Unit 5
Stereoccontrolled 1,2–Addition of Allylmetal Compounds to Carbonyl Groups

- Substrate Control: Addition of Achiral Allylmetals to $\alpha$–Chiral Aldehydes
- Reagent Control: Addition of Chiral Allylmetals to Achiral Aldehydes
- Reagent Control: Addition of Allylmetals to Achiral Aldehydes (w/ Chiral Lewis Acids)
- Addition of Chiral Allylmetals to $\alpha$–Chiral Aldehydes
- Crotymetal Additions: 3,4-Stereochemistry (Intrinsic Diastereoselection)
- Crotymetal Additions to $\alpha$–Chiral Aldehydes

Reagent Control: Addition of Chiral Allylmetals to Achiral Aldehydes

Allylboron Compounds

H. C. Brown
1912-2004
Allyltitanium Compounds

Reviews:
"Synthesis and Reactivity of Allyltitanium Derivatives" Szymoniak and Moise, C. 
"Chiral Titanium Complexes for Enantioselective Addition of Nucleophiles to Carbonyl Groups" 
"In the Arena of Enantioselective Synthesis, Titanium Complexes Wear the Laurel Wreath" Ramon, D. J.; Yus, M. *Chem. Rev.* **2006**, *106*, 2126

![Diagram of (R,R)-(TADDOL)CpTi](image)

Dieter Seebach
*TADDOL Ligands*

Allylsilicon Compounds


★ Reagent Control: Addition of Allylmetals to Achiral Aldehydes
(w/ Chiral Lewis Acids)

Allylstannanes

![Diagram of Allylstannanes](image)


Useful recent review: "BINOL: A Versatile Chiral Reagent" 
### Allylmetal Showdown

![Chemical structures and reactions]

<table>
<thead>
<tr>
<th>Method</th>
<th>Cost</th>
<th>Selectivity</th>
<th>Preparation (steps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roush</td>
<td>$5</td>
<td>80:20</td>
<td>2 (Storable)</td>
</tr>
<tr>
<td>Carriera</td>
<td>$14</td>
<td>80:20</td>
<td>0</td>
</tr>
<tr>
<td>(only non-enolizable)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brown</td>
<td>$14</td>
<td>98:2</td>
<td>1 (in situ)</td>
</tr>
<tr>
<td>Leighton</td>
<td>$20</td>
<td>94:6</td>
<td>1 (Storable)</td>
</tr>
<tr>
<td>(pseudoephedrine)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Keck</td>
<td>$19</td>
<td>98:2</td>
<td>0</td>
</tr>
<tr>
<td>Duthaler</td>
<td>$414</td>
<td>97:3</td>
<td>2 (Storable)</td>
</tr>
</tbody>
</table>

★ Addition of Chiral Allymetals to α-Chiral Aldehydes
(Double Asymmetric Synthesis)

![Chemical structures and reactions]
**Addition of Chiral Allylmetals to α-Chiral Aldehydes**

(Double Asymmetric Synthesis)

![Chemical structures and reactions](image)

- (R,R)\((TADDOL)\)CpTi
- (+)-Ipc\(_2\)B

- PhCHO → PhCH\(_2\)OH + PhCH\(_2\)OH
  - 99.5%
  - 0.5%

- PhCHO → PhCH\(_2\)OH + PhCH\(_2\)OH
  - 97%
  - 3%

- PhCHO → PhCH\(_2\)OH + PhCH\(_2\)OH
  - 95%
  - 5%

- PhCHO → PhCH\(_2\)OH + PhCH\(_2\)OH
  - 67%
  - 33%

![Chemical structures and reactions](image)

- (i-Pro)\(_2\)CpTi
- (R,R)\((TADDOL)\)CpTi
- (S,S)\((TADDOL)\)CpTi

- OCONC\(_2\)t-Bu → OCONC\(_2\)t-Bu + OCONC\(_2\)t-Bu
  - 37%
  - 63%

- OCONC\(_2\)t-Bu → OCONC\(_2\)t-Bu + OCONC\(_2\)t-Bu
  - 93%
  - 98%

- OCONC\(_2\)t-Bu → OCONC\(_2\)t-Bu + OCONC\(_2\)t-Bu
  - 95%
  - 0.5%

- OCONC\(_2\)t-Bu → OCONC\(_2\)t-Bu + OCONC\(_2\)t-Bu
  - 99.5%

![Chemical structures and reactions](image)

- PhCH\(_2\)CHO → PhCH\(_2\)OH + PhCH\(_2\)OH
  - 86%
  - 5%

- PhCH\(_2\)CHO → PhCH\(_2\)OH + PhCH\(_2\)OH
  - 86%
  - 98%

- PhCH\(_2\)CHO → PhCH\(_2\)OH + PhCH\(_2\)OH
  - 86%
  - 2%