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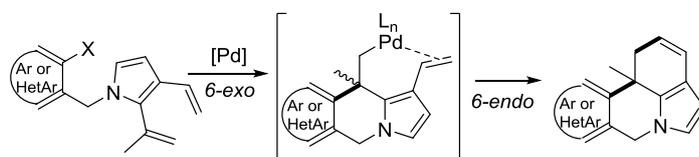
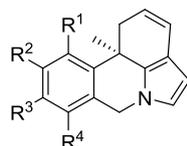
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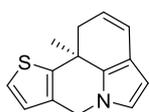

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Intramolecular enantioselective Mizoroki-Heck reactions of 2-alkenyl (o-halobenzyl)pyrroles

 Estibaliz Coya (estibaliz.coya@ehu.es), Nuria Sotomayor, and Esther Lete

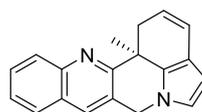
 Departamento de Química Orgánica II, Facultad de Ciencia y Tecnología, UPV/EHU,
 P.O. Box 644, 48080 Bilbao, Spain

Asymmetric Mizoroki-Heck reaction is one of most important palladium(0)-catalyzed C-C bond-forming reactions, which has allowed the preparation of optically active molecules with tertiary and quaternary stereocenters. In particular, Heck-Heck cascade reactions are a powerful synthetic strategy for rapidly increasing structural and stereochemical complexity, allowing the construction of polycyclic frameworks in a one-pot operation. For this purpose, the σ -alkylpalladium intermediate, resulting from the migratory insertion of the arylpalladium to the alkene, may undergo an insertion with an alkene in inter- or intramolecular way, so carbopalladation is repeated one or several times prior to β -hydride elimination. In connection with our work in palladium-catalyzed reactions,¹ we have developed the enantioselective palladium-catalyzed Heck-Heck cascade reaction of *N*-benzyl 2,3-dialkenylpyrroles, using chiral ligands for palladium. A 6-exo Mizoroki-Heck reaction generates the quaternary stereocenter, giving rise to the σ -alkylpalladium intermediate that undergoes a 6-endo insertion to give the Lycorane framework. Details of these transformations will be given.


 Reaction conditions: Pd(OAc)₂, (R)-BINAP, PMP, CH₃CN, reflux, 24h

 up to 75% yield,
 up to 72% ee

 R¹, R², R³, R⁴ = H, OCH₃, OBn, etc.


46%, 66% ee



11%, 99% ee

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¹. (a) Lage, S.; Martínez Estibaleiz, U. Sotomayor, N. Lete, E. *Adv. Synth. Catal.* **2009**, *351*, 2460. (b) Coya, E.; Sotomayor, N. Lete, E. *Adv. Synth. Catal.* **2014**, *356*, 1853.