Novel Atropisomeric Chiral Dienes in Lewis Base Organocatalysis

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 aldehyde allylation of aldehydes 2 with trichlorosilanes 3 (see Review below). Products 4 were isolated in moderate to excellent yields and in good to excellent enantiomeric 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 allylation reaction as well as the promising results obtained in the ring opening of meso-epoxides with silicon tetrachloride.

Applications:

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\begin{align*}
1 & \quad \text{ZnCl}_2, \text{ZnCl}_2 \\
(\text{M}^+\text{(-)} & \text{-1}) 1 \quad \text{DIPEA} (1.5 \text{ equiv}) \\
\text{R}^1 & \quad \text{Ar, alkényl} \\
\text{R}^2 & \quad \text{Ar, alk} \\
\text{Ph} & \quad \text{Ph} \\
\text{SiCl}_4 & \quad \text{CH}_2\text{Cl}_2, -78^\circ\text{C} \\
(\text{M}^+\text{(-)} & \text{-1}) 1 \quad \text{93\% yield} \\
\text{er} & \quad 92:8
\end{align*}
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