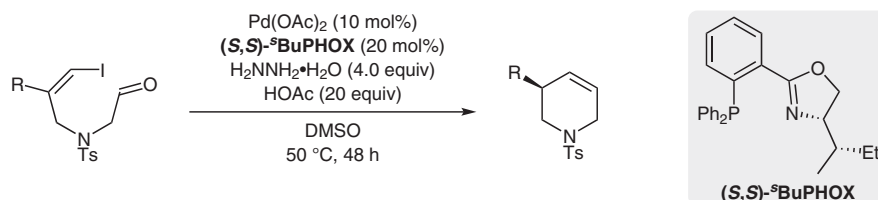


An Asymmetric Intramolecular Heck-Type Reaction of in situ Generated Hydrazones



Category

Metals in Synthesis

Key words

Heck-type reaction

hydrazones

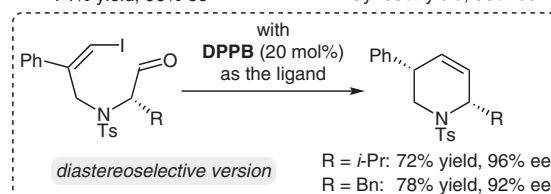
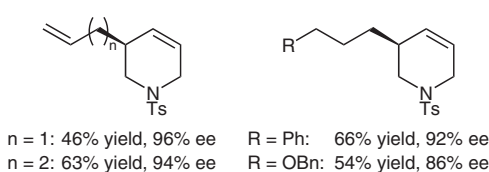
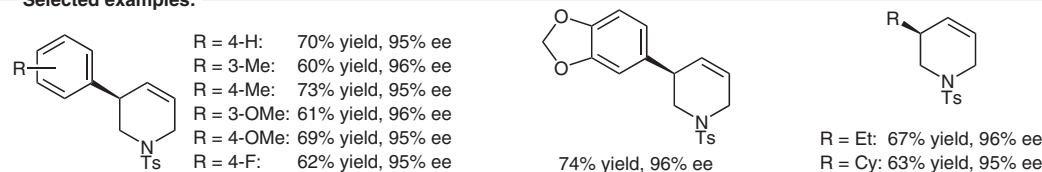
palladium catalysis

[1,5]-sigmatropic rearrangement

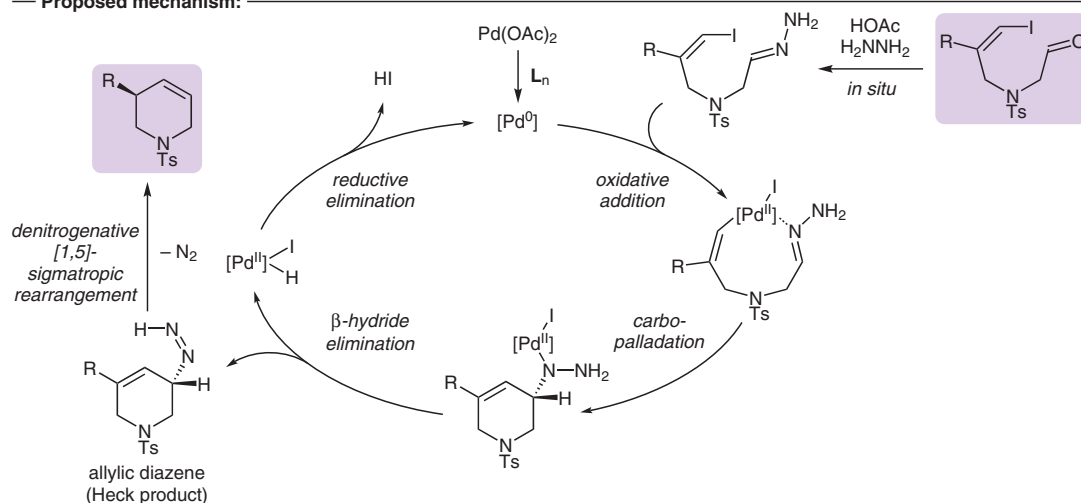
tetrahydropyridines

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Selected examples:



Proposed mechanism:



Significance: Tong and co-workers have disclosed a domino sequence of a hydrazone-type Heck reaction followed by a stereospecific denitrogenative [1,5]-sigmatropic rearrangement to access 3-substituted tetrahydropyridines in good yields and excellent enantioselectivities.

Comment: Using chiral substrates derived from amino alcohols, high diastereoselectivities were obtained using DPPB [1,4-bis(diphenylphosphino)-butane] as the ligand (see dashed box). Mechanistic studies such as deuterium-labeling experiments support the shown mechanism.