
Enantioselective 1,2-Difunctionalization of Dienes Enabled by Chiral Palladium Complex-Catalyzed Cascade Arylation/Allylic Alkylation Reaction


**Palladium-Catalyzed Enantioselective 1,2-Difunctionalization of 1,3-Dienes

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\begin{array}{c}
\text{Ar} = \text{CO}_2\text{Me} \\
\text{MeO}_2\text{C} \\
\end{array}
\]

Selected examples:

- Ar\(^1\) = Me, Ar\(^2\) = Ph, Pd(OAc)\(_2\) (5 mol%), ligand (10 mol%), MTBE, 80 °C, 72 h
- Ar\(^1\) = 4-F, Ar\(^2\) = 4-Cl, Pd(OAc)\(_2\) (5 mol%), ligand (10 mol%), MTBE, 80 °C, 72 h

**Significance:** The authors report a palladium-catalyzed enantioselective three-component coupling of 1,3-dienes with aryl iodides and sodium dialkylmalonates by using a H\(_8\)-BINOL-based phosphoramidite ligand. A series of chiral 1,2-difunctionalized products were prepared in good yields (≤93%) with high regio- and enantioselectivities (15:1 or better and ≤98% ee).

**Comment:** This reaction proceeds by a palladium-catalyzed cascade arylation and asymmetric allylic alkylation reaction, which provides an important alternative strategy for the enantioselective difunctionalization of 1,3-dienes, leading to synthetically useful chiral chemicals.

**Selected examples:**

- Ar\(^1\) = 4-F, Ar\(^2\) = 4-Cl, Pd(OAc)\(_2\) (5 mol%), ligand (10 mol%), MTBE, 80 °C, 72 h
- Ar\(^1\) = 4-F, Ar\(^2\) = 4-Cl, Pd(OAc)\(_2\) (5 mol%), ligand (10 mol%), MTBE, 80 °C, 72 h

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