# Master internship (6 months):
# Empowering Silver(I) Complexes in Catalysis

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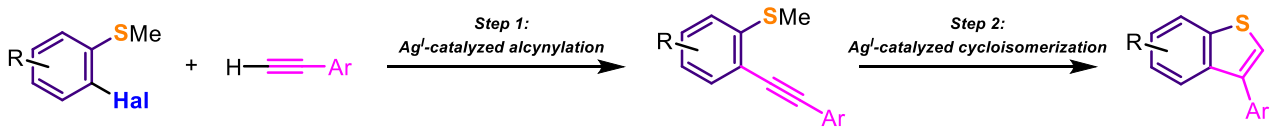
**Project:**

Carbon-Carbon and Carbon-Heteroatom bonds formation is of great interest for the construction of scaffolds in several areas such as pharmaceuticals or molecular materials. Concerning green chemistry field, homogeneous catalysis represents a powerful tool to succeed the formation of these bonds. Transition metals such as palladium and copper are frequently used as catalysts. Regarding the 12 principles of *Green Chemistry* introduced by Paul Anastas and John Warner,[1] the use of coinage metals reveals to be fully adapted to the development of sustainable processes. Silver is a coinage metal commonly employed for its moderate Lewis acidity, its halogenophilicity and as a one-electron oxidant.[2] In this context, we will focus our attention on silver(I) complexes. Its use for cycloisomerization reactions of carbonyl or amide functions[3] onto alkynyl derivatives has been intensively studied in our laboratory.

Despite these reactivities, the redox properties of silver are still not well understood. Indeed, it is generally accepted that silver is only involved in one-electron redox chemistry.[2] This fact was denied in 2014 by Ribas group's discovery: the authors reported the experimental evidence of a two-electron redox Ag(I)/Ag(III) catalytic process where the triazamacrocycle-Ag(III) intermediate has been fully characterized[4] and further extended their work with the use of acyclic ligands.[5] Apart from these two publications, reports about the Ag(I)/Ag(III) redox properties are very scarce and often lack mechanistic evidence.[6]

We are currently working on the development of a silver(I)-catalyzed Sonogashira-type reaction. Conditions have been found to allow the formation of the alcynylation product with a home-made silver(I) complex. To tune the conditions more deeply, optimization needs to be continued, including synthesis of new ligands for the metal complex. We envisioned to study the mechanism of this catalytic cycle by some electrochemical experiments allowing us to possibly point out the Ag(I)/Ag(III) process.

In addition to this work, silver-catalyzed cycloisomerisation reaction will be applied to the synthesis of benzothiophene derivatives functionalized at their C3 position, by cyclisation of alkynylthioanisoles. Indeed, benzothiophene derivatives represent an important class of sulfur-containing heterocycles for the design of biological active compounds.[7] Inspired by the knowledge of our team about cycloisomerization reactions of carbonyl and amide functions,[3] we wish to further study the ability of silver(I) complexes to promote cyclization of heteroatoms - here sulfur ones - onto a triple bond. Our research should ideally achieve the synthesis of benzothiophene derivatives by silver catalysis in one-pot, starting from thioanisole and alkyne (Scheme 1).




***Scheme 1.*** *Envisioned synthetic route to access C3-functionalized benzothiophene derivatives.*

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