\textbf{Asymmetric Synthesis of }\alpha,\beta\text{-Thioepoxy Carbonyls by Rhodium Catalysis}

\begin{equation}
\text{RH}_{2}(\text{OAc})_{4} \cdot 2\text{H}_{2}\text{O} (2 \text{ mol}%) \\
\underbrace{\begin{array}{c}
\text{R} \text{H} \\
\text{OCH}_{2}\text{Cl}_{2}, -20 \degree \text{C}, 18 \text{ h}
\end{array}}_{\text{cis}} \\
\begin{array}{c}
\text{cis} \\
\text{trans}
\end{array}
\end{equation}

Selected examples:

\begin{itemize}
\item 65\% yield \\
\text{cis/trans} = 93:7
\item 61\% yield \\
\text{cis/trans} = 92:8
\item 69\% yield \\
\text{cis/trans} = 86:14
\item 61\% yield \\
\text{cis/trans} = 1:99
\end{itemize}

Synthetic transformations of thiirane products:

Proposed reaction pathway:

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

\textbf{Comment:} Computational studies indicate formation of thiocarbonyl ylide intermediate A. Reaction with an aldehyde yields a tricyclic adduct, with preferential formation of \textit{anti,exo}–product B by 0.8–1.2 kcal/mol, which collapses to the \textit{cis} product by an \textit{SN}_{2} reaction. However, when the aryl substituent is anisyl, the \textit{trans} product forms by an \textit{SN}_{1} mechanism.