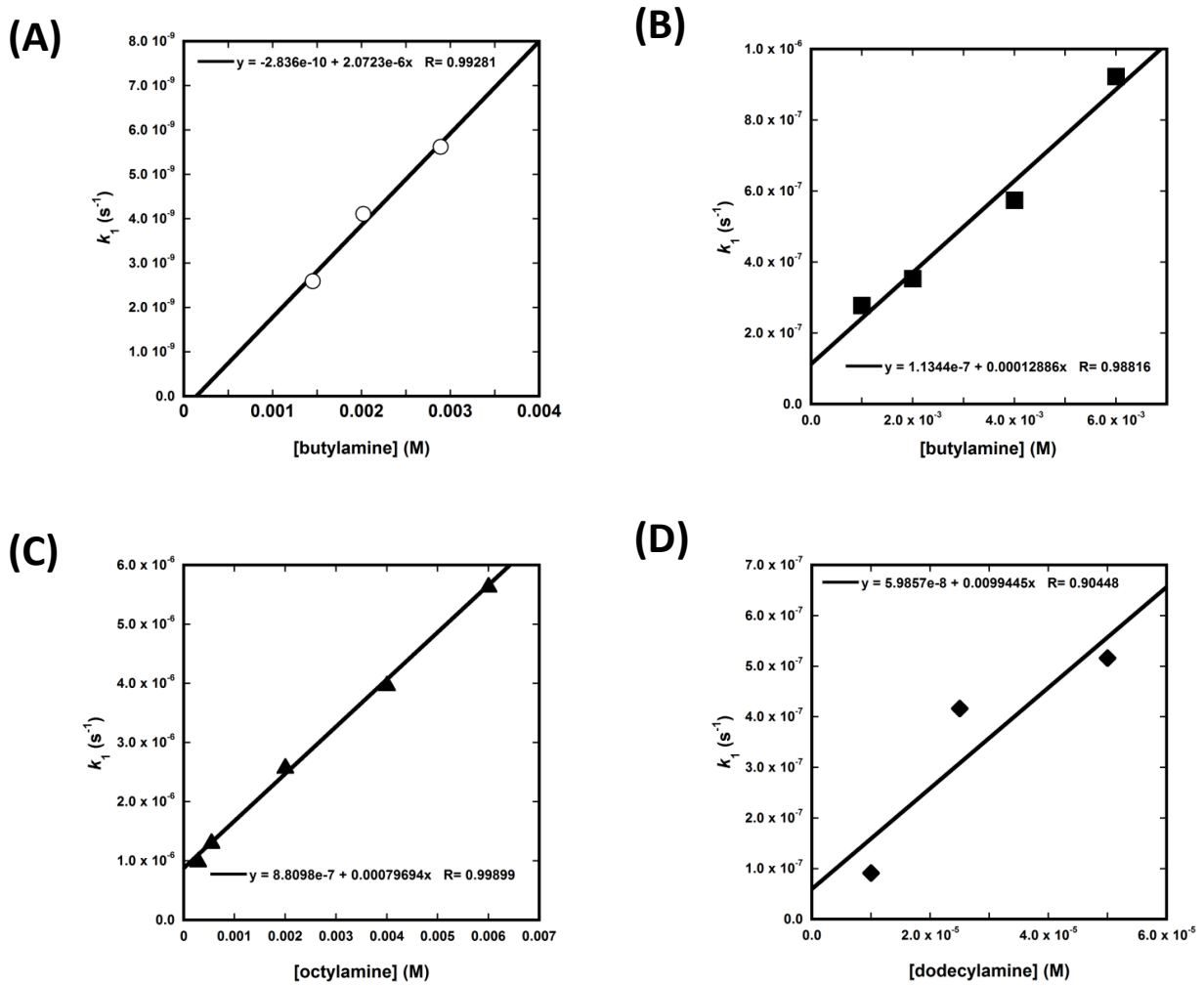
Electronic Supplementary Information for

The effect of the hydrophobic environment on the retro-aldol reaction: Comparison to a computationally-designed enzyme

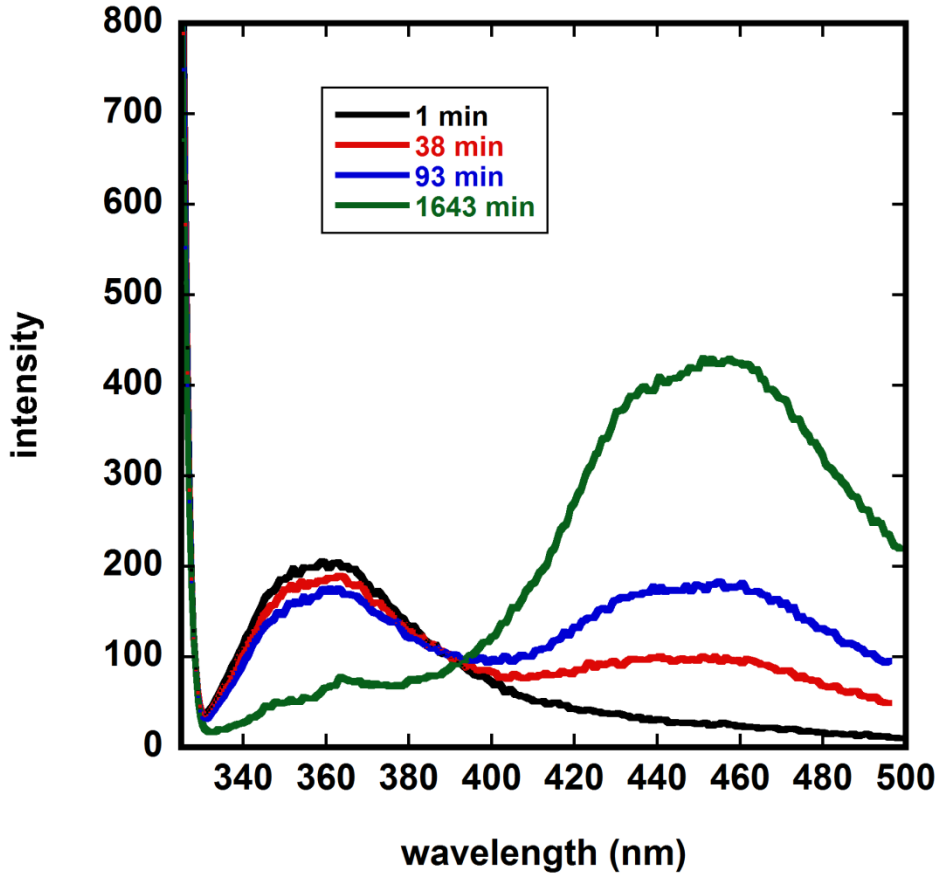
Joshua Schmidt,[a] Clayton Ehasz,[a] Michael Epperson,[a] Kimberly Klas,[a] Justin Wyatt,[a] Mirko Hennig,[b] and Marcello Forconi*[a]

[a] College of Charleston, Department of Chemistry and Biochemistry, 66 George Street, Charleston, SC, 29424, USA. E-mail: forconim@cofc.edu. [b] Medical University of South Carolina, Department of Biochemistry and Molecular Biology, 70 President Street, Charleston, 29425, SC, USA.

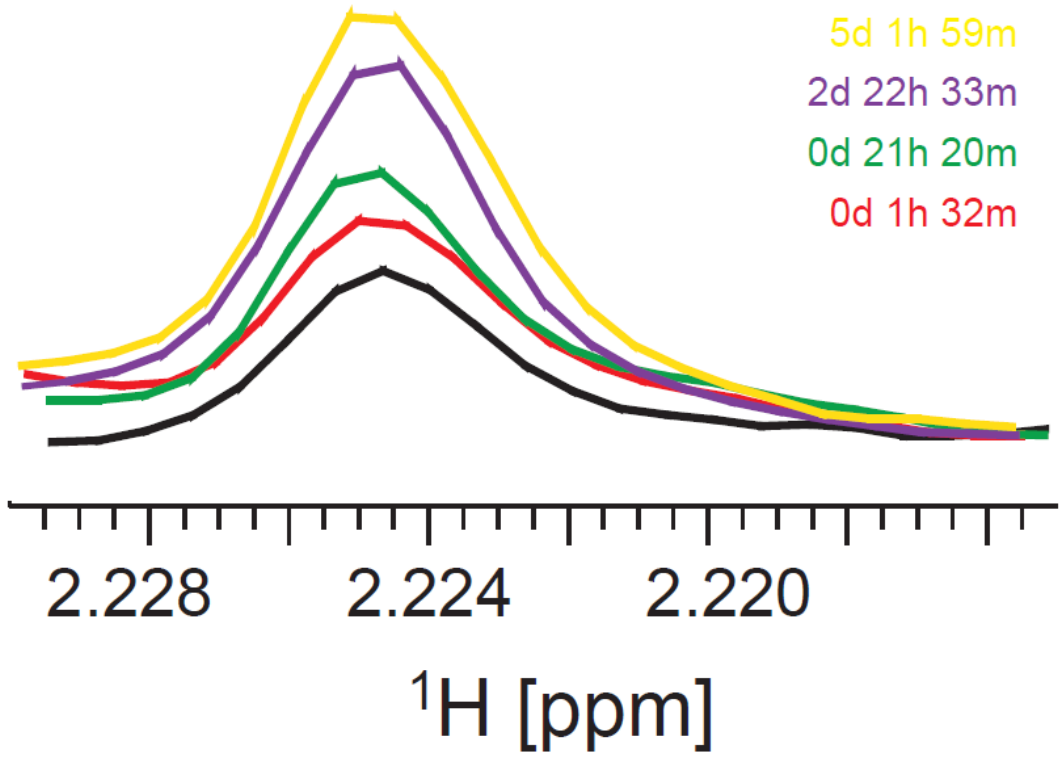
SUPPLEMENTARY FIGURE 1. Individual plots for the first order rate constant as a function of amine concentration for retro-aldol reactions carried out at pH 7.5 in the presence of 300 µM methodol. (A) butylamine; (B) butylamine and CTAC; (C) octylamine and CTAC; (D) dodecylamine and CTAC. Values obtained in CTAC were corrected for partial saturation of methodol. This correction changes the values by only two-fold.



SUPPLEMENTARY FIGURE 2. Typical evolution of fluorescence over time for retro-aldol reactions of methodol. Appearance of 6-methoxy-2-naphthaldehyde was monitored with excitation at 330 nm and emission at 452 nm, as described in Experimental.



SUPPLEMENTARY FIGURE 3. NMR spectra of reactions of 4-hydroxy-4-methyl-2-pentanone (HMP) in the presence of 1.0 mM CTAC and 4.0 mM butylamine at pH 7.5, zoomed at the acetone peak. To avoid excessive crowding, only every second time point is reported. The black line represents the spectra before addition of HMP; the small quantity of acetone present in this condition is probably due to residual acetone in the reaction vessel.



SUPPLEMENTARY FIGURE 4. Observed rate constant for retro-aldol reaction of methodol at pH 7.5 in the presence of 4 μM bovine serum albumin (BSA). The two symbols represent two different replicates for the reaction. The second-order rate constant (k_{cat}/K_M) was calculated using points at low substrate concentration. Apparent saturation could be due to methodol solubility, rather than enzyme saturation, as previously observed (see reference 8).