Asymmetric C–H Functionalization Using Chiral CpXCo(III) Catalysis

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\begin{align*}
\text{Synthesis of the cobalt complex:} & \\
& 1. \text{Co}_2(\text{CO})_8 (1.1 \text{ equiv}), \text{CO} (1 \text{ atm}), \text{CH}_2\text{Cl}_2, 37^\circ \text{C}, 6 \text{ h} \\
& 2. \text{I}_2 (1.2 \text{ equiv}), \text{Et}_2\text{O}, \text{r.t.}, 1 \text{ h}
\end{align*}
\]

Selected examples:

- 87% yield, 99% ee
- 61% yield, 98% ee
- 87% yield, 99% ee
- 85% yield, 99% ee
- 68% yield, 82% ee
- 74% yield, 89% ee
- 78% yield, 85% ee
- 77% yield, 92% ee
- 74% yield, 73% ee
- 53% yield, 75% ee

**Significance:** This work is an important advance in catalytic C–H functionalizations for the following reasons: (1) it is the first example of asymmetric C–H functionalization using a chiral CpX-ligated bound Co(III) complex; (2) it outperforms competing rhodium-catalyzed methods; (3) reactions with alkyl alkenes give regioisomeric products opposite to those with rhodium complexes.

**Comment:** The authors systematically studied the effect of various substituents on the CpX ligand in the C–H functionalization of chlorobenzamides, a benchmark for chiral CpRh(III) catalysis. The presence of the tert-butyl group greatly influences the approach of the olefin, whereas the naphthyl backbone acts to orient and align the metallocene.