Supporting Information for

Molecular Structure of the Photo-Oxidation Product of Ellagic Acid in Solution

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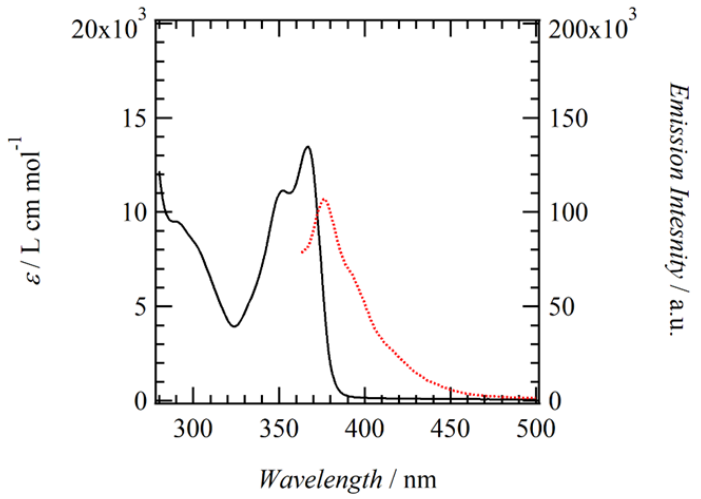


Figure S1. UV (solid line) and fluorescence (dashed line) spectra of **EA** in THF.

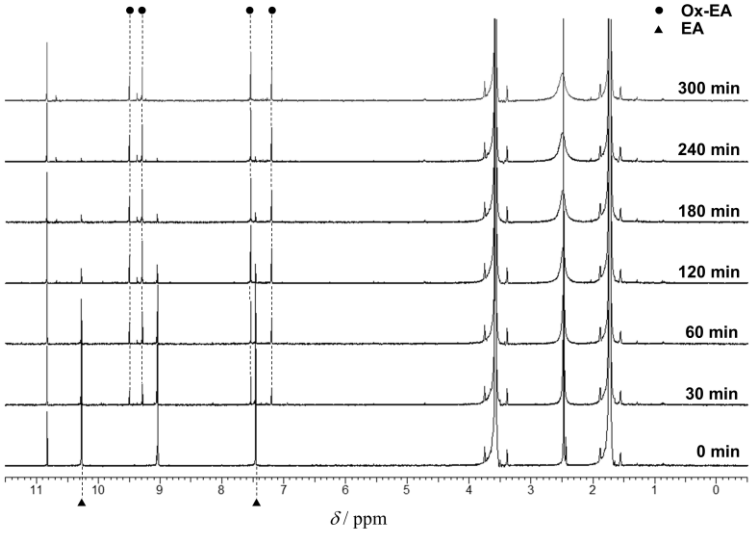


Figure S2. Time-course 1H NMR spectra of EA in THF-d8 upon photo irradiation.

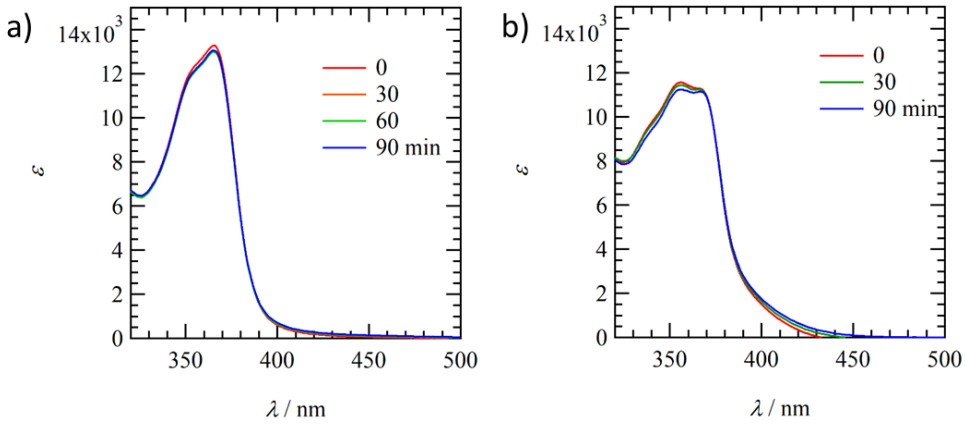


Figure S3. Absorption spectral changes of **EA** by photo irradiation in a) CH_3OH and b) DMF. After 90 min photo irradiation, there were no spectral changes of **EA**.

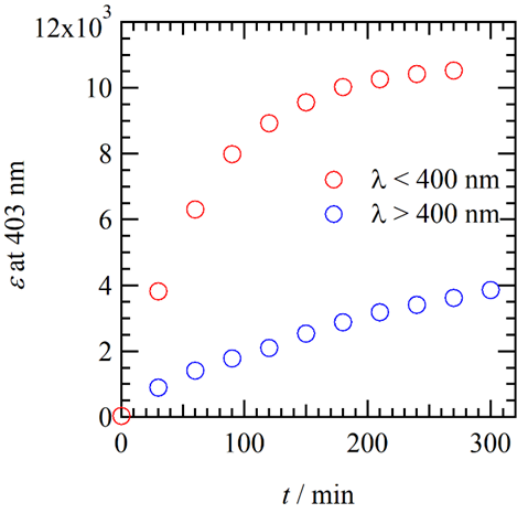


Figure S4. Wavelength dependent absorption spectral changes of **EA** by photo irradiation in THF. Two kinds of optical filters **I** (red: λ_{ex} = 280-400 nm) and **II** (blue: λ_{ex} > 400 nm) were used for the photoreaction.

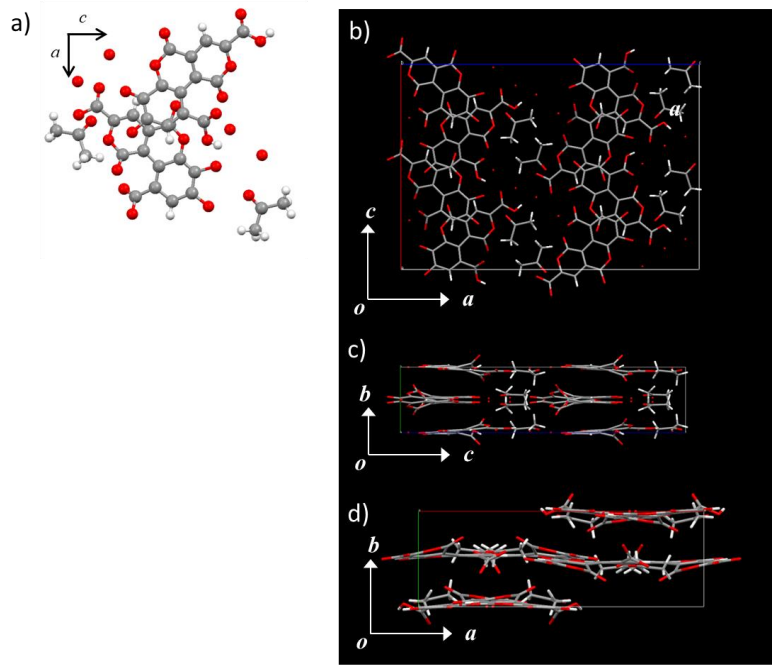
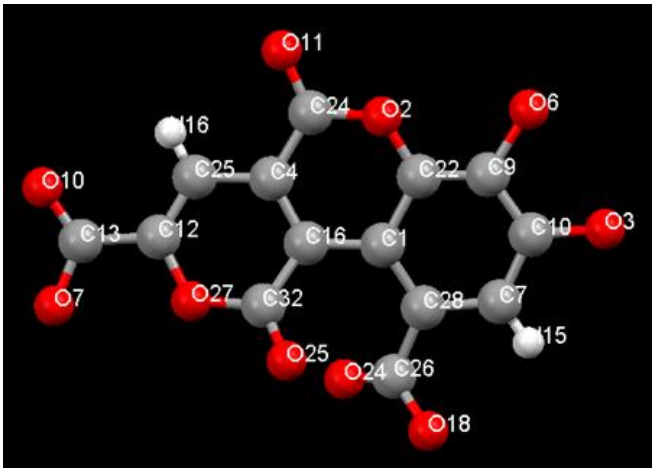


Figure S5. Crystal structure of (**Ox-EA**)(acetone)$(H_2O)_2$. a) Crystallographically independent structural units of two **Ox-EA**, two acetones, and four H_2O molecules. Unit cell viewed along the b) *b* axis, c) *a* axis, and d) *c* axis.



atom	atom	distance (Å)
O2	C24	1.340(17)
O7	C13	1.316(18)
O10	C13	1.239(18)
C1	C16	1.446(19)
C1	C28	1.42(2)
O27	C12	1.359(16)
C7	C10	1.41(2)
O18	C26	1.285(17)
C9	C10	1.394(19)
C12	C13	1.47(2)
C16	C32	1.479(18)
C26	C28	1.46(2)
O2	C22	1.327(17)
O3	C10	1.399(17)
O6	C9	1.450(17)
O9	C14	1.174(18)
O11	C24	1.295(18)
C1	C22	1.47(2)
O27	C32	1.372(15)
C7	C28	1.44(2)
C9	C22	1.30(2)
C12	C25	1.32(2)
O24	C26	1.245(16)
O25	C32	1.218(15)

Figure S6. Atomic numbering scheme of **Ox-EA** and the selective bond-lengths.

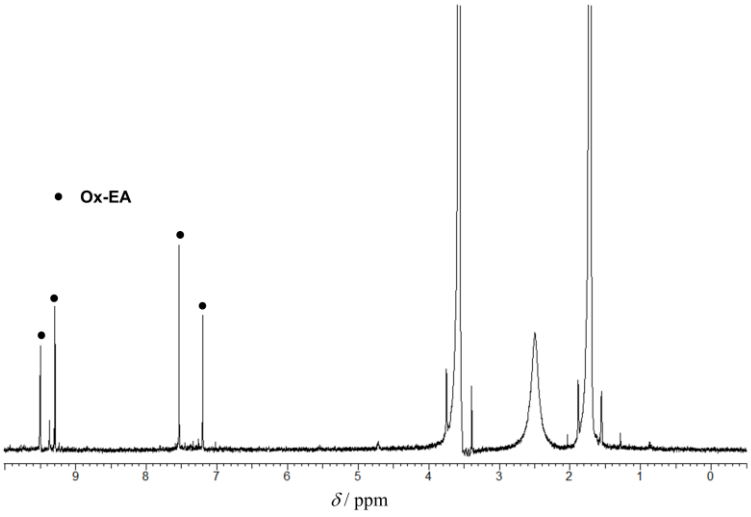


Figure S7. ^{1}H NMR spectrum of the crude product of **EA** after photo irradiation.

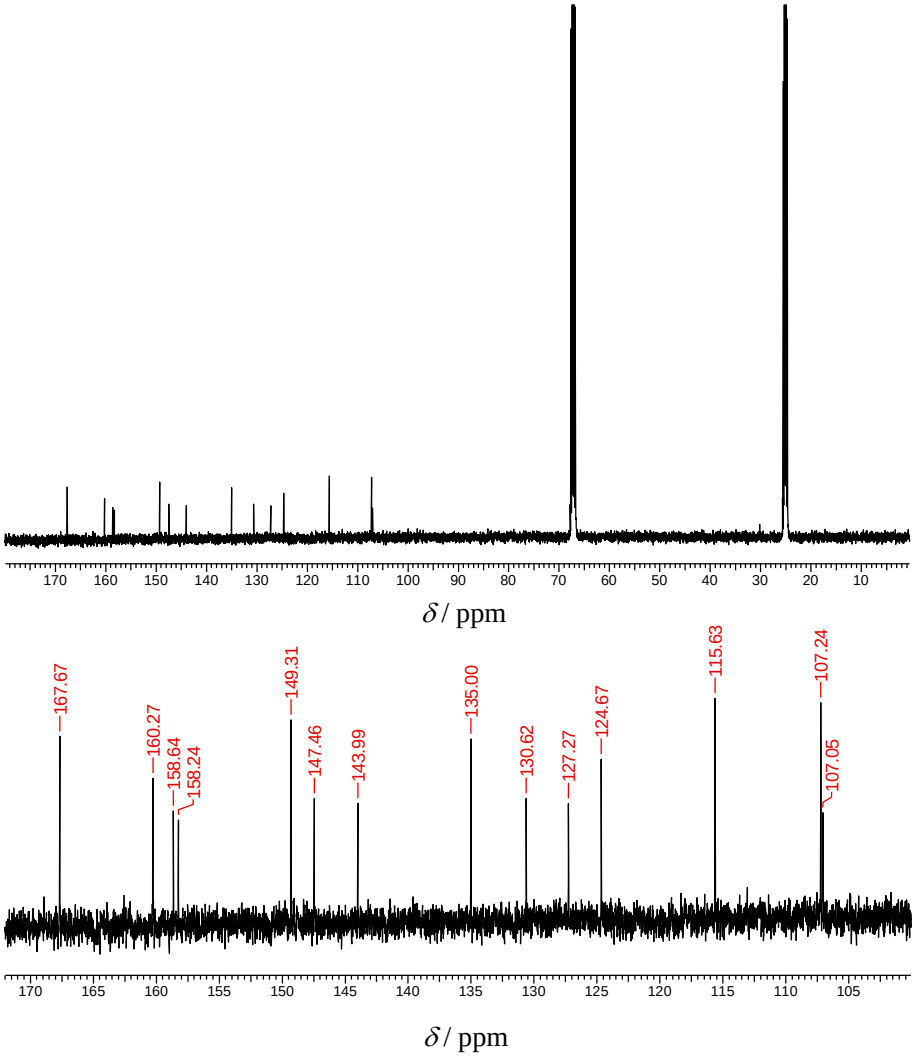


Figure S8. ^{13}C NMR spectra of **Ox-EA** in THF d_8.

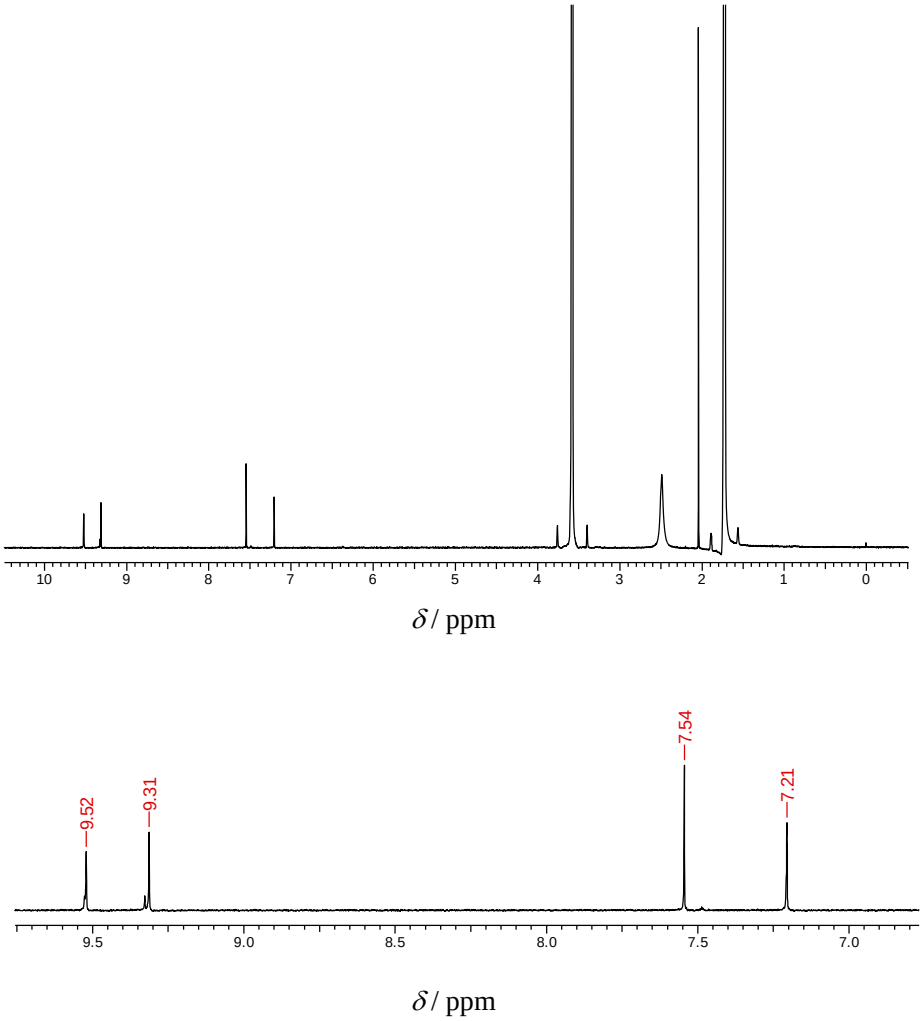
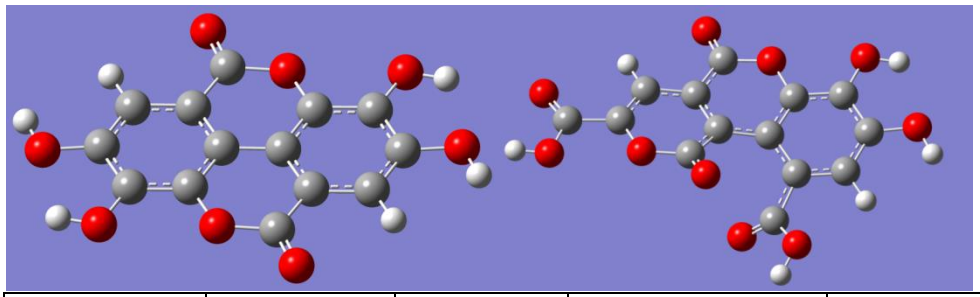


Figure S9. ^{1}H NMR spectra of **Ox-EA** in THF d_8.



	EA (vacuum)	**EA** (THF)	**Ox-EA** (vacuum)	**Ox-EA** (THF)
HOMO (eV)	-6.0859	-6.0026	-6.3536	-6.2660
LUMO (eV)	-1.8459	-1.9062	-3.0357	-3.0869
ΔE (eV)	4.239	4.096	3.318	3.179

Figure S10. Theoretical DFT calculations of **EA** (left) and **Ox-EA** (right) based on B3LYP/6-31G(d, p) basis set. HOMO and LUMO energy level of **EA** and **Ox-EA**.

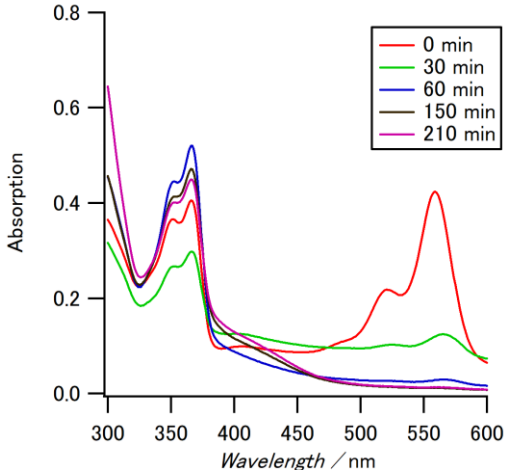


Figure S11. Time-dependent UV-vis spectra of **EA** in THF upon photo-irradiation with rose bengal.

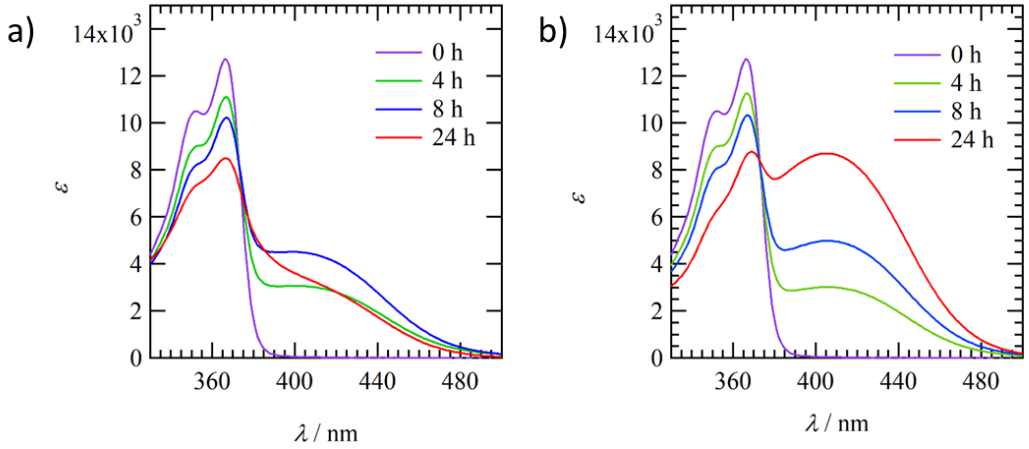
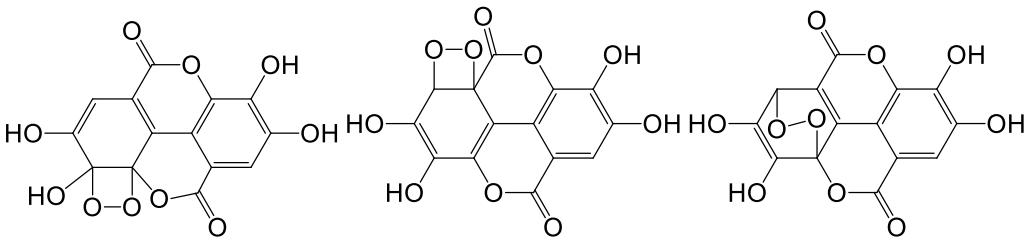
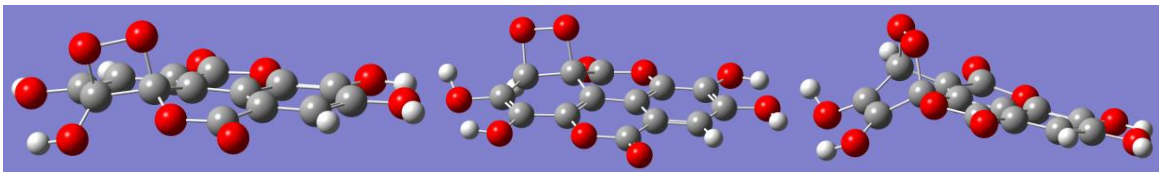


Figure S12. **BHT** dependent absorption spectra a) without **BHT** and b) with **BHT** during the photo-irradiation of 24 h





	[2+2]-1	**[2+2]-2**	**[4+2]**
Δ*E* vs [2+2]-1 (in vacuum)	0	+61.0	+73.6 kJ mol^{-1}
Δ*E* vs [2+2]-1 (THF solvation)	0	+66.9	+74.6 kJ mol^{-1}

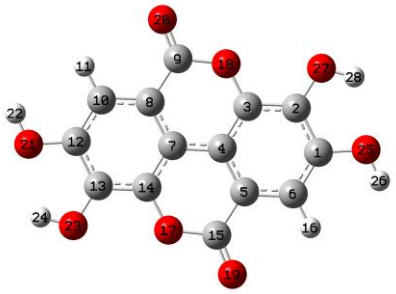
Figure S13. Energy calculations using DFT calculation based on a B3LYP/6-31G (*d*, *p*) basis set for the reaction intermediates of **[2+2]-1**, **[2+2]-2**, and **[4+2]** cyclization products, respectively.

Cartesian Coordinates for optimized structures.

a. Optimized structure of **EA**

E(RB3LYP) = -1138.93127751 a.u.

Number of imaginary frequency: 0



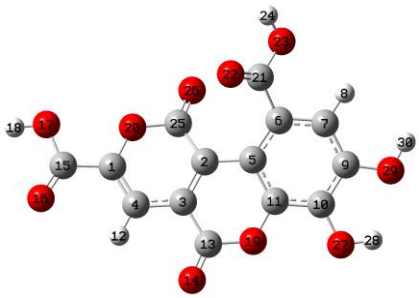
Atom No.	Element	Cartesian Coordinates		
		X	Y	Z
1	C	3.444764	−0.503247	0.000205
2	C	2.939655	0.818291	0.000007
3	C	1.555257	1.002372	0.000050
4	C	0.706271	−0.108599	−0.000009
5	C	1.221115	−1.413474	0.000112
6	C	2.607309	−1.609849	0.000169
7	C	−0.706286	0.108597	−0.000028
8	C	−1.221119	1.413488	−0.000093
9	C	−0.302305	2.562888	−0.000139
10	C	−2.607299	1.609850	−0.000022
11	H	−3.000733	2.621543	−0.000119
12	C	−3.444757	0.503236	0.000059
13	C	−2.939667	−0.818289	0.000077
14	C	−1.555255	−1.002389	0.000023

Atom No.	Element	Cartesian Coordinates		
		X	Y	Z
15	C	0.302344	−2.562881	−0.000092
16	H	3.000731	−2.621545	0.000231
17	O	−1.062917	−2.281046	0.000003
18	O	1.062908	2.281053	−0.000071
19	O	0.635150	−3.723768	−0.000548
20	O	−0.635159	3.723776	−0.000190
21	O	−4.815347	0.563695	−0.000059
22	H	−5.108318	1.483760	0.001251
23	O	−3.771917	−1.880293	0.000254
24	H	−4.680860	−1.540726	0.000121
25	O	4.815356	−0.563693	0.000427
26	H	5.108348	−1.483752	−0.001298
27	O	3.771905	1.880286	−0.000018
28	H	4.680836	1.540691	−0.000478

b. Optimized structure of **Ox-EA**

E(RB3LYP) = -1289.37050772 a.u.

Number of imaginary frequency: 0



Atom No.	Element	Cartesian Coordinates		
		X	Y	Z
1	C	−3.207596	−0.144906	−0.089603
2	C	−0.423704	0.004105	−0.064561
3	C	−1.074976	−1.200447	0.112059

Atom No.	Element	Cartesian Coordinates		
		X	Y	Z
16	O	−5.366056	−1.092953	0.206201
17	O	−5.199162	1.117871	−0.242042
18	H	−6.164731	1.028697	−0.172819

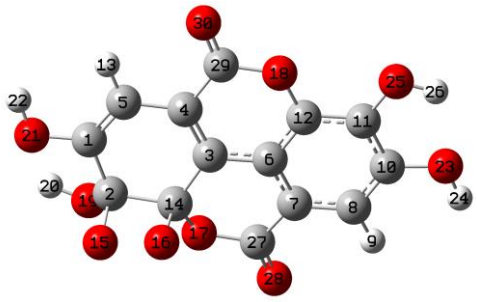
4	C	−2.501289	−1.278023	0.122197
5	C	1.025162	0.062512	0.016459
6	C	1.818060	1.236948	0.104294
7	C	3.203804	1.149866	−0.015936
8	H	3.797714	2.055556	0.050588
9	C	3.830088	−0.086128	−0.169718
10	C	3.087188	−1.271151	−0.146527
11	C	1.693868	−1.177977	−0.036243
12	H	−3.004288	−2.214557	0.319212
13	C	−0.318842	−2.461599	0.254858
14	O	−0.806382	−3.541460	0.479036
15	C	−4.694351	−0.109256	−0.023529

19	O	1.034700	−2.374590	0.019402
20	O	−2.603522	1.030023	−0.397762
21	C	1.243276	2.530495	0.574373
22	O	0.355797	2.626108	1.395200
23	O	1.896960	3.603926	0.073710
24	H	1.479779	4.380524	0.483359
25	C	−1.226488	1.150995	−0.546859
26	O	−0.808590	2.136465	−1.101165
27	O	3.677220	−2.484739	−0.224443
28	H	4.634609	−2.342526	−0.285139
29	O	5.181276	−0.262067	−0.290967
30	H	5.633793	0.591044	−0.280148

c. Optimized structure of **[2+2]-1**

E(RB3LYP) = -1289.21925001 a.u.

Number of imaginary frequency: 0



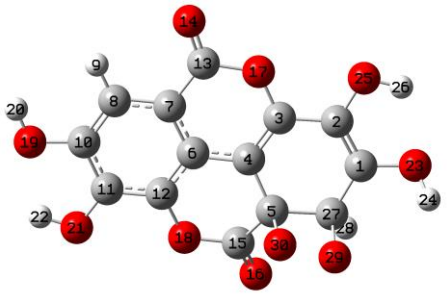
Atom No.	Element	Cartesian Coordinates		
		X	Y	Z
1	C	−3.212674	0.860786	−0.187140
2	C	−2.872221	−0.613469	−0.073629
3	C	−0.425015	0.251563	0.045061
4	C	−0.879488	1.534131	−0.024463
5	C	−2.295322	1.844533	−0.117560
6	C	0.960938	−0.052755	0.009228
7	C	1.399664	−1.384925	−0.062803
8	C	2.768250	−1.655870	−0.070596
9	H	3.106465	−2.685172	−0.141284
10	C	3.671714	−0.597772	−0.012635
11	C	3.246885	0.749151	0.019264
12	C	1.873392	1.008788	0.015603
13	H	−2.573283	2.891682	−0.186511
14	C	−1.380020	−0.882162	0.227395
15	O	−3.185487	−1.080599	1.278098

Atom No.	Element	Cartesian Coordinates		
		X	Y	Z
16	O	−1.734858	−1.027950	1.619775
17	O	−0.928144	−2.095337	−0.311714
18	O	1.440677	2.303342	0.018885
19	O	−3.444987	−1.368595	−1.056744
20	H	−4.309305	−0.982634	−1.268752
21	O	−4.547544	1.020950	−0.383129
22	H	−4.760079	1.958999	−0.490751
23	O	5.033712	−0.741917	−0.008884
24	H	5.273084	−1.677127	−0.037968
25	O	4.135348	1.763154	0.044875
26	H	5.025279	1.376409	0.040129
27	C	0.410113	−2.466715	−0.248460
28	O	0.689128	−3.627212	−0.419299
29	C	0.091615	2.643616	−0.056207
30	O	−0.196486	3.814721	−0.118516

d. Optimized structure of **[2+2]-2**

E(RB3LYP) = -1289.19602156 a.u.

Number of imaginary frequency: 0



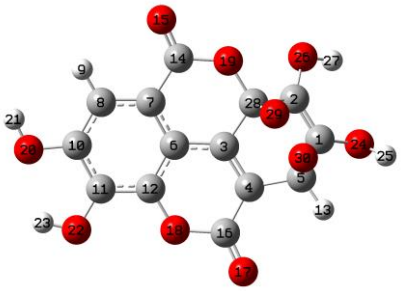
Atom No.	Element	Cartesian Coordinates		
		X	Y	Z
1	C	3.314487	0.098540	−0.233673
2	C	2.652339	1.280257	−0.169567
3	C	1.197052	1.293601	−0.075905
4	C	0.476373	0.140076	−0.022472
5	C	1.147338	−1.166277	0.121698
6	C	−0.944674	0.195564	−0.014304
7	C	−1.597393	1.439572	0.040243
8	C	−3.000131	1.489038	0.082934
9	H	−3.497162	2.452890	0.131004
10	C	−3.715266	0.304648	0.057901
11	C	−3.071811	−0.958251	−0.038348
12	C	−1.681936	−0.992459	−0.085750
13	C	−0.804100	2.668002	0.027888
14	O	−1.220090	3.797883	0.078666
15	C	0.303689	−2.317961	−0.433417

Atom No.	Element	Cartesian Coordinates		
		X	Y	Z
16	O	0.767394	−3.314048	−0.919499
17	O	0.599561	2.504579	−0.084308
18	O	−1.059094	−2.213243	−0.276413
19	O	−5.082965	0.211864	0.096796
20	H	−5.477254	1.092374	0.138275
21	O	−3.791350	−2.095660	−0.100701
22	H	−4.730302	−1.852739	−0.063829
23	O	4.678844	0.145185	−0.416379
24	H	5.097664	−0.527189	0.140534
25	O	3.273452	2.480929	−0.228985
26	H	4.226799	2.302719	−0.274433
27	C	2.649038	−1.237568	−0.171741
28	H	2.974535	−1.905410	−0.976039
29	O	2.850109	−1.889774	1.120646
30	O	1.466100	−1.500632	1.529124

e. Optimized structure of **[4+2]**

f. E(RB3LYP) = -1289.19112173 a.u.

g. Number of imaginary frequency: 0



Atom No.	Element	Cartesian Coordinates		
		X	Y	Z
1	C	3.203283	−0.382876	−0.535686
2	C	2.656492	0.838865	−0.622072
3	C	0.469411	−0.146915	0.017936
4	C	1.010324	−1.381286	0.081932

Atom No.	Element	Cartesian Coordinates		
		X	Y	Z
16	C	0.164930	−2.562411	0.046328
17	O	0.512308	−3.712739	0.140306
18	O	−1.214515	−2.301610	−0.151393
19	O	0.883901	2.250663	0.258972

5	C	2.476164	−1.289566	0.427603	20	O	−4.995229	0.522480	−0.245800
6	C	−0.917937	0.081733	−0.048256	21	H	−5.294944	1.438160	−0.178922
7	C	−1.421841	1.385598	0.023877	22	O	−3.955262	−1.920834	−0.328682
8	C	−2.802067	1.574333	−0.036719	23	H	−4.865666	−1.585757	−0.352690
9	H	−3.212782	2.577359	0.024311	24	O	4.338693	−0.738495	−1.229719
10	C	−3.629808	0.458671	−0.169738	25	H	4.988403	−1.111593	−0.616418
11	C	−3.127877	−0.862774	−0.222306	26	O	3.094575	1.914377	−1.311383
12	C	−1.741987	−1.045410	−0.147233	27	H	3.930507	1.659475	−1.733354
13	H	2.956510	−2.253656	0.601351	28	C	1.431011	0.972878	0.257657
14	C	−0.487962	2.519290	0.202751	29	O	1.882526	0.717258	1.655891
15	O	−0.826065	3.671715	0.285855	30	O	2.504712	−0.613412	1.750863