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Atropisomeric Chiral Dienes in Asymmetric Catalysis: C2-Symmetric (Z,Z)-2,3-Bis[1-(diphenylphosphynyl)-ethylidene]tetralin as a Highly Active Lewis Base Organocatalyst


Novel Atropisomeric Chiral Dienes in Lewis Base Organocatalysis

The authors report a novel tetraline-based, atropisomeric, and configurationally stable chiral diene catalyst 1, which was successfully employed in the Lewis base catalyzed alkylation of aldehydes 2 with trichlorosilanes 3 (see Review below). Products 4 were isolated in moderate to excellent yields and in good to excellent enantio-meric ratios. Catalyst 1 also proved to be effective in a single example of enantioselective ring opening of a meso-epoxide to afford a 1,2-chlorohydrin.

**Applications:**

\[
\begin{align*}
\text{R}^1 & \quad \text{H} \\
\text{R}^2 & \quad \text{SiCl}_3
\end{align*}
\]

15 examples 55–92% yield ee from 89.5:10.5 to 96.5:3.5

\[
\begin{align*}
\text{R}^1 & \quad \text{Ar}, \text{alkenyl} \\
\text{R}^2 & \quad \text{Ar}, \text{Alk}
\end{align*}
\]

93% yield ee = 92.8

\[
\begin{align*}
\text{OH} & \quad \text{Cl} \\
\text{H}_2\text{O}_2
\end{align*}
\]

99% yield

\[
\begin{align*}
\text{PPh}_2 & \quad \text{PPh}_2 \\
\text{PPh}_2 & \quad \text{PPh}_2
\end{align*}
\]

\[
\begin{align*}
\text{ZrCp}_2 & \quad \text{PPh}_2 \\
\text{PPh}_2 & \quad \text{PPh}_2
\end{align*}
\]

resolution

**Significance:** The authors report a novel tetraline-based, atropisomeric, and configurationally stable chiral diene catalyst 1, which was successfully employed in the Lewis base catalyzed alkylation of aldehydes 2 with trichlorosilanes 3 (see Review below). Products 4 were isolated in moderate to excellent yields and in good to excellent enantio-meric ratios. Catalyst 1 also proved to be effective in a single example of enantioselective ring opening of a meso-epoxide to afford a 1,2-chlorohydrin.

**Comment:** Chiral atropisomeric biaryl scaffolds have been well studied and extensively applied in asymmetric catalysis. Yet, atropisomeric conjugated dienes have found limited application in asymmetric synthesis due to their low racemization-energy barrier. The authors avoid this major drawback by designing a catalyst bearing an extended conjugated system involving a diene and two phosphinoxide moieties, thus generating a stable conjugated helical system. Catalyst 1 proved to be configurationally stable even for prolonged periods (24 h) at high temperatures (135 °C). Its potential is well described by the reported alkylation reaction as well as the promising results obtained in the ring opening of meso-epoxides with silicon tetrachloride.


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