

# **The assignment of the absolute configuration of non-cyclic sesquiterpenes by vibrational and electronic circular dichroism: the example of chiliadenus lopadusanus metabolites**

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TABLE S1

Isomer	S.I.(1.00)	S.I.(0.99)	S.I.(0.98)	S.I.(0.97)	S.I.(0.96)	S.I.(0.95)	$\Delta G$ spectra average
(3S,9R)	0.10	0.31	0.42	0.27	0.12	0.08	
(3S,9S)	0.03	-0.06	-0.04	0.24	0.19	-0.02	
Isomer	Sim_NN(1.00)	Sim_NN(0.99)	Sim_NN(0.98)	Sim_NN(0.97)	Sim_NN(0.96)	Sim_NN(0.95)	
(3S,9R)	0.05	0.18	0.26	0.15	0.07	0.04	
(3S,9S)	0.01	-0.03	-0.02	0.13	0.10	-0.01	

Isomer	S.I.(1.00)	S.I.(0.99)	S.I.(0.98)	S.I.(0.97)	S.I.(0.96)	S.I.(0.95)	$\Delta E$ spectra average
(3S,9R)	0.22	0.38	0.54	0.29	0.08	0.10	
(3S,9S)	-0.04	-0.10	0.04	0.26	0.28	0.09	
Isomer	Sim_NN(1.00)	Sim_NN(0.99)	Sim_NN(0.98)	Sim_NN(0.97)	Sim_NN(0.96)	Sim_NN(0.95)	
(3S,9R)	0.12	0.22	0.34	0.16	0.04	0.05	
(3S,9S)	-0.04	-0.05	0.02	0.15	0.16	0.05	

Isomer	S.I.(1.00)	S.I.(0.99)	S.I.(0.98)	S.I.(0.97)	S.I.(0.96)	S.I.(0.95)	$\Delta G$ spectra average
(3R,9S)	-0.10	-0.31	-0.42	-0.27	-0.12	-0.01	
(3R,9R)	-0.03	0.06	0.04	-0.24	-0.19	0.02	
Isomer	Sim_NN(1.00)	Sim_NN(0.99)	Sim_NN(0.98)	Sim_NN(0.97)	Sim_NN(0.96)	Sim_NN(0.95)	
(3R,9S)	-0.05	-0.18	-0.26	-0.15	-0.07	-0.03	
(3R,9R)	-0.01	0.03	0.02	-0.13	-0.10	0.01	

Isomer	S.I.(1.00)	S.I.(0.99)	S.I.(0.98)	S.I.(0.97)	S.I.(0.96)	S.I.(0.95)	$\Delta E$ spectra average
(3R,9S)	-0.22	-0.43	-0.54	-0.29	-0.08	-0.15	
(3R,9R)	0.08	0.10	-0.04	-0.26	-0.28	-0.09	
Isomer	Sim_NN(1.00)	Sim_NN(0.99)	Sim_NN(0.98)	Sim_NN(0.97)	Sim_NN(0.96)	Sim_NN(0.95)	
(3R,9S)	-0.12	-0.25	-0.34	-0.16	-0.04	-0.08	
(3R,9R)	0.04	0.05	-0.02	-0.15	-0.16	-0.05	

FIGURE S1

Isomer	S.I.(1.00)	S.I.(0.99)	S.I.(0.98)	S.I.(0.97)	S.I.(0.96)	S.I.(0.95)	$\Delta G$ spectra average
(3S,9R)	0.10	0.31	0.42	0.27	0.12	0.08	
(3S,9S)	0.03	-0.06	-0.04	0.24	0.19	-0.02	
Isomer	Sim_NN(1.00)	Sim_NN(0.99)	Sim_NN(0.98)	Sim_NN(0.97)	Sim_NN(0.96)	Sim_NN(0.95)	
(3S,9R)	0.05	0.18	0.26	0.15	0.07	0.04	
(3S,9S)	0.01	-0.03	-0.02	0.13	0.10	-0.01	

Isomer	S.I.(1.00)	S.I.(0.99)	S.I.(0.98)	S.I.(0.97)	S.I.(0.96)	S.I.(0.95)	$\Delta E$ spectra average
(3S,9R)	0.22	0.38	0.54	0.29	0.08	0.10	
(3S,9S)	-0.04	-0.10	0.04	0.26	0.28	0.09	
Isomer	Sim_NN(1.00)	Sim_NN(0.99)	Sim_NN(0.98)	Sim_NN(0.97)	Sim_NN(0.96)	Sim_NN(0.95)	
(3S,9R)	0.12	0.22	0.34	0.16	0.04	0.05	
(3S,9S)	-0.04	-0.05	0.02	0.15	0.16	0.05	

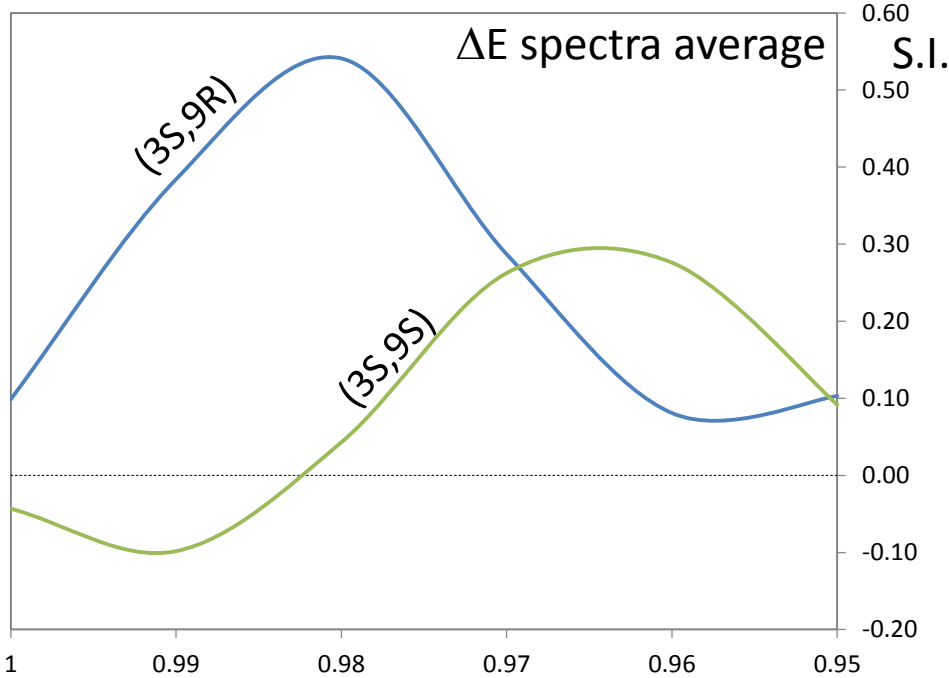
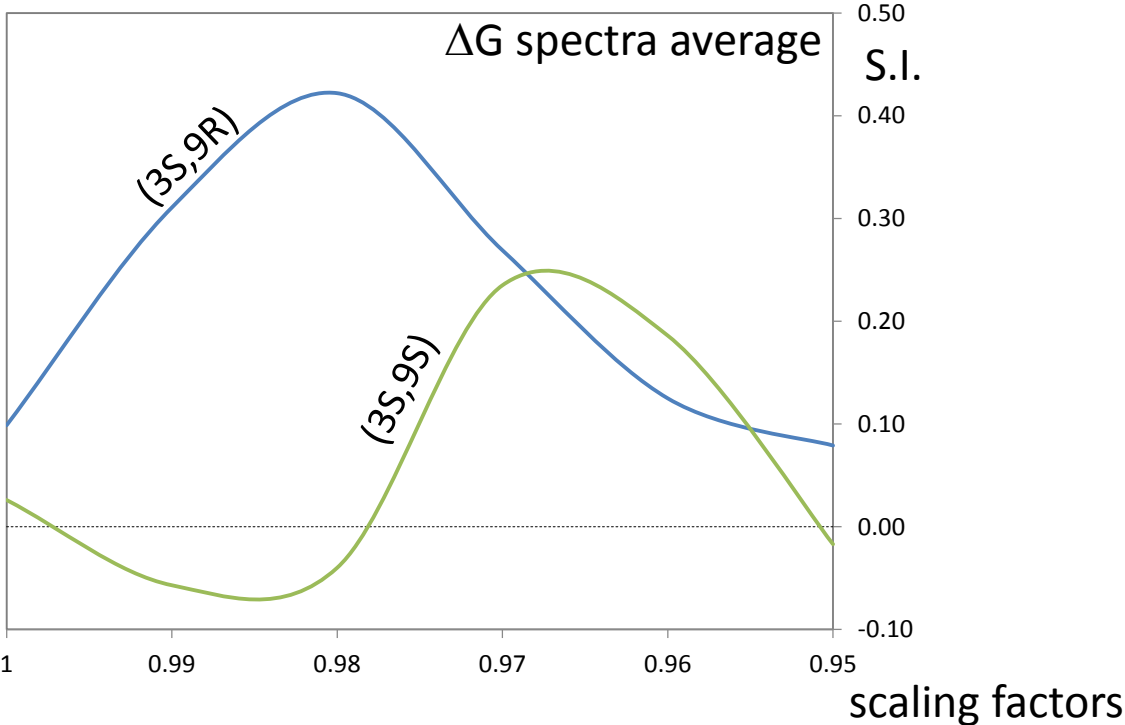


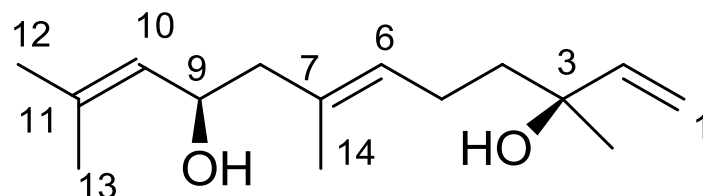
TABLE S2

1: AC (3*S*,9*R*) Computed Poputation Factors $\Delta E$ 

CONFORMERS	$\Delta E$	% pop
337	0.000000	12.5
44	0.042573	11.7
360	0.134554	10.0
23	0.307920	7.5
21	0.307982	7.5
26	0.328297	7.2
6	0.329300	7.2
79	0.329551	7.2
58	0.486803	5.5
18	0.559409	4.9
165	0.947522	2.5
124	0.981757	2.4
323	1.104899	1.9
196	1.230111	1.6
118	1.334256	1.3
250	1.403289	1.2
60	1.432820	1.1
19	1.568879	0.9
81	1.596844	0.8
227	1.663368	0.8
59	1.681802	0.7
262	1.879683	0.5
104	1.909842	0.5
269	1.967150	0.5
80	1.975928	0.4
154	1.978248	0.4
65	1.978310	0.4
2	2.169545	0.3
28	2.188669	0.3
127	2.400971	0.2

Conformational Search B3LYP/6-31G\* on 368 conformers.  
 Re-optimized with frequency calculated at B3LYP/6-311++G(2d,p)

§ Original numbering of the conformers from the MM conformational search has been maintained



1, CL1, 9-Hydroxynerylolidol

 $\Delta G$ 

CONFORMERS	$\Delta G$	% pop
337	0.000000	28.1
360	0.030723	26.7
323	0.779361	7.5
104	1.010097	5.1
80	1.065273	4.7
79	1.106655	4.3
23	1.136124	4.1
6	1.350558	2.9
44	1.586937	1.9
18	1.622049	1.8
227	1.636470	1.8
59	1.673463	1.7
269	1.701051	1.6
58	1.771902	1.4
26	1.826451	1.3
165	2.101077	0.8
124	2.129292	0.8
21	2.215191	0.7
118	2.361909	0.5
60	2.415204	0.5
196	2.597034	0.4
28	2.650956	0.3
81	2.855358	0.2
262	2.980758	0.2
65	2.982012	0.2
154	2.985147	0.2
250	3.069792	0.2
19	3.377022	0.1
2	3.546312	0.1
127	3.853542	0.0

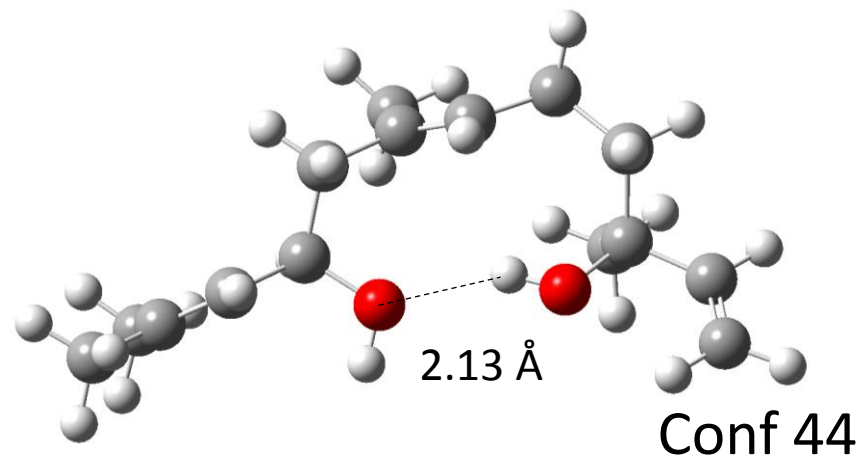
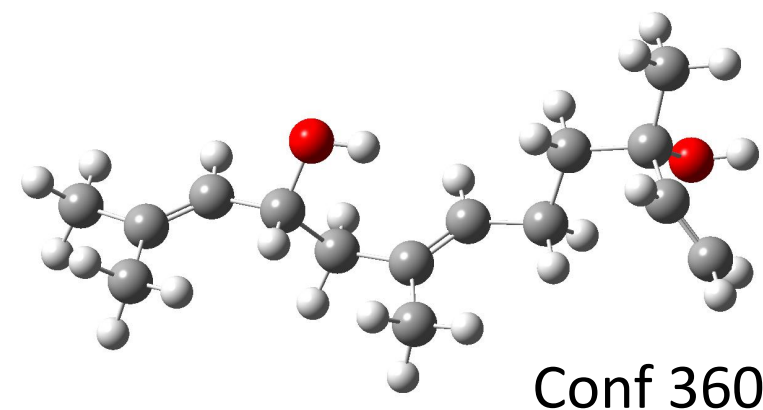
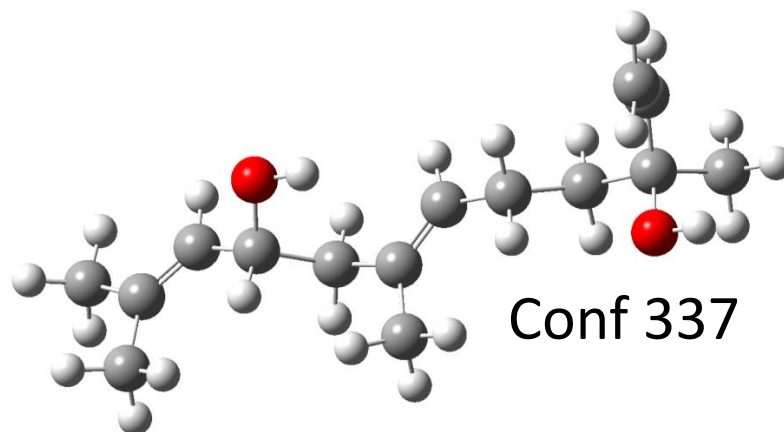
(3*S*,9*R*)-1

FIGURE S2

# Populations; Conformers for ( $\geq 10\%$ )-P.F.-based on $\Delta E$

CONFORMERS     $\Delta E$     % pop

337	0.000000	12.5
44	0.042573	11.7
360	0.134554	10.0
23	0.307920	7.5
21	0.307982	7.5
26	0.328297	7.2
6	0.329300	7.2
79	0.329551	7.2
58	0.486803	5.5
18	0.559409	4.9
165	0.947522	2.5
124	0.981757	2.4
323	1.104899	1.9
196	1.230111	1.6
118	1.334256	1.3
250	1.403289	1.2
60	1.432820	1.1
19	1.568879	0.9
81	1.596844	0.8
227	1.663368	0.8
59	1.681802	0.7
262	1.879683	0.5
104	1.909842	0.5
269	1.967150	0.5
80	1.975928	0.4
154	1.978248	0.4
65	1.978310	0.4
2	2.169545	0.3
28	2.188669	0.3
127	2.400971	0.2



(3*S*,9*R*)-1

FIGURE S3

Populations; Conformers for P.F. (9%-5%) based on  $\Delta E$  $\Delta E$ 

CONFORMERS	$\Delta E$	% pop
337	0.000000	12.5
44	0.042573	11.7
360	0.134554	10.0
23	0.307920	7.5
21	0.307982	7.5
26	0.328297	7.2
6	0.329300	7.2
79	0.329551	7.2
58	0.486803	5.5
18	0.559409	4.9
165	0.947522	2.5
124	0.981757	2.4
323	1.104899	1.9
196	1.230111	1.6
118	1.334256	1.3
250	1.403289	1.2
60	1.432820	1.1
19	1.568879	0.9
81	1.596844	0.8
227	1.663368	0.8
59	1.681802	0.7
262	1.879683	0.5
104	1.909842	0.5
269	1.967150	0.5
80	1.975928	0.4
154	1.978248	0.4
65	1.978310	0.4
2	2.169545	0.3
28	2.188669	0.3
127	2.400971	0.2

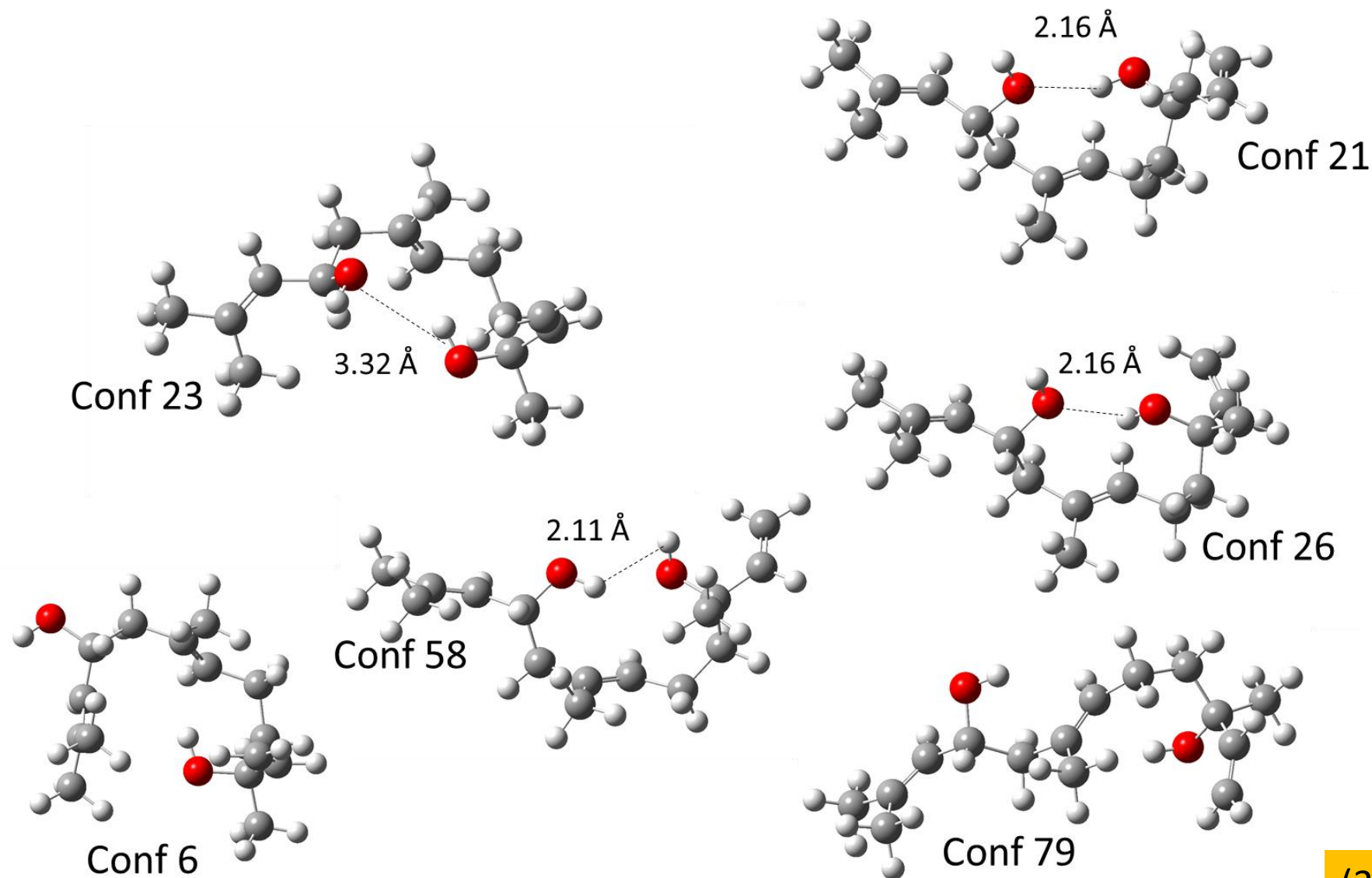
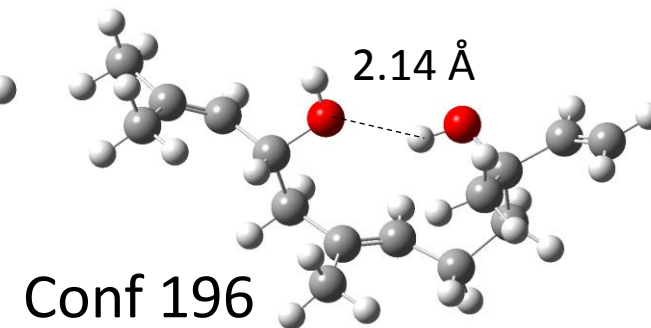
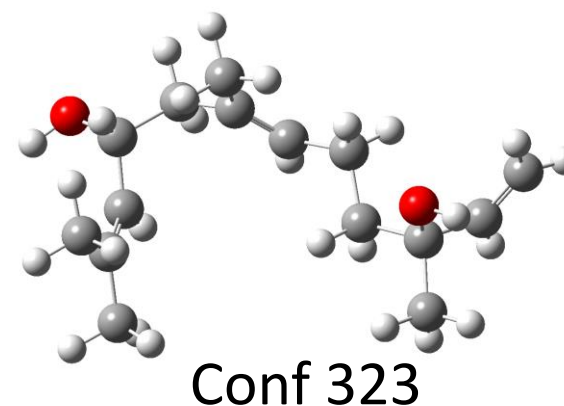
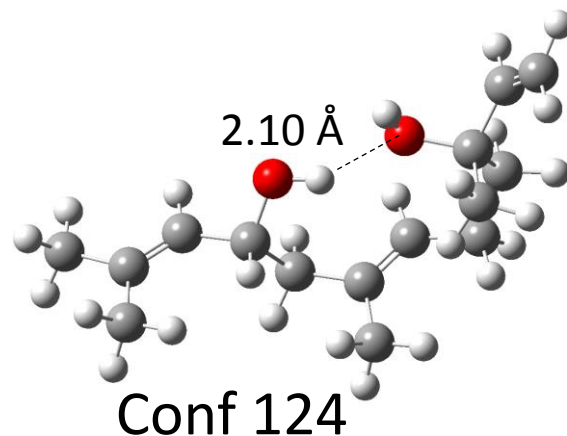
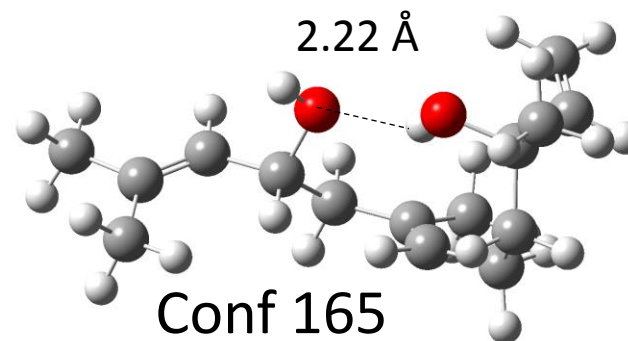
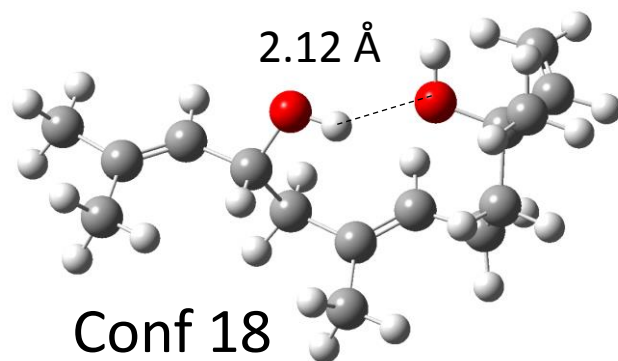
(3*S*,9*R*)-1

FIGURE S4

# Populations; Conformers for P.F. (5%-1.5%) based on $\Delta E$

CONFORMERS     $\Delta E$     % pop

337	0.000000	12.5
44	0.042573	11.7
360	0.134554	10.0
23	0.307920	7.5
21	0.307982	7.5
26	0.328297	7.2
6	0.329300	7.2
79	0.329551	7.2
58	0.486803	5.5
18	0.559409	4.9
165	0.947522	2.5
124	0.981757	2.4
323	1.104899	1.9
196	1.230111	1.6
118	1.334256	1.3
250	1.403289	1.2
60	1.432820	1.1
19	1.568879	0.9
81	1.596844	0.8
227	1.663368	0.8
59	1.681802	0.7
262	1.879683	0.5
104	1.909842	0.5
269	1.967150	0.5
80	1.975928	0.4
154	1.978248	0.4
65	1.978310	0.4
2	2.169545	0.3
28	2.188669	0.3
127	2.400971	0.2



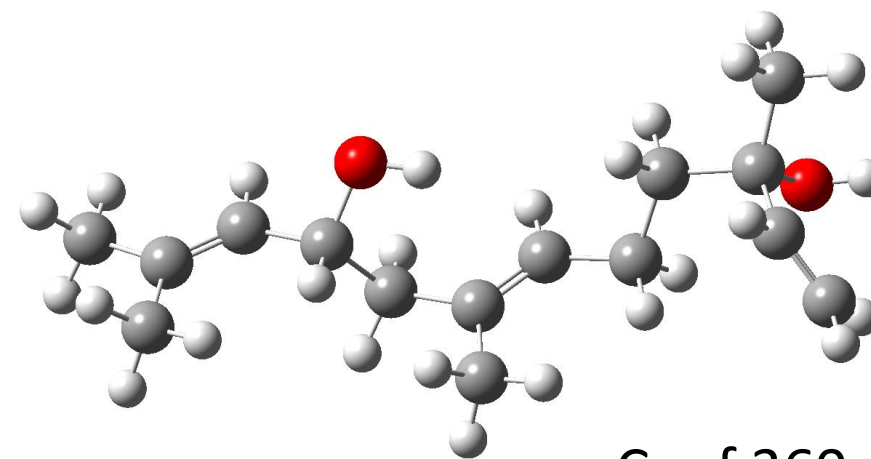
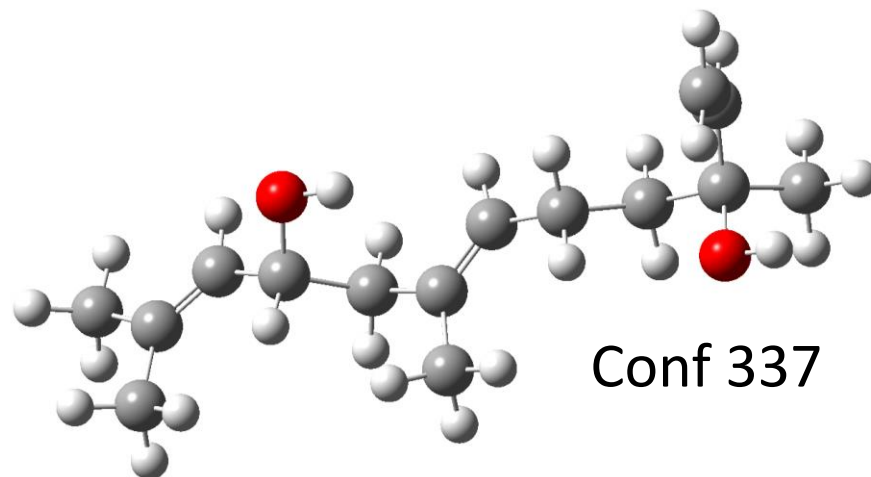
(3*S*,9*R*)-1



FIGURE S5

Populations; Conformers for ( $\geq 20\%$ )-P.F.-based on  $\Delta G$  $\Delta G$ 

CONFORMERS	$\Delta G$	% pop
337	0.000000	28.1
360	0.030723	26.7
323	0.779361	7.5
104	1.010097	5.1
80	1.065273	4.7
79	1.106655	4.3
23	1.136124	4.1
6	1.350558	2.9
44	1.586937	1.9
18	1.622049	1.8
227	1.636470	1.8
59	1.673463	1.7
269	1.701051	1.6
58	1.771902	1.4
26	1.826451	1.3
165	2.101077	0.8
124	2.129292	0.8
21	2.215191	0.7
118	2.361909	0.5
60	2.415204	0.5
196	2.597034	0.4
28	2.650956	0.3
81	2.855358	0.2
262	2.980758	0.2
65	2.982012	0.2
154	2.985147	0.2
250	3.069792	0.2
19	3.377022	0.1
2	3.546312	0.1
127	3.853542	0.0



Conf 360

(3*S*,9*R*)-1

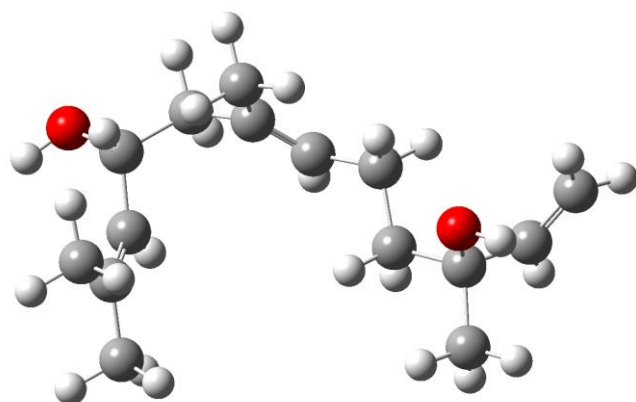


FIGURE S6

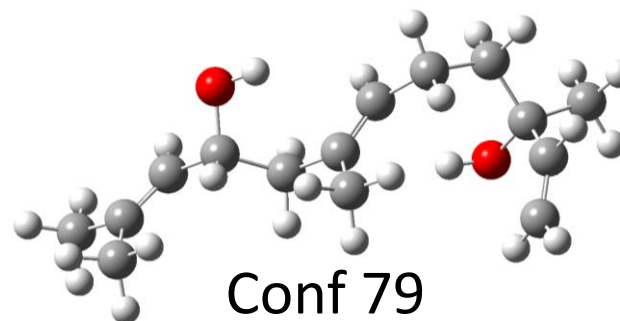
# Populations; Conformers for (9% – 2%)P.F.-based on $\Delta G$

 $\Delta G$ 

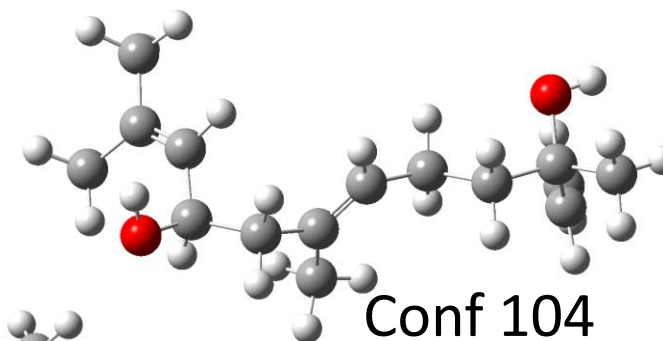
CONFORMERS	$\Delta G$	% pop
337	0.000000	28.1
360	0.030723	26.7
323	0.779361	7.5
104	1.010097	5.1
80	1.065273	4.7
79	1.106655	4.3
23	1.136124	4.1
6	1.350558	2.9
44	1.586937	1.9
18	1.622049	1.8
227	1.636470	1.8
59	1.673463	1.7
269	1.701051	1.6
58	1.771902	1.4
26	1.826451	1.3
165	2.101077	0.8
124	2.129292	0.8
21	2.215191	0.7
118	2.361909	0.5
60	2.415204	0.5
196	2.597034	0.4
28	2.650956	0.3
81	2.855358	0.2
262	2.980758	0.2
65	2.982012	0.2
154	2.985147	0.2
250	3.069792	0.2
19	3.377022	0.1
2	3.546312	0.1
127	3.853542	0.0



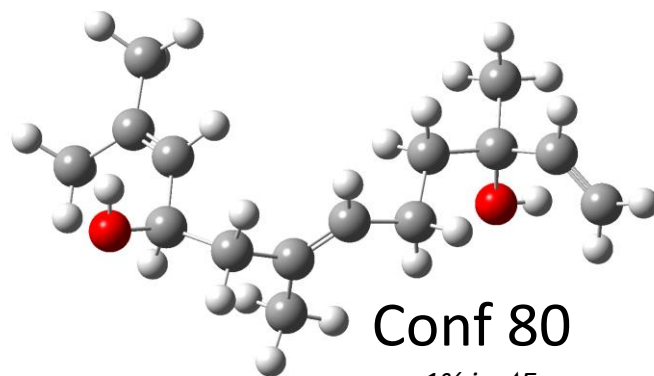
Conf 323



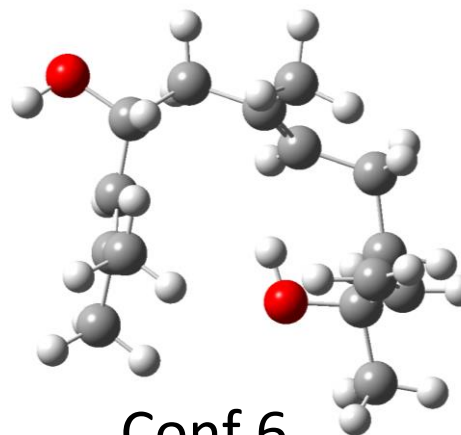
Conf 79



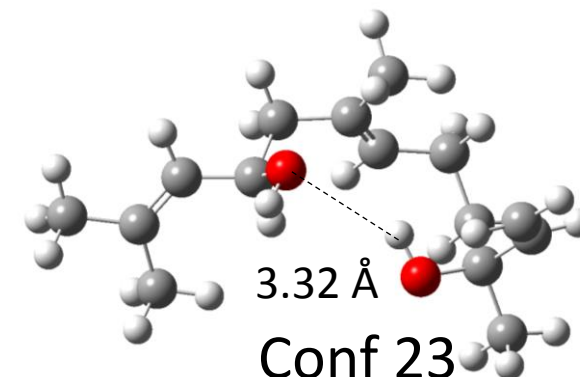
Conf 104

<1% in  $\Delta E$ 

Conf 80

<1% in  $\Delta E$ 

Conf 6



3.32 Å

Conf 23

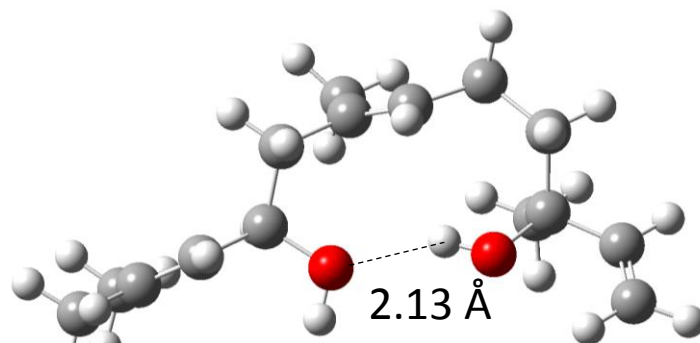
(3*S*,9*R*)-1

FIGURE S7

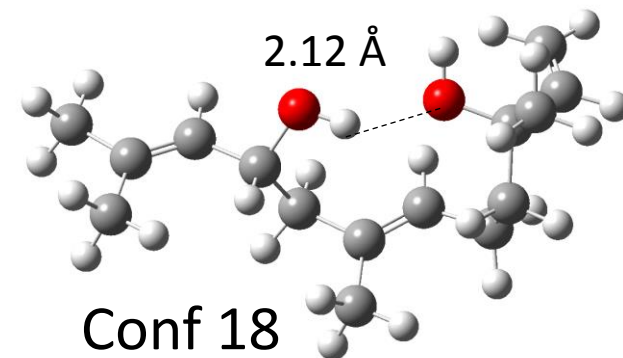
# Populations; Conformers for (2% – 1%)P.F.-based on $\Delta G$

## $\Delta G$

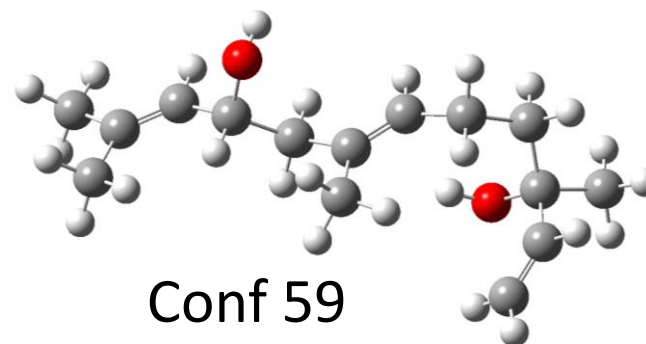
CONFORMERS	$\Delta G$	% pop
337	0.000000	28.1
360	0.030723	26.7
323	0.779361	7.5
104	1.010097	5.1
80	1.065273	4.7
79	1.106655	4.3
23	1.136124	4.1
6	1.350558	2.9
44	1.586937	1.9
18	1.622049	1.8
227	1.636470	1.8
59	1.673463	1.7
269	1.701051	1.6
58	1.771902	1.4
26	1.826451	1.3
165	2.101077	0.8
124	2.129292	0.8
21	2.215191	0.7
118	2.361909	0.5
60	2.415204	0.5
196	2.597034	0.4
28	2.650956	0.3
81	2.855358	0.2
262	2.980758	0.2
65	2.982012	0.2
154	2.985147	0.2
250	3.069792	0.2
19	3.377022	0.1
2	3.546312	0.1
127	3.853542	0.0



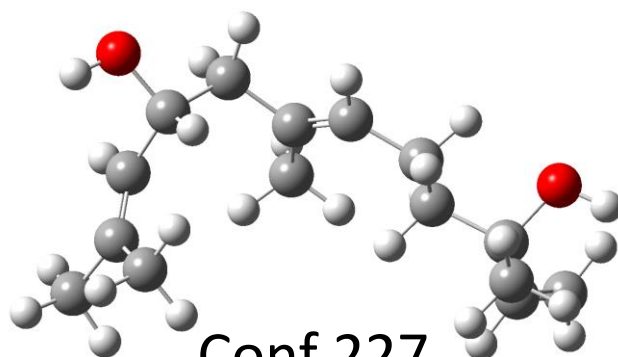
Conf 44

11.7% in  $\Delta E$ 

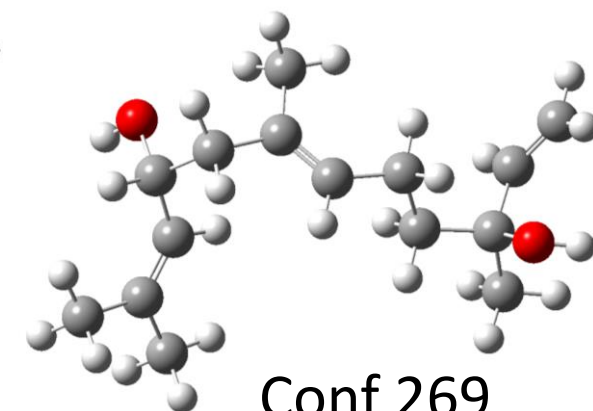
Conf 18



Conf 59

<1% in  $\Delta E$ 

Conf 227

<1% in  $\Delta E$ 

Conf 269

<1% in  $\Delta E$ 

(3S,9R)-1

TABLE S3

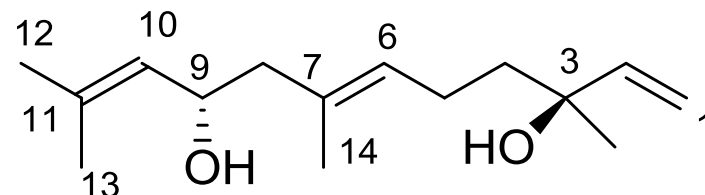
# 1: AC (3S,9S) Computed Poputation Factors

Conformational Search B3LYP/6-31G\* on 264 conformers.

Re-optimized with frequency calculated at B3LYP/6-311++G(2d,p)

§ Original numbering of the conformers from the MM conformational search has been maintained

$\Delta E$		
CONFORMERS	$\Delta E$	% pop
16	0.000000	45.8
1	0.732775	13.3
4	0.742180	13.1
61	1.209358	6.0
38	1.271870	5.4
57	1.512324	3.6
90	1.643367	2.9
2	1.684373	2.7
153	1.800368	2.2
85	1.967526	1.7
24	2.009472	1.5
14	2.208921	1.1
48	2.655157	0.5
115	2.944643	0.3
240	4.159581	0.0



**1, CL1, 9-Hydroxynerylidol**

$\Delta G$		
CONFORMERS	$\Delta G$	% pop
4	0.000000	73.4
1	0.732775	9.9
38	0.742180	5.3
57	1.209358	3.2
16	1.271870	1.5
61	1.512324	1.5
14	1.643367	1.4
2	1.684373	1.2
90	1.800368	0.8
153	1.967526	0.6
24	2.009472	0.6
85	2.208921	0.3
48	2.655157	0.2
115	2.944643	0.1
240	4.159581	0.1

FIGURE S8

# Populations; Conformers for ( $\geq 20\%$ )-P.F.-based on $\Delta E$

 $\Delta E$ 

CONFORMERS	$\Delta E$	% pop
16	0.000000	45.8
1	0.732775	13.3
4	0.742180	13.1
61	1.209358	6.0
38	1.271870	5.4
57	1.512324	3.6
90	1.643367	2.9
2	1.684373	2.7
153	1.800368	2.2
85	1.967526	1.7
24	2.009472	1.5
14	2.208921	1.1
48	2.655157	0.5
115	2.944643	0.3
240	4.159581	0.0

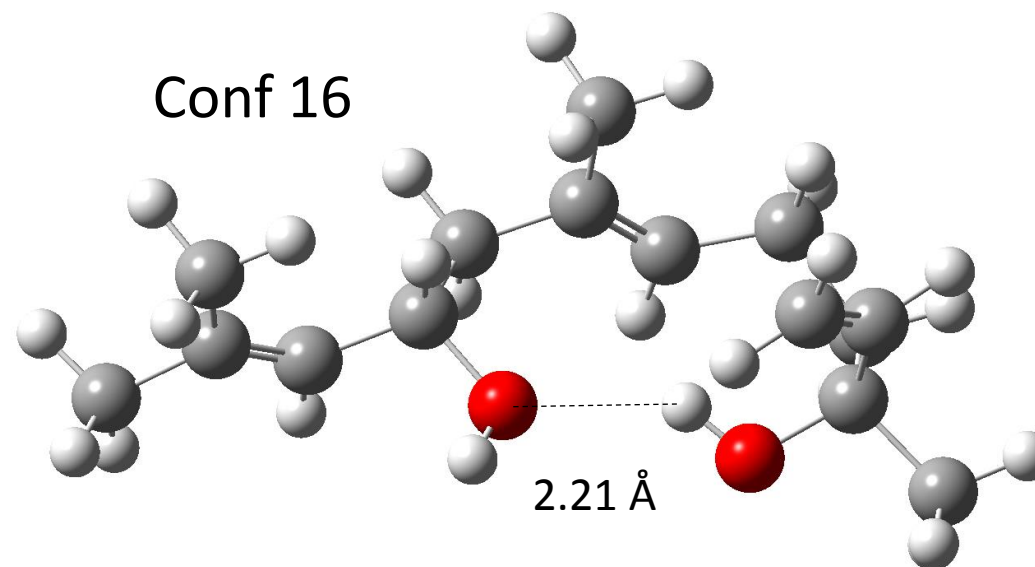


FIGURE S9

Populations; Conformers for (20%-10%)-P.F.-based on  $\Delta E$  $\Delta E$ 

CONFORMERS	$\Delta E$	% pop
16	0.000000	45.8
1	0.732775	13.3
4	0.742180	13.1
61	1.209358	6.0
38	1.271870	5.4
57	1.512324	3.6
90	1.643367	2.9
2	1.684373	2.7
153	1.800368	2.2
85	1.967526	1.7
24	2.009472	1.5
14	2.208921	1.1
48	2.655157	0.5
115	2.944643	0.3
240	4.159581	0.0

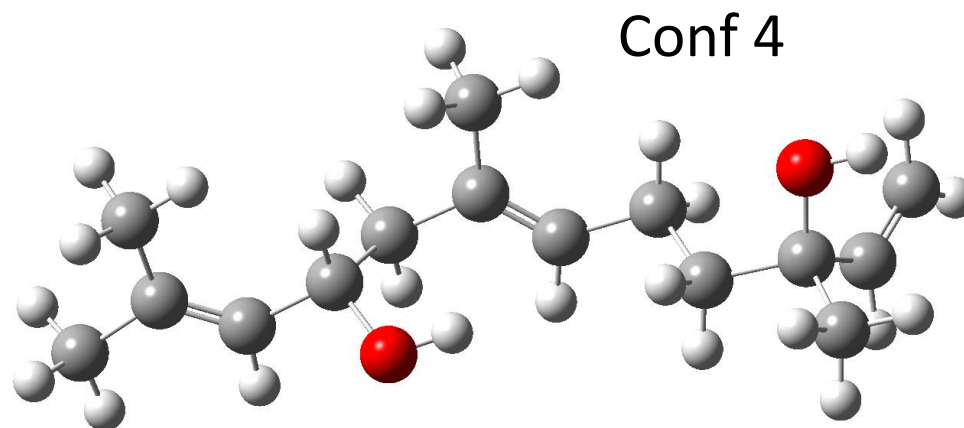
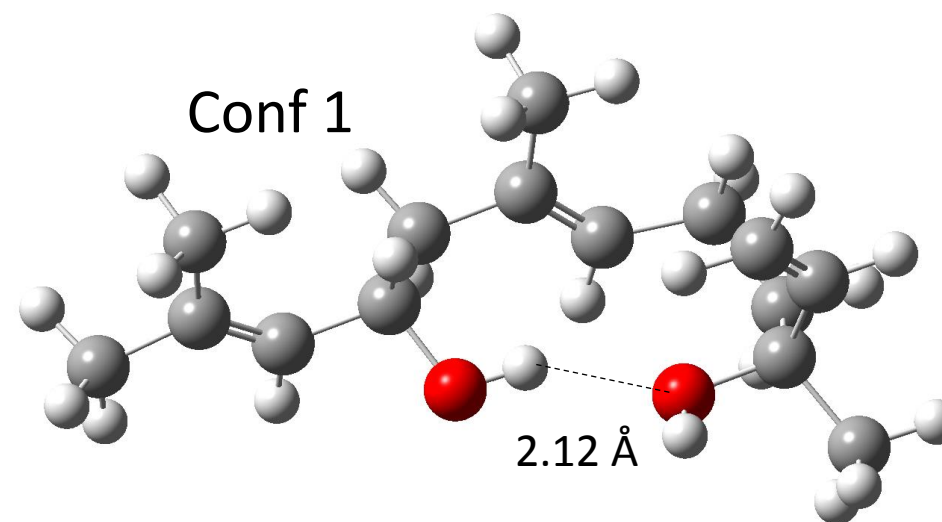


FIGURE S10

# Populations; Conformers for P.F. (10%-3%) based on $\Delta E$

 $\Delta E$ 

CONFORMERS	$\Delta E$	% pop
16	0.000000	45.8
1	0.732775	13.3
4	0.742180	13.1
61	1.209358	6.0
38	1.271870	5.4
57	1.512324	3.6
90	1.643367	2.9
2	1.684373	2.7
153	1.800368	2.2
85	1.967526	1.7
24	2.009472	1.5
14	2.208921	1.1
48	2.655157	0.5
115	2.944643	0.3
240	4.159581	0.0

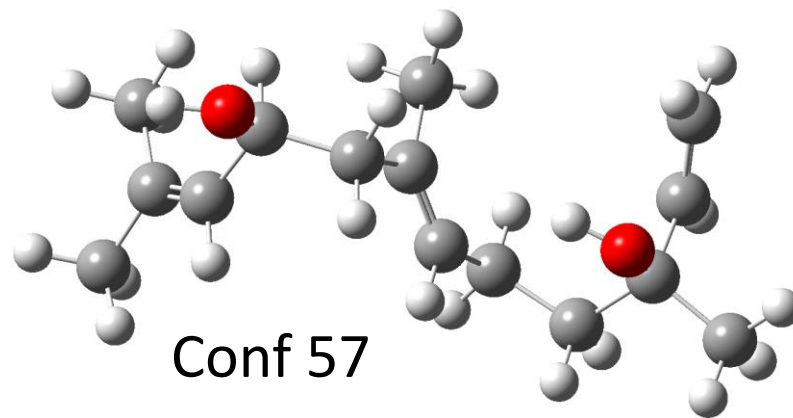
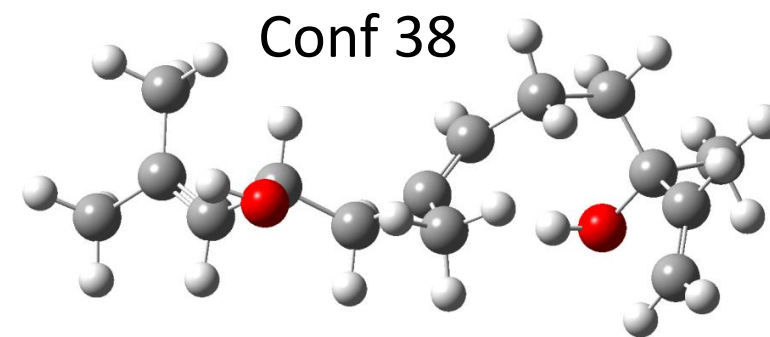
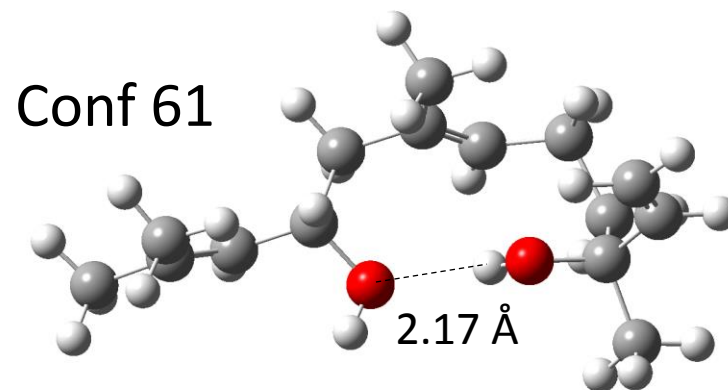




FIGURE S11

Populations; Conformers for P.F. based on  $\Delta E$  (<3%) $\Delta E$ **CONFORMERS**    $\Delta E$    % pop

16	0.000000	45.8
1	0.732775	13.3
4	0.742180	13.1
61	1.209358	6.0
38	1.271870	5.4
57	1.512324	3.6
90	1.643367	2.9
2	1.684373	2.7
153	1.800368	2.2
85	1.967526	1.7
24	2.009472	1.5
14	2.208921	1.1
48	2.655157	0.5
115	2.944643	0.3
240	4.159581	0.0

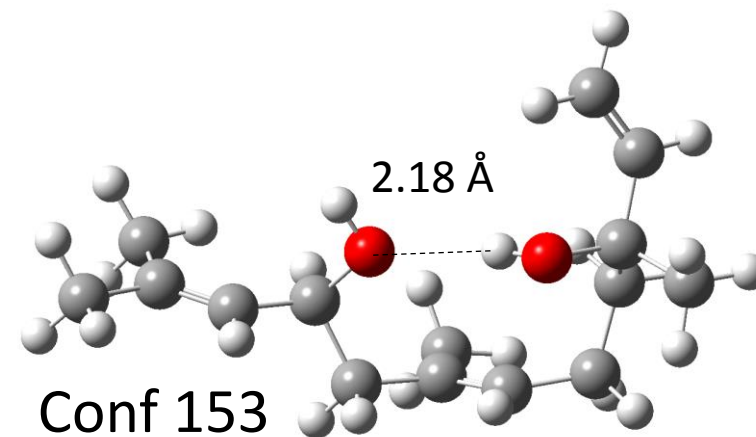
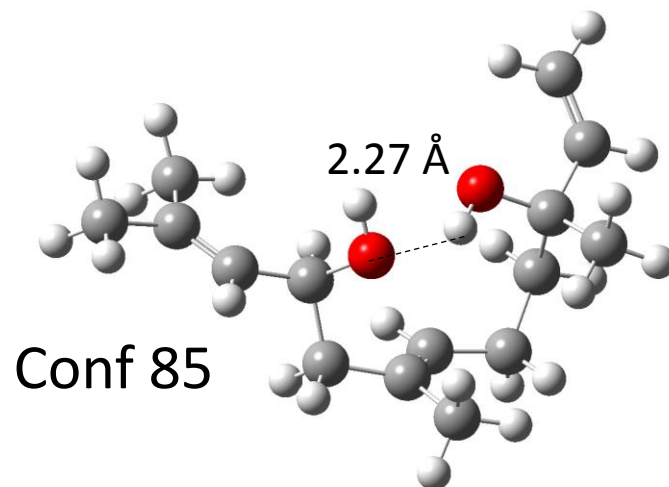
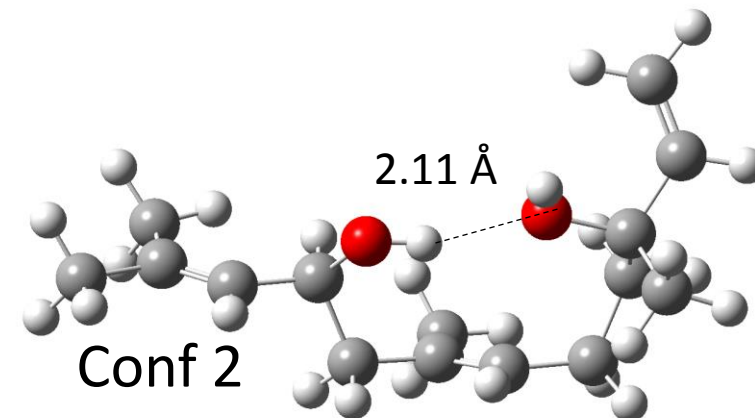
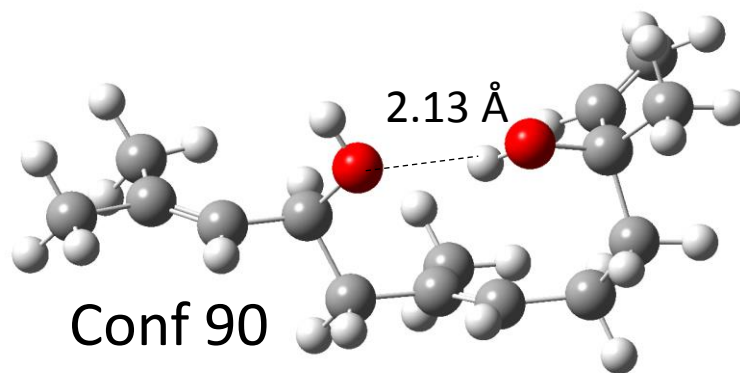




FIGURE S12

# Populations; Conformers for ( $\geq 20\%$ )-P.F.-based on $\Delta G$

 $\Delta G$ 

CONFORMERS	$\Delta G$	% pop
4	0.000000	73.4
1	0.732775	9.9
38	0.742180	5.3
57	1.209358	3.2
16	1.271870	1.5
61	1.512324	1.5
14	1.643367	1.4
2	1.684373	1.2
90	1.800368	0.8
153	1.967526	0.6
24	2.009472	0.6
85	2.208921	0.3
48	2.655157	0.2
115	2.944643	0.1
240	4.159581	0.1

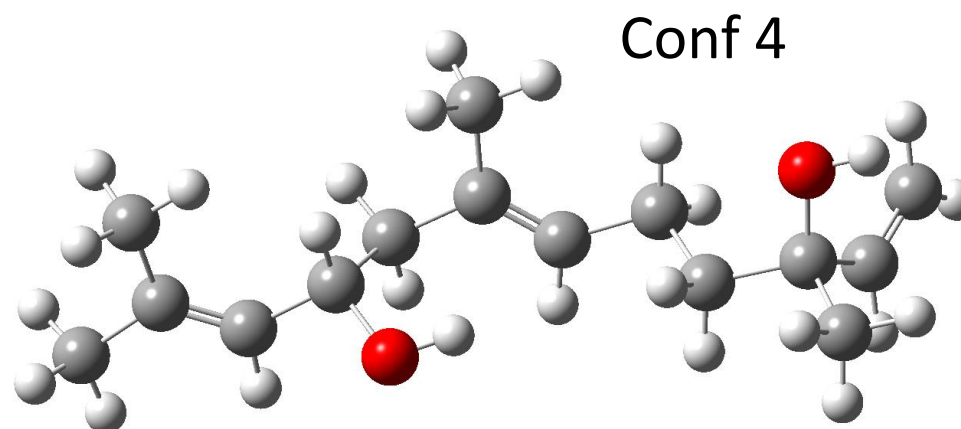
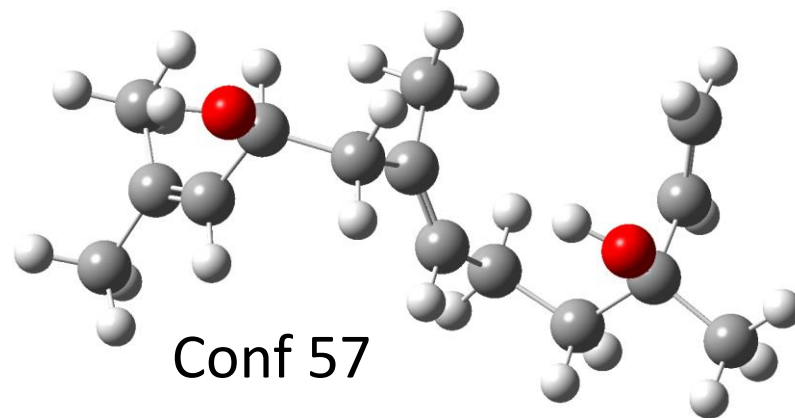
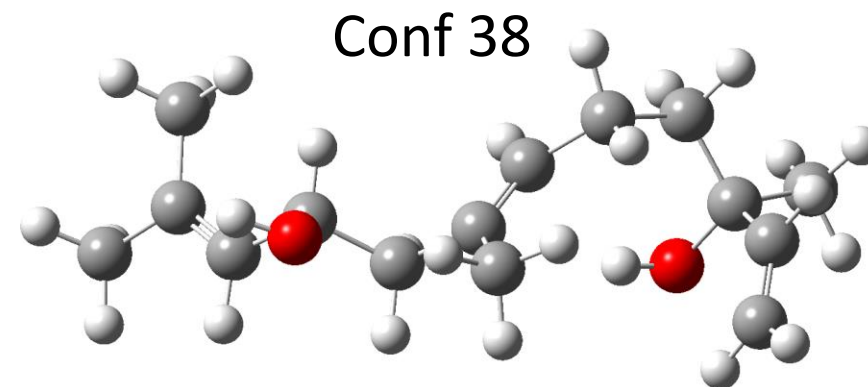
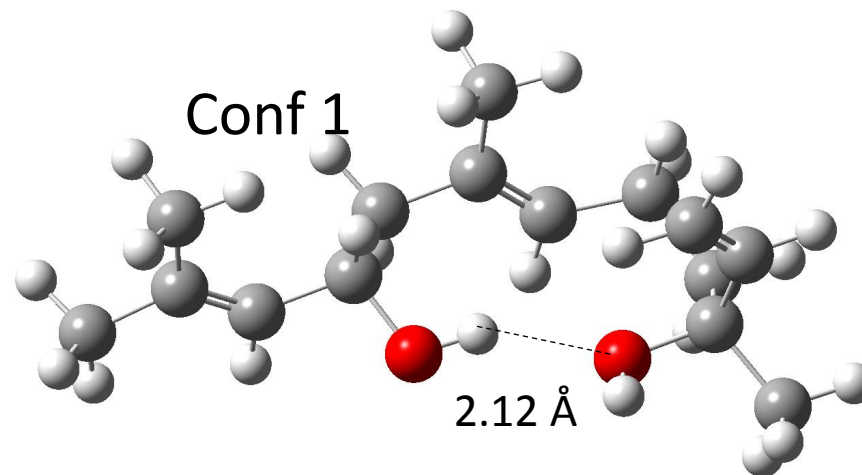


FIGURE S13

Populations; Conformers for (10%-3%) based on  $\Delta G$ 

$\Delta G$		
CONFORMERS	$\Delta G$	% pop
4	0.000000	73.4
1	0.732775	9.9
38	0.742180	5.3
57	1.209358	3.2
16	1.271870	1.5
61	1.512324	1.5
14	1.643367	1.4
2	1.684373	1.2
90	1.800368	0.8
153	1.967526	0.6
24	2.009472	0.6
85	2.208921	0.3
48	2.655157	0.2
115	2.944643	0.1
240	4.159581	0.1



(3S,9S)-1

FIGURE S14

Populations; Conformers for (3%-1%) based on  $\Delta G$ 

$\Delta G$		
CONFORMERS	$\Delta G$	% pop
4	0.000000	73.4
1	0.732775	9.9
38	0.742180	5.3
57	1.209358	3.2
16	1.271870	1.5
61	1.512324	1.5
14	1.643367	1.4
2	1.684373	1.2
90	1.800368	0.8
153	1.967526	0.6
24	2.009472	0.6
85	2.208921	0.3
48	2.655157	0.2
115	2.944643	0.1
240	4.159581	0.1

