

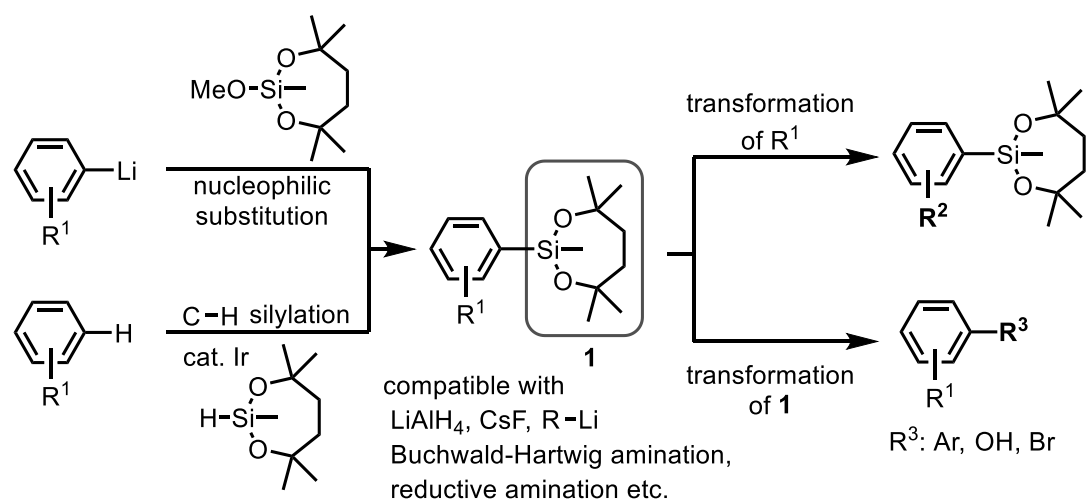
## Development of 7-Membered Dialkoxysilyl Group and Its Application to Organic Synthesis

(Graduate School of Science, Kyoto University) ○Hayate Saito, Jun Shimokawa, Hideki Yorimitsu

**Keywords:** Organosilicon; Silyl Group; Steric Protection; Cyclic Structure

Even modestly reactive organometallic compounds such as organoboronate esters and alkoxysilanes are often difficult to purify and to selectively modify at another functional group in the compounds while maintaining the organometallic moieties. For example,  $\text{ArSi}(\text{OMe})_3$  has good reactivity for cross-coupling reactions whereas it easily undergoes hydrolysis of the  $\text{Si}-\text{OMe}$  moieties and does not survive under various reaction conditions. Thus, a stable organometallic moiety that can be reliably activated under specific conditions would be highly desirable as a powerful tool for organic synthesis.

In an attempt to develop a new alkoxysilyl group that is orthogonal to various functional group transformations, a 7-membered dialkoxysilyl group **1** was found to be compatible with strong nucleophiles such as  $\text{CsF}$ , organolithiums, and even  $\text{LiAlH}_4$ .<sup>1)</sup> Computational studies revealed that the 7-membered structure is highly stabilized not only kinetically but also thermodynamically. While **1** showed the excellent stability, the  $\text{C}-\text{Si}$  bond in arylsilanes bearing **1** could be transformed with the aid of an appropriate activator. In addition, **1** was easily introduced onto arenes with retaining various functional groups by iridium-catalyzed  $\text{C}-\text{H}$  silylation with the corresponding hydrosilane. Nucleophilic substitution of the corresponding methoxysilane with aryllithiums also afforded a series of arylsilanes. To prove the advantages of silyl group **1** in organic synthesis, we conducted a shorter synthesis of a bioactive molecule employing iterative halogen-lithium exchanges, which other conventional alkoxysilyl groups cannot endure.



1) H. Saito, J. Shimokawa, H. Yorimitsu, *submitted*.