Activation of carbonyl compounds with chiral amines by formation of either an enamine or an iminium ion opens up various possibilities in the field of asymmetric catalysis [1, 2]. Existing catalyst families are based on proline or imidazolidinone structures. Selectivity in the formation of either an (E)- or (Z)- enamine/iminium ion is essential for an enantioselective course of the reaction. In addition, the attack of the activated species is envisioned to proceed in a chiral environment to obtain high enantioface differentiation.

In this work, the synthesis of chiral amines based on the octahydromethanoisoindol-backbone 1 was realized. Catalyst design required geminal α-dimethylation to direct the enamine or iminium ion selectively to (E)-formation.

To achieve this new amine synthesis, the lactam motif of a currently used hydrogen-bond donating catalyst precursor 2 [3] was protected. After activation, dimethylation with a methyl cerium reagent [4] and subsequent deprotection, secondary amines were obtained in good yields. Installation of catalytic active or sterical demanding entities gave either bifunctional catalysts 3 or a sterical demanding amine 4 for covalent catalysis.