

The present work focusses on the development and application of squaramide- and cyclodiphosph(V)azane-based hydrogen-bonding catalysts. These applications include the employment in asymmetric organocatalyses and the investigation of the influence of various substitution-patterns of the cyclodiphosph(V)azane catalysts on the binding-strength in anion recognition and the catalytic activity in various non-enantioselective organocatalyses.

In the first part of this work, the synthesis of the hitherto inaccessible product of the Michael-addition of 4-hydroxycoumarin and  $\beta$ -nitrostyrene was achieved through enantioselective catalysis by squaramide catalysts known from the literature. Yields up to 92 % and an enantiomeric excess up to 81 % were achieved. Through computational DFT-methods combined with the measurement of the specific rotation of a scalemic mixture of the product, the absolute configuration of the product was determined as *R*. Additionally DFT-computations of transition structures were performed to rationalize the experimental results.

In the second part of this work, the variety of achiral derivatives of the new (to organocatalytic purposes) four-membered cyclodiphosph(V)azan motif was broadened. The influence of structural variations on the properties of this motif was evaluated by X-ray crystal structures of all new compounds and the activity as anion receptors, in the counter-ion catalysis (an N-Acyl-Mannich reaction of an isoquinoline-derivative and a silylketene acetal) and the Diels-Alder reaction of methyl vinyl ketone with cyclopentadiene. The combination of the 3,5-(CF<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>-substitution of the exocyclic N-atoms and the oxidation of the phosphorous atoms with oxygen proved to be the superior pattern in anion-receptors as well as in the counter-ion catalysis. DFT-computations of the anion-binding support these experimental results, as well as the theoretical superiority of the O(=P)-cyclodiphosph(V)azane catalyst with 3,5-(CF<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>-substitution over *Schreiners Katalysator* in the Diels-Alder reaction in cyclohexane and chloroform (reaction barrier cyclodiphosph(V)azan:  $\Delta G_{TS-cHex} = 20,9$  kcal/mol,  $\Delta G_{TS-Chloroform} = 21,2$  kcal/mol; *Schreiners Katalysator*:  $\Delta G_{TS-cHex} = 23,4$  kcal/mol,  $\Delta G_{TS-Chloroform} = 23,9$  kcal/mol).

A new chiral cyclodiphosph(V)azane with quinine-substitution of the exocyclic N-atoms was synthesized and characterized by X-ray in fundamental experiments. An increase of the enantioselectivity in the Michael-Addition of 2-hydroxynaphthochinone to  $\beta$ -nitrostyren from 0 % *e.e.* for the corresponding cyclodiphosph(V)azane with (*R,R*)-*N,N*-dimethyl diaminocyclohexane substitution to 39 % *e.e.* for the new chiral cyclodiphosph(V)azan catalyst was achieved. This increase of the selectivity is connected to the stabilization of the orientation of the two NH-functionalities in such a manner, that a bifurcated activation of the substrate can be achieved. DFT-computations revealed a small destabilization of said orientation of 0,63 kcal/mol for the new quinine-substituted

cyclodiphosph(V)azane compared to a significant destabilization of 2,08 kcal/mol for the corresponding (*R,R*)-DMDACH catalyst.