Supporting Information for

Mechanism of Alcohol Oxidation by $Fe^{V}(O)$ at Room Temperature

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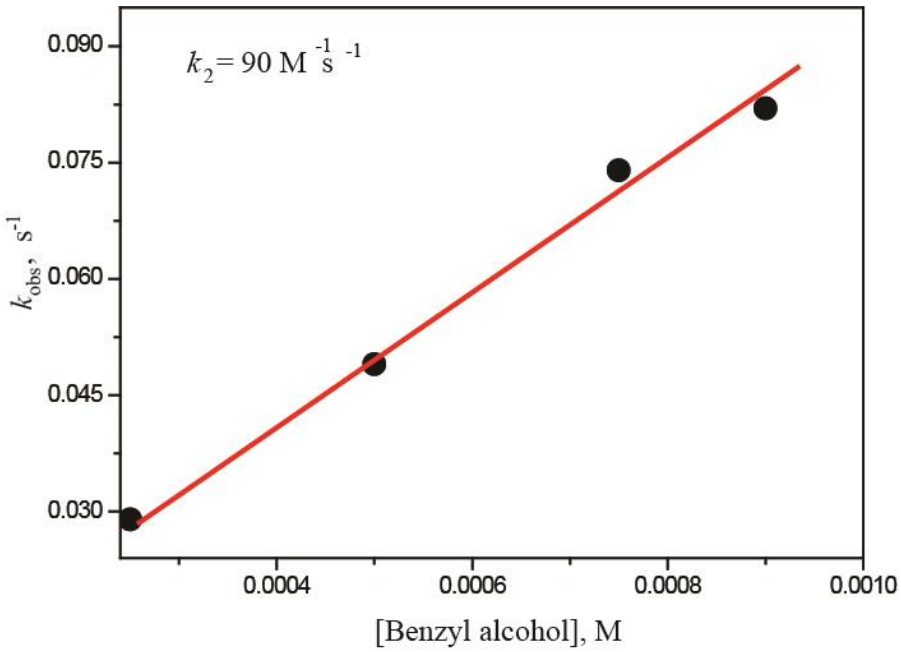
[≠] Indicates equal contribution



Fiugure SI 1 Plot of k_{obs} against the concentration of benzyl alcohol to determine the second-order rate constant

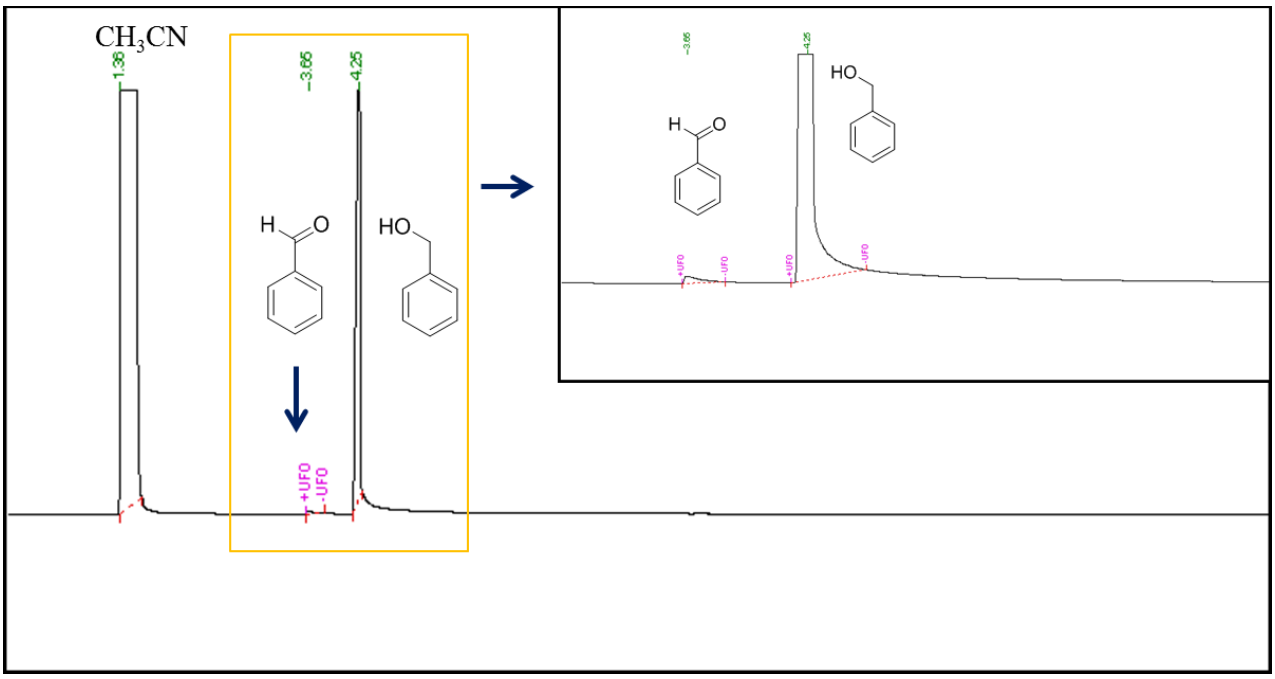
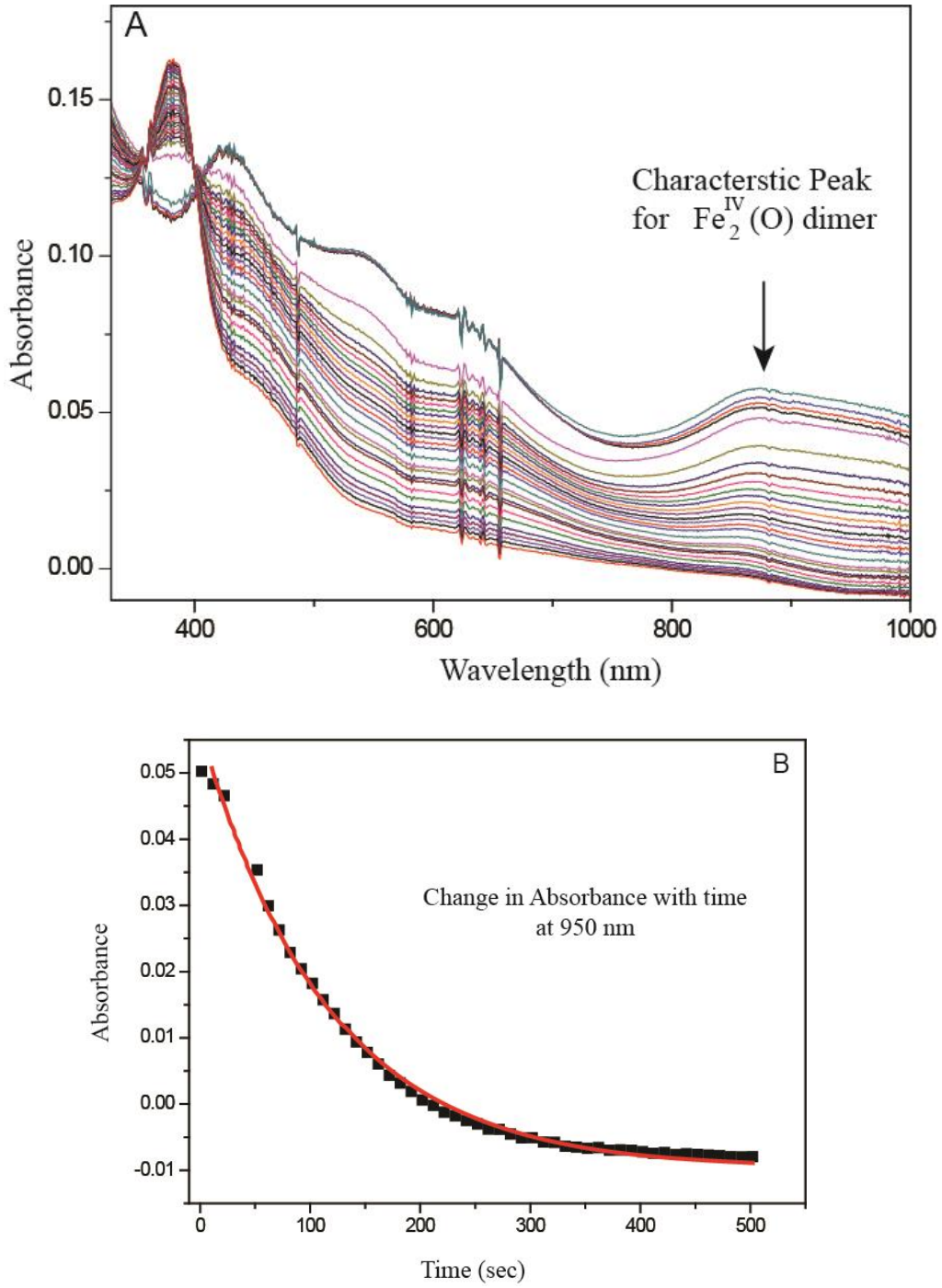


Figure SI 2 GC chromatogram of reaction with 500 equiv benzyl alcohol with $Fe^{V}(O)$ (5 x 10^{-5} M) benzaldehyde R_t = 3.6 and benzyl alcohol R_t = 4.25



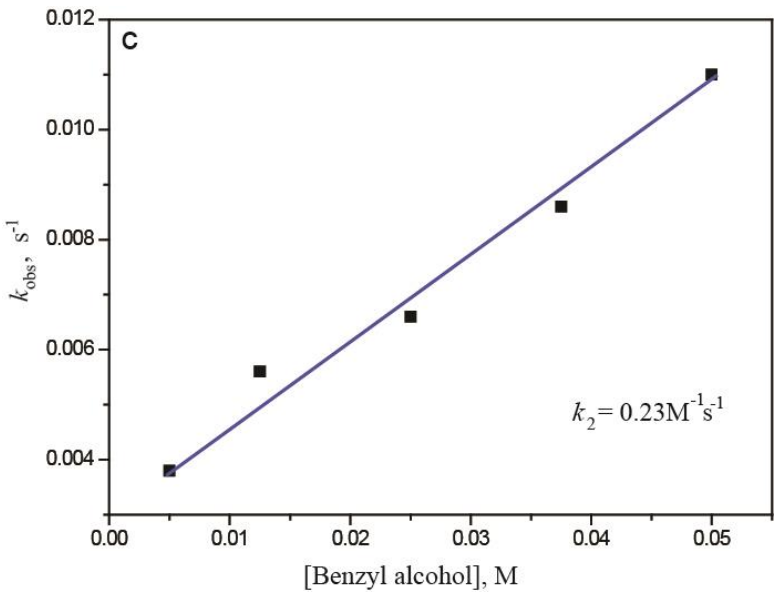


Figure SI 3 **(A)** Uv-vis spectral changes upon reaction of μ-oxo-Fe^{IV} dimer (5 x 10^{-5} M) with benzyl alcohol (2.5 mM). **(B)** Absorbance *vs* time plot at 950 nm for reaction of μ-oxo-Fe^{IV} dimer (5 x 10^{-5} M) with benzyl alcohol (2.5 mM) to determine $k_{obs.}$ **(C)** Plot of k_{obs} against the concentration of benzyl alcohol's to determine the second-order rate constant for reaction of μ-oxo-Fe^{IV} dimer (5 x 10^{-5} M) with benzyl alcohol (2.5 mM).

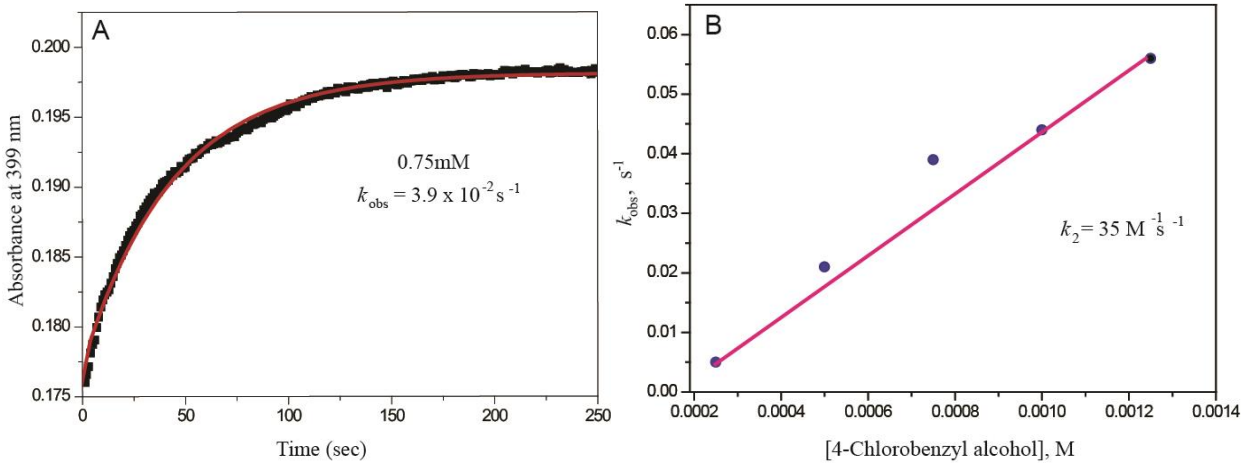


Figure SI 4 Absorbance at 399 nm *vs* time to determine k_{obs} of **(A)** 4-Chlorobenzyl alcohol oxidation (0.75 mM, 15 equiv.) Red line is the first order fit according to the equation [($A_t = A_\alpha - (A_\alpha - A_0)e^{-k_{obs}t}$)]. **(B)** Plot of k_{obs} against the concentration of 4-chloro benzyl alcohol to determine the second-order rate constant.

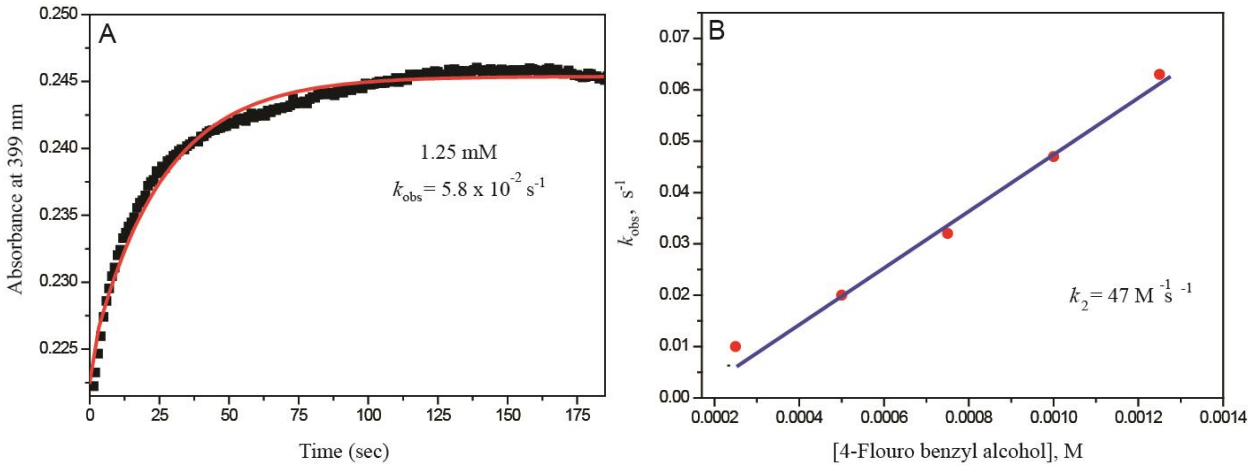


Figure SI 5 Absorbance at 399 nm *vs* time to determine k_{obs} of **(A)** 4-Fluoro benzyl alcohol oxidation (1.25 mM, 25 equiv). Red line is the first order fit according to the equation [($A_t = A_\alpha - (A_\alpha - A_0)e^{-k_{obs}t}$)]. **(B)** Plot of k_{obs} against the concentration of 4-Fluoro benzyl alcohol to determine the second-order rate constant

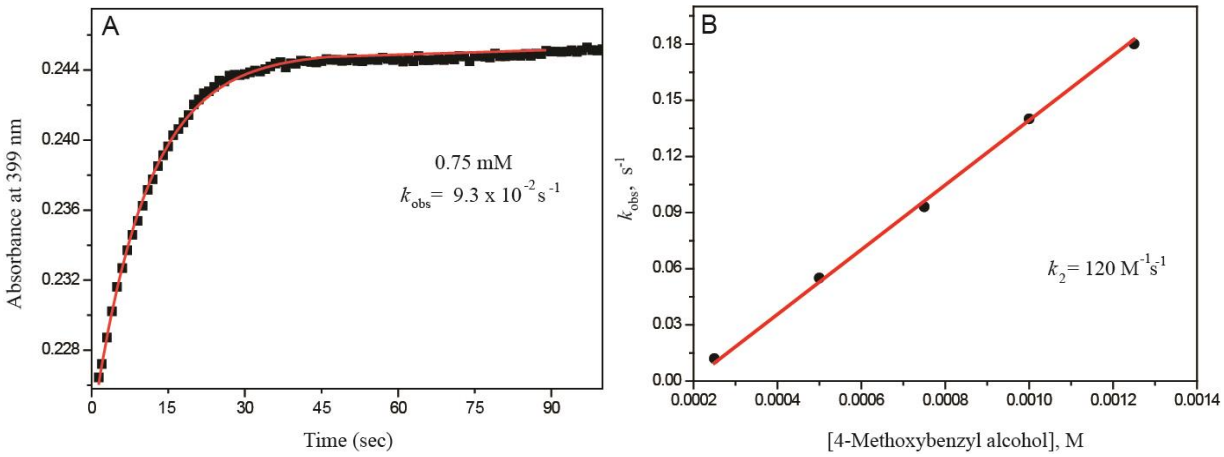


Figure SI 6 Absorbance at 399nm *vs* time to determine k_{obs} of **(A)** 4-Methoxy benzyl alcohol oxidation (0.75 mM, 15 equiv). Red line is the first order fit according to the equation [($A_t = A_\alpha - (A_\alpha - A_0)e^{-k_{obs}t}$)]. **(B)** Plot of k_{obs} against the concentration of 4-Methoxy benzyl alcohol's to determine the second-order rate constant.

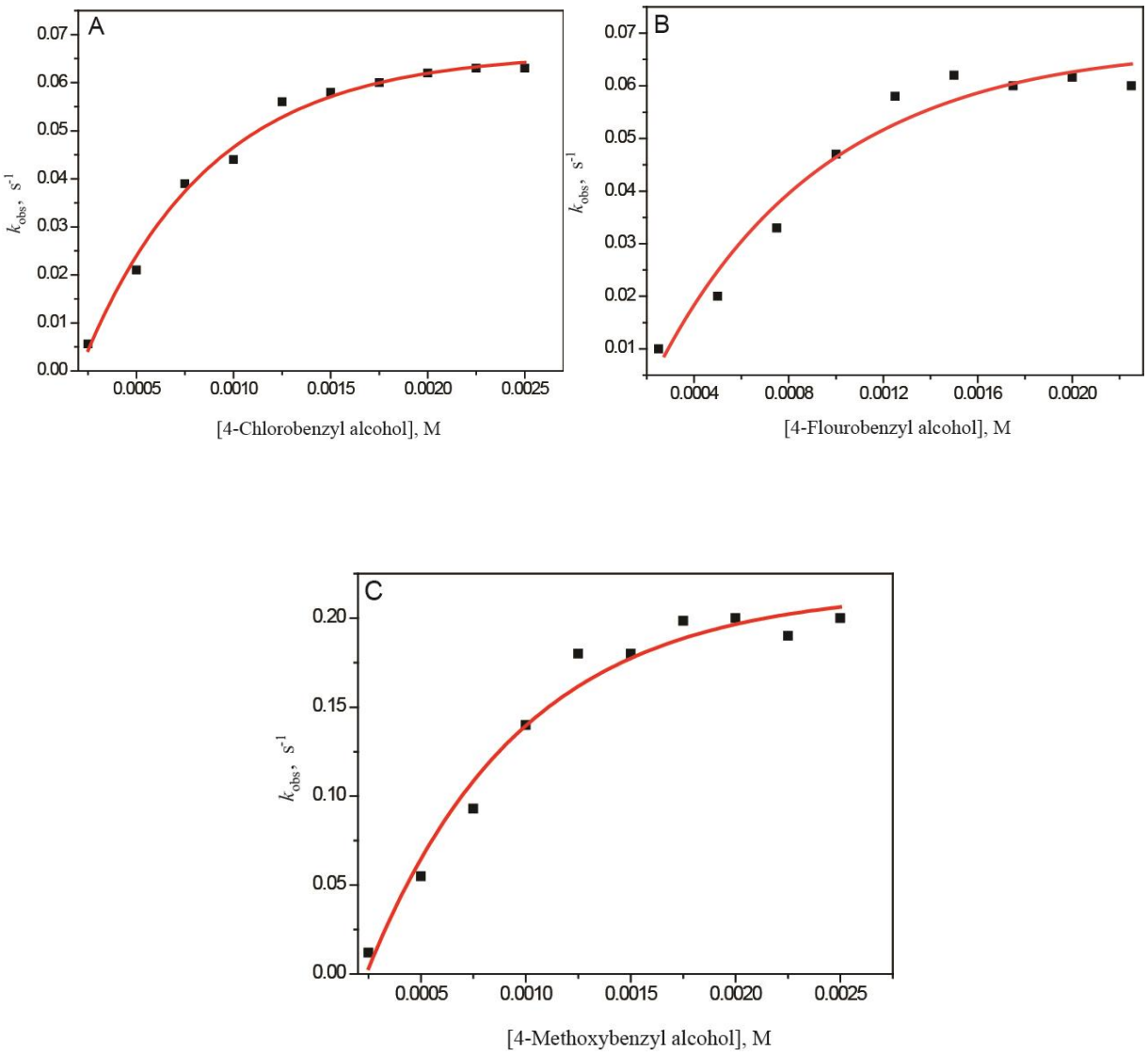


Figure SI 7 Plot of k_{obs} vs substrate to determine the binding constant *K* and first order rate constant *k*. **(A)** Chlorobenzyl alcohol **(B)** Flourobenzyl alcohol **(C)** Methoxybenzyl alcohol

Substituents	Equilibrium constant $K(M^{-1})$	Rate constant $k(s^{-1})$	k_2 ($M^{-1}s^{-1}$) (experimentally determined)
-OMe	300 ± 15	0.52 ± 0.020	120 ± 10
-F	300 ± 21	0.19 ± 0.008	47 ± 5
-Cl	350 ± 20	0.14 ± 0.004	35 ± 5

SI Table Equilibrium constant (*K*), Rate constant (*k*) and second order rate constant of substituted benzyl alcohols

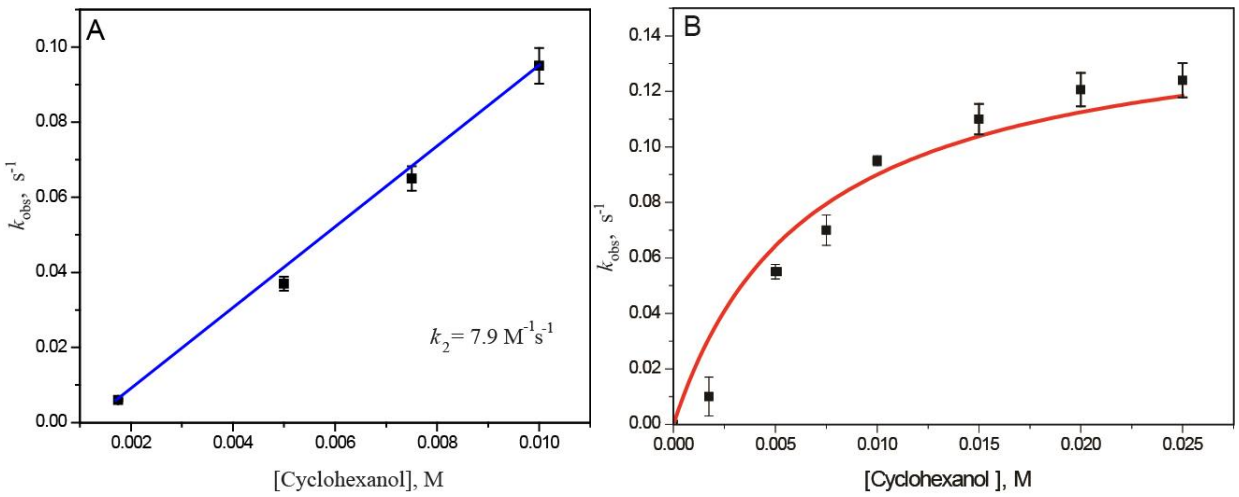


Figure SI 8 (A) Plot of k_{obs} against the concentration of cyclohexanol to determine the second-order rate constant. **(B)** Plot of k_{obs} vs substrate to determine the binding constant *K* and first order rate constant *k* for oxidation of cyclohexanol

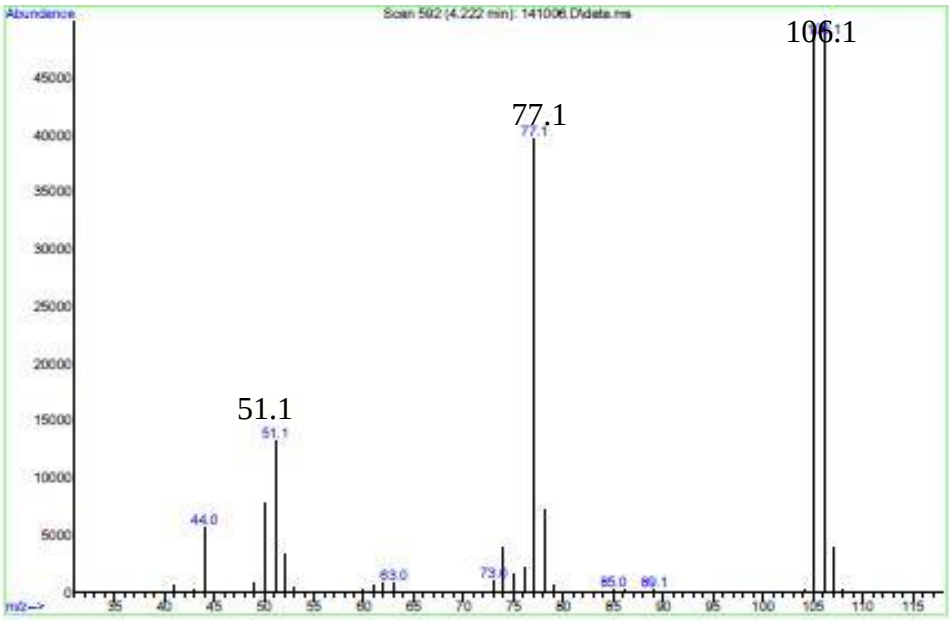


Figure SI 9 GC-MS data for the formation of benzaldehyde product when benzyl alcohol oxidation was carried out with $Fe^{V}(^{16}O)$.

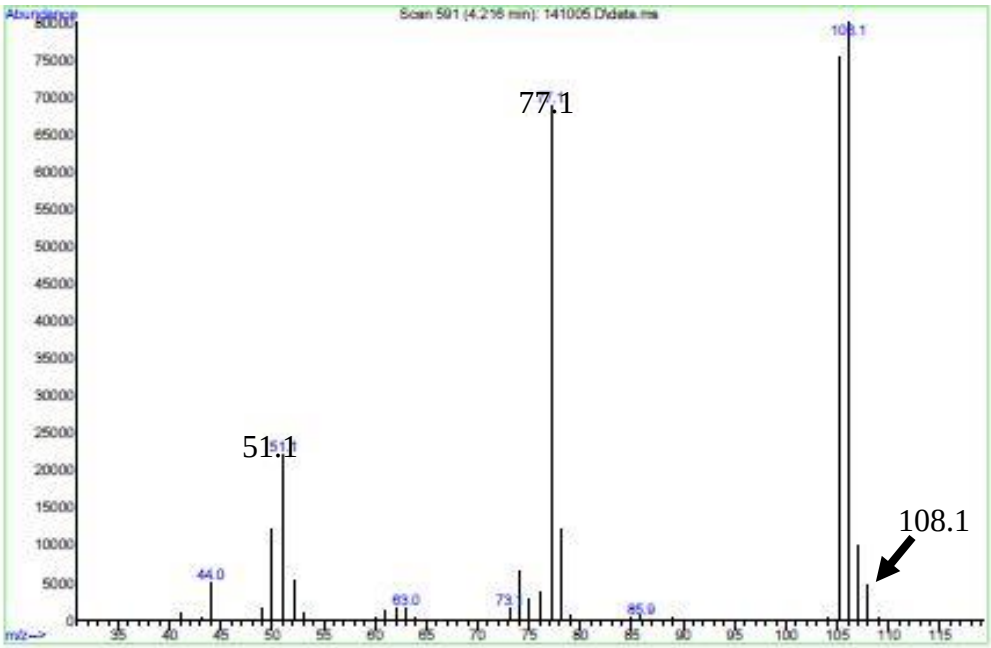


Figure SI 10 GC-MS data showing <5% incorporation of ^{18}O in benzaldehyde product when benzyl alcohol oxidation was carried out with $Fe^{V}(^{18}O)$.

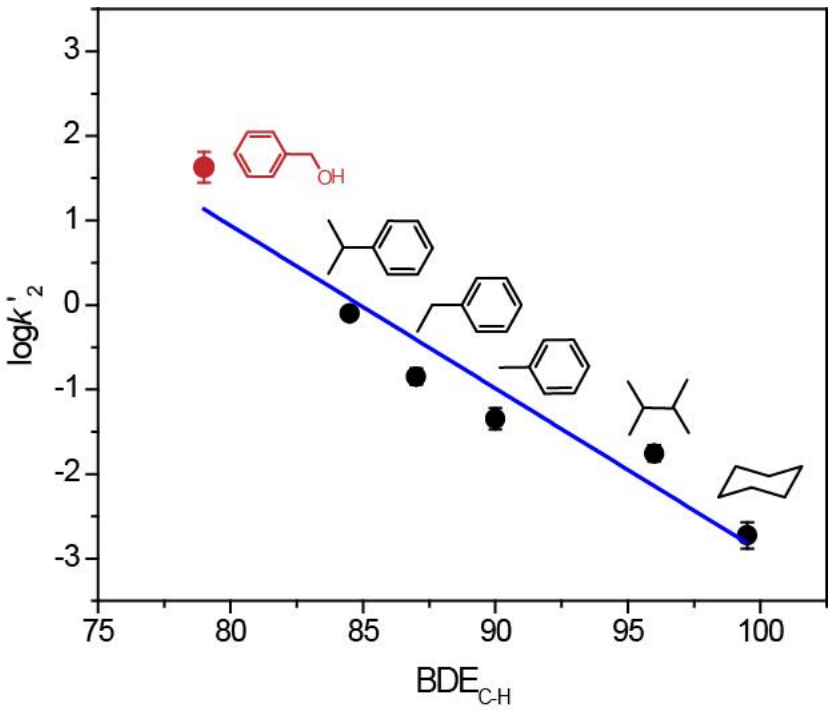


Figure SI 11 logk'_2 vs BDE_{C-H} of various hydrocarbons for the reaction with $Fe^{V}(O)$. The substrates represented with black circles have been published earlier by us.[21] Benzyl alcohol (this work) is represented with a red circle.