Nickel-Catalyzed Asymmetric Claisen Rearrangement

**Significance:** The authors present an asymmetric propargyl and allyl Claisen rearrangement using a readily available chiral N,N'-dioxide–nickel(II) complex. Product allyl and allenyl compounds were obtained with good yield and excellent enantio- and diastereoselectivities.

**Comment:** This rearrangement works with relatively inexpensive metal (nickel) under mild reaction conditions. The produced β-keto esters with all-carbon quaternary stereogenic centers with allenyl and allyl substituents are highly useful chiral building blocks.

**Selected examples:**

<table>
<thead>
<tr>
<th>Reaction Conditions</th>
<th>Yields/Enantiomeric Excesses</th>
<th>Stereochemical Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>L/Ni(OTf)_2 (1:1, 5–10 mol%) CH_2Cl_2, 35 °C 24–96 h</td>
<td>88% yield 98% ee</td>
<td>88% yield 97% ee dr = 99:1</td>
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<tr>
<td>L/Ni(BF_4)_2·6H_2O (1:1, 0.5–2 mol%) CH_2Cl_2, 35 °C 1–48 h</td>
<td>91% yield 98% ee</td>
<td>95% yield 97% ee dr = 98:2</td>
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<td>95% yield 96% ee dr = 99:1</td>
<td>95% yield 95% ee dr = 97:3</td>
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**Stereochemical model:**

This rearrangement works with relatively inexpensive metal (nickel) under mild reaction conditions. The produced β-keto esters with all-carbon quaternary stereogenic centers with allenyl and allyl substituents are highly useful chiral building blocks.