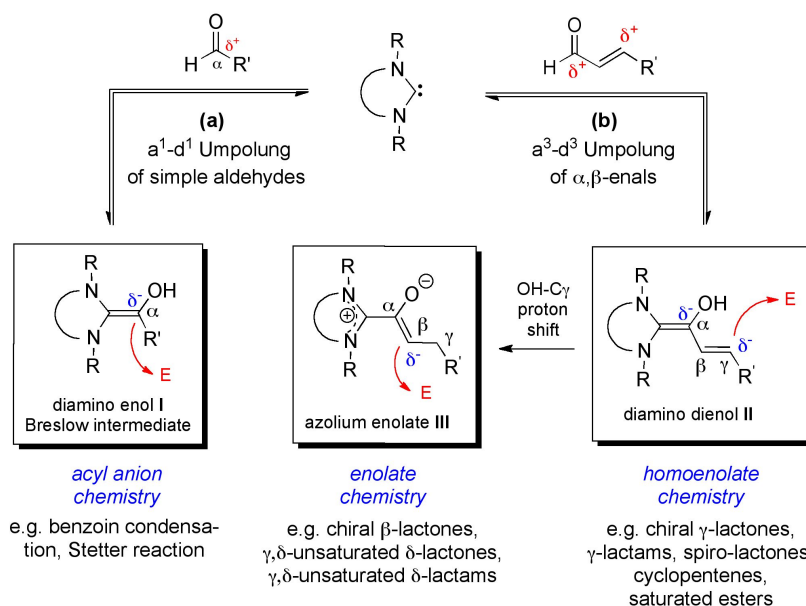


Carbene Catalysis and the Breslow Intermediate

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Both in B₁-enzymes and in organocatalytic Umpolung, catalysis by N-heterocyclic carbenes hinges on the formation of the so-called Breslow-intermediates [(di)amino enols] **I** (Scheme, reaction a), in which the innate polarity of e.g. an aldehyde substrate is inverted from electrophilic to nucleophilic. In the related a³-d³ Umpolung ("conjugate Umpolung"; Scheme, reaction b), the diamino dienol **II**, a homoenolate equivalent, is assumed to be pivotal. OH-C γ proton shift in the diamino dienol **II** leads to the azolium enolate **III**, an enolate equivalent. The lecture will report the generation and characterization, by NMR and X-ray crystal structures, of intermediates **I-III** and their transformations which support the reactivity patterns shown in the Scheme.



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