Palladium-Catalyzed Vinylborylation of Alkenes

Significance: The trapping of alkyl–palladium(II) species in situ with various nucleophiles has emerged as an important strategy for the synthesis of complex molecules. The crucial requirement for the success of this approach is the formation of palladium intermediates lacking β-hydrogen atoms. In this work, the authors present an extension of this class of transformations in the synthesis of enantioenriched tetrahydropyridines through palladium-catalyzed vinylborylation of alkenes.

Comment: The combination of alkenyl vinyliodides and bis(pinacolato)diboron in the presence of a chiral palladium catalyst and Ag₂CO₃ allows the synthesis of tetrahydropyridines. An all-carbon quaternary center is formed in moderate to good yields, enantioselectivities, and, in a few examples, high diastereoselectivity. The nature of the linkage between the two alkene moieties was found to deeply affect the enantioselectivity of the transformation. A 5 mmol scale reaction was carried out, providing the desired product in slightly lower yield and with 94% ee.

Selected examples:

- [Pd₂(MeO-dba)₃] (5.0 mol%)
  - ligand (15.0 mol%)
  - Ag₂CO₃ (2.0 equiv)
  - B₂pin₂ (2.0 equiv)

R¹ R² R₃

PhMe or 1,4-dioxane
25–40 °C, 12–36 h
(0.2 mmol scale)

- >20 examples
- 44–95% yield
- 33–97% ee
- dr > 20:1

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