

# The synthesis of structurally complex allylic amines, alcohols and carbamates by dual photocatalysis

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The main goal of the project was devoted to the development of a convenient strategy for the preparation of complex allylic systems, particularly allylic alcohols and allylamines, bearing aliphatic substituents. The second task was concerned on a regioselective functionalization of an internal double bond of allylamines.

The modular strategy of synthesis of complex allyl systems (allyl alcohols, allylamines and derivatives) starting from 3-bromoallyl alcohols and *N*-(3-bromoallyl)amines as a structural platform for a divergent functionalization was reported. Proposed method involved a dual photoredox/Ni-catalyzed cross-coupling reaction of the mentioned starting systems with various alkyl bromides. Further studies involved determination of possible variation of aliphatic part that can be introduced into allyl system, as well as variation of double bond substitution patterns and type of *O*- and *N*-substituents. Overall, the reaction showed excellent scope and chemoselectivity. Furthermore, this approach was employed to the synthesis of complex allyl carbamates, which were next subjected to Ichikawa reaction, a unique transformation to construct allyamine derivatives, especially nonracemic  $\alpha$ -*tert*-allylamines, with tetrasubstituted carbon stereogenic center. Their synthesis by other methods is highly challenging.

In the second part of research, the regioselective functionalization of allylamines' internal double bond was investigated. Application of Wacker oxidation of the obtained allylamines allowed for regioselective formation of  $\beta$ -amino ketones. This includes synthesis of challenging  $\beta$ -amino ketone motifs, which synthesis *via* common approaches, like Mannich or aza-Michael reaction, and enamine hydrogenation, is highly problematic or even impossible. Above this, hydroacylation and hydroesterification of allylamines was investigated.

Finally, an extraordinarily broad reaction scope of both cross-coupling and oxidation protocols allowed to employ them in synthesis of selected biologically relevant structures, such as direct precursors of drug compounds as well as alkaloids.