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Supplementary Material

O_3-initiated oxidation mechanisms and kinetics of catechol

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Table S1. The energy barriers and exothermic value of catechol + O_3 → IM2 are obtained with several different functionals, with and without dispersion corrections.

Functionals	with dispersion corrections		without dispersion corrections	
	$\Delta E^{\neq}$	$\Delta_r E$	$\Delta E^{\neq}$	$\Delta_r E$
M062X/aug-cc-pVDZ	-	-	6.08	-37.92
B2PLYP/ aug-cc- pVDZ	6.04	-37.67	8.51	-35.56
wB97X/ aug-cc- pVDZ	7.35	-28.14	9.29	-30.70

Table S2. The energy barriers ($\Delta E^{\neq}$) of catechol + O_3 → IM1 at various levels of theory. Units of $\Delta E^{\neq}$ is kcal mol^{-1}.

Methods	Energy barriers $\Delta E^{\neq}$ (kcal mol^{-1})	Note
CCSD(T)/6-311++g(3df,2p)	7.45	
M06-2X/aug-cc-pVDZ	8.09	ZPEs from
M06-2X/ aug-cc-pVTZ	8.70	M06-2X/6-31+g(d,p)
M06-2X/6-311++g (3df, 2p)	8.10	

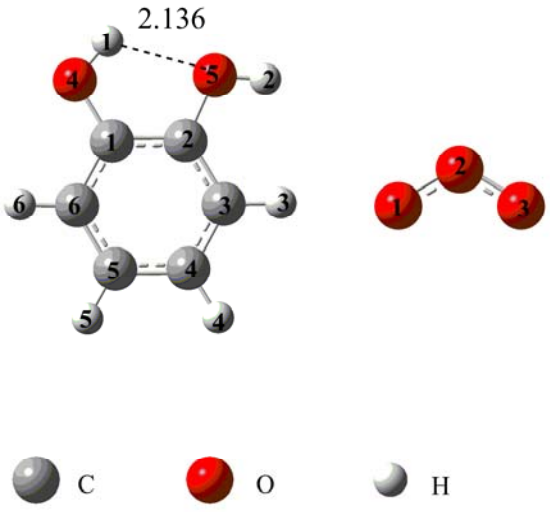


Fig. S1. The global minima structures of reactants with atom numbers and a hydrogen bond length (in Å) at M06-2X/6-31+G(d,p) level.

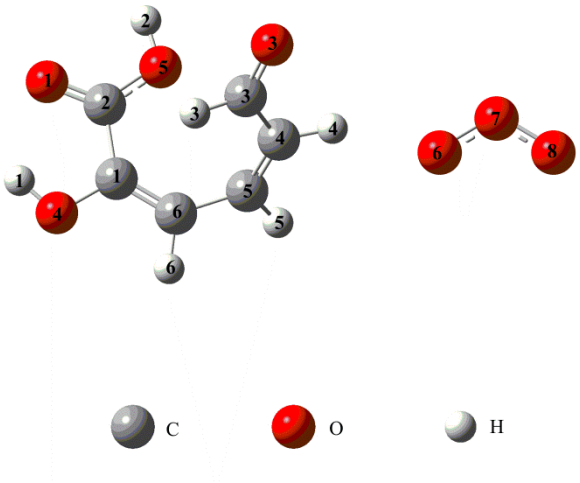


Fig. S2. The chemical structure for P2 and ozone with atom numbers at M06-2X/6-31+G(d,p) level.

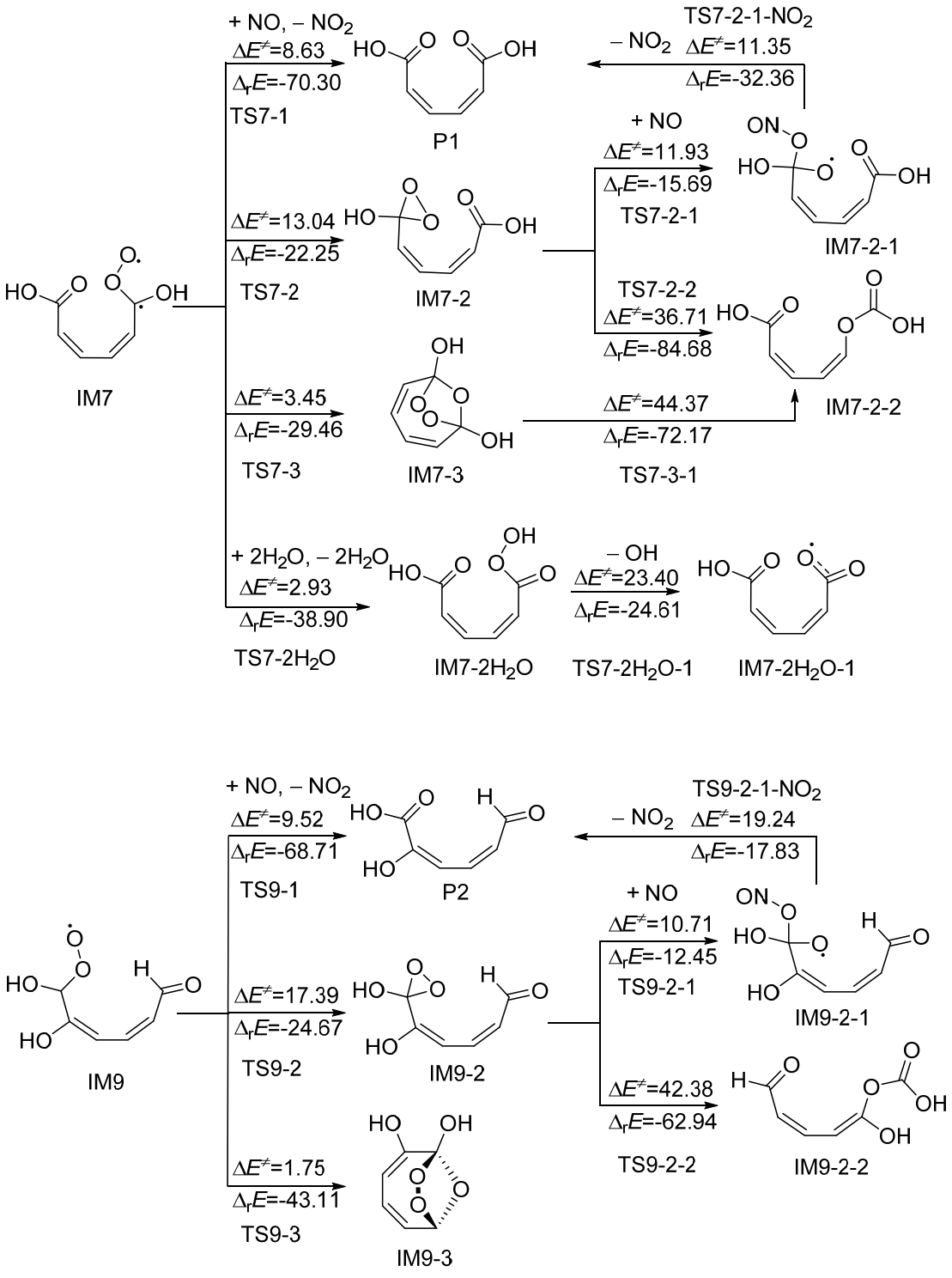


Fig. S3. The detailed mechanisms within reaction heats (Δ_rE) and energy barriers ($\Delta E^{\neq}$) of the further reaction for the Criegee intermediates IM7, IM8, IM9, IM10, IM11, IM12, IM13, IM14, IM15 and IM16. Units of $\Delta E^{\neq}$ and Δ_rE are kcal mol^{-1}. TS: transition state, IM: intermediate, P: product.

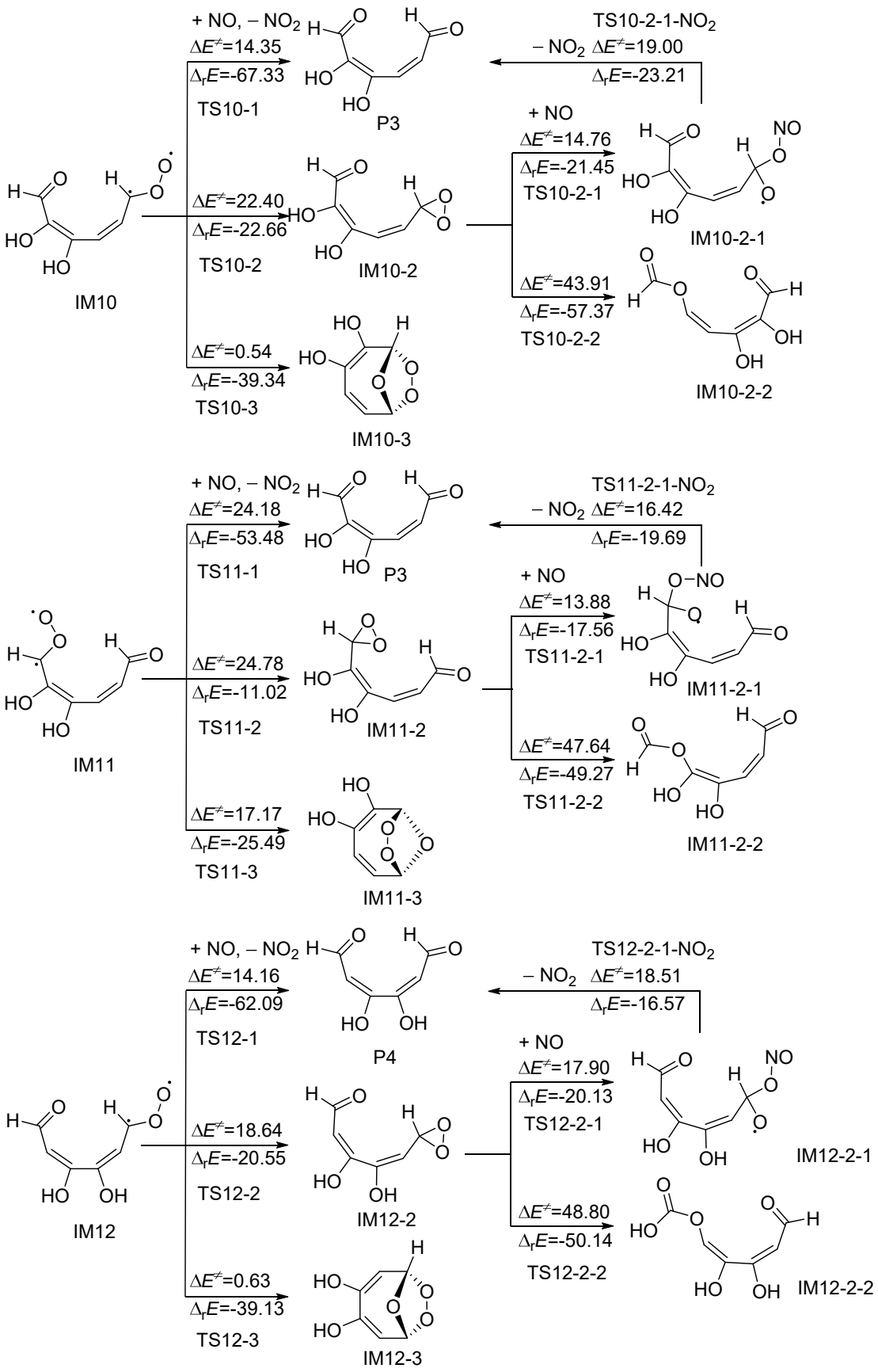


Fig. S3. Continued.

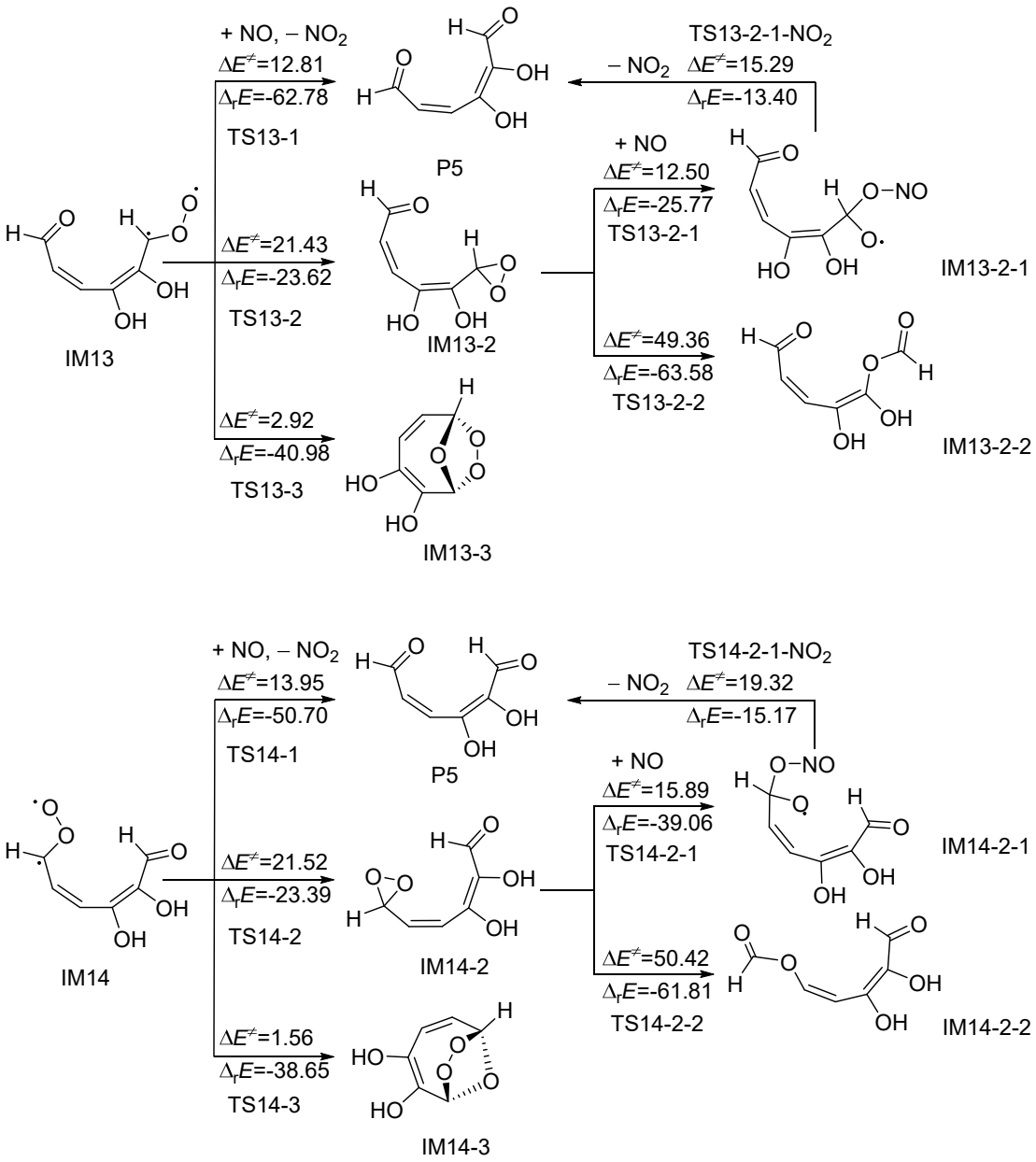


Fig. S3. Continued.

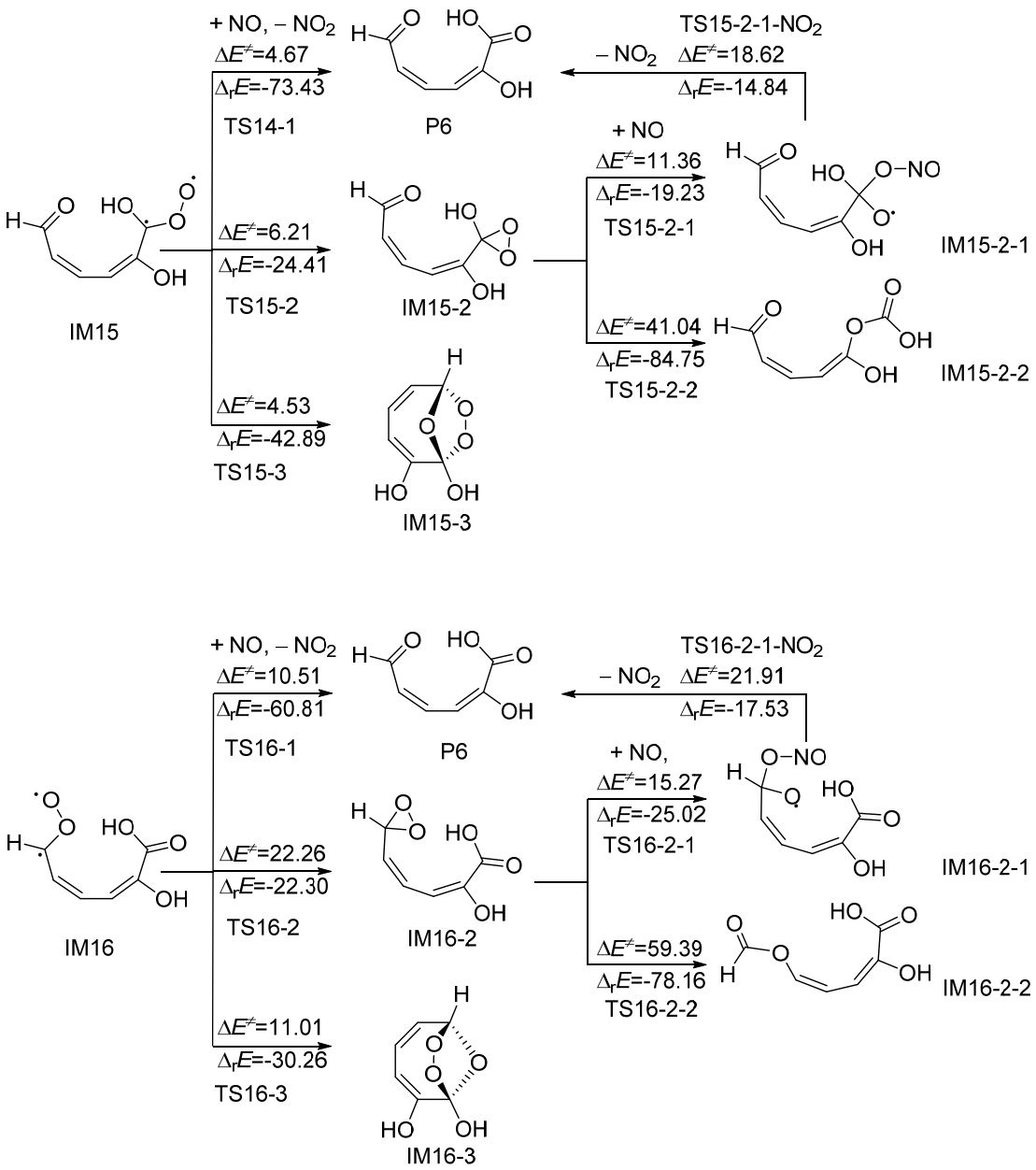


Fig. S3. Continued.

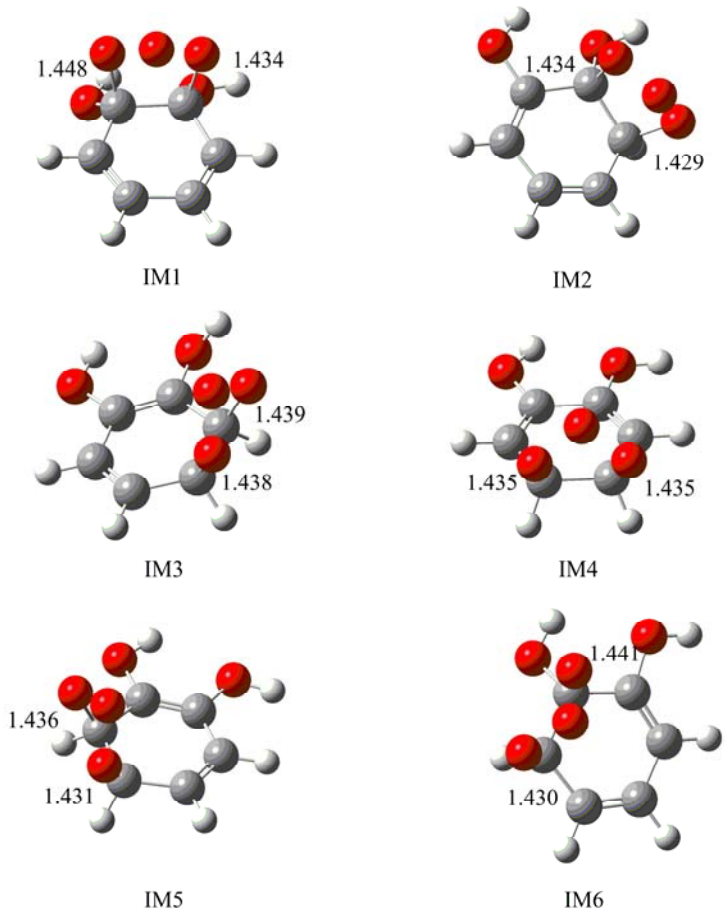
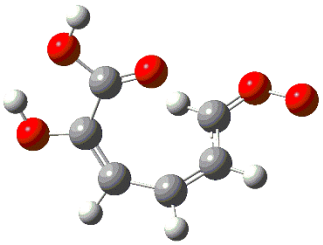
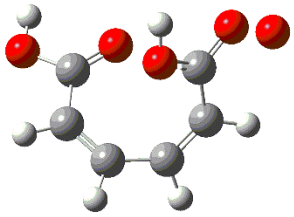


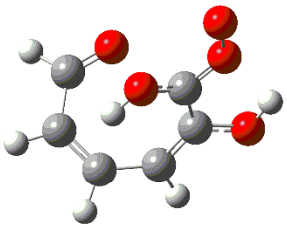
Fig. S4. M06-2X/6-31+G(d,p) optimized geometries for the primary ozonides and Criegee intermediates involved in reaction of catechol + O_3. Bond lengths are in Å.



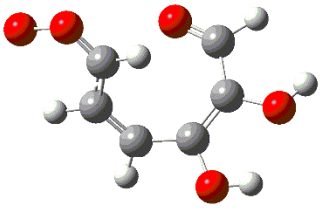
IM7



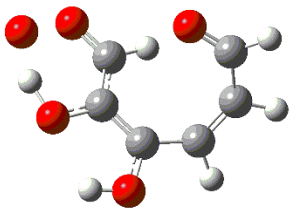
IM8



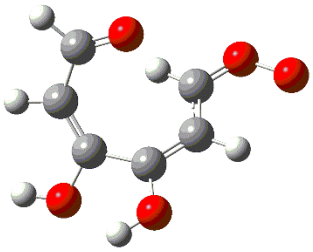
IM9



IM10



IM11



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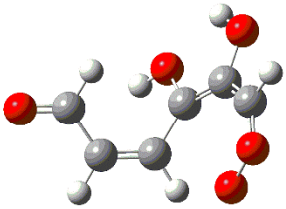
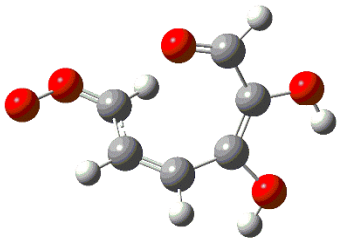
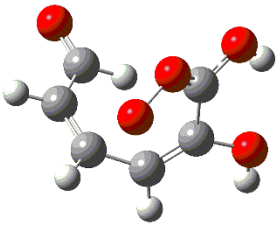


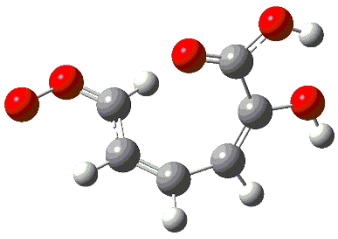
IM13



IM14



IM15



IM16

Fig. S4. Continued.

Table S3. The changes of Gibbs free energy (ΔG_{gas}, ΔG_{aq}) and free energy of activation ($\Delta G^{\neq}_{gas}$, $\Delta G^{\neq}_{aq}$) of elementary reactions. K_{gas} and K_{aq} are the equilibrium constants. Units of ΔG_{gas}, ΔG_{aq}, $\Delta G^{\neq}_{gas}$ and $\Delta G^{\neq}_{aq}$ are kcal mol^{-1}.

Reactions	$\Delta G^{\neq}_{gas}$	ΔG_{gas}	$\Delta G^{\neq}_{aq}$	ΔG_{aq}	K_{gas}	K_{aq}
R+O_3→TS1→IM1	18.76	-24.91	18.39	-25.35	8.09×10^{-2}	1.84×10^{-1}
R+O_3→TS2→IM2	18.45	-25.16	20.02	-23.91	1.14×10^{-1}	1.01×10^{-1}
R+O_3→TS3→IM3	20.46	-21.65	20.83	-21.59	3.23×10^{-4}	2.72×10^{-4}
R+O_3→TS4→IM4	19.83	-23.15	18.39	-25.35	4.04×10^{-3}	1.38×10^{-1}
R+O_3→TS5→IM5	22.84	-20.64	21.02	-23.28	5.87×10^{-5}	4.35×10^{-3}
R+O_3→TS6→IM6	19.58	-23.59	17.88	-25.16	7.68×10^{-3}	1.02×10^{-1}
IM1→TS7→IM7	17.26	-29.81	16.82	-45.18	1.36×10^{24}	1.43×10^{33}
IM2→TS8→IM8	20.83	-22.15	18.51	-36.40	2.57×10^{18}	5.32×10^{26}
IM2→TS9→IM9	30.75	-7.34	26.29	-23.53	3.31×10^{7}	1.85×10^{17}
IM3→TS10→IM10	29.05	-6.59	23.47	-20.47	9.35×10^{6}	9.87×10^{14}
IM3→TS11→IM11	29.62	-19.95	26.79	-25.10	5.61×10^{16}	2.44×10^{18}
IM4→TS12→IM12	29.12	-7.40	24.28	-23.85	3.48×10^{7}	3.45×10^{17}
IM5→TS13→IM13	32.13	-6.59	27.92	-13.81	9.04×10^{6}	1.40×10^{10}
IM5→TS14→IM14	29.49	-7.91	25.66	-18.57	8.36×10^{7}	4.17×10^{13}
IM6→TS15→IM15	31.25	-7.09	24.66	-21.46	2.91×10^{7}	6.04×10^{15}
IM6→TS16→IM16	23.28	-12.36	19.95	-34.20	2.92×10^{16}	1.27×10^{25}
IM8+NO→TS8-1→P2+NO_2	26.92	-64.32	32.00	-54.97	1.38×10^{47}	9.54×10^{47}
IM8→TS8-2→IM8-2	21.59	-23.59	23.83	-24.54	1.93×10^{17}	1.66×10^{6}
IM8-2→TS8-2-1→IM8-2-1	23.22	-13.37	23.41	-16.50	1.35×10^{8}	5.37×10^{3}
IM8-2-1→TS8-2-1-NO_2→P2+NO_2	22.34	-27.36	19.52	-13.93	1.63×10^{40}	4.89×10^{55}
IM8-2→TS8-2-2→IM8-2-2	51.27	-72.04	52.90	-65.07	6.84×10^{52}	5.48×10^{47}
IM8→TS8-3→IM8-3	11.73	-29.68	20.08	-16.82	5.92×10^{21}	3.34×10^{13}
IM8-3→TS8-3-1→P4	37.84	-63.75	30.75	-54.84	5.49×10^{46}	1.00×10^{39}
IM8+H_2O→IM08-H_2O	-	-10.17	-	-21.65	1.13×10^{-12}	4.98×10^{-11}
IM08-H_2O→TS8-H_2O→IM8-H_2O+H2O	6.15	-8.85	24.16	-6.28	1.90×10^{-4}	6.42×10^{-2}
IM8-H_2O→TS8-H_2O-CO_2→IM8-H_2O-CO_2+CO_2	27.30	-6.21	28.74	-1.88	2.67×10^{14}	8.53×10^{12}

Table S4. Detail energy of reactants, intermediates, transition states and products. Units of Zero, Zero $G_{correct}$, SP, G_{water} are hartree while Gibbs free energy of salvation ($G_{solvation}$) is kcal mol^{-1}.

Species	Zero-point correction /6-31+G(d,p)	Thermal $G_{correct}$ /6-31+G(d,p)	SP /aug-cc-pVDZ	G_{water} /aug-cc-pVDZ	$G_{solvation}$ /aug-cc-pVDZ
R	0.1100	0.0796	-382.6055	-382.6240	-7.83
O_3	0.0081	-0.0156	-225.3555	-225.3602	-2.99
TS1	0.1224	0.0853	-607.9524	-607.9762	-11.61
IM1	0.1224	0.0886	-608.0253	-608.0492	-11.99
TS7	0.1202	0.0871	-607.9963	-608.0209	-11.53
IM7	0.1209	0.0838	-608.0680	-608.1164	-24.73
TS2	0.1201	0.0857	-607.9533	-607.9740	-9.69
IM2	0.1232	0.0894	-608.0265	-608.0477	-10.22
TS8	0.1207	0.0874	-607.9913	-608.0162	-11.57
IM8	0.1208	0.0835	-608.0559	-608.0998	-21.92
TS9	0.1200	0.0865	-607.9746	-608.0029	-13.54
IM9	0.1202	0.0841	-608.0329	-608.0799	-24.06
TS3	0.1205	0.0859	-607.9503	-607.9729	-10.97
IM3	0.1240	0.0900	-608.0215	-608.0466	-11.35
TS10	0.1204	0.0863	-607.9715	-608.0035	-15.82
IM10	0.1198	0.0826	-608.0246	-608.0698	-22.71
TS11	0.1211	0.0875	-607.9718	-607.9994	-13.1
IM11	0.1184	0.0820	-608.0453	-608.0766	-13.94
TS4	0.1200	0.0850	-607.9504	-607.9759	-12.72
IM4	0.1241	0.0901	-608.0240	-608.0507	-13.46
TS12	0.1205	0.0864	-607.9739	-608.0083	-17.17
IM12	0.1202	0.0833	-608.0290	-608.0819	-27.3
TS5	0.1199	0.0851	-607.9457	-607.9718	-13.14
IM5	0.1232	0.0877	-608.0176	-608.0450	-13.98
TS13	0.1204	0.0862	-607.9649	-607.9990	-16.97
IM13	0.1199	0.0821	-608.0225	-608.0614	-18.23
TS14	0.1204	0.0864	-607.9693	-608.0028	-16.74
IM14	0.1198	0.0827	-608.0252	-608.0696	-22.12
TS6	0.1199	0.0854	-607.9512	-607.9771	-12.88
IM6	0.1232	0.0893	-608.0239	-608.0496	-13
TS15	0.1196	0.0854	-607.9702	-608.0064	-18.15
IM15	0.1191	0.0817	-608.0276	-608.0762	-24.48
TS16	0.1202	0.0866	-607.9841	-608.0151	-15.28
IM16	0.1209	0.0840	-608.0496	-608.0988	-25.23

NO	0.0048	-0.0152	-129.8665	-129.8673	1.77
TS8-1	0.1252	0.0816	-737.8928	-737.9294	-23.35
P2	0.1171	0.0816	-532.9939	-533.0218	-10.98
NO_2	0.0092	-0.0147	-205.0296	-205.0315	3.25
TS8-2	0.1193	0.0826	-608.0206	-608.0609	-19.57
IM8-2	0.1219	0.0855	-608.0955	-608.1409	-10.85
TS8-2-1	0.1267	0.0848	-737.9395	-737.8654	-9.09
IM8-2-1	0.1285	0.0870	-738.0000	-737.9592	-11.66
TS8-2-1-NO_2	0.1249	0.0834	-737.9608	-737.9165	-13.66
TS8-2-2	0.1174	0.0794	-608.0077	-608.0505	-20.55
IM8-2-2	0.1223	0.0850	-608.2098	-608.2441	-13.27
TS8-3	0.1208	0.0873	-608.0410	-608.0716	-11.14
IM8-3	0.1249	0.0921	-608.1118	-608.1352	-14.23
TS8-3-1	0.1206	0.0877	-608.0471	-608.0818	-17.27
IM8-3-1	0.1219	0.0859	-608.2072	-608.2164	-11.29
H_2O	0.0216	0.0040	-76.4086	-76.4222	-7.09
IM08-H_2O	0.1452	0.1066	-684.4998	-684.5756	-22.67
TS8-H_2O	0.1409	0.1032	-684.4866	-684.5337	-23.45
IM8-H_2O	0.1202	0.0841	-608.0568	-608.1349	-24.49
TS8-H_2O-CO_2	0.1176	0.0798	-608.0390	-608.0648	-8.77
IM8-H_2O-CO_2	0.1045	0.0710	-419.4822	-419.5065	-9.54
CO_2	0.0052	-0.0088	-188.5491	-188.5537	2.68