Pd-Catalyzed Asymmetric Ring Opening of Azabenzonorbornadienes

**Significance:** In the presence of electron-rich chiral spirophosphine ligands, I$_2$ as key additive, and zinc powder as reducing agent, Pd(MeCN)$_2$Cl$_2$ efficiently catalyzes the ring opening of azabenzonorbornadiene with various 2-iodobenzoates. The resulting enantioenriched cis-dihydrobenzo[c]phenanthridinones serve as core structure of numerous optically active natural products.

**Comment:** The use of easily available organic halides instead of organometallic reagents and the construction of fused ring systems with multiple stereocenters via the tandem asymmetric ring-opening–cyclization process make the strategy remarkably efficient. A direct application of the present methodology was demonstrated via the concise total synthesis of (+)-chelidonine.

**Selected examples:**

- 80% yield, 85% ee
- 67% yield, 76% ee
- 82% yield, 81% ee
- 78% yield, 80% ee

**Application:** Formal synthesis of (+)-chelidonine:

- 97% yield
- 88% yield, 82% ee
- 78% yield, 94% ee
- 88% yield, 82% ee

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