



Expert opinion on the Ph.D. thesis titled “Synthesis of aromatic compounds possessing the fluorene unit”

The submitted Ph.D. thesis focuses on the preparation of fluorene-based polycyclic aromatic hydrocarbons by means of cyclotrimerization reactions. The topic of the thesis corresponds with the scientific interests of the supervisor's research group. In addition to the synthesis of the target compounds, the photophysical properties of the synthesized compounds are reported. Therefore, I consider the thesis interesting not only from the perspective of organic synthesis, but also in light of the potential applications in the field of materials chemistry. The thesis is organized in a standard fashion so that it includes introduction, aims, results and discussion, conclusion, and experimental sections, as well as a list of abbreviations and a references section. The thesis is 209 numbered pages in length, and it features 158 citations. In the introductory section, the importance of fluorene derivatives and the possibility of their preparation are discussed, including the utility of cyclotrimerization experiments. The aims of the thesis are then clearly defined in a separate section. This is followed by the presentation and discussion of the results, which runs to a total of 64 pages (or 30% of the entire thesis). Next comes the experimental section, which is 80 pages in length (or 38% of the thesis).

The thesis is written in a readable manner, with the findings being logically arranged in tables, diagrams, and figures. The use of colors serves to greatly clarify the more complex diagrams. I also consider the sample of fluorescence properties (Figure 5) to be a valuable addition in terms of improving the readability of the thesis. While reading the thesis, I was pleasantly surprised by the enormous amount of experimental work that has been performed, as illustrated by the synthesis of more than 20 of the target fluorenes. This reflects the diligence and dedication with which the student has approached the project. Thus, it is not surprising that the experimental section of the thesis is 80 pages long. Furthermore, the experimental section is clearly written, which enhances the reproducibility of the performed experiments.

I regret to say that, even in this case, the ambiguities and errors that accompany the majority of scholarly texts have not been completely eliminated. As an example, the indication of the yields of the prepared compounds can be mentioned. In Scheme 17, it is stated that compound **11g** was obtained in yields ranging from 80–91%, whereas in the experimental section only an isolated yield of 91% is given. Therefore, in this case, further clarification of the yields of the prepared compounds is desirable. Moreover, I was surprised by the method used to number the benzene rings of the fluorinated substrates, which is not in accordance with established principles of nomenclature. The numbering of the substances in Scheme 18 is confusing, and I was able to confirm the structure of substance **13** in Scheme 20. Furthermore, it is disappointing that the student did not attach copies of the ^1H and ^{13}C NMR spectra of selected spirofluorene derivatives in order to demonstrate the purity of the synthesized substances.



The thesis contains only minimal grammatical and typographical errors, including:

- Inconsistent ligand notation. For example, Table 1 uses $[\text{Rh}(\text{cod})_2]\text{BF}_4$ (page 47), whereas the general procedure for cyclotrimerization uses $\text{Ni}(\text{COD})(\text{DQ})$ (page 194).
- Inconsistent use of hyphenation when writing multiplets for the ^1H NMR spectra. Traditionally, two numeric values and a dash should not be separated by spaces.
- Page 49, lines 15 and 16: “electro-donating” should read “electron-donating.”

The following questions arose while I was reading this Ph.D. thesis:

1. The optimization of the reaction conditions for the cyclotrimerization of diyne **1a** (Table 1, page 47) was essentially conducted under ligandless conditions. Yet, it has previously been shown (*Org. Lett.* **2003**, *5*, 3659; *Org. Biomol. Chem.* **2013**, *11*, 7653) that the progress of a cyclotrimerization reaction can be influenced by the use of a suitable ligand or complex. Why has the reaction of alkynes **1a** and **2h** not been performed with other ligands?
2. With a few exceptions, I consider the bathochromic shifts of the prepared spirofluorene derivatives to be only minimal. Is this typical for spirofluorene derivatives? The photophysical properties (especially the UV/Vis) also strongly depend on the solvent used. Have other solvents been used to measure the photophysical properties of the prepared compounds?
3. The spectrum of substance **19** when measured at 55 °C (Figure 17) appears similar to an H-F decoupled spectrum (Figure 16). Was an attempt made to measure the ^1H NMR spectrum of substance **19** in a different solvent at 55 °C so as to avoid the overlapping of the signals?
4. How many values does the interval for the isolated yield of compound **11g** (80–91%) comprise? Can this pattern be extrapolated to the other isolated yields of the synthesized compounds?

Let me conclude this report by stating that the presented Ph.D. thesis includes a collection of high-quality original results. The aims of the thesis were achieved, and Mgr. Ilaria Caivano published five papers (three as the first author). Thus, I recommend the Ph.D. thesis as the basis for defending the Ph.D. academic degree.

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