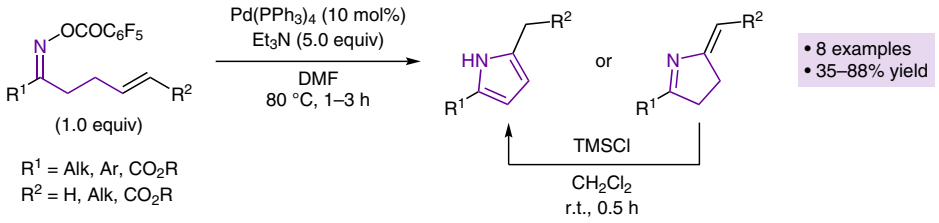
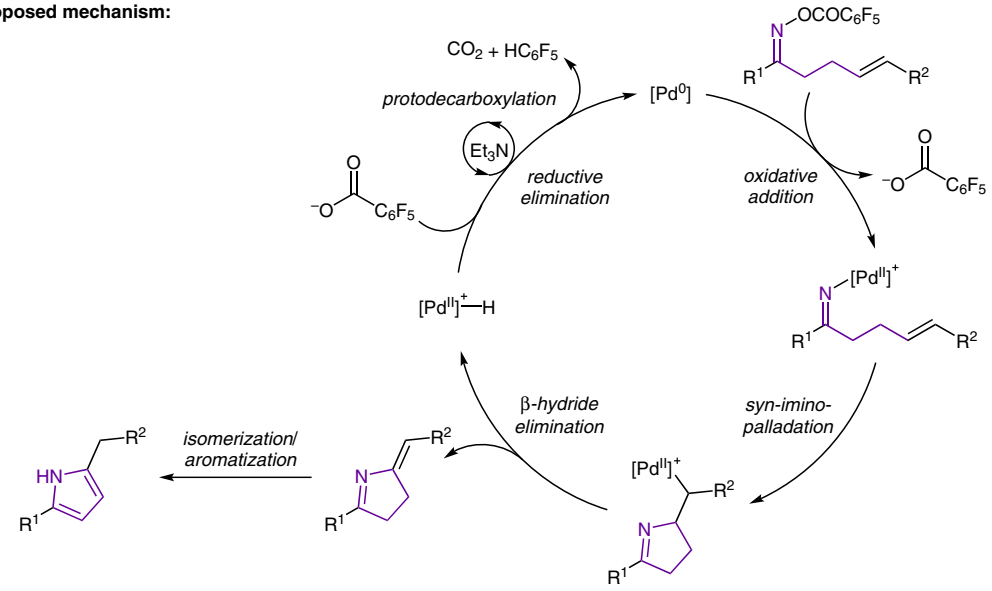
H. TSUTSUI, K. NARASAKA* (THE UNIVERSITY OF TOKYO, JAPAN)

Synthesis of Pyrrole Derivatives by the Heck-Type Cyclization of γ,δ-Unsaturated Ketone *O*-Pentafluorobenzoyloximes
Chem. Lett. **1999**, *28*, 45–46, DOI: 10.1246/cl.1999.45.

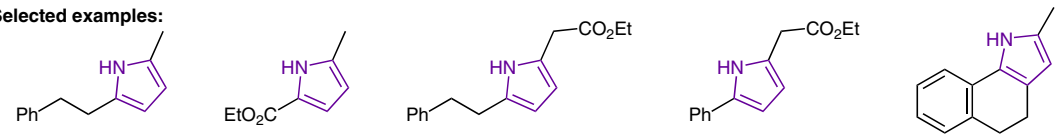
The Narasaka–Heck Cyclization



Proposed mechanism:



Selected examples:



81% yield | 45% yield | 75% yield | 88% yield | 78% yield

Significance: Based on the finding that palladium(0) can cleave the N–O bond of sulfonyloximes, Tsutsui and Narasaka reported a catalytic protocol coupled with an intramolecular Heck-type cyclization to form pyrroles. Competing Beckmann rearrangement of the oxime derivatives could be suppressed by changing from the sulfonyl- to the pentafluorophenylacyl N-protecting group.

Comment: In the following years, this method was successfully extended to access various N-heterocycles (see Review below). An enantioselective version for the synthesis of dihydropyrroles bearing a stereogenic center at the 2-position was introduced by Bower and co-workers (*Chem. Sci.* **2017**, *8*, 1981).

Review: M. Kitamura, K. Narasaka *Chem. Rec.* **2002**, *2*, 268–277.

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Category
Metals in Synthesis

Key words
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oximes
palladium catalysis
pyrroles