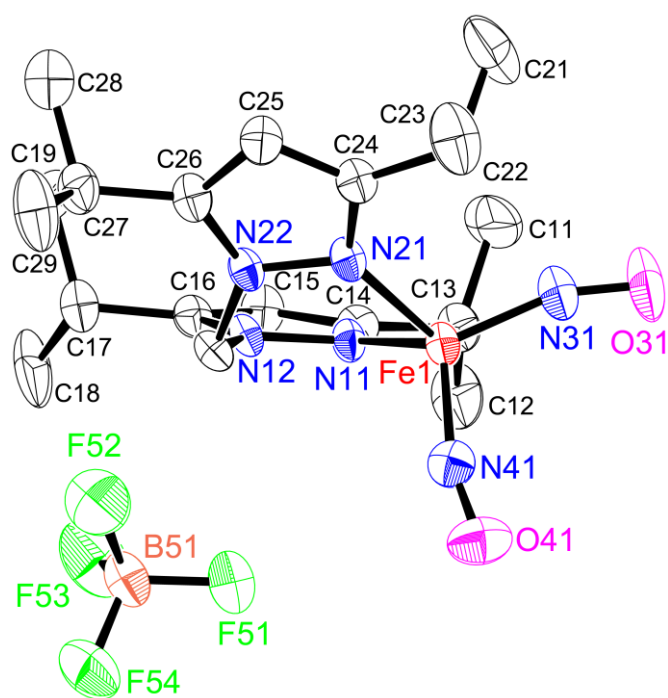
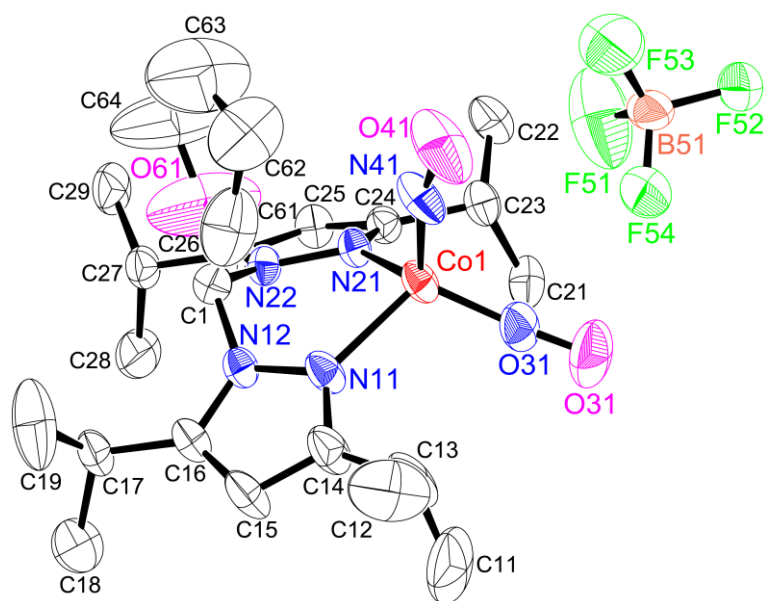


Supplementary Materials: Structures and Properties of Dinitrosyl Iron and Cobalt Complexes Ligated by Bis(3,5-diisopropyl-1-pyrazolyl)methane

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Figure S1. Crystal structure of $[\text{Fe}(\text{NO})_2(\text{L1}'')](\text{BF}_4)$.Figure S2. Crystal structure of $[\text{Co}(\text{NO})_2(\text{L1}'')](\text{BF}_4) \cdot \text{thf}$.

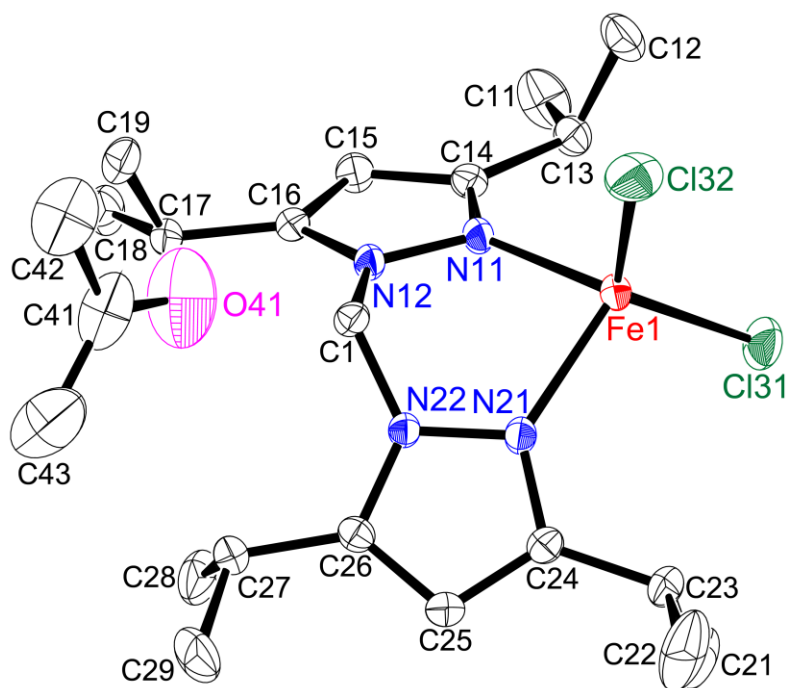


Figure S3. Crystal structure of $[\text{FeCl}_2(\text{L1}'')](\text{CH}_3)_2\text{CO}$.

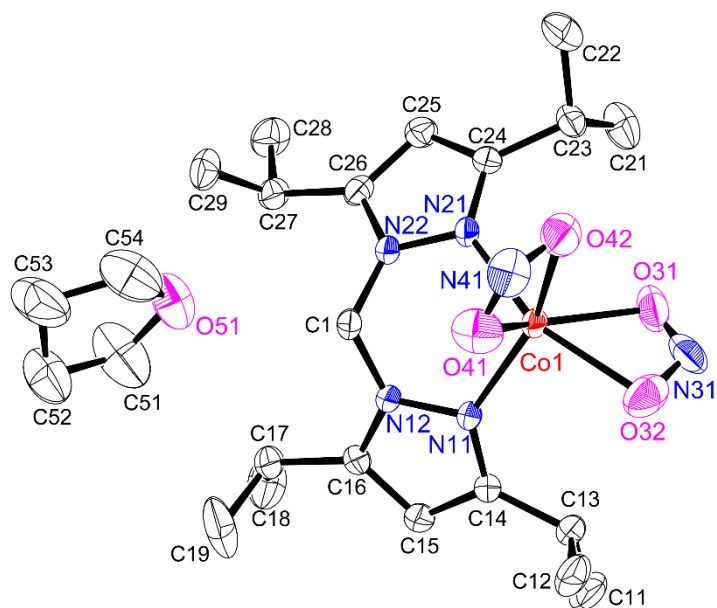


Figure S4. Crystal structure of $[\text{Co}(\text{NO}_2)_2(\text{L1}'')]\cdot\text{thf}$.

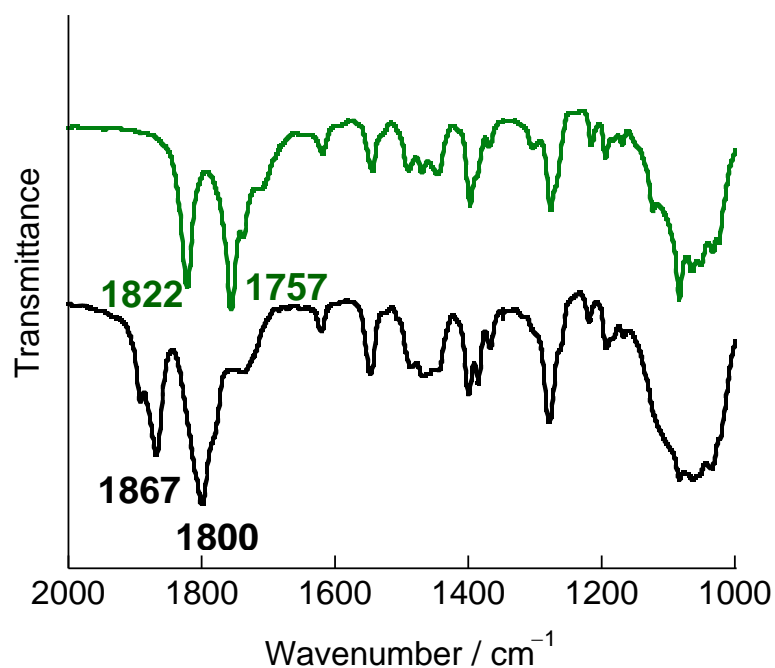


Figure S5. IR spectra of $[\text{Fe}(\text{NO})_2(\text{L1}'')](\text{BF}_4)$ (green, top) and $[\text{Co}(\text{NO})_2(\text{L1}'')](\text{BF}_4)$ (black, bottom) in the solid state (KBr).

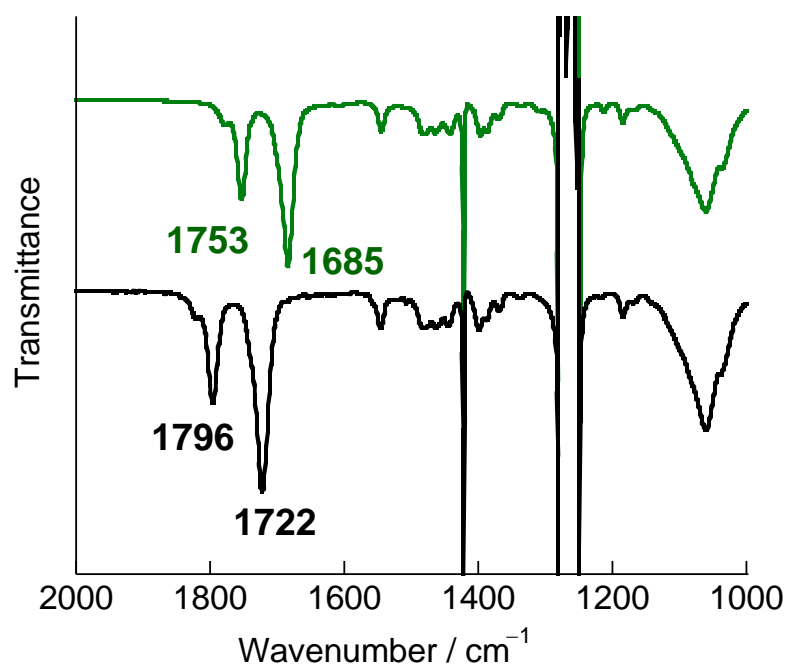


Figure S6. IR spectra of $[\text{Fe}(^{15}\text{N}^{18}\text{O})_2(\text{L1}'')](\text{BF}_4)$ (green, top) and $[\text{Co}(^{15}\text{N}^{18}\text{O})_2(\text{L1}'')](\text{BF}_4)$ (black, bottom) in solution (CH_2Cl_2).

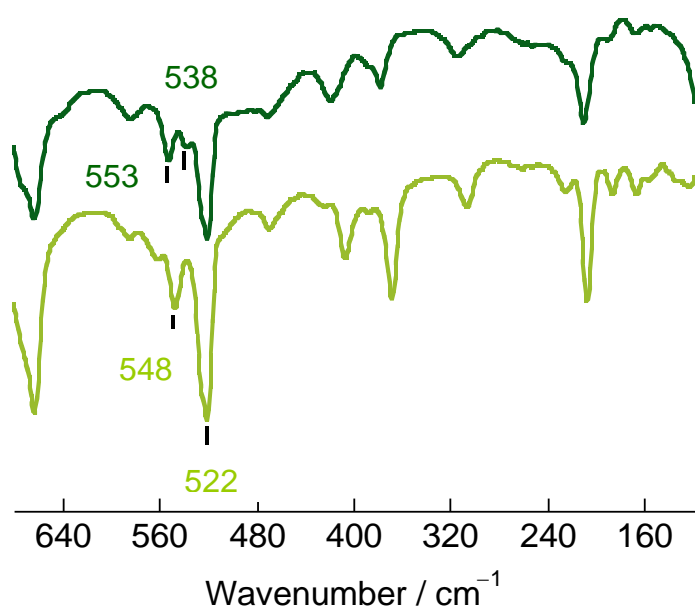


Figure S7. Far-IR spectra of $[\text{Fe}(\text{NO})_2(\text{L1''})](\text{BF}_4)$ (top, deep green) and $[\text{Fe}^{15}\text{N}^{18}\text{O})_2(\text{L1''})](\text{BF}_4)$ (bottom, yellow green).

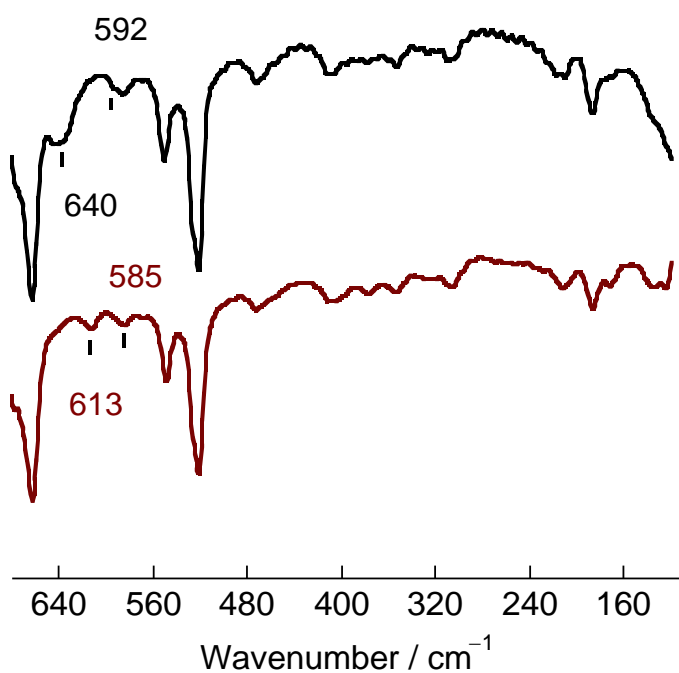


Figure S8. Far-IR spectra of $[\text{Co}(\text{NO})_2(\text{L1''})](\text{BF}_4)$ (top, black) and $[\text{Co}^{15}\text{N}^{18}\text{O})_2(\text{L1''})](\text{BF}_4)$ (bottom, brown).

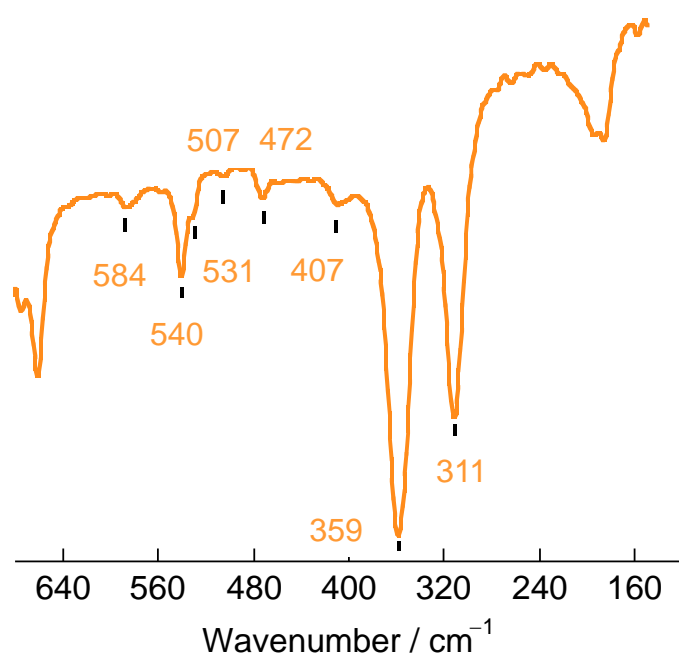


Figure S9. Far-IR spectra of $[\text{FeCl}_2(\text{L1}'')](\text{BF}_4)$ (CsI pellet).

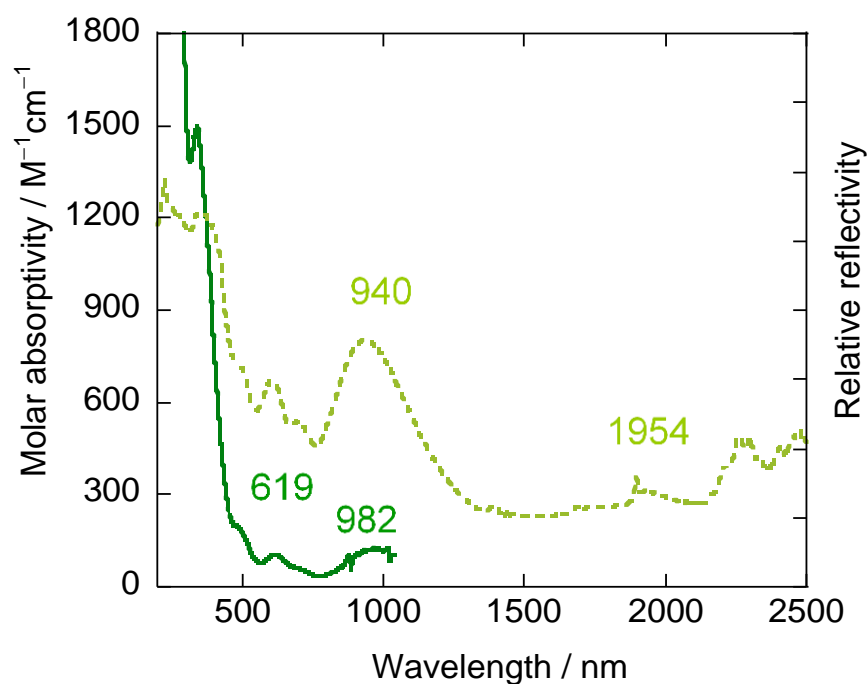


Figure S10. UV-vis (solid line, in CH_2Cl_2) and diffuse reflectance (dotted line, solid) spectra of $[\text{Fe}(\text{NO})_2(\text{L1}'')](\text{BF}_4)$.

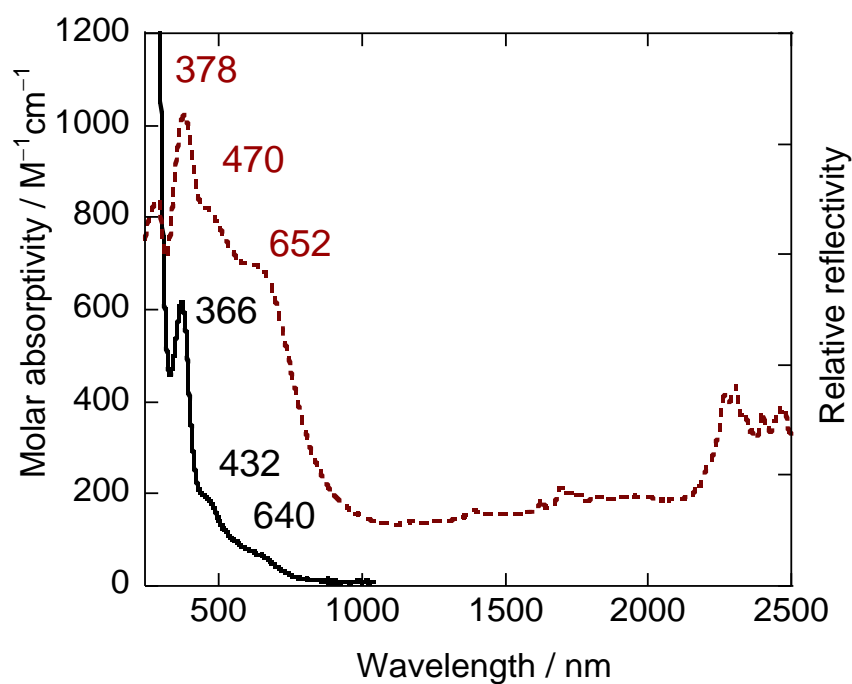


Figure S11. UV-vis (solid line, in CH_2Cl_2) and diffuse reflectance (dotted line) spectra of $[\text{Co}(\text{NO})_2(\text{L1}'')](\text{BF}_4)$.

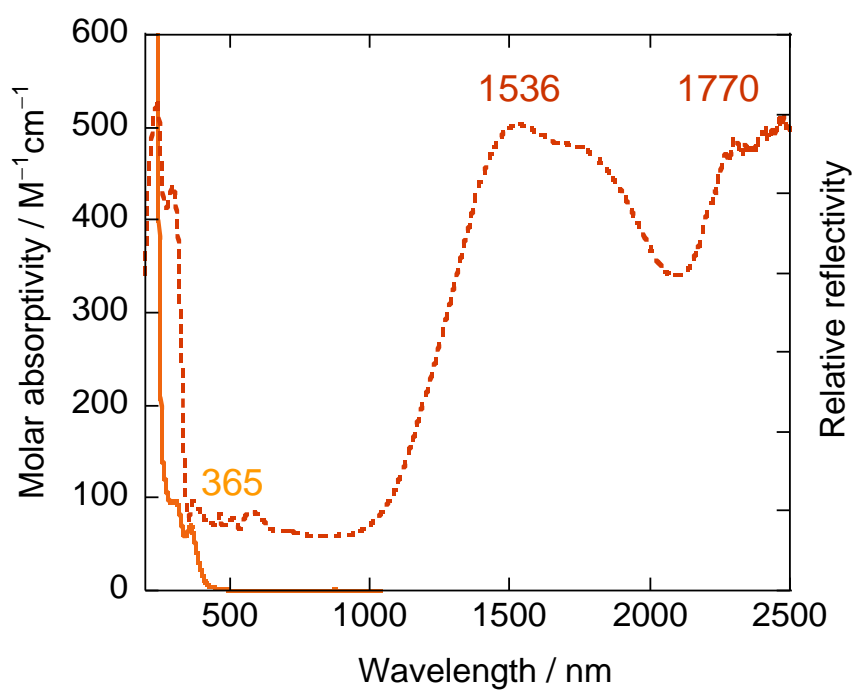


Figure S12. UV-vis (solid line, in CH_2Cl_2) and diffuse reflectance (dotted line) spectra of $[\text{FeCl}_2(\text{L1}'')]$.

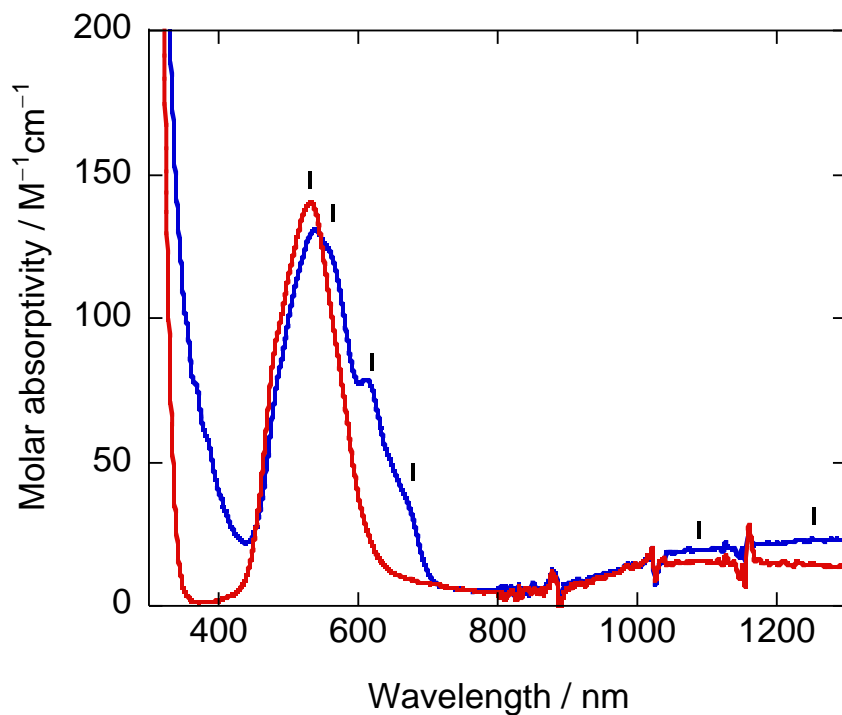
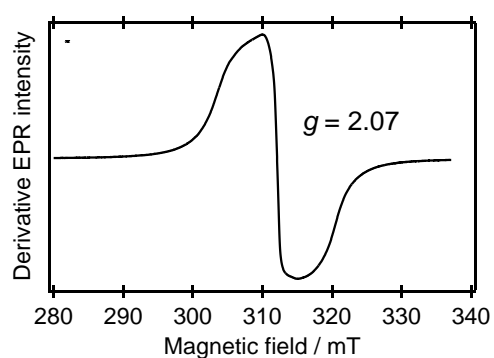


Figure S13. UV-vis spectra of $[\text{Co}(\kappa^2\text{-O}_2\text{NO})_2(\text{L1}'')]$ (red) and $[\text{Co}(\kappa^2\text{-O}_2\text{N})_2(\text{L1}'')]$ (blue) in CH_2Cl_2 .

(a) solid state



(b) solution state

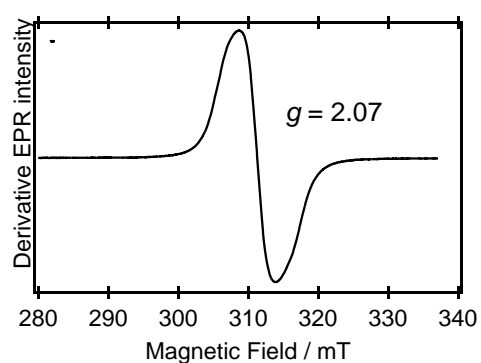
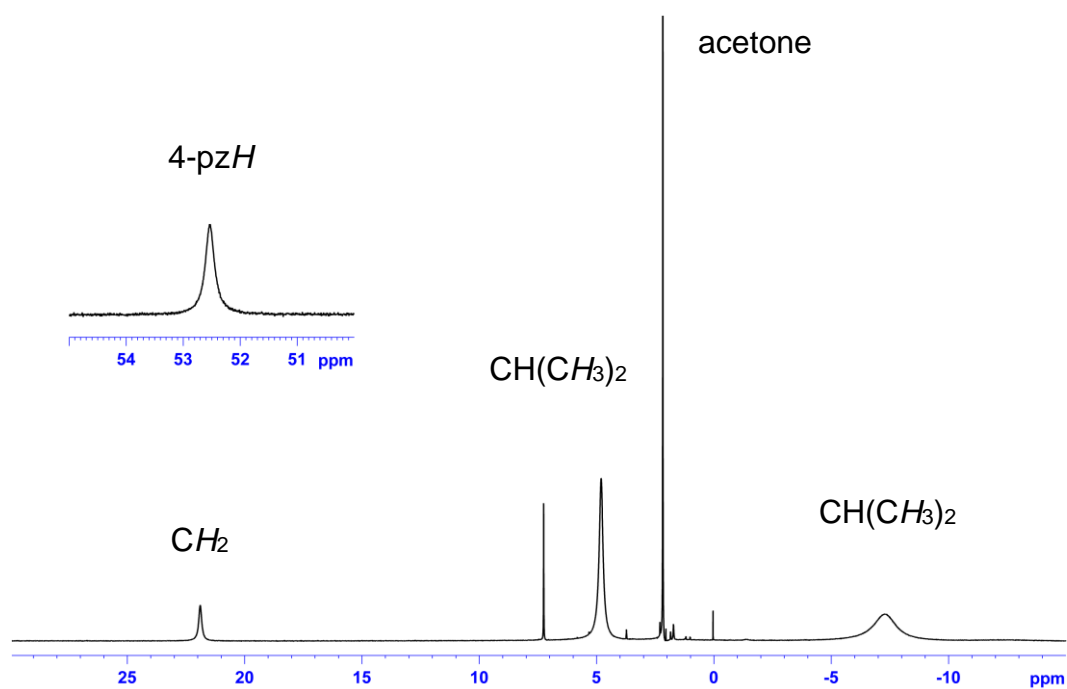
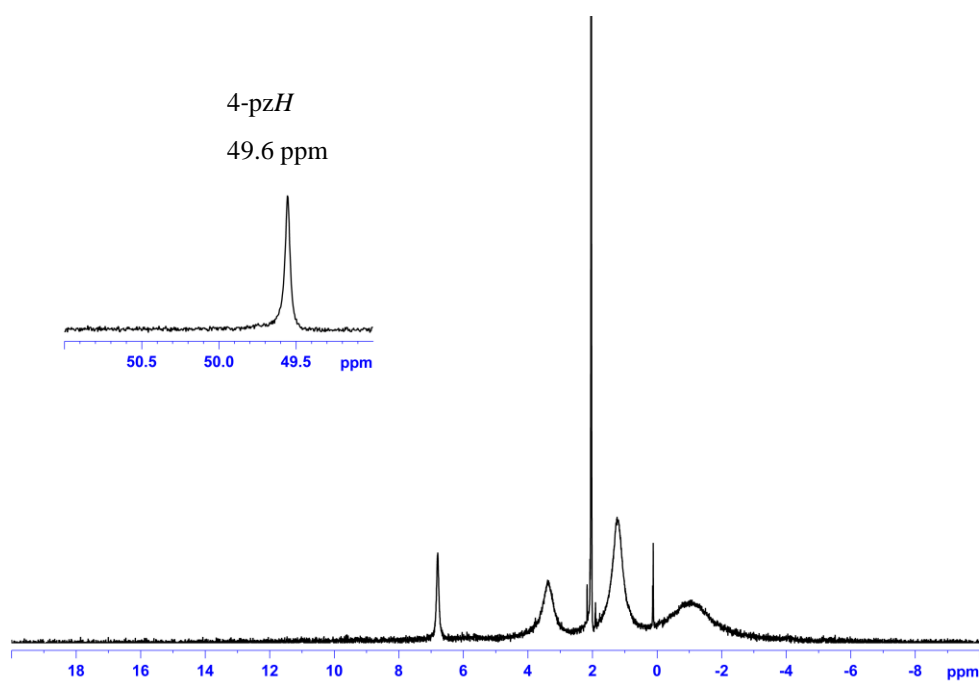


Figure S14. EPR spectra of $[\text{Fe}(\text{NO})_2(\text{L1}'')](\text{BF}_4)$ in solid (left) and frozen dichloromethane solution (right) at 130 K.

Figure S15. ^1H -NMR spectrum of $[\text{FeCl}_2(\text{L1}'')]$ in CDCl_3 at room temperature.Figure S16. ^1H -NMR spectrum of $[\text{Co}(\kappa^2\text{-O}_2\text{NO})_2(\text{L1}'')]$ in $(\text{CD}_3)_2\text{CO}$ at room temperature.

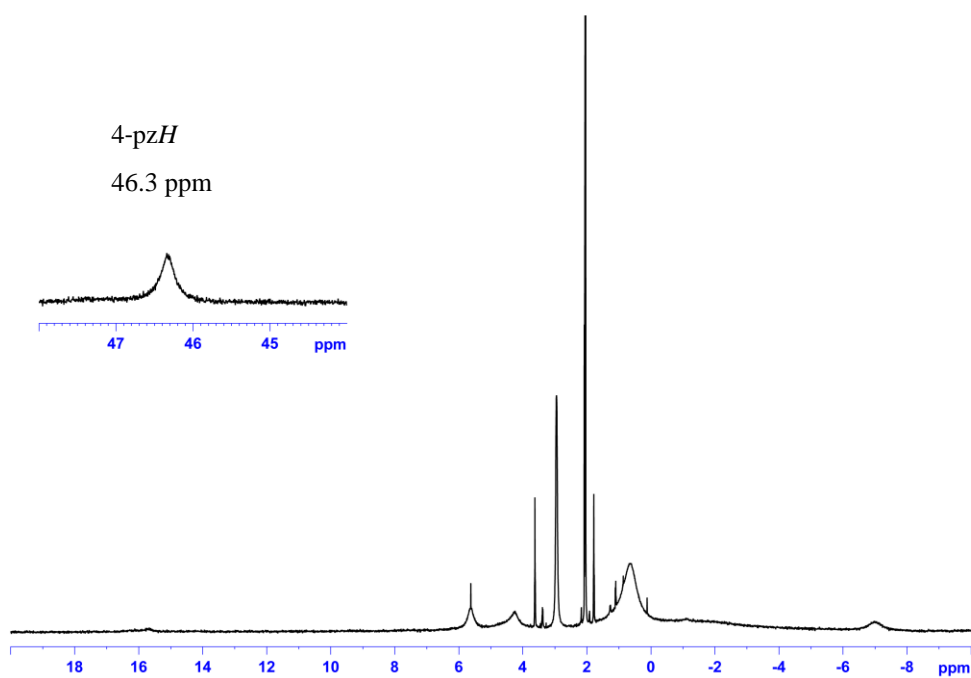


Figure S17. ^1H -NMR spectrum of $[\text{Co}(\kappa^2\text{-O}_2\text{N})_2(\text{L1}'')]$ in $(\text{CD}_3)_2\text{CO}$ at room temperature.

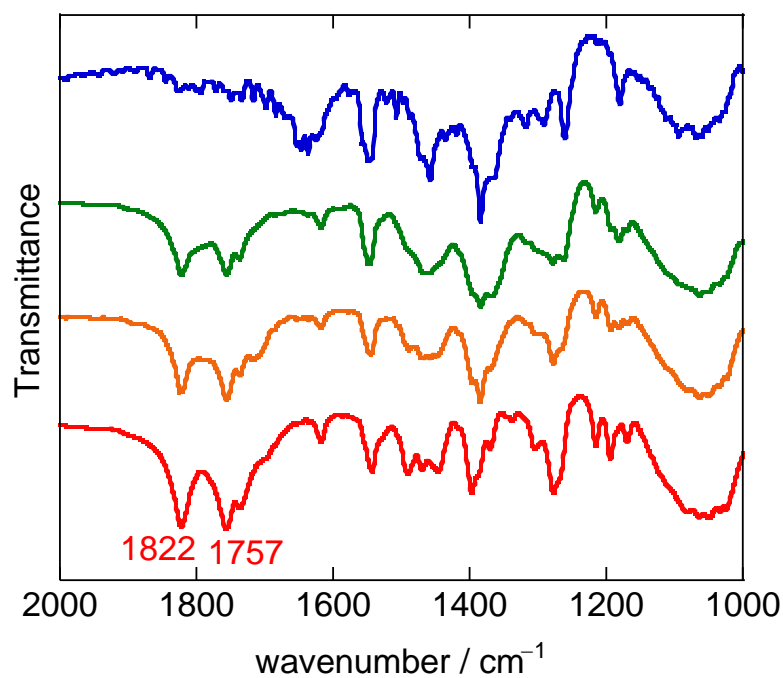


Figure S18. IR spectral changes of $[\text{Fe}(\text{NO})_2(\text{L1}'')](\text{BF}_4)$ under argon atmospheres at room temperature (KBr) (red: start, orange: one week after, green: two weeks after, blue: three weeks after).

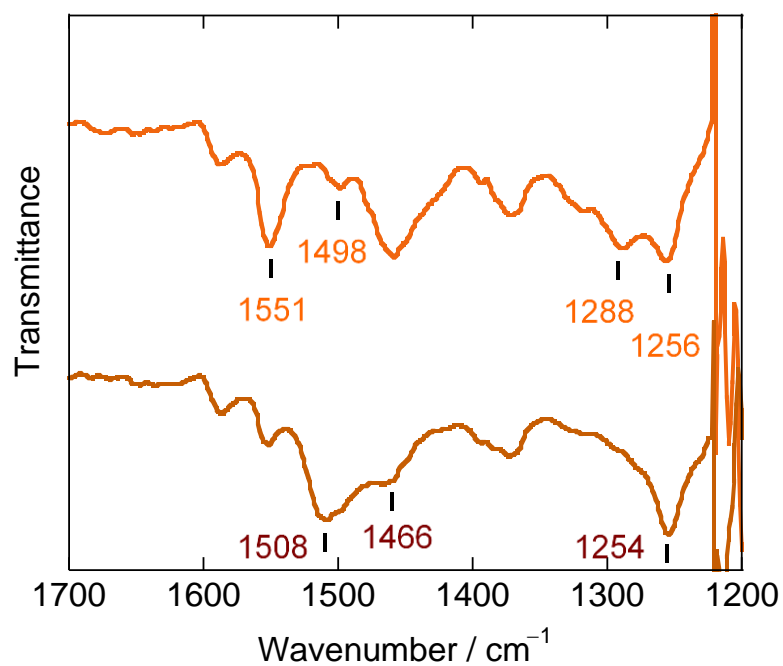


Figure S19. IR spectral changes during the O_2 reaction of $[\text{Fe}(\text{NO})_2(\text{L1}'')](\text{BF}_4)$ in solution (RT, CH_2Br_2). (top: normal NO and bottom: isotope labelled).

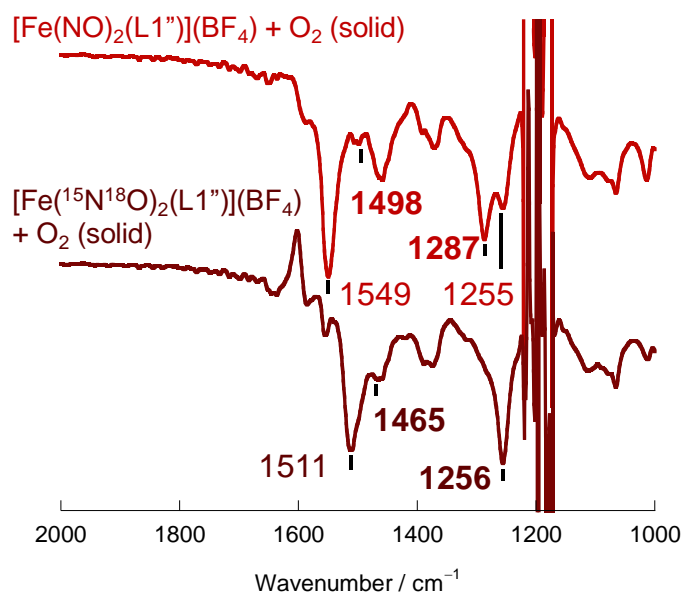


Figure S20. IR spectral changes during the O_2 reaction of $[\text{Fe}(\text{NO})_2(\text{L1}'')](\text{BF}_4)$ in the solid (RT, CH_2Br_2). (top: normal NO and bottom: isotope labelled).

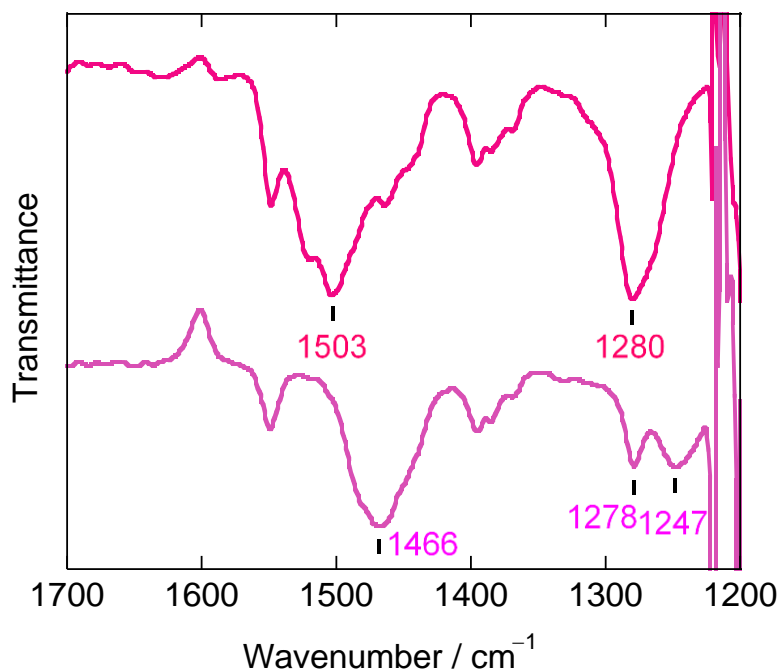


Figure 21. IR spectral changes during the dioxygen reaction of $[\text{Co}(\text{NO})_2(\text{L1}'')](\text{BF}_4)$ in solution (RT, CH_2Br_2). (top: normal NO and bottom: isotope labelled).

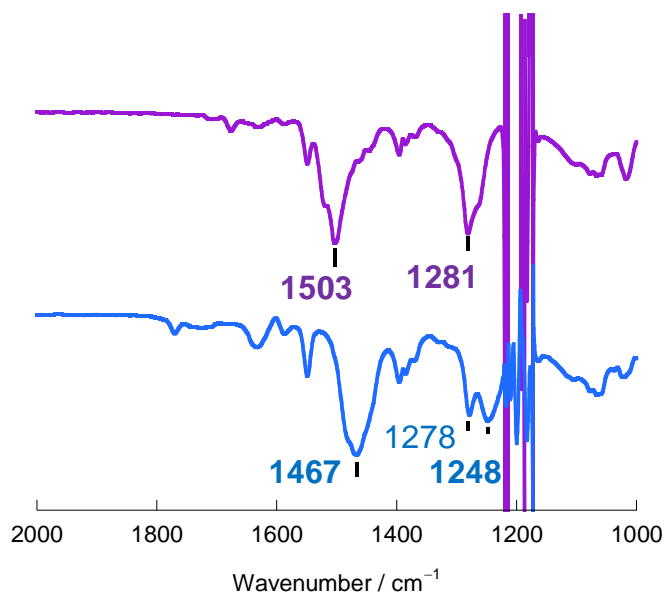


Figure S22. IR spectral changes during the O_2 reaction of $[\text{Co}(\text{NO})_2(\text{L1}'')](\text{BF}_4)$ in the solid (RT, CH_2Br_2). (top: normal NO and bottom: isotope labelled).

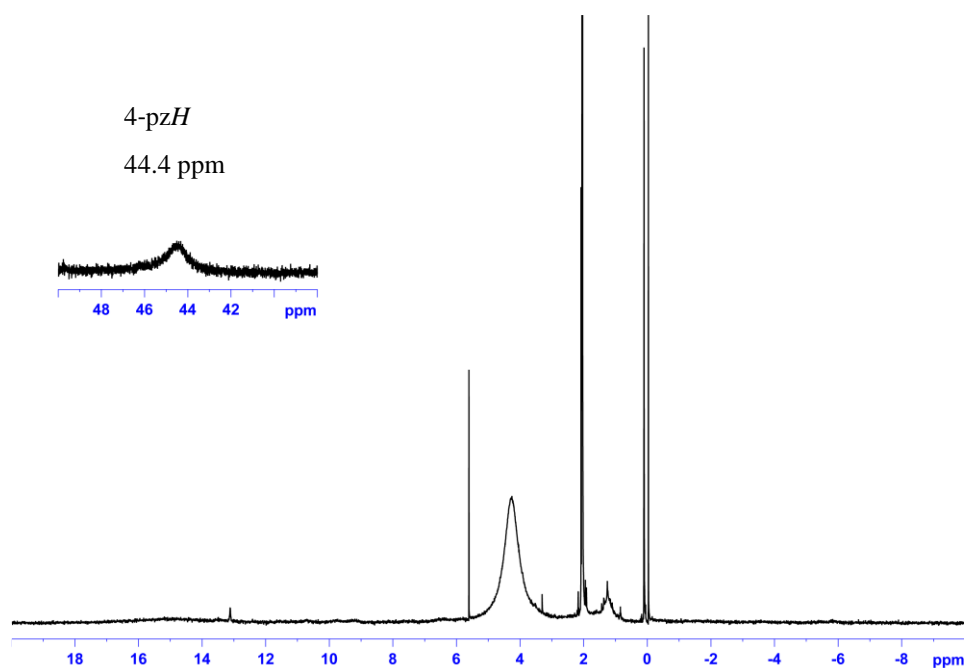


Figure S23. ^1H -NMR spectrum of the products of the O_2 reaction of $[\text{Co}(\text{NO})_2(\text{L1}'')](\text{BF}_4)$ in solution. Taken in $(\text{CD}_3)_2\text{CO}$ at room temperature.

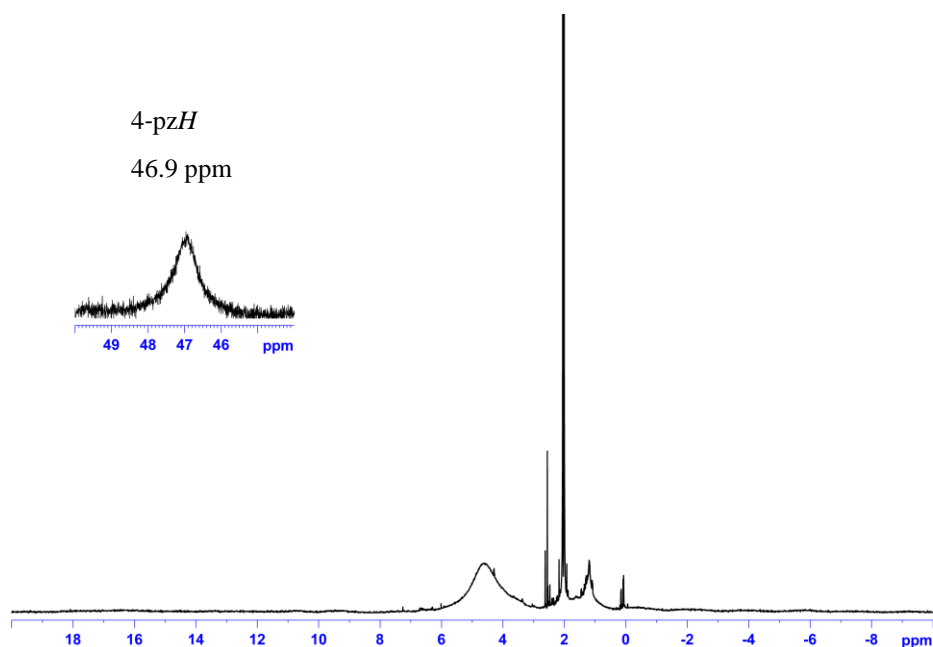


Figure S24. ^1H -NMR spectrum of the products of the O_2 reaction of $[\text{Co}(\text{NO})_2(\text{L1}'')](\text{BF}_4)$ in the solid. Taken in $(\text{CD}_3)_2\text{CO}$ at room temperature.