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Umpolung by N-Heterocyclic Carbenes: Generation and Reactivity of the Elusive 2,2-Diamino Enols (Breslow Intermediates)
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Organo- and Biocatalysis

Key words
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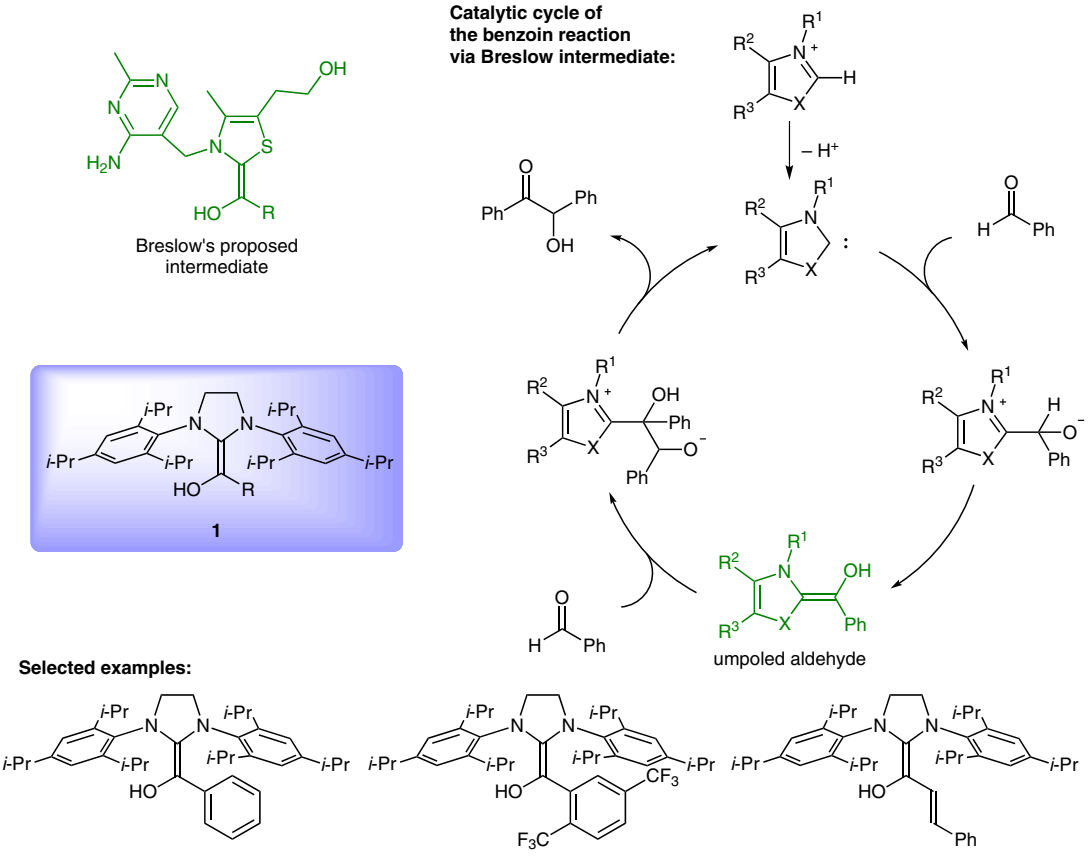
NMR Characterization of Breslow Intermediates



Significance: The generation of 2,2-diamino enols **1** from the corresponding N-heterocyclic carbenes and aldehydes has been reported. Species like **1** are commonly invoked as intermediates in aldehyde-umpolung reactions such as the benzoin reaction, and are known as Breslow intermediates. Different Breslow intermediates were characterized by NMR methods for the first time, and are shown to possess the expected benzoin reactivity.

Comment: In 1958, Breslow proposed that thiamine-mediated reactions in biochemistry rely on carbene reactivity and invoked the intermediates that today bear his name (*J. Am. Chem. Soc.* **1958**, *80*, 3719). In the current report the identification of relatively unreactive Breslow intermediates such as **1** by combination of aromatic aldehydes with a saturated carbene was crucial for making the intermediates detectable. More common Breslow intermediates with unsaturated N-heterocyclic carbenes remain to be characterized. For a previous characterization of aza analogues of Breslow intermediates, see: *J. Am. Chem. Soc.* **2012**, *134*, 6143.

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