Electronic Supplementary Material (ESI) for New Journal of Chemistry.

MECHANISTIC AND KINETIC STUDY OF LIMONA KETONE OXIDATION INITIATED BY HYDROXYL RADICAL: IMPACT OF INDOOR AIR POLLUTION

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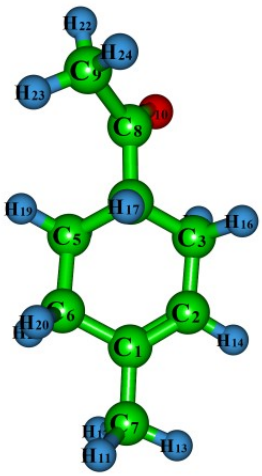

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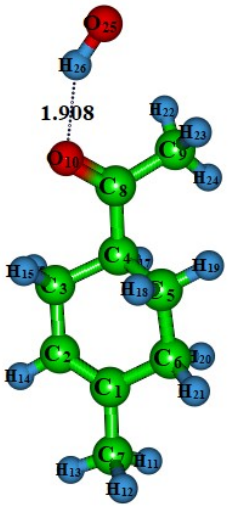

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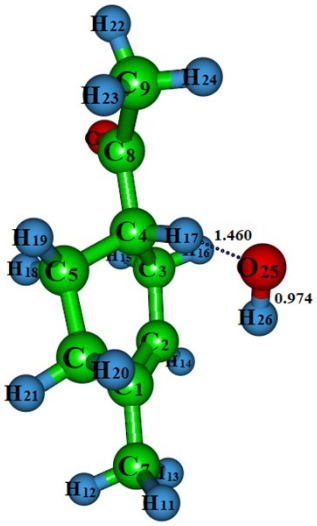

RC1

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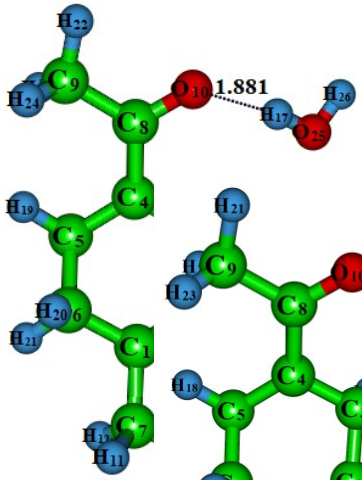

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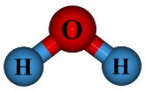

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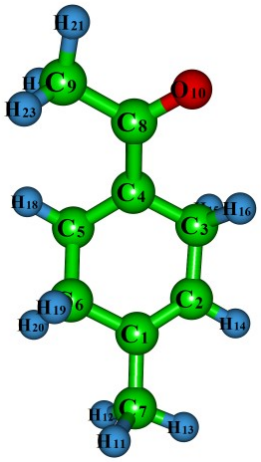

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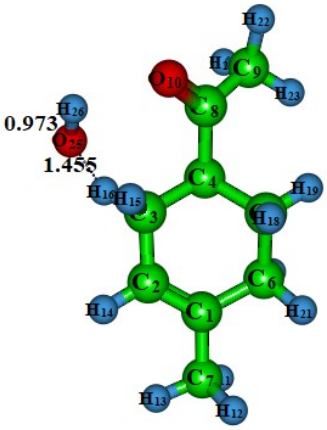

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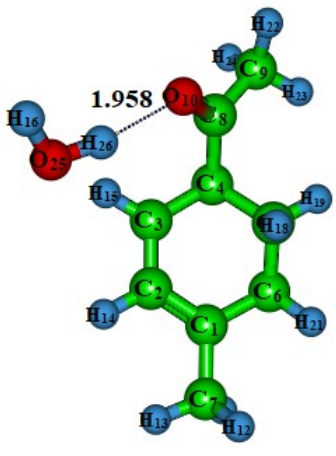

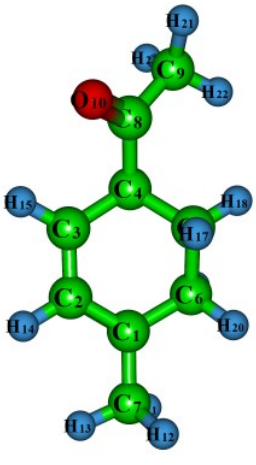

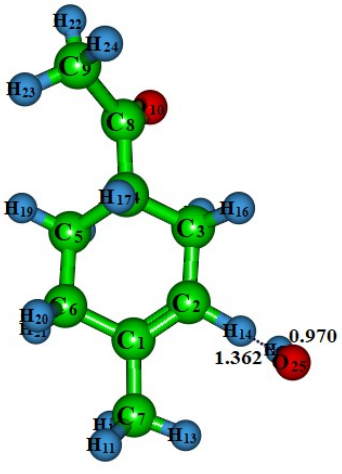

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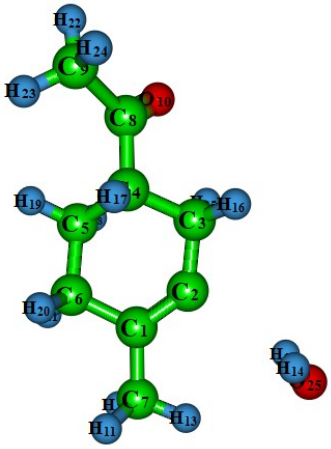

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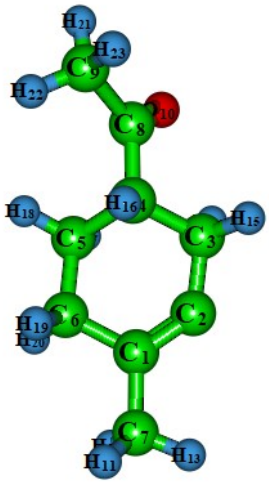

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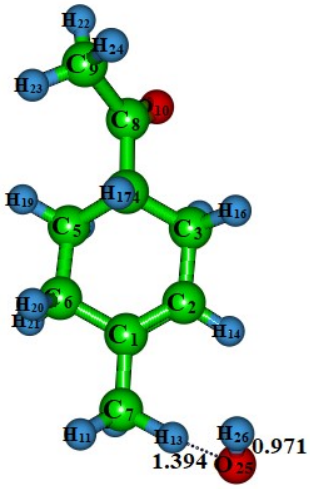

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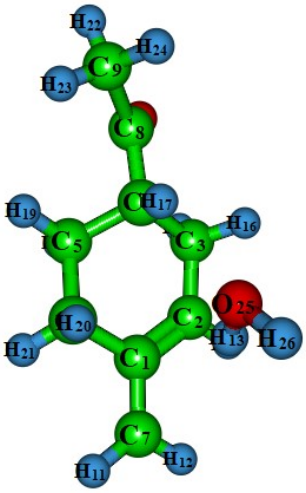

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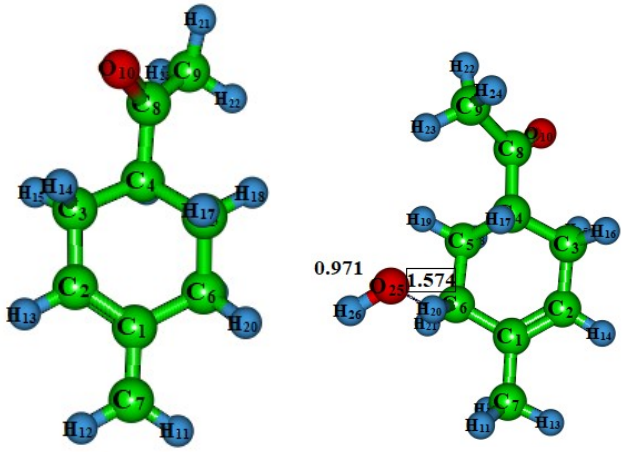

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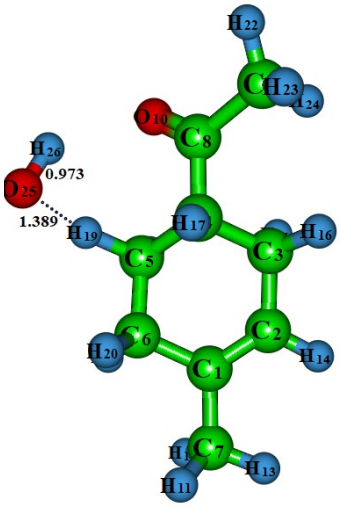

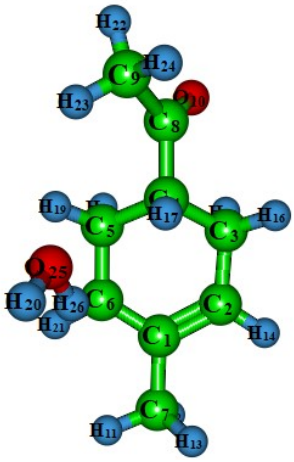

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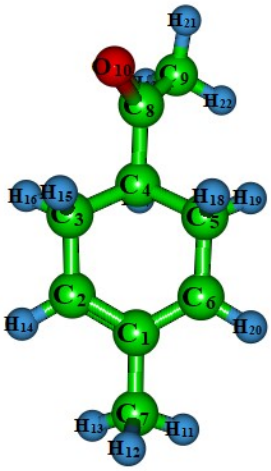

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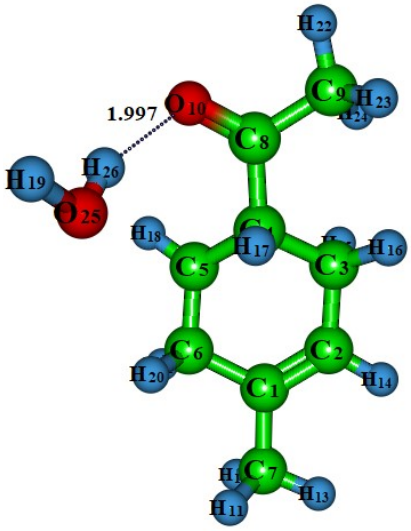

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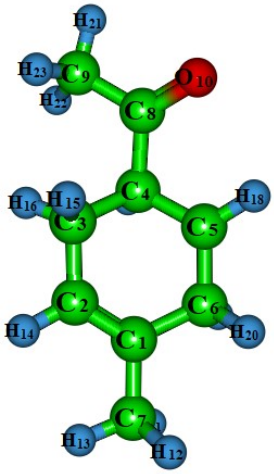

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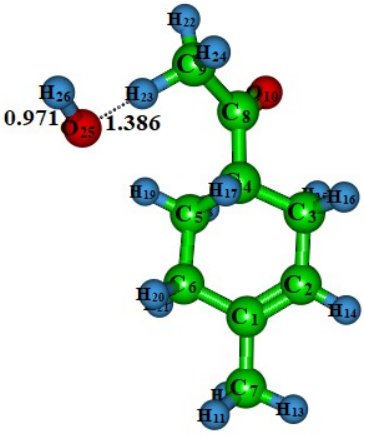

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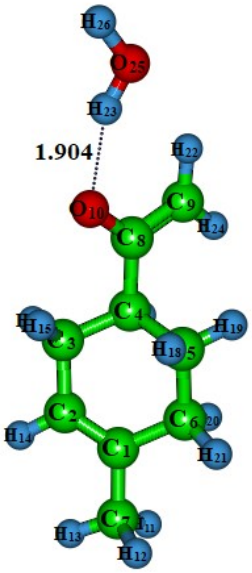

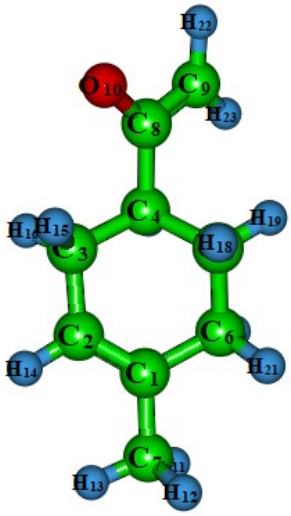

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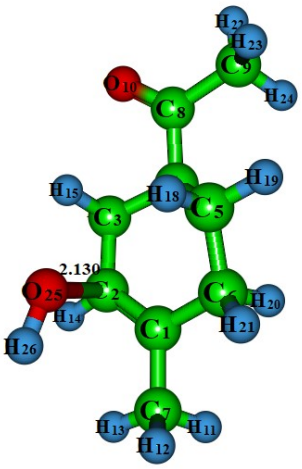

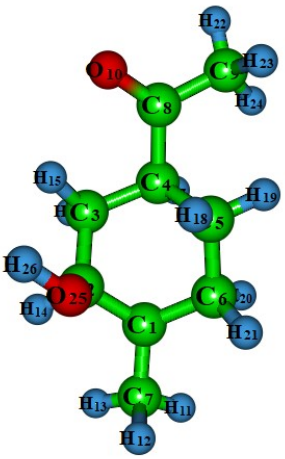

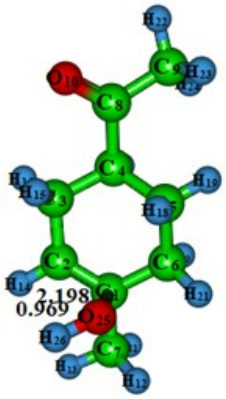

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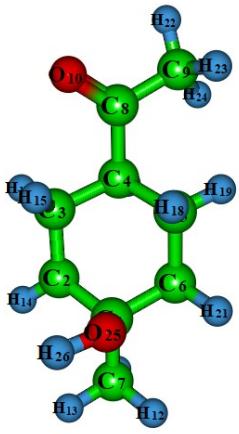
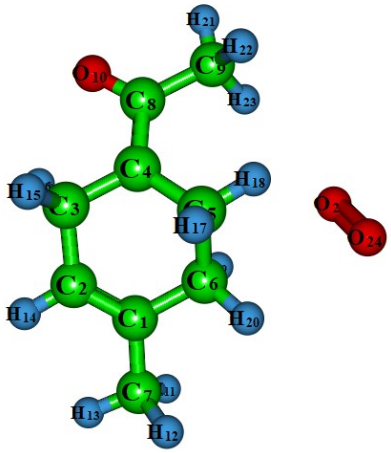
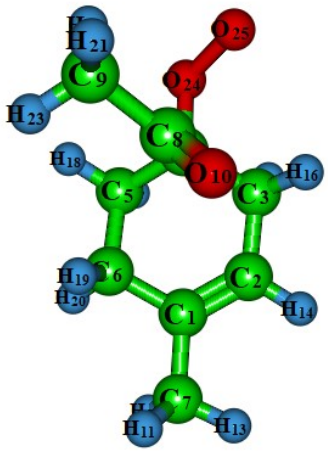


I9

Figure S1 Optimized structures of initial-H-abstraction and OH addition of LK with OH calculated at M06-2X/6-311+G(d,p) level of theory



I1+O_2



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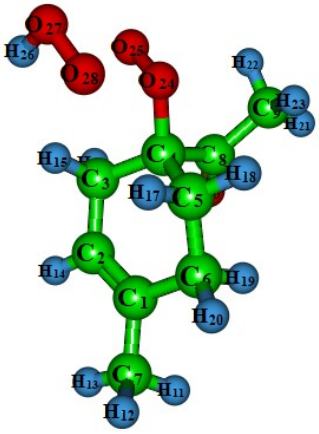

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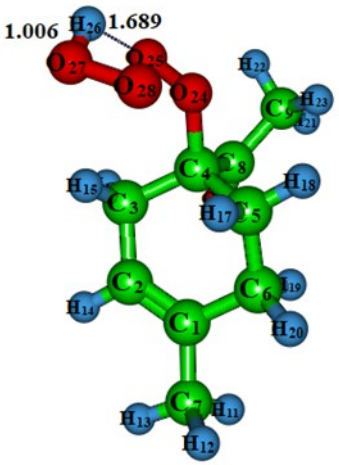

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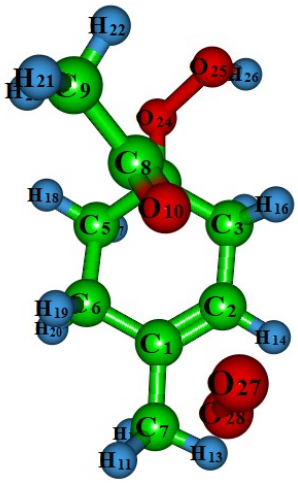

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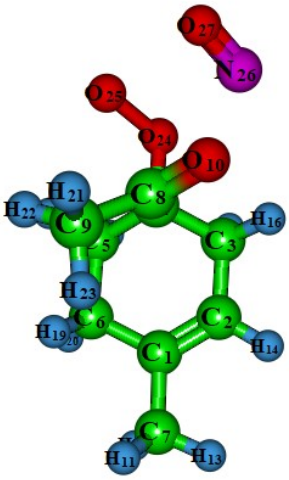
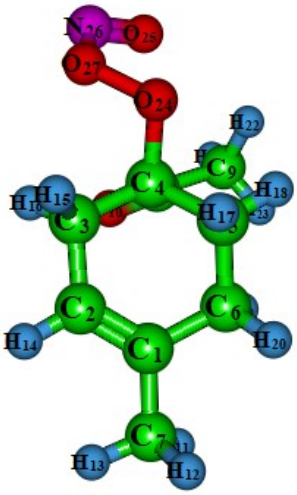


I10+NO



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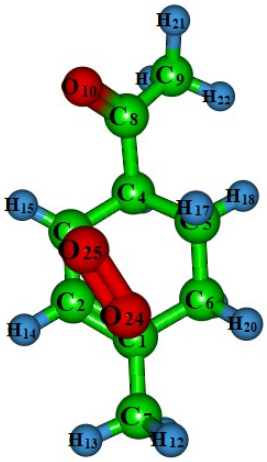

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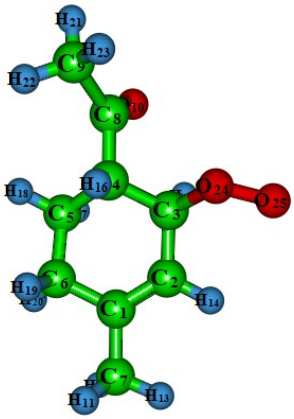

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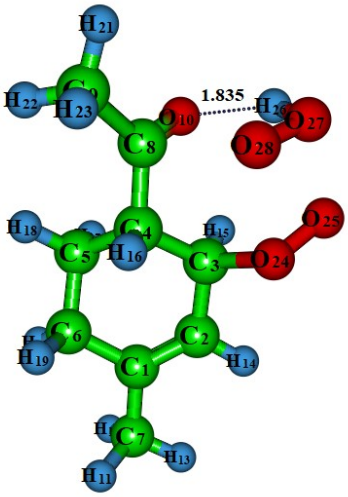

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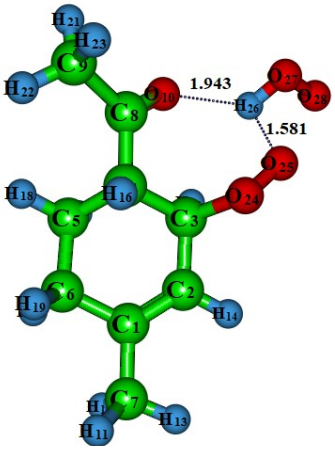

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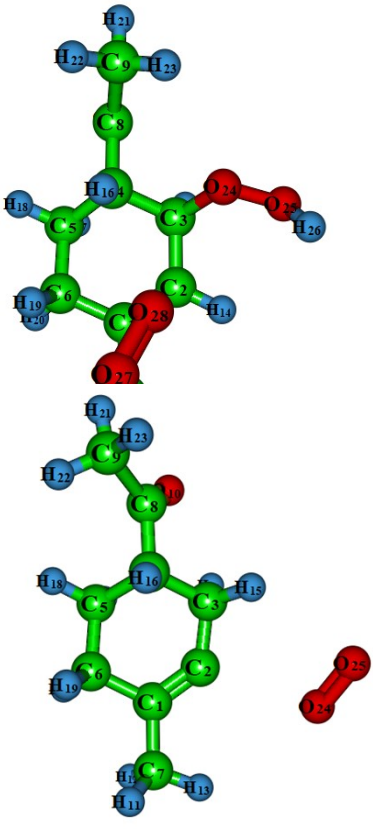
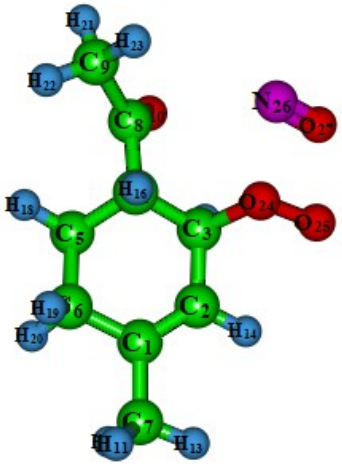
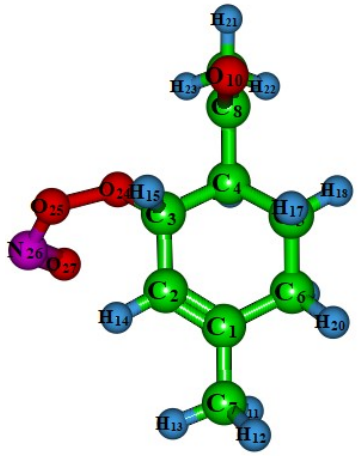




I11+NO



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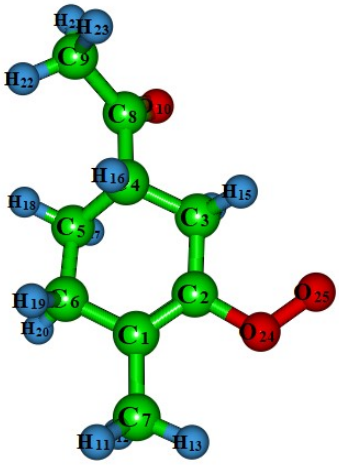

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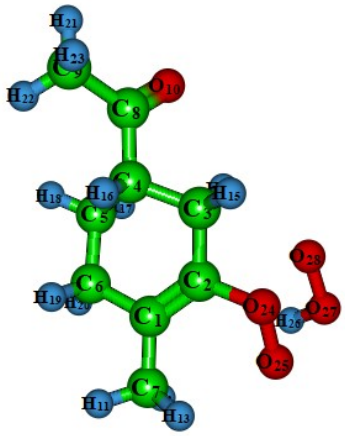

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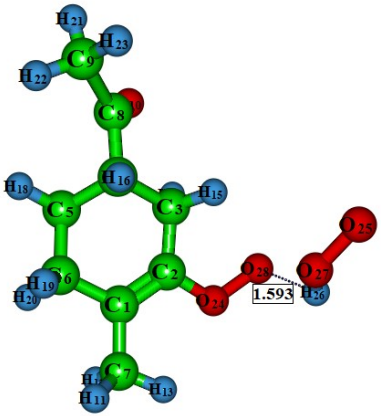

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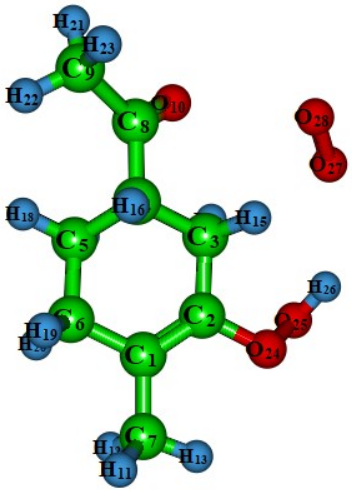

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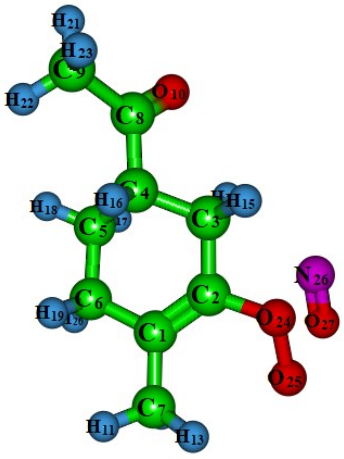

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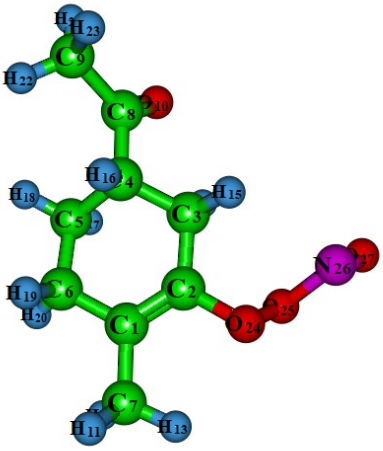

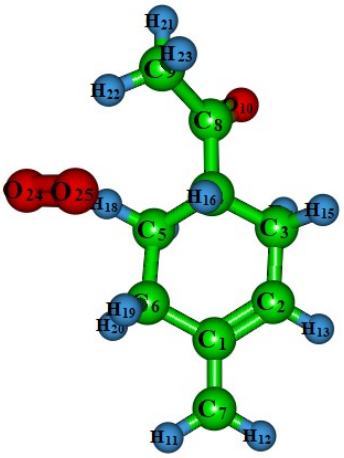

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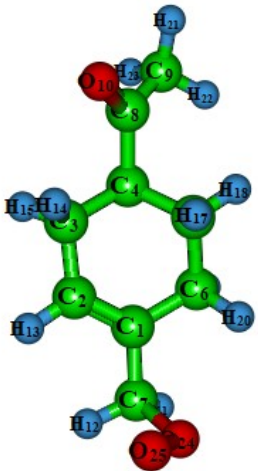

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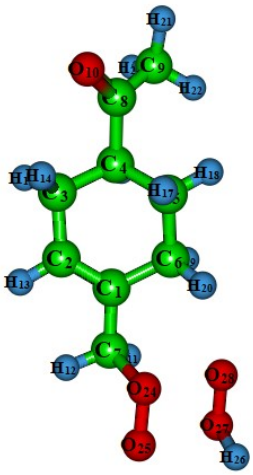

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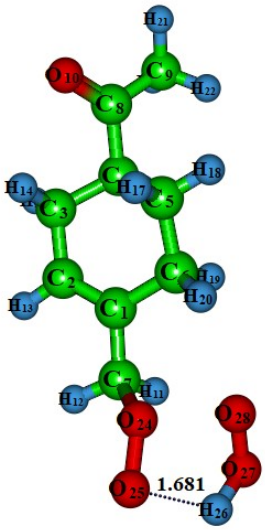

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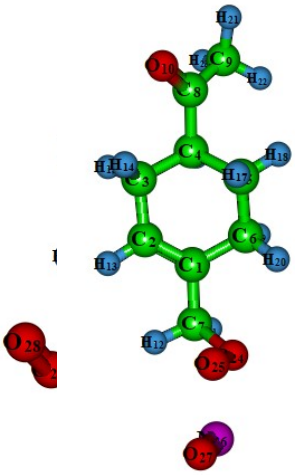

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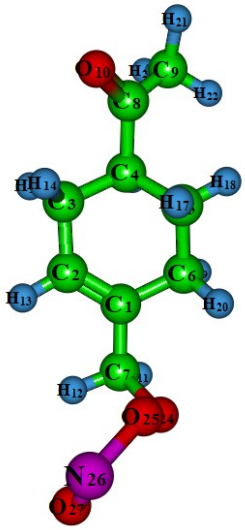

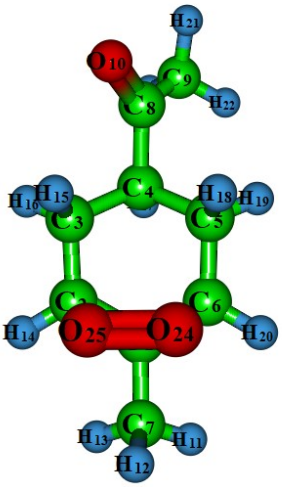

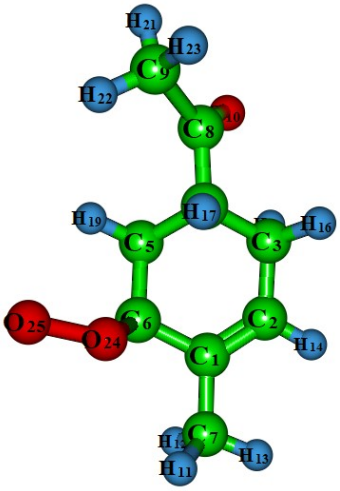

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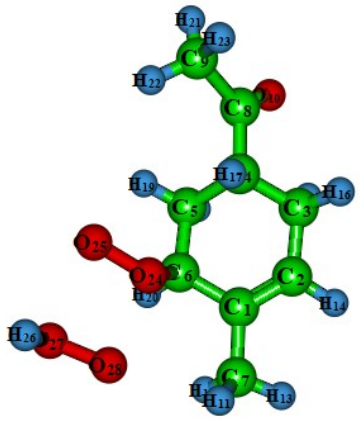

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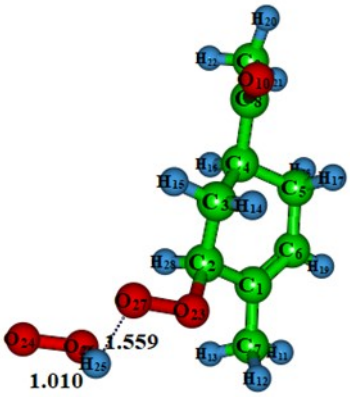

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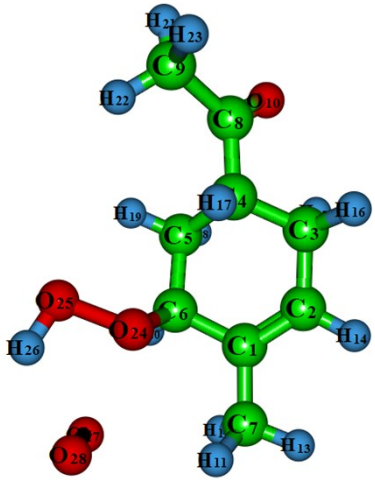
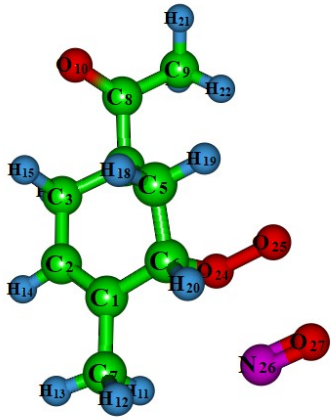
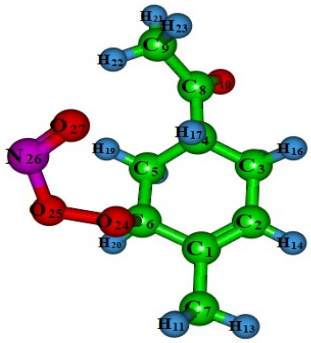


I14+HO_2



TS14



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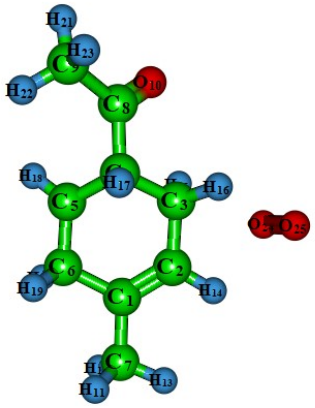
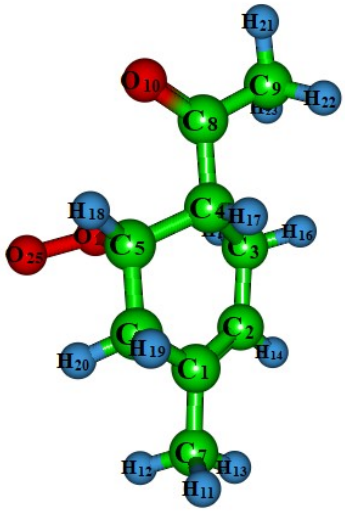


I14+NO



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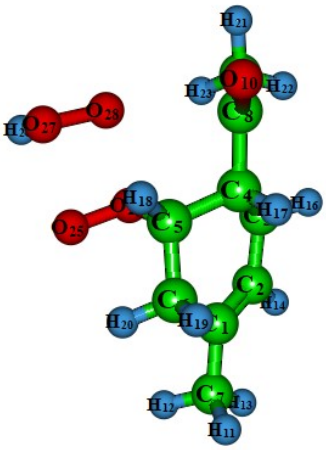
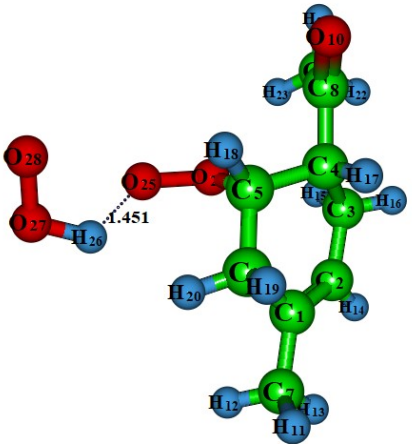
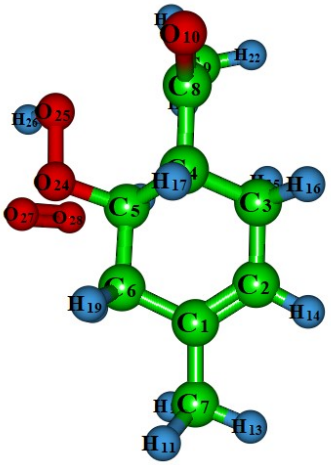


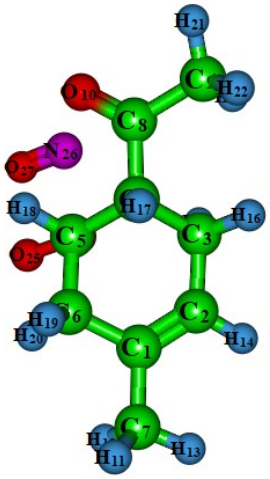
I6+O_2



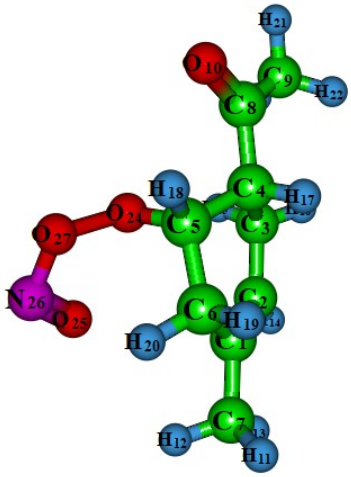
I15



I15+HO_2



TS15

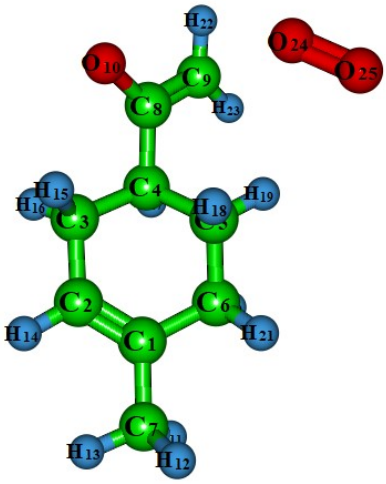


P11

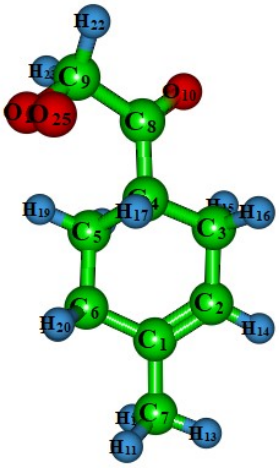
I15+NO

P12

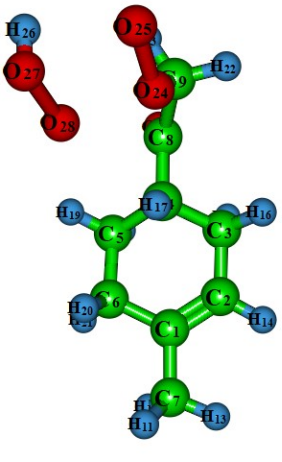
I7+O_2

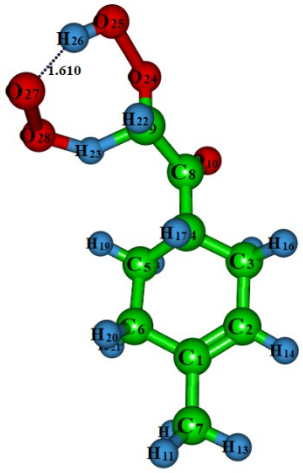


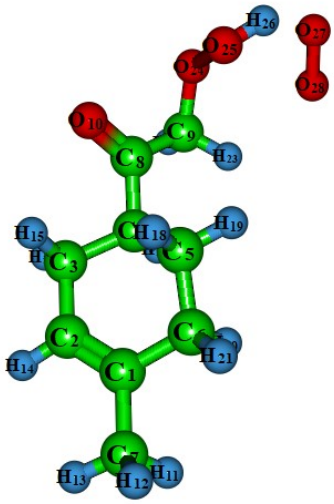
I16

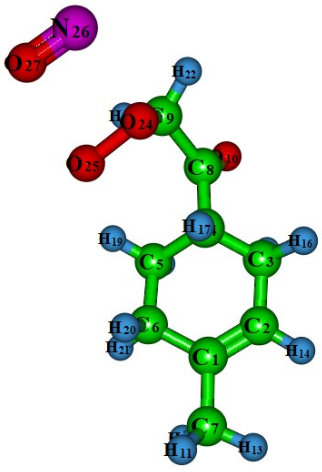


I16+HO_2

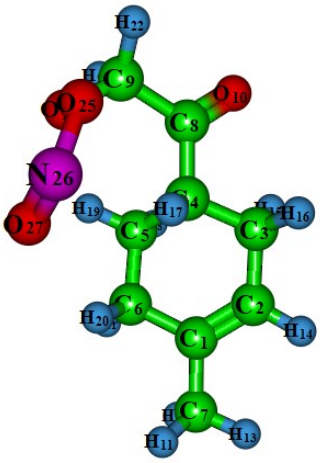








TS16



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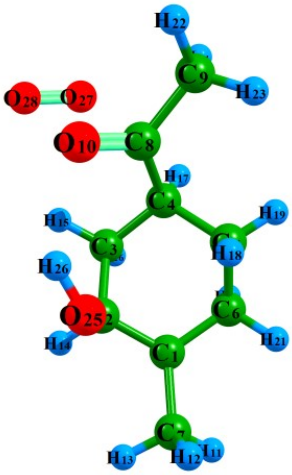
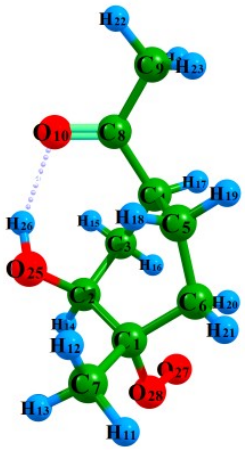


I16+NO



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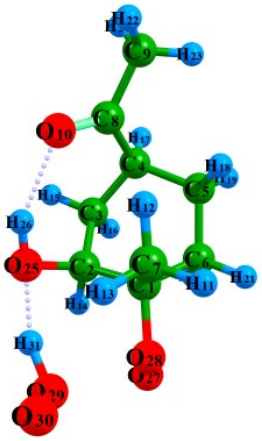
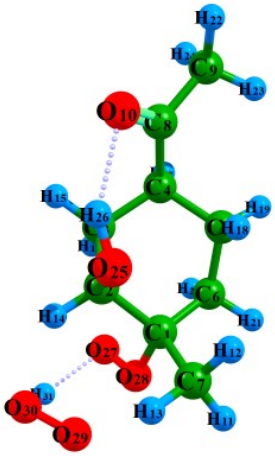
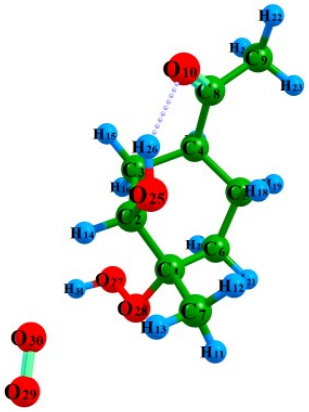


I8+O2



I17

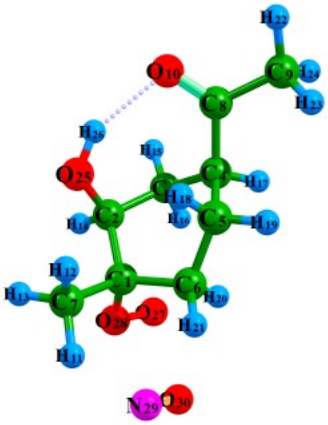


I17+HO_2

TS17

P15

I17+NO



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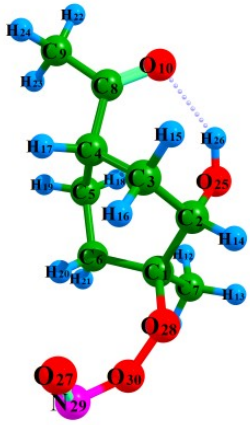

I9+O_2

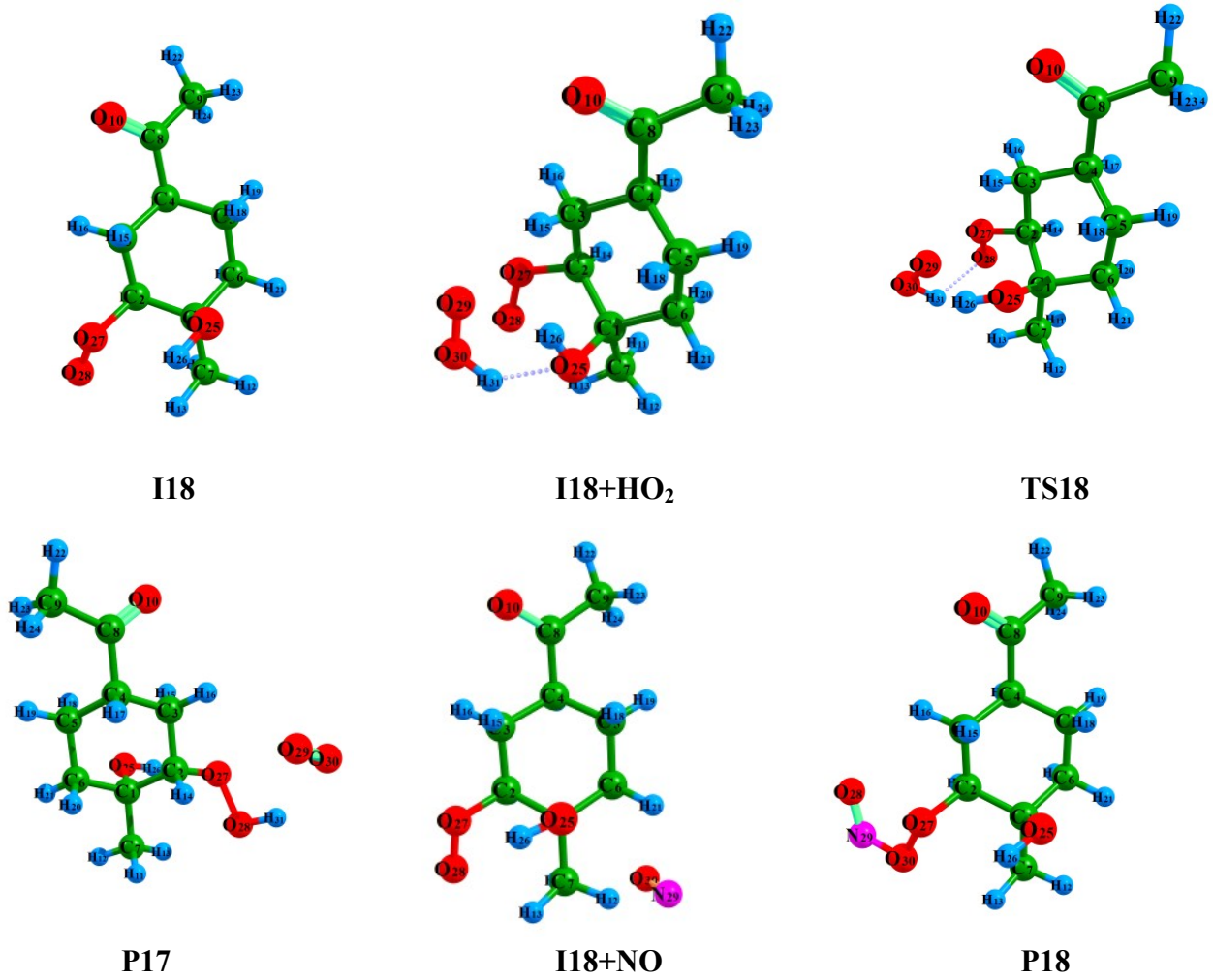

Figure S2 Optimized structures of secondary reactions of LK with O_2, HO_2 and NO calculated at M06-2X/6-311+G(d,p) level of theory

Table S1: Relative energy, enthalpy and Gibb's free energy of initial reaction mechanism of LK with OH calculated at M06-2X, ωB97X-D and CCSD(T)/ 6-311+G(d,p) level of theory.

REACTION PATHWAYS	M06-2X			ωB97X-D			CCSD(T)
	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	ΔE
R	0	0	0	0	0	0	0
RC1	-8.51	-6.56	1.13	-7.85	-6.11	1.58	-4.82
TS1	-1.65	-2.60	6.51	-4.16	-4.42	4.69	-0.33
IC1	-37.95	-36.25	-29.20	-38.22	-36.33	-29.33	-32.65
I1+H_2O	-29.47	-29.64	-30.82	-30.05	-30.24	-31.34	-25.51
TS2	-1.37	-2.19	7.07	-3.62	-3.94	5.21	0.64

IC2	-38.71	-37.60	-31.03	-39.85	-38.70	-32.69	-36.29
I2+H_2O	-31.40	-32.17	-33.57	-32.77	-33.42	-34.83	-29.68
TS3	3.22	1.64	10.11	0.94	-0.73	7.70	4.95
IC3	-12.84	-11.51	-6.14	-12.12	-10.84	-5.26	-9.98
I3+H_2O	-8.26	-8.17	-9.42	-7.38	-7.28	-8.54	-6.83
TS4	3.69	2.31	10.50	-1.49	-1.74	6.21	5.66
IC4	-33.94	-33.21	-26.52	-34.77	-33.88	-27.42	-31.73
I4+H_2O	-27.69	-28.23	-28.99	-28.98	-29.39	-30.13	-26.28
TS5	-0.55	-1.46	6.27	-2.33	-1.76	5.86	0.78
IC5	-36.31	-35.77	-29.69	-37.26	-36.82	-32.11	-33.58
I5+H_2O	-30.43	-31.44	-33.54	-31.73	-32.62	-34.80	-28.97
TS6	-1.43	-2.50	7.11	-3.47	-4.45	5.20	0.64
IC6	-24.70	-24.04	-17.06	-24.26	-23.56	-15.63	-20.78
I6+H_2O	-17.67	-18.94	-20.35	-17.31	-18.56	-20.00	-14.86
TS7	3.54	2.03	10.41	0.55	-0.63	7.91	5.03
IC7	-29.87	-28.15	-20.75	-29.08	-27.33	-20.24	-26.22
I7+H_2O	-21.40	-21.70	-22.48	-21.06	-21.33	-22.25	-19.16
TS8	-6.60	-4.70	5.80	-8.96	-6.74	3.90	-3.92
I8	-30.95	-27.32	-18.53	-33.06	-29.22	-19.55	-25.98
TS9	-7.27	-5.45	4.52	-9.22	-7.40	2.53	-5.12
I9	-35.58	-32.37	-21.89	-34.12	-30.93	-20.48	-31.04

Table S2: Relative energy, enthalpy and Gibb's Free energy of initial reaction mechanism of LK with OH calculated at MP2/6-311+G(d,p) level of theory.

Reaction Energy	ΔE	ΔH	ΔG
R	0	0	0
RC1	-6.24	-4.62	2.57
TS1	2.38	1.10	10.31
IC1	-32.30	-29.01	-22.42
I1+H_2O	-23.58	-22.04	-23.28

TS2	4.73	4.67	13.32
IC2	-33.52	-32.11	-26.45
I2+H_2O	-26.97	-27.23	-28.36
TS3	9.75	9.29	17.93
IC3	-11.43	-8.74	-1.60
I3+H_2O	-4.81	-3.76	-4.75
TS4	8.11	7.53	15.93
IC4	-29.69	-28.53	-21.62
I4+H_2O	-23.81	-23.99	-24.63
TS5	5.26	4.96	13.18
IC5	-31.55	-30.73	-25.50
I5+H_2O	-26.27	-26.79	-29.17
TS6	3.36	2.46	12.06
IC6	-24.25	-22.13	-15.77
I6+H_2O	-17.45	-17.40	-18.75
TS7	6.98	5.67	15.00
IC7	-26.08	-23.83	-16.54
I7+H_2O	-17.67	-17.46	-18.39
TS8	3.50	6.38	16.37
I8	-28.41	-24.58	-15.36
TS9	1.19	3.97	14.28
I9	-33.67	-30.38	-19.95

Table S3: Relative energy, enthalpy and Gibbs Free energy of reaction mechanism of LK with O_2, NO and HO_2 calculated at M06-2X and ωB97X-D with 6-311+G(d,p) level of theory.

REACTION PATHWAYS	M06-2X			ωB97-XD		
	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG
I1+O_2	0	0	0	0	0	0
I10	-24.97	-22.24	-16.81	-20.83	-17.86	-3.07
I10+HO_2	0	0	0	0	0	0
TS10	-0.57	-1.83	-1.38	0.74	-1.04	-0.67
P1	-29.71	-31.07	-34.73	-19.24	-20.68	-24.96
I10+NO	0	0	0	0	0	0
P2	-32.08	-31.77	-31.58	-28.63	-28.65	-29.44
I2+O_2	0	0	0	0	0	0
I11	-20.94	-17.70	-14.46	-18.42	-15.01	-6.13
I11+HO_2	0	0	0	0	0	0
TS11	22.34	19.49	17.32	22.35	19.15	15.98
P3	-22.47	-24.31	-28.20	-12.39	-14.42	-19.36
I11+NO	0	0	0	0	0	0
P4	-32.67	-32.39	-32.96	-29.10	-28.91	-29.87
I3+O_2	0	0	0	0	0	0
I12	-46.02	-43.42	-38.83	*	*	*
I12+HO_2	0	0	0	0	0	0
TS12	12.66	10.41	8.85	11.56	9.36	7.82
P5	-29.10	-30.37	-33.63	-19.78	-21.12	-25.36
I12+NO	0	0	0	0	0	0
P6	-35.09	-34.84	-34.51	-31.60	-31.48	-30.93
I4+O_2	0	0	0	0	0	0
I13	-22.71	-18.82	-15.21	-19.55	-15.65	-6.68
I13+HO_2	0	0	0	0	0	0
TS13	1.57	0.14	0.50	3.20	1.16	1.36
P7	-24.86	-26.23	-29.77	-14.79	-16.11	-19.42
I13+NO	0	0	0	0	0	0
P8	-35.77	-35.34	-34.91	-31.39	-31.16	-30.95
I5+O_2	0	0	0	0	0	0
I14	-22.17	-18.65	-14.96	-19.76	-16.16	-6.77
I14+HO_2	0	0	0	0	0	0
TS14	20.93	18.58	16.91	19.87	17.41	15.53
P9	-25.68	-26.91	-29.28	-15.21	-16.62	-19.96
I14+NO	0	0	0	0	0	0
P10	-36.02	-35.60	-34.92	-31.68	-31.38	-30.19
I6+O_2	0	0	0	0	0	0
I15	-37.44	-32.82	-25.54	-34.62	-30.04	-12.54
I15+HO_2	0	0	0	0	0	0
TS15	22.78	19.71	18.59	21.81	18.99	17.57
P11	-24.46	-25.78	-28.52	-14.62	-16.01	-17.65

I15+NO	0	0	0	0	0	0
P12	-32.80	-32.47	-32.46	-29.13	-28.95	-30.30
I7+O_2	0	0	0	0	0	0
I16	-26.28	-22.60	-18.18	-24.69	-20.87	-9.79
I16+HO_2	0	0	0	0	0	0
TS16	6.67	2.23	2.09	11.48	7.26	7.47
P13	-28.92	-30.13	-33.51	-18.07	-19.39	-24.08
I16+NO	0	0	0	0	0	0
P14	-33.93	-33.35	-32.92	-29.66	-29.43	-27.75
I8 + O_2	0	0	0	0	0	0
I17	-36.58	-36.15	-35.20	-32.84	-32.14	-30.98
I17+HO_2	0	0	0	0	0	0
TS17	2.90	2.43	2.71	2.35	2.04	1.91
P15	-51.47	-50.92	-51.04	-49.87	-48.05	-49.47
I17+NO	0	0	0	0	0	0
P16	-33.50	-31.85	-32.01	-29.58	-28.74	-28.01
I9+O_2	0	0	0	0	0	0
I18	-35.98	-33.24	-31.52	-34.89	-34.14	-33.85
I18+HO_2	0	0	0	0	0	0
TS18	3.88	3.56	3.01	4.14	3.98	3.84
P17	-27.97	-26.54	-26.37	-26.18	-25.69	-26.01
I18+NO	0	0	0	0	0	0
P18	-89.56	-86.48	-87.05	-87.25	-86.14	-86.48

***denotes structure not converged**

Table S4: Relative energy, enthalpy and Gibbs Free energy of reaction mechanism of LK with O_2, NO and HO_2 calculated at MP2/6-311+G(d,p) level of theory.

Reaction Energy	ΔE	ΔH	ΔG

I1+O_2	0	0	0
I10	-23.68	-22.24	-16.00
I10+NO	0	0	0
P2	-9.83	-10.20	-10.27
I2+O_2	0	0	0
I11	-19.64	-16.69	-11.77
I11+NO	0	0	0
P4	-6.51	-7.13	-8.44
I3+O_2	0	0	0
I12	*	*	*
I12+NO	0	0	0
P6	-9.71	-10.39	-10.86
I4+O_2	0	0	0
I13	-18.75	-13.83	-9.51
I13+NO	0	0	0
P8	-8.58	-9.01	-9.37
I5+O_2	0	0	0
I14	-20.32	-15.41	-10.13
I14+NO	0	0	0
P10	-8.34	-8.83	-8.99
I6+O_2	0	0	0
I15	-29.60	-29.06	-19.07
I15+NO	0	0	0
P12	-7.36	-7.96	-8.45
I7+O_2	0	0	0
I16	-21.82	-18.62	-13.02
I16+NO	0	0	0
P14	-8.44	-8.94	-8.56

Reaction of HO_2 : Reactants of HO_2 structures are not converged in MP2 method

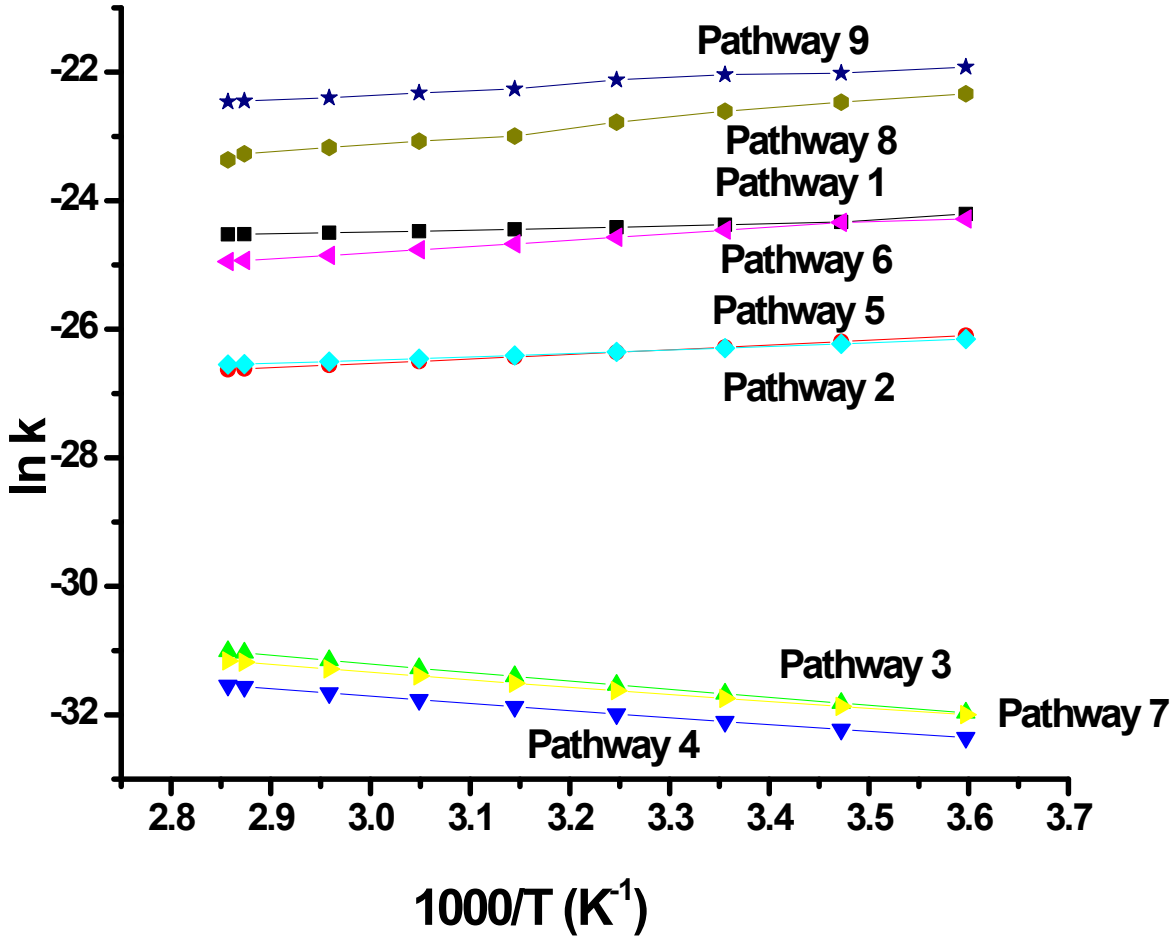

Figure S3 Arrhenius plot for the initial reaction mechanism of LK with OH