Pd-Catalyzed Asymmetric Ring Opening of Azabenzenonorbornadienes

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 azabenzenonorbornadiene 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.

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