CONQUEST will focus on new transition metal catalyzed approaches for the construction of quaternary and tetrasubstituted tertiary carbon stereocenters enabled through decarboxylative allylation reactions. Compounds featuring acyclic quaternary stereocenters are attractive targets as the development of new scaffolds with such a structural element are valuable to increase the chemical space that is exploited by medicinal and fine-chemical chemists to develop new and/or improved drug molecules. While the synthesis of such highly dense stereocenters through decarboxylation methods has been traditionally dominated by metal catalysts comprising Rh or Ir, new approaches that would alleviate the use of these expensive systems by more economical and sustainable ones that comprise of either Pd, Co or Ni would provide impetus for the creation of new potential for chiral synthons and active pharmaceutical ingredients (APIs) in the discovery of new biologically active or pharma-relevant platform molecules. Three new catalytic approaches are proposed to advance the synthesis of quaternary stereocenters. First, a dual Co/photocatalyst (PC) mediated transformation of vinyl cyclic carbonates is examined that allows for in situ umpolung of the initial electrophilic Co(allyl) species enabling its crosscoupling with (electrophilic) aldehyde reagents offering a straightforward and diastereoselective route to homo-allylic alcohols. Second, a reductive Ni-assisted crosscoupling of linear carbonates will produce branched products derived from a single substrate and forged through a cross-electrophile coupling with an in situ, putative formation of a Ni(III)-bis(allyl) species from which the target product is reductively eliminated. Lastly, a dual Pd/PC mediated arylation of aryl,vinyl cyclic carbonates and arylboronate reagents allows to develop a enantiodivergent synthesis of alfa,alfa-heterodiaryl homoallylic alcohols and amines. Reverting the nature of the aryl groups present in the reagents offers a direct route to both product enantiomers. The experimental studies are complemented by extensive mechanistic studies to unravel the origin of the enantio-control and regio-selectivity of these manifolds as to rationalize the research outcomes, and to iterate towards the use of improved and intensified ligand engineering approaches.

**SUMMARY**

CONQUEST will focus on new transition metal catalyzed approaches for the construction of quaternary and tetrasubstituted tertiary carbon stereocenters enabled through decarboxylative allylation reactions. Compounds featuring acyclic quaternary stereocenters are attractive targets as the development of new scaffolds with such a structural element are valuable to increase the chemical space that is exploited by medicinal and fine-chemical chemists to develop new and/or improved drug molecules. While the synthesis of such highly dense stereocenters through decarboxylation methods has been traditionally dominated by metal catalysts comprising Rh or Ir, new approaches that would alleviate the use of these expensive systems by more economical and sustainable ones that comprise of either Pd, Co or Ni would provide impetus for the creation of new potential for chiral synthons and active pharmaceutical ingredients (APIs) in the discovery of new biologically active or pharma-relevant platform molecules. Three new catalytic approaches are proposed to advance the synthesis of quaternary stereocenters. First, a dual Co/photocatalyst (PC) mediated transformation of vinyl cyclic carbonates is examined that allows for in situ umpolung of the initial electrophilic Co(allyl) species enabling its crosscoupling with (electrophilic) aldehyde reagents offering a straightforward and diastereoselective route to homo-allylic alcohols. Second, a reductive Ni-assisted crosscoupling of linear carbonates will produce branched products derived from a single substrate and forged through a cross-electrophile coupling with an in situ, putative formation of a Ni(III)-bis(allyl) species from which the target product is reductively eliminated. Lastly, a dual Pd/PC mediated arylation of aryl,vinyl cyclic carbonates and arylboronate reagents allows to develop a enantiodivergent synthesis of alfa,alfa-heterodiaryl homoallylic alcohols and amines. Reverting the nature of the aryl groups present in the reagents offers a direct route to both product enantiomers. The experimental studies are complemented by extensive mechanistic studies to unravel the origin of the enantio-control and regio-selectivity of these manifolds as to rationalize the research outcomes, and to iterate towards the use of improved and intensified ligand engineering approaches.

**Decarboxylative approaches in asymmetric allylic alklylation reactions**

- **state of the art**
  - dominated by Rh and Ir catalysis
  - low diversity of quaternary carbons
  - limited mechanistic knowledge

- **CONQUEST**
  - new Ni, Pd and Co catalysis
  - wider diversity of quaternary carbons
  - better mechanistic understanding

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