The Supporting Information for the paper:

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

Jadwiga Frelek,*[a] Aleksandra Butkiewicz,[a] Marcin Górecki,[a] Ryszard K. Wojcieszczyk,[b] Roman Luboradzki,[c] Marcin Kwit,[d] Michał F. Rode,[e] and Wojciech J. Szczepek,*[f]

[a] *Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, Warsaw, Poland*
[b] *University of Technology and Humanities in Radom, Chrobrego 27, 26-600 Radom, Poland*
[c] *Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, Warsaw, Poland*
[d] *Department of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland*
[e] *Institute of Physics, Polish Academy of Sciences, al. Lotników 32/46, 02-668 Warsaw, Poland*
[f] *Pharmaceutical Research Institute, Rydygiera 8, 01-793 Warsaw, Poland*

Contents

Single crystal X-ray diffraction measurements for 8a

Single crystal X-ray diffraction measurements were carried out on a Agilent Supernova diffractometer, at 100K with graphite monochromated Cu Kα radiation (1.54184 Å). Colourless crystal of approximate dimensions 1.0 x 0.1 x 0.1 mm (long needle) was used. The data reduction was made by using CrysAlisPRO software.[1] The structures were solved by direct methods and refined on F^2 by full-matrix least-squares by using SHELXS97 and SHELXL97.[2] All non-hydrogen atoms were refined as anisotropic while hydrogen atoms were placed in calculated positions, and refined in riding mode. Formula: $C_{29}H_{46}O_4$ monoclinic, space group $P2_1$, a=11.4050(2) b=6.18540(10) c=18.2916(3)Å, β=90.4610(10)^o, R_1= 0.0297 (I>2σ(I)), wR_2= 0.0769 for all data. Crystallographic data: CIF CCDC 882503.

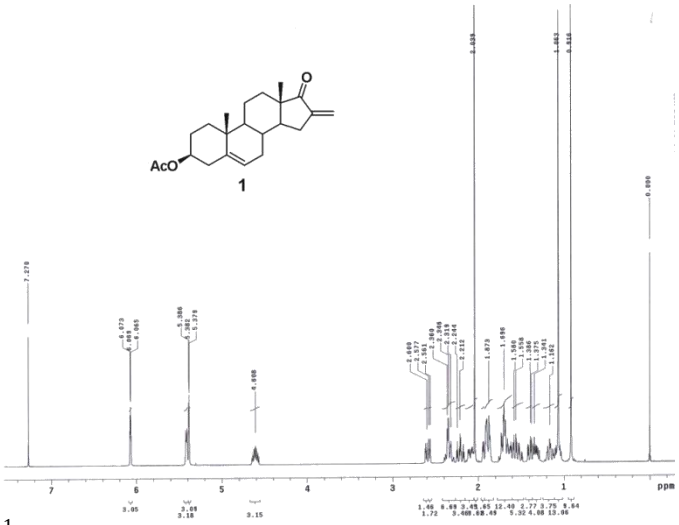
Overview of computational methods

In the first step the conformational analysis was performed using HyperChem program applying MM2 force field method. In order to simplify computation, the C_8H_{17} side chain at C(17) was replaced by the place-holder methyl group for all cholestane analogues. Next, the conformers found following this procedure were subjected to the quantum chemical geometry optimization using B3LYP density functional and TZVP basis set (Gaussian09 program package). Since ECD experiments were conducted in acetonitrile (or methanol) as solvent, the geometry optimization was evaluated for solvation effect using the polarizable continuum model (PCM) for acetonitrile (or methanol) implemented in G09 program. The calculations were done in a similar fashion for all discussed compounds.

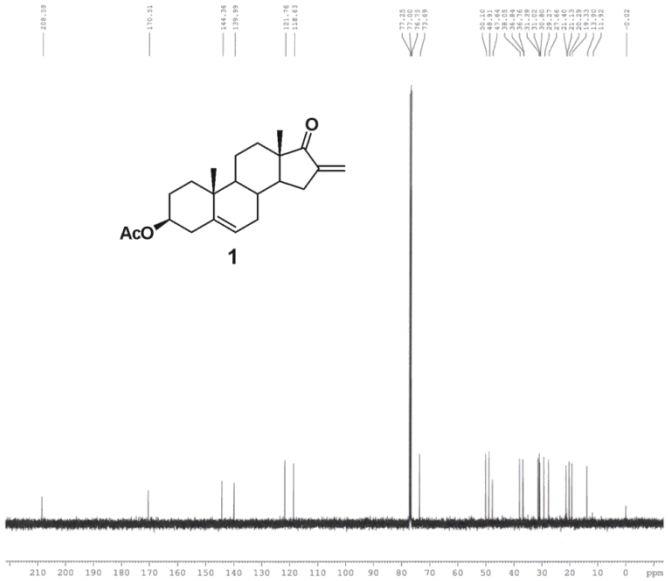
The theoretical ECD spectra were simulated using B3LYP functional and TZVP basis set with PCM model for acetonitrile (or methanol) as solvent. Determination of the origin of electronic transitions for a group of model compounds was conducted using the basis of DFT calculation at the B3LYP/TZVP level of theory and with the use of NBO method.[3] When necessary, the calculated spectra were wavelength corrected to match the experimental UV

maxima. Throughout the work, the calculated values of the rotatory strength (*R*) are given in 10^{-40} cgs units.

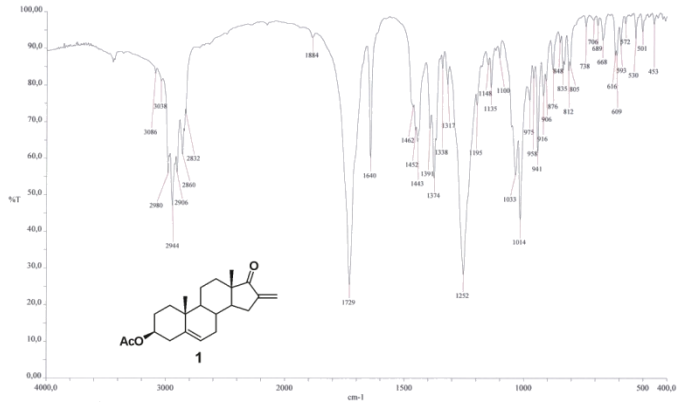
Copies of ^{1}H NMR, ^{13}C NMR and IR spectra of synthesized compounds



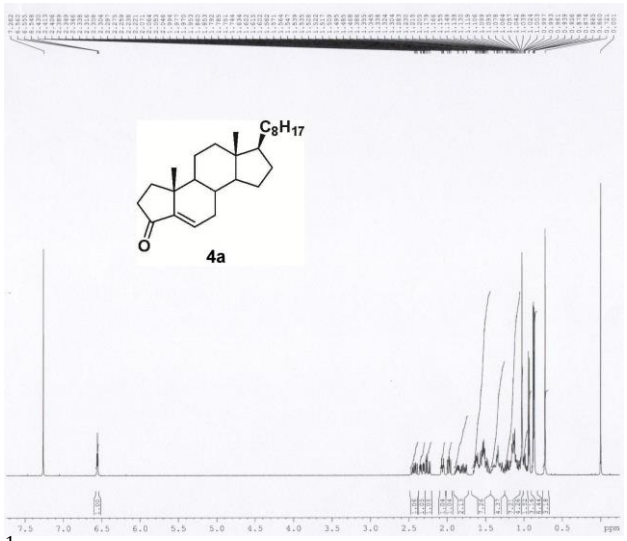
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1**.



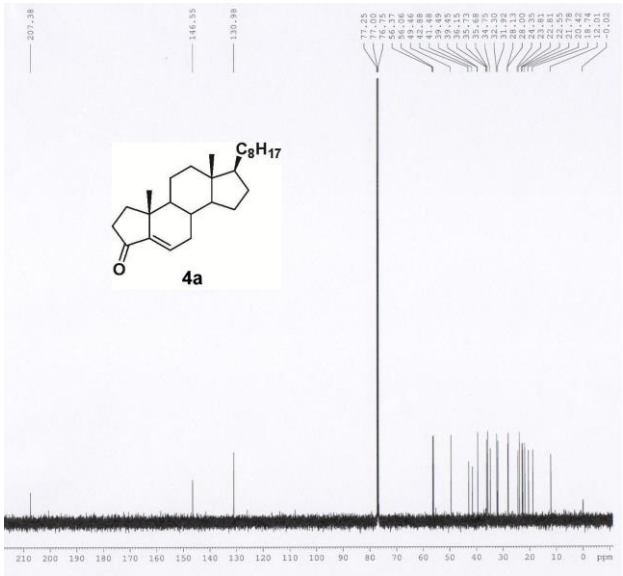
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1**.



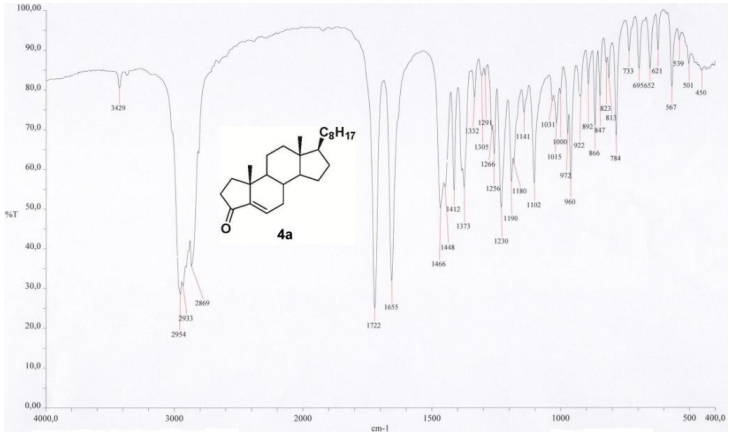
IR spectrum of compound **1** (in KBr).



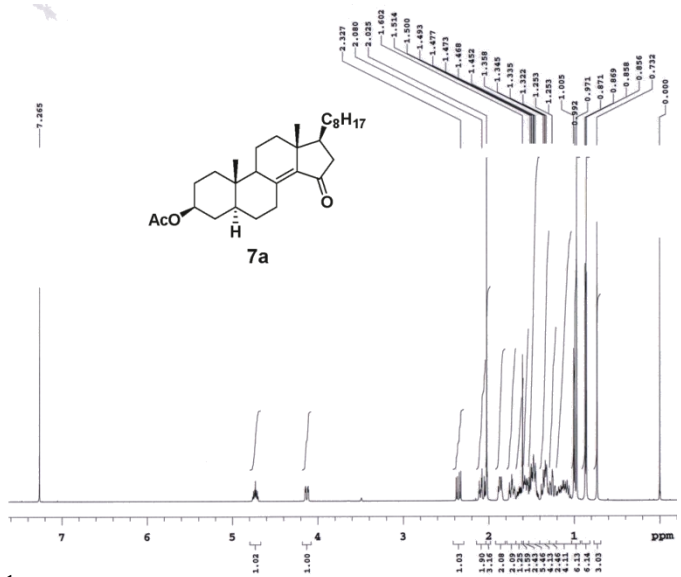
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4a**.



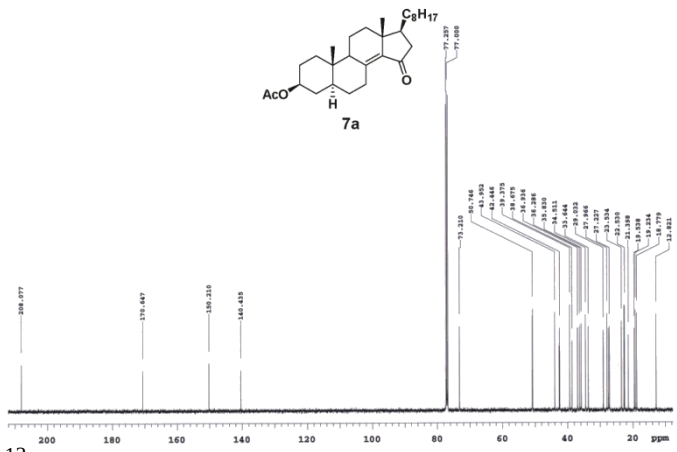
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4a**.



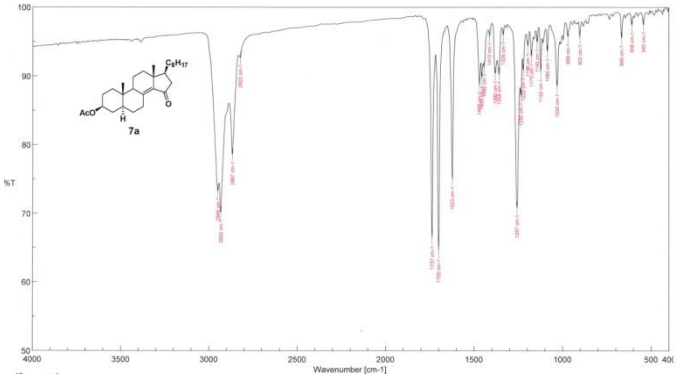
IR spectrum of compound **4a** (in KBr).



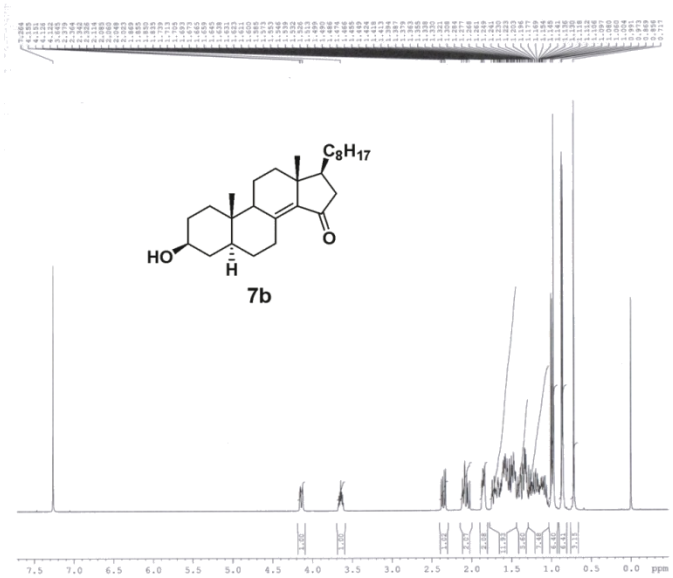
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **7a**.



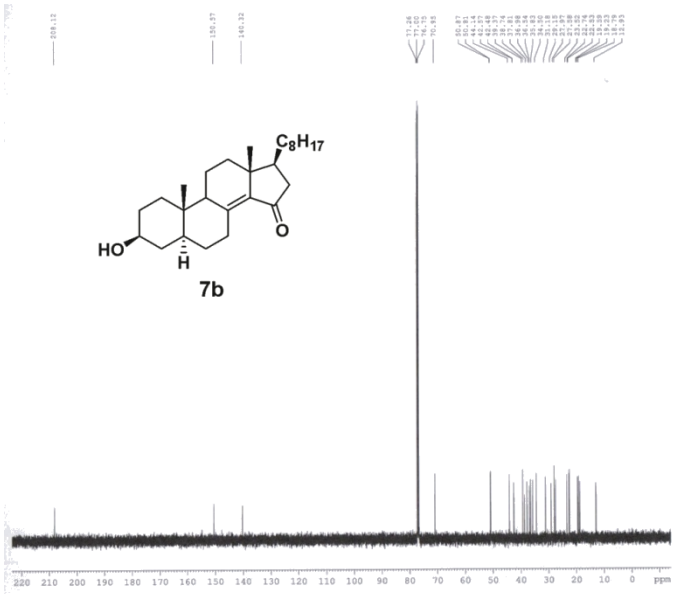
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **7a**.



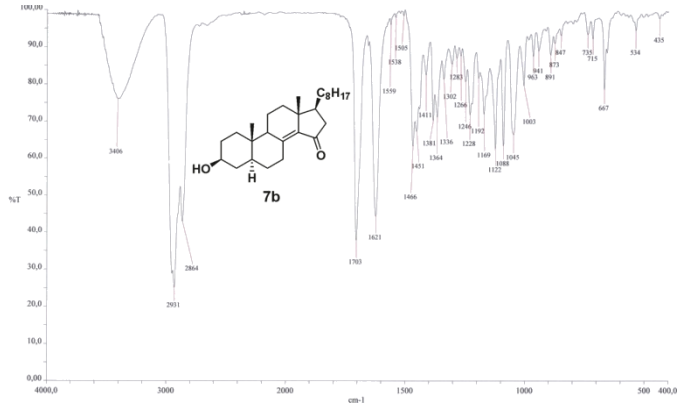
IR spectrum of compound **7a** (in KBr).



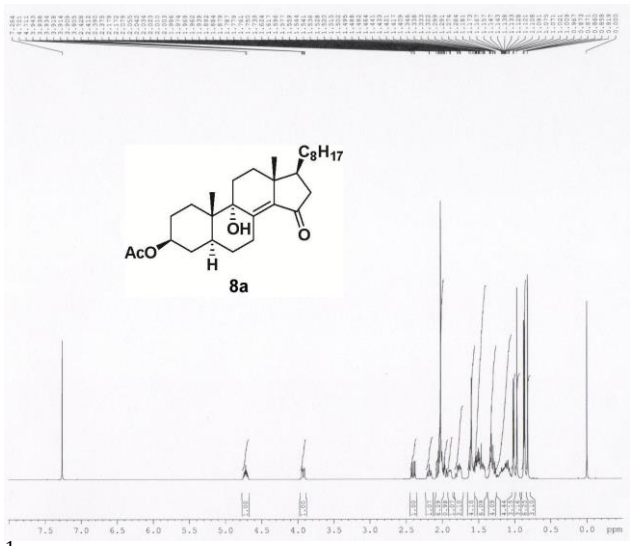
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **7b**.



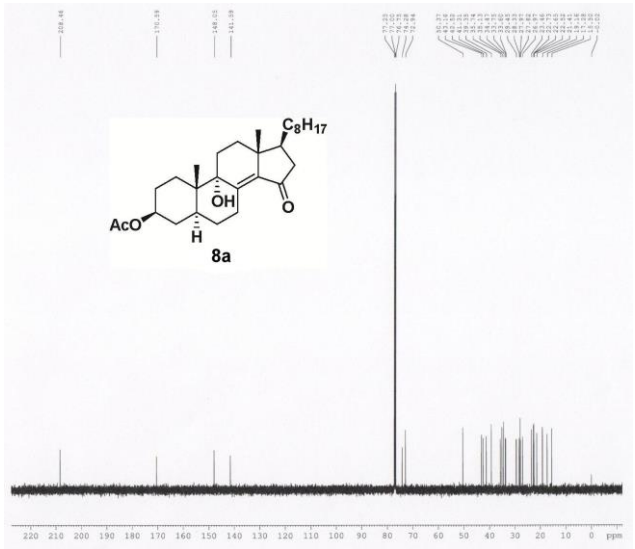
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **7b**.



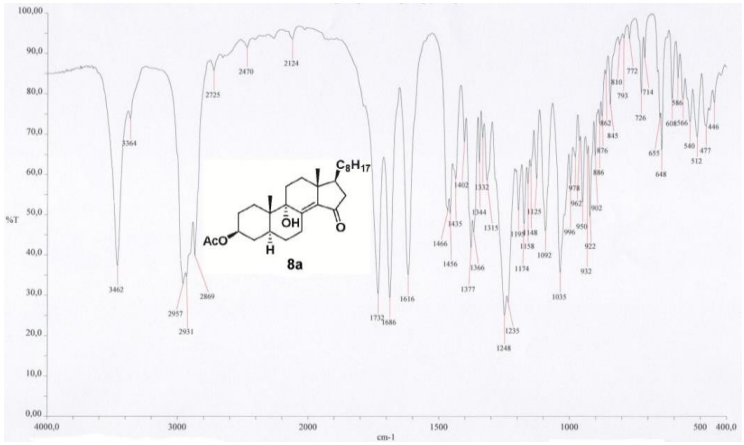
IR spectrum of compound **7b** (film from CH_2Cl_2).



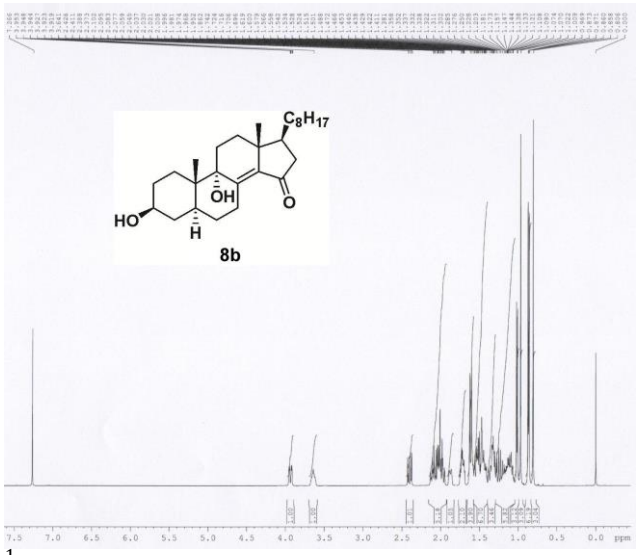
^{1}H NMR (500 MHz. $CDCl_3$) spectrum of compound **8a**.



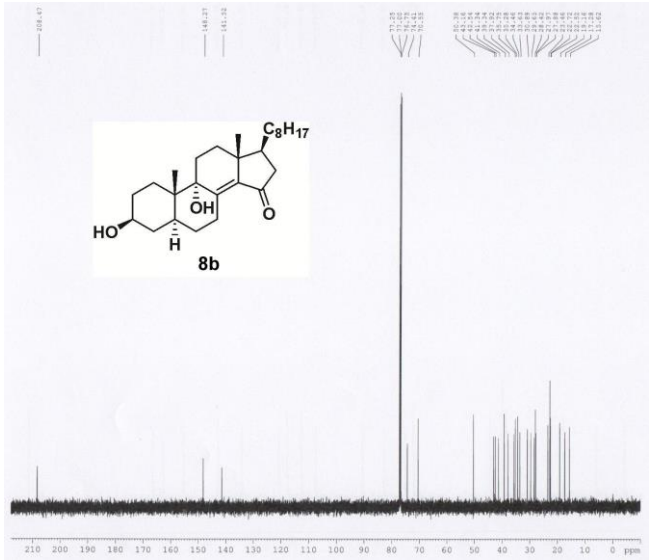
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **8a**.



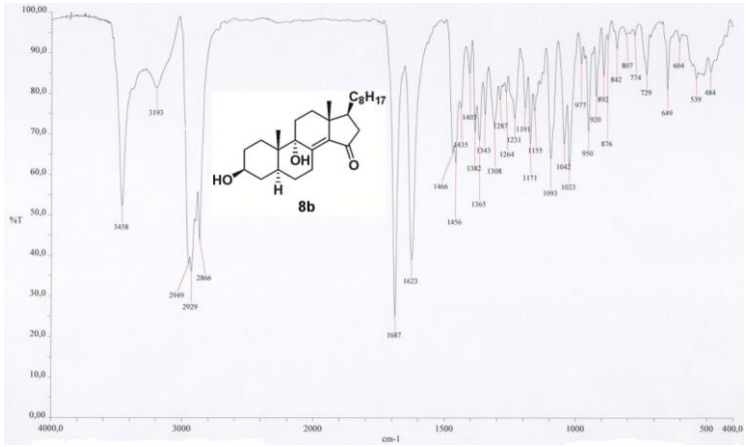
IR spectrum of compound **8a** (in KBr).



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **8b**.



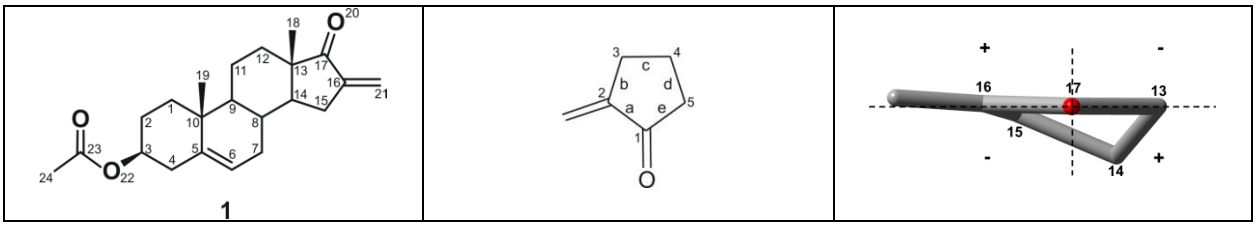
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **8b**.



IR spectrum of compound **8b** (film from CH_2Cl_2).

Conformational and spectral analysis of 1 in acetonitrile

For model compound **1** seven conformers in the range of 0-5 kcal/mol were found. Two major conformers **1**(1) and **1**(2), based on their internal energies, are populated in the conformational equillibrium in 50.9% and 48.8%, respectively. Populations of other conformers were below 0.4%. Therefore, these minor conformers were excluded from further consideration. All conformers possess nearly planar enone chromophoric system. The five-membered ketone ring in conformers of **1** exists in conformation close to envelope E(14α) (all investigated compounds are viewed along the axis of the O=C bond with C=C bond on the left side of the cyclopentanone ring). Beyond that, both main conformers show conformational differences mostly for the substituent at C(3) carbon atom. The Boltzmann-averaged ECD spectrum of conformers **1**(1) and **1**(2) was used for comparison with the experimental spectrum of **1**.



Overview of the conformational analysis for conformers 1(1) and 1(2) of compound 1.

Conformer	ΔG (kcal.mol^{-1})	Population (%)	Torsion angles [°]						
			enone	a	b	c	d	e	2-3-22-23
1(1)	0.00	50.9	+2.9	+5.8	+19.5	−37.5	+40.8	−28.4	+89.7
1(2)	0.03	48.8	+3.2	+6.0	+19.4	−37.5	+40.9	−28.6	+150.4

Calculated at B3LYP/TZVP level of theory total energies, relative energies and conformer distribution at 25° C for individual conformers of compound 1.

Conformer	Energy [Hartree]	ΔG [kcal mol^{-1}]	Distribution [%]
1	-1082.32816	0.00	50.9
2	-1082.32812	0.03	48.8
3	-1082.32290	3.30	0.2
4	-1082.32142	4.23	0.0
5	-1082.32139	4.25	0.0
6	-1082.32098	4.51	0.0

7	-1082.32094	4.53	0.0

Cartesian coordinates for individual conformers of compound 1.

Input orientation of compound **1** conf. 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.559122	0.618867	0.511730
2	6	0	3.058666	0.617240	0.729222
3	6	0	1.715201	-1.561504	-0.699491
4	6	0	3.223041	-1.602021	-0.428520
5	6	0	3.781009	-0.193620	-0.344071
6	6	0	0.886354	-0.745335	0.334770
7	1	0	1.339336	-2.585234	-0.741624
8	1	0	1.550711	-1.127019	-1.691174
9	6	0	-0.563587	-0.565009	-0.227431
10	6	0	0.885779	-1.481186	1.695940
11	6	0	0.890004	1.772107	0.483853
12	6	0	-1.365411	-1.887618	-0.279072
13	1	0	-0.440596	-0.229346	-1.266220
14	6	0	-1.338243	0.575356	0.484206
15	6	0	-0.592235	1.903244	0.315887
16	1	0	-1.407980	0.354327	1.554356
17	6	0	-2.743784	0.661750	-0.107583
18	1	0	-0.974531	2.642266	1.027440
19	1	0	-0.804999	2.320605	-0.678236
20	6	0	-2.805102	-1.733907	-0.803658
21	6	0	-3.543065	-0.658009	-0.008402
22	1	0	-1.403250	-2.336026	0.714950
23	1	0	-0.842246	-2.606163	-0.912989
24	1	0	-2.603634	0.834114	-1.184616
25	6	0	-3.733481	1.747600	0.358861
26	1	0	-3.324658	-2.693601	-0.743423
27	1	0	-2.786194	-1.447334	-1.859984
28	6	0	-3.819073	-1.119798	1.445712
29	6	0	-4.901254	-0.210270	-0.542753
30	6	0	-5.042298	1.255478	-0.226294
31	1	0	-3.474881	2.745145	0.003536
32	1	0	-3.787150	1.793658	1.451103
33	1	0	0.204301	-1.004167	2.402131
34	1	0	1.875921	-1.477871	2.151125
35	1	0	0.587212	-2.524562	1.584337
36	1	0	-2.896953	-1.339709	1.980873
37	1	0	-4.424275	-2.028425	1.427890
38	1	0	-4.362286	-0.370034	2.022887
39	1	0	3.430152	1.642699	0.741598
40	1	0	3.304262	0.172254	1.699964
41	1	0	3.725336	-2.151996	-1.227769
42	1	0	3.436703	-2.128700	0.505589
43	1	0	3.702489	0.309651	-1.308393
44	1	0	1.446180	2.700224	0.590581
45	8	0	5.199163	-0.306326	-0.013727
46	6	0	6.042907	0.647373	-0.446269
47	8	0	5.699478	1.607284	-1.102882
48	6	0	7.455121	0.360755	-0.012937
49	1	0	7.507581	0.318032	1.076056

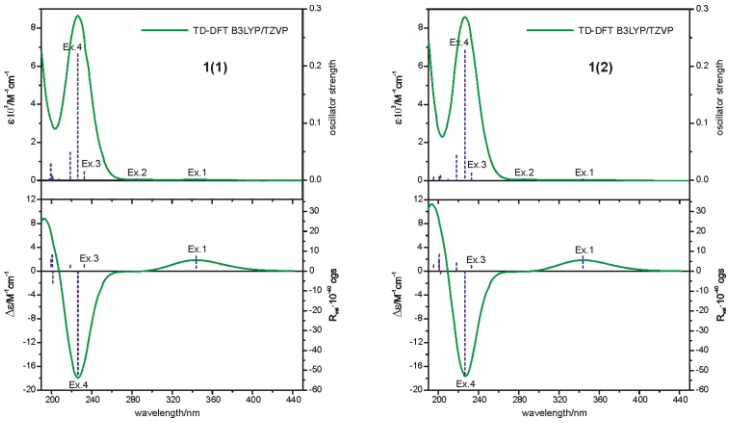
50	1	0	8.118909	1.137780	-0.382468
51	1	0	7.772730	-0.610331	-0.395486
52	8	0	-5.725788	-0.904669	-1.106458
53	6	0	-6.150636	1.943045	-0.490903
54	1	0	-7.006734	1.450768	-0.938091
55	1	0	-6.238493	3.001441	-0.276195

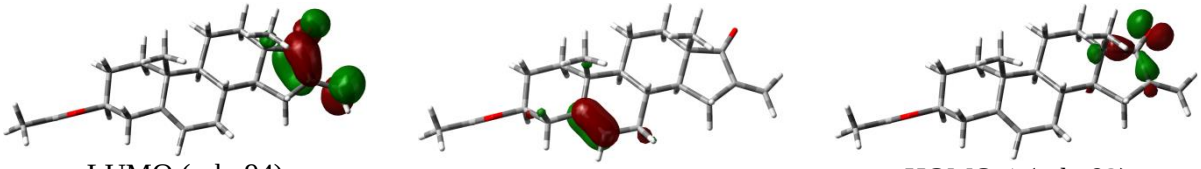
Input orientation of compound **1** conf. 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.474424	0.933841	0.503155
2	6	0	2.960730	1.055934	0.769663
3	6	0	1.810719	-1.355421	-0.435354
4	6	0	3.305463	-1.270575	-0.108355
5	6	0	3.776438	0.174186	-0.167968
6	6	0	0.894922	-0.483639	0.471513
7	1	0	1.497344	-2.399111	-0.376485
8	1	0	1.663099	-1.042726	-1.474460
9	6	0	-0.543304	-0.466385	-0.148510
10	6	0	0.890677	-1.056199	1.909954
11	6	0	0.735817	2.027934	0.312076
12	6	0	-1.251946	-1.839067	-0.071027
13	1	0	-0.405211	-0.241422	-1.214740
14	6	0	-1.409146	0.694842	0.406874
15	6	0	-0.745519	2.038243	0.087085
16	1	0	-1.484744	0.603831	1.495321
17	6	0	-2.806125	0.610578	-0.206526
18	1	0	-1.197530	2.834040	0.687873
19	1	0	-0.949957	2.311025	-0.957816
20	6	0	-2.689830	-1.846411	-0.621915
21	6	0	-3.511835	-0.742242	0.041050
22	1	0	-1.277458	-2.183538	0.963438
23	1	0	-0.668300	-2.580501	-0.619984
24	1	0	-2.659371	0.666335	-1.294840
25	6	0	-3.876260	1.669685	0.122716
26	1	0	-3.142048	-2.827828	-0.456848
27	1	0	-2.676206	-1.680687	-1.703961
28	6	0	-3.769300	-1.051020	1.538483
29	6	0	-4.891865	-0.457906	-0.546925
30	6	0	-5.138892	1.021117	-0.408165
31	1	0	-3.683492	2.635122	-0.345312
32	1	0	-3.947788	1.838186	1.201944
33	1	0	0.162214	-0.540016	2.537411
34	1	0	1.862972	-0.945603	2.389445
35	1	0	0.650809	-2.120555	1.913067
36	1	0	-2.838472	-1.133605	2.096813
37	1	0	-4.303054	-1.999440	1.625898
38	1	0	-4.375087	-0.282778	2.021436
39	1	0	3.271876	2.096945	0.667293
40	1	0	3.188669	0.753291	1.797253
41	1	0	3.870493	-1.877947	-0.818587
42	1	0	3.509630	-1.668096	0.889500
43	1	0	3.717277	0.547710	-1.190859
44	1	0	1.228082	2.997403	0.320393
45	8	0	5.168378	0.274286	0.263510
46	6	0	6.142376	0.150873	-0.655262

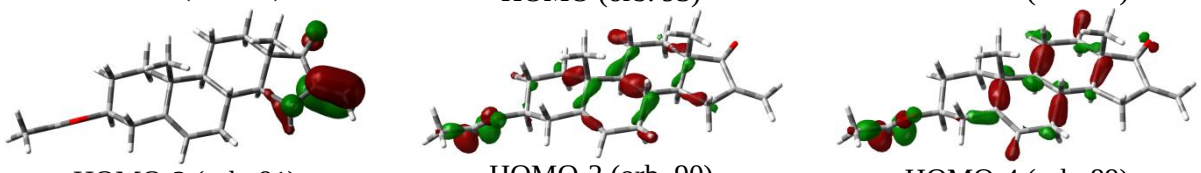
47	8	0	5.939486	-0.027956	-1.837392
48	6	0	7.503380	0.256661	-0.022159
49	1	0	7.667295	-0.601342	0.632767
50	1	0	7.569041	1.155841	0.590880
51	1	0	8.268432	0.273681	-0.793847
52	8	0	-5.659082	-1.270800	-1.026910
53	6	0	-6.287227	1.593649	-0.761612
54	1	0	-7.101285	0.993872	-1.152584
55	1	0	-6.449666	2.661604	-0.676808

Computed UV (top) and ECD (bottom) spectra of conformers 1(1) and 1(2) of compound 1





LUMO (orb. 94) HOMO (orb. 93) HOMO-1 (orb. 92)



HOMO-2 (orb. 91) HOMO-3 (orb. 90) HOMO-4 (orb. 89)

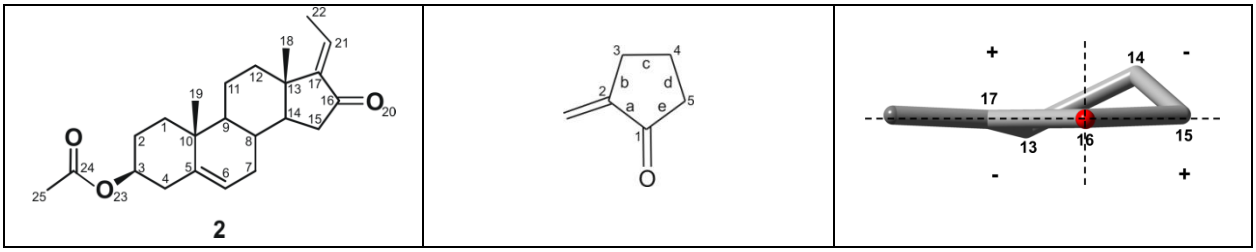
Conformer 1(1)

Excited State 1: 352.70 nm f=0.0013 Rotatory Strength (*R*) 8.4985
92 -> 94 0.69262
Excited State 2: 293.16 nm f=0.0015 Rotatory Strength (*R*) -0.3621
93 -> 94 0.70342
Excited State 3: 241.55 nm f=0.0148 Rotatory Strength (*R*) 2.8720
85 -> 94 -0.10036
87 -> 94 0.11982
89 -> 94 -0.42975
90 -> 94 0.46791
91 -> 94 0.24979
Excited State 4: 235.10 nm f=0.2210 Rotatory Strength (*R*) -51.2567
88 -> 94 -0.20492
89 -> 94 0.28861
91 -> 94 0.58913

Conformer 1(2)
Excited State 1: 352.48 nm f=0.0013 Rotatory Strength (*R*) 8.5848
92 -> 94 0.69311
Excited State 2: 293.52 nm f=0.0016 Rotatory Strength (*R*) -0.3463
93 -> 94 0.70389
Excited State 3: 241.52 nm f=0.0123 Rotatory Strength (*R*) 2.5334
85 -> 94 -0.11133
89 -> 94 -0.36874
90 -> 94 0.52885
91 -> 94 -0.23106
Excited State 4: 235.02 nm f=0.2277 Rotatory Strength (*R*) -50.5919
88 -> 94 -0.23905
90 -> 94 0.24062
91 -> 94 0.60018

Conformational and spectral analysis of 2 in methanol

Enone **2** has five conformers in the range of 0-5 kcal/mol. The two lowest energy conformers **2**(1) and **2**(2), based on their internal energies, are populated in the conformational equillibrium in 50.4 % and 49.3 %, respectively. Populations of other conformers were below 0.3%, therefore these minor conformers were excluded from further consideration. All conformers of **2** possess nearly planar enone chromophoric system. The five-membered ketone ring in both major conformers exists essentially as an envelope E(14β) conformation. Similarly, as in the case of compound **1**, two lowest energy conformers of enone **2** show conformational differences mostly for the substituent at C(3) carbon atom. The Boltzmann-averaged ECD spectrum of conformers **2**(1) and **2**(2) was used for comparison with the literature data of *cis*-enone **2**.



Overview of the conformational analysis for compound 2.

Conformer	Δ*G* (kcal.mol^{-1})	Population (%)	Torsion angles [°]						
			enone	a	b	c	d	e	2-3-23-24
2(1)	0.00	50.4	+4.1	+6.1	−28.1	+40.2	−36.8	+19.1	+89.1
2(2)	0.01	49.3	+4.3	+6.3	−28.2	+40.3	−36.7	+18.9	+151.1

Calculated at B3LYP/TZVP level of theory total energies, relative energies and conformer distribution at 25° C for individual conformers of compound 2.

Conformer	Energy [Hartree]	Δ*G* [kcal mol^{-1}]	Distribution [%]
1	-1121.65095	0.00	50.4
2	-1121.65093	0.01	49.3
3	-1121.64565	3.33	0.2
4	-1121.64426	4.20	0.0
5	-1121.64374	4.52	0.0

Cartesian coordinates for individual conformers of compound 2.

Input orientation of compound **2** conf. 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.783011	1.029431	0.393801
2	6	0	3.279409	1.113271	0.615166
3	6	0	1.990859	-1.382087	-0.226786
4	6	0	3.494863	-1.326587	0.061179
5	6	0	4.029554	0.071766	-0.206498
6	6	0	1.138388	-0.348657	0.563765
7	1	0	1.629644	-2.390356	-0.016881
8	1	0	1.835146	-1.209819	-1.296930
9	6	0	-0.308929	-0.342923	-0.032574
10	6	0	1.136988	-0.716243	2.067632
11	6	0	1.089644	2.122511	0.072052
12	6	0	-1.083989	-1.649674	0.238892
13	1	0	-0.181434	-0.267679	-1.121124
14	6	0	-1.112639	0.915895	0.374430
15	6	0	-0.394794	2.174272	-0.126728
16	1	0	-1.176170	0.972362	1.466102
17	6	0	-2.520177	0.815589	-0.212340
18	1	0	-0.796057	3.061985	0.372720
19	1	0	-0.609267	2.319888	-1.194771
20	6	0	-2.534130	-1.663026	-0.280595
21	6	0	-3.320901	-0.446410	0.231994
22	1	0	-1.101464	-1.851848	1.310714
23	1	0	-0.552805	-2.489246	-0.214465
24	1	0	-2.383605	0.695588	-1.296289
25	6	0	-3.503285	1.977323	-0.048391
26	1	0	-2.997380	-2.600259	0.033058
27	1	0	-2.540741	-1.655108	-1.375270
28	6	0	-3.520868	-0.532734	1.764561
29	6	0	-4.684330	-0.145692	-0.387906
30	6	0	-4.823232	1.345341	-0.468633
31	1	0	-3.286472	2.854419	-0.657793
32	1	0	-3.586417	2.310830	0.991905
33	1	0	0.433398	-0.094506	2.623776
34	1	0	2.119170	-0.570334	2.516696
35	1	0	0.865794	-1.761672	2.222653
36	1	0	-2.578881	-0.624250	2.303629
37	1	0	-4.129784	-1.407230	2.003587
38	1	0	-4.040855	0.342979	2.156272
39	1	0	3.636025	2.113930	0.365090
40	1	0	3.518628	0.942852	1.670634
41	1	0	4.015221	-2.052182	-0.567465
42	1	0	3.703140	-1.592947	1.101134
43	1	0	3.959994	0.303051	-1.270018
44	1	0	1.625331	3.059748	-0.058415
45	8	0	5.435597	0.163100	0.178290
46	6	0	6.376831	-0.143892	-0.731921
47	8	0	6.132265	-0.490582	-1.867893
48	6	0	7.758752	0.002704	-0.154655
49	1	0	8.501713	-0.226388	-0.913910
50	1	0	7.878823	-0.673091	0.693643
51	1	0	7.904799	1.019561	0.212360
52	6	0	-5.692207	-0.925146	-0.798551
53	8	0	-5.816486	1.960383	-0.818245
54	6	0	-5.823229	-2.410918	-0.780023

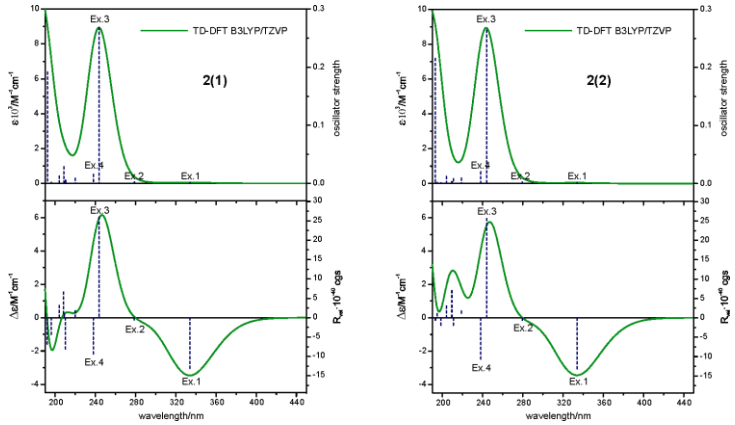
55	1	0	-6.552789	-0.393714	-1.201241
56	1	0	-4.997841	-2.917259	-0.288049
57	1	0	-5.906969	-2.796344	-1.801576
58	1	0	-6.752430	-2.690851	-0.274212

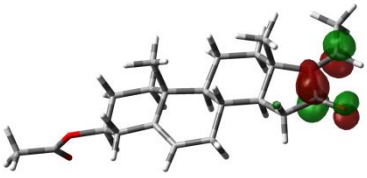
Input orientation of compound **2** conf. 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.858819	0.694784	0.444442
2	6	0	3.361999	0.652476	0.628914
3	6	0	1.892769	-1.623592	-0.493323
4	6	0	3.403449	-1.698443	-0.246403
5	6	0	4.021748	-0.316713	-0.349333
6	6	0	1.124190	-0.649000	0.445810
7	1	0	1.471643	-2.626296	-0.401534
8	1	0	1.725217	-1.307302	-1.528352
9	6	0	-0.326519	-0.466472	-0.113229
10	6	0	1.118659	-1.214181	1.886355
11	6	0	1.235979	1.864729	0.294734
12	6	0	-1.187760	-1.743390	-0.010455
13	1	0	-0.207530	-0.248868	-1.183447
14	6	0	-1.038587	0.772819	0.480815
15	6	0	-0.244083	2.041003	0.147339
16	1	0	-1.088502	0.677374	1.570378
17	6	0	-2.454463	0.853023	-0.087175
18	1	0	-0.575966	2.870431	0.780209
19	1	0	-0.467341	2.354730	-0.882059
20	6	0	-2.638101	-1.584387	-0.503958
21	6	0	-3.336268	-0.403242	0.188564
22	1	0	-1.210840	-2.091647	1.023170
23	1	0	-0.720408	-2.545307	-0.585738
24	1	0	-2.335010	0.879758	-1.179242
25	6	0	-3.353555	2.042532	0.258563
26	1	0	-3.163328	-2.523496	-0.320363
27	1	0	-2.649323	-1.419643	-1.586114
28	6	0	-3.527423	-0.692736	1.697637
29	6	0	-4.681141	0.073280	-0.357044
30	6	0	-4.718484	1.566239	-0.219691
31	1	0	-3.082884	2.980729	-0.225476
32	1	0	-3.401524	2.230239	1.336881
33	1	0	0.491657	-0.610686	2.544652
34	1	0	2.120588	-1.223210	2.314914
35	1	0	0.750288	-2.240752	1.908376
36	1	0	-2.586033	-0.901973	2.204094
37	1	0	-4.175769	-1.562742	1.822125
38	1	0	-4.001429	0.142621	2.215647
39	1	0	3.776978	1.653635	0.505602
40	1	0	3.613283	0.320650	1.642354
41	1	0	3.863428	-2.365514	-0.979229
42	1	0	3.616728	-2.113434	0.742337
43	1	0	3.940568	0.066483	-1.367320
44	1	0	1.832456	2.773728	0.277477
45	8	0	5.442066	-0.451022	-0.036277
46	6	0	6.310840	0.412607	-0.591152
47	8	0	5.989124	1.300902	-1.351355
48	6	0	7.719053	0.133317	-0.140327

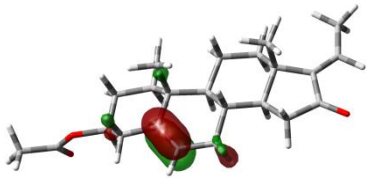
49	1	0	8.414156	0.758709	-0.694284
50	1	0	7.963586	-0.919177	-0.285535
51	1	0	7.808548	0.348171	0.926353
52	6	0	-5.742554	-0.569714	-0.858828
53	8	0	-5.671173	2.289676	-0.456309
54	6	0	-5.973335	-2.030355	-1.055720
55	1	0	-6.568474	0.070354	-1.164443
56	1	0	-5.179646	-2.656851	-0.659131
57	1	0	-6.091997	-2.254176	-2.121052
58	1	0	-6.914651	-2.320497	-0.578931

Computed UV (top) and ECD (bottom) spectra of conformers 2(1) and 2(2) of compound 2

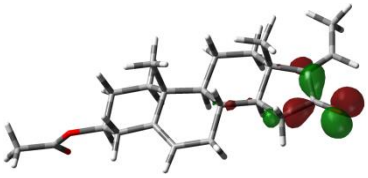




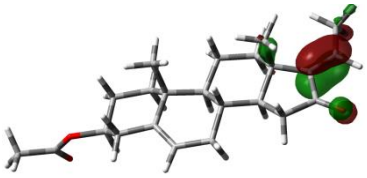
LUMO (orb. 98)



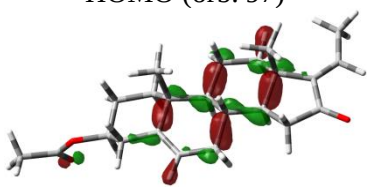
HOMO (orb. 97)



HOMO-1 (orb. 96)



HOMO-2 (orb. 95)



HOMO-3 (orb. 94)

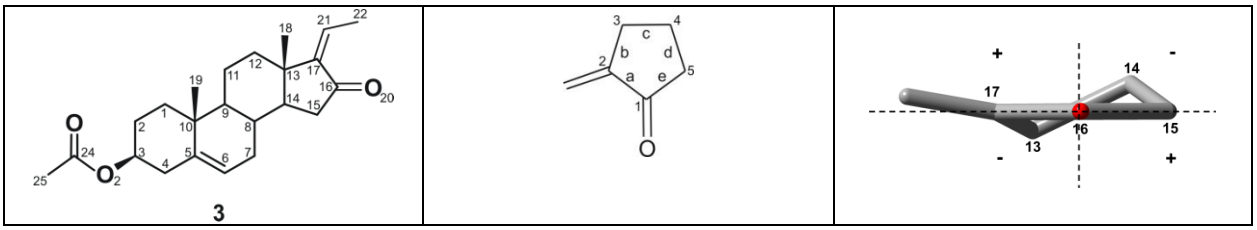
Conformer 2(1)

Excited State 1: 334.13 nm f=0.0015 Rotatory Strength (*R*) -14.2836
95 -> 98 0.14358
96 -> 98 0.68069
Excited State 2: 278.82 nm f=0.0023 Rotatory Strength (*R*) -0.6750
97 -> 98 0.70642
Excited State 3: 243.89 nm f=0.2685 Rotatory Strength (*R*) 21.8451
94 -> 98 0.14050
95 -> 98 0.66477
96 -> 98 -0.14690
Excited State 4: 238.01 nm f=0.0157 Rotatory Strength (*R*) -10.8972
93 -> 98 -0.11166
94 -> 98 0.65991
95 -> 98 -0.13802

Conformer 2(2)
Excited State 1: 333.95 nm f=0.0015 Rotatory Strength (*R*) -14.1615
95 -> 98 0.14663
96 -> 98 0.68026
Excited State 2: 279.35 nm f=0.0023 Rotatory Strength (*R*) -0.6759
97 -> 98 0.70650
Excited State 3: 243.97 nm f=0.2643 Rotatory Strength (*R*) 21.5606
94 -> 98 0.15411
95 -> 98 0.66025
96 -> 98 -0.14862
Excited State 4: 238.17 nm f=0.0205 Rotatory Strength (*R*) -12.1897
89 -> 98 -0.10638
93 -> 98 -0.18076
94 -> 98 0.64431

Conformational and spectral analysis of 3 in acetonitrile

Similarly to compound **2**, for steroid **3** five conformers in the range of 0-5 kcal/mol were found. The two lowest energy confromers **3**(1) and **3**(2), based on their internal energies, were found to have populations of 50.8% and 48.9%, respectively. Distribution of other minor conformers were below 0.3%, therefore the minor conformers were excluded from further consideration. For conformers of compound **3** the cyclopentanone five-membered ring adopts a half-chair HC(13α,14β) conformation and the enone torsion angles show nonplanarity of the chromophore. The two lowest energy conformers of enone **3** show conformational differences mostly for the substituent at C(3) carbon atom. The Boltzmann-averaged ECD spectrum of conformers **3**(1) and **3**(2) was used for comparison with the experimental spectrum of **3**.



Overview of the conformational analysis for compound 3.

Conformer	ΔG (kcal.mol^{-1})	Population (%)	Torsion angles [°]						
			enone	a	b	c	d	e	2-3-23-24
3(1)	0.00	50.8	+12.4	+10.6	−31.7	+41.5	−35.4	+15.6	+151.1
3(2)	0.02	48.9	+12.4	+10.5	−31.7	+41.5	−35.5	+15.6	+89.0

Calculated at B3LYP/TZVP level of theory total energies, relative energies and conformer distribution at 25° C for individual conformers of compound 3.

Conformer	Energy [Hartree]	ΔG [kcal mol^{-1}]	Distribution [%]
1	-1121.65671	0.00	50.8
2	-1121.65667	0.02	48.9
3	-1121,65129	3.40	0.2
4	-1121,65001	4.21	0.0
5	-1121,64952	4.51	0.0

Cartesian coordinates for individual conformers of compound 3.
Input orientation of compound **3** conf. 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.883821	0.660242	0.464948
2	6	0	3.389357	0.650682	0.635439
3	6	0	1.969000	-1.610656	-0.575328
4	6	0	3.483678	-1.656730	-0.346756
5	6	0	4.065792	-0.256277	-0.390033
6	6	0	1.185856	-0.701937	0.416308
7	1	0	1.575758	-2.627609	-0.527139
8	1	0	1.781411	-1.250353	-1.592323
9	6	0	-0.277772	-0.537944	-0.115165
10	6	0	1.216294	-1.330910	1.829855
11	6	0	1.229879	1.818605	0.366726
12	6	0	-1.100845	-1.845394	-0.051733
13	1	0	-0.180629	-0.277369	-1.177979
14	6	0	-1.012787	0.661757	0.534831
15	6	0	-0.255526	1.960832	0.238025
16	1	0	-1.043906	0.524763	1.620673
17	6	0	-2.439650	0.725777	-0.008057
18	1	0	-0.602897	2.758923	0.902201
19	1	0	-0.497421	2.303275	-0.777934
20	6	0	-2.557829	-1.700789	-0.526862
21	6	0	-3.267393	-0.568194	0.221796
22	1	0	-1.104005	-2.231924	0.968302
23	1	0	-0.614922	-2.610484	-0.660720
24	1	0	-2.341239	0.812281	-1.099132
25	6	0	-3.384714	1.853743	0.416261
26	1	0	-3.074988	-2.654727	-0.385999
27	1	0	-2.579570	-1.483083	-1.599686
28	6	0	-3.437716	-0.926748	1.718261
29	6	0	-4.631300	-0.129884	-0.302408
30	6	0	-4.753286	1.336084	-0.026632
31	1	0	-3.181534	2.821742	-0.042261
32	1	0	-3.399819	2.003098	1.501218
33	1	0	0.582191	-0.775315	2.522520
34	1	0	2.223900	-1.331589	2.245049
35	1	0	0.876039	-2.367135	1.809952
36	1	0	-2.486916	-1.112728	2.216249
37	1	0	-4.045931	-1.830003	1.804818
38	1	0	-3.949108	-0.137242	2.271600
39	1	0	3.775698	1.667340	0.552880
40	1	0	3.658856	0.281972	1.631267
41	1	0	3.952824	-2.276321	-1.114627
42	1	0	3.718159	-2.112494	0.618997
43	1	0	3.967586	0.170720	-1.388940
44	1	0	1.802546	2.742841	0.381674
45	8	0	5.491428	-0.368926	-0.092488
46	6	0	6.334610	0.540229	-0.612784
47	8	0	5.985818	1.453446	-1.330391
48	6	0	7.752127	0.278142	-0.181315
49	1	0	7.847318	0.476444	0.888210
50	1	0	8.429973	0.927323	-0.729307
51	1	0	8.015356	-0.766580	-0.347240
52	6	0	-5.527818	-0.906333	-0.925249
53	8	0	-5.752161	2.029578	-0.126274
54	6	0	-6.863068	-0.523014	-1.475536
55	1	0	-5.260748	-1.951932	-1.065882

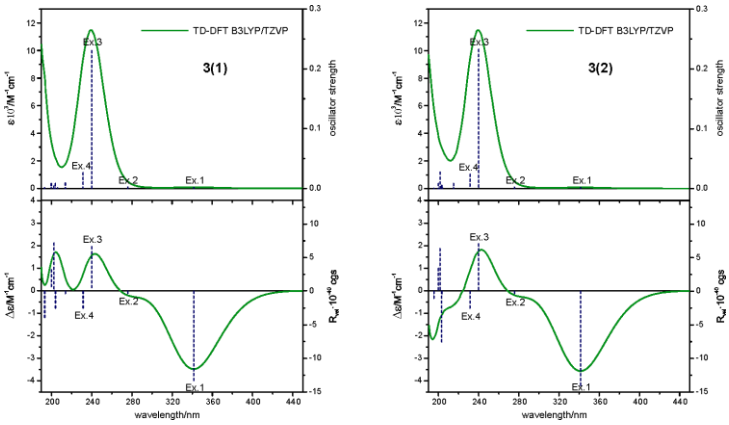
56	1	0	-7.061680	0.541073	-1.389481
57	1	0	-7.651872	-1.069363	-0.946751
58	1	0	-6.935380	-0.826023	-2.524551

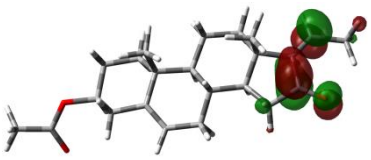
Input orientation of compound **3** conf. 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.809636	1.021567	0.375016
2	6	0	3.307620	1.142965	0.565344
3	6	0	2.060220	-1.401960	-0.183816
4	6	0	3.567594	-1.304745	0.074089
5	6	0	4.065262	0.096642	-0.242698
6	6	0	1.197655	-0.365176	0.591878
7	1	0	1.726660	-2.411634	0.062191
8	1	0	1.881193	-1.265452	-1.255508
9	6	0	-0.258871	-0.407539	0.019018
10	6	0	1.227146	-0.692031	2.104459
11	6	0	1.087037	2.091732	0.041199
12	6	0	-0.996177	-1.730100	0.329558
13	1	0	-0.150388	-0.355015	-1.073003
14	6	0	-1.084134	0.844855	0.409880
15	6	0	-0.401445	2.106919	-0.129667
16	1	0	-1.133094	0.922807	1.500913
17	6	0	-2.497743	0.703436	-0.152007
18	1	0	-0.813114	2.995977	0.359003
19	1	0	-0.639091	2.225670	-1.196106
20	6	0	-2.447651	-1.781625	-0.181378
21	6	0	-3.246531	-0.573530	0.318167
22	1	0	-1.000084	-1.909223	1.405680
23	1	0	-0.446438	-2.564293	-0.111019
24	1	0	-2.378229	0.580638	-1.237552
25	6	0	-3.524092	1.825746	0.029271
26	1	0	-2.906454	-2.721011	0.141480
27	1	0	-2.456755	-1.783375	-1.276278
28	6	0	-3.433669	-0.642621	1.853196
29	6	0	-4.621353	-0.339906	-0.300537
30	6	0	-4.844360	1.139480	-0.321891
31	1	0	-3.370762	2.697289	-0.607505
32	1	0	-3.578486	2.182078	1.063604
33	1	0	0.519564	-0.070223	2.655323
34	1	0	2.213247	-0.513548	2.532682
35	1	0	0.980268	-1.738294	2.290410
36	1	0	-2.486695	-0.678171	2.390491
37	1	0	-3.998021	-1.542902	2.106596
38	1	0	-3.995715	0.211342	2.235055
39	1	0	3.637443	2.144111	0.282482
40	1	0	3.570520	1.006161	1.620204
41	1	0	4.092484	-2.036648	-0.543470
42	1	0	3.800968	-1.536335	1.117080
43	1	0	3.970239	0.296996	-1.310520
44	1	0	1.599738	3.036657	-0.121983
45	8	0	5.476081	0.229860	0.111806
46	6	0	6.406311	-0.083753	-0.807102
47	8	0	6.148043	-0.461937	-1.930015
48	6	0	7.795930	0.086311	-0.255364
49	1	0	7.899555	1.057101	0.229253

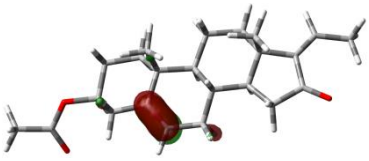
50	1	0	8.524716	-0.013705	-1.055457
51	1	0	7.981140	-0.680916	0.499299
52	6	0	-5.449234	-1.283215	-0.768753
53	8	0	-5.882949	1.729849	-0.570047
54	6	0	-6.790710	-1.108430	-1.403204
55	1	0	-5.112085	-2.315241	-0.694550
56	1	0	-7.052224	-0.064734	-1.549875
57	1	0	-7.559570	-1.575538	-0.777785
58	1	0	-6.820561	-1.632863	-2.363024

Computed UV (top) and ECD (bottom) spectra of conformers 3(1) and 3(2) of compound 3

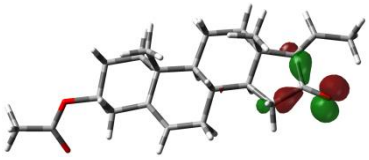




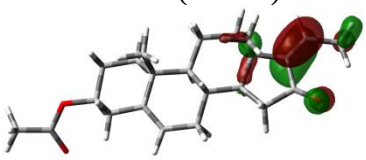
LUMO (orb. 98)



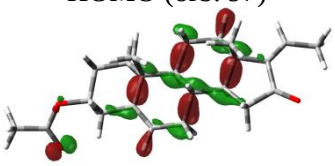
HOMO (orb. 97)



HOMO-1 (orb. 96)



HOMO-2 (orb. 95)



HOMO-3 (orb. 94)

Conformer 3(1)

Excited State 1: 348.36 nm f=0.0017 Rotatory Strength (*R*) -15.1512
95 -> 98 0.13015
96 -> 98 0.68544
Excited State 2: 282.94 nm f=0.0024 Rotatory Strength (*R*) -0.8989
97 -> 98 0.70652
Excited State 3: 247.04 nm f=0.2305 Rotatory Strength (*R*) 5.6341
94 -> 98 0.17242
95 -> 98 0.65727
96 -> 98 -0.13046
Excited State 4: 238.40 nm f=0.0267 Rotatory Strength (*R*) -3.7349
93 -> 98 -0.20529
94 -> 98 0.63341
95 -> 98 -0.17425

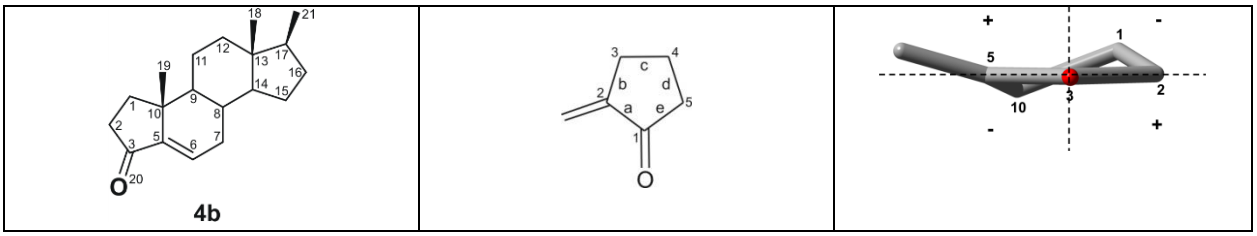
Conformer 3(2)

Excited State 1: 348.40 nm f=0.0017 Rotatory Strength (*R*) -15.2028

95 -> 98 0.13081
96 -> 98 0.68513
Excited State 2: 282.60 nm f=0.0023 Rotatory Strength (*R*) -0.8824
97 -> 98 0.70650
Excited State 3: 246.98 nm f=0.2327 Rotatory Strength (*R*) 5.7287
94 -> 98 0.17066
95 -> 98 0.65915
96 -> 98 -0.13191
Excited State 4: 238.30 nm f=0.0238 Rotatory Strength (*R*) -3.6329
91 -> 98 -0.10766
93 -> 98 -0.12538
94 -> 98 0.65226
95 -> 98 -0.16546

Conformational and spectral analysis of 4b in acetonitrile

For compound **4b** (17β-methyl analog of compound **4a**) only one low energy conformer in the range 0-5 kcal/mol was found. It has skewed enone chromophore and the cyclopentanone five membered ring is in a half-chair HC(10α,1β) conformation. The theoretical ECD spectrum of **4b(1)** was used for comparison with the experimental spectrum of **4a**.



Overview of the conformational analysis for compound 4b

Conformer	ΔG (kcal.mol^{-1})	Population (%)	Torsion angles [°]					
			enone	a	b	c	d	e
4b(1)	0.00	100.0	+18.5	+10.0	−26.6	+33.0	−27.9	+11.4

Calculated at B3LYP/TZVP level of theory total energies, relative energies and conformer distribution at 25° C for individual conformers of compound 4b.

Conformer	Energy [Hartree]	ΔG [kcal mol^{-1}]	Distribution [%]
1	-816.38840	0.00	100.0

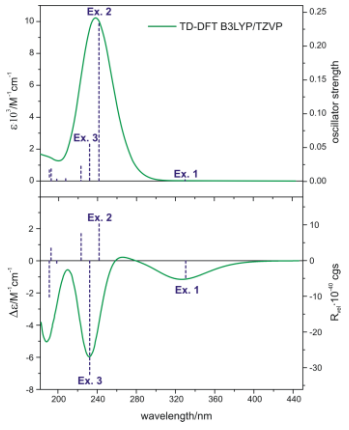
Cartesian coordinates for individual conformers of compound 4b.

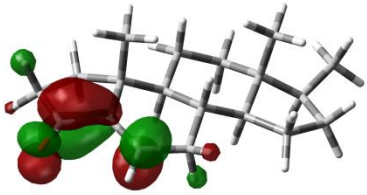
Input orientation of compound **4b** conf. 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	19.498749	19.419554	4.254073
2	6	0	18.127916	19.336922	4.809066
3	6	0	18.723291	21.662544	4.442533
4	6	0	20.039195	20.827370	4.420278
5	1	0	18.847287	22.615545	4.957314
6	1	0	18.415064	21.877607	3.416223
7	6	0	20.973640	21.154497	3.228275
8	6	0	20.742716	20.952289	5.790999

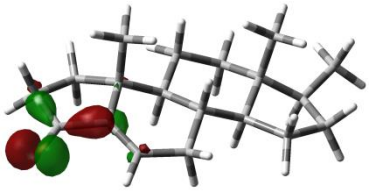
9	6	0	20.082433	18.460151	3.532238
10	6	0	21.595300	22.562279	3.295388
11	1	0	20.336675	21.129258	2.333275
12	6	0	22.033706	20.034269	3.030316
13	6	0	21.362781	18.667212	2.789041
14	1	0	22.635457	19.955014	3.940573
15	6	0	22.948824	20.413254	1.864520
16	1	0	22.059409	17.854683	3.021534
17	1	0	21.138655	18.546130	1.719826
18	6	0	22.558523	22.860884	2.133567
19	6	0	23.647625	21.786314	2.021972
20	1	0	22.127725	22.689227	4.240107
21	1	0	20.793392	23.306094	3.299502
22	1	0	22.290035	20.522973	0.990742
23	6	0	24.080817	19.463779	1.438065
24	1	0	22.997577	23.854344	2.270535
25	1	0	21.996223	22.891332	1.193194
26	6	0	24.585095	21.841703	3.244776
27	6	0	24.473224	21.814289	0.706950
28	6	0	25.019697	20.362741	0.582774
29	1	0	23.709851	18.603416	0.878878
30	1	0	24.607697	19.071282	2.311786
31	6	0	25.544658	22.893351	0.574634
32	1	0	23.748819	21.968464	-0.101355
33	1	0	26.047812	20.310314	0.949520
34	1	0	25.045781	20.046056	-0.461735
35	1	0	20.081572	20.631066	6.598664
36	1	0	21.028653	21.985271	5.995436
37	1	0	21.637371	20.330567	5.841224
38	1	0	24.063822	21.624203	4.176377
39	1	0	25.021082	22.838379	3.342601
40	1	0	25.408720	21.130982	3.161501
41	1	0	26.340467	22.767854	1.312266
42	6	0	17.674167	20.758665	5.116010
43	8	0	17.461403	18.328013	4.974709
44	1	0	19.576250	17.505881	3.411649
45	1	0	25.124319	23.894875	0.698967
46	1	0	26.007373	22.853429	-0.415117
47	1	0	16.653652	20.918689	4.766071
48	1	0	17.660498	20.883984	6.203257

Computed UV (top) and ECD (bottom) spectrum of conformer 4b(1) of compound 4b

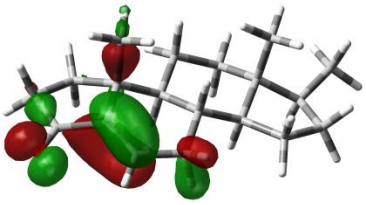




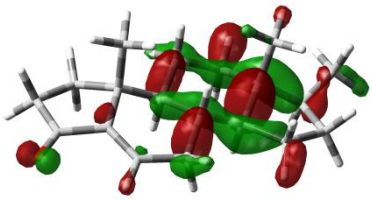
LUMO (orb. 76)



HOMO (orb. 75)



HOMO-1 (orb. 74)



HOMO-2 (orb. 73)

Conformer 4b(1)

Excited State 1: 335.37 nm f=0.0006 Rotatory Strength (*R*) -6.1578

74 -> 76 0.25022

75 -> 76 0.65098

Excited State 2: 246.95 nm f=0.2309 Rotatory Strength (*R*) 8.1241

73 -> 76 0.19949

74 -> 76 0.60921

75 -> 76 -0.26297

Excited State 3: 237.31 nm f=0.0551 Rotatory Strength (*R*) -33.1082

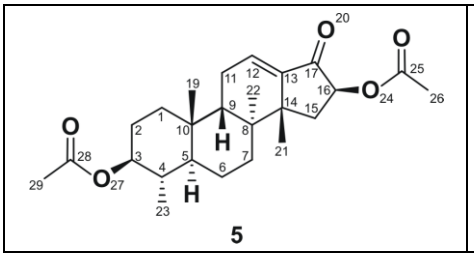
72 -> 76 -0.11208

73 -> 76 0.64787

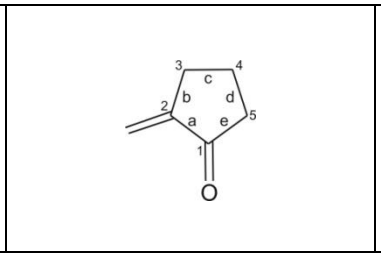
74 -> 76 -0.21522

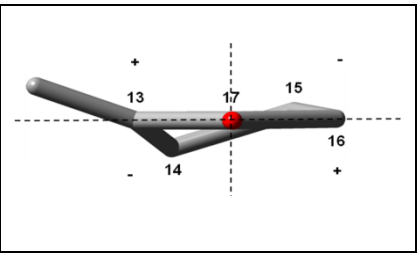
Conformational and spectral analysis of 5 in acetonitrile

For model compound **5** two conformers in the range of 0-5 kcal/mol were found. The five-membered ketone ring in conformers of **5** exists in conformation close to envelope E(14α). The enone torsion angles equal +23.4° and +24.4°, and show nonplanarity of the chromophore. The Boltzmann-averaged ECD spectrum of conformers **5**(1) and **5**(2) was used for comparison with the experimental spectrum of **5**.



5





Overview of the conformational analysis for compound 5

Conformer	ΔG (kcal.mol^{-1})	Population (%)	Torsion angles [°]							
			enone	a	b	c	d	e	17-16-24-25	4-3-27-28
5(1)	0.00	60.1	+24.4	+15.7	−27.6	+29.0	−20.6	+3.4	−112.4	+147.8
5(2)	0.41	39.9	+23.4	+15.4	−27.5	+29.2	−21.0	+3.9	−152.6	+147.2

Calculated at B3LYP/TZVP level of theory total energies, relative energies and conformer distribution at 25° C for individual conformers of compound 5.

Conformer	Energy [Hartree]	ΔG [kcal mol^{-1}]	Distribution [%]
1	-1350.438033	0.00	60.1
2	-1350.437646	0.41	39.9

Cartesian coordinates for individual conformers of compound 5.

Input orientation of compound **5** conf. 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.162338	0.151294	1.669685
2	6	0	-4.660294	-0.440013	0.357993
3	6	0	-3.731827	-1.529818	-0.188715
4	6	0	-2.261040	-1.047763	-0.249384
5	6	0	-1.733289	-0.504629	1.112358
6	6	0	-2.701237	0.605256	1.589620
7	8	0	-4.734906	0.622802	-0.652792
8	1	0	-5.667597	-0.837242	0.479296
9	6	0	-4.246308	-2.058031	-1.534340
10	1	0	-3.800815	-2.353605	0.529724
11	6	0	-0.241400	0.038898	0.973504
12	6	0	-1.707144	-1.618468	2.186688
13	1	0	-2.644331	1.456833	0.908325
14	1	0	-2.394433	0.970587	2.572939
15	1	0	-4.799618	0.991304	1.955357
16	1	0	-4.291830	-0.606110	2.446477
17	1	0	-2.276909	-0.194237	-0.929184
18	6	0	-1.332337	-2.118406	-0.862271
19	6	0	0.567049	-0.484356	-0.271957
20	6	0	0.163923	-1.944852	-0.527117
21	1	0	0.264739	-0.389843	1.837306
22	6	0	-0.028312	1.553996	1.137816
23	1	0	-1.379163	-1.201381	3.142446
24	1	0	-1.016863	-2.420826	1.926877
25	1	0	-2.683024	-2.074297	2.349740
26	1	0	-1.466700	-2.113761	-1.945403
27	1	0	-1.646178	-3.112310	-0.528734
28	6	0	0.289930	0.351941	-1.547163
29	6	0	2.094090	-0.346763	0.108831
30	1	0	0.767195	-2.359793	-1.339908
31	1	0	0.400426	-2.538533	0.355742
32	6	0	-5.874312	1.320573	-0.773647
33	8	0	-6.867407	1.122680	-0.104750
34	6	0	-5.754301	2.382861	-1.833629
35	6	0	2.350605	1.074787	0.589144
36	6	0	1.417179	1.923270	1.033580
37	1	0	-5.307944	-2.308547	-1.464648
38	1	0	-4.129287	-1.313775	-2.324376
39	1	0	-3.715484	-2.959969	-1.837868
40	1	0	-0.576977	2.138945	0.389483
41	1	0	-0.407025	1.900602	2.103149
42	1	0	0.595113	-0.194496	-2.441108
43	1	0	-0.764400	0.585582	-1.665674
44	1	0	0.825834	1.301046	-1.543126
45	6	0	3.111343	-0.469232	-1.073675
46	6	0	2.557354	-1.343180	1.200352
47	1	0	-5.077146	3.165273	-1.484591

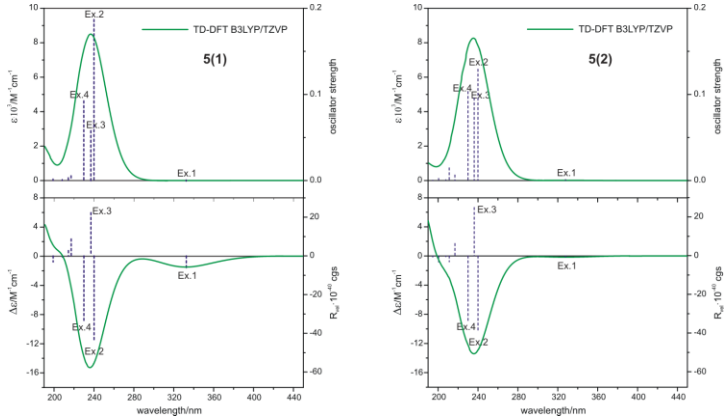
48	1	0	-6.730723	2.816754	-2.032987
49	1	0	-5.333431	1.966522	-2.748787
50	6	0	3.737640	1.464905	0.287049
51	1	0	1.700897	2.944531	1.272884
52	6	0	4.288442	0.456789	-0.744342
53	1	0	2.670795	-0.123311	-2.005715
54	1	0	3.446047	-1.494496	-1.229391
55	1	0	1.952375	-1.291298	2.104777
56	1	0	3.587290	-1.128227	1.490095
57	1	0	2.535233	-2.367719	0.827068
58	8	0	5.391074	-0.261426	-0.138266
59	1	0	4.667294	0.990609	-1.613914
60	8	0	4.373848	2.402377	0.730396
61	6	0	6.641179	-0.060913	-0.617295
62	8	0	6.898962	0.675395	-1.541475
63	6	0	7.642139	-0.875971	0.152000
64	1	0	7.364345	-1.930355	0.128960
65	1	0	8.631550	-0.742852	-0.276889
66	1	0	7.647798	-0.559294	1.196235

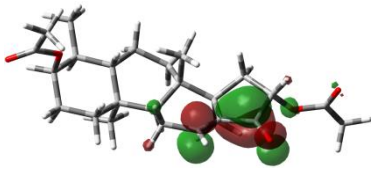
Input orientation of compound **5** conf. 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.157831	0.373988	1.613060
2	6	0	-4.614381	-0.460545	0.424464
3	6	0	-3.639839	-1.595876	0.090761
4	6	0	-2.187480	-1.076570	-0.046348
5	6	0	-1.700299	-0.272645	1.195897
6	6	0	-2.715056	0.865657	1.460626
7	8	0	-4.709670	0.398950	-0.762291
8	1	0	-5.609329	-0.865958	0.605658
9	6	0	-4.117000	-2.380554	-1.138338
10	1	0	-3.686851	-2.276780	0.947249
11	6	0	-0.229416	0.296446	0.967893
12	6	0	-1.642938	-1.174438	2.452673
13	1	0	-2.684465	1.580801	0.635971
14	1	0	-2.434347	1.415672	2.362576
15	1	0	-4.831757	1.224216	1.739989
16	1	0	-4.267182	-0.238902	2.511219
17	1	0	-2.219793	-0.365948	-0.873479
18	6	0	-1.210125	-2.207634	-0.436195
19	6	0	0.615977	-0.415728	-0.152189
20	6	0	0.274655	-1.912701	-0.133105
21	1	0	0.280196	0.057464	1.900513
22	6	0	-0.076634	1.823228	0.847390
23	1	0	-2.602809	-1.632322	2.689167
24	1	0	-1.342166	-0.581357	3.320243
25	1	0	-0.918839	-1.981376	2.341483
26	1	0	-1.330185	-2.416258	-1.500805
27	1	0	-1.490848	-3.129732	0.081812
28	6	0	0.328425	0.157005	-1.563780
29	6	0	2.131222	-0.149378	0.207286
30	1	0	0.904100	-2.445378	-0.852039
31	1	0	0.525904	-2.319717	0.846054
32	6	0	-5.873833	1.011528	-1.025769
33	8	0	-6.868685	0.906142	-0.338749

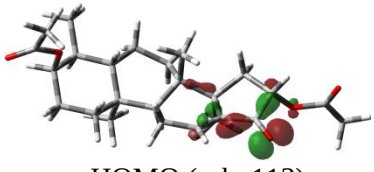
34	6	0	-5.780987	1.841101	-2.278702
35	6	0	2.326893	1.344999	0.415747
36	6	0	1.355228	2.223814	0.685580
37	1	0	-5.168651	-2.657511	-1.028899
38	1	0	-4.019836	-1.788745	-2.050577
39	1	0	-3.547793	-3.300560	-1.270270
40	1	0	-0.636512	2.236431	-0.000594
41	1	0	-0.481081	2.328925	1.728326
42	1	0	0.652491	-0.542181	-2.336490
43	1	0	-0.729894	0.339815	-1.727349
44	1	0	0.842881	1.101931	-1.738896
45	6	0	3.168866	-0.451311	-0.923707
46	6	0	2.615932	-0.907946	1.468159
47	1	0	-5.046953	2.636827	-2.139999
48	1	0	-6.750701	2.275690	-2.506456
49	1	0	-5.444187	1.225265	-3.113510
50	6	0	3.702043	1.727440	0.055342
51	1	0	1.596457	3.282321	0.730498
52	6	0	4.308336	0.565633	-0.757866
53	1	0	2.733120	-0.301293	-1.909072
54	1	0	3.536862	-1.476187	-0.882518
55	1	0	2.001977	-0.706205	2.344862
56	1	0	3.636294	-0.610383	1.715373
57	1	0	2.627532	-1.984807	1.294486
58	8	0	5.437241	0.067662	0.000491
59	1	0	4.676674	0.936269	-1.713352
60	8	0	4.288686	2.763404	0.304849
61	6	0	6.443524	-0.518871	-0.686544
62	8	0	6.441393	-0.647752	-1.889362
63	6	0	7.531855	-0.980054	0.240685
64	1	0	7.147728	-1.769022	0.889913
65	1	0	8.369981	-1.359968	-0.337123
66	1	0	7.857461	-0.157843	0.878411

Computed UV (top) and ECD (bottom) spectra of conformers 5(1) - 5(2) of compound 5

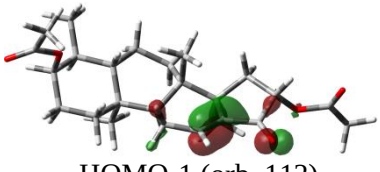




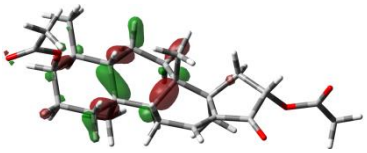
LUMO (orb. 114)



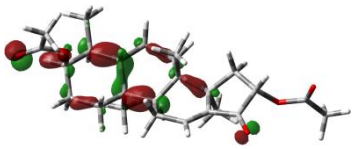
HOMO (orb. 113)



HOMO-1 (orb. 112)



HOMO-2 (orb. 111)



HOMO-3 (orb. 110)

Conformer 5(1)

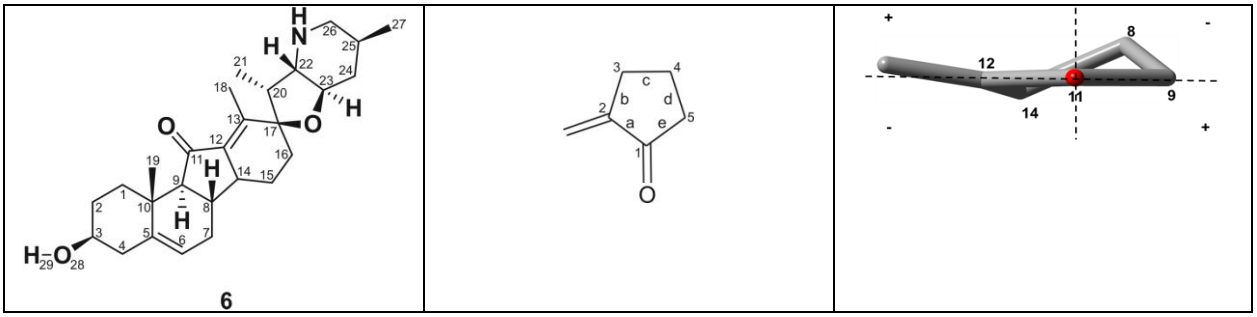
Excited State 1: 352.56 nm f=0.0002 Rotatory Strength (*R*) -6.7768
112 ->114 -0.26192
113 ->114 0.64114
Excited State 2: 259.86 nm f=0.1875 Rotatory Strength (*R*) -45.5477
110 ->114 0.21682
111 ->114 -0.25799
112 ->114 0.55459
113 ->114 0.24935
Excited State 3: 256.83 nm f=0.0596 Rotatory Strength (*R*) 22.3706
106 ->114 -0.12151
111 ->114 0.63441
112 ->114 0.18359
113 ->114 0.13288
Excited State 4: 249.82 nm f=0.0957 Rotatory Strength (*R*) -33.8154
109 ->114 -0.19865
110 ->114 0.60148
112 ->114 -0.27211

Conformer 5(2)

Excited State 1: 348.21 nm f=0.0006 Rotatory Strength (*R*) -0.5421
110 ->114 0.11521
112 ->114 -0.31706
113 ->114 0.61017
Excited State 2: 260.39 nm f=0.1305 Rotatory Strength (*R*) -40.4320
110 ->114 -0.22192
111 ->114 -0.36489
112 ->114 0.47872
113 ->114 0.27020
Excited State 3: 256.65 nm f=0.0956 Rotatory Strength (*R*) 25.0125
110 ->114 -0.16137
111 ->114 0.57750
112 ->114 0.23711
113 ->114 0.21132
Excited State 4: 250.38 nm f=0.1038 Rotatory Strength (*R*) -34.0285
109 ->114 -0.20107
110 ->114 0.57106
112 ->114 0.31900

Conformational and spectral analysis of 6 in acetonitrile

Conformational analysis done for jervine **6** identified the existence of six conformers in the range of 0-5 kcal/mol. The cyclopentanone five-membered ring in conformers of enone **6** adopts nearly an envelope E(8β) conformation. The enone torsion angles were found in the range from $+14.0^{o}$ to $+14.7^{o}$ and show nonplanarity of the chromophore. The Boltzmann-averaged ECD spectrum of conformers **6**(1) - **6**(6) was used for comparison with the experimental spectrum of **6**.



Overview of the conformational analysis for compound 6.
CA – absolute configuration at nitrogen atom

Conformer	ΔG (kcal.mol^{-1})	Population (%)	CA	Torsion angles [°]						
				enone	a	b	c	d	e	2-3-28-29
6(1)	0.00	18.3	*R*	+14.2	+5.0	−27.1	+38.6	−35.9	+19.3	+176.7
6(2)	0.04	17.1	*S*	+14.7	+5.3	−27.4	+38.8	−35.8	+19.1	+176.7
6(3)	0.05	16.8	*R*	+14.2	+5.0	−27.1	+38.6	−35.9	+19.3	+60.3
6(4)	0.06	16.5	*R*	+14.0	+4.8	−27.0	+38.7	−36.0	+19.5	−60.7
6(5)	0.08	16.0	*S*	+14.7	+5.3	−27.4	+38.8	−35.9	+19.1	+60.4
6(6)	0.10	15.4	*S*	+14.5	+5.2	−27.3	+38.8	−36.0	+19.2	−60.6

Calculated at B3LYP/TZVP level of theory total energies, relative energies and conformer distribution at 25° C for individual conformers of compound 6.

Conformer	Energy [Hartree]	ΔG [kcal mol^{-1}]	Distribution [%]
1	-1333.21933	0.00	18.3
2	-1333.21927	0.04	17.1
3	-1333.21926	0.05	16.8
4	-1333.21923	0.06	16.5
5	-1333.21920	0.08	16.0
6	-1333.21917	0.10	15.4

Cartesian coordinates for individual conformers of compound 6.
Input orientation of compound **6** conf. 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.699717	0.629012	0.783456
2	6	0	6.110775	0.236359	1.162754
3	6	0	4.692047	-1.118576	-1.013131
4	6	0	6.102405	-1.548518	-0.600341
5	6	0	6.878308	-0.382558	-0.010446
6	6	0	3.856561	-0.477750	0.130404
7	1	0	4.142592	-1.970374	-1.415708
8	1	0	4.775614	-0.388356	-1.825371
9	6	0	2.593737	0.180085	-0.465494
10	6	0	3.480370	-1.548795	1.179088
11	6	0	4.257843	1.873519	0.996300
12	1	0	2.910361	0.732686	-1.364759
13	6	0	1.925578	1.203049	0.460302
14	6	0	2.865525	2.373824	0.706828
15	1	0	1.716208	0.717575	1.420585
16	6	0	0.578075	1.476728	-0.225968
17	1	0	2.518354	2.990530	1.541804

18	1	0	2.881822	3.037155	-0.168683
19	6	0	0.180051	0.101577	-0.732937
20	1	0	0.769923	2.133280	-1.087964
21	1	0	2.863324	-1.123967	1.972407
22	1	0	4.364153	-1.977413	1.650727
23	1	0	2.926608	-2.363552	0.710583
24	1	0	6.647720	1.109698	1.542074
25	1	0	6.095754	-0.505235	1.969639
26	1	0	6.636502	-1.941183	-1.469246
27	1	0	6.065646	-2.353867	0.139283
28	1	0	7.018762	0.383230	-0.784795
29	8	0	8.164789	-0.873671	0.401487
30	1	0	8.683152	-0.128530	0.728828
31	6	0	1.431281	-0.682302	-0.957640
32	8	0	1.532537	-1.783907	-1.474454
33	6	0	-0.531597	2.095177	0.608805
34	6	0	-1.085632	-0.355233	-0.810065
35	6	0	-2.264015	0.564092	-0.464569
36	6	0	-1.828594	2.011777	-0.193070
37	6	0	-1.421366	-1.778936	-1.161409
38	1	0	4.945534	2.595281	1.429778
39	1	0	-0.305917	3.136559	0.850881
40	1	0	-0.634656	1.553697	1.553973
41	8	0	-2.815058	0.019768	0.786749
42	6	0	-3.442711	0.454876	-1.533065
43	1	0	-2.641661	2.524014	0.323952
44	1	0	-1.678384	2.535257	-1.140213
45	1	0	-2.305514	-2.107388	-0.617158
46	1	0	-0.595153	-2.448273	-0.940813
47	1	0	-1.632116	-1.881541	-2.230520
48	6	0	-4.234438	0.143425	0.707755
49	6	0	-4.541955	-0.268556	-0.723740
50	1	0	-3.114565	-0.188575	-2.348355
51	6	0	-3.917376	1.764794	-2.166555
52	1	0	-4.519388	1.197236	0.853435
53	6	0	-5.009223	-0.710415	1.689149
54	7	0	-5.942603	-0.086054	-1.089146
55	1	0	-4.352734	-1.344820	-0.786147
56	6	0	-6.788626	-0.837578	-0.140210
57	6	0	-6.512905	-0.575071	1.358989
58	1	0	-3.128671	2.230388	-2.758030
59	1	0	-4.263681	2.497369	-1.435407
60	1	0	-4.745432	1.551728	-2.845038
61	1	0	-4.822557	-0.409049	2.723573
62	1	0	-4.696566	-1.755486	1.586823
63	1	0	-6.643446	-1.904598	-0.345138
64	1	0	-7.833474	-0.610842	-0.363126
65	1	0	-6.803066	0.462636	1.564823
66	6	0	-7.367224	-1.490417	2.237071
67	1	0	-7.199354	-1.285881	3.296967
68	1	0	-7.125200	-2.541862	2.057437
69	1	0	-8.432257	-1.352961	2.034590
70	1	0	-6.187824	0.898760	-1.045501

Input orientation of compound **6** conf. 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	4.688595	0.653097	0.777303
2	6	0	6.095813	0.270131	1.179711
3	6	0	4.700235	-1.133941	-0.979486
4	6	0	6.107263	-1.552824	-0.544386
5	6	0	6.875973	-0.373488	0.028245
6	6	0	3.852923	-0.469344	0.141796
7	1	0	4.155708	-1.995187	-1.368523
8	1	0	4.790734	-0.421476	-1.806576
9	6	0	2.594416	0.171955	-0.480320
10	6	0	3.469350	-1.518086	1.210052
11	6	0	4.244196	1.902160	0.955417
12	1	0	2.917460	0.702977	-1.390184
13	6	0	1.917868	1.216451	0.415051
14	6	0	2.854455	2.394093	0.640014
15	1	0	1.702113	0.754430	1.385494
16	6	0	0.574382	1.470120	-0.287000
17	1	0	2.499056	3.031614	1.455666
18	1	0	2.878570	3.034758	-0.252058
19	6	0	0.182518	0.080430	-0.757335
20	1	0	0.771416	2.102077	-1.166101
21	1	0	2.844559	-1.077550	1.988667
22	1	0	4.349780	-1.935075	1.698079
23	1	0	2.921141	-2.343612	0.754083
24	1	0	6.628295	1.152031	1.545278
25	1	0	6.072841	-0.453632	2.002347
26	1	0	6.650065	-1.962728	-1.399861
27	1	0	6.064801	-2.342742	0.211466
28	1	0	7.024092	0.375472	-0.760994
29	8	0	8.158476	-0.854170	0.464257
30	1	0	8.672695	-0.101488	0.780727
31	6	0	1.436435	-0.704311	-0.958887
32	8	0	1.542151	-1.817139	-1.450252
33	6	0	-0.541534	2.110671	0.522275
34	6	0	-1.080475	-0.385566	-0.821901
35	6	0	-2.263790	0.535748	-0.499182
36	6	0	-1.835731	1.994577	-0.280622
37	6	0	-1.406453	-1.820081	-1.136484
38	1	0	4.927148	2.634584	1.378372
39	1	0	-0.321287	3.160386	0.731051
40	1	0	-0.646388	1.600002	1.484239
41	8	0	-2.804356	0.031374	0.770230
42	6	0	-3.452668	0.381976	-1.555147
43	1	0	-2.652020	2.522814	0.214528
44	1	0	-1.685096	2.482696	-1.246266
45	1	0	-2.309332	-2.130485	-0.613009
46	1	0	-0.588878	-2.482193	-0.865948
47	1	0	-1.579529	-1.958037	-2.208435
48	6	0	-4.223684	0.163181	0.695797
49	6	0	-4.542117	-0.314927	-0.708936
50	1	0	-3.125626	-0.293818	-2.344632
51	6	0	-3.927781	1.667012	-2.236770
52	1	0	-4.499269	1.224031	0.780331
53	6	0	-4.995559	-0.622125	1.733258
54	7	0	-5.948626	-0.057444	-0.995397
55	1	0	-4.339714	-1.397726	-0.726895
56	6	0	-6.780702	-0.845498	-0.065306
57	6	0	-6.499778	-0.490553	1.405198

58	1	0	-3.132427	2.112452	-2.835656
59	1	0	-4.286691	2.416405	-1.531315
60	1	0	-4.750878	1.435848	-2.914715
61	1	0	-4.797259	-0.256992	2.744362
62	1	0	-4.695055	-1.674720	1.693913
63	1	0	-6.614349	-1.928044	-0.197895
64	1	0	-7.830139	-0.646768	-0.292818
65	1	0	-6.778712	0.560072	1.543607
66	6	0	-7.355971	-1.342292	2.343411
67	1	0	-7.178237	-1.071157	3.386410
68	1	0	-7.124376	-2.405156	2.230569
69	1	0	-8.421036	-1.207627	2.139800
70	1	0	-6.173019	-0.326240	-1.947807

Input orientation of compound **6** conf. 3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.700163	0.633679	0.782904
2	6	0	6.112137	0.246920	1.164645
3	6	0	4.692419	-1.117426	-1.010456
4	6	0	6.100573	-1.547755	-0.588751
5	6	0	6.877405	-0.374963	-0.000056
6	6	0	3.856865	-0.474225	0.131446
7	1	0	4.142457	-1.968174	-1.414563
8	1	0	4.780620	-0.387620	-1.822650
9	6	0	2.594000	0.182668	-0.465356
10	6	0	3.480319	-1.543300	1.182071
11	6	0	4.256020	1.877014	0.997485
12	1	0	2.910793	0.735780	-1.364256
13	6	0	1.924391	1.204597	0.460593
14	6	0	2.863036	2.375855	0.709130
15	1	0	1.714464	0.718137	1.420231
16	6	0	0.577269	1.477774	-0.226485
17	1	0	2.514992	2.990763	1.545078
18	1	0	2.878664	3.040734	-0.165230
19	6	0	0.180430	0.102525	-0.734085
20	1	0	0.769338	2.134676	-1.088172
21	1	0	2.861019	-1.117432	1.973019
22	1	0	4.363765	-1.969112	1.656828
23	1	0	2.928770	-2.360183	0.714579
24	1	0	6.651922	1.119916	1.536188
25	1	0	6.096861	-0.489347	1.976710
26	1	0	6.633377	-1.947680	-1.457221
27	1	0	6.060914	-2.349319	0.154616
28	1	0	7.018441	0.387833	-0.777549
29	8	0	8.164116	-0.772781	0.503539
30	1	0	8.672895	-1.140935	-0.229029
31	6	0	1.432352	-0.680491	-0.958221
32	8	0	1.534575	-1.782050	-1.474972
33	6	0	-0.533155	2.095441	0.607830
34	6	0	-1.084923	-0.355109	-0.811864
35	6	0	-2.264029	0.563246	-0.466144
36	6	0	-1.829751	2.011240	-0.194564
37	6	0	-1.419630	-1.778879	-1.163895
38	1	0	4.943241	2.599639	1.430141
39	1	0	-0.308216	3.136939	0.850081

40	1	0	-0.636283	1.553832	1.552915
41	8	0	-2.814288	0.018334	0.785266
42	6	0	-3.442971	0.453190	-1.534275
43	1	0	-2.643344	2.522962	0.322135
44	1	0	-1.679557	2.534781	-1.141676
45	1	0	-2.304082	-2.107971	-0.620518
46	1	0	-0.593253	-2.447855	-0.942791
47	1	0	-1.629404	-1.881260	-2.233224
48	6	0	-4.233721	0.141661	0.706904
49	6	0	-4.541729	-0.270465	-0.724442
50	1	0	-3.114795	-0.190399	-2.349440
51	6	0	-3.918289	1.762731	-2.168063
52	1	0	-4.518853	1.195412	0.852636
53	6	0	-5.007916	-0.712236	1.688701
54	7	0	-5.942574	-0.088292	-1.089289
55	1	0	-4.352279	-1.346697	-0.786850
56	6	0	-6.788083	-0.839783	-0.139864
57	6	0	-6.511749	-0.577058	1.359182
58	1	0	-3.129854	2.228513	-2.759753
59	1	0	-4.264793	2.495350	-1.437055
60	1	0	-4.746357	1.549153	-2.846366
61	1	0	-4.820818	-0.410776	2.723018
62	1	0	-4.695185	-1.757278	1.586301
63	1	0	-6.642877	-1.906817	-0.344705
64	1	0	-7.833054	-0.613190	-0.362348
65	1	0	-6.801897	0.460653	1.565019
66	6	0	-7.365634	-1.492355	2.237736
67	1	0	-7.197320	-1.287686	3.297535
68	1	0	-7.123630	-2.543808	2.058117
69	1	0	-8.430762	-1.354978	2.035696
70	1	0	-6.187943	0.896489	-1.045719

Input orientation of compound **6** conf. 4

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.702435	0.635315	0.780776
2	6	0	6.118303	0.252874	1.154037
3	6	0	4.692673	-1.116029	-1.012912
4	6	0	6.107428	-1.539984	-0.605678
5	6	0	6.885464	-0.367567	-0.018511
6	6	0	3.860093	-0.474842	0.132344
7	1	0	4.143409	-1.969301	-1.412770
8	1	0	4.773015	-0.386874	-1.826452
9	6	0	2.593886	0.178672	-0.461281
10	6	0	3.489431	-1.544597	1.184297
11	6	0	4.257208	1.878524	0.994261
12	1	0	2.906842	0.730410	-1.362362
13	6	0	1.925147	1.202098	0.463657
14	6	0	2.863070	2.374950	0.707630
15	1	0	1.716905	0.717746	1.424764
16	6	0	0.577264	1.473066	-0.222860
17	1	0	2.516153	2.991366	1.542921
18	1	0	2.876074	3.037874	-0.168255
19	6	0	0.180255	0.096613	-0.726896
20	1	0	0.768758	2.127947	-1.086210
21	1	0	2.873136	-1.119563	1.978052

22	1	0	4.375151	-1.970027	1.655401
23	1	0	2.936821	-2.361921	0.718959
24	1	0	6.657635	1.126613	1.524451
25	1	0	6.104248	-0.482409	1.969051
26	1	0	6.639522	-1.932636	-1.475793
27	1	0	6.070923	-2.348572	0.132903
28	1	0	7.027112	0.393182	-0.791252
29	8	0	8.220696	-0.735591	0.362067
30	1	0	8.162798	-1.426117	1.034943
31	6	0	1.432013	-0.687148	-0.949112
32	8	0	1.533939	-1.790966	-1.461036
33	6	0	-0.533079	2.092614	0.610109
34	6	0	-1.085314	-0.360458	-0.804391
35	6	0	-2.264130	0.559877	-0.463148
36	6	0	-1.829017	2.008009	-0.193342
37	6	0	-1.420673	-1.784973	-1.152738
38	1	0	4.944260	2.602745	1.424500
39	1	0	-0.307677	3.134340	0.850933
40	1	0	-0.637167	1.552422	1.555901
41	8	0	-2.818333	0.018215	0.787913
42	6	0	-3.440428	0.448916	-1.534215
43	1	0	-2.642826	2.521106	0.321644
44	1	0	-1.677390	2.529986	-1.141064
45	1	0	-2.306565	-2.111526	-0.610177
46	1	0	-0.595370	-2.454027	-0.927870
47	1	0	-1.628313	-1.890432	-2.222187
48	6	0	-4.237352	0.143932	0.705601
49	6	0	-4.542383	-0.271162	-0.725512
50	1	0	-3.111005	-0.197129	-2.346920
51	6	0	-3.912189	1.757609	-2.172395
52	1	0	-4.520874	1.198601	0.847878
53	6	0	-5.015725	-0.705886	1.687604
54	7	0	-5.941993	-0.087612	-1.094388
55	1	0	-4.354466	-1.347836	-0.784940
56	6	0	-6.791228	-0.835187	-0.145222
57	6	0	-6.518433	-0.568709	1.353825
58	1	0	-3.121636	2.220705	-2.763367
59	1	0	-4.259290	2.492526	-1.443978
60	1	0	-4.738961	1.543619	-2.852148
61	1	0	-4.830728	-0.402039	2.721604
62	1	0	-4.704817	-1.751813	1.588797
63	1	0	-6.647082	-1.903009	-0.346662
64	1	0	-7.835238	-0.607607	-0.371183
65	1	0	-6.807140	0.470139	1.555899
66	6	0	-7.376360	-1.479896	2.232694
67	1	0	-7.210061	-1.272906	3.292362
68	1	0	-7.136231	-2.532325	2.056281
69	1	0	-8.440712	-1.340707	2.027836
70	1	0	-6.185847	0.897674	-1.054047

Input orientation of compound **6** conf. 5

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.689024	0.658621	0.776282
2	6	0	6.097463	0.282475	1.181030
3	6	0	4.700674	-1.134040	-0.975067

4	6	0	6.105643	-1.552018	-0.530914
5	6	0	6.874919	-0.364657	0.038335
6	6	0	3.853344	-0.465824	0.143832
7	1	0	4.155768	-1.994961	-1.364313
8	1	0	4.795318	-0.423077	-1.803047
9	6	0	2.594666	0.173474	-0.479908
10	6	0	3.469762	-1.511376	1.215278
11	6	0	4.242162	1.906698	0.954613
12	1	0	2.917750	0.703781	-1.390188
13	6	0	1.916535	1.218164	0.414087
14	6	0	2.851733	2.396678	0.639585
15	1	0	1.700021	0.756501	1.384514
16	6	0	0.573607	1.470317	-0.289440
17	1	0	2.495326	3.033534	1.455325
18	1	0	2.875257	3.037701	-0.252261
19	6	0	0.182931	0.079754	-0.758166
20	1	0	0.771144	2.101149	-1.169245
21	1	0	2.842687	-1.069085	1.991010
22	1	0	4.350019	-1.924672	1.706713
23	1	0	2.923942	-2.339670	0.761388
24	1	0	6.632567	1.164479	1.537753
25	1	0	6.074785	-0.435126	2.009361
26	1	0	6.647100	-1.970150	-1.385359
27	1	0	6.060847	-2.336949	0.229789
28	1	0	7.022437	0.380327	-0.755045
29	8	0	8.157358	-0.748567	0.563247
30	1	0	8.674264	-1.131186	-0.156125
31	6	0	1.437553	-0.704405	-0.957812
32	8	0	1.544257	-1.818007	-1.447251
33	6	0	-0.543207	2.111554	0.518016
34	6	0	-1.079733	-0.387178	-0.822622
35	6	0	-2.263755	0.533794	-0.501501
36	6	0	-1.836785	1.993323	-0.285523
37	6	0	-1.404608	-1.822356	-1.135357
38	1	0	4.924545	2.640595	1.375806
39	1	0	-0.323657	3.161728	0.725196
40	1	0	-0.648440	1.602433	1.480755
41	8	0	-2.803872	0.031271	0.768798
42	6	0	-3.452686	0.377254	-1.557093
43	1	0	-2.653684	2.522072	0.208068
44	1	0	-1.685826	2.479631	-1.252026
45	1	0	-2.307855	-2.132500	-0.612352
46	1	0	-0.586927	-2.483586	-0.862951
47	1	0	-1.576503	-1.962006	-2.207282
48	6	0	-4.223233	0.162744	0.694415
49	6	0	-4.541851	-0.318200	-0.709314
50	1	0	-3.125448	-0.300093	-2.345153
51	6	0	-3.928291	1.660724	-2.241318
52	1	0	-4.498911	1.223729	0.776855
53	6	0	-4.994841	-0.620435	1.733659
54	7	0	-5.948442	-0.061487	-0.996018
55	1	0	-4.339274	-1.401009	-0.725143
56	6	0	-6.780276	-0.847612	-0.064075
57	6	0	-6.499118	-0.489462	1.405606
58	1	0	-3.132993	2.105493	-2.840777
59	1	0	-4.287803	2.411189	-1.537307
60	1	0	-4.751070	1.427875	-2.919078
61	1	0	-4.796308	-0.253192	2.743953

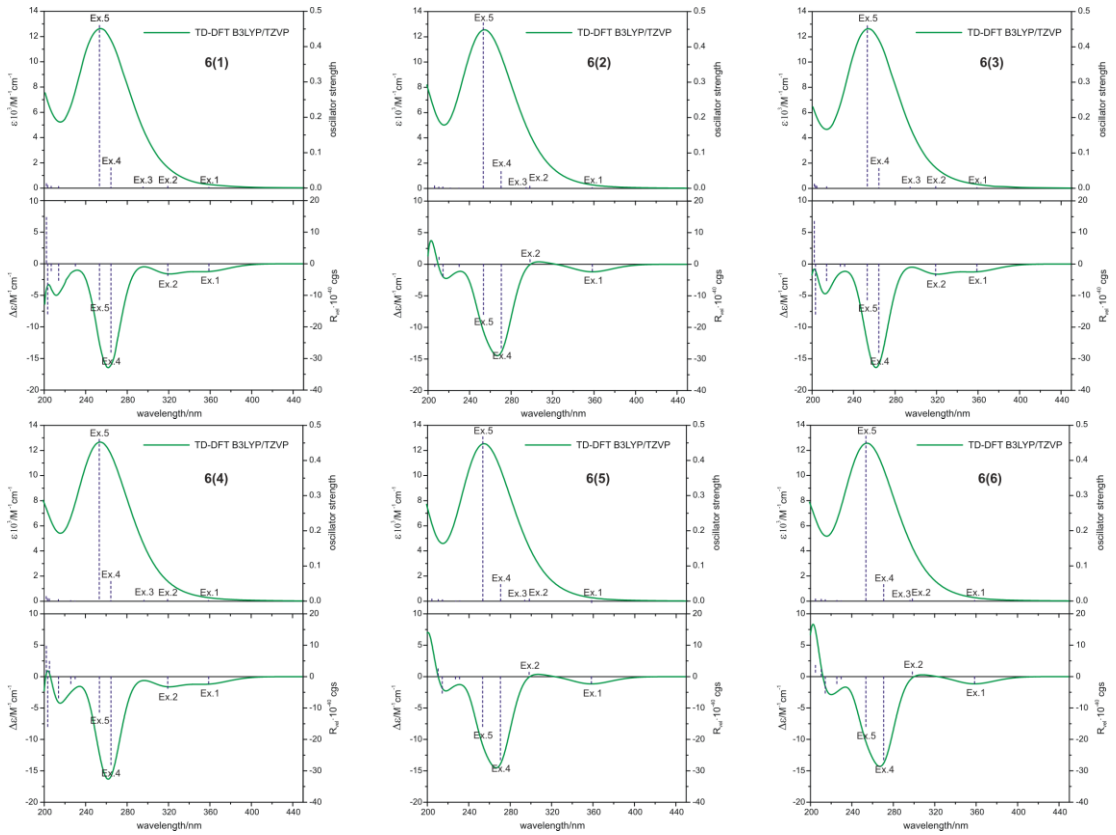
62	1	0	-4.694378	-1.673122	1.696447
63	1	0	-6.613806	-1.930419	-0.194331
64	1	0	-7.829770	-0.649488	-0.291852
65	1	0	-6.777924	0.561495	1.541738
66	6	0	-7.355236	-1.339005	2.345869
67	1	0	-7.177407	-1.065417	3.388213
68	1	0	-7.123680	-2.402139	2.235516
69	1	0	-8.420317	-1.204778	2.142042
70	1	0	-6.173019	-0.332279	-1.947818

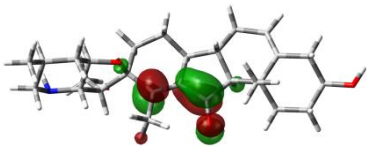
Input orientation of compound **6** conf. 6

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.691455	0.658891	0.774588
2	6	0	6.103392	0.285421	1.170838
3	6	0	4.700985	-1.130209	-0.980747
4	6	0	6.112202	-1.544007	-0.551412
5	6	0	6.883392	-0.359263	0.020057
6	6	0	3.856519	-0.466249	0.142850
7	1	0	4.156508	-1.992346	-1.368042
8	1	0	4.788517	-0.417974	-1.808370
9	6	0	2.594564	0.171315	-0.476296
10	6	0	3.478604	-1.514604	1.213487
11	6	0	4.243839	1.906593	0.954229
12	1	0	2.913895	0.702081	-1.387620
13	6	0	1.917623	1.215605	0.419096
14	6	0	2.852305	2.395075	0.642032
15	1	0	1.703233	0.754078	1.390087
16	6	0	0.573579	1.467040	-0.282589
17	1	0	2.497270	3.031901	1.458376
18	1	0	2.873133	3.035781	-0.250097
19	6	0	0.182648	0.076541	-0.751134
20	1	0	0.769918	2.098113	-1.162480
21	1	0	2.854647	-1.074591	1.993016
22	1	0	4.361054	-1.928785	1.700465
23	1	0	2.931517	-2.342270	0.760099
24	1	0	6.638431	1.167117	1.528384
25	1	0	6.080808	-0.432468	2.000848
26	1	0	6.653259	-1.952949	-1.408416
27	1	0	6.069734	-2.338180	0.202454
28	1	0	7.033963	0.385234	-0.766694
29	8	0	8.214263	-0.719203	0.423277
30	1	0	8.148729	-1.396631	1.108689
31	6	0	1.437069	-0.707859	-0.951031
32	8	0	1.543425	-1.822354	-1.438444
33	6	0	-0.542792	2.107756	0.525837
34	6	0	-1.080273	-0.389599	-0.816331
35	6	0	-2.263976	0.532353	-0.496822
36	6	0	-1.836137	1.991304	-0.278356
37	6	0	-1.405983	-1.824555	-1.129173
38	1	0	4.926232	2.641007	1.374483
39	1	0	-0.322760	3.157550	0.734412
40	1	0	-0.648387	1.597359	1.487866
41	8	0	-2.807678	0.029205	0.771703
42	6	0	-3.450524	0.378109	-1.555444
43	1	0	-2.653012	2.519736	0.215604

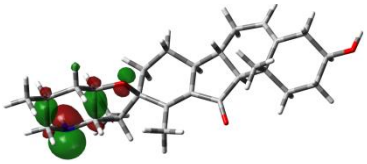
44	1	0	-1.684320	2.479102	-1.243958
45	1	0	-2.309796	-2.133969	-0.606726
46	1	0	-0.588946	-2.486333	-0.856221
47	1	0	-1.577296	-1.964120	-2.201208
48	6	0	-4.226686	0.162735	0.694049
49	6	0	-4.542640	-0.316579	-0.710819
50	1	0	-3.122242	-0.299134	-2.343155
51	6	0	-3.922881	1.662563	-2.240042
52	1	0	-4.501037	1.224053	0.776661
53	6	0	-5.001969	-0.620131	1.730781
54	7	0	-5.948178	-0.057574	-1.000673
55	1	0	-4.341551	-1.399652	-0.727148
56	6	0	-6.783453	-0.843166	-0.071360
57	6	0	-6.505256	-0.486581	1.399254
58	1	0	-3.125807	2.106311	-2.837892
59	1	0	-4.282605	2.413349	-1.536482
60	1	0	-4.744725	1.431166	-2.919426
61	1	0	-4.805297	-0.254026	2.741852
62	1	0	-4.703028	-1.673244	1.693403
63	1	0	-6.618346	-1.926132	-0.202061
64	1	0	-7.832079	-0.643251	-0.301547
65	1	0	-6.782757	0.564703	1.535531
66	6	0	-7.364897	-1.335510	2.336842
67	1	0	-7.188940	-1.063119	3.379815
68	1	0	-7.134859	-2.398929	2.226069
69	1	0	-8.429293	-1.199335	2.130758
70	1	0	-6.170850	-0.327322	-1.953214

Computed UV (top) and ECD (bottom) spectra of conformers 6(1) - 6(6) of compound 6

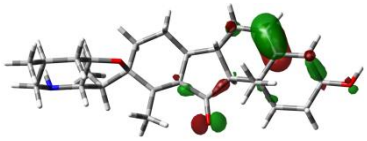




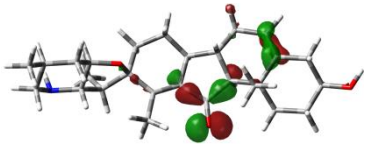
LUMO (orb. 117)



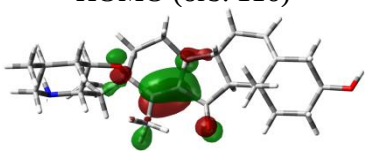
HOMO (orb. 116)



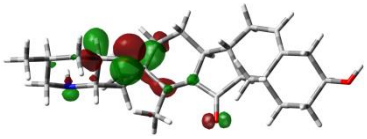
HOMO-1 (orb. 115)



HOMO-2 (orb. 114)



HOMO-3 (orb. 113)



HOMO-4 (orb. 112)

Conformer 6(1)

Excited State 1: 358.80 nm f=0.0019 Rotatory Strengths (*R*) -4.3555
114 ->117 0.58383
115 ->117 -0.36514
Excited State 2: 319.06 nm f=0.0049 Rotatory Strengths (*R*) -3.6435
116 ->117 0.70314
Excited State 3: 295.31 nm f=0.0026 Rotatory Strengths (*R*) 0.0536
114 ->117 0.37443
115 ->117 0.59839
Excited State 4: 264.42 nm f=0.0569 Rotatory Strengths (*R*) -27.6755
112 ->117 0.60115
113 ->117 -0.35861
Excited State 5: 253.27 nm f=0.4601 Rotatory Strengths (*R*) -13.6473
112 ->117 0.34766
113 ->117 0.59232

Conformer 6(2)

Excited State 1: 358.42 nm f=0.0019 Rotatory Strengths (*R*) -4.6130
112 ->117 -0.10022
114 ->117 0.57856
115 ->117 -0.37097
Excited State 2: 298.26 nm f=0.0059 Rotatory Strengths (*R*) 1.4332
116 ->117 0.70247
Excited State 3: 294.84 nm f=0.0022 Rotatory Strengths (*R*) -0.1874
114 ->117 0.38257
115 ->117 0.59032
Excited State 4: 270.61 nm f=0.0475 Rotatory Strengths (*R*) -26.4567
112 ->117 0.55815
113 ->117 -0.42523
Excited State 5: 253.40 nm f=0.4682 Rotatory Strengths (*R*) -18.1975
112 ->117 0.40993
113 ->117 0.55052

Conformer 6(3)

Excited State 1: 358.88 nm f=0.0019 Rotatory Strengths (*R*) -4.3246
114 ->117 0.54517
115 ->117 -0.42039
Excited State 2: 319.10 nm f=0.0049 Rotatory Strengths (*R*) -3.6219
116 ->117 0.70313
Excited State 3: 294.36 nm f=0.0030 Rotatory Strengths (*R*) 0.0109
114 ->117 0.43172
115 ->117 0.55897
Excited State 4: 264.45 nm f=0.0562 Rotatory Strengths (*R*) -27.4194
112 ->117 0.60217
113 ->117 -0.35604

Excited State 5: 253.25 nm f=0.4601 Rotatory Strengths (*R*) -13.9157
112 ->117 0.34443
113 ->117 0.59407

Conformer 6(4)
Excited State 1: 358.84 nm f=0.0019 Rotatory Strengths (*R*) -4.3935
114 ->117 0.58881
115 ->117 -0.35699
Excited State 2: 319.24 nm f=0.0048 Rotatory Strengths (*R*) -3.6047
116 ->117 0.70314
Excited State 3: 296.47 nm f=0.0025 Rotatory Strengths (*R*) -0.2757
114 ->117 0.36594
115 ->117 0.60366
Excited State 4: 264.48 nm f=0.0561 Rotatory Strengths (*R*) -27.4587
112 ->117 0.60358
113 ->117 -0.35409
Excited State 5: 253.34 nm f=0.4604 Rotatory Strengths (*R*) -13.6605
112 ->117 0.34315
113 ->117 0.59546

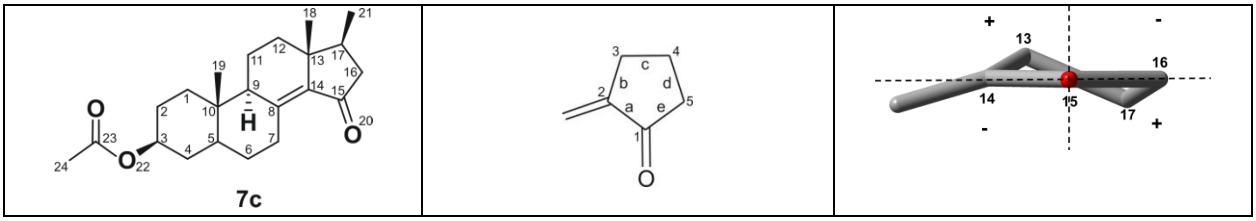
Conformer 6(5)
Excited State 1: 358.50 nm f=0.0019 Rotatory Strengths (*R*) -4.3956
114 ->117 0.53866
115 ->117 -0.42659
Excited State 2: 298.30 nm f=0.0058 Rotatory Strengths (*R*) 1.3735
116 ->117 0.70337
Excited State 3: 293.89 nm f=0.0027 Rotatory Strengths (*R*) -0.1894
114 ->117 0.43994
115 ->117 0.55055
Excited State 4: 270.64 nm f=0.0471 Rotatory Strengths (*R*) -26.2673
112 ->117 0.55904
113 ->117 -0.42366
Excited State 5: 253.38 nm f=0.4676 Rotatory Strengths (*R*) -18.7111
112 ->117 0.40819
113 ->117 0.55192

Conformer 6(6)
Excited State 1: 358.48 nm f=0.0019 Rotatory Strengths (*R*) -4.4858
114 ->117 0.58485
115 ->117 -0.36096
Excited State 2: 298.44 nm f=0.0061 Rotatory Strengths (*R*) 1.4899
116 ->117 0.69902
Excited State 3: 296.00 nm f=0.0018 Rotatory Strengths (*R*) -0.6000
114 ->117 0.37194
115 ->117 0.59303
Excited State 4: 270.69 nm f=0.0470 Rotatory Strengths (*R*) -26.2232
112 ->117 0.56099
113 ->117 -0.42124
Excited State 5: 253.47 nm f=0.4687 Rotatory Strengths (*R*) -17.5441
112 ->117 0.40619
113 ->117 0.55393

Conformational and spectral analysis of 7c in acetonitrile

For *cis*-enone **7c (**17β-methyl analog of **7a**) five conformers in the range of 0-5 kcal/mol were found. Two of these conformers, *i.e.*, **7c**(1) and **7c**(2) are found to have populations of 53.5% and 46.3%, respectively. The highest energy conformers were excluded

from further consideration due to their insignificant share of the total population (below 0.3%). All conformers show a non-planar enone moiety and their cyclopentanone rings adopt half-chair HC(13β,17α) conformation. The two lowest energy conformers of enone **7c** show conformational differences mostly for the substituent at C(3) carbon atom. The Boltzmann-averaged ECD spectrum for two lowest energy conformers of **7c** was used in comparison with the experimental spectra of **7a** and **7b**.



Overview of the conformational analysis for compound 7c

C Onformer	ΔG (kcal.mol^{-1})	Population (%)	Torsion angles [°]						
			enone	a	b	c	d	e	2-3-22-23
7c(1)	0.00	53.5	−21.3	−11.6	+29.9	−36.7	+30.5	−12.1	+90.5
7c(2)	0.09	46.3	−20.9	−11.5	+29.8	−36.6	+30.5	−12.2	+149.1

Calculated at B3LYP/TZVP level of theory total energies, relative energies and conformer distribution at 25° C for individual conformers of compound 7c.

Conformer	Energy [Hartree]	ΔG [kcal mol^{-1}]	Distribution [%]
1	-1083.56493	0.00	53.5
2	-1083.56479	0.09	46.3
3	-1083.55967	3.30	0.2
4	-1083.55787	4.43	0.0
5	-1083.55766	4.56	0.0

Cartesian coordinates for individual conformers of compound 7c.

Input orientation of compound **7c** conf.1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.422507	0.994086	-0.345493
2	6	0	2.842460	1.198357	0.201123
3	6	0	1.730636	-1.492198	-0.252730
4	6	0	3.161345	-1.304272	0.271649
5	6	0	3.737904	0.030429	-0.183247
6	6	0	0.774565	-0.339689	0.133422
7	1	0	1.344654	-2.443829	0.117390
8	1	0	1.759804	-1.571535	-1.345336
9	6	0	-0.586503	-0.508918	-0.636869
10	6	0	0.534392	-0.341157	1.656444
11	1	0	1.517628	0.905948	-1.436641
12	6	0	0.518009	2.196891	-0.078661
13	6	0	-1.262939	-1.874486	-0.409293
14	1	0	-0.317388	-0.452959	-1.701653
15	1	0	0.982971	3.102908	-0.476973
16	1	0	0.403813	2.355364	0.997401
17	6	0	-1.496442	0.686986	-0.405060
18	6	0	-0.859687	2.015315	-0.733130

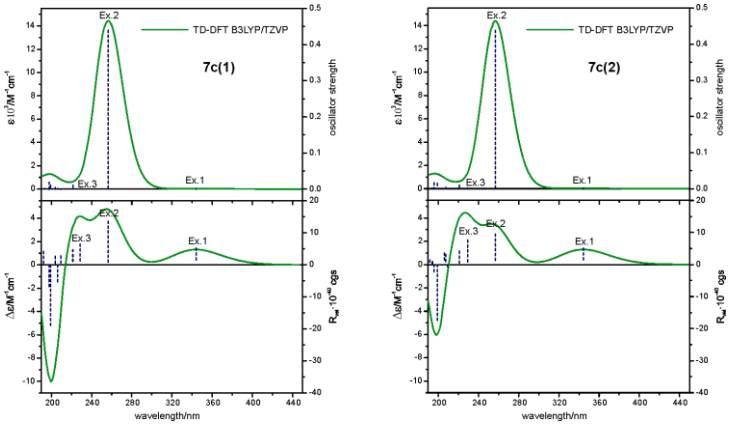
19	6	0	-2.788806	0.541928	-0.047020
20	1	0	-1.521202	2.836247	-0.475078
21	1	0	-0.718496	2.038195	-1.822381
22	6	0	-2.754955	-1.857597	-0.746006
23	6	0	-3.499077	-0.804863	0.084083
24	1	0	-1.136851	-2.193181	0.626019
25	1	0	-0.760997	-2.626953	-1.020276
26	6	0	-3.810081	1.614324	0.079059
27	1	0	-3.183508	-2.850045	-0.580540
28	1	0	-2.886236	-1.626362	-1.808465
29	6	0	-3.586393	-1.232860	1.565159
30	6	0	-4.915458	-0.470133	-0.489474
31	6	0	-5.182541	0.961154	-0.003771
32	6	0	-6.034188	-1.460339	-0.179841
33	1	0	-4.796292	-0.426523	-1.577718
34	1	0	-5.630619	0.973298	0.996265
35	1	0	-5.841612	1.539247	-0.653649
36	1	0	-0.240236	0.368868	1.947164
37	1	0	1.436532	-0.083577	2.210606
38	1	0	0.222278	-1.327787	2.001322
39	1	0	-2.594116	-1.329533	2.005319
40	1	0	-4.092725	-2.195393	1.663276
41	1	0	-4.133878	-0.503623	2.165978
42	1	0	3.257833	2.124055	-0.205899
43	1	0	2.831449	1.306994	1.288859
44	1	0	3.793319	-2.120712	-0.084470
45	1	0	3.177129	-1.340708	1.364105
46	1	0	3.893068	0.017440	-1.262957
47	8	0	5.037459	0.257587	0.446535
48	1	0	-6.256076	-1.500206	0.888514
49	1	0	-5.780141	-2.470031	-0.510929
50	1	0	-6.951804	-1.166679	-0.695317
51	6	0	6.146722	-0.168949	-0.181364
52	8	0	6.142776	-0.740357	-1.251261
53	6	0	7.381603	0.160584	0.613323
54	1	0	7.331657	-0.318293	1.592449
55	1	0	7.442921	1.237460	0.777082
56	1	0	8.264964	-0.182469	0.081383
57	8	0	-3.637270	2.814871	0.237395

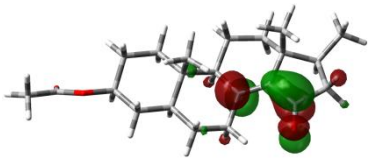
Input orientation of compound **7c** conf.2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.501041	0.753758	-0.280401
2	6	0	2.936383	0.808111	0.265297
3	6	0	1.625988	-1.745956	-0.391139
4	6	0	3.067677	-1.709364	0.134606
5	6	0	3.741351	-0.392715	-0.217022
6	6	0	0.759729	-0.561607	0.097795
7	1	0	1.170217	-2.693540	-0.098581
8	1	0	1.646815	-1.734604	-1.486822
9	6	0	-0.614171	-0.567602	-0.670325
10	6	0	0.523770	-0.670751	1.617703
11	1	0	1.584068	0.745881	-1.375877
12	6	0	0.691147	1.995112	0.091667
13	6	0	-1.393584	-1.890599	-0.543644

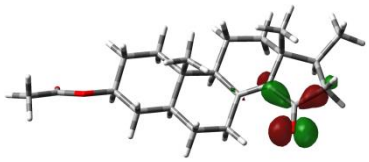
14	1	0	-0.345382	-0.450121	-1.730458
15	1	0	1.222479	2.893507	-0.234262
16	1	0	0.591036	2.072089	1.178133
17	6	0	-1.431796	0.673328	-0.342944
18	6	0	-0.697226	1.972045	-0.565396
19	6	0	-2.734601	0.600591	-0.000189
20	1	0	-1.295182	2.815730	-0.235753
21	1	0	-0.555598	2.075034	-1.649962
22	6	0	-2.878153	-1.735670	-0.874691
23	6	0	-3.544573	-0.694319	0.031921
24	1	0	-1.294262	-2.294662	0.464542
25	1	0	-0.949159	-2.630826	-1.211245
26	6	0	-3.673354	1.735048	0.204083
27	1	0	-3.380944	-2.702506	-0.782376
28	1	0	-2.987631	-1.417252	-1.916937
29	6	0	-3.667477	-1.220554	1.478269
30	6	0	-4.929772	-0.213824	-0.512876
31	6	0	-5.090590	1.194254	0.076215
32	6	0	-6.119738	-1.138611	-0.274797
33	1	0	-4.803826	-0.100141	-1.595343
34	1	0	-5.540213	1.167923	1.075386
35	1	0	-5.701890	1.866100	-0.528650
36	1	0	-0.205264	0.059593	1.969974
37	1	0	1.440927	-0.515747	2.184860
38	1	0	0.150982	-1.660994	1.884398
39	1	0	-2.685356	-1.414295	1.909158
40	1	0	-4.237091	-2.151871	1.508975
41	1	0	-4.167233	-0.500893	2.130172
42	1	0	3.415468	1.730460	-0.071601
43	1	0	2.938758	0.827093	1.358496
44	1	0	3.637581	-2.537897	-0.292492
45	1	0	3.082517	-1.839709	1.219799
46	1	0	3.895264	-0.322886	-1.294840
47	8	0	5.059578	-0.403803	0.415904
48	1	0	-6.349766	-1.238453	0.787873
49	1	0	-5.937228	-2.137801	-0.676988
50	1	0	-7.010770	-0.743309	-0.768574
51	6	0	6.069759	0.254581	-0.177813
52	8	0	5.963181	0.857254	-1.225034
53	6	0	7.335691	0.151237	0.629504
54	1	0	7.534851	-0.886663	0.896694
55	1	0	7.219856	0.714314	1.557826
56	1	0	8.168734	0.558928	0.062887
57	8	0	-3.412481	2.905118	0.447461

Computed UV (top) and ECD (bottom) spectra of conformers 7c(1) and 7c(2) of compound 7c

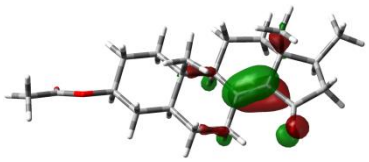




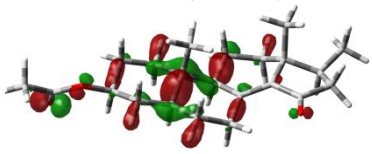
LUMO (orb. 95)



HOMO (orb. 94)



HOMO-1 (orb. 93)



HOMO-3 (orb. 91)

Conformer 7c(1)

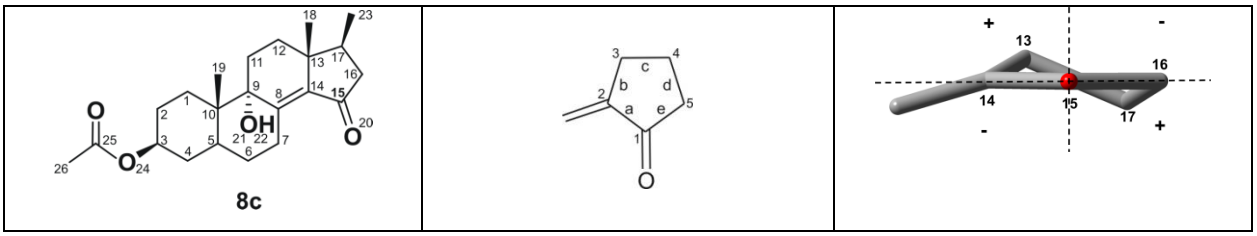
Excited State 1: 347.59 nm f=0.0012 Rotatory Strengths (*R*) 6.0584
93 -> 95 -0.16533
94 -> 95 0.67837
Excited State 2: 260.21 nm f=0.4396 Rotatory Strength (*R*) 12.0810
93 -> 95 0.67932
94 -> 95 0.16608
Excited State 3: 232.36 nm f=0.0018 Rotatory Strength (*R*) 6.7165
84 -> 95 0.10898
90 -> 95 -0.21529
91 -> 95 0.62983
92 -> 95 -0.14966

Conformer 7c(2)

Excited State 1: 347.96 nm f=0.0012 Rotatory Strength (*R*) 5.9101
93 -> 95 -0.16769
94 -> 95 0.67784
Excited State 2: 260.45 nm f=0.4385 Rotatory Strength (*R*) 8.1173
93 -> 95 0.67871
94 -> 95 0.16862
Excited State 3: 232.76 nm f=0.0021 Rotatory Strength (*R*) 7.8798
84 -> 95 0.10361
90 -> 95 0.36910
91 -> 95 -0.28699
92 -> 95 0.50406

Conformational and spectral analysis of 8c in acetonitrile

In the case of compound **8c** (17β-methyl analog of **8a**) nine conformers in the range of 0-5 kcal/mol were found. Six conformers [**8c**(1) - **8c**(6)], based on their internal energies, were found to have populations of 36.6%, 34.7%, 10.8%, 10.7%, 3.6%, and 3.4%, respectively. Populations of other conformers were below 0.3%, therefore these conformers were excluded from further consideration. All conformers have skewed enone chromophoric systems with enone torsion angles from –22.4° to –24.3°. Very similar torsion angle, –23.1°, was found for compound **8a** from the experimental crystallographic data. The five-membered cyclopentanone ring of all conformers exists in a half-chair HC(13β,17α) conformation. The six lowest energy conformers of enone **8c** show conformational differences for the substituent at C(3) carbon atom as well as for the 9α-hydroxyl substituent. The Boltzmann-averaged ECD spectrum for six lowest energy conformers of **8c** was used in comparison with the experimental spectra of **8a** and **8b**.



Overview of the conformational analysis for compound 8c

SCXRD = single crystal X-ray diffraction

Conformer	ΔG (kcal.mol^{-1})	Pop. (%)	Torsion angles [°]							
			enone	a	b	c	d	e	22-21-9-8	2-3-24-25
SCXRD **of 8a**	–	–	−23.1	−13.5	+28.9	−33.1	+25.7	−8.1	−76.9	+82.7
8c(1)	0.00	36.6	−22.8	−13.6	+31.5	−37.4	+30.0	−10.6	−62.9	+90.7
8c(2)	0.03	34.7	−22.4	−13.5	+31.3	−37.2	+29.8	−10.6	−63.2	+148.8
8c(3)	0.73	10.8	−23.0	−13.6	+31.5	−37.4	+30.0	−10.6	+51.1	+91.1
8c(4)	0.73	10.7	−22.8	−13.6	+31.4	−37.3	+29.9	−10.5	+50.3	+149.1
8c(5)	1.38	3.6	−24.3	−14.2	+31.9	−37.6	+29.8	−10.1	−168.9	+90.6
8c(6)	1.41	3.4	−23.9	−14.1	+31.7	−37.4	+29.7	−10.2	−169.0	+148.4

Calculated at B3LYP/TZVP level of theory total energies, relative energies and conformer distribution at 25° C for individual conformers of compound 8c.

Conformer	Energy [Hartree]	ΔG [kcal mol^{-1}]	Distribution [%]
1	-1158.812965	0.00	36.6
2	-1158.812914	0.03	34.7
3	-1158.811805	0.73	10.8
4	-1158.811801	0.73	10.7
5	-1158.810766	1.38	3.6
6	-1158.810715	1.41	3.4
7	-1158.807786	3.25	0.2
8	-1158.806676	3.95	0.1
9	-1158.805543	4.66	0.0

Cartesian coordinates for individual conformers of compound 8c.

Input orientation of compound **8c** conf. 1

Center Atomic Atomic Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	1.441697	1.001455	-0.331065
2	6	0	2.860470	1.225124	0.212157
3	6	0	1.758754	-1.488860	-0.122798
4	6	0	3.179281	-1.265775	0.416776
5	6	0	3.757710	0.040651	-0.109090
6	6	0	0.795062	-0.319017	0.191348
7	1	0	1.805818	-1.625537	-1.205190
8	1	0	1.369782	-2.418677	0.296372
9	6	0	-0.575858	-0.526758	-0.561271
10	6	0	0.541744	-0.248332	1.713187
11	1	0	1.533728	0.885922	-1.414931
12	6	0	0.537405	2.208267	-0.082573
13	6	0	-1.254059	-1.857046	-0.182557
14	8	0	-0.252523	-0.560680	-1.978763
15	1	0	0.997198	3.105334	-0.506499
16	1	0	0.434395	2.391652	0.990978
17	6	0	-1.482791	0.696015	-0.348782
18	6	0	-0.847153	2.014704	-0.718170
19	6	0	-2.770667	0.558808	0.023305
20	1	0	-0.720695	2.018597	-1.806508
21	1	0	-1.506130	2.837980	-0.462462
22	6	0	-2.746182	-1.884381	-0.516073
23	6	0	-3.491648	-0.772508	0.227078
24	1	0	-1.126121	-2.055849	0.880357
25	1	0	-0.735965	-2.656260	-0.713494
26	6	0	-3.794782	1.641442	0.111597
27	1	0	-3.159898	-2.863456	-0.261966
28	1	0	-2.894825	-1.756295	-1.594082
29	6	0	-3.600696	-1.096870	1.733773
30	6	0	-4.898093	-0.464086	-0.383852
31	6	0	-5.167165	0.990068	0.026525
32	6	0	-6.022971	-1.435435	-0.039167
33	1	0	-4.763237	-0.476617	-1.470924
34	1	0	-5.640539	1.053353	1.012585
35	1	0	-5.805981	1.539519	-0.666907
36	1	0	1.415373	0.127948	2.243305
37	1	0	0.324512	-1.234466	2.124912
38	1	0	-0.292787	0.406392	1.963900
39	1	0	-4.147718	-0.323017	2.275839
40	1	0	-2.615394	-1.173228	2.193110
41	1	0	-4.118585	-2.044956	1.889747
42	1	0	3.277327	2.129884	-0.238364
43	1	0	2.849181	1.387919	1.293372
44	1	0	3.178831	-1.236136	1.509679
45	1	0	3.817681	-2.100420	0.119072
46	1	0	3.915890	-0.030861	-1.185953
47	8	0	5.055439	0.303181	0.511721
48	1	0	-6.260590	-1.419115	1.026325
49	1	0	-5.766401	-2.461251	-0.313685
50	1	0	-6.932010	-1.167418	-0.582797
51	6	0	6.167365	-0.154428	-0.088406
52	8	0	6.168640	-0.781779	-1.126547
53	6	0	7.398802	0.217821	0.692835
54	1	0	7.349019	-0.216600	1.692537
55	1	0	7.454286	1.301237	0.807974
56	1	0	8.285175	-0.144652	0.179083

57	8	0	-3.617111	2.842051	0.244137
58	1	0	-1.074237	-0.688271	-2.468446

Input orientation of compound **8c** conf. 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.519889	0.769287	-0.260911
2	6	0	2.949428	0.842046	0.299468
3	6	0	1.653141	-1.744414	-0.262719
4	6	0	3.080993	-1.674816	0.295435
5	6	0	3.759618	-0.379202	-0.116595
6	6	0	0.776517	-0.537756	0.151644
7	1	0	1.697643	-1.789002	-1.352779
8	1	0	1.193360	-2.675438	0.073997
9	6	0	-0.603767	-0.582790	-0.611434
10	6	0	0.521634	-0.578598	1.674508
11	1	0	1.610480	0.736162	-1.350541
12	6	0	0.705859	2.015816	0.085140
13	6	0	-1.382188	-1.883874	-0.338757
14	8	0	-0.278593	-0.527296	-2.028016
15	1	0	1.232966	2.908030	-0.263935
16	1	0	0.609101	2.118312	1.170164
17	6	0	-1.417721	0.684715	-0.300325
18	6	0	-0.685083	1.976264	-0.566260
19	6	0	-2.712812	0.616845	0.065875
20	1	0	-1.282954	2.823851	-0.247591
21	1	0	-0.549875	2.055586	-1.650575
22	6	0	-2.871948	-1.769408	-0.663412
23	6	0	-3.529840	-0.668760	0.173761
24	1	0	-1.270490	-2.178572	0.703445
25	1	0	-0.927340	-2.673784	-0.937047
26	6	0	-3.652503	1.763342	0.242990
27	1	0	-3.360237	-2.731578	-0.489016
28	1	0	-3.011347	-1.540718	-1.726115
29	6	0	-3.654321	-1.102467	1.651267
30	6	0	-4.912475	-0.211421	-0.396894
31	6	0	-5.070160	1.224567	0.122277
32	6	0	-6.104918	-1.119590	-0.112541
33	1	0	-4.785419	-0.152838	-1.483427
34	1	0	-5.534257	1.250562	1.114473
35	1	0	-5.667858	1.870348	-0.523171
36	1	0	0.252483	-1.583024	2.003138
37	1	0	-0.280267	0.094417	1.978046
38	1	0	1.410861	-0.292813	2.234399
39	1	0	-4.235753	-2.022296	1.738737
40	1	0	-4.143907	-0.338002	2.257622
41	1	0	-2.674328	-1.281844	2.092972
42	1	0	3.432242	1.748340	-0.074022
43	1	0	2.943300	0.911103	1.390770
44	1	0	3.073456	-1.742862	1.386478
45	1	0	3.660424	-2.525038	-0.072215
46	1	0	3.923658	-0.363915	-1.194964
47	8	0	5.071467	-0.357972	0.529754
48	1	0	-6.993869	-0.747174	-0.627168
49	1	0	-6.336189	-1.162858	0.953634
50	1	0	-5.925260	-2.138620	-0.462550

51	6	0	6.090232	0.263016	-0.088531
52	8	0	5.996665	0.810063	-1.167082
53	6	0	7.348855	0.193121	0.733895
54	1	0	7.555402	-0.836968	1.025473
55	1	0	7.218572	0.774527	1.648705
56	1	0	8.183637	0.595027	0.165794
57	8	0	-3.384970	2.934313	0.462196
58	1	0	-1.105368	-0.557324	-2.524831

Input orientation of compound **8c** conf. 3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.441108	0.997405	-0.328042
2	6	0	2.859009	1.220122	0.218641
3	6	0	1.757210	-1.492465	-0.127922
4	6	0	3.176205	-1.271818	0.416443
5	6	0	3.757027	0.036051	-0.103295
6	6	0	0.792062	-0.325216	0.185006
7	1	0	1.806363	-1.627382	-1.211019
8	1	0	1.365904	-2.423002	0.287232
9	6	0	-0.581459	-0.535161	-0.576648
10	6	0	0.534537	-0.253596	1.706686
11	1	0	1.560241	0.891363	-1.414015
12	6	0	0.535745	2.204734	-0.084038
13	6	0	-1.258492	-1.860683	-0.196396
14	8	0	-0.358236	-0.665198	-2.007075
15	1	0	0.996591	3.102511	-0.504322
16	1	0	0.429231	2.383749	0.989212
17	6	0	-1.485670	0.689549	-0.361751
18	6	0	-0.849239	2.013126	-0.719822
19	6	0	-2.769443	0.557505	0.020705
20	1	0	-1.510086	2.831729	-0.454107
21	1	0	-0.735232	2.055606	-1.812031
22	6	0	-2.751428	-1.882976	-0.522709
23	6	0	-3.491655	-0.772156	0.226791
24	1	0	-1.116852	-2.062077	0.863662
25	1	0	-0.746943	-2.657752	-0.736762
26	6	0	-3.789947	1.643506	0.115593
27	1	0	-3.167589	-2.861064	-0.267386
28	1	0	-2.889034	-1.744574	-1.598466
29	6	0	-3.594532	-1.096270	1.733987
30	6	0	-4.899989	-0.458665	-0.377259
31	6	0	-5.163915	0.995736	0.036421
32	6	0	-6.025727	-1.427521	-0.028384
33	1	0	-4.769754	-0.470402	-1.464817
34	1	0	-5.632042	1.058854	1.025047
35	1	0	-5.804936	1.547957	-0.652825
36	1	0	0.327650	-1.241989	2.117876
37	1	0	-0.309039	0.390740	1.953911
38	1	0	1.401222	0.133530	2.240816
39	1	0	-4.116753	-2.041721	1.891577
40	1	0	-4.133909	-0.320263	2.280844
41	1	0	-2.606932	-1.179380	2.187257
42	1	0	3.276484	2.126581	-0.227356
43	1	0	2.841572	1.379136	1.299978
44	1	0	3.172123	-1.245801	1.509449

45	1	0	3.815555	-2.105425	0.117949
46	1	0	3.918576	-0.032234	-1.179981
47	8	0	5.051519	0.298078	0.522160
48	1	0	-6.936761	-1.156877	-0.567417
49	1	0	-6.258252	-1.411855	1.038295
50	1	0	-5.772554	-2.453552	-0.305210
51	6	0	6.166698	-0.149851	-0.080770
52	8	0	6.171137	-0.769739	-1.123083
53	6	0	7.395407	0.225070	0.703068
54	1	0	7.340062	-0.199138	1.706745
55	1	0	7.453125	1.309563	0.807678
56	1	0	8.283080	-0.143893	0.196245
57	8	0	-3.607128	2.843482	0.247468
58	1	0	-0.060519	0.175516	-2.371655

Input orientation of compound **8c** conf. 4

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.519089	0.765991	-0.261958
2	6	0	2.950155	0.839418	0.295845
3	6	0	1.653689	-1.746220	-0.267566
4	6	0	3.081362	-1.677941	0.290776
5	6	0	3.761018	-0.382205	-0.119042
6	6	0	0.776250	-0.542043	0.146933
7	1	0	1.697000	-1.789695	-1.358275
8	1	0	1.193395	-2.677556	0.067207
9	6	0	-0.610123	-0.591514	-0.619002
10	6	0	0.523797	-0.578831	1.670925
11	1	0	1.631110	0.740750	-1.353716
12	6	0	0.704957	2.012697	0.084170
13	6	0	-1.385558	-1.887060	-0.336397
14	8	0	-0.398312	-0.629089	-2.056506
15	1	0	1.231286	2.905956	-0.262197
16	1	0	0.608313	2.109899	1.168984
17	6	0	-1.421043	0.678615	-0.307371
18	6	0	-0.688072	1.974607	-0.562586
19	6	0	-2.712642	0.615109	0.066158
20	1	0	-1.287952	2.816314	-0.232405
21	1	0	-0.564726	2.094624	-1.647846
22	6	0	-2.874817	-1.771022	-0.658843
23	6	0	-3.531469	-0.668458	0.176460
24	1	0	-1.262695	-2.178100	0.704927
25	1	0	-0.935056	-2.677011	-0.937897
26	6	0	-3.649226	1.764756	0.243779
27	1	0	-3.365541	-2.731476	-0.480015
28	1	0	-2.998123	-1.538861	-1.720153
29	6	0	-3.657779	-1.096933	1.655270
30	6	0	-4.912232	-0.207641	-0.396205
31	6	0	-5.067633	1.229238	0.122019
32	6	0	-6.107215	-1.112662	-0.112773
33	1	0	-4.783058	-0.150372	-1.482463
34	1	0	-5.532486	1.256872	1.113836
35	1	0	-5.663205	1.876254	-0.524195
36	1	0	0.267993	-1.585690	2.002117
37	1	0	-0.287509	0.083876	1.972177
38	1	0	1.408523	-0.279442	2.231292

39	1	0	-4.244406	-2.013257	1.744837
40	1	0	-4.142057	-0.328810	2.261458
41	1	0	-2.678271	-1.281910	2.095904
42	1	0	3.431971	1.746074	-0.077385
43	1	0	2.941313	0.908559	1.386759
44	1	0	3.073023	-1.747314	1.381734
45	1	0	3.660969	-2.527634	-0.077611
46	1	0	3.927862	-0.366289	-1.197078
47	8	0	5.070154	-0.360132	0.530818
48	1	0	-6.994656	-0.738840	-0.629047
49	1	0	-6.340117	-1.154511	0.953139
50	1	0	-5.928999	-2.132320	-0.461620
51	6	0	6.088933	0.267013	-0.082258
52	8	0	5.995327	0.819414	-1.157895
53	6	0	7.345831	0.195617	0.742314
54	1	0	7.555060	-0.835850	1.027049
55	1	0	7.211593	0.770042	1.660946
56	1	0	8.180477	0.604209	0.178835
57	8	0	-3.377572	2.934975	0.461947
58	1	0	-0.051443	0.216959	-2.360100

Input orientation of compound **8c** conf. 5

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.436274	0.993829	-0.366255
2	6	0	2.852042	1.230135	0.180221
3	6	0	1.758428	-1.488705	-0.114009
4	6	0	3.172868	-1.256280	0.438041
5	6	0	3.754650	0.041012	-0.107099
6	6	0	0.788823	-0.317392	0.173704
7	1	0	1.841699	-1.638960	-1.195119
8	1	0	1.366601	-2.417277	0.304766
9	6	0	-0.584668	-0.537614	-0.590261
10	6	0	0.529594	-0.226611	1.693800
11	1	0	1.531376	0.859745	-1.448331
12	6	0	0.530346	2.204267	-0.142452
13	6	0	-1.262994	-1.862474	-0.196534
14	8	0	-0.365592	-0.541011	-2.026633
15	1	0	0.990710	3.093739	-0.581456
16	1	0	0.423936	2.406737	0.927340
17	6	0	-1.486625	0.687075	-0.381829
18	6	0	-0.852328	1.996614	-0.778056
19	6	0	-2.762655	0.556656	0.025856
20	1	0	-1.511483	2.825752	-0.542160
21	1	0	-0.722953	1.971354	-1.865834
22	6	0	-2.756672	-1.883795	-0.518396
23	6	0	-3.488540	-0.770831	0.236427
24	1	0	-1.119014	-2.056910	0.865191
25	1	0	-0.757916	-2.677733	-0.720734
26	6	0	-3.777058	1.645470	0.134736
27	1	0	-3.174304	-2.861121	-0.263239
28	1	0	-2.898181	-1.742421	-1.593475
29	6	0	-3.587734	-1.097400	1.743111
30	6	0	-4.898022	-0.450616	-0.362216
31	6	0	-5.154605	1.004341	0.054546
32	6	0	-6.026735	-1.415186	-0.010903

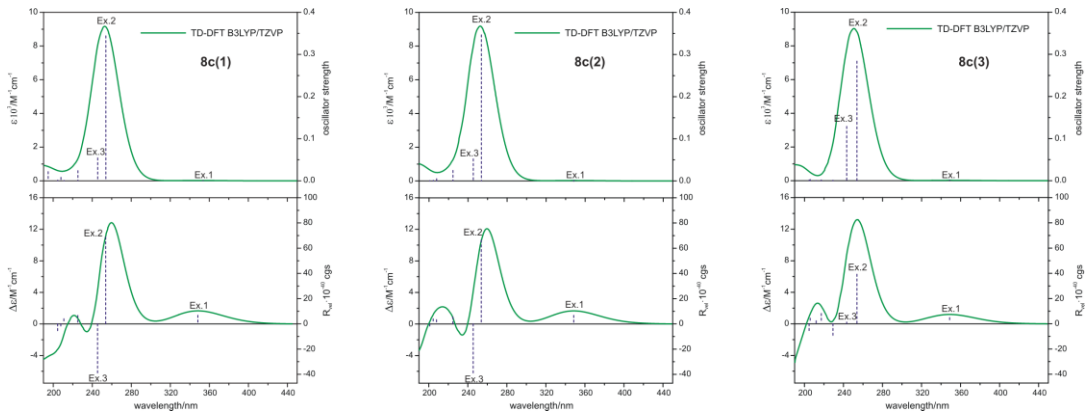
33	1	0	-4.771522	-0.461124	-1.450189
34	1	0	-5.622989	1.068221	1.042936
35	1	0	-5.792680	1.560643	-0.634227
36	1	0	0.312728	-1.207437	2.118542
37	1	0	-0.308234	0.428928	1.930161
38	1	0	1.398800	0.160283	2.224074
39	1	0	-4.113909	-2.040593	1.901179
40	1	0	-4.121831	-0.319656	2.292647
41	1	0	-2.599419	-1.185666	2.193876
42	1	0	3.271105	2.125425	-0.286740
43	1	0	2.832254	1.416700	1.257518
44	1	0	3.157067	-1.206899	1.529746
45	1	0	3.814756	-2.095896	0.163399
46	1	0	3.924945	-0.052496	-1.180526
47	8	0	5.044530	0.317672	0.522281
48	1	0	-6.938517	-1.139259	-0.545994
49	1	0	-6.255247	-1.400425	1.056654
50	1	0	-5.779491	-2.441897	-0.290610
51	6	0	6.163402	-0.152327	-0.056184
52	8	0	6.175228	-0.803423	-1.079315
53	6	0	7.386317	0.241083	0.727742
54	1	0	7.318390	-0.149933	1.744036
55	1	0	7.449319	1.328070	0.797695
56	1	0	8.276923	-0.148891	0.242234
57	8	0	-3.588623	2.843066	0.279710
58	1	0	0.048085	-1.378935	-2.265630

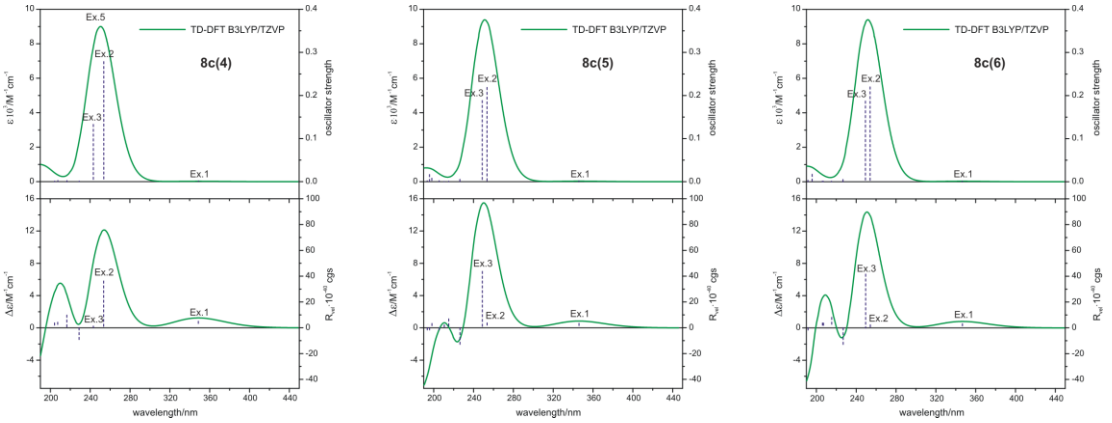
Input orientation of compound **8c** conf. 6

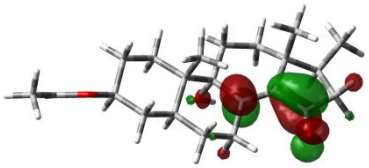
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.514004	0.765065	-0.293056
2	6	0	2.939750	0.852513	0.274943
3	6	0	1.653648	-1.744989	-0.246614
4	6	0	3.074926	-1.664464	0.326959
5	6	0	3.756532	-0.376408	-0.104512
6	6	0	0.769898	-0.533991	0.138776
7	1	0	1.734569	-1.808383	-1.336468
8	1	0	1.191839	-2.674412	0.091174
9	6	0	-0.612803	-0.592737	-0.637804
10	6	0	0.509614	-0.552297	1.661552
11	1	0	1.609111	0.710612	-1.382070
12	6	0	0.696873	2.017912	0.022418
13	6	0	-1.391171	-1.888542	-0.345193
14	8	0	-0.388142	-0.502218	-2.070297
15	1	0	1.224693	2.902886	-0.343479
16	1	0	0.594574	2.143309	1.104532
17	6	0	-1.422033	0.677740	-0.336310
18	6	0	-0.690911	1.960796	-0.634756
19	6	0	-2.705224	0.614777	0.064597
20	1	0	-0.550815	2.004869	-1.720543
21	1	0	-1.289444	2.817485	-0.342496
22	6	0	-2.881780	-1.770358	-0.659342
23	6	0	-3.526869	-0.666731	0.183915
24	1	0	-1.264464	-2.176201	0.697227
25	1	0	-0.950395	-2.696061	-0.934721
26	6	0	-3.634926	1.765851	0.257490

27	1	0	-3.373860	-2.729762	-0.479373
28	1	0	-3.012416	-1.534722	-1.719271
29	6	0	-3.642565	-1.097034	1.662847
30	6	0	-4.911169	-0.200719	-0.376557
31	6	0	-5.056821	1.236512	0.143713
32	6	0	-6.106877	-1.101595	-0.082849
33	1	0	-4.791224	-0.143423	-1.463822
34	1	0	-5.516148	1.265758	1.138010
35	1	0	-5.653202	1.886329	-0.499006
36	1	0	1.393216	-0.249873	2.222096
37	1	0	0.246331	-1.553047	2.005999
38	1	0	-0.299079	0.119134	1.949401
39	1	0	-4.229324	-2.012913	1.756237
40	1	0	-4.122061	-0.328791	2.272657
41	1	0	-2.660331	-1.282614	2.097127
42	1	0	3.424261	1.750571	-0.115794
43	1	0	2.924688	0.947401	1.364223
44	1	0	3.051856	-1.710354	1.418602
45	1	0	3.658854	-2.521678	-0.015975
46	1	0	3.933494	-0.384610	-1.180968
47	8	0	5.059520	-0.339911	0.557090
48	1	0	-6.997403	-0.724472	-0.591369
49	1	0	-6.330741	-1.142631	0.985040
50	1	0	-5.935607	-2.121940	-0.433246
51	6	0	6.087561	0.262045	-0.065574
52	8	0	6.007746	0.780390	-1.159116
53	6	0	7.336287	0.209045	0.772790
54	1	0	7.543938	-0.816770	1.078649
55	1	0	7.192508	0.800130	1.679229
56	1	0	8.176004	0.607498	0.209609
57	8	0	-3.357071	2.932935	0.484532
58	1	0	-0.035511	-1.347252	-2.373488

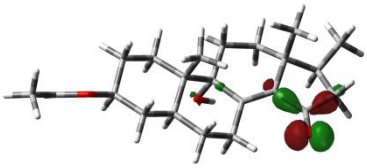
Computed UV (top) and ECD (bottom) spectra of conformers 8c(1) - 8c(6) of compound 8c



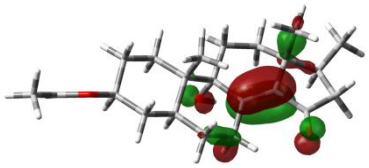




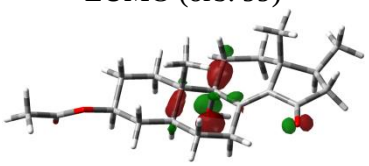
LUMO (orb. 99)



HOMO (orb. 98)



HOMO-1 (orb. 97)



HOMO-2 (orb. 96)

Conformer 8c(1)

Excited State 1: 353.49 nm f=0.0010 Rotatory Strength (*R*) 7.2065
98 -> 99 0.69335
Excited State 2: 258.98 nm f=0.3440 Rotatory Strength (*R*) 66.2041
96 -> 99 0.20377
97 -> 99 0.66728
Excited State 3: 250.73 nm f=0.0546 Rotatory Strength (*R*) -41.9339
96 -> 99 0.65429
97 -> 99 -0.20039
98 -> 99 0.10148

Conformer 8c(2)

Excited State 1: 353.81 nm f=0.0011 Rotatory Strength (*R*) 7.2216
98 -> 99 0.69320
Excited State 2: 258.99 nm f=0.3466 Rotatory Strength (*R*) 63.9186
96 -> 99 0.19225
97 -> 99 0.66885
Excited State 3: 250.85 nm f=0.0523 Rotatory Strength (*R*) -41.8853
95 -> 99 -0.16395
96 -> 99 0.63992
97 -> 99 -0.19466
98 -> 99 0.10266

Conformer 8c(3)

Excited State 1: 353.82 nm f=0.0011 Rotatory Strength (*R*) 5.3319
98 -> 99 0.69406
Excited State 2: 258.81 nm f=0.2839 Rotatory Strength (*R*) 37.7614
96 -> 99 -0.21917
97 -> 99 0.66061

Excited State 3: 248.33 nm f=0.1291 Rotatory Strength (*R*) 1.0277
94 -> 99 -0.12215
96 -> 99 0.64343
97 -> 99 0.22302

Conformer 8c(4)
Excited State 1: 354.10 nm f=0.0011 Rotatory Strength (*R*) 5.5070
98 -> 99 0.69400
Excited State 2: 259.01 nm f=0.2787 Rotatory Strength (*R*) 34.7810
96 -> 99 -0.22008
97 -> 99 0.65847
Excited State 3: 248.59 nm f=0.1330 Rotatory Strength (*R*) 0.8583
95 -> 99 -0.18032
96 -> 99 0.63185
97 -> 99 0.22893

Conformer 8c(5)
Excited State 1: 350.06 nm f=0.0014 Rotatory Strength (*R*) 3.9906
97 -> 99 0.10294
98 -> 99 0.68950
Excited State 2: 257.80 nm f=0.2188 Rotatory Strength (*R*) 3.0952
96 -> 99 -0.35606
97 -> 99 0.59709
Excited State 3: 253.01 nm f=0.1884 Rotatory Strength (*R*) 41.7459
96 -> 99 0.60410
97 -> 99 0.34646

Conformer 8c(6)
Excited State 1: 350.33 nm f=0.0014 Rotatory Strength (*R*) 3.8875
97 -> 99 0.10573
98 -> 99 0.68917
Excited State 2: 257.83 nm f=0.2200 Rotatory Strength (*R*) 1.8498
96 -> 99 -0.35398
97 -> 99 0.59703
Excited State 3: 253.10 nm f=0.1872 Rotatory Strength (*R*) 39.9738
96 -> 99 0.60245
97 -> 99 0.34573

Table S1. Dependence of the calculated *R* (given in 10^{-40} cgs units) on torsion angles ω and τ and calculated $\Delta R = R_{\tau+5^\circ} - R_{\tau-5^\circ}$ on torsion angle ω for s-*cis* acrolein (**13**)

		ω [°]										
		−25	**−20**	**−15**	**−10**	**−5**	**0**	**+5**	**+10**	**+15**	**+20**	**+25**
τ [°]	**−5**	**2.688**	**2.359**	**1.914**	**1.384**	**0.788**	**0.148**	**−0.511**	**−1.148**	**−1.728**	**−2.251**	**−2.692**
	−4	**2.723**	**2.355**	**1.904**	**1.365**	**0.760**	**0.123**	**−0.541**	**−1.149**	**−1.768**	**−2.266**	**−2.704**
	−3	**2.713**	**2.346**	**1.878**	**1.343**	**0.733**	**0.096**	**−0.578**	**−1.193**	**−1.767**	**−2.276**	**−2.696**
	−2	**2.715**	**2.330**	**1.864**	**1.331**	**0.705**	**0.071**	**−0.599**	**−1.219**	**−1.807**	**−2.288**	**−2.739**
	−1	**2.706**	**2.334**	**1.846**	**1.296**	**0.677**	**0.024**	**−0.626**	**−1.243**	**−1.808**	**−2.298**	**−2.705**
	0	**2.707**	**2.311**	**1.827**	**1.271**	**0.660**	**0.000**	**−0.638**	**−1.267**	**−1.843**	**−2.308**	**−2.720**
	+1	**2.691**	**2.310**	**1.806**	**1.246**	**0.620**	**−0.037**	**−0.686**	**−1.296**	**−1.847**	**−2.321**	**−2.709**
	+2	**2.696**	**2.279**	**1.786**	**1.213**	**0.602**	**−0.061**	**−0.705**	**−1.316**	**−1.873**	**−2.332**	**−2.725**
	+3	**2.657**	**2.289**	**1.769**	**1.191**	**0.555**	**−0.099**	**−0.733**	**−1.350**	**−1.885**	**−2.348**	**−2.713**
	+4	**2.692**	**2.265**	**1.748**	**1.169**	**0.543**	**−0.121**	**−0.763**	**−1.366**	**−1.911**	**−2.354**	**−2.725**
	+5	**2.684**	**2.271**	**1.716**	**1.141**	**0.516**	**−0.154**	**−0.792**	**−1.386**	**−1.917**	**−2.360**	**−2.738**
Δ*R*			**−0.088**	**−0.198**	**−0.243**	**−0.272**	**−0.302**	**−0.281**	**−0.238**	**−0.189**	**−0.109**	

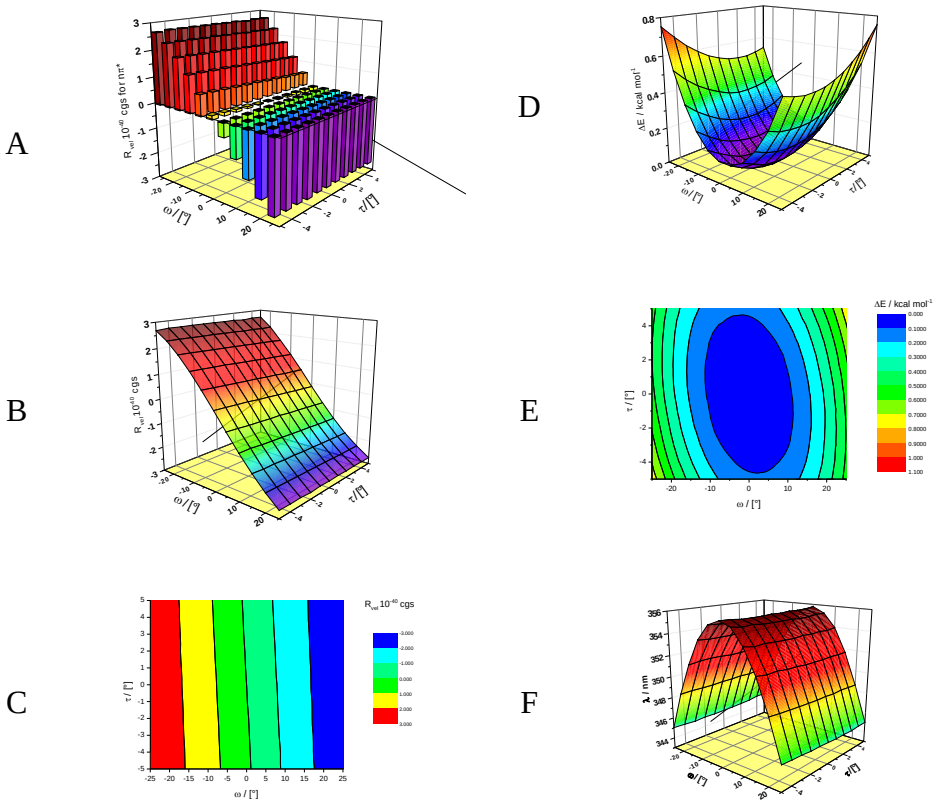


Figure S1. Rotatory strength (A, B, C), 3D or 2D energy surface (D or E) and excitation energy (F) of the lowest-energy electronic transition of s-*cis* acrolein (**13**) as a function of torsion angles ω and τ calculated at the B3LYP/aug-cc-pVDZ/PCM (acetonitrile) level of theory.

Table S2. Dependence of the calculated R (given in 10^{-40} cgs units) on torsion angles ω and τ and calculated $\Delta R = R_{\tau+5^\circ} - R_{\tau-5^\circ}$ on torsion angle ω for *P*–helical conformers of 2-methylenecyclopentanone (**14**)

		ω [°]										
		−25	**−20**	**−15**	**−10**	**−5**	**0**	**+5**	**+10**	**+15**	**+20**	**+25**
τ [°]	**−5**	**5.765**	**5.721**	**5.487**	**5.101**	**4.553**	**3.856**	**3.023**	**2.131**	**1.251**	**0.392**	**−0.403**
	−4	**5.803**	**5.736**	**5.490**	**5.091**	**4.546**	**3.833**	**2.994**	**2.105**	**1.221**	**0.379**	**−0.397**
	−3	**5.712**	**5.741**	**5.487**	**5.084**	**4.528**	**3.804**	**2.963**	**2.075**	**1.199**	**0.361**	**−0.428**
	−2	**5.843**	**5.748**	**5.493**	**5.077**	**4.513**	**3.770**	**2.931**	**2.046**	**1.175**	**0.346**	**−0.433**
	−1	**5.755**	**5.754**	**5.484**	**5.063**	**4.489**	**3.751**	**2.902**	**2.016**	**1.149**	**0.326**	**−0.458**
	0	**5.877**	**5.756**	**5.476**	**5.051**	**4.470**	**3.718**	**2.869**	**1.986**	**1.127**	**0.306**	**−0.469**
	+1	**5.786**	**5.756**	**5.468**	**5.036**	**4.443**	**3.631**	**2.837**	**1.956**	**1.105**	**0.281**	**−0.482**
	+2	**5.894**	**5.762**	**5.463**	**5.019**	**4.413**	**3.599**	**2.799**	**1.926**	**1.077**	**0.264**	**−0.499**
	+3	**5.802**	**5.758**	**5.451**	**5.000**	**4.385**	**3.561**	**2.769**	**1.899**	**1.053**	**0.242**	**−0.509**
	+4	**5.905**	**5.760**	**5.437**	**4.984**	**4.354**	**3.589**	**2.729**	**1.867**	**1.028**	**0.221**	**−0.516**
	+5	**5.816**	**5.752**	**5.424**	**4.960**	**4.325**	**3.553**	**2.700**	**1.839**	**1.002**	**0.203**	**−0.529**
ΔR[a]			**+0.031**	**−0.063**	**−0.141**	**−0.228**	**−0.303**	**−0.323**	**−0.292**	**−0.249**	**−0.189**	

Table S3. Dependence of the calculated R (given in 10^{-40} cgs units) on torsion angles ω and τ and calculated $\Delta R = R_{\tau+5^\circ} - R_{\tau-5^\circ}$ on torsion angle ω for *M*–helical conformers of 2-methylenecyclopentanone (**14**)

		ω [°]										
		−25	**−20**	**−15**	**−10**	**−5**	**0**	**+5**	**+10**	**+15**	**+20**	**+25**
τ [°]	**−5**	**0.531**	**−0.198**	**−1.002**	**−1.837**	**−2.697**	**−3.554**	**−4.326**	**−4.961**	**−5.425**	**−5.755**	**−5.918**
	−4	**0.514**	**−0.215**	**−1.031**	**−1.862**	**−2.740**	**−3.526**	**−4.354**	**−4.982**	**−5.436**	**−5.757**	**−5.911**
	−3	**0.429**	**−0.244**	**−1.052**	**−1.899**	**−2.768**	**−3.561**	**−4.386**	**−5.002**	**−5.452**	**−5.762**	**−5.897**
	−2	**0.500**	**−0.265**	**−1.079**	**−1.927**	**−2.804**	**−3.596**	**−4.415**	**−5.017**	**−5.461**	**−5.762**	**−5.911**
	−1	**0.405**	**−0.284**	**−1.105**	**−1.957**	**−2.836**	**−3.633**	**−4.443**	**−5.037**	**−5.470**	**−5.758**	**−5.888**
	0	**0.469**	**−0.302**	**−1.128**	**−1.985**	**−2.870**	**−3.717**	**−4.470**	**−5.047**	**−5.475**	**−5.757**	**−5.886**
	+1	**0.377**	**−0.326**	**−1.148**	**−2.017**	**−2.901**	**−3.751**	**−4.489**	**−5.066**	**−5.487**	**−5.754**	**−5.860**
	+2	**0.433**	**−0.345**	**−1.176**	**−2.047**	**−2.929**	**−3.771**	**−4.511**	**−5.075**	**−5.489**	**−5.749**	**−5.837**
	+3	**0.350**	**−0.363**	**−1.198**	**−2.076**	**−2.963**	**−3.805**	**−4.528**	**−5.085**	**−5.490**	**−5.741**	**−5.820**
	+4	**0.395**	**−0.376**	**−1.224**	**−2.105**	**−2.994**	**−3.830**	**−4.547**	**−5.090**	**−5.489**	**−5.733**	**−5.791**
	+5	**0.303**	**−0.392**	**−1.246**	**−2.134**	**−3.023**	**−3.856**	**−4.558**	**−5.102**	**−5.490**	**−5.719**	**−5.768**
Δ*R*			**−0.194**	**−0.244**	**−0.297**	**−0.326**	**−0.302**	**−0.232**	**−0.141**	**−0.065**	**+0.036**	

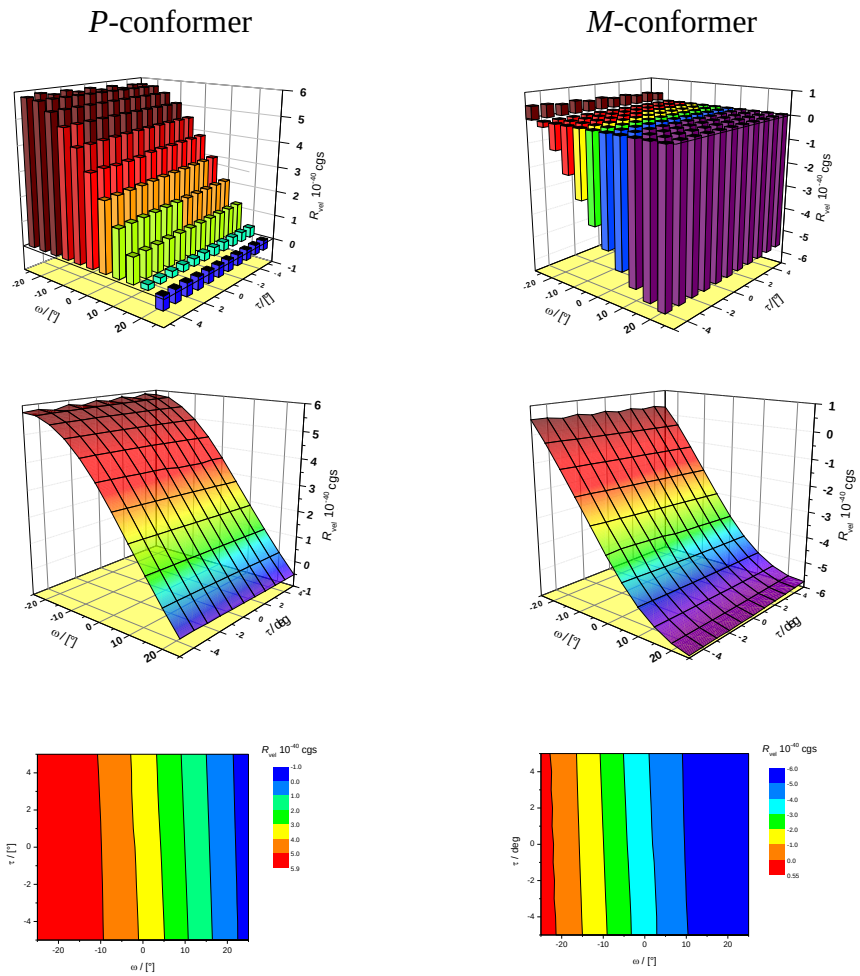


Figure S2. Rotatory strength of the lowest-energy electronic transition of two conformers of 2-methylenecyclopentanone (**14**) as a function of torsion angles ω and τ calculated at the B3LYP/aug-cc-pVDZ/PCM (acetonitrile) level of theory.

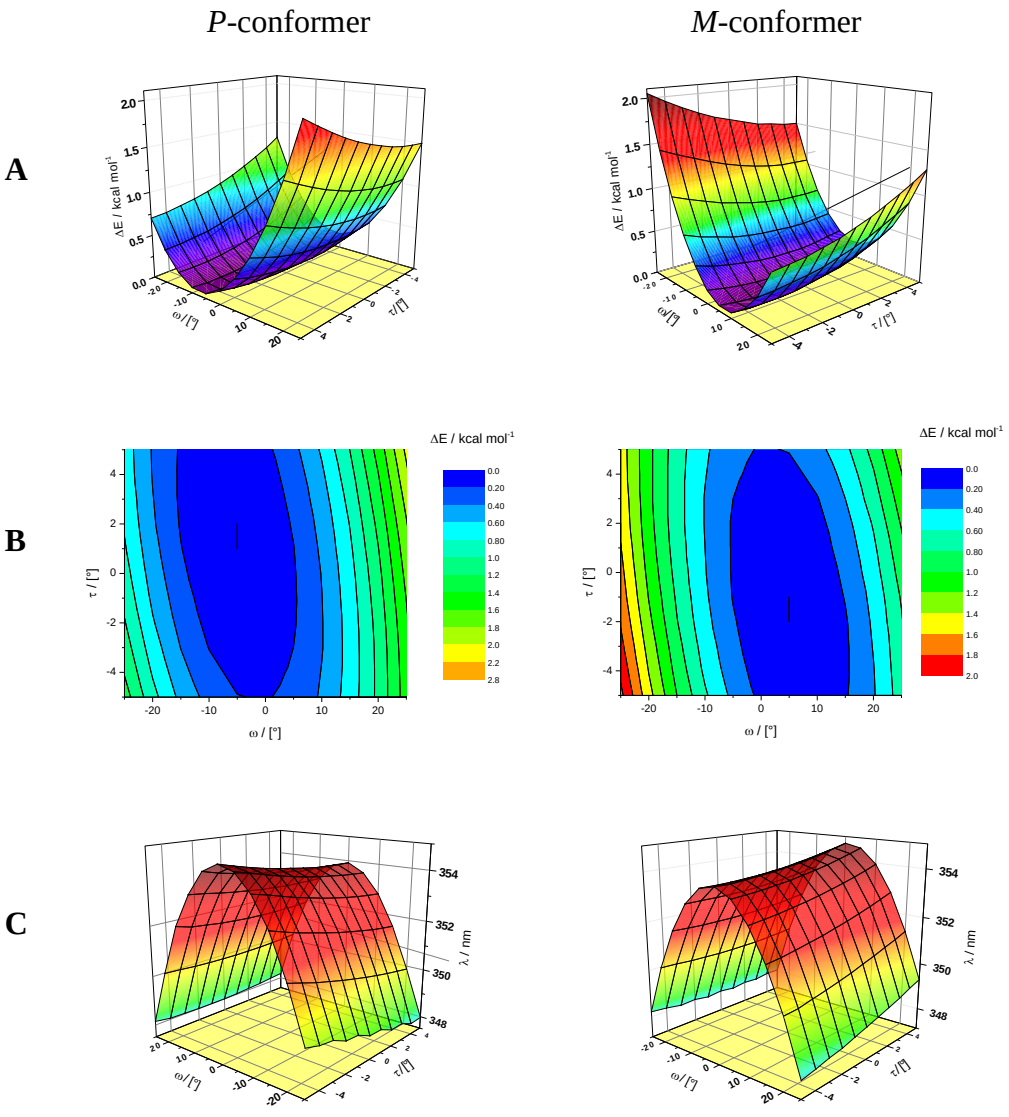
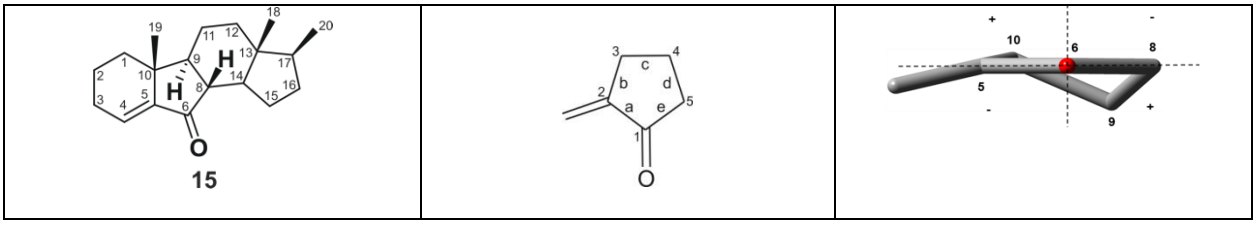


Figure S3. 3D or 2D energy surface (A or B) and excitation energy (C) of two conformers of 2-methylenecyclopentanone (**14**) as a function of torsion angles ω and τ calculated at the B3LYP/aug-cc-pVDZ/PCM (acetonitrile) level of theory.

Conformational and spectral analysis of 15 in acetonitrile

For model compound **15** one conformer in the range of 0-5 kcal/mol was found. Its cyclopentanone five-membered ring adopts conformation close to an envelope E(9α) and the enone torsion angles show nonplanarity of the chromophore.



Overview of the conformational analysis for conformer 15(1) of compound 15.

Conformer	ΔG (kcal.mol^{-1})	Population (%)	Torsion angles [°]					
			enone	a	b	c	d	e
15(1)	0.00	100.0	−15.6	−4.1	+26.9	−39.3	+38.0	−20.8

Calculated at B3LYP/TZVP level of theory total energies, relative energies and conformer distribution at 25° C for individual conformers of compound 15.

Conformer	Energy [Hartree]	ΔG [kcal mol^{-1}]	Distribution [%]
1	-815.99724	0.00	100.0

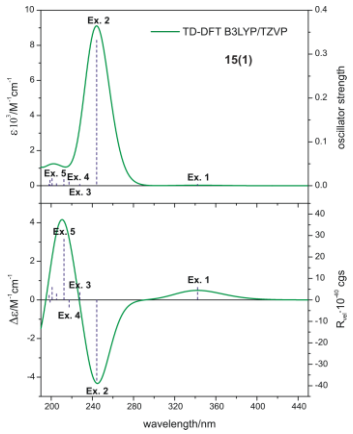
Cartesian coordinates for individual conformers of compound 15.

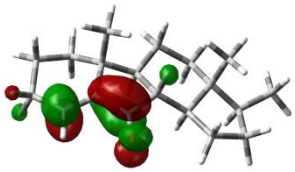
Input orientation of compound **15** conf.1

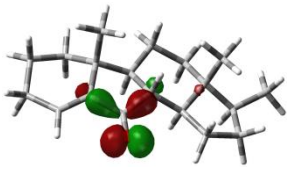
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.969094	-0.475888	-0.099806
2	6	0	-2.057381	-0.154246	-1.393489
3	6	0	0.516743	-0.606847	-0.267418
4	6	0	0.419052	0.418234	-1.407907
5	6	0	-0.880749	0.271743	-2.215910
6	6	0	-0.672886	-0.486992	0.703116
7	1	0	0.526515	-1.616458	-0.691787
8	1	0	1.460511	-0.477025	0.268984
9	6	0	-0.920062	-1.755886	1.569146
10	6	0	-0.532491	0.781832	1.569566
11	6	0	-0.035087	-2.081039	2.771891
12	1	0	-0.828152	-2.603192	0.875619
13	6	0	-2.421460	-1.685269	1.942167
14	1	0	-2.575013	-0.888560	2.682047
15	6	0	-2.854680	-3.012558	2.543694
16	6	0	-0.520468	-3.383247	3.451434
17	6	0	-2.015833	-3.338726	3.816787
18	1	0	1.004146	-2.206154	2.454667
19	1	0	-0.042822	-1.257487	3.490095
20	1	0	-2.590384	-3.786315	1.810982
21	6	0	-4.303134	-3.286653	2.969765
22	1	0	-0.350929	-4.220602	2.764919
23	1	0	0.084690	-3.579333	4.341477
24	6	0	-2.242612	-2.321421	4.953383
25	6	0	-2.650449	-4.707166	4.189075
26	6	0	-4.173422	-4.483817	3.956211
27	1	0	-4.940526	-3.514389	2.115804
28	1	0	-4.737777	-2.415917	3.465816
29	6	0	-2.315633	-5.288835	5.560136
30	1	0	-2.296621	-5.419161	3.434372
31	1	0	-4.673468	-4.263646	4.902505
32	1	0	-4.640514	-5.387864	3.560754
33	1	0	-1.370425	0.906179	2.257079
34	1	0	0.384535	0.742737	2.161877
35	1	0	-0.492382	1.676516	0.947753
36	1	0	-1.964472	-1.306474	4.668823
37	1	0	-1.632232	-2.587442	5.818806
38	1	0	-3.282070	-2.292566	5.282733
39	1	0	1.276053	0.311945	-2.076587

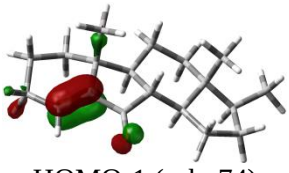
40	1	0	0.478634	1.428394	-0.996171
41	1	0	-0.754840	-0.474912	-3.010971
42	1	0	-1.114452	1.203862	-2.741527
43	1	0	-1.237345	-5.406748	5.696272
44	6	0	-3.056135	-1.144917	0.668205
45	8	0	-4.225014	-1.246704	0.331708
46	1	0	-3.009774	-0.277550	-1.902557
47	1	0	-2.691341	-4.660833	6.370950
48	1	0	-2.769750	-6.276599	5.675514

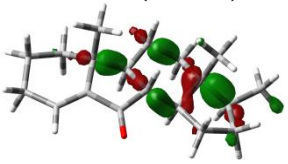
Computed UV (top) and ECD (bottom) spectra of conformer 15(1) of compound 15

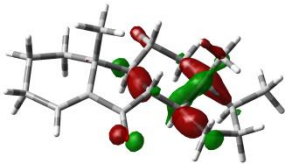


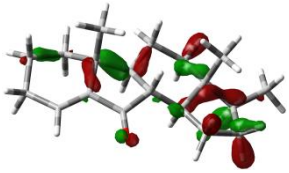

LUMO (orb. 76)

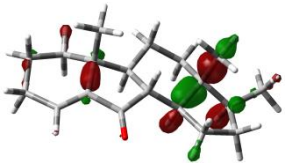

HOMO (orb. 75)


HOMO-1 (orb. 74)


HOMO-2 (orb. 73)


HOMO-3 (orb. 72)


HOMO-5 (orb. 70)


HOMO-6 (orb. 69)

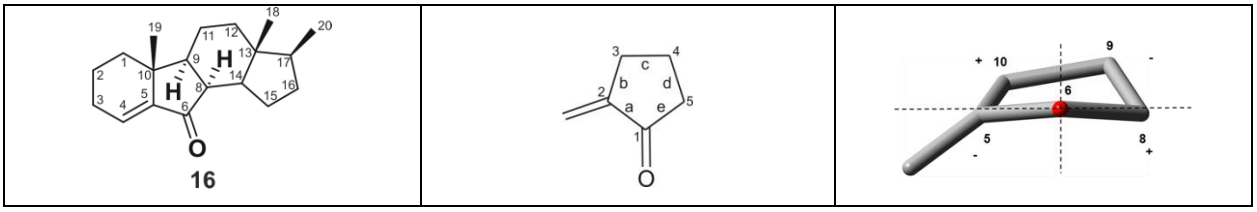
Conformer 15(1)

Excited State 1: 342.31 nm f=0.0011 Rotatory Strength (*R*) 6.5935
74 -> 76 0.10634
75 -> 76 0.68834
Excited State 2: 244.30 nm f=0.3318 Rotatory Strength (*R*) -35.0941
74 -> 76 0.67605
75 -> 76 -0.11508
Excited State 3: 227.78 nm f=0.0028 Rotatory Strength (*R*) 3.1446
70 -> 76 0.11334
72 -> 76 0.28157

73 -> 76 0.62800
Excited State 4: 217.42 nm f=0.0084 Rotatory Strength (*R*) -3.3794
70 -> 76 -0.13221
72 -> 76 0.61905
73 -> 76 -0.24946
74 -> 76 -0.10660
Excited State 5: 212.49 nm f=0.0144 Rotatory Strength (*R*) 27.7738
67 -> 76 0.22630
68 -> 76 -0.25804
69 -> 76 0.40776
70 -> 76 0.41387
73 -> 76 -0.12493

Conformational and spectral analysis of 16 in acetonitrile

For model compound **16** two conformers in the range of 0-5 kcal/mol were found. Based on their internal energies, conformers **16**(1) and **16**(2) are populated in the conformational equillibrium in 98.7% and 1.3%, respectively. Therefore the higher energy conformer **16**(2) was excluded from further consideration. The five-membered ketone ring in conformer **16**(1) exists in a conformation close to envelope E(8α).



Overview of the conformational analysis for conformer 16(1).

Conformer	ΔG (kcal.mol^{-1})	Population (%)	Torsion angles [°]					
			enone	a	b	c	d	e
16(1)	0.00	98.7	−37.6	−24.7	+5.6	+15.3	−30.3	+33.5

Calculated at B3LYP/TZVP level of theory total energies, relative energies and conformer distribution at 25° C for individual conformers of compound 16.

Conformer	Energy [Hartree]	ΔG [kcal mol^{-1}]	Distribution [%]
1	-815.98209	0.00	98.7
2	-815.97800	4.33	1.3

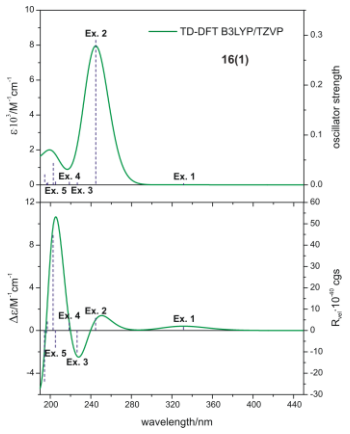
Cartesian coordinates for individual conformers of compound 16.

Input orientation of compound **16** conf.1

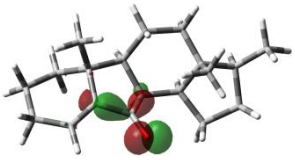
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.661528	-0.257117	0.476088
2	6	0	-1.976464	0.514534	-0.568498
3	6	0	0.451347	-0.946376	-0.574882
4	6	0	0.425393	0.309852	-1.462333
5	6	0	-0.966627	0.991826	-1.568080
6	6	0	-0.244782	-0.705235	0.785356
7	1	0	1.488501	-1.257519	-0.417608
8	6	0	-0.443747	-2.045139	1.605294
9	6	0	0.520462	0.385711	1.561655

10	6	0	-0.117049	-1.944734	3.111059
11	1	0	0.205790	-2.816430	1.182468
12	6	0	-2.420125	-3.547702	2.297211
13	6	0	-0.608345	-3.141100	3.942913
14	6	0	-2.124222	-3.333173	3.798047
15	1	0	-0.554753	-1.038866	3.532257
16	1	0	0.963449	-1.838791	3.232406
17	1	0	-1.799207	-4.413293	2.028104
18	6	0	-3.870202	-4.054865	2.250965
19	1	0	-0.101443	-4.055922	3.613994
20	1	0	-0.330584	-2.985635	4.990146
21	6	0	-2.883197	-2.141344	4.410925
22	6	0	-2.680165	-4.672707	4.357869
23	6	0	-3.996770	-4.893540	3.556258
24	1	0	-4.575563	-3.225190	2.246901
25	1	0	-4.062055	-4.647700	1.354065
26	6	0	-2.851115	-4.782228	5.870659
27	1	0	-1.967192	-5.446650	4.051501
28	1	0	-4.857584	-4.565572	4.144078
29	1	0	-4.148432	-5.954472	3.347770
30	1	0	1.533500	0.055527	1.803691
31	1	0	0.019950	0.657943	2.489725
32	1	0	0.600169	1.295408	0.967349
33	1	0	-2.673929	-1.204257	3.897334
34	1	0	-3.963775	-2.285864	4.379770
35	1	0	-2.597605	-2.010758	5.457318
36	1	0	1.152467	1.028733	-1.082474
37	1	0	0.766167	0.044701	-2.465193
38	1	0	-1.396616	0.825047	-2.561138
39	1	0	-0.855092	2.079433	-1.493099
40	1	0	-3.186233	-5.786203	6.144602
41	6	0	-1.927771	-2.453296	1.353236
42	1	0	-1.965671	-2.874157	0.336637
43	6	0	-2.659290	-1.128353	1.147729
44	8	0	-3.833358	-0.877062	1.356964
45	1	0	-3.022887	0.717122	-0.780413
46	1	0	-1.910894	-4.596277	6.396828
47	1	0	-3.593965	-4.076103	6.248093
48	1	0	-0.055959	-1.772209	-1.083547

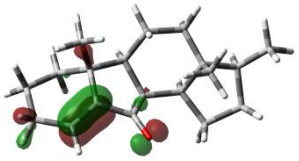
Computed UV (top) and ECD (bottom) spectra of conformer 16(1) of compound 16



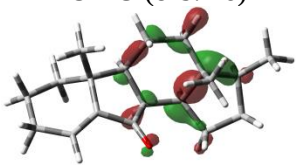
LUMO (orb. 76)



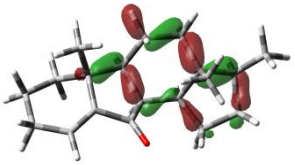
HOMO (orb. 75)



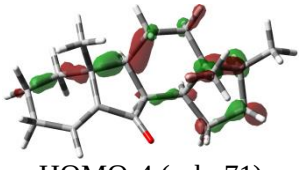
HOMO-1 (orb. 74)



HOMO-2 (orb. 73)



HOMO-3 (orb. 72)



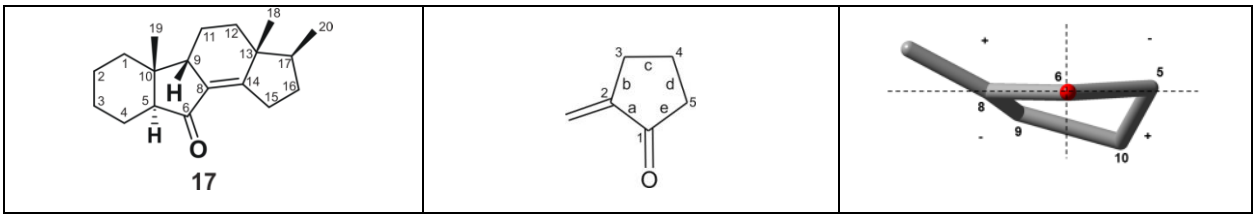
HOMO-4 (orb. 71)

Conformer 16(1)

Excited State 1: 331.50 nm f=0.0004 Rotatory Strength (*R*) 2.0273
74 -> 76 -0.16926
75 -> 76 0.67691
Excited State 2: 244.76 nm f=0.2898 Rotatory Strength (*R*) 5.4332
74 -> 76 0.66540
75 -> 76 0.17273
Excited State 3: 226.51 nm f=0.0038 Rotatory Strength (*R*) -10.2475
68 -> 76 0.10178
73 -> 76 0.68598
Excited State 4: 218.65 nm f=0.0056 Rotatory Strength (*R*) 3.5518
70 -> 76 -0.10199
71 -> 76 0.21348
72 -> 76 0.65981
Excited State 5: 205.07 nm f=0.0060 Rotatory Strength (*R*) -8.1784
67 -> 76 -0.12219
70 -> 76 -0.12599
71 -> 76 0.63418
72 -> 76 -0.22008

Conformational and spectral analysis of 17 in acetonitrile

For model compound **17** one conformer in the range of 0-5 kcal/mol was found. Its cyclopentanone five-membered ring adopts conformation close to an envelope E(5β) and the enone torsion angles show nonplanarity of the chromophore.



Overview of the conformational analysis for conformer 17(1).

Conformer	ΔG (kcal.mol^{-1})	Population (%)	Torsion angles [°]					
			enone	a	b	c	d	e
17(1)	0.00	100.0	+32.2	+16.3	+7.9	−28.3	+38.6	−34.2

Calculated at B3LYP/TZVP level of theory total energies, relative energies and conformer distribution at 25 °C for individual conformers of compound 17.

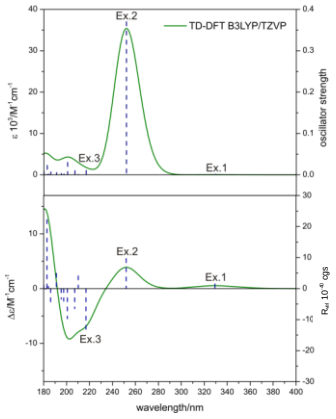
Conformer	Energy [Hartree]	ΔG [kcal mol^{-1}]	Distribution [%]
1	-816.24784720	0.00	100.0

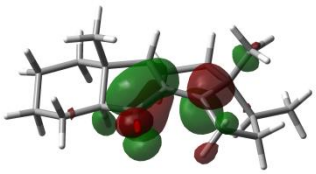
Cartesian coordinates for individual conformers of compound 17.

Input orientation of compound **17** conf.1

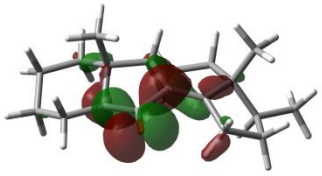
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.982070	-0.698001	-1.455831
2	6	0	-3.608041	0.491522	-2.359433
3	6	0	-2.133005	0.923419	-2.222234
4	6	0	-1.757314	1.165698	-0.753374
5	6	0	-2.101913	-0.114051	0.046778
6	6	0	-3.571919	-0.498898	0.016469
7	6	0	-0.244849	1.384350	-0.414316
8	6	0	-0.092470	0.765298	0.967999
9	6	0	-1.335351	0.056363	1.346608
10	6	0	0.841814	0.768774	-1.306369
11	6	0	2.219042	1.153652	-0.739058
12	6	0	2.394450	0.968856	0.802903
13	6	0	1.115044	0.550092	1.510776
14	6	0	3.331438	-0.227385	1.172384
15	6	0	2.955093	-0.568583	2.626109
16	6	0	1.443315	-0.271180	2.735652
17	8	0	-1.648314	-0.381849	2.444006
18	6	0	-2.515092	2.390939	-0.200124
19	6	0	2.896928	2.294768	1.421331
20	6	0	4.826533	-0.018593	0.952177
21	1	0	-5.056335	-0.888394	-1.525788
22	1	0	-3.481887	-1.598116	-1.831382
23	1	0	-3.809239	0.228707	-3.401641
24	1	0	-4.260834	1.338772	-2.132088
25	1	0	-1.952775	1.821195	-2.822057
26	1	0	-1.493650	0.135582	-2.632076
27	1	0	-3.738782	-1.419917	0.580624
28	1	0	-4.186436	0.272551	0.487708
29	1	0	0.769714	1.134272	-2.333740
30	1	0	0.726939	-0.318967	-1.340778
31	1	0	2.998253	0.587706	-1.255625
32	1	0	2.394221	2.204050	-0.985897
33	1	0	3.011117	-1.064661	0.540008
34	1	0	3.192121	-1.604398	2.873801
35	1	0	3.523682	0.060685	3.315277
36	1	0	1.194405	0.267776	3.653079
37	1	0	0.837067	-1.180002	2.753084
38	1	0	-3.597000	2.285857	-0.260307
39	1	0	-2.261683	2.575709	0.847152
40	1	0	-2.235121	3.281676	-0.767931
41	1	0	3.828745	2.609522	0.946818
42	1	0	2.159686	3.084626	1.266025
43	1	0	3.076149	2.209856	2.494621
44	1	0	5.222962	0.766495	1.599477
45	1	0	5.372801	-0.937768	1.177862
46	1	0	5.052264	0.250344	-0.082685
47	1	0	-1.552447	-0.932049	-0.447807
48	1	0	-0.054054	2.462399	-0.382387

Computed UV (top) and ECD (bottom) spectra of conformer 17(1) of compound 17

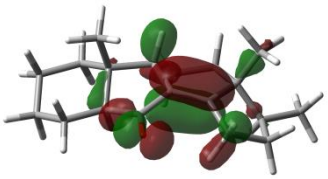




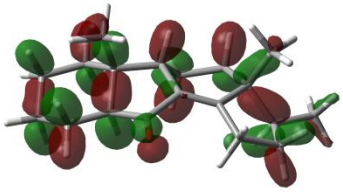
LUMO (orb. 76)



HOMO (orb. 75)



HOMO-1 (orb. 74)



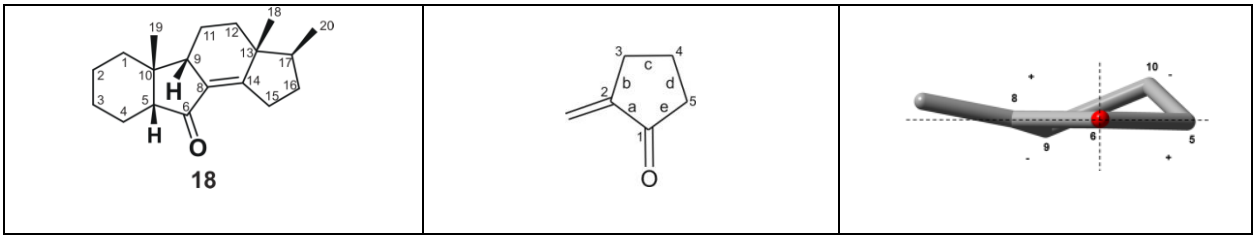
HOMO-2 (orb. 73)

Conformer 17(1)

Excited State 1: 329.26 nm f=0.0006 Rotatory Strengths (*R*) 1.7055
74 -> 76 0.26448
75 -> 76 0.64553
Excited State 2: 252.04 nm f=0.3785 Rotatory Strengths (*R*) 9.6694
74 -> 76 0.64252
75 -> 76 -0.26508
Excited State 3: 216.92 nm f=0.0106 Rotatory Strengths (*R*) -13.5364
73 -> 76 0.69447

Conformational and spectral analysis of 18 in acetonitrile

For model compound **18** two conformers in the range of 0-5 kcal/mol were found. Based on their internal energies, conformers **18**(1) and **18**(2) are populated in the conformational equillibrium in 84.7% and 15.3%, respectively. The five-membered ketone rings in conformers **18**(1) and **18**(2) exists in two slightly different conformations close to an envelope E(10β).



Overview of the conformational analysis for conformer 18(1).

Conformer	ΔG (kcal.mol^{-1})	Population (%)	Torsion angles [°]					
			enone	a	b	c	d	e
18(1)	0.00	84.7	+12.0	+4.7	−26.8	+37.5	−34.8	+19.5
18(2)	1.71	15.3	+5.8	−2.8	−19.8	+33.7	−35.4	+24.4

Calculated at B3LYP/TZVP level of theory total energies, relative energies and conformer distribution at 25 °C for individual conformers of compound 18.

Conformer	Energy [Hartree]	ΔG [kcal mol^{-1}]	Distribution [%]
1	-816.010529	0.00	84.7
2	-816.008913	1.71	15.3

Cartesian coordinates for individual conformers of compound 18.

Input orientation of compound **18** conf. 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.346764	2.736310	2.212041
2	6	0	1.183121	3.318242	1.405629
3	6	0	0.488956	2.231766	0.575582
4	6	0	1.434959	1.487251	-0.397284
5	6	0	2.709072	1.018731	0.367205
6	6	0	3.361334	2.044248	1.296319
7	6	0	0.824495	0.118341	-0.848347
8	6	0	1.099837	-0.793245	0.328746
9	6	0	2.290882	-0.293790	1.034888
10	6	0	-0.637231	0.089782	-1.363338
11	6	0	-1.603864	-0.680237	-0.449660
12	6	0	-1.037791	-2.032049	0.026555
13	6	0	0.288393	-1.783952	0.727489
14	6	0	-1.885135	-2.679188	1.166297
15	6	0	-0.864181	-3.520188	1.952532
16	6	0	0.428128	-2.681213	1.934572
17	8	0	2.862027	-0.812225	1.985459
18	6	0	1.775926	2.365866	-1.604128
19	6	0	-0.838639	-2.997933	-1.162425
20	6	0	-3.138519	-3.438835	0.742460
21	1	0	2.844722	3.521789	2.787042
22	1	0	1.955852	2.016980	2.940223
23	1	0	0.453447	3.780872	2.076102
24	1	0	1.552266	4.117439	0.754380
25	1	0	-0.340555	2.667581	0.012709
26	1	0	0.045240	1.509471	1.269039
27	1	0	4.134337	1.546915	1.887398
28	1	0	3.869327	2.799317	0.688381

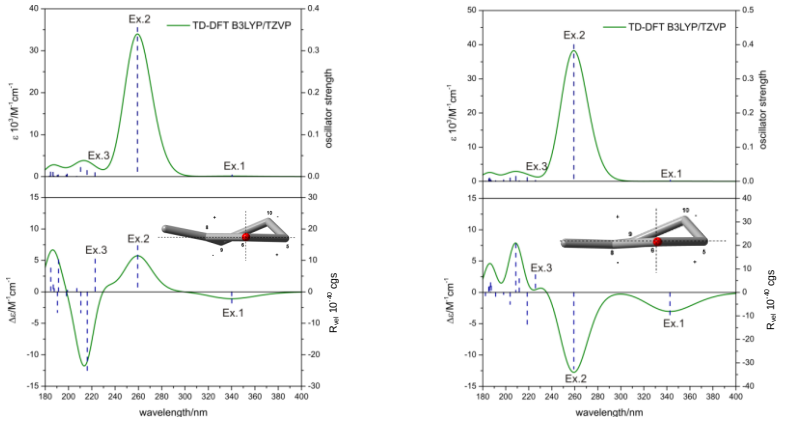
29	1	0	1.464078	-0.220061	-1.673711
30	1	0	-0.649721	-0.364092	-2.355882
31	1	0	-1.010830	1.106720	-1.500771
32	1	0	-2.550149	-0.835892	-0.975995
33	1	0	-1.829821	-0.079435	0.435813
34	1	0	-2.197399	-1.853686	1.817707
35	1	0	-0.706035	-4.480078	1.452568
36	1	0	-1.206012	-3.739713	2.965259
37	1	0	0.524727	-2.071844	2.838088
38	1	0	1.334970	-3.287358	1.888263
39	1	0	2.245063	3.305401	-1.306928
40	1	0	0.874925	2.615114	-2.170804
41	1	0	2.464506	1.849288	-2.277790
42	1	0	-0.108875	-2.602725	-1.869712
43	1	0	-1.778630	-3.147516	-1.697889
44	1	0	-0.477984	-3.973744	-0.832866
45	1	0	-2.895687	-4.319960	0.144878
46	1	0	-3.813236	-2.809672	0.156732
47	1	0	-3.689956	-3.780222	1.621985
48	1	0	3.448098	0.711927	-0.387710

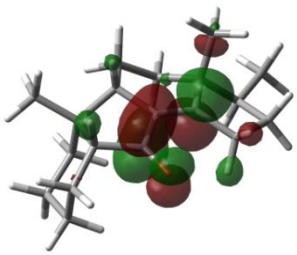
Input orientation of compound **18** conf. 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.525921	-1.705690	-1.290295
2	6	0	-3.298452	-0.486136	-2.185525
3	6	0	-2.048825	0.292030	-1.754500
4	6	0	-2.084666	0.771567	-0.282733
5	6	0	-2.470336	-0.424290	0.636156
6	6	0	-3.643883	-1.291833	0.179336
7	6	0	-0.651639	1.132337	0.241543
8	6	0	-0.063019	-0.201002	0.651049
9	6	0	-1.152593	-1.169987	0.853447
10	6	0	0.312676	1.845574	-0.710348
11	6	0	1.690765	1.982477	-0.053244
12	6	0	2.290892	0.651662	0.470734
13	6	0	1.257024	-0.440354	0.678817
14	6	0	3.257513	-0.069495	-0.520398
15	6	0	3.310223	-1.525542	0.003434
16	6	0	1.958224	-1.775203	0.725121
17	8	0	-1.053381	-2.345659	1.179255
18	6	0	-3.041106	1.957403	-0.121840
19	6	0	2.987869	0.925399	1.826496
20	6	0	4.631911	0.562537	-0.716316
21	1	0	-2.689115	-2.402500	-1.410416
22	1	0	-4.426799	-2.243826	-1.597324
23	1	0	-3.185205	-0.798169	-3.227589
24	1	0	-4.180659	0.161638	-2.152845
25	1	0	-1.898889	1.152281	-2.412019
26	1	0	-1.180403	-0.360181	-1.899190
27	1	0	-3.704992	-2.172919	0.822889
28	1	0	-4.574392	-0.733775	0.322690
29	1	0	-0.792500	1.770641	1.124480
30	1	0	-0.060498	2.837647	-0.977832
31	1	0	0.400908	1.275546	-1.638271
32	1	0	2.392854	2.444236	-0.752491

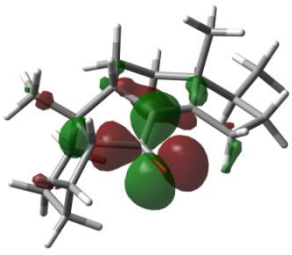
33	1	0	1.597662	2.678988	0.785134
34	1	0	2.748350	-0.077656	-1.491366
35	1	0	3.470958	-2.234357	-0.810097
36	1	0	4.147095	-1.644259	0.694926
37	1	0	1.353687	-2.546014	0.249149
38	1	0	2.109457	-2.104851	1.757313
39	1	0	-4.054585	1.713192	-0.445018
40	1	0	-2.704512	2.811527	-0.715300
41	1	0	-3.093452	2.273612	0.923131
42	1	0	2.254570	1.252993	2.565806
43	1	0	3.728520	1.719951	1.715742
44	1	0	3.495242	0.044744	2.222382
45	1	0	5.216685	0.550384	0.205957
46	1	0	4.558071	1.598358	-1.056384
47	1	0	5.197969	0.010969	-1.471239
48	1	0	-2.706907	-0.010795	1.627997

Computed UV (top) and ECD (bottom) spectra of conformers 18(1) (left) and **18(2)** (right) **of compound 18.**

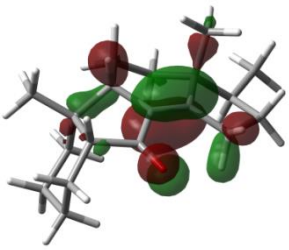




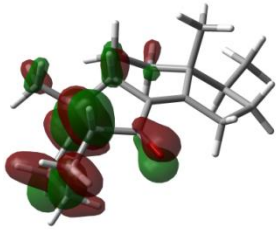
LUMO (orb. 76)



HOMO (orb. 75)



HOMO-1 (orb. 74)



HOMO-2 (orb. 73)

Conformer 18(1)

Excited State 1: 340.14 nm f=0.0012 Rotatory Strength (*R*) -3.6543
74 -> 76 -0.36526
75 -> 76 0.59716
Excited State 2: 259.40 nm f=0.3648 Rotatory Strength (*R*) 14.6558
74 -> 76 0.59338
75 -> 76 0.36309
Excited State 3: 222.92 nm f=0.0098 Rotatory Strength (*R*) 10.4086
72 -> 76 0.15483
73 -> 76 0.68616

Conformer 18(2)
Excited State 1: 342.70 nm f=0.0006 Rotatory Strength (*R*) -10.2961
75 -> 76 0.69918
Excited State 2: 259.15 nm f=0.4095 Rotatory Strength (*R*) -32.6289
74 -> 76 0.69552
Excited State 3: 225.80 nm f=0.0024 Rotatory Strength (*R*) 7.5160
72 -> 76 -0.18659
73 -> 76 0.67839

Table S4. Conformations of 2-methylenecyclopentanone unit of important conformers of investigated enones **1-8** and **15-18**

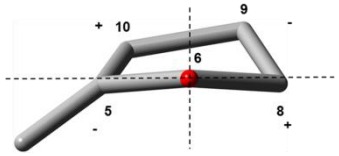
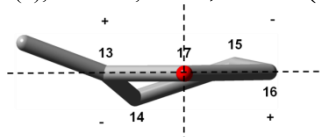
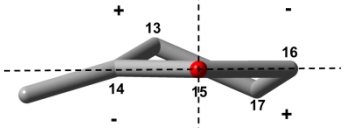
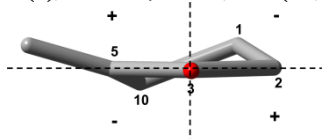
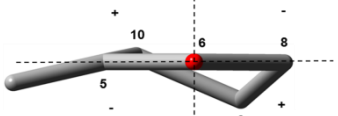
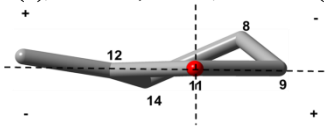
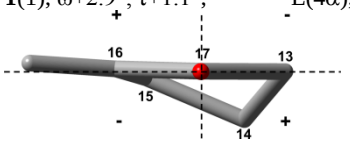
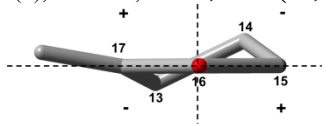
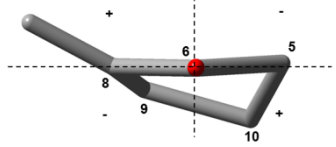
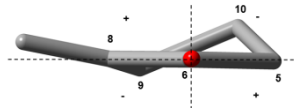
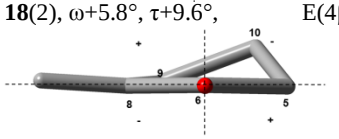
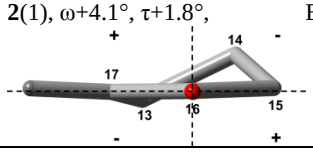
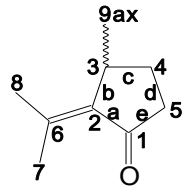
P-helical conformers	*M*-helical conformers
16(1), ω−37.6°, τ+16.1°, E(5α), *R*+ 	**5**(1), ω+24.4°, τ−5.5°, E(3α), *R*− 
8c(1), ω−22.8°, τ+1.4° HC(3β,4α), *R*+ **7c**(1), ω−21.3°, τ+0.6° HC(3β,4α), *R*+ 	**4b**(1), ω+18.5°, τ−6.4°, HC(3α,4β), *R*− 
15(1), ω−15.6°, τ+7.3°, E(4α), *R*+ 	**6**(1), ω+14.2°, τ−0.6°, E(4β), *R*− 
1(1), ω+2.9°, τ+1.1°, E(4α), *R*+ 	**3**(1), ω+12.4°, τ−1.0°, HC(3α,4β), *R*− 
17(1), ω+32.2°, τ−10.3°, E(5β), *R*+ 	**18**(1), ω+12.0°, τ−4.0°, E(4β), *R*− 
	18(2), ω+5.8°, τ+9.6°, E(4β), *R*− 
	2(1), ω+4.1°, τ+1.8°, E(4β), *R*− 

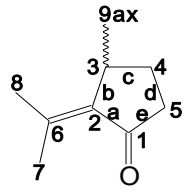
Table S5. Selected torsion angles of 2-methylenecyclopentanone unit for all conformers of investigated enones **1-8c** and **15-18**. For clarity the positive values are given in red whereas the negative ones are in blue. *R* is given in 10^{-40} cgs units.



Torsion angles: σ = 9_{ax}–C3–C2–C6
ω = O=C1–C2–C6
τ= C1–C2–C6–7

	Torsion angles [°]									
Conf.	σ	ω	τ	a	b	c	d	e	nπ*R*	ππ*R*
***P*-helical conformers**										
16(1)	+83.1	−37.6	+16.1	−24.7	+5.6	+15.3	−30.3	+33.5	+2.0	+5.4
8c(5)	+103.3	−24.3	+1.4	−14.2	+31.9	−37.6	+29.8	−10.1	+4.0	+3.1
8c(6)	+102.7	−23.9	+1.4	−14.1	+31.7	−37.4	+29.7	−10.2	+3.9	+1.8
8c(3)	+102.2	−23.0	+2.3	−13.6	+31.5	−37.4	+30.0	−10.6	+5.3	+37.8
8c(4)	+101.9	−22.8	+2.4	−13.6	+31.4	−37.3	+29.9	−10.5	+5.5	+34.8
8c(1)	+101.9	−22.8	+1.4	−13.6	+31.5	−37.4	+30.0	−10.6	+7.2	+66.2
8c(2)	+101.4	−22.4	+1.5	−13.5	+31.3	−37.2	+29.8	−10.6	+7.2	+63.9
7c(1)	+100.4	−21.3	+0.6	−11.6	+29.9	−36.7	+30.5	−12.1	+6.1	+12.1
7c(2)	+100.1	−20.9	+0.7	−11.5	+29.8	−36.6	+30.5	−12.2	+5.9	+8.1
15(1)	+100.8	−15.6	+7.3	−4.1	+26.9	−39.3	+38.0	−20.8	+6.6	−35.1
1(1)	+83.3	+2.9	+1.1	+5.8	+19.5	−37.5	+40.8	−28.4	+8.5	−51.3
1(2)	+83.0	+3.2	+1.0	+6.0	+19.4	−37.5	+40.9	−28.6	+8.6	−50.6
17(1)	−75.7	+32.2	−10.3	+16.3	+7.9	−28.3	+38.6	−34.2	+1.7	+9.7
***M*-helical conformers**										
5(1)	−104.5	+24.4	−5.5	+15.7	−27.6	+29.0	−20.6	+3.4	−6.8	−45.6
5(2)	−104.6	+23.4	−5.6	+15.4	−27.5	+29.2	−21.0	+3.9	−0.5	−40.4
4b(1)	−101.0	+18.5	−6.4	+10.0	−26.6	+33.0	−27.9	+11.4	−6.2	+8.1
6(2)	−100.6	+14.7	−0.8	+5.3	−27.4	+38.8	−35.8	+19.1	−4.6	−26.5
6(5)	−100.6	+14.7	−0.8	+5.3	−27.4	+38.8	−35.9	+19.1	−4.4	−26.3
6(6)	−100.5	+14.5	−0.8	+5.2	−27.3	+38.8	−36.0	+19.2	−4.5	−26.2
6(1)	−100.1	+14.2	−0.6	+5.0	−27.1	+38.6	−35.9	+19.3	−4.3	−27.7
6(3)	−100.1	+14.2	−0.6	+5.0	−27.1	+38.6	−35.9	+19.3	−4.3	−27.4
6(4)	−100.0	+14.0	−0.6	+4.8	−27.0	+38.7	−36.0	+19.5	−4.4	−27.5
3(1)	−94.8	+12.4	−1.0	+10.6	−31.7	+41.5	−35.4	+15.6	−15.2	+5.6
3(2)	−94.7	+12.4	−1.0	+10.5	−31.7	+41.5	−35.5	+15.6	−15.2	+5.7
18(1)	−103.4	+12.0	−4.0	+4.7	−26.8	+37.5	−34.8	+19.5	−3.7	+14.7
18(2)	−91.9	+5.8	+9.6	−2.8	−19.8	+33.7	−35.4	+24.4	−10.3	−32.6
2(2)	−87.9	+4.3	+1.7	+6.3	−28.2	+40.3	−36.7	+18.9	−14.2	+21.6
2(1)	−87.6	+4.1	+1.8	+6.1	−28.1	+40.2	−36.8	+19.1	−14.3	+21.8

Table S6. Selected torsion angles of 2-methylenecyclopentanone unit for some conformers of investigated enones **1-8c** and **15-18**. For clarity the positive values are given in red whereas the negative ones are in blue. *R* is given in 10^{-40} cgs units.

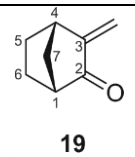


Torsion angles: σ = 9_{ax}–C3–C2–C6
ω = O=C1–C2–C6
τ = C1–C2–C6–7
trans1 = C1–C2–C6–8
cis2 = C3–C2–C6–8
trans2 = C3–C2–C6–7

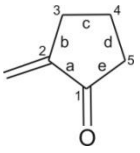
	Torsion angles [°]								
Conf.	σ	ω	τ	trans1	cis2	trans2	b	nπ*R	ππ*R
***P*-helical conformers**									
16(1)	+83.1	−37.6	+16.1	−156.5	+1.6	+174.2	+5.6	+2.0	+5.4
8c(6)	+102.7	−23.9	+1.4	−172.5	−2.3	+172.5	+31.7	+3.9	+1.8
8c(1)	+101.9	−22.8	+1.4	−172.5	−2.3	+171.6	+31.5	+7.2	+66.2
8c(4)	+101.9	−22.8	+2.4	−173.5	−4.0	+170.9	+31.4	+5.5	+34.8
7c(1)	+100.4	−21.3	+0.6	−173.5	−3.7	+170.4	+29.9	+6.1	+12.1
15(1)	+100.8	−15.6	+7.3	−167.8	−1.5	+173.6	+26.9	+6.6	−35.1
1(1)	+83.3	+2.9	+1.1	−178.9	−1.5	+178.4	+19.5	+8.5	−51.3
17(1)	–75.7	+32.2	−10.3	+160.3	+2.8	−167.8	+7.9	+1.7	+9.7
***M*-helical conformers**									
5(1)	–104.5	+24.4	−5.5	+170.6	+1.2	−174.9	−27.6	−6.8	−45.6
5(2)	–104.6	+23.4	−5.6	+170.6	+1.4	−174.7	−27.5	−0.5	−40.4
4b(1)	–101.0	+18.5	−6.4	+168.9	0.0	−175.3	−26.6	−6.2	+8.1
6(1)	–100.1	+14.2	−0.6	+176.2	+4.4	−172.4	−27.1	−4.4	−27.7
3(1)	–94.8	+12.4	−1.0	+178.3	+0.4	−178.9	−31.7	−15.2	+5.6
18(1)	–103.4	+12.0	−4.0	+169.2	−2.4	−175.5	−26.8	−3.7	+14.7
18(2)	–91.9	+5.8	+9.6	−179.2	+7.9	−163.3	−19.8	−10.3	−32.6
2(1)	–87.6	+4.1	+1.8	−177.6	+0.3	+179.7	−28.1	−14.3	+21.8

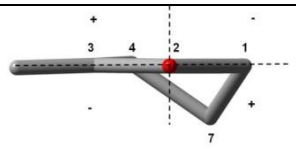
Conformational and spectral analysis of 19 in acetonitrile

For model compound **19** one conformer in the range of 0-5 kcal/mol was found.



19





Overview of the conformational analysis for conformer 19(1) of compound 19.

Conformer	ΔG (kcal.mol^{-1})	Population (%)	Torsion angles [°]					
			enone	a	b	c	d	e
19(1)	0.00	100.0	3.0	0.8	+35.1	–54.2	+53.6	–33.8

Calculated at B3LYP/TZVP level of theory total energies, relative energies and conformer distribution at 25° C for individual conformers of compound 19.

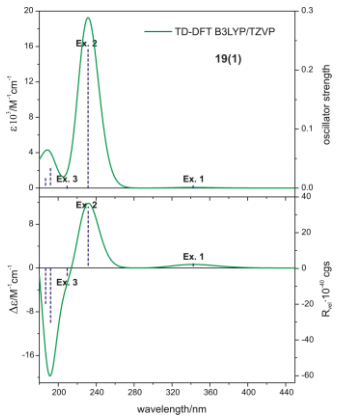
Conformer	Energy [Hartree]	ΔG [kcal mol^{-1}]	Distribution [%]
1	-386.07409	0.00	100.0

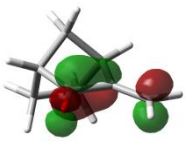
Cartesian coordinates for individual conformers of compound 19.

Input orientation of compound **19** conf.1

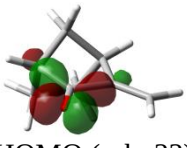
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.513353	0.644981	-0.849618
2	6	0	1.380112	-0.909485	-0.843123
3	6	0	0.686658	1.089668	0.396112
4	6	0	-0.769327	0.845736	0.032864
5	6	0	-0.919835	-0.651909	0.034442
6	6	0	0.456521	-1.179196	0.376092
7	6	0	0.941061	-0.088140	1.364356
8	1	0	1.146424	1.098886	-1.770669
9	1	0	2.549850	0.957647	-0.719849
10	1	0	2.348972	-1.387253	-0.690793
11	1	0	0.957924	-1.299203	-1.769224
12	1	0	0.469778	-2.206431	0.734100
13	1	0	1.994552	-0.192507	1.627939
14	1	0	0.344800	-0.037487	2.276747
15	1	0	0.889660	2.099510	0.743423
16	6	0	-2.058468	-1.299193	-0.193823
17	1	0	-2.970019	-0.751373	-0.404496
18	1	0	-2.119427	-2.380800	-0.172524
19	8	0	-1.624120	1.673031	-0.219809

Computed UV (top) and ECD (bottom) spectra of conformer 19(1) of compound 19



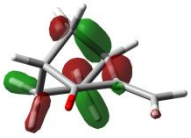


LUMO (orb. 34)



HOMO (orb. 33)

HOMO-1 (orb. 32)



HOMO-2 (orb. 31)

Conformer 19(1)

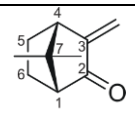
Excited State 1: 342.44 nm f=0.0008 Rotatory Strength (*R*) 2.7266

33 -> **34** 0.69671

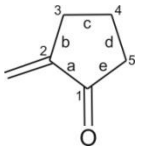
Excited State 2: 231.47 nm f=0.2347 Rotatory Strength (*R*) 31.3357
32 -> **34** 0.69111
Excited State 3: 209.38 nm f=0.0021 Rotatory Strength (*R*) -6.0548
31 -> **34** 0.69840

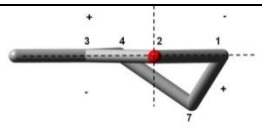
Conformational and spectral analysis of 20 in acetonitrile

For model compound **20** one conformer in the range of 0-5 kcal/mol was found.



20





Overview of the conformational analysis for conformer 20(1) of compound 20.

Conformer	ΔG (kcal.mol^{-1})	Population (%)	Torsion angles [°]					
			enone	a	b	c	d	e
20(1)	0.00	100.0	1.1	0.0	+34.9	–54.0	+53.8	–35.1

Calculated at B3LYP/TZVP level of theory total energies, relative energies and conformer distribution at 25° C for individual conformers of compound 20.

Conformer	Energy [Hartree]	ΔG [kcal mol^{-1}]	Distribution [%]
1	-464.67289	0.00	100.0

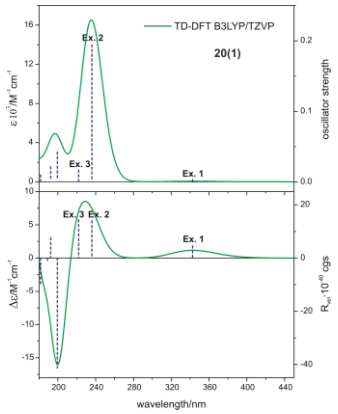
Cartesian coordinates for individual conformers of compound 20.

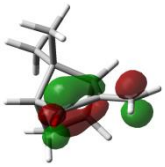
Input orientation of compound **20** conf.1

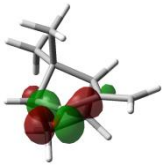
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.518146	-1.712213	-0.716355
2	6	0	0.486600	-1.665474	0.842573
3	6	0	0.314643	-0.221793	-1.130894
4	6	0	-1.143584	0.060474	-0.810634
5	6	0	-1.205049	0.096519	0.693668
6	6	0	0.216177	-0.165497	1.140285
7	6	0	1.036343	0.556710	0.015121
8	1	0	-0.256430	-2.356620	-1.133417
9	1	0	1.473530	-2.074935	-1.093844
10	1	0	1.435474	-1.984189	1.273579
11	1	0	-0.292137	-2.301285	1.262790
12	1	0	0.434859	0.142765	2.161858
13	6	0	2.547186	0.312439	0.084015
14	6	0	0.805038	2.073048	-0.041414
15	1	0	0.595725	0.013094	-2.155576
16	6	0	-2.308292	0.316223	1.401360
17	1	0	-3.257045	0.483230	0.903850
18	1	0	-2.301363	0.341583	2.484565
19	8	0	-2.066757	0.203500	-1.589194
20	1	0	2.822749	-0.740339	0.098708
21	1	0	2.958002	0.775620	0.984893
22	1	0	3.040320	0.771431	-0.776227
23	1	0	1.224028	2.553139	0.846303
24	1	0	-0.249748	2.346469	-0.094685

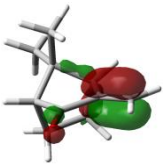
25 1 0 1.302839 2.499420 -0.915595

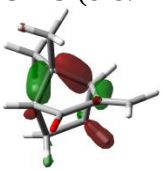
Computed UV (top) and ECD (bottom) spectra of conformer 20(1) of compound 20




LUMO (orb. 42)


HOMO (orb. 41)

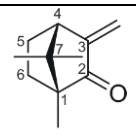

HOMO-1 (orb. 40)

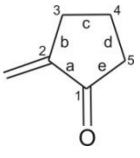

HOMO-2 (orb. 39)

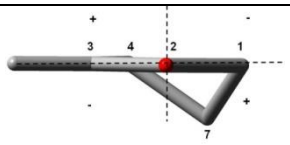
Conformer 20(1)
Excited State 1: 342.56 nm f=0.0007 Rotatory Strength (*R*) 5.3778
41 -> **42** 0.69993
Excited State 2: 235.87 nm f=0.1944 Rotatory Strength (*R*) 14.7805
39 -> 42 -0.14303
40 -> **42** 0.68134
Excited State 3: 221.88 nm f=0.0170 Rotatory Strength (*R*) 13.6809
39 -> **42** 0.68648
40 -> 42 0.13380

Conformational and spectral analysis of 21 in acetonitrile

For model compound **21** one conformer in the range of 0-5 kcal/mol was found.


21





Overview of the conformational analysis for conformer 21(1) of compound 21.

Conformer	Δ*G* (kcal.mol^{-1})	Population (%)	Torsion angles [°]					
			enone	a	b	c	d	e
21(1)	0.00	100.0	□1.1	□0.1	+35.0	–53.9	+52.9	–34.3

Calculated at B3LYP/TZVP level of theory total energies, relative energies and conformer distribution at 25° C for individual conformers of compound 21.

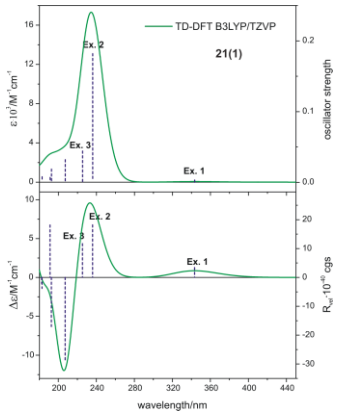
Conformer	Energy [Hartree]	ΔG [kcal mol^{-1}]	Distribution [%]
1	-503.977016	0.00	100.0

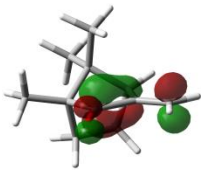
Cartesian coordinates for individual conformers of compound 21.

Input orientation of compound **21** conf.1

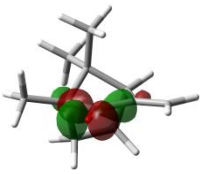
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.530455	0.264883	-1.738575
2	6	0	0.091995	-1.223731	-1.629259
3	6	0	0.484048	0.798444	-0.265996
4	6	0	-1.014910	0.869733	0.026811
5	6	0	-1.473452	-0.558086	0.124365
6	6	0	-0.227947	-1.376798	-0.118588
7	6	0	0.871365	-0.488619	0.555127
8	1	0	-0.116939	0.849647	-2.393897
9	1	0	1.545736	0.363128	-2.123907
10	1	0	0.890930	-1.901511	-1.929513
11	1	0	-0.777736	-1.450783	-2.245344
12	1	0	-0.286725	-2.406372	0.232566
13	6	0	2.301356	-0.982554	0.309679
14	6	0	0.678897	-0.330890	2.070102
15	6	0	1.243388	2.086474	-0.028535
16	6	0	-2.722444	-0.936283	0.376311
17	1	0	-3.502197	-0.197530	0.523498
18	1	0	-3.003249	-1.980300	0.448893
19	8	0	-1.697659	1.869501	0.140644
20	1	0	2.556307	-1.082550	-0.743704
21	1	0	2.440419	-1.960097	0.778718
22	1	0	3.022881	-0.298267	0.761329
23	1	0	0.819626	-1.292927	2.569005
24	1	0	-0.311623	0.036955	2.341939
25	1	0	1.414931	0.363204	2.481451
26	1	0	2.300782	1.965864	-0.271375
27	1	0	1.166296	2.412101	1.010829
28	1	0	0.845326	2.887990	-0.654286

Computed UV (top) and ECD (bottom) spectra of conformer 21(1) of compound 21

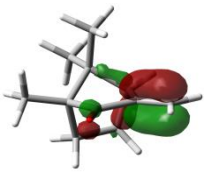




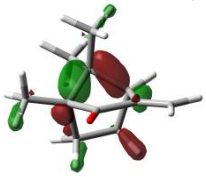
LUMO (orb. 46)



HOMO (orb. 45)



HOMO-1 (orb. 44)

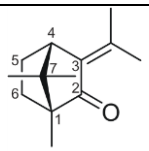


HOMO-2 (orb. 43)

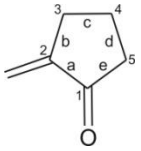
Conformer 21(1)
Excited State 1: 343.38 nm f=0.0007 Rotatory Strength (*R*) 4.3294
45 -> **46** 0.69975
Excited State 2: 236.07 nm f=0.1819 Rotatory Strength (*R*) 18.8383
43 -> 46 -0.20632
44 -> **46** 0.66492
Excited State 3: 225.42 nm f=0.0443 Rotatory Strength (*R*) 11.3086
43 -> **46** 0.66778
44 -> 46 0.19910

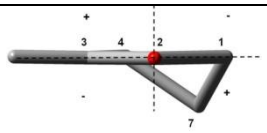
Conformational and spectral analysis of 22 in acetonitrile

For model compound **22** one conformer in the range of 0-5 kcal/mol was found.



22





Overview of the conformational analysis for conformer 22(1) of compound 22.

Conformer	Δ*G* (kcal.mol^{-1})	Population (%)	Torsion angles [°]					
			enone	a	b	c	d	e
22(1)	0.00	100.0	+0.3	+0.3	+34.7	–54.0	+53.0	–34.8

Calculated at B3LYP/TZVP level of theory total energies, relative energies and conformer distribution at 25° C for individual conformers of compound 22.

Conformer	Energy [Hartree]	Δ*G* [kcal mol^{-1}]	Distribution [%]
1	-582.587489	0.00	100.0

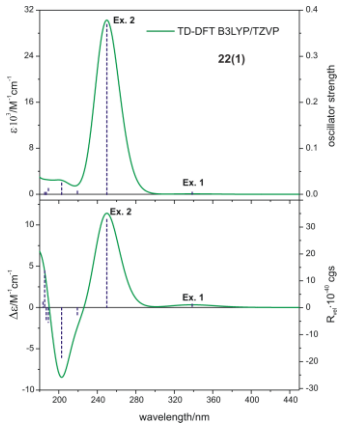
Cartesian coordinates for individual conformers of compound 22.

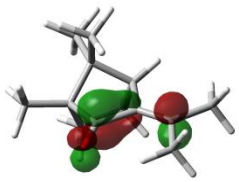
Input orientation of compound **22** conf.1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.313085	0.149748	-1.703548
2	6	0	0.489692	-1.168461	-1.657342
3	6	0	1.280711	0.679609	-0.230312

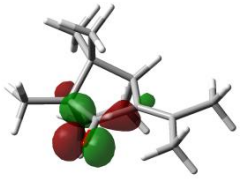
4	6	0	-0.167545	1.155345	-0.058759
5	6	0	-1.003503	-0.083847	-0.032866
6	6	0	0.008894	-1.210462	-0.183198
7	6	0	1.242717	-0.653325	0.595441
8	1	0	0.899969	0.883956	-2.397295
9	1	0	2.346931	-0.025130	-2.003823
10	1	0	1.105906	-2.035272	-1.898060
11	1	0	-0.350975	-1.162081	-2.350978
12	1	0	-0.333451	-2.187821	0.149470
13	6	0	2.502825	-1.517423	0.463756
14	6	0	0.972300	-0.445304	2.092543
15	6	0	2.329720	1.722530	0.093803
16	6	0	-2.343619	-0.171877	0.067630
17	6	0	-3.251085	1.018980	0.211610
18	6	0	-3.071666	-1.487812	0.046366
19	8	0	-0.515147	2.324209	0.009892
20	1	0	2.817141	-1.682482	-0.565215
21	1	0	2.329051	-2.496526	0.918340
22	1	0	3.338704	-1.055698	0.994414
23	1	0	0.821049	-1.409918	2.583686
24	1	0	0.089647	0.164854	2.287967
25	1	0	1.825131	0.037717	2.574737
26	1	0	2.206779	2.602578	-0.540827
27	1	0	3.334623	1.328239	-0.070444
28	1	0	2.258340	2.054656	1.131576
29	1	0	-2.713994	1.960866	0.185298
30	1	0	-3.804221	0.949515	1.154375
31	1	0	-4.002217	1.010233	-0.584890
32	1	0	-3.674113	-1.599100	0.953521
33	1	0	-2.414335	-2.349348	-0.038519
34	1	0	-3.773947	-1.509126	-0.793206

Computed UV (top) and ECD (bottom) spectra of conformer 22(1) of compound 22

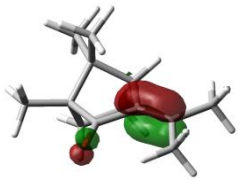




LUMO (orb. 54)



HOMO (orb. 53)



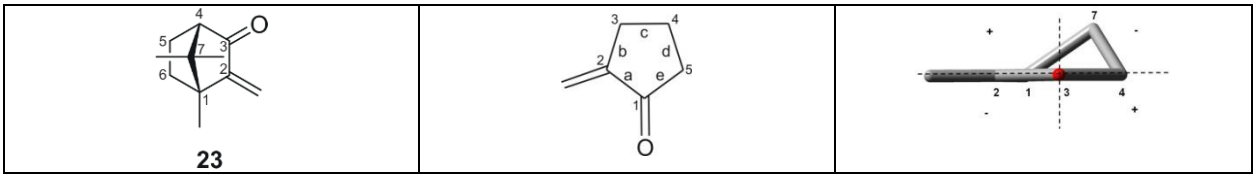
HOMO-1 (orb. 52)

Conformer 22(1)

Excited State 1: 338.61 nm f=0.0010 Rotatory Strength (*R*) 1.8204
52 -> 54 0.11060
53 -> 54 0.69207
Excited State 2: 249.76 nm f=0.3690 Rotatory Strength (*R*) 33.1651
52 -> 54 0.69083
53 -> 54 -0.10880

Conformational and spectral analysis of 23 in acetonitrile

For model compound **23** one conformer in the range of 0-5 kcal/mol was found.



Overview of the conformational analysis for conformer 23(1) of compound 23.

Conformer	ΔG (kcal.mol^{-1})	Population (%)	Torsion angles [°]					
			enone	a	b	c	d	e
23(1)	0.00	100.0	+0.9	−0.2	−34.1	+53.2	−53.8	+35.2

Calculated at B3LYP/TZVP level of theory total energies, relative energies and conformer distribution at 25° C for individual conformers of compound 23.

Conformer	Energy [Hartree]	ΔG [kcal mol^{-1}]	Distribution [%]
1	-503.975761	0.00	100.0

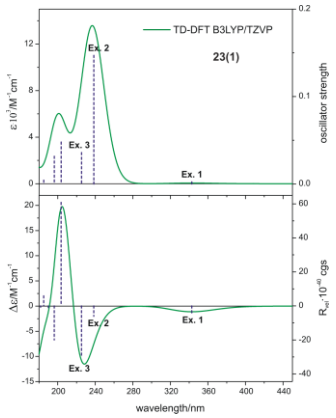
Cartesian coordinates for individual conformers of compound 23.

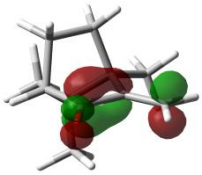
Input orientation of compound **23** conf.1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.502196	0.284428	-1.748301
2	6	0	0.206910	-1.236017	-1.606938
3	6	0	0.357161	0.833976	-0.295171
4	6	0	-1.127613	0.713725	0.015498
5	6	0	-1.385537	-0.759977	0.161050
6	6	0	-0.039311	-1.415294	-0.078669
7	6	0	0.929617	-0.371900	0.556216
8	1	0	-0.188911	0.785420	-2.426311
9	1	0	1.510929	0.464676	-2.121391
10	1	0	1.053263	-1.846321	-1.920252
11	1	0	-0.654162	-1.555323	-2.195165
12	1	0	0.022747	-2.440612	0.280985
13	6	0	2.410564	-0.679497	0.307582
14	6	0	0.727545	-0.216452	2.070143
15	6	0	0.969030	2.205679	-0.081883
16	8	0	-2.449106	-1.300981	0.398450
17	6	0	-2.060748	1.650685	0.149410
18	1	0	2.664408	-0.795551	-0.744343
19	1	0	2.686520	-1.605026	0.818834
20	1	0	3.037438	0.116464	0.715451
21	1	0	1.020115	-1.135430	2.583563

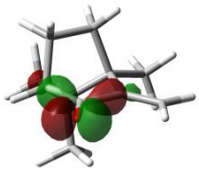
22	1	0	-0.305201	0.002432	2.345498
23	1	0	1.350592	0.591266	2.460475
24	1	0	0.511482	2.943732	-0.745284
25	1	0	2.038699	2.192561	-0.299489
26	1	0	0.833261	2.552547	0.944664
27	1	0	-1.841866	2.706806	0.050471
28	1	0	-3.085350	1.374066	0.371068

Computed UV (top) and ECD (bottom) spectra of conformer 23(1) of compound 23

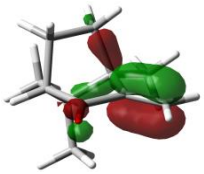




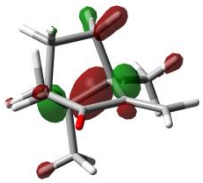
LUMO (orb. 46)



HOMO (orb. 45)



HOMO-1 (orb. 44)



HOMO-2 (orb. 43)

Conformer 23(1)

Excited State 1: 342.80 nm f=0.0007 Rotatory Strength (*R*) -5.1445
45 -> 46 0.69968
Excited State 2: 238.40 nm f=0.1471 Rotatory Strength (*R*) -6.4744
43 -> 46 -0.24267
44 -> 46 0.65364
Excited State 3: 225.21 nm f=0.0360 Rotatory Strength (*R*) -28.5097
43 -> 46 0.65479
44 -> 46 0.22287

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