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 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:**

1. $[\text{Cp}_2\text{ZrCl}_2], \text{Mg}$
2. CuCl, Ph$_2$PCl
3. DIPEA (1.5 equiv)

- **R**$^1$ = Ar, alkanyl
- **R**$^2$ = Ar, Alk

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