

Stereoselective S_N1 at Non-Classical Carbocation

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Nucleophilic substitution at sp³ carbon center is one of the most fundamental and common transformations in organic synthesis. While the stereochemical outcome for a S_N2 reaction proceeds with inversion of configuration, the unimolecular nucleophilic substitution S_N1 provides, in most cases, a racemic product in addition to potential elimination of a proton, as well as undesired hydride and alkyl rearrangements. Therefore, the control of the stereochemical outcome for a S_N1-type reactions remains very complex. Here, we intend to develop a predictable and reliable approach that would control the stereochemistry for a S_N1-type transformation, opening new avenues in stereoselective synthesis in acyclic systems through the use of non-classical carbocations.

We are proposing a strategy that would produce either inversion or retention of configuration for a given S_N1 reaction for the preparation of regio-, diastereo- and enantiomerically enriched acyclic products possessing several adjacent stereocenters. Then, we will use the well-known skeletal rearrangements of carbocations as an approach of molecular editing to create a new *stereodefined* C–C bond at a position remote from the original carbocation, with a complete stereocontrol, even in the presence of sensitive functional groups.