K.-L. HUANG, C. GUO, L.-J. CHENG, L.-G. XIE, Q.-L. ZHOU, X.-H. XU,* S.-F. ZHU* (NANKAI UNIVERSITY, TIANJIN, P. R. OF CHINA)

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.

SYNFACTS Contributors: Hisashi Yamamoto, Sukalyan Bhadra
Synfacts 2014, 10(1), 0057 Published online: 13.12.2013
DOI: 10.1055/s-0033-1340438; Reg-No.: H15913SF