

Supporting Information

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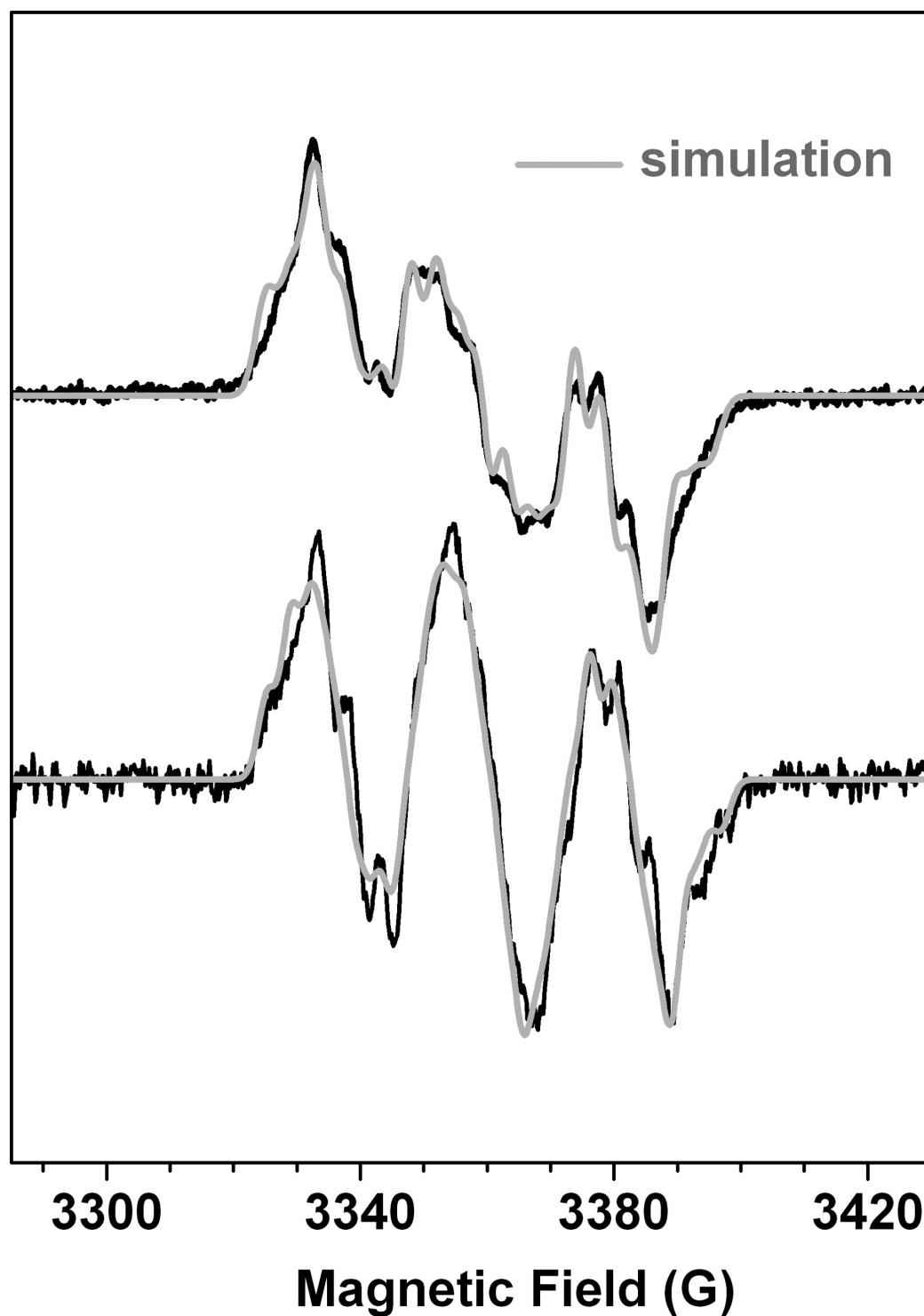


Fig. S1. Simulations (gray traces) of the 9-GHz EPR spectra of the Trp* formed on reaction of the D179W+R258E+R272D variant of CiP and the E250+E168Q variant of lignin peroxidase (LiP) with 5-fold excess hydrogen peroxide. Simulations were performed by using the "esfit" routine of the EasySpin simulation package with Perturbation option enabled [Stoll S, Schweiger A (2006) EasySpin, a comprehensive software package for spectral simulation and analysis in EPR *J Magn Reson* 178:42–55].

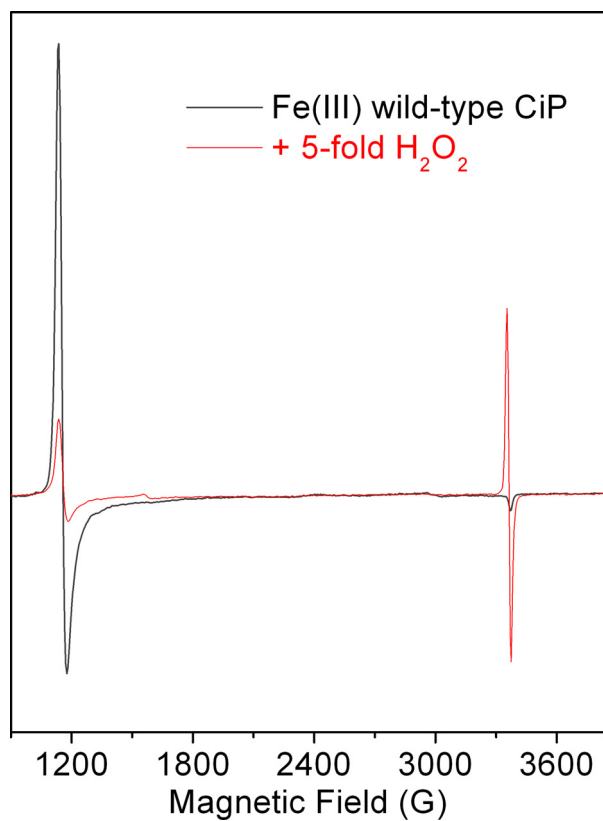


Fig. S2. The 9-GHz EPR spectra of *Coprinus cinereus* peroxidase (CiP) (WT) in the resting state (black trace) and on reaction with 5-fold excess hydrogen peroxide (gray trace). Experimental conditions: 4 K; modulation amplitude, 2 G; modulation frequency, 100 kHz. The dramatic decrease of the ferric EPR signal (75%) with the concomitant appearance of a low proportion of a Tyr* signal (red trace) implied the formation of the EPR-silent [Fe(IV)=O] intermediate.

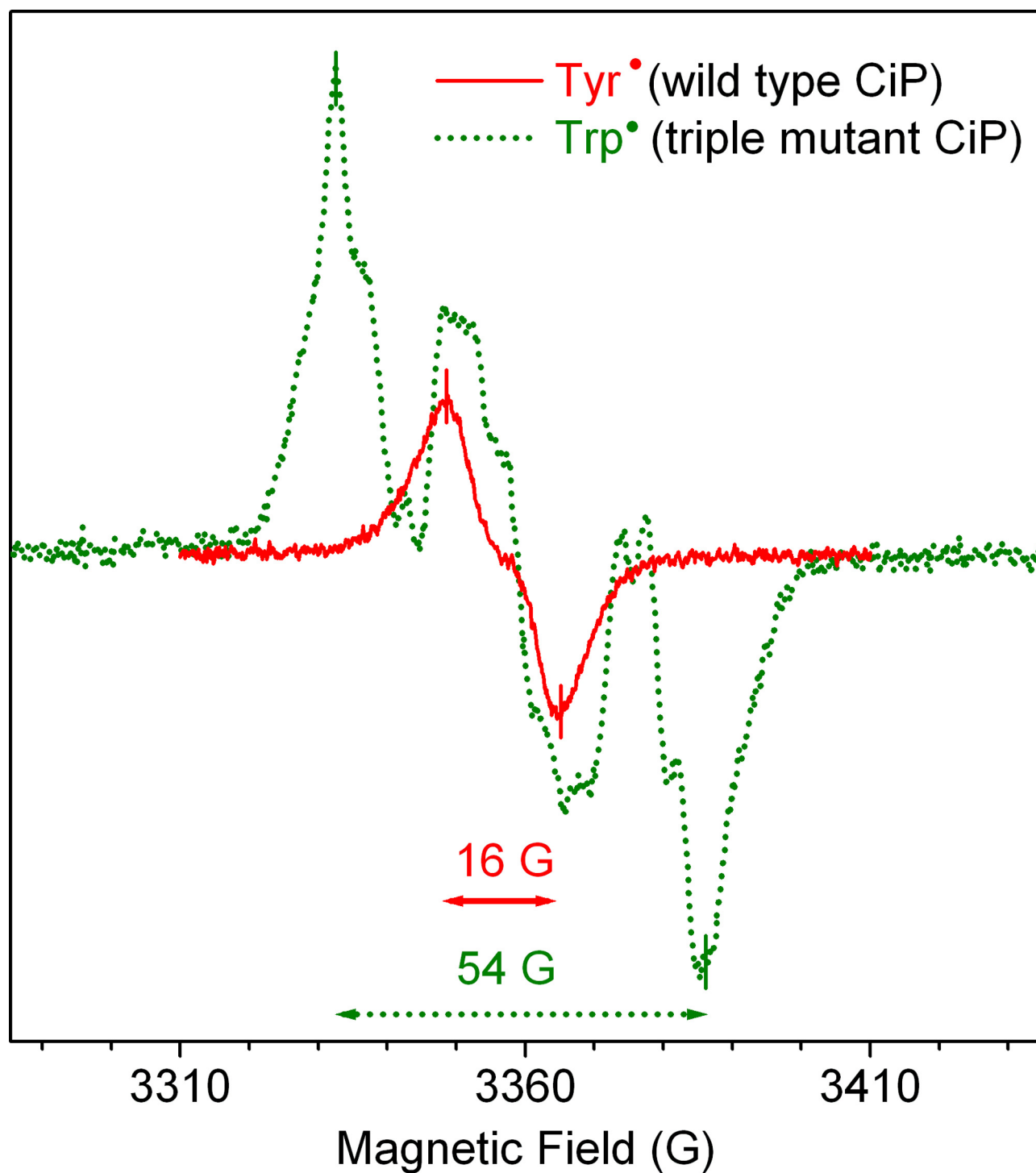


Fig. S3. Comparison of the Trp[•] (green trace) and the Tyr[•] (red trace) formed on reaction with 5-fold excess H₂O₂ of the D179W+R258E+R272D variant and the WT CiPs, respectively. Spin quantification showed that the Tyr[•] yield in the WT enzyme represented only 10% of the Trp[•] in the triple variant. Experimental conditions: 40 K; modulation amplitude, 1 G; modulation frequency, 100 kHz.

Other Supporting Information Files

[Table S1 \(PDF\)](#)