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Scope of the 2(5H)-Furanone Helicity Rule: A Combined ECD, VCD, and DFT Investigation

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Table S1: Comparison of ^{1}H-NMR ($CDCl_3$, 400 MHz) and ^{13}C ($CDCl_3$, 100 MHz) data of the isolated compound with that reported for rolliniastatin-1 (PETIT *et al.*, 1987: $CDCl_3$, 300 MHz for ^{1}H NMR / 75 MHz for ^{13}C NMR).

H/C	δ_H (ppm), *J* (Hz)		δ_C (ppm)	
	Isolated Compound	**PETIT *et al.*, 1987**	**Isolated Compound**	**PETIT *et al.*, 1987**
1	-	-	174.6	174.5
2	-	-	131.1	131.1
3α	2.49 (*ddt*, 1.6; 3.3; 15.3)	2.50 (*dddd*, 1.6; 3.5; 15.1)	33.2	33.2
3β	2.37 (*ddt*, 1.6; 8.3; 15.3)	2.36 (*dddd*, 1.4; 8.1; 15.1)		
4	3.82 (*m*)	3.85 (*m*)	69.9	69.9
5	1.23-1.47 (*m*)	1.45 (*m*)	37.3	37.4
6	1.23-1.47 (*m*)	1.25 (*m*)	26.0	26.0
7-12	1.23-1.47 (*m*)	1.25 (*m*)	29.3-29.6	29.3-29.6
13	1.23-1.47 (*m*)	1.25 (*m*)	25.7	25.7
14	1.23-1.47 (*m*)	1.50 (*m*)	34.1	34.1
15	3.38 (*m*)	3.38 (*m*)	73.9	74.0
16	3.88 (*m*)	3.85 (*m*)	83.0	83.0
17	1.71-1.93 (*m*)	1.7-1.9 (*m*)	28.6	28.7
18	1.71-1.93 (*m*)	1.7-1.9 (*m*)	23.7	27.8
19	3.87 (*m*)	3.85 (*m*)	81.1	81.1
20	3.84 (*m*)	3.85 (*m*)	81.0	81.0
21	1.71-1.93 (*m*)	1.7-1.9 (*m*)	27.8	27.8
22	1.71-1.93 (*m*)	1.7-1.9 (*m*)	28.3	28.4
23	3.88 (*m*)	3.85 (*m*)	83.0	83.0
24	3.84 (*m*)	3.85 (*m*)	71.7	71.8

25	1.23-1.47 (*m*)	1.45 (*m*)	32.7	32.8
26	1.23-1.47 (*m*)	1.25 (*m*)	25.5	25.5
27-31	1.23-1.47 (*m*)	1.25 (*m*)	29.3-29.6	29.3-29.6
32	1.23-1.47 (*m*)	1.25 (*m*)	31.8	31.9
33	1.23-1.47 (*m*)	1.25 (*m*)	22.6	22.6
34	0.84 (*t*, 6.7)	0.85 (*t*)	14.0	14.1
35	7.17 (q_{dist}, 1.4)	7.16 (*ddd*, 1.5)	151.7	151.7
36	5.03 (*dq*, 1.4 e 6.8)	5.02 (*dddq*, 1.5)	77.9	77.9
37	1.40 (*d,* 6.8)	1.41 (*d*)	19.0	19.1

Table S2: Different levels of theory tested for geometry optimisation of the (*SR*)-lactone fragment (**b**).

	Conformation - Boltzmann distribution (%)/relative energy ($kcal^{-1}$)					
Level of theory	C1	C2	C3	C4	C5	C6
wB97XD/aug-cc-pVTZ	35 / 0.0	21 / 0.3	18 / 0.4	11 / 0.7	8 / 0.9	7 / 1.0
B3LYP/6-31G(d)	6 / 1.0	18 / 0.5	14 / 0.6	39 / 0.0	11 / 0.7	11 / 0.7
B3PW91/6-311G(dp)	4 / 1.1	15 / 0.4	12 / 0.5	30 / 0.0	10 / 0.6	28 / 0.3
MP2/6-31G(d)	10 / 0.8	9 / 0.8	13 / 0.6	37 / 0.0	10 / 0.8	21 / 0.3

Table S3: Analysis of the most relevant transitions calculated for the simple lactone fragment (**a**) at the CAM-B3LYP/PCM(ACN)/TZVP level.

	Excited State	**λ/nm**	**$R/10^{-40}$ cgs[a]**	**Excitations[b] (MO)**	**Coeficients[b]**
Simple Lactone fragment	1 (n-π*)	229.07	-0.64	25 → 27	0.67
	2 (π-π*)	193.71	29.90	26 → 27	0.69

[a]Rotational strengths calculated through dipole lenght formalism.

[b]Only single excitations with coefficients larger than 0.2 (absolute value) were listed.

Figure S1: ^{1}H NMR spectra of the isolated compound (400 MHz, $CDCl_3$).

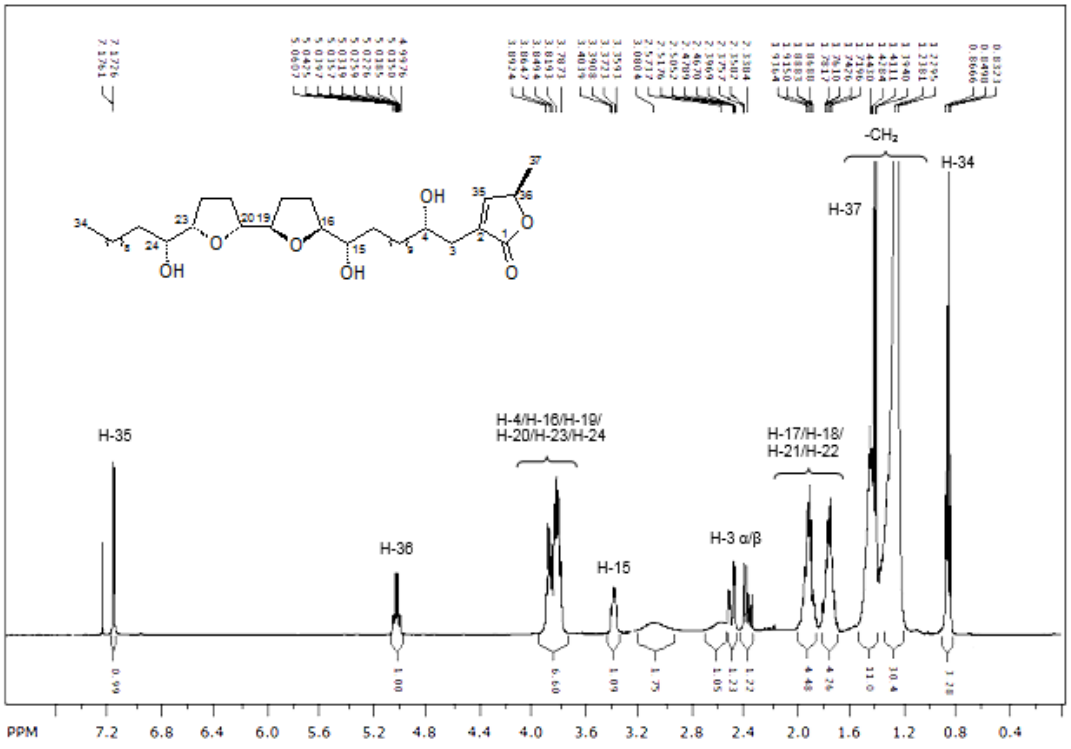


Figure S2: ^{13}C NMR spectra of the isolated compound (100 MHz, $CDCl_3$).

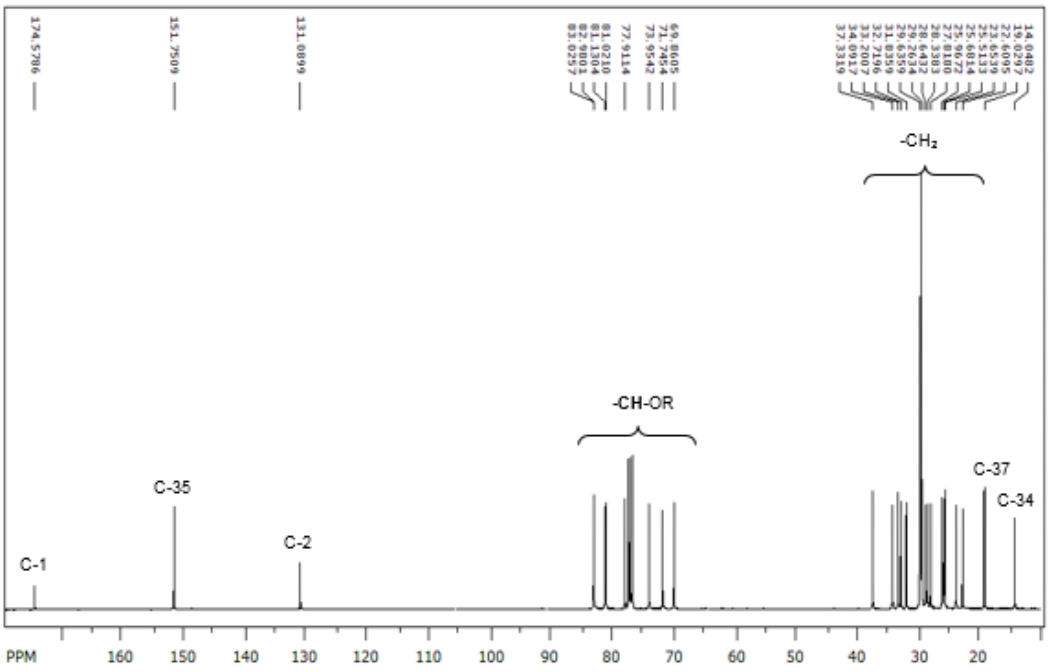


Figure S3: COSY spectra of the isolated compound (400 MHz, $CDCl_3$).

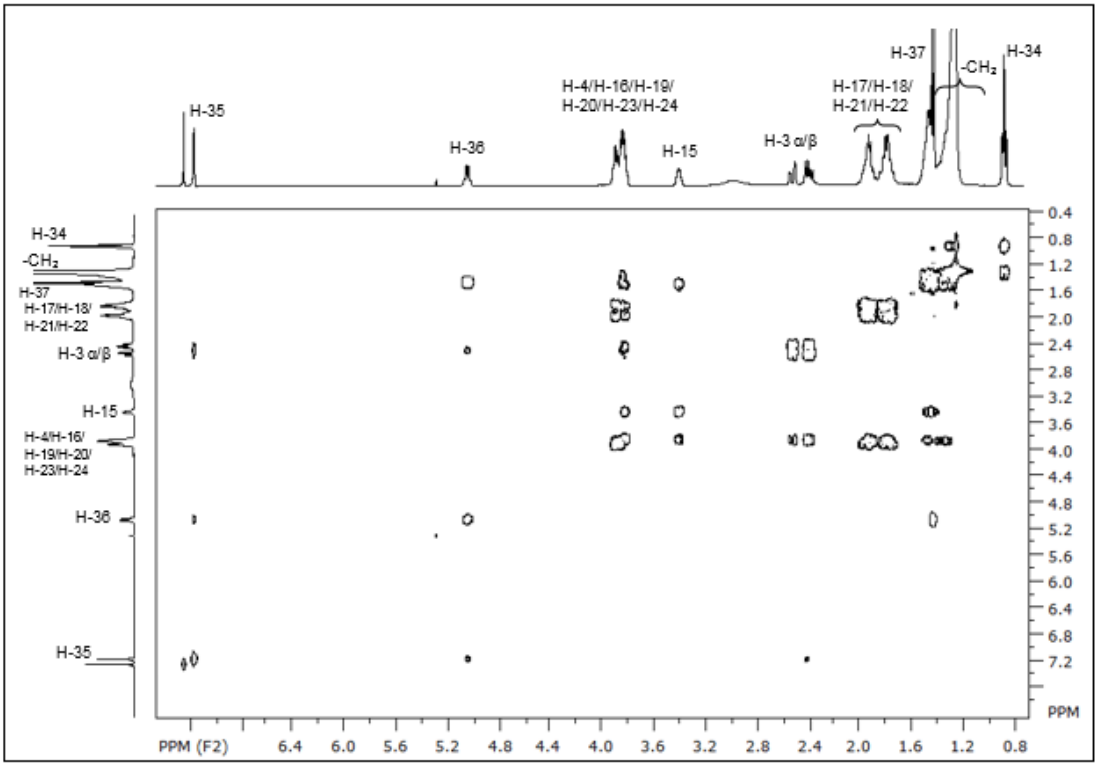


Figure S4: HSQC correlation map of the isolated compound (400 MHz, $CDCl_3$).

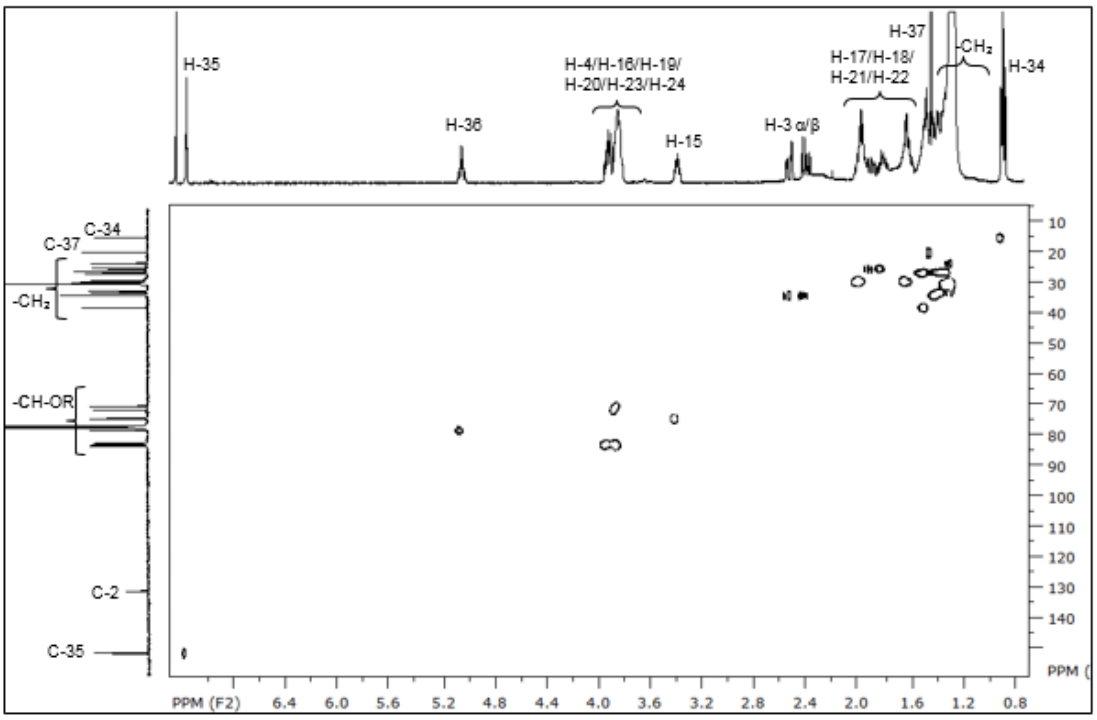


Figure S5: HMBC correlation map of the isolated compound (400 MHz, $CDCl_3$).

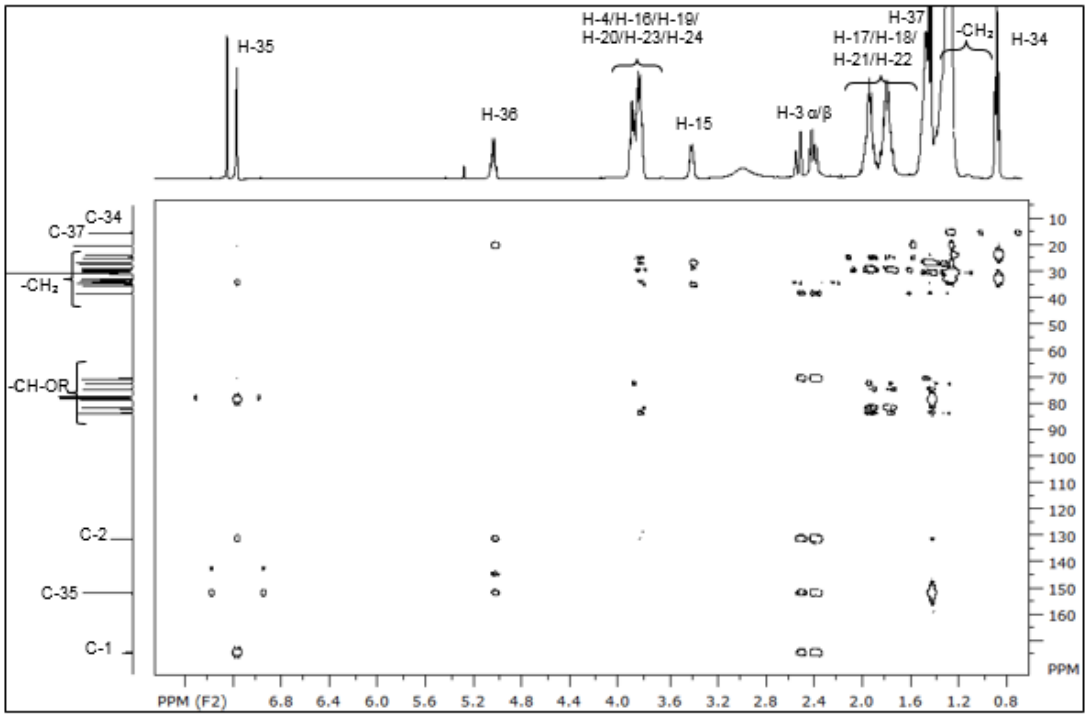
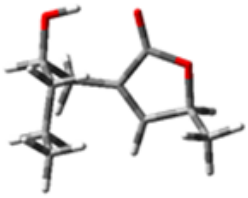
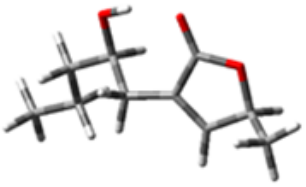


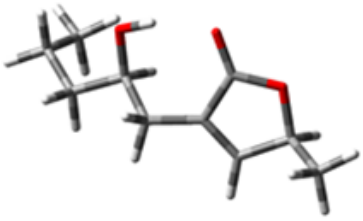
Figure S6: Structure of the 6 lowest-energy conformers of the (*SR*)-lactone fragment (**b**) at the wB97XD/cc-pVTZ level.



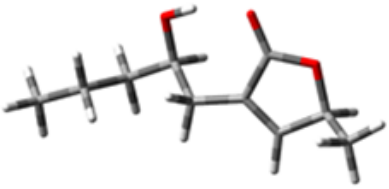
Conf. 1, 0.0 kcal^{-1} (35%)



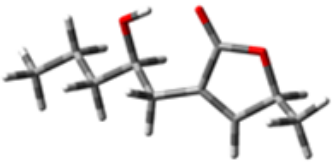
Conf. 2, +0.3 kcal^{-1} (21%)



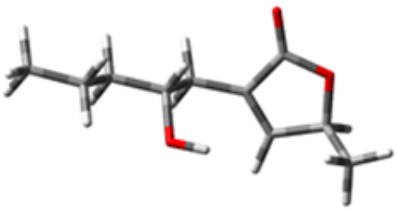
Conf. 3, +0.4 kcal^{-1} (18%)



Conf. 4, +0.7 kcal^{-1} (11%)



Conf. 5, +0.9 kcal^{-1} (8%)



Conf. 6, +1.0 kcal^{-1} (7%)

Figure S7: Calculated ECD spectrum at the wB97XD/PCM(ACN)/TZVP level for the (*SR*)-lactone fragment (**b**).

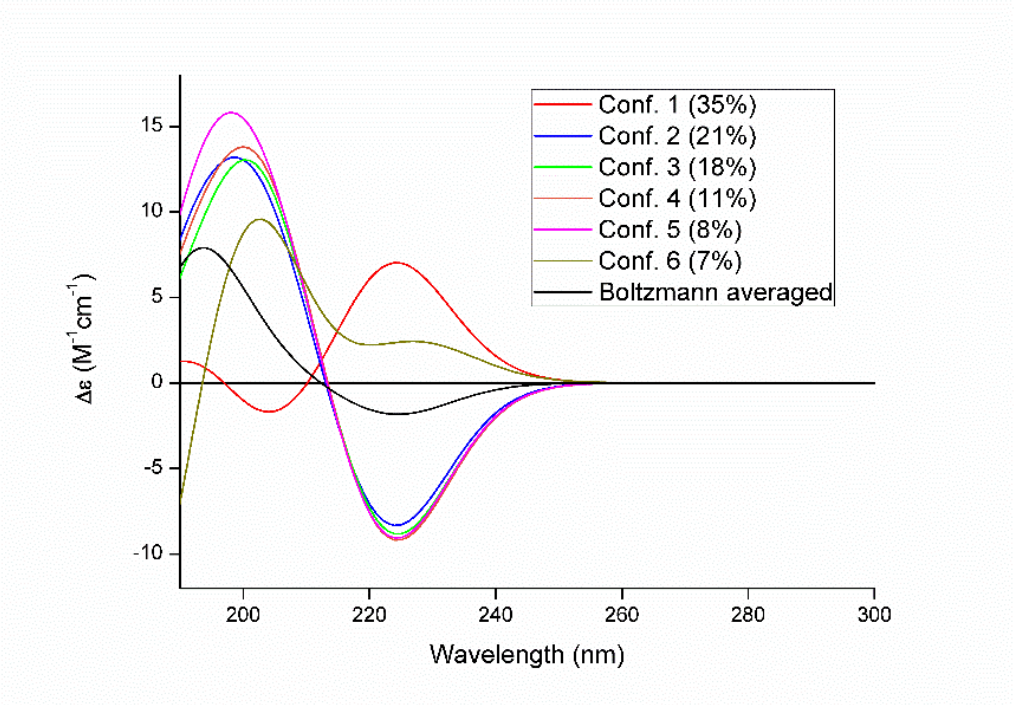


Figure S8: Calculated ECD spectrum at the wB97XD/PCM(ACN)/aug-cc-pVTZ level for the (*SR*)-lactone fragment (**b**).

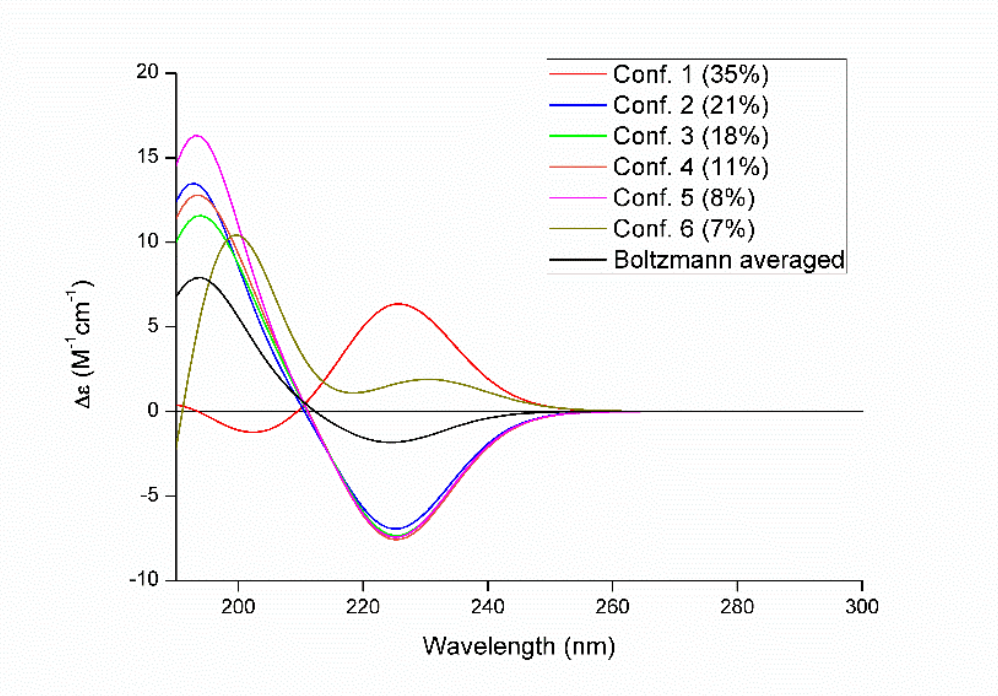


Figure S9: Calculated ECD spectrum at the CAM-B3LYP/PCM(ACN)/TZVP level for the (*RR*)-lactone fragment (**c**).

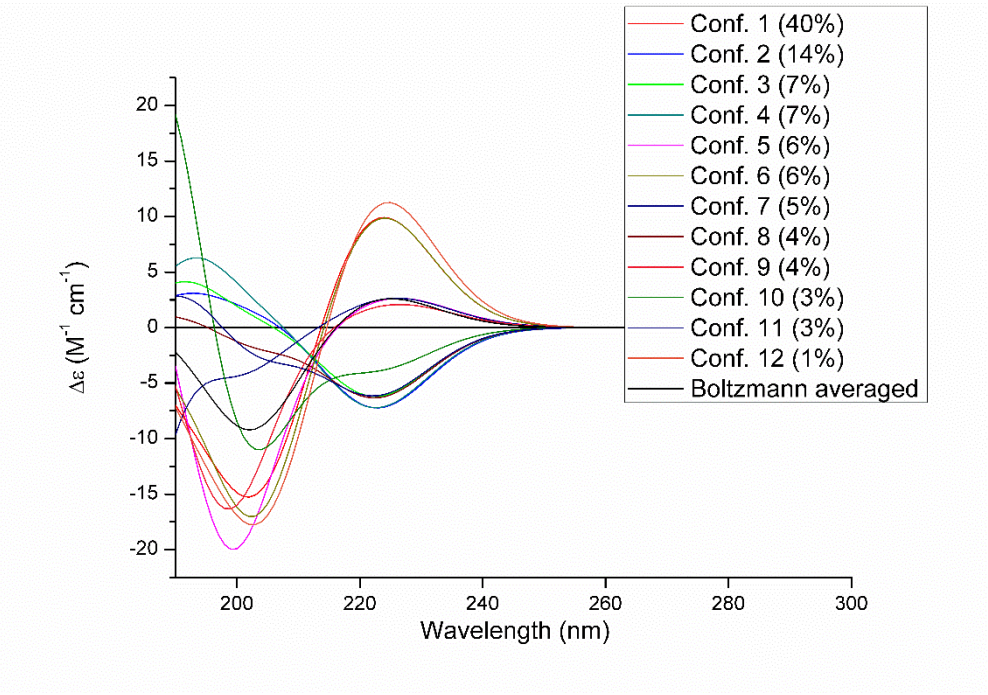


Figure S10: (Left) Experimental ECD spectrum of the synthetic simple lactone (**a**, α,β-unsaturated butenolide) in ACN; (Right) Calculated ECD at the CAM-B3LYP/PCM(ACN)/TZVP//B3LYP/6-31G(d) level for the (*S*)-simple lactone fragment (**a**).

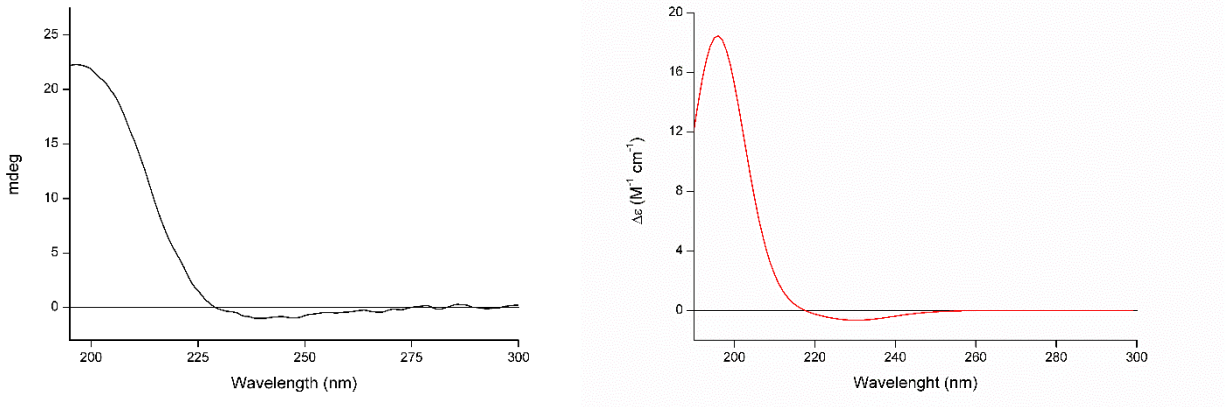


Figure S11: Calculated ECD spectrum at the wB97XD/PCM(ACN)/aug-cc-pVTZ//B3LYP/6-31G(d) level for the (*S*)-simple lactone fragment (**a**).

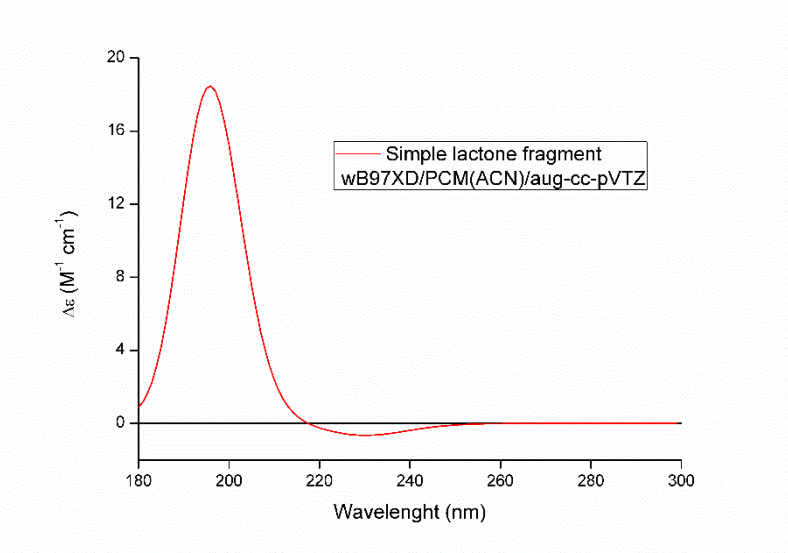


Figure S12: Most relevant molecular orbitals of the (*S*)-simple lactone fragment (**a**) at the CAM-B3LYP/PCM(ACN)/TZVP level.

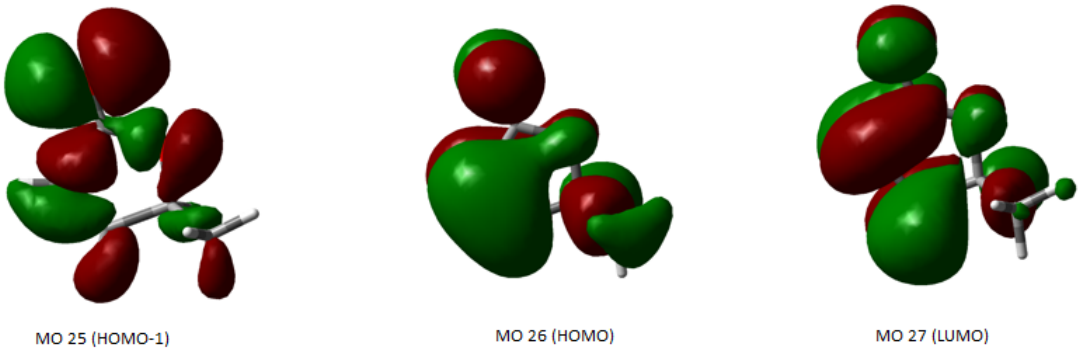


Figure S13: Simulated VCD spectra of conformers 1 (black) and 2 (red) of the (*SR*)-lactone fragment (**b**) at the B3LYP/6-31G(d) level.

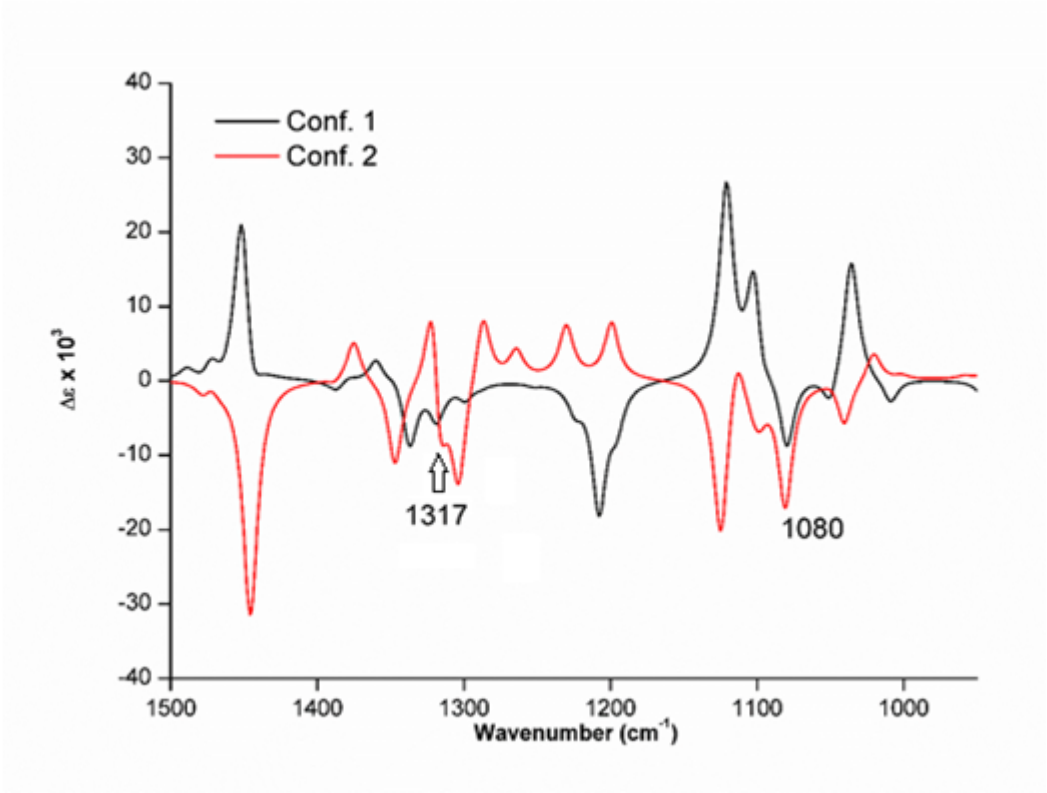


Figure S14: Simulated VCD spectra of conformers 1 (black) and 2 (red) of the (*SR*)-lactone fragment (**b**) at the B3PW91/6-311G(d,p) level.

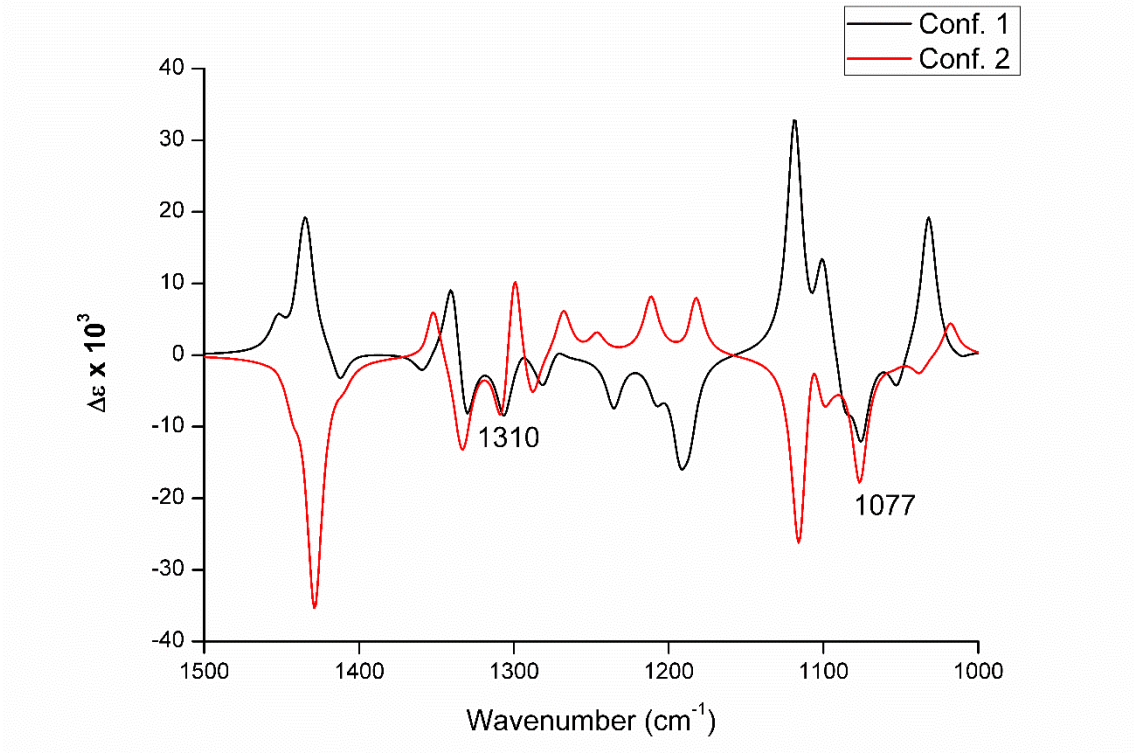


Figure S15: Displacement vectors of selected vibrational modes for Conf. 2 of (*SR*)-lactone fragment (b): band at 1080 cm^{-1} (Left); band at 1317 cm^{-1} (Right).

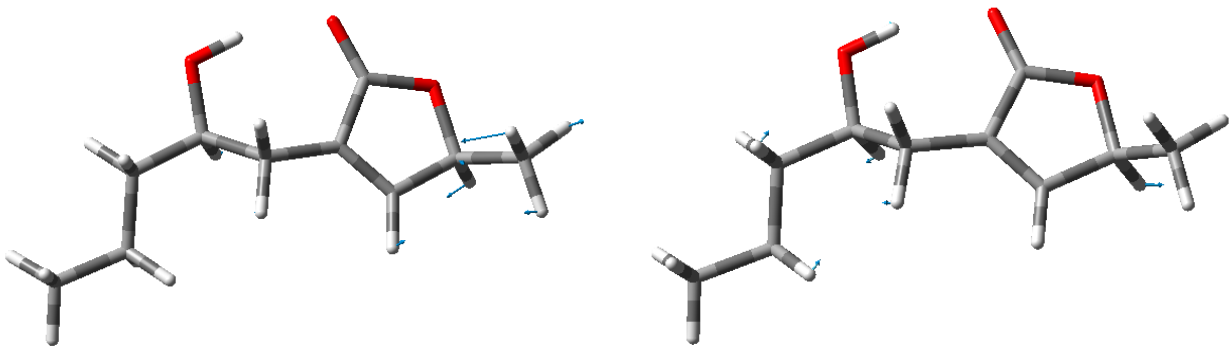


Figure S16: Displacement vectors of selected vibrational modes for the (*S*)-simple lactone fragment (**a**): band at 1108 cm^{-1} (Left); band at 1323 cm^{-1} (Right).