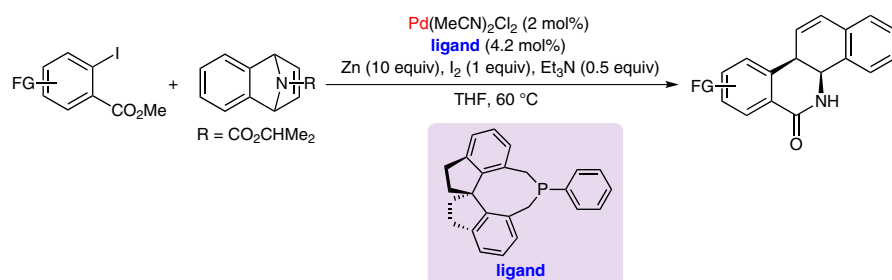


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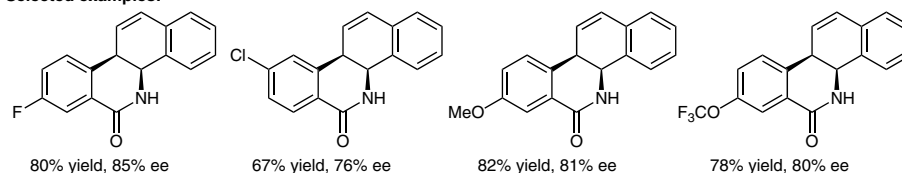
Enantioselective Palladium-Catalyzed Ring-Opening Reaction of Azabenzonorbornadienes with Methyl 2-Iodobenzoate: An Efficient Access to *cis*-Dihydrobenzo[*c*]phenanthridinones

Adv. Synth. Catal. **2013**, 355, 2833–2838.

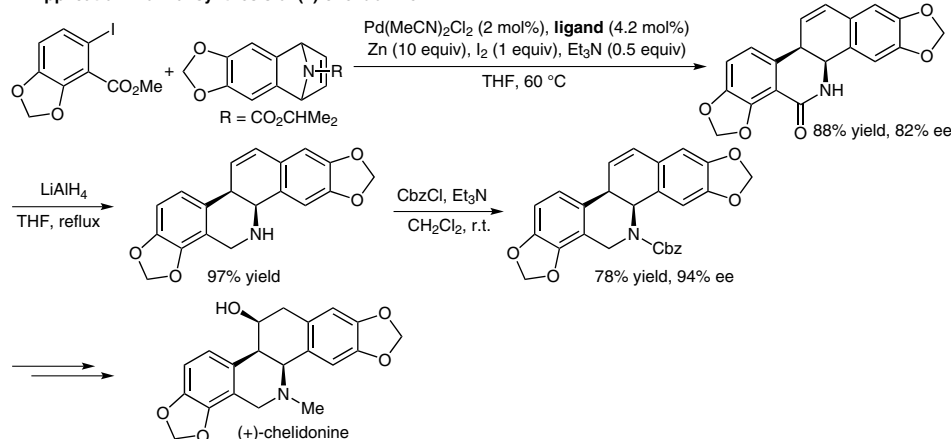
Pd-Catalyzed Asymmetric Ring Opening of Azabenzonorbornadienes



Selected examples:



Application: Formal synthesis of (+)-chelidonine:



Significance: In the presence of electron-rich chiral spirophosphine ligands, I_2 as key additive, and zinc powder as reducing agent, $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ 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.

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