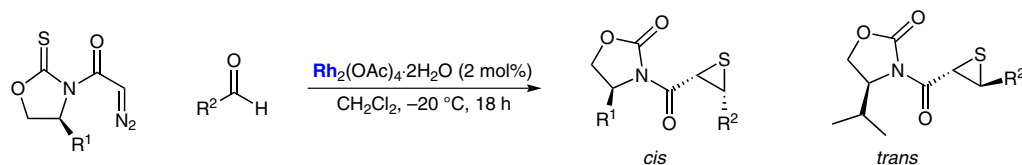


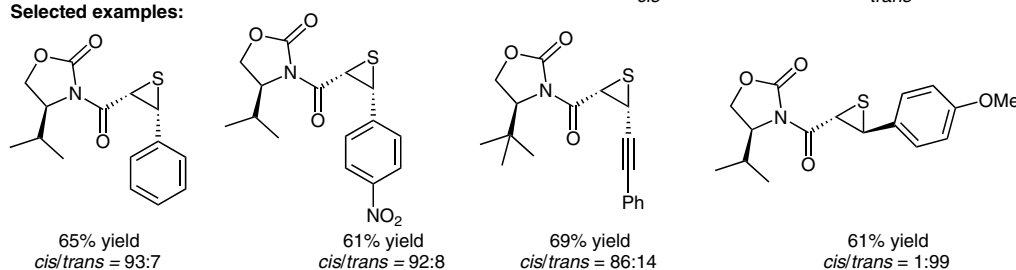
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*N*-(Diazoacetyl)oxazolidin-2-thiones as Sulfur-Donor Reagents: Asymmetric Synthesis of Thiiranes from Aldehydes  
*Angew. Chem. Int. Ed.* **2012**, *51*, 10856–10860.

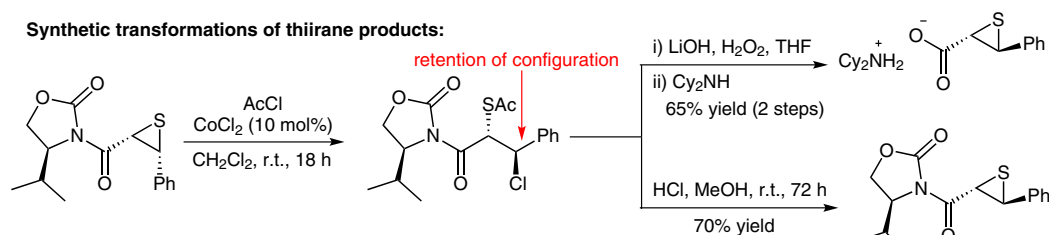
## Asymmetric Synthesis of $\alpha,\beta$ -Thioepoxy Carbonyls by Rhodium Catalysis



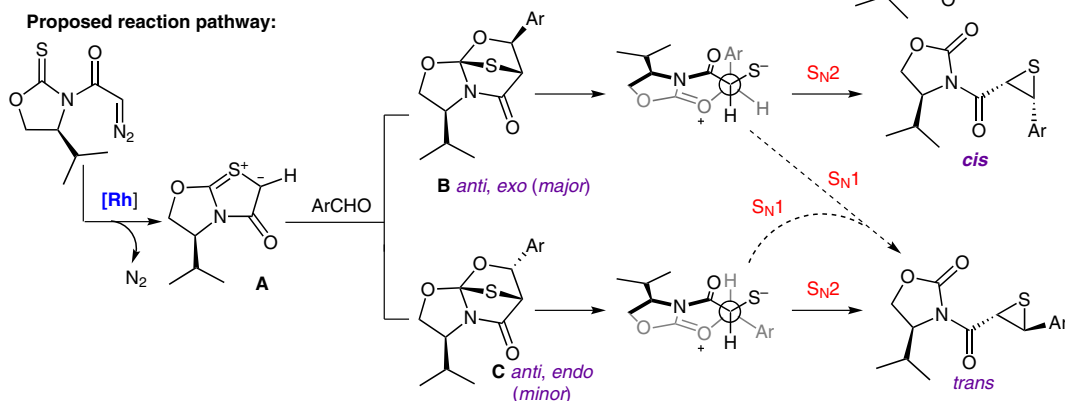
Selected examples:



Synthetic transformations of thirane products:



Proposed reaction pathway:



**Significance:** Stereoselective formation of C–S bonds is a difficult yet important challenge. This report describes the use of diazo thianes as intramolecular sulfur-donor reagents. Under rhodium catalysis, reaction with aldehydes forms thiiranes with high selectivity.

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**Comment:** Computational studies indicate formation of thiocarbonyl ylide intermediate **A**. Reaction with an aldehyde yields a tricyclic adduct, with preferential formation of *anti,exo*-product **B** by 0.8–1.2 kcal/mol, which collapses to the *cis* product by an S<sub>N</sub>2 reaction. However, when the aryl substituent is anisyl, the *trans* product forms by an S<sub>N</sub>1 mechanism.