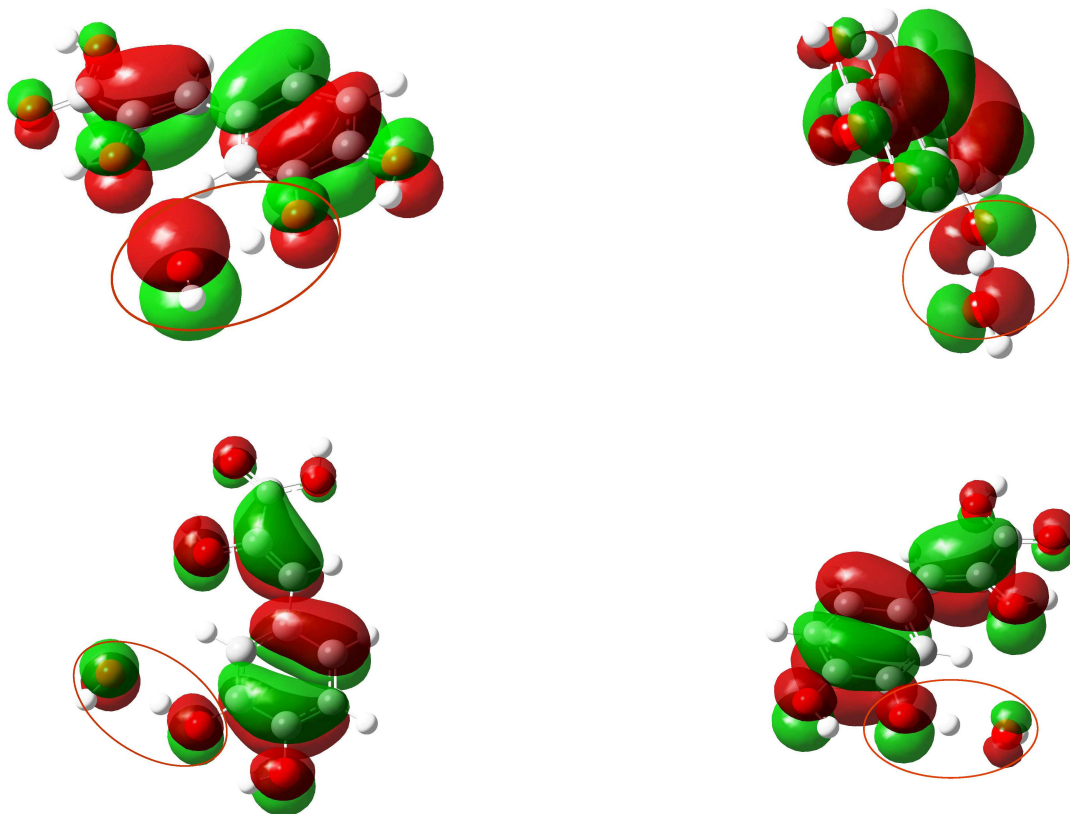


## 0.1 Supplementary information



**Fig.S1** SOMO distributions on a transition state structure in the reaction of D-DHPPA with  $\bullet\text{OH}$  radical in cyclohexane (top left), benzene (top right), methanol (bottom left) and water (bottom right).

**Table S1:** Reaction free energies (in kJ/mol) related to CPCET, ET-PT, PT-ET and PT mechanisms in different media, at B3LYP/6-31+G(d) level of theory. RFE-PT(X), RFE-CPCET(X) and RFE-ET(X) are the reaction free energies involving the reactive oxygen specie X and, related to PT, CPCET and ET mechanisms, respectively.

Attack site	Media	$\text{ROH} \longrightarrow \text{RO}^- + \text{H}^+$ $\bullet\text{OH} + \text{H}^+ \longrightarrow \text{H}_2\text{O}^+$ [RFE-PT(2)(OH)]	$\text{ROH} \longrightarrow \text{ROH}^+ + \text{e}^-$ $\bullet\text{OH} + \text{e}^- \longrightarrow \text{OH}^-$ [RFE-ET(1)(OH)]	$\text{ROH} \longrightarrow \text{RO}^\bullet + \bullet\text{H}$ $\bullet\text{OH} + \bullet\text{H} \longrightarrow \text{H}_2\text{O}$ $\Delta G^\ddagger$	$\text{ROH} \longrightarrow \text{RO}^\bullet + \bullet\text{H}$ $\bullet\text{OH} + \bullet\text{H} \longrightarrow \text{H}_2\text{O}$ [RFE-CPCET(OH)]	$\text{ROH} \longrightarrow \text{RO}^\bullet + \bullet\text{H}$ $\text{OBr}^- + \text{H}^\bullet \longrightarrow \text{HOBr}^-$ [RFE-CPCET(OBr <sup>-</sup> )]	$\text{ROH} \longrightarrow \text{RO}^- + \text{H}^+$ $\text{OBr}^- + \text{H}^+ \longrightarrow \text{HOBr}$ [RFE-PT(OBr <sup>-</sup> )]
DHPPA <sub>3</sub>	vacuum	795	539	31	-166	-64	-99
	cyclohexane	524	276	47	-164	-48	-48
	benzene	496	250	54	-164	-46	-44
	methanol	263	31	72	-158	-32	-7
	DMSO	258	28	76	-158	-32	-7
	water	253	21	78	-159	-33	-6
DHPPA <sub>4</sub>	vacuum	811	39	68	-148	-45	-83
	cyclohexane	536	276	-	-155	-38	-36
	benzene	508	250	79	-156	-38	-32
	methanol	265	31	93	-166	-40	-6
	DMSO	259	28	92	-166	-40	-6
	water	254	21	91	-165	-39	-5
DHPPA <sub>8</sub>	vacuum	819	539	-	-155	-53	-75
	cyclohexane	542	276	-	-161	-45	-29
	benzene	514	250	-	-162	-44	-26
	methanol	265	31	-	-169	-43	-5
	DMSO	261	28	-	-169	-43	-4
	water	255	21	-	-171	-46	-4