M. SUGIURA, C. MORI, S. KOBAYASHI\* (THE UNIVERSITY OF TOKYO, JAPAN) Enantioselective Transfer Aminoallylation: Synthesis of Optically Active Homoallylic Primary Amines J. Am. Chem. Soc. 2006, 128, 11038-11039.

## Synthesis of Homoallylic Amines via 2-Aza-**Cope Rearrangement**

## General concept:

R<sup>1</sup> H 
$$R^2$$
  $H^+$ ,  $-H_2O$   $H^+$ ,  $-H_2O$   $H^2$   $H^3$   $H^3$   $H^4$ ,  $-H_2O$   $H^2$   $H^3$   $H^3$   $H^4$ ,  $-H_2O$   $H^2$   $H^3$   $H^3$   $H^4$   $H^4$ 

Realization:

R = Ph, 2-thienyl, 2-furanyl, 3-pyridyl, Bn, PhCH<sub>2</sub>CH<sub>2</sub>, Cy, BnOCH<sub>2</sub>CH<sub>2</sub>, BOM

14 examples 57-92% yield er: up to 99:1

Significance: The enantioselective transfer aminoallylation catalyzed by a Brønsted acid leading to homoallylic primary amines 6 is described. Starting from aldehyde 1 and chiral homoallylamine 2, an imine-intermediate 3 is formed, which can undergo a 2-aza-Cope rearrangement to imine 4. Finally, the homoallylic amine 6 is released after cleavage of the imine bond with hydroxylamine. The authors have employed camphorsulfonic acid as a catalyst, leading to homoallylic amines 6 in good yields and excellent enantiomeric ratios.

Comment: Homoallylic amines are typically prepared by addition of allylic nucleophiles to imine electrophiles. In most cases, protected homoallylic amines are obtained although the formation of primary homoallylic amines would be highly desirable. The same group has recently reported a non-asymmetric variant starting from aldehydes, ammonia and an allylboronate yielding the primary amines directly (Chem. Commun. 2005, 104-106). Now, they report a highly enantioselective approach to homoallylic primary amines 6 via a 2aza-Cope rearrangement using the optically active amine 5.

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Category

Organo- and **Biocatalysis** 

Key words

aminoallylation

homoallylic amines

aza-Cope rearrangement

