Cyclohexenylamines and Cyclohexenols by Rhodium-Catalyzed Cycloaddition

1,1-Disubstituted alkenes:

\[
\begin{align*}
\text{[Rh(cod)₂]BF₄ (5–10 mol%)} & \quad \text{L* (5–10 mol%)} \\
\text{CH₂Cl₂, r.t., 16 h} & \quad \text{(0.2 mmol scale)} \\
\end{align*}
\]

Selected examples:

- TsN
  - 92% yield
  - 98% ee
  - H₈-BINAP

- Ph
  - 69% yield
  - 92% ee
  - Segphos

- BnO₂C
  - 74% yield
  - 97% ee
  - H₈-BINAP

- Et
  - 88% yield
  - 97% ee
  - Segphos

- t-Bu
  - 48% yield
  - 98% ee
  - TsN

Monosubstituted alkenes:

\[
\begin{align*}
\text{[Rh(cod)₂]BF₄ (5–10 mol%)} & \quad \text{L* (5–10 mol%)} \\
\text{CH₂Cl₂, r.t., 16 h} & \quad \text{major} \quad \text{or} \quad \text{minor} \\
& \quad \text{(0.2 mmol scale)} \\
\end{align*}
\]

Selected examples:

- TsN
  - 48% yield
  - 98% ee
  - or
  - 23% yield
  - 84% ee

- TsN
  - 45% yield
  - >99% ee
  - or
  - 39% yield
  - >99% ee

Significance: Transition-metal-catalyzed [2+2+2] cycloadditions of diynes or enynes with unsaturated moieties have become an attractive method for the stereoselective construction of carbocycles. Herein, Tanaka and co-workers report a regiodivergent asymmetric rhodium-catalyzed [2+2+2] cycloaddition generating cyclohexenylamines and cyclohexenols.

Comment: The rhodium-catalyzed [2+2+2] cycloaddition of enynes bearing 1,1-disubstituted olefins provided the desired products in moderate to excellent yields with good enantiomeric excess. Interestingly, when enynes with monosubstituted olefins were employed, a different regioisomer was obtained, which was confirmed to be formed in moderate yields and with excellent enantiomeric excess.

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