

Supporting information for

A Peroxynitrite Dicopper Complex: Formation via Cu-NO and Cu-O₂ Intermediates and Reactivity via O-O Cleavage Chemistry

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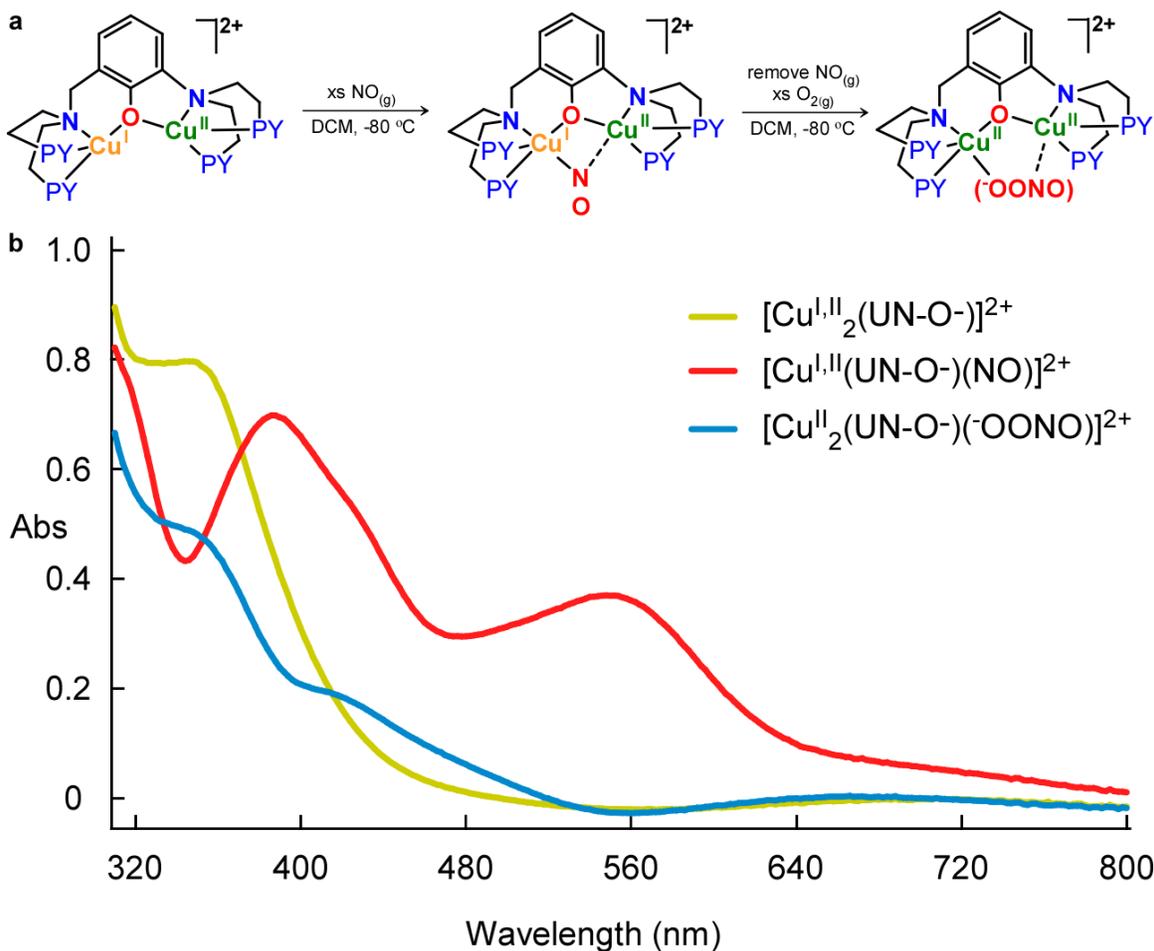


Figure S1. (a) $[\text{Cu}^{\text{I,II}}_2(\text{UN-O}^-)(\text{DMF})]^{2+}$ (**1**) reacts with excess $\text{NO}_{(\text{g})}$ to form nitrosyl complex $[\text{Cu}^{\text{I,II}}_2(\text{UN-O}^-)(\mu\text{-NO})]^{2+}$ (**2**) at $-80\text{ }^\circ\text{C}$ in dichloromethane (DCM) solvent with $\lambda_{\text{max}} = 383\text{ nm}$ ($3500\text{ M}^{-1}\text{cm}^{-1}$) and 546 nm ($1900\text{ M}^{-1}\text{cm}^{-1}$). After removing excess $\text{NO}_{(\text{g})}$ and adding excess $\text{O}_{2(\text{g})}$, peroxynitrite complex $[\text{Cu}^{\text{II}}_2(\text{UN-O}^-)(\text{-OONO})]^{2+}$ (**4**) was formed over the course of 10 minutes at $-80\text{ }^\circ\text{C}$. (b) UV-Vis spectrum change starting from $[\text{Cu}^{\text{I,II}}_2(\text{UN-O}^-)(\text{DMF})]^{2+}$ (**1**), yellow spectrum, upon addition of $\text{NO}_{(\text{g})}$ to form the nitrosyl complex $[\text{Cu}^{\text{I,II}}(\text{UN-O}^-)(\text{NO})]^{2+}$ (**2**), red spectrum. After removing excess $\text{NO}_{(\text{g})}$ and adding excess $\text{O}_{2(\text{g})}$, peroxynitrite complex $[\text{Cu}^{\text{II}}_2(\text{UN-O}^-)(\text{-OONO})]^{2+}$ (**4**) is shown in blue spectrum with $\lambda_{\text{max}} = 355$ (sh, $2500\text{ M}^{-1}\text{cm}^{-1}$), 420 (sh, $1000\text{ M}^{-1}\text{cm}^{-1}$) and 680 nm ($450\text{ M}^{-1}\text{cm}^{-1}$).

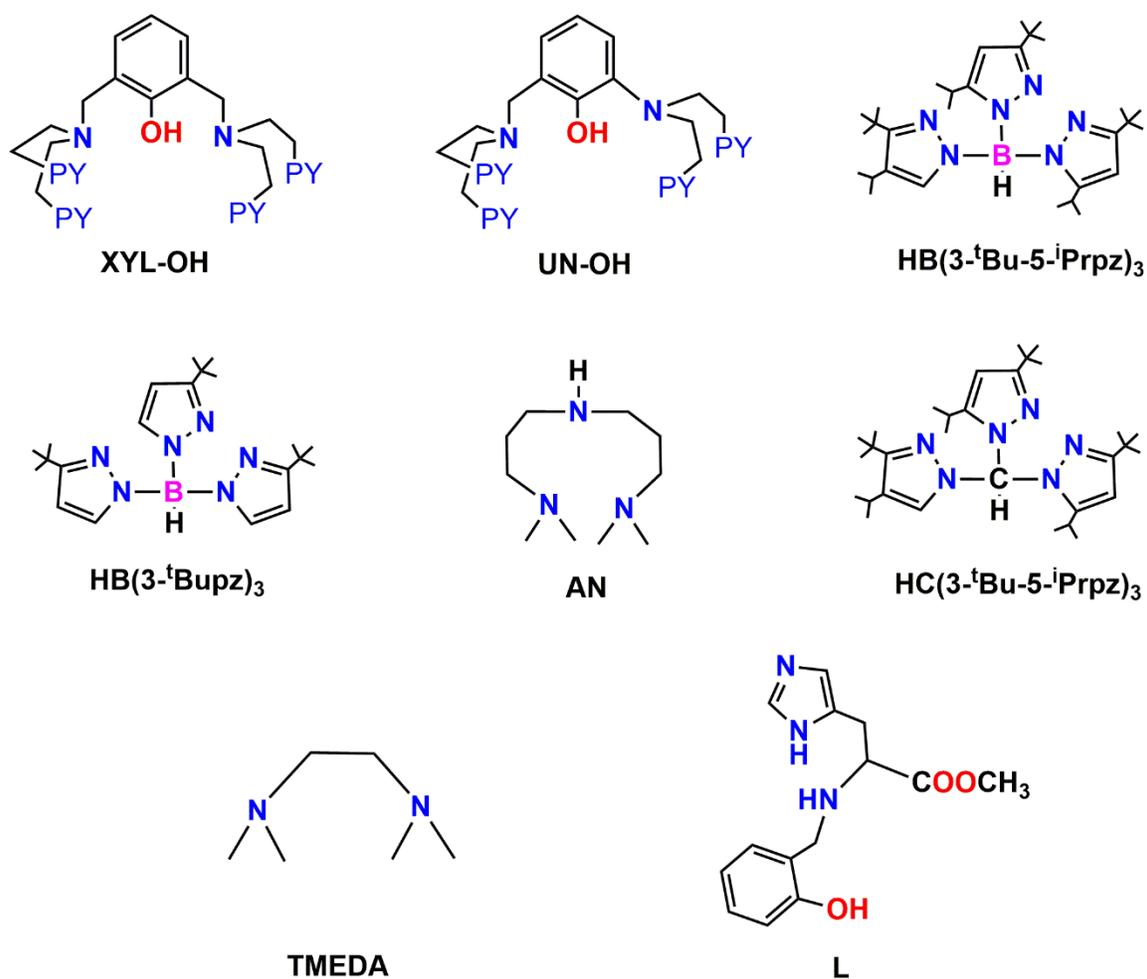


Figure S2. Drawings of the ligands and IUPAC names listed in main text, Table 1. XYL-OH = 2,6-bis((bis(2-(pyridin-2-yl)ethyl)amino)methyl)phenol; UN-OH = 2-(bis(2-(pyridin-2-yl)ethyl)amino)-6-((bis(2-(pyridin-2-yl)ethyl)amino)methyl)phenol; HB(3-^tBu-5-ⁱPrpz)₃ = hydrotris(3-tert-butyl-5-isopropyl-1-pyrazolyl)borate; HB(^tBupz)₃ = hydrotris(3-tert-butyl-1-pyrazolyl)borate; AN = N1-(3-(dimethylamino)propyl)-N3,N3-dimethylpropane-1,3-diamine; HC(3-^tBu-5-ⁱPrpz)₃ = tris(3-tert-butyl-5-isopropyl-1-pyrazolyl)methane; TMEDA = N,N,N',N'-tetramethylethylenediamine; L = methyl(2-hydroxybenzyl)histidinate.

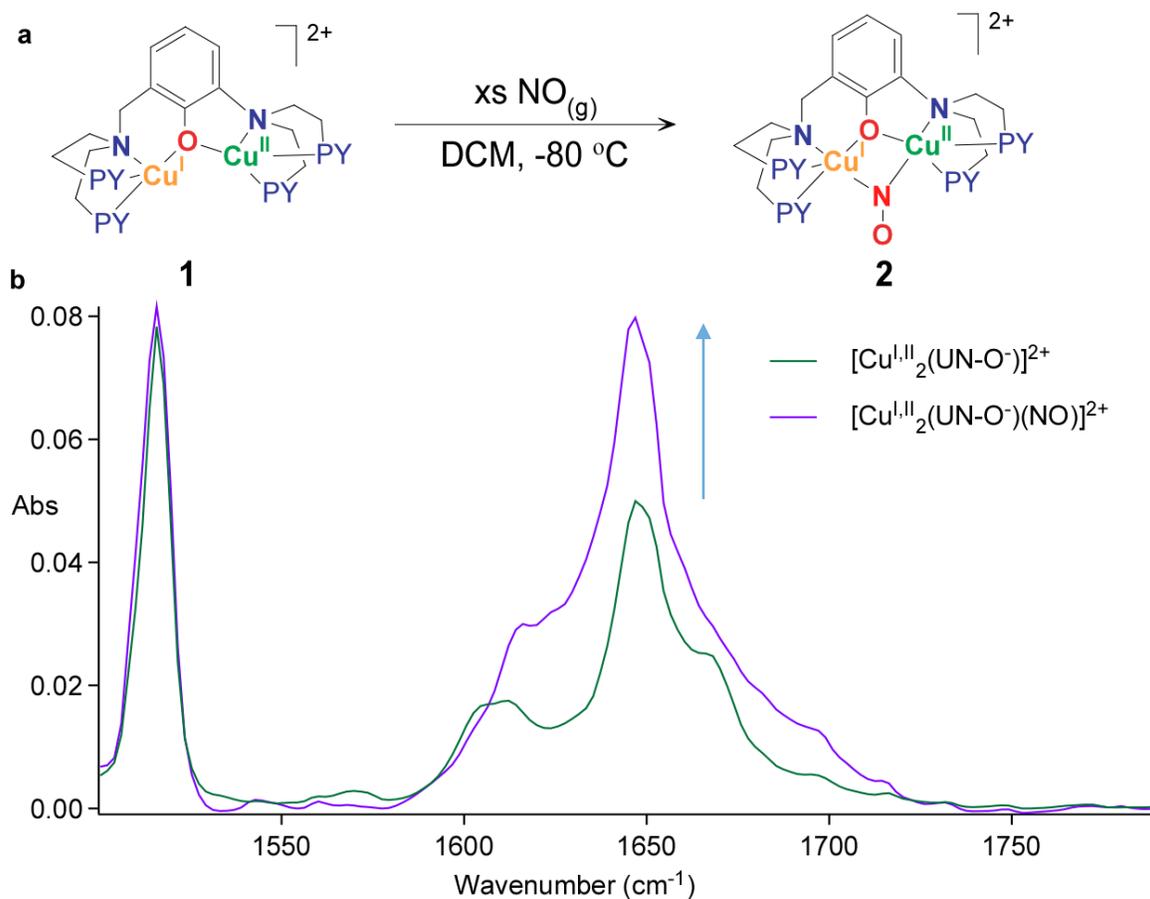


Figure S3. (a) $[\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(\text{UN-O}^-)]^{2+}$ (**1**) reacts with excess labeled $^{15}\text{NO}_{(\text{g})}$ to form $[\text{Cu}^{\text{I,II}}(\text{UN-O}^-)(\text{NO})]^{2+}$ (**2**) complex at $-80\text{ }^\circ\text{C}$ in dichloromethane (DCM) solvent. (b) Low-temperature ($-80\text{ }^\circ\text{C}$) infrared spectroscopy of the complex **1** (green colored spectrum) reacts with $^{15}\text{NO}_{(\text{g})}$ to form complex **2** (purple colored spectrum), $\nu(^{15}\text{N-O}) = 1645\text{ cm}^{-1}$, which is down-shifted from the $\nu(\text{N-O})$ at 1670 cm^{-1} (Figure 1 in the main text). Note the band from complex **2** $\nu(^{15}\text{N-O})$ at 1645 cm^{-1} overlaps with the band in the starting mixed-valent complex **1** which has the absorption band at 1650 cm^{-1} .

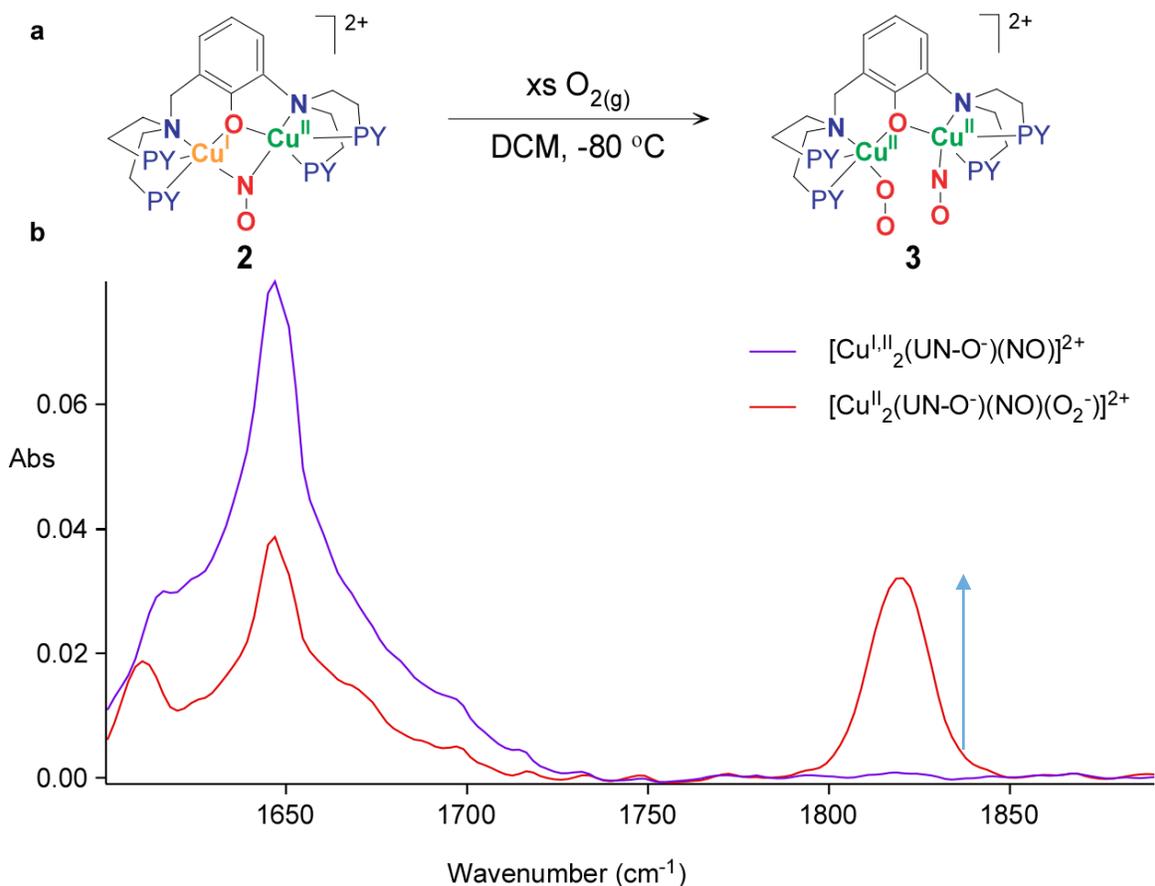


Figure S4. (a) ¹⁵NO labeled complex [Cu^{I,II}₂(UN-O⁻)(¹⁵NO)]²⁺ (**2**) (excess ¹⁵NO_(g) removed) reacts with excess O_{2(g)} to form [Cu^{II}₂(UN-O⁻)(¹⁵NO)(O₂⁻)]²⁺ (**3**) complex at -80 °C. (b) Low-temperature infrared spectroscopy of the complex **2** (spectrum in purple color) with $\nu(^{15}\text{N-O})$ at 1645 cm⁻¹ reacts with O_{2(g)} to form complex **3** (spectrum in red color) at -80 °C with $\nu(^{15}\text{N-O})$ at 1820 cm⁻¹.

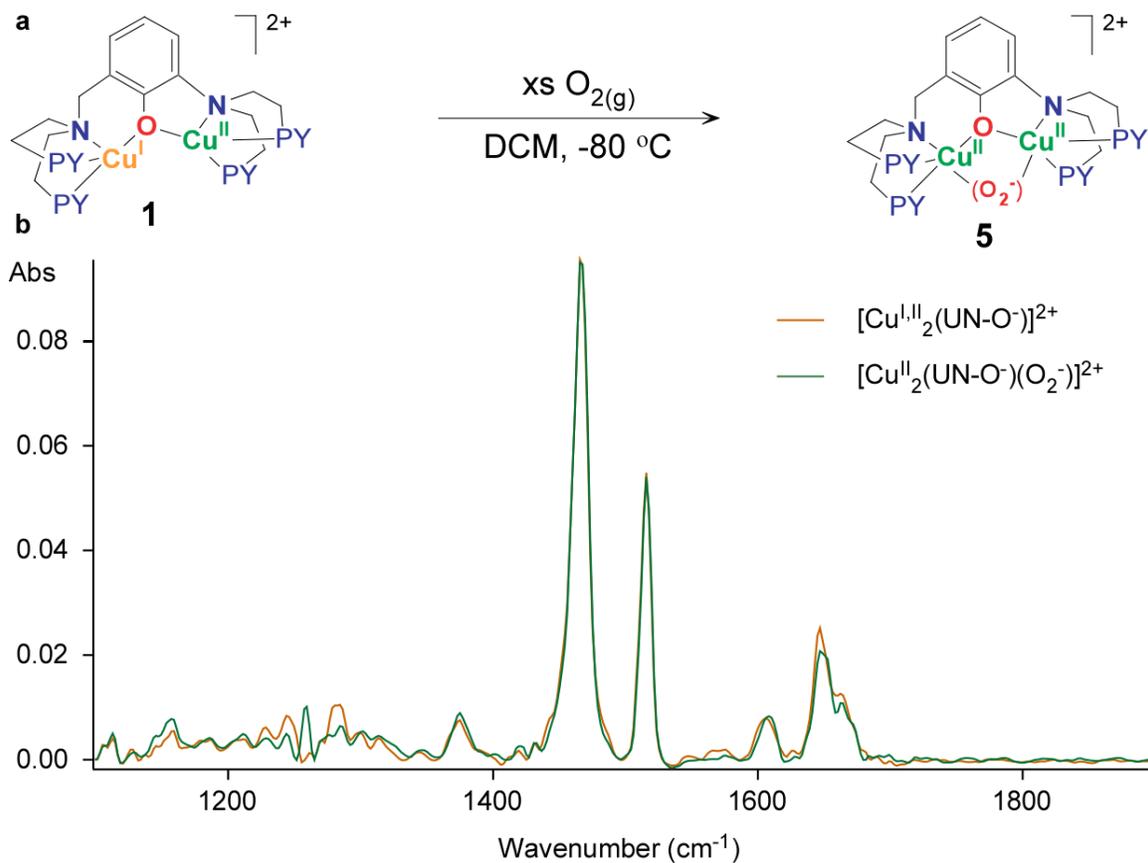


Figure S5. (a) [Cu^ICu^{II}(UN-O)]²⁺ (**1**) reacts with excess O_{2(g)} to form superoxide dicopper(II) complex [Cu^{II}₂(UN-O)(O₂⁻)]²⁺ (**5**) at -80 °C in dichloromethane (DCM) solvent. (b) Low-temperature (-80 °C) infrared spectroscopy of the complex **1** in orange color spectrum reacts with O_{2(g)} to form complex **5** in green color spectrum.

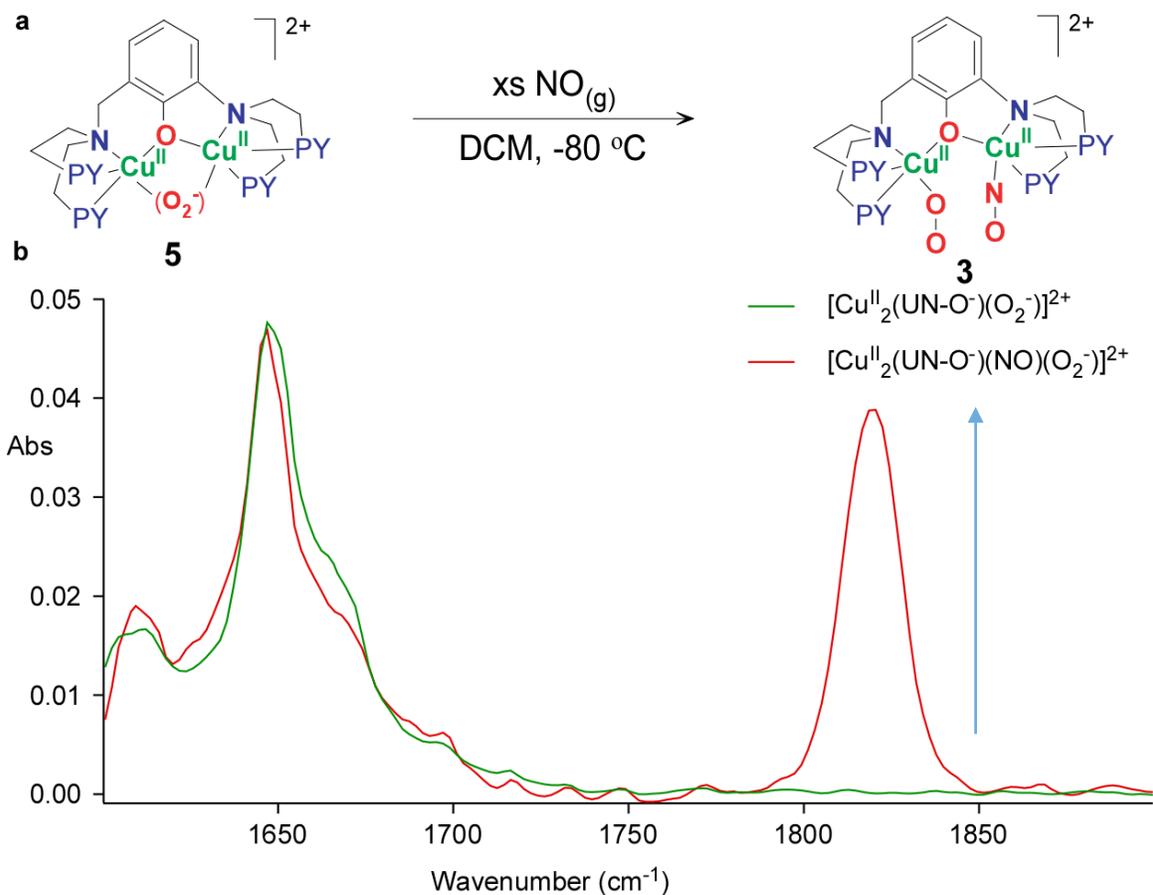


Figure S6. (a) $[\text{Cu}^{\text{II}}_2(\text{UN-O}^-)(\text{O}_2^-)]^{2+}$ (**5**) (excess $\text{O}_{2(\text{g})}$ removed) reacts with $^{15}\text{NO}_{(\text{g})}$ to form $[\text{Cu}^{\text{II}}_2(\text{UN-O}^-)(^{15}\text{NO})(\text{O}_2^-)]^{2+}$ (**3**) complex at $-80\text{ }^\circ\text{C}$ in DCM. $^{15}\text{NO}_{(\text{g})}$ was directly added into the solution of the superoxide complex $[\text{Cu}^{\text{II}}_2(\text{UN-O}^-)(\text{O}_2^-)]^{2+}$ (**5**) using a gas-tight syringe. (b) Low-temperature ($-80\text{ }^\circ\text{C}$) infrared spectroscopy for the formation of the superoxide and nitrosyl complex $[\text{Cu}^{\text{II}}_2(\text{UN-O}^-)(\cdot^{15}\text{NO})(\text{O}_2^-)]^{2+}$ (**3**) with $\nu(^{15}\text{N-O})$ at 1820 cm^{-1} (red colored spectrum) from the reaction of ^{15}NO and **5** (green colored spectrum).

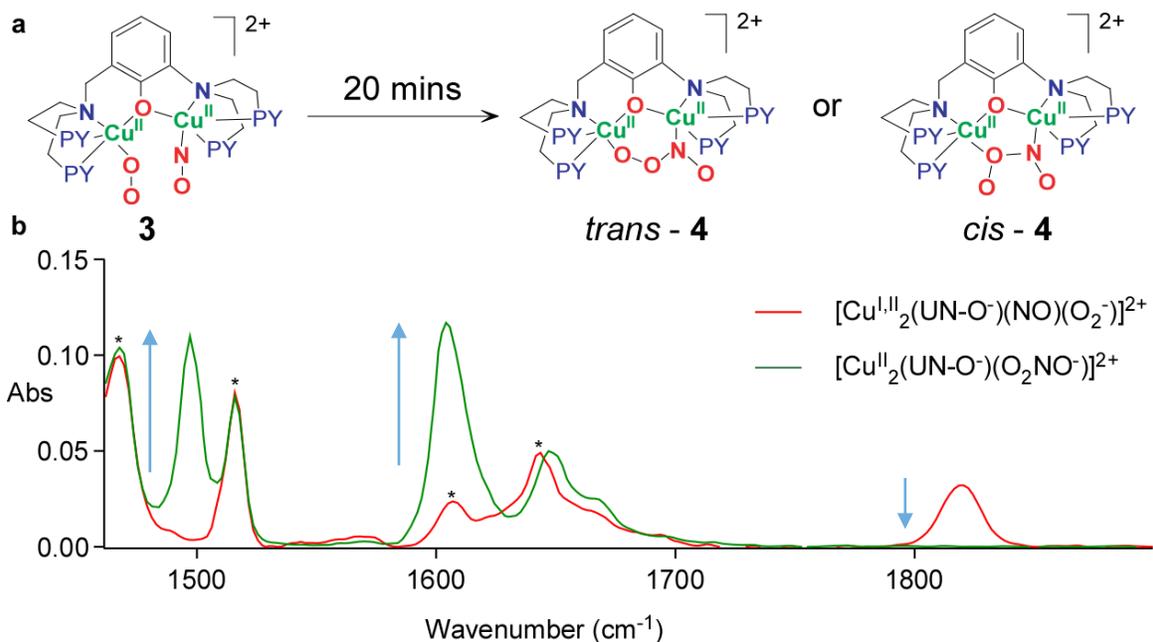


Figure S7. (a) The solution of $[\text{Cu}^{\text{II}}_2(\text{UN-O}^-)(^{15}\text{NO})(\text{O}_2^-)]^{2+}$ (**3**) gradually transforms to produce *trans*- and *cis*- isomers of $[\text{Cu}^{\text{II}}_2(\text{UN-O}^-)(\text{OO}^{15}\text{N=O})]^{2+}$ (**4**) at $-80\text{ }^\circ\text{C}$. (b) Low-temperature infrared spectroscopy of the complex **3** in red color spectrum gradually changes to complex **4** in green color spectrum over the course of 20 mins at $-80\text{ }^\circ\text{C}$ by the appearance of new IR bands for *cis*- $[\text{Cu}^{\text{II}}_2(\text{UN-O}^-)(\text{OO}^{15}\text{N=O})]^{2+}$ with $\nu(^{15}\text{N-O}) = 1500\text{ cm}^{-1}$ and *trans*- $[\text{Cu}^{\text{II}}_2(\text{UN-O}^-)(\text{OO}^{15}\text{N=O})]^{2+}$ with $\nu(^{15}\text{N-O}) = 1614\text{ cm}^{-1}$. These bands are shifted from 1520 cm^{-1} and 1640 cm^{-1} in the samples prepared with unlabeled NO (see Figure 3 of the main text). The bands marked in asterisks do not change over time.

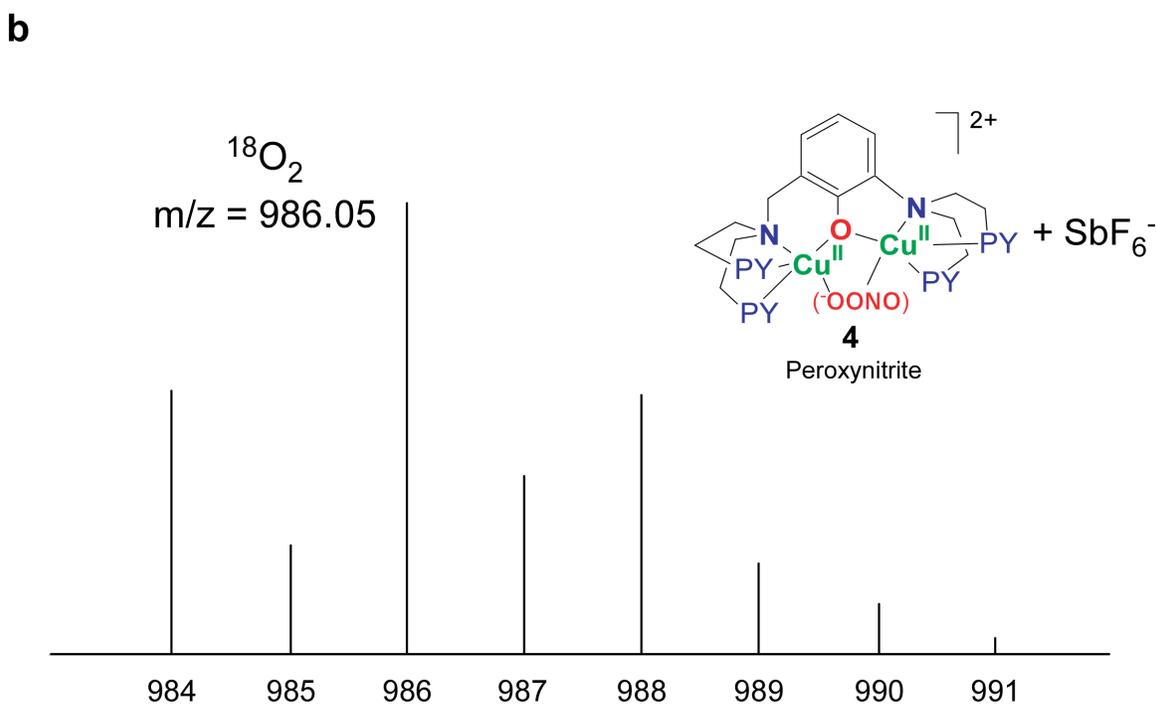
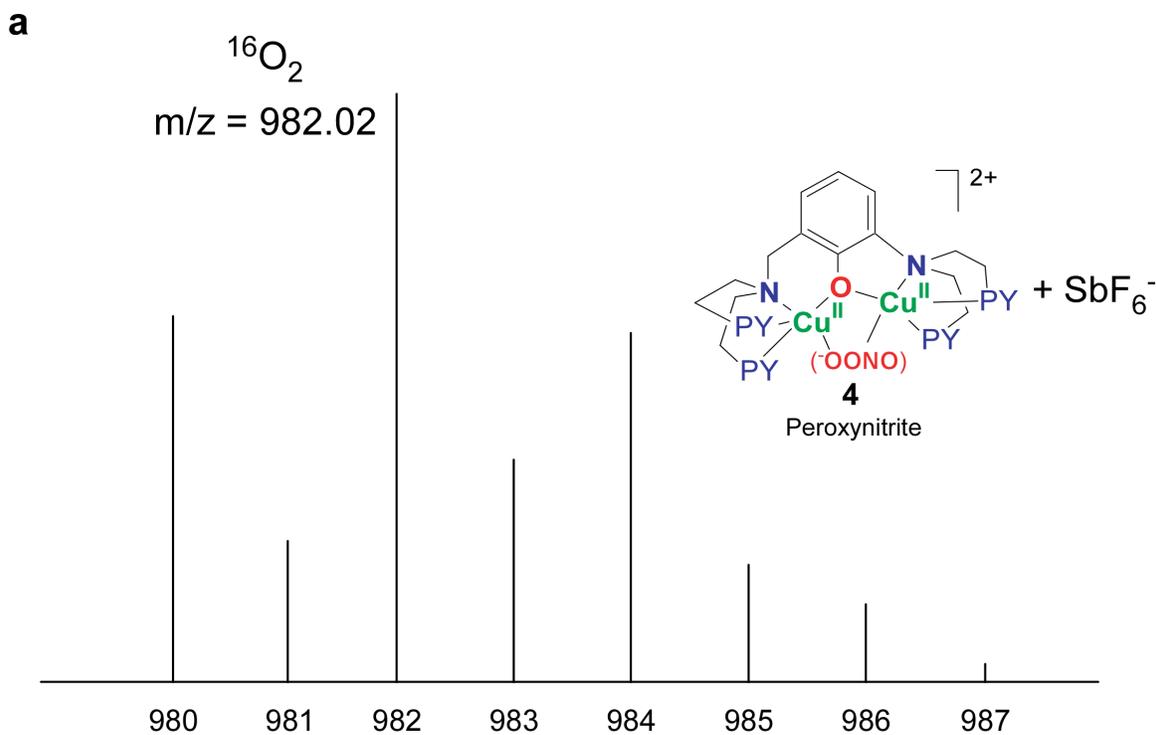


Figure S8. (a) Chemdraw predicted isotope distributions for $[\text{Cu}^{\text{II}}_2(\text{UN-O}^-)(^-\text{OON}=\text{O})]^{2+}$ (**4**) with one SbF_6^- anion. (b) Chemdraw predicted isotope distributions for $[\text{Cu}^{\text{II}}_2(\text{UN-O}^-)(^-\text{O}^{18}\text{ON}=\text{O})]^{2+}$ (**4**) with one SbF_6^- anion.

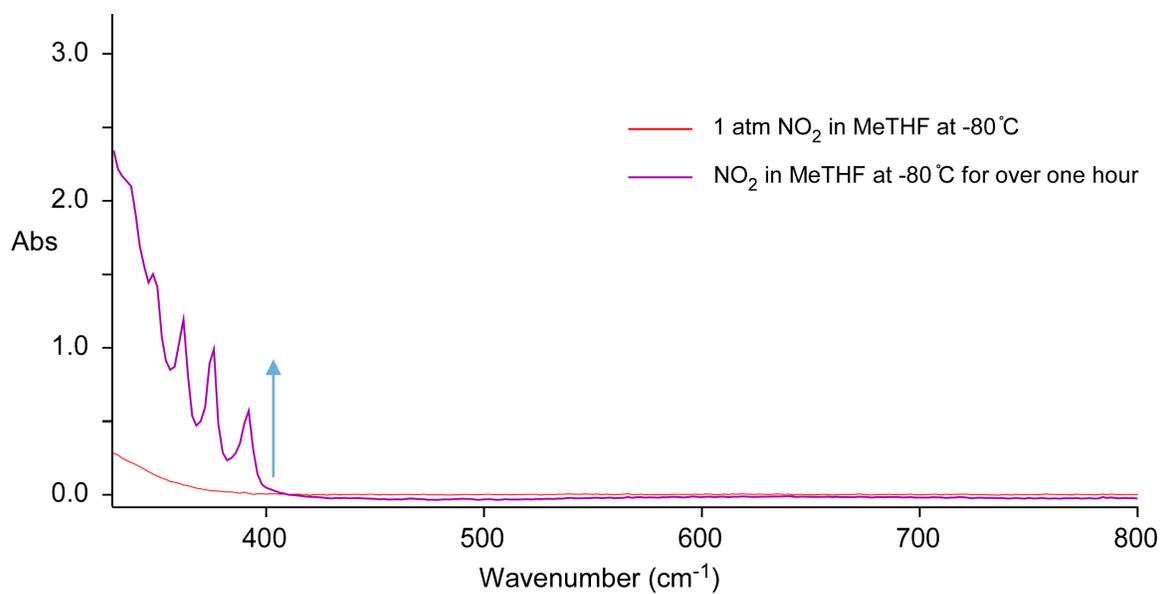


Figure S9. UV-Vis spectrum of ~ one atmosphere nitrogen dioxide bubbled through the MeTHF solution in a 10 mm Schlenk cuvette at $-80\text{ }^{\circ}\text{C}$ (red colored spectrum). Over the course of one hour at $-80\text{ }^{\circ}\text{C}$, the red colored spectrum gradually changes to the purple colored spectrum featuring multiple sharp bands in the 330 nm to 400 nm region.

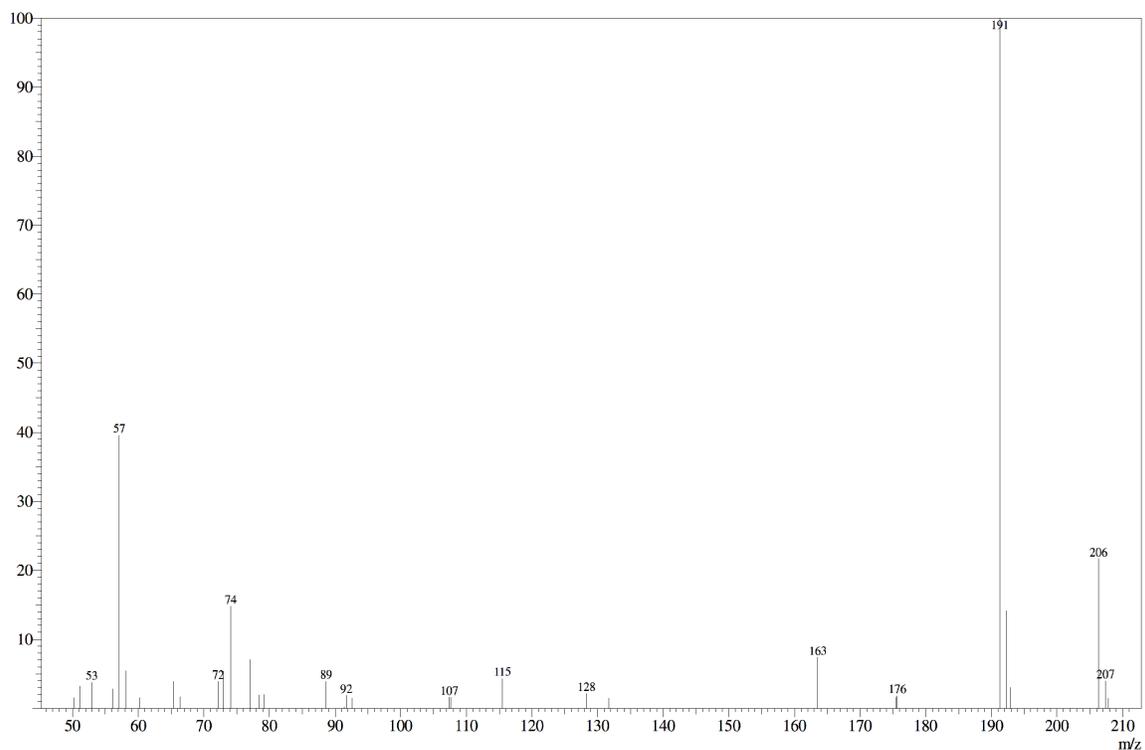


Figure S10. GC-MS spectrum of the original 2,4-di-*tert*-butyl phenol (DTBP).

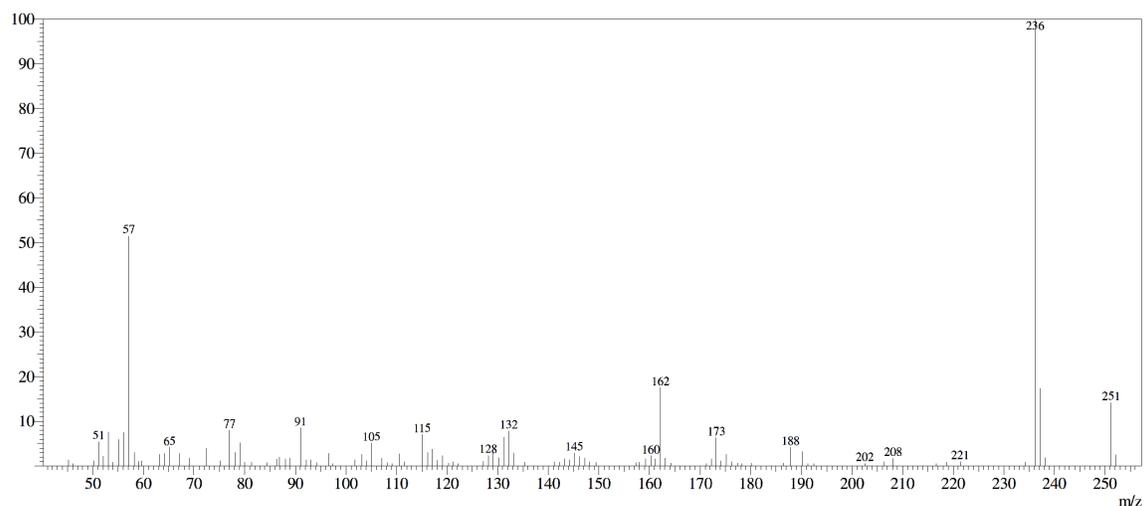


Figure S11. GC-MS spectrum of the organic part of the reaction adding one equiv of DTBP to the peroxyntirite complex in DCM at -80 °C. All of the starting DTBP was consumed and the only product observed *o*-nitrated phenol with retention time at 10.8 minutes which is consistent with authentic 2,4-di-*tert*-Butyl-6-nitrophenol.

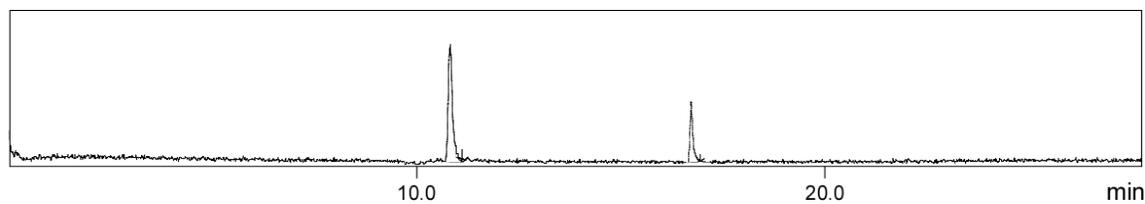


Figure S12. GC chromatogram of the organic part of the reaction adding one equiv of DTBP to the peroxyxynitrite complex in MeTHF at $-80\text{ }^{\circ}\text{C}$. The peak with retention time at 10.8 mins corresponds to 60% of the final products while the peak with retention time at 16.6 mins corresponds to 40% of the final products.

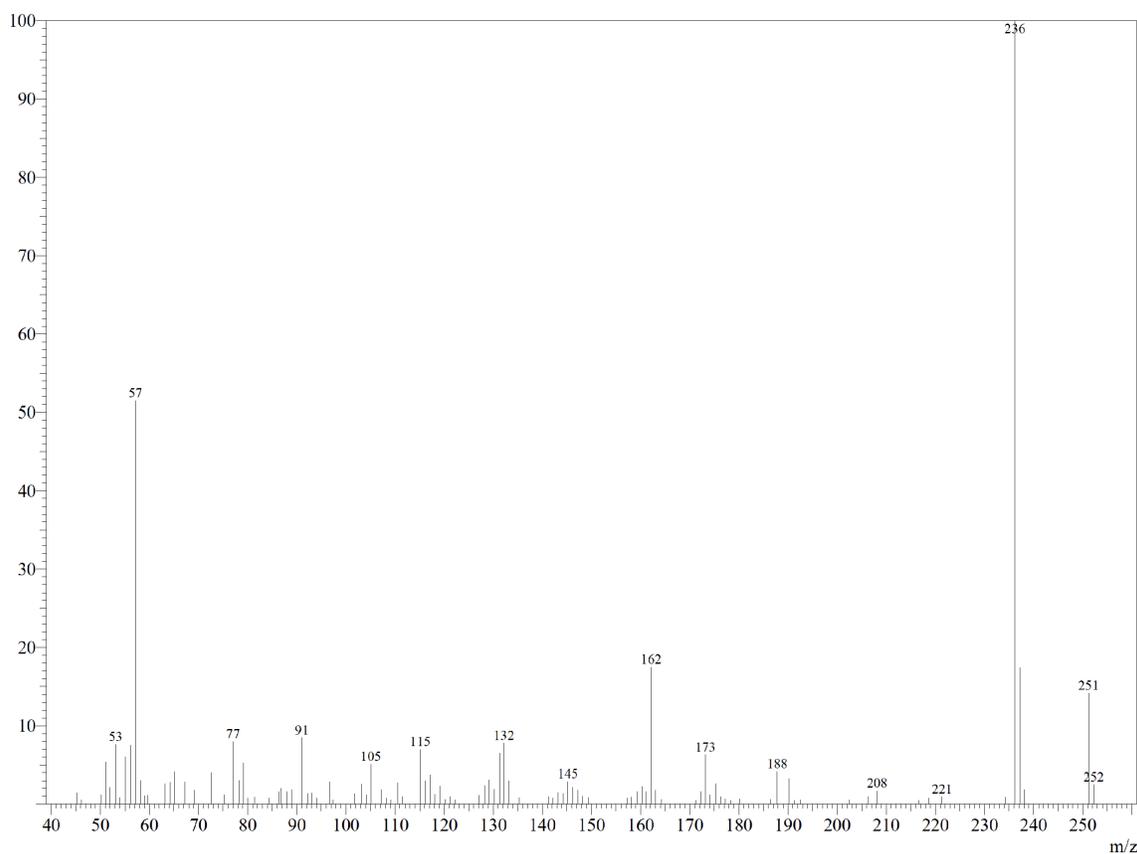


Figure S13. GC-MS spectrum of the organic part of the reaction adding one equiv of DTBP to the peroxyxynitrite complex in MeTHF at $-80\text{ }^{\circ}\text{C}$. The resulting product of bis-phenol dimer (retention time 10.8 mins) confirmed by comparison with authentic 2,4-di-*tert*-Butyl-6-nitrophenol.

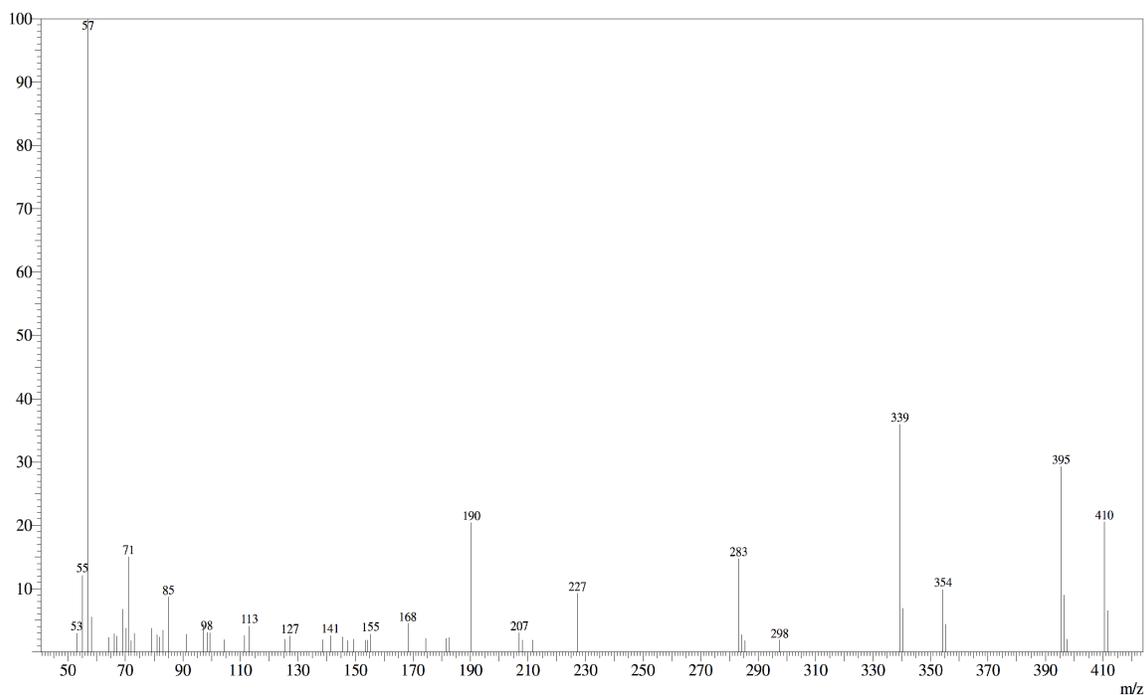


Figure S14. GC-MS spectrum of the organic part of the reaction adding one equiv of DTBP to the peroxyxynitrite complex in MeTHF at $-80\text{ }^{\circ}\text{C}$. The resulting product of bis-phenol dimer (retention time 16.6 mins) confirmed by comparison with authentic 4,4',6,6'-tetra-*tert*-butyl-2,2'-biphenol.