

Supplementary Material

An enantiopure building block for naturally occurring hydroporphyrins and vitamin B₁₂ from Hagemann's ester

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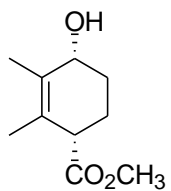
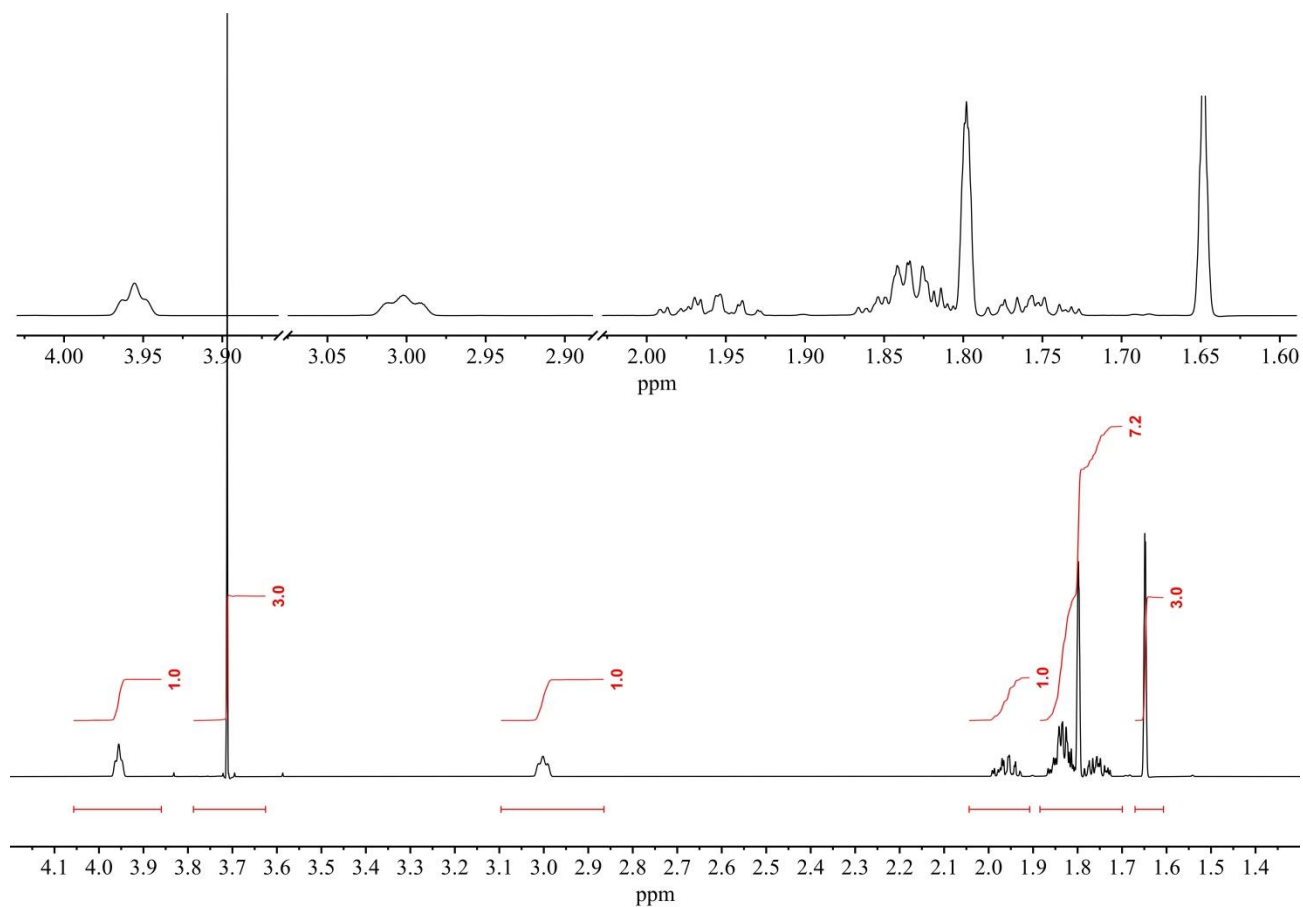
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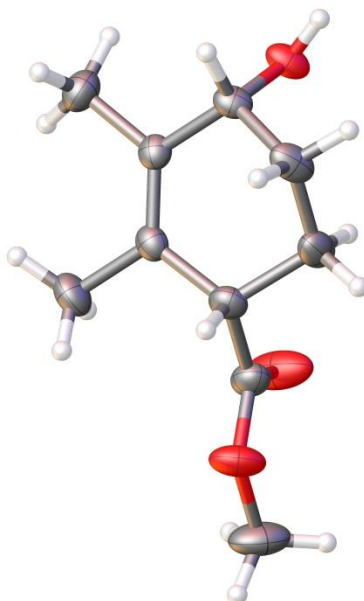
Email: mont@uni-bremen.de

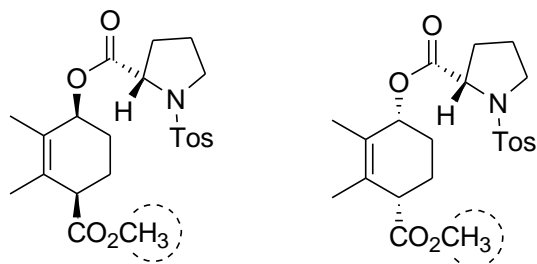
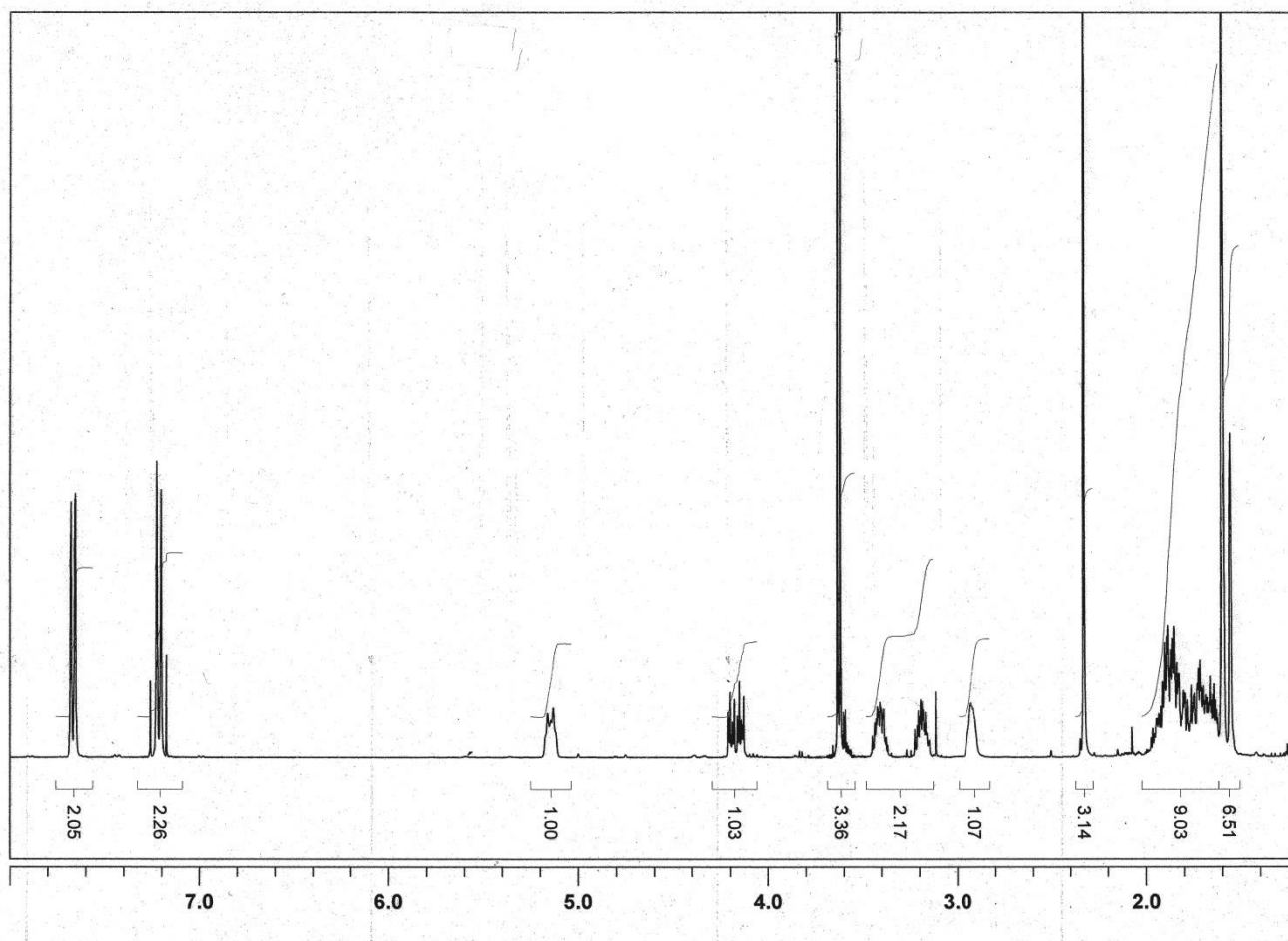
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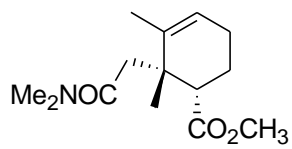
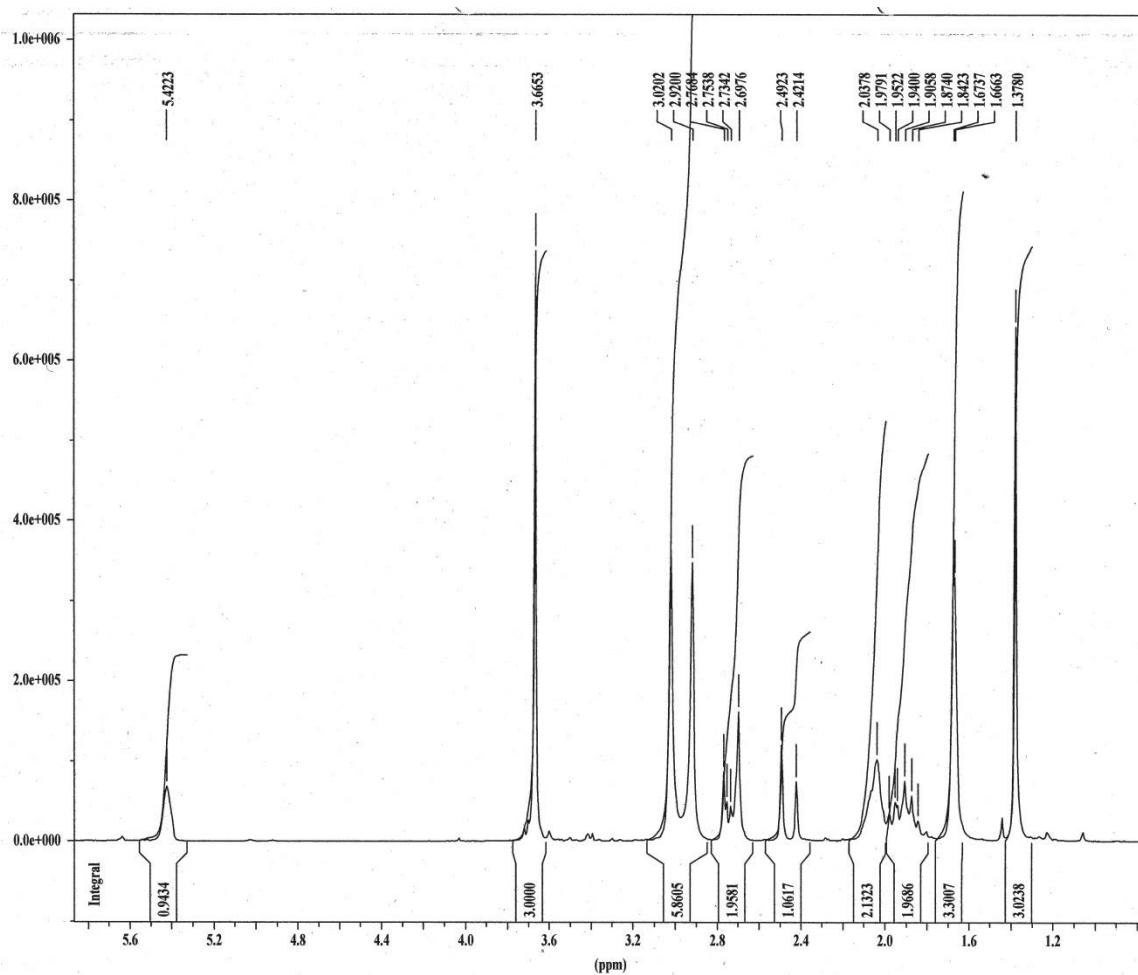
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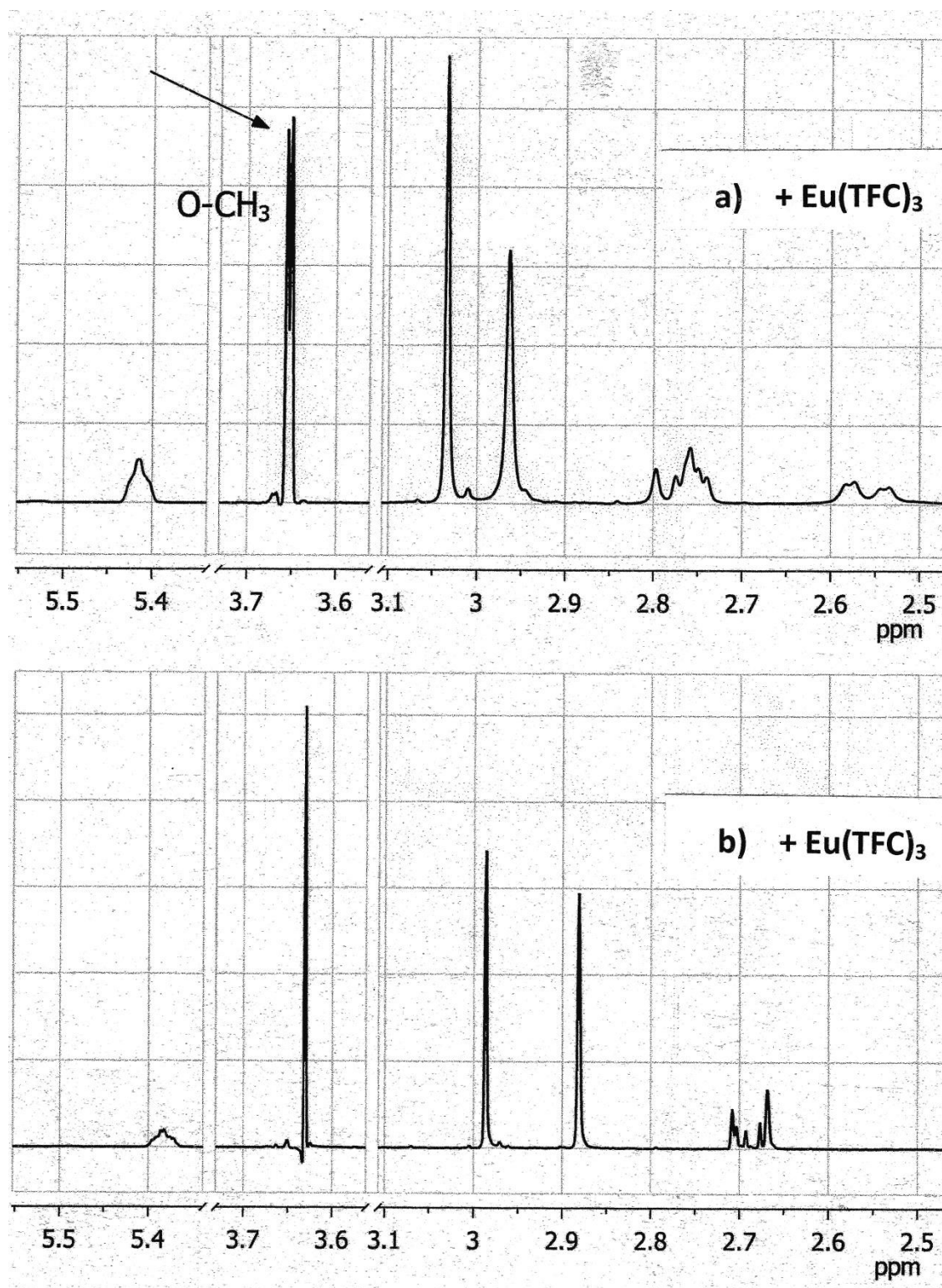
Compound 5/*rac*-5**¹H NMR (600 MHz, CDCl₃)**

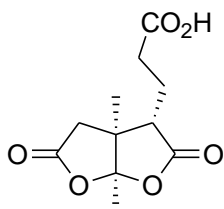
X-Ray crystal-structure analysis of *rac*-5: C₁₀H₁₆O₃ M 184.23, thermal ellipsoids are shown at 50% level. Monoclinic, space group P2₁/n, D_c = 1.1212 [Mg/m³], Z = 8, unit cell a = 1289.2(2), b = 776.60(10), c = 2114.1(3) [pm], α = 90°, β = 107.420(10)°, γ = 90°, V = 2.0196(5) [nm³], μ(MoKα) = 0.088[mm⁻¹], wR₂ = 0.1388. Deposition Number: CCDC 2040266.



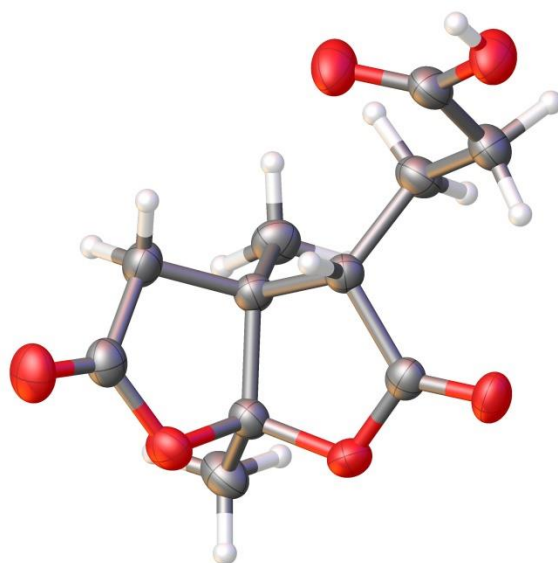
Compounds 14/15**¹H NMR (360 MHz, CDCl₃)**

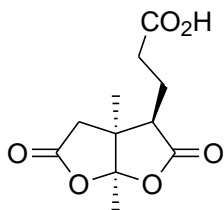
Compound 2**¹H NMR (360 MHz, CDCl₃)**



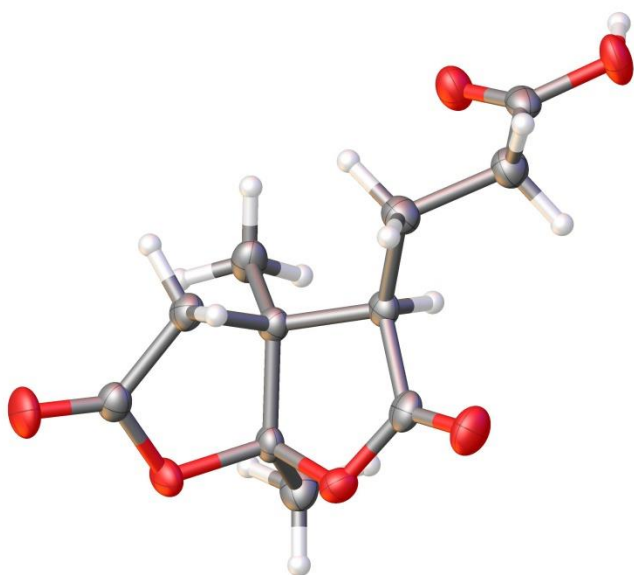
Compound *rac*-8

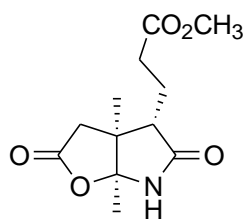
X-Ray crystal-structure analysis of *rac*-8: C₁₁H₁₄O₆ M 242.22, thermal ellipsoids are shown at 50 % level. Monoclinic, space group P2₁/c, D_c = 1.422 [Mg/m³], Z = 4, unit cell a = 675.30(10), b = 1701.1(2), c = 1037.70(10) [pm], $\alpha = 90^\circ$, $\beta = 108.340(10)^\circ$, $\gamma = 90^\circ$, V = 1.1315(2) [nm³], $\mu(\text{MoK}\alpha) = 0.117$ [mm⁻¹], wR₂ = 0.1129. Deposition Number: CCDC 2040263.



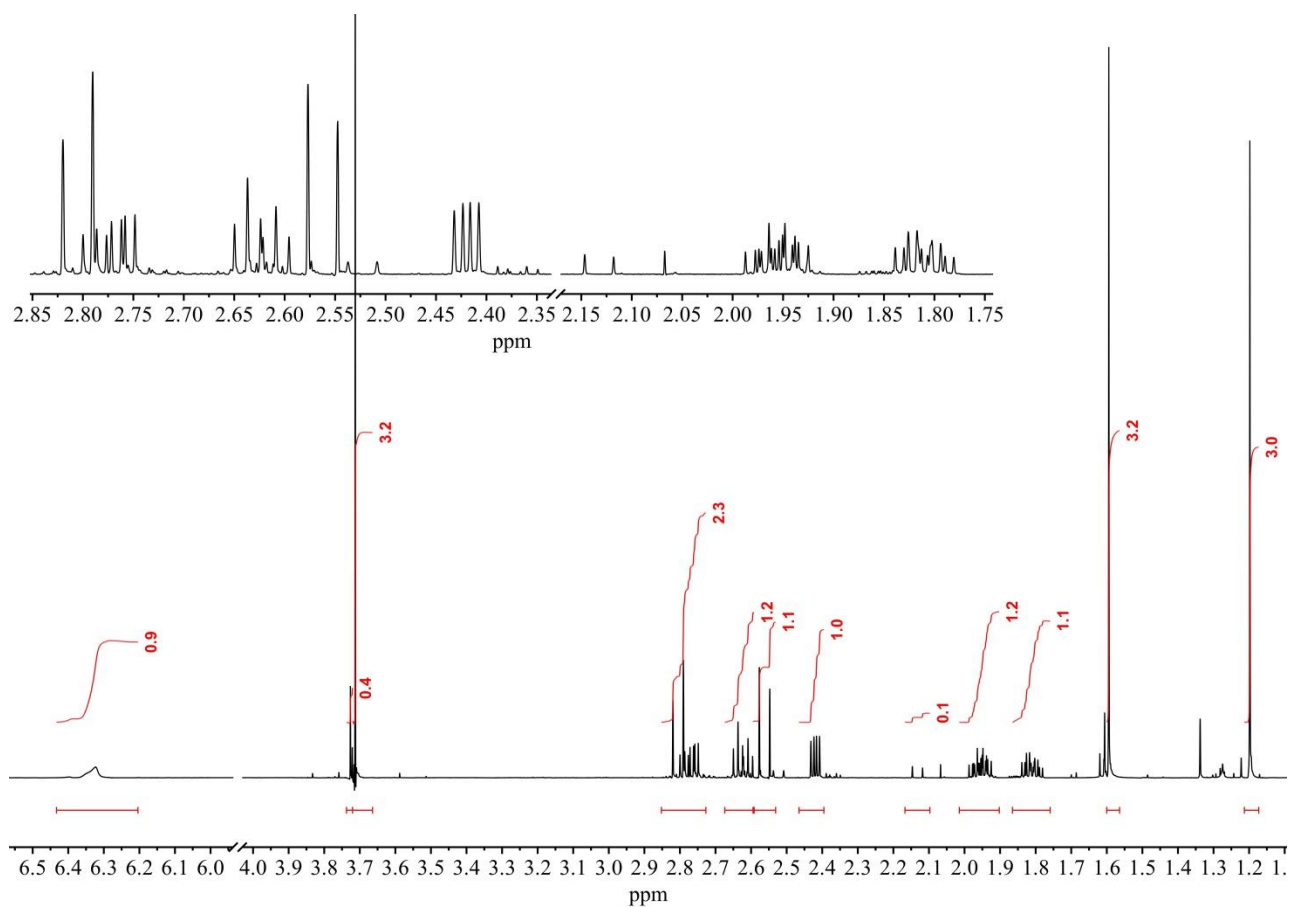
Compound *epi-rac-8*

X-Ray crystal-structure analysis of *epi-rac-8*: C₁₁H₁₄O₆ M 242.22, thermal ellipsoids are shown at 50 % level. Monoclinic, space group P2₁/c, D_C = 1.433 [Mg/m³], Z = 4, unit cell a = 811.00(10), b = 2001.5(3), c = 714.8(3) [pm], α = 90°, β = 104.62(2)°, γ = 90°, V = 1.1224(5) [nm³], μ(MoKα) = 0.118 [mm⁻¹], wR₂ = 0.1762. Deposition Number: CCDC 2040267.

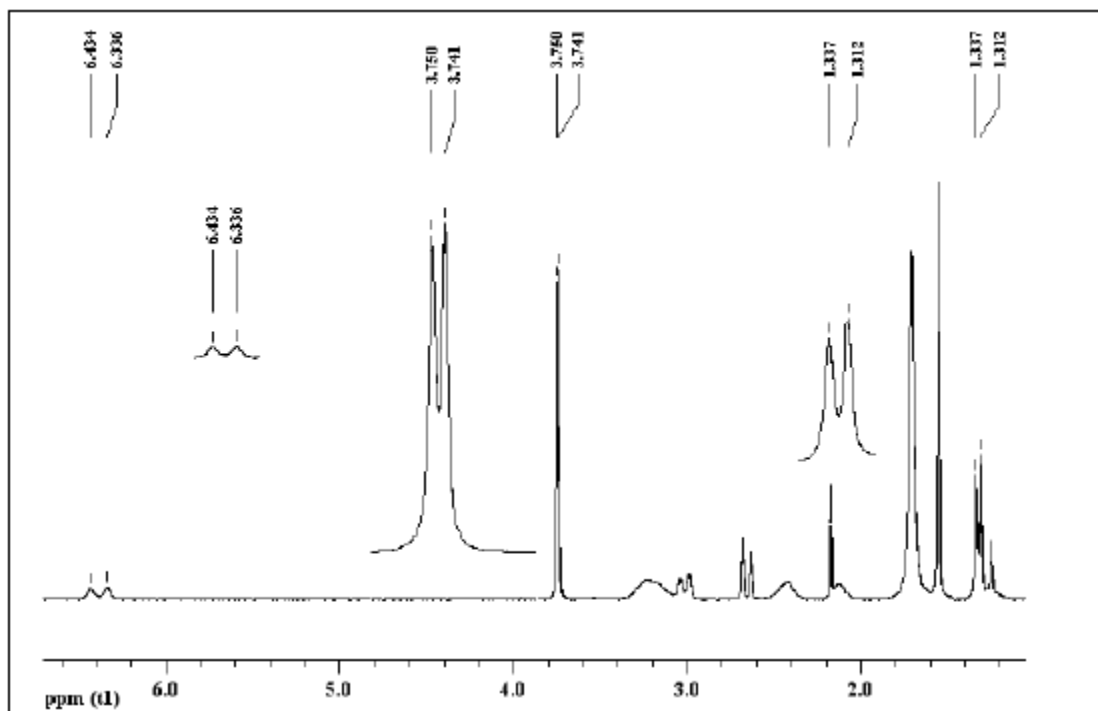


Compound 3/*rac*-3

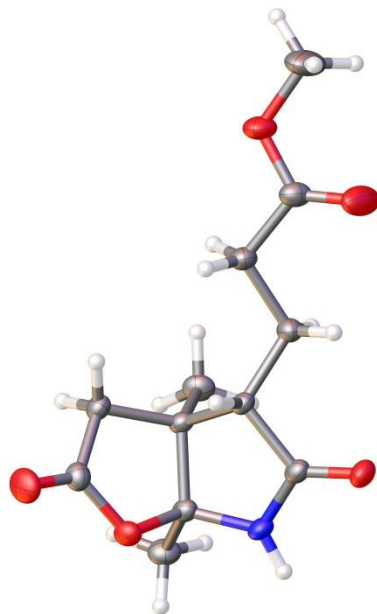
¹H NMR (600 MHz, CDCl₃): 3 + trace of 2-*epi*-3

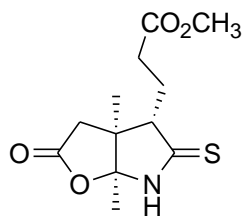


^1H NMR (360 MHz, CDCl_3) shift experiment on *rac*-3 with $\text{Eu}(\text{TFC})_3$. Split off of -NH, $-\text{CO}_2\text{CH}_3$ and $1-\text{CH}_3$ signals.

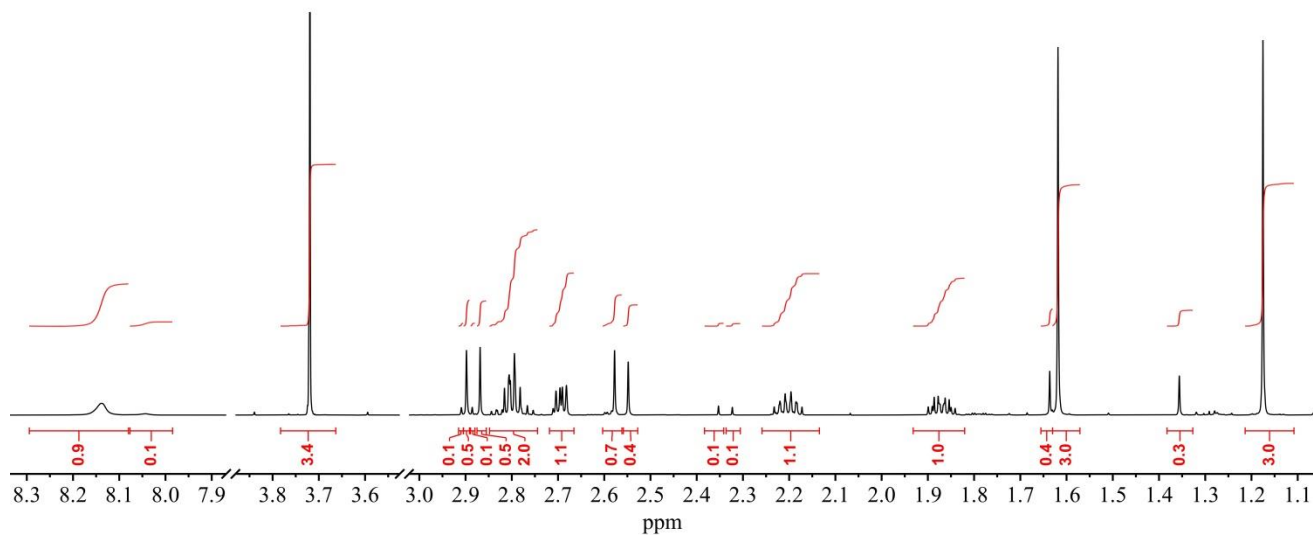
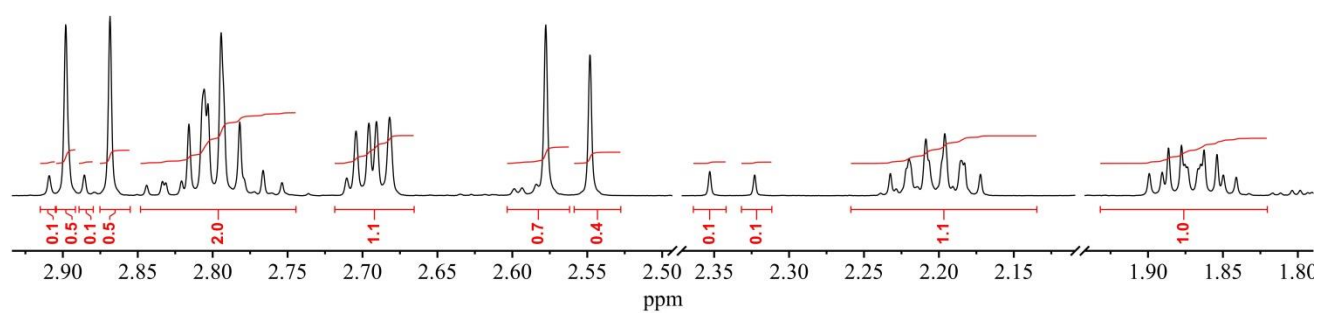


X-Ray crystal-structure analysis of *rac*-3: $\text{C}_{12}\text{H}_{17}\text{NO}_3$ M 255.27, thermal ellipsoids are shown at 50 % level. Triclinic, space group P-1, $D_c = 1.340$ [Mg/m^3], $Z = 2$, unit cell $a = 669.80(10)$, $b = 859.80(10)$, $c = 1189.1(2)$ [pm], $\alpha = 98.470(10)^\circ$, $\beta = 104.930(10)^\circ$, $\gamma = 101.950(10)^\circ$, $V = 0.63259(16)$ [nm^3], $\mu(\text{MoK}\alpha) = 0.105$ [mm^{-1}], $wR_2 = 0.1297$. Deposition Number : CCDC 2040265.

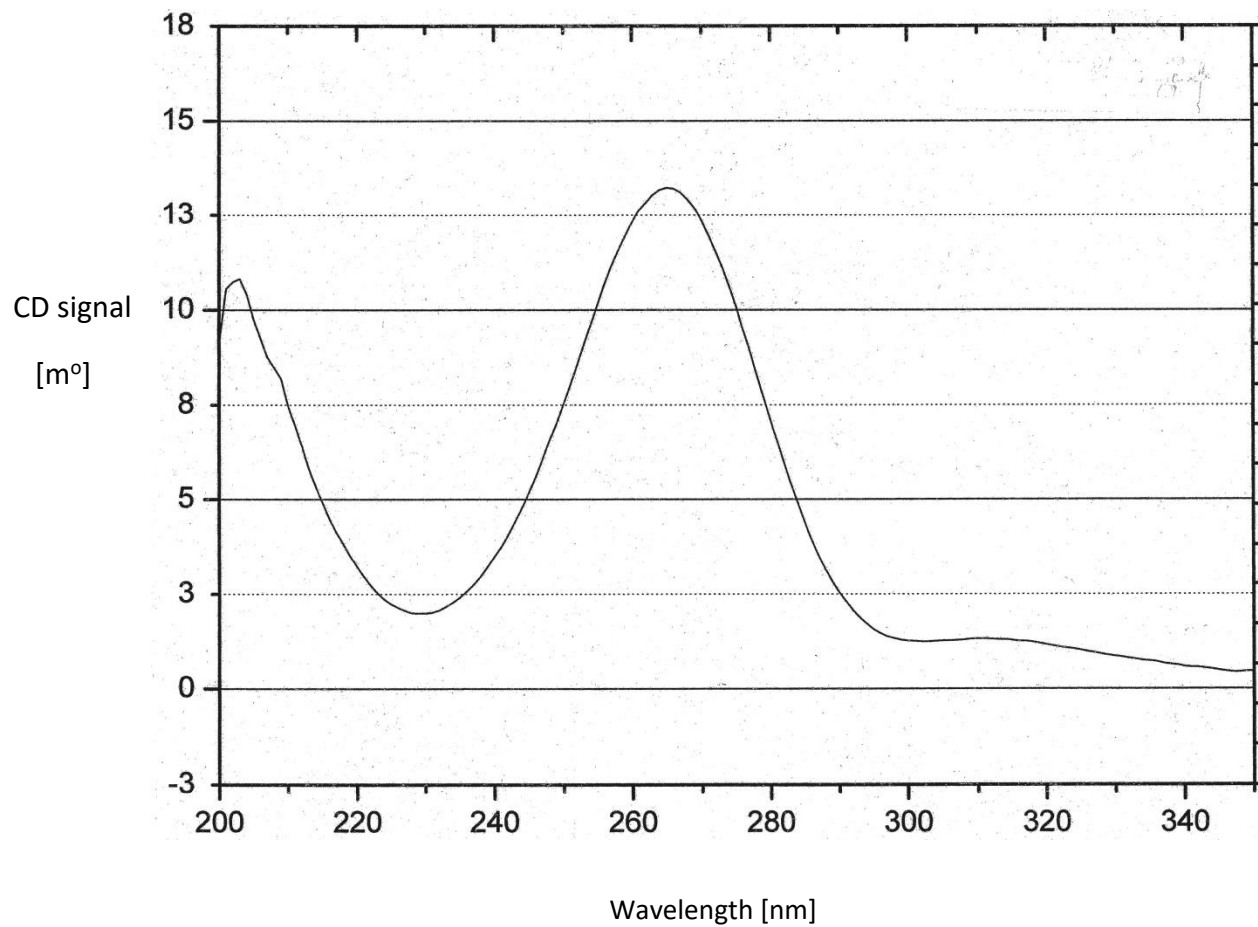


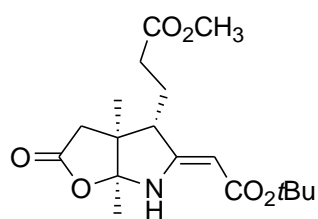
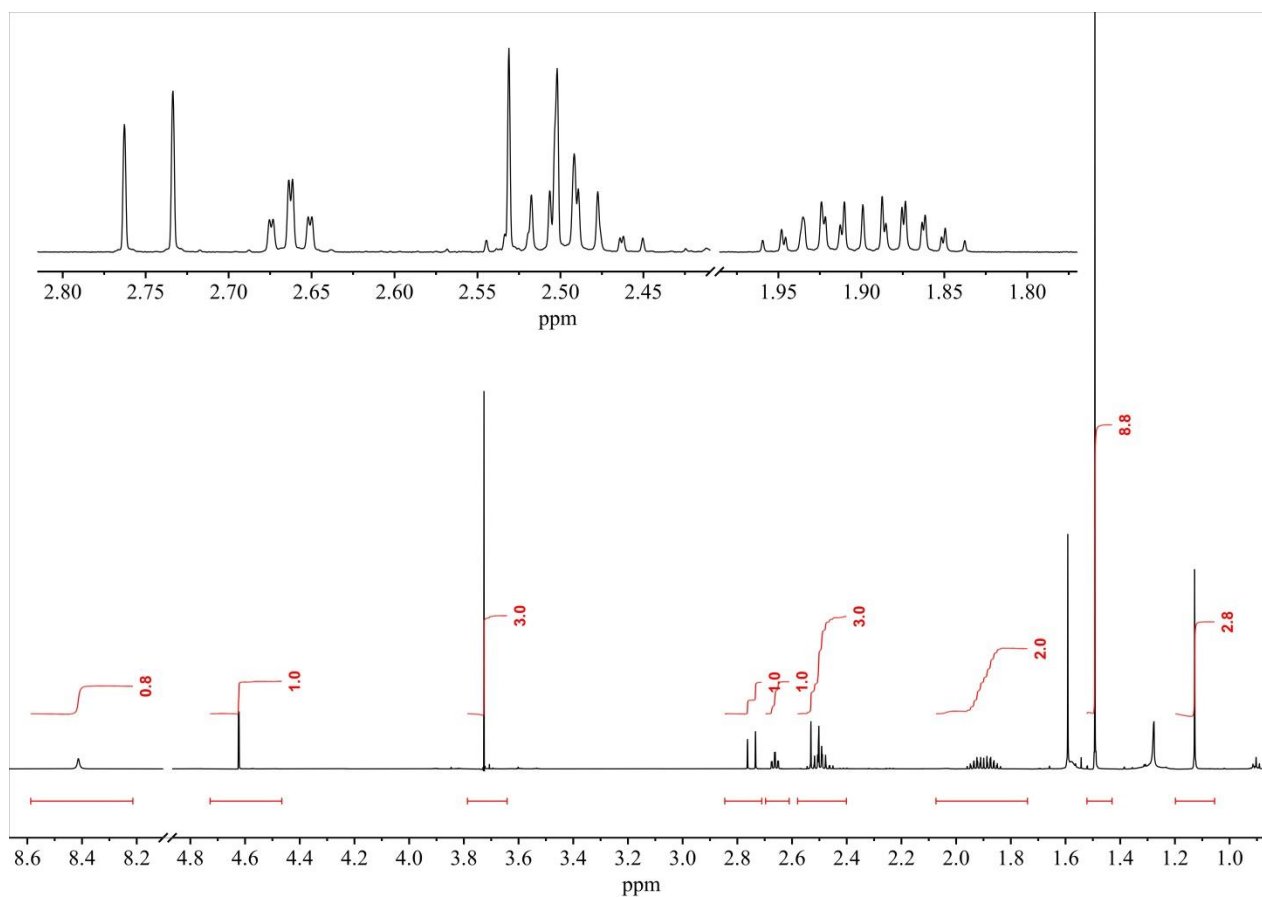
Compound 10

¹H NMR (600 MHz, CDCl₃): 10 + ca. 10 % of 2-*epi*-10

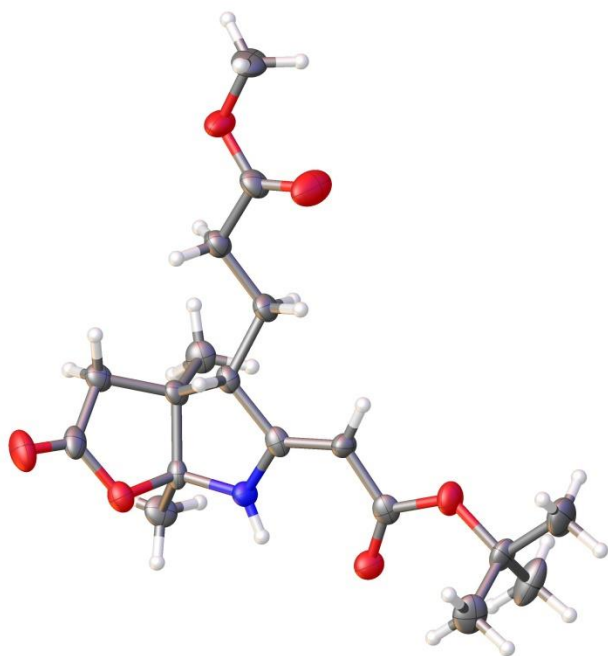


CD spectrum in CH₃OH [$c = 9.40 \times 10^{-5}$ M, $\Theta(\lambda) = 1415$ (267 nm)]



Compound 12/rac-12**¹H NMR (600 MHz, CDCl₃)**

X-Ray crystal-structure analysis of *rac*-12: $C_{18}H_{27}NO_6$ M 353.41, thermal ellipsoids are shown at 50 % level. Monoclinic, space group $P2_1/n$, $D_c = 1.247$ [Mg/m^3], $Z = 4$, unit cell $a = 669.1(2)$, $b = 3324.9(6)$, $c = 852.5(2)$ [pm], $\alpha = 90^\circ$, $\beta = 96.91(2)^\circ$, $\gamma = 90^\circ$, $V = 1.8828(8)$ [nm^3], $\mu(MoK\alpha) = 0.093$ [mm^{-1}], $wR_2 = 0.2179$. Deposition Number: CCDC 2040264.



CD spectrum of 12 in CH_3OH [$c = 2.86 \times 10^{-5} M$, $\Theta(\lambda) = 7944$ (265)]

