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

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\begin{align*}
&\text{Selected examples:} \\
&\text{Ar}=\text{MeO}_2\text{C} \quad \text{CO}_2\text{Me} \\
&\text{Na}^+\text{Pd(OAc)}_2 (5 \text{ mol\%}) \quad \text{ligand (10 mol\%)} \\
&\text{MTBE, } 80 ^\circ\text{C, 72 h} \\
&\text{Ar} \quad \text{Ar} \quad \text{CO}_2\text{Me} \\
&\text{MeO}_2\text{C} \quad \text{MeO}_2\text{C} \\
&\text{71\% yield, 86\% ee, regioselectivity } \geq 15:1 \\
&\text{62\% yield, 94\% ee, regioselectivity } \geq 15:1 \\
&\text{Selected examples:} \\
&\text{Ar}^1=\text{MeO}_2\text{C} \quad \text{CO}_2\text{Me} \\
&\text{Na}^+\text{Pd(OAc)}_2 (5 \text{ mol\%}) \quad \text{ligand (10 mol\%)} \\
&\text{MTBE, } 80 ^\circ\text{C, 72 h} \\
&\text{Ar}^1 \quad \text{Ar}^2 \quad \text{CO}_2\text{Me} \\
&\text{MeO}_2\text{C} \quad \text{MeO}_2\text{C} \\
&\text{90\% yield, 95\% ee, regioselectivity } \geq 15:1 \\
&\text{71\% yield, 98\% ee, regioselectivity } \geq 15:1 \\
&\text{Significance:} \quad \text{Comment:} \\
&\text{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\text{-BINOL-based phosphoramidite ligand. A series of chiral 1,2-difunctionalized products were prepared in good yields (\geq 93\%) with high regio- and enantioselectivities (15:1 or better and } \leq 98\% \text{ ee).} \\
&\text{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.}
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Synfacts 2016, 12(1), 0047 Published online: 16.12.2015
DOI: 10.1055/s-0035-1561018; Reg-No.: H16315SF