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


**Catalytic \textit{gem}-Difluoropropargylation Using Aryl and Alkenyl Boron Reagents**

**Significance:** The authors report the first palladium-catalyzed \textit{gem}-difluoropropargylation of organoboron reagents using \textit{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 \((\text{o-Tol})_3\text{P}\) can be used. The late-stage introduction of the fluoro substituents is suitable for applications in the synthesis of complex molecules.

**Selected examples:**

\[
\text{ArB(OH)}_2 + \text{Br}_2 \xrightarrow{\text{Pd}_2(\text{dba})_3 (0.5 \text{ mol\%})} \xrightarrow{(\text{o-Tol})_3\text{P} (3 \text{ mol\%})} \xrightarrow{\text{K}_2\text{CO}_3 (3.0 \text{ equiv})} \text{dioxane, 80 °C, 24 h} \xrightarrow{\text{Ar}} \text{F} \quad \text{F} \quad \text{TIPS} 
\]

77% yield 

58% yield 

79% yield 

90% yield 

78% yield 

84% yield 

67% yield 

87% yield