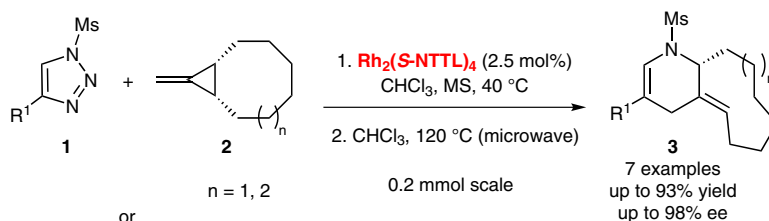


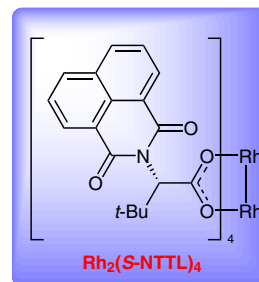
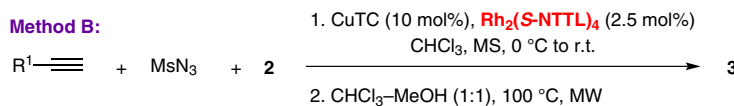
T. MIURA,\* T. NAKAMURO, C.-J. LIANG, M. MURAKAMI\* (KYOTO UNIVERSITY, JAPAN)  
Synthesis of *trans*-Cycloalkenes via Enantioselective Cyclopropanation and Skeletal Rearrangement  
*J. Am. Chem. Soc.* **2014**, *136*, 15905–15908.

## Synthesis of *trans*-Cycloalkenes via Cyclopropanation and Rearrangement

### Method A:



### Method B:

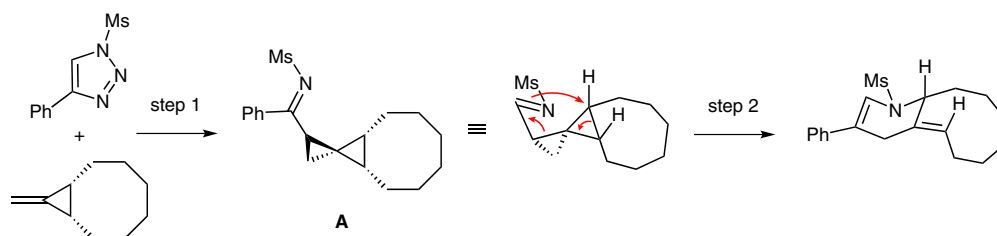


### Substrate scope: Method A

$\text{R}^1$	Yield (%)	ee (%)
Ph	88	97
4-MeOC <sub>6</sub> H <sub>4</sub>	82	98
4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	91	97
2-Naph	88	96
3-thienyl	93	93
1-cyclohexenyl	83	98

93% yield  
97% ee

### Proposed mechanism:



**Significance:** There are few ways to access chiral medium-sized rings possessing a *trans* double bond (for selected examples, see: A. Deiters et al. *Chem. Eur. J.* **2002**, *8*, 1833; X.-N. Wang et al. *J. Am. Chem. Soc.* **2014**, *136*, 9802). Such motifs often exhibit planar chirality and may find application in the synthesis of complex polycyclic frameworks. The authors report an efficient procedure for the asymmetric synthesis of piperidine-fused *trans*-cycloalkenes **3** from triazoles **1** and methylenecyclopropanes **2**.

**Comment:** The reaction is initiated by the in situ formation of an  $\alpha$ -imino rhodium carbenoid from triazole **1**. Cyclopropanation of the exocyclic methylene group of **2** leads to the formation of spirocyclic intermediate **A**, which can then undergo a thermal rearrangement under microwave irradiation to give *trans*-cycloalkene **3**. The authors propose a concerted mechanism, which draws similarity to the retro-Claisen [3,3]-sigmatropic rearrangement.

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