Reactivity and Intramolecular Interactions in Linalool: A Computational Study Using Reactivity Descriptors, NCI, NBO, and QTAIM Analyses

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Table S1. xyz coordinates of *S* and *R* enantiomers optimized at the MP2/6-311++G(2d,2p) level of theory in the aqueous phase using the PCM solvation model

S enantiomer			
Atom	x	y	z
C	4.2441	-0.5311	0.0204
C	2.8577	0.0507	-0.0324
C	1.8661	-0.5745	-0.6922
C	0.4394	-0.1176	-0.7988
C	-0.4333	-0.7664	0.279
C	-1.9151	-0.3941	0.2036
C	-2.6873	-1.1286	1.2975
C	-2.0897	1.0914	0.3812
C	-2.5786	1.9311	-0.5366
O	-2.3683	-0.8338	-1.0864
C	2.6873	1.3507	0.7043
H	-2.3412	-0.8229	2.2828
H	-3.7511	-0.906	1.2251
H	-2.5431	-2.2015	1.1906
H	-2.8725	1.5833	-1.5157
H	-2.6846	2.9838	-0.3215
H	-1.7939	1.4766	1.3516
H	-3.3195	-0.6841	-1.1237
H	-0.357	-1.853	0.2079
H	-0.0594	-0.4812	1.2637
H	0.3687	0.9649	-0.7179
H	0.0442	-0.384	-1.7778
H	2.1033	-1.5227	-1.1651
H	3.3471	2.1131	0.2887
H	1.6687	1.7246	0.6745
H	2.9718	1.2257	1.7494
H	4.9698	0.1658	-0.4002

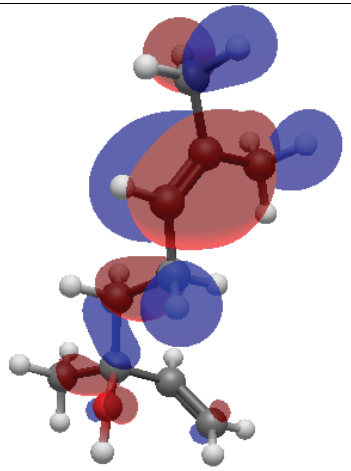
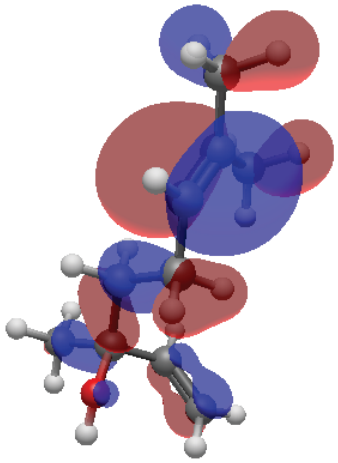
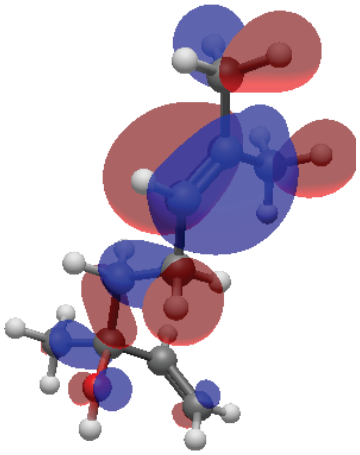
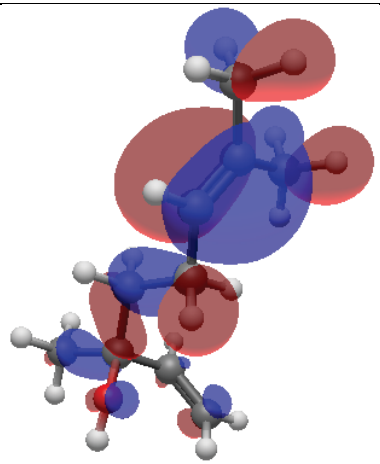
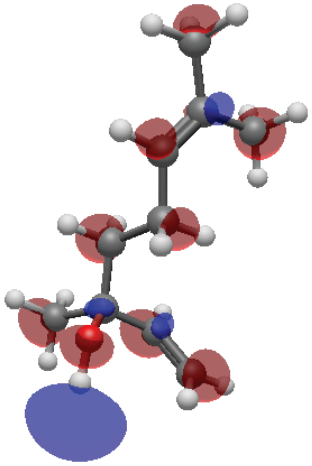
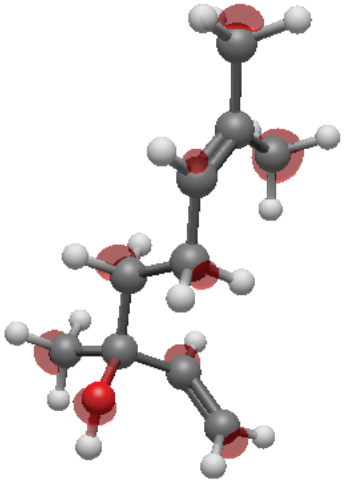
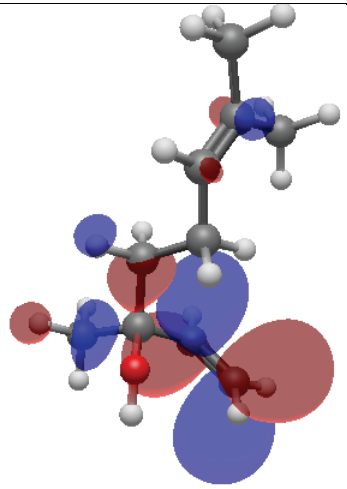
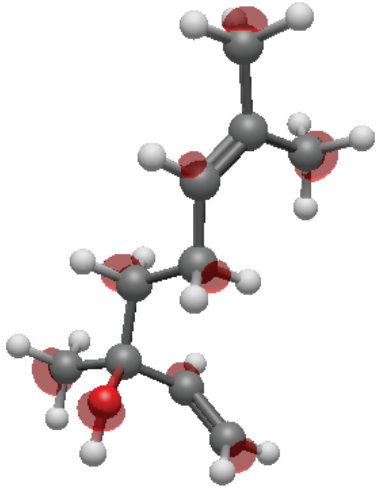
R enantiomer			
Atom	x	y	z
C	-4.2441	-0.5311	0.0205
C	-2.8577	0.0507	-0.0324
C	-1.8661	-0.5745	-0.6922
C	-0.4394	-0.1176	-0.7987
C	0.4333	-0.7664	0.279
C	1.9152	-0.3941	0.2036
C	2.6873	-1.1286	1.2974
C	2.0897	1.0914	0.3813
C	2.5786	1.9311	-0.5365
O	2.3683	-0.8337	-1.0864
C	-2.6874	1.3508	0.7041
H	-4.5457	-0.7147	1.0521
H	-4.9698	0.1656	-0.4003
H	-4.3056	-1.467	-0.5293
H	-2.1033	-1.5228	-1.1649
H	-0.3687	0.9649	-0.7179
H	-0.0442	-0.384	-1.7778
H	0.0595	-0.4813	1.2637
H	0.357	-1.8531	0.2079
H	1.7939	1.4766	1.3516
H	2.6847	2.9838	-0.3213
H	2.8726	1.5834	-1.5157
H	3.3195	-0.684	-1.1238
H	-1.6688	1.7247	0.6744
H	-2.9719	1.2258	1.7493
H	-3.3472	2.1131	0.2885
H	2.3413	-0.823	2.2827

H	4.5457	-0.7147	1.052	H	3.7511	-0.906	1.225
H	4.3057	-1.4669	-0.5295	H	2.5431	-2.2016	1.1905

Table S2. Values of Ionization potential and electronic affinities at the X/6-311++G(2d,2p) level of theory. Both enantiomers R and S shows the same values and are the values reported in this Table

X	I / eV	A / eV
B3LYP	6.449	0.7587
M06	6.462	0.6916
M06L	6.254	0.3598
ωB97XD	6.496	0.1789
MP2	5.187	-0.0200

Table S3. Local reactivity evaluated within the frozen-core approximation for *S* enantiomer, according to equations (9)–(11) for (a) electrophilic (f^-), (b) nucleophilic (f^+), and (c) free radical attacks (f^0). In all cases, the isosurfaces were generated at an isovalue of 0.02 e/Å³.

	B3LYP	M06	M06L	ωB97XD
f^-				
f^+				

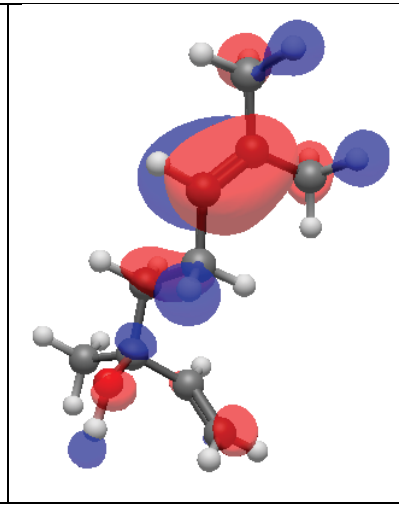
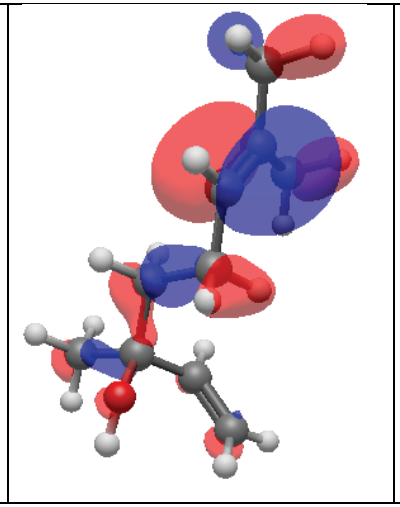
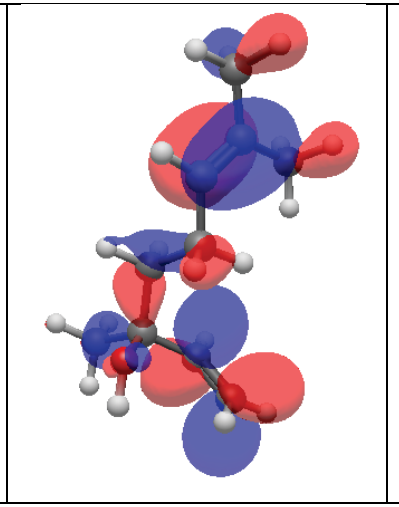
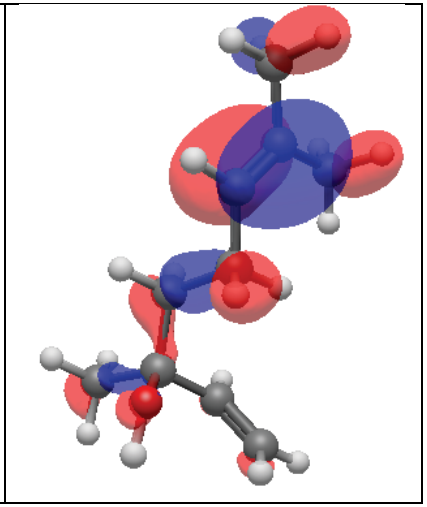
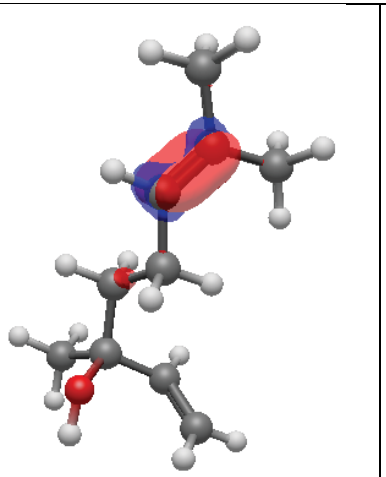
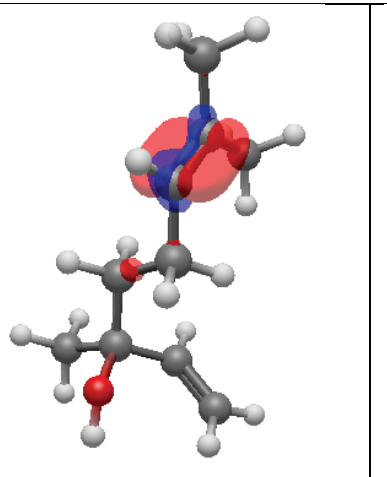
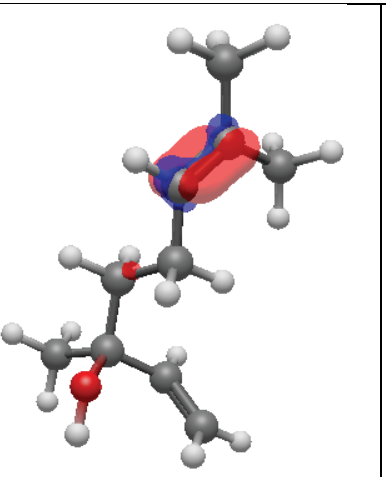
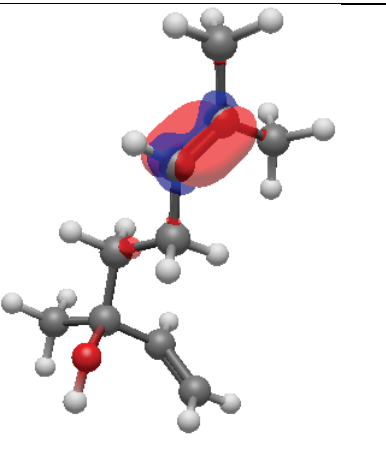
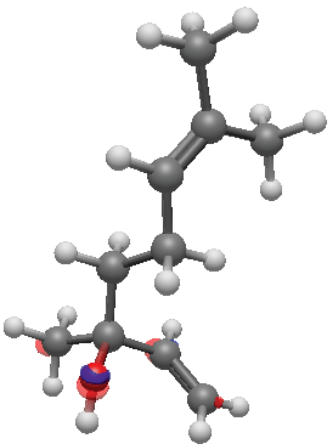
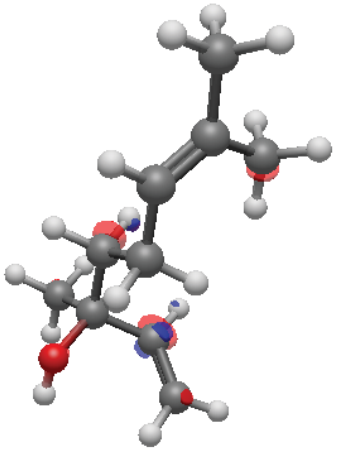
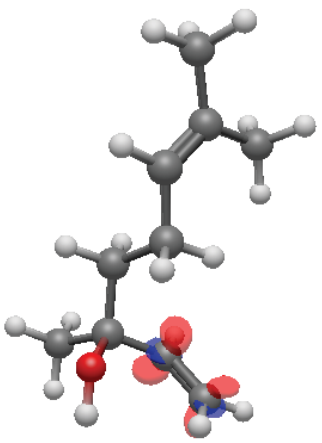
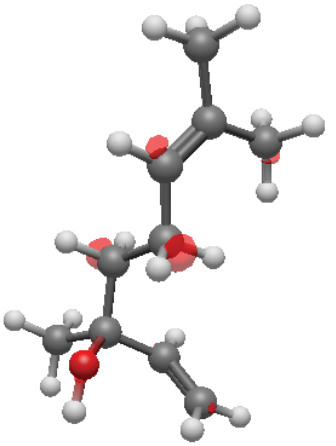
f^0				

Table S4. Local reactivity evaluated within the frozen-core approximation for *S* enantiomer, according to equations (12)–(14) for (a) electrophilic (f^-), (b) nucleophilic (f^+), and (c) free radical attacks (f^0). In all cases, the isosurfaces were generated at an isovalue of 0.02 e/Å³.

	B3LYP	M06	M06L	ωB97XD

				
f				

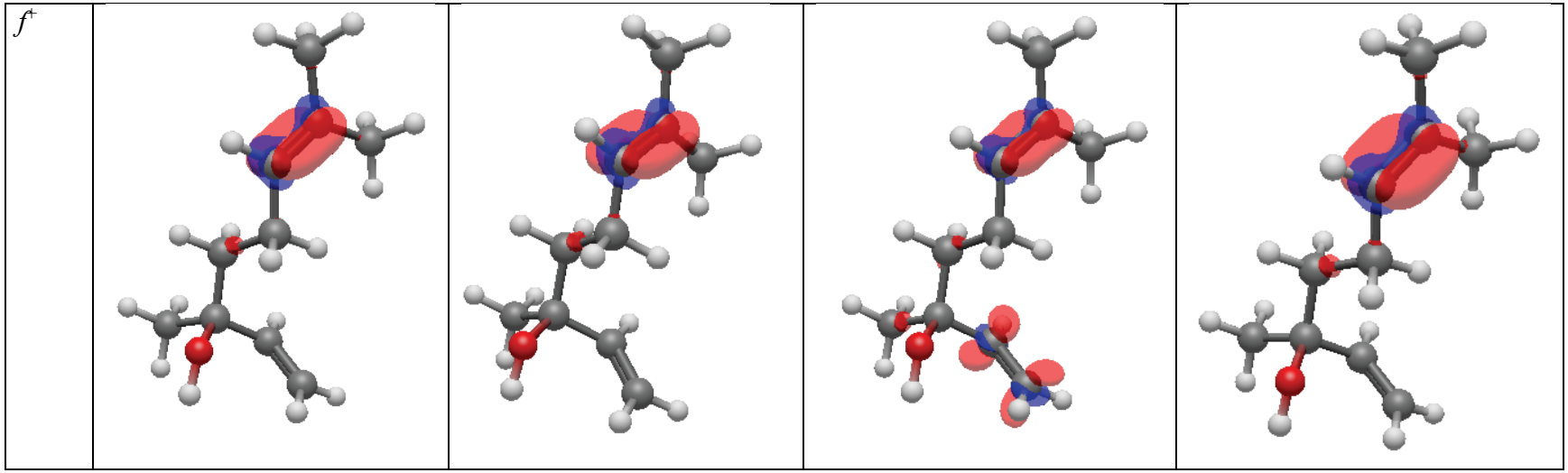


Table S5. Fukui function values for *S* and *R* enantiomer, at the X/6-311++G(2d,2p) level of theory (where B3LYP, M06, M06L, and ωB97XD), for electrophilic attacks $f^-(r)$, nucleophilic attacks $f^+(r)$, and radical attacks $f^0(r)$, according to equations (15), (16), and (17). An internal atomic labeling scheme is used and it is reported in figure 1 in the manuscript. Cn and Hn refer to the atoms of the main skeleton numbered according to the compound's structure; Hna/Hnb/Hnc indicate non-equivalent hydrogens attached to the same carbon; and labels such as $C_{M1\text{-}2}$ identify the carbon of the methyl substituent bonded to carbon 3. An equivalent notation is used for the hydrogens.

	B3LYP			M06			M06L			ωB97xd		
Atom	f(-)	f(+)	f(0)	f(-)	f(+)	f(0)	f(-)	f(+)	f(0)	f(-)	f(+)	f(0)
C1	0.020	0.054	0.037	0.020	0.031	0.025	0.046	0.264	0.155	0.010	0.031	0.021
H1a	0.007	0.034	0.021	0.007	0.010	0.008	0.014	0.119	0.066	0.004	0.034	0.019
H1b	0.008	0.055	0.032	0.008	0.028	0.018	0.016	0.130	0.073	0.005	0.031	0.018
C2	0.005	0.050	0.027	0.003	0.048	0.025	0.022	0.146	0.084	-0.001	0.020	0.009
H2	0.006	0.131	0.068	0.005	0.165	0.085	0.012	0.058	0.035	0.003	0.051	0.027
C3	0.008	0.015	0.012	0.008	0.012	0.010	0.012	0.015	0.014	0.006	0.010	0.008

C_{M1}	0.010	0.045	0.027	0.009	0.032	0.020	0.018	0.018	0.018	0.006	0.015	0.010
H_{M1-a}	0.006	0.090	0.048	0.006	0.108	0.057	0.011	0.012	0.012	0.004	0.028	0.016
H_{M1-b}	0.009	0.057	0.033	0.009	0.014	0.011	0.014	0.019	0.016	0.007	0.012	0.009
H_{M1-c}	0.006	0.028	0.017	0.006	0.013	0.010	0.011	0.020	0.015	0.004	0.021	0.013
O	0.010	0.035	0.022	0.007	0.010	0.008	0.029	0.016	0.022	0.005	0.035	0.020
H_O	0.009	0.109	0.059	0.008	0.014	0.011	0.015	0.029	0.022	0.006	0.056	0.031
C4	0.023	0.026	0.024	0.022	0.032	0.027	0.023	0.012	0.017	0.021	0.027	0.024
H4a	0.016	0.020	0.018	0.018	0.016	0.017	0.017	0.019	0.018	0.015	0.045	0.030
H4b	0.018	0.084	0.051	0.015	0.118	0.066	0.018	0.012	0.015	0.017	0.052	0.034
C5	0.034	0.011	0.023	0.031	0.009	0.020	0.030	0.012	0.021	0.032	0.041	0.037
H5a	0.022	0.014	0.018	0.027	0.014	0.020	0.020	0.025	0.023	0.022	0.028	0.025
H5b	0.043	0.012	0.028	0.033	0.006	0.020	0.037	0.014	0.025	0.042	0.105	0.074
C6	0.194	0.008	0.101	0.202	0.008	0.105	0.164	0.007	0.085	0.215	0.042	0.128
H6	0.061	0.007	0.034	0.066	0.006	0.036	0.052	0.006	0.029	0.067	0.066	0.066
C7	0.167	0.009	0.088	0.169	0.013	0.091	0.141	0.009	0.075	0.182	0.022	0.102
C_{M2}	0.040	0.021	0.031	0.038	0.061	0.050	0.034	0.006	0.020	0.041	0.038	0.039
H_{M2-a}	0.045	0.006	0.026	0.047	0.019	0.033	0.041	0.006	0.023	0.048	0.027	0.038
H_{M2-b}	0.024	0.031	0.027	0.023	0.083	0.053	0.020	0.009	0.015	0.025	0.051	0.038
H_{M2-c}	0.044	0.029	0.036	0.045	0.097	0.071	0.039	0.004	0.021	0.044	0.040	0.042
C8	0.043	0.004	0.024	0.043	0.008	0.025	0.037	0.003	0.020	0.044	0.016	0.030
H8a	0.047	0.002	0.024	0.048	0.006	0.027	0.041	0.003	0.022	0.048	0.012	0.030
H8b	0.047	0.007	0.027	0.049	0.013	0.031	0.042	0.004	0.023	0.048	0.015	0.032
H8c	0.028	0.003	0.015	0.029	0.006	0.017	0.024	0.002	0.013	0.029	0.021	0.025

Table S6. Bond Critical Points for S and R enantiomers obtained at the MP2/6-311++G(2d,2p) level of theory.

Bond Critical Point	$\rho(r_c)$ / a.u.	$\nabla^2\rho(r_c)$ / a.u.
1	0.278541	-0.762104
2	0.278322	-0.760981
3	0.284105	-0.710234
4	0.301245	-0.845612
5	0.282134	-0.994562
6	0.298451	-0.832104
7	0.281995	-0.991243
8	0.300124	-0.840129
9	0.282004	-0.992315
10	0.302145	-0.849912
11	0.281874	-0.990412
12	0.281903	-0.991102
13	0.451294	-0.152431
14	0.449812	-0.149872
15	0.265412	-0.680412
16	0.448712	-0.145612
17	0.450123	-0.151123
18	0.385412	-0.451243
19	0.341203	-2.104512
20	0.021451	0.084512
21	0.018742	0.075412
22	0.148512	-0.065412
23	0.021451	0.15421
24	0.020984	0.149872
25	0.008451	0.025412
26	0.005412	0.018742
27	0.004123	0.031245
28	0.003981	0.029812
29	0.012451	0.054123