The Additional Supporting Information for the paper:

Structure – Chiroptical Properties Relationship of *Cisoid* Enones with α-Methylenecyclopentanone Unit.

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Contents

1. Theoretical UV-absorption spectra of selected *cis*-enone molecules (1, 2, 3, and 6)

To locate the position of the charge-transfer state and confirm the correct assignment of other states in the UV-absorption spectrum the additional calculations were done using the TURBOMOLE program package[1,2] making use of the Resolution-of-the-Identity (RI) approximation for the evaluation of the electron-repulsion integrals.[3]

Firstly, the equilibrium geometries of the most stable conformers of the selected molecular systems in their closed-shell singlet ground state (S_0) were determined with the MP2 method[4] with the default def-SV(P) basis set. Secondly, the excitation energies and response properties of the lowest excited singlet states were calculated using the CC2 method[5,6] and the correlation-consistent Valence Double Zeta basis set with polarization functions on all atoms (cc-pVDZ)[7] was used in this calculations.

References

1. TURBOMOLE, V5.9 2006, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2006, TURBOMOLE GmbH, since 2006; available from http://www.turbomole.com.
2. R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*, 1989, **162**, 165.
3. F.Weigend and M. Häser, *Theor. Chem. Acc.*, 1997, **97**, 331.
4. C. Møller and M.S. Plesset, *Phys. Rev.*, 1934, **46**, 0618.
5. O. Christiansen, H. Koch and P. Jorgensen, *Chem. Phys. Lett.*, 1995, **243**, 409.
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The UV-absorption spectra of the four selected *cis*-enones **1**, **2**, **3** and **6** present several common features. The lowest lying excited singlet state for these molecules is always of the nπ* orbital nature. This locally-excited state results from local excitations within the enone-part of the molecule. The respective excitation energy values, *ΔE*, for these enones are given in Supporting Information and compared to the experimental findings. While usually the nπ* states are dark - non-absorbing states - the S_1(nπ*) state is also characterized by low oscillator strength, *f*.

The excitation energies to the second and higher excited states are lying in the far-UV region of the spectrum, over 2 electron volts above that to the S_1(nπ*) state, in the range of 6 to 7 eV. In the case of the enones **1**-**3** the only one strongly absorbing ππ* excited state (*f*~0.3) is present in this UV-range; it is the S_3(ππ*) state for the enone **1** (of *ΔE*=6.29 eV), the S_2(ππ*) state for the enone **2** (5.95 eV), and S_2(ππ*) state for the enone **3** (of *ΔE*=5.89 eV). In the case of the enone **6** there are two strong absorbing ππ*-excited states lying close to each other. These are the S_3(ππ*) and S_4(ππ*) excited states of *ΔE* equal 5.55 and 5.67 eV, respectively, among which the former is stronger absorbing than the latter.

In the case of the molecule **1** the excitation energy to the S_2(ππ*) state of 6.28 eV (197 nm) corresponds to the experimental value of 228 nm at the absorption maximum (compare Table 1). In the case of enone **2**, the maximum absorption band S_2(ππ*) is red-shifted by ~0.4 eV in comparison to the S_3(ππ*) state of **1**. It should be noted that the excitation-energy values calculated with the CC2 method are always larger than those found experimentally. The ππ* absorbing states of molecules **1**, **2** and **3** result from local excitations within the enone part (enone to enone* excitation) and, in analogy to the S_1(nπ*) states, can be classified as the LE(ππ*) states.

The second nπ* state of the studied molecules, S_2(nπ*) for **1** and S_3(nπ*) for **2** is also dark, but differently as for the S_1(nπ*) state, the electron density is moved, upon excitation from the carbon skeleton toward the opposite enone molecule side – the ester-end of the molecule.

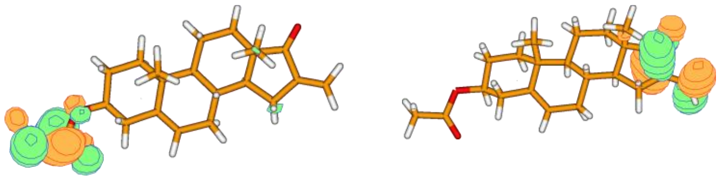
The remaining issue in this analysis is the presence of the charge-transfer (CT) state in the UV absorption spectrum of the *cis*-enones **1**, **2**, **3** and **6**. The CT-state should be characterized by a large change in dipole moment in comparison to the ground state. The change of the dipole moment value might be, in turn, visualized by the change of the shape and localization of the molecular orbitals occupied by the electrons. The values of the ground- and excited-state dipole moments calculated with the CC2 method are gathered in the Tables AS1, AS3, AS5 and AS7, while the most important HF-orbitals illustrating the electron excitations are also given in the Tables AS2, AS4, AS6 and AS8.

The CT-states for the studied molecules are of ππ*-orbital nature and involve substantial shift of electron density from the isolated double bond present in the carbon skeleton to the enone part of the molecule. This is reflected in a large change of the excited-state dipole moment in comparison to its ground-state value.

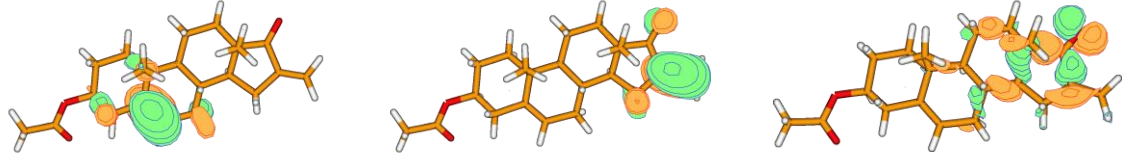
Table AS1. Vertical excitation energies (*ΔE*), oscillator strength (*f*), dipole moment (*μ*) and dominant electronic configurations of the lowest energy conformer **1**(1) of *cis*-enone **1** calculated with the CC2/cc-pVDZ method at the geometry optimized at the MP2/def-SV(P) level. Experimental values (in nm) taken form Table 1.

	ΔE/ eV(λ)	*f*	*μ / D*	*electronic structure*
S_0	0.0	-	2.3	-
S_1 (nπ*)	**3.67 (338) [expt. 348]**	**0.0006**	**3.8**	**0.88*(91→94)**
S_2 (nπ*)	6.08 (204)	0.0015	1.5	0.53*(88→97)+0.53*(86→97)
S_3 (ππ*)	**6.29 (197) [expt. 226]**	**0.3172**	**3.5**	**0.96*(92→94)**
S_4 (ππ*)/(nπ*)	6.50 (191)	0.0077	23.5	0.86*(93→94)−0.42*(90→94)
S_5 (nπ*)/(ππ*)	6.67 (186)	0.0003	16.3	0.75*(90→94)+0.47*(93→94)
S_6 (nπ*)	6.86 (181)	0.0085	13.1	0.67*(89→94)+**0.38*(91→94)**

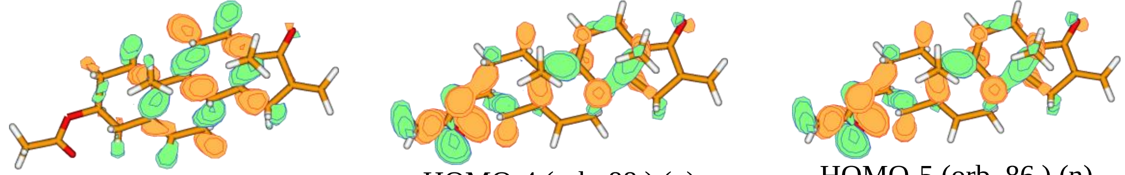
Table AS2. The two highest occupied π-orbitals (92 and 93), the four highest occupied n orbitals (86, 88, 90 and 91), and the two lowest unoccupied π* orbitals (94 and 97) of the lowest energy conformer **1**(1) of *cis*-enone **1**, determined at the equilibrium geometry of the electronic ground state.



LUMO+1 (orb. 97) (π*) LUMO (orb. 94) (π*)



HOMO (orb. 93) (π) HOMO-1 (orb. 92) (π) HOMO-2 (orb. 91) (n)

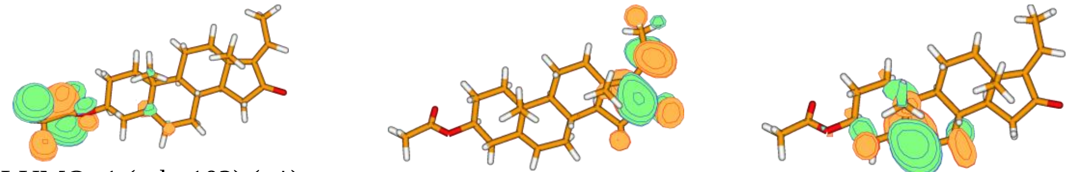


HOMO-3 (orb. 90) (n) HOMO-4 (orb. 88) (n) HOMO-5 (orb. 86) (n)

Table AS3. Vertical excitation energies (*ΔE*), oscillator strength (*f*), dipole moment (*μ*) and dominant electronic configurations of the lowest energy conformer **2**(1) of the *cis*-enone **2** calculated with the CC2/cc-pVDZ method at the geometry optimized at the MP2/def-SV(P) level. Experimental values (in nm) taken form Table 1.

	ΔE/ *eV*(*λ*)	*f*	*μ* / *D*	*electronic structure*
S$_0$	0.0	-	2.9	-
S$_1$ (nπ*)	**3.77 (329) [expt. 345]**	**0.0010**	**2.7**	**0.88*(95→98)**
S$_2$ (ππ*)	**5.95 (208) [expt. 243]**	**0.2921**	**5.5**	**0.96*(96→98)**
S$_3$ (nπ*)	6.08 (204)	0.0014	2.2	0.65*(91→02)+0.35*(90→102) −0.33(93→102)
S$_4$ (nπ*) / (ππ*)	6.46 (192)	0.0038	12.4	0.79*(94→98)+0.32*(97→98)
S$_5$ (ππ*)	6.75 (184)	0.0073	25.6	0.93*(97→98)
S$_6$ (nπ*) / (ππ*)	7.02 (177)	0.0077	9.9	0.43*(93→98)−**0.36*(95→98)** +0.33*(94→98)

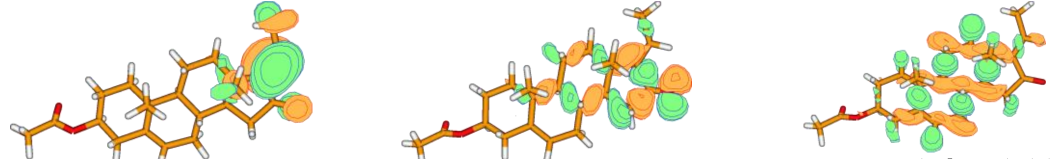
Table AS4. The two highest occupied π-orbitals (96 and 97), the five highest occupied n orbitals (90, 91, 93, 94 and 95), and the two lowest unoccupied π* orbitals (98 and 102) of the lowest energy conformer **2**(1) of the *cis*-enone **2**, determined at the equilibrium geometry of the electronic ground state.



LUMO+1 (orb. 102) (π*)

LUMO (orb. 98) (π*)

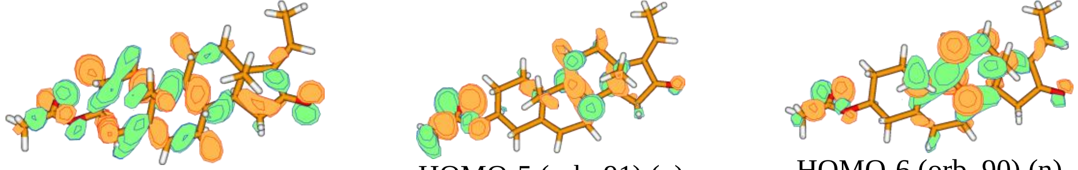
HOMO (orb. 97) (π)



HOMO-1 (orb. 96) (π)

HOMO-2 (orb. 95) (n)

HOMO-3 (orb. 94) (n)



HOMO-4 (orb. 93) (n)

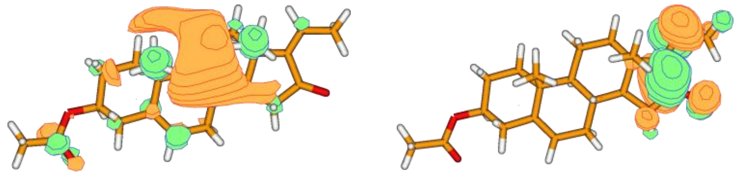
HOMO-5 (orb. 91) (n)

HOMO-6 (orb. 90) (n)

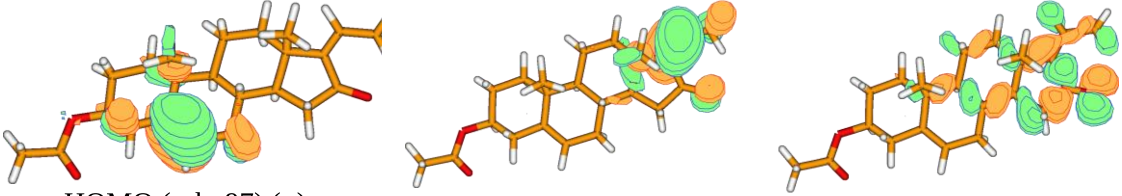
Table AS5. Vertical excitation energies (*ΔE*), oscillator strength (*f*), dipole moment (*μ*) and dominant electronic configurations of the lowest energy conformer **3**(1) of *cis*-enone **3** calculated with the CC2/cc-pVDZ method at the geometry optimized at the MP2/def-SV(P) level. Experimental values (in nm) taken form Table 1.

	ΔE/ *eV*(*λ*)	*f*	*μ* / *D*	*electronic structure*
S$_0$	0.0	-	3.4	-
S$_1$ (nπ*)	**3.64 (341) [expt. 348]**	**0.0013**	**2.3**	**0.89*(95→98)**
S$_2$ (ππ*)	**5.89 (211) [expt. 240]**	**0.2713**	**6.5**	**0.95*(96→98)**
S$_3$ (nσ*)	6.08 (204)	0.0015	2.1	0.49*(92→101)+0.44*(90→101)
S$_4$ (nπ*)/(ππ*)	6.43 (193)	0.0076	15.3	0.72*(94→98)−0.49*(97→98)

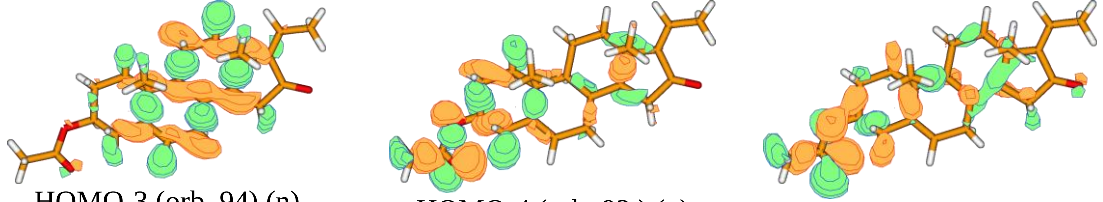
Table AS6. The two highest occupied π-orbitals (96 and 97), the four highest occupied n orbitals (90, 92, 94 and 95), and the two lowest unoccupied orbitals: π* (98) and σ* (101) of the lowest energy conformer **3**(1) of *cis*-enone **3**, determined at the equilibrium geometry of the electronic ground state.



LUMO+1 (orb. 101) (σ*)   LUMO (orb. 98) (π*)



HOMO (orb. 97) (π)   HOMO-1 (orb. 96) (π)   HOMO-2 (orb. 95) (n)

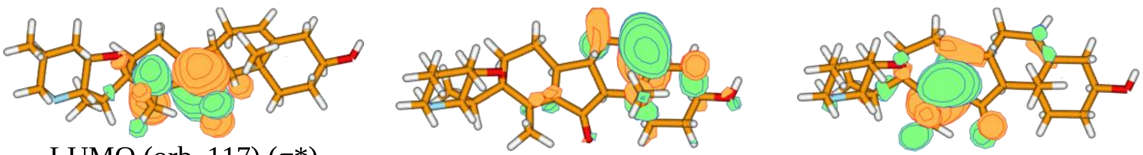


HOMO-3 (orb. 94) (n)   HOMO-4 (orb. 92) (n)   HOMO-5 (orb. 90) (n)

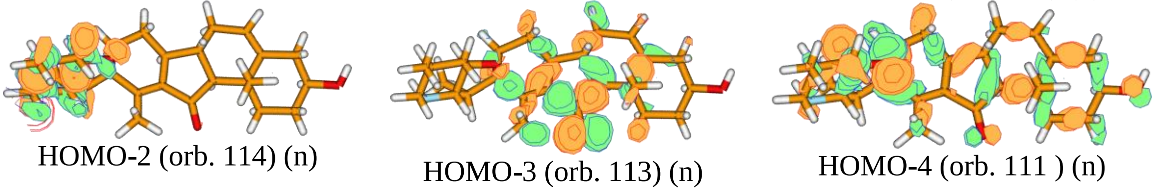
Table AS7. Vertical excitation energies (*ΔE*), oscillator strength (*f*), dipole moment (*μ*) and dominant electronic configurations of the lowest energy conformer **6**(1) of *cis*-enone **6** calculated with the CC2/cc-pVDZ method at the geometry optimized at the MP2/def-SV(P) level. Experimental values (in nm) taken form Table 1.

	ΔE/ eV(λ)	*f*	*μ / D*	*electronic structure*
S_0	0.0	-	4.4	-
S_1 (nπ*)	**3.50 (354) [expt 357]**	**0.0011**	**2.9**	**+0.90*(113→117)**
S_2 (nπ*)	5.13 (242)	0.0698	20.0	−0.74*(114→117)+0.43*(111→117) **+0.34*(115→117)**
S_3 (ππ*)	**5.55 (223) [expt 252]**	**0.3164**	**6.8**	−0.74*(116→117)+**0.56*(115→117)**
S_4 (ππ*)	**5.67 (219) [expt 252]**	**0.1719**	**9.1**	**+0.71*(115→117)**+0.61*(116→117)

Table AS8. The two highest occupied π-orbitals (115 and 116), the three highest occupied n orbitals (111, 113, and 114), and the lowest unoccupied π* orbital (117) of the lowest energy conformer **6**(1) of *cis*-enone **6**, determined at the equilibrium geometry of the electronic ground state.



LUMO (orb. 117) (π*)   HOMO (orb. 116) (π)   HOMO-1 (orb. 115) (π)



HOMO-2 (orb. 114) (n)   HOMO-3 (orb. 113) (n)   HOMO-4 (orb. 111) (n)

2. Additional conformational and spectral analysis of enone 4b

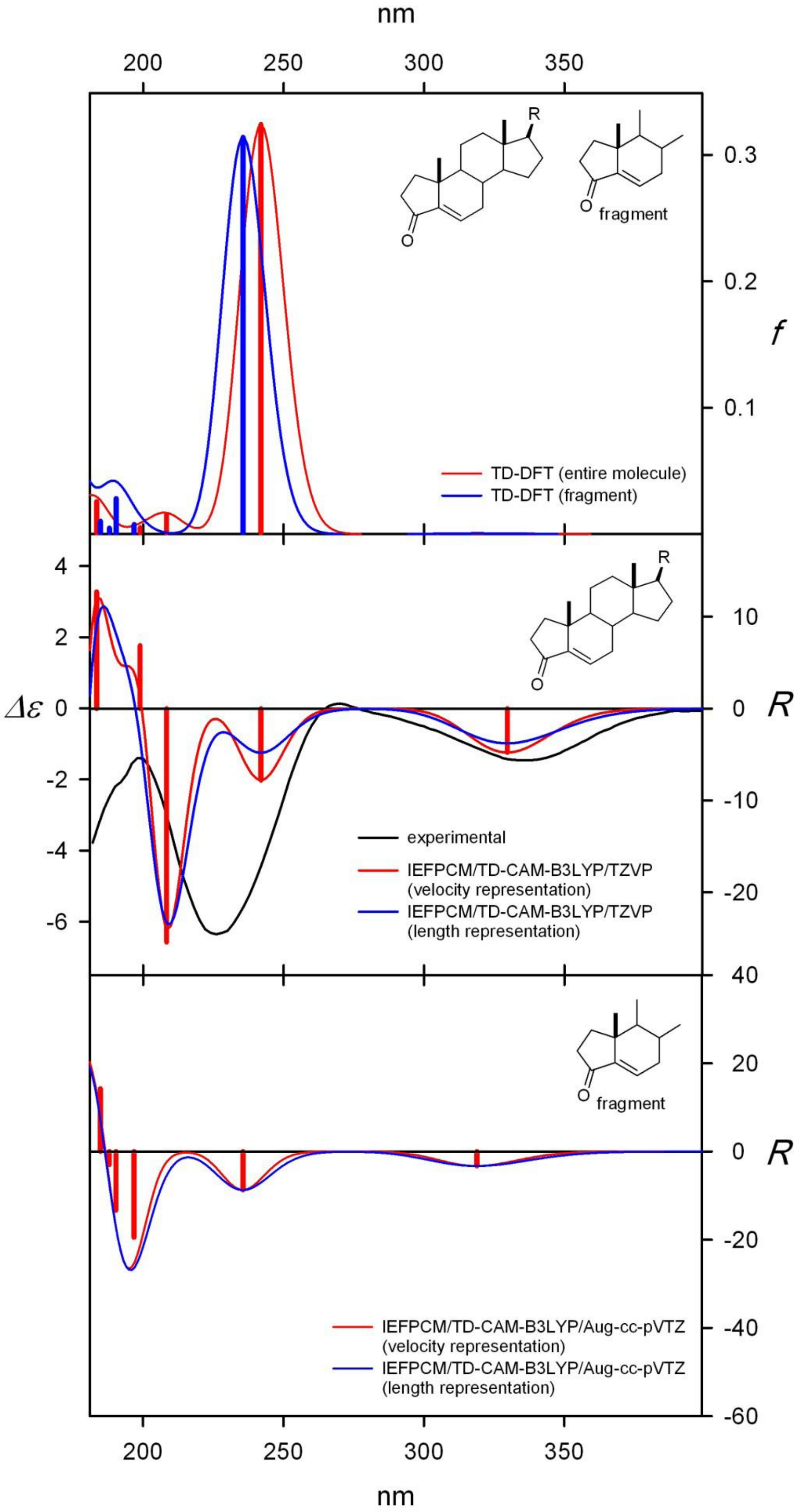


Figure AS1. UV and CD spectra calculated for conformer of **4b** at IEFPCM/TD-CAM-B3LYP/TZVP level.

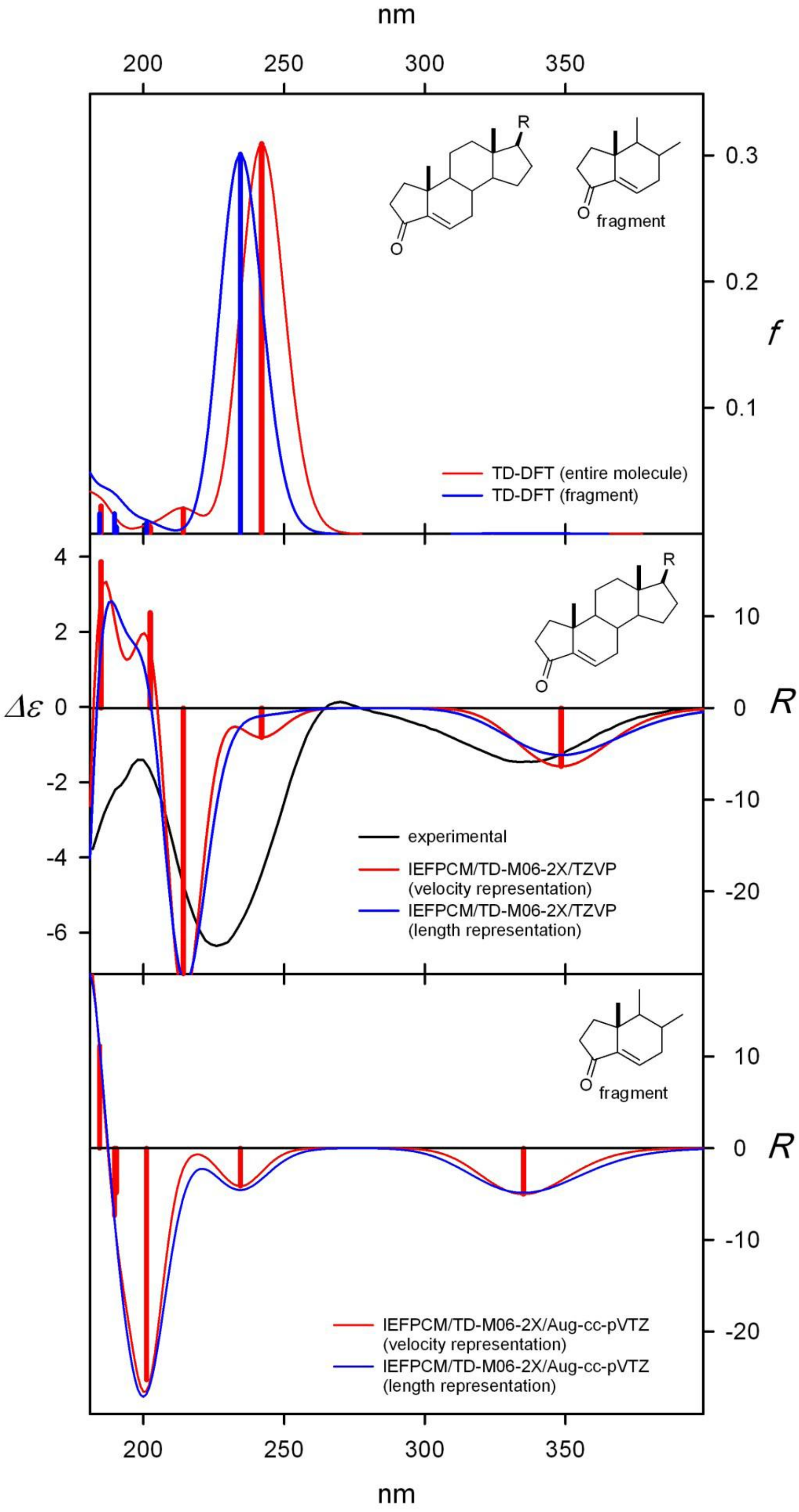


Figure AS2. UV and CD spectra calculated for conformer of **4b** at IEFPCM/TD-M06-2X/TZVP level.

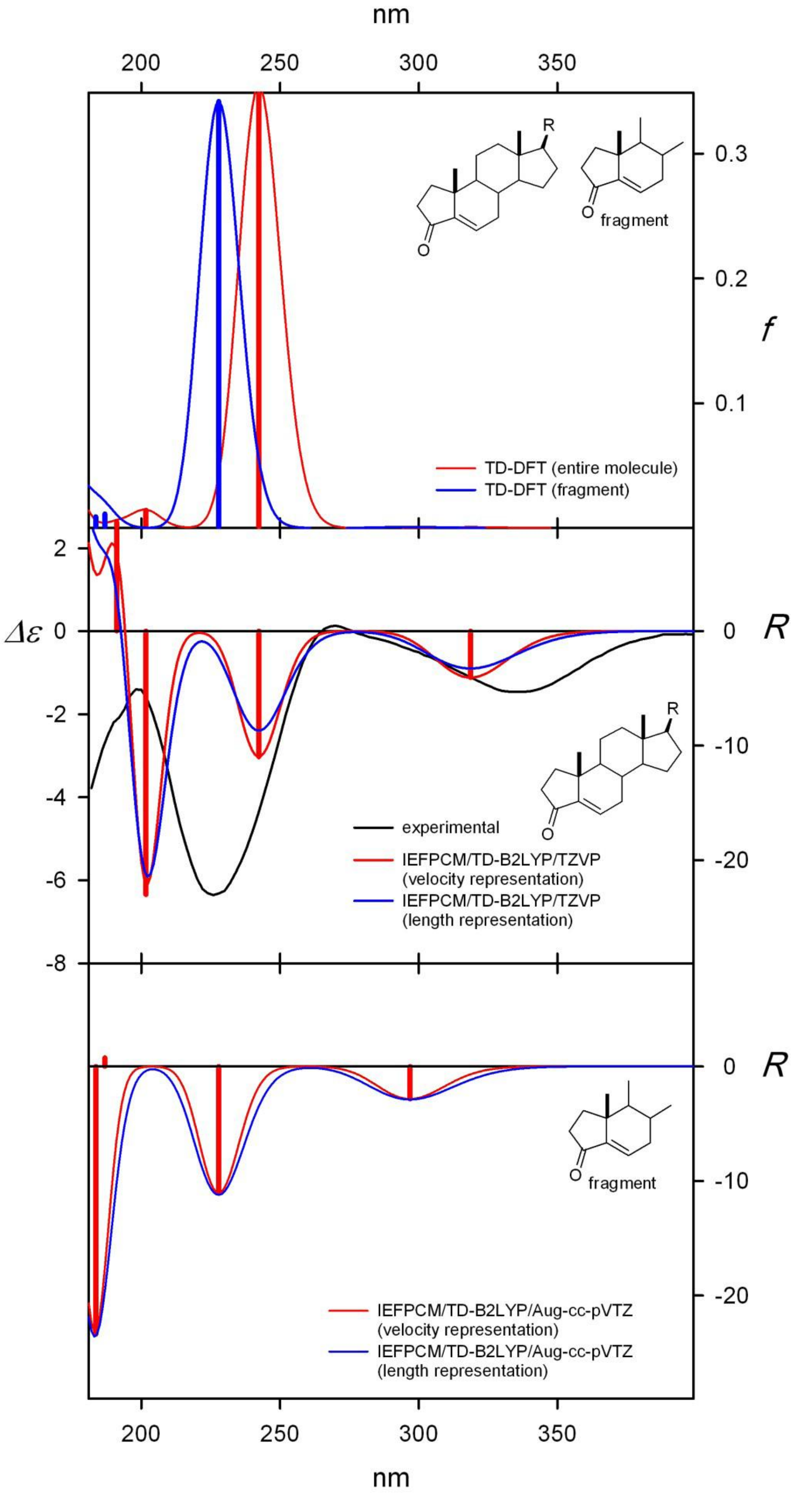


Figure AS3. UV and CD spectra calculated for conformer of **4b** at IEFPCM/TD-B2LYP/TZVP level.

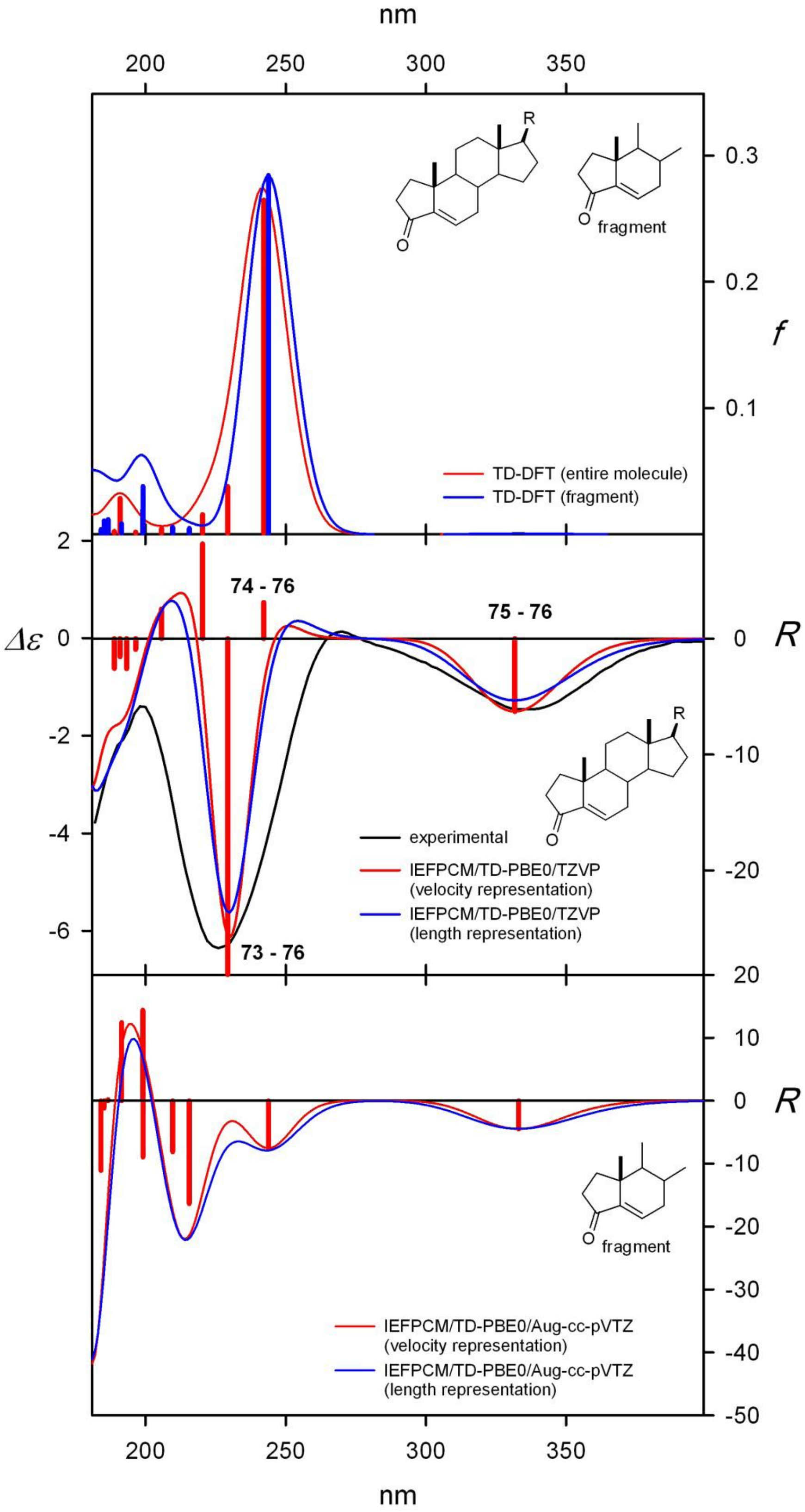


Figure AS4. UV and CD spectra calculated for conformer of **4b** at IEFPCM/TD-PBE0/TZVP level.

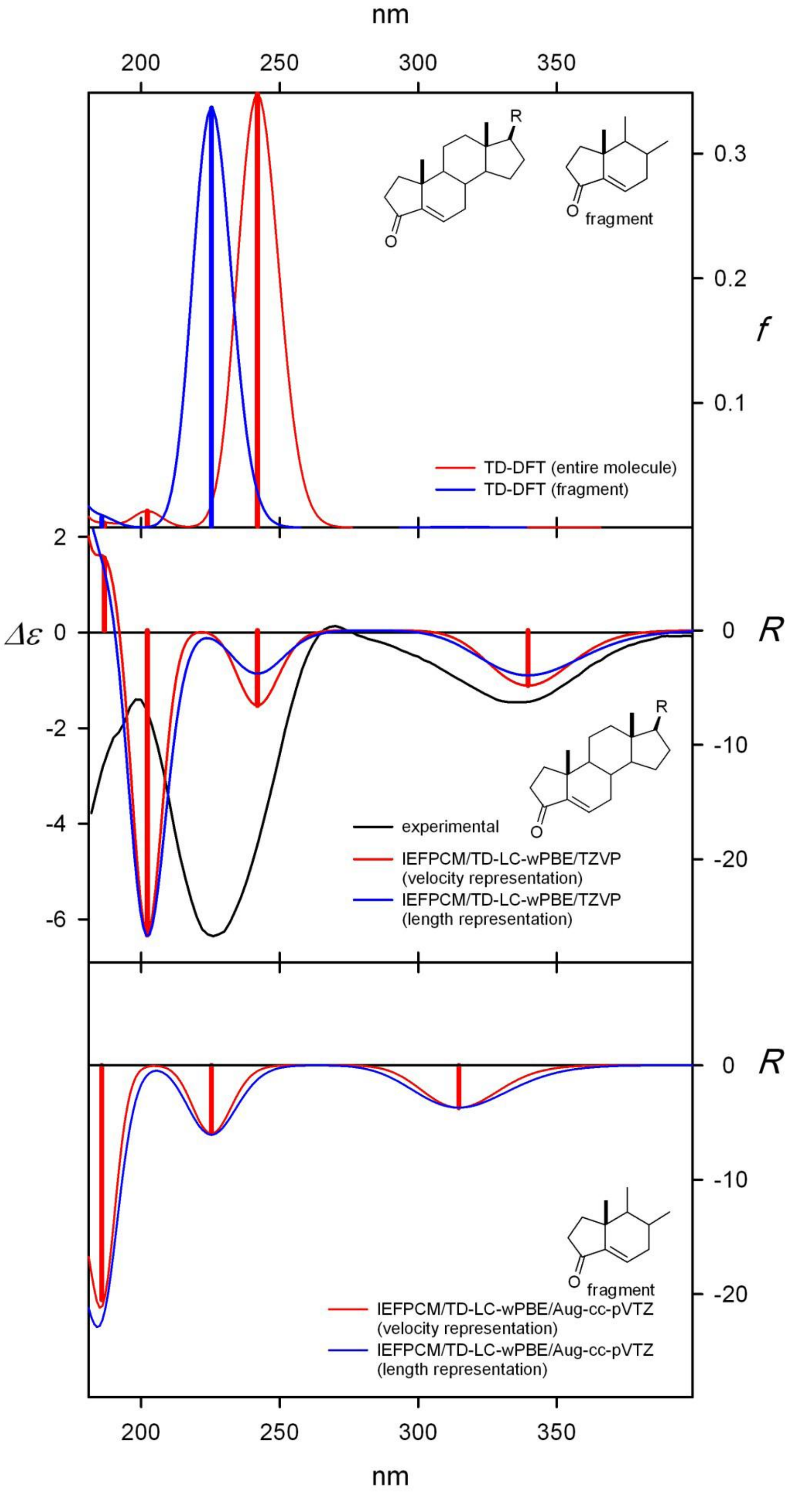


Figure AS5. UV and CD spectra calculated for conformer of **4b** at IEFPCM/TD-LC-wPBE/TZVP level.

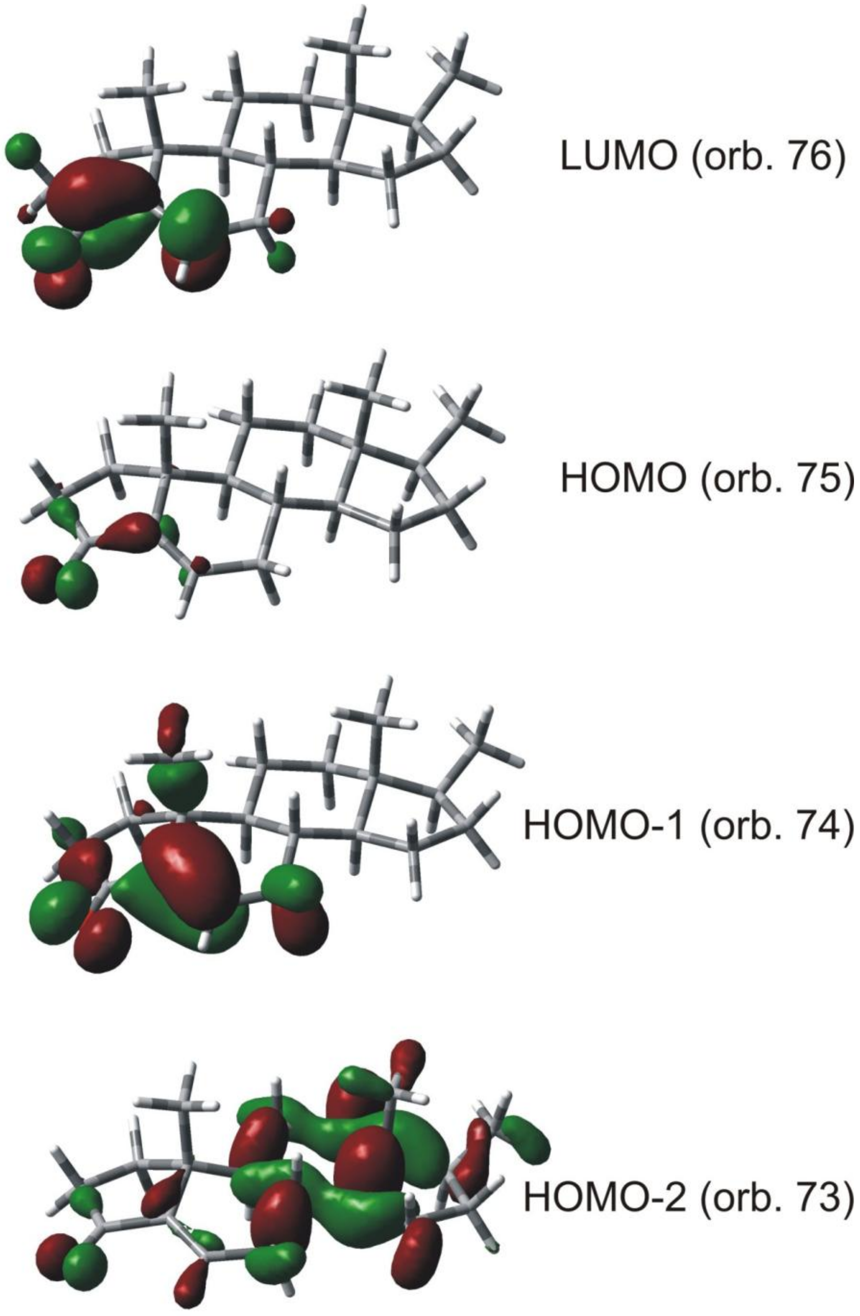


Figure AS6. The PBE0/TZVP HOMO-2 to HOMO and LUMO molecular Kohn–Sham orbitals of the conformer of **4b**.

Among five different levels of theory used to calculate Boltzmann-averaged ECD spectrum of *cis*-enone **4b** only the one simulated at IEFPCM/TD-PBE0/TZVP level of theory is in good agreement with the experimental ECD data for diagnostic bands corresponding to the nπ* and $\pi\pi$* transitions.

3. Additional conformational and spectral analysis of enone 6 (jervine)

Table AS9. Total energies (in Hartree), relative energies (ΔE, ΔG in kcal mol^{-1}), percentage populations (Pop.), absolute configuration at nitrogen atoms (CA) and values of torsion angles ω, α and β [in °] calculated at the IEFPCM/B3LYP/TZVP level for individual conformers of jervine.

							Torsion angle[a]			
Conformer	Energy	ΔE	Pop.	ΔG	Pop.	CA	ω	α	β	γ
3	−1333.21933	0.00	18	0.00	20	R	14.2	176.2	3.4	58.4
3a	−1333.21927	0.04	17	0.24	14	S	14.7	176.0	3.5	58.4
1	−1333.219256	0.05	17	0.03	20	R	14.2	176.2	3.2	−60.5
2	−1333.219232	0.06	17	0.03	19	R	14.0	176.3	3.3	−178.5
1a	−1333.219196	0.08	16	0.28	13	S	14.7	176.0	3.3	−60.5
2a	−1333.219171	0.10	15	0.23	14	S	14.5	176.1	3.3	−178.7

[a] ω = O=C-C=C; α = trans1 = (O=)C-C=C-C(-O-); β = C(10)-C(5)=C(6)-C(7); γ = H-O-C(3)-H

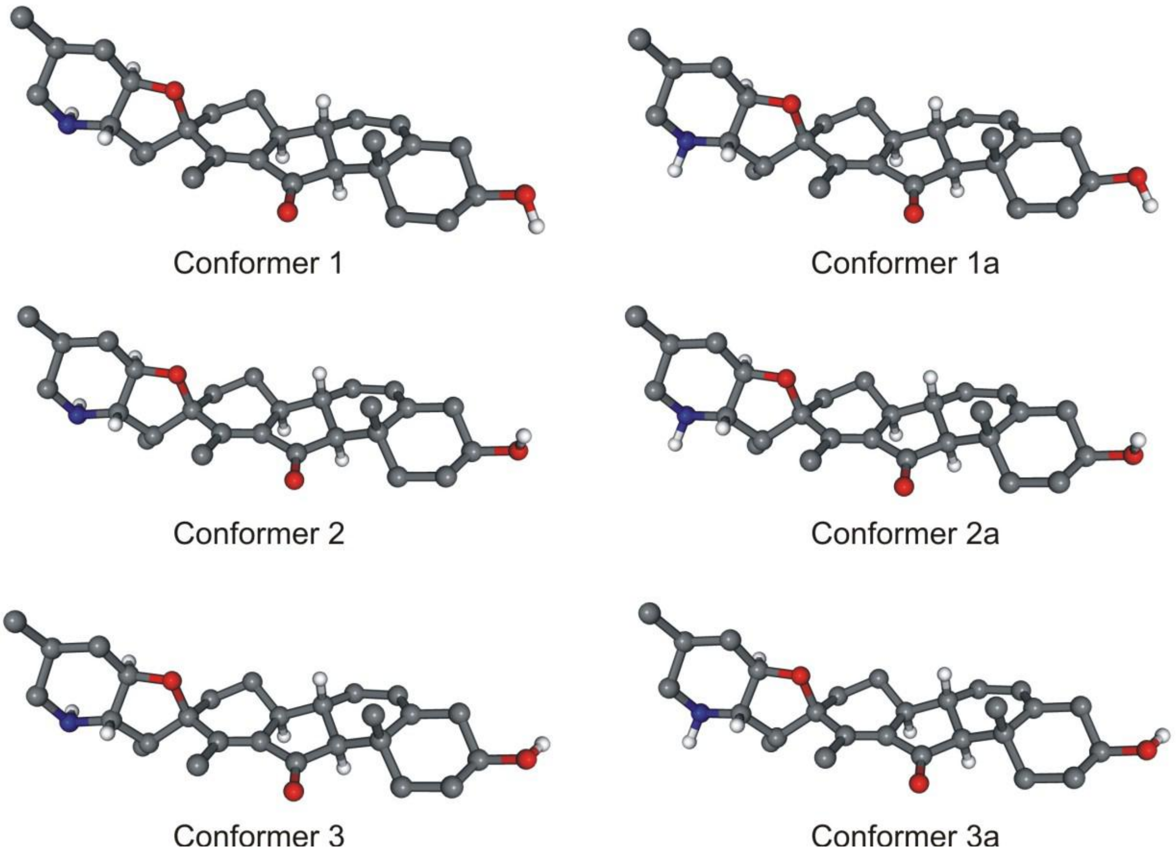

Conformer 1
Conformer 1a
Conformer 2
Conformer 2a
Conformer 3
Conformer 3a

Figure AS7. Structures of individual conformers of jervine calculated at the IEFPCM/B3LYP/TZVP level. Some hydrogen atoms were omitted for clarity.

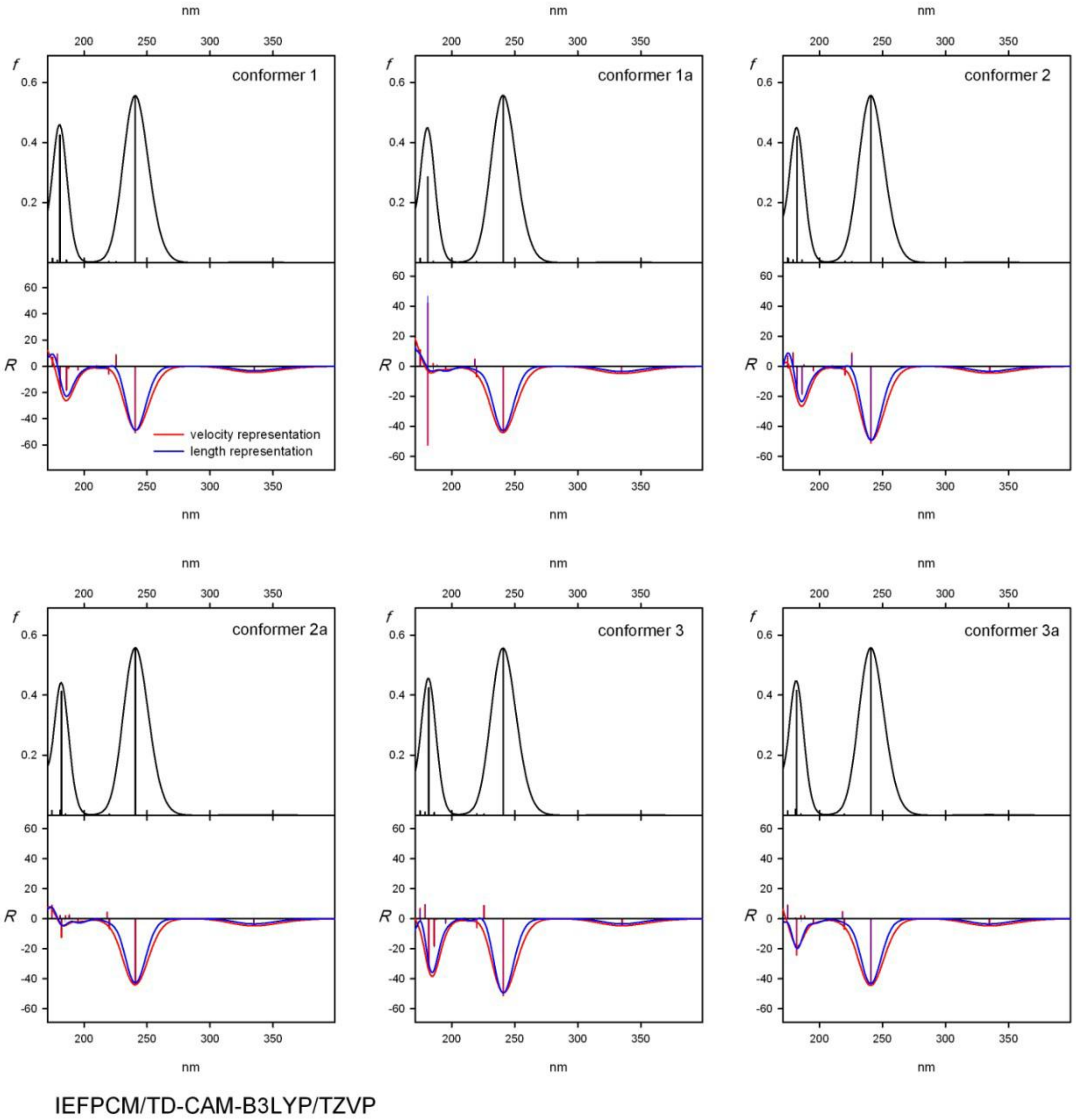


Figure AS8. UV and CD spectra calculated for individual conformers of jervine at IEFPCM/TD-CAM-B3LYP/TZVP level.

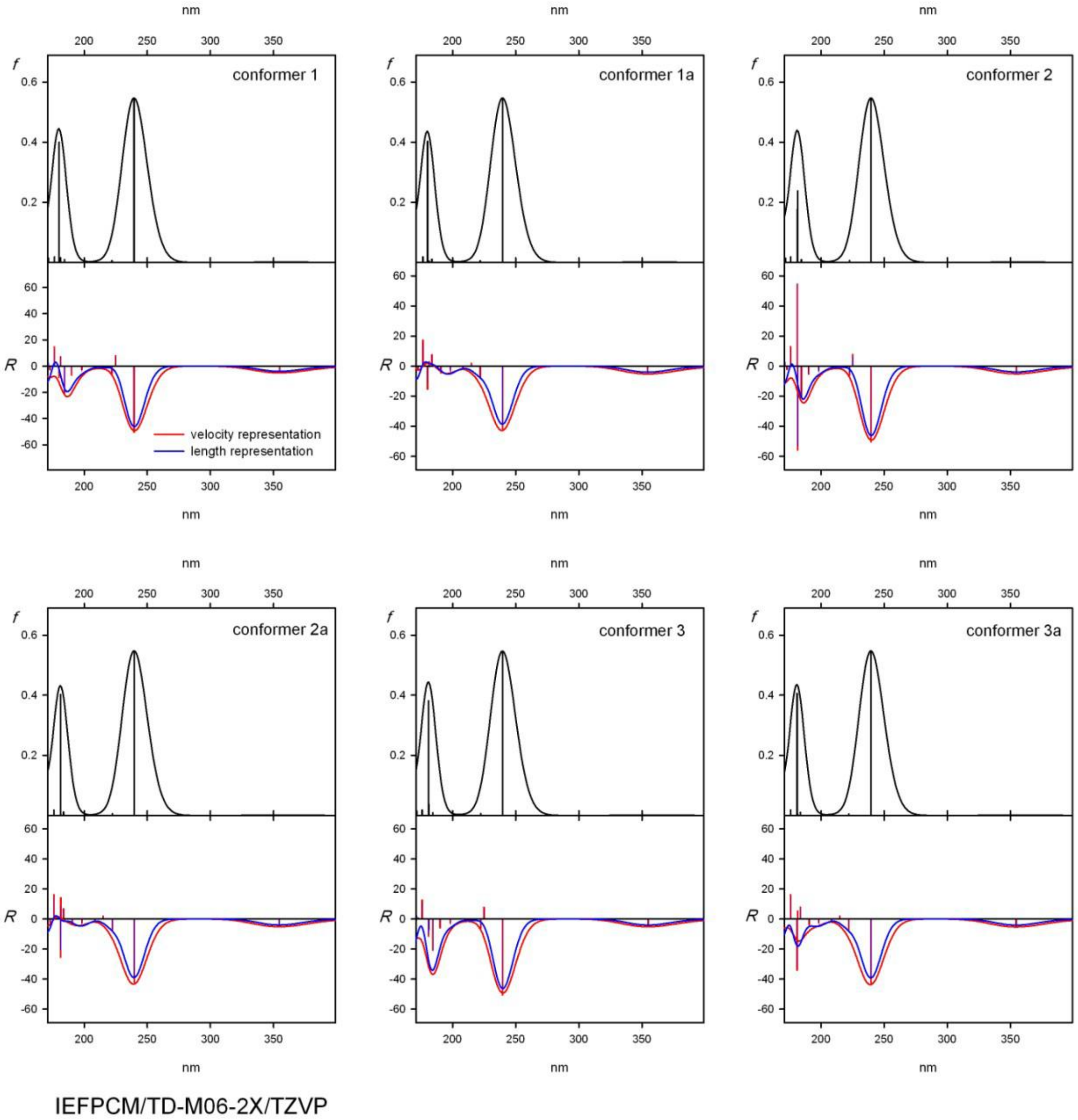
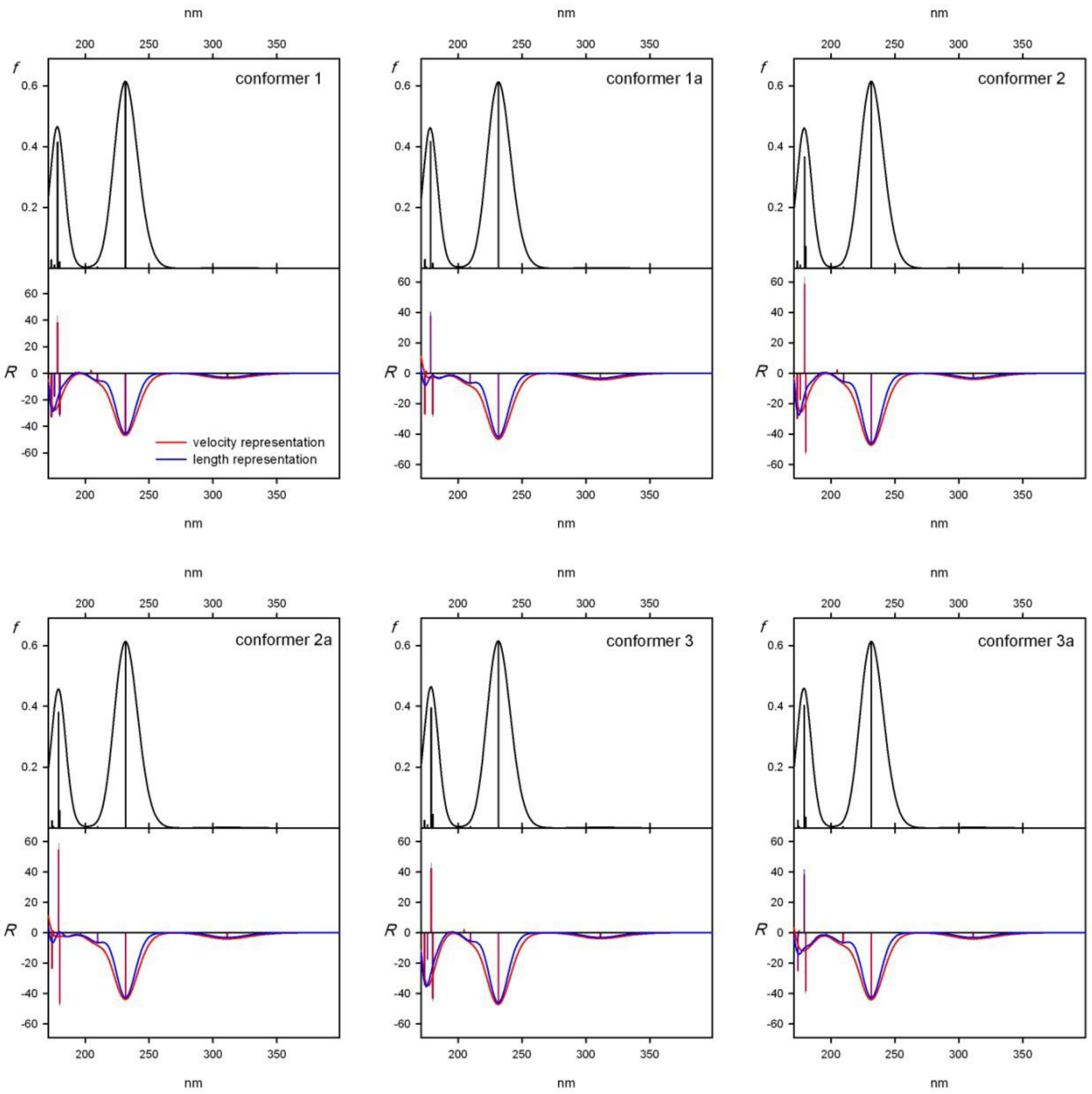


Figure AS9. UV and CD spectra calculated for individual conformers of jervine at IEFPCM/TD-M06-2X/TZVP level.



IEFPCM/TD-B2LYP/TZVP

Figure AS10. UV and CD spectra calculated for individual conformers of jervine at IEFPCM/TD-23LYP/TZVP level.

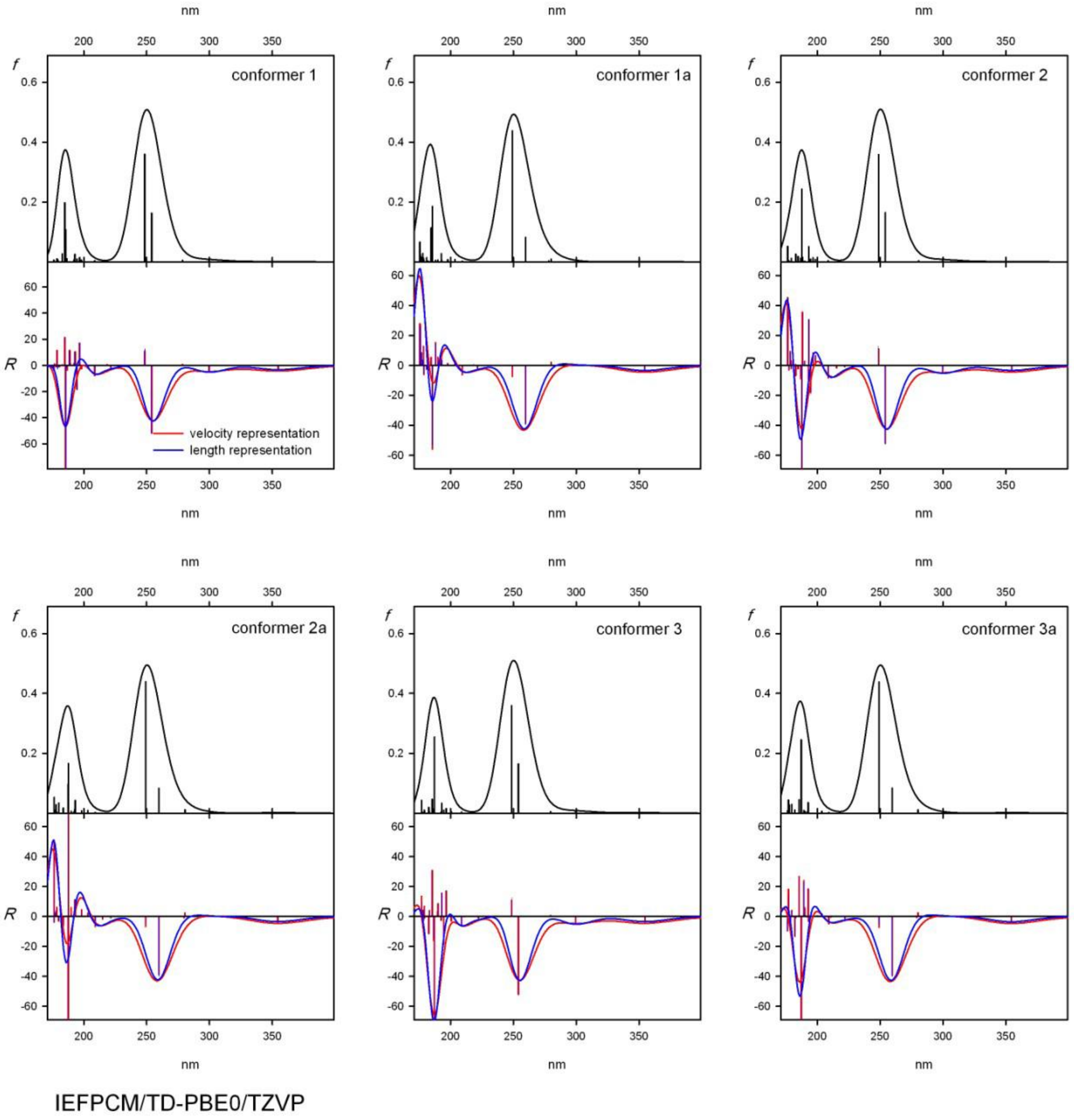


Figure AS11. UV and CD spectra calculated for individual conformers of jervine at IEFPCM/TD-PBE0/TZVP level.

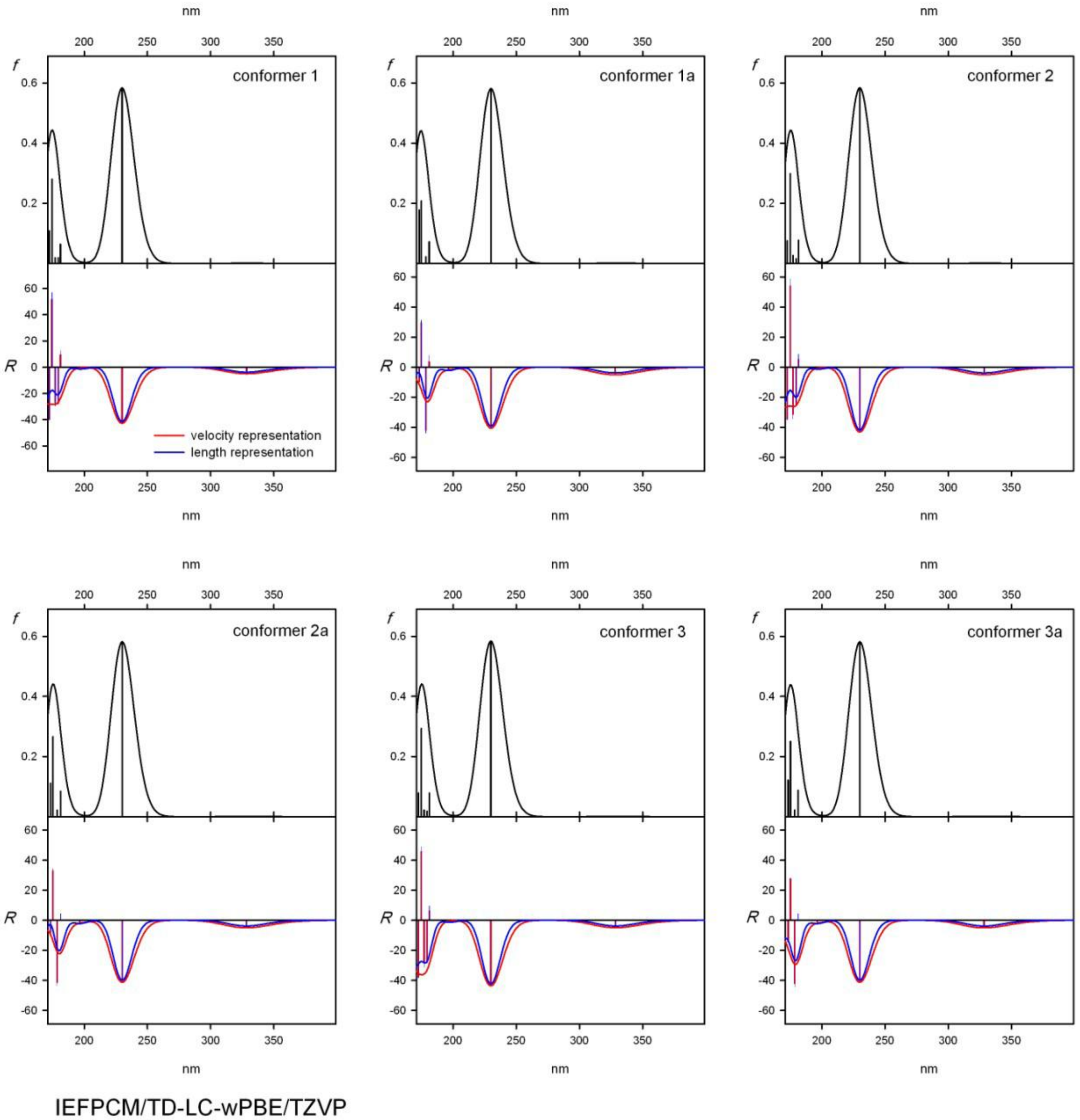


Figure AS12. UV and CD spectra calculated for individual conformers of jervine at IEFPCM/TD-LC-wPBE/TZVP level.

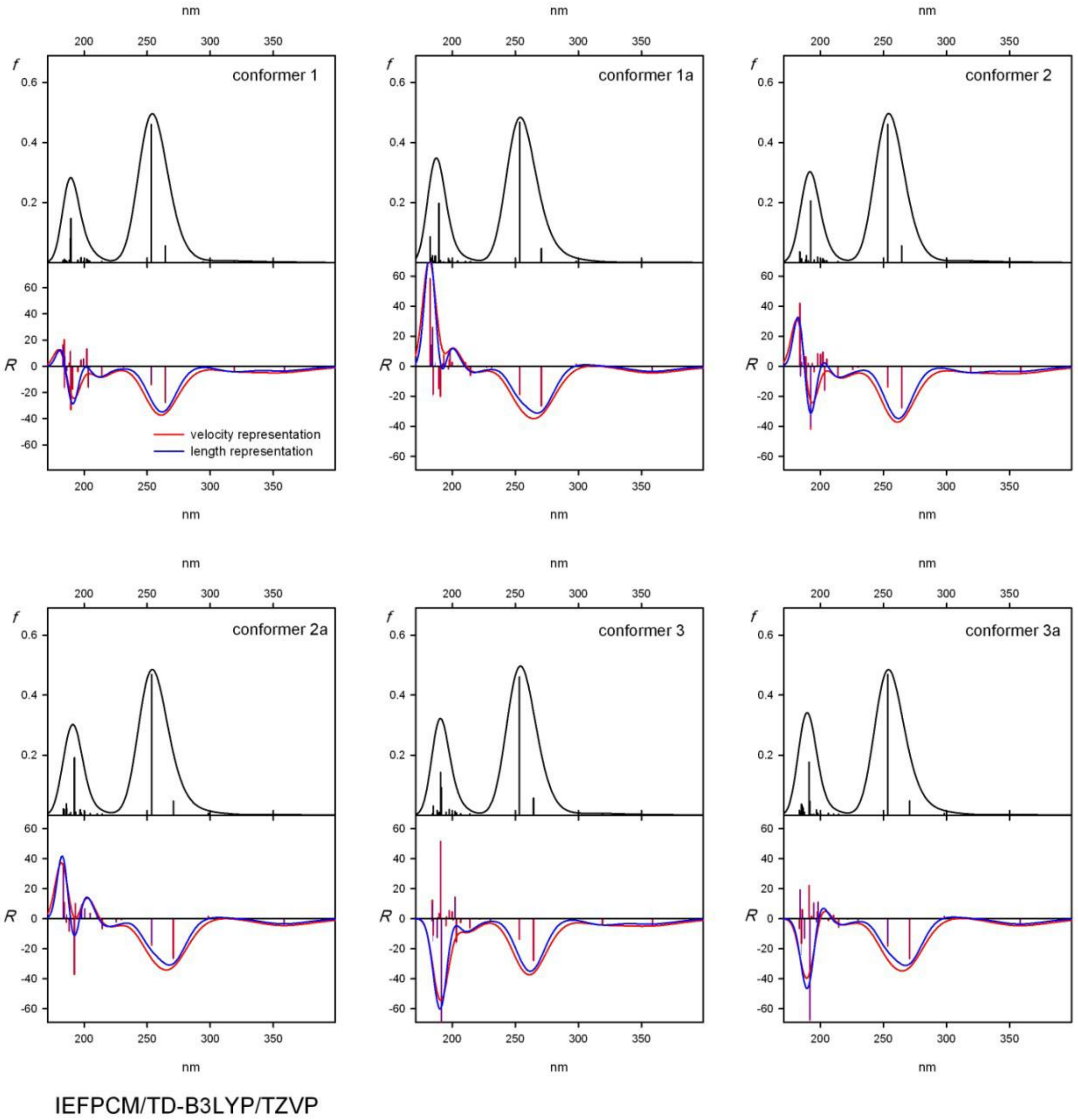


Figure AS13. UV and CD spectra calculated for individual conformers of jervine at IEFPCM/TD-B3LYP/TZVP level.

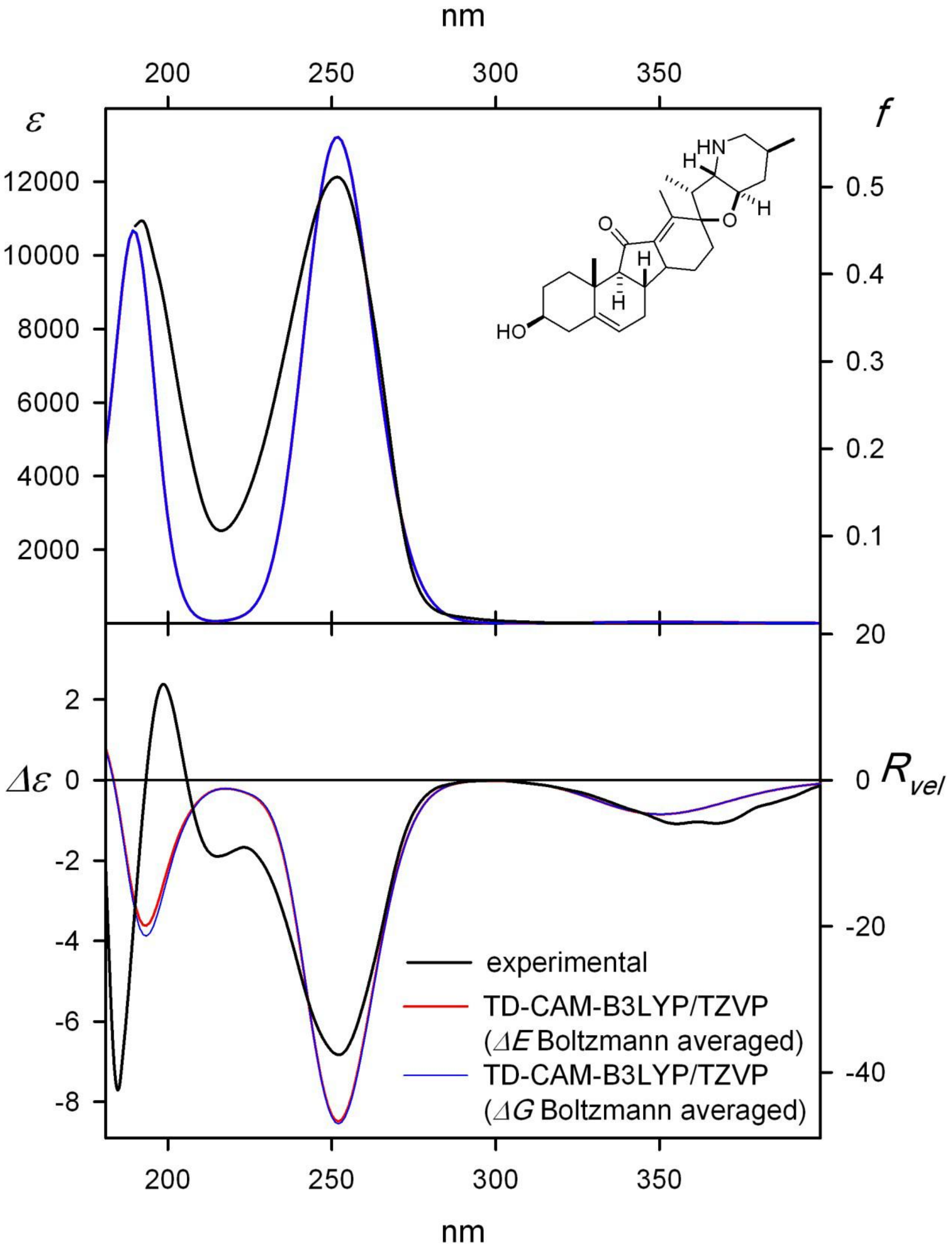


Figure AS14. UV (upper panel) and CD (lower panel) spectra of jervine, experimental measured in acetonitrile solution (solid black lines) and *ΔE*- and *ΔG*-based Boltzmann averaged (red and blue lines, respectively) calculated at the IEFPCM/TD-CAM-B3LYP/TZVP level. All calculated spectra were wavelength corrected to match the experimental UV maxima.

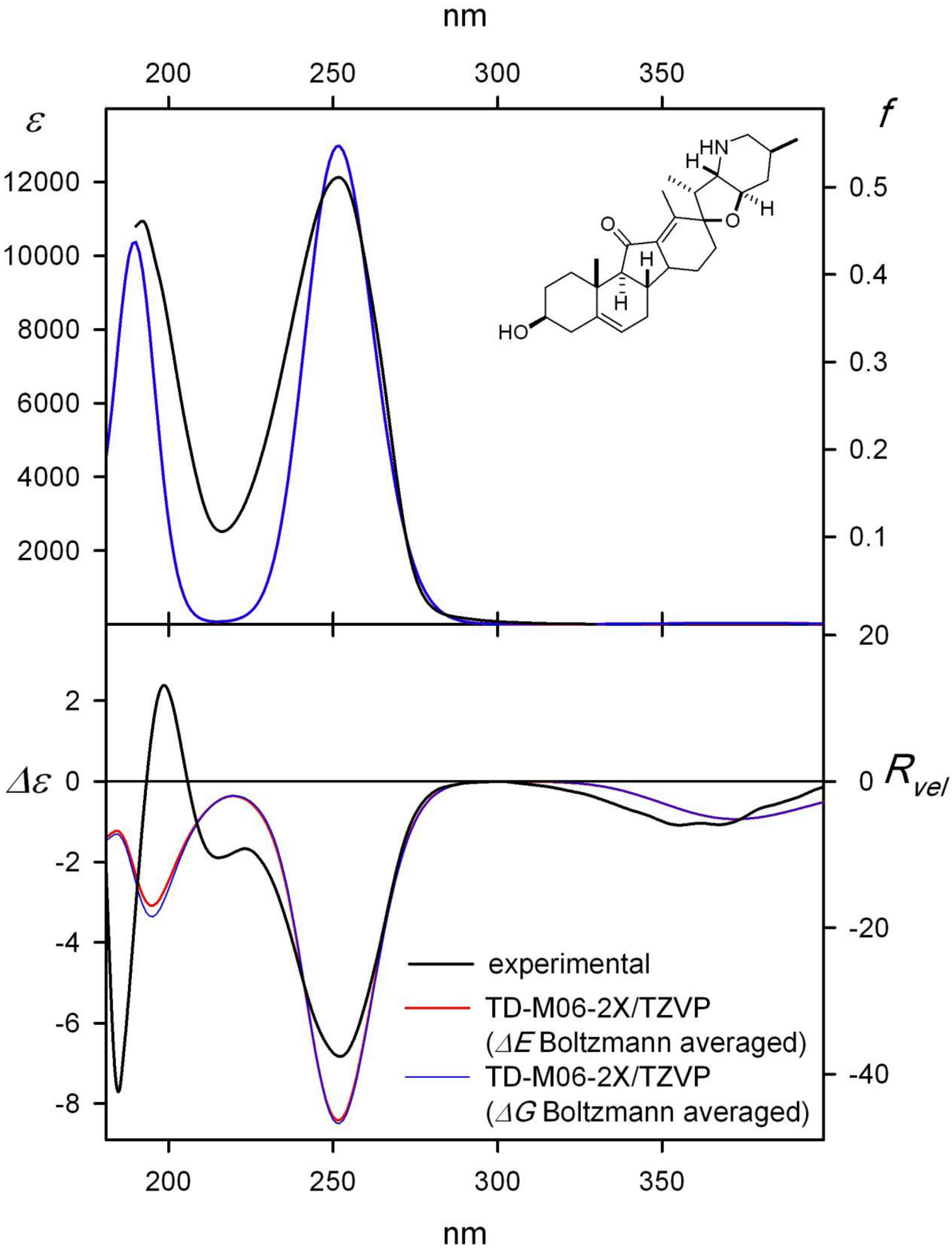


Figure AS15. UV (upper panel) and CD (lower panel) spectra of jervine, experimental measured in acetonitrile solution (solid black lines) and *ΔE*- and *ΔG*-based Boltzmann averaged (red and blue lines, respectively) calculated at the IEFPCM/TD-M06-2X/TZVP level. All calculated spectra were wavelength corrected to match the experimental UV maxima.

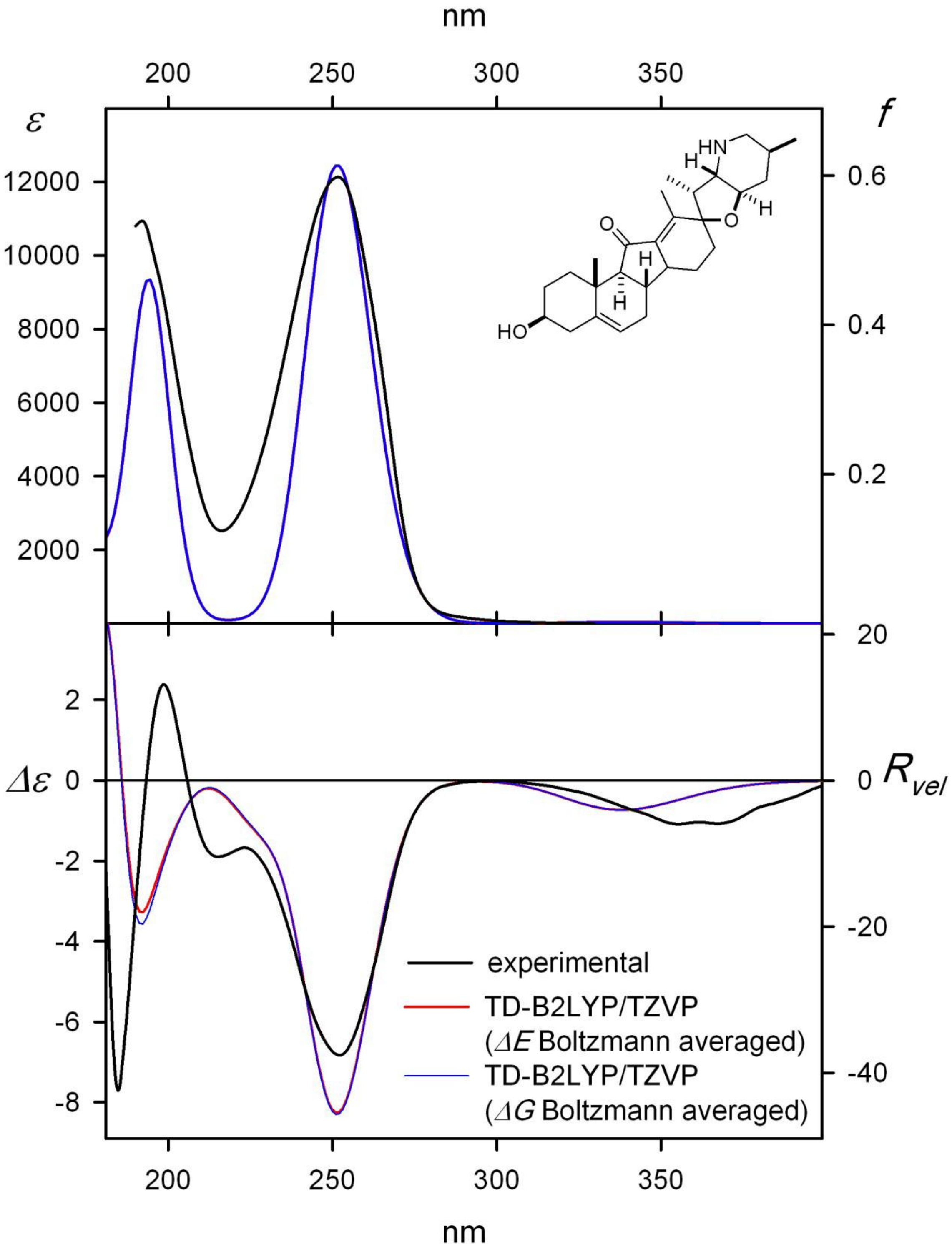


Figure AS16. UV (upper panel) and CD (lower panel) spectra of jervine, experimental measured in acetonitrile solution (solid black lines) and *ΔE*- and *ΔG*-based Boltzmann averaged (red and blue lines, respectively) calculated at the IEFPCM/TD-B2LYP/TZVP level. All calculated spectra were wavelength corrected to match the experimental UV maxima.

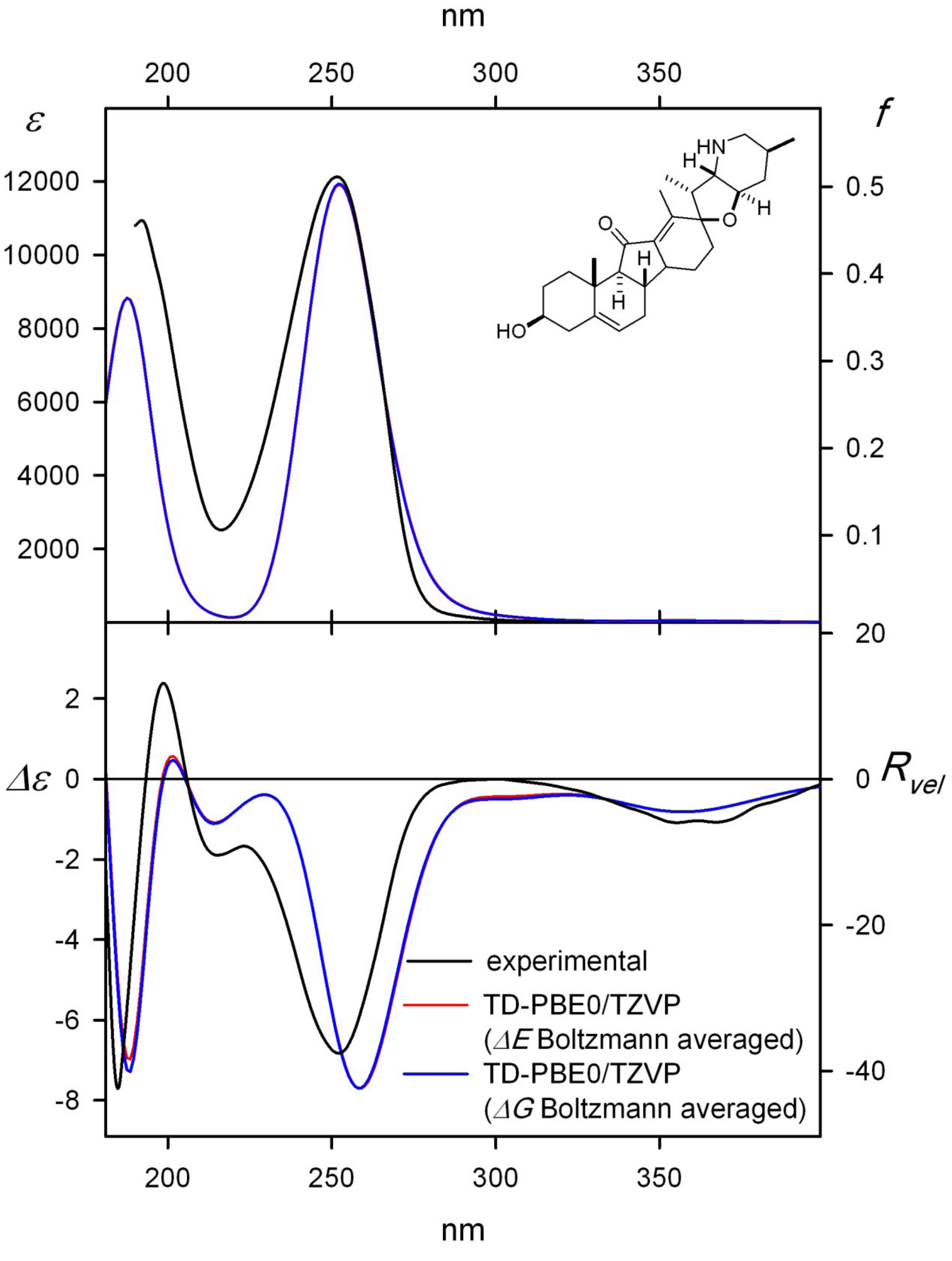


Figure AS17. UV (upper panel) and CD (lower panel) spectra of jervine, experimental measured in acetonitrile solution (solid black lines) and *ΔE*- and *ΔG*-based Boltzmann averaged (red and blue lines, respectively) calculated at the IEFPCM/TD-PBE0/TZVP level. All calculated spectra were wavelength corrected to match the experimental UV maxima.

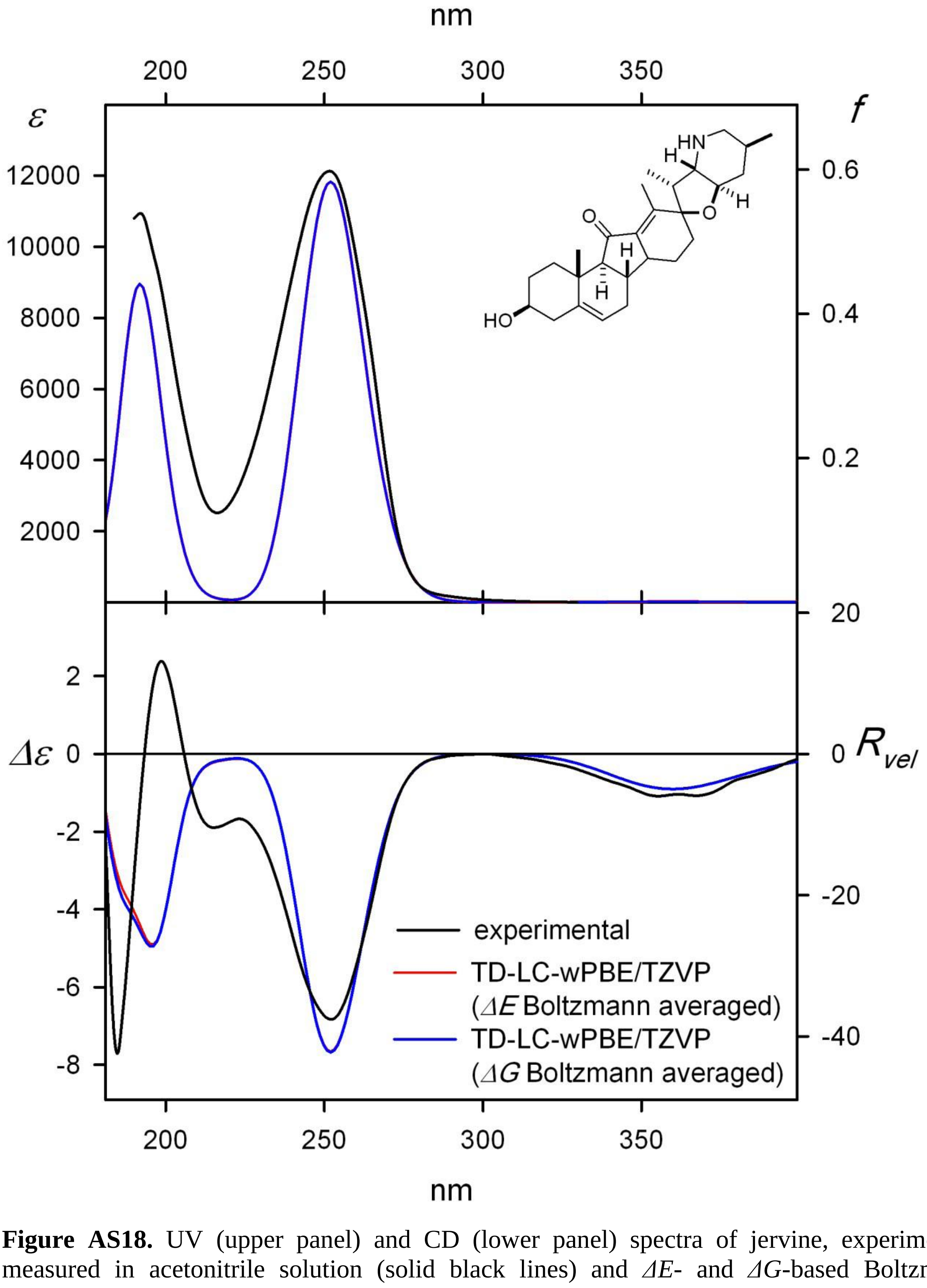


Figure AS18. UV (upper panel) and CD (lower panel) spectra of jervine, experimental measured in acetonitrile solution (solid black lines) and *ΔE*- and *ΔG*-based Boltzmann averaged (red and blue lines, respectively) calculated at the IEFPCM/TD-LC-wPBE/TZVP level. All calculated spectra were wavelength corrected to match the experimental UV maxima.

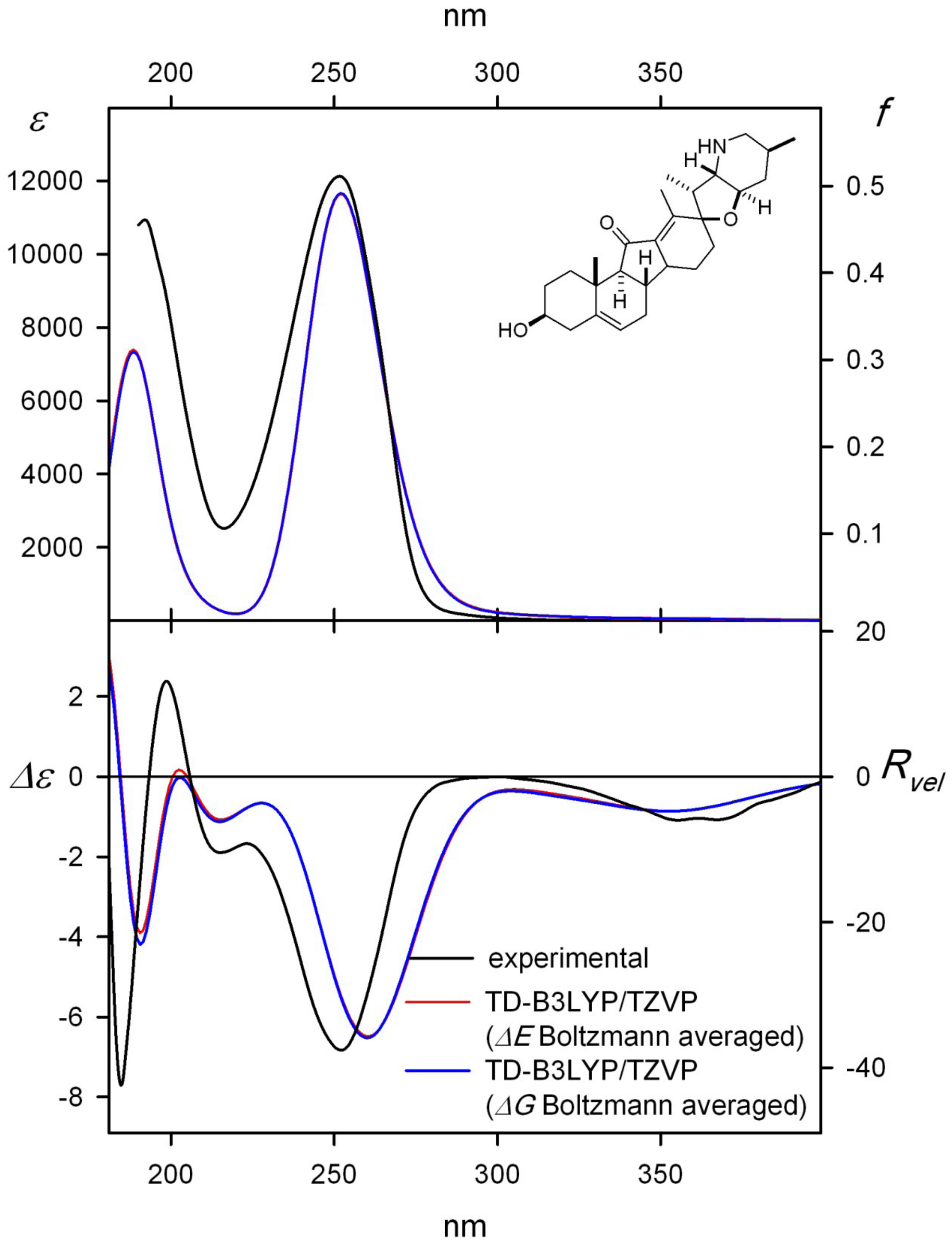


Figure AS19. UV (upper panel) and CD (lower panel) spectra of jervine, experimental measured in acetonitrile solution (solid black lines) and *ΔE*- and *ΔG*-based Boltzmann averaged (red and blue lines, respectively) calculated at the IEFPCM/TD-B3LYP/TZVP level. All calculated spectra were wavelength corrected to match the experimental UV maxima.

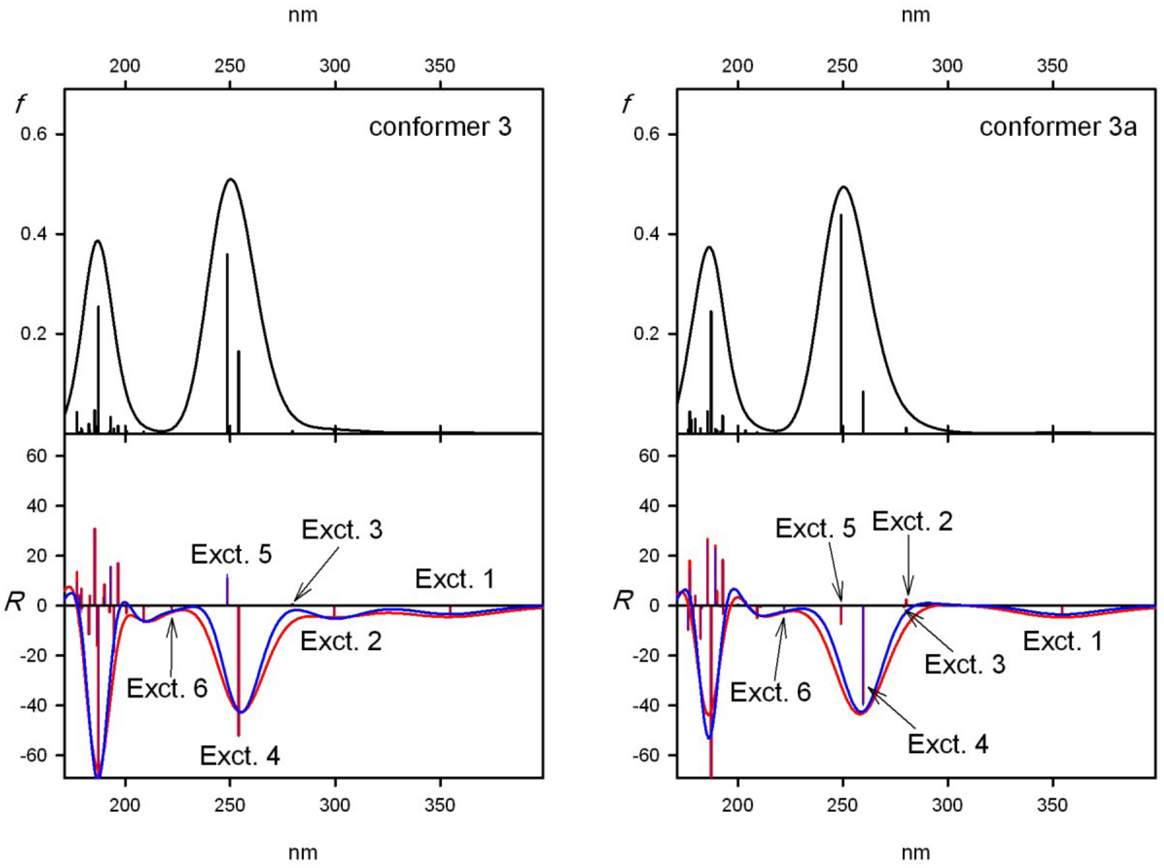


Figure AS20. UV and CD spectra calculated for 3 and 3a conformer of jervine at IEFPCM/TD-PBE0/TZVP level.

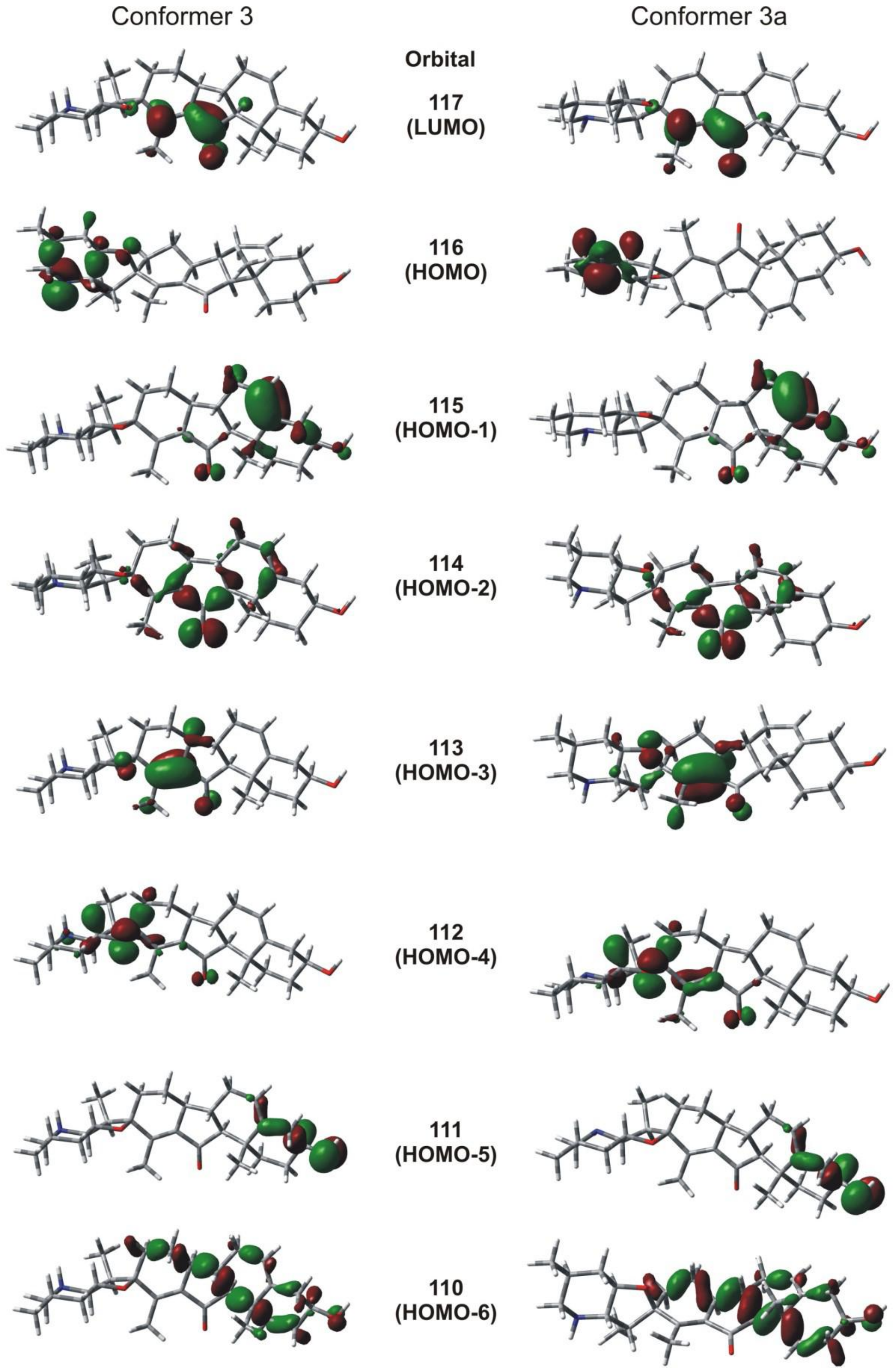


Figure AS21. The PBE0/TZVP HOMO-6 to HOMO and LUMO molecular Kohn–Sham orbitals of the 3 and 3a conformers of jervine.

Table AS10. Energies, oscillator strengths and orbitals involved in the first 6 electronic transitions (bold indicates the main contribution to given electronic transition).

Electronic transition	Conformer **3**			Conformer **3a**		
	Energy[nm]	f	Orbitals involved	Energy [nm]	f	Orbitals involved
1	354.7	1.80e-3	**114→117** 115→117	354.3	1.90e-3	112→117 **114→117** 115→117
2	299.6	6.60e-3	**116→117**	280.1	0.011	115→117 **116→117**
3	279.5	4.80e-3	114→117 **115→117**	279.0	1.60e-3	114→117 **115→117** 116→117
4	254.0	0.165	**112→117** 113→117	259.6	0.084	**112→117** 113→117
5	248.6	0.359	**112→117** **113→117** 114→117	249.0	0.438	112→117 **113→117** 114→117
6	222.1	5.00e-4	**110→117** 111→117	222.0	4.00e-4	**110→117** 111→117

Among six different levels of theory used to calculate Boltzmann-averaged ECD spectrum of jervine **6** only two ones simulated at IEFPCM/TD-PBE0/TZVP and IEFPCM/TD-B3LYP/TZVP levels of theory are in good agreement with the experimental ECD data for diagnostic bands corresponding to the nπ* and ππ* transitions.

4. Additional conformational and spectral analysis of s-*cis*-acrolein (13)

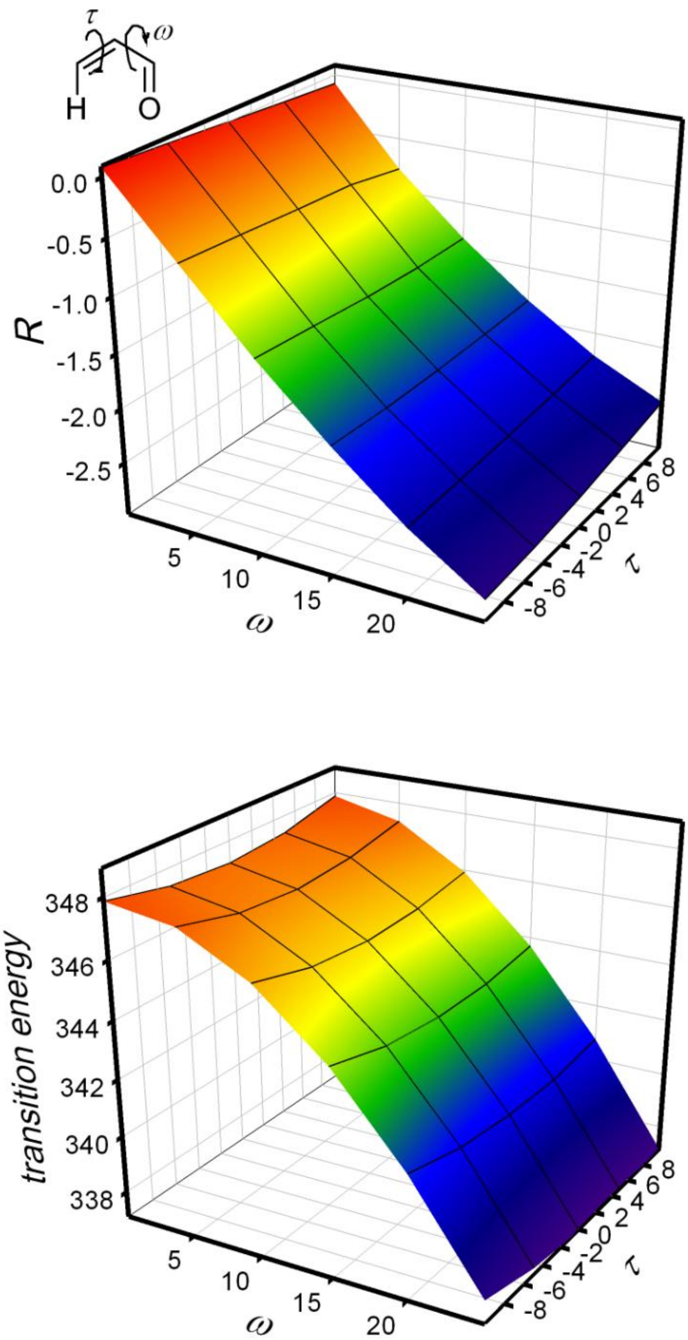


Figure AS22. Rotatory strength (upper panel) and excitation energy of the lowest-energy electronic transition of s-*cis*-acrolein (**13**) as a function of torsion angles ω and τ, calculated at the PCM/B3LYP/Aug-cc-pVTZ level of theory.

5. Additional conformational and spectral analysis of 2-methylenecyclopentanone (14)

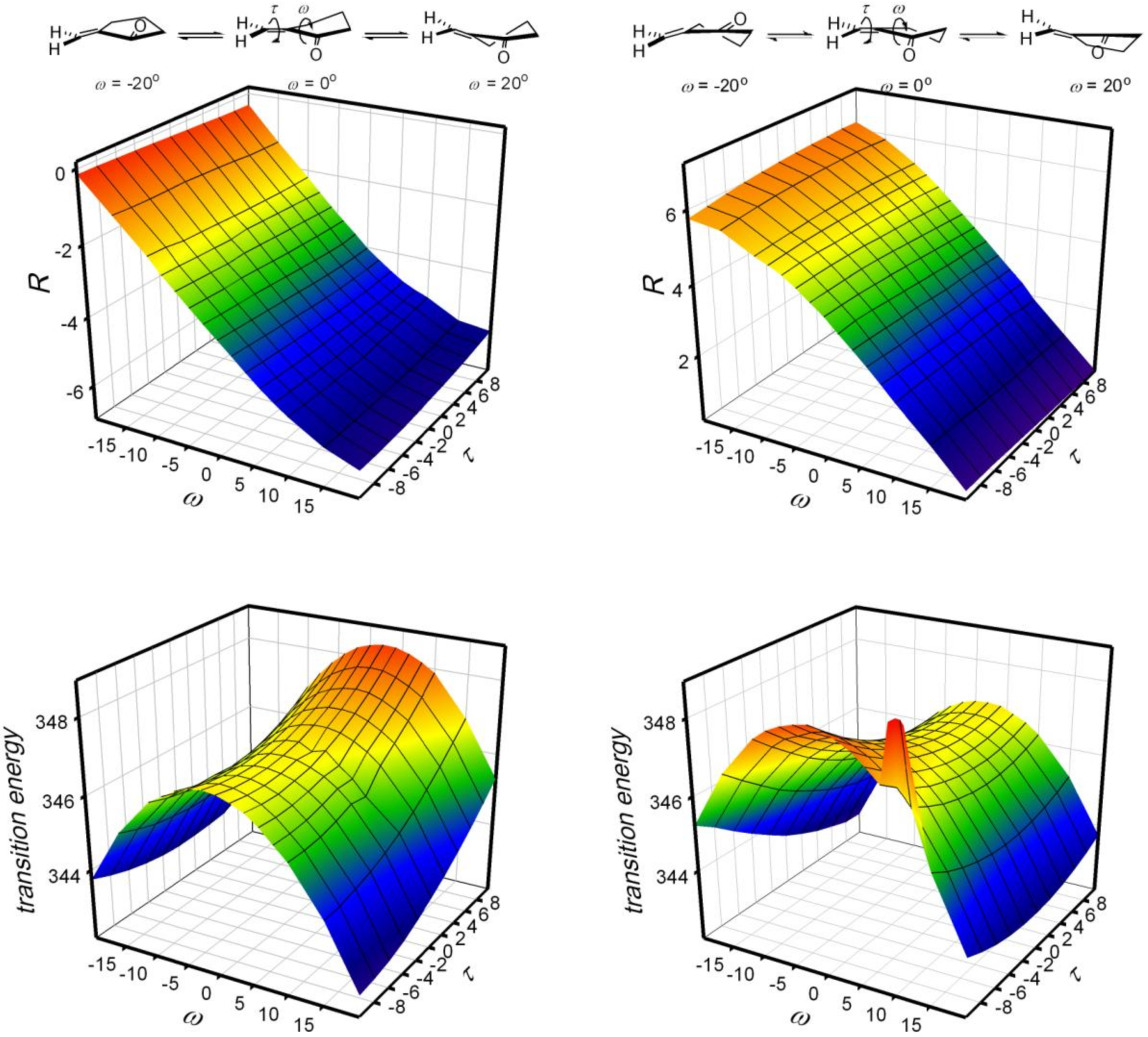
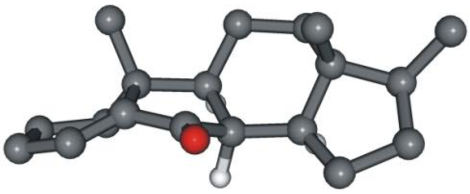
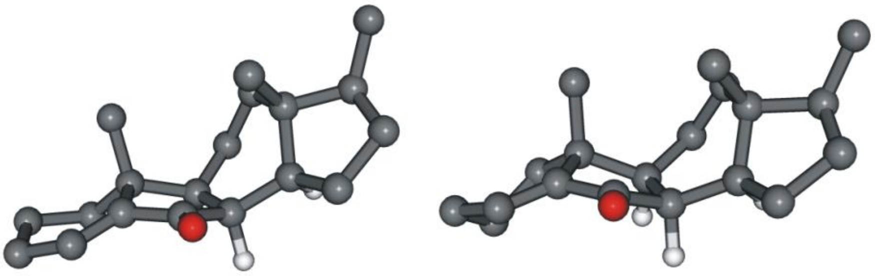


Figure AS23. Rotatory strength (upper panels) and excitation energy of the lowest-energy electronic transition of two conformers of 2-methylenecyclopantanone (**14**) as a function of torsion angles ω and τ, calculated at the PCM/B3LYP/Aug-cc-pVTZ level of theory.

6. Additional conformational and spectral analysis of enone 16



conformer 1



conformer 2 conformer 3

Figure AS24. Structures of individual conformers of **16** optimized at the PCM/B3LYP/TZVP level of theory. Some hydrogen atoms were omitted for clarity.

Table AS11. Relative energies, populations and values of torsion angles ω and τ calculated for **16** at the PCM/B3LYP/TZVP level.

Conformer	ΔE [kcal mol^{-1}]	Pop. [%]	ΔG [kcal mol^{-1}]	Pop. [%]	ω [O=C-C=C]	τ [(O=)C-C=C-H]
Conf. 1	0.00	100	0.00	100	−37.5	+16.1
Conf. 2	2.09	-	2.57	-	−29.3	+9.8
Conf. 3	5.63	-	6.13	-	−32.5	+11.8

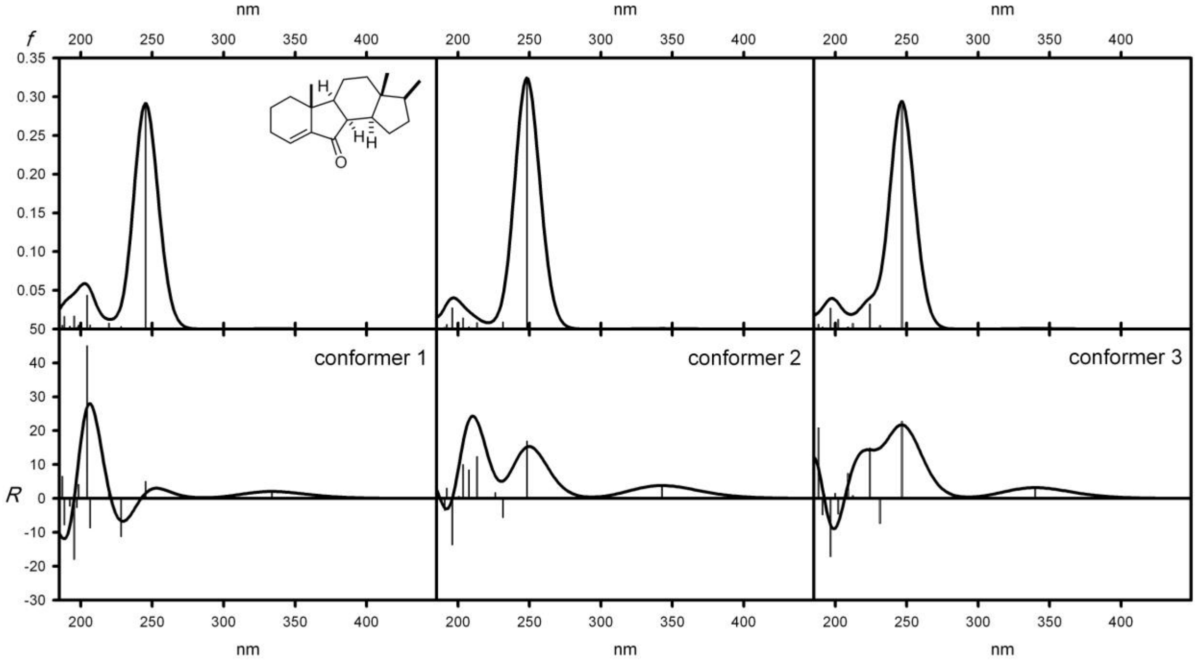


Figure AS25. UV (upper panel) and CD spectra (lower panel) calculated at the PCM/B3LYP/TZVP level for individual conformers of **16**.

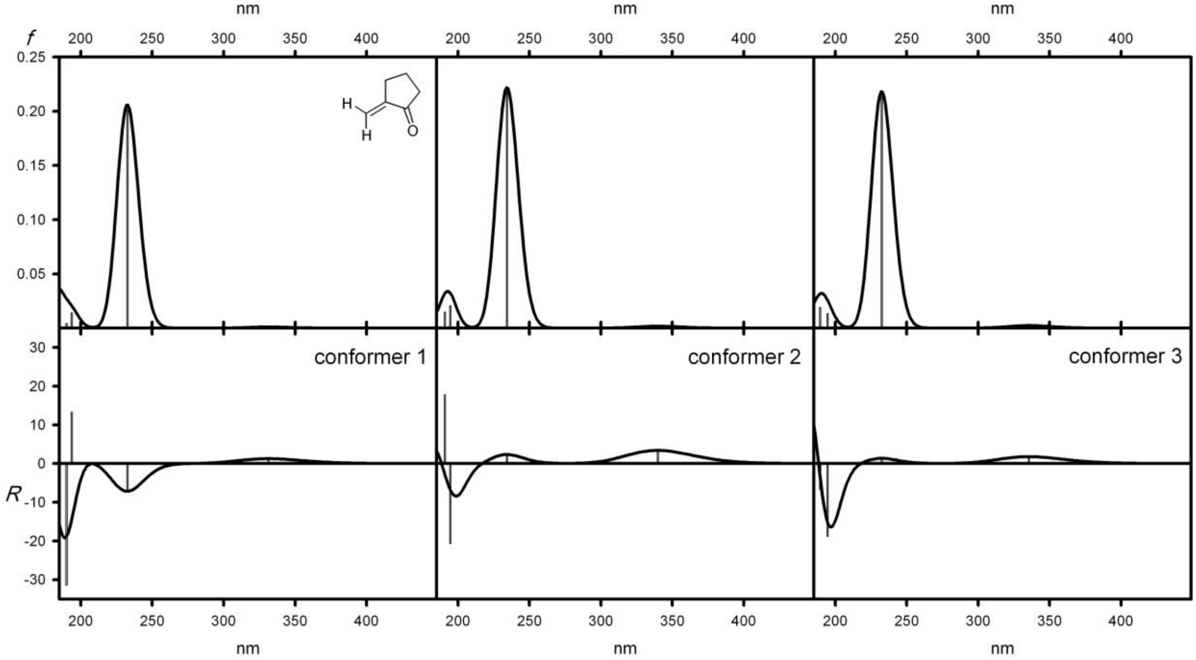


Figure AS26. UV (upper panel) and CD spectra (lower panel) calculated at the PCM/B3LYP/TZVP level for individual conformers of 2-methylenecyclopentanone. Conformation of cyclopentanone ring is the same as in the parent conformer of **16**.