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 enantioselective 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:**

<table>
<thead>
<tr>
<th>R¹</th>
<th>R²</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>Ar</td>
<td>4</td>
</tr>
<tr>
<td>Ar</td>
<td>Alk</td>
<td>4</td>
</tr>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>4</td>
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</tbody>
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**Conditions:**

- **1.** [Cp₂ZrCl₂], Mg
- **2.** CuCl, Ph₂PCl

**Yields:**

- 67% yield
- 99% yield
- 93% yield
- 99% yield

**ER:**

- From 89:10 to 96:4
- 92:8
- 92:8
- 93% yield

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