

Referees opinion on the PhD thesis of **MSc. Reinhard Peter Kaiser: Development of new syntheses of condensed aromatic compounds.**

The aim of this work was to develop a new synthetic methodology based on [2+2+2] cyclotrimerization of appropriately substituted diynols for the synthesis of 9,9'-spirobifluorenes and dispiroindeno[2,1-*c*]fluorenes. Subsequently it was necessary to synthesize differently substituted derivatives and to study the dependence of their photophysical properties on the substitution. The last aim was to use the developed a procedure for the synthesis of [7]-helical dispiroindeno[2,1-*c*]fluorenes.

For the cyclotrimerization the Wilkinson catalyst gave the best results yielding 1,2,3,4-substituted fluorenols – the key intermediates for the synthesis of the target compounds. The study of the first derivatives showed, that the photophysical properties are influenced mainly by the presence of phenylsubstituent in position 4. Therefore, using an optimized methodology three new sets of 4-substituted 9,9'-spirobifluorenes were synthesized. These compounds contained 4-phenyl group bearing electron donor and electron acceptor substituents, 4-substituted biphenyl derivatives, substituted diphenylethynyl- and one carborane derivative. Also several 9,9'-spirobifluorenes with the fused  $\pi$ -aromatic hydrocarbons at position 4 were synthesized. It was shown, that the emission maxima were red-shifted in the presence of electron deficient *para*-substituents and the quantum yields were generally high. In contrast to the parent biphenyl derivative neither the biphenyl substituted derivatives nor the diphenylethynyl substituted derivatives showed a significant red shift of emission, only the relative quantum yields increased. From the fused  $\pi$ -aromatic hydrocarbon derivatives only phenantryl-, antranyl- and pyrenyl-derivatives showed the red shifted emission. The quantum yield was very high in the case of antranyl-derivative. These results indicate the existence of  $\pi$ -conjugation breaking between the 4-substituent and the fluorene, which was in several cases proved by X-ray analysis. The cyclotrimerization approach was also successfully used for the preparation of symmetrical and nonsymmetrical dispiroindeno[2,1-*c*]fluorenes and [7]-helical dispiroindeno[2,1-*c*]fluorenes starting from the corresponding triyndiols. In addition, the analysis of photophysical properties of these compounds was accomplished. The [7]-helical dispiroindeno[2,1-*c*]fluorenes show very high quantum yields and fluorescence emission maxima in the blue region, which might be useful for the applications in materials science.

From the formal point of view, the thesis is divided by the classical way, containing Literature overview, Results and discussion, Experimental and Reference sections. The thesis is written in English, the text seems to be written carefully, with minimum of formal mistakes, several of them are listed below. However, in my opinion, the language, especially of the part Results and discussion, might be better. It is sometime difficult to understand meaning of complicated sentences.

Pg. 21, Scheme 19B: The second structure of **II** is wrong.

Pg. 23, Scheme 22A: AgSBF<sub>6</sub>.

Pg. 79: The diastereoisomers of the triyne **20**, are not *cis/trans*-isomers.

Pg. 202: The Czech Abstract contains two versions of the first sentence.

The whole text Wilkinson catalyst, not Wilkinson's catalyst. The same holds for Autor's publications.

To summarize the above, MSc. Reinhard Peter Kaiser has done a lot of good synthetic work. He worked up and optimized a new general and robust synthetic procedure for the synthesis of substituted 9,9'-spirobifluorenes and dispiroindeno[2,1-*c*]fluorenes with a potential use in the material science. The four or six step procedure is based on [2+2+2] cyclotrimerization of alkynes catalysed by Wilkinson catalyst as the key step and starts from commercially available materials. The obtained compounds were subjected to the study of photophysical properties, and the structure of each structural type was confirmed by X-ray analysis. The results were published in two high impacted journals (*Chem. Eur. J.*, and *Chem. Biomol. Chem.*).

I have a following question:

Your methodology proved to be very useful also for very interesting fluorene derivatives with [7]-helical structure. What is your opinion on the possibility to extend your methodology for the synthesis of [9]-helical fluorenes or even for higher analogues?

MSc. Reinhard Peter Kaiser proved that he is a good synthetic chemist with a broad practical and theoretical knowledge capable of an independent scientific work. This can be documented by the fact, that the obtained results have been already published in two respected scientific journals. Therefore, **I recommend** his thesis for further processing **to obtain PhD degree**.

Prague 9. 9. 2018

Prof. Dalimil Dvořák, CSc.