Supporting Information for

Selective C–H Bond Cleavage by a High Spin Fe^{IV}–Oxido Complex

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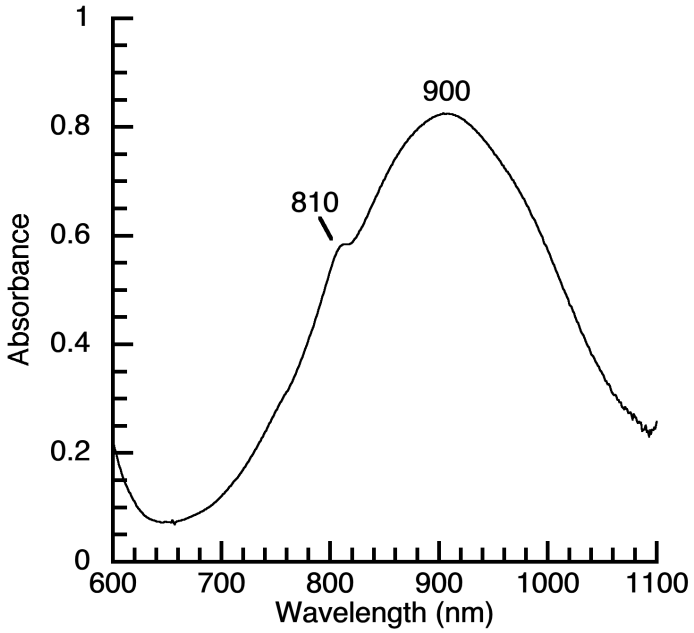


Figure S1. Electronic absorption spectrum of $[Fe^{IV}pop(O)]^-$ generated using 9.23 mM $K[Fe^{II}pop(OH_2)]$ in the presence of 2.08 equiv of 18c6 + 1.06 equiv of IBX-iPr in DMF:THF at –80 ºC, highlighting the low-energy region.

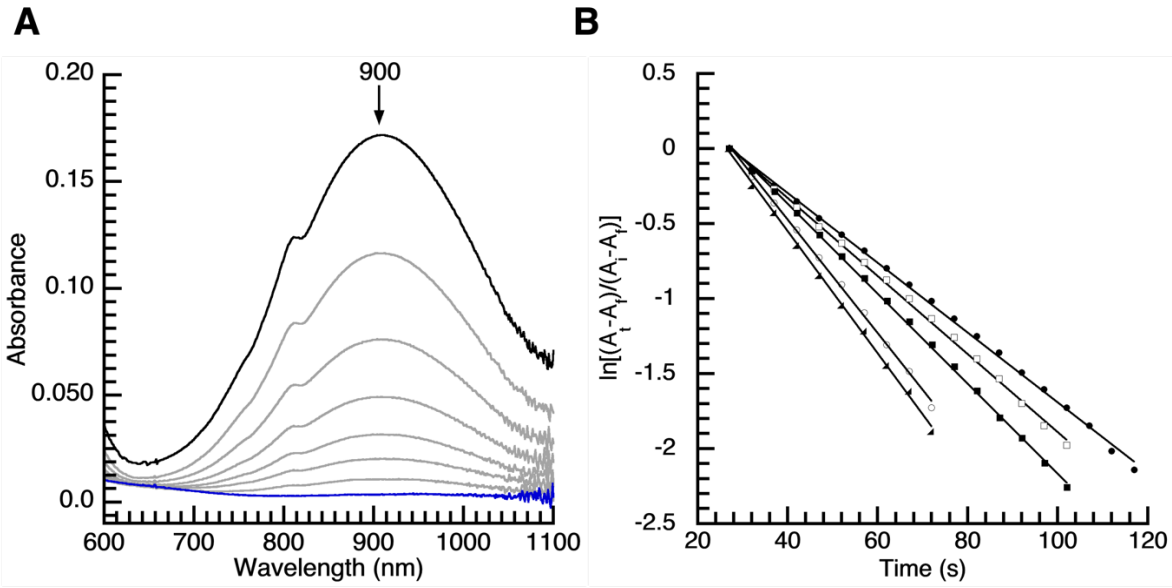


Figure S2. (A) Electronic absorption spectrum showing the disappearance of the 900 nm *d–d* band from the reaction of $[Fe^{IV}pop(O)]^-$ (1.9 mM) and BzOH under pseudo first-order rate conditions in DMF at –20 ºC. (B) The corresponding plot of $\ln\left(\frac{A_t - A_f}{A_i - A_f}\right)$ vs. time associated with the disappearance of the 900 nm *d–d* band for different concentrations of BzOH.

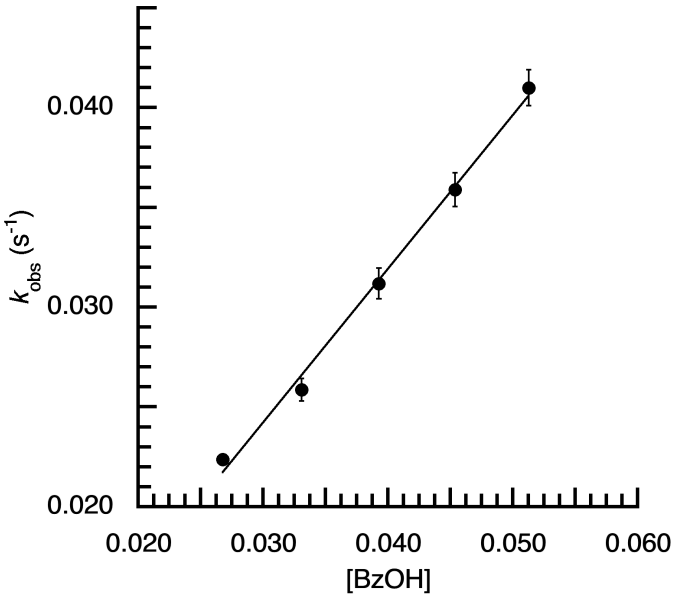


Figure S3. Plot of k_{obs} vs. the concentration of benzyl alcohol in DMF at –20 °C.

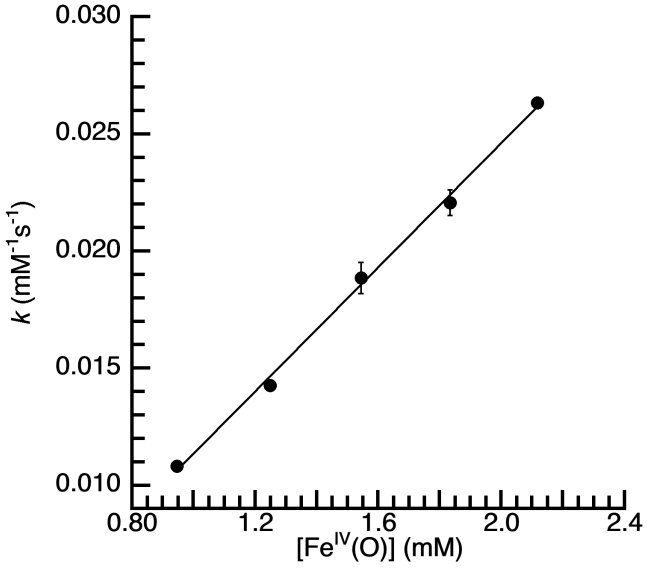


Figure S4. Plot of k vs. the concentration of $[Fe^{IV}pop(O)]^-$ in DMF at –20 °C.

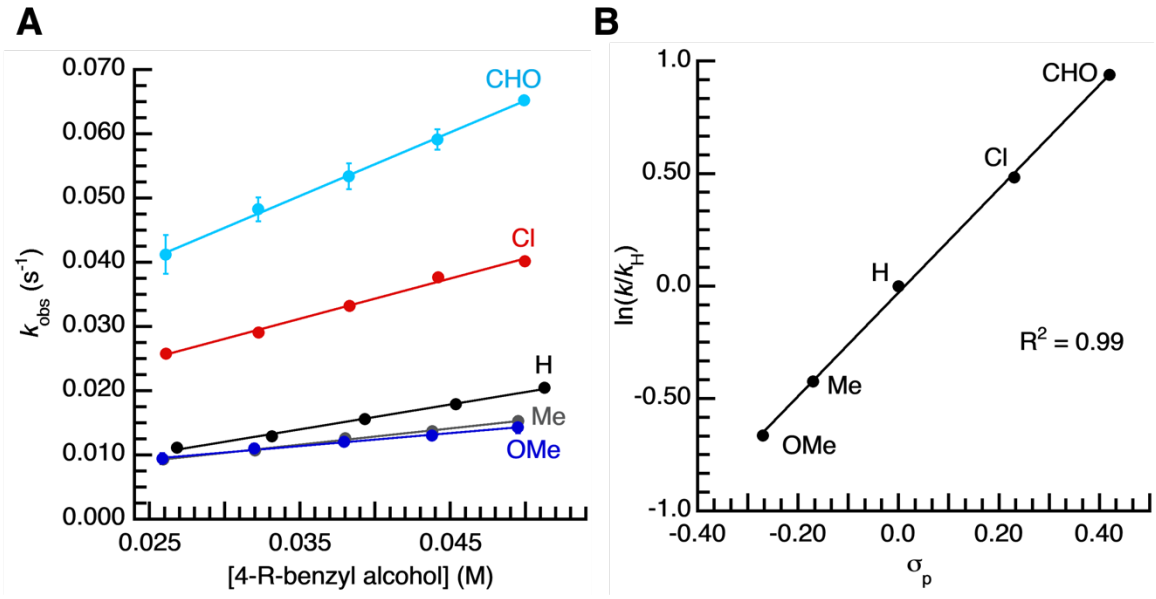


Figure S5: (A) Plot of k_{obs} vs. the concentration of 4-R-BzOH in DMF at –20 °C and (B) the corresponding Hammett plot.

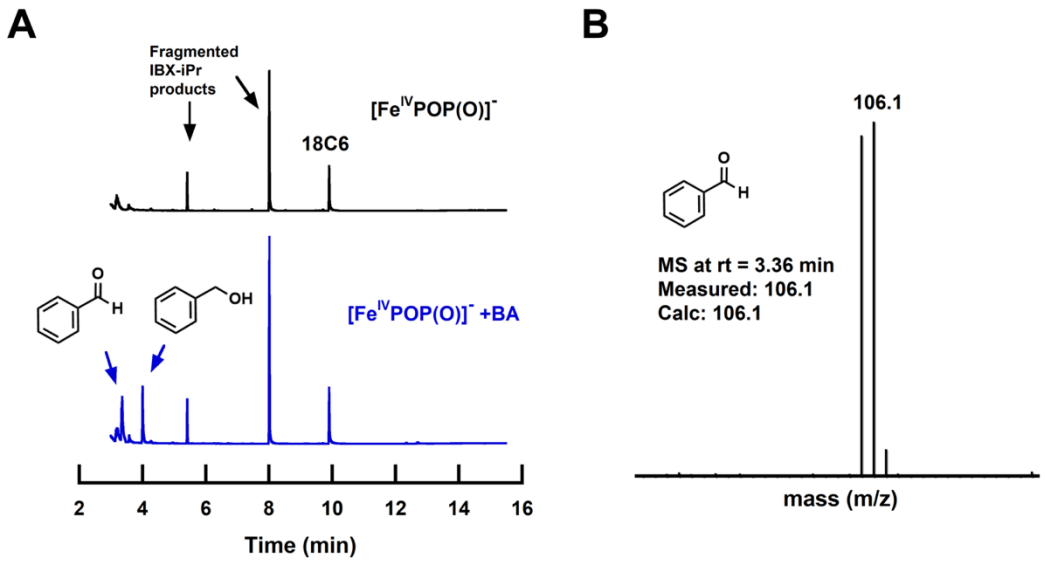


Figure S6. (A) Gas chromatograph of the organic products from the reaction of [Fe^{IV}pop(O)]$^-$ with BzOH (1:1) and (B) the corresponding mass spectrum at retention time (rt) 3.36 min in CH_2Cl_2.

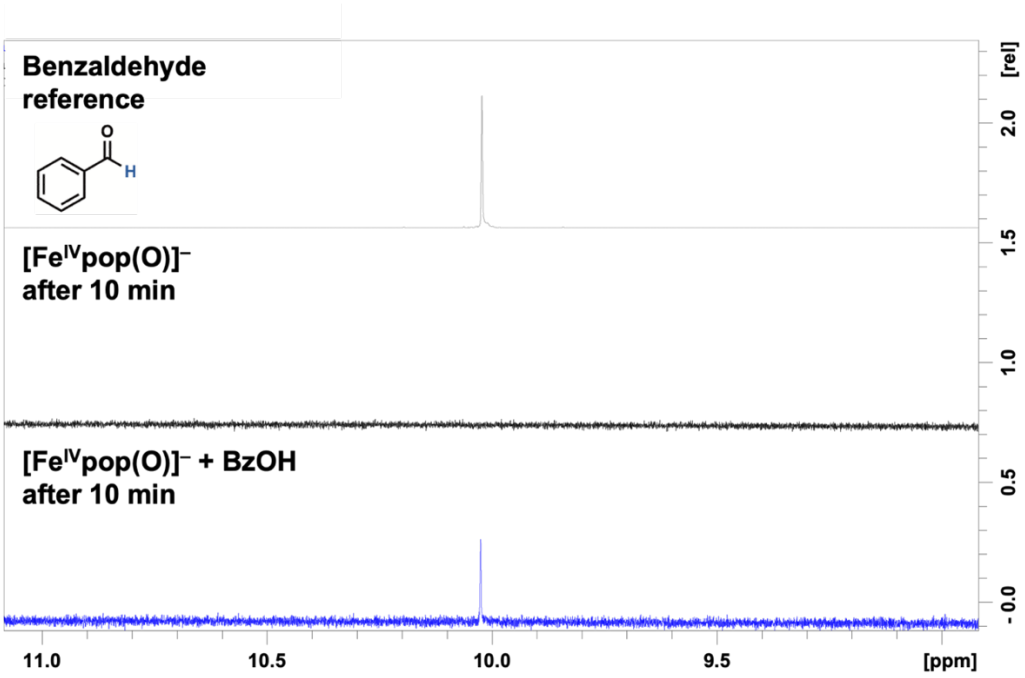


Figure S7. ^{1}H NMR spectrum in d_6-DMSO of an authentic sample of benzaldehyde (grey), the extracted organic product from the reaction of $[Fe^{IV}pop(O)]^-$ without BzOH (black), and the extracted organic product from the reaction of $[Fe^{IV}pop(O)]^-$ with BzOH (1:1) (blue).

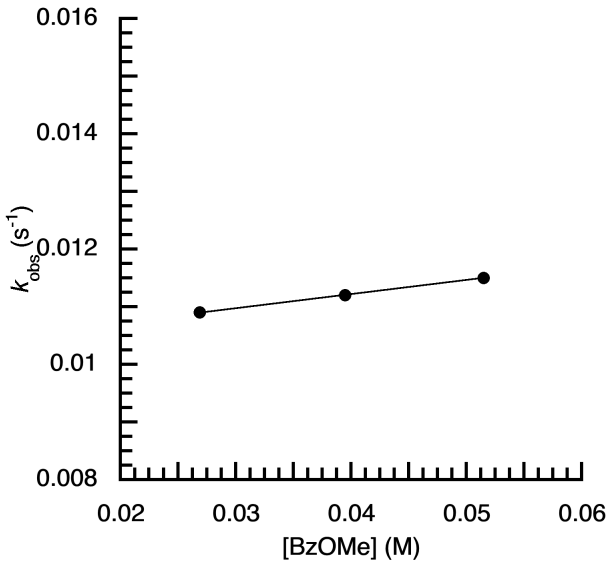


Figure S8. Plot of k_{obs} vs. the concentration of BzOMe in DMF at –20 °C.

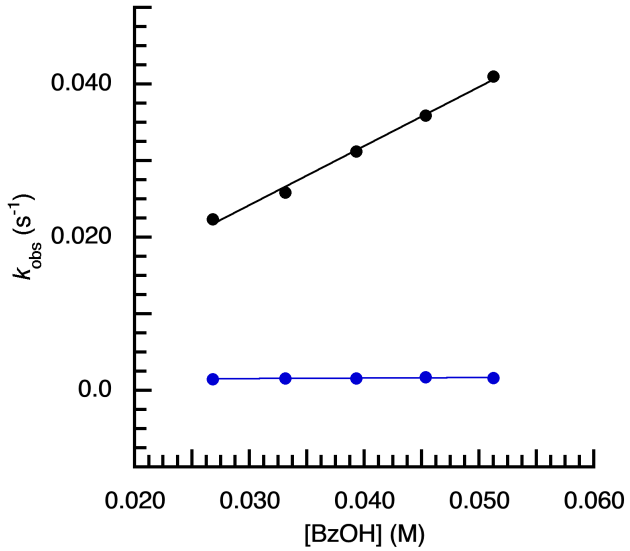
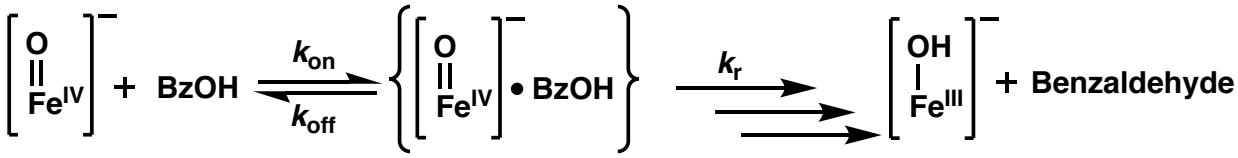


Figure S9. Plot of k_{obs} vs. the concentration of BzOH in DMF at –20 °C using either $[Fe^{IV}pop(O)]^-$ (black) or $[Fe^{IV}pop(O)]^-$ or $[Fe^{IV}poat(O)]^-$ (blue) as the oxidant.



Scheme S1. Expression for the proposed pre-equilibrium between the Fe^{IV}–oxido complex and substrate.

Table S1. Second order rate constants (k) and the corresponding substituent constant (σ) for each respective *para*-substituted benzyl alcohol.

R	k **($M^{-1}s^{-1}$)**	σ
OMe	0.100	-0.27
Me	0.127	-0.17
H	0.193	0
Cl	0.314	0.23
CHO	0.495	0.42

Table S2. Crystallographic Information for $\{K[Fe^{II}pop(OH_2)]\}_2$

Complex	**$\{K[Fe^{II}pop(OH_2)]\}$**
Empirical Formula	$C_{84}H_{86}Fe_2K_2N_8O_{20}P_6$
Fw	1903.32
T (K)	133(2)
Crystal System	Triclinic
Space Group	$P\bar{1}$
a (Å)	14.427(3)
b (Å)	16.428(3)
c (Å)	20.699(4)
α (º)	99.145(2)
β (º)	98.055(2)
γ (º)	111.423(2)
V ($Å^3$)	4402.8(13)
Z	2
δ_{calcd} (Mg/m^3)	1.436
GOF on F^2	1.038
R1	0.0392
wR2	0.1080