Review report on PhD thesis „Synthesis and reactivity of hypervalent sulphur fluorides" submitted by Javier Ajenjo Bárcenas.

Ph.D. thesis submitted by Javier Ajenjo is focused on the synthesis of pentafluorosulfanylated aromatic compounds. Special attention has been paid to extension and improvement of a method using elementary fluorine which has still been used for very limited substrate scope. The thesis also follows the research from group of supervisor dealing with aromatic nucleophilic substitution reactions.

The thesis is written in a "classic" form with an introductory part, results and discussion and experimental. In the introduction (23 pages), author brings brief overview of hypervalent sulphur compounds which is accompanied by subchapters focused on synthesis and properties of pentafluorosulfanylated compouds. Number of references in this part (135) is in usual range. Results and discussion part is devided into two main chapters. In the first one, fluorination of diaryl disulfides or thiophenols, originally used for *para*- and *meta*- nitro derivatives only, was shown to be applicable also for variety of aromatic compounds. Although the method was optimized, it has some limitations from the point of view of the substrate structure. This is clearly stated in conclusion part. Nice piece of "engineering" work was done in development of combined batch-flow-process for fluorination. The second part of the results and discussion is focused on substitution reactions on pentafluorosulfanylbenzenes with the aim to study further derivatization of these compounds both with vicarious and $S_NAr$ reactions.

Experimental reflects structure of Results and discussion part. It contains also data on the synthesis of starting compounds: disulfides and thiophenols. Surprisingly, this is not mentioned in results and discussion part. Although only known methods are applied to prepare disulfide and thiophenol, short comment and the corresponding scheme would be useful for readers. One should take in mind that the synthesis of precursors was substantial part of the work.

Overall, the thesis is logically constructed. Style of presentation is on good level. Conclusions are supported by relevant data and they are clearly stated. Schemes, Figures and other illustrations meet standard criteria for publishing in the area of organic chemistry. New compounds are adequately characterized by $^{1}H$, $^{19}F$ and $^{13}C$ NMR and by HR-MS, physical parameters (melting points) are given. On the other hand, there are some formal details, which could be improved, e.g. missing acidification of the reaction mixture in Scheme 28; for clarity I also recommend to use entries in all cases in the text discussing Table 4 (pages 30-32); carbon NMR data are given using 2 decimal places which is unusual.

There are some comments and recommendations, which should be addressed within the defence:

1. There is an attempt to direct fluorination of pyridine containing substrates (p. 41). Unfortunately, the author finished work in this issue after first set of experiments Approach to heteroaromatic compounds with pentafluorosulfanyl group would be

desirable. Have been done any other experiments not described in the theses? There are other possibilities for substrate modification before being fluorinated. What about the reactivity of *N*-oxides?

2. On page 49, oversimplified scheme for vicarious substitution is given. Unfortunately, it is misleading. The process described in Scheme 48 is rather "ipso-substitution" as a leaving group attached to the nucleophile (typical for vicarious substitution) is not shown.
3. Statement on page 49 on nitro group arrangement relative to benzene ring "which is planar to the ring" is not accurate. It should be "which can be planar to the ring".
4. The yields of fluorinations are poor, sometimes good but not great. Are there any by-products or it is because of unreacted starting material?

**Evaluation:**

I would like to conclude that the research in the thesis is original with high scientific value. The results have been published in 2 papers in impacted journals. In both of them, applicant is the first author. Despite some comments, the applicant clearly demonstrated skills and the ability to work independently in the areas of synthetic organic chemistry. Therefore I recommend **PhD thesis to be accepted** and doctoral degree to be awarded to author after successful defence.

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