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Atropisomeric Chiral Dienes in Asymmetric Catalysis: C₂-Symmetric (Z,Z)-2,3-Bis[1-(diphenylphosphoryl)-ethyidene]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 allylation of aldehydes 2 with trichlorosilanes 3 [see Review below]. Products 4 were isolated in moderate to excellent yields and in good to excellent enantioselectivities. 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:

\[ R^1 = \text{Ar}, \text{alkenyl} \]
\[ R^2 = \text{Ar}, \text{Alk} \]

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 allylation of aldehydes 2 with trichlorosilanes 3 [see Review below]. Products 4 were isolated in moderate to excellent yields and in good to excellent enantioselectivities. 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.


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