Enantioselective Intermolecular Ruthenium-Catalyzed Cycloaddition

**Significance:** Metal-catalyzed cycloaddition is one of the most active areas of research. The authors have developed an enantioselective intermolecular cycloaddition of benzocyclobutenone with tetralone-derived ketols through a C–C bond oxidative addition catalyzed by a chiral ruthenium–DM-SEGPHOS complex.

**Comment:** This ruthenium-catalyzed intermolecular cycloaddition merging C–C bond activation and transfer hydrogenation coupling proceeds smoothly in moderate to high yield with excellent enantio-, diastereo-, and regioselectivities. The obtained products can be transformed into the corresponding compounds containing dione and amine motifs.

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**Selected examples:**

<table>
<thead>
<tr>
<th>Transformation</th>
<th>OMe</th>
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</tr>
</thead>
<tbody>
<tr>
<td>+ R2</td>
<td>OMe</td>
<td>OMe</td>
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<tr>
<td>+ Ru3(CO)12 (2 mol%) + (R)-DM-SEGPHOS (6 mol%)</td>
<td>TIPSO</td>
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<tr>
<td>m-xylenes (1 M)</td>
<td>150 °C, 24 h</td>
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<tr>
<td>Yield</td>
<td>96% yield (X-ray)</td>
<td>97% yield</td>
<td>71% yield</td>
<td>73% yield</td>
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<tr>
<td>dr</td>
<td>&gt; 20:1</td>
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<td>er</td>
<td>&gt; 97:3</td>
<td>&gt; 98:2</td>
<td>&gt; 96:4</td>
<td>&gt; 97:3</td>
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**Transformation:**

1. TBAF (1.5 equiv), THF (0.1 M), 25 °C
2. DMP (1.5 equiv), CH2Cl2 (0.2 M), 25 °C

73% yield in 2 steps

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