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 alkylation 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 alkylation reaction as well as the promising results obtained in the ring opening of meso-epoxides with silicon tetrachloride.

Applications:

1. **Alkylation of Aldehydes with Trichlorosilanes**

   - **Reagents:** (M)-(+)-1 (0.1–10 mol%), rBu₄NI (1.2 equiv), DIPEA (3.0 equiv), CH₂Cl₂, –78°C
   - **Products:** 4
   - **Yield:** 93%
   - **E.r.:** 92:8

2. **Ring Opening of Mesoclad Epoxides**

   - **Reagents:** (M)-(+)-1 (10 mol%), DIPEA (1.5 equiv), CH₂Cl₂, ~78°C
   - **Products:** 4
   - **Yield:** 93%
   - **E.r.:** 92:8

**Key words**: atropisomerism, chiral dienes, Lewis base catalysis, aldehyde alkylation

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