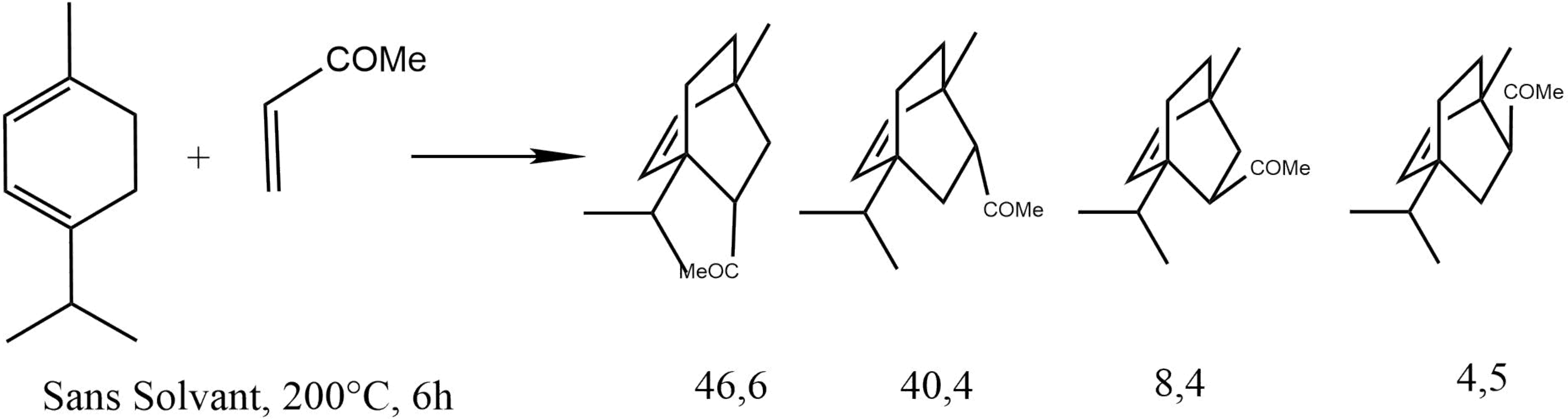
Sélectivité en synthèse organique


COMe
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Sans Solvant, 200°C, 6h
46,6
40,4
8,4
4,5

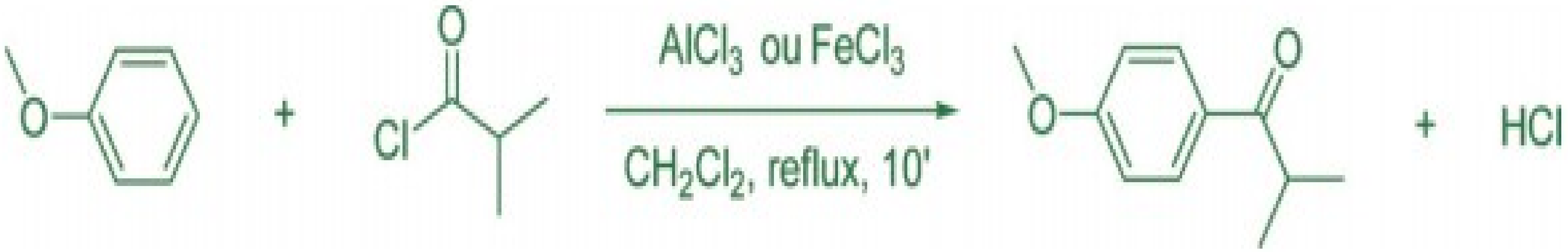

Figure 1 : Équation de la réaction de Friedel-Crafts.

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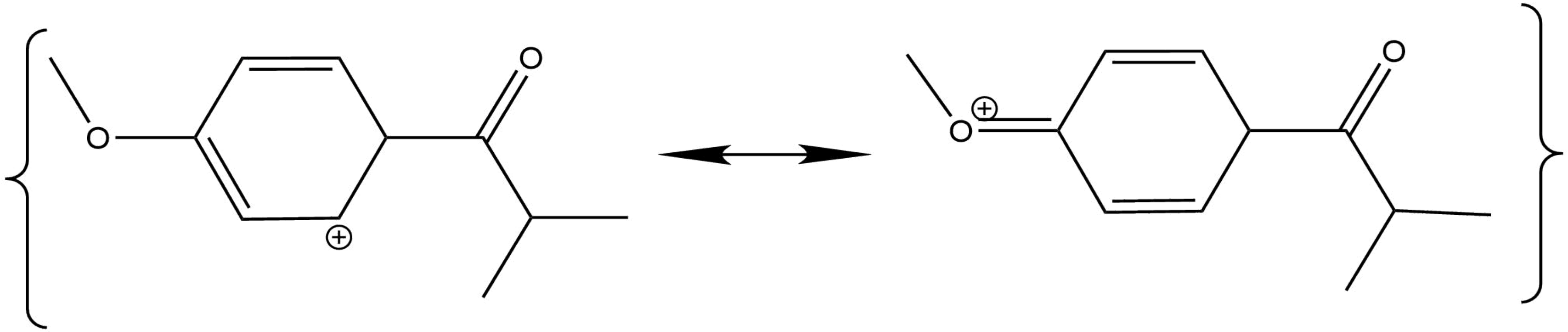
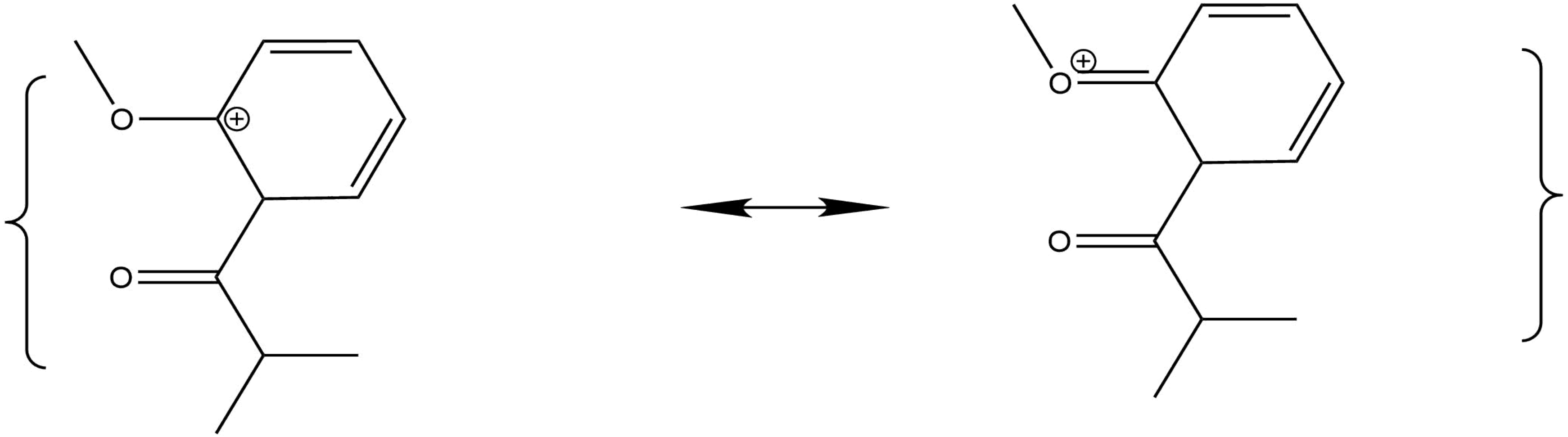
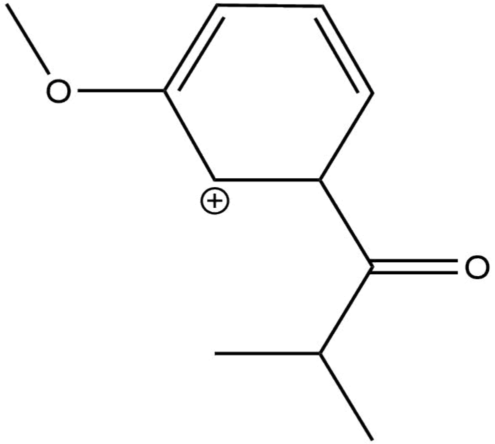
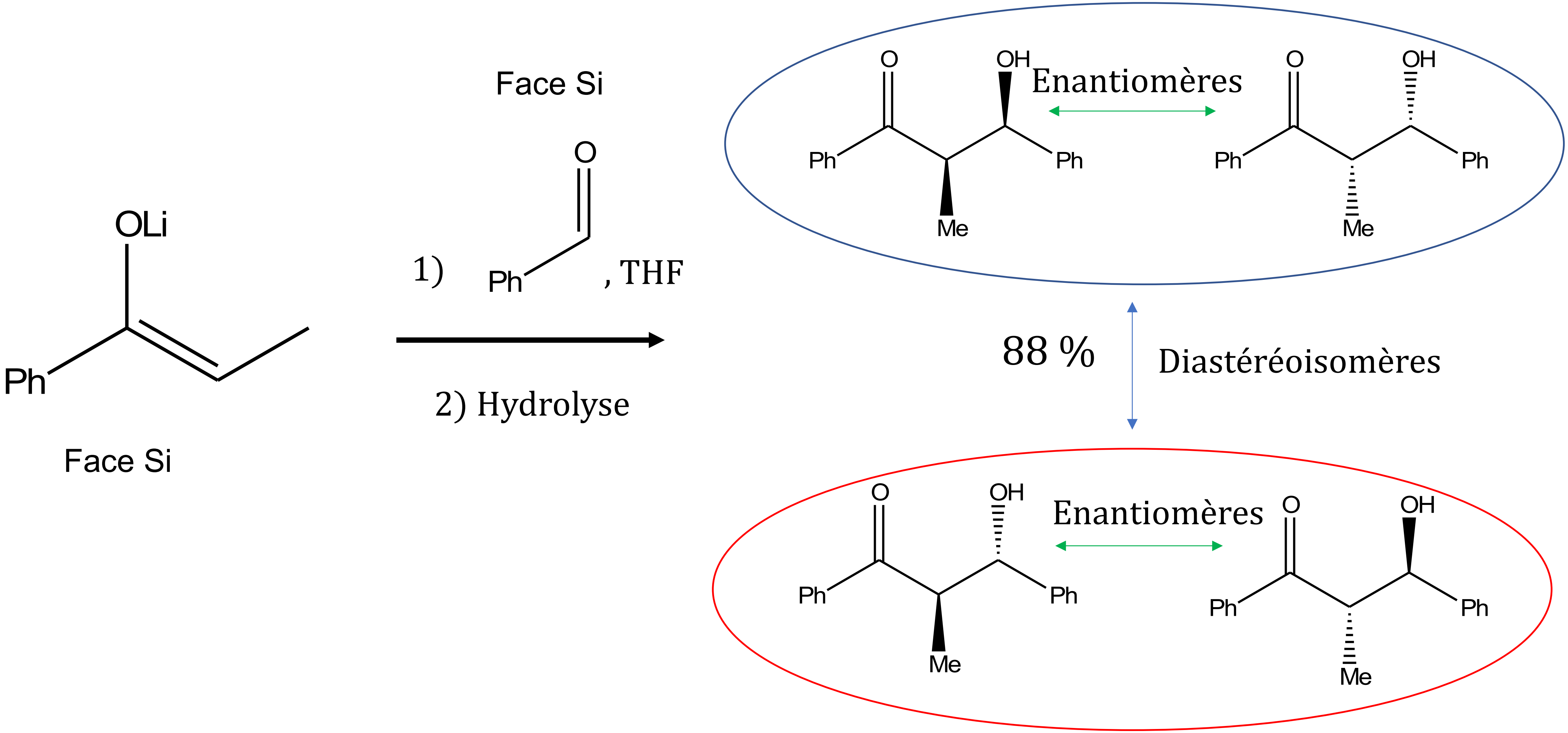








Face Si

Face Si

1) , THF

2) Hydrolyse

Enantiomères

Enantiomères

88 %

Diastéréoisomères

12 %

Modèle de Zimmerman-Traxler

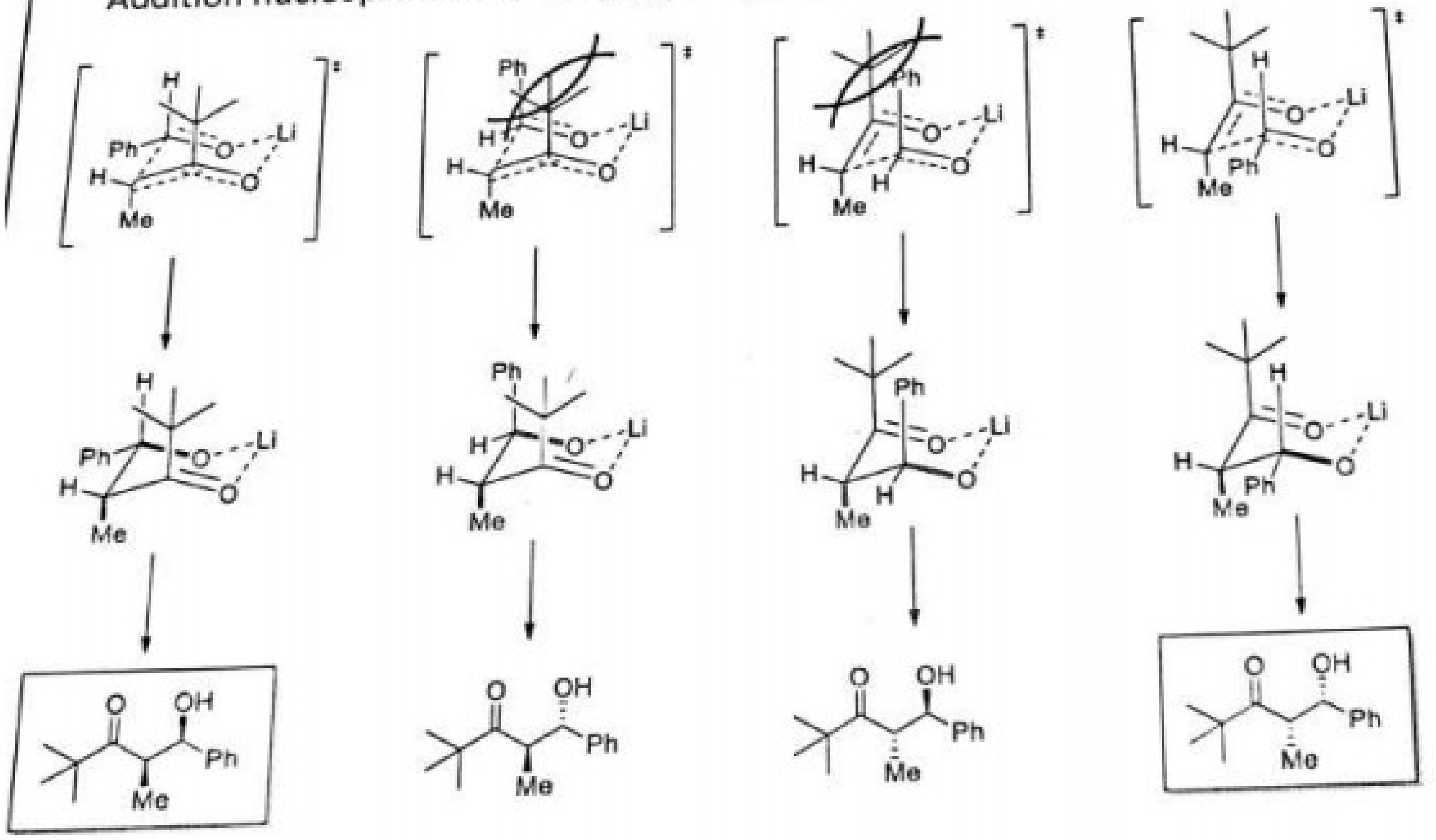
1. Pour l’attaque de l’énolate sur le carbonyle on dessine un état de transition cyclique à 6 centres en conformation chaise, le métal est coordiné par les deux atomes d’oxygène.

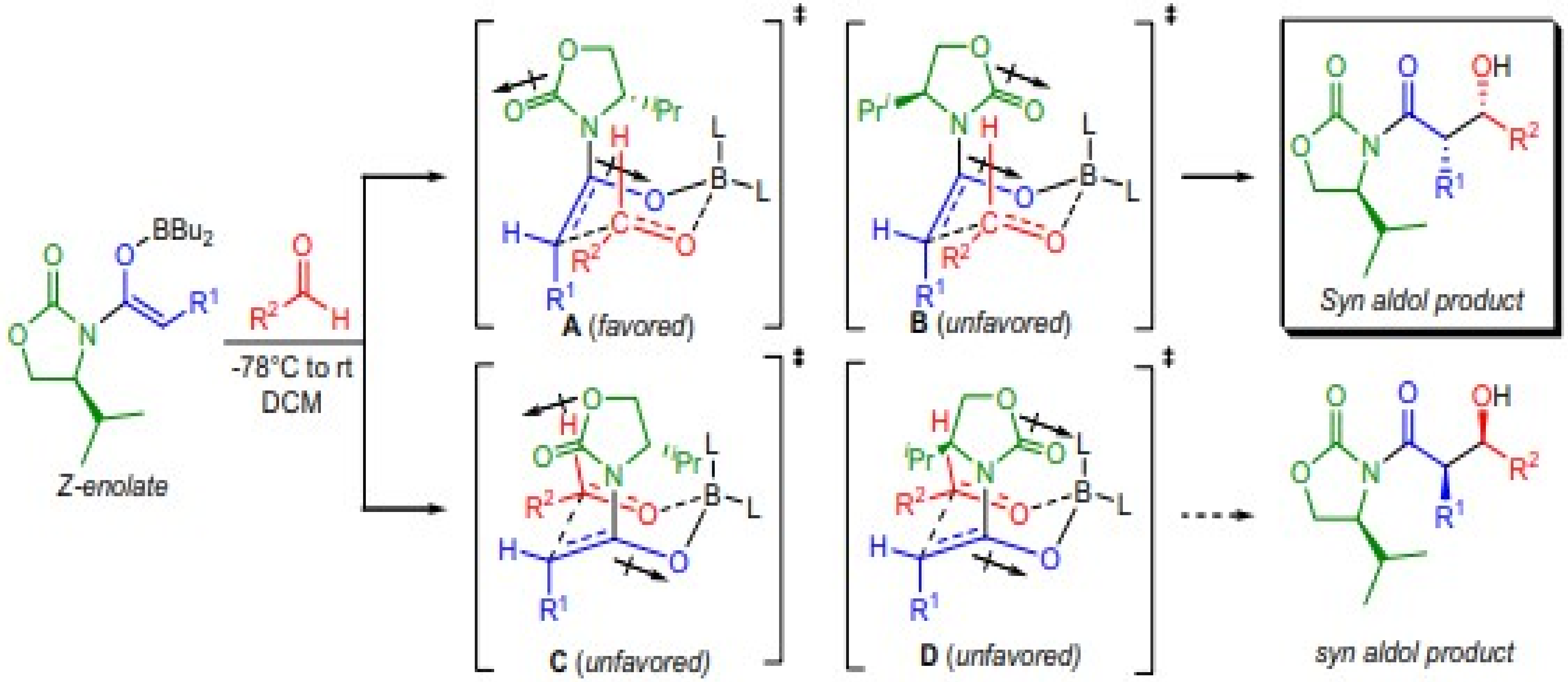
2. En fonction de la stéréochimie de l’énolate on place les substituants

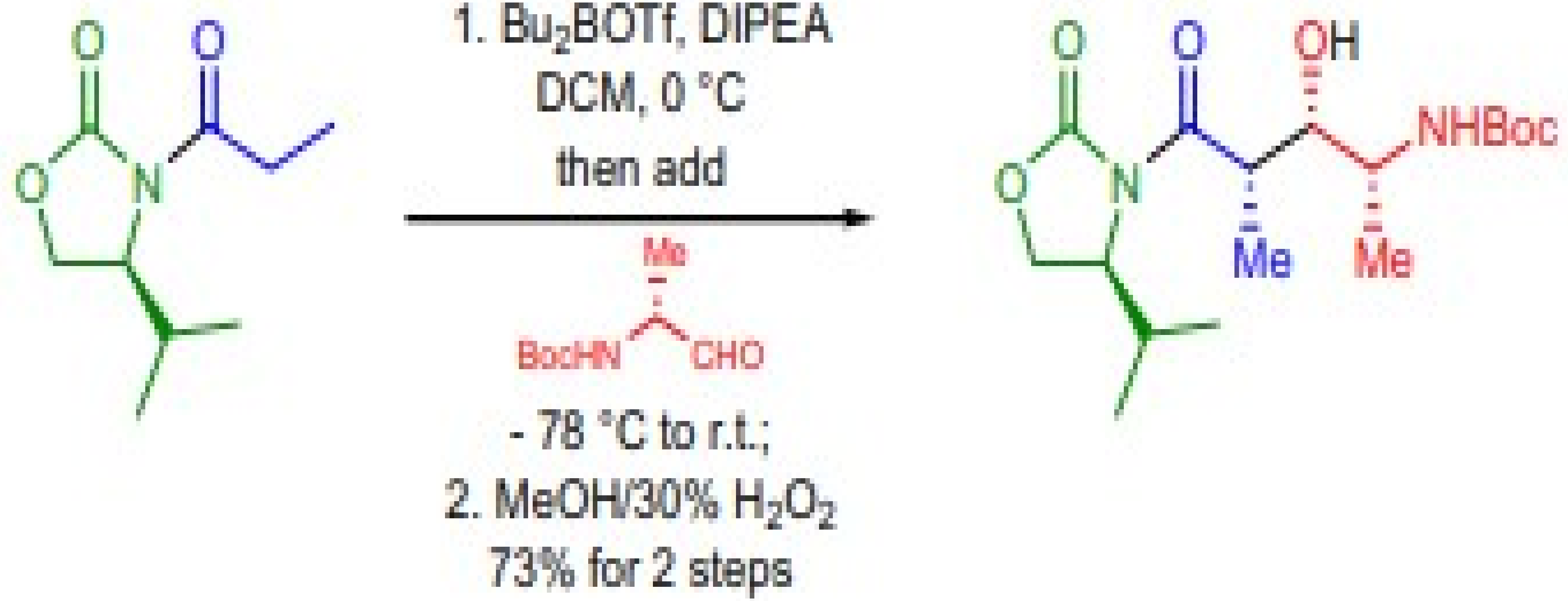
3. On place les substituants du carbonyle de l’ordre à minimiser les interactions 1,3 diaxiales.

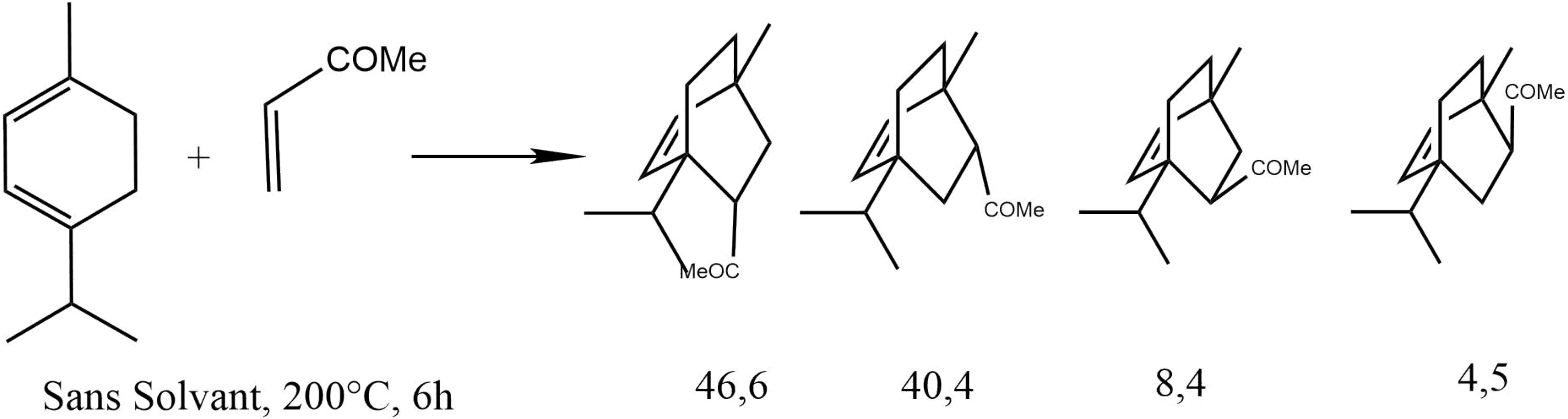
4. On détermine les stéréodescripteurs des centres stéréogènes formés

Addition nucléophile sur un carbonyle — Aldolisation :Zimmerman Traxler

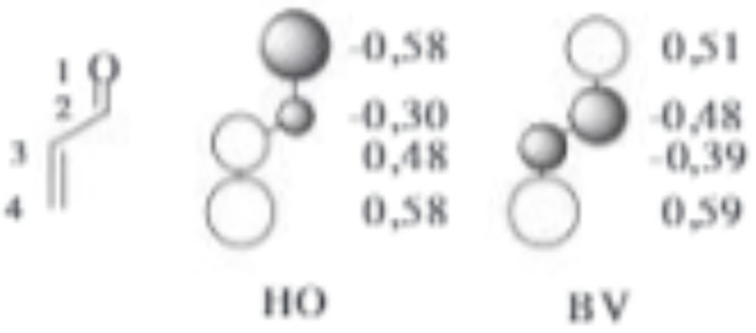



O
BBu2
R1
O
N
O
iPr
Z-enolate
R2
H
-78°C to rt
DCM
‡
A (favored)
B (unfavored)
C (unfavored)
D (unfavored)
B
L
L
Syn aldol product
syn aldol product
OH
R2
R1


1. Bu_2BOTf, DIPEA
DCM, 0 °C
then add
Me
BocHN
CHO
- 78 °C to r.t.;
2. MeOH/30% H_2O_2
73% for 2 steps
O
O
O
N
OH
NHBoc
Me
Me

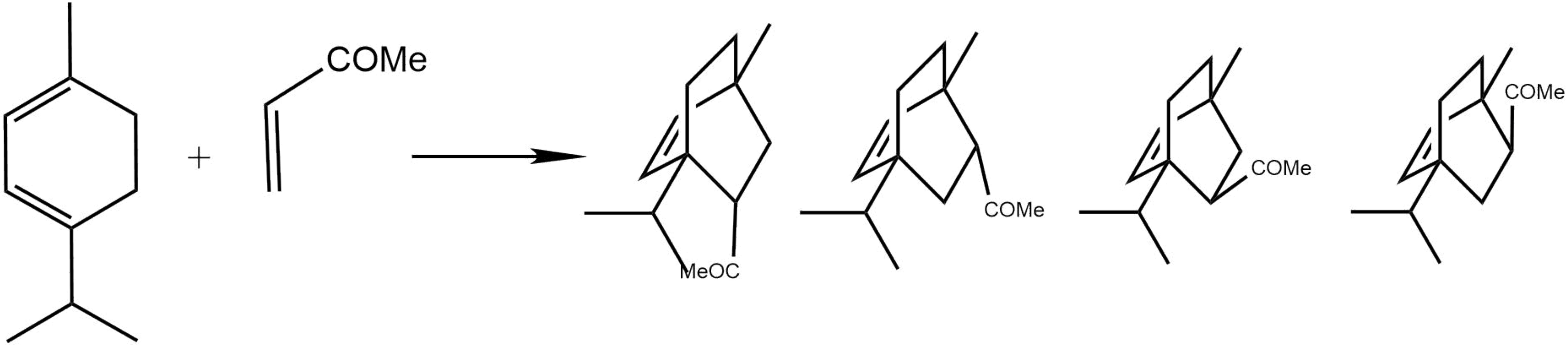


Sans Solvant, 200°C, 6h


1 O
2
3
4
-0,58
-0,30
0,48
0,58
0,51
-0,48
-0,39
0,59
HO
BV

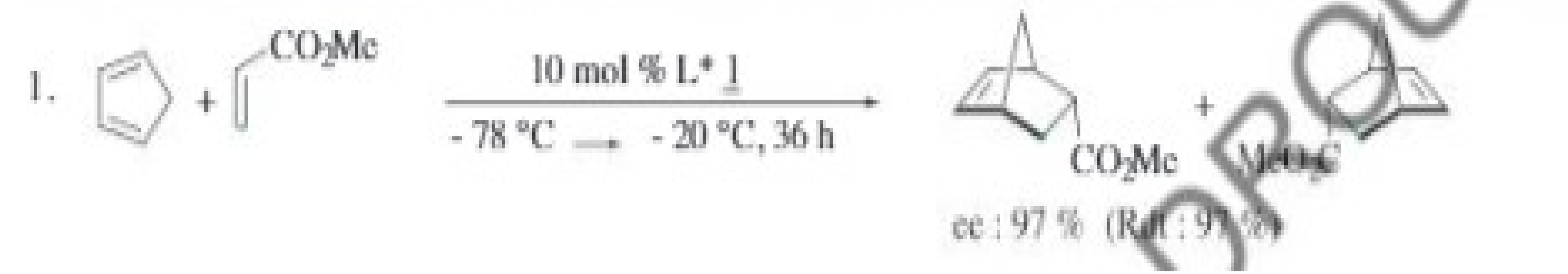

H ⊕
O
-0,47
0,08
0,67
0,57
0,41
-0,72
-0,10
0,55
HO
BV

Drouin, ICO



Sans Solvant, 200°C, 6h	46,6	40,4	8,4	4,5
CH_2Cl_2, $SnCl_4$,$5H_2O$ (1,0éq), 0°C, 1h	71,3	24,5	3,9	0,4

Tableau 8.6 (a) : Exemples de cycloadditions [4+2] acido-catalysées énantio- ou (et) dia- stéréosélectives[1,2,3]

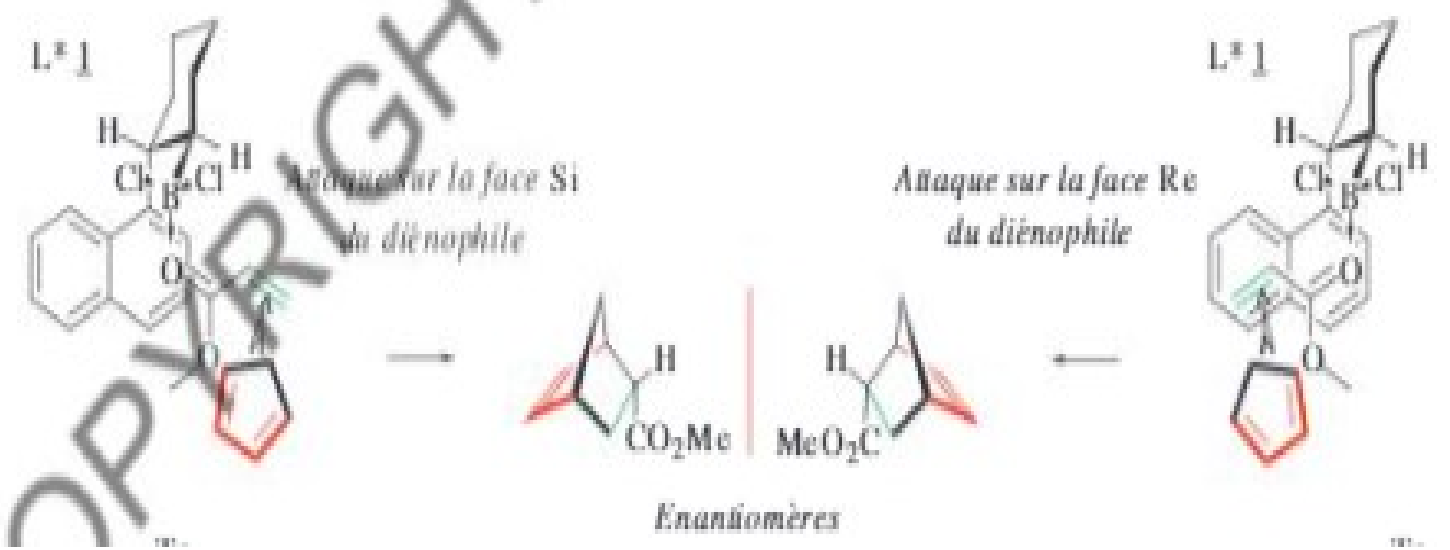


ee : 97 % (Réf : 97 %)

Drouin, ICO

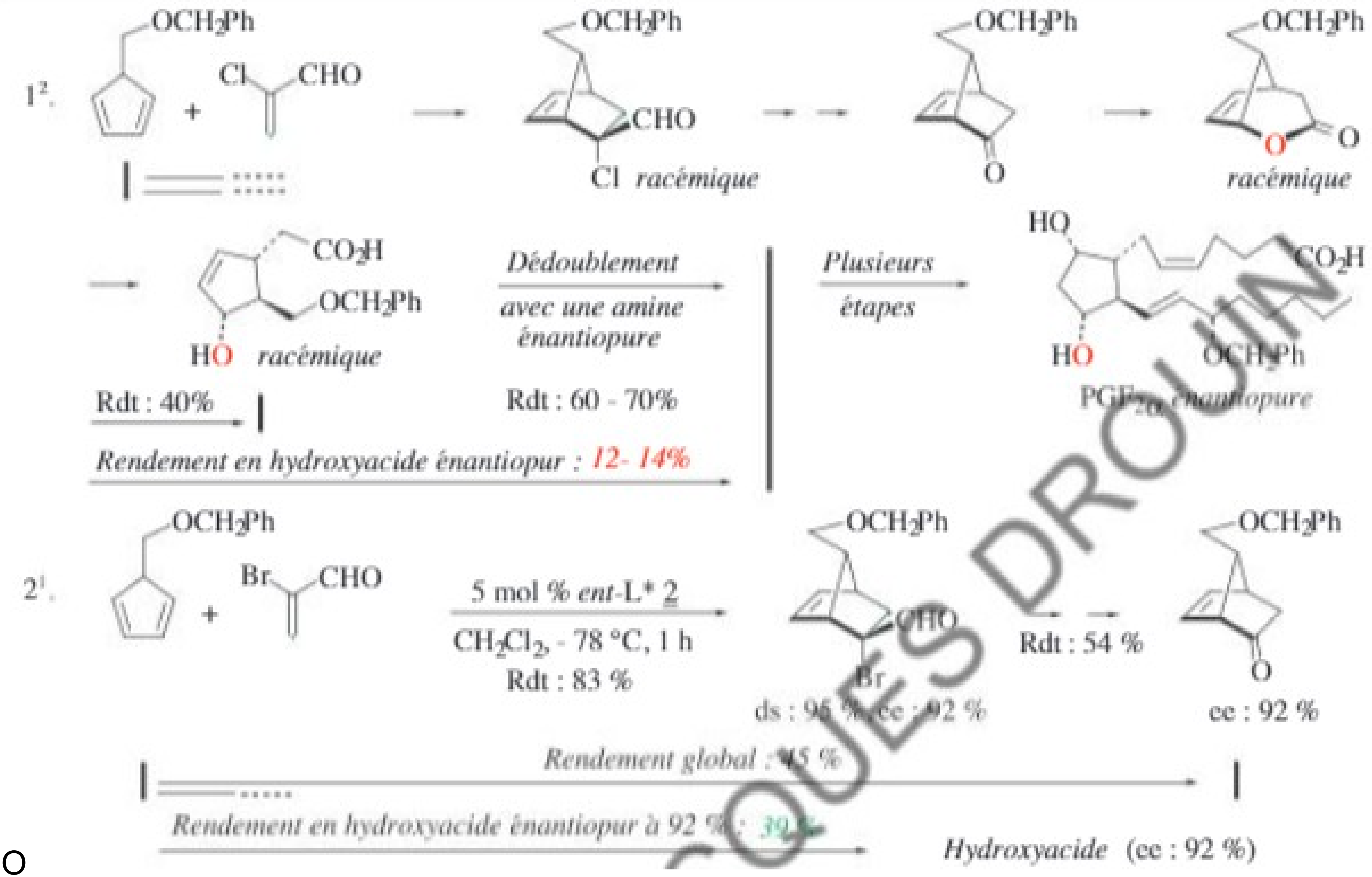
Tableau 8.6 (a) : Exemples de cycloadditions [4+2] acido-catalysées énantio- ou (et) dia- stéréosélectives[1,2,3]

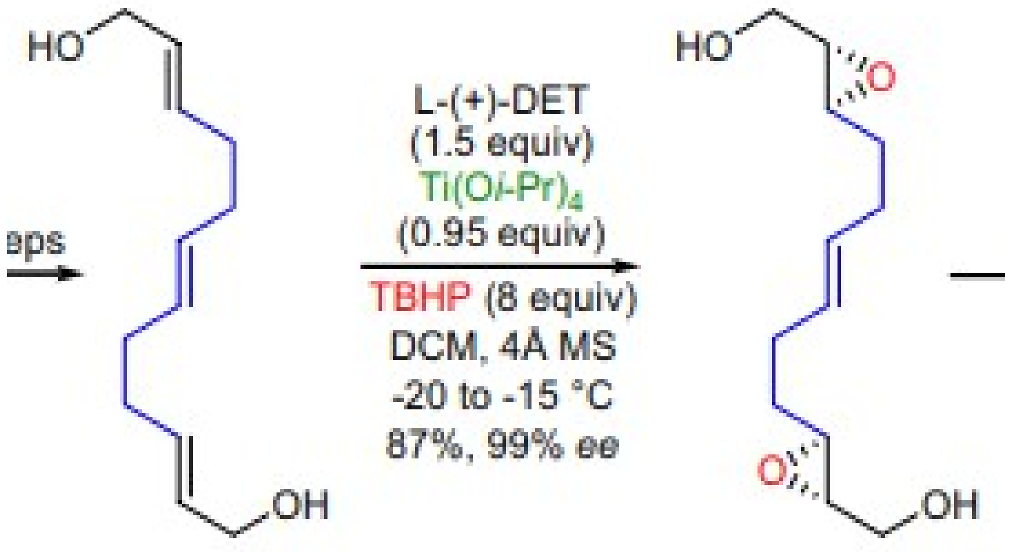
4. L'énantiomère majoritaire est seul représenté.



Drouin, ICO

Tableau 8.6 (b) : Deux synthèses de la prostaglandine PGF2α par E. J. Corey[1]





Transition state of epoxidation: