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27 HSKIKI

VELI LOŠINJ
2021

**27th CROATIAN MEETING
OF CHEMISTS AND CHEMICAL ENGINEERS**

WITH INTERNATIONAL PARTICIPATION • 5th SYMPOSIUM "VLADIMIR PRELOG"
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BOOK OF ABSTRACTS



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METAL-FREE SULFUR DIOXIDE-ASSISTED GLYCOSYLATION WITH GLYCOSYL FLUORIDES

Krista Gulbe,^{a,*} Jevgeņija Lugiņina,^a Edijs Jansons,^a Artis Kinēns,^{b,c} Māris Turks^a

^a Institute of Technology of Organic Chemistry, Faculty of Materials Science and Applied Chemistry, Riga Technical University, P. Valdena str. 3, Riga, LV-1048, Latvia

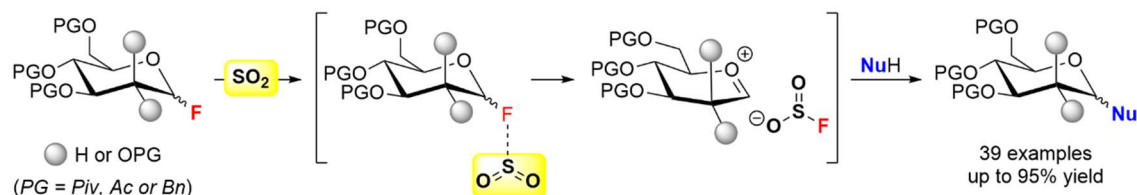
^b Latvian Institute of Organic Synthesis, Aizkraukles str. 21, Riga, LV-1006, Latvia

^c Department of Chemistry, University of Latvia, Jelgavas str. 1, Riga, LV-1004, Latvia

* Krista.Gulbe@rtu.lv

Liquid SO₂ is a polar solvent that possesses Lewis acid properties. It is known to facilitate Lewis acid promoted and/or carbenium ion mediated chemical transformations.^[1] Apart from that, SO₂ has an affinity towards fluoride ion that leads to covalent bonding in the form of relatively stable fluorosulfite anion (FSO₂⁻).^[2]

Based on the aforementioned physico-chemical properties of SO₂, we have developed sulfur dioxide-assisted glycosylation with glycosyl fluorides as glycosyl donors in liquid SO₂ without an external promoter.^[3] The novel synthetic method was demonstrated with variously protected mannosyl and glucosyl fluorides, and series of *O*-, *S*- and *C*-glycosides were obtained in moderate to excellent yields. The α/β-selectivity of glycosylation was proposed to be substrate-controlled presenting thermodynamic equilibrium. The formation of fluorosulfite species during the glycosylation in the presence of SO₂ was proved by both ¹⁹F NMR spectroscopy and DFT calculations.



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