

Report on the Thesis entitled “*Computational Insights into Organic and Organometallic Catalysis*” by Xinglong Zhang.

In this thesis, different transformations in organic and organometallic chemistry have been thoroughly studied in detail by means of computational tools. To this end, state-of-the-art Density Functional Theory (DFT) calculations have been carried out to gain more insight into the reaction mechanisms and the nature of the intermediates and transition states involved in the studied reactions. In most cases, the work is not limited to showing the computed reaction profiles but tries to rationalize the factors controlling the more favourable and selective reaction pathways. In all cases the computational studies have been tied into experimental work from several different collaborating groups.

Chapter 1 is introductory, and covers the basic to advanced concepts of computational chemistry, and DFT calculations in particular. It provides a thorough overview of this area. Chapters 2 and 3 are concerned with calculations supporting two mechanistically distinct organocatalytic transformations, the first concerning cyclobutane synthesis, and second looking at a catalytic variant of the Staudinger reduction. Chapters 4-8 are all concerned with transition metal catalysis, and on C-H functionalization reactions in particular. Each chapter deals with a different type of substrate, and as such each is again mechanistically distinct. Each of these research chapters follows a similar pattern, and details the challenges to be overcome, the approach taken, and the results achieved. Each also has a short conclusion section.

Overall, the work is clearly of high quality. This is not only our personal view but it is objectively supported by the publication of many of the results derived from this thesis in high impact international journals such as *Angewandte Chemie*. So far three manuscripts have so far been published, but it is likely that at least a further three will be forthcoming. The thesis stands out for its clarity in the presentation of both objectives and results as well as the conclusions derived from them. The thesis is well written in scientific English. In addition, the bibliography is extensive and up-to-date, documenting exhaustively the precedents directly related to the research work. There are a small number of minor errors which should be corrected in a revision.

The results obtained and presented in this thesis greatly contribute to the current understanding of the reaction mechanisms involved in the selected catalysed transformations. The results are convincingly reported and discussed in a critical manner. As mentioned above, there is no doubt about the significance of the results since many of them have been already reported in internationally reputed scientific journals.

The viva examination took place on 25th November, in Oxford, and lasted 1 hour 40 minutes. The candidate was able to answer a range of questions, both on the details of their project, and also computational and organic chemistry more widely. It was a convincing performance, which clearly demonstrated that the candidate was the author of the thesis.

In summary, this is an excellent thesis that clearly documents the precedents directly related to the research. The used methodology is up-to-date and perfectly suited to the pursued objectives. Moreover, the results derived from the present work are relevant not only for the selected transformations but also for the development of future experimental studies. Therefore, we can only evaluate this doctoral thesis very positively. The award of the DPhil degree is strongly recommended by these examiners.

Date:

25/11/19

Prof. Dr. Michael Willis (internal examiner)
Prof. Dr. Israel Fernández (external examiner)

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- corrections received 3/12/19

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