

Supporting Information for Kinetics of an Air and Water Stable Ruthenium(IV) Catalyst
for the Deprotection of Allyl Alcohol

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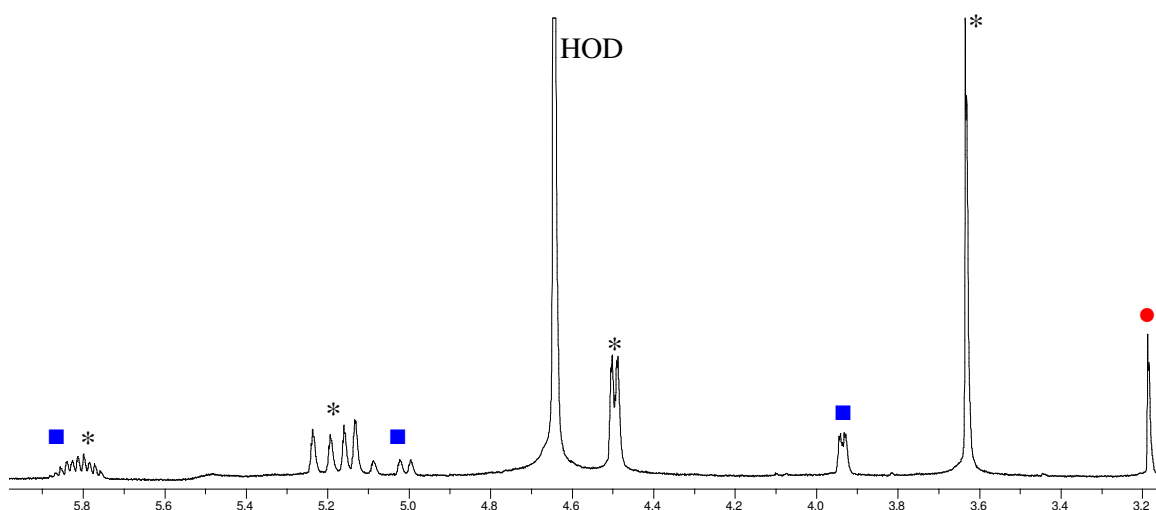


Figure S1. ^1H -NMR spectrum of partially converted allyl methyl carbonate. The resonances marked with * are due to allyl methyl carbonate, with ● are due to methanol and with ■ are due to allyl alcohol.

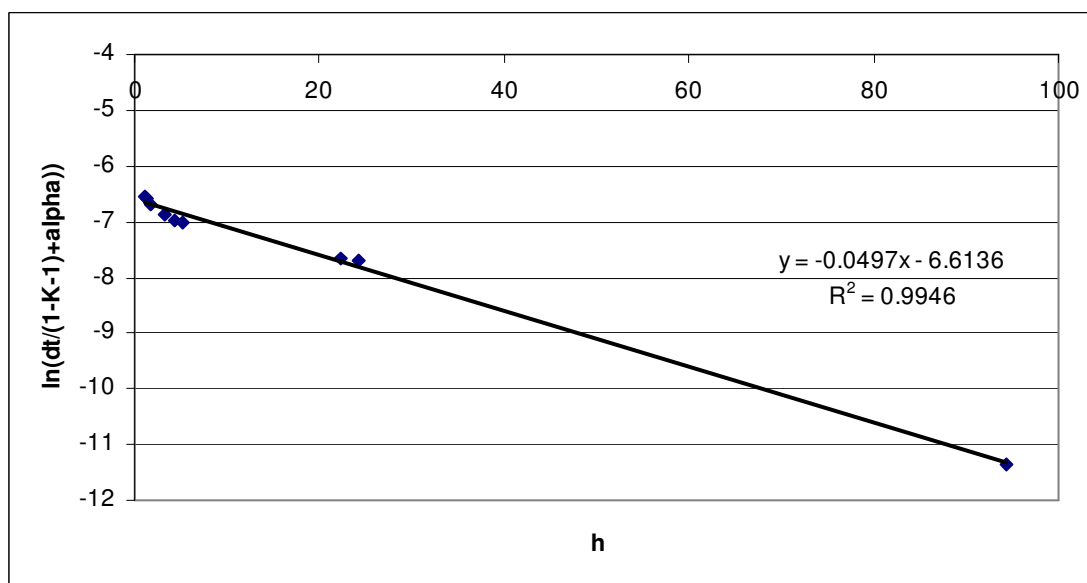


Figure S2. Slow approach to equilibrium (eq S3; from Espenson, Chemical Kinetics and Reaction Mechanisms) of the reaction shown in eq S1, R=H. Thermodynamic data extracted from plot using eqs S1-S3: $K_{\text{eq}} = 0.0075$; $\Delta G^\circ = 2.90$ kcal/mol; $[4]_e = 0.0047\text{M}$; $[\text{RuII}]_e = 0.0027\text{M}$; $[\text{allyl alcohol}]_e = 0.0027\text{M}$; $[\text{D}_2\text{O}]_e = 0.48\text{M}$, $\alpha = 1.1898$.
 $k_1 = 0.0116 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$ and $k_{-1} = 1.54 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$

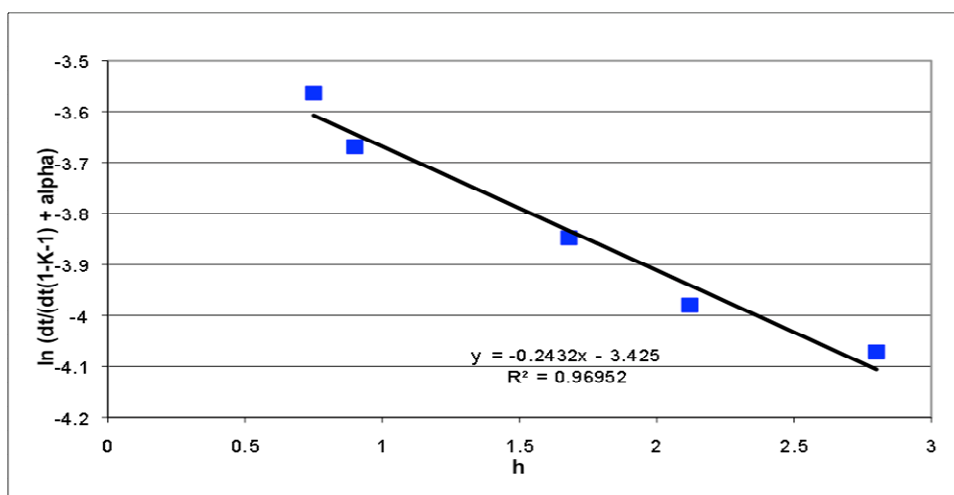
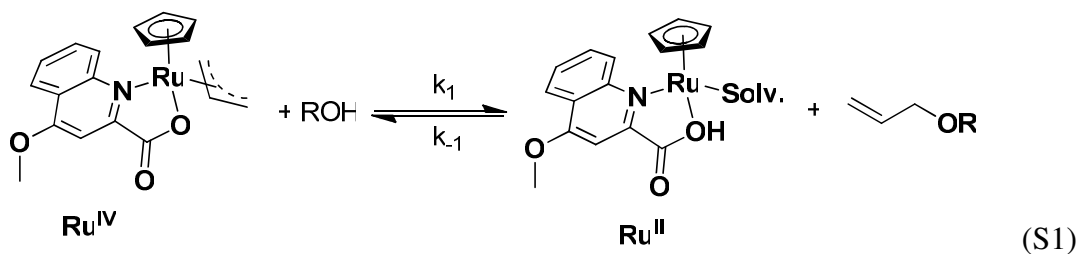


Figure S3. Slow approach to equilibrium of **4** and CD₃OD in acetone-d₆.

Thermodynamic data extracted from plot using eqs S1-S3 (R=CD₃): $K_{eq} = 0.0828$; $\Delta G^\circ = 1.45$ kcal/mol; $[4]_e = 0.0042$ M; $[Ru^{II}]_e = 0.0057$ M; [allyl methyl ether]_e = 0.0057 M; $[CD_3OD]_e = 0.0933$ M, $\alpha = 0.2341$. $k_1 = 0.238 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ and $k_{-1} = 2.87 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$



$$[A] = [A]_e + \delta \quad (S2)$$

$$\ln \left\{ \frac{\delta_t}{\delta_t(1 - K^{-1}) + \alpha} \right\} = -k_1 \alpha t + C \quad (S3)$$

where $\alpha = [Ru^{IV}]_e + [ROH]_e + K^{-1}([Ru^{II}]_e + [\text{allyl alcohol/ether}]_e)$

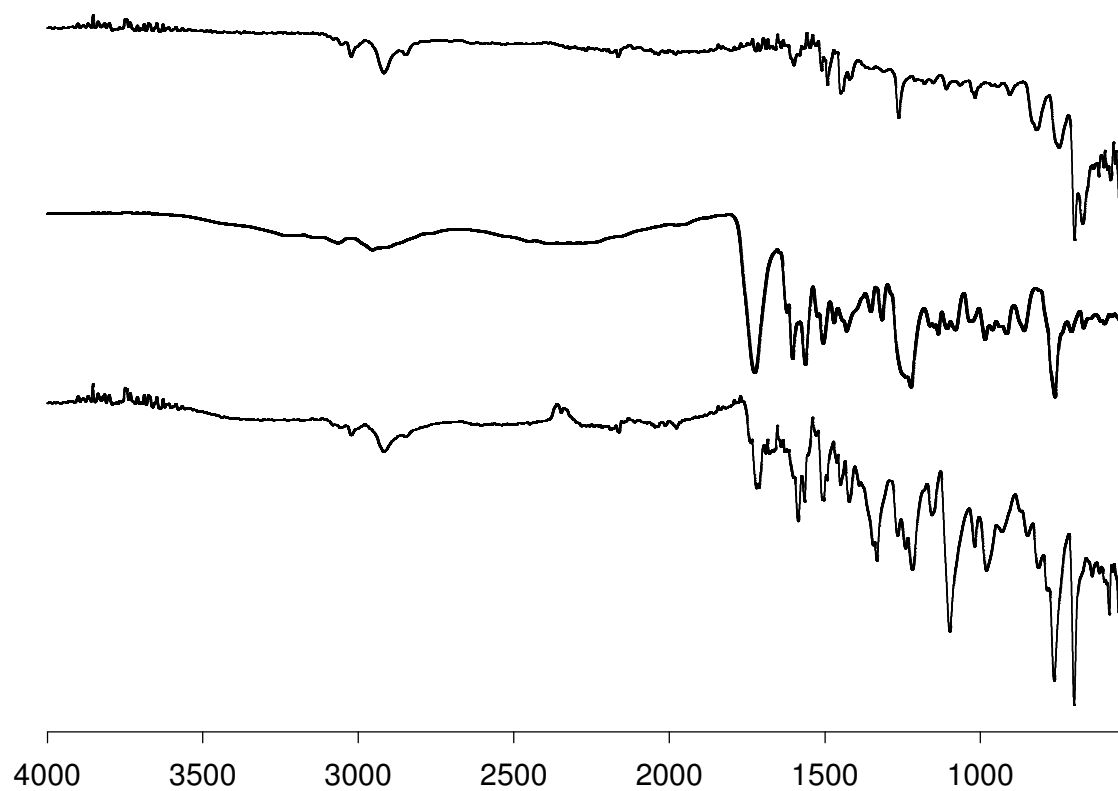


Figure S4. IR spectra of A) IR spectrum of Merrifield's peptide resin, 1% crosslinked B) **3**, and C) **PS-3**.

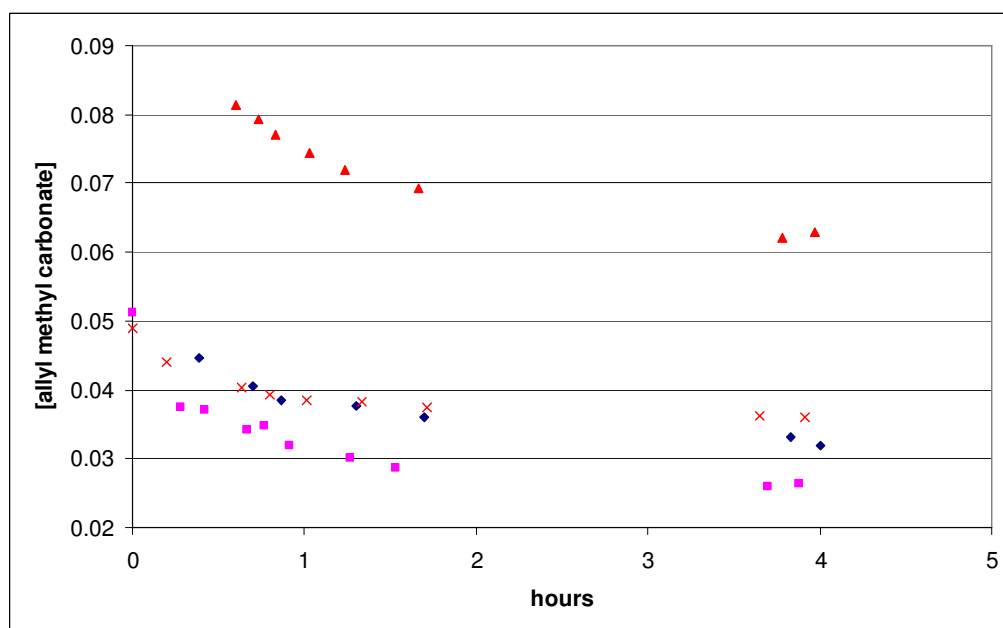


Figure S5. Plot of [allyl methyl ether] versus hours. Initial reaction conditions, all reactions under air in methanol-d₄:

- (▲) [4] = 1.8 mM, [allyl methyl carbonate] = 100 mM, [allyl methyl ether] = 0.0 M;
- (X) [4] = 1.8 mM, [allyl methyl carbonate] = 49 mM, [allyl methyl ether] = 0.0 M;
- (◆) [4] = 3.6 mM, [allyl methyl carbonate]_o = 51 mM, [allyl methyl ether]_o = 0.274 M;
- (■) [4] = 3.6 mM, [allyl methyl carbonate]_o = 51 mM, [allyl methyl ether]_o = 0.0 M;