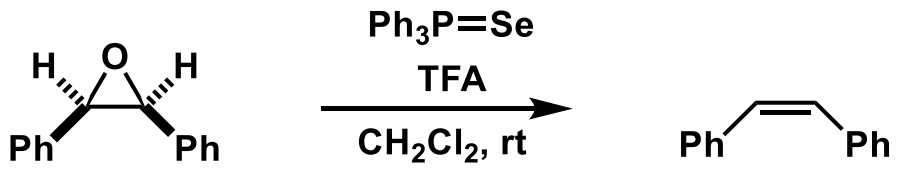
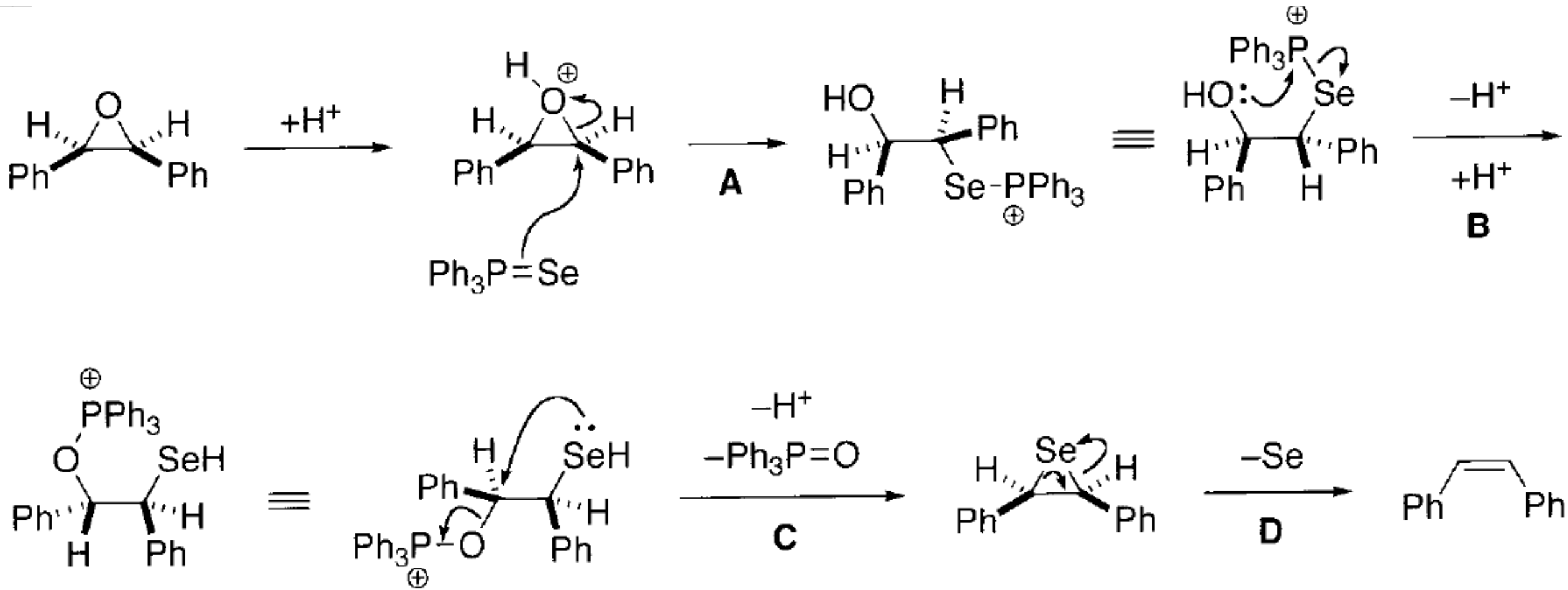
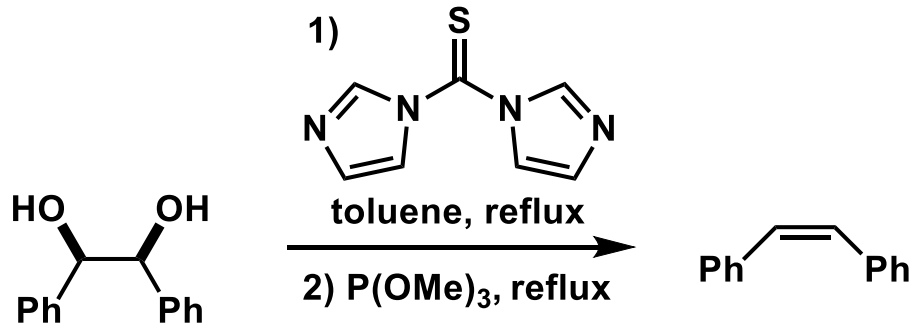
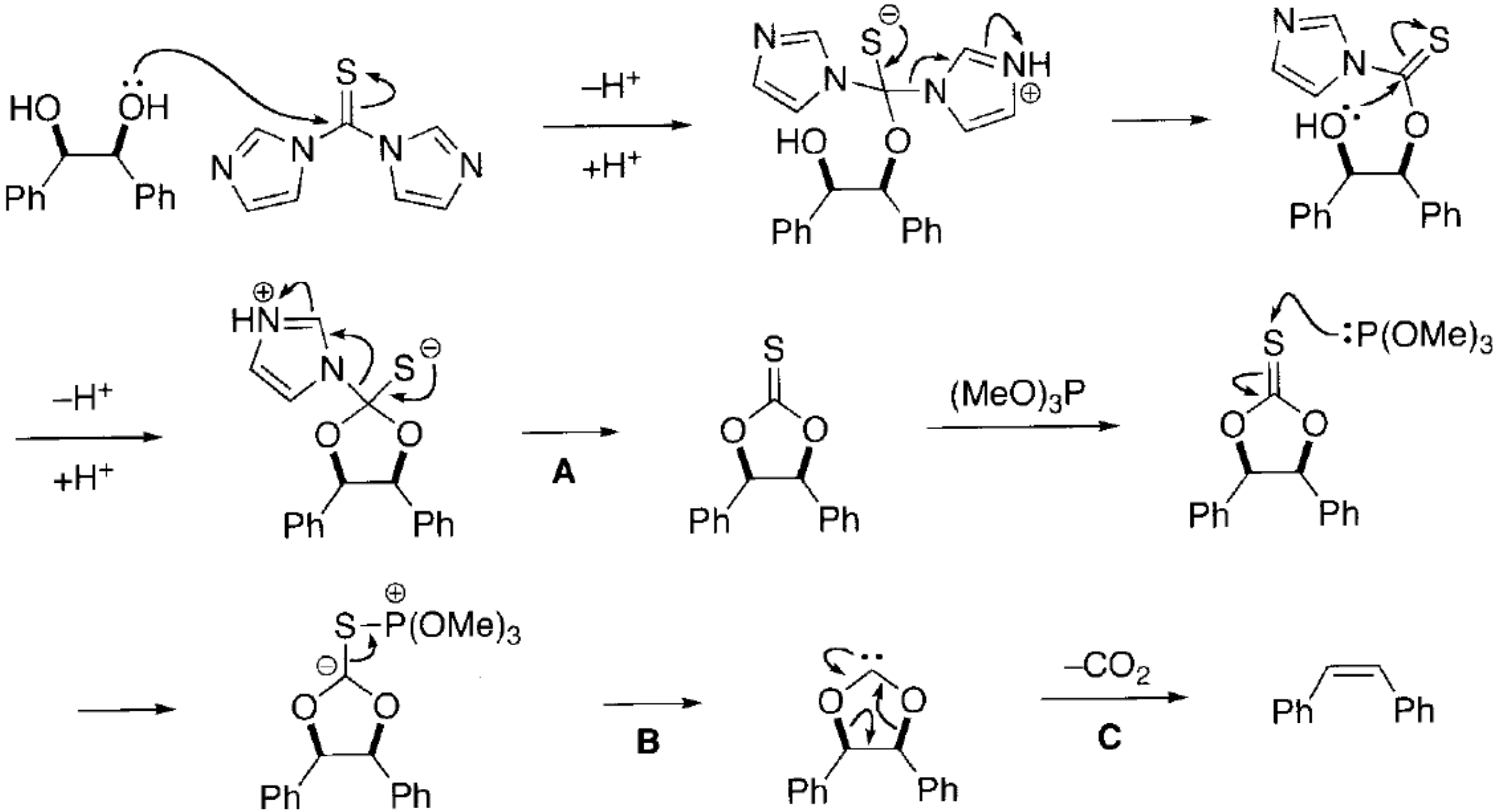
1.

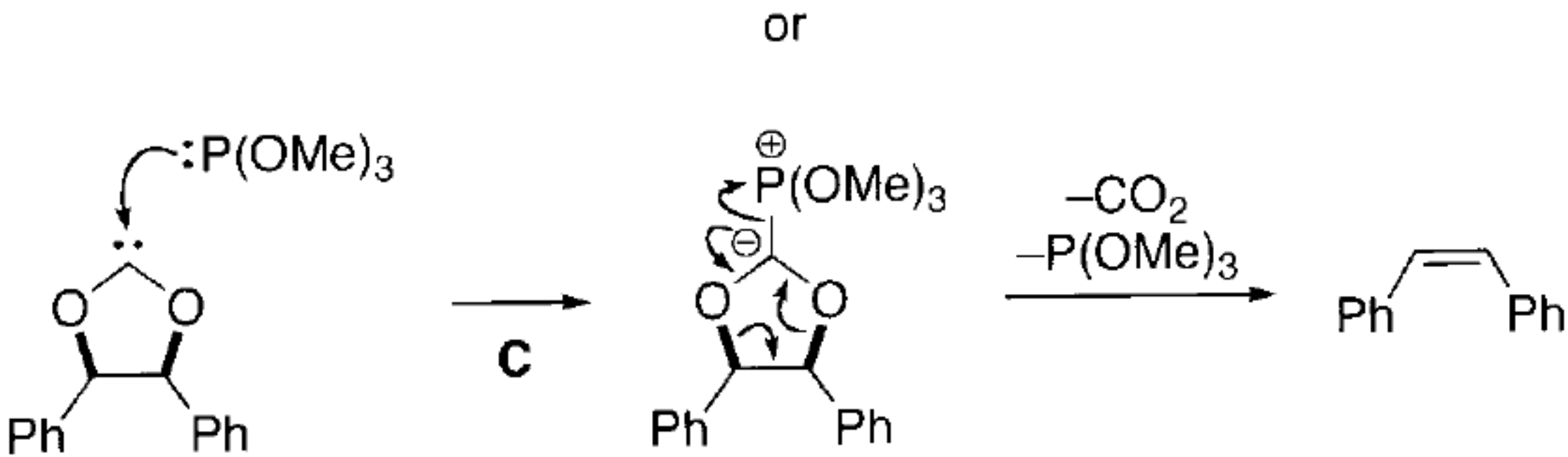



+H+
Ph3P=Se
A
HO
H
Ph
Se-PPh3
Ph3P
Se
HO:
–H+
+H+
B
PPh3
O
SeH
Ph
H
–H+
–Ph3P=O
C
Se
–Se
D

2.

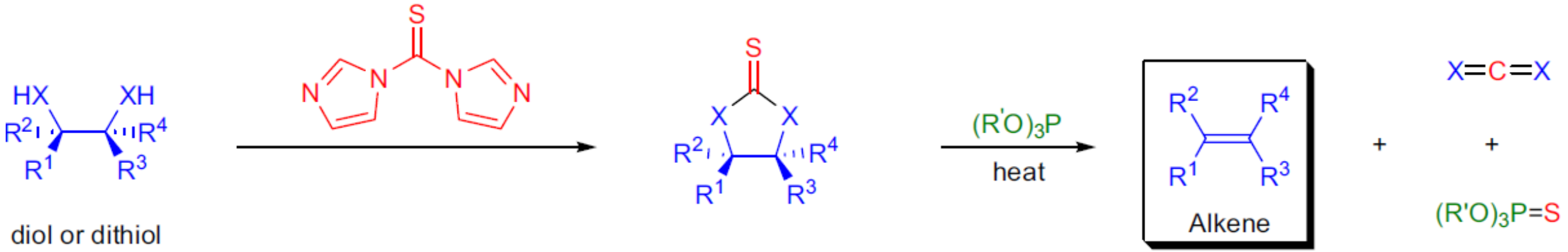



HO
OH
Ph
Ph
S
N
N
N
N
–H+
+H+
S
NH
HO
O
Ph
Ph
HO
O
Ph
Ph
HN
N
S
O
O
Ph
Ph
–H+
+H+
A
S
O
O
Ph
Ph
(MeO)3P
S
:P(OMe)3
O
O
Ph
Ph
S–P(OMe)3
O
O
Ph
Ph
B
O
O
Ph
Ph
–CO2
C
Ph
Ph

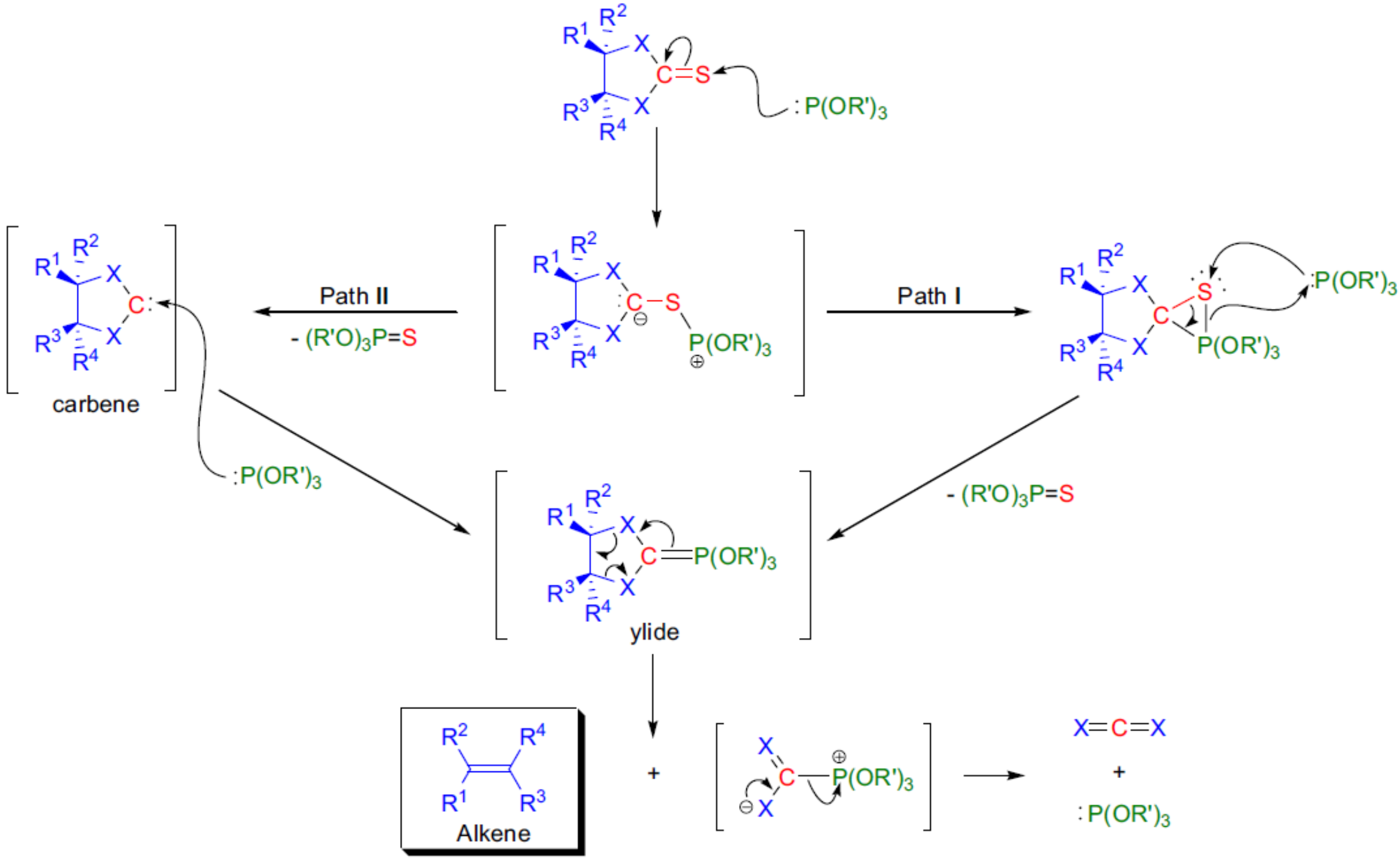

or
:P(OMe)3
O
O
Ph
Ph
c
⊕
P(OMe)3
⊖
O
O
Ph
Ph
–CO2
–P(OMe)3
Ph
Ph

Corey-Winter olefination （P110）

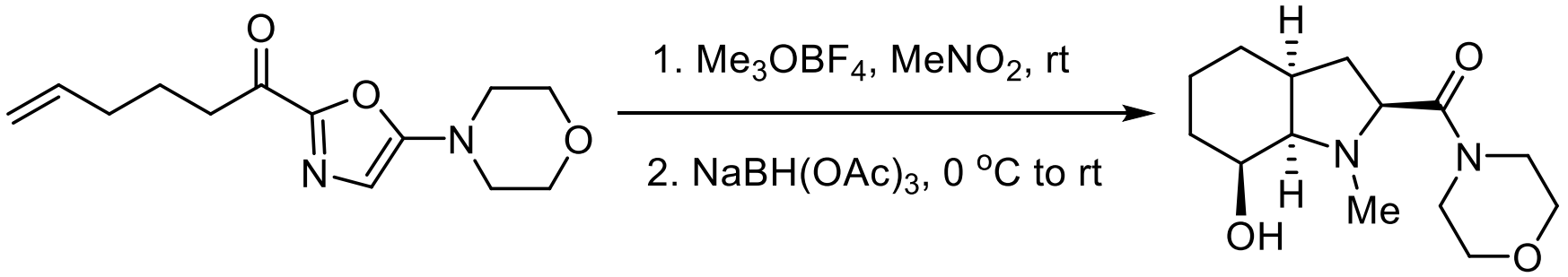
- 邻二醇与1,1-硫代羰基二咪唑反应生成硫代碳酸酯，再经亚磷酸酯促使的顺式还原热消除从而转化为相应的烯烃。
- 用硫代光气使反应温度降低很多，温和的条件使带有多种官能团的复杂分子也可应用。
- 能够立体专一地合成各种取代烯烃，也可以高产率地合成高张力烯烃。



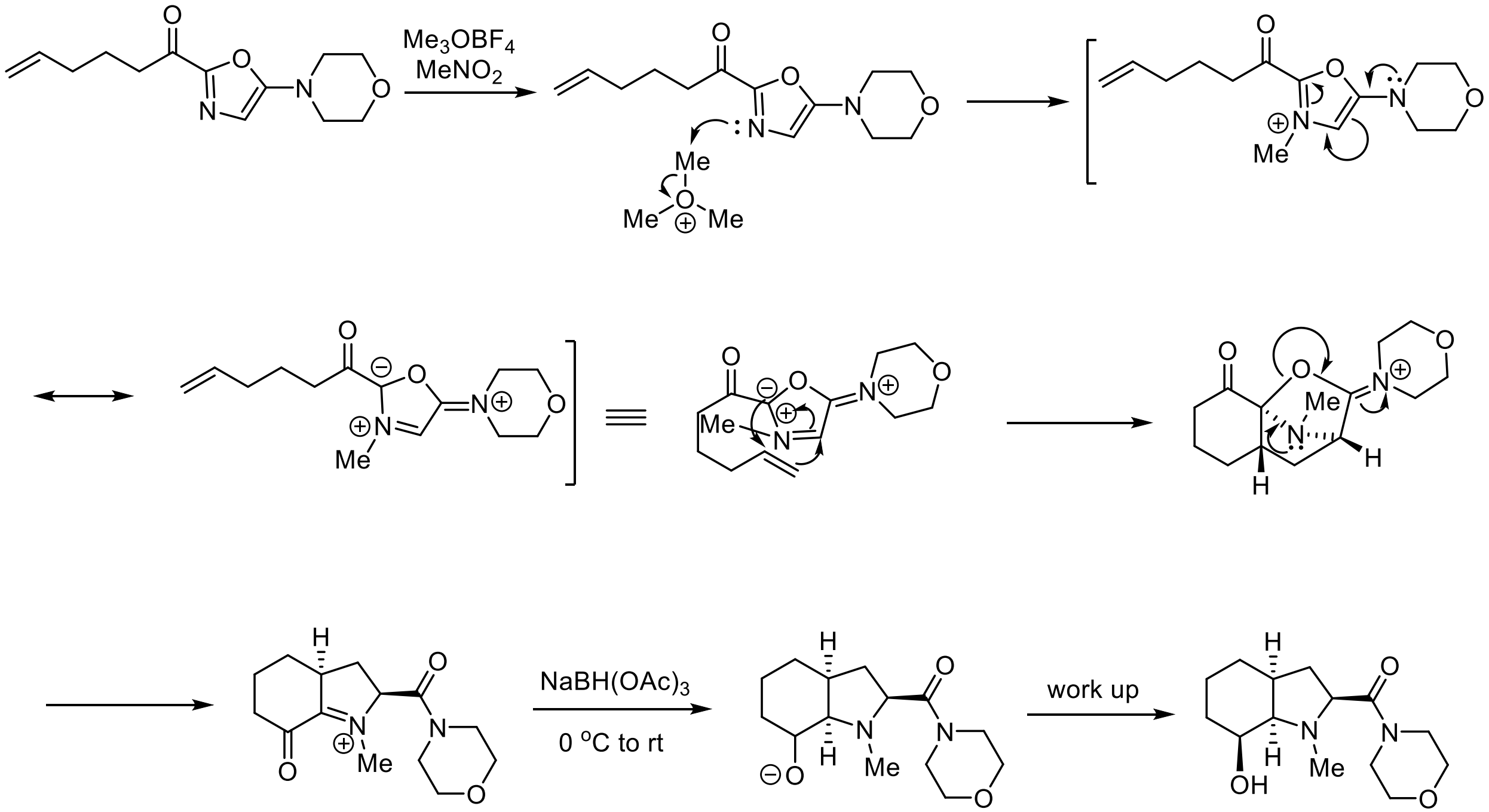
R^1, R^2, R^3, R^4 = H, alkyl, aryl; R' = Me, Et; substrate: X = O (1,2-diol), X = S, 1,2-dithiol;
cyclic intermediate: X = O (cyclic 1,2-thionocarbonate), X = S (cyclic 1,2-trithiocarbonate)


Path II
- (R'O)3P=S
Path I
carbene
:P(OR')3
- (R'O)3P=S
ylide
Alkene
+
+
:P(OR')3

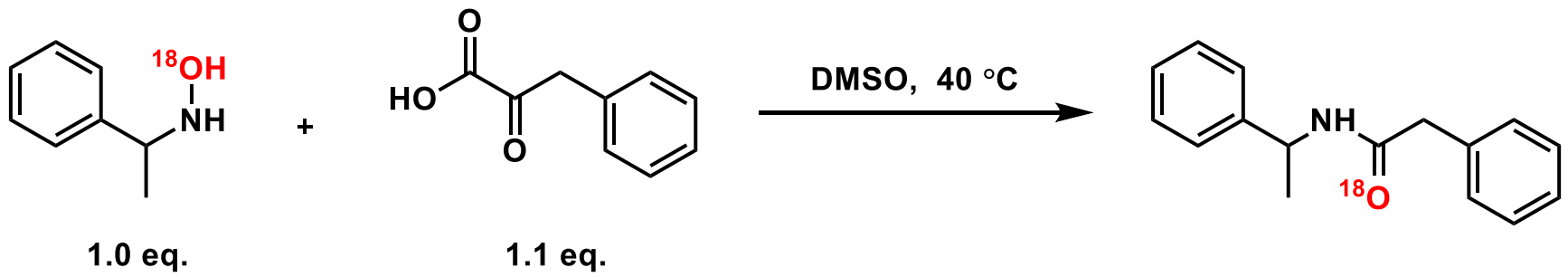
3.



J. Org. Chem. **2012**, *77*, 10416.

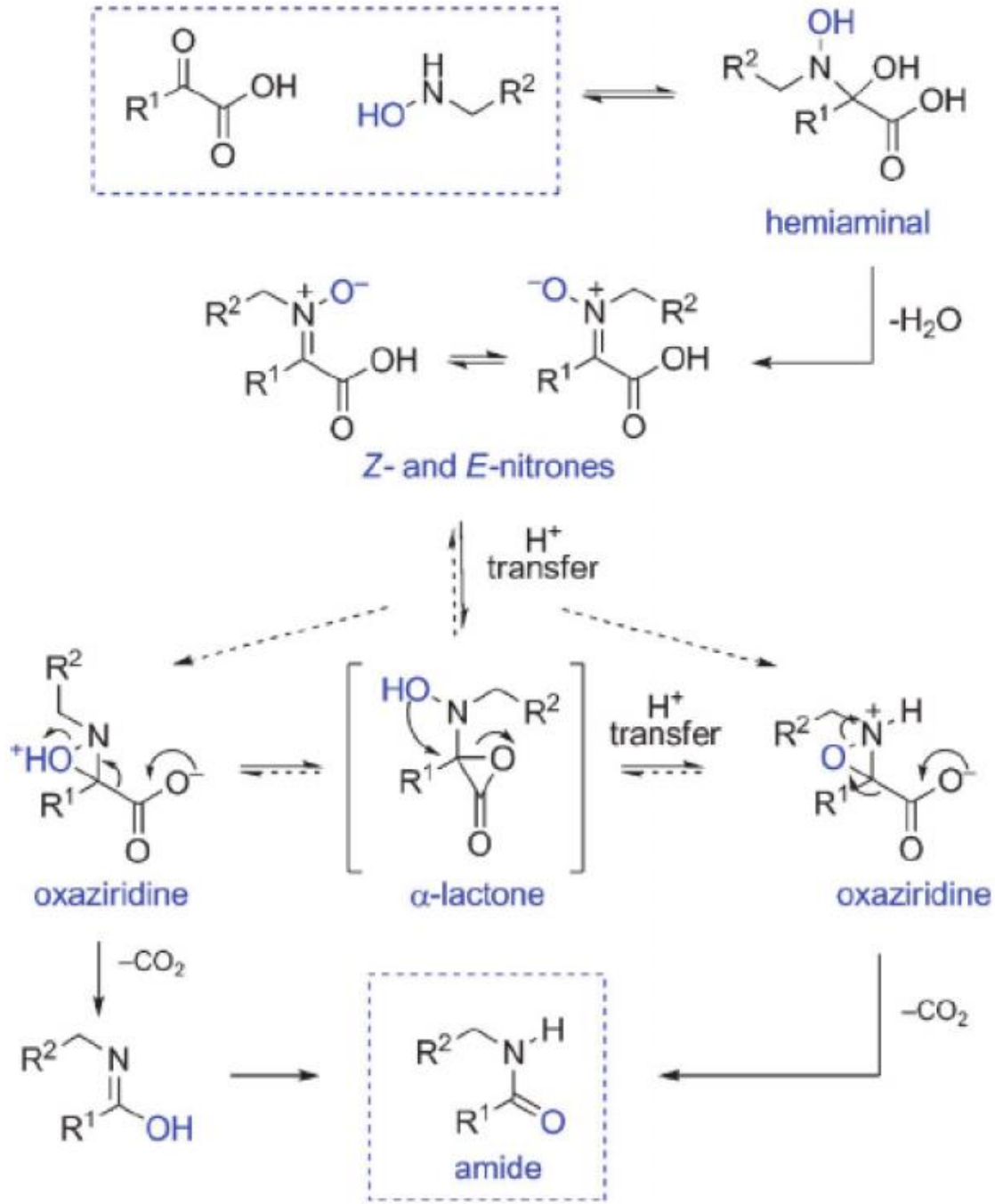

Me3OBF4
MeNO2
NaBH(OAc)3
0 °C to rt
work up

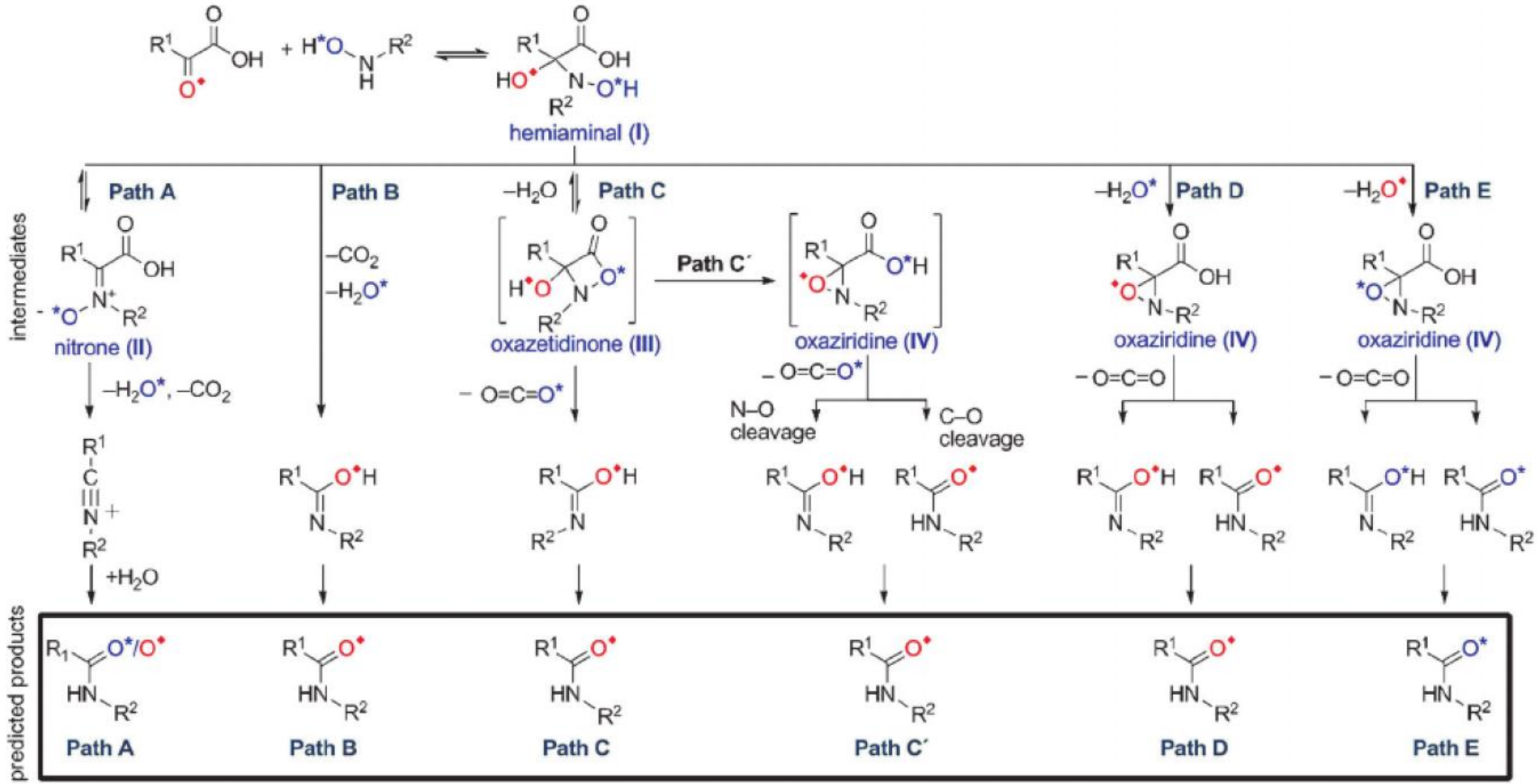
4.



1.0 eq. **1.1 eq.**

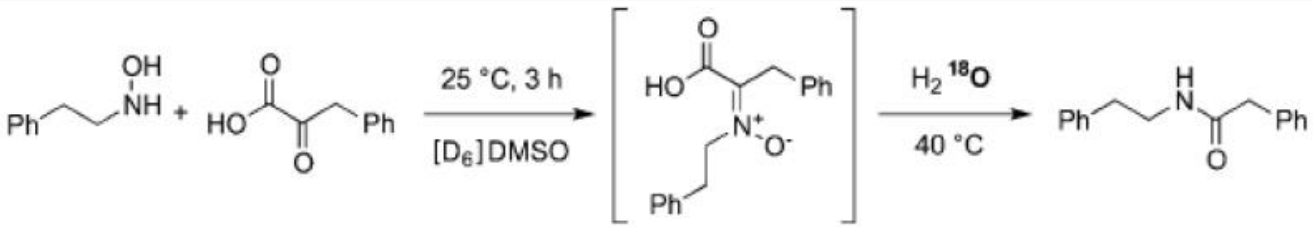
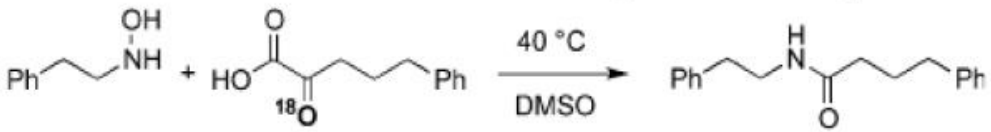
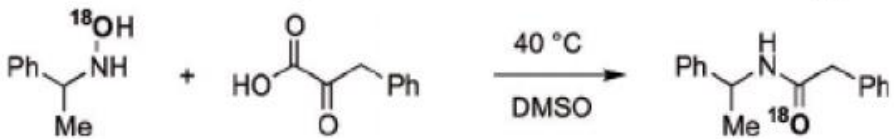
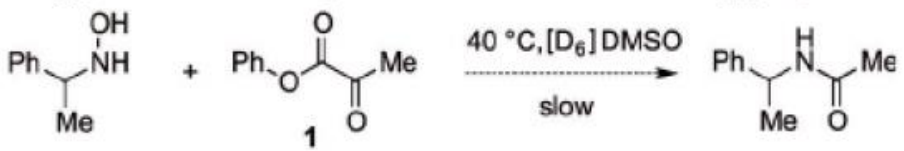
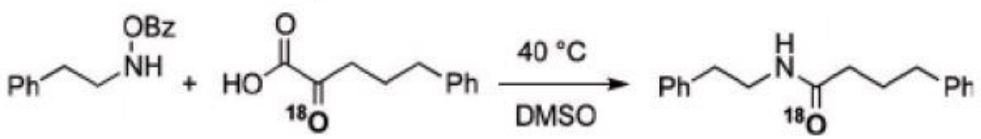
Angew. Chem. Int. Ed., **2012**, *51*, 513.

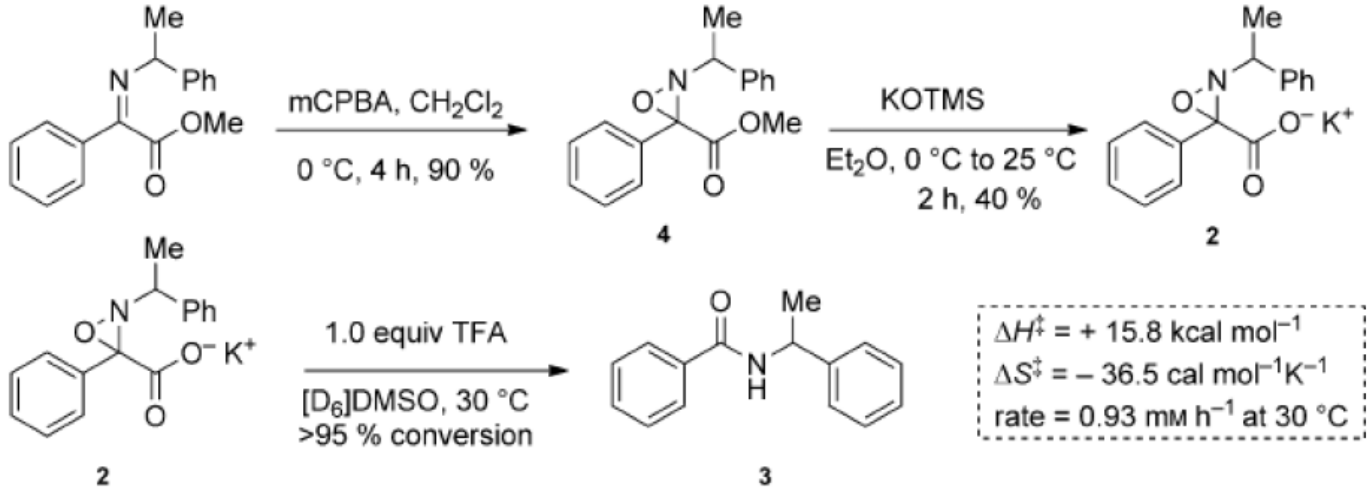

hemiaminal
-H2O
Z- and E-nitrones
H+ transfer
oxaziridine
α-lactone
H+ transfer
oxaziridine
–CO2
–CO2
amide



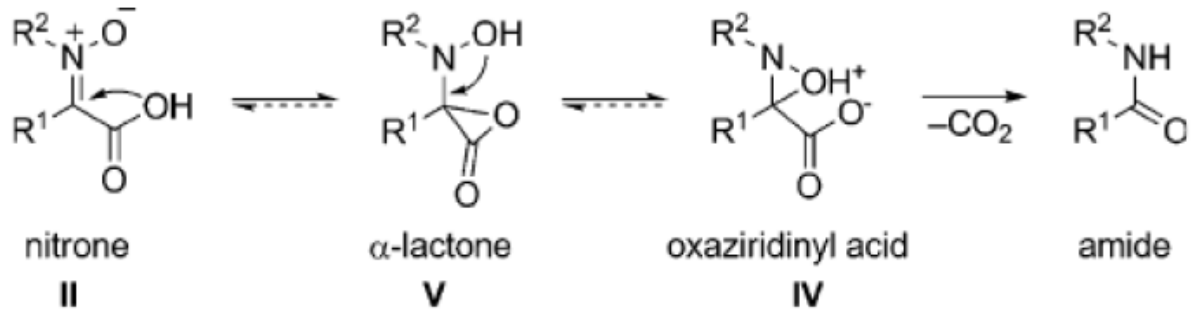
Scheme 2. Possible mechanistic pathways for type I KAHA ligations.

Table 1: Exclusion of pathways and mechanistic probes.

Entry		Label transfer	Path excluded
1		0%	A
2		0%	B, C, C′, D
3		>80%	A, B, C, C′, D
4		–	C
5		>80%	A, C, C′, E



Scheme 3. Synthesis and rearrangement of α-oxaziridinyl acid **2**. mCPBA = *m*-chloroperoxybenzoic acid, TMS = trimethylsilyl, TFA = trifluoroacetic acid.



Scheme 4. Proposed pathway from nitrone to oxaziridine via an α-lactone intermediate.