Supplementary Information

Degradation of methyl salicylate through Cl initiated atmospheric oxidation - A theoretical study

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Table S1 The selected geometrical parameters (bond length R, in Å, bond angle, θ and dihedral angle, ϕ in degrees) on the potential energy surface of the favourable reaction path calculated at M06-2X/6-311++G(d,p) level of theory.

Geometrical parameters	M06-2X/6-311++G(d,p)		
	MeSA+Cl	**TS1**	**I1**
R(C3-H16)	1.082	1.083	6.640
R(H16-C120)	3.775	3.772	1.296
θ(C3-H16-Cl20)	85.3	70.7	167.8
	I1+O_2	**-**	**I2**
R(C3-O16)	5.288	Barrierless	1.399
R(O16-O20)	1.188		1.309
θ(C3-O16-O20)	99.7		112.3
	I2+NO	**TS4**	**I3**
R(N21-O22)	1.156	1.164	1.192
R(O20-N21)	1.425	1.390	1.185
θ(C3-O16-O20)	107.9	115.7	86.3
ϕ(C3-O16-O20- N21)	-120.6	-1.37	-169.9

Table S2 The global reactivity parameters, hardness (η), softness $1/\eta$, electrophilicity index (ω), activation hardness (Δn^*) in eV calculated at M06-2X/6-311++G(d,p) level of theory.

Stationary point	η	$1/\eta$	ω	Δn^*
MeSA+Cl	4.389	0.227	2.095	0.739
TS1	3.650	0.273	2.637	
I1	3.681	0.271	2.720	
I1+O_2	4.279	0.233	2.340	
I2	3.633	0.275	3.023	barrierless
I2+HO_2	4.848	0.206	2.265	
TS2	3.193	0.313	3.630	1.655
P1	3.615	0.276	2.850	
I2+NO_2	4.492	0.222	2.294	
TS3	3.405	0.293	3.655	1.087
P2	3.564	0.280	3.066	
I2+NO	3.452	0.289	3.166	
TS4	3.591	0.278	3.072	-0.139
I3	3.176	0.314	2.824	
I3+O_2	2.086	0.479	4.300	*
P3	2.494	0.400	6.619	

*Indicates structure not converged

Δn^* has been calculated for pre-reactive reactants

η has been calculated by the equation (9) given in the text above

Table S3 The global reactivity parameters, Homo, lumo, energy gap (ΔE) in eV calculated at M06-2X/6-311++G(d,p) level of theory.

Reaction	Homo	Lumo	ΔE
MeSA	-7.916	-0.661	7.254
TS1	-8.038	-0.737	7.301
I1	-8.156	-0.794	7.362
O_2	-9.353	-3.239	6.114
I2	-8.320	-1.053	7.267
HO_2	-10.750	-0.293	10.457
TS2	-8.008	-1.622	6.386
P1	-8.156	-0.924	7.231
NO_2	-10.038	-1.156	8.882
TS3	-8.402	-1.592	6.810
P2	-8.240	-1.111	7.129
NO	-7.943	-1.416	6.527
TS4	-8.289	-1.106	7.182
I3	-7.411	-1.059	6.352
P3	-8.242	-3.252	4.989

Table S4 NOFFs (unit in electrons) of methyl salicylate with Cl radical of initial reaction and peroxy radical with their reactivities calculated at M06-2X/6-311++G(d,p) level of theory.

Stationay point	Bond parameter	Bonding orbital BD		Anti-bonding orbital BD*		Reactivity
		f^{+}_{nbo}	f^{-}_{nbo}	f^{+}_{nbo}	f^{-}_{nbo}	
MeSA	**C3-H16**	-0.988	0.988	-0.005	0.006	**Electrophilic**
	C3-C2	-0.988	0.985	-0.011	0.012	**Electrophilic**
	C3-C4	-0.989	0.987	-0.006	0.007	**Electrophilic**
TS1	**C3-H16**	0.988	-0.987	0.006	-0.004	**Nucleophilic**
	C3-C2	0.987	-0.991	0.011	-0.011	**Nucleophilic**
	C3-C4	0.988	-0.991	0.007	-0.005	**Nucleophilic**
I1	**C3-C2**	0.979	-0.995	0.010	-0.021	**Nucleophilic**
	C3-C4	0.983	-0.996	0.006	-0.010	**Nucleophilic**
O_2	**O16-O20**	-1.000	1.000 (electrophilic)	0	0	**Inactive**
I2	**C3-C2**	0.988	-0.988	0.023	-0.019	**Nucleophilic**
	C3-C4	0.990	-0.986	0.012	-0.008	**Nucleophilic**
	C3-O16	0.992	-0.997	0.022	-0.022	**Nucleophilic**
	O16-O20	0.989	-0.997	0.000	-0.018	**Nucleophilic**

Electrophilic- This captures the ability of the NBO to donate electrons

Nucleophilic- This captures the ability of the NBO to accept electrons

Inactive- It means that orbital prefers to neither accept nor donate electrons

Table S5 NOFFs (unit in electrons) of peroxy radical with HO_2, NO_2, NO radical and their corresponding intermediates, transistion state and products with their reactivities calculated at M06-2X/6-311++G(d,p) level of theory.

Reaction	Bond parameter	Bonding orbital BD		Anti-bonding orbital BD*		Reactivity
		f^{+}_{nbo}	f^{-}_{nbo}	f^{+}_{nbo}	f^{-}_{nbo}	
HO_2	H21-O22	0.996	-0.998	0.024	-0.000	Nucleophilic
	O22-O23	0.998	-0.999	0.000	-0.001	Nucleophilic
TS2	C3-C2	-0.983	0.982	-0.015	0.015	Electrophilic
	C3-C4	-0.989	0.987	-0.010	0.011	Electrophilic
	C3-O16	-0.997	0.996	-0.017	0.018	Electrophilic
	O16-O20	-0.994	0.995	-0.010	0.008	Electrophilic
	O22-O23	-0.979	0.975	-0.008	0.008	Electrophilic
P1	C3-C2	-0.988	0.985	-0.020	0.019	Electrophilic
	C3-C4	-0.989	0.987	-0.011	0.012	Electrophilic
	C3-O16	-0.995	0.996	-0.012	0.012	Electrophilic
	O16-O20	-0.990	1.004	-0.008	0.021	Electrophilic
	O20-H21	-1.000	1.001	-0.003	0.004	Electrophilic
NO_2	O22-N21	0.999	-0.992	0.023	-0.027	Nucleophilic
	N21-O23	0.999	-0.981	0.023	-0.006	Nucleophilic
TS3	C3-C2	-0.986	0.984	-0.395	0.395	Electrophilic
	C3-C4	-0.990	0.988	-0.011	0.012	Electrophilic
	C3-O16	-0.996	0.996	-0.015	0.014	Electrophilic
	O16-O20	-0.985	0.991	-0.031	0.037	Electrophilic
	O22-N21	-0.996	0.996	-0.032	0.026	Electrophilic
	N21-O23	-0.998	1.000	-0.035	0.025	Electrophilic
	O22-O23	-0.993	0.995	-0.123	0.114	Electrophilic
P2	C3-C2	-0.986	0.982	-0.017	0.017	Electrophilic
	C3-C4	-0.990	0.987	-0.011	0.012	Electrophilic
	C3-O16	-0.995	0.995	-0.016	0.015	Electrophilic
	O16-O20	-0.992	0.994	-0.017	0.021	Electrophilic
	O22-N21	-0.993	0.995	-0.147	0.134	Electrophilic
	N21-O23	-0.998	0.997	-0.517	0.513	Electrophilic
NO	N21-O22	0	-1	0	0	Inactive
TS4	C3-C2	-0.987	0.985	-0.021	0.020	Electrophilic
	C3-C4	-0.990	0.987	-0.012	0.012	Electrophilic
	C3-O16	-0.995	0.996	-0.016	0.015	Electrophilic
	O16-O20	-0.988	0.999	-0.029	0.044	Electrophilic
	N21-O22	-0.999	1.000	-0.078	0.100	Electrophilic
	O20-N21	-0.994	0.999	-0.070	0.061	Electrophilic
I3	C3-C2	0.982	-0.991	0.037	-0.035	Nucleophilic
	C3-C4	0.987	-0.993	0.024	-0.021	Nucleophilic
	C3-O16	0.996	-0.997	0.004	-0.005	Nucleophilic
P3	C3-C2	0.979	-0.995	0.010	-0.021	Nucleophilic
	C3-C4	0.983	-0.996	0.006	-0.010	Nucleophilic

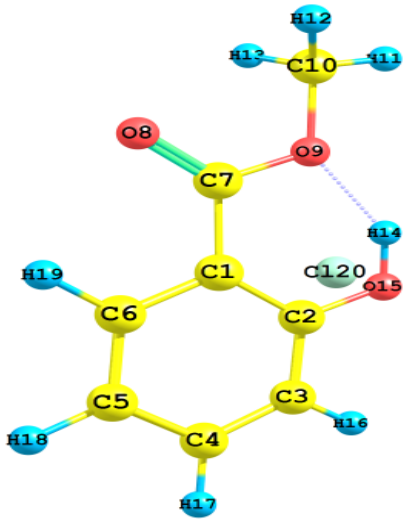
Electrophilic- This captures the ability of the NBO to donate electrons

Nucleophilic- This captures the ability of the NBO to accept electrons

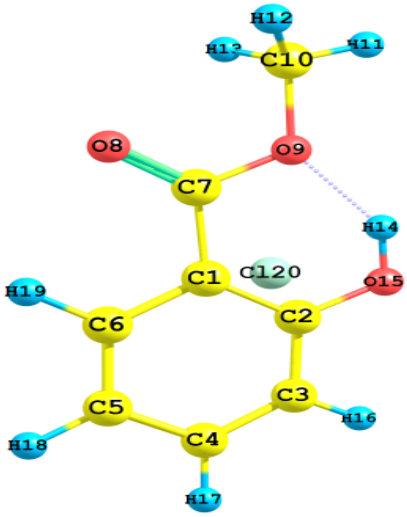
Inactive- It means that orbital prefers to neither accept nor donate electrons

Table S6 Topological analysis of reactants, transition states, intermediates and products of methyl salicylate with Cl radical calculated at M06-2X/6-311++G(d,p) level of theory (values are in atomic units).

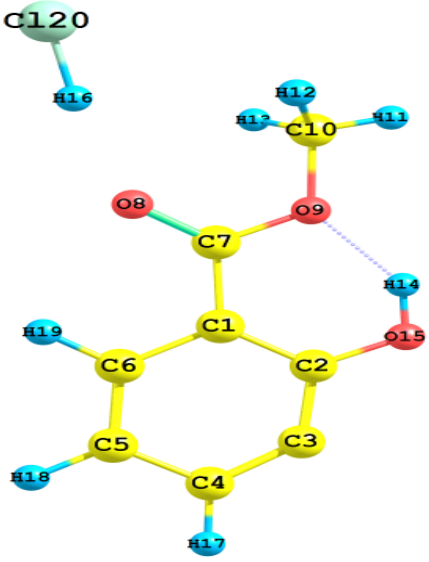
Reaction	Bond parameter	$\rho(r)$	$\nabla^2\rho(r)$	ε	V(r)	G(r)	H(r)
MeSA	C3-H16	0.2802	-0.9620	0.0205	-0.3160	0.0377	-0.2782
	C3-C2	0.3096	-0.8778	0.2156	-0.4202	0.1003	-0.3198
	C3-C4	0.3116	-0.8724	0.2094	-0.4291	0.1055	-0.3236
TS1	C3-H16	0.2806	-0.9655	0.0187	-0.3155	0.0370	-0.2784
	C3-C2	0.3085	-0.8743	0.2046	-0.4153	0.0984	-0.3169
	C3-C4	0.3121	-0.8753	0.2083	-0.4303	0.1057	-0.3245
I1	C3-C2	0.3127	-0.8849	0.2026	-0.4304	0.1046	-0.3258
	C3-C4	0.3211	-0.9185	0.1964	-0.4679	0.1191	-0.3488
O_2	O16-O20	0.5614	-0.8980	0.0378	-1.2198	0.4976	-0.7221
I2	C3-C2	0.3082	-0.8657	0.2698	-0.4048	0.0941	-0.3106
	C3-C4	0.3179	-0.9097	0.2531	-0.4492	0.1109	-0.3383
	C3-O16	0.2656	-0.3308	0.0474	-0.6541	0.2857	-0.3684
	O16-O20	0.4045	-0.2978	0.0219	-0.7110	0.3183	-0.3927
HO_2	O22-O23	0.4206	-0.3851	0.0198	-0.7505	0.3271	-0.4234
	H21-O22	0.3618	-2.5691	0.0277	-0.7659	0.0618	-0.7040
TS2	C3-C2	0.3086	-0.8714	0.2688	-0.4045	0.0933	-0.3111
	C3-C4	0.3156	-0.8943	0.2388	-0.4513	0.1138	-0.3374
	C3-O16	0.2613	-0.2331	0.0196	-0.6621	0.3019	-0.3601
	O16-O20	0.3931	-0.2747	0.0208	-0.6668	0.2991	-0.3677
	H21-O23	0.2504	-1.3749	0.1213	0.0900	-0.5238	-0.4337
	O22-O23	0.2716	0.2449	0.1182	0.2466	-0.4321	-0.1854
P1	C3-C2	0.3079	-0.8673	0.2621	-0.4039	0.0935	-0.3104
	C3-C4	0.3177	-0.9094	0.2514	-0.4441	0.1084	-0.3357
	C3-O16	0.2832	-0.3532	0.0495	-0.7198	0.3157	0.4040
	O16-O20	0.2924	-0.0187	0.0022	-0.4116	0.2035	-0.2081
NO_2	N21-O22	0.5384	-1.3663	0.0574	-1.2335	0.4459	-0.7875
	N21-O23	0.5314	-1.3096	0.0581	-1.2018	0.4372	-0.7646
TS3	C3-C2	0.3164	-0.9036	0.2437	-0.4394	0.1067	-0.3326
	C3-C4	0.3089	-0.8695	0.2786	-0.4060	0.0943	-0.3117
	C3-O16	0.2692	-0.2254	0.0141	-0.6961	0.3199	-0.3762
	O16-O20	0.2935	0.0260	0.0054	-0.4249	0.2157	-0.2092
	N21-O20	0.2931	-0.2292	0.0397	-0.3999	0.1713	-0.2286
	N21-O22	0.5434	-1.2831	0.1140	-1.1996	0.4394	-0.7602
	N21-O23	0.5499	-1.3262	0.1137	-1.2275	0.4480	-0.7795
P2	C3-C2	0.3081	-0.8665	0.2743	-0.4035	0.0934	-0.3100
	C3-C4	0.3153	-0.8931	0.2440	-0.4433	0.1100	-0.3333
	C3-O16	0.2650	-0.2441	0.0239	-0.6735	0.3062	-0.3673
	O16-O20	0.3298	-0.0906	0.0230	-0.5034	0.2403	-0.2630
NO	N21-O22	0.5727	-1.8902	0.1044	-1.6401	0.5837	-1.0563
TS4	C3-C2	0.3084	-0.8702	0.2623	-0.4030	0.0927	-0.3103
	C3-C4	0.3099	-0.8766	0.2710	-0.4349	0.1079	-0.3270
	C3-O16	0.2694	-0.2016	0.0058	-0.7020	0.3258	-0.3762
	O16-O20	0.2833	0.0429	0.0977	-0.3964	0.2036	-0.1928
	O21-N21	0.3327	-0.3838	0.0933	-0.5419	0.2230	-0.3189
	N21-O22	0.5785	-1.8406	0.0971	-1.4197	0.4798	-0.9399
I3	C3-C2	0.3125	-0.9250	0.1962	-0.4108	0.0898	-0.3210
	C3-C4	0.3222	-0.9681	0.1822	-0.4446	0.1013	-0.3433
	C3-O16	0.2864	-0.6068	0.0467	-0.635	0.2416	-0.3933
P3	C3-C2	0.3139	-0.8902	0.2046	-0.4338	0.1056	-0.3282
	C3-C4	0.3206	-0.9162	0.1940	-0.4667	0.1188	-0.3478



Reactant

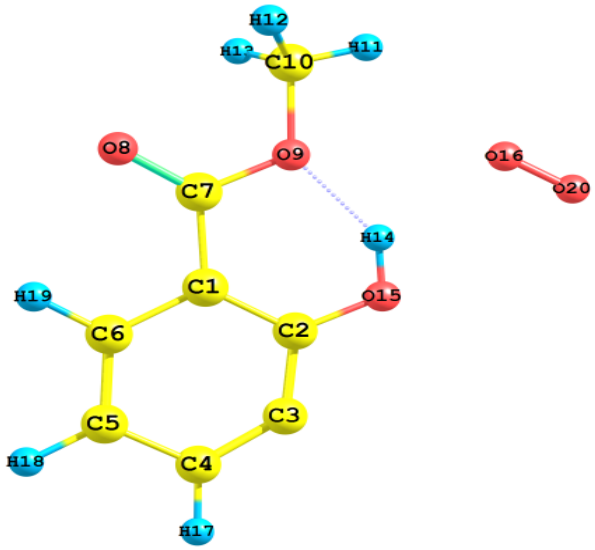


TS1

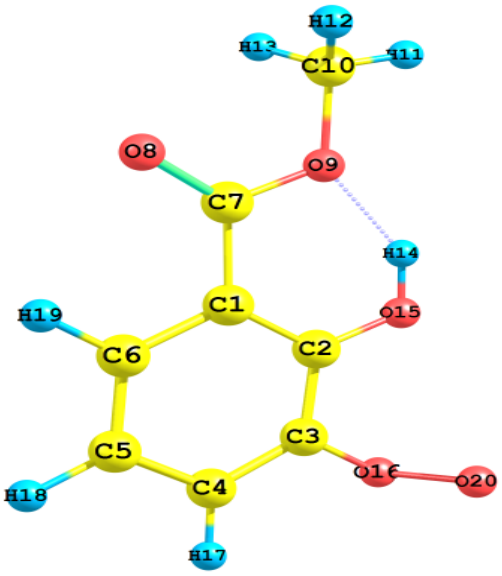


I1

Fig.S1

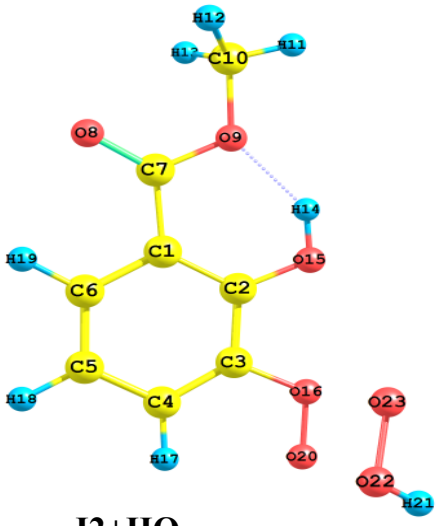


I1+O_2

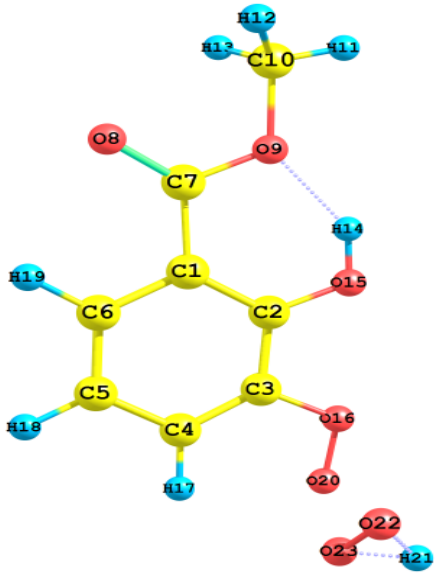


I2

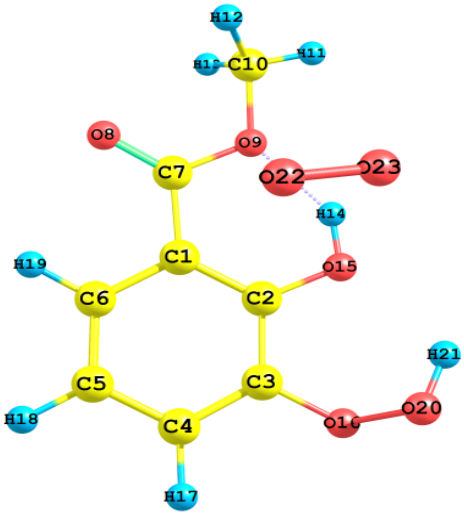
Fig.S1 contd...



I2+HO_2

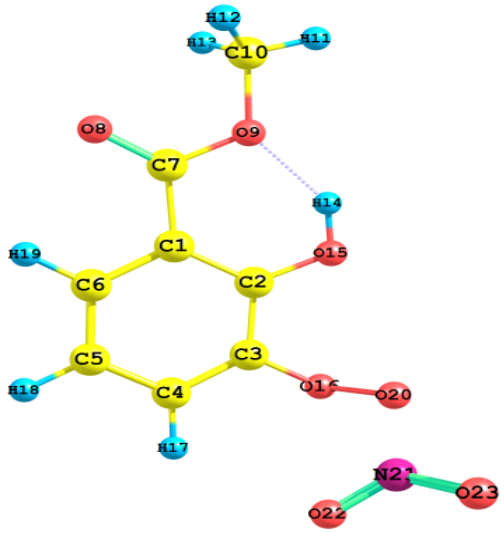


TS2

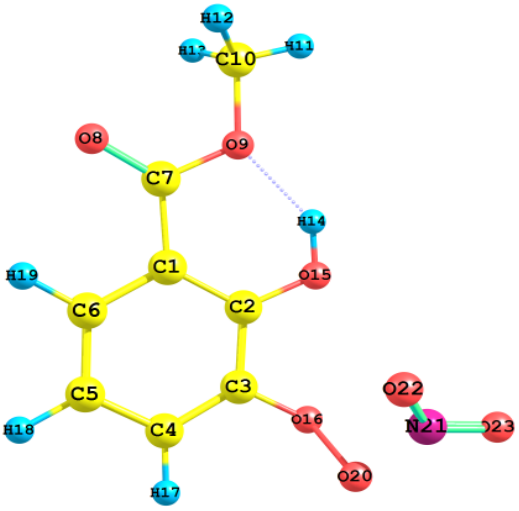


P1

Fig. S2



I2+NO_2



TS3

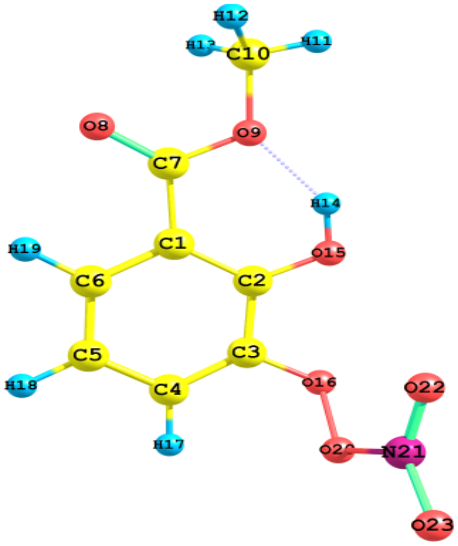


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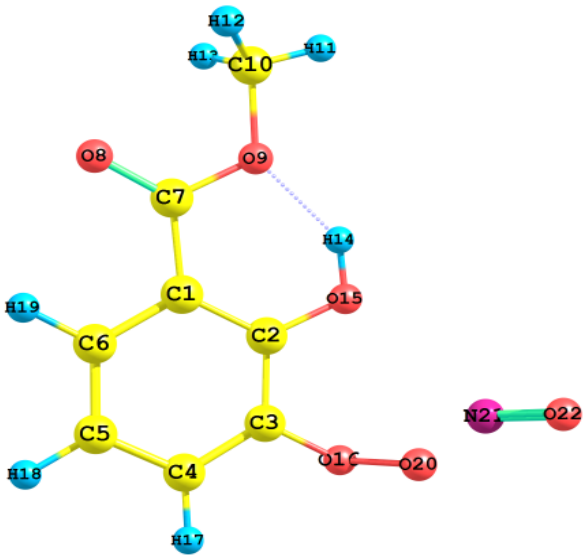
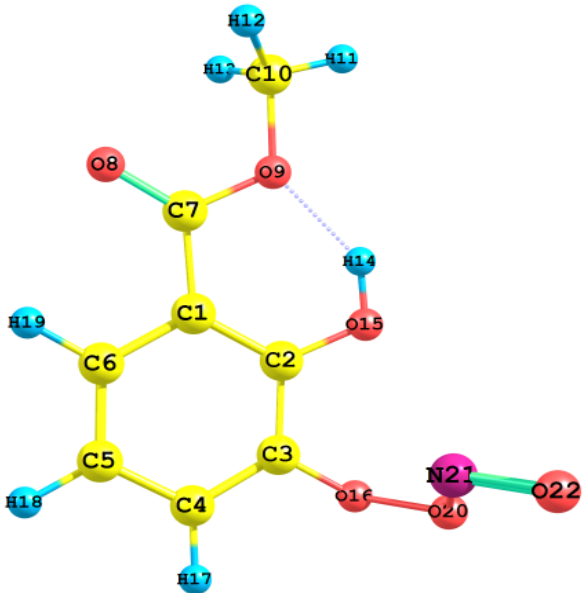
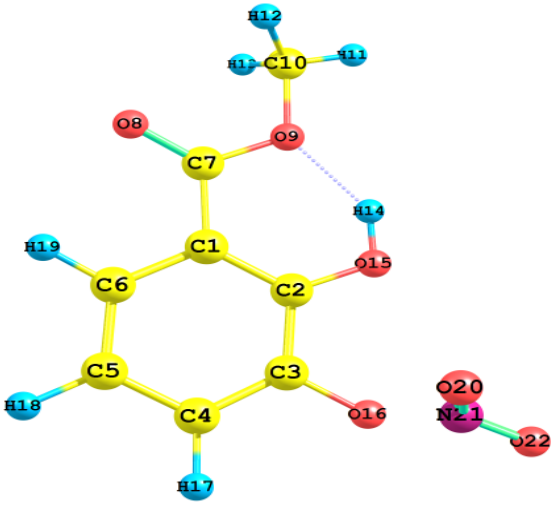
Fig.S2 contd...



I2+NO



TS4



I3

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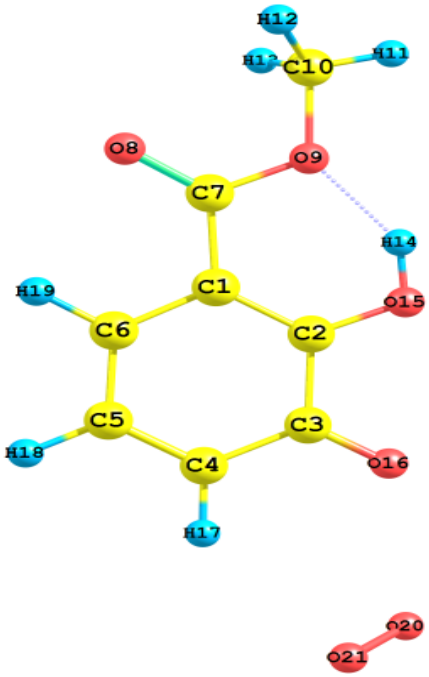
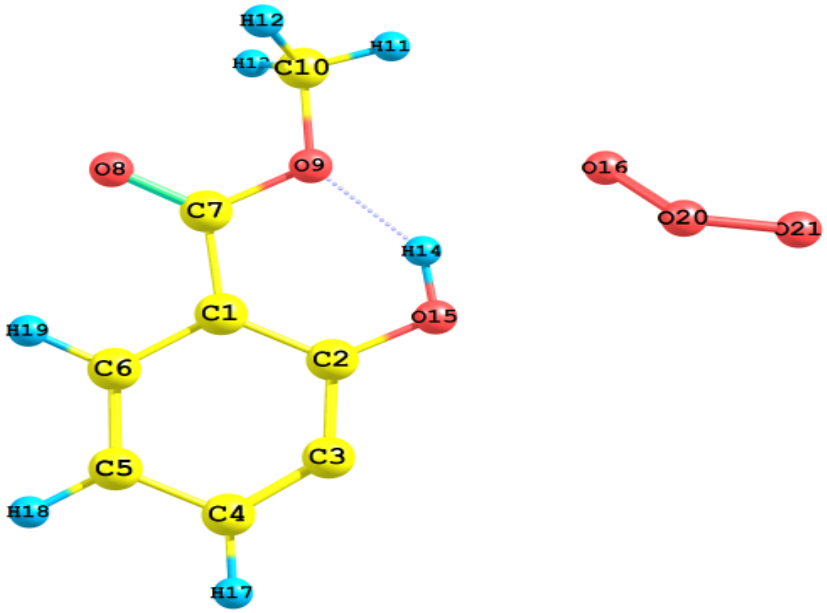
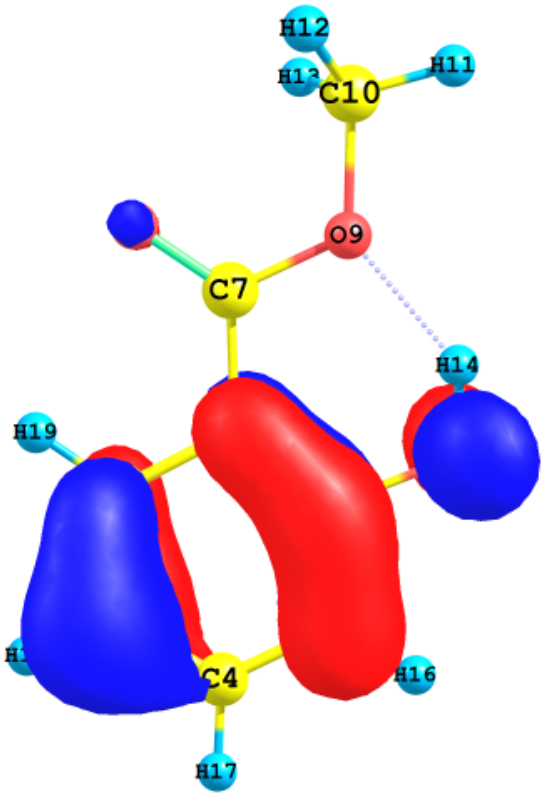


I3+O2



P3

Fig.S2 contd...



Reactant-HOMO

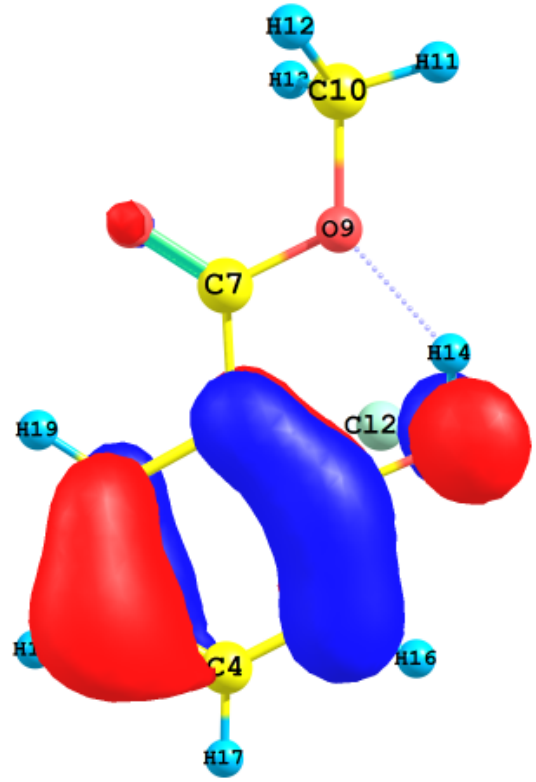
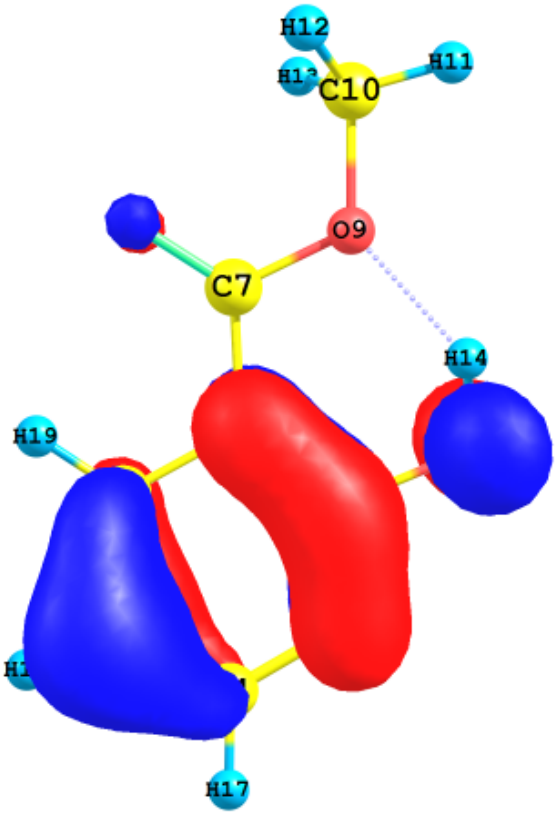
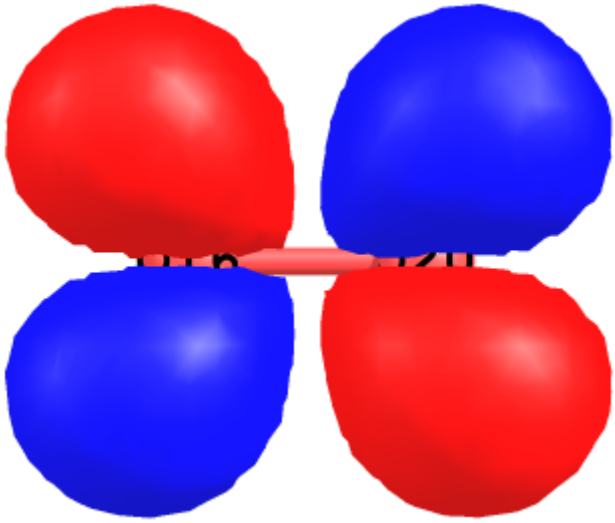


Fig.S3 **TS1-HOMO**

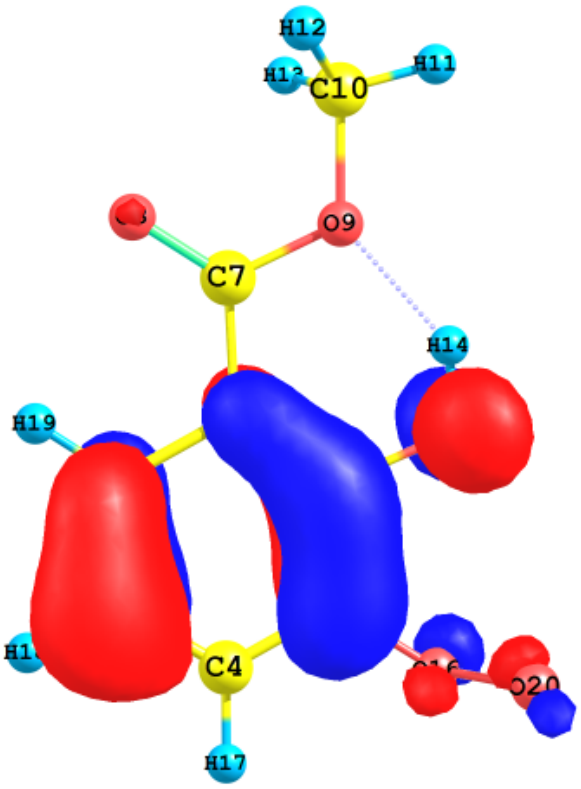


I1-HOMO



O_2-HOMO

Fig.S3 contd...



I2-HOMO

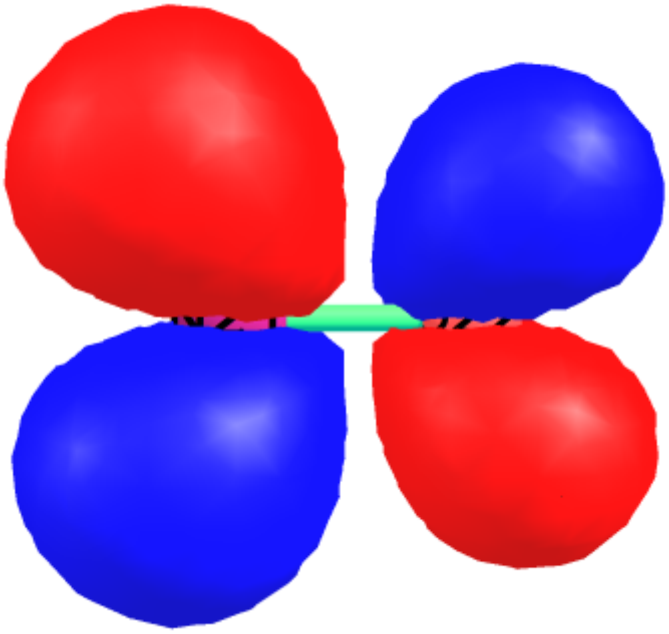
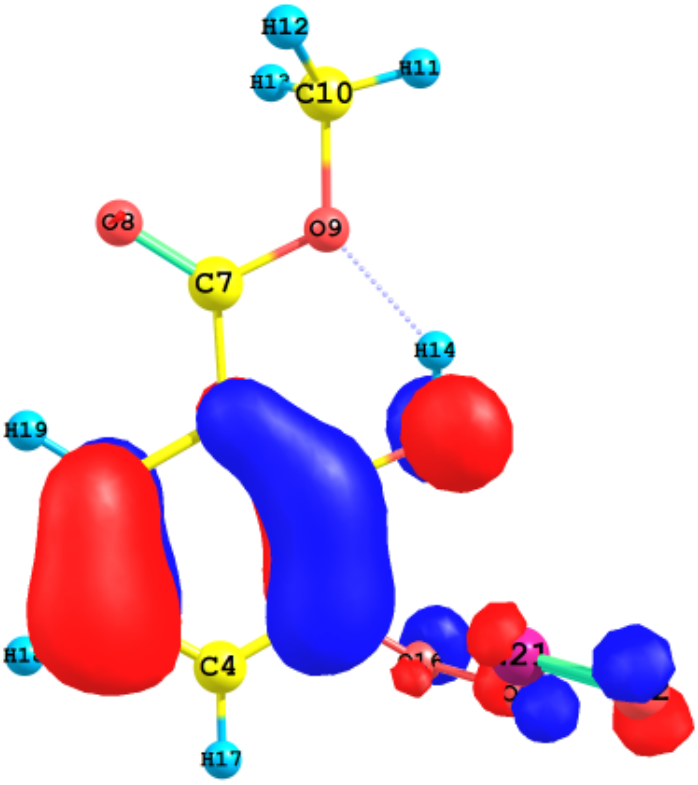


Fig.S3contd...

NO-HOMO



TS4-HOMO

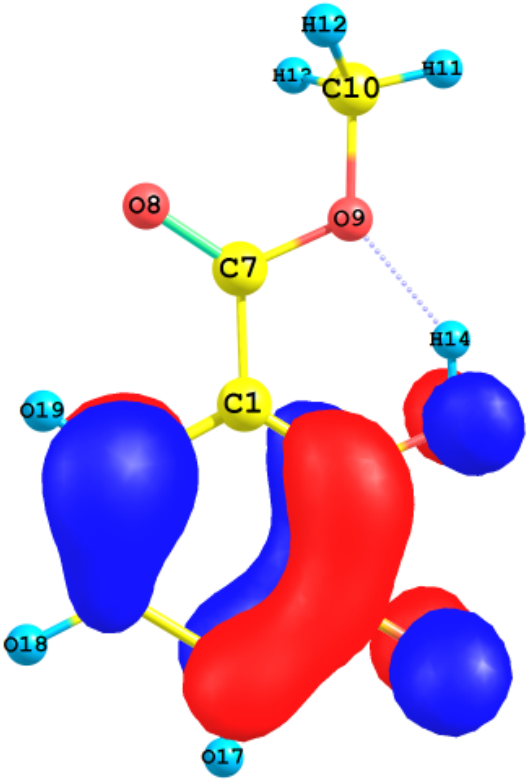
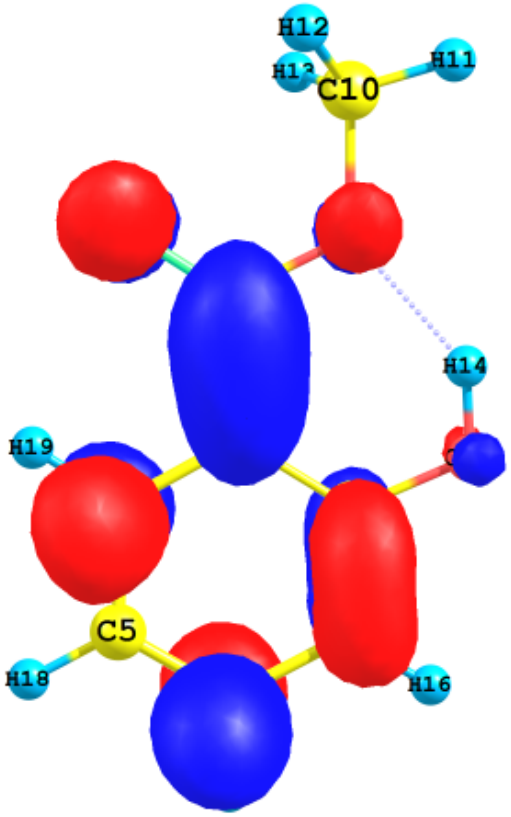
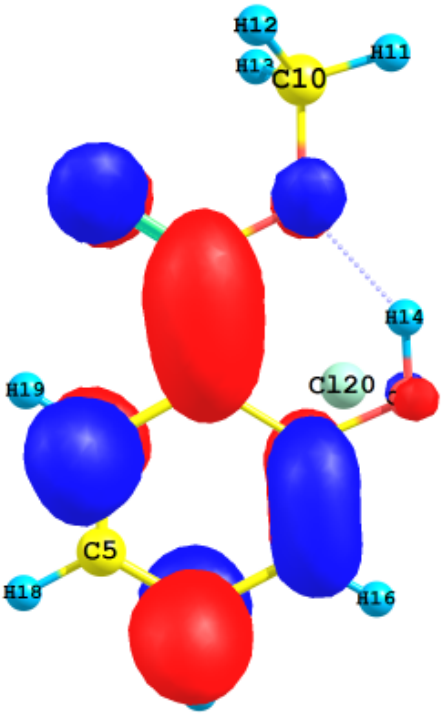


Fig.S3 contd...

I3-HOMO

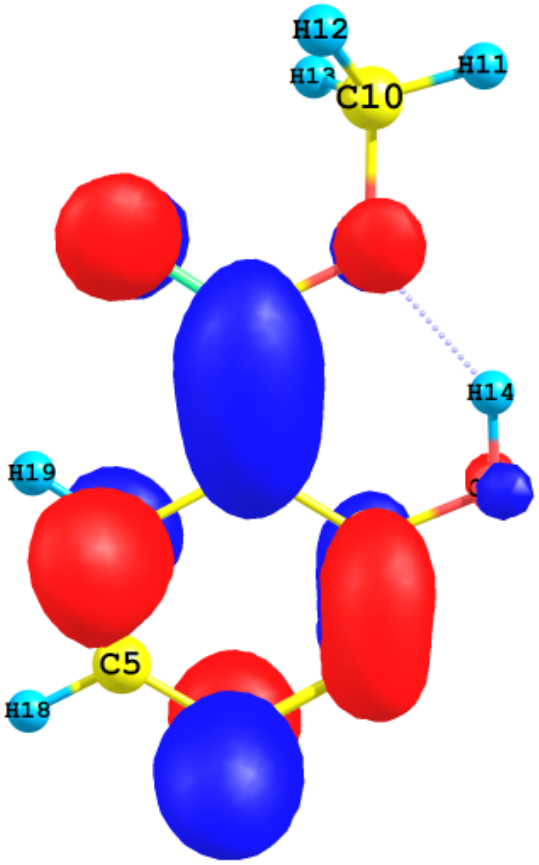


Reactant-LUMO

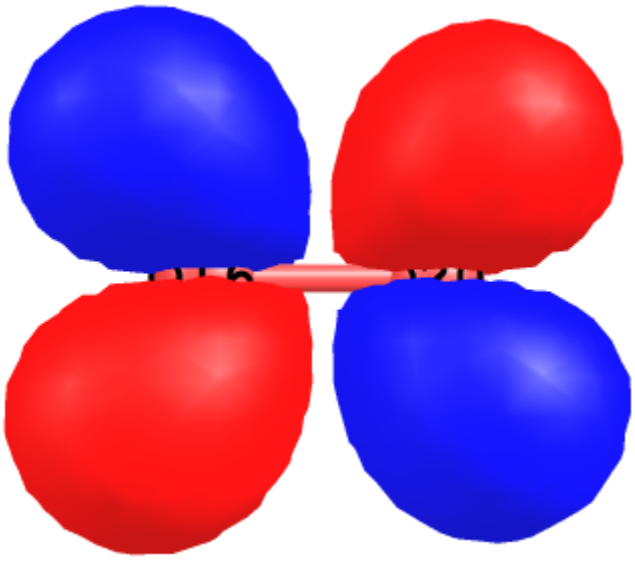


TS1-LUMO

Fig.S4

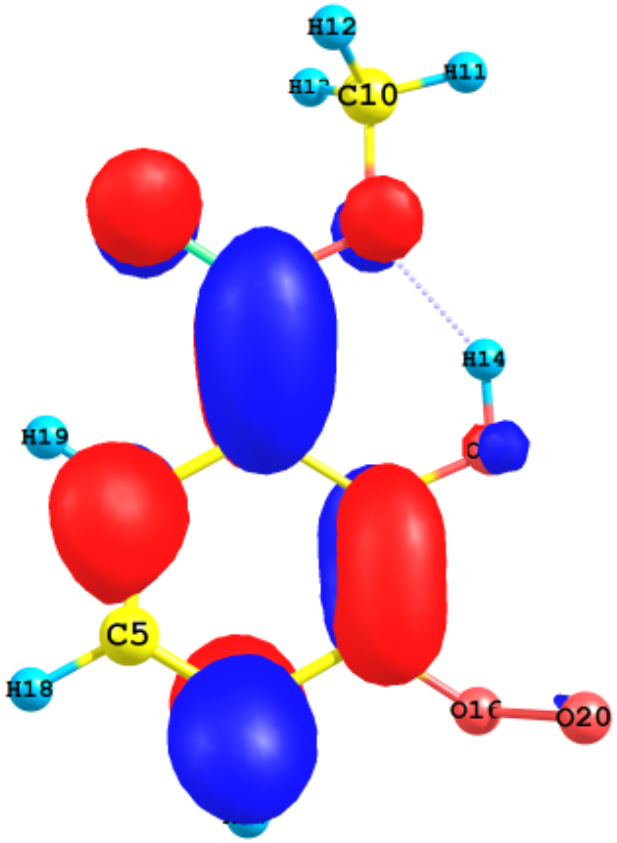


I1-LUMO

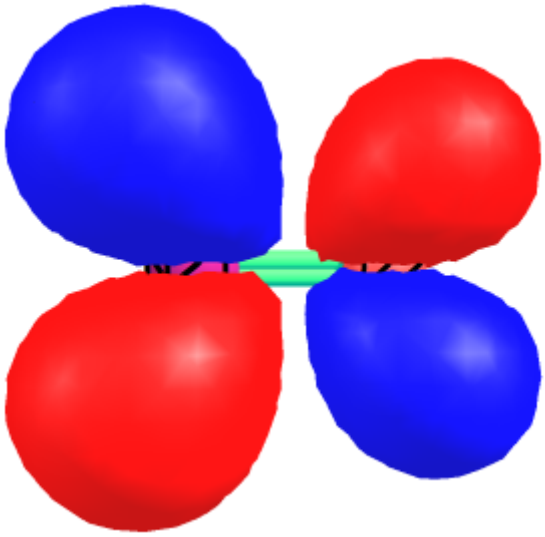


O_2-LUMO

Fig.S4 contd...

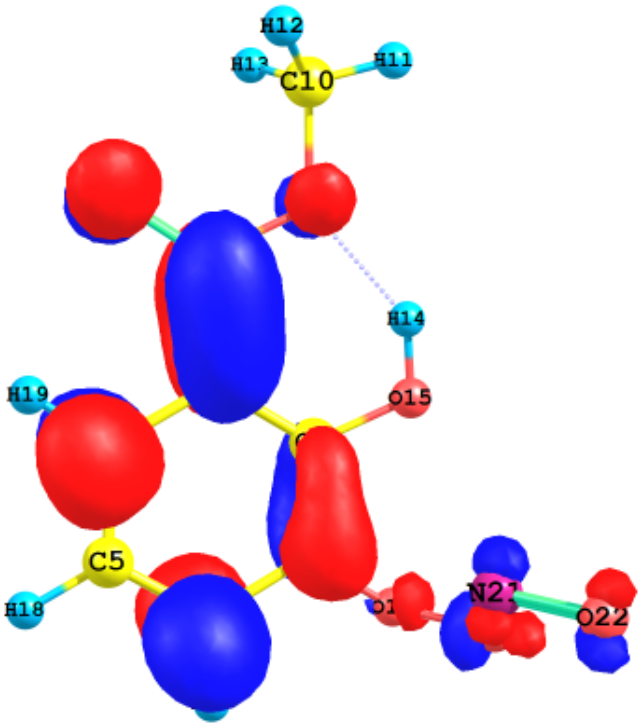


I2-LUMO



NO-LUMO

Fig.S4 contd...



TS4-LUMO

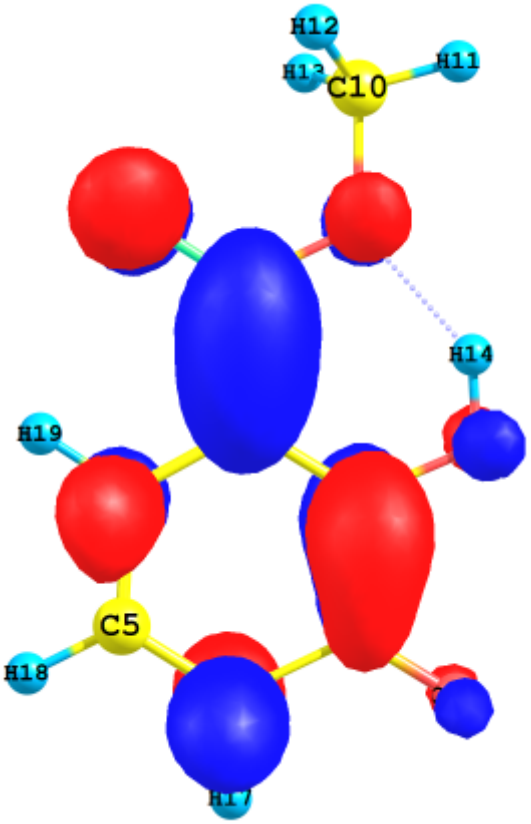


Fig.S4 contd...

I3-LUMO

TABLE CAPTIONS

Table S1 The selected geometrical parameters (bond length R, in Å, bond angle, θ and dihedral angle, ϕ in degrees) on the potential energy surface of the favourable reaction path calculated at M06-2X/6-311++G(d,p) level of theory.

Table S2 The global reactivity parameters, hardness (η), softness $1/\eta$, electrophilicity index (ω), activation hardness (Δn^*) in eV calculated at M06-2X/6-311++G(d,p) level of theory.

Table S3 The global reactivity parameters, Homo, lumo, energy gap (ΔE) in eV calculated at M06-2X/6-311++G(d,p) level of theory.

Table S4 NOFFs (unit in electrons) of methyl salicylate with Cl radical of initial reaction and peroxy radical with their reactivities calculated at M06-2X/6-311++G(d,p) level of theory.

Table S5 NOFFs (unit in electrons) of peroxy radical with HO_2, NO_2, NO radical and their corresponding intermediates, transistion state and products with their reactivities calculated at M06-2X/6-311++G(d,p) level of theory.

Table S6 Topological analysis of reactants, transition states, intermediates and products of methyl salicylate with Cl radical calculated at M06-2X/6-311++G(d,p) level of theory (values are in atomic units).

FIGURE CAPTIONS

Fig.S1 The optimized structures of the reactive species corresponding to the formation of peroxy radical I2 from the Cl-initiated reaction of Methyl salicylate at M06-2X/6-311++G(d,p) level of theory.

Fig.S2 The optimized structures of the reactive species corresponding to the reactions of peroxy radical I2 with HO_2, NO_2 and NO at M06-2X/6-311++G(d,p) level of theory.

Fig.S3 The density plot of highest occupied molecular orbital (HOMOs) of most favourable reaction pathway calculated at M06-2X/6-311++G(d,p) level of theory. Here red region indicates the positive phase and the blue region indicates the negative phase. The contour shown is 0.05 a.u.

Fig.S4 The density plot of lowest unoccupied molecular orbital (LUMOs) of most favourable reaction pathway calculated at M06-2X/6-311++G(d,p) level of theory. Here red region indicates the positive phase and the blue region indicates the negative phase. The contour shown is 0.05 a.u.