Dear Dr. Kai Rossen,

We ask you to consider the publication of the manuscript "The first study of the thermal and storage stability of arenediazonium triflates comparing to 4-nitrobenzenediazonium tosylate and tetrafluoroborate by calorimetric methods" in Organic Process Research & Development.

Albeit being versatile substrates in organic chemistry, diazonium salts suffer from serious drawbacks limiting their application, especially on an industrial scale. In most cases, they are unstable, explosive and cannot be stored as a dry solid under normal conditions, whereas the few known stable diazonium salts are too expensive for the industrial use.

Aiming to address these challenges, we have recently prepared and characterized arenediazonium tosylates (Org.Lett **2008**, *10*, 3961-3964) and triflates (Eur.J.Org.Chem **2019**, 665-674) that appeared to be highly reactive as well as stable under normal conditions. Importantly, they can be easily synthesized and are inexpensive, therefore, have high chances to be widely used in industry. Overall, arenediazonium tosylates and triflates can be considered as prospective candidates to the “ideal” diazonium salts. However, in order to achieve this, their stability and safety should be studied systematically and quantitatively. The latter is the main goal of the manuscript proposed for the consideration.

Our original endeavor to use the known methods in order to conduct the studies required was not successful as, surprisingly, generally accepted and standardized methods for assessing safety and storage stability of diazonium salts are not available.

Therefore, herein, for the first time we have quantitively assessed the storage stability of some arenediazonium triflates comparing to arenediazonium tosylate and tetrafluoroborate using isothermal flow calorimetry and DSC/TGA. We have determined diazonium salt decomposition energies and proposed possible mechanism of the processes observed. As a result, we have shown that indeed, arenediazonium triflates are significantly more stable and safe comparing to widely used arenediazonium tetrafluoroborates.

The given approach can be proposed as a standard procedure for the quantitative analysis of the storage stability and explosiveness of a wide range of aromatic diazonium salts.

We believe that our results would be attractive for chemists working in both academia and industry. As such, we hope that our paper would contribute to the discovery of new application areas of diazonium salts, intensify their usage and increase safety while handling these compounds.

We confirm that this manuscript has not been published elsewhere and is not under consideration by another journal.

All authors have approved the manuscript and agree with its submission to *Organic Process Research & Development*.

Please address all correspondence to: Alexander Bondarev, Alexander.A.Bondarev@gmail.com and Prof. Dr. Victor Filimonov, e-mail: filimonov@tpu.ru and

We look forward to hearing from you at your earliest convenience.

On behalf of all authors

Yours sincerely,
Victor Filimonov

The Kizhner Research Center
School of Advanced Manufacturing Technologies
National Research Tomsk Polytechnic University
Tomsk, 634050 Russia

filimonov@tpu.ru

Alexander Bondarev,
The Scientific Research Institute of Biological Medicine
Altai State University
Barnaul, 656049 Russia

Alexander.A.Bondarev@gmail.com