

PhD position available in ISCR (Rennes), 36 months from October 2022

Title: New lithium-calcium bases for original aromatic compounds functionalization	
Supervisors: Prof. Florence Mongin (50%), Dr. William Erb (50%)	
Place: Chimie Organique et Interfaces (COrint Team), Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS, Campus de Beaulieu, Université de Rennes 1 (France)	
Contact: florence.mongin@univ-rennes1.fr, +33 (0)2 23 23 69 31, https://iscr.univ-rennes1.fr/florence-mongin	
Financial support: Agence Nationale de la Recherche	Net salary: ≈ 1550 €
Keywords: strong bases, aromatic compounds, heterocycles, asymmetric synthesis	
<p>Overview of the research project:</p> <p>More abundant and biocompatible than widely used transition metals, alkali and alkaline earth metals are attractive alternatives for developing more sustainable synthetic strategies. While the use of bimetallic organic bases for the functionalization of aromatic compounds has revolutionized organic synthesis (<i>Angew. Chem. Int. Ed.</i> 2007, <i>46</i>, 3802; <i>Chem. Rev.</i> 2013, <i>113</i>, 7563; <i>Chem. Rev.</i> 2019, <i>119</i>, 8332), bimetallic bases containing calcium have been scarcely studied. A whole section of organic chemistry therefore remains to be discovered, with potential applications in the conversion of renewable resources and asymmetric synthesis.</p> <p>Despite all the recent advances in organic synthesis, the directed functionalization of aromatic ethers still represents an unmet challenge. Thus, our first goal will be to identify new calcium or lithium-calcium bases with which challenging aromatic substrates will be selectively deprotometallated owing to the specific properties of alkaline earth metals. Furthermore, the arylmetals formed should exhibit unexpected reactivities, allowing their reaction with an unprecedented range of original electrophiles.</p> <p>Achieving the regioselective functionalization of compounds with several reactive centres has always been a major concern of chemists. This is why our second goal will be to find calcium or lithium-calcium bases able to discriminate between C_{sp²}-H and C_{benzylic}-H. Whenever possible, the generated arylmetals or benzylmetals will be identified by high resolution analytical methods, while plausible mechanistic pathways will be delineated by state-of-the-art DFT calculations to rationalize their formation.</p> <p>As asymmetric synthesis currently represents a key process in modern organic chemistry, our third goal will be to identify suitable chiral, enantiopure lithium-calcium bases to perform enantioselective deprotometallation of suitable prochiral substrates toward either biologically active products or ligands.</p> <p>The PhD student will benefit from the collaborative network established around the BiMeDep ANR program for the synthesis, isolation and characterization of calcium bases (Y. Sarazin, Rennes, France), the identification and characterization of lithium-calcium bases and arylmetals (NMR spectroscopy and mass spectrometry; H. Oulyadi, C. Afonso, Rouen, France) and the DFT calculations to validate or invalidate reaction pathways (S. Kahlal, J. Y. Saillard). Thus, the development of this original project around new lithium-calcium bases to functionalize aromatic compounds will allow the PhD student to acquire various and valuable skills.</p>	
<p>Scientific and general skills that will be acquired by the PhD student:</p> <ul style="list-style-type: none"> - Organic synthesis (deprotometallation-trapping sequences, enantioselective reactions) - Analysis of the prepared compounds (NMR, GC-MS, IR, etc.) - Bibliography, presentation of results, team work 	
<p>Selection criteria:</p> <p>Skills and interest in organic synthesis and in standard characterization tools (at least a five-month training period), interest for organometallics will be an advantage but is not mandatory, background in organic chemistry</p>	
<p>Application:</p> <ul style="list-style-type: none"> - Detailed CV and Motivation letter (10 lines in the email) - Names and emails of two contacts (for recommendations) - Transcripts of marks for Master 1 or 2nd year of Engineer School - When possible, transcripts of marks for the 1st semester of M2 - An interview will be planned for the candidates best fulfilling the criteria. 	