

Supporting Information

Are Reactions Between Metal Cyanides and Aryl Diazonium Ions Really Outer-Sphere Electron Transfer Processes?

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Plots of $-RT\ln k_8$ and $-RT\ln k_9$ ($= \Delta G^\ddagger - RT\ln Z_{\text{col}}$; see eq 6) against the corresponding values of $-FE_{1/2, \text{ZC}_6\text{H}_4\text{N}_2^+}$ ($\propto \Delta G^0$) give straight lines with slopes of 1.31 ± 0.17 and 0.77 ± 0.14 , respectively (Figure S1). All data are taken from ref S1.

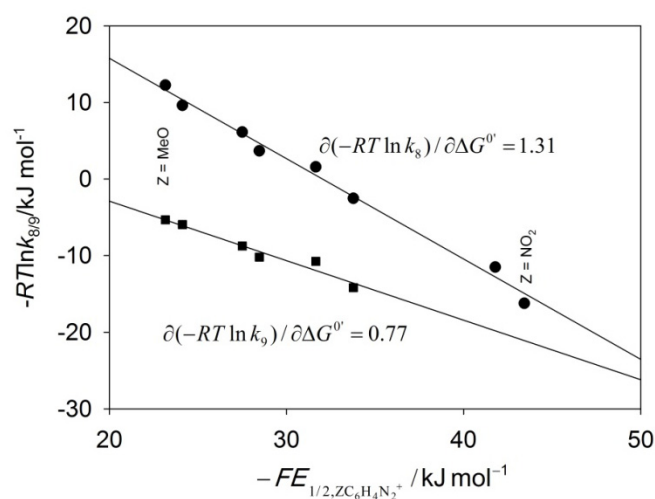


Figure S1. Plots of $-RT\ln k_8$ and $-RT\ln k_9$ vs $-FE_{1/2, \text{ZC}_6\text{H}_4\text{N}_2^+}$ for the reactions between a number of $\text{ZC}_6\text{H}_4\text{N}_2^+$ compounds with $\text{Fe}(\text{CN})_6^{4-}$ in water (eq 8) and with decamethylferrocene, $(\text{Me}_5\text{Cp})_2\text{Fe}$, in acetonitrile (eq 9), respectively.

Under oxygenated conditions the main non-ionic product from the reaction between $\text{NO}_2\text{C}_6\text{H}_4\text{N}_2^+$ and $\text{Fe}(\text{CN})_6^{4-}$ is 4-nitrophenol as evidenced by the recorded optical spectra (Figure S2).

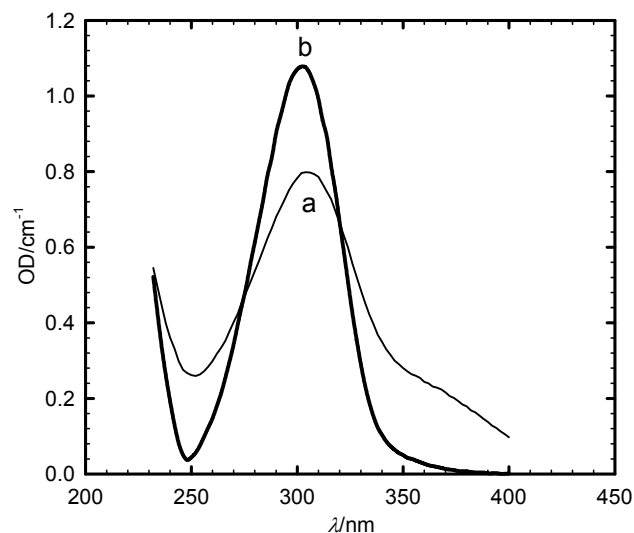


Figure S2. Optical spectra of a) oxygen-saturated reaction mixture containing 10^{-4} M $\text{NO}_2\text{C}_6\text{H}_4\text{N}_2^+$ and 10^{-4} M $\text{Fe}(\text{CN})_6^{4-}$ and b) 10^{-4} M solution of an authentic sample of 4-nitrophenol.

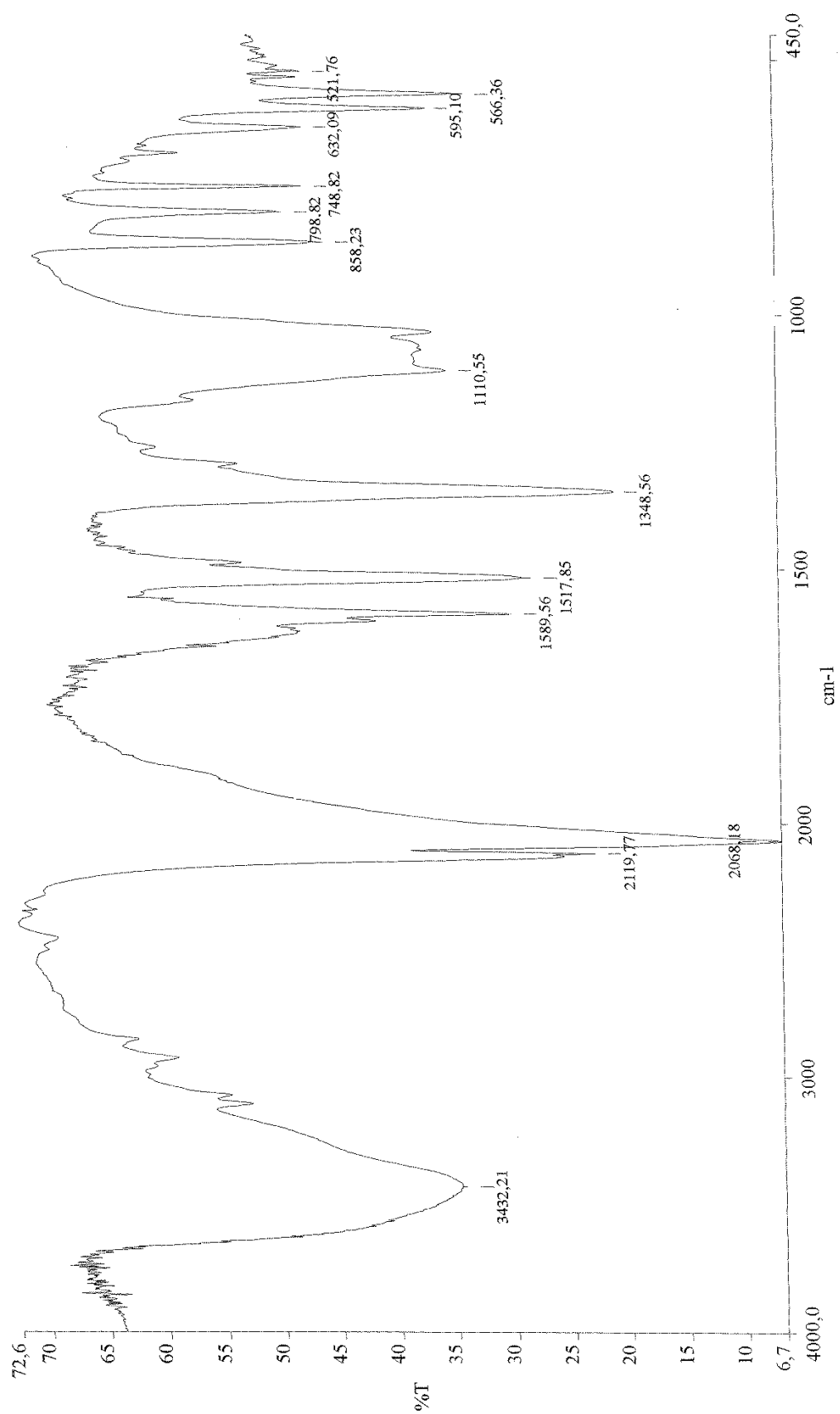


Figure S3. IR spectrum of $\text{NO}_2\text{C}_6\text{H}_4(\text{NC})\text{Fe}(\text{CN})_5^{3-}$.

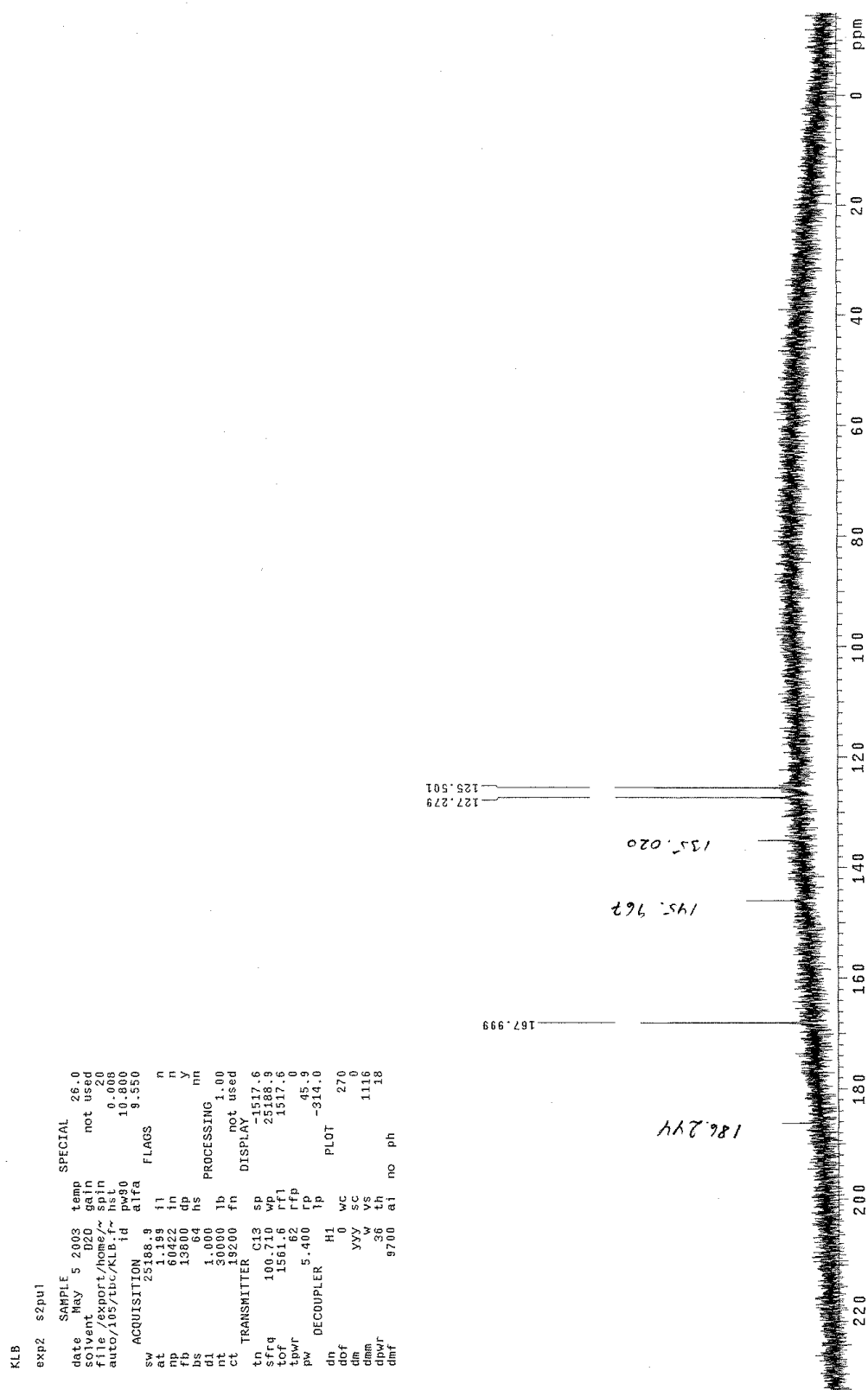


Figure S4. ^{13}C NMR spectrum of $\text{NO}_2\text{C}_6\text{H}_4(\text{NC})\text{Fe}(\text{CN})_5^{3-}$.

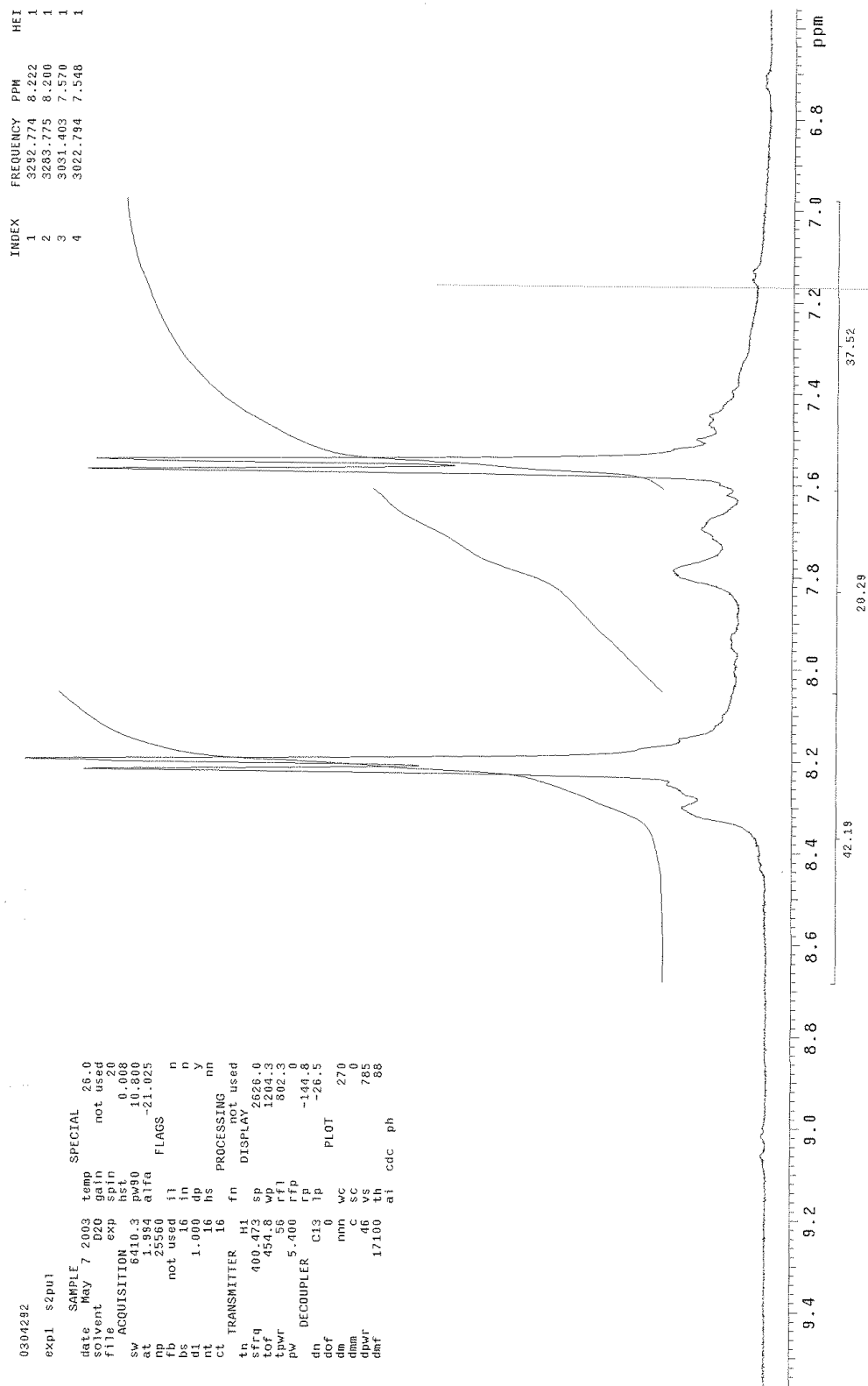


Figure S5. ^1H NMR spectrum of $\text{NO}_2\text{C}_6\text{H}_4(\text{NC})\text{Fe}(\text{CN})_5^{3-}$.

References

- (S1) Doyle, M. P.; Guy, J. K.; Brown, K. C.; Mahapatro, S. N.; VanZyl, C. M.; Pladzewicz, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 1536–1540.