Cyclohexane Desymmetrization via Rhodium-Catalyzed C–H Activation

**Significance:** The authors report a site- and stereoselective desymmetrization of cyclohexanes via a rhodium-complex-catalyzed C–H functionalization.

**Comment:** The method does not require any directing group and can be applied to unactivated C–H bonds, which presents a limitation for similar methods.

**Selected examples:**

1. **Disubstituted cyclohexanes:**
   - 73% yield, 97% ee
   - 75% yield, 92% ee

2. **Tri- and tetrasubstituted cyclohexanes:**
   - 58% yield, 96% ee, rr = 9:9:1, dr = 7:7:1
   - 41% yield, 83% ee, rr > 50:1, dr = 25:1

R1 = Ar, Het(Ar)
R2 = H, Alk
n = 0, 1, 2

**R1**

\[
\text{R}^1 \text{CO}_2 \text{CH}_2 \text{CCl}_3
\]

**R2**

\[
\text{R}^2 \text{CO}_2 \text{CH}_2 \text{CCl}_3
\]

**Rh2(S-TPPTTL)4 (0.5 mol%)**

CH2Cl2, 40 °C, 2 h

**35 examples up to 89% yield up to 99% ee**