Chapter 4
Functional Group Transformations: Oxidation and Reduction

Oxidation states (numbers)

<table>
<thead>
<tr>
<th>-4</th>
<th>-2</th>
<th>0</th>
<th>+2</th>
<th>+4</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Chemical structure" /></td>
<td><img src="image2" alt="Chemical structure" /></td>
<td><img src="image3" alt="Chemical structure" /></td>
<td><img src="image4" alt="Chemical structure" /></td>
<td><img src="image5" alt="Chemical structure" /></td>
</tr>
</tbody>
</table>

Less E.N. than C = -1
More E.N. than C = +1
C = 0

4.8 – Terminology for Reduction of Carbonyl Compounds

Chemoselective reagent – reacts selectively with one FG in the presence of others

\[ \text{chemoselective} \]

![Chemical structure](image6) \rightarrow ![Chemical structure](image7)

Zn(BH₄)₂, THF
RT, 5 min
100%

Ranu, B. C. Synlett. 1993, 885-892

Regioselective reaction – reagent adds at only one of several regions (places)

\[ \text{regioselective} \]

![Chemical structure](image8) \rightarrow ![Chemical structure](image9)

NaBH₄, THF
0 °C, 2 h
62%

Kar, A.; Argade, N. P. Synthesis 2005, 2284-2286
4.8 – Terminology for Reduction of Carbonyl Compounds

**Stereoselective reaction** – one stereoisomer is formed preferably over other(s)

![Stereoselective reaction](image)


**Stereospecific reaction** – one isomer of the SM gives only one product isomer

![Stereospecific reaction](image)

Decicco, C. P.; Grover, P. *Synlett.* 1997, 529-530

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**Prochiral Center** – sp² hybridized C, which may become chiral upon addition

![Prochiral Center](image)

**Stereogenic Carbon** – general term for chiral atom, asymmetric atom, etc.

![Stereogenic Carbon](image)

Careful – molecules without stereogenic carbon may still be chiral (i.e. asymmetric)
4.8 – Terminology for Reduction of Carbonyl Compounds

**Stereoisomers** – molecules with the same formula but different spatial arrangements

**Enantiomers** – molecules that are related as non-superimposable mirror images

**Diastereomers** – stereoisomers not related as mirror images

**Asymmetric Induction** – preferential formation of one stereoisomer (enantiomer or diastereomer over another. Controlled by another chiral entity in either the substrate, the reagent, a catalyst, or even solvent

**Enantioselective Reaction** – preferential formation of one of two enantiomers when an achiral starting material is used

**Enantiomeric Excess** – a measure of the ratios of the two possible enantiomers formed in an enantioselective reaction (%ee)

**Diastereomeric Excess** – [% major diastereomer - % minor diastereomer] (%de)

**Racemate** – racemic mixture, i.e. equal amounts of two enantiomers ([α]D = 0)

**Homochiral** – same sense of chirality as a related molecule

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4.9 – Nucleophilic Reducing Agents

<table>
<thead>
<tr>
<th>Hydride Donors</th>
<th>Amines</th>
<th>Alcohol</th>
<th>Alcohol</th>
<th>Alcohol</th>
<th>Alcohol</th>
<th>Alcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiAlH₄</td>
<td>Aamine</td>
<td>Alcohol</td>
<td>Alcohol</td>
<td>Alcohol</td>
<td>Aamine</td>
<td>Alcohol</td>
</tr>
<tr>
<td>N₂H₄</td>
<td>Aamine</td>
<td>Alcohol</td>
<td>Alcohol</td>
<td>Alcohol</td>
<td>Aamine</td>
<td>Alcohol</td>
</tr>
<tr>
<td>Na₂(OCH₂Bu₂)</td>
<td>Aamine</td>
<td>Alcohol</td>
<td>Alcohol</td>
<td>Alcohol</td>
<td>Aamine</td>
<td>Alcohol</td>
</tr>
<tr>
<td>AlH₃</td>
<td>Aamine</td>
<td>Alcohol</td>
<td>Alcohol</td>
<td>Alcohol</td>
<td>Aamine</td>
<td>Alcohol</td>
</tr>
<tr>
<td>NaBH₄</td>
<td>Aamine</td>
<td>Alcohol</td>
<td>Alcohol</td>
<td>Alcohol</td>
<td>Aamine</td>
<td>Alcohol</td>
</tr>
<tr>
<td>NaCNBH₃</td>
<td>Aamine</td>
<td>Alcohol</td>
<td>Alcohol</td>
<td>Alcohol</td>
<td>Aamine</td>
<td>Alcohol</td>
</tr>
<tr>
<td>Na₂(C₂H₃)O₂BH</td>
<td>Aamine</td>
<td>Alcohol</td>
<td>Alcohol</td>
<td>Alcohol</td>
<td>Aamine</td>
<td>Alcohol</td>
</tr>
<tr>
<td>B₂H₆</td>
<td>Aamine</td>
<td>Alcohol</td>
<td>Alcohol</td>
<td>Alcohol</td>
<td>Aamine</td>
<td>Alcohol</td>
</tr>
<tr>
<td>Li(THF)BH</td>
<td>Aamine</td>
<td>Alcohol</td>
<td>Alcohol</td>
<td>Alcohol</td>
<td>Alcohol</td>
<td>Alcohol</td>
</tr>
<tr>
<td>H₂ (catalyst)</td>
<td>Aamine</td>
<td>Alcohol</td>
<td>Alcohol</td>
<td>Alcohol</td>
<td>Aamine</td>
<td>Alcohol</td>
</tr>
</tbody>
</table>

**Abbreviations:**
- **Amine:** Amine groups
- **Aldehyde:** Aldehyde groups
- **Alcohol:** Alcohol groups
- **Acid Sphere:** Acid groups
- **Ester:** Ester groups
- **Amide:** Amide groups
- **Carboxylic Acid:** Carboxylic acid groups

**Notes:**
- α-Alkyl esters are reduced to the corresponding alcohols.
- Indicates no reaction or no productive reaction (alkohols are deprotonated in many instances).
4.9 – Nucleophilic Reducing Agents

4 LiH + AlCl₃ → LiAlH₄ + 3 LiCl

Powerful reducing agent - ust use aprotic solvent, not chemoselective


4.9 – Nucleophilic Reducing Agents

![Chemical Reaction Diagram]


![Chemical Reaction Diagram]


4.9 – Nucleophilic Reducing Agents - Selective

\[
\text{LiAlH}_4 + 3 \text{ROH} \xrightarrow{\text{THF or Ether}} \text{LiAlH(OH)₃} + 3 \text{H}_2
\]

Ketone to alcohol

![Chemical Reaction Diagram]


Nitrile to aldehyde

![Chemical Reaction Diagram]

4.9 – Nucleophilic Reducing Agents - Selective

Acid chloride to aldehyde


\[
\text{Na}([\text{t-BuO}])_2\text{AlH}
\]

\[
\begin{array}{c}
\text{COCl} \\ \text{STBA, diglyme} \\ \text{THF, } -78^\circ \text{C}
\end{array}
\xrightarrow{100\%}
\begin{array}{c}
\text{CHO}
\end{array}
\]

\[
\begin{array}{c}
\text{CHO} \\ \text{STBA, diglyme} \\ \text{THF, } -78^\circ \text{C}
\end{array}
\xrightarrow{93\%}
\begin{array}{c}
\text{CHO}
\end{array}
\]
diglyme = \(\text{CH}_3\text{OCH}_2\text{CH}_2\text{O}\)


Amide to aldehyde


\[
\begin{array}{c}
\text{NMe}_2 \\ \text{LiAIH(DEt)}_2, \text{ether}
\end{array}
\xrightarrow{0^\circ \text{C}, 1 \text{ h}}
\begin{array}{c}
\text{CH}_2
\end{array}
\]

89% de

4.9 – Nucleophilic Reducing Agents – Red-Al

\[
\text{Na} \left[ \text{AlH}_2\left(\text{OCH}_2\text{CH}_2\text{OCH}_3\right)_2\right]
\]

Sodium Bis(2-methoxyethoxy)aluminum hydride – Red-Al

\[\text{18} \quad \text{19: } R = \text{OH} \quad \text{20: } R = \text{SH} \quad \text{21: } R = \text{H}\]

c) Na[AlH(2MeOEt)2], toluene, −78 °C, 0.5 h


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4.9 – Nucleophilic Reducing Agents - Red-Al

\[\text{X} = \text{Boc, Z} \]

\[\text{R} = \text{amino acid side chain}\]

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boc-Phe-OH</td>
<td>Boc-Phe-ol</td>
<td>95</td>
</tr>
<tr>
<td>Z-Phe-OH</td>
<td>Z-Phe-ol</td>
<td>92</td>
</tr>
<tr>
<td>Boc-Val-OH</td>
<td>Boc-Val-ol</td>
<td>84</td>
</tr>
<tr>
<td>Boc-Trp-OH</td>
<td>Boc-Trp-ol</td>
<td>87</td>
</tr>
<tr>
<td>Boc-Cys(Bzl)-OH</td>
<td>Boc-Cys(Bzl)-ol</td>
<td>98</td>
</tr>
<tr>
<td>Boc-Tyr(Bzl)-OH</td>
<td>Boc-Tyr(Bzl)-ol</td>
<td>89</td>
</tr>
<tr>
<td>Boc-Lys(Zb)-OH</td>
<td>Boc-Lys(Zb)-ol</td>
<td>75</td>
</tr>
</tbody>
</table>

Amide survives, acid gets reduced

4.9 – Nucleophilic Reducing Agents – NaBH₄

\[ \text{B(OCH₃)₃} + 4 \text{NaH} \rightarrow \text{NaBH₄} + 3 \text{NaOCH₃} \]


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4.9 – Nucleophilic Reducing Agents - NaBH₄

\[ \text{Ar} \quad \text{O} \quad \text{CH}_2 \quad \text{CH}_3 \quad \text{ONa} \quad \text{NaBH₄} \quad 90^\circ \text{C} \rightarrow \text{Ar} \quad \text{O} \quad \text{CH}_2 \quad \text{CH}_3 \quad \text{ONa} \]


4.9 – Nucleophilic Reducing Agents - NaBH₄

Fexofenadine (antihistamine)


4.9 – Nucleophilic Reducing Agents - NaBH₄

Okaramine N synthesis

Luche reduction


4.9 – Nucleophilic Reducing Agents - LiBH₄

Lithium borohydride is commonly used for the selective reduction of esters and lactones to the corresponding alcohols in the presence of carbonylic acids, tertiary amides, and nitrites. Aldehydes, ketones, epoxides, and several other functional groups can also be reduced by lithium borohydride.


![Reaction Diagram](image)

**ZnBH₄**

Zn(BH₄)₂

Less basic than NaBH₄ but short shelf-life

4.9 – Nucleophilic Reducing Agents - Selectrides

Among hydride sources, lithium triethylborohydride (Super Hydride, LiEt₃BH) has been shown to rapidly reduce alkyl bromides efficiently, even those derived from hindered alcohols.

\[
\text{Reductant} \quad \text{LiEt}_3\text{BH} \quad \text{OH} \quad \text{CH}_2=\text{CH} \quad \text{CH}_2=\text{CH} \quad \text{OTs} \quad \text{54%} \quad \text{80%} \quad \text{25%} \quad \text{15%} \quad \text{0%}
\]


\[
\text{BnOH} \quad \text{CH}_3\text{CHO} \quad \text{CH}_2=\text{CH} \quad \text{LiEt}_3\text{BH}, \text{THF} \quad \text{H}_2\text{O}, \text{NaOH (aq)} \quad \text{CH}_3\text{OH}
\]

92%


\[
\text{H}_{2}\text{O} \quad \text{H}_{2}\text{O} \quad \text{H}_{2}\text{O} \quad \text{LiEt}_{3}\text{BH}, \text{Int.} \quad \text{OH} \quad \text{H}_{2}\text{O}
\]

72%


4.9 – Nucleophilic Reducing Agents – NaBH₃CN

\[
\text{NaBH}_{3}\text{CN} \quad \text{CH}_2\text{O} \quad \text{84%}
\]


\[
\text{OTBS} + \text{H}_2\text{C} \quad \text{AcO-CH}_2\text{CHO} \quad \text{Na}\text{(AcO)}_2\text{BH}, \text{Sn(OTf)}_2 \quad \text{4 A MS, CHCl}_3 \quad 0^\circ \text{C}
\]

66%

4.9 – Nucleophilic Reducing Agents – NaBH₃CN


4.9 – Nucleophilic Reducing Agents – NaBH₃CN


2-deoxymugineic acid
4.9 – Nucleophilic Reducing Agents – NaBH₃CN

- Two possible mechanisms for reduction of ketopyrazones by sodium cyanoborohydride have been suggested. Direct hydride attack by sodium cyanoborohydride on an iminium ion is proposed in most cases.

- However, reduction of an azohydrazone is proposed when inductive effects and/or conformational constraints favor tautomerization of the hydrazone to an azohydrazone.


4.9 – Nucleophilic Reducing Agents – NaBH₃CN

DIBAL-H reacts slowly with electron poor compounds, and more quickly with electron rich compounds. In short it is an electrophilic reducing agent. While the mechanism by which LIAH₂ reacts is complex, LIAH₂ can be thought of as a nucleophilic reducing agent.


- The mechanism for this "alkene walk" reaction apparently proceeds through a diazene intermediate which transfers hydride by 1,5-sigmatropic rearrangement.


4.10 – Electrophilic Reducing Agents

Dilisobutylaluminum Hydride (DIBAL): i-Bu₂AlH

- At low temperatures, DIBAL reduces esters to the corresponding aldehydes, and lactones to lactols.

- Typically, toluene is used as the reaction solvent, but other solvents have also been employed, including dichloromethane.


DIBAL-H reacts slowly with electron poor compounds, and more quickly with electron rich compounds. In short it is an electrophilic reducing agent. While the mechanism by which LIAH₂ reacts is complex, LIAH₂ can be thought of as a nucleophilic reducing agent.

4.10 – Electrophilic Reducing Agents

1. DIBAL, CH₂Cl₂, –78 °C
2. CH₃OH, –60 °C
3. potassium sodium tertate

88%


OTBS

\[ \text{DIBAL-H (1M in PhMe)} \]

\[ \text{CH}_2\text{Cl}_2, -78^\circ \text{C}, 2\text{h} \]

R

\[ \text{OTBS} \]

82%


4.10 – Electrophilic Reducing Agents

\[ \text{DIBAL-THF} \]

\[ -100 \rightarrow -78^\circ \text{C} \]

(+)-stereomer D

Swern, 62%  \[ R = \text{CH}_3\text{OH} \]

62%  \[ R = \text{CHO} \]

16%

4.10 – Electrophilic Reducing Agents

- Nitriles are reduced to imines, which hydrolyze upon work-up to furnish aldehydes.

\[
\text{DIBAL, other} \rightarrow -78{\degree}C \rightarrow \text{60%}
\]


- Borane complexes: BH₄⁺L
  - Borane is commonly used for the reduction of carboxylic acids in the presence of esters, lactones, amides, halides and other functional groups. In addition, borane rapidly reduces aldehydes, ketones, and alkynes.

  - Borane is commercially available as a neat complex with tetrahydrofuran (THF) or dimethylsulfoxide or in solution. In addition, gaseous diborane (B₂H₆) is available.

  - The borane-dimethylsulfoxide complex exhibits improved stability and solubility compared to the borane-THF complex.

  - Competing hydroboration of carbon-carbon double bonds can limit the usefulness of borane-THF as a reducing agent.


4.10 – Electrophilic Reducing Agents

\[ \text{R} - \text{O}-\text{H} + \text{BH}_3 \xrightarrow{(-3\text{H}_2)} \text{R} - \text{O}-\text{H} \]

1. BH₃/THF (1 eq.)
2. THF, -18 °C to rt
3. H₂O workup

\[ \text{O} \xrightarrow{1. \text{BH}_3/\text{THF}, 0 °C} \text{O} \xrightarrow{2. \text{dihydropyrimidin. THF}} \text{O} \xrightarrow{\text{TeOH}, 0 °C} \]


\[ \text{HO}_2\text{C} = \text{CO}_2\text{Et} \xrightarrow{\text{BH}_3/\text{THF}, 0 → 25 °C} \text{HOCH}_2\text{CO}_2\text{Et} \]


4.11 – Regio- and Chemoselective Reductions

\[ \text{O} \xrightarrow{\text{Reductant}} \text{CH}_2 + \text{OH} \]

51% 49%
50% 50%
50%
100%


\[ \text{O} \xrightarrow{\text{Zn(BH}_3\text{)₃, THF}} \text{OH} \]

Ranu, B. C. Synlett. 1993, 885-892

\[ \text{O} \xrightarrow{\text{0.5 eq. NaBH}_4, \text{EtOH}, -30 °C, 15 \text{ min}} \text{O} \]

4.11 – Regio- and Chemoselective Reductions

Attack from underneath favoured?

Mat Maust (Schering-Plough)

4.12 – Diastereoselective Reductions of Cyclic Ketones

<table>
<thead>
<tr>
<th>Conditions</th>
<th>cis (%)</th>
<th>trans (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(Oi-Pr)_3, i-PrOH</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>LiAlH_4, THF</td>
<td>76</td>
<td>24</td>
</tr>
<tr>
<td>LiAlH(Ot-Bu)_3, THF</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>NaBH_4, MeOH</td>
<td>77</td>
<td>23</td>
</tr>
<tr>
<td>LiBH(sec-Bu)_3, THF</td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>Li-trisiamylborohydride</td>
<td>&lt;1</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>
4.12 – Diastereoselective Reductions of Cyclic Ketones

Mitsunobu reaction

4.13 – Inversion of Secondary Alcohol Configuration

Mitsunobu reaction
4.14 – Diastereofacial Selectivity in Acyclic Systems

Re, Si

A stereoheterotopic face of a trigonal atom is designated Re if the ligands of the trigonal atom appear in a clockwise sense in order of CIP priority when viewed from that side of the face. The opposite arrangement is termed Si.

See also enantiotopic, and illustrated under prochirality.

1996, 68, 2216


4.14 – Diastereofacial Selectivity in Acyclic Systems

enantiotopic

Constitutionally identical atoms or groups in molecules which are related by symmetry elements of the second kind only (mirror plane, inversion centre or rotation-reflection axis). For example the two groups e in a grouping Cabc are enantiotopic. Replacement of one of a pair of enantiotopic groups forms one of a pair of enantiomers. Analogously, if complexation or addition to one of the two faces defined by a double bond or other molecular plane gives rise to a chiral species, the two faces are called enantiotopic.

See also prochiral, diastereotopic.

1996, 68, 2207

Enantiotopic faces of the carbonyl
4.14 – Diastereofacial Selectivity in Acyclic Systems

diastereotopic
Constitutionally equivalent atoms or groups of a molecule which are not symmetry related. Replacement of one of two diastereotopic atoms or groups results in the formation of one of a pair of diastereoisomers. In the example below the two hydrogen atoms of the methylene group C-3 are diastereotopic.

\[
\begin{array}{cc}
\text{Me} & \text{Me} \\
\text{H} & \text{H} \\
\text{Me} & \text{Me}
\end{array}
\quad \quad
\begin{array}{cc}
\text{Me} & \text{Me} \\
\text{H} & \text{H} \\
\text{Me} & \text{Me}
\end{array}
\]

See also prochirality, enantiotopic, heterotopic. 1996, 68, 2206

asymmetric induction
The traditional term describing the preferential formation in a chemical reaction of one enantiomer or diastereoisomer over the other as a result of the influence of a chiral feature present in the substrate, reagent, catalyst or environment.

Example: enantioselective reduction i.e asymmetric induction

The reductions so far (except the MPV reaction) have been concerned with *kinetically controlled* reactions (i.e. irreversible) that involve the formation of tetrahedral (sp³) carbon atoms within a molecular framework.

Because of the conformational mobility of acyclic compounds, it is important to recognize an important precept known as **The Curtin Hammett Principle:**

The ratio of products obtained from a group of equilibrating conformers is *determined by transition state energies*, not conformer concentrations.

Enantiomers are equal in energy, therefore enantiomeric transition states are also equal in energy. It is impossible to achieve any selectivity (without the addition of a chiral reagent), and a racemic mixture is formed.

If there is a chiral centre in the substrate we form diastereomers, then the transition state energies need not be equal and we should observe some selectivity. This forms the basis for all diastereoselectivity (and also for all enantioselectivity – except that the chirality is not in the substrate).

http://www-teach.ch.cam.ac.uk/teach/C5/C5_part2.pdf
4.14 – Diastereotopicity – Asymmetric Induction

1st example: 1,2-diastereoselectivity; the chiral center at C-2 influences the outcome of the reduction – asymmetric induction

2nd example: chiral center too far away to have any influence

1,3-diastereoselectivity also possible (later)

4.14 – Models for Predicting Mode of Asymmetric Induction

the substituents on the chiral center adjacent to the carbonyl group are labeled L (large), M (medium) and S (small), reflecting their approximate size

Each model predicts the correct configuration of the favored diastereomer from LiAlH₄ reduction of 3-phenyl-2-butanone. Original Cram model (1952) updated by Karabatsos and then Felkin and Ahn.

http://www.cem.msu.edu/~reusch/VirtualText/sterslct.htm
4.14 – Models for Predicting Mode of Asymmetric Induction

Felkin-Ahn model takes into account:
1. The Bürgi-Dunitz trajectory of the nucleophile (107-109°)
2. Conformational (torsional) issues in both reactant and the transition state
3. Stereoelectronic considerations (C-L σ donation into C=O π*)
4.14 – Chelation-controlled Addition Reactions

1. A heteroatom with lone pairs available for coordination to a metal ion.
2. A metal ion that favours coordination to both C=O and the heteroatom. E.g.:
   - Mg$^{2+}$, Zn$^{2+}$, Al$^{3+}$, Ce$^{3+}$ and Ti$^{4+}$ are excellent
   - Li$^+$ is sometimes okay
   - Na$^+$ and K$^+$ are bad

When to Use Which Model?

- Use Felkin-Anh model: consider rxns on conformations with the largest group perpendicular to C=O
- Use chelation model: consider rxns on conformations with C=O and heteroatom held close together in space

Transition states with different metal counterions:

With Na$^+$

With Mg$^{2+}$
4.14 – Examples of Cram/Felkin-Ahn vs. Chelation

Rationale using chelation model (Zn$^{2+}$)


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Rationale using Felkin-Ahn model

4.14 – Examples of Cram/Felkin-Ahn vs. Chelation


4.14 – Hydroxyl-directed Reduction of β-Hydroxy Ketones

- Chelate formed at low temperature in the first step
- **External** nucleophile then added (NaBH₄)
- Nucleophile attack from underneath to avoid CH₃
- *Syn* stereochemistry achieved from remote location
4.14 – Hydroxyl-directed Reduction of β-Hydroxy Ketones

- Reagent chelates to hydroxyl to form complex
- **Internal** nucleophile then adds in an intramolecular sense
- Nucleophile attack directed by 6-membered transition state
- *Anti* stereochemistry achieved from remote location

![Reaction Scheme]

4.15 – Enantioselective Reductions

**Alpine-Borane**

**Diastereomeric TS**

Steric clash makes this TS higher in energy

Lower energy TS leads to major product, although products are of equal energy.
4.15 – Enantioselective Reductions

Corey-Bakshi-Shibata Reduction

\[ \text{1 mol-%} \]

\[ \text{1 eq. BH}_3 \text{ (in THF)} \]

\[ \text{THF, 0-30°C, 80 min} \]

\[ \text{ex > 98.5} \]

\[ \text{97% (rac)} \]


4.15 – Enantioselective Reductions

\[ \text{5 mol% (R)-NaaCB5} \]

\[ \text{1 eq. BH}_3 \text{ (in THF)} \]

\[ \text{THF, -16°C, 3 h} \]

\[ \text{95% (rac)} \]

\[ \text{ee: 94%} \]


*In situ* formation of the Oxazaborolidine catalyst

4.15 – Enantioselective Reductions

<table>
<thead>
<tr>
<th>Ketone</th>
<th>Yield (%)</th>
<th>ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>97</td>
<td>97</td>
</tr>
<tr>
<td>Cl-</td>
<td>82</td>
<td>90</td>
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<td></td>
<td>81</td>
<td>99</td>
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<tr>
<td></td>
<td>87</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>89</td>
<td>50</td>
</tr>
</tbody>
</table>


4.15 – Enantioselective Reductions

Proposed catalytic cycle