Supporting Information

Mechanistic insight into degradation of cetirizine under UV/chlorine treatment: Experimental and quantum chemical studies

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[#] Boyi Zhu and Fangyuan Cheng contributed equally to this work.

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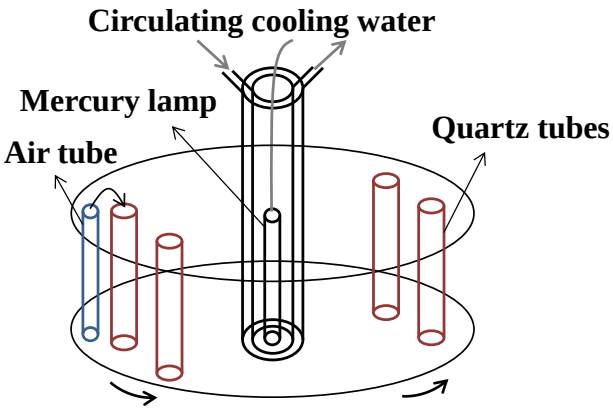


Figure S1. Photochemical reactor system diagram

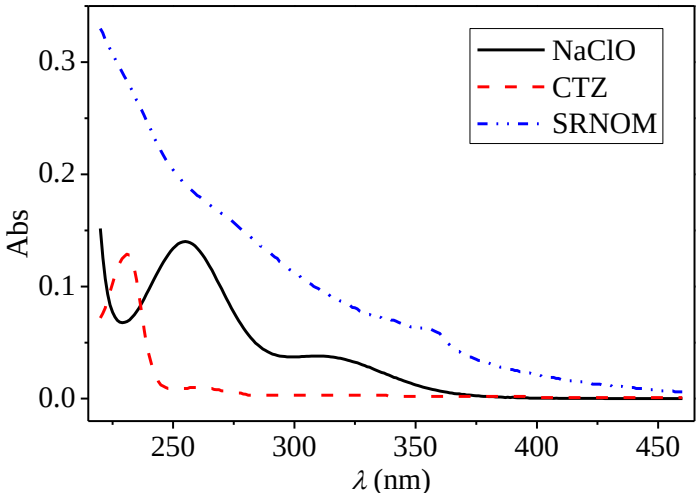


Figure S2. UV-Vis absorption spectra of NaClO (500 μM), CTZ (10 μM), and SRNOM (10 mg L^{-1})

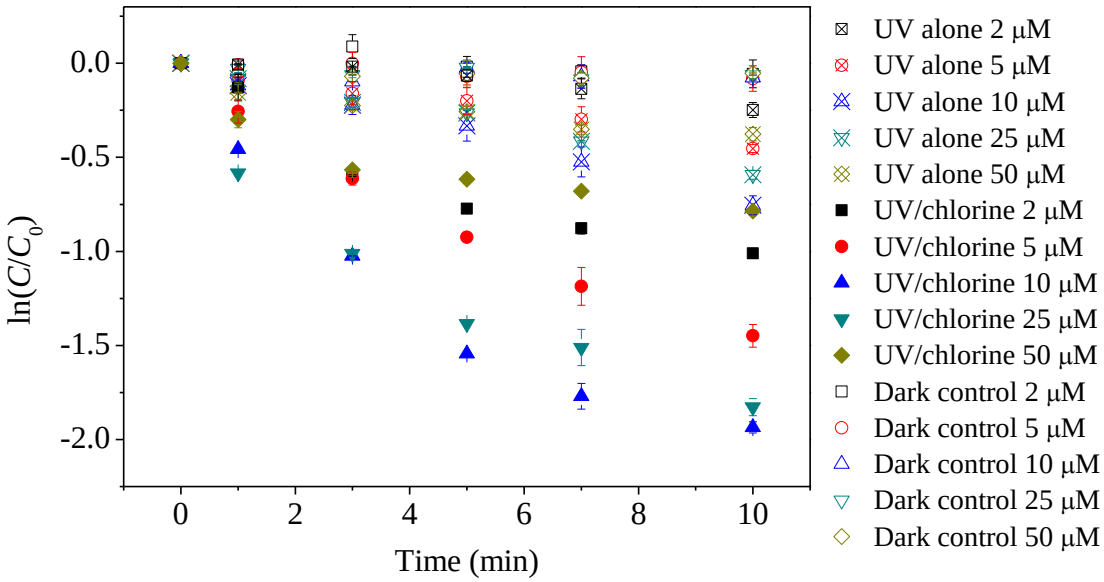


Figure S3. Degradation kinetics of CTZ with different concentrations in UV/chlorine system (pH = 7.0, $[\text{Free chlorine}]_0$ = 100 μM, the concentration values in the figure are for CTZ).

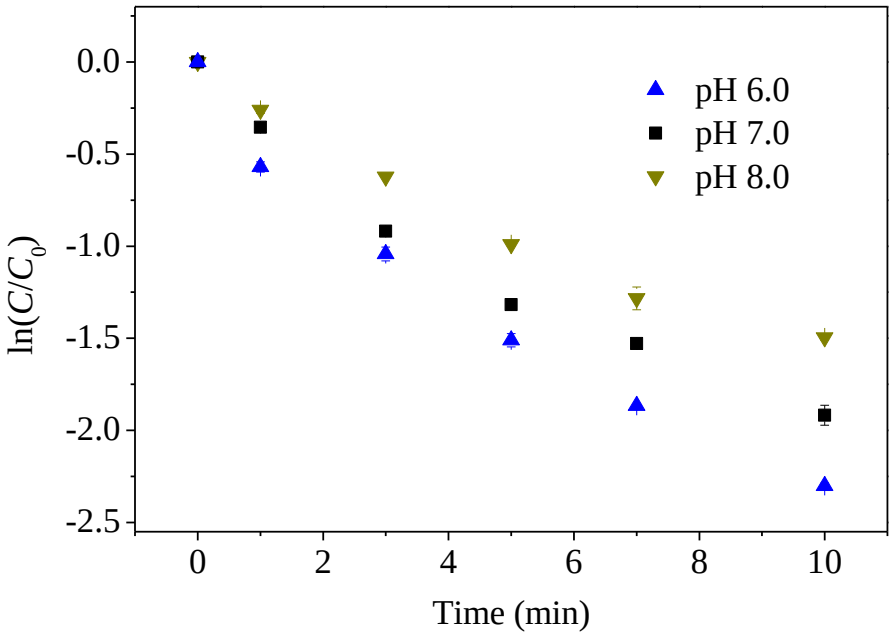


Figure S4. Degradation kinetics of CTZ in UV/chlorine system with different pH values ($[\text{CTZ}]_0$ = 10 μM, $[\text{Free chlorine}]_0$ = 100 μM).

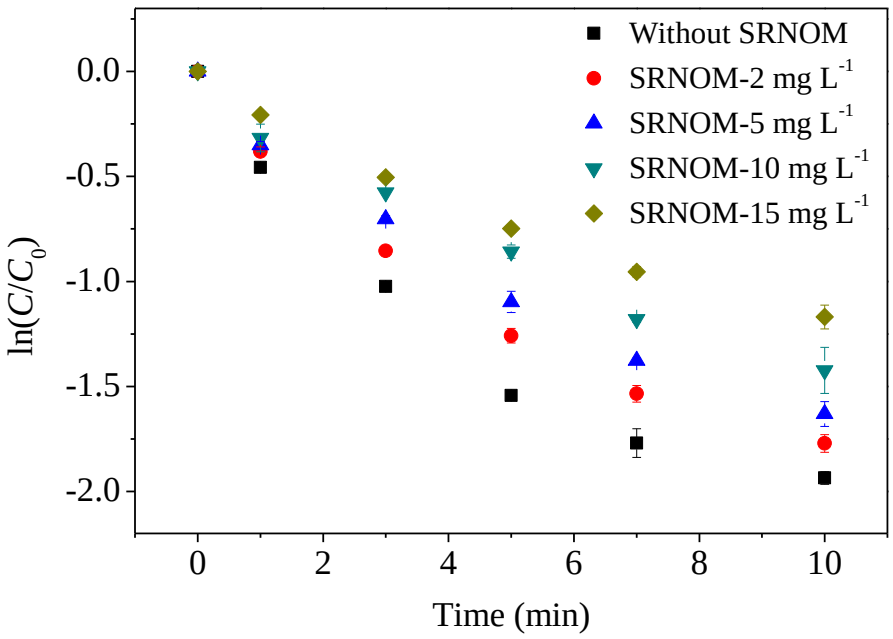


Figure S5. Degradation kinetics of CTZ in UV/chlorine system in the presence of SRNOM with different concentration (pH = 7.0, $[CTZ]_0$ = 10 μM, $[Free\ chlorine]_0$ = 100 μM).

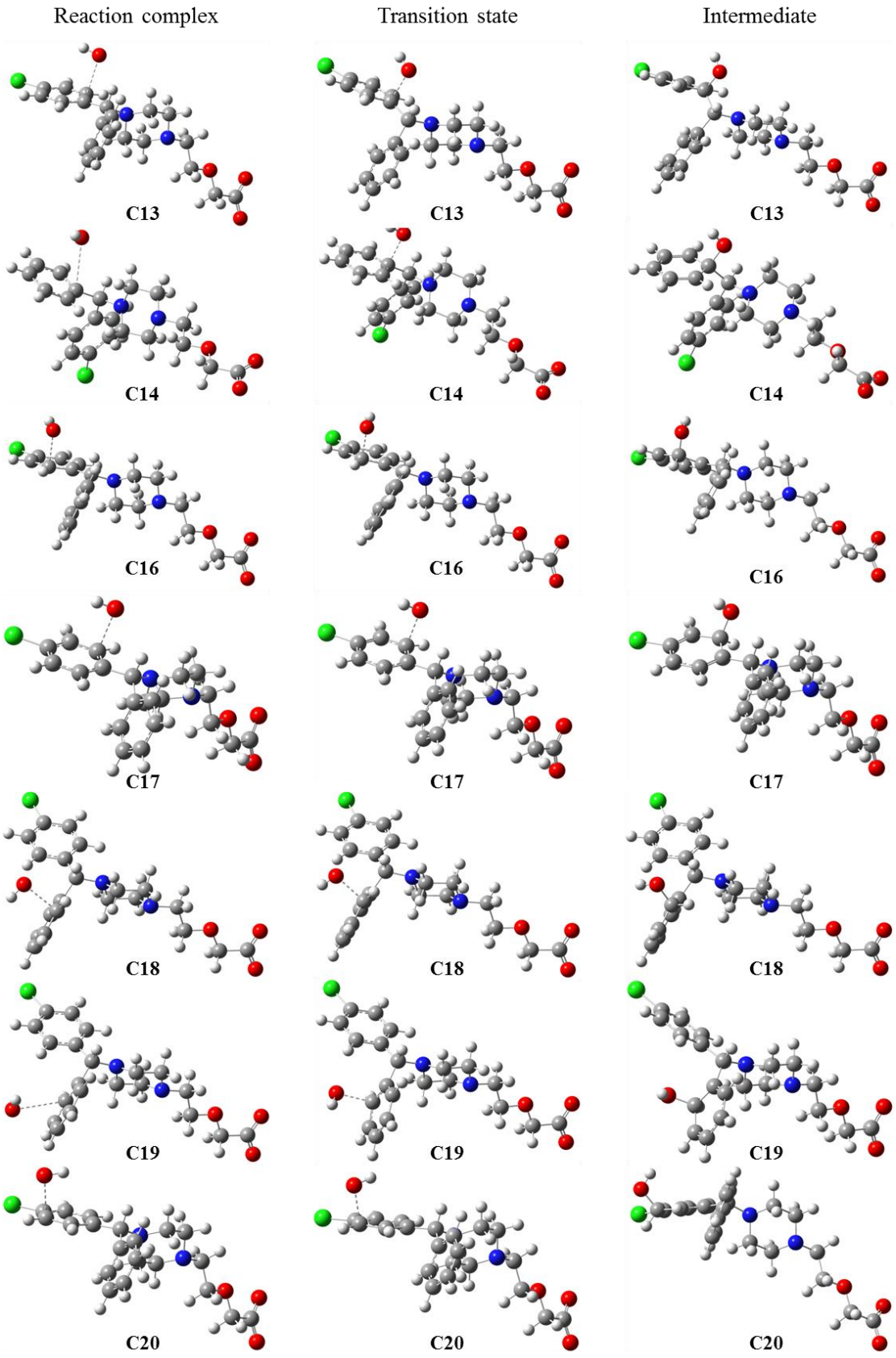
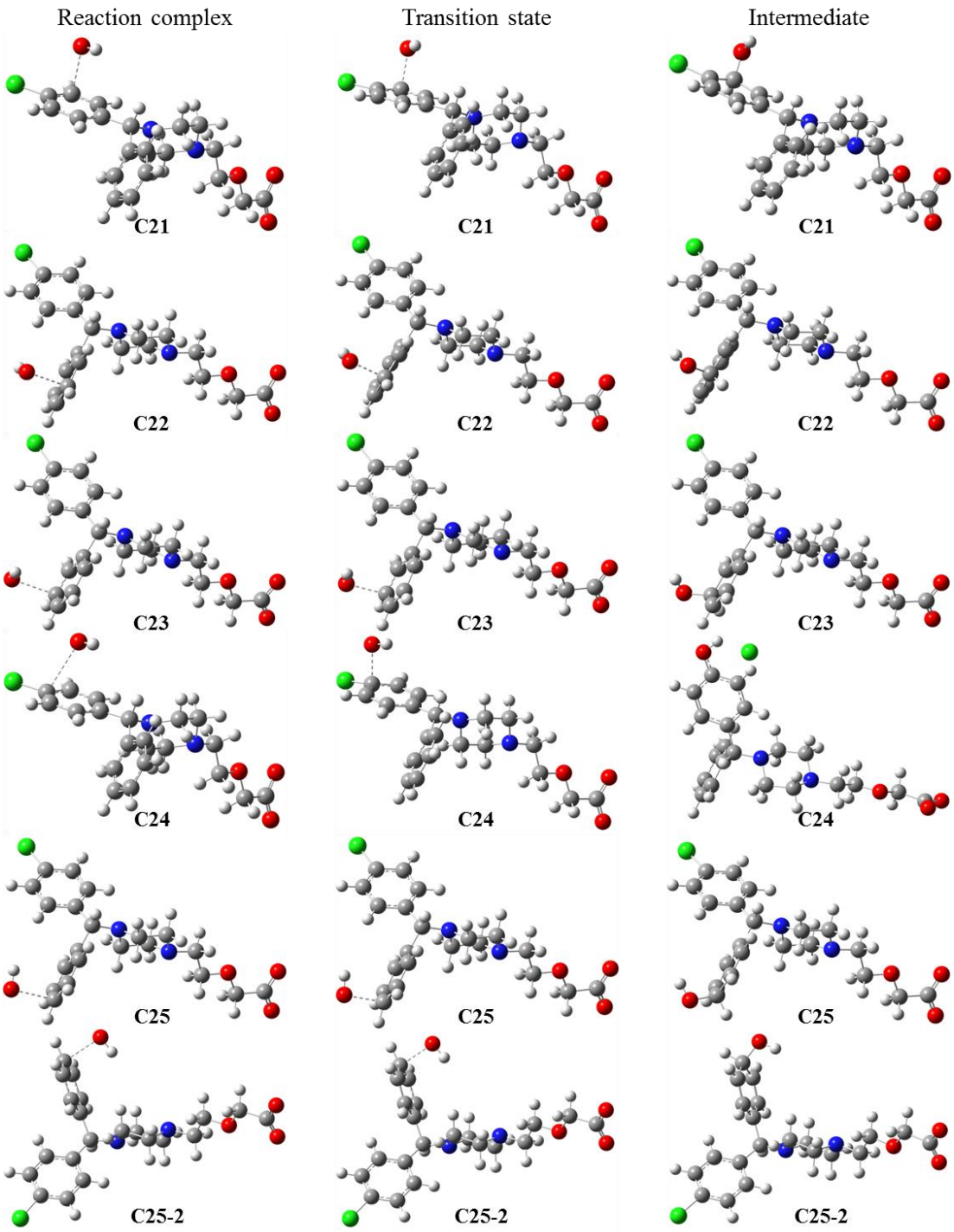


Figure S6. Reaction complexes, transition states and intermediates of the addition reaction pathways of CTZ with HO•



Continued Figure S6. Reaction complexes, transition states and intermediates of the addition reaction pathways of CTZ with HO•

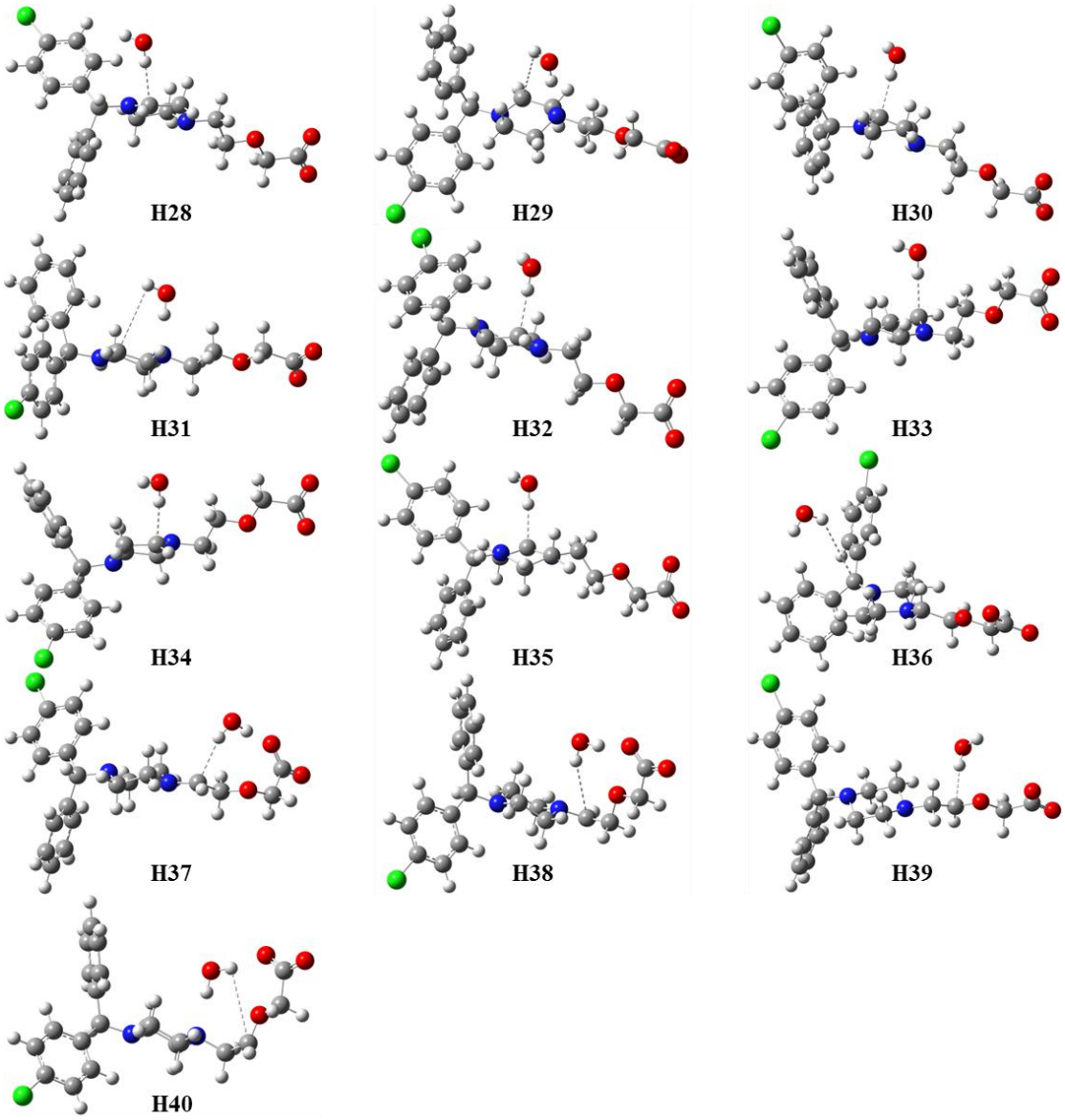


Figure S7. Reaction intermediates of barrierless H-abstraction reaction pathways of CTZ with HO•

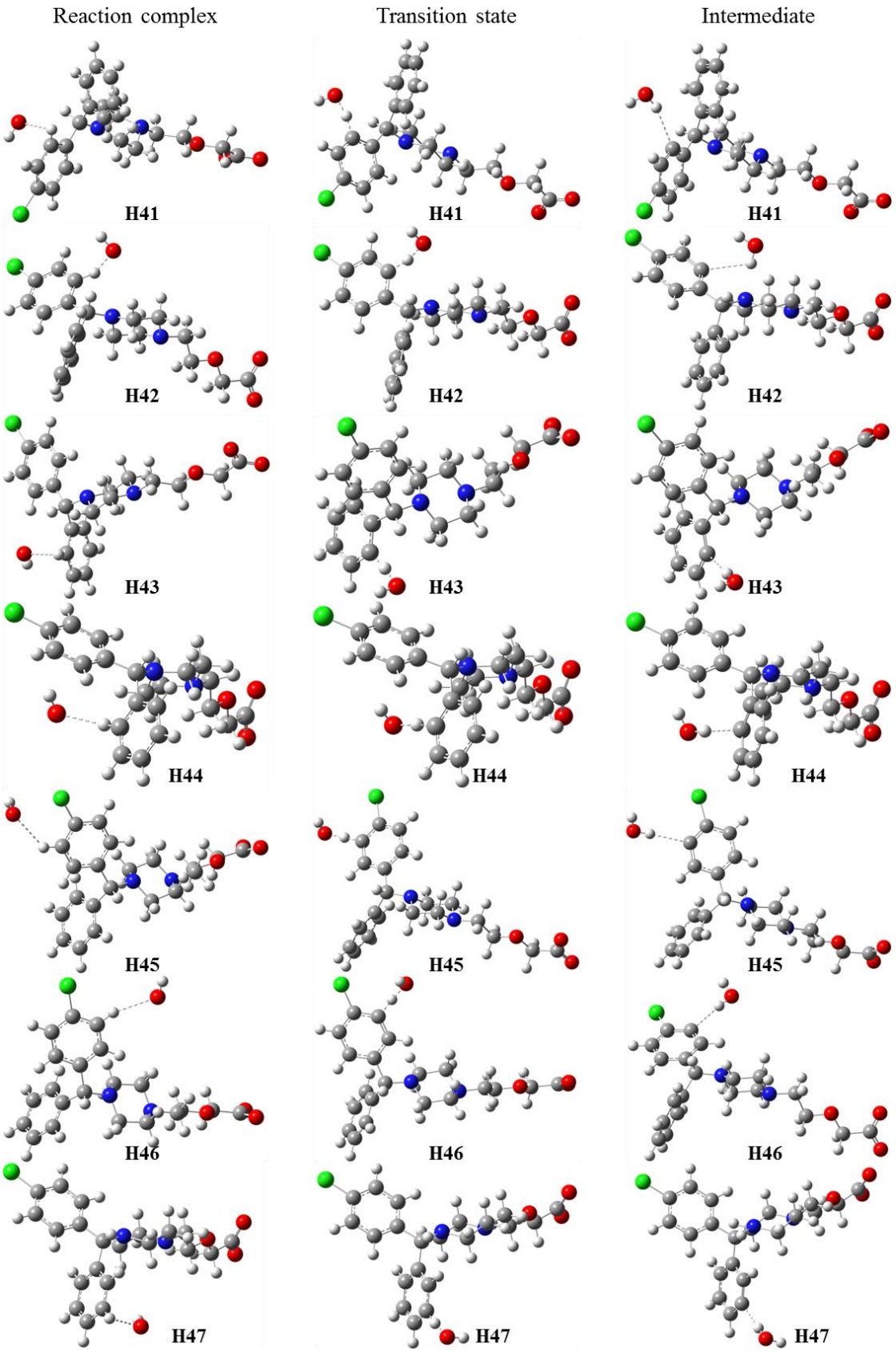
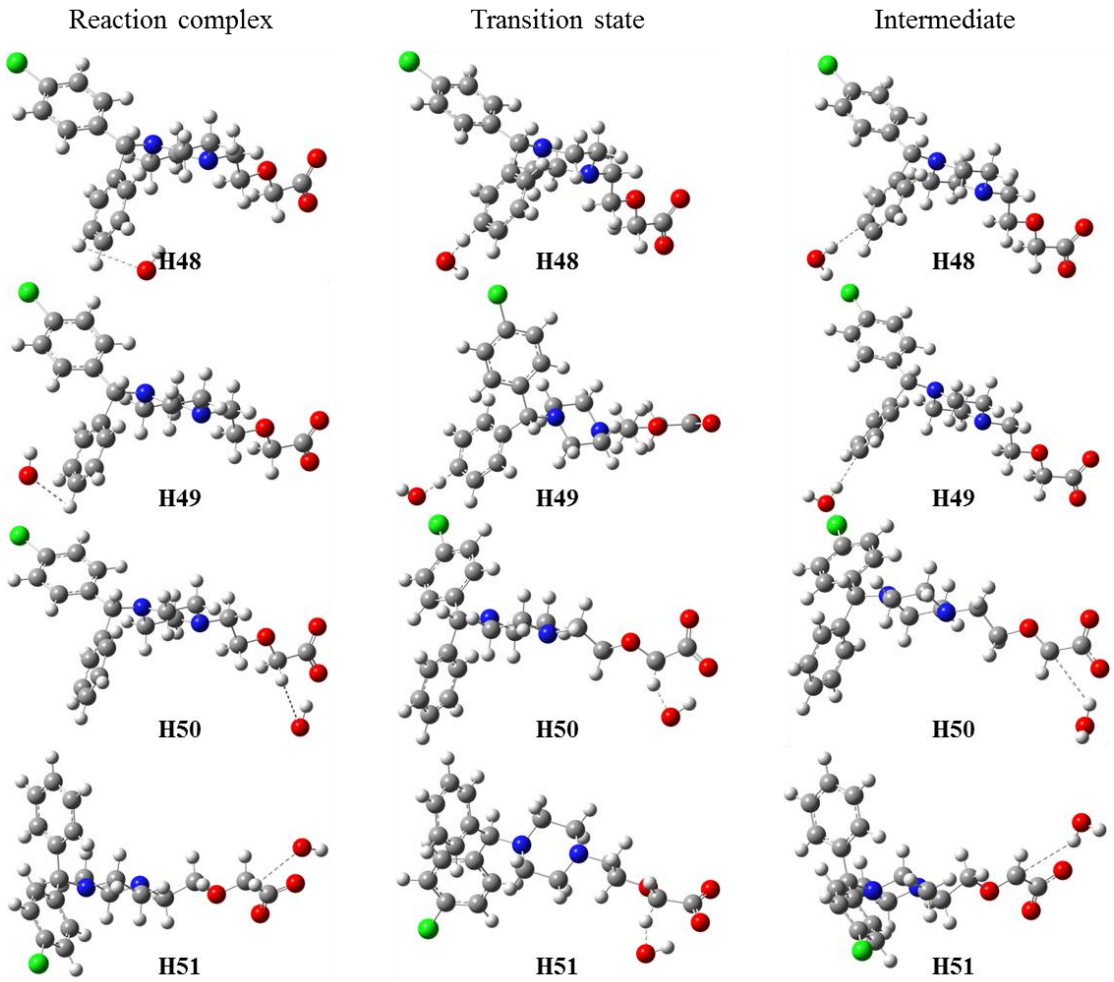


Figure S8. Reaction complexes, transition states and intermediates of the hydrogen abstraction pathways of CTZ with HO•



Continued Figure S8. Reaction complexes, transition states and intermediates of the hydrogen abstraction pathways of CTZ with HO•

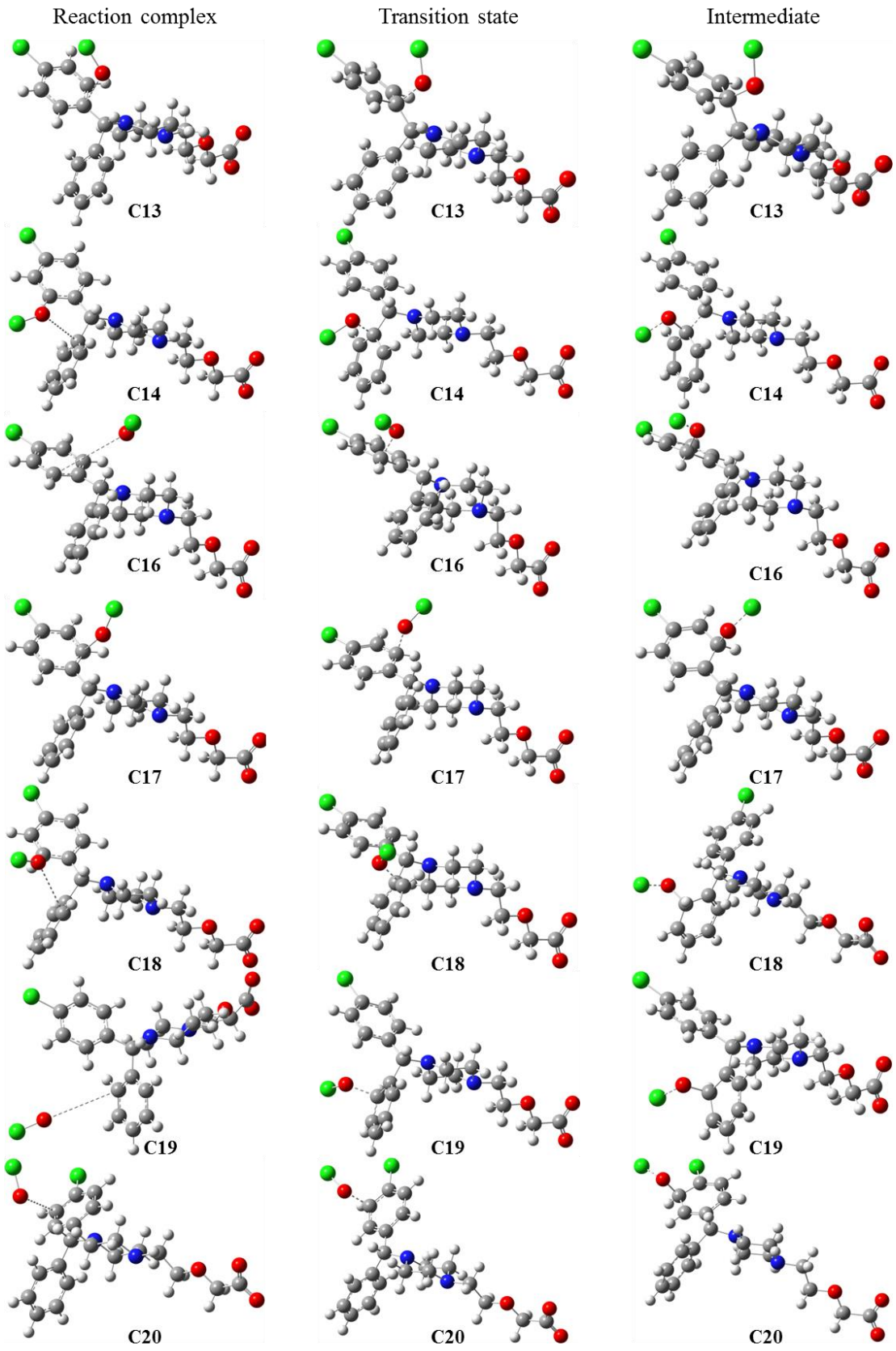
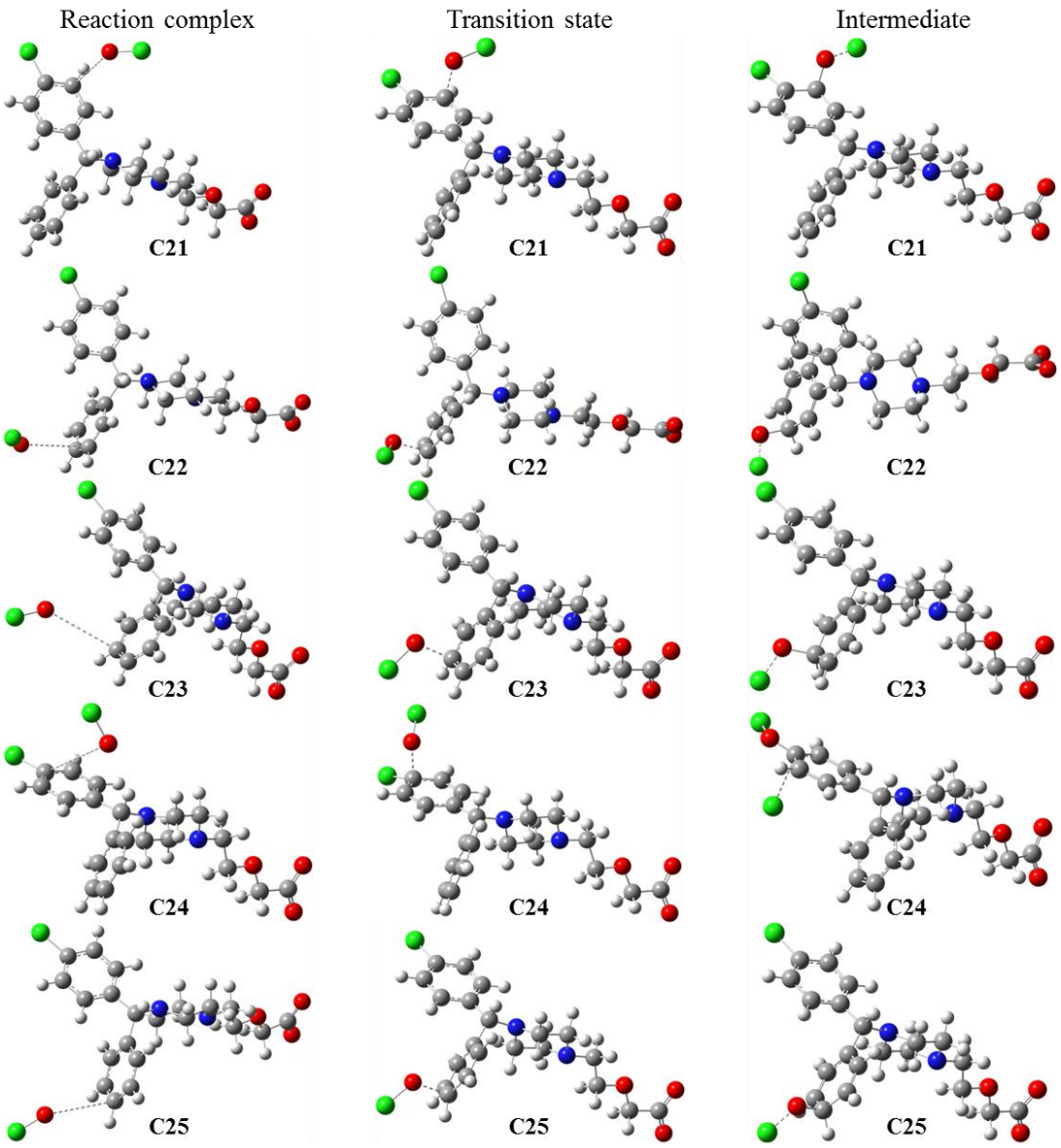


Figure S9. Reaction complexes, transition states and intermediates of the addition reaction pathways of CTZ with ClO•



Continued Figure S9. Reaction complexes, transition states and intermediates of the addition reaction pathways of CTZ with ClO•

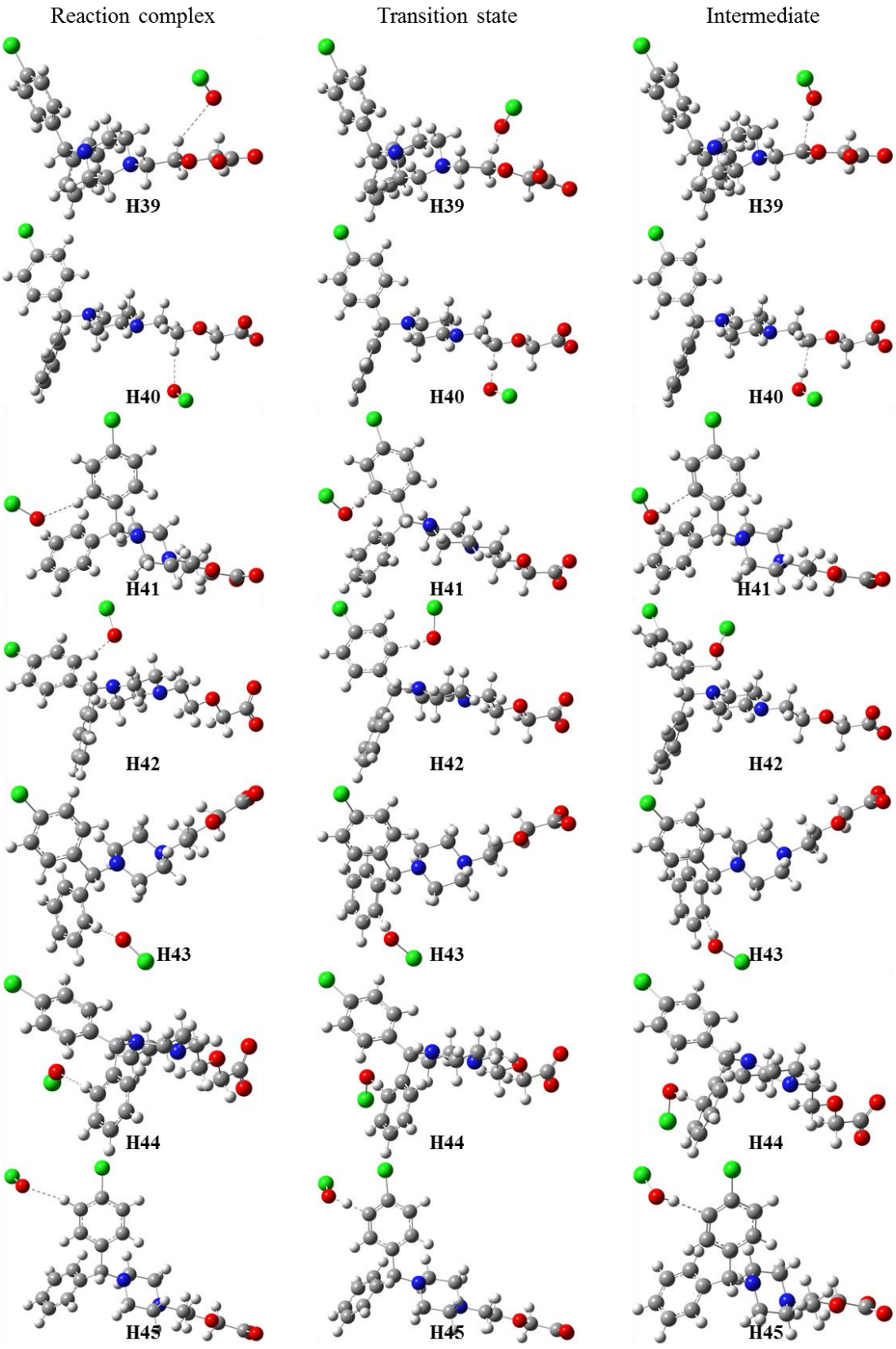
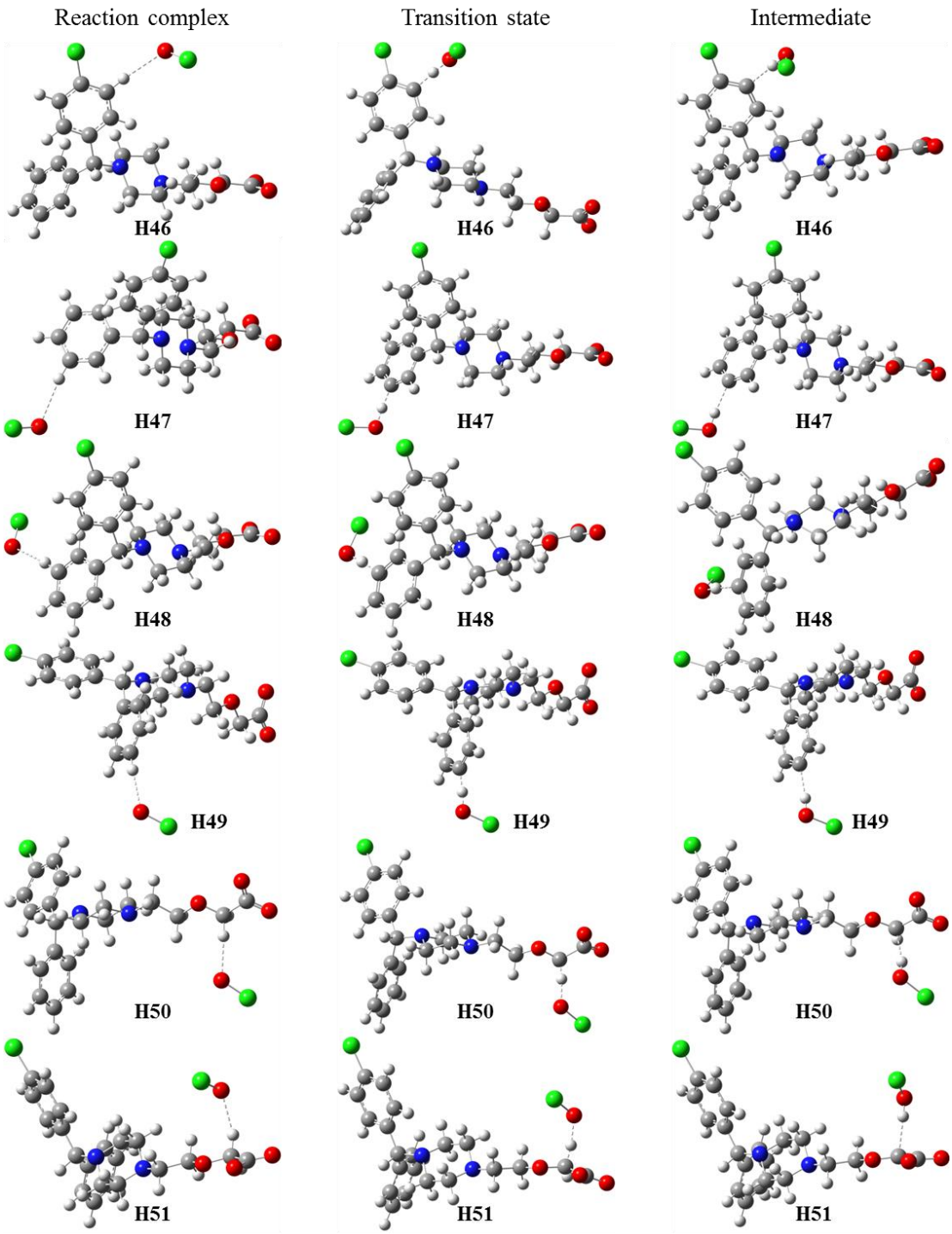


Figure S10. Reaction complexes, transition states and intermediates of the hydrogen abstraction reaction pathways of CTZ with ClO•



Continued Figure S10. Reaction complexes, transition states and intermediates of the hydrogen abstraction reaction pathways of CTZ with $ClO^{\bullet}$

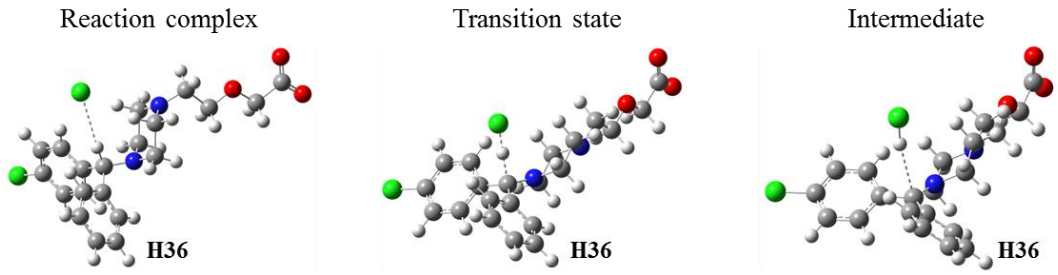


Figure S11. Reaction complexes, transition states and intermediates of the hydrogen abstraction reaction of H36 of CTZ with $Cl^{\bullet}$

Table S1 Contribution ratio of different reactive species and UV degradation to the degradation of CTZ (10 μM) in UV/chlorine system ([Free chlorine]$_0$ = 100 μM).

Items		$HO^{\bullet}$	$Cl^{\bullet}$	$ClO^{\bullet}$	UV	Others
Ratio	PBS	35.3%	7.3%	17.1%	38.7%	1.6%
	With SRNOM	29.6%	4.8%	21.2%	42.2%	2.2%

Table S2 Calculated Gibbs free energy change (Δ*G*), enthalpy change (Δ*H*) and activation free energy ($\Delta G^{\ddagger}$) values for possible reaction pathways of HO• with CTZ (in kcal mol^{-1})

Pathways		Sites	**Δ*G***	**Δ*H***	**$\Delta G^{\ddagger}$**
HO•	addition	C13	-6.94	-9.87	4.20
		C14	-5.61	-8.64	5.59
		C16	-10.10	-12.46	0.87
		C17	-9.78	-12.35	1.80
		C18	-9.13	-11.06	1.04
		C19	-6.06	-8.14	4.18
		C20	-11.01	-13.09	0.89
		C21	-10.99	-13.20	1.12
		C22	-8.89	-12.02	2.16
		C23	-9.69	-11.56	1.50
		C24 (-Cl)	-31.58	-31.68	4.57
		C25	-9.89	-12.29	1.39
	H-abstraction	H28	-23.21	-28.20	barrierless
		H29	-25.96	-32.83	barrierless
		H30	-21.94	-26.91	barrierless
		H31	-26.78	-33.26	barrierless
		H32	-25.19	-30.99	barrierless
		H33	-20.90	-26.95	barrierless
		H34	-22.06	-28.21	barrierless
		H35	-24.77	-30.75	barrierless
		H36	-40.08	-44.81	barrierless
		H37	-26.62	-35.20	barrierless
		H38	-28.47	-37.18	barrierless
		H39	-21.53	-26.98	barrierless
		H40	-26.25	-35.36	barrierless
		H41	-8.12	-5.59	4.92
		H42	-2.66	-9.38	10.52
		H43	-8.47	-5.22	2.78
		H44	-8.64	-8.21	3.57
		H45	-6.69	-4.82	3.82
		H46	-6.58	-6.12	4.18
		H47	-8.59	-5.28	1.66
		H48	-7.84	-5.05	2.69
		H49	-6.95	-4.41	2.84
		H50	-30.98	-29.70	2.50
		H51	-34.38	-32.75	1.72

Table S3 Calculated Gibbs free energy change (ΔG), enthalpy change (ΔH) and activation free energy ($\Delta G^{\ddagger}$) values for possible reaction pathways of ClO$^{\bullet}$ with CTZ (in kcal mol^{-1})

Pathways		Sites	ΔG	ΔH	$\Delta G^{\ddagger}$
ClO$^{\bullet}$	addition	C13	10.06	6.73	12.97
		C14	16.69	10.28	19.00
		C16	8.92	4.09	12.69
		C17	9.15	4.34	13.34
		C18	9.76	4.28	13.17
		C19	11.32	7.79	14.56
		C20	11.24	4.71	14.54
		C21	11.24	4.71	14.54
		C22	10.83	3.85	14.72
		C23	10.90	3.77	14.90
		C24 (-Cl)	-2.18	-6.40	17.21
		C25	9.64	3.16	13.56
	H-abstraction	H39	-3.28	-5.47	4.63
		H40	-3.55	-6.79	4.66
		H41	15.60	15.24	19.09
		H42	18.90	10.71	24.65
		H43	17.30	14.93	18.91
		H44	14.82	14.00	18.50
		H45	19.21	17.90	20.93
		H46	19.57	17.42	21.46
		H47	14.69	15.52	16.02
		H48	18.42	14.95	18.11
		H49	15.98	15.55	17.59
		H50	-9.54	-11.36	2.22
		H51	-9.11	-10.33	1.83