

Important notes:

Do **NOT** write outside the grey boxes. Any text or images outside the boxes **will** be deleted.

Do **NOT** alter the structure of this form. Simply enter your information into the boxes. The form will be automatically processed – if you alter its structure your submission will not be processed correctly.

Do not include keywords – you can add them when you submit the abstract online.

Title:

Reaction of introverted and extroverted allylsilanes with mCPBA

Authors & affiliations:

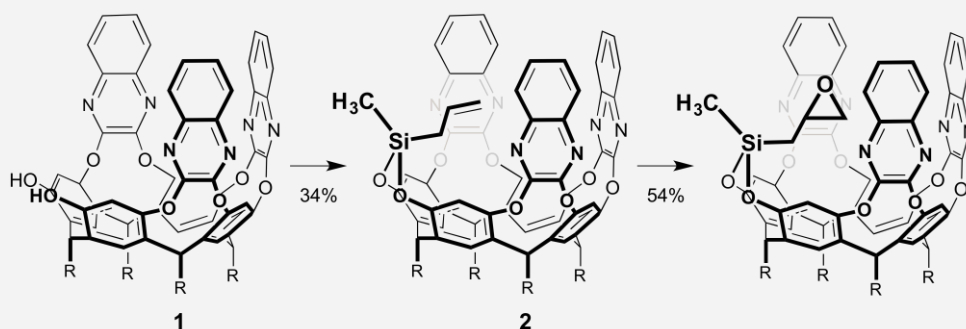
T. Iwasawa^{*†}, K. Ohashi[†], K. Ito[†]
Ryukoku University, Department of Materials Chemistry, Seta, Otsu, Japan
iwasawa@rins.ryukoku.ac.jp

Abstract: (Your abstract must use **Normal style** and must fit in this box. Your abstract should be no longer than 300 words. The box will 'expand' over 2 pages as you add text/diagrams into it.)

Natural supramolecular systems integrate inwardly directed functions. Binding site of enzymes, polypeptides, and RNA strands can fold around a substrate, and in the folded state the functionality converges on the substrate. The introverted functionalities in biological macromolecules play quintessential roles in catalysis.

In a similar vein, synthetic approach to the chemical space with introverted functionality has been pioneered, particularly by Rebek and co-workers. They use the deepened cavitand derived from Högberg's resorcinarene scaffold and 4 aromatic exteriors. The functional substituent is up in the interior space, like a fishing line, toward the tapered end. Indeed, there are many parallels between the synthetic and natural systems: the introverted functionality can recognize guests, accelerate and catalyze reactions, and stabilize reactive intermediates. Despite the relevant role played by inwardly functionalized cavitands in supramolecular chemistry, the organization of reaction sites inside the space is underrepresented due to the synthetic difficulty in functionalizing concave surfaces. To overcome this intrinsic problem would expand the possibilities and importance of functionalized cavitands.

Herein we report a novel synthesis of self-folded silyl-cavitands endowed with inwardly directed allyl group (Scheme 1). The reactions of triquinoxaline-spanned cavitand **1** with allyl(dichloro)methylsilane yielded introverted allyl **2** in 34% yield. NMR analyzing elucidated the cavity of **2** definitely holds allyl moiety; functionalizing the concave surfaces was successfully achieved. In addition, the allyl **2** underwent epoxidation with *meta*-chloroperbenzoic acid (mCPBA) in 54% yield, and higher reactivity of **2** than the corresponding extroverted allyl was observed through competitive experiments.



Scheme 1. Synthesis of introverted allyl **2**, and the following epoxidation.