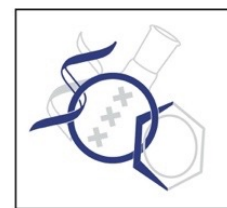




UvA

Incorporation of Directional and Quinone-Functionalized Macrocycles in Covalently Synthesized Rotaxanes



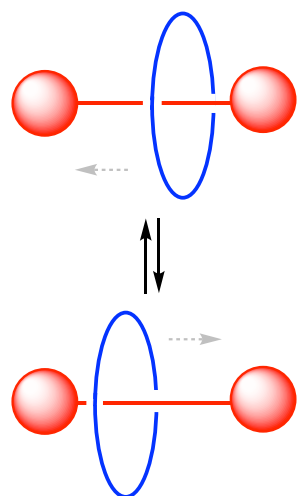
Milo Cornelissen

Supervisors: Prof. dr. Jan van Maarseveen, Dr. Francesco Mutti

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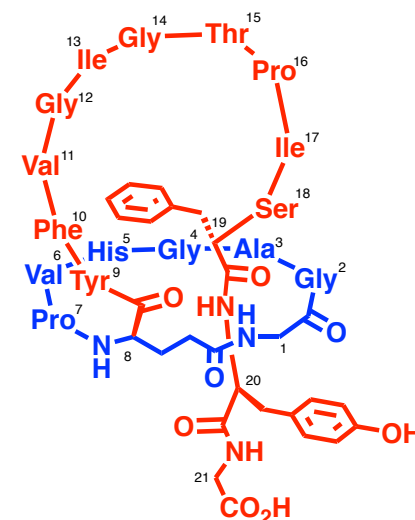
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Introduction



Translational motion in a rotaxane.

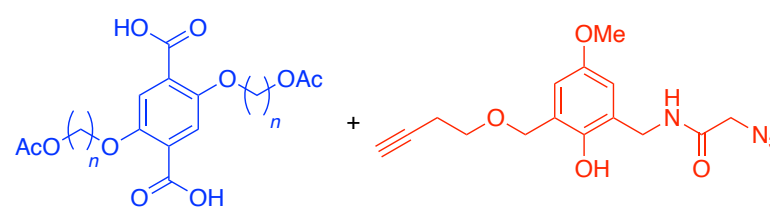
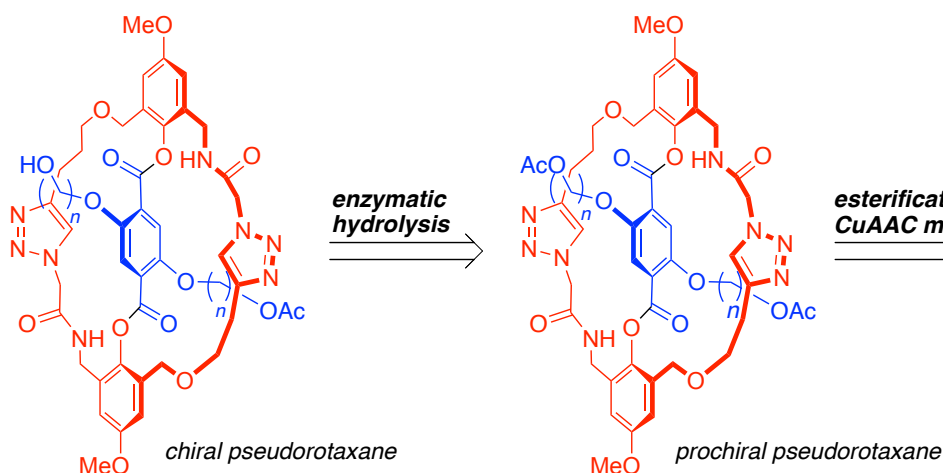
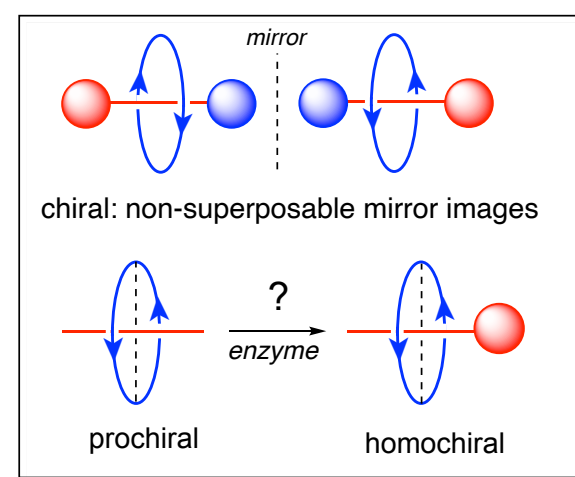
- The mechanical bond in rotaxanes enables movement of the ring over and around the thread.
- This molecular motion could be controlled to create new catalysts and and construct molecular machines.
- Natural products such as lasso peptides possess the same interlocked structure and show promising antibacterial and anticancer activity.



Lasso peptide microcin J25.

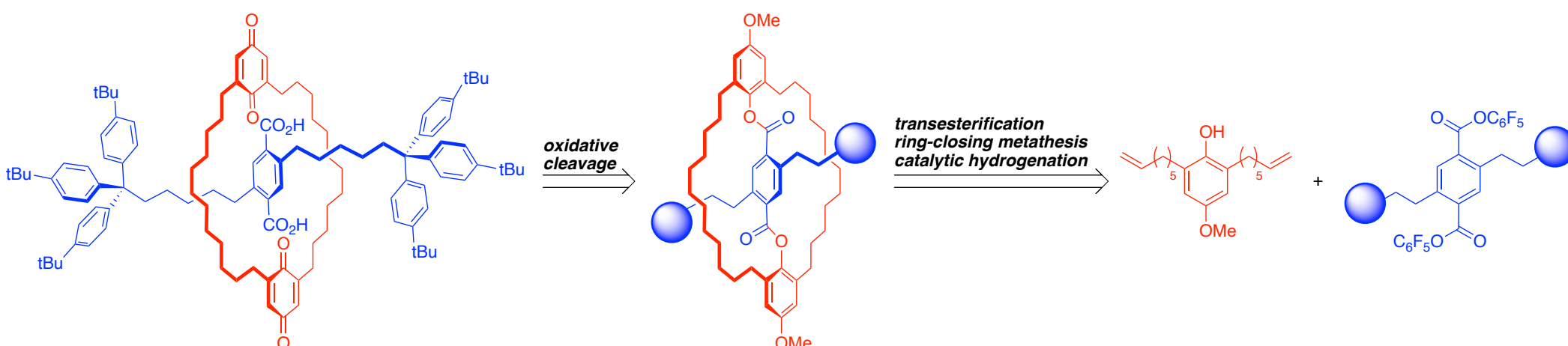
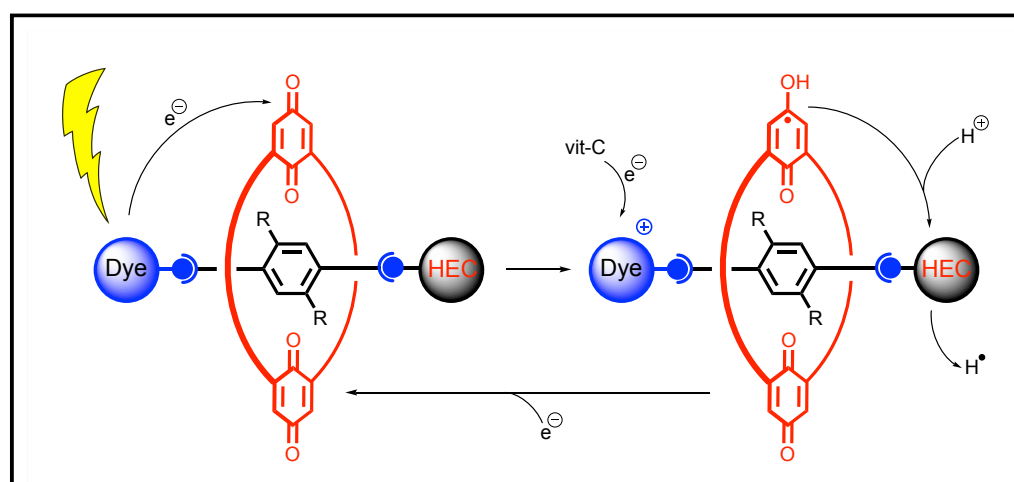
Mechanically Chiral Rotaxanes

- Directional components give rise to mechanical chirality, which is found in lasso peptides and mechanically interlocked catalysts.
- An enantioselective approach towards mechanically chiral rotaxanes is developed, using an enzyme that differentiates the two faces of a directional ring.



Quinone-Functionalized Rotaxanes

- Quinones serve as electron transporters in mitochondria and chloroplasts to fuel the cell.
- Similarly, a rotaxane with quinone ring could be used for unidirectional electron transport in a light-driven hydrogen evolution catalyst (HEC).
- Prerotaxanes with an all-carbon thread were synthesized to enable oxidation to the quinone.



Conclusion & Outlook

- The building blocks for the directional rotaxane were successfully synthesized. Directed evolution and optimization of the tether length are the next steps towards asymmetric hydrolysis.
- The synthesis was established of two prerotaxanes with an all-carbon thread. Oxidative cleavage is now attempted with various oxidants and electrochemically.