STATEMENT

by Prof. Svetlana Dimitrova Simova, DSc. - IOCCP-BAS,

member of the scientific jury in regard to the PhD Thesis
submitted for awarding the educational and scientiflc degree
"DOCTOR"
higher education field "Natural Sciences, Mathematics and Informatics",
professional field 4.2. "Chemical Sciences",
doctoral program "Organic Chemistry"

presented by **Martin Antoniev Ravutsov**

Topic: "Sulfonamide-directed ortho-metalation as a tool for regio- and stereoselective synthesis of multifunctional aromatic compounds"

Head: Prof. DSc Vladimir Dimitrov, DSc.

By order № RD-09-20 / 21.01.2021 of the Director of IOCCP - BAS I have been confirmed as a member of the scientific jury for the procedure for promotion of a PhD Thesis for obtaining the educational and scientific degree "Doctor" of Martin Antoniev Ravutsov, full-time doctoral student at IOCCP - BAS in professional field 4.2."Chemical Sciences", doctoral program "Organic Chemistry" on the topic "Sulfonamide-directed *ortho*-metalation as a tool for regio- and stereoselective synthesis of multifunctional aromatic compounds"

General presentation of the candidate

PhD thesis, abstract and presented by Assist. Martin Ravutsov set of documents meet the requirements for acquiring the education and scientific degree **Doctor** is in accordance with the Act on Development of the Academic Staff in the Republic of Bulgaria, the Regulations under it as well the regulations for acquiring scientific degrees and holding academic positions at BAS and IOCCP-BAS. Martin Ravutsov graduated Bachelor (2011) and Master (2012) in chemistry with qualification "Organic Chemistry" in the Faculty of Chemistry and Pharmacy at Sofia University "St. Kliment Ohridski". In the period 2013 – 2015 he was a PhD student in the lab "Organic Synthesis and Stereochemistry" at IOCCP-BAS. Since 2016, he was appointed as an assistant and since 2018 as a chemist at the institute. In addition to working on his PhD thesis, throughout the period at the IOCCP he performed various scientific, applied and administrative tasks.

Aims of the PhD Thesis and timeliness of the research topic

The PhD Thesis develops methods of asymmetric organic synthesis and aims to develop approaches for sulfonamide-directed *ortho*-metalation as an effective tool for regio- and stereoselective synthesis of multifunctional aromatic compounds. The obtained products are intended for application in asymmetric synthesis and medical chemistry. PhD thesis presents research in a promising scientific field as the specific goals and the objectives are clearly defined, with deep knowledge of the current trends and developments in the field of asymmetric organic synthesis. The research in the PhD Thesis is

directed in two main directions: i) synthesis of chiral P-containing naphthalene ligands for Pd-catalyzed asymmetric allyl substitution and ii) synthesis of ferrocensulfonamides with potential biological activity against *Mycobacterium tuberculosis*.

Main results and contributions of the PhD Thesis

The results obtained in the dissertation have both fundamental and scientifically applied character. They enrich existing knowledge in the field of asymmetric organic synthesis and contribute to the development of new chiral catalytic and bioactive products. Scientific results and contributions can be summarized as follows:

- An effective method for regioselective *ortho*-lithiation of 1- and 2-substituted naphthylsulfonamides has been developed.
- Through regioselective ortho-lithiation of 2-naphthylsulfonamids, followed by reaction with diphenylphosphine chiral P, O-ligands were synthesized possessing moderate catalytic activity in a model reaction of the Pd-catalyzed asymmetric allylic substitution.
- A practical method for the preparation of 1,2-disubstituted planar chiral derivatives of ferrocene has been developed by diastereoselective ortho-lithiation directed by chiral sulfonamide groups. A number of pure diastereoisomers have been obtained, the configuration of which has been unambiguously determined by NMR spectroscopy and X-ray diffraction analysis.
- *In vitro* antibacterial activity of 11 new compounds against a standard laboratory strain H37Rv and the multi-drug resistant strain 43 of *Mycobacterium tuberculosis* have been determined.

Research on the topic of the dissertation are summarized in three scientific publications, two out of print in *Monatshefte für Chemie* (IF 1.285, Q3) and *ChemSusChem* (IF 7.804, Q1), and a work accepted for publication in *Organometallics* (IF 3.804, Q1). The results have been presented at 12 international and national scientific forums and 3 citations have been noticed so far.

Assessment of the candidate's personal contribution

The personal contribution of Martin Ravutsov during preparation of the PhD Thesis is appreciable, clear and indisputable. I would also like to mention the candidate's taking responsibility for additional tasks, such as participation in 10 international and national projects and a large number of public procurements. I could describe Martin Ravutsov as an erudite, correct, communicative colleague, with a high chemical culture and significant intellectual capacity. I welcome the writing of the PhD Thesis in English, which can contribute to better publicity of the research done in the country and abroad.

Critical remarks and recommendations

I have no critical remarks on the substance of the PhD Thesis and the presented materials of Martin Ravutsov. I was not able to clarify the formal role of Assoc. Prof. G. Dobrikov in the presented work.

CONCLUSION

The dissertation ***contains scientific and applied results, which represent an original contribution to science*** and **meet all the** requirements of the Act on Development of the Academic Staff in the Republic of Bulgaria. The PhD Thesis and the presented materials **fully** comply with the specific requirements of IOCCP-BAS, adopted in connection with the Rules of BAS for application of the Act on Development of the Academic Staff in the Republic of Bulgaria.

The dissertation shows that the doctoral student **Martin Antoniev Ravutsov has** in-depth theoretical knowledge and professional skills in the doctoral program "Organic Chemistry" by **demonstrating** qualities and skills for independent research.

Due to the foregoing, I confidently give a ***positive assessment*** of the submitted PhD Thesis, abstract, results and offerings, and ***propose to the scientific jury to award the educational and scientific degree "Doctor"*** to **Martin Antonieva Ravutsov** in field of higher education: "Natural Sciences, Mathematics and Informatics", professional field 4.2."Chemical Sciences" doctoral program"Organic Chemistry"

February 16, 2021.

Reviewer: Svetlana Simova

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/Prof. Svetlana Simova, DSc./