## Two enantiomers, two pathways, one intermediate



## Synthesis A:

- Why $\mathrm{CeCl}_{3}$ is used for the first step?
- Give the structure of 1
- Explain the mechanism between 2 and 3
- Give the 3 missing steps between 3 and 4
- Give the last 2 steps missing

(-)-Carvone



Intermediate A




1. L-selectride then $\mathrm{H}_{3} \mathrm{O}^{+}(80 \%)$ 2. PCC (95\%)
2. TMSCI, Lil, HMDS, then PhSeCl
3. $\mathrm{H}_{2} \mathrm{O}_{2}$, pyr 3. $\mathrm{AcOH}, \mathrm{mW}$



4
$\stackrel{3}{ } \stackrel{\text { steps }}{ }$

## Synthesis B:

- Give the 3 missing steps between 6 and 7
- Give the mechanism of the reaction between 7 and 8
- Explain the formation of 10



[^0]
## Two enantiomers, two pathways, one intermediate SOLUTIONS

## Synthesis A:





Intermediate A

1. 1,2-addition of the Grignard reagents with Luche conditions

2. Reactions between $\mathbf{1}$ and $\mathbf{2}$

3. Reactions between 2 and $\mathbf{3}$

4. Radical Cyclization and epimerization
a)


18
b)


14a


12


14b

Scheme 4. a) Postulated samarium-templated ring closure of radical 18 to form hydroxy ketone 12; and b) base-mediated equilibration of of hydroxy ketones $\mathbf{1 4 a}$ and 14b.

## Synthesis B:

- Give the 3 missing steps between 6 and 7
- Give the mechanism of the reaction between 7 and 8
- Explain the formation of 10

$n$-BuLi, $\mathrm{Ph}_{3} \mathrm{P}+\mathrm{CHOMe} \cdot \mathrm{Cl}^{-}$ then NBS , then $\mathrm{Zn}-\mathrm{NH}_{4} \mathrm{Cl}$


> | 1. $\mathrm{OsO}_{4}$ |
| :--- |
| 2. $\mathrm{NalO}_{4}$ |
| 3. KOH |
| $\begin{array}{c}39 \% \\ 4 \text { steps }\end{array}$ |


10



1. MeMgBr
2. PCC
$\leftarrow \frac{2 . \text { PCC }}{65 \%}$
(three steps)

8

Intermediate A
2. Homologation reaction between $\mathbf{7}$ and $\mathbf{8}$

3. Reaction between $\mathbf{9}$ and $\mathbf{1 0}$

Scheme 1. Selective C-H Insertion of Alkylidene Carbenes



[^0]:    Intermediate A

