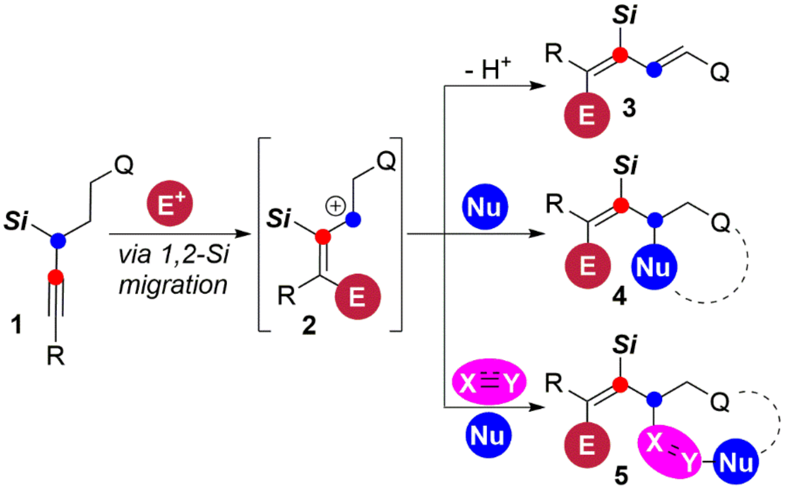
Synthesis of allylic systems and heterocycles with highly functionalized olefin side chain from propargyl silanes via 1,2-silyl shift

Māris Turks, Rūdolfs Beļaunieks, Rasma Kroņkalne, Mikus Puriņš, Artjoms Ubaidullajevs, Rebeka Anna Līpiņa

Faculty of Materials Science and Applied Chemistry, Riga Technical University, P. Valdena str. 3, Riga 1048, Latvia
e-mail: maris.turks@rtu.lv

A non-vertical stabilization of β-silyl carbocations (formation of cyclic silonium ion) can lead to 1,2-silyl migration.[1] Recently, we have applied this phenomenon in the Brønsted acid catalyzed synthesis of silyldienes **3** from propargylsilanes **1** ($E^+ = H^+$).[2]

Herein, we report a further development of this methodology, which profits from the vinyl cation - allyl cation rearrangement via 1,2-silyl shift. Electrophiles like H^+, Br^+, I^+, $PhSe^+$ and *in situ* generated organocopper(III) species can be used for the transformation **1** + $E^+ \rightarrow$ **2**. The latter is prone to accept various nucleophiles in either intramolecular or intermolecular manner. These include alcohols, carboxylic acids, oximes, acyl and sulfonyl amides, carbamates and thioacetates. In this way highly functionalized allylic systems or heterocycles with substituted olefin side chain are obtained. The latter are shown to undergo further transformations by reactions like C-C cross-coupling reactions of vinyl halide or vinyl silane moieties, and allylic substitution. We have also extended this methodology to multicomponent approach by combining propargyl silane, incoming electrophile and nitrile for the Ritter type process, which is terminated by nucleophilic attack. Preliminary studies suggest that the transformation **1** → **4** can be performed in the enantioselective fashion in the presence of chiral Brønsted acids.



Acknowledgements: This work has been supported by the Latvian Council of Science Grant LZP-2023/1-0576. R.B and R.K thank the European Social Fund within the project 8.2.2.0/20/I/008 and Riga Technical University Doctoral Student Grant.

References:

1. R. Belaunieks, M. Puriņš, M. Turks, *Synthesis* **2020**, *52*, 2147.
2. M. Puriņš, A. Mishnev, M. Turks, *J. Org. Chem.* **2019**, *84*, 3595.