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Ústav organické chemie a biochemie
Akademie věd České republiky, v. v. i.
Institute of Organic Chemistry and Biochemistry
of the Czech Academy of Sciences

The assessment of the PhD Thesis by

Manfred Karras

Faculty of Science, University of Potsdam
Faculty of Science, Charles University

"Synthesis of Enantiomerically Pure Helical Aromatics such as NHC Ligands and Their Use in Asymmetric Catalysis"

Co-supervisor:

RNDr. Ivo Starý, CSc.

Institute of Organic Chemistry and Biochemistry, Prague
Czech Academy of Science

The submitted PhD Thesis by Manfred Karras presents the important achievements in asymmetric synthesis of enantiopure aminohelicenes and the application of their NHC congeners to enantioselective olefin metathesis. Actually, he developed the first helically chiral Ru-based catalyst and demonstrated its promising efficiency the chirality transfer.

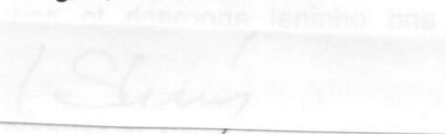
The submitted PhD Thesis presents a modern and original approach to new molecular materials for applications to asymmetric catalysis and material science and, accordingly, it follows modern trends of contemporary aromatic chemistry. I really appreciate his results attained demonstrating the applicant's ability to conduct a high-standard research in the perspective field of science. I have no doubt about the validity and originality of the acquired data that are well documented and convincingly presented.

The first part of the Thesis ("Introduction", 23 pp) expresses the importance of chirality in chemistry. Helicenes as iconic helically chiral molecules are briefly presented along with their syntheses published in the literature. They are now under the spotlight and the number of the related papers is rapidly increasing. Attention is paid also to NHC ligands/transition metal complexes and enantioselective olefin metathesis (along with the general principles of asymmetric catalysis). This part of the Thesis is concise and adequately organised covering the important aspects later on experimentally explored. The second part of the Thesis ("Objectives", 2 pp) aptly presents the goals, specifies the target compounds along with the proposed synthetic

methodologies in an illustrative way. The third part of the Thesis ("Results and Discussion", 40 pp) is a quintessence of the original research performed by Manfred Karras. He clearly describes his successful effort to develop asymmetric synthesis of the properly functionalised enantiopure helicenes, namely amino[6]helicenes (on a multigram scale) and corresponding imidazolium salts as precursors to NHC ligands. Most importantly, he succeeded in developing the first helically chiral Ru catalyst and demonstrated its efficiency in enantioselective ring-closing olefin metathesis of a prochiral triene. He paid attention also to the mechanistic issues and explanation of the chirality transfer employing a theoretical model. The conclusions drawn from experimental results are adequate and correct. The fourth part of the Thesis ("Conclusion and Outlook", 1 p) summarises the results achieved in a concise way. The fifth part of the Thesis ("Experimental", 50 pp) presents the experimental details. The new compounds were systematically characterised in a publication-like style. The sixth part of the Thesis ("Literature", 156 references) presents the literature resources discussed. He is a co-author of three original papers related to the Thesis that were already published in international peer-reviewed journals (the fourth one will be submitted to press soon).

Evidently, the PhD Thesis by Manfred Karras describes his successful and original synthetic effort to prepare attractive functionalised non-planar aromatics in an enantiopure form. Moreover, he showed their promising application as chiral ligands to enantioselective catalysis. It follows modern trends of contemporary science. Summing up, the submitted PhD Thesis meets the requirements for the PhD Thesis in organic chemistry and convincingly demonstrates the ability of the author to conduct high-quality research in the respective area of science. Therefore, it provides clear evidence that the candidate is worthy of unconditional admission to the defence of his PhD Thesis. I recommend accepting the Thesis without corrections.

Prague, 3 October 2018



RNDr. Ivo Starý, CSc.