Synthesis of Indanes by Enantioselective Direct Arylation

**Significance:** Transition-metal-catalyzed C–H functionalization reactions are becoming increasingly practical; however, highly enantioselective variants are rare (see Review below). The authors have identified a catalytic system which allows for the desymmetrization of enantiotopic aryl C–H bonds using a palladium-catalyzed direct arylation.

**Comment:** The key step in the catalytic cycle is proposed to involve a concerted metalation–deprotonation (CMD) reaction. The use of a chiral monodentate ligand is required to induce enantioselectivity, and bulky taddol-based phosphoramidite ligands were optimal. The reaction is performed at room temperature using NaHCO₃ as a base, making the process exceptionally mild.

**Selected examples:**

- 93% yield, 93% ee
- 94% yield, 91% ee
- 97% yield, 87% ee
- 98% yield, 93% ee
- 80% yield, 45% ee

**Mechanistic model:**

**Equation:**

\[
\text{OTf} \quad \text{Ar} \quad \text{Ar} \quad \text{Pd(OAc)} \quad (5 \text{ mol%}) \quad \text{ligand} \quad (12 \text{ mol%}) \quad \text{NaHCO}_3 \quad (3 \text{ equiv}) \quad \text{DMAc, r.t.} \]

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