Asymmetric Redox-Relay Oxidative Heck Arylations

**Significance:** The generation of stereogenic centers which are remote to functional groups via carbon–carbon bond formation is currently an interesting topic in organic chemistry. Herein, the authors report a highly efficient palladium-catalyzed oxidative Heck reaction of alkenyl alcohols furnishing optical active aldehydes via a redox-relay process.

**Comment:** The authors demonstrated that the strategy of the redox-relay process is applicable even on an η2-position, for the site-selective and highly enantioselective arylation of alkenyl alcohols. Additionally, preliminary mechanistic investigations are conducted for rationalizing the stereochemical course of the palladium- and copper-catalyzed reaction.

**Selected examples:**

<table>
<thead>
<tr>
<th>Ar B(OH)2 (3.0 equiv)</th>
<th>Pd(MeCN)2(OTs)2 (6.0 mol%)</th>
<th>Cu(OTf)2 (6.0 mol%)</th>
<th>ligand (13 mol%)</th>
<th>R1</th>
<th>R2</th>
<th>Ar</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar = cyclohexene</td>
<td>R1 = Me, Et, i-Pr</td>
<td>R2 = H, Me</td>
<td>n = 0–5</td>
<td>27 examples</td>
<td>0.5 mmol scale up to 85% yield er up to 99:1 major/minor = 1.2:1 to 49:1</td>
<td>1 example</td>
<td>10 mmol scale</td>
</tr>
</tbody>
</table>

**Rationalization of stereochemical course:**

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

**Key words:** oxidative Heck reaction, redox relay, palladium, copper, alkenyl alcohols