Electronic Supplementary Information:

Base catalysed decomposition of anthracene endoperoxide

M. Klaper, P. Wessig and T. Linker*

Department of Chemistry, University of Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Golm, Germany
E-Mail: linker@uni-potsdam.de

1. General information

All compounds were used as purchased without further purification. If nothing else mentioned all reactions were carried out under inert gas atmosphere (nitrogen gas or argon) in dry glassware with dried solvents. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker Avance 300 MHz NMR and analysed with Top Spin. Chemical shifts (δ-scale) are reported in ppm with TMS (0 ppm) as internal standard for ^{1}H NMR ($CDCl_3$: 7.26, DMSO-d_6: 2.50) and the residual solvent signal ($CDCl_3$: 77.16 ppm, DMSO-d_6: 39.51) for ^{13}C NMR. HRMS were recorded on an ESI-Q-TOF maXis mass spectrometer from Bruker Daltonik. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer with ATR. Melting points were recorded on Mel-Temp with Fluke 51 II thermometer. Elemental analyses were determined by Vario EL III from elementar. Thin layer chromatography (tlc) was performed on tlc Silica gel 60 F_{254} plates from Merck.

2. Experimental procedures and compound characterization data

Anthraquinone and anthrone were identified by comparison with NMR spectra of commercially available compounds.

2.1. Synthesis of starting and reference material

Anthracene-9,10-endoperoxide (**2a**)

Anthracene (178 mg, 1 mmol) was dissolved in dichloromethane (110 mL). Methylene blue (10 mg, 3 mol%, 0.03 mmol) was added. The mixture was cooled to –78°C and irradiated by a high pressure sodium lamp (400 W) for 9 h.

The solvent was removed at 0 °C by a passing nitrogen stream. The crude product was then isolated by column chromatography (solvent: $CHCl_3$/hexane 3:1). The solvent was removed in the same manner. The anthracene endoperoxide (**2a**) was isolated as a white solid (193 mg, 0.92 mmol, 92 %). $R_f = 0.33$ ($CHCl_3$/hexane 3:1); m.p.: 156.3°C (decomposition); IR $\tilde{\nu}$ (cm^{-1}) 3023, 2358, 1463, 1172, 769; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.05 (s, 2 H), 7.17–7.23 (m, 4 H), 7.31–7.37 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 79.5 (d), 123.7 (d), 128.1 (d), 138.2 (s); HRMS (ESI-Q-TOF): *m/z* calcd for $C_{14}H_{10}O_2$: 210.0681 [M$^+$], found: 210.0689; elemental analysis: calcd (%) for $C_{14}H_{10}O_2$: C 79.98, H 4.802, found: C 79.80, H 4.833.

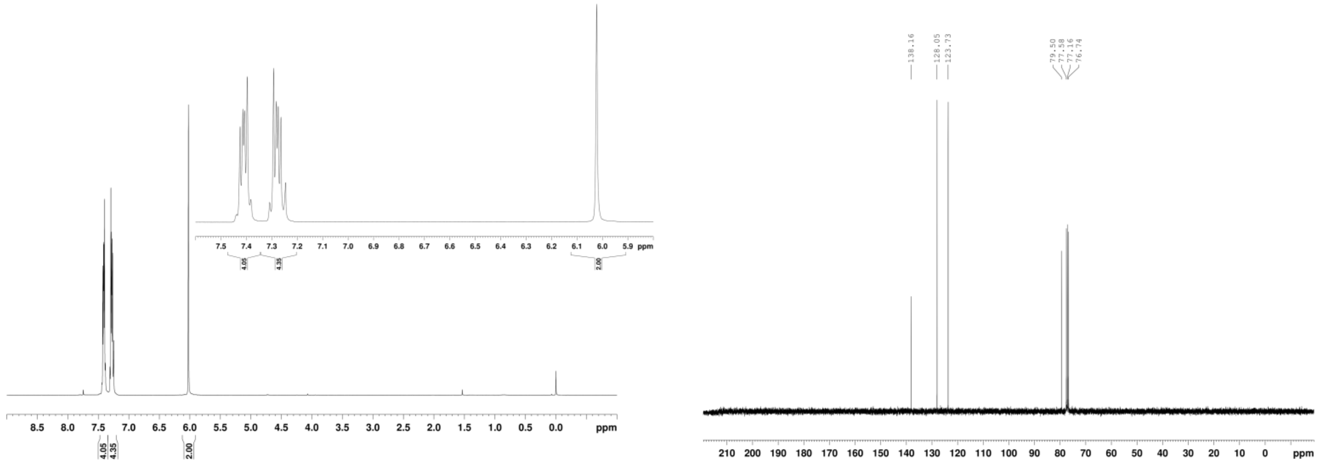


Fig. S1 and S2. NMR spectra of anthracene-9,10-endoperoxide (**2a**).

9,10-Dihydro-9,10-dihydroxy anthracene

The anthracene endoperoxide (**2a**, 105 mg, 0.5 mmol) was dissolved in dichloromethane (15 mL) and methanol (1 mL). Thiourea (57 mg, 0.75 mmol) was added at room temperature without inert atmosphere. The reaction was stirred over night.

Water (25 mL) was added, the mixture was separated. The organic phase was washed with saturated sodium chloride solution, filtered through a small bed of silica gel, which was rinsed with DCM (75 mL) before the product was eluted with diethyl ether (2 x 25 mL). The product (102 mg, 0.48 mmol, 96 %) was found in the second ether fraction as a white solid.

R_f = 0.35 (diethyl ether); m.p. 158.2 °C; IR $\tilde{\nu}$ (cm^{-1}) 3401, 1703, 1362, 1228; ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.35 (d, J = 3.3 Hz, 2 H), 6.35 (d, J = 3.6 Hz, 2 H), 7.22–7.35 (m, 4 H), 7.58–7.70 (m, 4 H); ^{13}C NMR (300 MHz, DMSO-d_6): δ 66.3 (d), 122.9 (d), 125.9 (d), 139.3 (s); HRMS (ESI-Q-TOF): *m/z* calcd for $C_{14}H_{12}O_2$: 212.0837 [M$^+$], found: 212.0839; elemental analysis: calcd (%) for $C_{14}H_{12}O_2$: C 79.22, H 5.704; found: C 79.40, H 5.472.

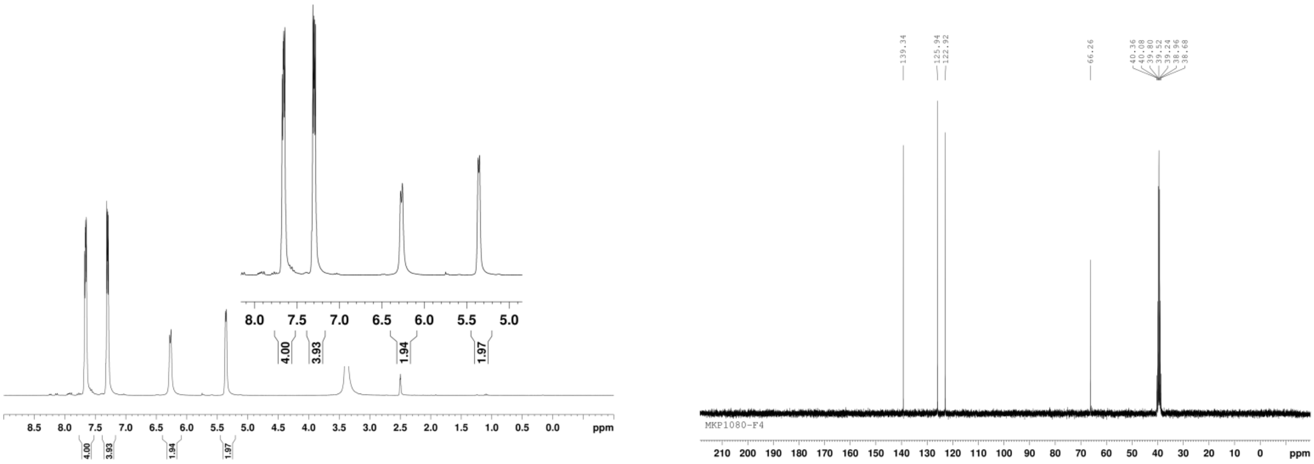


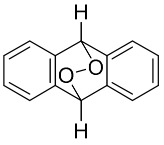
Fig. S3 and S4. NMR spectra of 9,10-dihydro-9,10-dihydroxy anthracene.

2.2. Reactions of EPOs 2a in Schlenck equipment

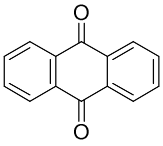
Decomposition of EPOs

The corresponding endoperoxide (**2a**, 106 mg, 0.5 mmol) was dissolved in the appropriate solvent (V = 5.0 mL) in a Schlenck apparatus under argon. The appropriate acid or base was added. NMR samples were extracted and directly submitted (Table S1). All reactions were performed at least three times.

Table S1 Decomposition of EPO 2a under Schlenck conditions.



2a



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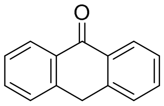


Anthrone

Entry	Base/Acid	Equivalents of Base/Acid	Solvent	Reaction Time	Temperature	Products (%)
1	H_2SO_4	0.05	$CDCl_3$	6 d	RT	**2a** (20), **3** (70), anthrone (5)
2	H_2SO_4	0.10	$CDCl_3$	6 d	RT	**2a** (19), **3** (75), anthrone (4)
3	H_2SO_4	0.50	$CDCl_3$	6 d	RT	**2a** (8), **3** (85), anthrone (7)
4	H_2SO_4	1.00	$CDCl_3$	12.5 h	RT	**2a** (trace), **3** (90), anthrone (10)
5	H_2SO_4	2.00	$CDCl_3$	5 h	RT	**2a** (0), **3** (90), anthrone (10)
6	H_2SO_4	10.00	$CDCl_3$	5 min	RT	**2a** (0), **3** (87), anthrone (13)
7	H_2SO_4	20.00	$CDCl_3$	5 min	RT	**2a** (0), **3** (82), anthrone (18)
8	H_2SO_4	0.05	$CDCl_3$	1 h	80 °C	**2a** (0), **3** (98), anthrone (trace)
9	NaOH	0.05	DCM-d_2	1 h	RT	**3** (100)
10	NaOH	0.10	DCM-d_2	45 min	RT	**3** (100)
11	NaOH	0.50	DCM-d_2	20 min	RT	**3** (100)
12	NaOH	1.00	DCM-d_2	5 min	RT	**3** (100)
13	NaOH	2.00	DCM-d_2	5 min	RT	**3** (100)
14	NaOH	10.00	DCM-d_2	5 min	RT	**3** (100)
15	NaOH	20.00	DCM-d_2	5 min	RT	**3** (100)
16	KOH	0.05	DCM-d_2	1 h	RT	**3** (100)
17	DBU	0.05	$CDCl_3$	1 h	RT	**3** (100)
18	NEt_3	0.05	$CDCl_3$	1 h	RT	**3** (100)
19	K_2CO_3	0.05	$CDCl_3$	1 h	RT	**3** (100)
20	Na_2CO_3	0.05	$CDCl_3$	1 h	RT	**3** (100)
21	$NaHCO_3$	0.05	$CDCl_3$	1 h	RT	**3** (100)
22	KOH	0.05	DMSO-d_6	1 h	RT	**3** (100)
23	NaOH	0.05	DMSO-d_6	1 h	RT	**3** (100)
24	DBU	0.05	DMSO-d_6	1 h	RT	**3** (100)
25	NEt_3	0.05	DMSO-d_6	1 h	RT	**3** (100)
26	K_2CO_3	0.05	DMSO-d_6	1 h	RT	**3** (100)
27	Na_2CO_3	0.05	DMSO-d_6	1 h	RT	**3** (100)
28	$NaHCO_3$	0.05	DMSO-d_6	1 h	RT	**3** (100)

2.3. Reactions of EPOs 2a and AQ (3)in the glove box

All solvents were degassed by five freeze-pump-thaw-cycles and directly transferred into the glove box. All reactions were performed at least four times.

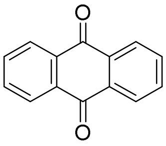
Decomposition of EPOs

The corresponding endoperoxide (**2a**, 64 mg, 0.3 mmol) was dissolved in the appropriate solvent (V = 3 mL). The appropriate base was weighted into a snap-cap vial and added in one portion. The solution was divided into five portions after 10 min and treated by additives as shown in Table S2. The NMR tubes were opened after the first NMR measurement.

*Reaction of anthraquinone (**3**) with NaBH$_4$*

AQ (**3**, 62 mg, 0.3 mmol) was dissolved in the appropriate solvent (V = 3 mL). NaBH$_4$ (6 mg, 0.15 mmol) was weighted into a snap-cap vial and added in one portion. The solution was divided into five portions after 6 h and treated by additives as shown in Table S2. The NMR tubes were opened after the first NMR measurement.

Table S2 Reactions of EPOs 2a and AQ (3) under glove box conditions and secondary reaction products after exposure to oxygen



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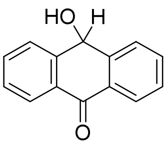

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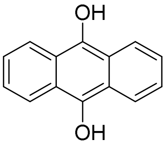

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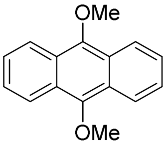

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Entry	Starting Material	Reagent (mol%)	Solvent	Additive	Initial Product	After Exposure to Oxygen
1	EPO **2a**	NaOH (2.5 mol%)	DCM-d_2	./.	**4/5**	**3**
2	EPO **2a**	NaOH (2.5 mol%)	DCM-d_2	CF_3COOD	**5-d_2**	**3**
3	EPO **2a**	NaOH (2.5 mol%)	DCM-d_2	DCl in D_2O	**5-d_2**	**3**
4	EPO **2a**	NaOH (2.5 mol%)	DCM-d_2	HCl in H_2O	**5-h_2**	**3**
5	EPO **2a**	NaOH (2.5 mol%)	DCM-d_2	MeI	**11**	**11**
6	EPO **2a**	KOH (2.5 mol%)	DCM-d_2	./.	**4/5**	**3**
7	EPO **2a**	DBU (2.5 mol%)	DCM-d_2	./.	**4/5**	**3**
8	EPO **2a**	NEt_3 (2.5 mol%)	DCM-d_2	./.	**4/5**	**3**
9	EPO **2a**	K_2CO_3 (2.5 mol%)	DCM-d_2	./.	**4/5**	**3**
10	EPO **2a**	Na_2CO_3 (2.5 mol%)	DCM-d_2	./.	**4/5**	**3**
11	EPO **2a**	$NaHCO_3$ (2.5 mol%)	DCM-d_2	./.	**4/5**	**3**
12	AQ (**3**)	$NaBH_4$ (50 mol%)	DCM-d_2	./.	**3**[1]	**3**
13	AQ (**3**)	$NaBH_4$ (50 mol%)	DCM-d_2	CF_3COOD	**3**[1]	**3**
14	AQ (**3**)	$NaBH_4$ (50 mol%)	DCM-d_2	DCl in D_2O	**3**[1]	**3**
15	AQ (**3**)	$NaBH_4$ (50 mol%)	DCM-d_2	HCl in H_2O	**3**[1]	**3**
16	AQ (**3**)	$NaBH_4$ (50 mol%)	DCM-d_2	MeI	**3**[1]	**3**
17	EPO **2a**	NEt_3 (2.5 mol%)	$CDCl_3$	./.	**4/5**	**3**
18	EPO **2a**	K_2CO_3 (2.5 mol%)	$CDCl_3$	./.	**4/5**	**3**
19	EPO **2a**	Na_2CO_3 (2.5 mol%)	$CDCl_3$	./.	**4/5**	**3**
20	EPO **2a**	$NaHCO_3$ (2.5 mol%)	$CDCl_3$	./.	**4/5**	**3**
21	EPO **2a**	$NaHCO_3$ (2.5 mol%)	$CDCl_3$	CF_3COOD	**5-d_2**	**3**
22	EPO **2a**	$NaHCO_3$ (2.5 mol%)	$CDCl_3$	DCl in D_2O	**5-d_2**	**3**
23	EPO **2a**	$NaHCO_3$ (2.5 mol%)	$CDCl_3$	HCl in H_2O	**5-h_2**	**3**
24	EPO **2a**	$NaHCO_3$ (2.5 mol%)	$CDCl_3$	MeI	**11**	**11**
25	EPO **2a**	NaOH (2.5 mol%)	DMSO-d_6	./.	**4/5**	**3**
26	EPO **2a**	NaOH (2.5 mol%)	DMSO-d_6	CF_3COOD	**5-d_2**	**3**
27	EPO **2a**	NaOH (2.5 mol%)	DMSO-d_6	DCl in D_2O	**5-d_2**	**3**
28	EPO **2a**	NaOH (2.5 mol%)	DMSO-d_6	HCl in H_2O	**5-h_2**	**3**
29	EPO **2a**	NaOH (2.5 mol%)	DMSO-d_6	MeI	**11**	**11**
30	EPO **2a**	DBU (2.5 mol%)	DMSO-d_6	./.	**4/5**	**3**
31	EPO **2a**	NEt_3 (2.5 mol%)	DMSO-d_6	./.	**4/5**	**3**
32	EPO **2a**	K_2CO_3 (2.5 mol%)	DMSO-d_6	./.	**4/5**	**3**
33	EPO **2a**	Na_2CO_3 (2.5 mol%)	DMSO-d_6	./.	**4/5**	**3**
34	EPO **2a**	$NaHCO_3$ (2.5 mol%)	DMSO-d_6	./.	**4/5**	**3**
35	AQ (**3**)	$NaBH_4$ (50 mol%)	DMSO-d_6	./.	**5-h_2**	**3**
36	AQ (**3**)	$NaBH_4$ (50 mol%)	DMSO-d_6	CF_3COOD	**5-d_2**	**3**
37	AQ (**3**)	$NaBH_4$ (50 mol%)	DMSO-d_6	DCl in D_2O	**5-d_2**	**3**
38	AQ (**3**)	$NaBH_4$ (50 mol%)	DMSO-d_6	HCl in H_2O	**5-h_2**	**3**
39	AQ (**3**)	$NaBH_4$ (50 mol%)	DMSO-d_6	MeI	**11**	**11**

[1] no reaction observed

Anthraquinone (**3**)

^{1}H NMR (300 MHz, CDCl$_3$): δ 7.7–7.82 (m, 4 H), 8.24–8.36 (m, 4 H); ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.95 (dd, *J* = 5.7, 3.3 Hz, 4 H), 8.23 (dd, *J* = 5.7, 3.3 Hz, 4 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 127.5 (d), 133.8 (s), 134.2 (d), 183.2 (s); ^{13}C NMR (75 MHz, DMSO-d_6): δ 127.5 (d), 133.8 (s), 134.2 (d), 183.2 (s).

p-Hydroxy anthrone (**4**)
^{1}H NMR (300 MHz, CDCl$_3$): δ 5.71 (s, 1 H), 7.49 (dd, *J* = 7.5, 0.6 Hz, 2 H), 7.67 (dd, *J* = 8.1, 0.6 Hz, 2 H), 7.86 (d, *J* = 7.5 Hz, 2 H), 8.24 (d, *J* = 8.1, 2 H); ^{1}H NMR (300 MHz, DMSO-d_6): δ 6.20 (s, 1 H), 7.49 (dd, *J* = 7.2, 0.6 Hz, 2 H), 7.77 (dd, *J* = 7.9, 0.6 Hz, 2 H), 7.97 (d, *J* = 7.2 Hz, 2 H), 8.09 (d, *J* = 7.9, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 70.6 (d), 127.4 (d), 128.2 (d), 128.7 (d), 134.7 (s), 135.7 (s), 139.3 (d), 180.6 (s).

9,10-Dihydroxy anthracene-h$_2$ (**5**)
^{1}H NMR (300 MHz, CDCl$_3$): δ 5.46 (s, 2 H), 7.34 (dd, *J* = 5.4, 3.3 Hz, 4 H), 7.57 (dd, *J* = 5.1, 3.3 Hz, 4 H); ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.60 (d, *J* = 4.8 Hz, 1 H), 5.77 (d, *J* = 4.8 Hz, 1 H), 7.29 (dd, *J* = 5.1, 3.4 Hz, 4 H), 7.57 (dd, *J* = 5.1, 3.8 Hz, 4 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 127.3 (d), 128.4 (d), 139.2 (s), 162.5 (s).

9,10-Dihydroxy anthracene-d$_2$ (**5**)
^{1}H NMR (300 MHz, DMSO-d_6): δ 7.42 (dd, *J* = 5.4, 3.3 Hz, 4 H), 8.34 (*J* = 5.1, 3.3 Hz, 4 H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 122.5 (d), 123.8 (d), 140.9 (s), 161.9 (s).

9,10-Dimethoxy anthracene (**11**)
^{1}H NMR (300 MHz, DMSO-d_6): δ 4.01 (s, 6 H), 7.56–7.68 (m, 4 H), 8.16–8.28 (m, 4 H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 67.5 (q), 122.8 (d), 125.5 (s), 126.2 (d), 146.4 (s).

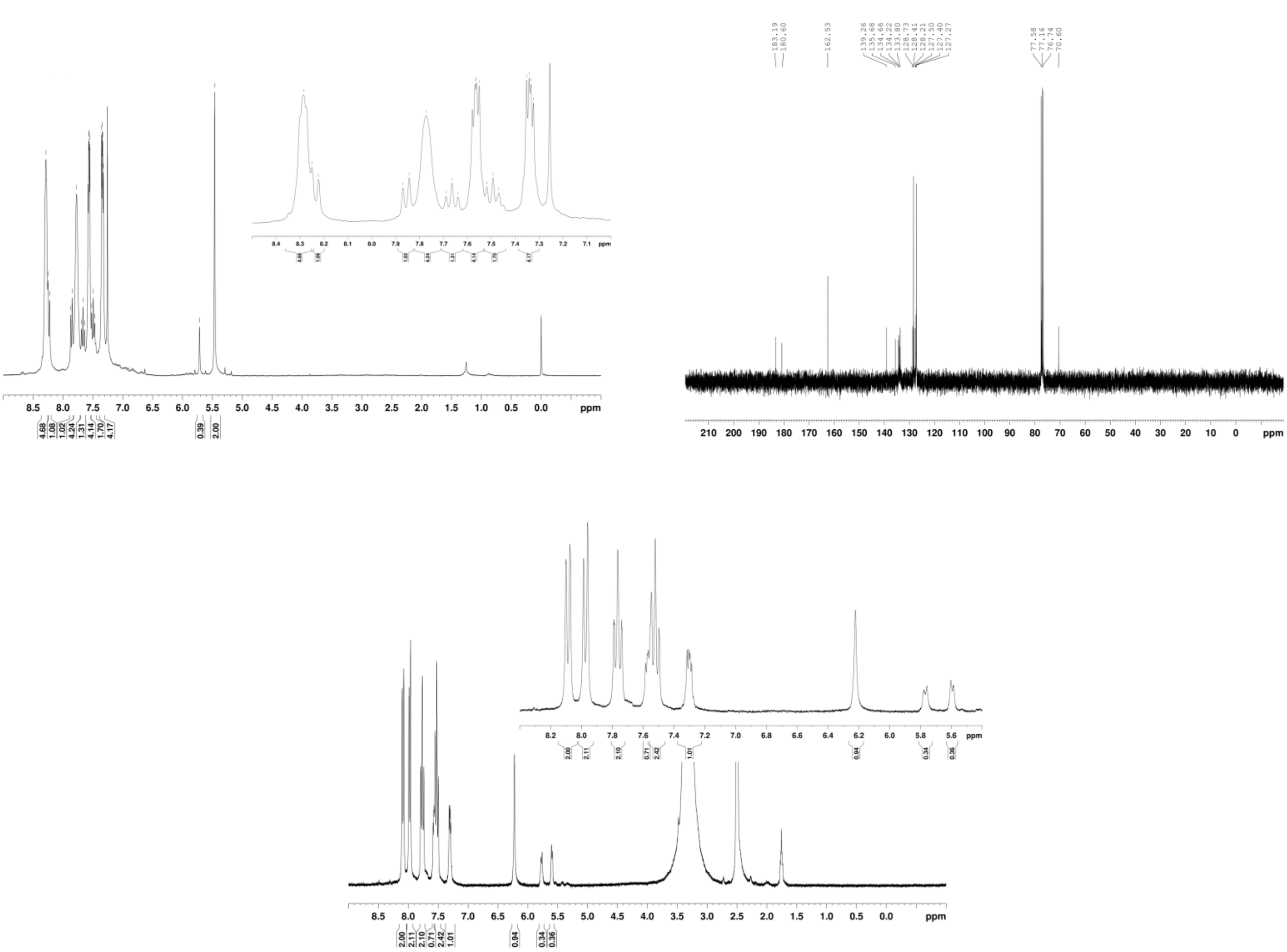

Fig. S5–S7. NMR spectra of glove box reactions. Top: decomposition of **2a** in $CDCl_3$ with catalytic amounts of NaOH; products: anthraquinone (**3**), *p*-hydroxy anthrone (**4**) and 9,10-dihydroxy anthracene (**5**). Bottom: decomposition of **2a** in DMSO-d_6 with catalytic amounts of NaOH; products: *p*-hydroxy anthrone (**4**) and 9,10-dihydroxy anthracene (**5**).

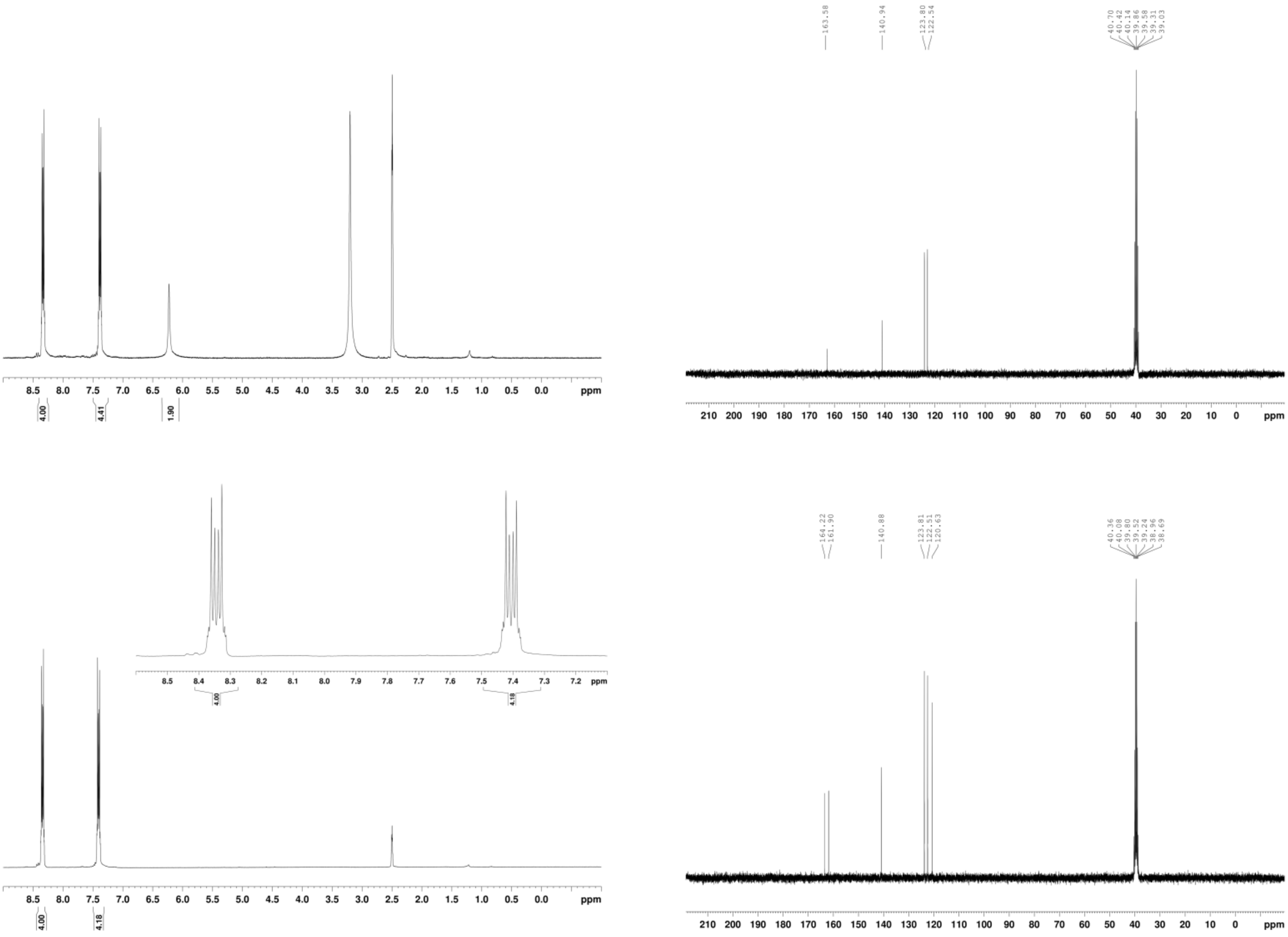

Fig. S8–S11. Top: NMR spectra of 9,10-dihydroxy anthracene-*h*$_2$ (**5**) in DMSO-*d*$_6$ with HCl/H_2O. Bottom: NMR spectra of 9,10-dihydroxy anthracene-*d*$_2$ (**5**) in DMSO-*d*$_6$ with TFA-*d*, same result for DCl/D_2O.

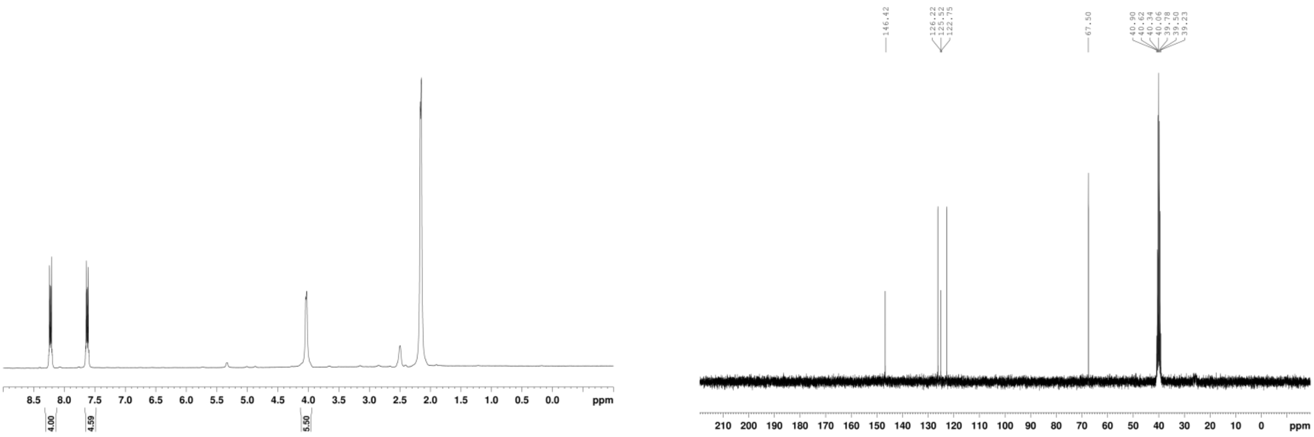

Fig. S12 and S13. NMR spectra of 9,10-dimethoxy anthracene (**11**).

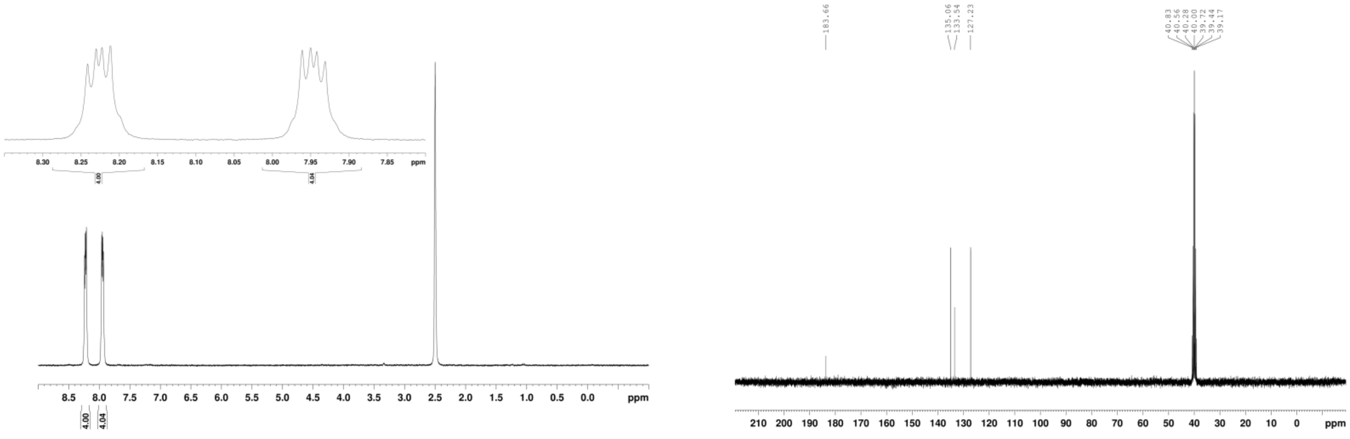

Fig. S14 and S15. NMR spectra of anthraquinone (**3**).

3. Absorption-, excitation- and fluorescence spectra

All spectra were recorded in deoxygenated DMSO-d_6 at a $5{\cdot}10^{-5}$ M solution in a sealed fluorescence cuvette at room temperature. The fluorescence lifetime is 17 µs. The sealed cuvette was opened for 90 s after the measurement of absorption-, emission- and excitation spectra and the decrease of the fluorescence intensity was monitored time-dependent. The first order rate constant $k_1 = 17.3\ \mathrm{s}^{-1}$ was determined from the slope of linearised fluorescence intensity ($\ln(I_{\mathrm{rel}})$ vs. t) at 520 nm, the half-life ($t_{½} = \ln(2)/k_1$) was calculated to be $t_{½}$ = 144 s ≈ 2.4 min.

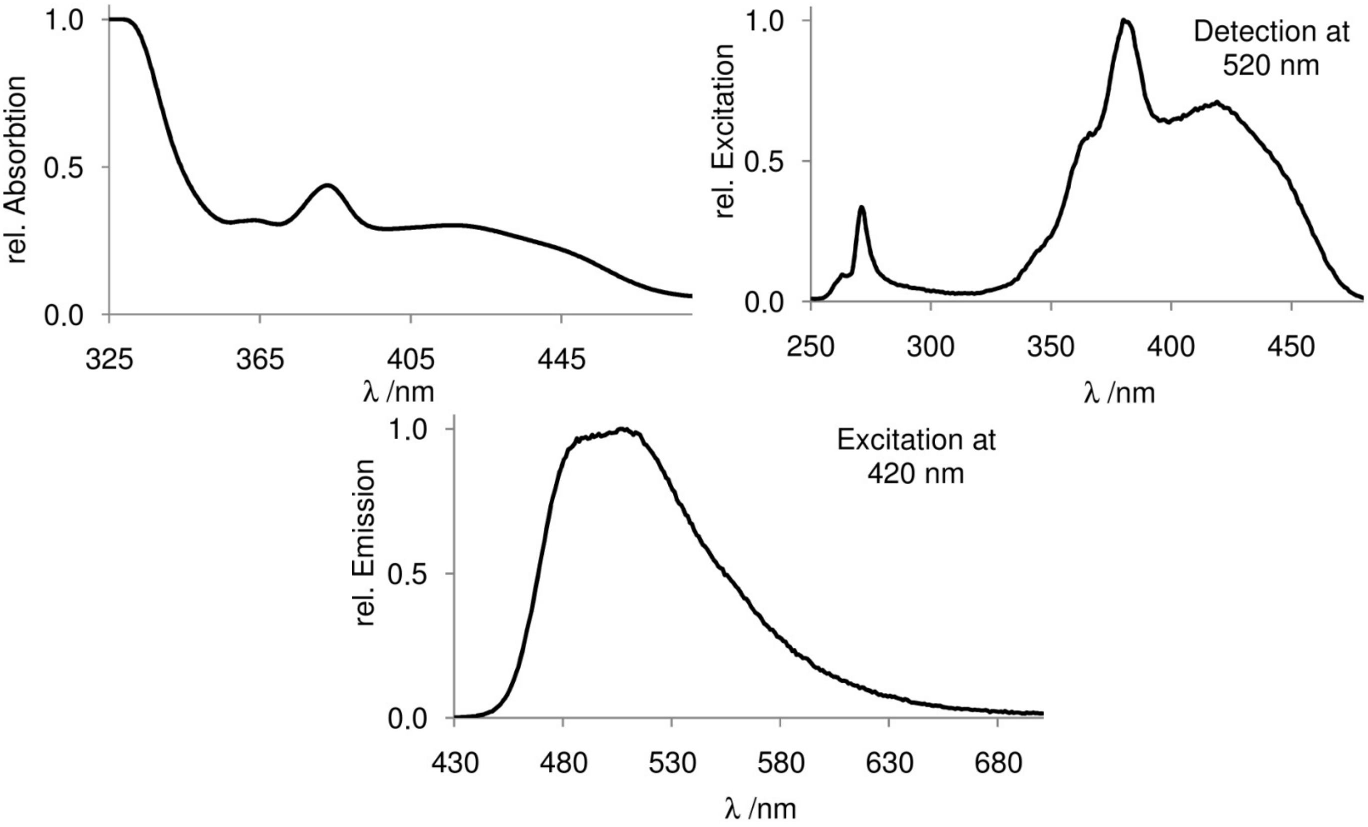

Fig. S16–S18. Top, left: Absorption spectrum of 9,10-dihydroxy anthracene (**5**). Top, right: excitation spectrum of 9,10-dihydroxy anthracene (**5**) with detection at 520 nm. Bottom: emission spectrum of 9,10-dihydroxy anthracene (**5**) with excitation at 420 nm.

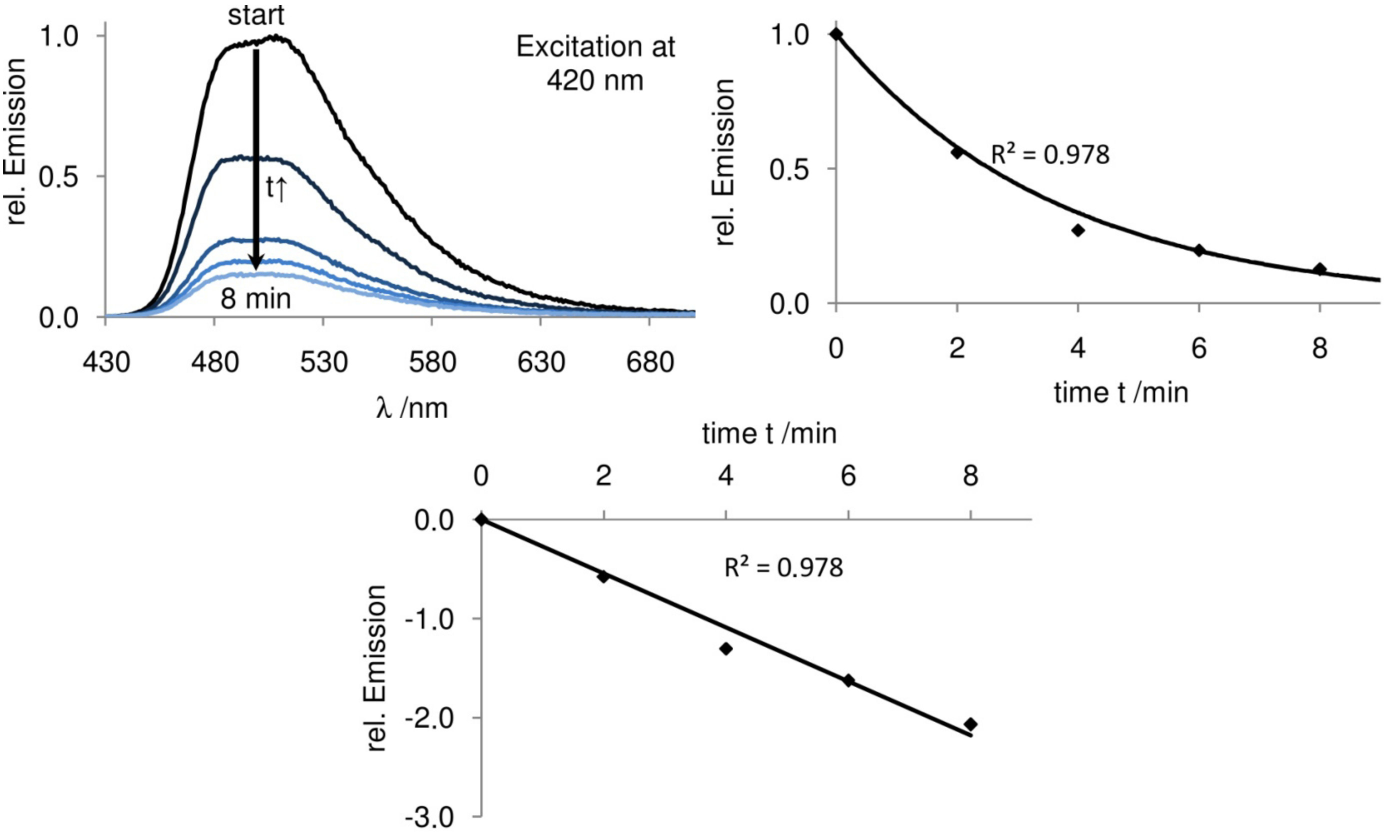

Fig. S19–S21. Top, left: fluorescence spectra of 9,10-dihydroxy anthracene (**5**) before (start) and after exposure to oxygen with chronological progress with excitation at 420 nm. Top, right: logarithmic intensity decrease of the fluorescence from 9,10-dihydroxy anthracene (**5**) at 520 nm with excitation at 420 nm. Bottom: Linearisation of the intensity decrease at 520 nm with excitation at 420 nm.

4. Detection of hydrogen peroxide

The absence of endoperoxide **2a** was confirmed by thin layer chromatography after the decomposition reaction and exposure to oxygen for the detection of hydrogen peroxide (H_2O_2). Furthermore, the sample was diluted with chloroform and extracted with water to remove the organic fraction. Afterwards, the aqueous phase was tested for H_2O_2.

4.1. Detection with Potassium Iodide

A few drops of the aqueous solution were added to a colorless solution of potassium iodide in water (10 %, 5 mL) in a test tube. The solution turned instantaneously brown, showing the presence of H_2O_2.

4.2. Detection with Potassium Dichromate

A few drops of the aqueous solution were added to a solution of potassium dichromate (0.1 M, 5 mL) and sulfuric acid (0.5 M, 0.1 mL) in a test tube. Afterwards, the aqueous phase was extracted with diethyl ether (5 mL), which turned blue, showing the presence of H_2O_2.

4.3. Detection with *p*-Nitrophenyl Boronic Acid[1]

Sodium carbonate (212 mg, 2 mmol) and a solution of *p*-nitrophenyl boronic acid in methanol (1 mmol, 0.05 M, 20 mL) were added to the aqueous extract from a 1 mmol decomposition reaction batch. The reaction was stirred for 2 h. Then the reaction was acidified with concentrated HCl (1 mL) and extracted with chloroform (3 x 10 mL). The organic phase was washed with sodium bicarbonate solution (25 mL) and saturated sodium chloride solution (25 mL) and was dried over sodium sulfate. The solvent was removed to give *p*-nitrophenol (118 mg, 0.85 mmol, 85 %).
^1H NMR (300 MHz, CD_3CN): δ 6.95 (ddd, *J* = 10.4, 3.3 and 2.8 Hz, 2 H), 8.09 (s, br, 1 H), 8.13 (ddd, *J* = 10.4, 3.3 and 2.8 Hz, 2 H); ^{13}C NMR (75 MHz, CD_3CN): δ 116.6 (d), 127.1 (d), 164.0 (s).

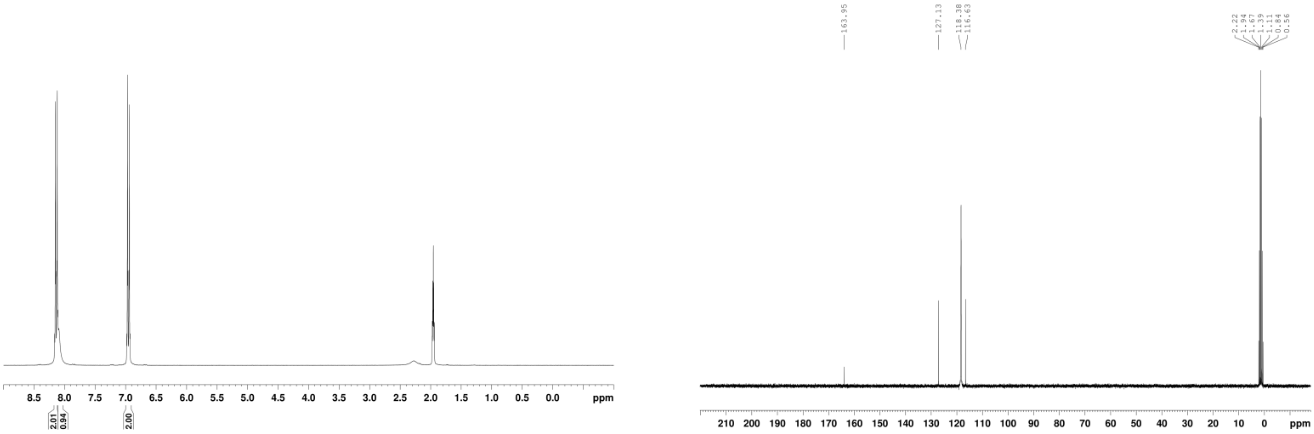

Fig. S22 and S23. NMR spectra of *p*-nitrophenol.

4.4. Detection with Enzyme-Mimetic Catalyst-Modified Nanoporous SiO_2-Cellulose Hybrid Composites Test Paper[2]

The H_2O_2 test paper was prepared as described in literature.[2] Some drops of the aqueous solution were put onto the test paper. It turned turquoise within 1 min (see Fig. S29 and S30).

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[1] G. Su and Y. Wei, M. Guo, *Am. J. Anayl. Chem.*, 2011, **2**, 879–884.

[2] Y. Jiang, W. Wang, X. Li, X. Wang, J. Zhou and X. Mu, *ACS Appl. Mater. Interfaces*, 2013, **5**, 1913–1916.

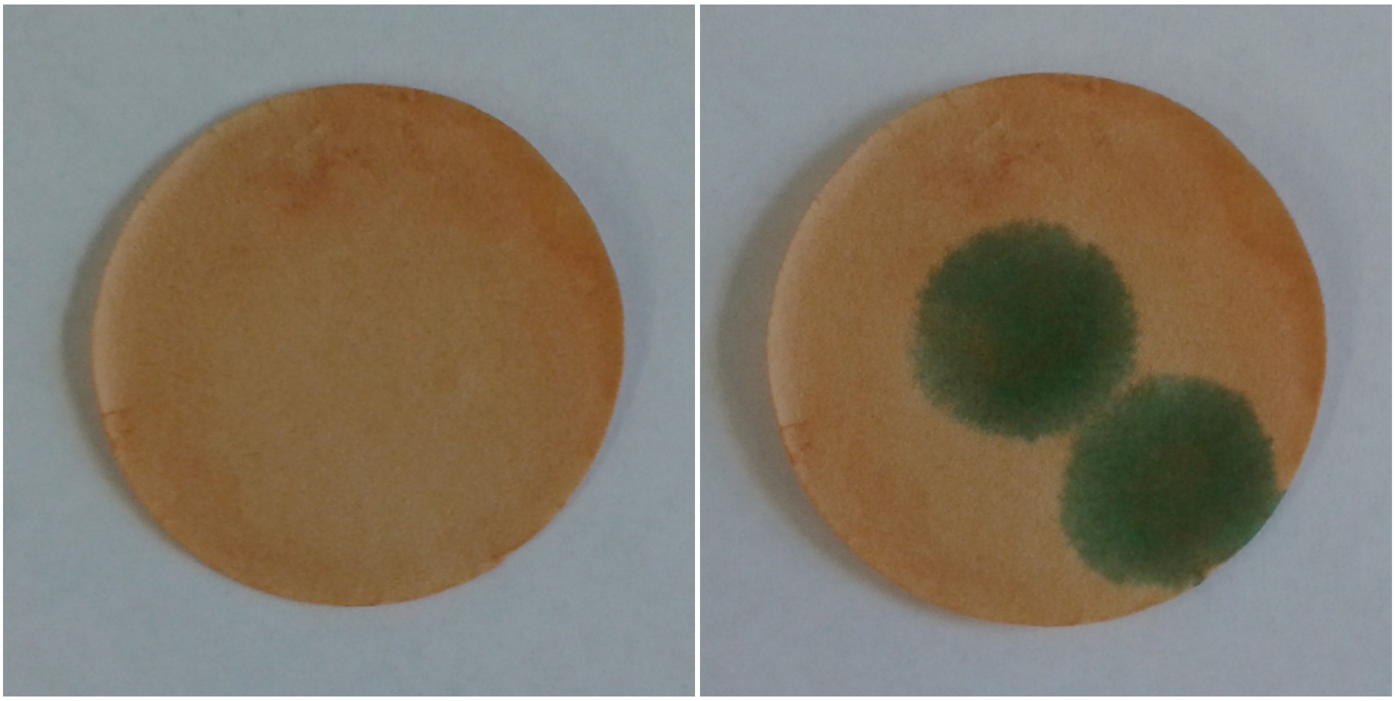
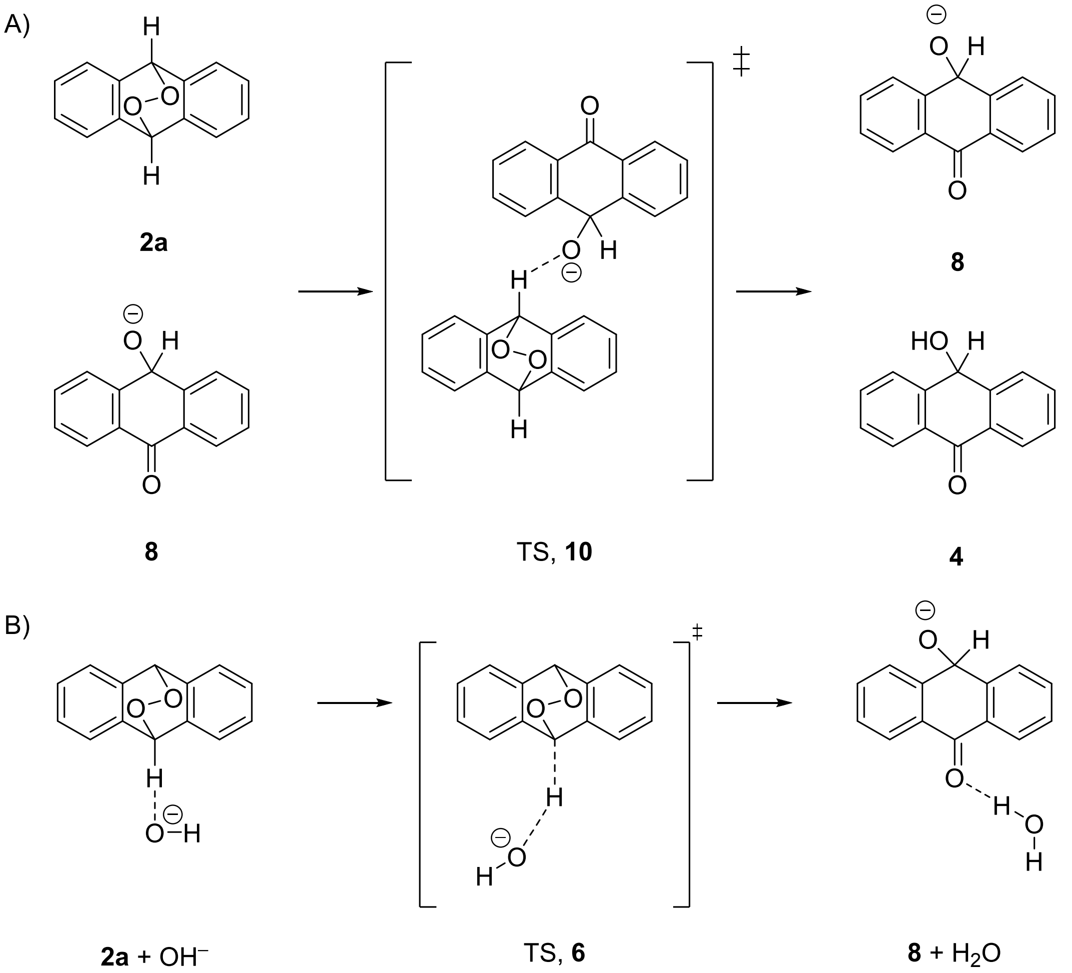


Fig. S24 and S25. Pictures from the detection of H_2O_2 with the enzyme-mimetic catalyst-modified nanoporous SiO_2-cellulose hybrid composites test paper. Left: before addition of the aqueous solution. Right: after addition of the aqueous solution.

5. Quantum chemical calculations - ring opening of 2a

Quantum chemical calculations were performed using the program package Gaussian 09[3], the DFT functionals B3LYP[4] and M062X[5] and the basis sets 6-31+G*[6] and 6-311++G**[7]. Stationary points were characterised by frequency analysis and energies were corrected by the zero-point vibrational energy. An attempt to optimise structure **7** led to the peroxide ring opened intermediate **8** (no imaginary frequencies). Counterpoise correction[8] of basis set superposition error (BSSE) was performed with structures **10**,[9] [**2a** + OH$^-$], **6**, [**8** + H_2O].

5.1. Energies



Scheme S1 Autocatalytic ring opening of **2a** (A) and ring-opening of **2a** by hydroxide (B).

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[3] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, GAUSSIAN 09 (Revision A.02) Gaussian Inc., Wallingford, CT, 2009.

[4] A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.

[5] Y. Zhao and D. G. Truhlar, *J. Phys. Chem.*, 2006, **110**, 5121–5129.

[6] R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724–728.

[7] A. D. McLean and G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639–5648.

[8] (a) S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553. (b) S. Simon, M. Duran and J. J. Dannenberg, *J. Chem. Phys.*, 1996, **105**, 11024–11031.

[9] The negative value might originate from an overestimation of the transition state **10** due to the BSSE, because this value is raised by 1 kcal·mol^{-1} by the single-point CP correction. More accurate values could be obtained by CP-optimization of the TS but failed due to convergence problems. We thank a reviewer for this helpful suggestion.

Table S3 Energies of calculated structures (path A).

Entry	Functional	E_{REL} (**2a** + **8**)	E_{REL} (**10**)[c)][d)]	E_{REL} (**4** + **8**)
1	a)	± 0 kcal/mol	–10.7 (–9.6) kcal/mol	**–72.8 kcal/mol**
2	b)	± 0 kcal/mol	–11.1 (–9.7) kcal/mol	**–77.2 kcal/mol**

a) B3LYP/6-31+G*//B3LYP/6-31+G*, b) M062X/6-311++G**//B3LYP/6-31+G*, c) Imaginary frequency –1074.5394 cm^{-1}, d) BSSE-CP corrected values in parentheses

Table S4 Energies of calculated structures (path B).[a)]

Entry	Functional	E_{REL} (**2a** + **OH^-**)	E_{REL} (**TS, 6**)[b)]	E_{REL} (**8** + H_2O)
1	a)	± 0 kcal/mol	–1.5 (–1.3) kcal/mol [c)]	–90.7 (–92.5) kcal/mol [c)]

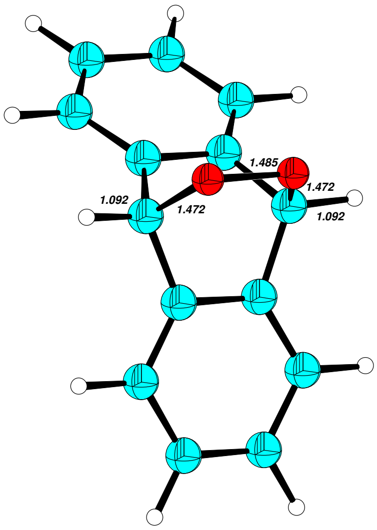
a) B3LYP/6-31+G*//B3LYP/6-31+G*, b) Imaginary frequency –296.5644 cm^{-1}, c) BSSE-CP-corrected energies in parentheses.

5.2. Geometries

5.2.1. EPO 2a

Imaginary frequencies: 0

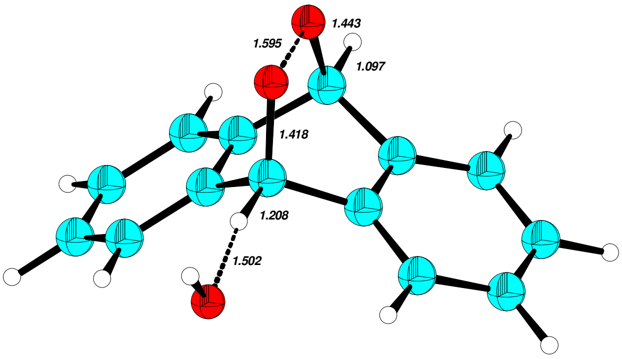
C	-3.386475	-0.699130	-1.042523
C	-3.386475	0.699132	-1.042522
C	-2.311638	1.411378	-0.488867
C	-1.238015	0.702355	0.039905
C	-1.238015	-0.702355	0.039905
C	-2.311639	-1.411378	-0.488868
C	0.000001	1.253681	0.707944
C	1.238022	0.702355	0.039917
C	1.238022	-0.702355	0.039915
C	0.000001	-1.253682	0.707942
C	2.311639	1.411379	-0.488868
C	3.386479	0.699132	-1.042516
C	3.386479	-0.699130	-1.042517
C	2.311639	-1.411378	-0.488870
O	-0.000010	0.742676	2.088590
O	-0.000009	-0.742679	2.088589
H	-4.226336	-1.239636	-1.471058
H	-4.226336	1.239638	-1.471056
H	-2.318478	2.498828	-0.477755
H	-2.318478	-2.498828	-0.477758
H	0.000000	2.338193	0.838981
H	0.000000	-2.338195	0.838977
H	2.318476	2.498829	-0.477759
H	4.226342	1.239638	-1.471048
H	4.226342	-1.239635	-1.471050
H	2.318476	-2.498828	-0.477763



5.2.2. Transition state 6-OH for base = OH$^-$

Imaginary frequencies: 1 (–296.5644 cm^{-1})

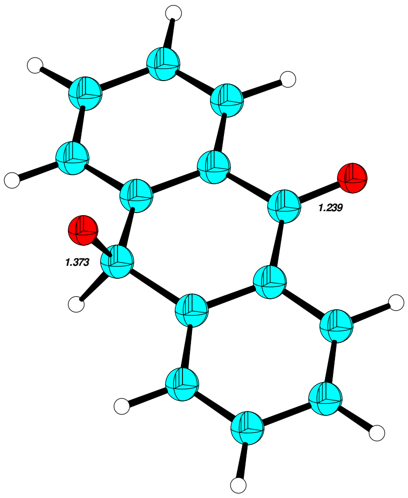
C	-3.363128	-1.057233	-1.025418
C	-3.340906	0.338101	-1.134400
C	-2.306221	-1.735966	-0.397347
C	-1.238277	-0.999935	0.107171
C	-1.226123	0.401673	0.010516
C	-2.270116	1.080388	-0.611512
C	0.000192	-1.521655	0.817465
C	1.238558	-0.999695	0.107164
C	1.226142	0.401915	0.010508
C	-0.000049	1.008527	0.664441
C	2.306640	-1.735531	-0.397342
C	3.363432	-1.056612	-1.025407
C	3.340959	0.338716	-1.134389
C	2.270026	1.080804	-0.611510
O	0.000152	-0.983935	2.156434
O	0.000010	0.605228	2.023756
H	-4.201050	-1.620779	-1.432667
H	-4.162471	0.851497	-1.631380
H	-2.321925	-2.822712	-0.313662
H	-2.219105	2.164983	-0.685116
H	0.000301	-2.611344	0.945018
H	2.322540	-2.822274	-0.313651
H	4.201458	-1.620008	-1.432648
H	4.162434	0.852263	-1.631360
H	2.218858	2.165388	-0.685132
H	-0.000301	2.213877	0.589198
O	-0.000968	3.600521	0.012776
H	-0.001077	4.213601	0.768034



5.2.3. *p*-Hydroxy anthrone anion 8

Imaginary frequencies: 0

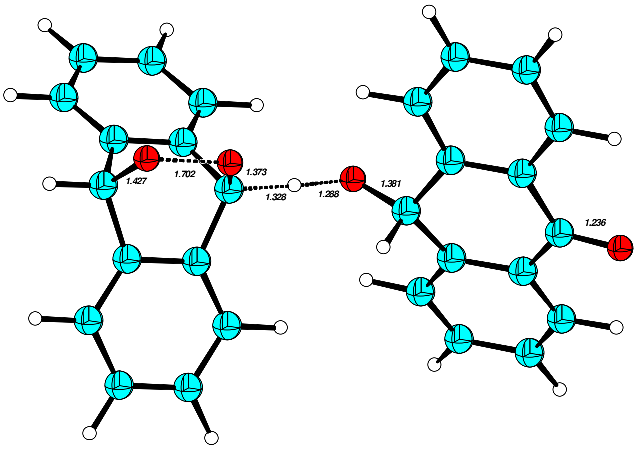
C	-3.693234	0.717199	-0.193119
C	-3.690990	-0.678935	-0.356867
C	-2.492228	-1.386569	-0.314261
C	-1.265695	-0.730780	-0.118411
C	-1.272749	0.670257	0.025470
C	-2.488499	1.383364	-0.003234
C	0.000000	-1.574813	0.040466
C	1.265695	-0.730780	-0.118411
C	1.272749	0.670257	0.025469
C	0.000000	1.423411	0.177814
C	2.492229	-1.386569	-0.314260
C	3.690991	-0.678934	-0.356866
C	3.693234	0.717199	-0.193120
C	2.488499	1.383364	-0.003235
O	-0.000001	-2.221031	1.252047
O	0.000000	2.644659	0.389304
H	-4.628340	1.271418	-0.221594
H	-4.628469	-1.207701	-0.516686
H	-2.493277	-2.469465	-0.419765
H	-2.461491	2.462927	0.113641
H	0.000000	-2.289409	-0.826605
H	2.493278	-2.469465	-0.419762
H	4.628470	-1.207701	-0.516683
H	4.628340	1.271419	-0.221595
H	2.461490	2.462927	0.113640



5.2.4. Transition state 10

Imaginary frequencies: 1 (–1074.5394 cm^{-1})

C	-2.713880	-0.707841	0.923906
C	-4.031527	-0.828015	0.450826
C	-4.147396	-0.476287	-1.027538
C	-3.572509	0.918800	-1.244546
C	-2.255011	1.037862	-0.764476
C	-1.758445	-0.280401	-0.184010
C	-5.050941	-1.254645	1.296161
C	-4.750160	-1.553561	2.634738
C	-3.439174	-1.430732	3.105545
C	-2.409282	-1.010786	2.248151
C	-4.203342	1.993730	-1.861967
C	-3.516388	3.211158	-1.993303
C	-2.209439	3.333309	-1.513774
C	-1.571421	2.242408	-0.901371
O	-3.369376	-1.407741	-1.777217
O	-1.786547	-1.227690	-1.176966
H	-5.178747	-0.563415	-1.397655
H	-0.524267	-0.273731	0.306109
H	-6.070933	-1.355044	0.925126
H	-5.540477	-1.883146	3.306863
H	-3.214434	-1.666002	4.144284
H	-1.383647	-0.921798	2.598473
H	-5.221005	1.892932	-2.238961
H	-4.002558	4.060206	-2.470168
H	-1.680030	4.278411	-1.618561
H	-0.551977	2.335669	-0.534562
C	3.695362	-3.647233	-1.140366
C	2.325455	-3.657205	-0.832840
C	1.688882	-2.494485	-0.404268
C	2.405302	-1.297021	-0.268513
C	3.780976	-1.289405	-0.572174
C	4.416775	-2.467003	-1.009761
C	1.649182	-0.023446	0.114532
C	2.586769	1.069823	0.621585
C	3.960399	1.083462	0.311720
C	4.597998	-0.059643	-0.398093
C	2.054420	2.127561	1.372896
C	2.861118	3.186738	1.783967
C	4.224957	3.210584	1.452229
C	4.769089	2.159044	0.724042
O	5.773085	-0.004439	-0.776117
O	0.582899	-0.241341	0.964098
H	4.188905	-4.556872	-1.476198
H	1.752852	-4.577159	-0.932292
H	0.629178	-2.493650	-0.169939
H	5.478810	-2.424924	-1.233551
H	1.279492	0.365942	-0.868038
H	1.003274	2.080615	1.639880
H	2.430852	3.996934	2.369922
H	4.853605	4.038707	1.772764
H	5.823994	2.135384	0.466326



5.2.5. *p*-Hydroxy anthrone 4

Imaginary frequencies: 0

C	3.687036	0.726608	-0.237083
C	3.686895	-0.664932	-0.397515
C	2.487270	-1.375020	-0.344406
C	1.274452	-0.708838	-0.137595
C	1.275846	0.687517	0.021921
C	2.486264	1.397706	-0.027980
C	0.002407	-1.514762	-0.010061
C	-1.268904	-0.702886	-0.145409
C	-1.271992	0.690424	0.039340
C	0.005482	1.442600	0.215724
C	-2.481942	-1.360510	-0.387846
C	-3.683593	-0.650716	-0.423344
C	-3.684215	0.734274	-0.218616
C	-2.481962	1.400196	0.005326
O	0.004887	2.645240	0.466559
O	0.067152	-2.145758	1.291491
H	4.620978	1.280841	-0.278532
H	4.621633	-1.194534	-0.563126
H	2.488968	-2.456732	-0.453457
H	2.456533	2.475771	0.096057
H	0.000975	-2.304512	-0.777049
H	-2.486107	-2.436026	-0.560181
H	-4.616092	-1.174337	-0.617945
H	-4.617928	1.289563	-0.246361
H	-2.451417	2.475935	0.148729
H	-0.792112	-2.561782	1.472720