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Atroposelective Synthesis of Axially Chiral Biaryls by Palladium-Catalyzed Asymmetric C–H Olefination Enabled by a Transient Chiral Auxiliary

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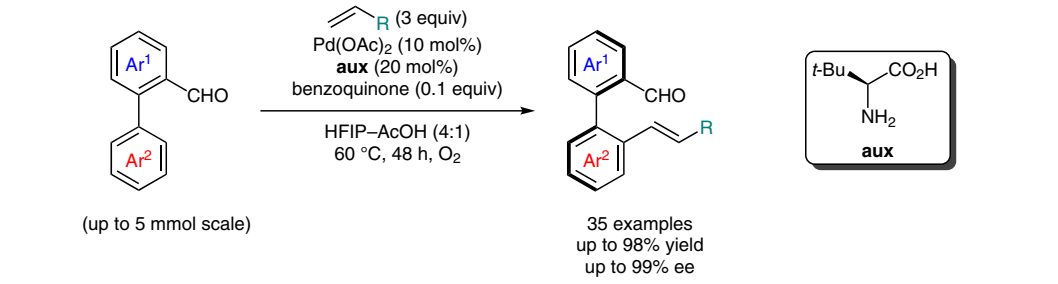
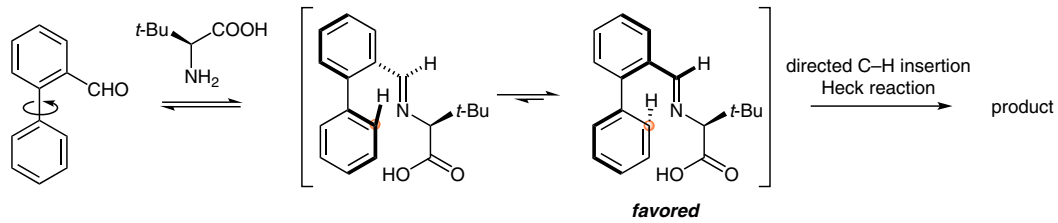
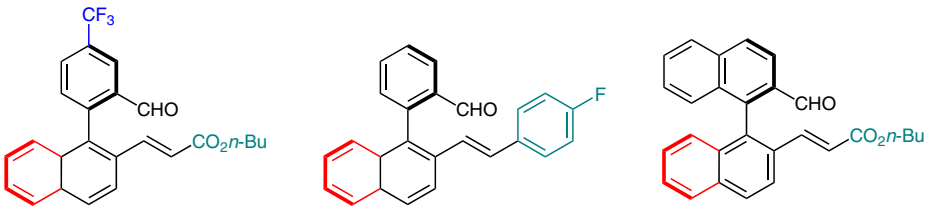
# Dynamic Kinetic Resolution Approach: Synthesis of Axially Chiral Biaryls




**Mechanism:**




**Selected examples:**




90% yield
99% ee

83% yield
97% ee

42% yield*
99% ee

* Substrates substituted at both the 6- and 2'-positions have restricted rotation; thus, products are formed by kinetic resolution.

**Significance:** Shi and co-workers report a protocol to access axially chiral biaryl systems by dynamic kinetic resolution. The approach relies on using *tert*-leucine as an inexpensive chiral auxiliary to allow selective C–H insertion into the favored atropisomer. Rotation is locked by a terminating Heck reaction.

**Comment:** The products are delivered in excellent yields and enantioselectivity. The reaction displays great scalability and is performed on up to 5 mmol. Additionally, both enantiomers can be accessed by simply using the amino acid of opposite chirality. The authors found that if the substrates are substituted at both the 6- and 2′-positions, the reaction does not exhibit dynamic reversibility and hence a maximum of 50% yield can be achieved in such cases.

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**Category**

**Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions**

**Key words**

**atroposelectivity**

**dynamic kinetic resolution**

**palladium catalysis**