

Table S1. Proton hyperfine couplings obtained from the simulations of the EPR spectra

| | g_i^* | A(H- β 1) [†] | A(H- β 2) [†] | A(H-5) [†] | A(H-7) [†] | A(N) [†] | Ref. |
|--------------------------------|---------|------------------------------|------------------------------|---------------------|---------------------|-------------------|-----------|
| CiP variant | | | | | | | This work |
| <i>xx</i> | 2.0035 | 2.77 | 1.56 | 0.97 | 0.53 | 0.18 | |
| <i>yy</i> | 2.0027 | 2.08 | 1.44 | 0.25 | 0.09 | 0.21 | |
| <i>zz</i> | 2.0022 | 2.18 | 1.56 | 1.12 | 0.37 | 0.87 | |
| LiP variant | | | | | | | This work |
| <i>xx</i> | 2.0035 | 3.14 | 1.34 | 0.52 | 0.03 | 0.20 | |
| <i>yy</i> | 2.0027 | 2.05 | 2.25 | 0.76 | 0.15 | 0.14 | |
| <i>zz</i> | 2.0022 | 2.44 | 1.97 | 0.87 | 0.38 | 0.74 | |
| <i>B. adusta</i> [‡] | | | | | | | 1 |
| <i>xx</i> | 2.0035 | 2.15 | 1.75 | 0.64 | ≤0.15 | ≤0.15 | |
| <i>yy</i> | 2.0025 | 2.30 | 1.95 | ≤0.15 | 0.62 | ≤0.15 | |
| <i>zz</i> | 2.0022 | 2.30 | 1.95 | 0.49 | 0.46 | 1.05 | |
| <i>P. eryngii</i> [‡] | | | | | | | 1 |
| <i>xx</i> | 2.0035 | 2.35 | 1.13 | 0.64 | ≤0.15 | ≤0.15 | |
| <i>yy</i> | 2.0025 | 2.75 | 1.13 | ≤0.15 | 0.62 | ≤0.15 | |
| <i>zz</i> | 2.0022 | 2.70 | 1.18 | 0.49 | 0.46 | 1.00 | |

*The g values were measured from the 285 GHz EPR spectrum of the CiP variant radical. The same values were used for the simulation of the LiP variant radical.

[†]Values are given in mT and are absolute values. It is noted that from theory, hyperfine values for ring protons are expected to be negative in the case of positive carbon spin density. For H-5 and H-7, the hyperfine tensors are oriented so that the x axis is aligned with the C-H bond. Euler angles were ($0^\circ 0^\circ 90^\circ$) for H-5 and ($0^\circ 0^\circ -150^\circ$) for H-7.

[‡] x axis for H-5 and H-7 hyperfine tensors are rotated 30° with respect to the g tensor x axis. The g values were measured from the 95-GHz EPR spectra.

1. Timofeevski SL, Nie G, Reading NS, Aust SD (2000) Substrate specificity of lignin peroxidase and a S168W variant of manganese peroxidase. *Arch Biochem Biophys* 373:147-153.

