M.Sc. Semester-IV
Core Course-9 (CC-9)
Synthetic Organic Chemistry

III. Photochemistry

4. Paternò-Büchi Reaction

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University Department of Chemistry
Dr. Shyama Prasad Mukherjee University, Ranchi

III Photochemistry 10 Hrs

Thermal versus photochemical reactions, Electronic excitations: n–π* and π–π* transitions. Singlet and Triplet energy states: Comparison of energies, Lifetimes and Reactivity. Jablonski diagram, Allowed and forbidden transitions: Fluorescence, Phosphorescence and Internal conversion and Intersystem crossing.

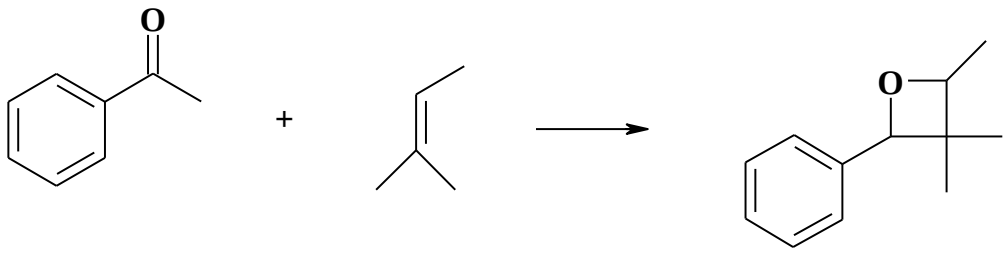
Photochemical reactions of saturated ketones : Norrish Type I and Norrish Type II reaction, Photoreduction of ketone, Photoaddition reactions, Paterno Buchi reaction. Photochemistry of simple olefins : Cis-trans isomerization, Di-pi methane rearrangement. Photooxidation : Formation of peroxy compounds, oxidative couplings : Barton reaction. Photo rearrangements : Photo-Fries rearrangement and Photo rearrangement of 2,5-Cyclohexadienones.

Coverage:

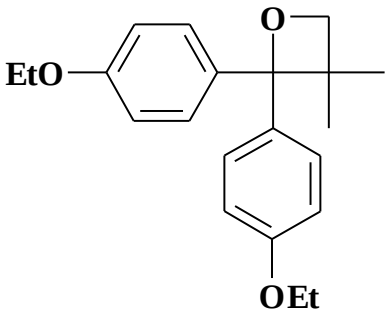
Photochemical Synthesis of Oxetanes : Paternò-Büchi Reaction

Photochemical synthesis of oxetanes

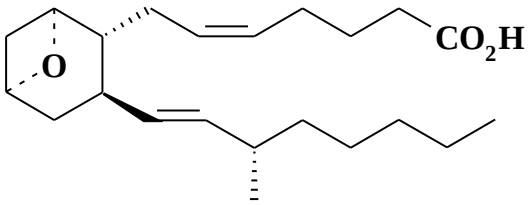
Paternò-Büchi Reaction



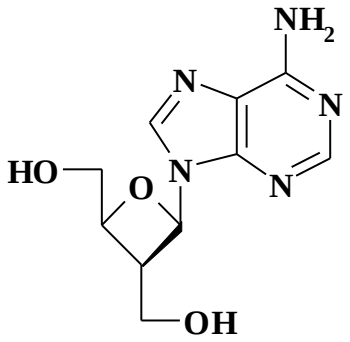
Paterno and Chieffi (1909), Buchi in 1954 mechanistic analysis



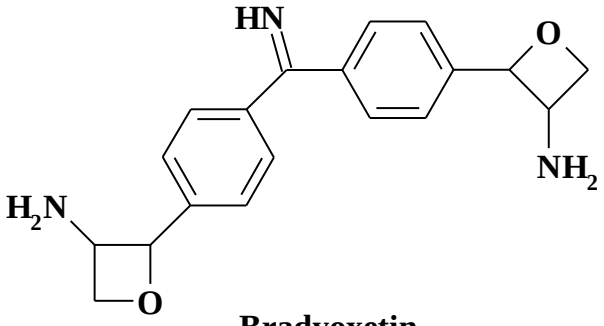
Insecticidal activity



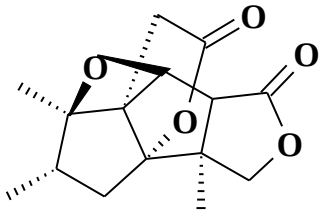
Thromboxane A_2



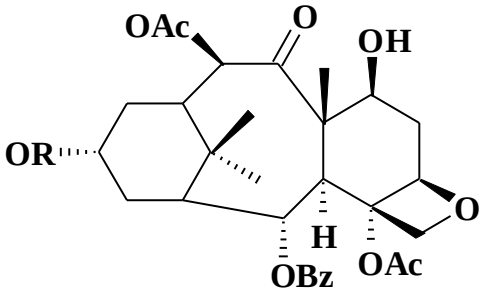
Oxetanocine



Bradyoxetin



Merrilactone A

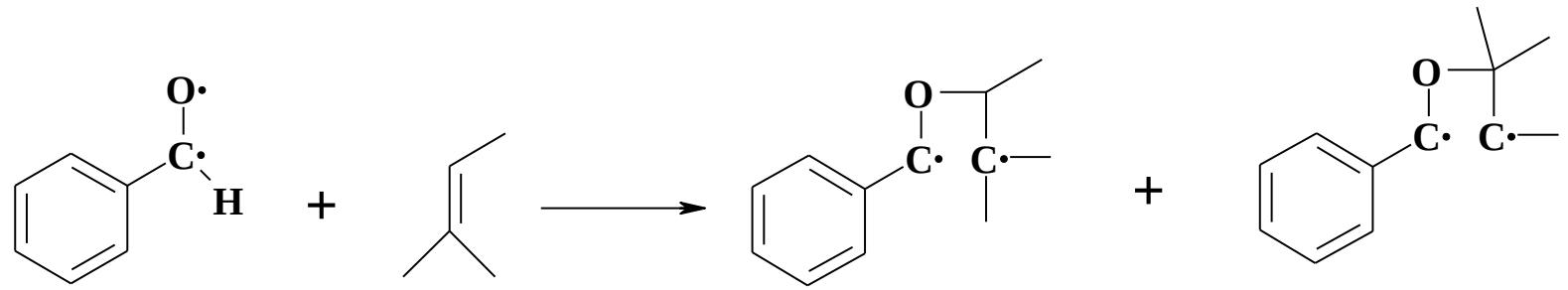


Palitaxel

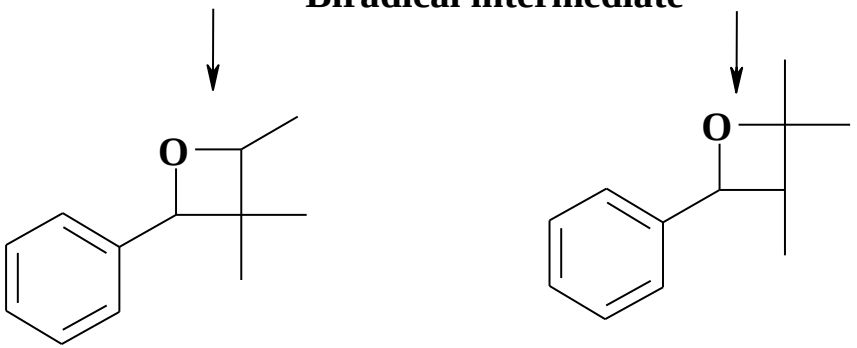
Reaction mechanism

$K_{isc\ aromatic} >> K_{isc\ aliphatic}$ (>>10^{10}/s)

responsible

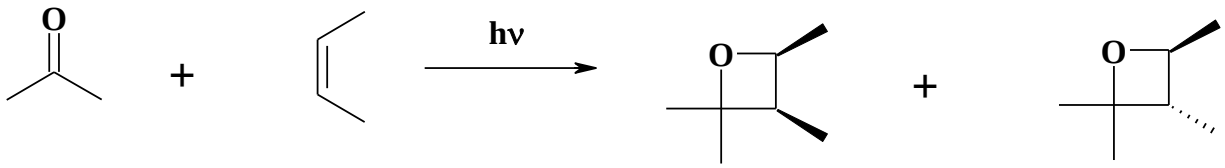


electrophile nucleophile Biradical intermediate

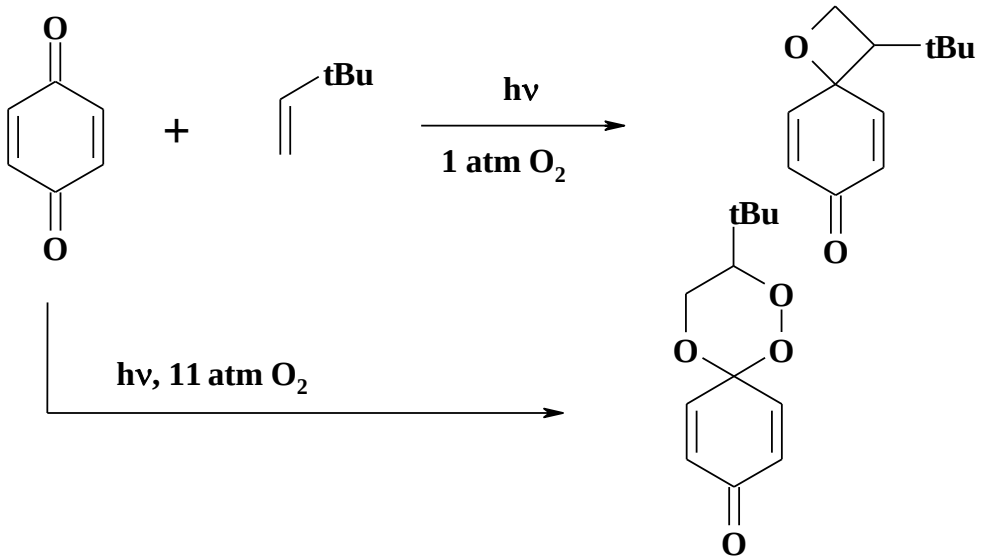


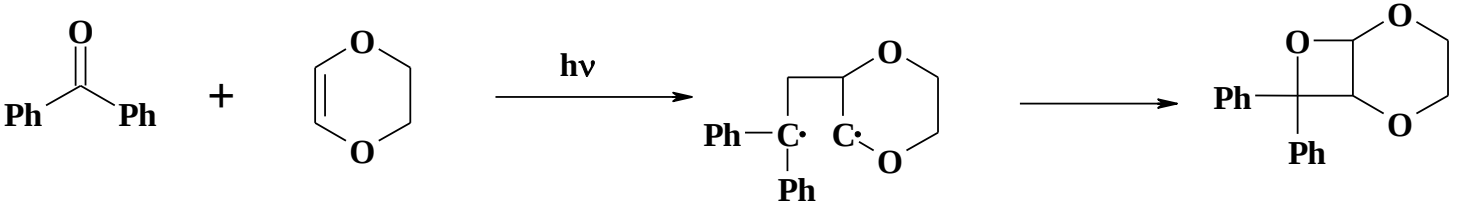
Major Minor

Intermediacy of biradical



1 1.6

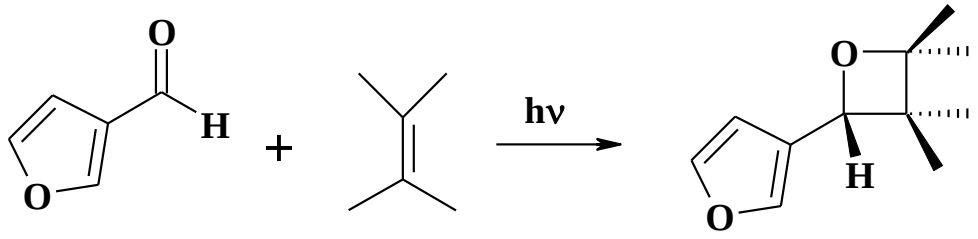




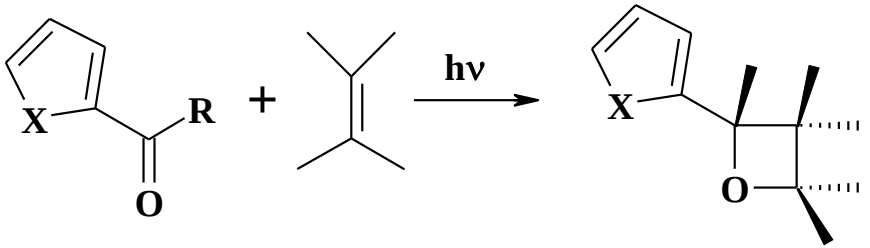
lifetime = 1.6 ns

Substrate spectrum of Paterno-Buchi Reaction

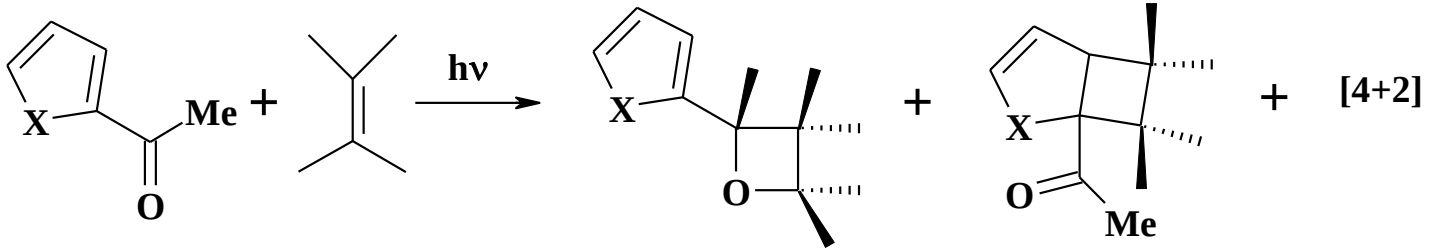
Aromatic ketones and aldehydes



54%

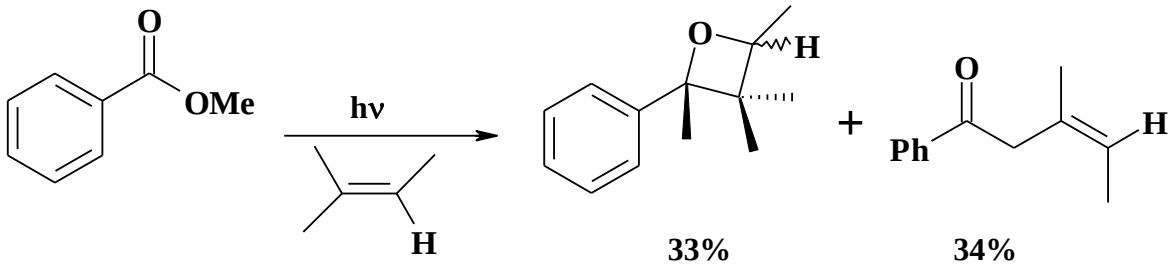


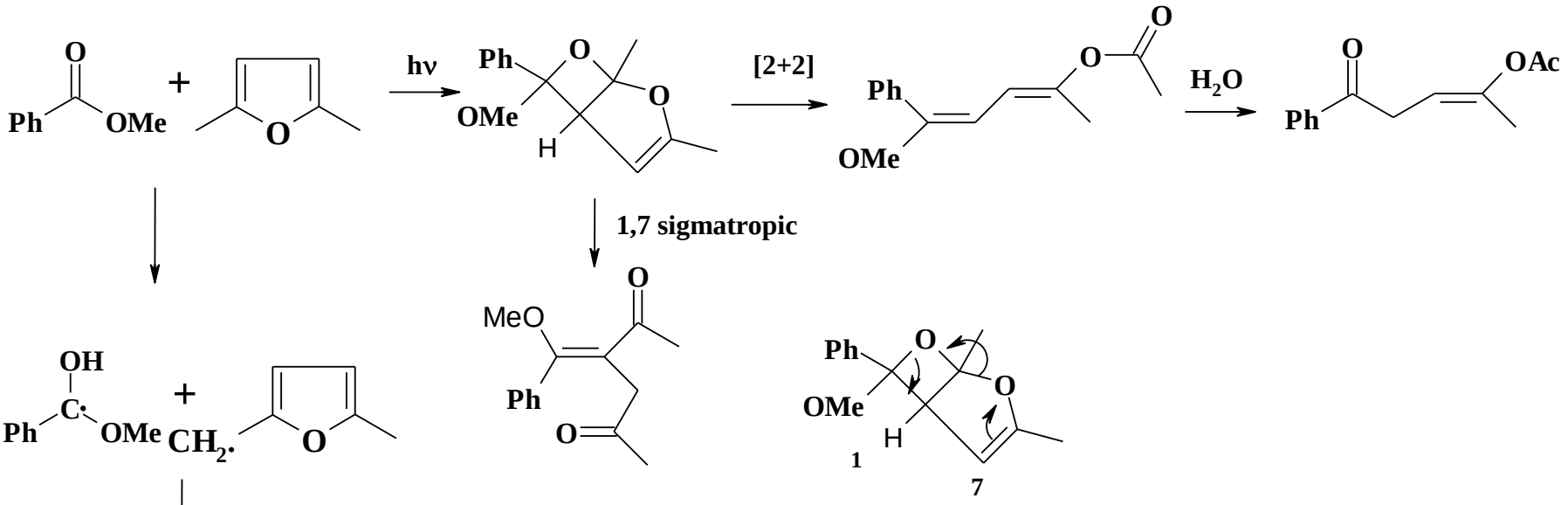
R = H, X = S, 46%
R = Ph, X = O, 27%
R = Ph, X = S, 76%

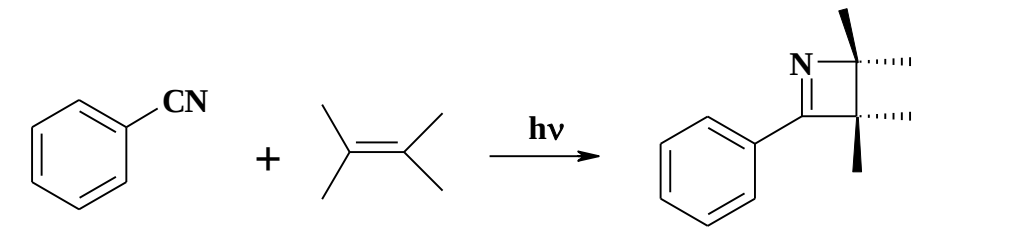


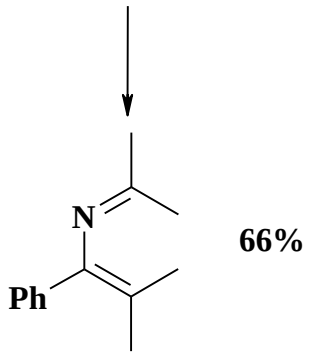
X = O	8%	33%	0%
X = S	11%	10%	38%

Carboxylic acid derivatives and nitriles

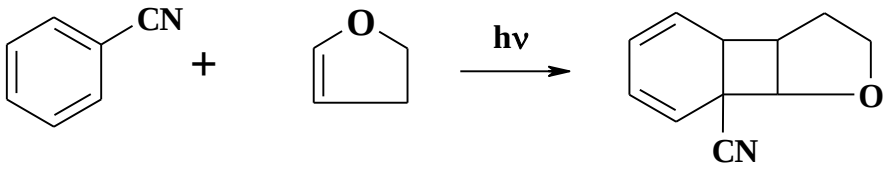


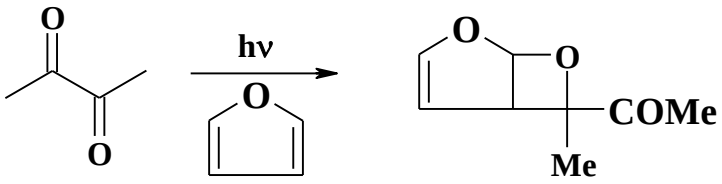


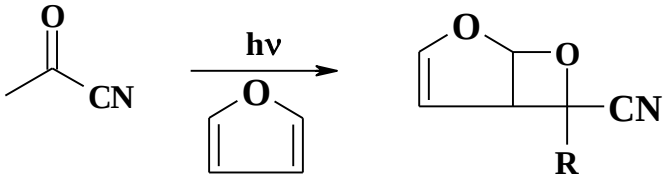




66%



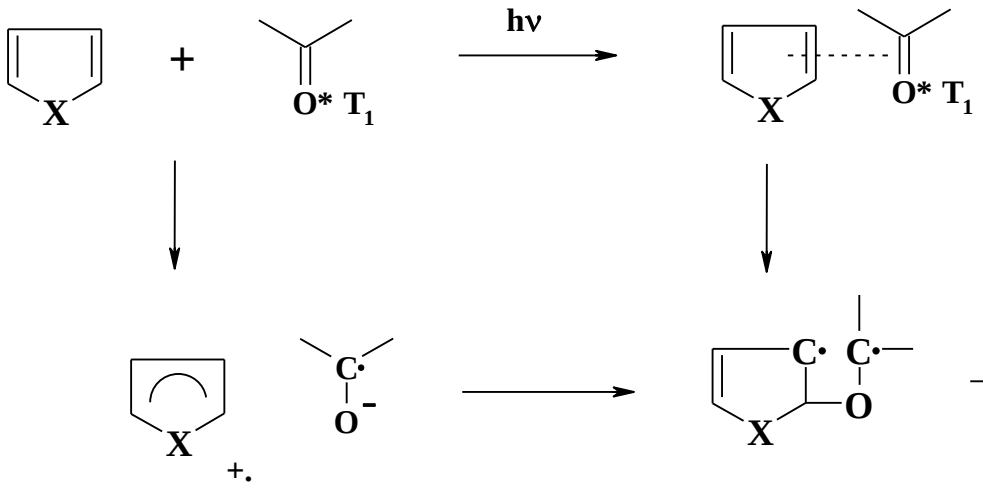


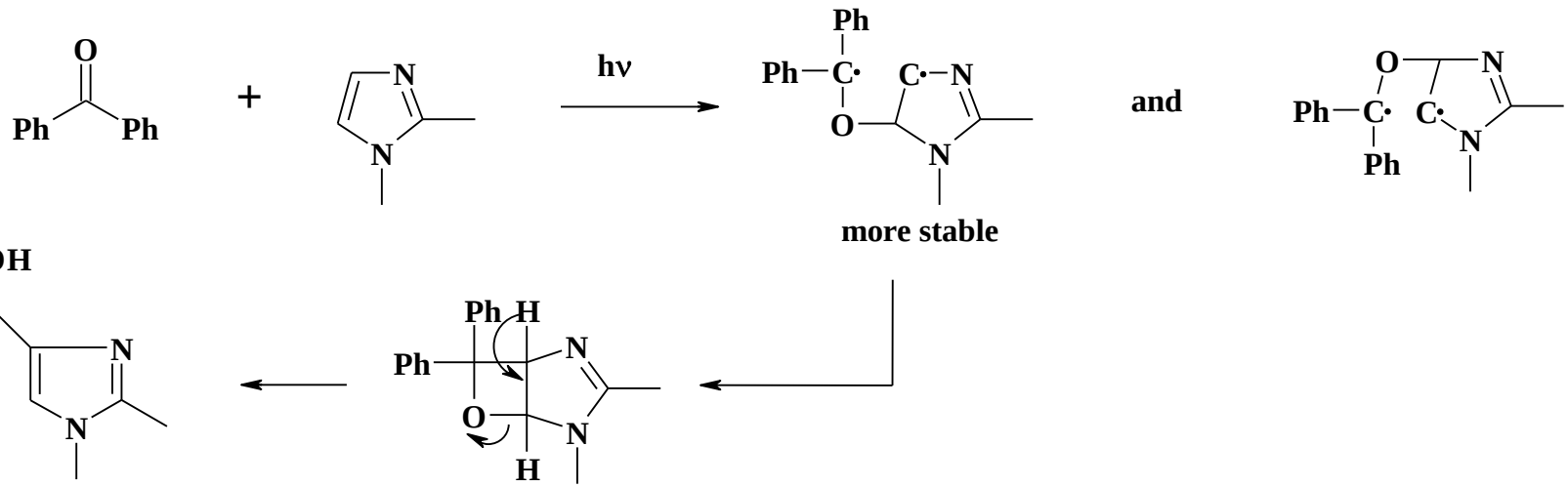


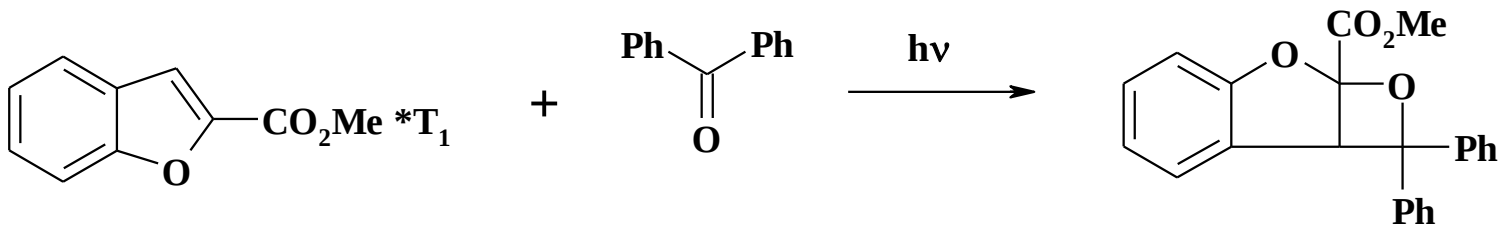
-55°C

R = Ph, endo/exo = 5.3:1

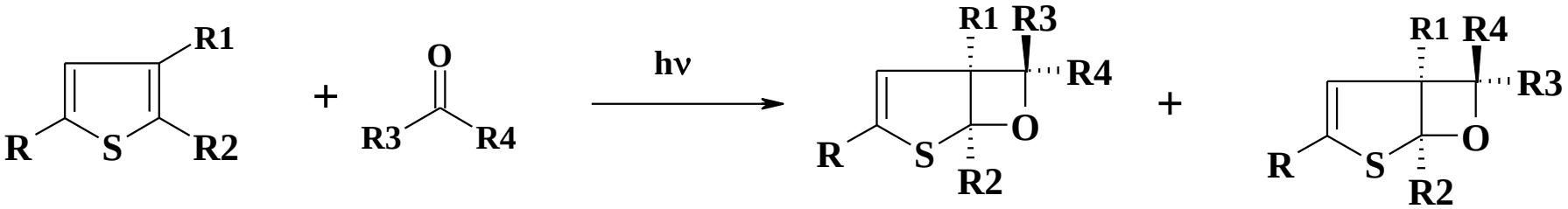
Oxetane formation: addition to heterocycles

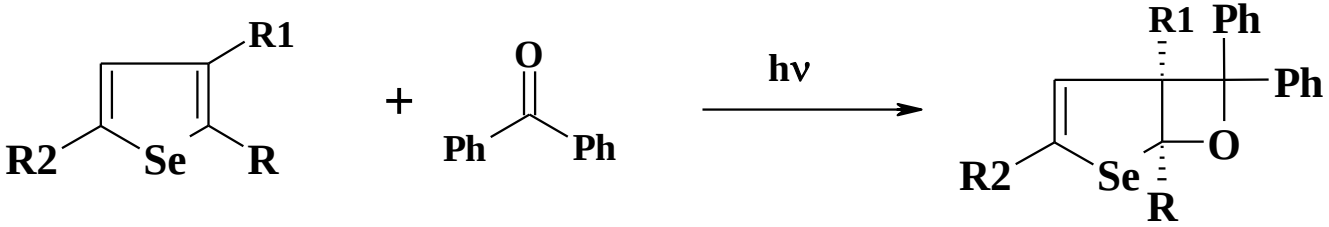




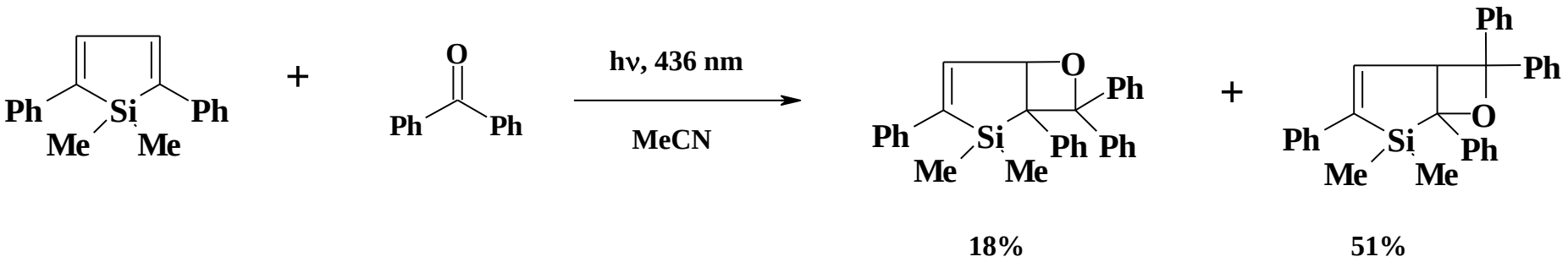


Methyl coumarilate



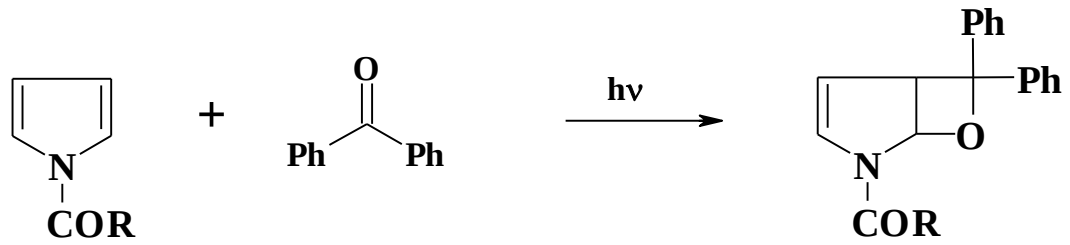


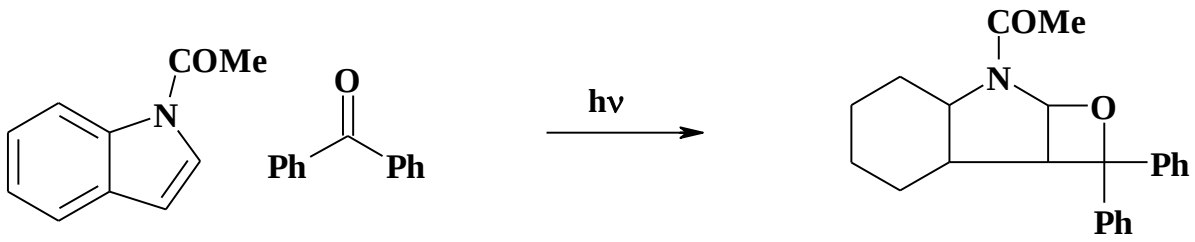
R1 = R2 = H, R = Me
R = R2 = H, R1 = Me
R1 = H, R = R2 = Me


Ph
Si
Ph
Me
Me
+
O
Ph
Ph
hν, 436 nm
MeCN
O
Ph
Ph
Si
Ph
Ph
Me
Me
+
Ph
Ph
Ph
O
Ph
Si
Me
Me

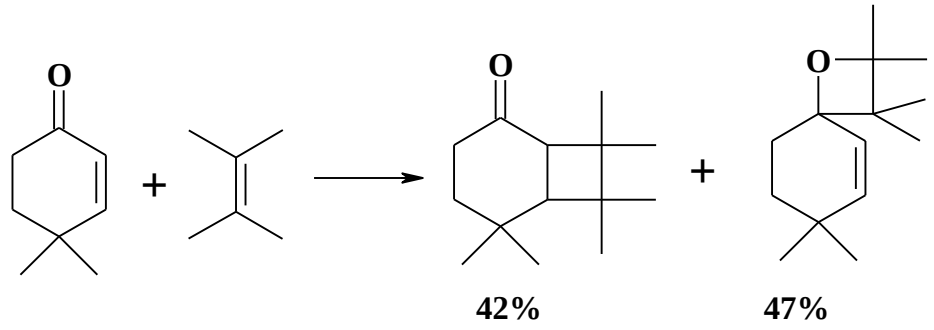
18%

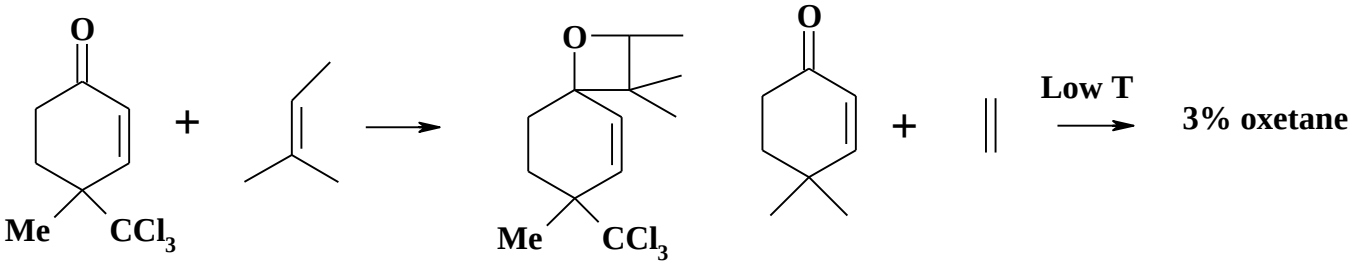
51%

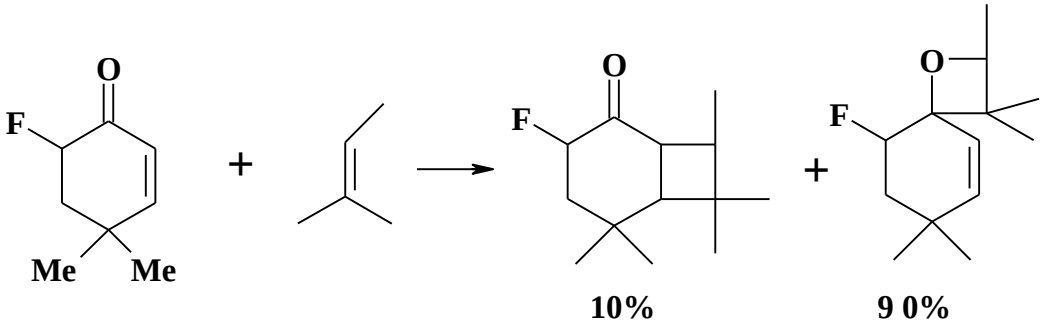

N
COR
+
O
Ph
Ph
hν
Ph
Ph
O
N
COR

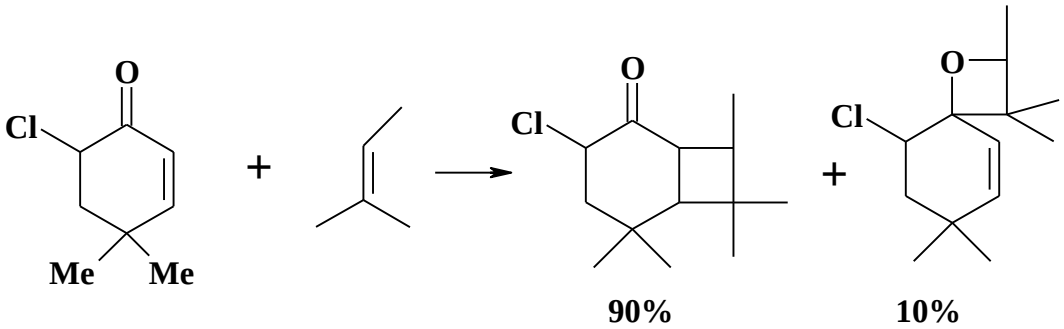

COMe
N
O
Ph
Ph
hν
COMe
N
O
Ph
Ph

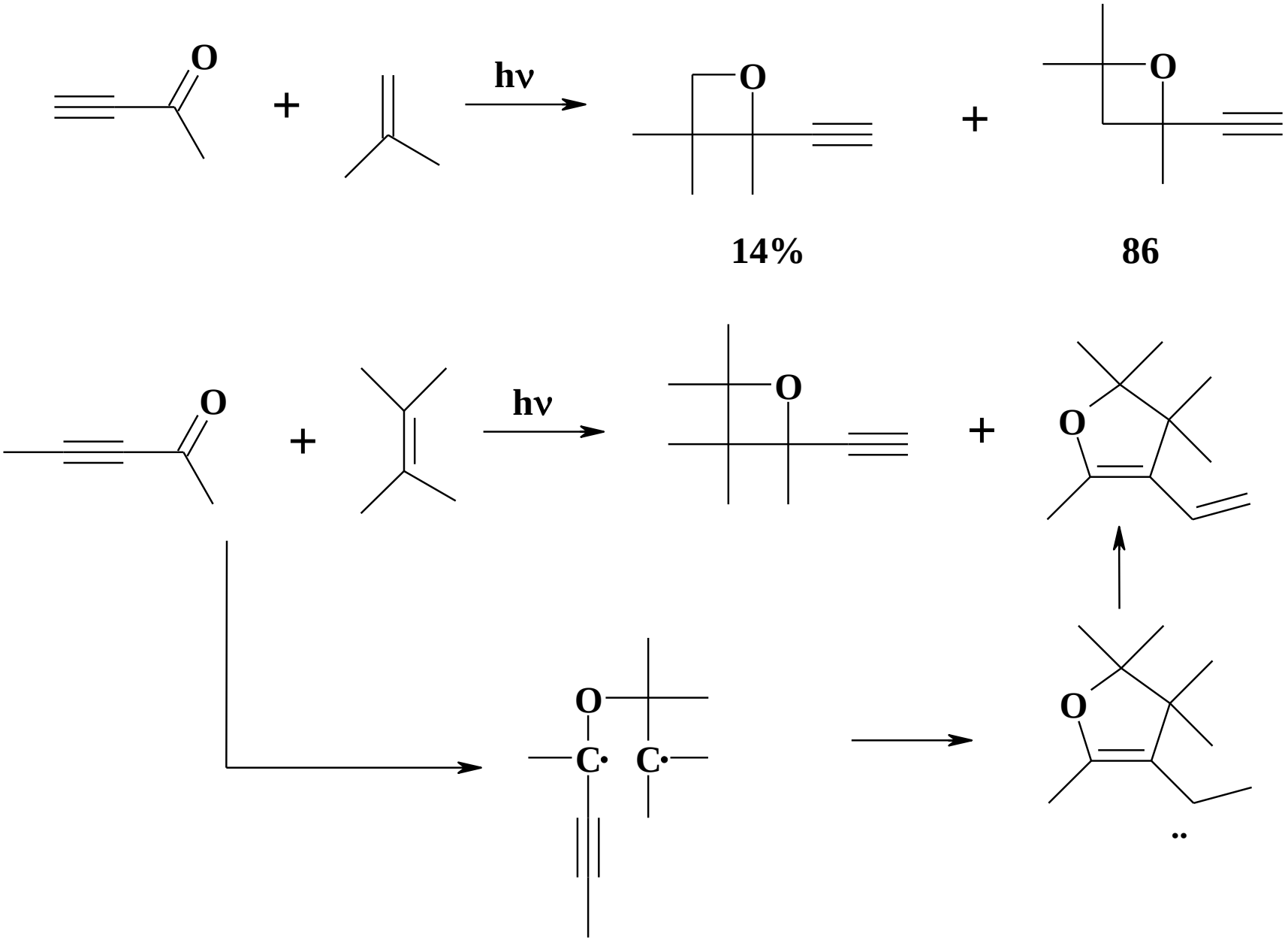
Enones and Ynones



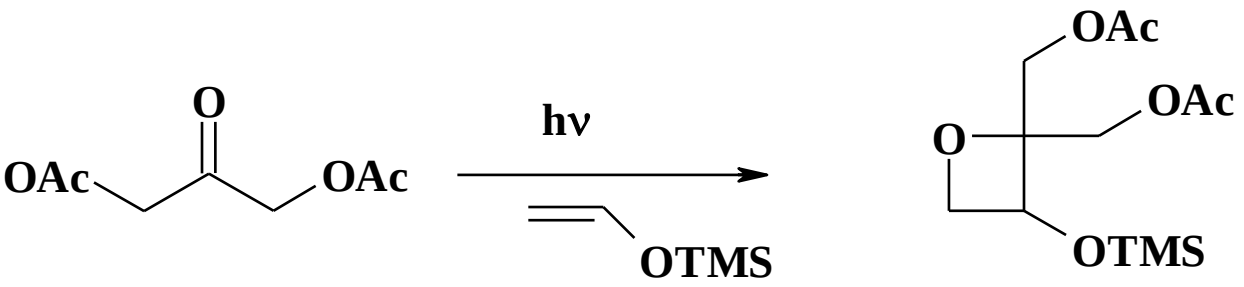


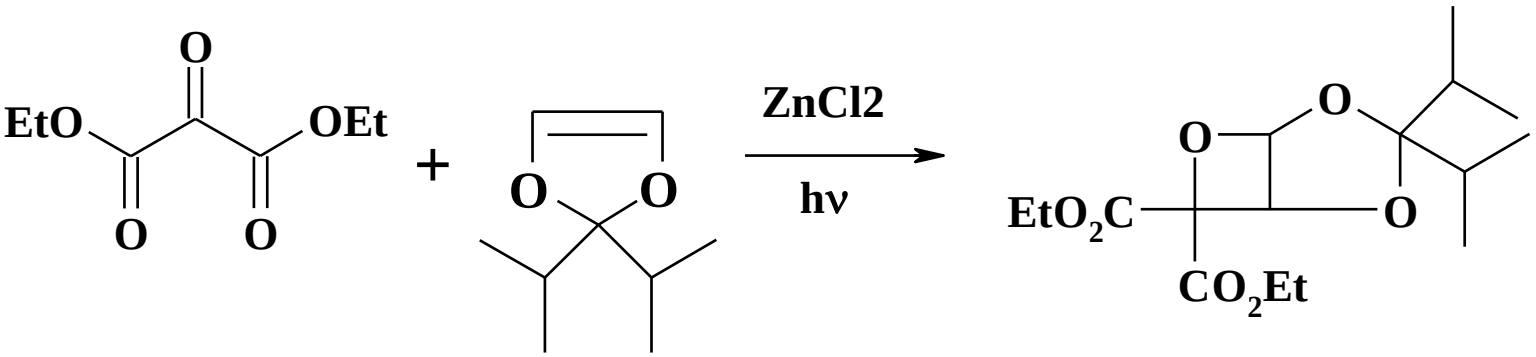


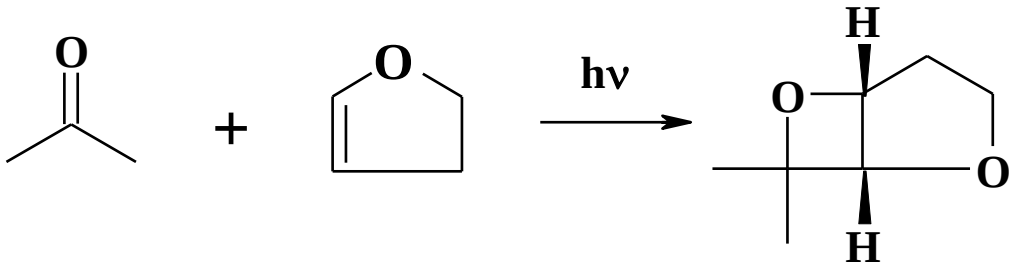


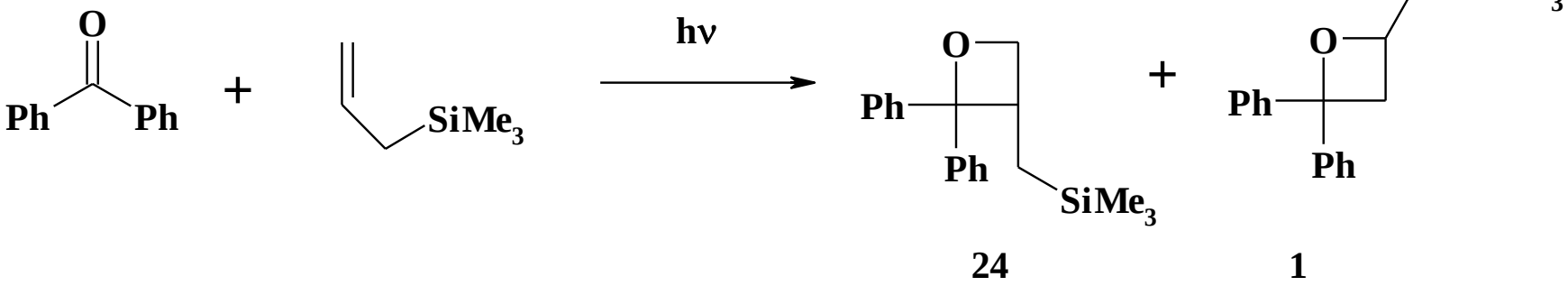

O
hν
O
O
14%
86
O
hν
O
O
O
C·
C·
O
O
..

Alkenes substituted with electron donor

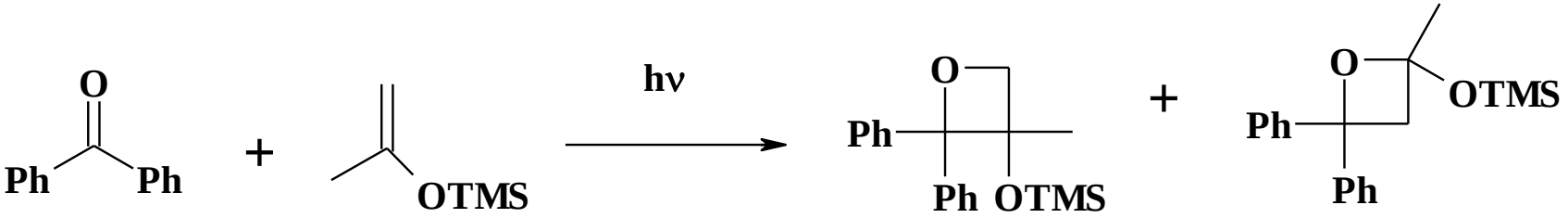




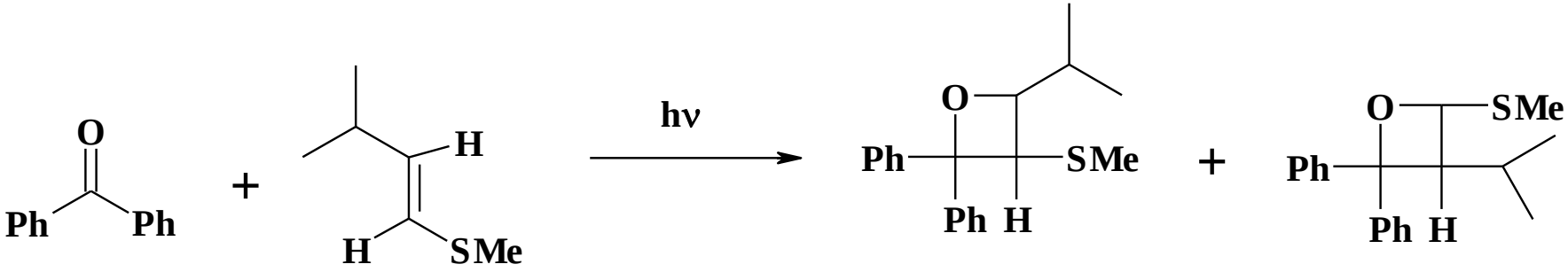



O
Ph
Ph
+
SiMe3
hν
O
Ph
Ph
SiMe3
+
SiMe3
O
Ph
Ph

24 1

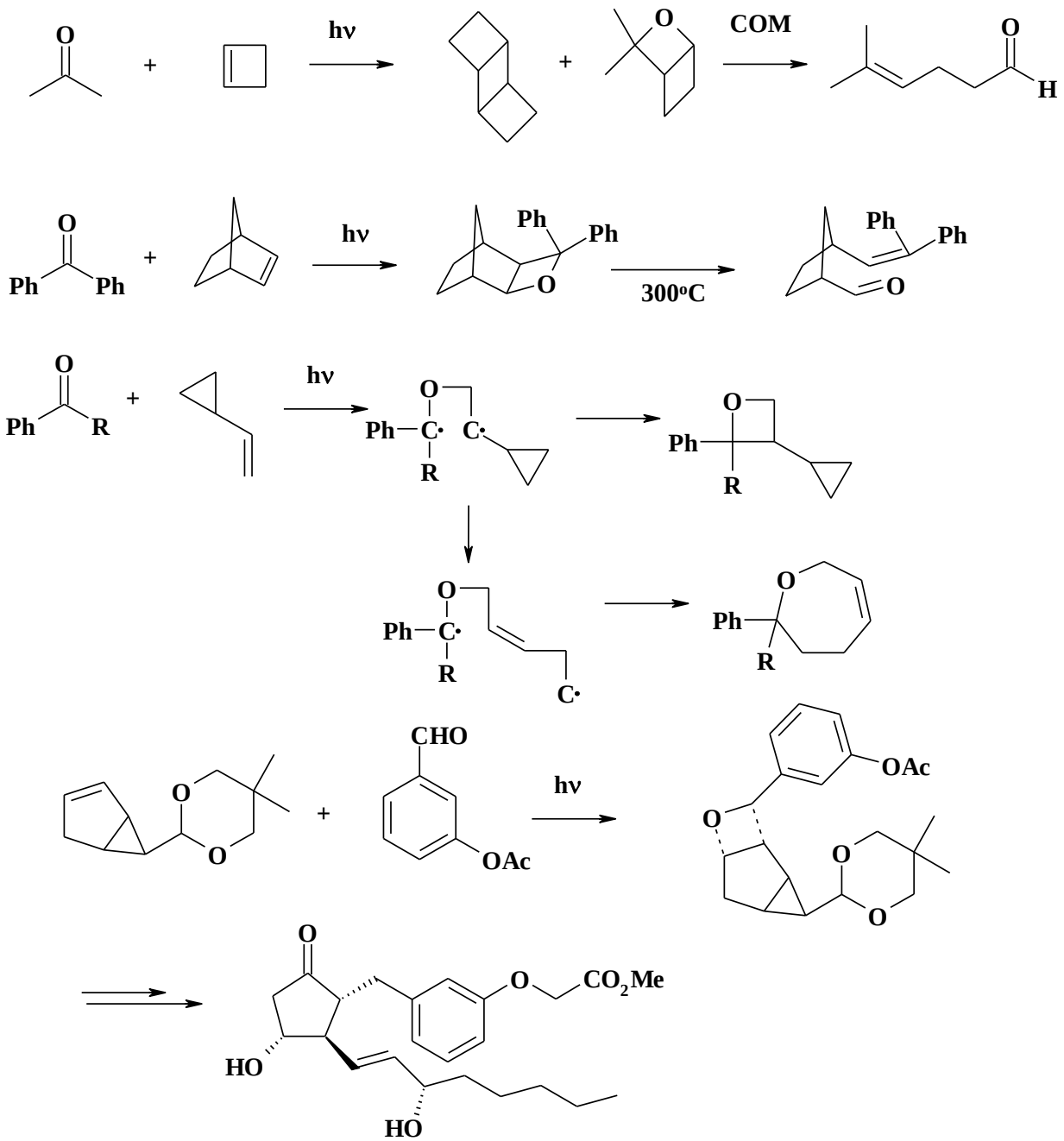

O
Ph
Ph
+
OTMS
hν
O
Ph
Ph
OTMS
+
O
OTMS
Ph
Ph

94 6

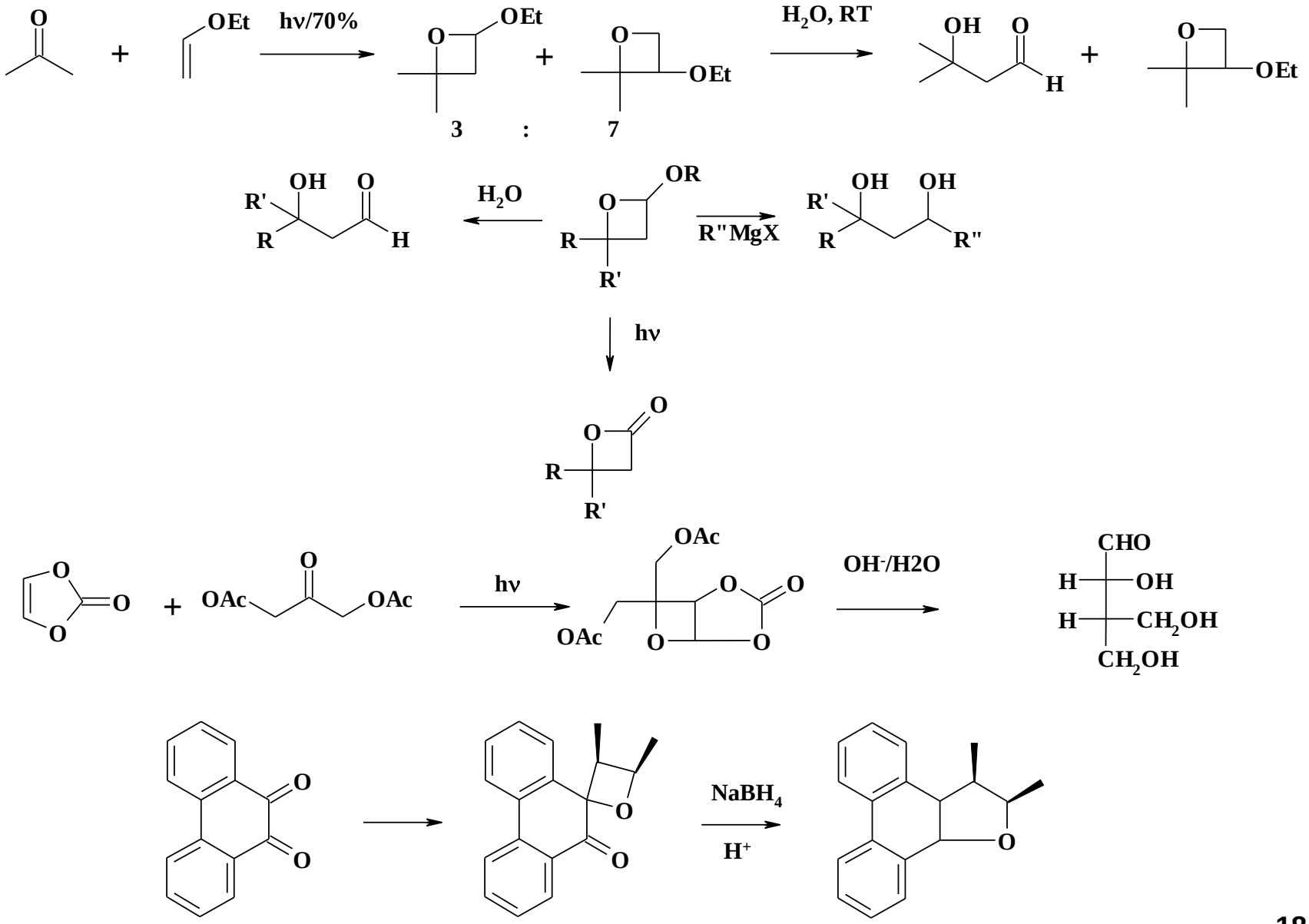

O
Ph
Ph
+
H
H
SMe
hν
O
Ph
SMe
Ph
H
+
O
SMe
Ph
Ph
H

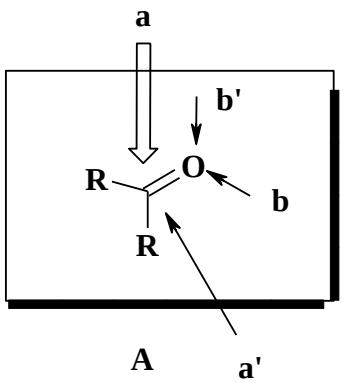
100 0

Miscelleneous Paterno-Buchi Reaction

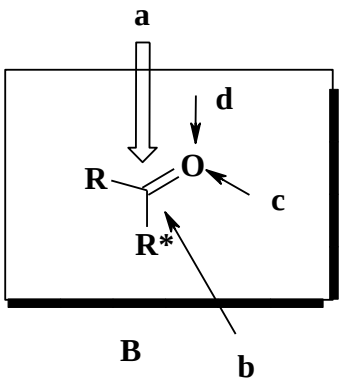


The Paterno-Buchi reaction as a photochemical aldol equivalent





enantiotopic faces a,a' and b,b'



diastereotopic faces a,b and c,d

↓

non prostereogenic carbonyl

↓

prostereogenic carbonyl

Parallel approach

↓

 # Nucleophilic attack of carbonyl (half filled π*) towards the alkene empty π*

 # Electron defficient alkenes favored this approach

Perpendicular approach

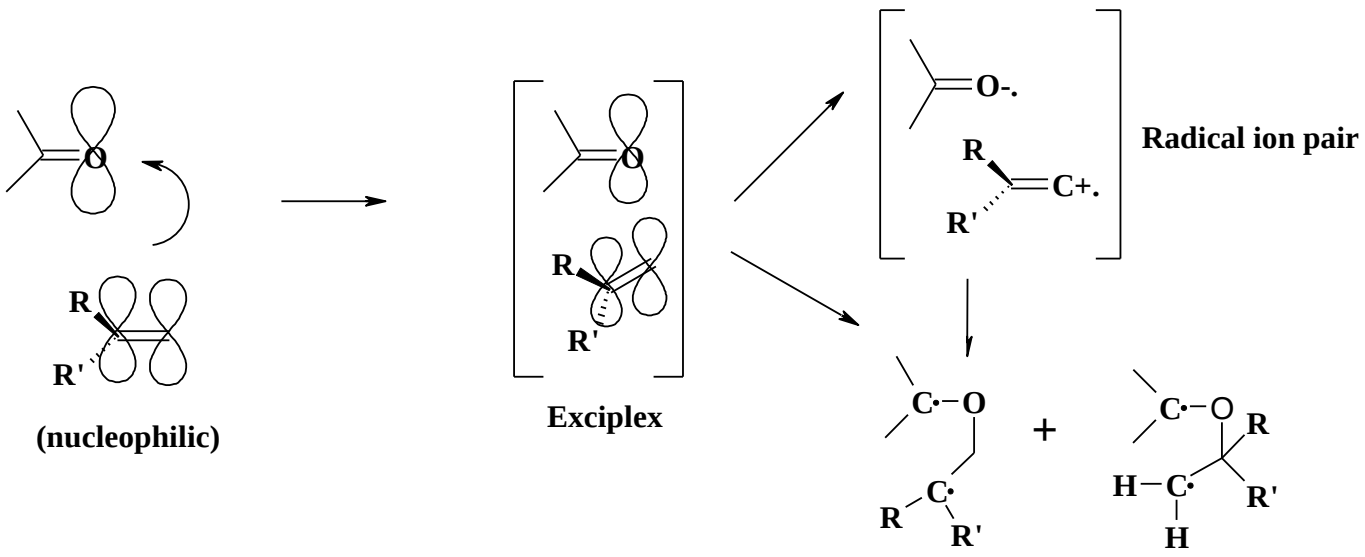
↓

#Nucleophilic attack of alkene toward carbonyl half filled n orbital

 # Electron rich alkenes favored this approach

 # Carbon-oxygen 1,4 biradical

Regioselectivity a closer look (Perpendicular approach)



 # nucleophilic attack of the filled π-orbitalof the olefin to the excited carbonyl oxygen (n-orbital) to form an exciplex

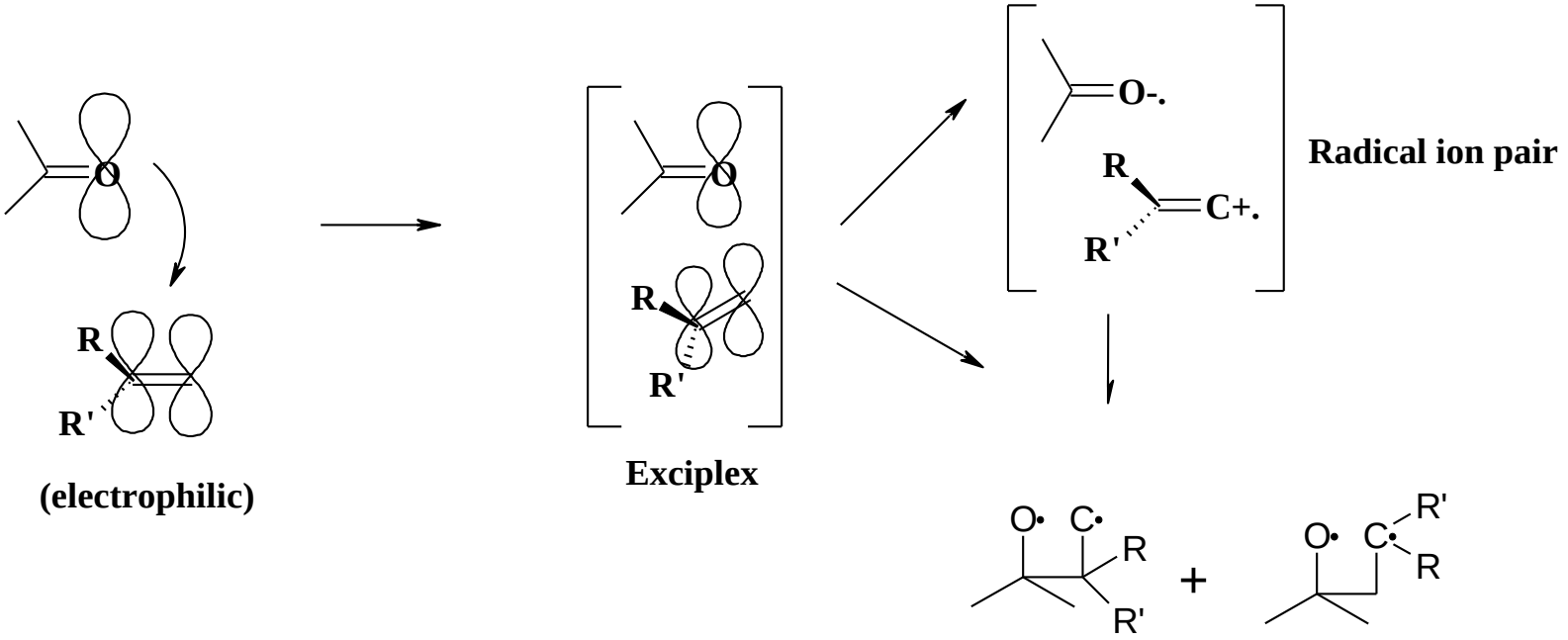
 # the attack results either in full or partial electorn transfer to generate a radical ion pair

 # the ion pair or exciplex combines to form a C-O bond resulting a diradical intermediate

 # the diradical if triplet lives long and undergoes other reactions before ISC

 # finally the singlet diradical closes to yield the oxetane

Regioselectivity a closer look (parallel approach)



 # nucleophilic attack of the carbonyl by its half filled π* to alkene π*

 # the attack results either in full or partial electorn transfer to generate a radical ion pair

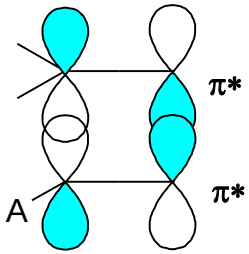
 # the ion pair or exciplex combines to form a C-C bond resulting a diradical intermediate

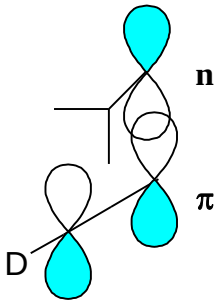
 # the diradical if triplet lives long and undergoes other reactions before ISC

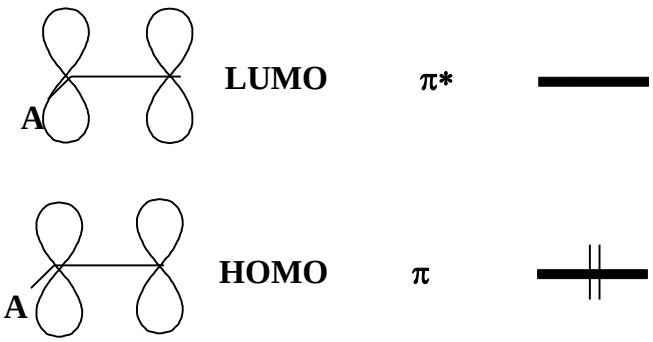
 # finally the singlet diradical closes to yield the oxetane

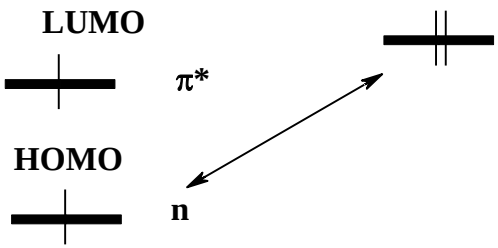
Parallel approach

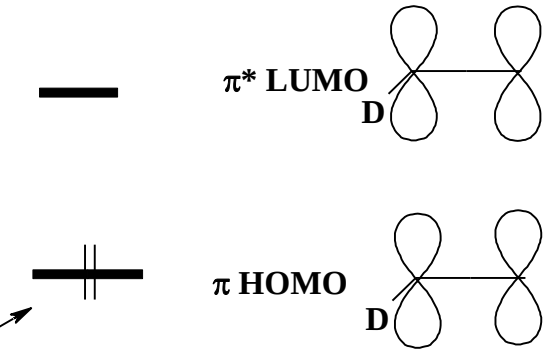
perpendicular approach

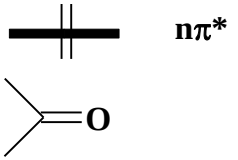


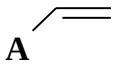








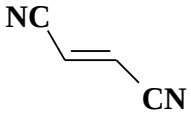


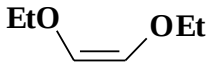


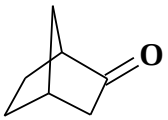
electron deficient alkene
A = electron acceptor

electronrich alkene
D = Donor

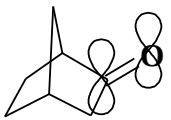
Fluorescence quenching of 2-norbornanone singlets by trans-DCE and cis-DEE



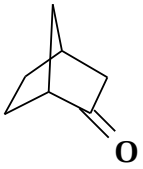




"edges"
(n-orbital attack)

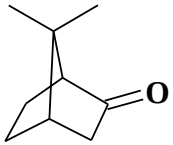


"faces"
(π-orbital attack)



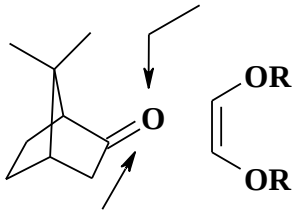
5.1

1.2

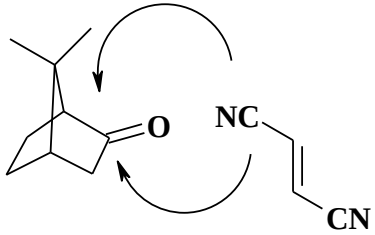


1.0

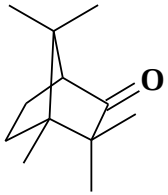
1.5



Fast

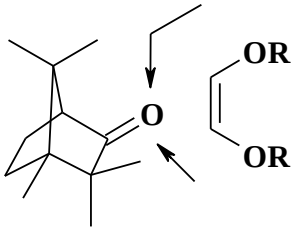


Slow

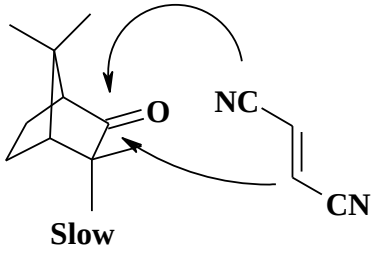


0.48

<0.03



Slow

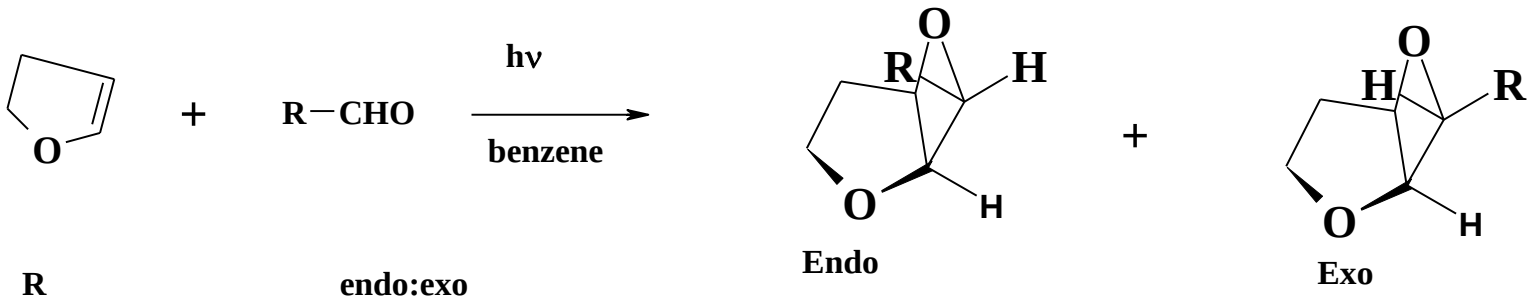


Slow

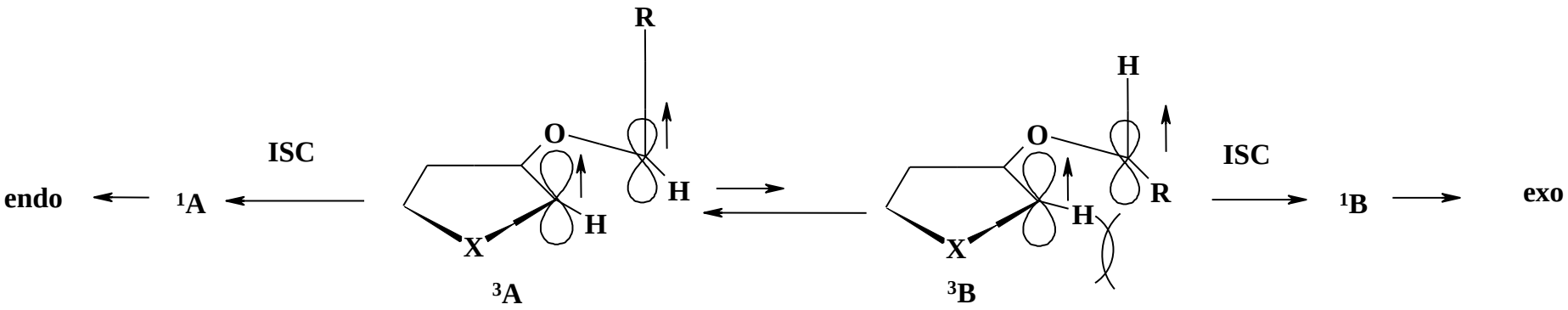
parallel approach
(π-orbital attack)

perpendicular approach
(n-orbital attack)

Intermediacy of diradical explains certain facts

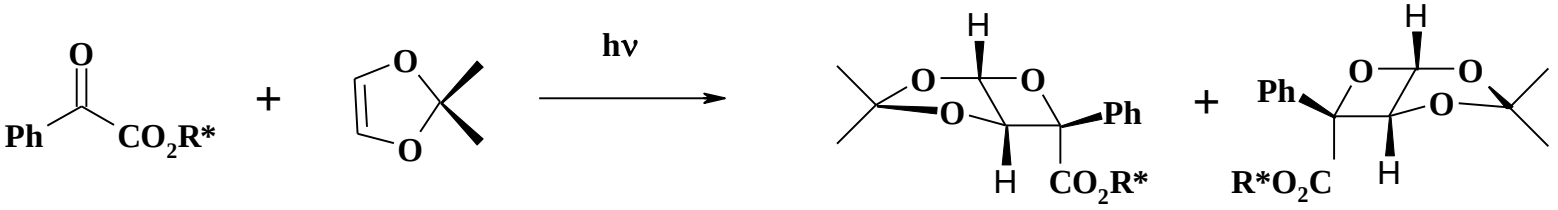


R	endo:exo
Me	45:55
ethyl	58:42
isobutyl	67:33
phenyl	88:12
o-tolyl	93:7
mesityl	>98:2

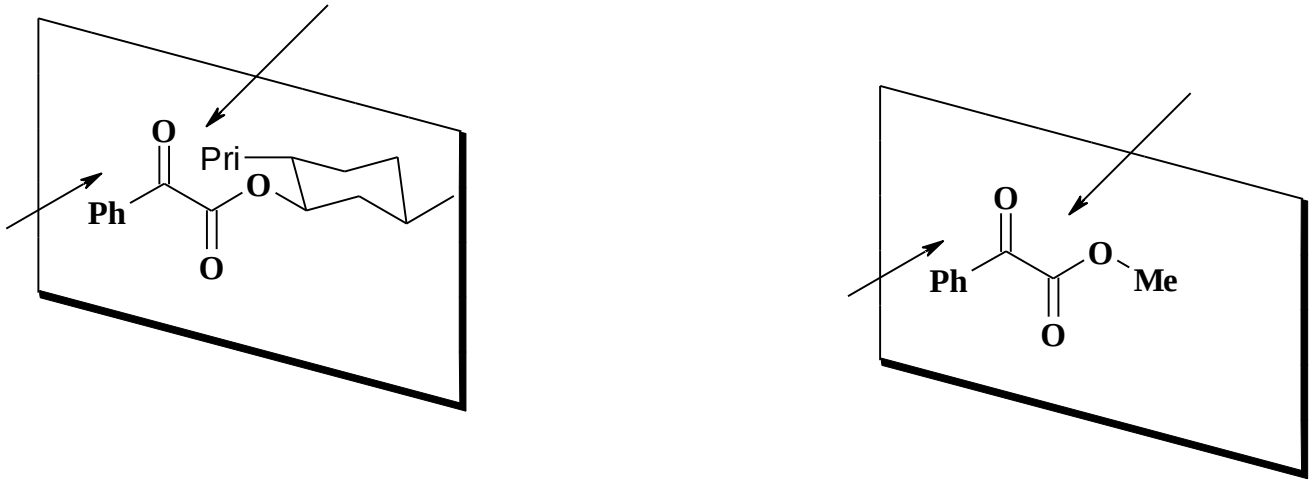


Perpendicular approach

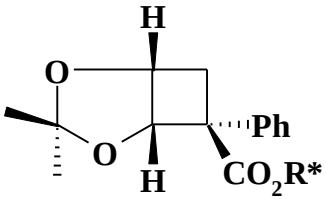
Enantiocontrol and diastereocontrol inPaterno-Buchi Reaction

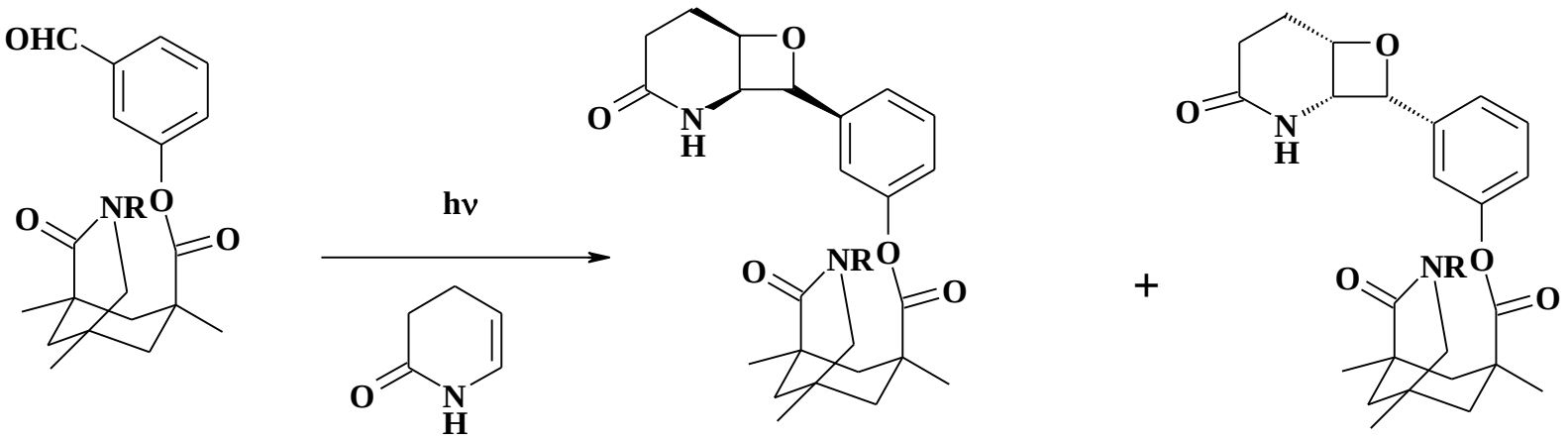


R* = (-) 8-phenyl menthyl; de>96%
R* = (-) menthyl; de 57%

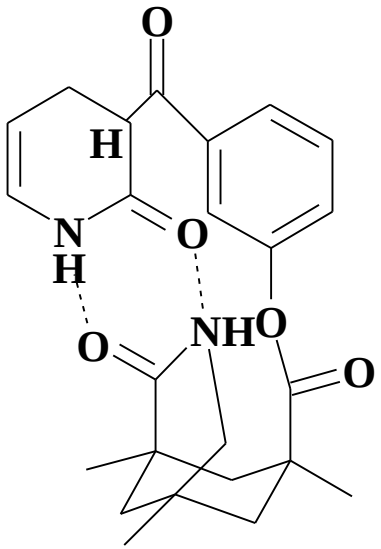


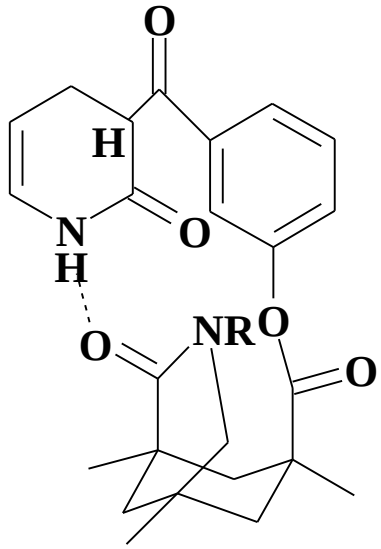
one face of carbonyl blocked by the menthyl group



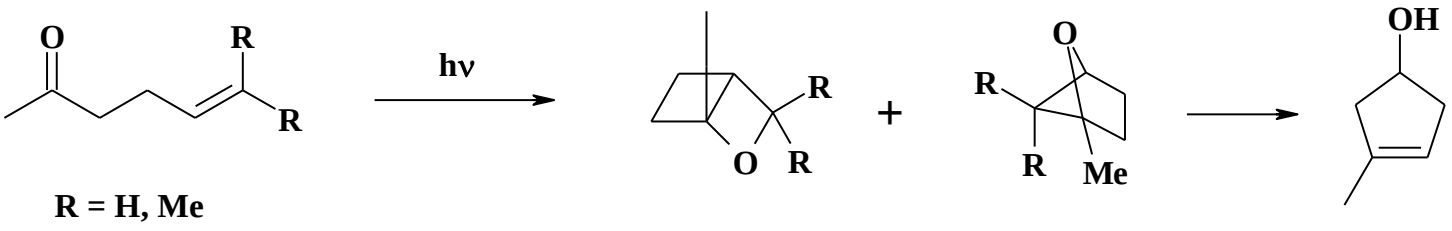


R = H acetonitrile 1:1
benzene 83:17
toluene 95:5
R = Me, benzene 1:1

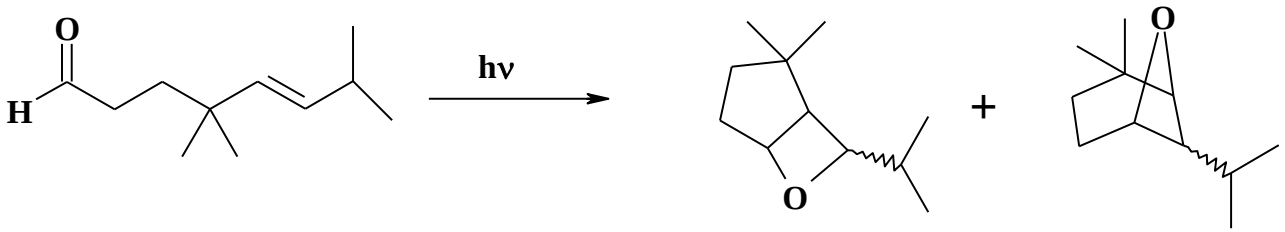


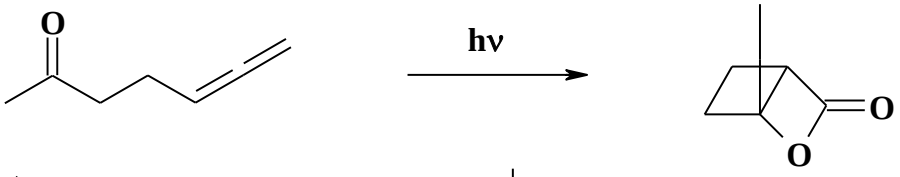


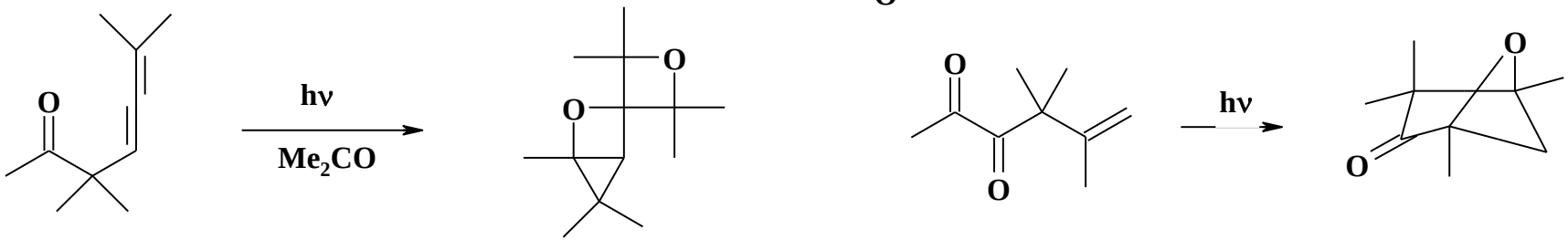
Intramolecular oxetane formation

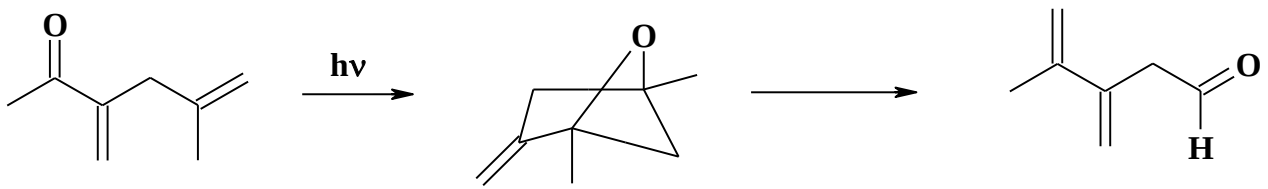


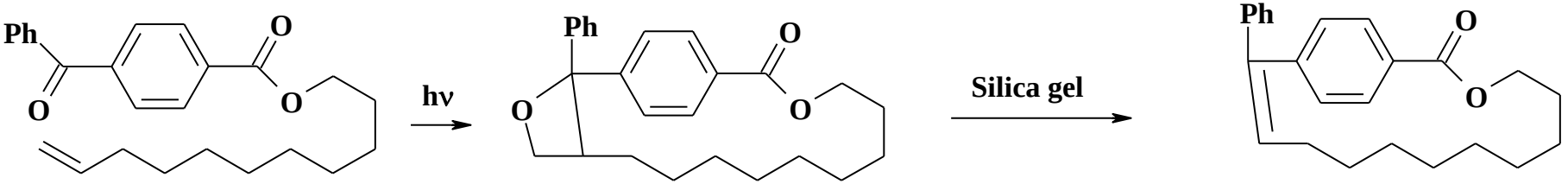
R = H, Me

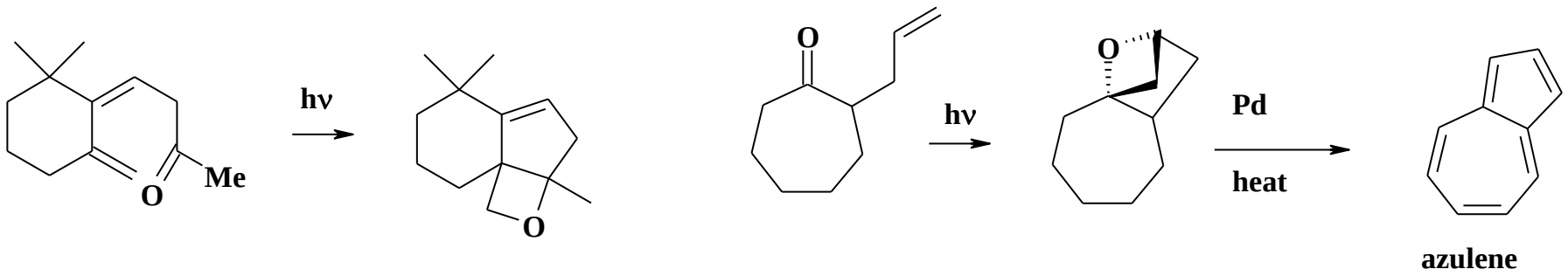




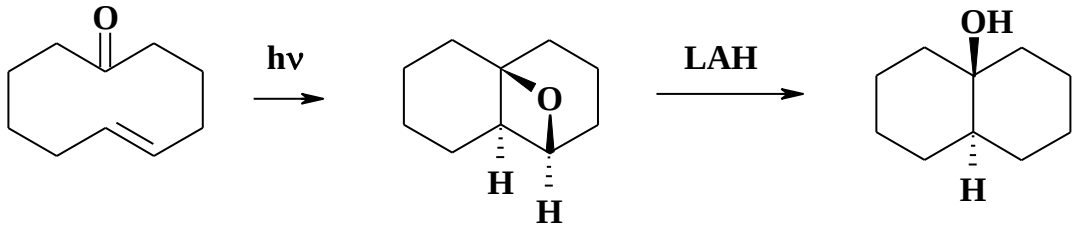


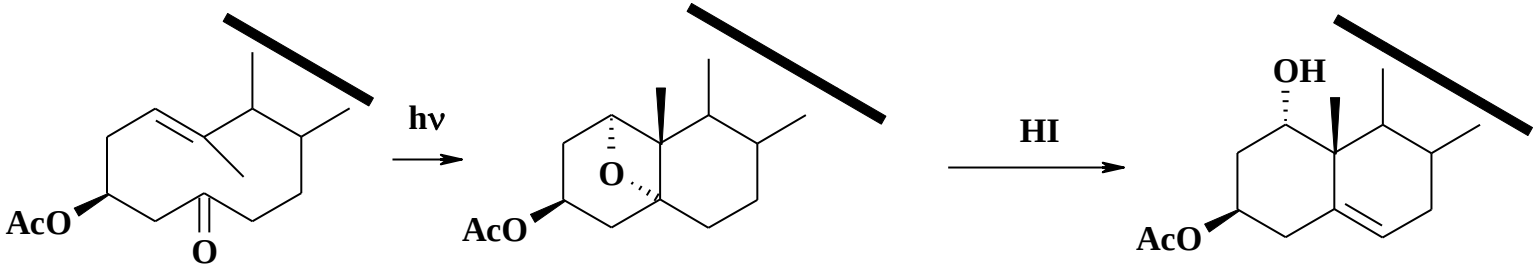




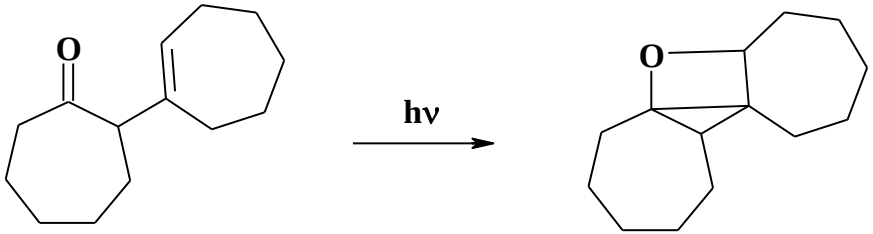


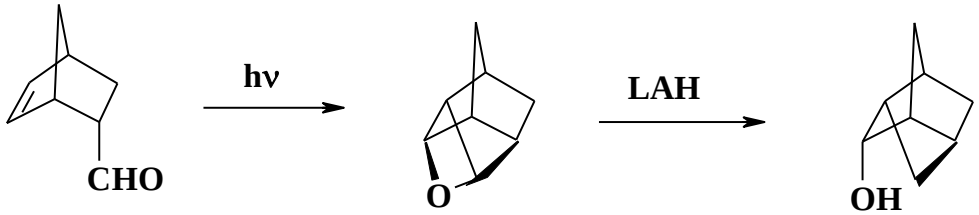
azulene

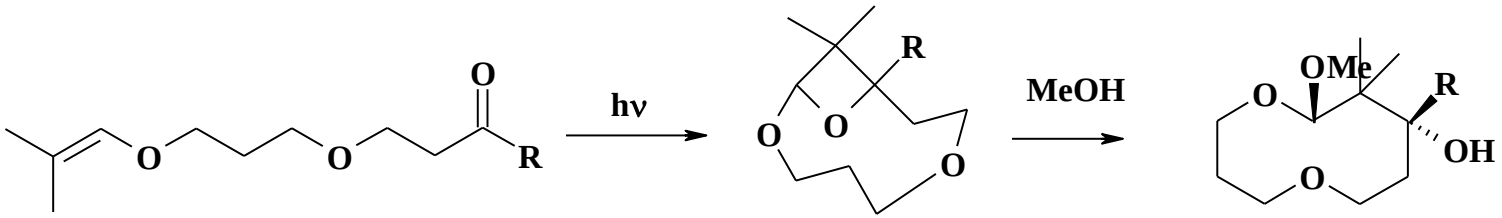


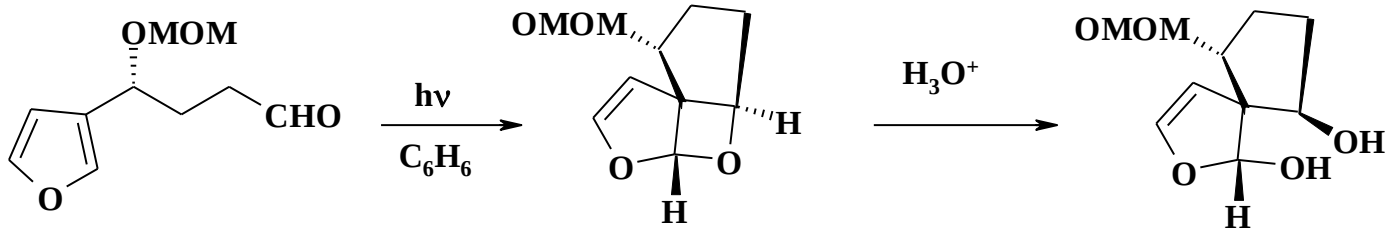


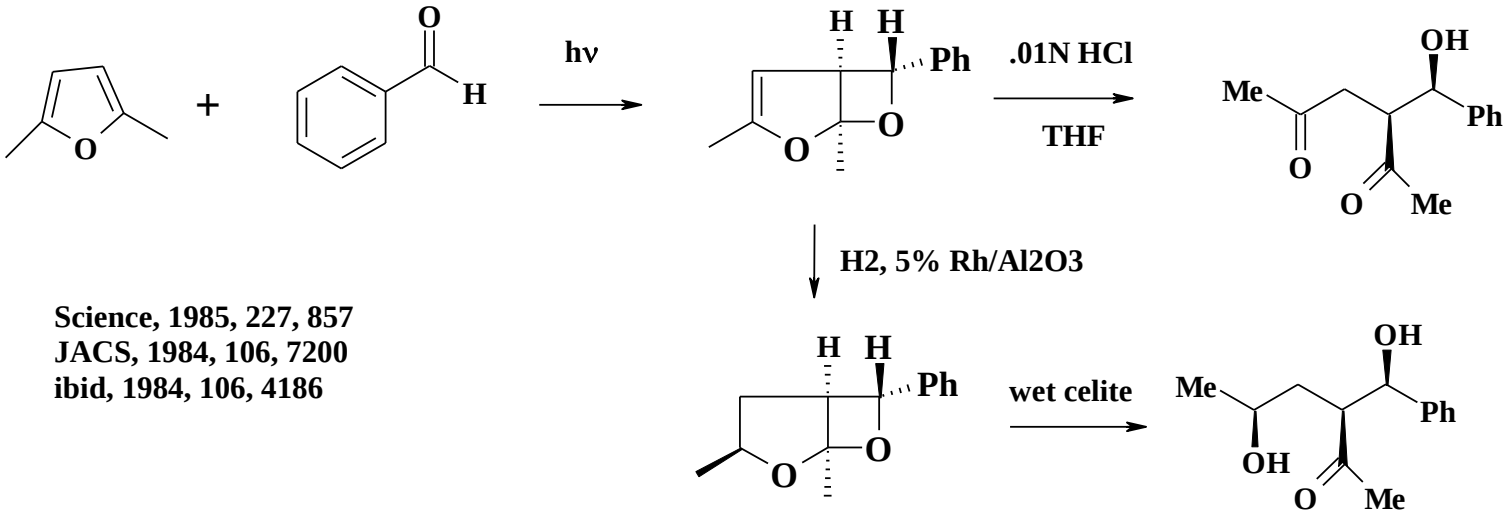
intermediate for 1α -hydroxy-vitamin D_3


O
hν
O

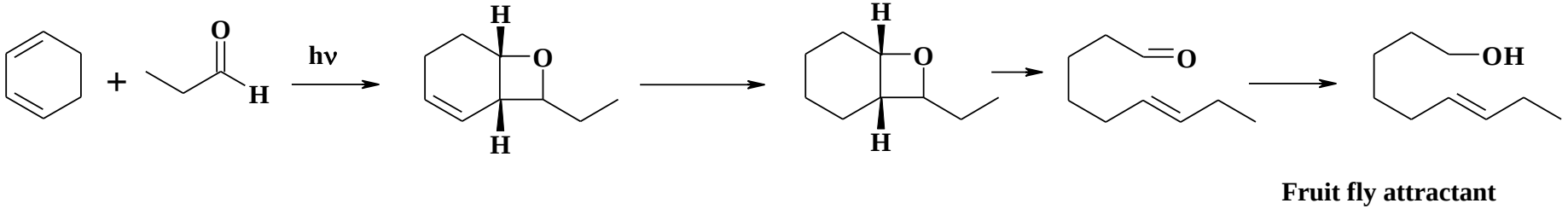

CHO
hν
O
LAH
OH


O
O
O
R
hν
R
O
O
O
MeOH
OMe
O
R
OH
O

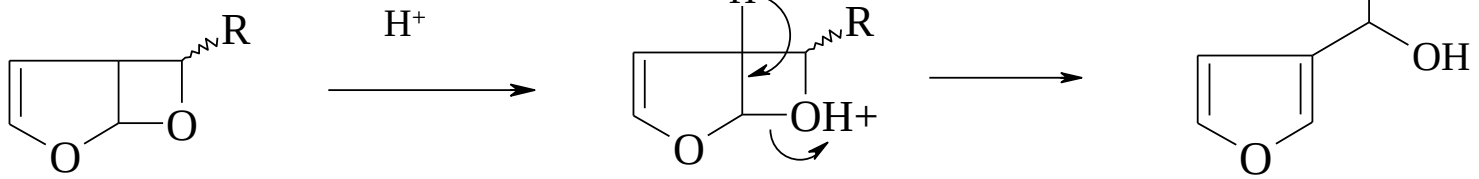

OMOM
CHO
O
hν
C6H6
OMOM
H
O
O
H
H3O+
OMOM
OH
O
OH
H



Science, 1985, 227, 857
JACS, 1984, 106, 7200
ibid, 1984, 106, 4186

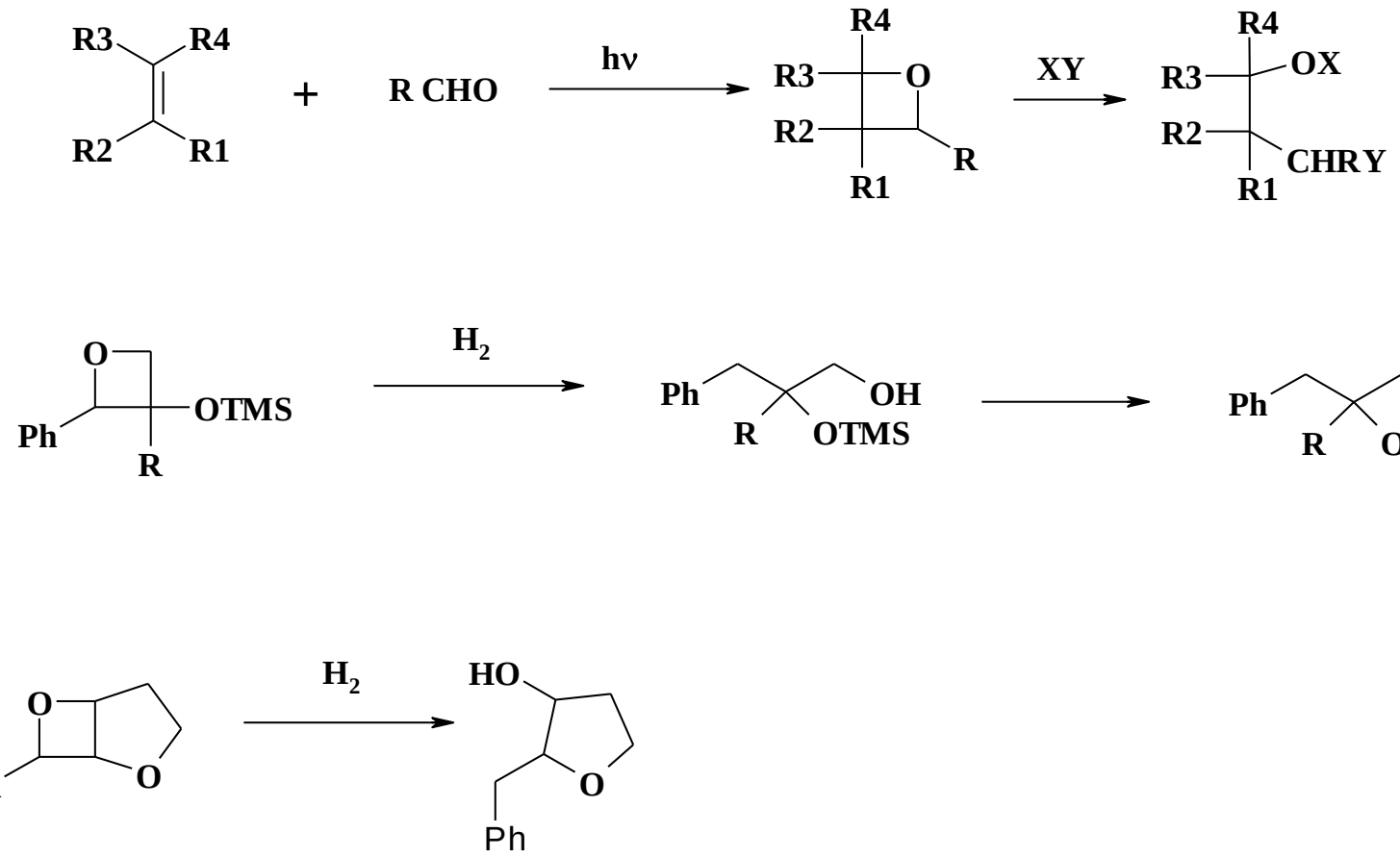


Fruit fly attractant

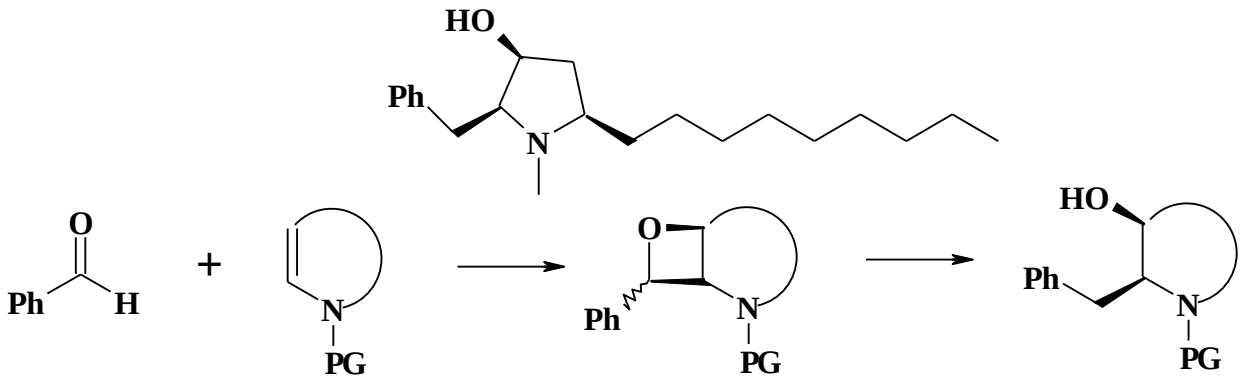


R = Me, Ph, CO_2nBu

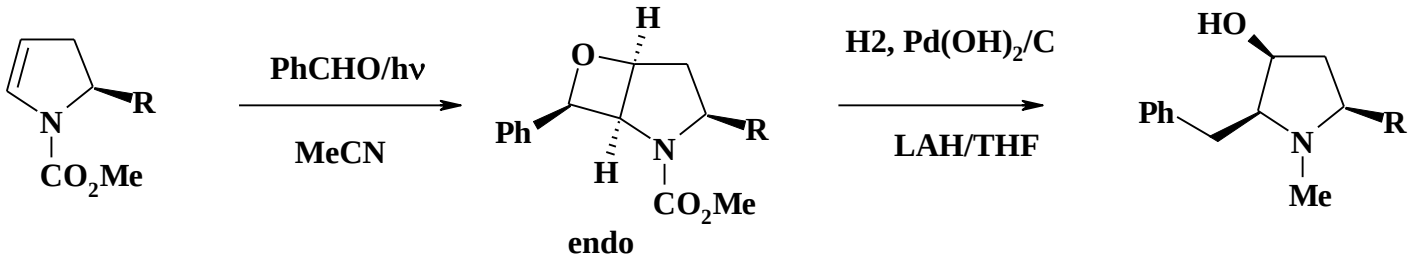
Carboxydroxylation strategy by reductive cleavage of oxetanes

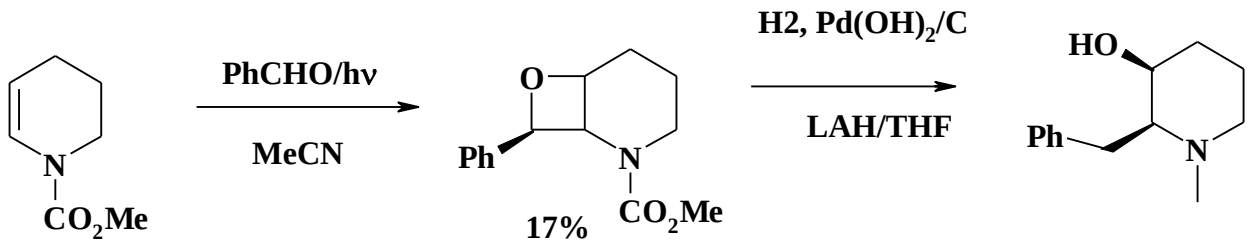


Total synthesis of (+)-Preussin

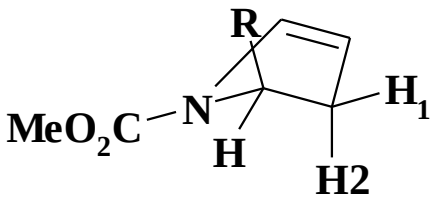


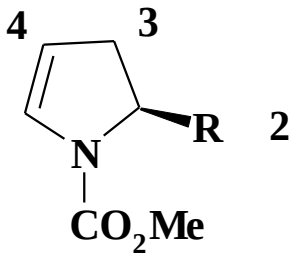
Carbohydroxylation strategy fo N-containing unsaturated heterocycles

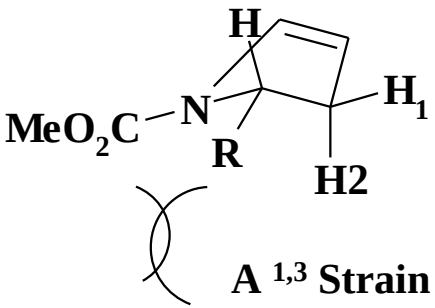




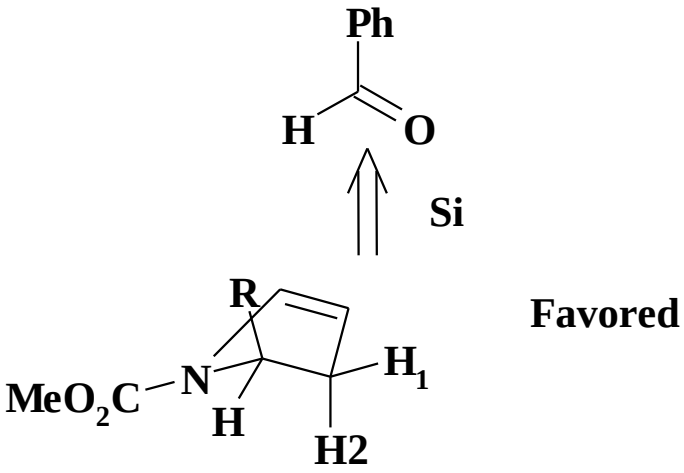
Chem.Eur.J, 2000, 6, 3838-48



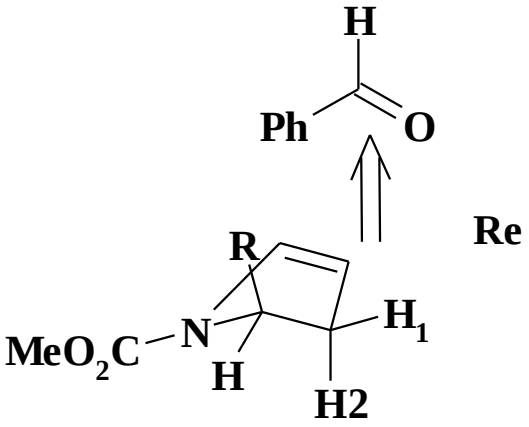




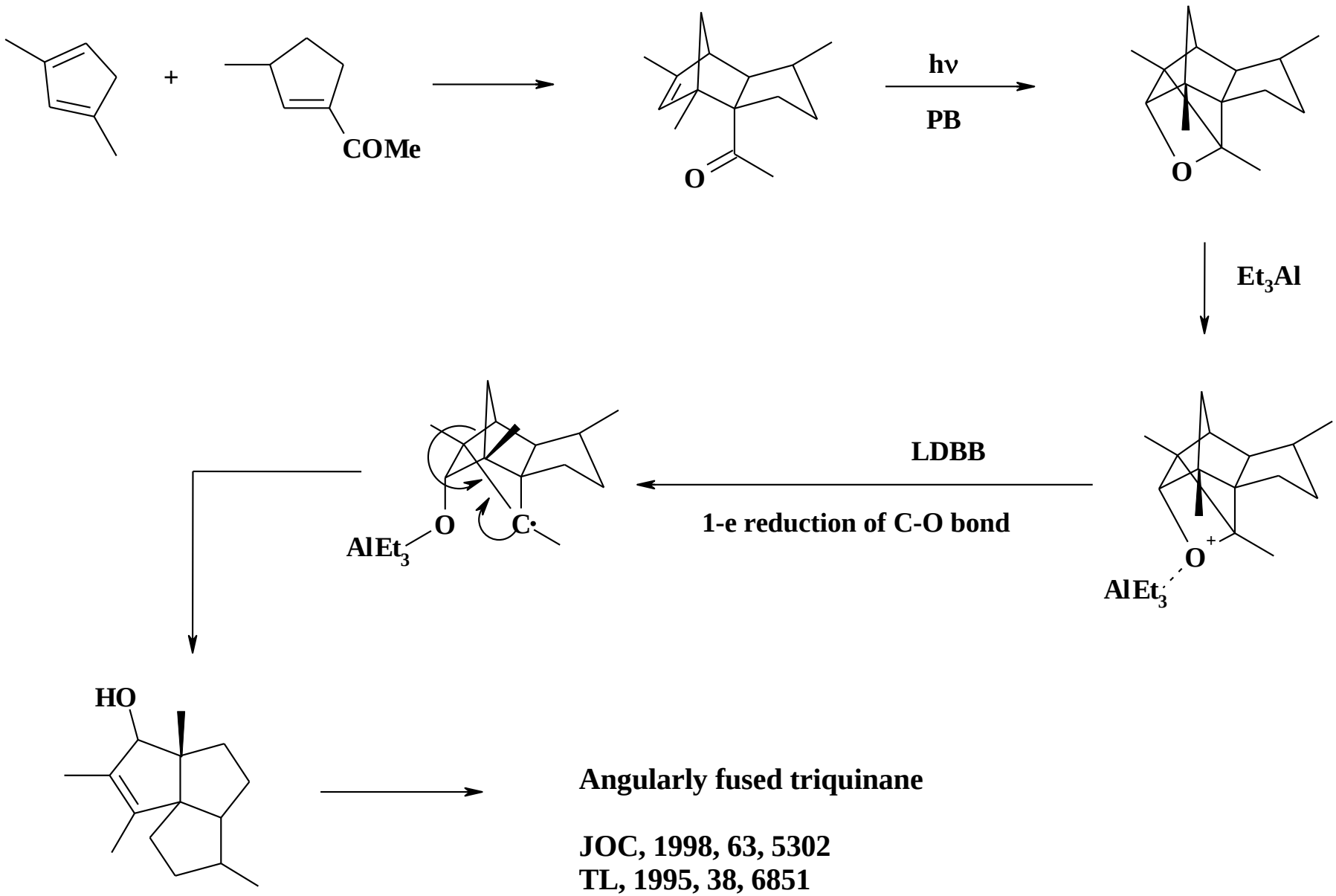
Pseudoaxial orientation of R



Favored



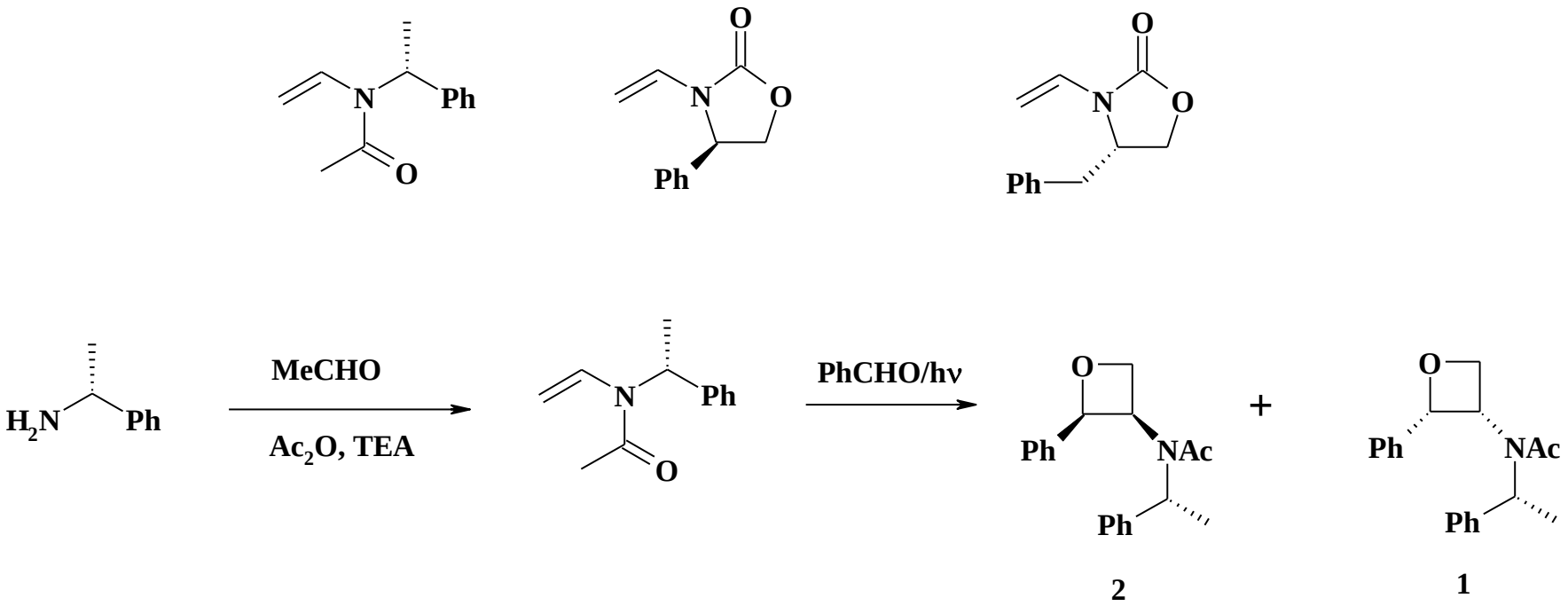
Possible explanation for the facial diastereoselectivity

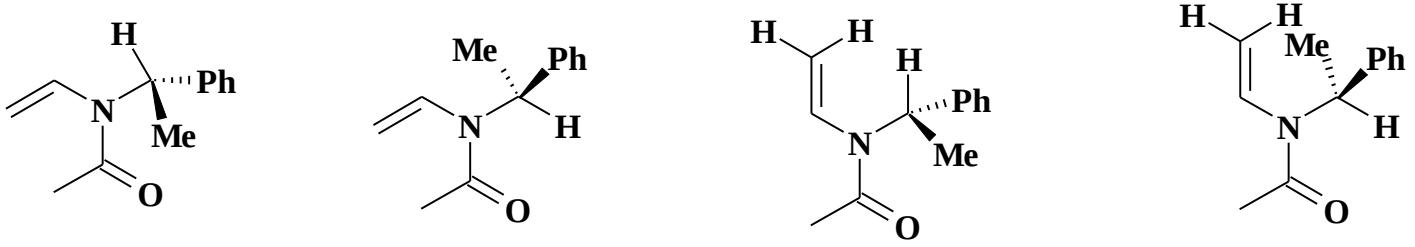


Angularly fused triquinane

JOC, 1998, 63, 5302
TL, 1995, 38, 6851

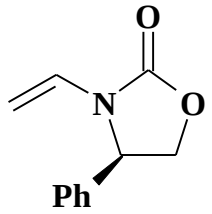
Chiral enamides and diastereoselective PB reaction

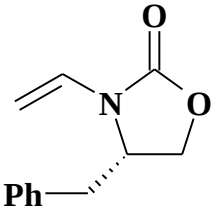


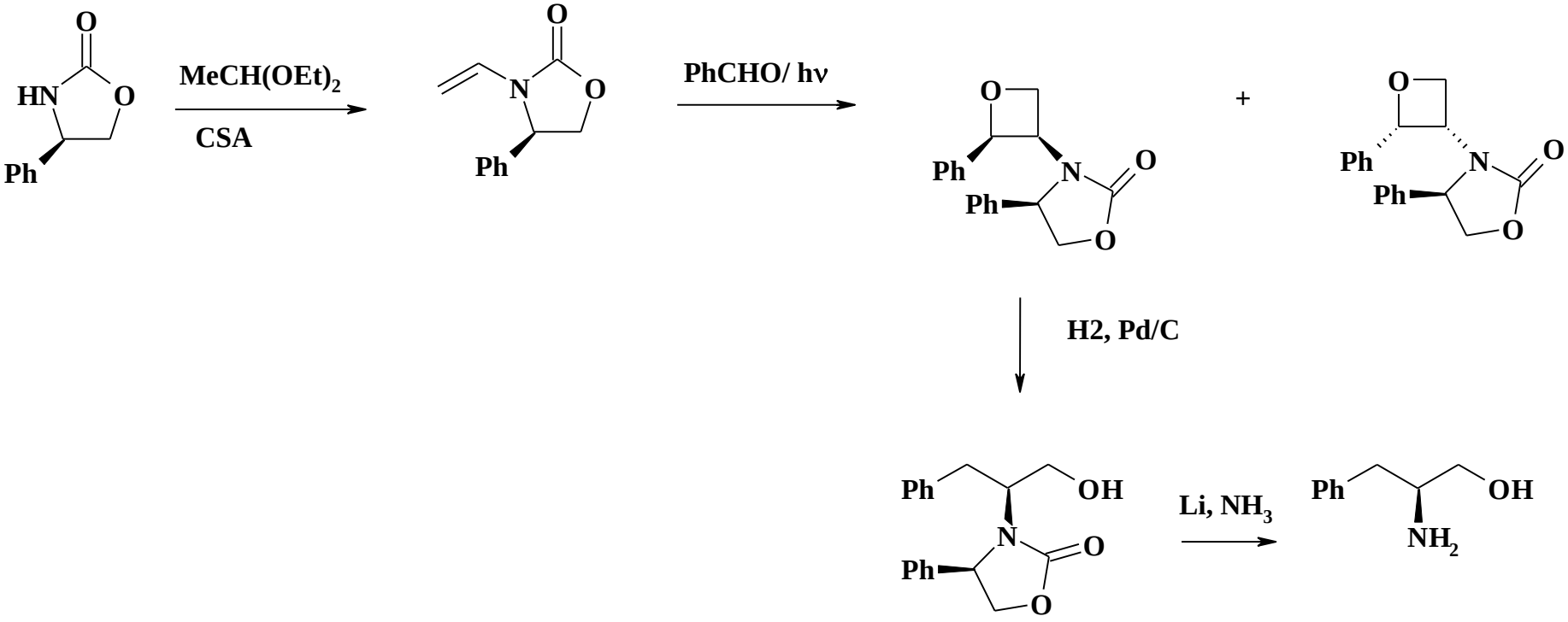


GS conformations of parent enamides

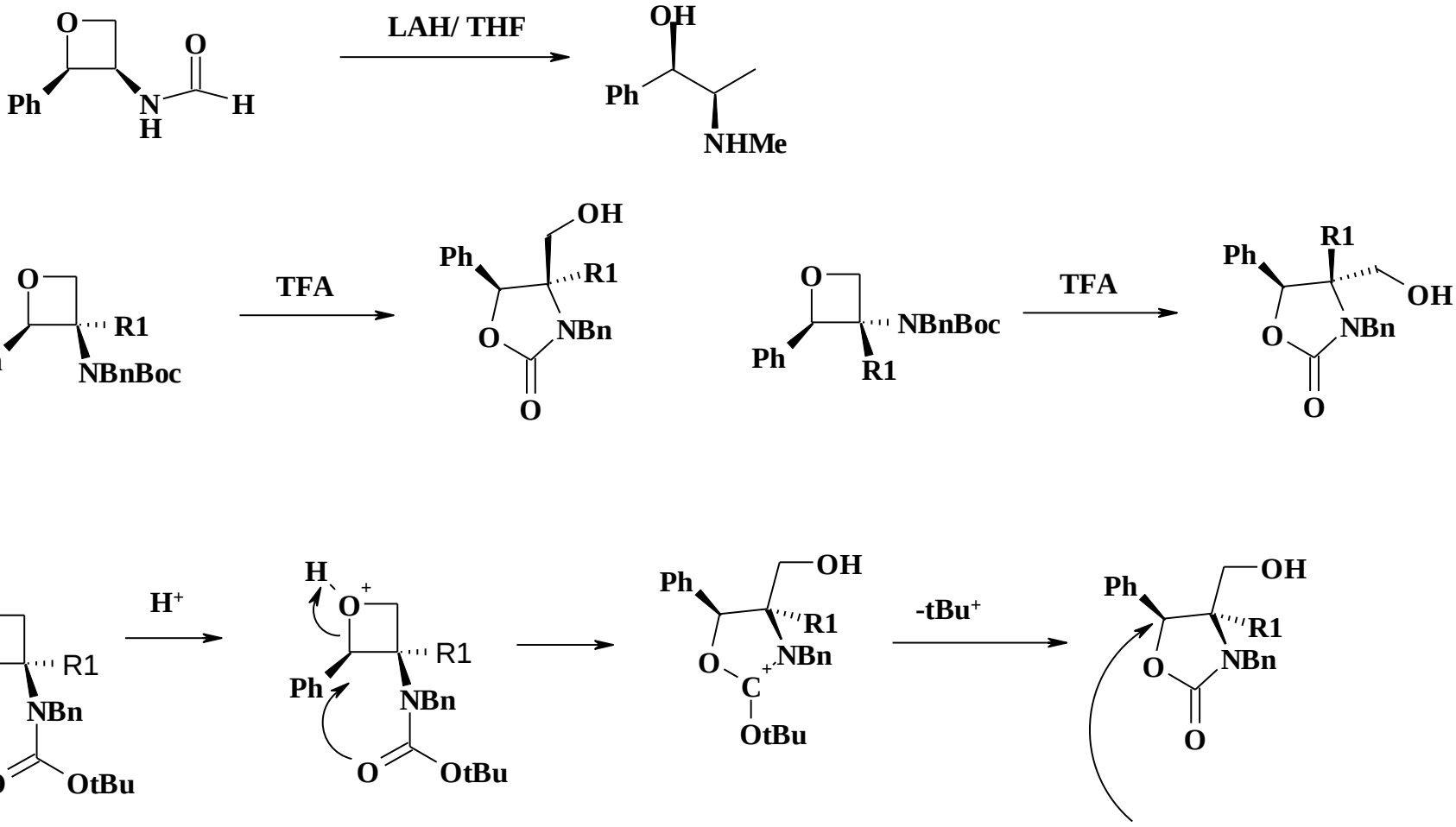
Chiral enamides and diastereoselective PB reaction



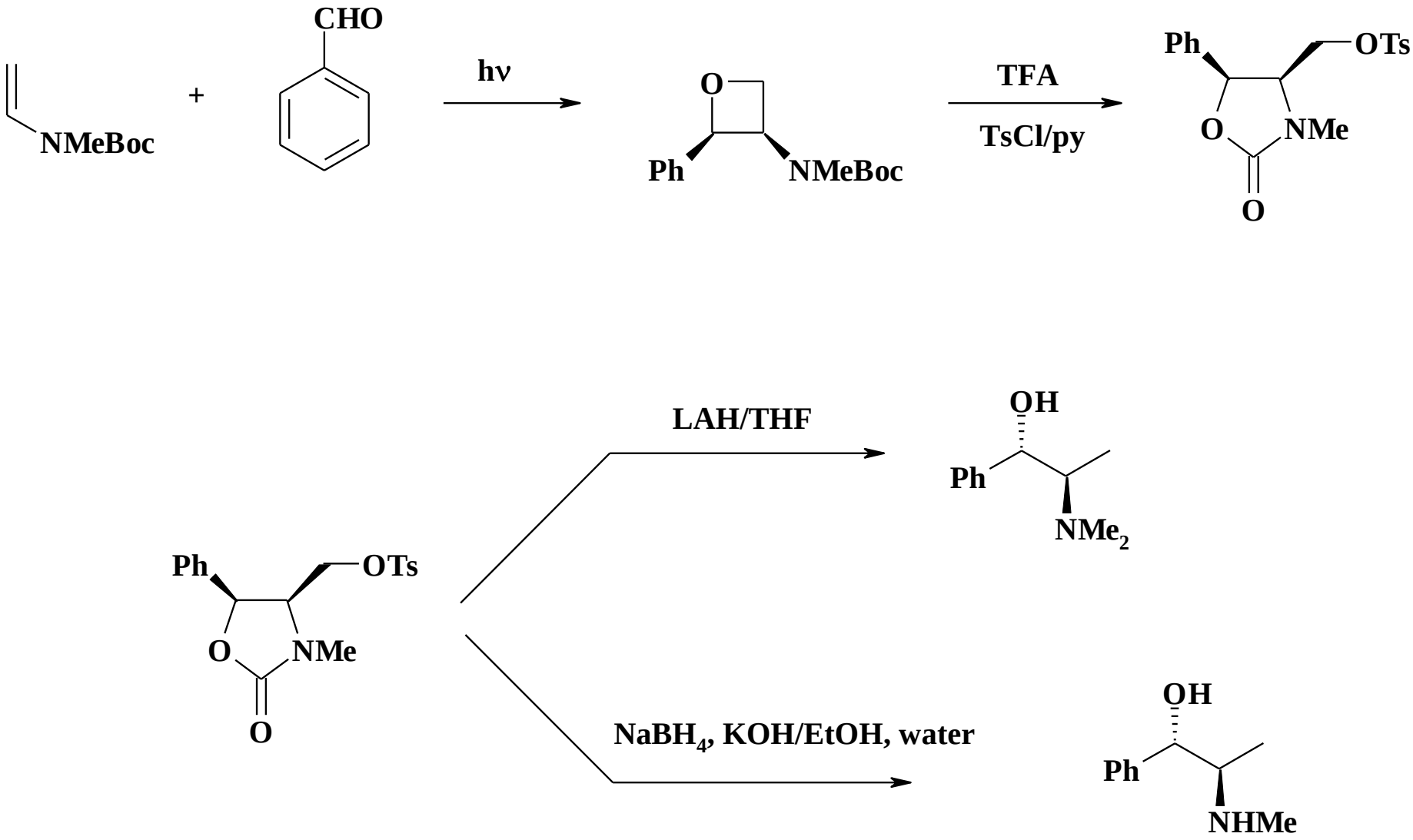




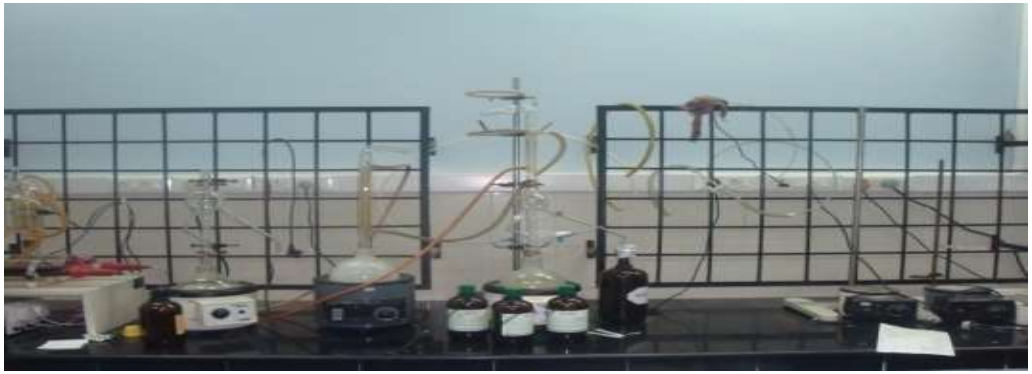
Ring opening of cis-aminooxetanes obtained by PB photocycloaddition



Tet.Lett, 1997, 38, 3707-10


NMeBoc
+
CHO
hν
O
Ph
NMeBoc
TFA
TsCl/py
Ph
OTs
O
NMe
O
LAH/THF
OH
Ph
NMe2
Ph
OTs
O
NMe
O
NaBH4, KOH/EtOH, water
OH
Ph
NHMe

Thank You



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