Project 2.1 Stereoselective dearomatization of nonactivated arenes via an „alkene walk" pathway: Rapid access to high-added value poly- and spirocyclic systems from readily available aromatic compounds

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Background:

Stereoselective dearomatizations, especially in non-activated arenes, allowing conversion of readily available planar aromatic compounds into three-dimensionally complex molecules with precise control of reaction site, regio- and stereoselectivity has long been an exciting challenge in organic synthesis. Due to their high resonance stabilization energy, dearomatizations of nonactivated arenes usually require the use of stoichiometric amounts of expensive and toxic transition metal activators or elevated temperatures and harsh reaction conditions. This makes achieving high stereoselectivity in these processes very difficult. In our approach aromatic substrates are initially transformed into highly active polyenes which can then further derivatized using the broad spectrum of well-established stereoselective reactions of alkenes and dienes conducted under mild reaction conditions, resulting in highly stereoselective dearomatizations. Further advantages of the method include high availability of substrates (in the case of chiral derivatives in both enantiomeric forms in high optical purity) and high chemo- and stereodiversity of the obtained products.

The candidate will be responsible for synthesizing of the starting materials and polyene intermediates, followed by an studies on their selective of transformations into variety of poly- and spirocyclic systems using selected literature protocols. The candidate will also be responsible for recording and interpreting spectral data, designing experiments, and preparing reports and materials for publications. Complementary theoretical studies on reaction mechanisms may be performed by the candidate or as part of a collaboration, depending on the scholar's interests.

Aim:

The aim of this research proposal is to establish a new methodology for the stereoselective dearomatization of nonactivated arenes via the virtually unexplored retro-ene reaction of in situ generated benzylic diazenes (a so called "alkene walk" process), and subsequent transformation of the so formed active polyene species into chiral poly- and spirocyclic molecules. As a result, a new and versatile tool for the synthesis of high-value organic molecules from cheap and readily available benzylic alcohols, halides, aldehydes (in combination with organometallics) and monosilyl diazenes will be added to the organic chemist's toolbox. Moreover, the possibility of synthesis of advanced polyaromatic systems via an additional re-aromatization process will be tested.

Requirements:

- A Master's degree in chemistry or related sciences (biotechnology, pharmacy) with an emphasis on organic chemistry is mandatory for this position,
- the candidate must possess basic organic synthesis laboratory and analytical (specific for organic chemistry – NMR, IR, HPLC, GC) skills,
- knowledge of the English language at a communicative level is also required