
**Studies towards enantioselective olefin metathesis – Asymmetric Ene-Yne
ring-rearrangement metathesis and immobilization of a chiral Ruthenium
catalyst**

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Abstract

The first part of the thesis involves studies of asymmetric Ene-Yne Ring Rearrangement Metathesis (aEYRRM) in which a short and flexible synthesis route for the generation of different precursors was developed allowing a specific modification of functional groups at each position. With these precursors aEYRRMs were conducted with different cross partners as well as various chiral Ruthenium catalysts exclusively affording the *exo* products in good yields and excellent enantioselectivities of up to 94%*ee*. This concept was then extended by an additional RCM step to generate enantiomerically enriched, cyclic *spiro* compounds which was realized by using substrates bearing another exocyclic double bond.

In the second part of the thesis the synthesis of a chiral, perfluorotagged Ruthenium catalyst **Ru-38** via Click chemistry is described. The functionalization was realized at the chiral NHC ligand with subsequent catalyst generation. A direct immobilization at the Ruthenium catalyst **Ru-27** could not be achieved due to self-metathesis of this catalyst. Studies for the synthesis of a heterogeneous catalyst with dendritic polyglycerolazide as well as the synthesis of a water-soluble catalyst with linear PEG-units were performed. These studies showed that generating a carbene was not possible due to a competing deprotonation of the triazole proton at the NHC ligand. **Ru-38** showed enhanced solubility in fluorinated solvents whereas their application in AROCM instead of non-fluorinated organic solvents gave no improvement in terms of enantioselectivity or *E/Z*-selectivity. **Ru-38** was successfully used in an AROCM in supercritical CO₂ representing the first asymmetric version of an olefin metathesis in supercritical CO₂.