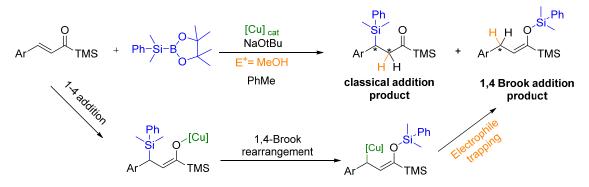
## COPPER CATALYZED 1, 4-BROOK REARRANGEMENT OF α, β-UNSATURATED ACYLSILANE

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Since its discovery in 1958,<sup>[1]</sup> the Brook rearrangement has been widely used in organic synthesis.<sup>[2]</sup> Among the multiple possibilities of this rearrangement, the regioselective formation of silyl enol ethers was initially report in the late 60's.<sup>[3]</sup> Among the few reported examples of 1,4-Brook rearrangement on silyl enol ethers,<sup>[4]</sup> only one of them used copper catalysis, <sup>[5]</sup> and none of them has been applied to  $\alpha$ , $\beta$ -unsaturated acylsilane

We propose hereby the extension of 1,4-Brook rearrangement to  $\alpha$ , $\beta$ -unsaturated acylsilane through the catalytic addition of a copper-silicon species. Such addition generates a nucleophilic copper intermediate, which will eventually trap an electrophilic species, *e.g.* a proton in this work. In addition, we highlight the selectivity towards the 1,4-rearrangement as no 1,2-Brook rearrangement is observed.



This reaction allows us to obtain a stereogenic center, moreover the nucleophilic copper intermediate formed allows us to consider the use of other electrophiles such as allylic halides, carbonyl electrophiles (acyl halides, ketones,...) and even a dual catalysis process with palladium.

<sup>[1]</sup> A. G. Brook, J. Am. Chem., Soc. 1958, 80, 1886

<sup>[2]</sup> a) W. H. Moser, Tetrahedron 2001, 57, 2065. b) P. Jankowski, Synlett 1994, 985

<sup>[3]</sup> a) A. G. Brook, J. Am. Chem. Soc. 1967, 89, 704. b) A. G. Brook, J. Organomet. Chem. 1967, 10, 235

<sup>[4]</sup> N. Toyooka, Tet. Lett. 2012, 53, 5955, X. She, Org. Lett. 2017, 19, 3478

<sup>[5]</sup> T. Takeda, J. Org. Chem. 2002, 67, 8450