SUPPLEMENTARY INFORMATION
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Additional information for the experimental section:

The concentrations of the 1,4-benzoquinone solutions were calculated based of the mass of the solid and the volume of the solution prepared.

A Mettler-Toledo Jewelry Balances semi-micro analytical balance (0.01 mg readability) was used for measurements of the masses of solid chemicals. Dissolution of 1,4-benzoquinone derivatives in water was aided using an EMMY-40-HC-EMAG ultrasonic bath at room temperature.

The electrode for pH measurement was calibrated with a freshly prepared 0.0500 mol dm^{-3} aqueous potassium hydrogen phthalate solution (pH 4.005±0.003). Typical buffer concentrations in the benzoquinone containing samples were 0.20-0.50 mol dm^{-3}.

All the solutions in this study were prepared in triply ion exchanged (Millipore) water.

The constant temperature for the kinetic measurements was ensured by using a Shimadzu TCC-CONTROLLER Peltier thermostat integrated into the cell holder of the spectrophotometer. The sampling time was between 1 and 180 s and the longest kinetic measurements took almost one day (20 h).

The temperature for the stopped-flow measurements was maintained within 25.0±0.1 °C during all stopped-flow measurements with a Julabo F-12 refrigerated/heated circulator.

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MicroMath model file for the calculation of pK_a values from spectrophotometric titrations at a single wavelength (a) and at *n* wavelengths (b)

(a)

```
// MicroMathScientistModel File
IndVars: PH, VTOT
DepVars: A, K
Params: PK, EHA, EA
H=10^(0-PH)
K=10^(0-PK)
XA=1/(1+(H/K))
XHA=1-XA
A=(EHA*VTOT*XHA+EA*VTOT*XA)/2.5
```

(b)

```
// MicroMathScientistModel File
IndVars: PH, VTOT
DepVars: A1, A2, … An, K
Params: PK, EHA1, EHA2, … EHAn, EA1, EA2, … EAn
H=10^(0-PH)
K=10^(0-PK)
XA=1/(1+(H/K))
XHA=1-XA
A1=(EHA1*VTOT*XHA+EA1*VTOT*XA)/2.5
A2=(EHA2*VTOT*XHA+EA2*VTOT*XA)/2.5

An=(EHAn*VTOT*XHA+EAn*VTOT*XA)/2.5
```

where PH is the measured pH of the solution, VTOT is the total volume of the solution after the pH adjustment measured in cm^3, A is the measured absorbance at a given wavelength, K is the K_a acid dissociation constant.

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MicroMath model file for the fitting of the kinetic scheme described by equations (3)-(5) of the main text

```
// MicroMathScientistModel File
Independent Variables: T
Dependent Variables: Q, QOH, DEC, A
Parameters: KF1, KF2, KF3, EQ, EQOH, EDEC, Q0,
Q'=-KF1*Q
QOH'=KF1*Q-KF2*QOH-2*KF3*QOH*QOH
DEC'=KF2*B +2*KF3*B*B
A=EQ*Q+EQOH*QOH+EDEC*DEC
// Initial conditions:
t=-8
Q=Q0
QOH=0
DEC=0
```

where T is the time, Q, QOH and DEC are the concentrations for the quinone, hydroxyquinone and decomposition product(s), A is the measured absorbance, KF1-KF3 are the apparent rate constants, EQ-EDEC are the molar absorption coefficients, Q0 is the initial concentration of the quinone derivative and 8 s (from the line "t=-8") is the mixing time before the kinetic measurement starts (this value is different for all measurements but usually between 7 and 10 s).

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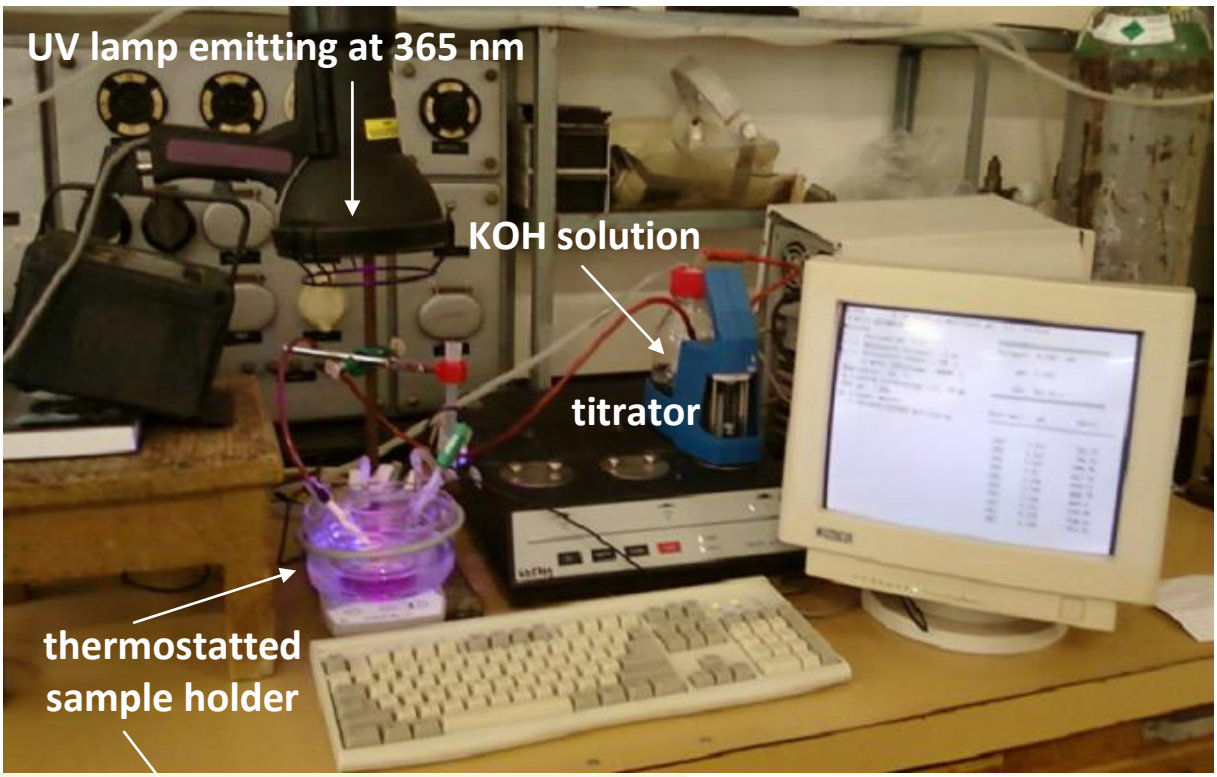
Experimental set-up for the photochemical preparation of hydroxyquinones



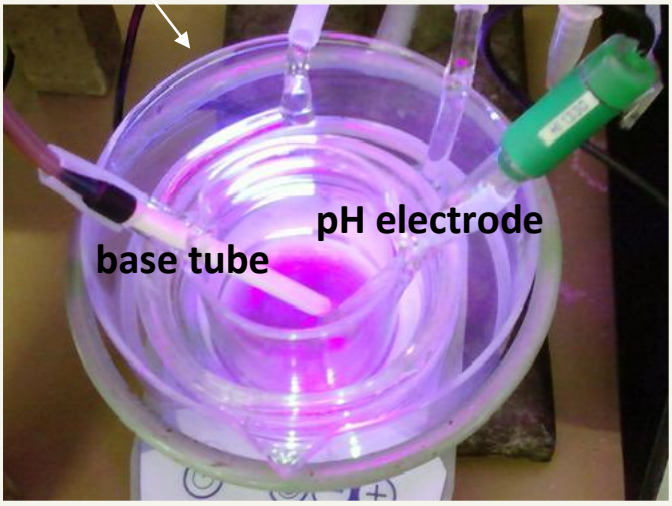


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Table S1: Pseudo-first order rate constants for the 2-methyl-1,4-benzoquinone (QMe) – H_2O_2 system at pH 6.5-6.7 and 25.0 °C

c(QMe), mmol dm^{-3}	c(H_2O_2), mol dm^{-3}	$k_{\Psi 1}$, s^{-1}	pH	ε_{490}(QMe), dm^3 mol^{-1} cm^{-1}	ε_{490}(QMe-O$^-$), dm^3 mol^{-1} cm^{-1}
1.00	0.094	$(1.58\pm0.04)\times10^{-3}$	6.70	16±1	817±20
0.99	0.18	$(2.904\pm0.001)\times10^{-3}$	6.68		
0.97	0.27	$(3.87\pm0.09)\times10^{-3}$	6.65		
0.97	0.33	$(4.73\pm0.09)\times10^{-3}$	6.60		
0.95	0.58	$(8.03\pm0.06)\times10^{-3}$	6.59		
0.89	1.08	$(1.17\pm0.06)\times10^{-2}$	6.50		

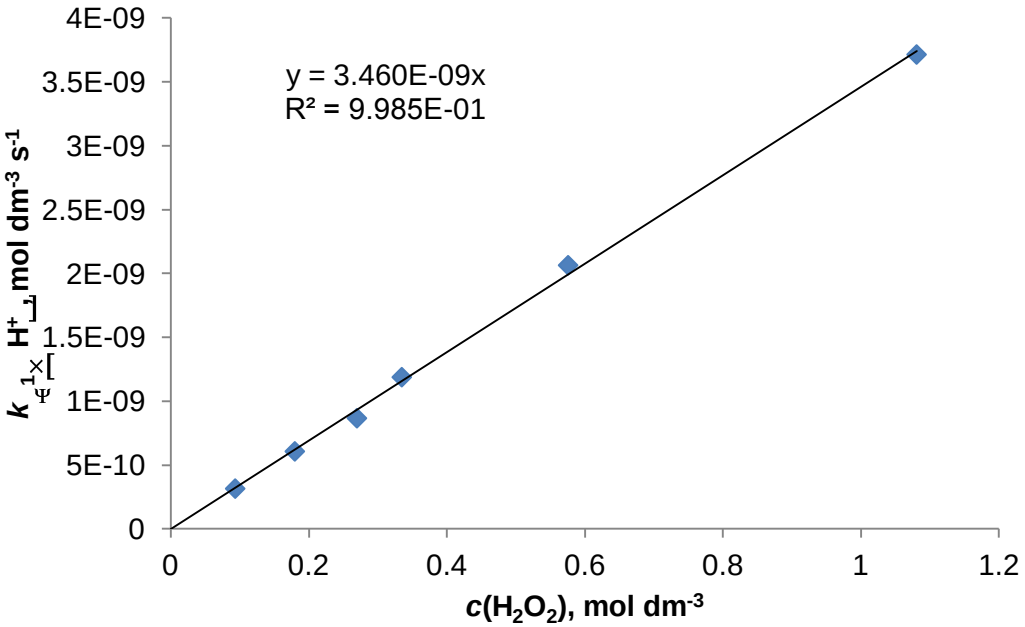

Figure S1: H_2O_2 concentration dependence of the $k_{\Psi 1}\times[H^+]$ values in the 2-methyl-1,4-benzoquinone (QMe) – H_2O_2 system at pH 6.5-6.7 and 25.0 °C. Here, a different fitting method was used because the pH range for the kinetic curves is too large to be considered as constant.

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Table S2: Pseudo-first order rate constants for the 1,4-benzoquinone (Q) – H_2O_2 system at pH 6.56-6.59 and 25.0 °C

c(Q), mmol dm^{-3}	c(H_2O_2), mol dm^{-3}	$k_{\Psi 1}$, s^{-1}	pH	ε_{480}(Q), dm^3 mol^{-1} cm^{-1}	ε_{480}(Q), dm^3 mol^{-1} cm^{-1}
1.00	0.022	$(9.4\pm0.1)\times10^{-4}$	6.59	24±1	1703±88
1.00	0.036	$(1.66\pm0.01)\times10^{-3}$	6.59		
1.00	0.054	$(2.39\pm0.02)\times10^{-3}$	6.59		
1.00	0.065	$(2.97\pm0.02)\times10^{-3}$	6.58		
0.99	0.094	$(4.35\pm0.04)\times10^{-3}$	6.58		
0.99	0.112	$(5.24\pm0.05)\times10^{-3}$	6.58		
0.99	0.180	$(8.5\pm0.1)\times10^{-3}$	6.57		
1.01	0.094	$(4.239\pm0.001)\times10^{-3}$*	6.56		
1.01	0.112	$(5.147\pm0.001)\times10^{-3}$*	6.56		
1.01	0.180	$(7.945\pm0.003)\times10^{-3}$*	6.56		

* Data obtained by stopped-flow measurements.

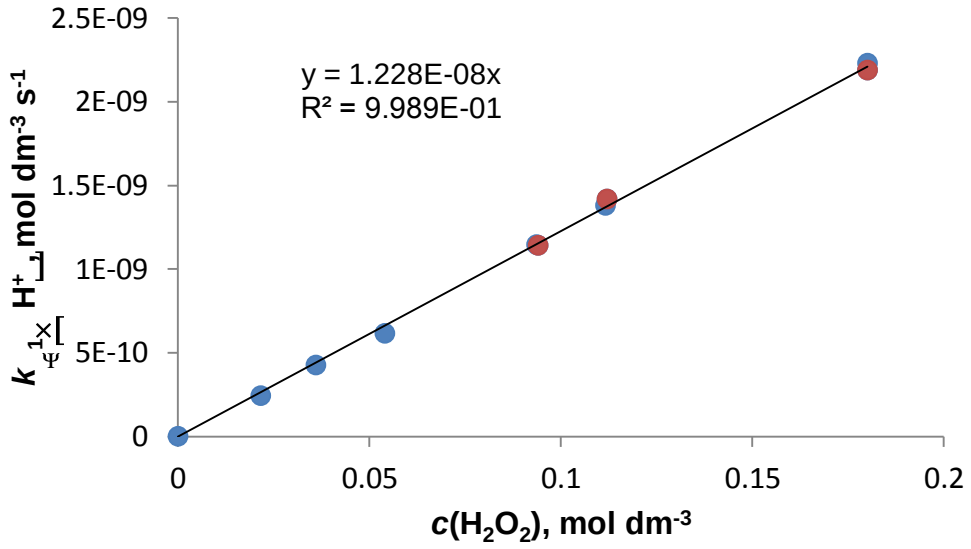

Figure S2: H_2O_2 concentration dependence of the $k_{\Psi 1}\times[H^+]$ values in the 1,4-benzoquinone (Q) – H_2O_2 system at pH 6.56-6.59 and 25.0 °C. Blue points are from spectrophotometric, red points are from stopped-flow measurements. Here, a different fitting method was used as in the main text of the paper taking into account the small differences in pH.

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Table S3: Pseudo-first order rate constants for the 2-chloro-1,4-benzoquinone (QCl) – H_2O_2 system at pH 6.54-6.56 and 25.0 °C

c(QCl), mmol dm^{-3}	c(H_2O_2), mol dm^{-3}	$k_{\Psi 1}$, s^{-1}	pH	ε_{510}(QCl), dm^3 mol^{-1} cm^{-1}	ε_{510}(QCl-O$^-$), dm^3 mol^{-1} cm^{-1}
1.00	0.022	$(1.20\pm0.02)\times10^{-2}$	6.55	28±1	823±10
1.00	0.029	$(1.36\pm0.01)\times10^{-2}$	6.56		
1.00	0.036	$(1.98\pm0.01)\times10^{-2}$	6.55		
1.00	0.047	$(2.40\pm0.01)\times10^{-2}$	6.55		
0.99	0.054	$(3.065\pm0.009)\times10^{-2}$	6.55		
0.99	0.065	$(3.56\pm0.01)\times10^{-2}$	6.55		
0.99	0.079	$(4.146\pm0.006)\times10^{-2}$	6.55		
0.99	0.094	$(4.85\pm0.02)\times10^{-2}$	6.54		

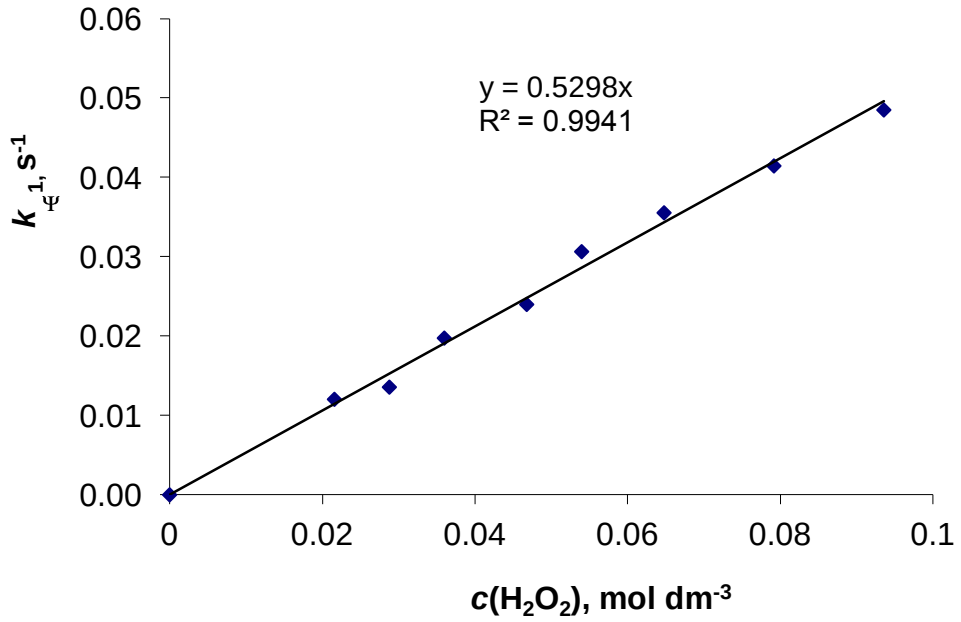

Figure S3: H_2O_2 concentration dependence of the $k_{\Psi 1}$ apparent rate constants in the 2-chloro-1,4-benzoquinone (QCl) – H_2O_2 system at pH 6.54-6.56 and 25.0 °C

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Table S4: Temperature dependent $k_{\Psi 1}$, k_1, k_b and Gibbs energy (or free energy) of activation values for the first step of the 2-methyl-1,4-benzoquinone – hydrogen peroxide reaction. c(QMe) = 9.5×10^{-4} mol dm^{-3}, c(H_2O_2) = 0.58 mol dm^{-3}, pH = 6.39

T, °C	$k_{\Psi 1}$, s^{-1}	k_1, s^{-1}	pK_a(H_2O_2)*	k_b, dm^3 mol^{-1} s^{-1}	, kJ mol^{-1}
10	(1.90±0.01)×10^{-3}	1.35×10^{-9}	11.97	1257	52.4
20	(4.09±0.09)×10^{-3}	2.90×10^{-9}	11.75	1637	53.7
25	(5.81±0.01)×10^{-3}	3.46×10^{-9}	11.65	1828	54.4
30	(8.26±0.01)×10^{-3}	5.84×10^{-9}	11.55	2065	55.0
35	(1.17±0.05)×10^{-2}	8.25×10^{-9}	11.45	2332	55.7
40	(1.67±0.03)×10^{-2}	1.18×10^{-8}	11.36	2690	56.3

*Data from M.G. Evans and N. Uri., *Trans. Faraday Soc.*, 1949, **45**, 224. (Ref. 60 of the main text)

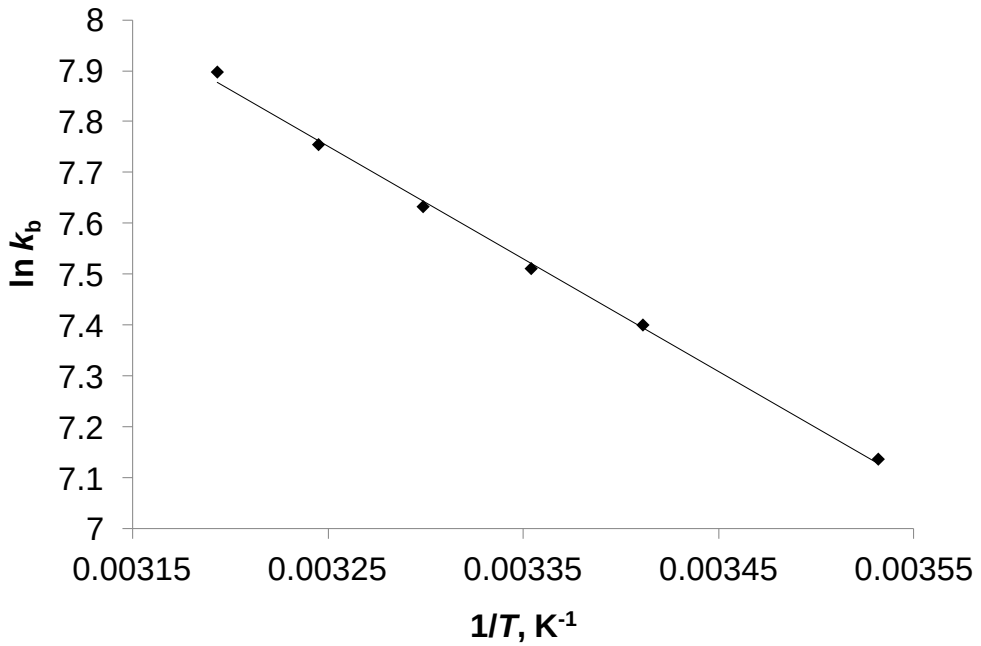

Figure S4: Arrhenius plot for the QMe + QMe-O$^-$ + H_2O reaction. c(QMe) = 9.49×10^{-4} mol dm^{-3}, c(H_2O_2) = 0.576 mol dm^{-3}, pH = 6.39. The pre-exponential factor from the plot was found to be (3.1±0.5)×10^6 dm^3 mol^{-1} s^{-1}.

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Table S5: $k_{\Psi 2}$ and $k_{\Psi 3}$ apparent rate constant for two different 1,4-benzoquinone derivatives as a function of $c(H_2O_2)$ and pH at 25.0 °C

Derivative	$c(H_2O_2)$, mol dm^{-3}	pH	$k_{\Psi 2}$, s^{-1}	$k_{\Psi 3}$, dm^3 mol^{-1} s^{-1}
2-methyl-1,4-benzoquinone (QMe)	0.094	6.70	cannot be determined	$(2.21\pm0.01)\times10^{-2}$
	0.18	6.68	$(8.91\pm0.07)\times10^{-5}$	$(4.48\pm0.01)\times10^{-2}$
	0.27	6.65	$(1.13\pm0.07)\times10^{-5}$	$(6.90\pm0.02)\times10^{-2}$
	0.33	6.60	$(1.53\pm0.09)\times10^{-5}$	$(8.03\pm0.09)\times10^{-2}$
	0.58	6.59	$(3.5\pm0.2)\times10^{-5}$	0.1235±0.0004
		5.69	$(8.82\pm0.08)\times10^{-6}$	0.152±0.001
	1.08	6.50	$(6.86\pm0.03)\times10^{-5}$	0.246±0.001

Name	$c(Q)$, mol dm^{-3}	$c(H_2O_2)$, mol dm^{-3}	pH
Sample A	9.4×10^{-4}	0.58	7.01
Sample B	9.5×10^{-4}		5.68
Sample C	8.7×10^{-4}	0.54	6.52
Sample D	8.7×10^{-4}		6.75
Sample E	8.4×10^{-4}	0.52	6.09
Sample F	8.4×10^{-4}		4.76
Sample G	9.1×10^{-4}	0.10	6.52

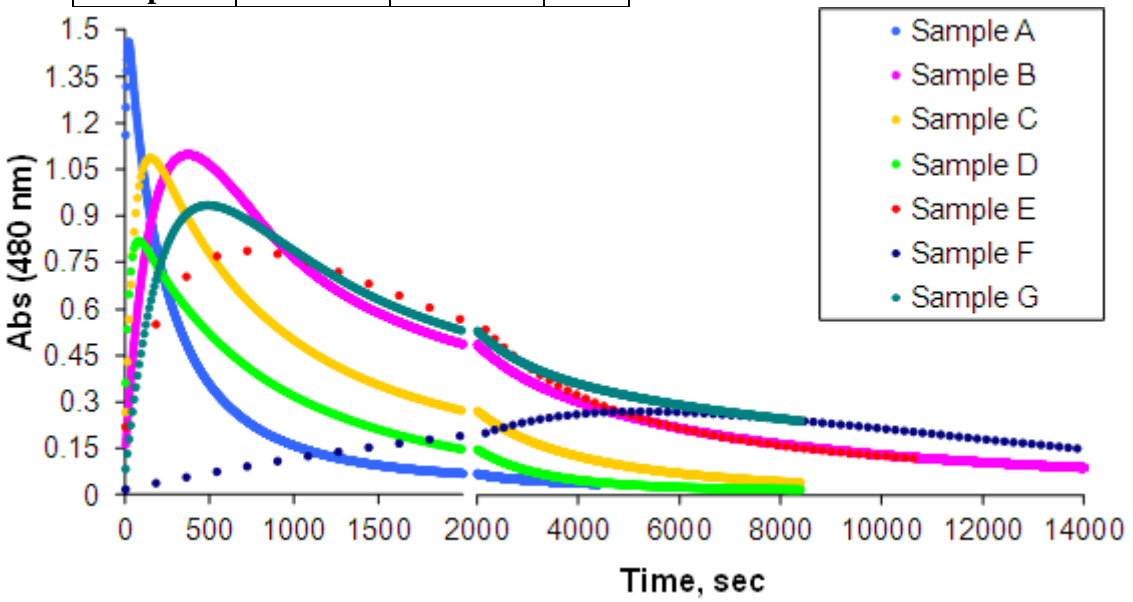

Figure S5: Kinetic curves measured for the reaction between 1,4-benzoquinone (Q) and hydrogen peroxide at 25.0 °C. $c(Q)$, $c(H_2O_2)$ and pH values are given in the table.

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Additional information for the DFT calculations:

$Q + OOH^- \rightarrow Q\text{-}OOH^2$

Using *in vacuo* calculations (B3LYP and MP2), we only found the structure of $Q\text{-}OOH^2$, but not $Q\text{-}OOH^1$. The $Q + OOH^-$ process had no energy barrier *in vacuo* when the anion was not farther than 350-450 pm from the quinone, the exact distance depending on the orientation of the anion.

$Q\text{-}OOH^2 \rightarrow EQ + OH^-$

$Q\text{-}OOH^2$ can be protonated on the oxygen that is not bonded to carbon in the −OOH group. This induces a barrierless O−O bond breaking and water formation with the B3LYP functional, but MP2 calculations gave a very small energy barrier (+6.7 kJ mol^{-1}).

Table S6: The main structural parameters of Q, Q–OOH^x (x = 1 – 3) and EQ at B3LYP/6-311G+(d,p) level

	Distances (pm), angles (°) and dihedral angles (°)				
	Q	**Q-OOH^1**	**Q-OOH^2**	**Q-OOH^3**	**EQ**
C1=O1	122.4	124.8	125.0	134.0	121.7
C4=O2	122.4	123.9	127.3	130.6	121.7
C1−O3	–	211.9	–	–	–
C2−O3	–	–	149.5	–	143.4
C3−O3	–	–	–	–	143.4
O3−O4	–	142.9	146.9	148.0	–
C1−C2	148.3	147.9	153.6	141.5	150.5
C2−C3	134.0	134.6	148.4	139.8	148.1
C3−C4	148.3	146.9	138.2	143.2	150.5
C4−C5	148.3	147.3	149.5	143.8	148.2
C5−C6	134.0	134.6	135.0	140.0	134.2
C6−C1	148.3	148.0	145.2	140.9	148.2
C1-O3-O4	–	117.4	–	–	–
C2-O3-O4	–	–	109.5	–	–
O1-C1-C4	180.0	167.2	170.7	177.5	164.9
O2-C4-C1	180.0	179.9	172.0	179.9	164.9
O1-C1-C2-O3	–	–	44.1	4.3	130.6
C1-C2-O3-O4	–	–	73.2	41.3	–
C2-C1-O3-O4	–	57.9	–	–	–

From the C-C and C=O bond lengths of Table S6, it can be seen that $Q\text{-}OOH^3$ has an aromatic ring while the others have the quinone structure.

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EQ + OOH^- → EQd + H_2O

Table S7: The relative Gibbs energies (kJ mol^{-1}) of the reaction between EQ + OOH^-

	B3LYP/6-31G(d) *in vacuo*	B3LYP/6-31G(d) PCM	MP2/6-31G(d) *in vacuo*
EQ + OOH^-	0.0	0.0	0.0
TS	7.5	–	–
EQd + H_2O	6.3	22.8	-16.4

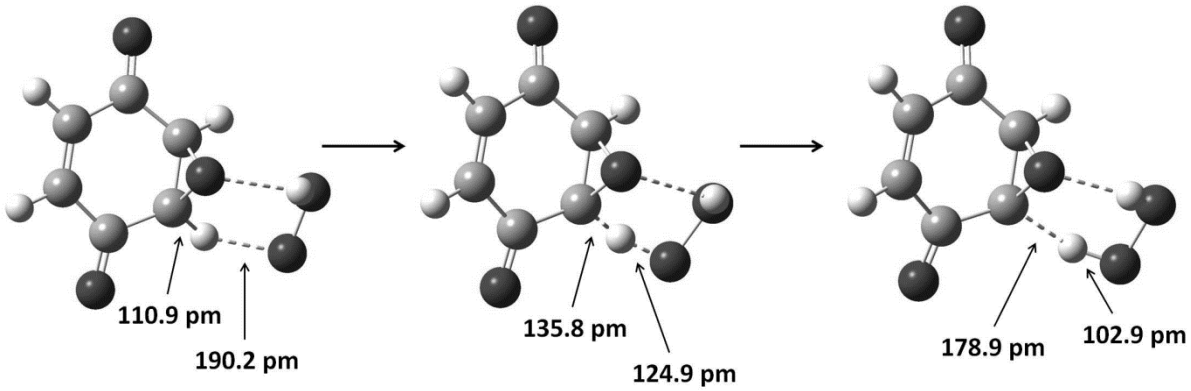

Figure S6: The reactant (EQ + OOH^-), transition state (TS) and product (EQd + H_2O) of the reaction between EQ and OOH^-

EQ → EQd + H^+
or EQ → EQd' + H^+

The deprotonation of the non-epoxide side (EQd') is a bit more favored compared to the epoxide side (EQd) (see: Table S8), however, the mechanism is blocked through EQd'.

Table S8: The relative Gibbs energies (kJ mol^{-1}) of EQd and EQd' at different levels

	B3LYP/6-31G(d) *in vacuo*	B3LYP/6-31G(d) PCM	MP2/6-31G(d) *in vacuo*
EQd	8.1	10.5	13.1
EQd'	0.0	0.0	0.0

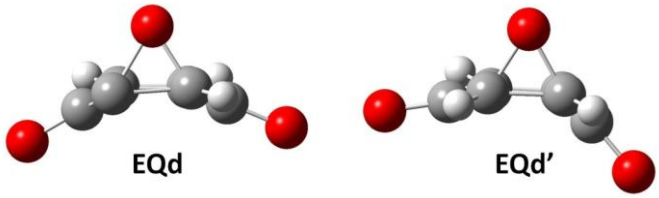

Figure S7: The optimized structures of EQd and EQd' at MP2 level

EQ + water cluster → Q–OH + water cluster

We also tried to find the minima of the protonation processes with water molecules, using B3LYP/6-31G(d) calculations *in vacuo*. We found that a $H_7O_3^+$ cluster could not protonate the epoxide oxygen of EQ and a H_6O_3 cluster could also not deprotonate any of the carbon atoms in EQ. We could find an auto-protonation process, where one of the carbon atoms can be deprotonated through two water molecules and the epoxide oxygen can be protonated. This process has a very high activation barrier (over 200 kJ mol^{-1}).

EQd + H_2O → Q–O^- + H_2O

Table S9: The relative Gibbs energies (kJ mol^{-1}) of the epoxide ring opening of the deprotonated EQ

	B3LYP/6-31G(d) *in vacuo*	B3LYP/6-31G(d) PCM	MP2/6-31G(d) *in vacuo*
EQd + H_2O	0.0	0.0	0.0
TS_5	43.0	–	–
Q–O^- + H_2O	-305.6	-311.4	-308.2

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Pathways for QMe → … → QMe-OH

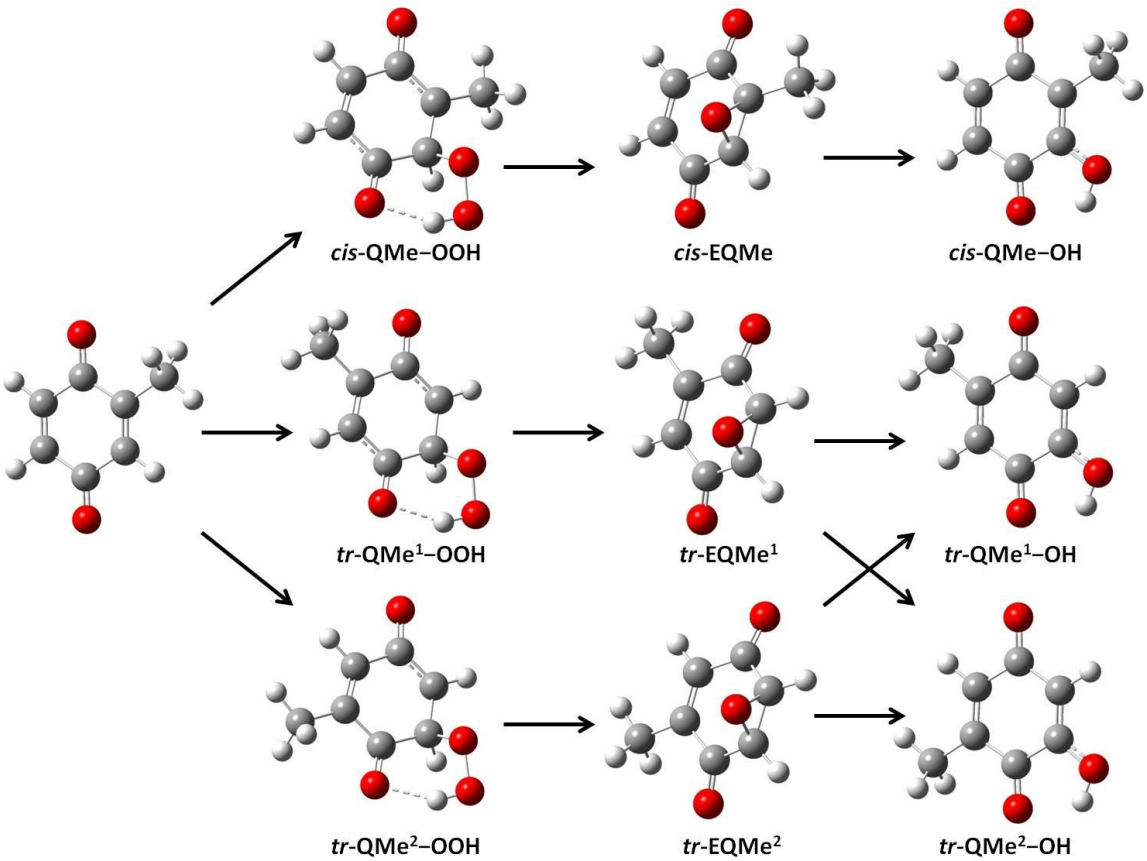

Figure S8: The intermediates of the 2-methyl-1,4-benzoquinone + H_2O_2 reaction

Table S10: The relative Gibbs energies (kJ mol^{-1}) of the QMe and QMe-OH forms, the reaction of EQ + OOH^- (1) and the epoxide ring opening of the deprotonated EQ (2)

	B3LYP/6-31G(d) *in vacuo*	B3LYP/6-31G(d) PCM	MP2/6-31G(d) *in vacuo*
***cis*-QMe–OOH**	12.1	13.3	9.1
***tr*-QMe^1–OOH**	0.0	0.0	0.0
***tr*-QMe^2–OOH**	10.5	6.7	8.9
***cis*-EQMe**	0.0	0.0	0.0
***tr*-$EQMe^1$**	2.5	1.1	8.7
***tr*-$EQMe^2$**	3.8	3.0	9.9
***cis*-QMe–OH**	5.6	4.9	2.8
***tr*-QMe^1–OH**	0.0	0.0	0.0
***tr*-QMe^2–OH**	3.9	2.7	3.5

It can be seen from Table 10 that the *trans* positions are favored for the bonding of OOH^-.

Here, we also found differences among the methods for the EQMe derivates (EQdMe). *In vacuo*, there is a chair conformation for the three isomers (*cis*-EQMe, *trans*-EQMe and *trans*-EQMe'), while MP2 shows boat conformations. On the other hand, PCM results show different conformations for the isomers (see Figure S9).

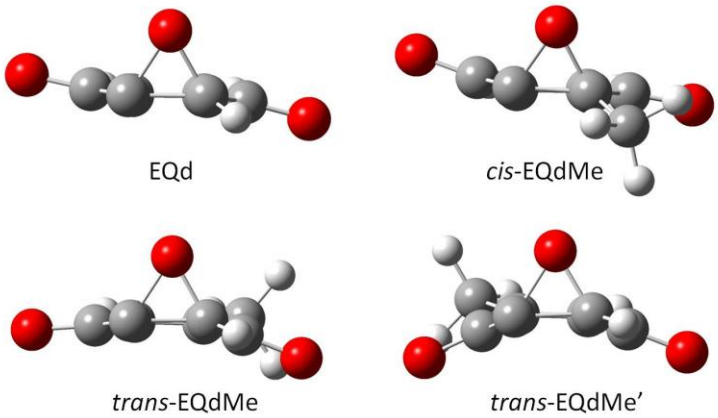

Figure S9: The different conformations of the EQ derivatives using PCM at B3LYP/6-31(d) level

SUPPLEMENTARY INFORMATION

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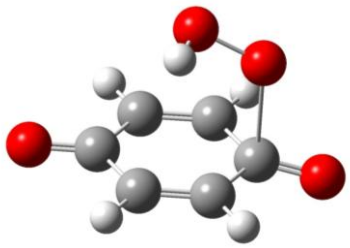
XYZ coordinates and the structures of the stationary points of the full mechanism at B3LYP level. IRC energy profiles are also summarized here.

Q-OOH[1]

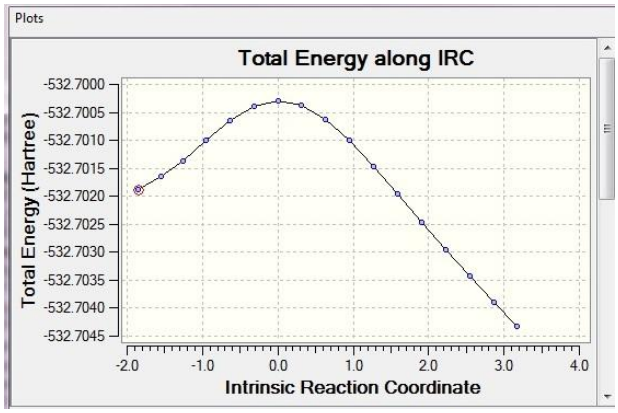
C	0.92712000	-0.54521100	1.21606100
C	1.67987700	-0.27431800	-0.01617000
C	0.91883600	-0.25790000	-1.27691200
C	-0.40943300	-0.47502200	-1.29526700
C	-1.18299900	-0.73659400	-0.06106100
C	-0.40268000	-0.75009800	1.19474700
H	1.49544600	-0.55990800	2.14015600
H	1.48275900	-0.06932900	-2.18460600
H	-0.97478400	-0.47401800	-2.22164700
H	-0.96304400	-0.94801200	2.10265900
O	2.90309700	-0.07578700	0.00030900
O	-2.34010700	-1.20189800	-0.11113300
O	-0.33820300	2.18179600	0.23923500
H	-0.05860000	2.26978600	-0.68473800
O	-1.49555100	1.34793300	0.15656200

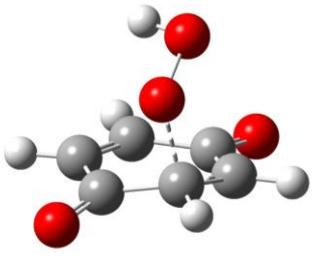


TS_1

Imaginary frequency: -220.3

C	0.76797800	0.40707800	1.14575700
C	1.65249800	-0.17899500	0.21969200
C	1.04421800	-1.05384600	-0.83785500
C	-0.25919500	-1.37550000	-0.86784700
C	-1.15783100	-0.86957600	0.18654800
C	-0.62603900	0.26358900	1.00336600
H	1.17105900	1.07343700	1.90054100
H	1.73843400	-1.45650800	-1.56975800
H	-0.67566900	-2.06416700	-1.59566600
H	-1.26499100	0.53340300	1.83783800
O	2.90887300	-0.05464100	0.21536000
O	-2.27292600	-1.35228700	0.37583900
O	-0.39117300	2.08547500	-0.95228100
H	-0.37788000	1.52348300	-1.74173400
O	-1.38486400	1.47568500	-0.13006800





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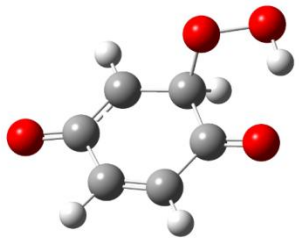
Q-OOH[2]

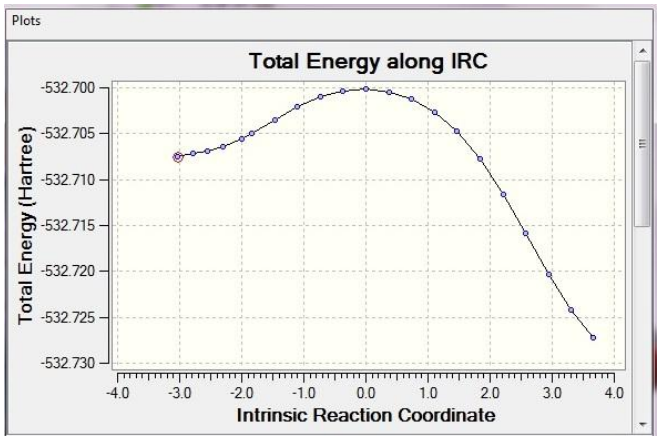
C	-1.92649100	-0.45099500	-0.00691200
C	-0.75893400	-1.15775500	0.21333900
C	0.55864700	-0.50312800	0.40509300
C	0.61633300	1.00589200	0.12446100
C	-0.63812400	1.72315400	-0.01562600
C	-1.79573000	1.03501100	-0.10657200
H	-0.80273500	-2.22802200	0.38651900
H	-0.59155400	2.80019700	-0.13775800
H	-2.72800600	1.56699800	-0.27708000
O	1.71422300	1.55754200	-0.00833400
O	-3.11248900	-0.93035100	-0.10946200
H	0.95035300	-0.64553100	1.42602100
O	1.51054100	-1.16446600	-0.48300000
O	2.87944300	-0.89831700	-0.02189800
H	2.90399700	0.07801400	-0.09884800

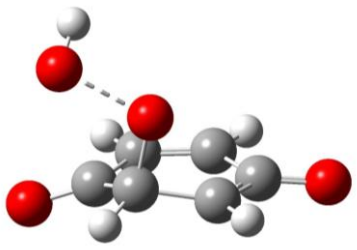


TS_2

Imaginary frequency: -297.1

C	-1.81210500	-0.26317900	0.02889400
C	-0.81961600	-0.87000600	0.84188700
C	0.57969100	-0.40222500	0.80459700
C	0.77891300	1.03557900	0.33402100
C	-0.21827800	1.55250900	-0.62297300
C	-1.41228600	0.95132800	-0.74768500
H	-1.06112900	-1.75391200	1.41667200
H	0.02623600	2.46741400	-1.15235700
H	-2.17497900	1.35335000	-1.40748000
O	1.71582100	1.71506000	0.72473400
O	-3.00011100	-0.65516100	-0.04941500
H	1.18728600	-0.60094800	1.69139600
O	0.80128000	-1.32051200	-0.23871700
O	2.61598200	-1.27732900	-0.77131200
H	2.38088600	-1.18641000	-1.70301100





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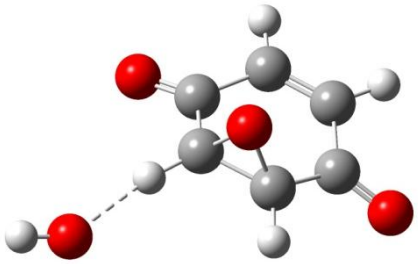
EQ + OH^-

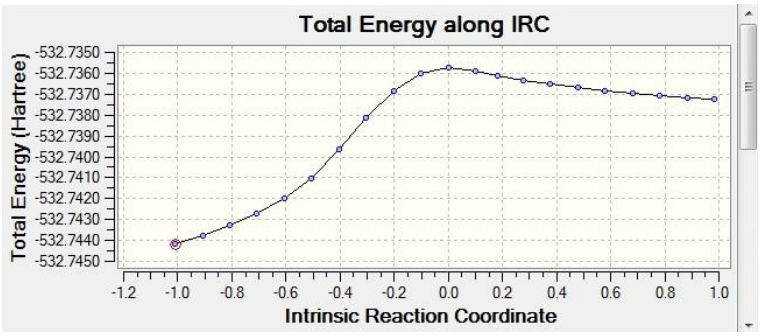
C	1.65305800	-0.75250500	-0.20626300
C	0.23922700	-1.15585300	0.10043300
C	-0.81350500	-0.11113900	0.16747600
C	-0.39062000	1.31641300	-0.04513300
C	1.05732800	1.62887800	0.05380500
C	1.99957300	0.67628700	-0.02142700
H	-0.02960000	-2.17174800	-0.17091000
H	1.31666500	2.67946100	0.12694700
H	3.05667700	0.91827100	-0.01459200
O	-1.20836400	2.18514000	-0.29789100
O	2.46939300	-1.56639400	-0.60401400
H	-1.86047100	-0.37576500	-0.04327000
O	-0.25178900	-0.69805100	1.36395400
O	-3.56444200	-1.11678400	-0.45132100
H	-4.51201900	-1.09400400	-0.27735100

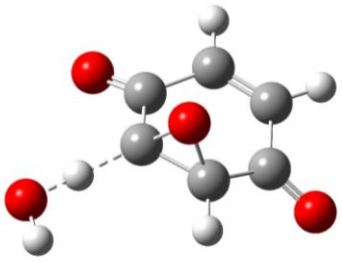


TS_4

Imaginary frequency: -1083.6

C	1.64387000	-0.67654300	-0.19425500
C	0.26227000	-1.15081300	0.09549300
C	-0.88957600	-0.18410600	0.11410800
C	-0.48301400	1.25560500	-0.06695000
C	0.93665200	1.65274000	0.14330400
C	1.92781100	0.75116300	0.07783500
H	0.07488000	-2.18819400	-0.17436600
H	1.13393600	2.70773400	0.30792300
H	2.97155000	1.03588600	0.16020000
O	-1.30521900	2.10506700	-0.39253300
O	2.49815500	-1.42084300	-0.66681200
H	-2.21384200	-0.66239100	-0.16867800
O	-0.26453400	-0.72471900	1.34608100
O	-3.31555400	-1.05552700	-0.37148200
H	-3.25738000	-2.01313200	-0.46432400





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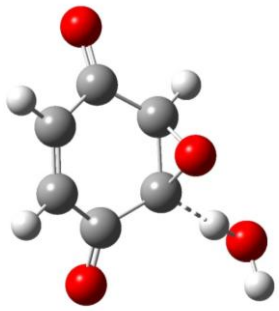
EQd + H_2O

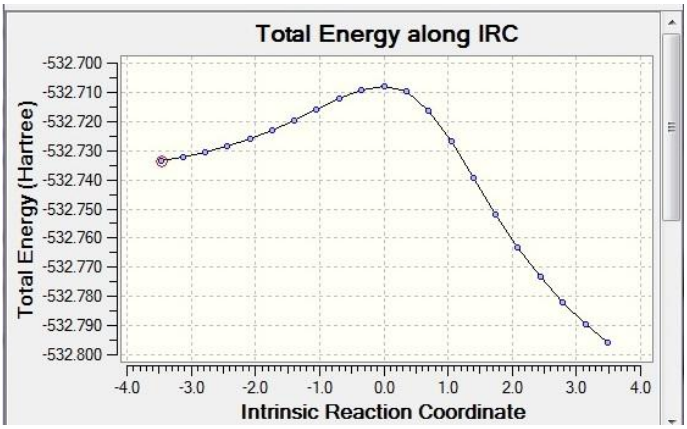
C	1.64354200	-0.72140400	-0.20026400
C	0.25682500	-1.15466500	0.10456300
C	-0.88194300	-0.15641800	0.11926600
C	-0.40885700	1.26486800	-0.07231000
C	1.01686600	1.62256800	0.17118100
C	1.97799800	0.68960100	0.09819200
H	0.04401400	-2.18959000	-0.15771000
H	1.24377000	2.66613400	0.36982500
H	3.03033100	0.93546600	0.19767500
O	-1.18797900	2.13959600	-0.44181200
O	2.46818200	-1.48135000	-0.70873800
H	-2.52438200	-0.73258100	-0.21474900
O	-0.24157900	-0.70567300	1.35482400
O	-3.45704700	-1.12960300	-0.39873100
H	-4.07293500	-0.53049100	0.03685000

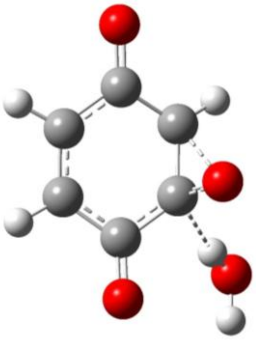


TS_5

Imaginary frequency: -844.1

C	1.91155900	-0.41855200	-0.16495600
C	0.66850800	-1.09766100	0.15494000
C	-0.50614900	-0.27710100	0.46805000
C	-0.72962100	1.10147200	0.09379300
C	0.47567000	1.62595900	-0.50109900
C	1.68981700	0.95030700	-0.55781100
H	0.57214400	-2.16548700	0.01474300
H	0.48427900	2.70171800	-0.66744500
H	2.55934100	1.48907700	-0.92392800
O	-1.73423800	1.78632400	0.42940600
O	2.99774600	-1.04903800	-0.34012700
H	-2.45580300	-1.04528400	-0.63458700
O	-0.28403500	-0.73465700	1.66793100
O	-3.26079800	-1.43241600	-1.01111400
H	-3.96806900	-0.84827400	-0.71505600





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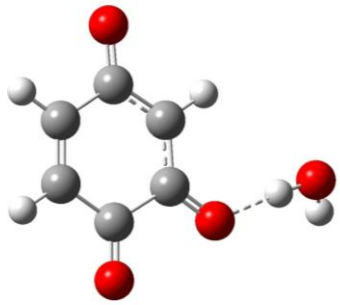
$Q\text{-}O^- + H_2O$

C	1.30091900	-1.32376900	0.00212700
C	-0.07879100	-0.98498800	0.05190300
C	-0.54440800	0.33165800	0.06046500
C	0.51501300	1.45832300	-0.00299000
C	1.94137100	1.07889700	-0.04079200
C	2.30321300	-0.20933900	-0.04015000
H	-0.79730100	-1.79748400	0.08870000
H	2.66146800	1.88964400	-0.07292200
H	3.34501300	-0.51147900	-0.07146000
O	0.17601200	2.63157100	-0.02427600
O	1.73987600	-2.49504300	-0.00688200
H	-3.12738500	-0.37017700	0.02036700
O	-1.75149500	0.69339300	0.11254700
O	-3.93672800	-0.93407800	-0.02089000
H	-4.52701300	-0.48193500	-0.63204600



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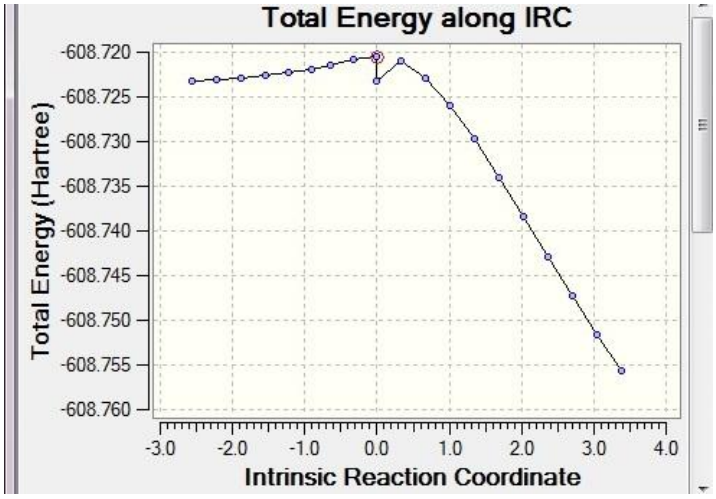
$Q\text{-}O^- + H_2O + OH^-$

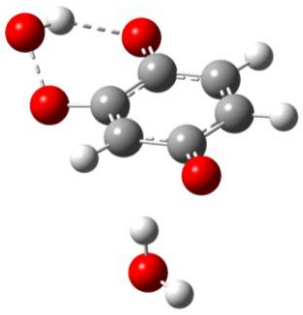
C	2.47264700	0.76452800	-0.97894800
C	1.09467200	0.75973200	-0.63297700
C	0.44465600	-0.34850900	-0.05384100
C	1.33334600	-1.57619500	0.30141700
C	2.76701500	-1.52792200	-0.04940200
C	3.29172000	-0.44259700	-0.63097600
H	0.49409400	1.61625600	-0.92603800
H	3.36017700	-2.40282000	0.19559700
H	4.34428900	-0.38728400	-0.88977400
O	0.84461500	-2.56301000	0.86035500
O	3.05873200	1.71249500	-1.55110700
H	1.36085600	1.87075800	1.33322500
O	-0.77436200	-0.43060800	0.20613600
O	1.43552300	2.35501700	2.17285300
H	1.43551500	3.28414300	1.91771700
O	-12.97915200	0.18170700	-0.36305900
H	-12.10212600	0.19992600	0.03620100

TS_3

Imaginary frequency: -492.0

C	1.63812800	-0.41168000	-0.73258100
C	0.58568200	0.53412200	-0.84910300
C	-0.65748500	0.35653800	-0.19903700
C	-1.00145200	-0.82960600	0.52136800
C	0.05600600	-1.77535400	0.62805600
C	1.30170700	-1.57312300	0.04579800
H	0.74062100	1.43993800	-1.43053400
H	-0.13862000	-2.69338400	1.17847200
H	2.07097800	-2.33374900	0.16123700
O	-2.21820900	-1.01671100	0.96435300
O	2.81590400	-0.25515300	-1.27592800
H	1.55395600	1.46029300	0.94606100
O	-1.58216200	1.34417000	-0.25577200
O	1.95487500	1.96446200	1.67734300
H	2.88905900	1.73202000	1.64338500
O	-2.92309900	0.77899100	-0.94937400
H	-3.02997700	0.06342700	-0.27060000





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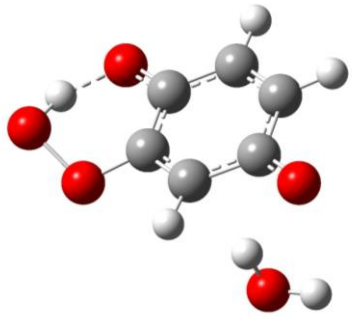
Q-OOH^{3} + H_2O

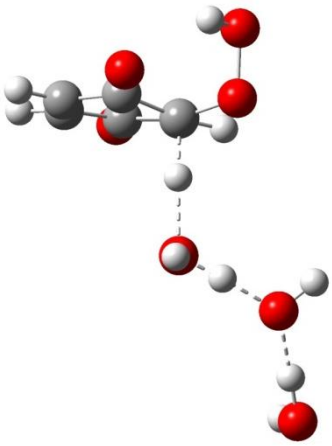
C	1.69471000	-0.41977200	-0.66844000
C	0.62399900	0.50744800	-0.87825600
C	-0.64752900	0.29909200	-0.33704700
C	-0.99423400	-0.83218300	0.43837500
C	0.05146700	-1.75725400	0.62452200
C	1.33927700	-1.55991000	0.11385500
H	0.79507600	1.38587900	-1.49538900
H	-0.16054500	-2.64831100	1.21210600
H	2.10706800	-2.30674600	0.30161700
O	-2.23626600	-0.96663500	0.92315100
O	2.88930300	-0.23451000	-1.16257200
H	1.45568800	1.50079200	0.95032800
O	-1.59073500	1.31097900	-0.51099700
O	1.80511700	2.03627000	1.68541800
H	2.73143500	1.77937500	1.74782900
O	-2.92527900	0.71507900	-0.74506500
H	-2.87198800	-0.02497400	0.00596400



Transition state of Q-OOH^{2} + OH^{-} + 2 H_2O system

Imaginary frequency: -334.8

C	1.33997300	1.96394300	-0.44533400
C	0.78908600	0.81783000	-0.99429400
C	0.81002700	-0.47761900	-0.27581700
C	1.83417500	-0.66651700	0.79848700
C	2.28874100	0.56054100	1.42682500
C	2.07371200	1.75904700	0.82514100
H	0.16531900	0.88128500	-1.88095800
H	2.90908400	0.47419200	2.31355200
H	2.49076100	2.65839200	1.27281600
O	2.25612900	-1.79434300	1.11367400
O	1.27623400	3.16403900	-0.92504400
H	-0.28134500	-0.54003500	0.46517400
O	0.62084600	-1.64336100	-1.06511200
O	-1.74183400	-0.56803300	1.35223700
H	-2.59796500	-0.63751300	0.71468900
O	1.89823400	-2.02535500	-1.69951300
H	2.34646700	-2.41723000	-0.92707500
H	-1.73037700	-1.36851200	1.88786800
O	-3.75538100	-0.67080700	-0.10436100
H	-5.11974600	0.12450700	-0.06316300
O	-6.00657700	0.61683900	0.00049800
H	-5.80618200	1.53212200	-0.21735500
H	-3.57151600	-1.08238500	-0.95462000



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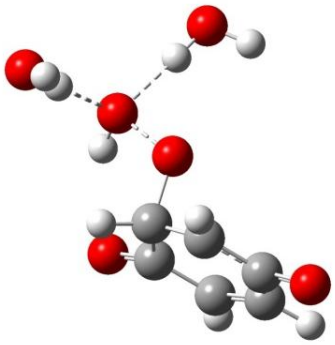
Transition state of TS_2 + 2 H_2O system

Imaginary frequency: -247.6

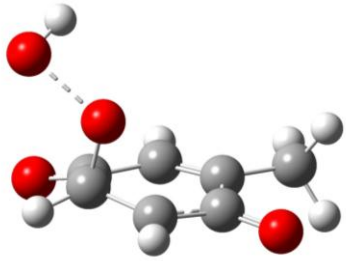
C	-2.40504900	0.60797400	0.67306300
C	-1.23837500	1.30105600	0.30465400
C	-0.22530900	0.70638600	-0.57346400
C	-0.62327000	-0.56357300	-1.32967900
C	-1.84993700	-1.25095100	-0.92250400
C	-2.65014700	-0.71547100	0.01519900
H	-1.04359800	2.28082900	0.72192600
H	-2.06885900	-2.20034200	-1.39947300
H	-3.55145100	-1.23056700	0.33362000
O	0.14041800	-1.02569300	-2.17375900
O	-3.28977100	1.03791600	1.46082200
H	0.29437700	1.39709800	-1.24455400
O	0.65549100	0.29183400	0.49238600
O	2.15265400	-0.32097600	-0.08840800
H	1.85029200	-0.77201000	-0.89505600
H	2.47905800	-1.44089300	1.28457500
H	3.08219600	1.20219900	-0.34260900
O	2.70246300	-2.03161000	2.03531400
H	1.87744000	-2.14207900	2.51879200
O	3.62494100	2.00910000	-0.47166300
H	3.14348900	2.70867300	-0.01837700



Transition state of Peroxo bond breaking of *tr*-QMe[1]

Imaginary frequency: -295.5

C	1.37350400	-0.82292800	-0.28269200
C	0.14607200	-1.31002300	-0.79812000
C	-1.09395900	-0.52041200	-0.70854000
C	-0.88612900	0.98437300	-0.57765700
C	0.34709700	1.41994300	0.08650700
C	1.40890400	0.59981400	0.23394900
H	0.09325100	-2.32708700	-1.16312600
H	0.39184600	2.46019800	0.39503500
O	-1.71908900	1.78143800	-0.99158700
O	2.43397000	-1.48920400	-0.27060300
H	-1.86908000	-0.73785000	-1.44839900
O	-1.34509600	-1.12262400	0.54301600
O	-2.99310200	-0.56308600	1.24064300
H	-2.58252600	-0.16346300	2.01742100
C	2.68585100	1.05615600	0.86834000
H	2.92484900	0.43044400	1.73386700
H	3.52214800	0.94817400	0.17250300
H	2.61800500	2.09584800	1.19022500



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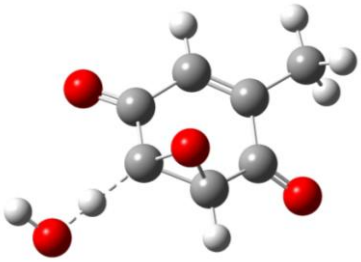
Transition state of Deprotonation of the epoxide form of *tr*-QMe[1]

Imaginary frequency: -1061.0

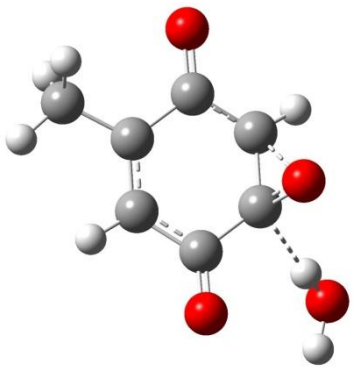
C	1.16630000	-0.97876600	-0.22068900
C	-0.25888500	-1.25172300	0.10746800
C	-1.26785500	-0.14141300	0.11259200
C	-0.66754100	1.22565900	-0.09133400
C	0.79250700	1.42229500	0.06459600
C	1.67638000	0.40651800	0.01460300
H	-0.58532600	-2.26063600	-0.13638100
H	1.12863800	2.44762000	0.19479200
O	-1.38330000	2.18398500	-0.37334400
O	1.88664900	-1.84915000	-0.69966000
H	-2.65114200	-0.43356200	-0.16222800
O	-0.70844500	-0.73495500	1.35438700
O	-3.77109500	-0.74893700	-0.39136600
H	-4.32691200	-0.07282000	0.01241100
C	3.16049000	0.59051500	0.10865600
H	3.56827400	0.00535000	0.93884700
H	3.64972900	0.22850800	-0.79964000
H	3.41788500	1.63949600	0.25671000



Transition state of Epoxide ring opening of *tr*-QMe[1]

Imaginary frequency: -858.4

C	1.41956500	-0.90802600	-0.00055300
C	0.04727900	-1.33282100	0.13958800
C	-0.97408700	-0.32410600	0.45498600
C	-0.84223800	1.10282000	0.24311600
C	0.49591200	1.41537200	-0.19707000
C	1.56128300	0.52103700	-0.24445200
H	-0.23853600	-2.34289800	-0.11956400
H	0.73008500	2.47853400	-0.23132000
O	-1.69978300	1.95751700	0.59077100
O	2.36329800	-1.73747100	-0.17520800
H	-2.83591100	-0.62216300	-0.82493200
O	-0.94159700	-0.91571100	1.62157500
O	-3.63698000	-0.78103800	-1.35164800
H	-4.15664700	0.02362700	-1.24441800
C	2.94246700	1.01101400	-0.57434900
H	3.65655500	0.70290200	0.19542100
H	3.29316200	0.56508900	-1.51138200
H	2.97070700	2.09678100	-0.67532200



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Transition state of Peroxo bond breaking of *tr*-QMe^2

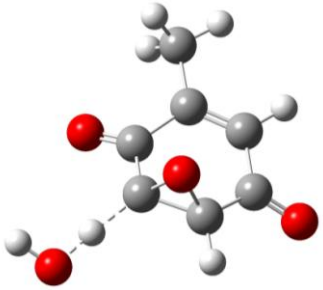
Imaginary frequency: -292.7

C	-1.87608400	-0.39478700	0.01928900
C	-0.98299000	-1.29011400	0.65798800
C	0.45505100	-0.97645600	0.73294700
C	0.80239900	0.50763900	0.66198800
C	-0.09129500	1.37254600	-0.15724000
C	-1.32913500	0.91911100	-0.43305000
H	-1.32887400	-2.26189900	0.98419300
O	1.77778100	0.95763400	1.24303200
O	-3.09942300	-0.61948600	-0.15525100
H	1.01680500	-1.45221400	1.54152700
O	0.64219100	-1.61405900	-0.51157500
O	2.44217900	-1.61227400	-0.99079100
H	2.26626900	-1.17287900	-1.83209500
C	0.41004900	2.73058400	-0.55418100
H	1.33199700	2.64956700	-1.13816500
H	-0.33486000	3.26256900	-1.14730100
H	0.64837200	3.33054900	0.32863500
H	-2.02950400	1.53865500	-0.98656600

Transition state of Deprotonation of the epoxide form of *tr*-QMe^2

Imaginary frequency: -1062.9

C	-0.92700200	1.57591700	-0.20708900
C	0.51177000	1.40341200	0.13598100
C	1.12971400	0.03535100	0.11740000
C	0.14956900	-1.07291600	-0.16532000
C	-1.32610300	-0.85243500	0.03602100
C	-1.80290300	0.40667800	-0.00973200
H	1.13628400	2.27040300	-0.06965000
O	0.54443300	-2.15970600	-0.57032700
O	-1.35886100	2.63857300	-0.65069400
H	2.54156300	-0.09935300	-0.12770400
O	0.74978400	0.73654000	1.36926400
O	3.71087300	-0.12783000	-0.32654000
H	4.02096200	-0.97074700	0.02333400
H	-2.86861400	0.60821700	0.04416400
C	-2.19672800	-2.05847100	0.21809500
H	-2.08964800	-2.74318300	-0.62713600
H	-1.89491900	-2.61464200	1.11163300
H	-3.24536200	-1.77652600	0.31958200



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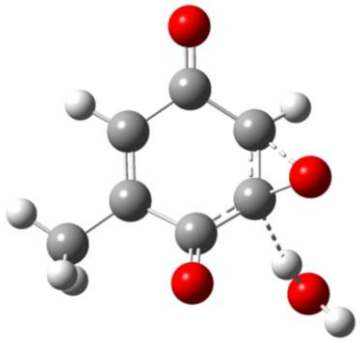
Transition state of Epoxide ring opening of *tr*-QMe^2

Imaginary frequency: -893.4

C	1.67224800	-0.97150500	-0.19041300
C	0.26296400	-1.48984600	-0.07386000
C	-0.74689200	-0.62732600	0.35514100
C	-0.54775400	0.74047100	0.55964600
C	0.65728000	1.29260600	-0.17845300
C	1.72941900	0.48272600	-0.38568500
H	0.05356400	-2.46701900	-0.49789100
O	-1.15586100	1.49582900	1.37201400
O	2.64539000	-1.71283800	-0.29469500
H	-2.35726400	-0.53592900	-0.95397000
O	-0.93589200	-1.63228400	1.32740300
O	-3.15797000	-0.61245500	-1.52090100
H	-3.89015000	-0.68976700	-0.89935100
H	2.67152800	0.87902900	-0.75216200
C	0.69305400	2.75699300	-0.47281000
H	-0.05056900	2.99650200	-1.24207000
H	0.41125100	3.32672500	0.41592900
H	1.67439700	3.07973700	-0.82243100



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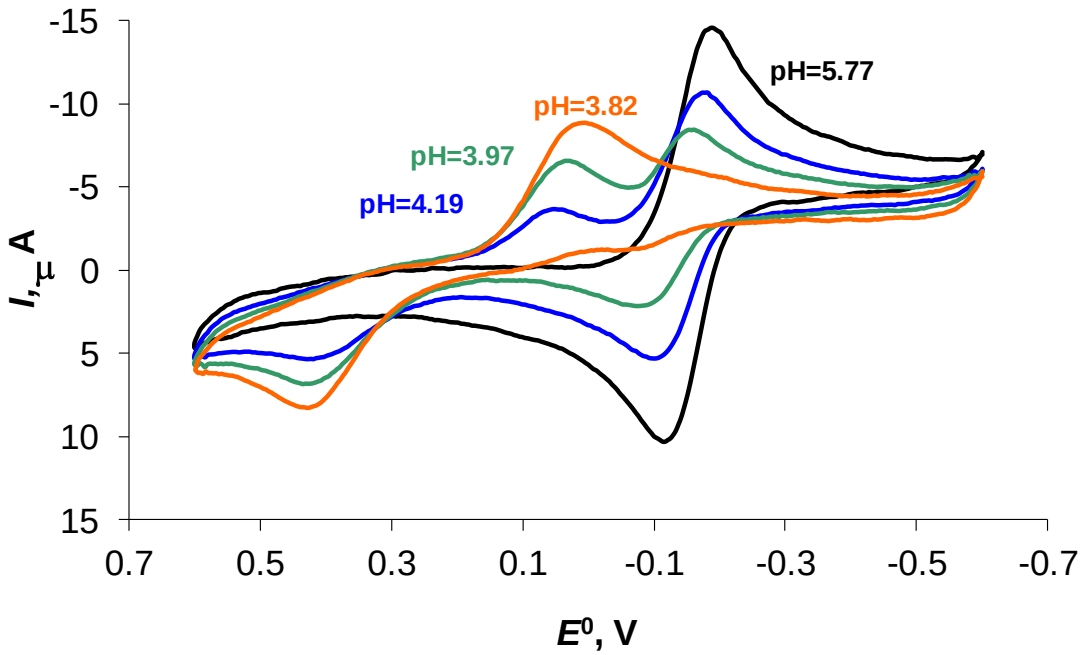

Figure S10: pH dependent cyclic voltammogram of 2-methyl -1,4-benzoquinone (QMe/QMe-H_2)

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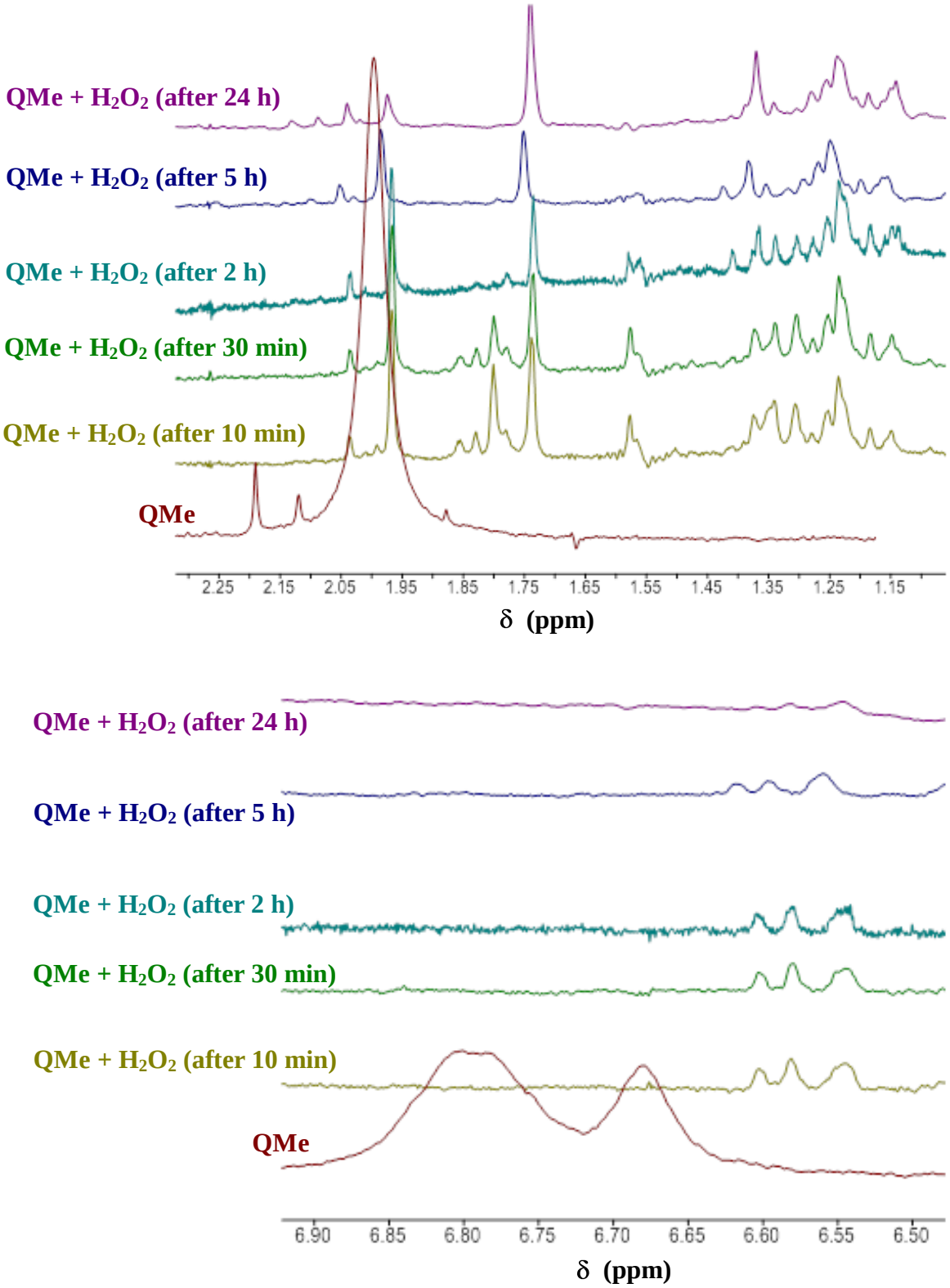

Figure S11: ^{1}H-NMR spectra measured for the reaction between 2-methyl-1,4-benzoquinone and hydrogen peroxide at pH 6.3 and 25 °C. Based on the color of the solution, the hydroxyquinone derivative was already formed after 10 min. c(QMe) = 4.57×10^{-3} mol dm^{-3}, c(H_2O_2) = 1.75 mol dm^{-3}