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Supporting Information

Autocatalytic Photodegradation of [Ru(II)(2,2'-bipyridine)$_2$DAD]$^+$ (DADH = 1,2-dihydroxyanthracene-9,10-dione) by Hydrogen Peroxide under Acidic Aqueous Conditions

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Table S1. [1]H NMR chemical shifts (ppm) for Δ–**RDAD** in CD_3CN at R.T.

Complex	Fragment	H_2	H_3	H_4	H_5	H_6	H_7	H_8
RDAD	**alizarin**	7.48 s	6.83 d	7.50 d	8.09m	7.70 t	7.52 t	7.62 d
			(7.9)	(7.8)		(7.6)	(7.6)	(8.0)
	bpy_a		8.44 d	7.89m	7.21 t	7.89m		
			(8.4)		(6.7)			
	bpy_b		8.52 d	8.09m	7.60 t	8.76 d		
			(8.1)		(6.5)	(5.6)		
	bpy_c		8.41 d	7.83m	7.18 t	7.83m		
			(8.1)		(6.8)			
	bpy_d		8.52 d	8.09m	7.50 t	8.62 d		
			(8.1)		(6.5)	(5.6)		

[1]Coupling constants (*J*) are in the brackets. Unit of *J* is Hz.

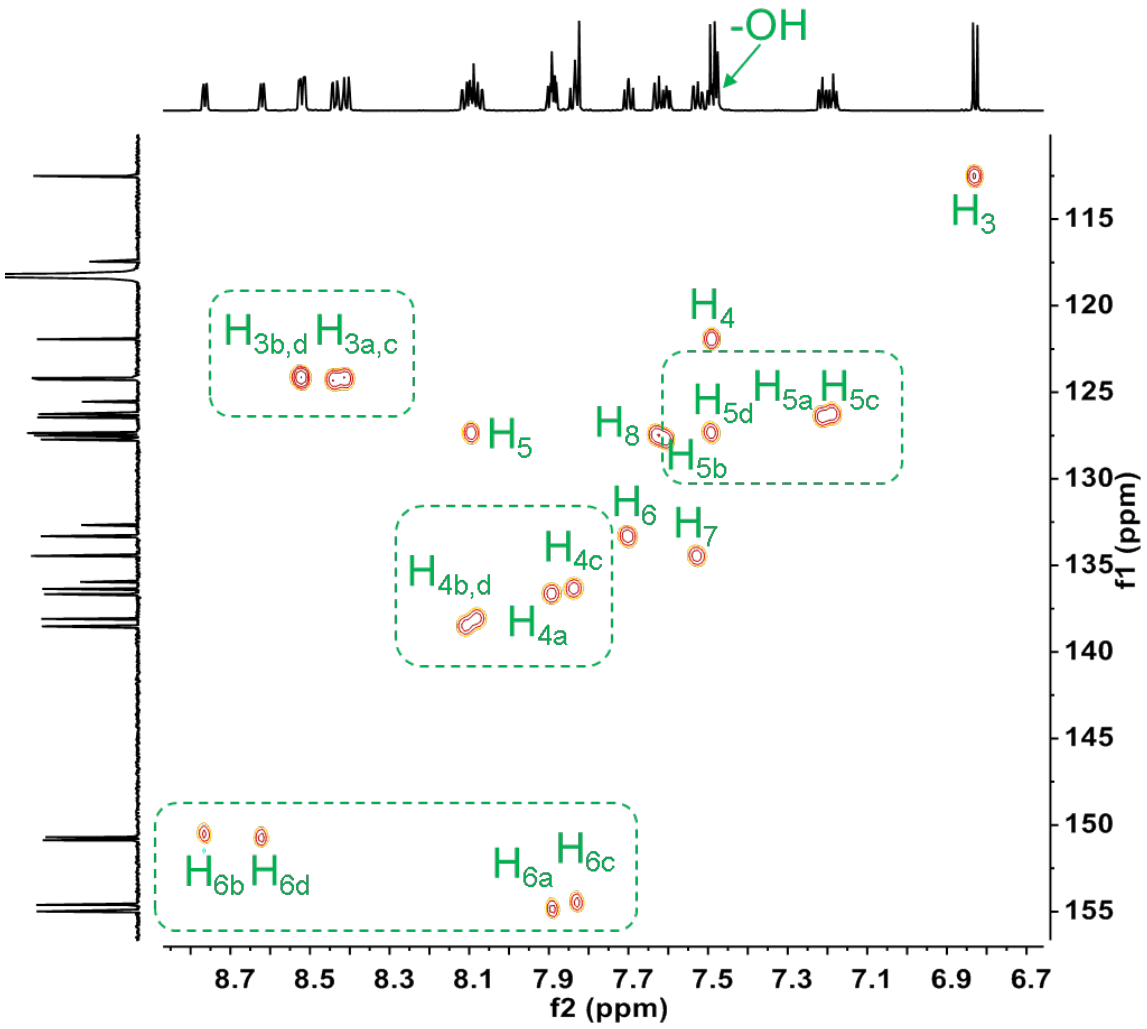


Figure S1. Labelled HSQC spectrum for Δ–**RDAD** in CD_3CN at R.T.

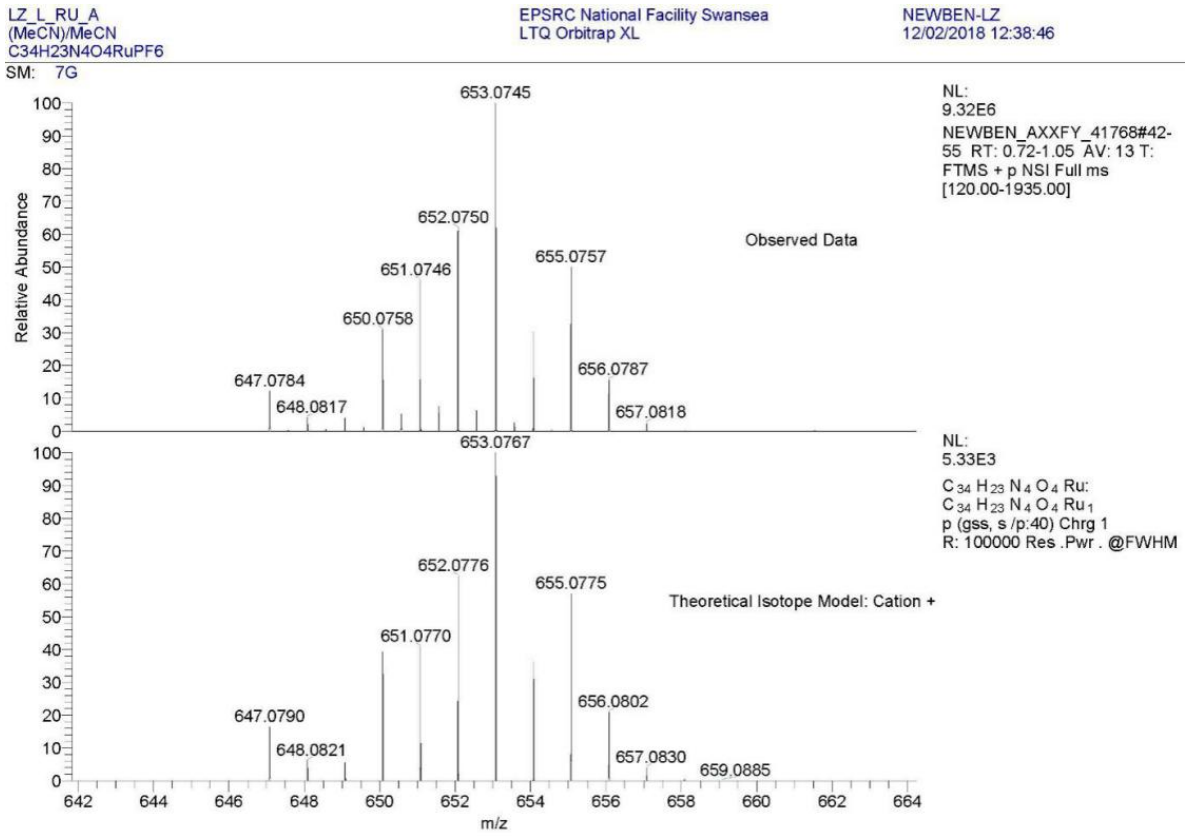


Figure S2. Observed and theoretical mass spectra for **RDAD** in $[M\text{-}PF_6]^+$ mode.

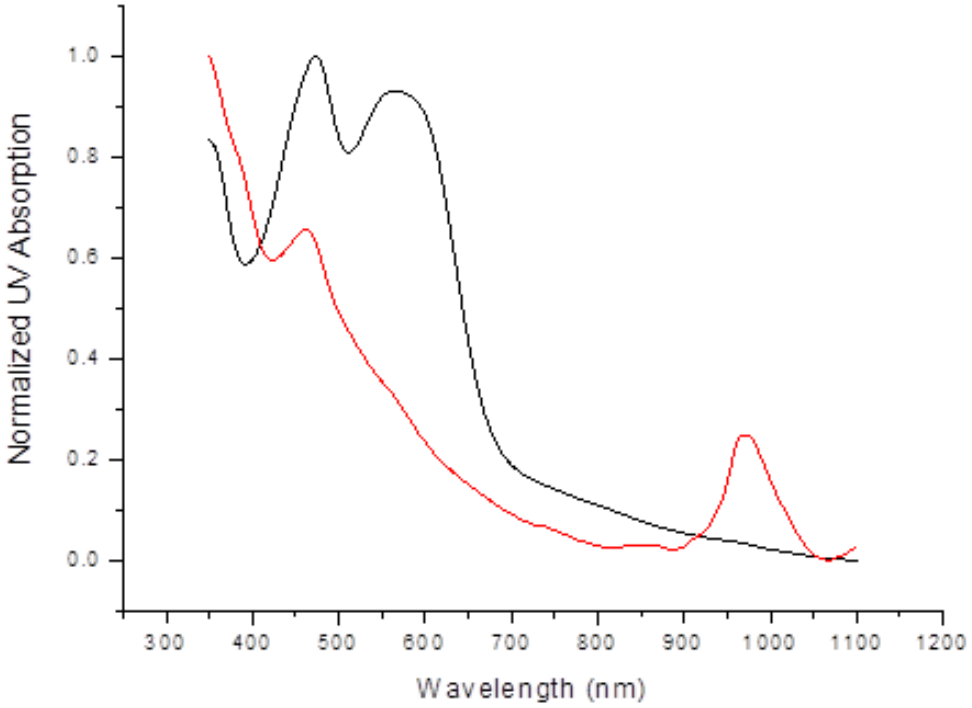


Figure S3. Comparison of UV-Vis absorption spectra in water after *in-situ* oxidation using PbO_2 and the conversion of $[Ru(bipy)_2L]^{2+}$ (black)) to $[Ru(bipy)_2L]^{3+}$ (red) , where L represents the alizarin ligand.

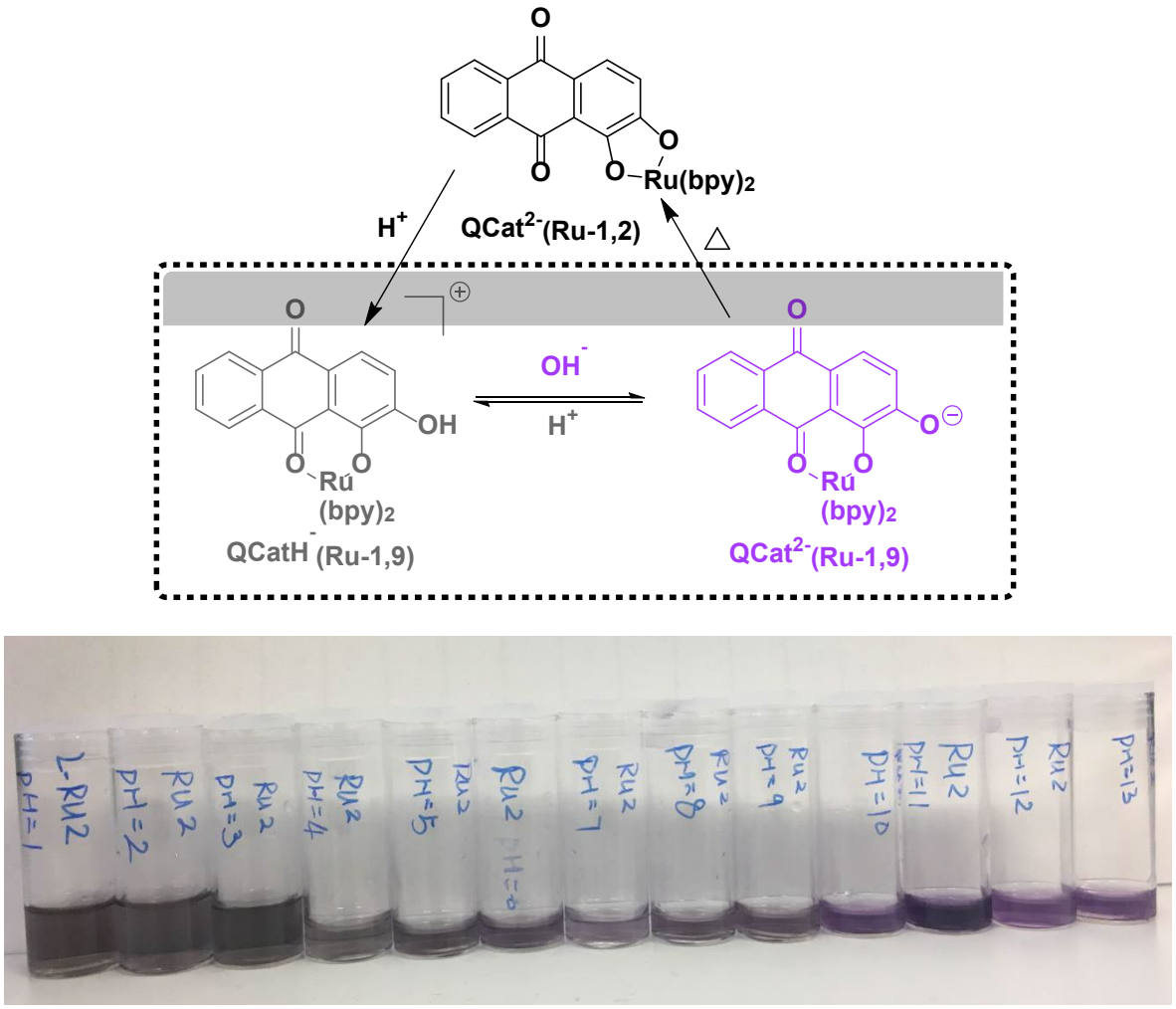
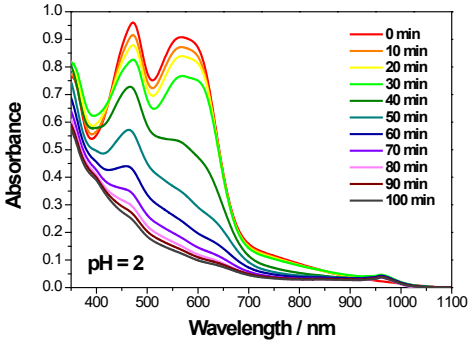
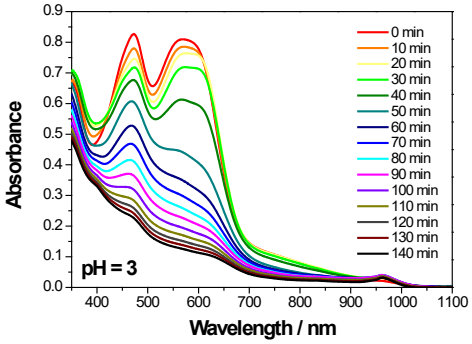


Figure S4. Interconversion of different ruthenium alizarin isomers with different environments (top). **RDAD** in different pH solutions (bottom).


Absorbance
Wavelength / nm
pH = 2
0 min
10 min
20 min
30 min
40 min
50 min
60 min
70 min
80 min
90 min
100 min


Absorbance
Wavelength / nm
pH = 3
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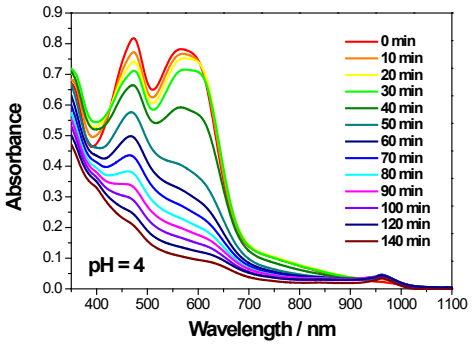
20 min
30 min
40 min
50 min
60 min
70 min
80 min
90 min
100 min
110 min
120 min
130 min
140 min


Absorbance
Wavelength / nm
pH = 4
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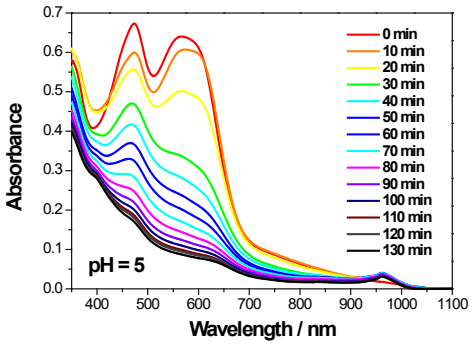
20 min
30 min
40 min
50 min
60 min
70 min
80 min
90 min
100 min
120 min
140 min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Wavelength / nm
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60 min
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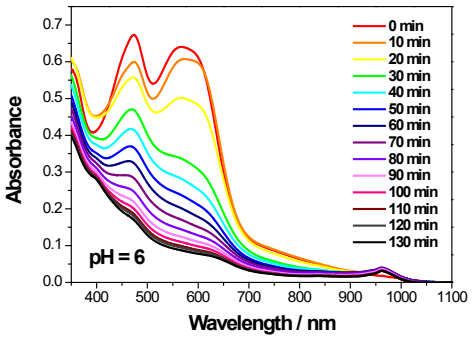
80 min
90 min
100 min
110 min
120 min
130 min


Absorbance
Wavelength / nm
pH = 6
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30 min
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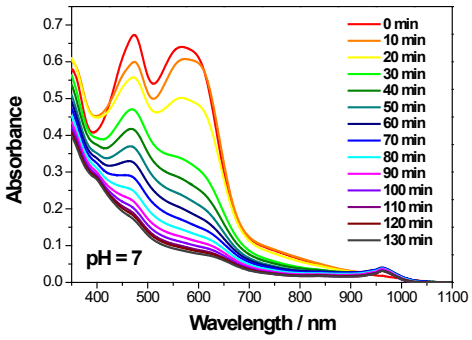
50 min
60 min
70 min
80 min
90 min
100 min
110 min
120 min
130 min


Absorbance
Wavelength / nm
pH = 7
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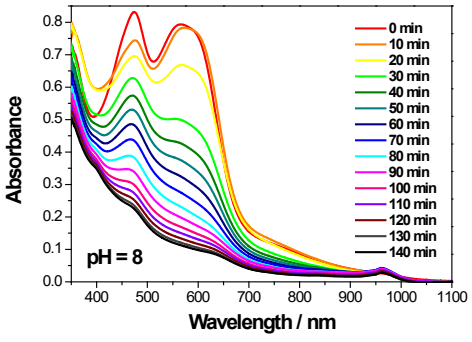
70 min
80 min
90 min
100 min
110 min
120 min
130 min


Absorbance
Wavelength / nm
pH = 8
0 min
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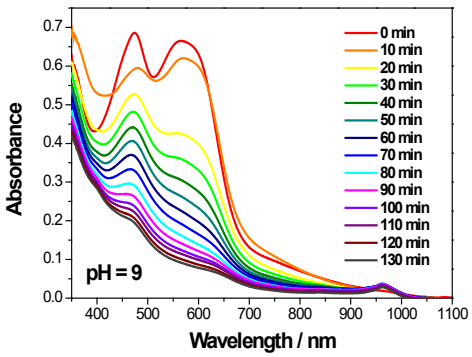
20 min
30 min
40 min
50 min
60 min
70 min
80 min
90 min
100 min
110 min
120 min
130 min
140 min


Absorbance
Wavelength / nm
pH = 9
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30 min
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50 min
60 min
70 min
80 min
90 min
100 min
110 min
120 min
130 min

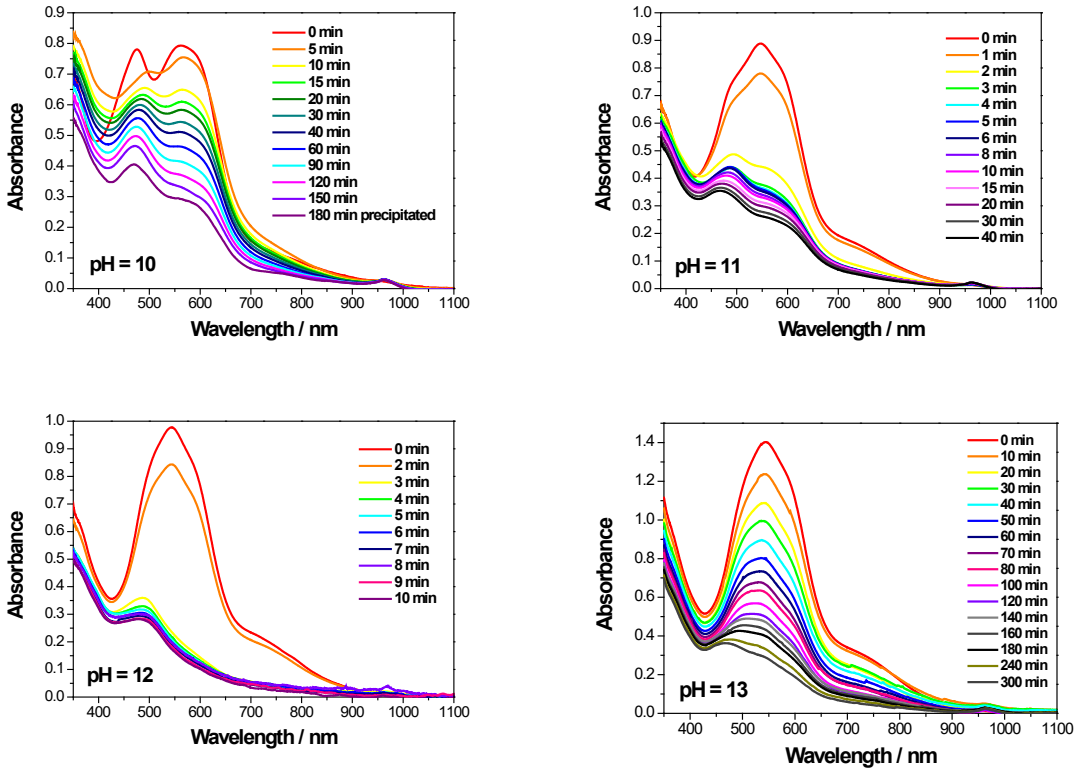
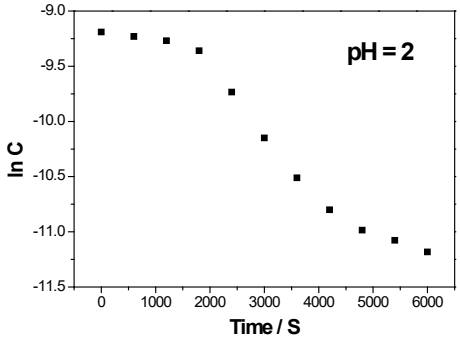
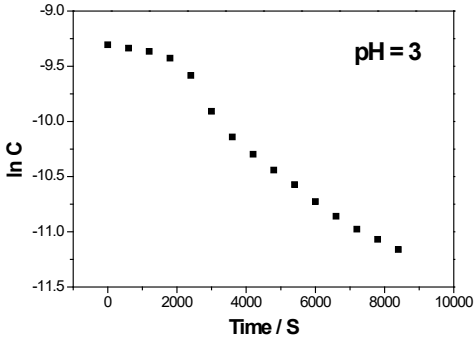
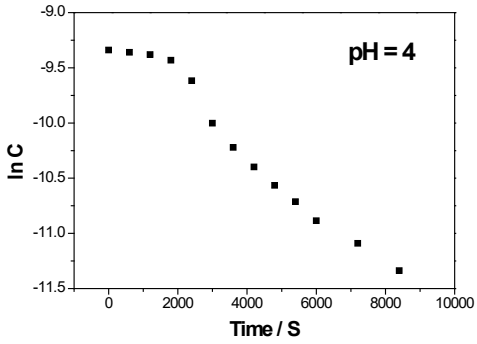
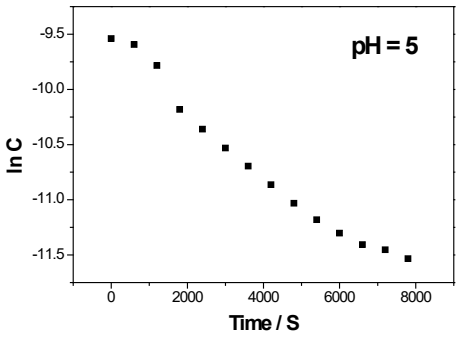


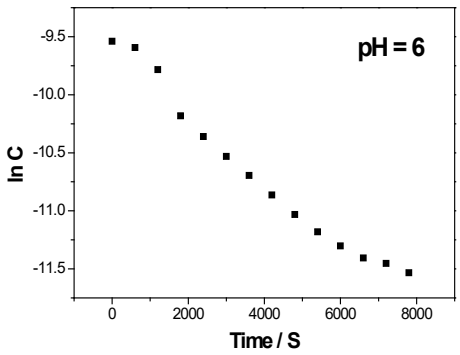
Figure S5. Degradation of **RDAD** with H_2O_2 in the aqueous buffer solution from pH 2 to pH 13. The solution was deoxygenated with N_2 before the measurement.

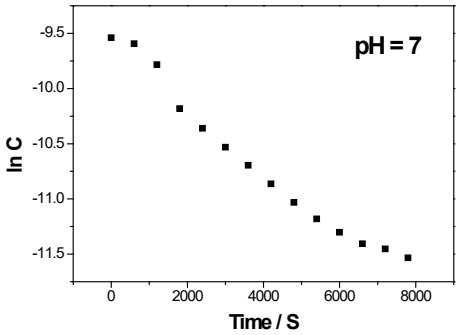

pH = 2
ln C
Time / S

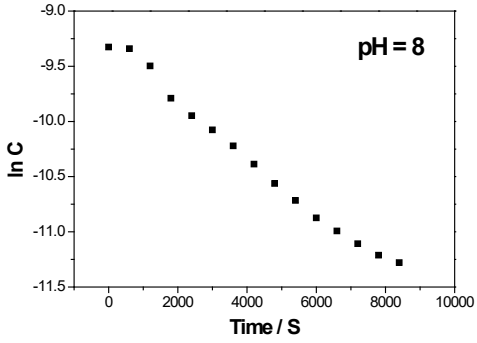

pH = 3
ln C
Time / S

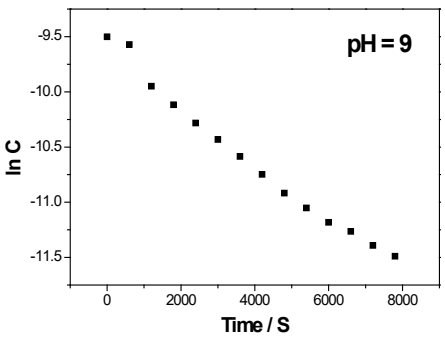

pH = 4
ln C
Time / S


pH = 5
ln C
Time / S


pH = 6
ln C
Time / S


pH = 7
ln C
Time / S


pH = 8
ln C
Time / S


pH = 9
ln C
Time / S

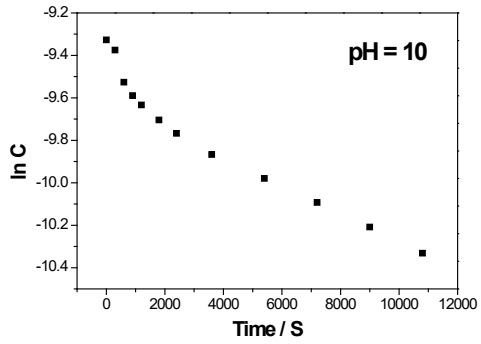


Figure S6. Concentration of **RDAD** versus time at 567 nm with H_2O_2 in the aqueous buffer solutions from pH 2 to pH 10.

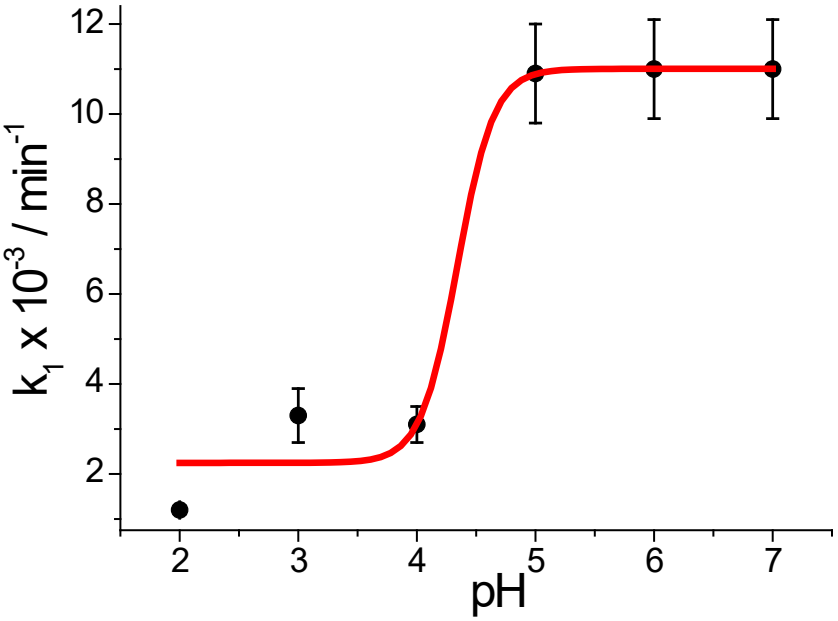


Figure S7. Plot of k_1 versus pH for **RDAD**.

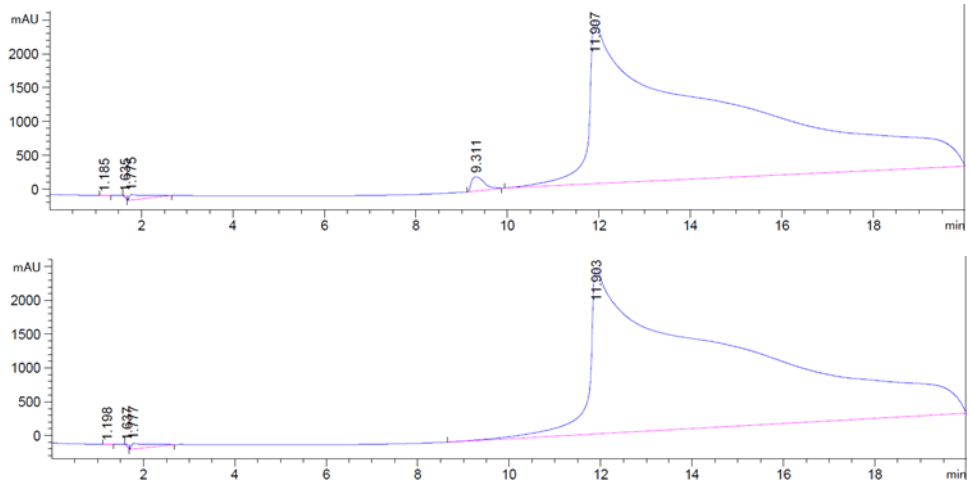


Figure S8. HPLC of Δ-**RDAD** (top) and solvent blank (bottom) measured at 250 nm.

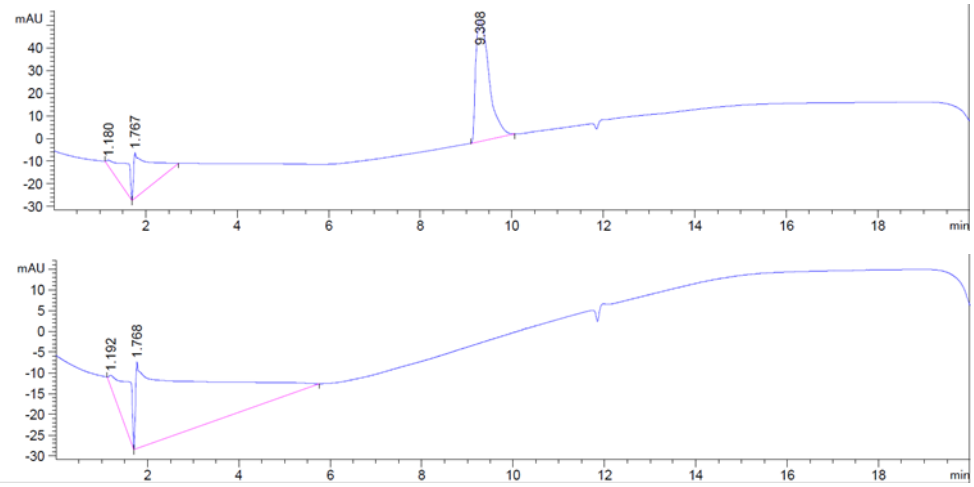


Figure S9. HPLC of Δ-**RDAD** (top) and solvent blank (bottom) measured at 567 nm.

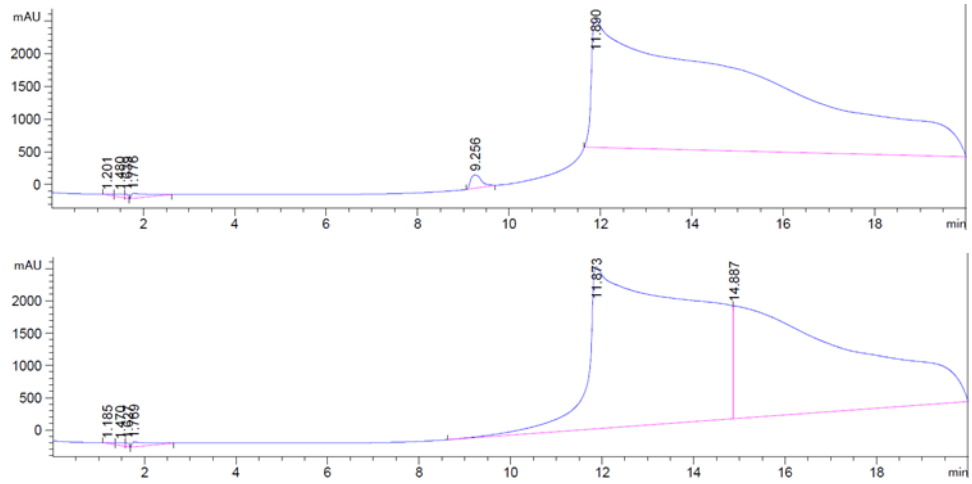


Figure S10. HPLC of Λ-**RDAD** (top) and solvent blank (bottom) measured at 250 nm.

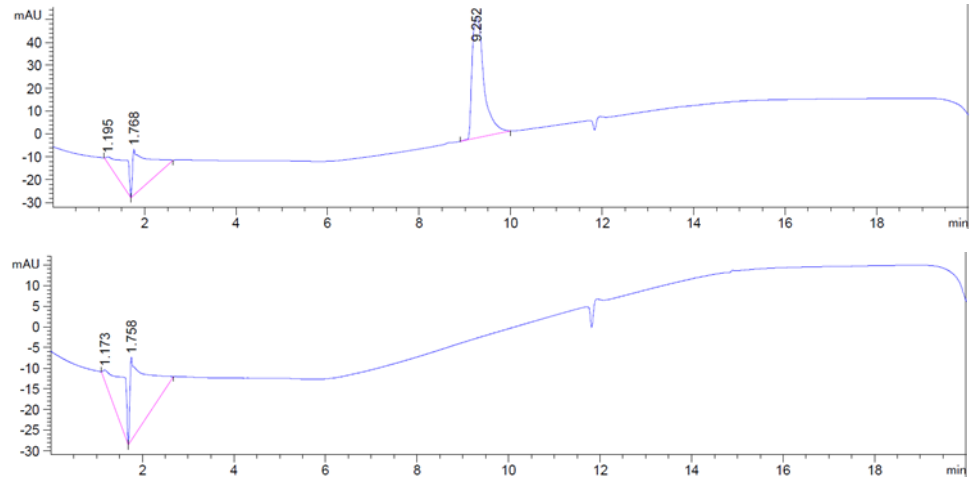


Figure S11. HPLC of Λ-**RDAD** (top) and solvent blank (bottom) measured at 567 nm.