

## Stereoselective Addition of Sulfenate Species to Electrophiles as a Versatile Synthetic Method of Chiral Sulfoxides

(<sup>1</sup>Department of Chemistry, Tokyo Institute of Technology, <sup>2</sup>Institute of Innovative Research, Tokyo Institute of Technology) ○Jian Zhang,<sup>1</sup> Keisuke Suzuki,<sup>2</sup> Ken Ohmori<sup>1</sup>

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During a course of our synthetic study on bioactive natural flavonoids, we found that epoxide **1** allows the nucleophilic attack of the sulfenate species **A** to give  $\beta$ -hydroxy sulfoxide **2** with *anti*-stereochemistry, albeit in a poor yield. Stimulated by these results, we assumed that this method would serve as a useful way to access various chiral sulfoxides, and thus, we decided to pursue this reaction.

First of all, we examined the diastereoselective ring-opening of epoxide by sulfenate anion **A**, and found that  $\text{MgBr}_2 \cdot \text{OEt}_2$  accelerates the reaction significantly, giving corresponding  $\beta$ -hydroxy sulfoxides in high yield with *anti*-selectivity. Secondly, we attempted the reaction of oxetane derivatives with **A** and discovered that an addition of catalytic  $\text{Sc}(\text{OTf})_3$  allows the diastereoselective synthesis of  $\gamma$ -hydroxy sulfoxides in excellent yield with high *anti*-selectivity. Finally, we successfully demonstrated the axial-to-central chirality transfer with allenes and sulfenate anion **A**, giving the *S*-chirogenic sulfoxide compounds in complete selective manner.

