

Text S6. Calculation of Electrostatic Contribution to Catalysis.

The slope of the dependence of phenolate affinity on pK_a (Figure 10) can be used to calculate the total electrostatic contribution to catalysis, which equals $10^{\text{slope} * (pK_a^{TS} - pK_a^{GS})}$. The maximal pK_a difference between the ground state and the transition state is 16. The average slope (based on all four correlations above) was 0.05 ± 0.10 , giving a maximum slope of 0.15, which would translate into a 250-fold rate enhancement. Similarly, the minimum slope of -0.05 would translate into a 6-fold barrier to catalysis. Also, the phenolates probed in Figure 10 spanned only ~ 2 pK_a units, so any nonlinearity over the larger pK_a difference between the ground state and transition state could lead to larger or smaller effects, although there was no indication of a significant change in slope over the extended pK_a range investigated with the *ortho*-F substituted phenolates (Figure S3).