Enantioselective Palladium-Catalyzed Ring-Opening Reaction of Azabenzonorbornadienes with Methyl 2-Iodobenzoate: An Efficient Access to cis-Dihydrobenzo[c]phenanthridinones

Pd-Catalyzed Asymmetric Ring Opening of Azabenzonorbornadienes

**Significance:** In the presence of electron-rich chiral spirophosphine ligands, I₂ as key additive, and zinc powder as reducing agent, Pd(MeCN)₂Cl₂ 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.