82nd International Scientific Conference of the University of Latvia
Organic Chemistry Session

2024.03.15. Riga, Jelgavas iela 1, 108. aud.

1	8:30	**Sandija Niedrīte**	Latvian Institute of Organic Synthesis
		SARS-COV-2 METHYLTRANSFERASE INHIBITORS CONTAINING (ADENOSYLTHIO)METHYL BENZOIC ACID ANALOGUES	
2	8:50	**Marija Ivanova**	Latvian Institute of Organic Synthesis
		ELABORATING THE NEW ROUTE TOWARD METHANOINDENE CAGE KEY INTERMEDIATE	
3	9:10	**Jānis Šadauskis**	Latvian Institute of Organic Synthesis University of Latvia
		ELECTROCHEMICAL SYNTHESIS OF PYROLLIDINE AND PIPERIDINE FRAGMENT-CONTAINING COMPOUNDS BY UTILIZING THE INTRAMOLECULAR HOFER-MOEST REACTION	
4	9:30	**Anete Patrīcija Raiskuma**	Latvian Institute of Organic Synthesis University of Latvia
		ORGANO-PHOTOREDOX CATALYZED RADICAL FLUOROMETHYLATION-CASCADE CYCLIZATION OF ARYL *N*-ACRYLAMIDES	
5	9:50	**Krišjānis Gercāns**	University of Latvia Riga Technical University
		INVESTIGATION OF RETRO-BROOK REACTION ON PROTECTED 2-PROPARGYL PHENOL	
6	10:10	**Emanuels Šūpulnieks**	Riga Technical University
		TRIMETHYLENEMETHANE CYCLOADDITION TO SULFUR DIOXIDE AS A NEW METHOD FOR SULTINE SYNTHESIS	
7	10:30	Ketrina Plantus	Latvian Institute of Organic Synthesis Riga Technical University
		SYNTHETIC APPLICATION OF 2-FLUOROCYCLOPROPYL-1-SULFINATE	
8	10:50	**Artjoms Ubaidullajevs**	Riga Technical University
		SYNTHESIS OF SUBSTITUTED CHROMANES VIA TANDEM 1,2-SILYL SHIFT – FRIEDEL–CRAFTS CYCLIZATION	
	11:10	**Launch break**	
9	11:50	**Dāgs Dāvis Līpiņš**	Riga Technical University
		C2 MODIFICATION OF QUINAZOLINE DERIVATIVES VIA AZIDE-TETRAZOLE TAUTOMERISM	
10	12:10	**Kristaps Leškovskis**	Riga Technical University
		SYNTHESIS AND ENERGETIC PROPERATIES OF NOVEL ANNULATED POLYAZIDOPYRIMIDINES AND THEIR SOLVATES	
11	12:30	**Laima Bērziņa**	Riga Technical University
		MELDRUM'S ACID BASED ANTIOXIDANT SYNTHESIS AND ANTIRADICAL ACTIVITY EVALUATION	
12	12:50	**Laura Laimiņa**	University of Latvia
		ETHER-FUNCTIONALIZED IMIDAZOLIUM IONIC LIQUIDS	
13	13:10	**Matīss Mārtiņš Drava**	University of Latvia
		SYNTHESIS OF ORGANIC LIGANDS FOR DEVELOPMENT OF METAL ION SENSORS	
14	13:30	**Artūrs Šilaks**	University of Latvia
		SYNTHESIS AND USE OF BIFUNCTIONAL NON-COVALENT MOLECULARLY IMPRINTED POLYMERS (MIPs) FOR SELECTIVE EXTRACTION OF CATECHOLAMINES AND THEIR METABOLITES	

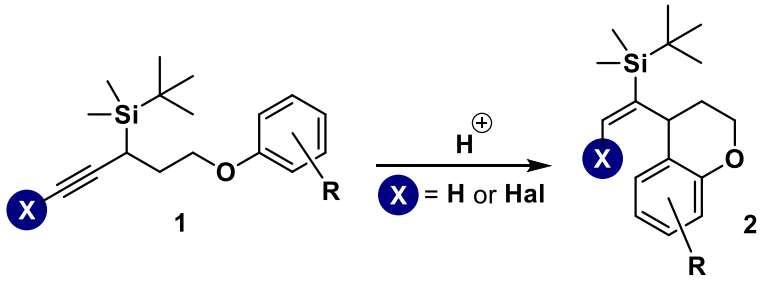
SYNTHESIS OF SUBSTITUTED CHROMANES VIA TANDEM 1,2-SILYL SHIFT – FRIEDEL–CRAFTS CYCLIZATION

Artjoms Ubaidullajevs, Rasma Kroņkalne, Māris Turks

Riga Technical University, Faculty of Natural Sciences and Technology, Institute of Chemistry and Chemical Technology, Paula Valdena 3, Riga, Latvia
e-mail: artjoms.ubaidullajevs@rtu.lv

Previously our scientific group has found 1,2-silyl shift approach to be a powerful tool to the formation of 5-membered cycles, both carbocycles [1] (indenes) and heterocycles [2] (tetrahydrofuranes, pyrrolidines, tetrahydrothiophenes and isoxazolidines).

In this work, we apply acid-induced 1,2-silyl shift for the formation of 6-membered rings. We have developed a convenient synthetic pathway to substituted chromanes. Key synthetic step (Scheme 1) to substituted chromane **2** involves protonation of alkynes **1** and 1,2-silyl shift with consequent Friedel–Crafts cyclization with yields up to 99 %.



Scheme 1. Chromane synthesis via tandem 1,2-silyl shift – Friedel–Crafts cyclization.

The starting material **1** can be obtained in 70-80 % yield from commercially available pent-4-yn-1-ol in 3 or 4 steps: O-silylation, retro-Brook rearrangement [3] under Schlosser conditions and modified Mitsunobu reaction [4] with corresponding phenols. In the additional step, haloalkyne (Hal = Cl, Br, I) synthesis was conducted, and the resulting aryl ether **1** undergoes acid-catalysed cyclization in the same fashion yielding chromane with *E*-selective alkene side chain.

References:

[1] Puriņš M., Mishnev, A., Turks, M. *J. Org. Chem.* **2019**, *84*, 3595-3611.
[2] Kroņkalne R., Beļaunieks, R., Ubaidullajevs, A., Mishnev, A., Turks, M. *J. Org. Chem.* **2023**, *88*, 13857-13870.
[3] Wang, X., Gao, Q., Buevich, A. V., Yasuda, N., Zhang, Y., Yang, R.-S., Zhang, L.-K., Martin, G. E., Williamson, T. R. *J. Org. Chem.* **2019**, *84*, 10024-10031.
[4] Hirose, D., Gazvoda, M., Košmrlj, J., Taniguchi, T. *J. Org. Chem.* **2018**, *83*, 4712-4729.