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Synthesis of α,α-Difluoromethylene Alkynes by Palladium-Catalyzed gem-Difluoropropargylation of Aryl and Alkenyl Boron Reagents


**Catalytic gem-Difluoropropargylation Using Aryl and Alkenyl Boron Reagents**

![Catalytic gem-Difluoropropargylation Using Aryl and Alkenyl Boron Reagents](image)

**Selected examples:**

- **ArB(OH)₂ + Br₂FF₃TIPS**
  - Pd₂(dba)₃ (0.5 mol%)
  - (o-Tol)₃P (3 mol%)
  - K₂CO₃ (3.0 equiv)
  - dioxane, 80 °C, 24 h
  - ArFF₃TIPS
  - 77% yield

- **F₂FF₃TIPS**
  - PhArFF₃TIPS
  - 58% yield

- **PhArFF₃TIPS**
  - 79% yield

- **PhOArFF₃TIPS**
  - 90% yield

- **NCArFF₃TIPS**
  - 78% yield

- **EtO₂C⁻ArFF₃TIPS**
  - 84% yield

- **O₂N⁻ArFF₃TIPS**
  - 67% yield

- **F₃C⁻ArFF₃TIPS**
  - 87% yield

**Significance:** The authors report the first palladium-catalyzed gem-difluoropropargylation of organoboron reagents using gem-difluoropropargyl bromides. A wide range of novel molecules with potential use as building blocks in organic synthesis were prepared. The reaction proceeds with high regioselectivity, broad substrate scope, and excellent functional group compatibility.

**Comment:** Whereas in previous reports special phosphine ligands with large bite angles or very bulky substituents needed to be applied, now a simple ligand (o-Tol)₃P can be used. The late-stage introduction of the fluoro substituents is suitable for applications in the synthesis of complex molecules.