## Diverse Mechanisms Observed in the Reactions of a Manganese Superoxo Complex with *para*-Substituted Phenols

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Reaction of a well-characterized  $Mn^{III}$ -superoxo species,  $Mn(BDP^{Br}P)(O_2^{\bullet})$  (1,  $H_2BDP^{Br}P = 2,6$ -bis((2-(*S*)-di(4-bromo)phenylhydroxylmethyl-1-pyrrolidinyl)methyl)-pyridine),<sup>1</sup> with 4-dimethylaminophenol at -80 °C proceeds via concerted proton electron transfer (CPET) to produce a  $Mn^{III}$ -hydroperoxo complex,  $Mn(BDP^{Br}P)(OOH)$  (2), alongside 4-dimethylaminophenoxy radical; whereas, upon treatment with 4-nitrophenol, complex 1 undergoes a proton transfer process to afford a  $Mn^{IV}$ -hydroperoxo complex,  $[Mn(BDP^{Br}P)(OOH)]^+$  (3).<sup>2</sup> Intriguingly, the reactions of 1 with 4-chlorophenol and 4-methoxyphenol follow two routes of CPET and sequential proton and electron transfer to furnish complex 2 in the end. UV-vis and EPR spectroscopic studies coupled with DFT calculations provided support for this wide mechanistic spectrum of activating various phenol O-H bonds by a single  $Mn^{III}$ -superoxo complex, 1.



## References:

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- "A Mechanistic Spectrum of O-H Bond Cleavage Observed for Reactions of Phenols with a Manganese Superoxo Complex" Tian, Y.-C.; Zhang, P; Lin, K.-T; Fu, C-W. Ye, S.\* Lee, W.-Z.;\* Chem. Eur. J. 2024, 30, e202401826.