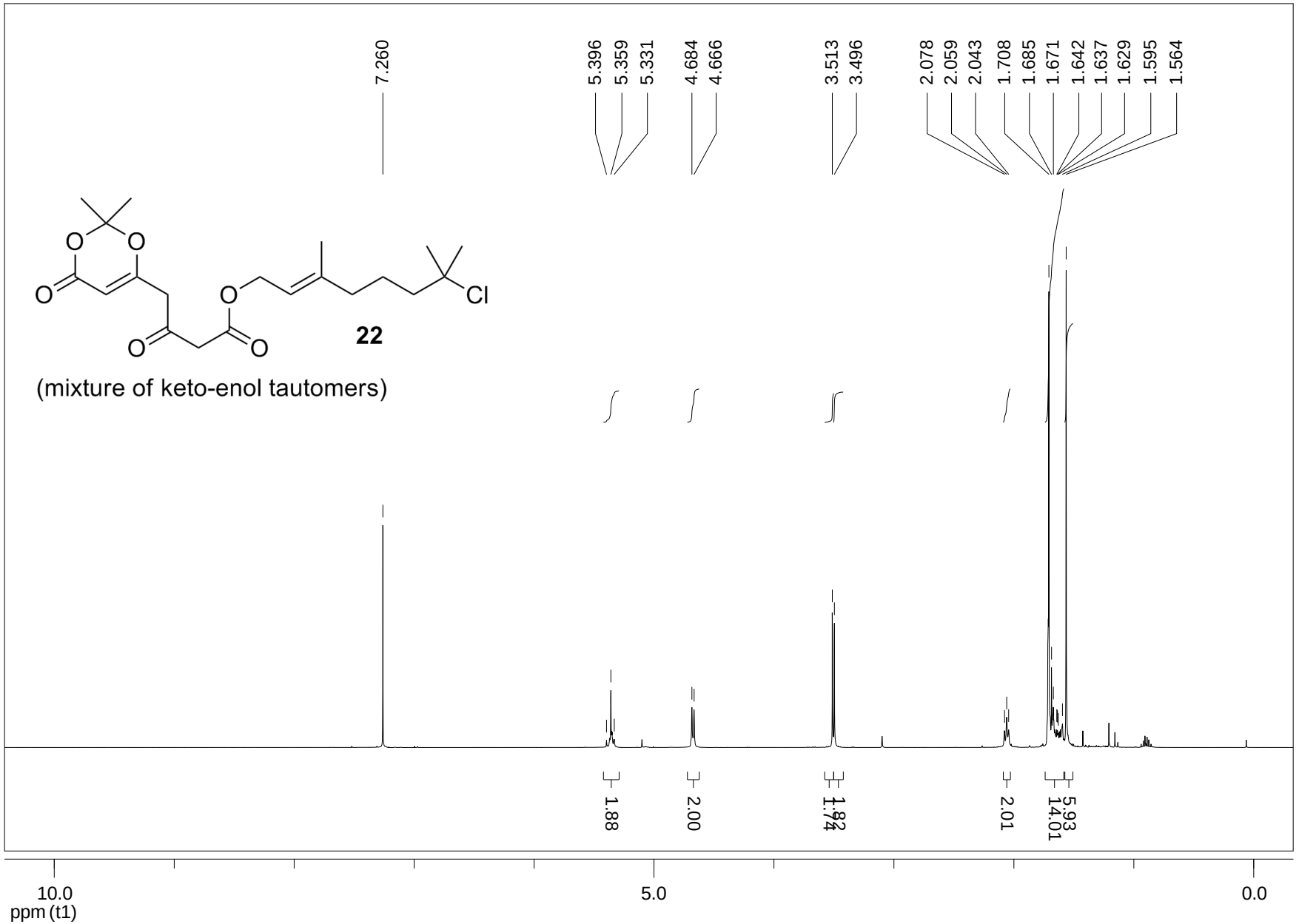
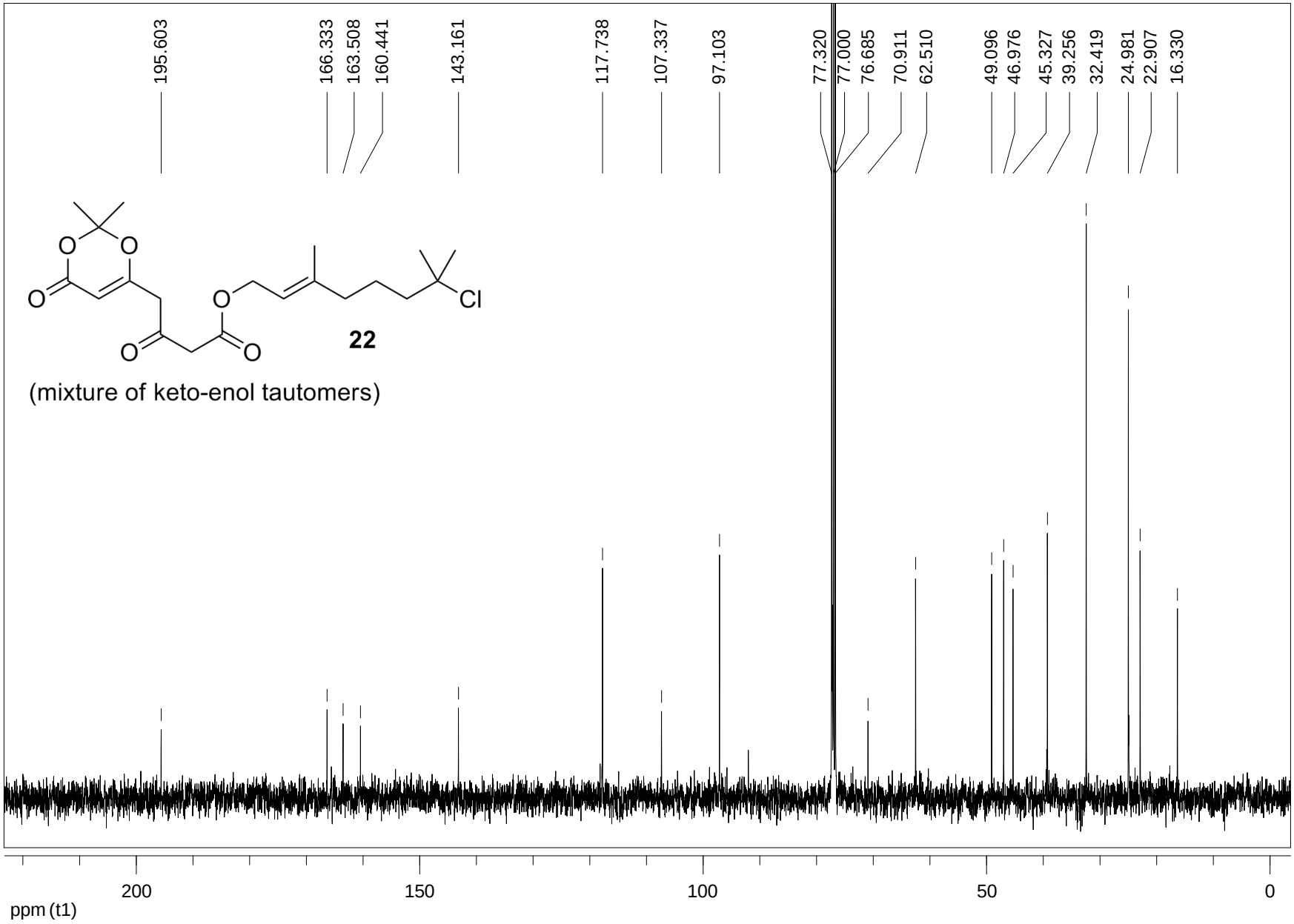


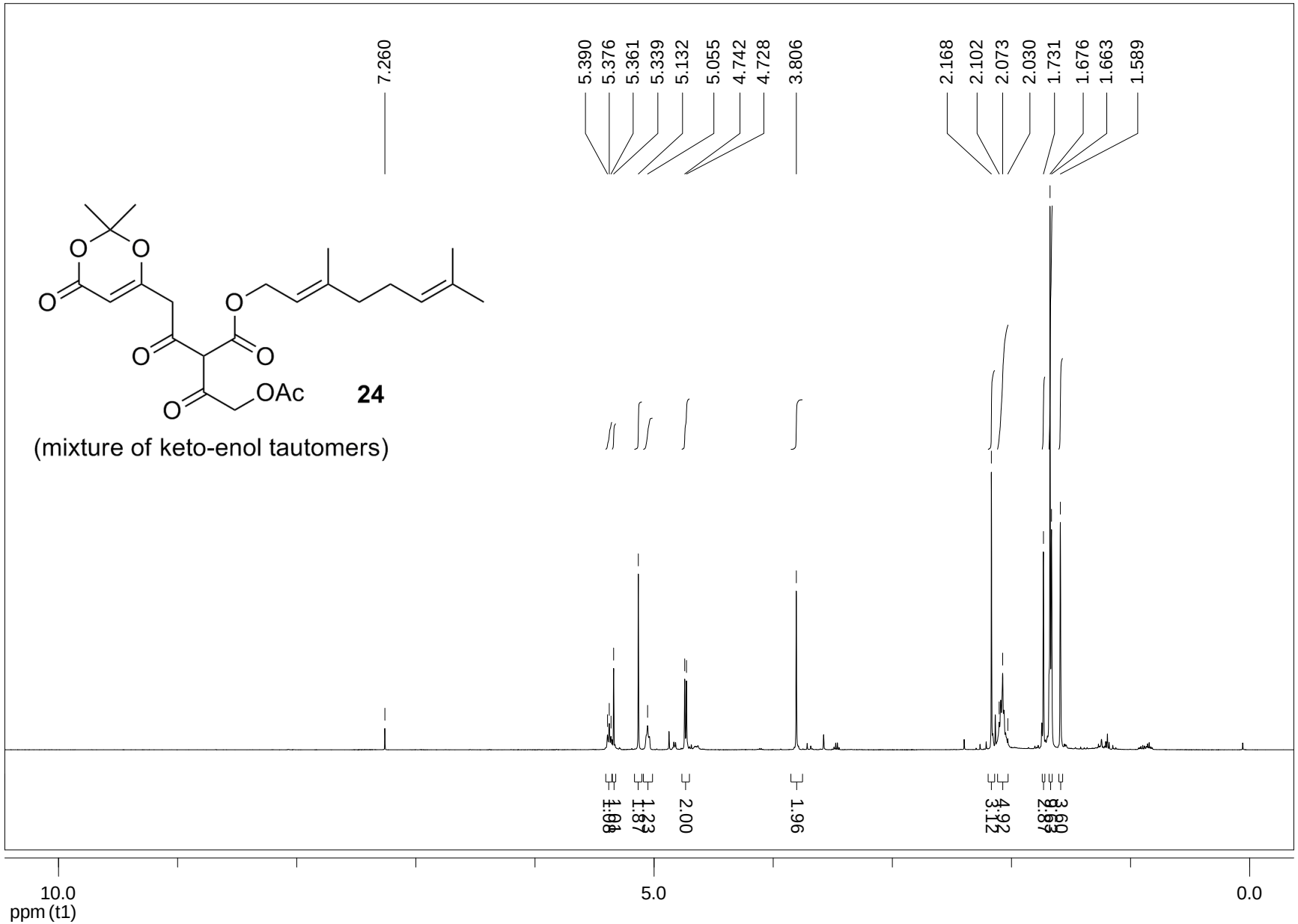
(*E*)-7-Chloro-3,7-dimethyloct-2-enyl 4-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)-3-oxobutanoate (22)



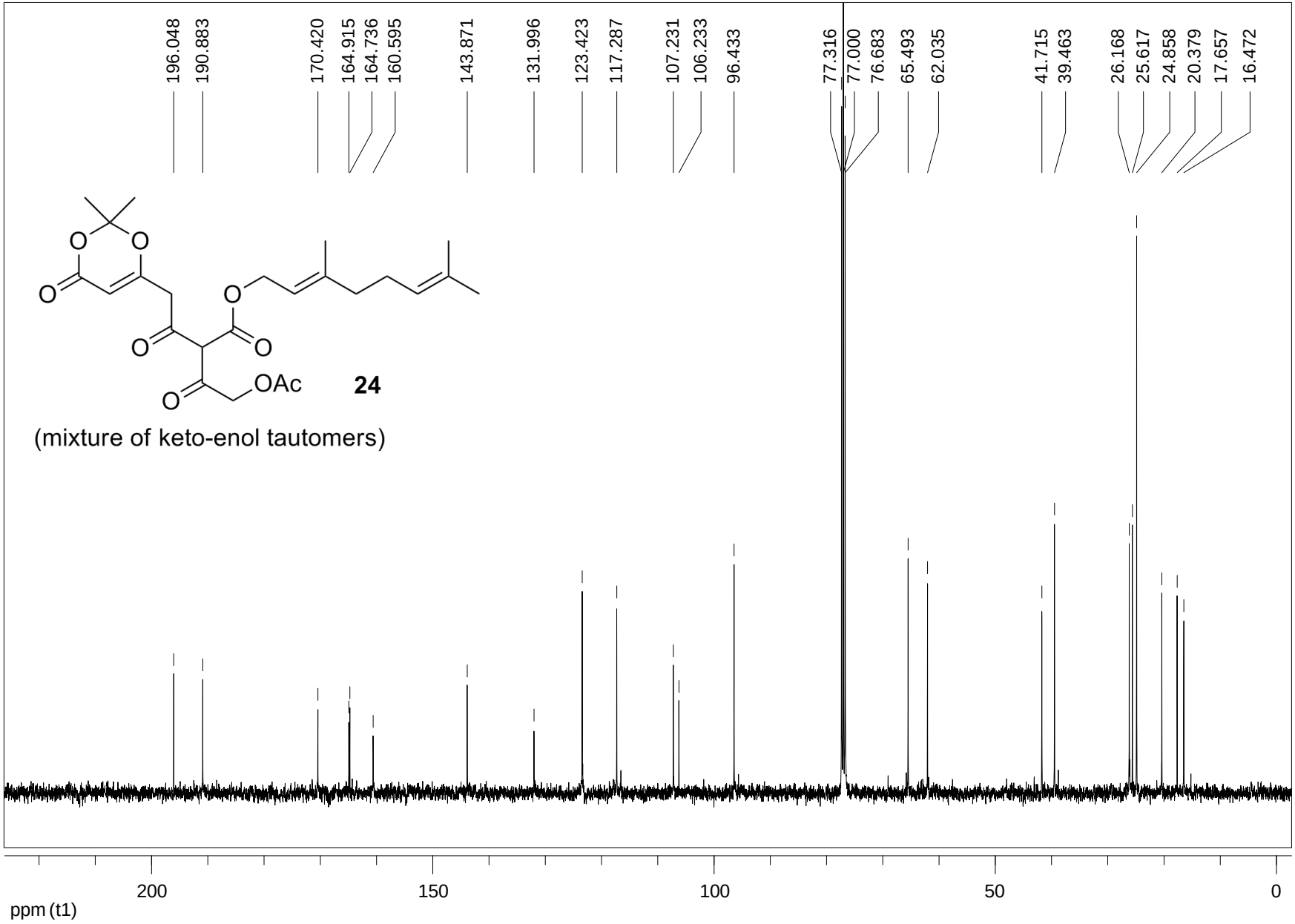
(*E*)-7-Chloro-3,7-dimethyloct-2-enyl 4-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)-3-oxobutanoate (22)



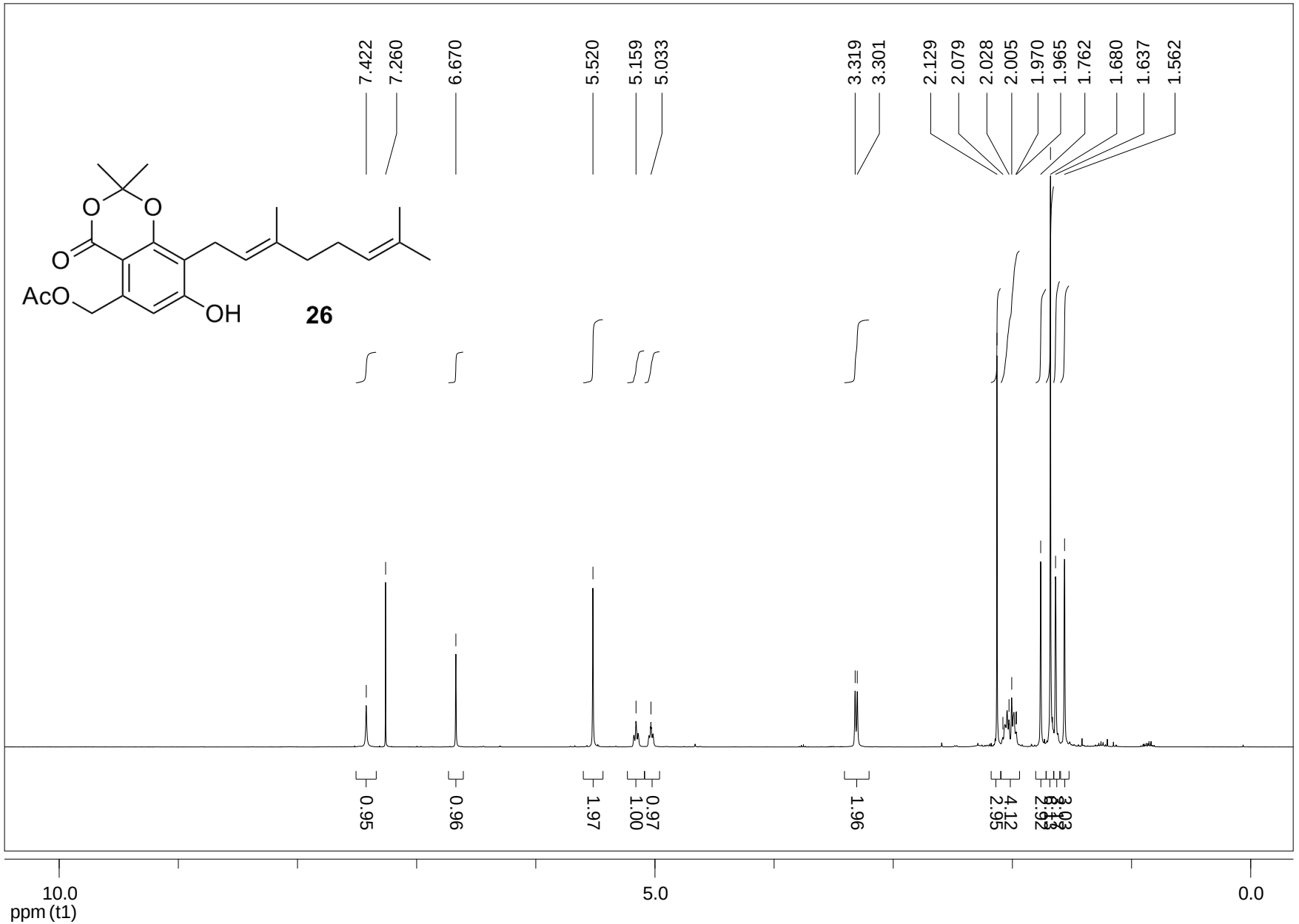
(*E*)-3,7-Dimethylocta-2,6-dienyl 4-acetoxy-2-(2-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)acetyl)-3-oxobutanoate (24)



(*E*)-3,7-Dimethylocta-2,6-dienyl 4-acetoxy-2-(2-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)acetyl)-3-oxobutanoate (24)



(*E*)-(8-(3,7-Dimethylocta-2,6-dienyl)-7-hydroxy-2,2-dimethyl-4-oxo-4*H*-benzo[*d*][1,3]dioxin-5-yl)methyl acetate (26)



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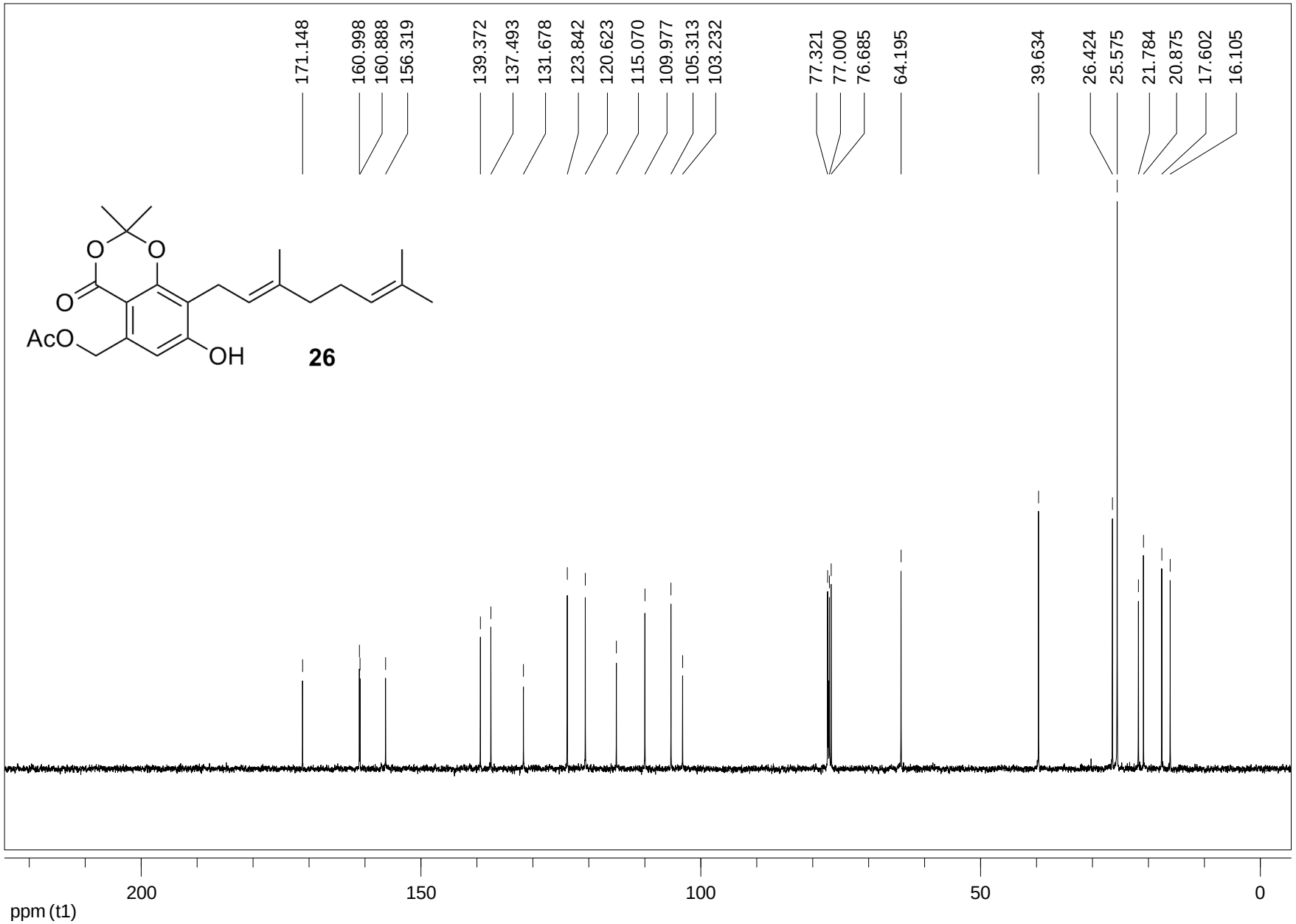
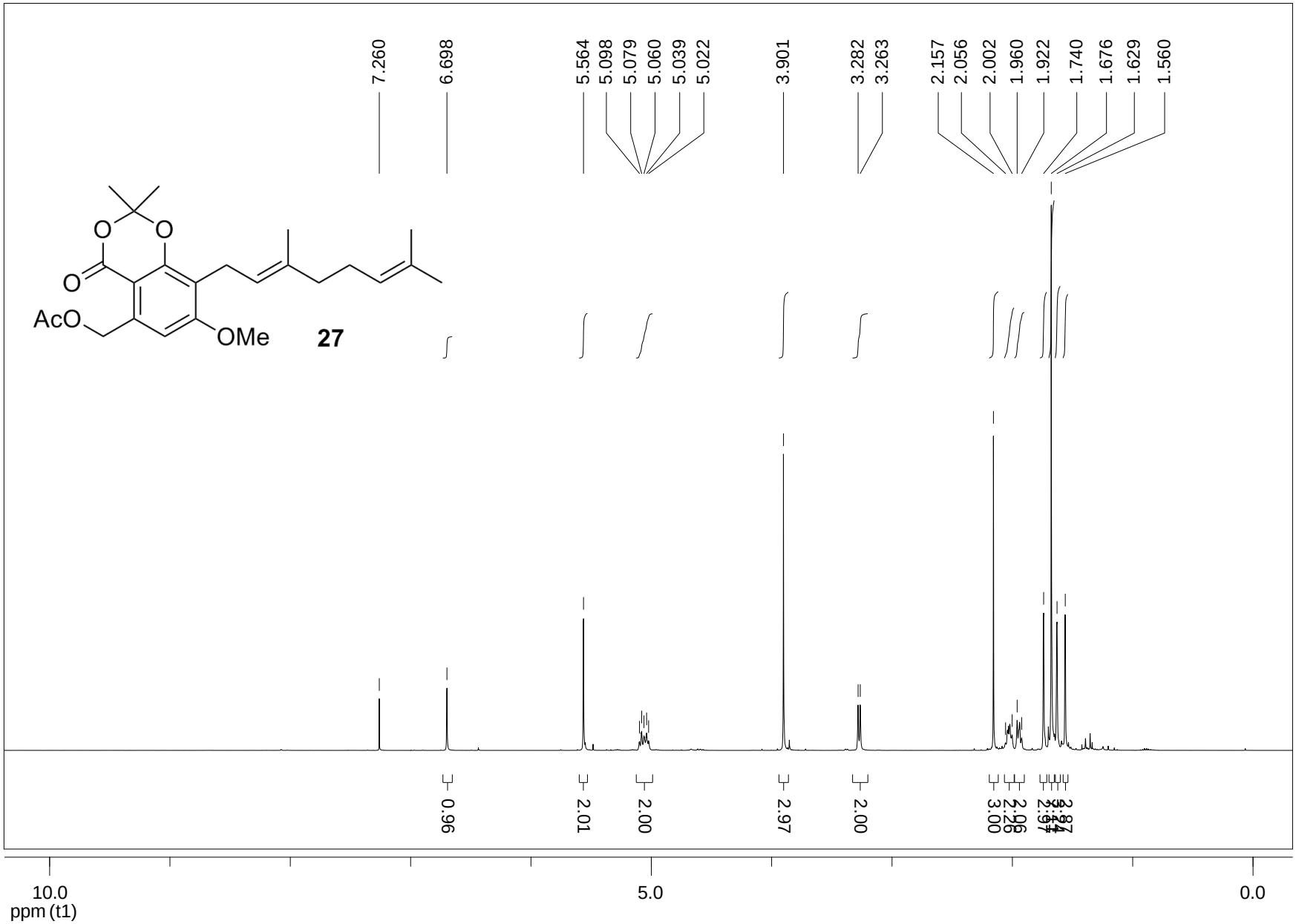
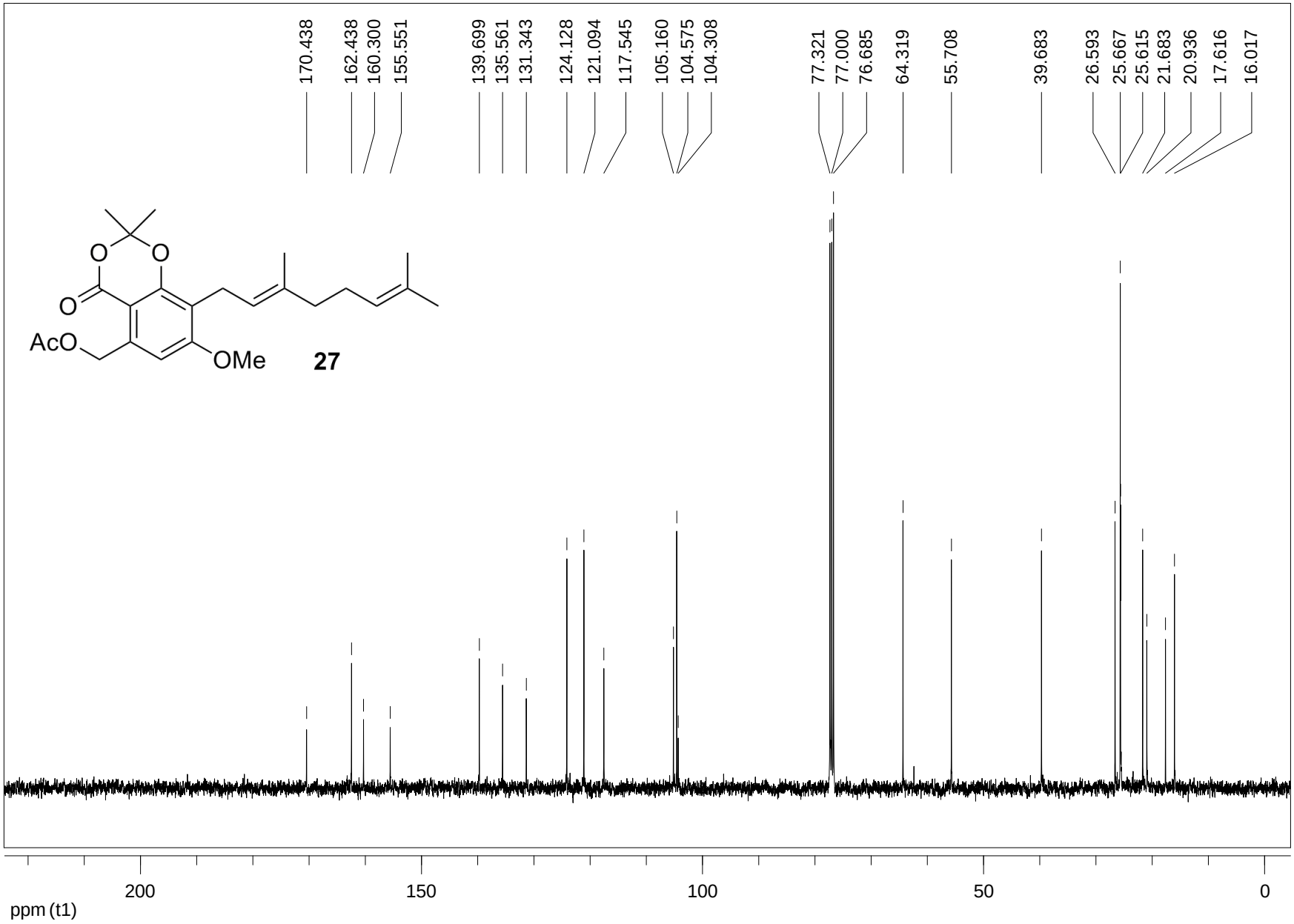


(*E*)-(8-(3,7-Dimethylocta-2,6-dienyl)-7-methoxy-2,2-dimethyl-4-oxo-4*H*-benzo[*d*][1,3]dioxin-5-yl)methyl acetate (27)



(*E*)-(8-(3,7-Dimethylocta-2,6-dienyl)-7-methoxy-2,2-dimethyl-4-oxo-4*H*-benzo[*d*][1,3]dioxin-5-yl)methyl acetate (27)



X-ray crystal structure of 2

Crystal data for **2**: $C_{19}H_{24}O_4$, M = 316.38, monoclinic, $P2_1/c$ (no. 14), a = 7.8863(2), b = 23.7456(5), c = 9.0571(2) Å, β = 97.213(3)°, V = 1682.66(7) Å^3, Z = 4, D_c = 1.249 g cm^{-3}, μ(Mo-Kα) = 0.086 mm^{-1}, T = 173 K, colorless tablets, Oxford Diffraction Xcalibur 3 diffractometer; 5677 independent measured reflections (R_{int} = 0.0202), F^2 refinement, R_1(obs) = 0.0502, wR_2(all) = 0.1367, 4342 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 65°], 256 parameters. CCDC 850168.

The C(12) to C(20) portion of the structure of **2** was found to be disordered. Two orientations were identified of *ca*. 75 and 25% occupancy, their geometries optimized, the thermal parameters of adjacent atoms restrained to be similar, and only the major occupancy non-hydrogen atoms were refined anisotropically.

The O–H proton on O(10) was located from a ΔF map and refined freely subject to an O–H distance constraint of 0.90 Å, and is involved in an intramolecular O–H···O hydrogen bond with O(2), the O···O and H···O separations being 3.0824(12) and ca. 2.38 Å respectively, with an O–H···O angle of ca. 135°.

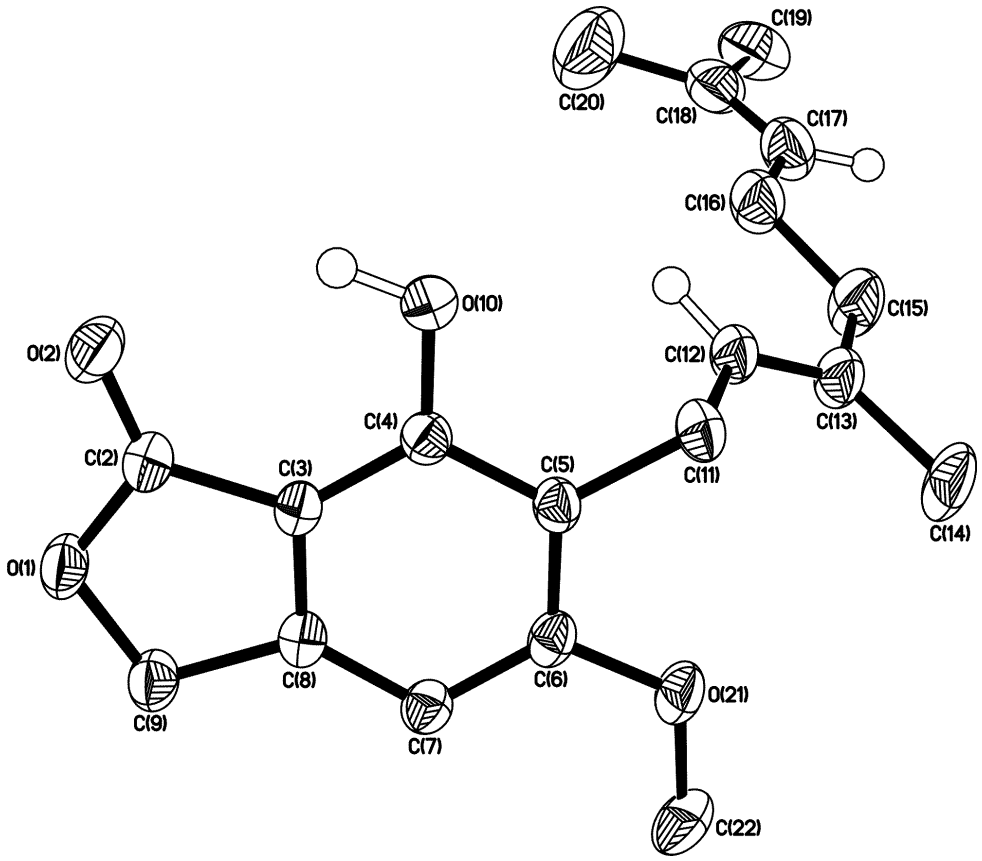


Figure S1. The molecular structure of **2** (50% probability ellipsoids).