STATEMENT

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Subject: Dissertation for awarding the educational and scientific degree 'Doctor' in the field of higher education "Natural Sciences, Mathematics and Informatics", professional field 4.2. "Chemical Sciences", Scientific specialty "Organic Chemistry", presented by **Martin Antoniev Ravutsov** (Scientific Jury according to order № РД-09-20/21.01.2021 of the Director of IOCCP-BAS).

Topic: "SULFONAMIDE-DIRECTED *ORTHO*-METALATION AS A TOOL FOR REGIO- AND STEREOSELECTIVE SYNTHESIS OF MULTIFUNCTIONAL AROMATIC COMPOUNDS"

Martin Rahutsov's thesis is in the field of stereoselective organic synthesis. The task is to develop an approach for the synthesis of enantiomeric (diastereoisomeric) pure multifunctional compounds with applications in asymmetric synthesis. Expected, this type of compounds may have diverse beneficial properties, including biological activity.

The synthetic tasks of the dissertation work are aimed at studying the ability of a chiral-modified sulfonamide group to direct regio- and stereoselective *ortho*-lithiation within aromatic systems. In this approach, chiral amines are used to obtain sulfonamide-substituted aromatic compounds, which are effectively involved in ortho-lithiation reactions due to the directing influence of sulfonamide functionality. After reaction with suitable electrophiles, a variety of multifunctional chiral compounds can be obtained. The experiments are focused on two types of reactions as follows:

- Study of regioselective ortho-lithiation of 1- and 2-naphthylsulfonamides as an opportunity to obtain different substituted chiral derivatives;
- Diastereoselective *ortho*-lithiation of ferrocenyl-sulfonamides substituted by means of different chiral groups in the amide residue – the aim is to study the influence of the chiral sulfonamide group on stereoselectivity; of particular interest is the isolation of 1,2-substituted ferrocene derivatives possessing a plane of chirality.

In the course of the experiments, Martin Rauvtsov optimized conditions for regioselective lithiation with subsequent introduction of functional groups in 1- and 2-naftylsulfonamide derivatives, demonstrating multifaceted possibilities for synthesis of structurally diverse organic compounds. In the case of the ferrocene derivatives, an efficient approach is optimized and a number of diastereoisomerally pure planar chiral compounds are isolated. All synthesized compounds have been

studied using NMR spectroscopy (one- and two-dimensional experiments), mass spectrometry and X-ray crystal structure analysis. A useful approach has been demonstrated for determining configuration in planar chiral ferrocene compounds.

I would like to emphasize that Martin Rauvtsov demonstrates experimental skills, which he conducts with enviable precision. He has mastered completely the basic modern physicochemical methods for the study of organic compounds. Martin Rauvtsov has acquired the necessary skills for conducting and solving research tasks independently, with which the main purpose of the PhD study is fulfilled.

Conclusion

The dissertation work of Martin Antoniev Ravutsov contains sufficient scientific and applied results that are of original contribution and meet the requirements laid down in the Law on Development of Academic Staff in the Republic Bulgaria, the Regulations for Implementation of the Low and the respective Rules of IOCCP-BAS.

Therefore, I am confidently giving my positive assessment of the results achieved in the dissertation work and propose to the scientific jury to award the educational and scientific degree "Doctor" of Martin Antoniev Ravutsov in the field of higher education: "Natural Sciences, Mathematics and Informatics", professional direction 4.2. "Chemical Sciences", Scientific Specialty "Organic Chemistry".

15.02.2021 Prof. Dr. Vladimir Dimitrov

Vladimir Dimitrov

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