

## *Summary*

The aim of my Thesis was to develop a general synthetic methodology for the preparation of long helicenes equipped with suitable functional groups that control their solubility or serve as anchoring groups for attachment to metallic surfaces, especially gold.

The well-established transition metal catalyzed [2+2+2] cyclootrimerization of triynes was selected as the key scaffold-forming transformation in the synthesis of long helicenes because of its high regioselectivity, atom efficiency, functional group tolerance and general robustness. A modular approach was used for the preparation of the starting oligoynes, thus enabling a high level of their structural diversity. Individual resorcinol-based aromatic building blocks were interconnected by Sonogashira cross-coupling reactions, providing complex cyclization precursors encompassing up to twelve alkyne units pre-arranged for the multiple [2+2+2] cycloisomerization to produce three six-membered rings from each set of three neighboring alkyne units. Thus, a small series of long helicenes with up to 19 rings constituting the helical scaffold was synthesized. The quadruple cyclization leading to the longest oxahelicene prepared to date was performed in a high-temperature-high-pressure flow reactor at 250 °C in the presence of  $\text{CpCo}(\text{CO})_2$ . The set of compounds includes racemic as well as optically pure helicenes functionalized by sulfur or nitrogen anchoring groups.

Sulfur anchoring groups were conveniently introduced into the helicene molecules by nucleophilic aromatic substitution employing the corresponding chloro helicenes. Due to its low reactivity in palladium catalyzed cross-coupling reactions, the chlorine substituent was advantageously carried through the synthesis to be eventually replaced by a sulfanyl group at high temperature (200 – 270 °C). A series of such helicenes with one or two sulfanyl or thioacetate groups attached at different positions was prepared using this approach including carba- and oxa- [5]-, [6]-, [7]- and [19]helicenes.

In parallel to the synthesis, a state-of-the-art break junction (BJ) instrument was designed and constructed in order to study single-molecule conductance of the newly prepared compounds in the STM as well as mechanically controllable BJ modes. Three new helicene molecules with sulfur-based anchor groups and the pyridooxa[9]helicene derivative were investigated, showing conductance in the order of  $10^{-3} G/G_0$ .