SUMMARY

The aim of my PhD Thesis was to explore the potential of helically chiral N-heterocyclic carbene (NHC) ligands in asymmetric catalysis. Helicenes and helicene-like molecules are inherently chiral. Their application in this field has been rather limited. To date, only a few examples of enantiopure helically chiral NHCs have been described in the literature.

Using a well-established method based on the diastereoselective metal catalysed [2+2+2] cycloisomerisation of centrally chiral triynes as the key step, I have synthesised a series of optically pure 2*H*-pyran based penta- and hexahelicenes bearing an amino group on the terminal benzene ring. The triynes were prepared by a sequence of Sonogashira and Mitsunobu coupling reactions using the commercially available (*S*)-but-3-yn-2-ol as the source of chirality. The resulting aminooxa[5]- and aminooxa[6]helicenes were then converted into the corresponding 1,3-disubstituted imidazolium salts, from which, upon deprotonation, the helically chiral N-heterocyclic carbenes were generated.

To evaluate the performance of the new helically chiral ligands, the enantioselective Ni^0-catalysed [2+2+2] intramolecular cycloisomerisation of prochiral triynes to nonracemic dibenzohelicenes was chosen as a model reaction. All the synthesised imidazolium salts provided, in the presence of a Ni^0 species and a base, highly active Ni^0-NHC complexes. In general, symmetrical imidazolium salt precursors provided higher enantiomeric excess than their unsymmetrical analogues, reaching with the symmetrical imidazolium salts up to 59% *ee* for dibenzo[6]helicene and 74% *ee* for dibenzo[7]helicene. These encouraging results prompted the introduction of bulky substituents onto the helical backbone in order to increase steric congestion around the metal centre and thus enforce the higher level of enantioselectivity. Oxahelicenes bearing a chlorine atom at different positions provided access to a small library of such ligands *via* Suzuki-Miyaura coupling. The stereochemical outcome of the new set of helically chiral NHC ligands ranged from 40% *ee* up to 66% *ee* for dibenzo[6]helicene and reached even 86% *ee* in case of dibenzo[7]helicene.

Although the novel helically chiral ligands show great promise in the enantioselective nickel catalysed [2+2+2] cycloisomerisation, further modification of the helical backbone hand in hand with molecular modelling is required in order to extend the substrate scope and improve the existing level of enantioselectivity by understanding better the mechanism of chirality transfer.