

## Abstract

In this work, the first successful generation of *aromatic* Breslow intermediates was achieved by employing benzimidazolin-2-ylidenes as N-heterocyclic carbene component. The focus was on the preparation, characterization (NMR, X-ray) and reactivity of these diamino enols, derived from the reaction of aromatic benzimidazolin-2-ylidenes and various aldehydes, is reported. Additionally, the annulation of various enals and electrophilic imine catalyzed by bis-Mes/Dipp-substituted benzimidazolium salts *via* reactive homoenolate selectively provided the diastereomeric  $\gamma$ -lactams. The *N*-substituents play an important role for the *cis* and *trans* selectivity in the lactam formation. The lactam formation utilizing these catalysts is also tolerant to a diverse range of solvents. Mes-disubstituted benzimidazolium salt catalyzed this transformation affording lactams in good yields (up to 85% yield, dr up to 5:1 in favor of the *cis*-isomer) whereas Dipp-disubstituted provided the desired product with up to 86% yield and up to 1:14 dr in favor of the *trans*-isomer. Furthermore, the novel electron-deficient NHC precursors, bearing C<sub>6</sub>F<sub>5</sub> or 3,5-bisCF<sub>3</sub>Ph groups which are attached on nitrogen atoms next to the carbene center, were prepared. These new salts were employed for the NHC-catalyzed generation of  $\gamma$ -butyrolactones however, they did not give promising results.