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Supporting Information

Supporting Online Information for

N-bridged diiron phthalocyanine catalyzes oxidation of benzene by H_2O_2 via benzene oxide with NIH shift evidenced using benzene-1,3,5-d_3 as a probe.

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Materials and Methods

Supplementary Figs.S1 to S11

References

Materials

Solvents and chemicals were obtained from Sigma-Aldrich and used without purification unless indicated. ***Synthesis of μ-nitrido-bis[tetra(tert-butyl)phthalocyaninatoiron] $(FePc^tBu_4)_2N$.*** Tetra-*tert*-butylphthalocyaninatoiron(II) was synthesised and purified as described previously [S1]. 0.4 g of $FePc^tBu_4$ and 2 g of NaN_3 were suspended in 70 ml of oxygen-free xylene under argon. The mixture was heated for 6 h at 150°C under intensive stirring. The reaction mixture was cooled and resulting dark blue solution was separated from undissolved material by filtration. The solution was chromatographed on Al_2O_3 (neutral) with CH_2Cl_2 to remove impurities. Then $(FePc^tBu_4)_2N$ complex was collected using CH_2Cl_2:EtOH (100:1) mixture as eluent. Evaporation of solvent afforded pure $(FePc^tBu_4)_2N$ as a dark blue powder (yield 0.25 g, 62 %). ESI-MS: 1599.9 [M]+ (100 %); calcd for $C_{96}H_{96}N_{17}Fe_2$: 1599.6. UV-Vis λ_{max} (log ε) (MeCN) : 219 (5.67); 272 (5.50); 340 (5.39); 637 (5.57). ^1H NMR (250 MHz, $CDCl_3$): 7.78 (s, 1H); 7.66 (s, 2H); 1.32 (s, 9 H). IR (KBr) 938 (ν_{as} Fe=N). ESR: Solid state or solution in acetone: singlet signal at g = 1.99.

Equipment and Methods

Liquid-state nuclear magnetic resonance spectra were obtained using a AM 250 Bruker spectrometer. The UV-vis spectra of solutions were recorded on a Perkin-Elmer Lambda 35 spectrophotometer. The reaction products were identified by GC-MS method (Hewlett Packard 5973/6890 system ; electron impact ionization at 70 eV, He carrier gas, 30m x 0.25 mm x 0.25 μm DB-5MS capillary column). The yield of phenol and conversion of benzene was determined by GC using methyl benzoate as the external standard (Agilent 4890D system; N_2 carrier gas, VF5-MS capillary column, 100 % dimethylpolysiloxane, 30 m x 0.25 mm, 0.25 μm coating). The labelling experiments were performed using 1:1 mixture of C_6H_6 and C_6D_6 controlling the exact ratio of this mixture by GS-MS. Isotopic composition of products was determined by GC-MS using m/z intensities of isotopomers. Each sample was analyzed three times and m/z intensiies were obtained by an integration of all scans of the peak [S2].

Determination of kinetic isotope effects on phenol formation.

Mass spectrum of phenol shows a very strong molecular peak without (M-1) and (M-2) fragmentation. Intermolecular KIE in oxidation of C_6H_6/C_6D_6 were determined from the intensities of molecular peaks of C_6H_5OH and C_6D_5OH.

Experimentally observed intensities of (M+1) signal due to ^{13}C natural content were in accordance with theoretical intensity: 1.08 % x 6 = 6.48 % with respect to M^+ signal. Therefore, intra- molecular KIE in oxidation of benzene-1,3,5-d_3 was calculated according to the following formalism:

Amount of phenol-d_2 = I_{96}

Amount of phenol-d_3 = $I_{97} – I_{96}$ x 0.0648

where I_{96} and I_{97} are intensities of signals at m/z 96 and 97, respectively.

Intra-molecular KIE = $I_{97} – I_{96}$ x 0.0648 / I_{96}

Determination of isotopic composition of 1,4-benzoquinone

Taking into account a clean molecular peak of benzoquinone (Supplementary Fig. 8A) without (M-1) and (M-2) fragmentations, isotopic composition of benzoquinone can be calculated after correction on ^{13}C natural abundance as follows.

Amount of benzoquinone-d_1 = I_{109}

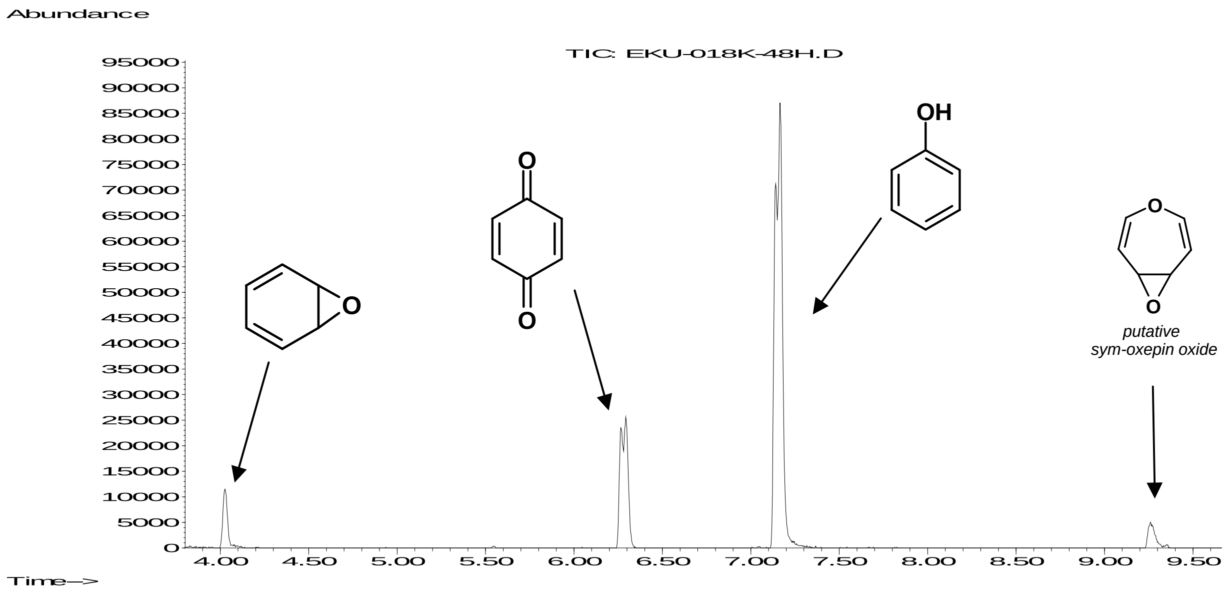
Amount of benzoquinone-d_2 = $I_{110} – I_{109}$ x 0.0648

Amount of benzoquinone-d_3 = I_{111} – ($I_{110} – I_{109}$ x 0.0648) x 0.0648

References

S1. J. Metz, O. Schneider, M. Hanack, *Inorg. Chem.* 1984, **23**, 1065.

S2. A. B. Sorokin, A. Robert, B. Meunier, *J. Am. Chem. Soc.* **1993**, *115*, 7293.



Supplementary Figure 1. Chromatogram of GC-MS analysis of the oxidation of 1:1 mixture of C_6H_6 and C_6D_6 at 25°C after 48 h. Reaction mixture: 0.5 mL MeCN, 0.5 mL C_6H_6/C_6D_6=1:1 mixture, $[(FePc^tBu_4)_2N] = 2.4 \times 10^{-4}$ M, 14 µL of H_2O_2 (35 %). Isotopomers do not have the same retention time on GC column [S2]. This phenomenon is well seen in the case of 1,4-benzoquinone and phenol. The deuterated compounds are eluted first.

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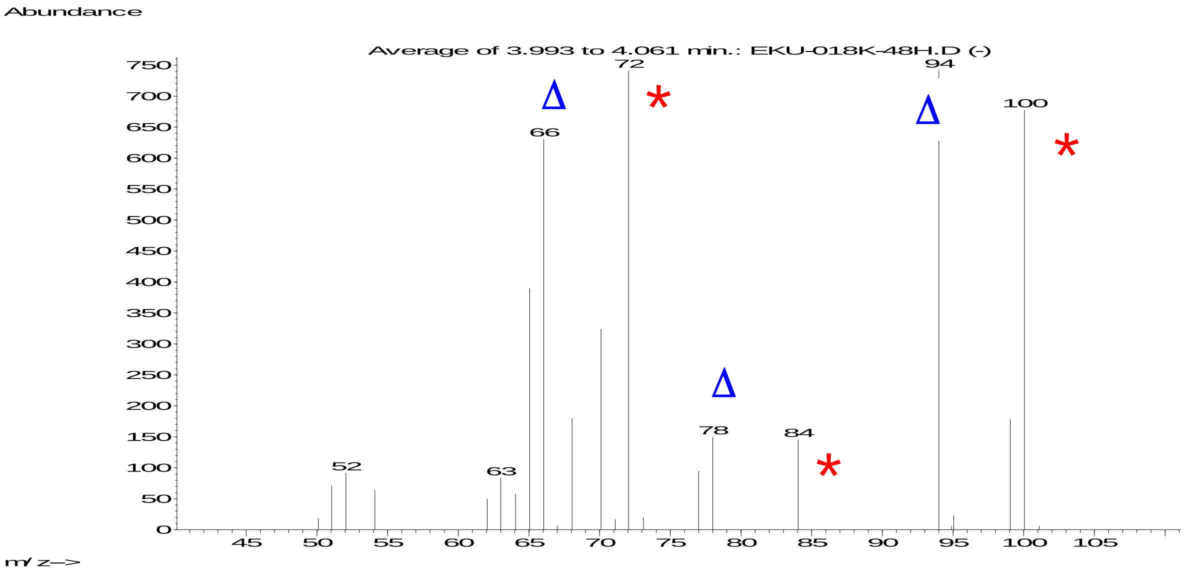
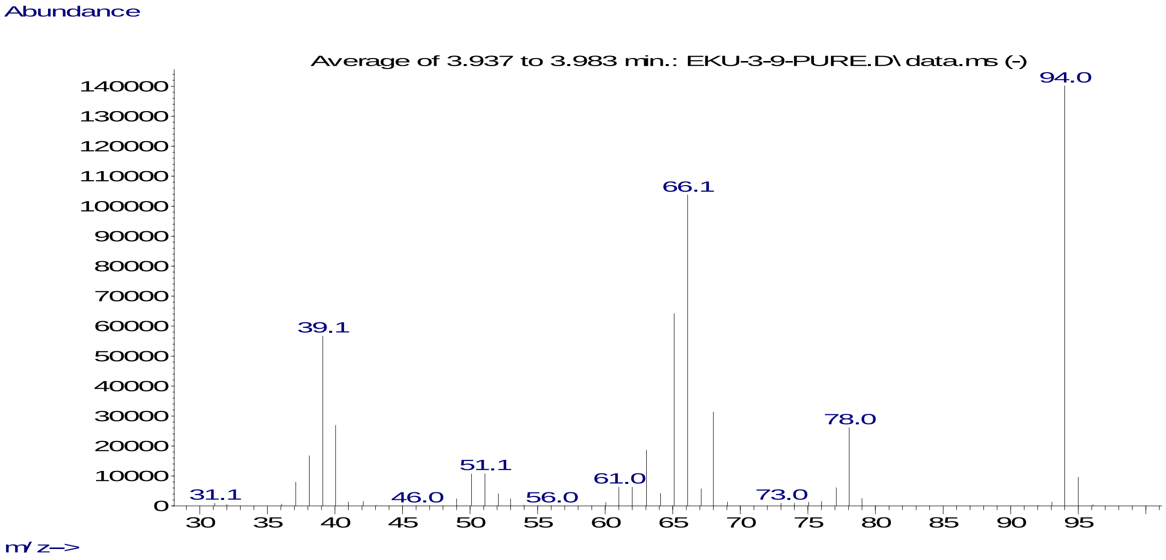
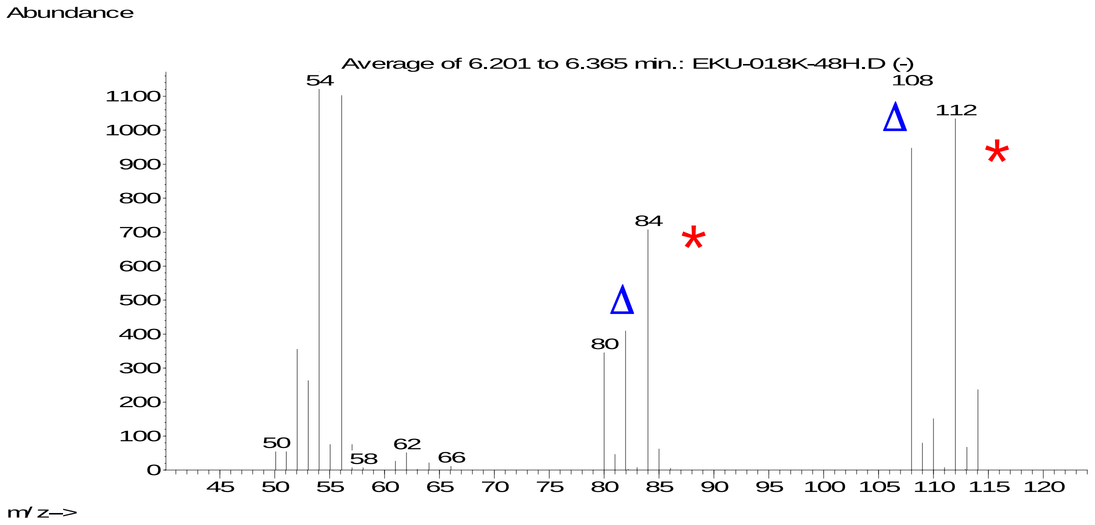


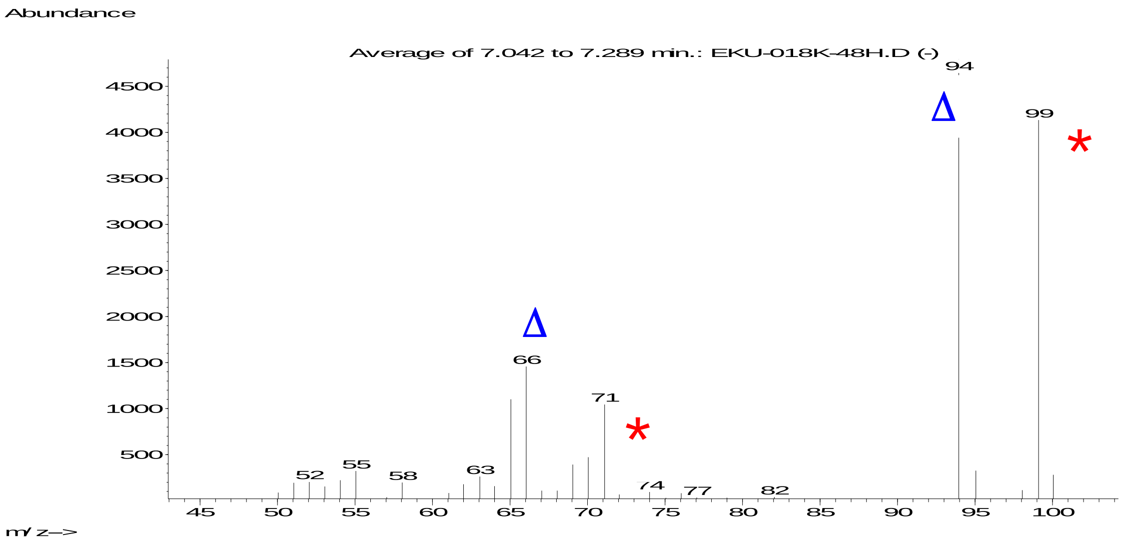
Supplementary Figure 2. Mass spectra of benzene oxides obtained from C_6H_6 (Δ, 94 $[M]^+$, 78 $[M\text{-}O]^+$, 66 $[M\text{-}CO]^+$) and C_6D_6 (*, 100 $[M]^+$, 84 $[M\text{-}O]^+$, 72 $[M\text{-}CO]^+$)



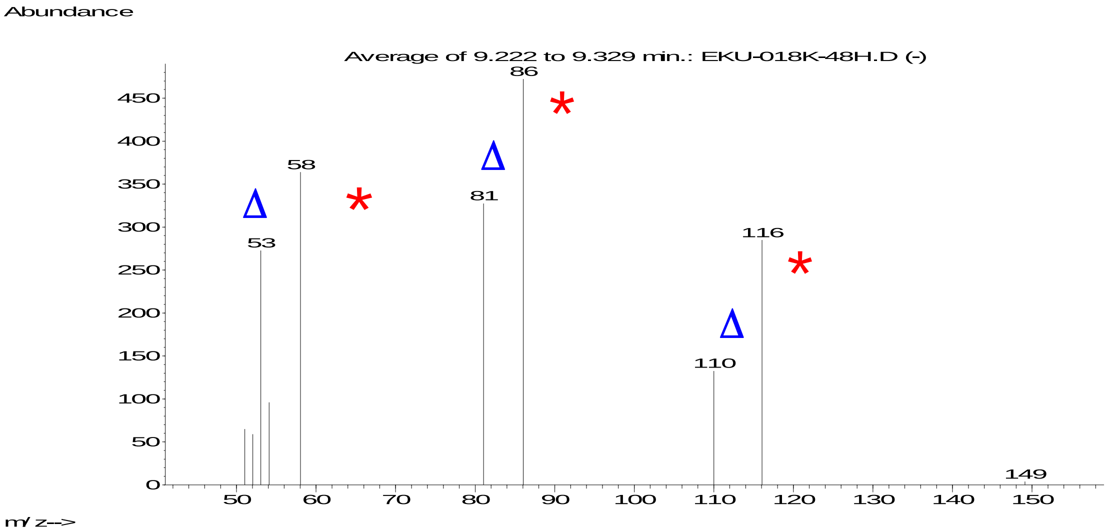
Supplementary Figure 3. Mass spectrum of the authentic benzene oxide prepared according to ref. 14 of the manuscript.



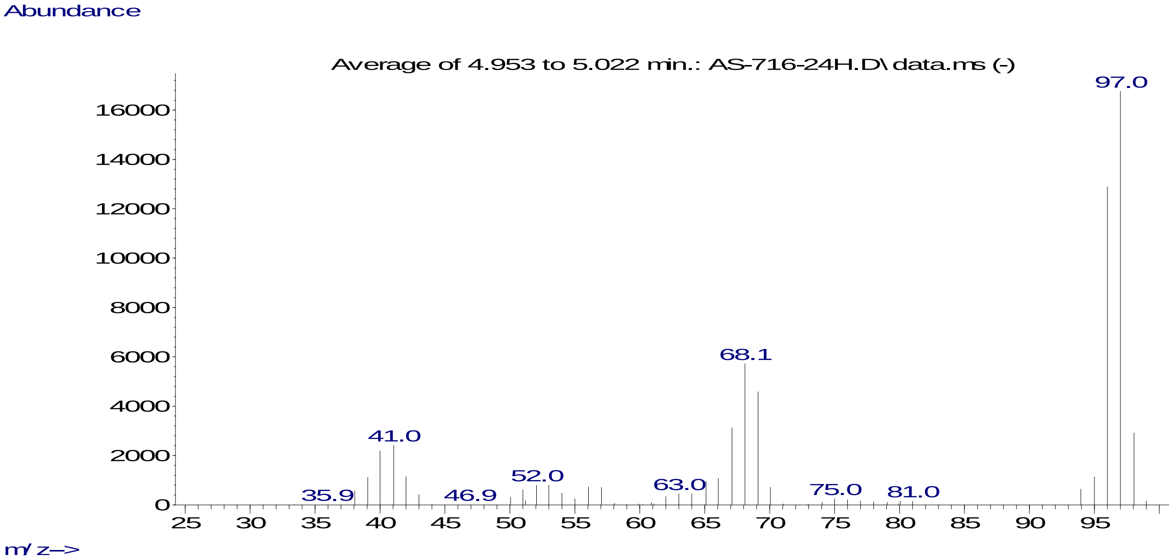
Supplementary Figure 4. Mass spectra of 1,4-benzoquinones obtained from C_6H_6 (Δ , 108 $[M]^+$, 80 $[M\text{-}CO]^+$) and C_6D_6 (* , 112 $[M]^+$, 84 $[M\text{-}CO]^+$)



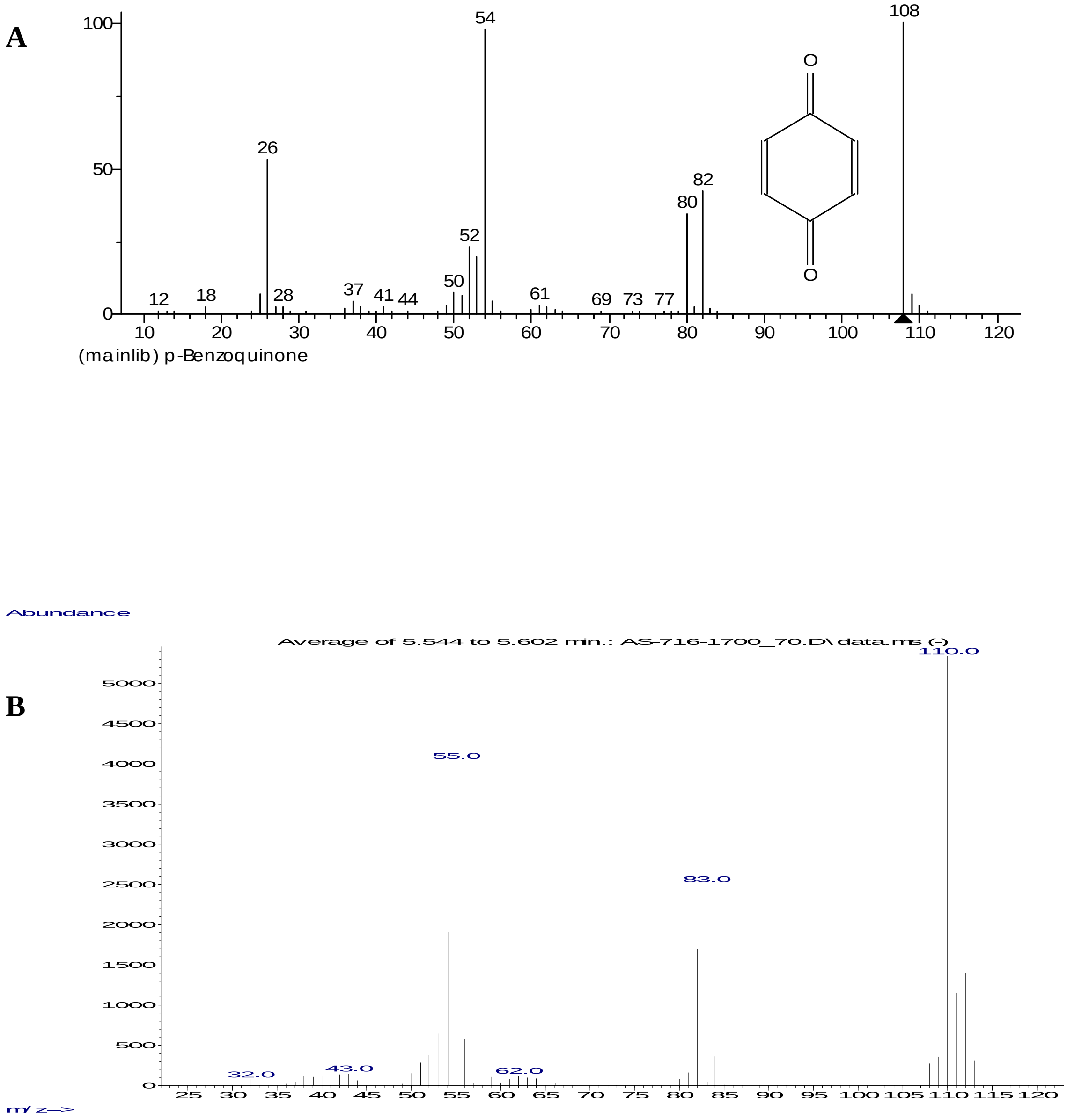
Supplementary Figure 5. Mass spectra of phenols obtained from C_6H_6 (Δ , 94 $[M]^+$, 66 $[M\text{-}CO]^+$) and C_6D_6 (* , 99 $[M]^+$, 71 $[M\text{-}CO]^+$). Inter-molecular KIE were determined from the intensities of m/z 94 and 99.



Supplementary Figure 6. Mass spectra of putative oxepin oxides obtained from C_6H_6 (Δ , 110 $[M]^+$, 81 $[M\text{-}CHO]^+$, 53 $[M\text{-}CHO\text{-}CO]^+$) and C_6D_6 (* , 116 $[M]^+$, 86 $[M\text{-}CDO]^+$, 58 $[M\text{-}CDO\text{-}CO]^+$). Molecular peaks of isotopomers of this product differ in m/z=6 indicating the presence of all H (D) atoms that is compatible with proposed oxepin oxide structure. Mass spectrum of sym-oxepin oxide published in ref. 15a of the manuscript : 110 $[M]^+$, base peak 81 $[M\text{-}CHO]^+$.

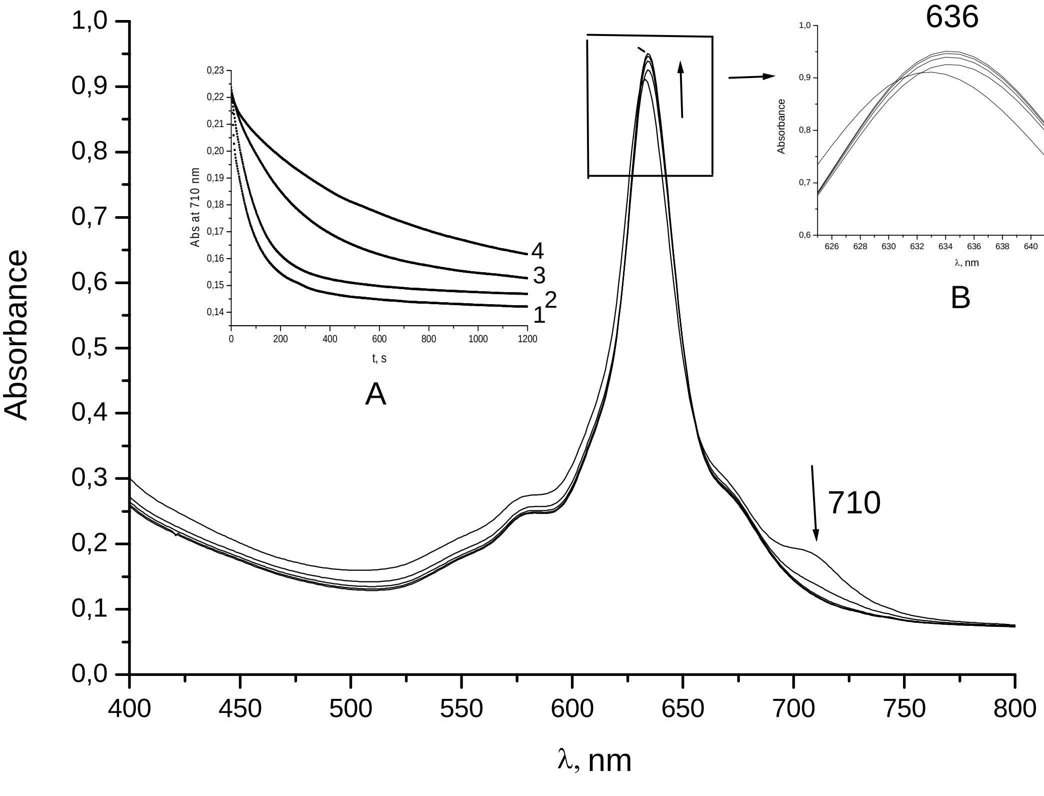


Supplementary Figure 7. Mass spectrum of phenol obtained in course of oxidation of benzene-1,3,5-d_3 used for determination of intra-molecular KIE.

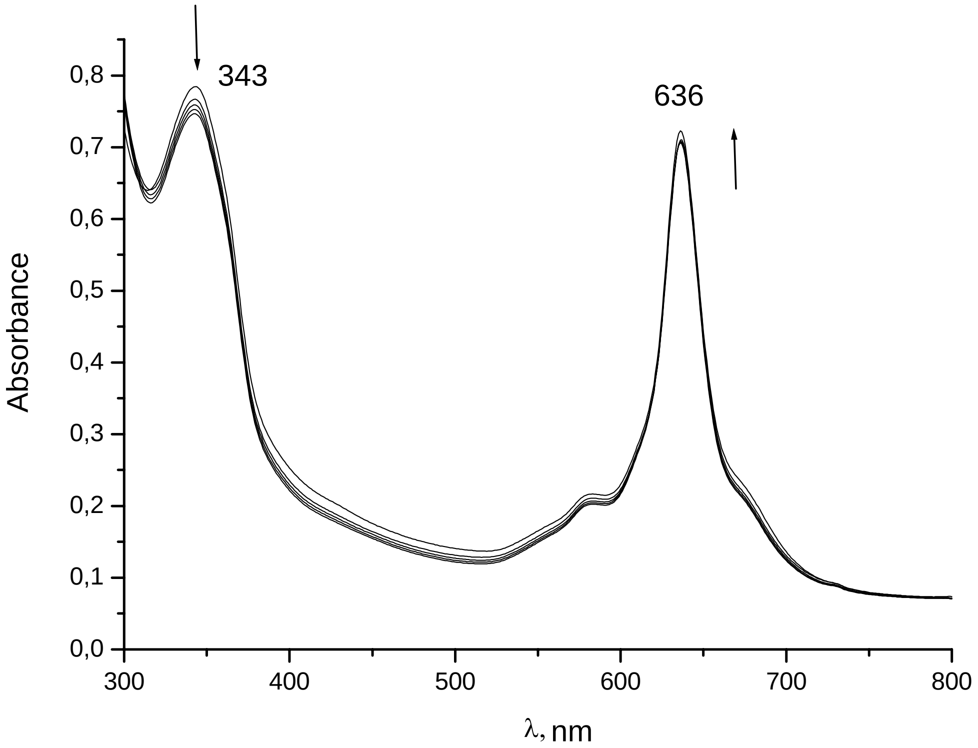


Supplementary Figure 8. Mass spectrum of benzoquinone (**A**) and benzoquinone obtained in course of oxidation of benzene-1,3,5-d_3 (**B**) used for determination of its isotopic composition to detect the NIH shift. Under conditions of GC-MS analysis (electron impact ionization at 70 eV) BQ could be partially reduced to corresponding hydroquinone. Relative intensity of hydroquinone signal increased along with the decreasing amount of sample injected. The analysis of benzoquinone isotopic composition was precise and reproducible when 0.5 -1 µl of the reaction mixture was analyzed with low split ratio.

Interaction of $(\mathrm{FePc^tBu_4})_2\mathrm{N}$ with hydrogen peroxide. Hydrogen peroxide (1000 fold excess) was added to the solution of $(\mathrm{FePc^tBu_4})_2\mathrm{N}$ in acetone or in MeCN in closed thermostated cuvette. The reaction was followed by UV-vis at λ=636 nm (Supplementary Fig. 9a and 9b). The changes of UV-vis spectra upon H_2O_2 addition were more pronounced in acetone. The intensity of Q band at 636 nm ($\pi - \pi^*$ phthalocyanine transition) was slightly increased and weak band at 710 nm disappeared. These changes indicate a metal-centered reaction with H_2O_2 without significant transformation of phthalocyanine macrocycle and monomerization. Monomeric phthalocyanine forms exhibit Q band in 665 – 680 nm region. The rate of the spectral changes correlates with H_2O_2 concentration (Inlet A). These observations indicate the interaction of H_2O_2 with diiron N-bridged phthalocyanine.

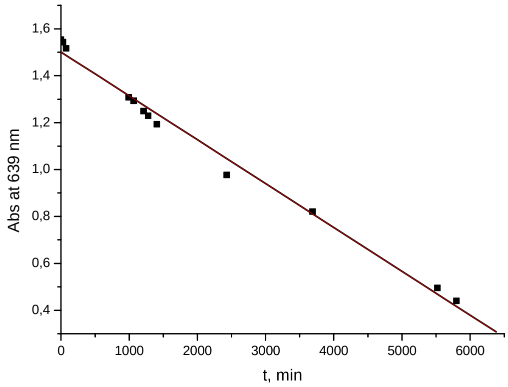


Supplementary Figure 9a. UV-Vis spectral changes during the reaction of $(\mathrm{FePc^tBu_4})_2\mathrm{N}$ with 1000 equivs of H_2O_2. Conditions: a) acetone, 25°C, $[(\mathrm{FePc^tBu_4})_2\mathrm{N}] = 1.12 \times 10^{-5}$ M. Inlet A : kinetic curves of interaction of $[(\mathrm{FePc^tBu_4})_2\mathrm{N}$ with H_2O_2; $[H_2O_2] = 3.4 \times 10^{-3}$ M (curve 1), 2.26×10^{-3}(curve 2), 5.65×10^{-4} (curve 3), $2.82\mathrm{x}10^{-4}$ (curve 4).



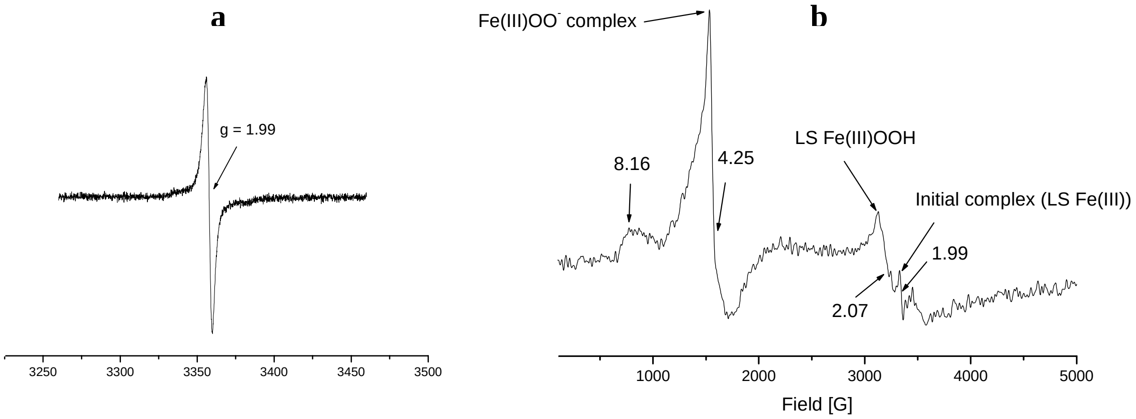
Supplementary Figure 9b. UV-Vis spectral changes during the reaction of $(FePc^tBu_4)_2N$ with 1000 equivs of H_2O_2. Conditions: MeCN, 25°C, $[(FePc^tBu_4)_2N] = 0.98 \times 10^{-5}$ M.

The life half-time ($\tau_{1/2}$) of μ-nitrido iron complex in the presence of H_2O_2 was determined from the decrease at λ=639 nm as indicated at Supplementary Fig. 10, where Abs = $A_t - A_\infty$. $\tau_{1/2}$ = 3470 min at 25°C, $\tau_{1/2}$ = 560 min at 60°C (not shown).



Supplementary Figure 10.

Degradation of μ-nitrido iron complex in the presence of 1000 equivs of H_2O_2 at 25°C.



Supplementary Figure 11. EPR spectra of $(FePc^tBu_4)_2N$ in acetone before (a) and after addition of 5 equivs of H_2O_2 (b). Conditions : capillary tube, 25°C, microwave frequency 9.392 GHz, power 40 mW, modulation 1.0 mT/100 kHz.