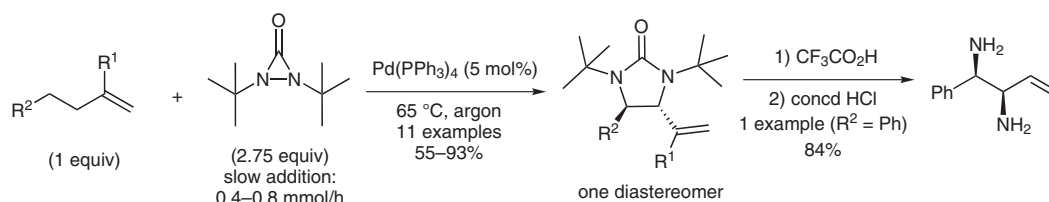


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A Pd(0)-Catalyzed Diamination of Terminal Olefins at Allylic and Homoallylic Carbons via Formal C–H Activation under Solvent-Free Conditions

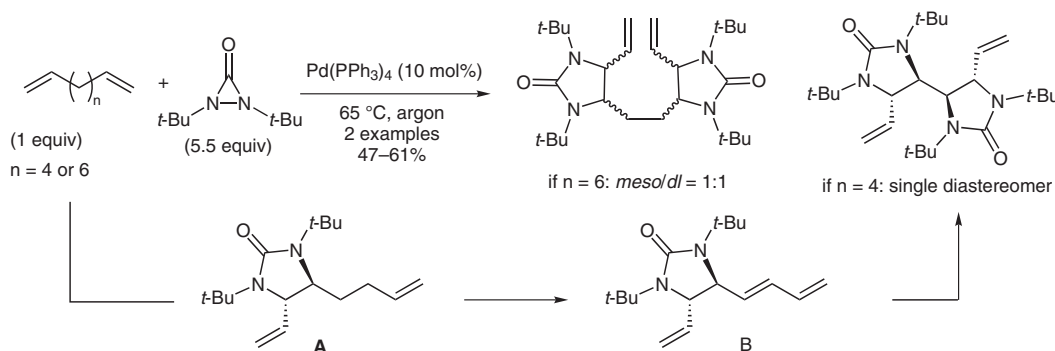
J. Am. Chem. Soc. **2007**, *129*, 7496–7497.

Palladium-Catalyzed Diamination of Olefins



R¹ = H, *n*-Bu, Ph, OMe

R² = Ph, Et, *n*-Hex, CH₂OBn, CH₂O*n*-Hex, CH₂CHCH₂, Me



Significance: Complementary to previous approaches to diaminate olefins and as an extension to the group's previous work in the area (H. Du, B. Zhao, Y. Shi *J. Am. Chem. Soc.* **2007**, *129*, 762), terminal olefins were diaminated at allylic and homoallylic carbons by a Pd-catalyzed C–H insertion under solvent-free conditions. The nitrogen source is di-*tert*-butyldiaziridinone, which can be synthesized in a few steps. The scope encompasses both monosubstituted and 1,1-disubstituted terminal olefins, and the resulting products can be converted into the free diamine by treatment with TFA and concentrated acid. Diamination is also possible, with 1,9-decadiene producing a 1:1 mixture of diastereomers and with 1,7-octadiene producing a single diastereomer.

Comment: Diamination of olefins is a potentially efficient strategy for synthesizing vicinal diamines. The present method needs to be solvent-free and have slow addition of the nitrogen source. The diamination results for 1,9-decadiene versus 1,7-octadiene suggest that the first diamination influences the stereochemical outcome of the second diamination unless the two olefins are too far apart. Although the exact mechanism is unknown, intermediates **A** and **B** have been isolated and both shown to lead to the product, which suggests that a conjugated diene is formed after the first diamination. The authors also speculate that Pd(0) inserts into the N–N bond of the diaziridinone, followed by coordination with the olefin, π -allyl formation, and nucleophilic attack of the amine moieties onto the olefin to furnish the product. A means of producing differentially protected diamines would be very attractive.

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Reactions

Key words

palladium

olefin diamination

C–H activation

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of the month