NANYANG TECHNOLOGICAL UNIVERSITY

17 April, 2008

Catalytic Reactions in Organic Synthesis

– Rhodium Complexes and Redox Catalysts –

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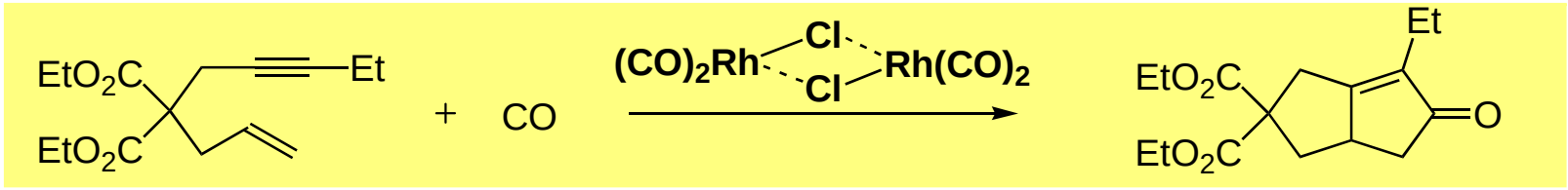
Rhodium Complexes

- Electron Deficient-Lower Valent Rh Complexes
- Bimetallic Rh Complexes

Redox Catalysts

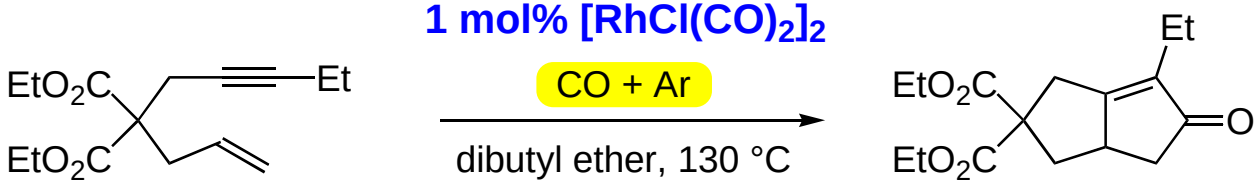
- Metal Catalyzed One-Electron Transfer
- Organic Electron Transfer Reagents

Brønsted & Lewis Acids and Bases
Metal Catalysts for Coupling, Addition, etc.
Organo-Catalysts
Biocatalysts

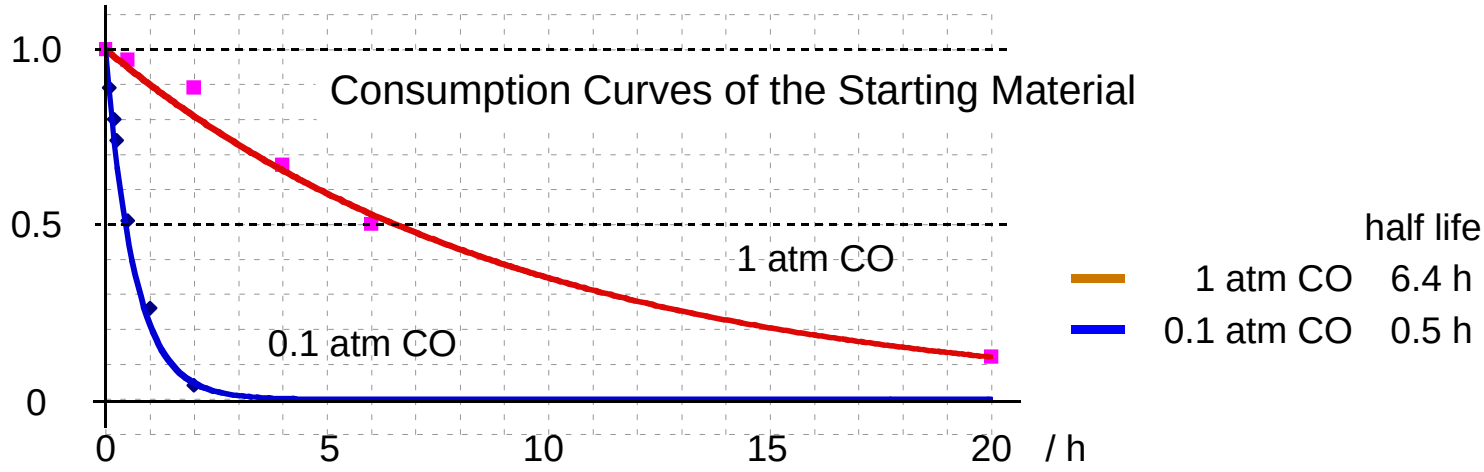


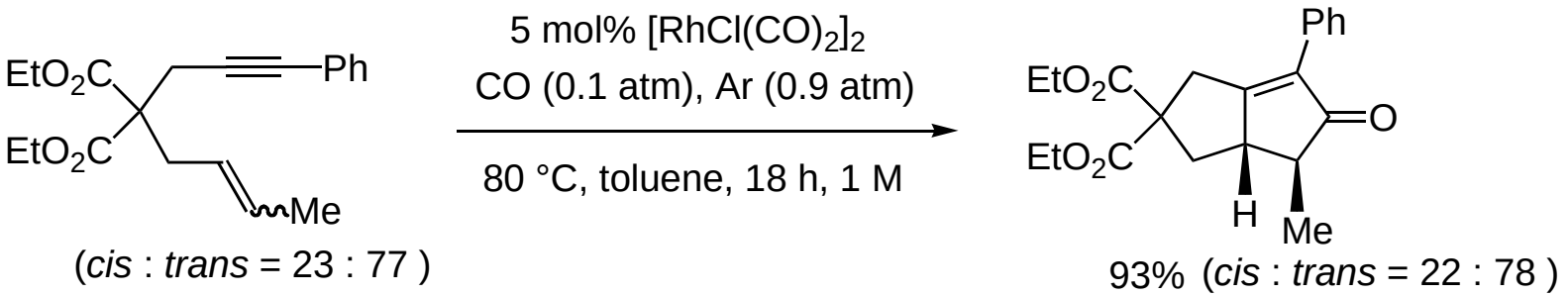
Catalytic Intramolecular Pauson–Khand Reactions (~1997)

			Catalyst	Solvent	CO / atm	Temp. / °C
Co	Jeong and Chung	2 mol%	Co(cod)(indenyl)	DME	15	100
	Jeong and Chung	3 mol%	$Co_2(CO)_8$ / $P(OPh)_3$	DME	3	120
	Chung	5 mol%	$Co(acac)_2$ / $NaBH_4$	CH_2Cl_2	30-40	100
	Jeong	2.5-5 mol%	$Co_2(CO)_8$	$scCO_2$	110-120	90
	Chung	1 mol%	$Co_4(CO)_{12}$	CH_2Cl_2	10	150
	Livinghouse	5 mol%	$Co_2(CO)_8$ / $h\nu$	DME	1	50-55
Ti	Buchwald	5-20 mol%	$CpTi(CO)_2$	Toluene	1	90
	Chung	5-20 mol%	(chiral Cp)$Ti(CO)_2$	Toluene	1	90
Ru	Murai	2 mol%	$Ru_3(CO)_{12}$	dioxane	10	160
	Mitsudo	2 mol%	$Ru_3(CO)_{12}$	DMAc	15	140



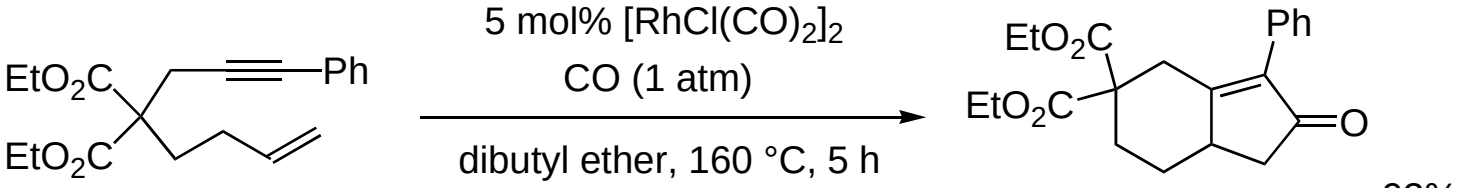
pressure / atm CO	Ar	time / h	yield / %	(recovery / %)
10	0	18	trace	(ca. 100)
3	0	36	70	(24)
1	0	18	91	–
0.2	0.8	5	90	–
0.1	0.9	2	92	–
0.05	0.95	3	85	–



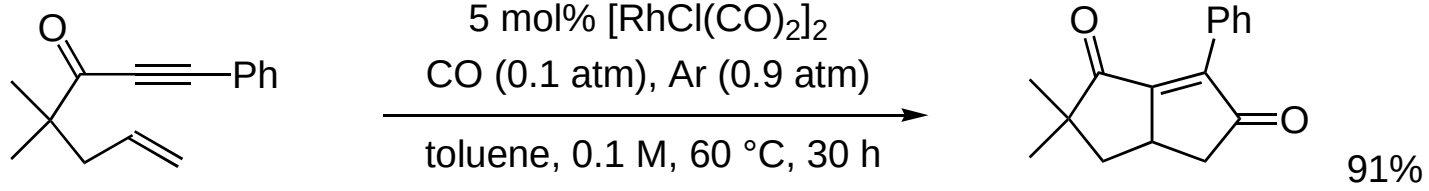


(*cis* : *trans* = 23 : 77)

93% (*cis* : *trans* = 22 : 78)



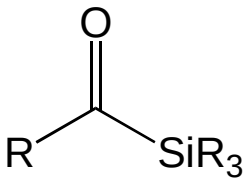
93%

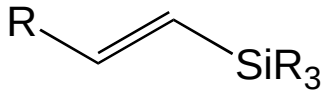


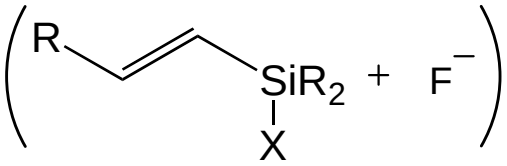
91%

J. Organomet. Chem. **2001**, *624*, 73.

Activation of Acyl and Vinyl Silanes with $[RhCl(CO)_2]_2$

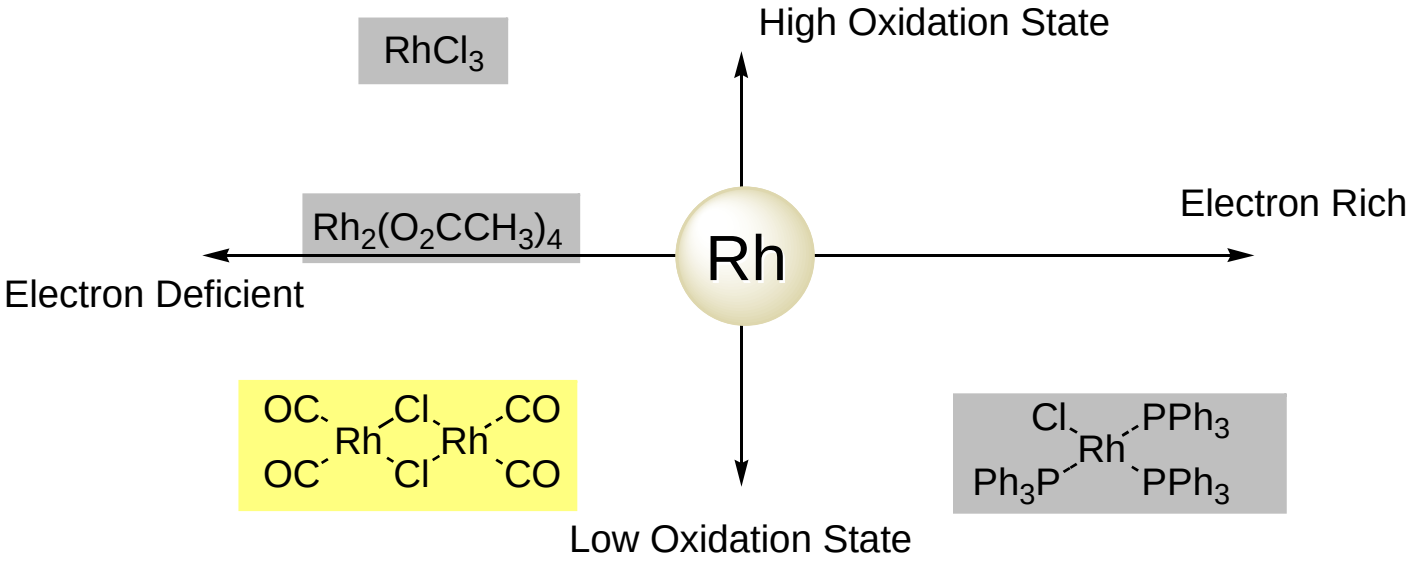


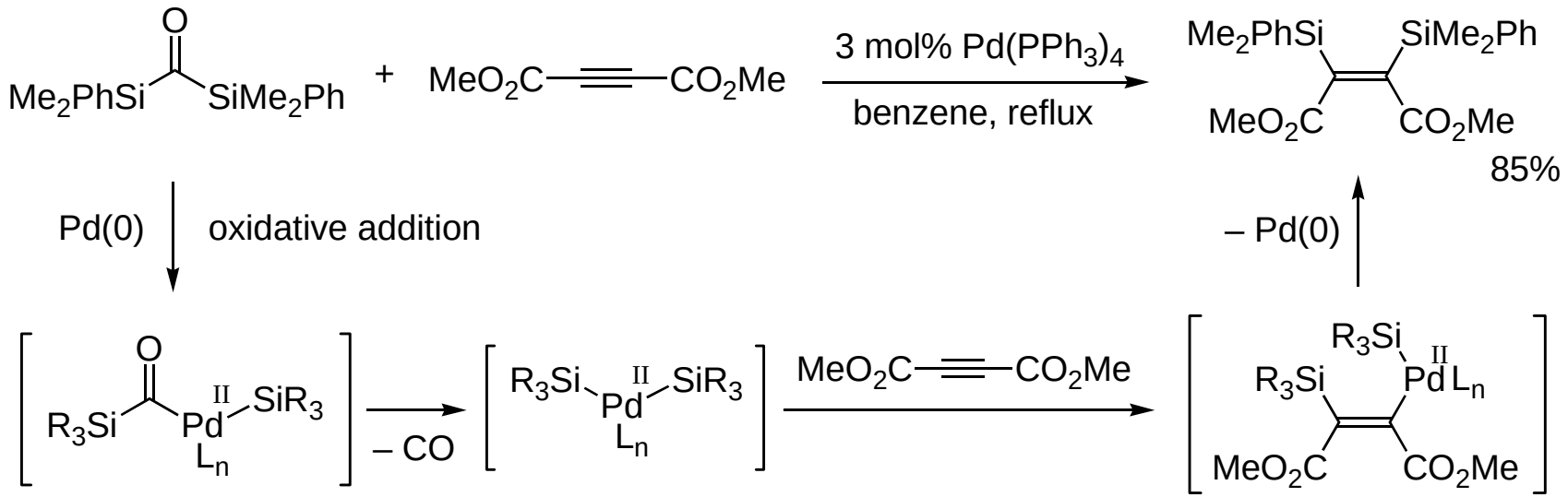


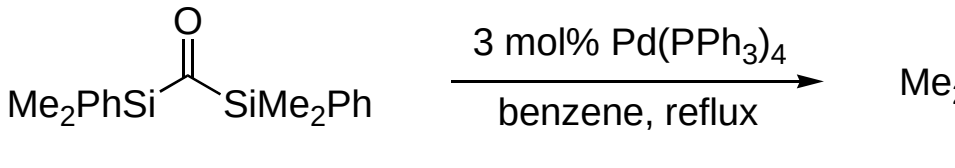


stable & isolable organometallic compounds

X = OR, Halogen: unstable

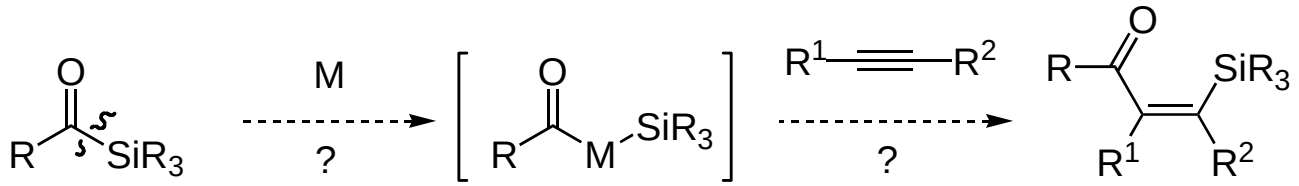


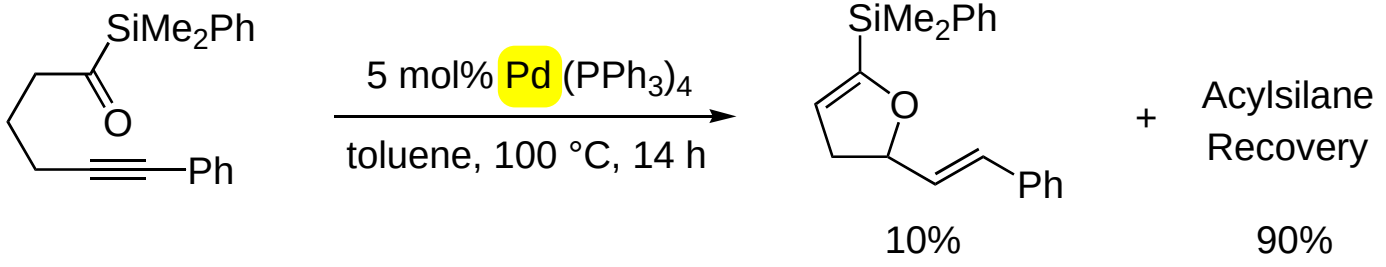


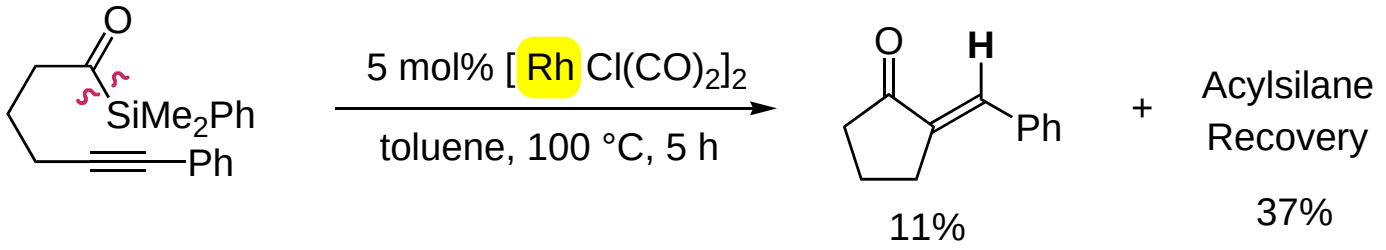


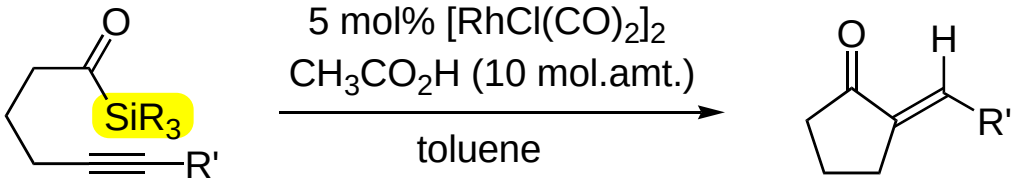
Chem. Lett., **1996**, 841.

Acylsilanes (Air–Stable Acyl Main Group Metal Compounds) (2001 –)



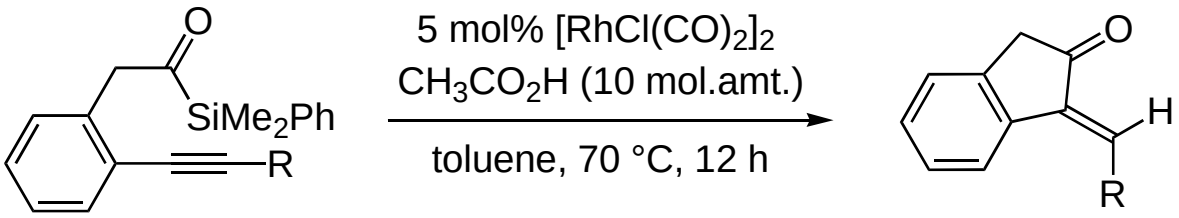






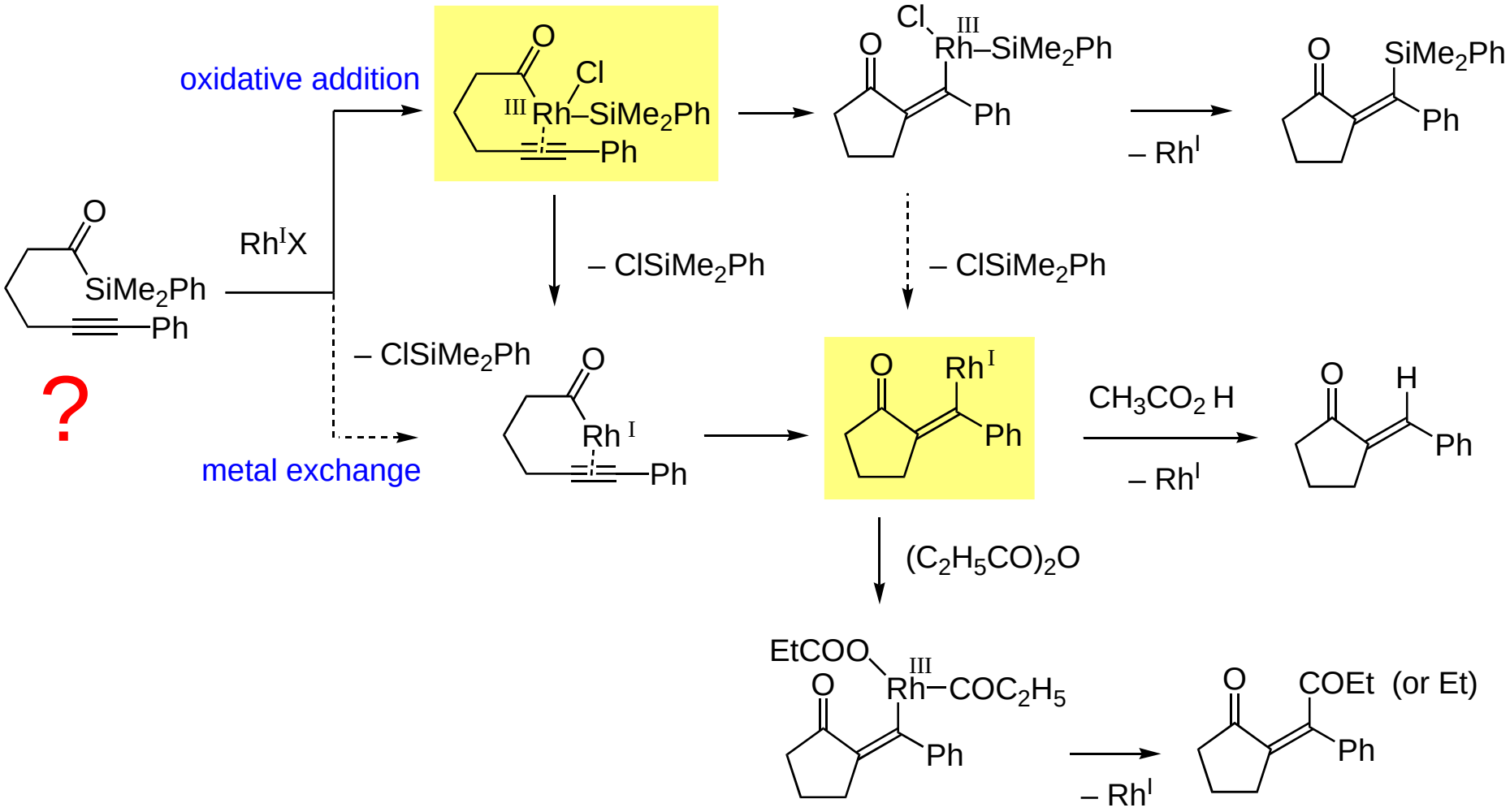
R'	SiR_3	temp.	time	yield
Ph	$SiMe_2Ph$	70 °C	12 h	82%
		100 °C	5 h	80%
$(CH_2)_2Ph$	$SiMe_2Ph$	70 °C	12 h	77%
Ph	$SiMe_3$	70 °C	24 h	77%
	$SiMe_3$	100 °C	3 h	81%

Chem. Lett. **2001**, 1210.

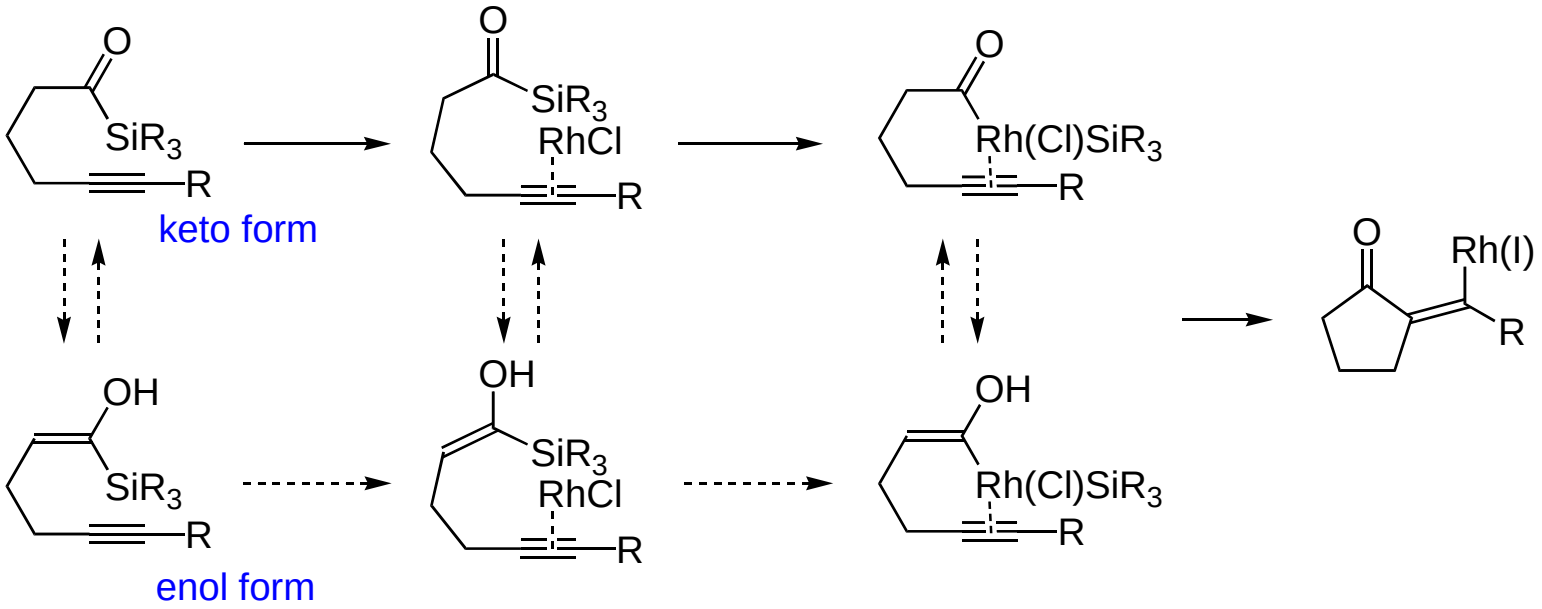


R = Ph: 52%
R = C_3H_7: 44%

1/2 $[RhCl(CO)_2]_2$ + CH_3CO_2H → (toluene-d_8, 80 °C, 5 h) No Reaction


oxidative addition
RhIX
SiMe2Ph
Ph
?
– ClSiMe2Ph
– ClSiMe2Ph
– ClSiMe2Ph
metal exchange
Cl
III
Rh–SiMe2Ph
Ph
O
– RhI
CH3CO2H
– RhI
(C2H5CO)2O
EtCOO
Rh–COC2H5
COEt (or Et)
H

Acylsilane or Vinylsilane ?



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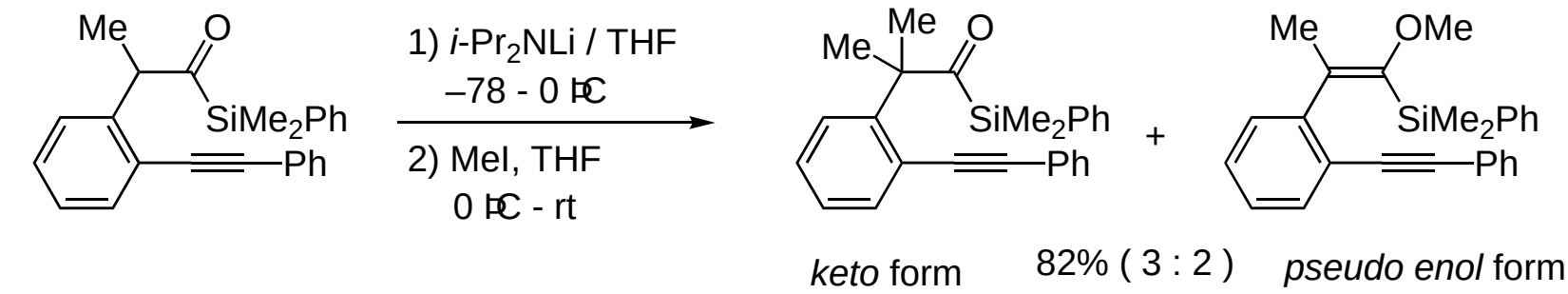
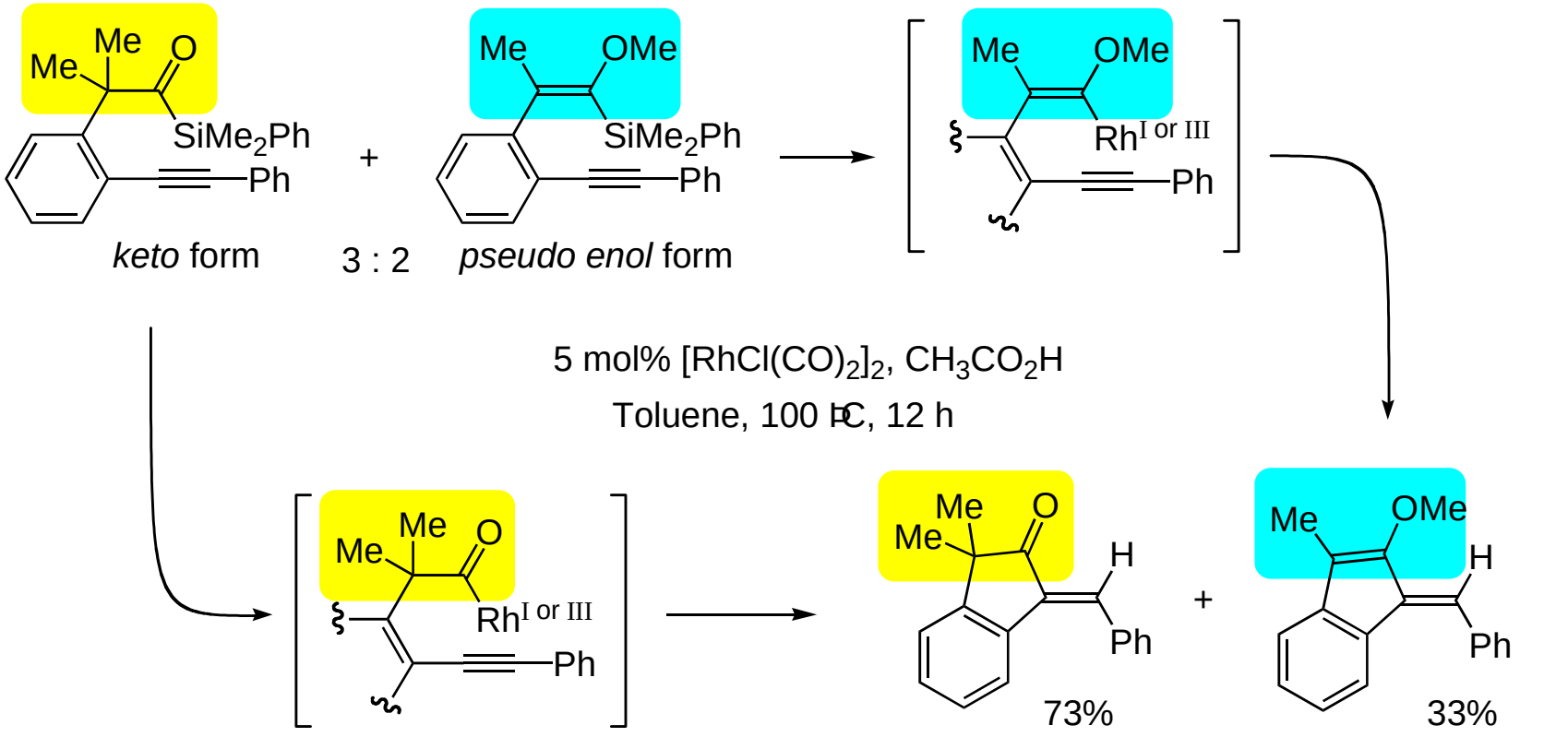
	pKa
R = $SiMe_3$	16.4
R = CH_3	19.3
i-C_3H_7OH	16.5

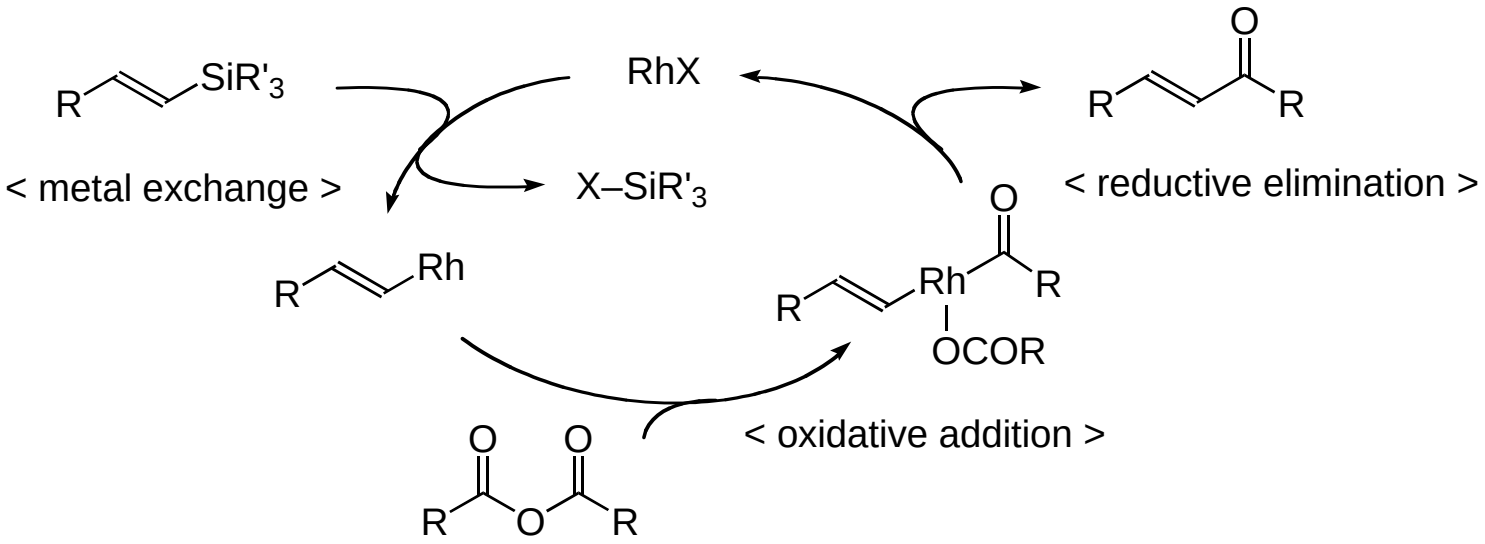
A. J. Kresge, J. B. Tobin

J. Am. Chem. Soc. **1990**, *112*, 2805.

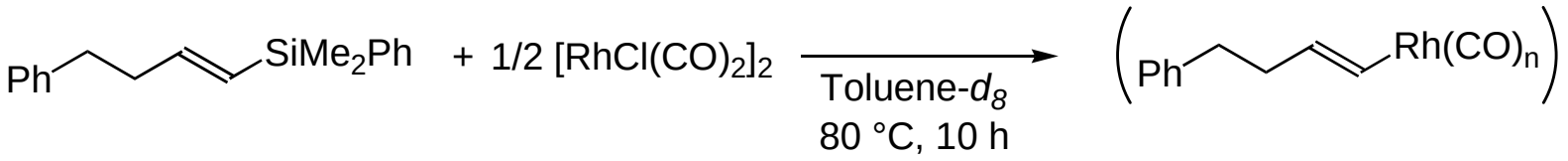

Me
O
SiMe2Ph
Ph
1) i-Pr2NLi / THF
–78 - 0 ºC
2) MeI, THF
0 ºC - rt
Me
OMe
+
keto form
82% (3 : 2)
pseudo enol form


Me
OMe
SiMe2Ph
Ph
+
keto form
3 : 2
pseudo enol form
RhI or III
5 mol% [RhCl(CO)2]2, CH3CO2H
Toluene, 100 ºC, 12 h
H
73%
33%
besed on keto form
based on pseudo enol form

Catalytic Acylation of Vinylsilanes



Stoichiometric Reaction

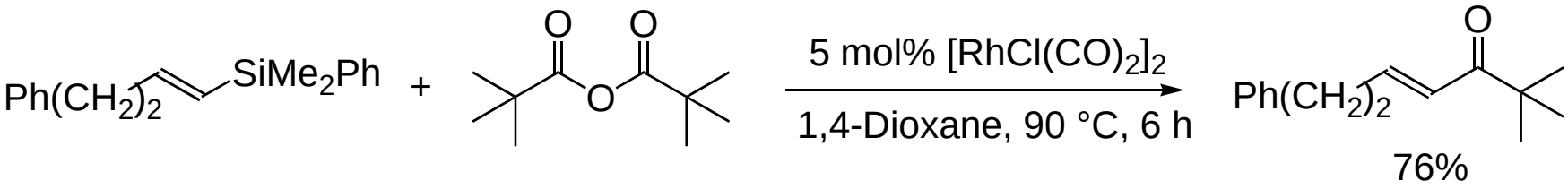


$\longrightarrow$ $Cl{-}SiMe_2Ph$ + $HO{-}SiMe_2Ph$ + $O(SiMe_2Ph)_2$

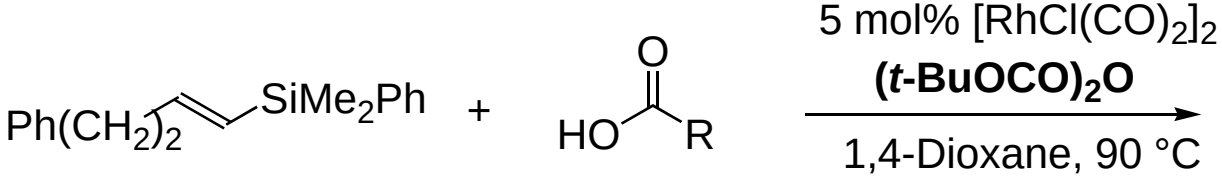
monitored by ^1H NMR (s, CH_3) 38% (δ 0.43) 9% (δ 0.23) 33% (δ 0.31)

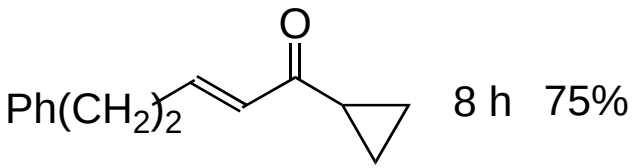
Catalytic Acylation of Vinylsilanes

with acid anhydrides

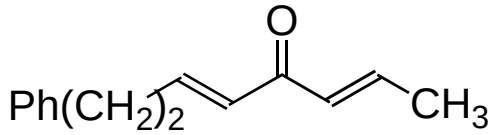


with carboxylic acids

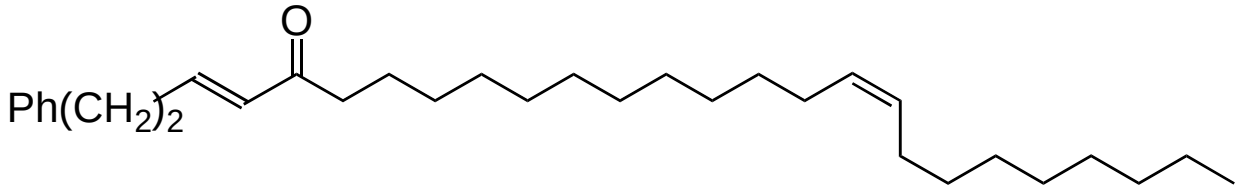




8 h 75%

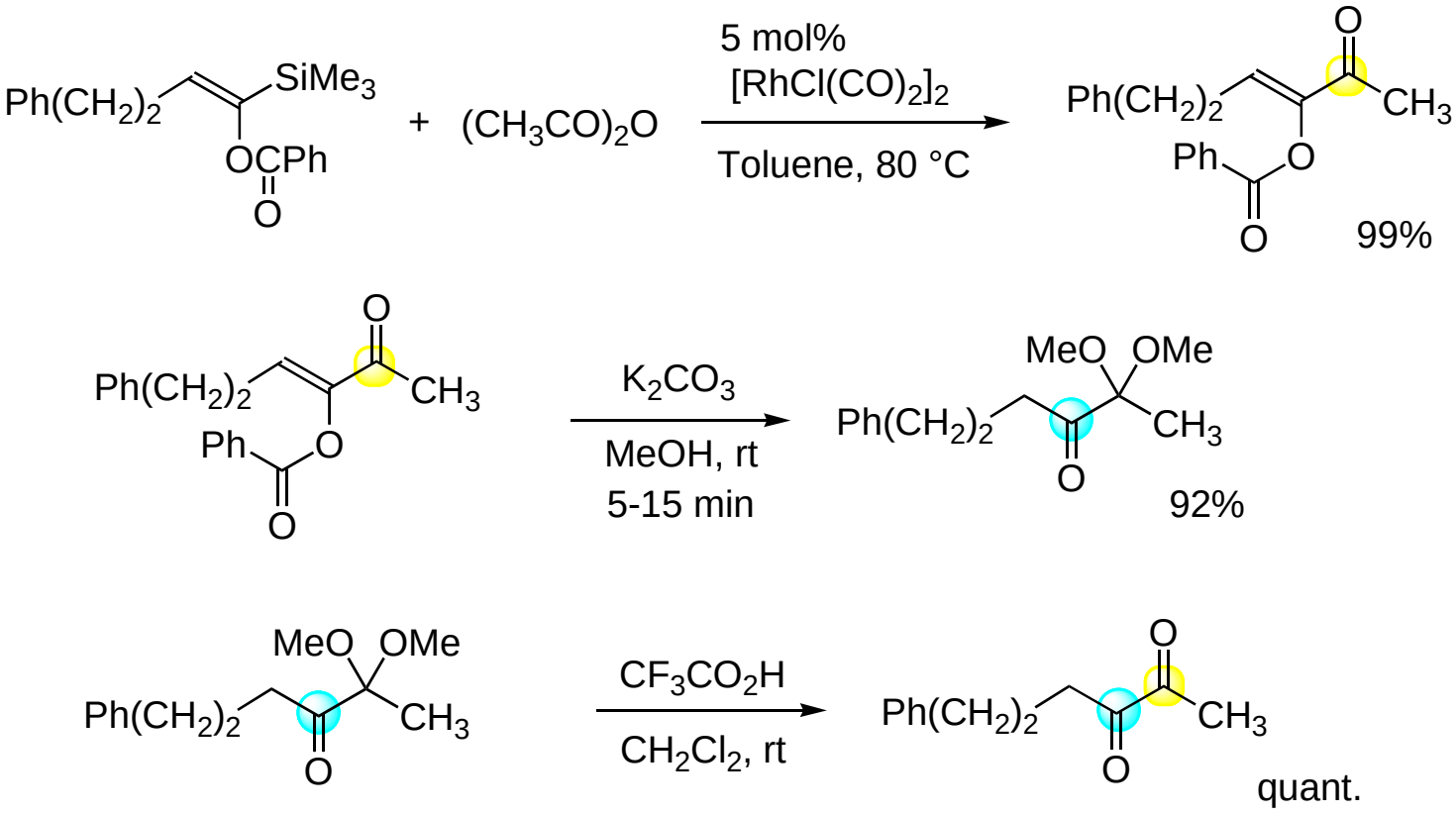


12 h 66%

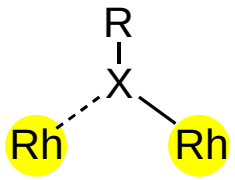


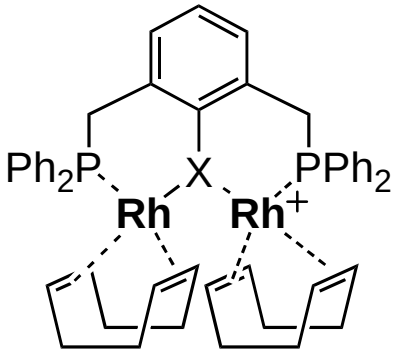
12 h 65%

Preparation of Unsymmetrical α-Diketones



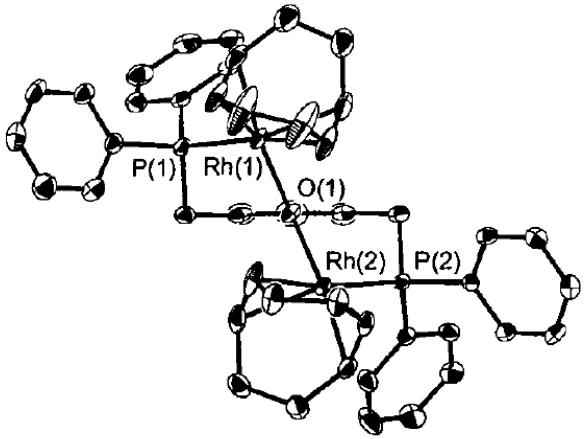
Hetroatom-Bridged Bimetallic Complexes

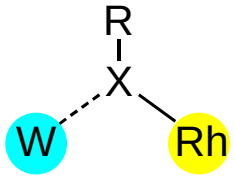


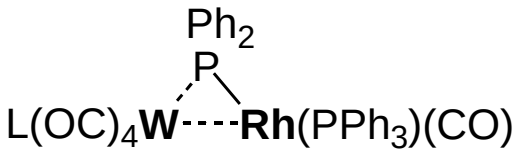


ClO_4^-

X = O, X = S

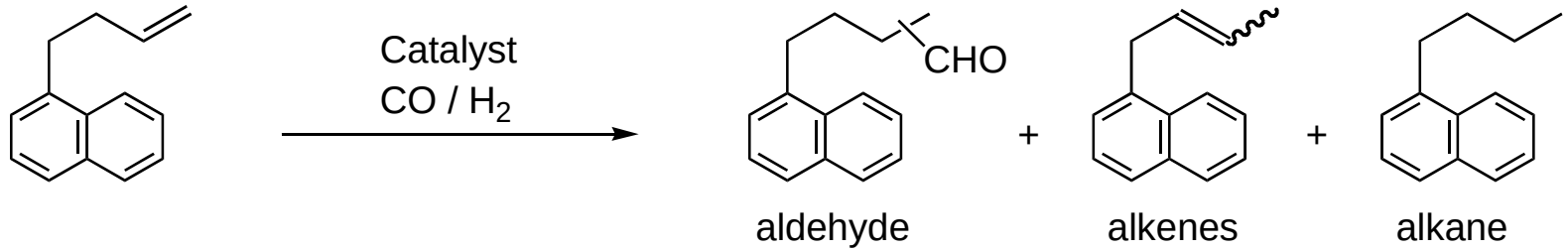


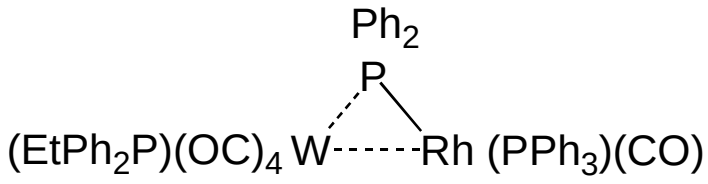


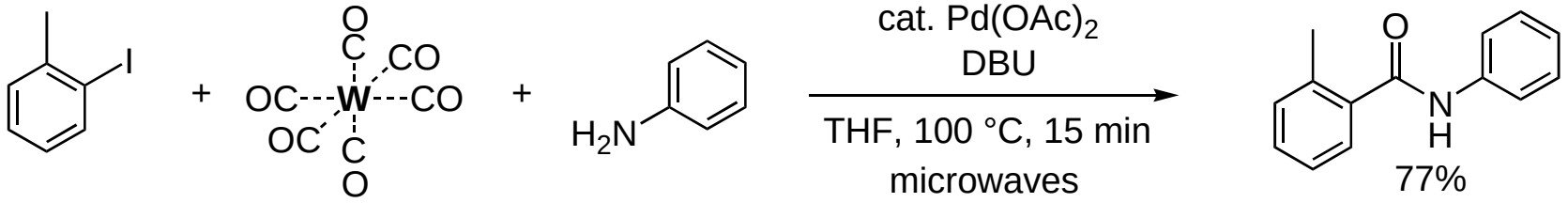


P. M. Shulman et al, *Organometallics,* **1987**, *6*, 101.

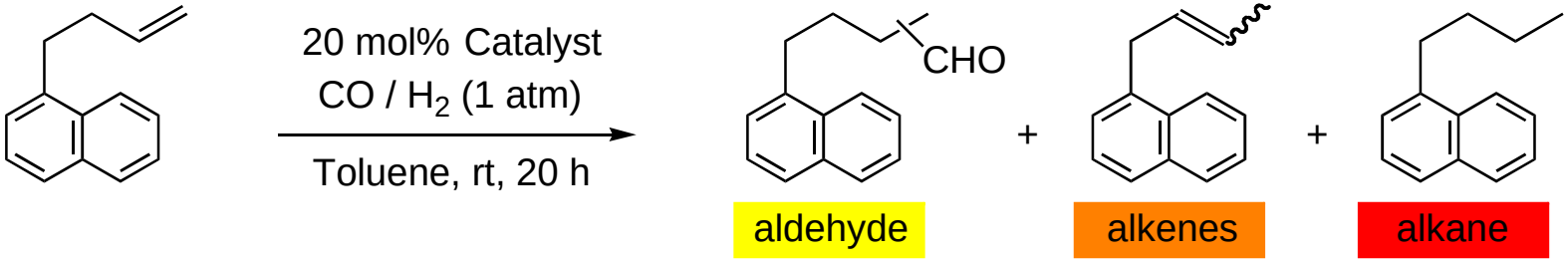
Hydroformylation of Alkenes

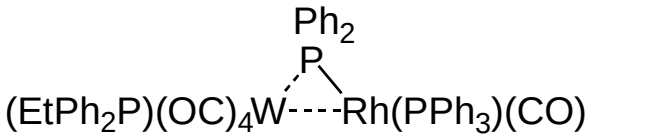




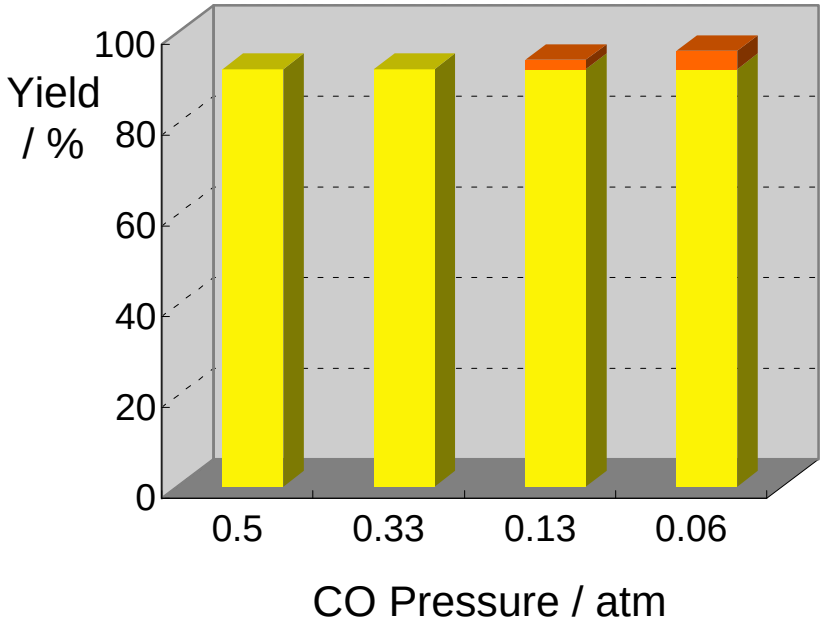


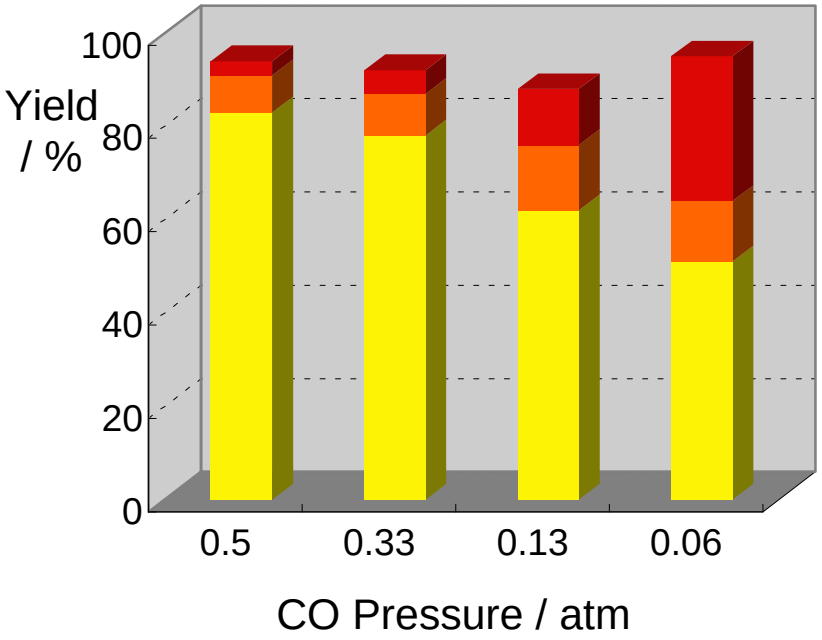
N. F. K. Kaiser, A. Hallberg, K. Larhed, *J. Comb. Chem.* **2002**, *4*, 109.

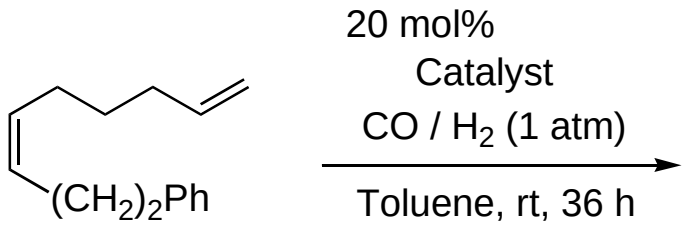

20 mol% Catalyst
CO / H2 (1 atm)
Toluene, rt, 20 h
CHO
+
+
aldehyde
alkenes
alkane

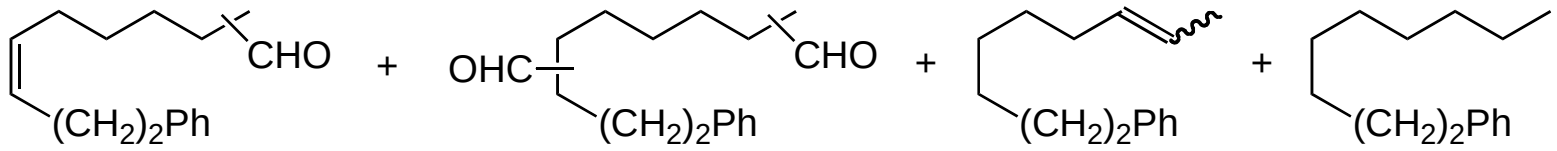

Ph2
P
(EtPh2P)(OC)4W
Rh(PPh3)(CO)

RhH(CO)(PPh$_3$)$_3$

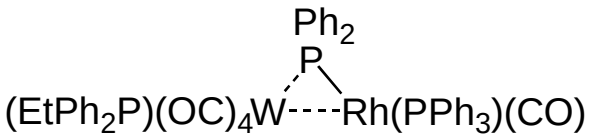

Yield
/ %
100
80
60
40
20
0
0.5
0.33
0.13
0.06
CO Pressure / atm


Yield
/ %
100
80
60
40
20
0
0.5
0.33
0.13
0.06
CO Pressure / atm





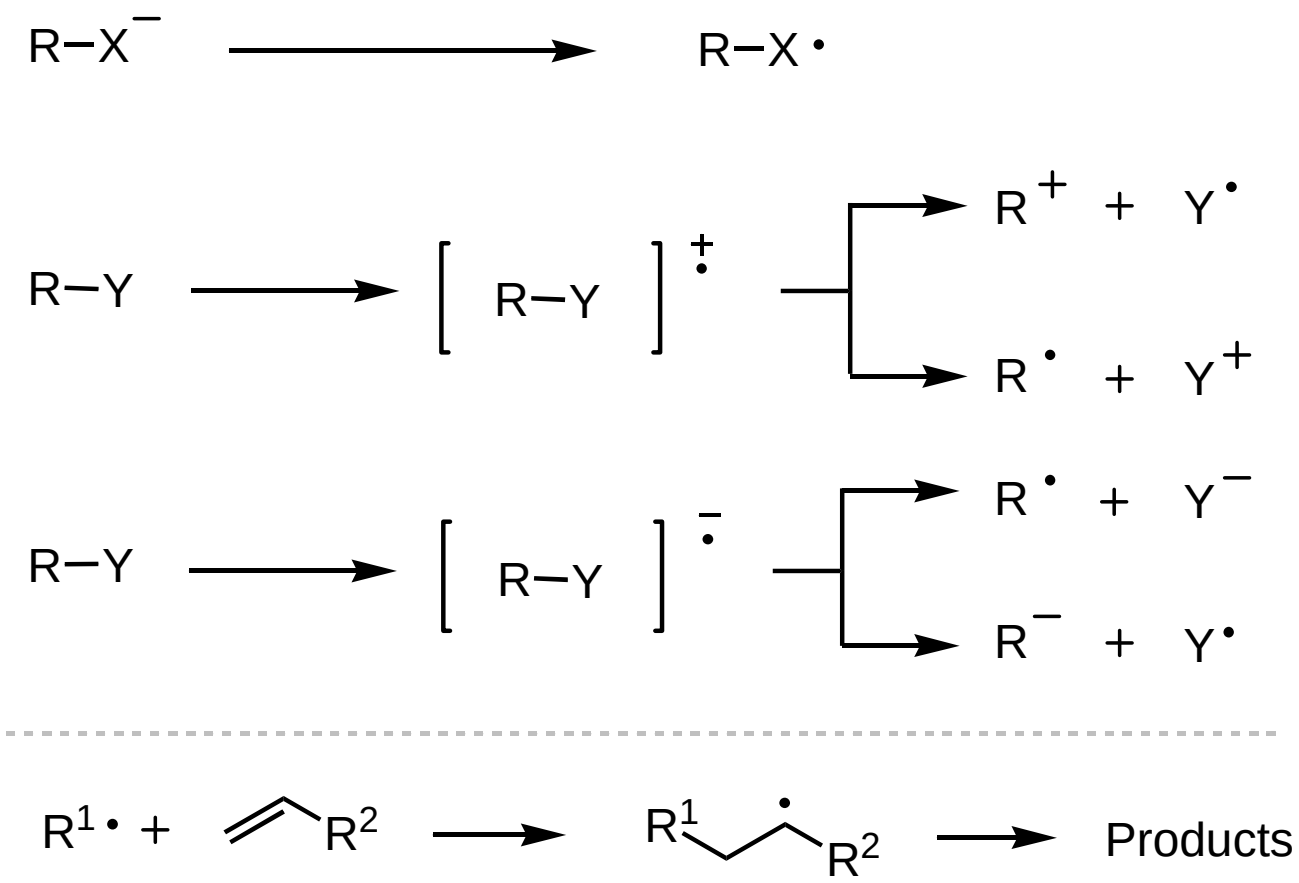
monoaldehyde dial alkenes alkane



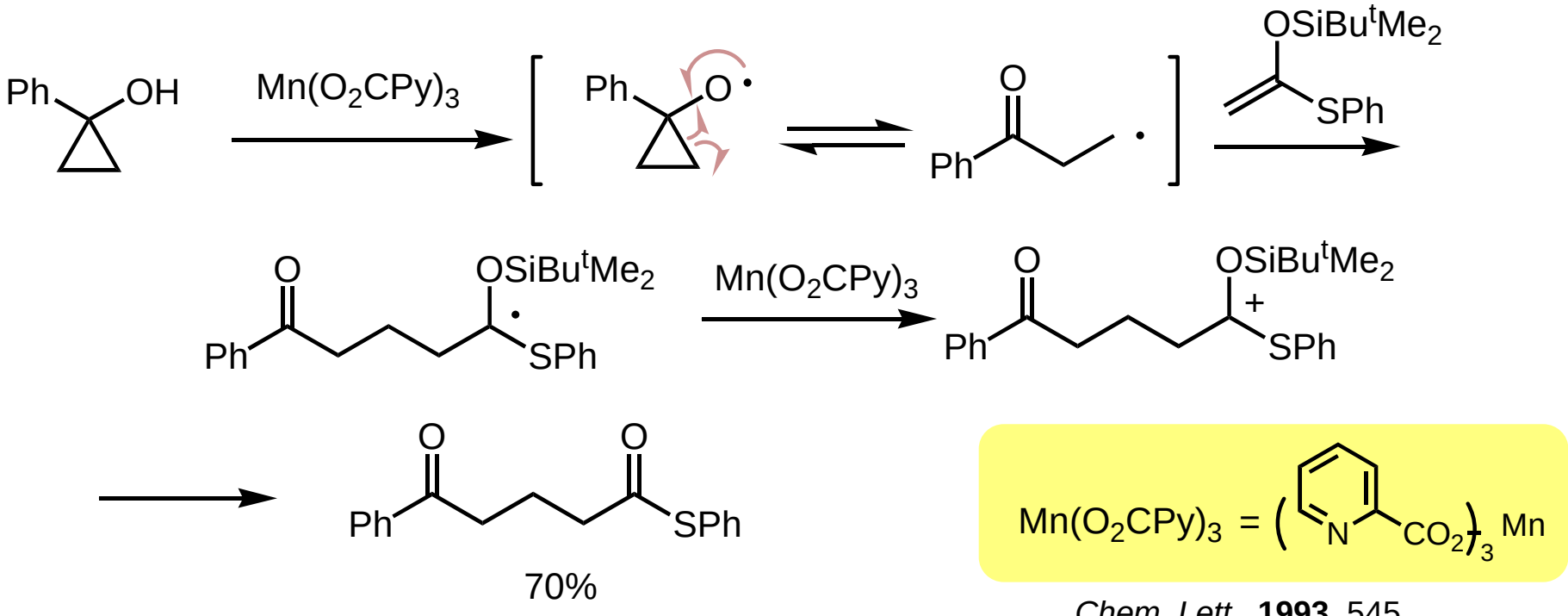
	monoaldehyde	dial	alkenes	alkane
	89% (*n* : *iso* = 2.5 : 1)	0%	4%	0%
$RhH(CO)(PPh_3)_3$	60% (*n* : *iso* = 2.5 : 1)	<12%	14%	10%

Redox-Catalysts for Generation of Radical Species

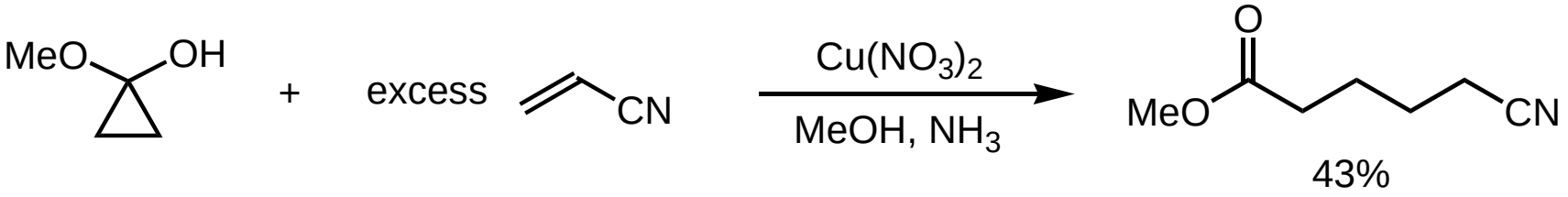
1989 - present



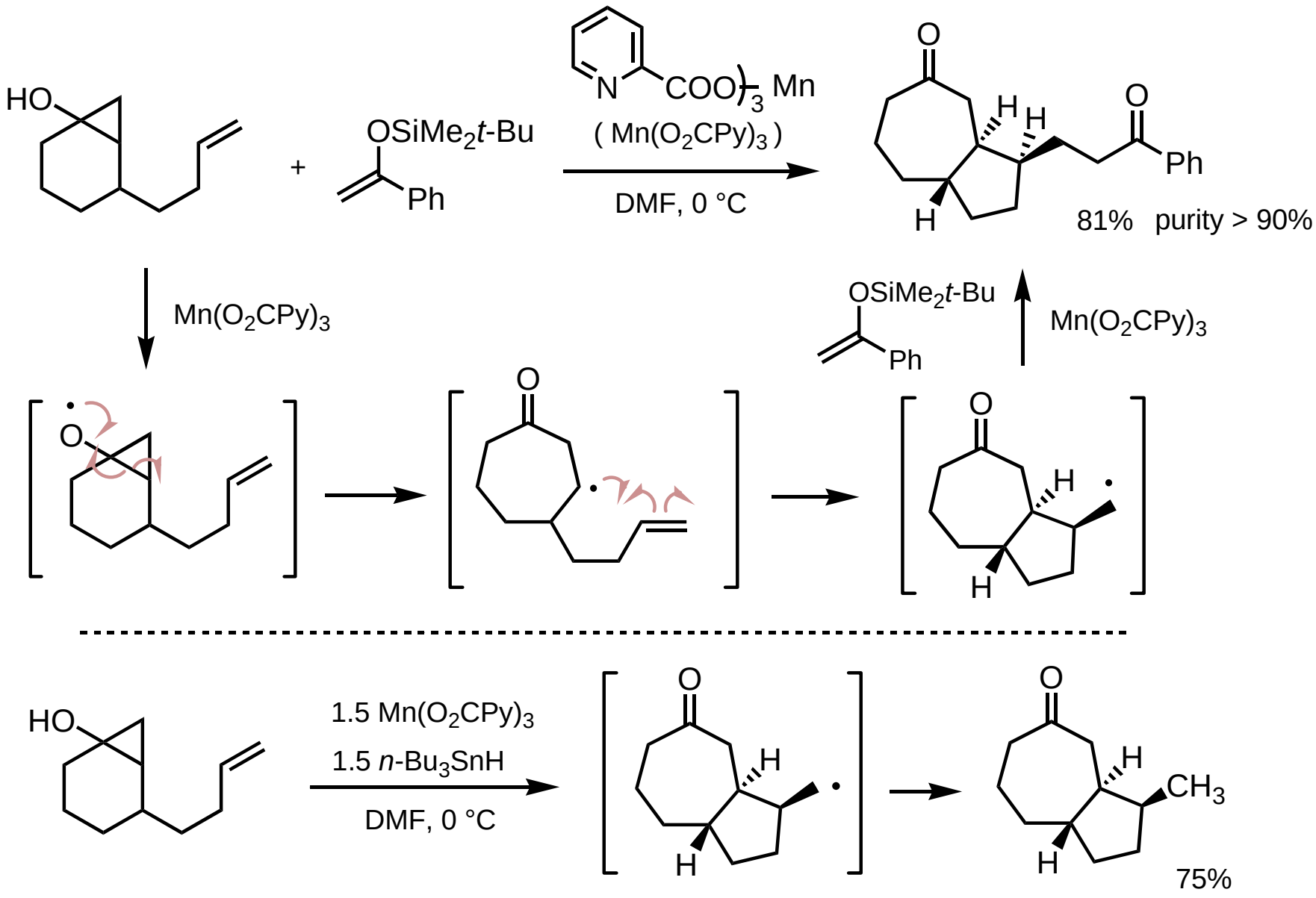
Generation of β-Keto Radicals: Intermolecular Addition to Olefins



Chem. Lett., **1993**, 545.



S. E. Schaafsma et al., *Tetrahedron Lett*., **1973**, 827.



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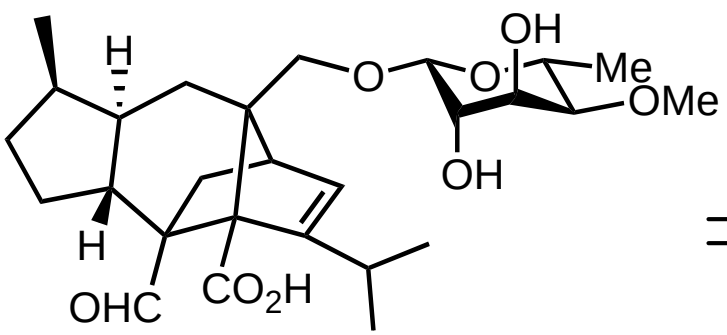
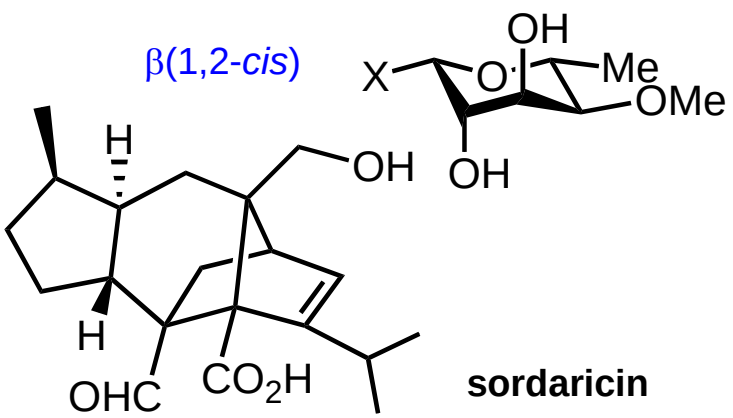
Synthesis of (–)-Sordarin

Synthesis of (–)-Sordarin: see *J. Am. Chem.Soc.*, **128**, 6931 (2006).



sordarin



sordaricin

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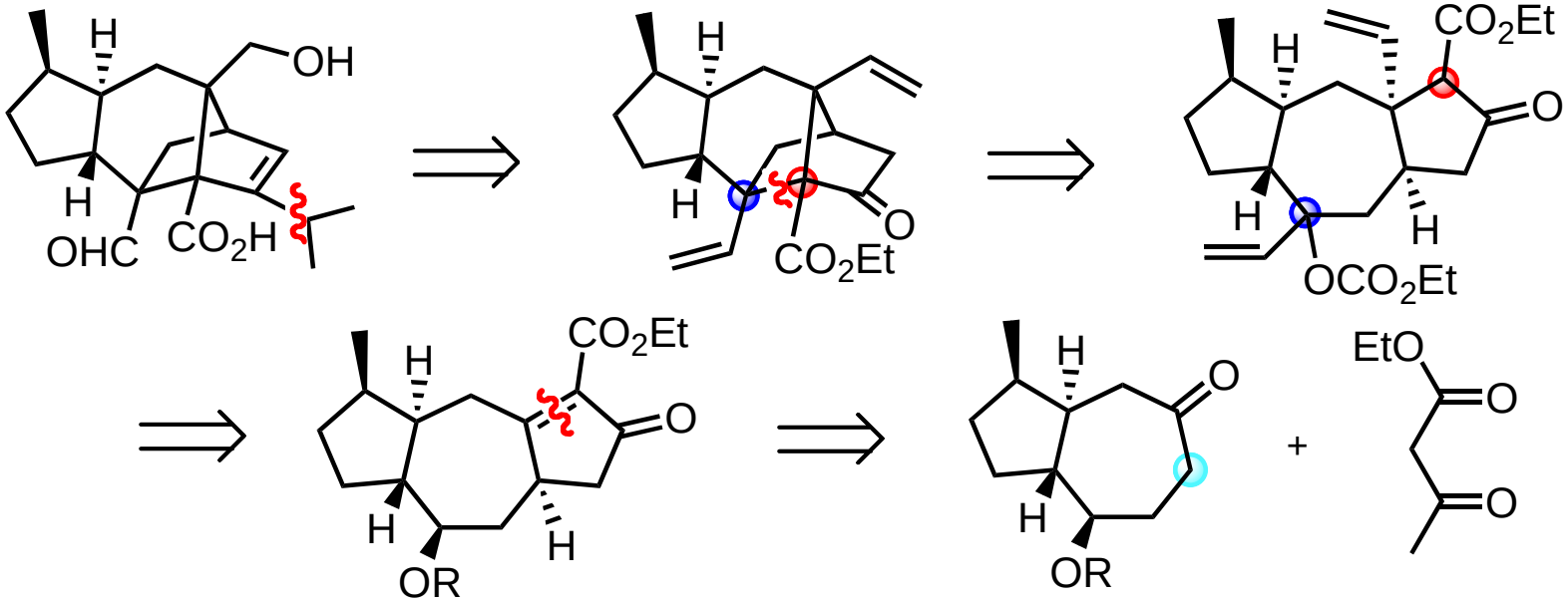
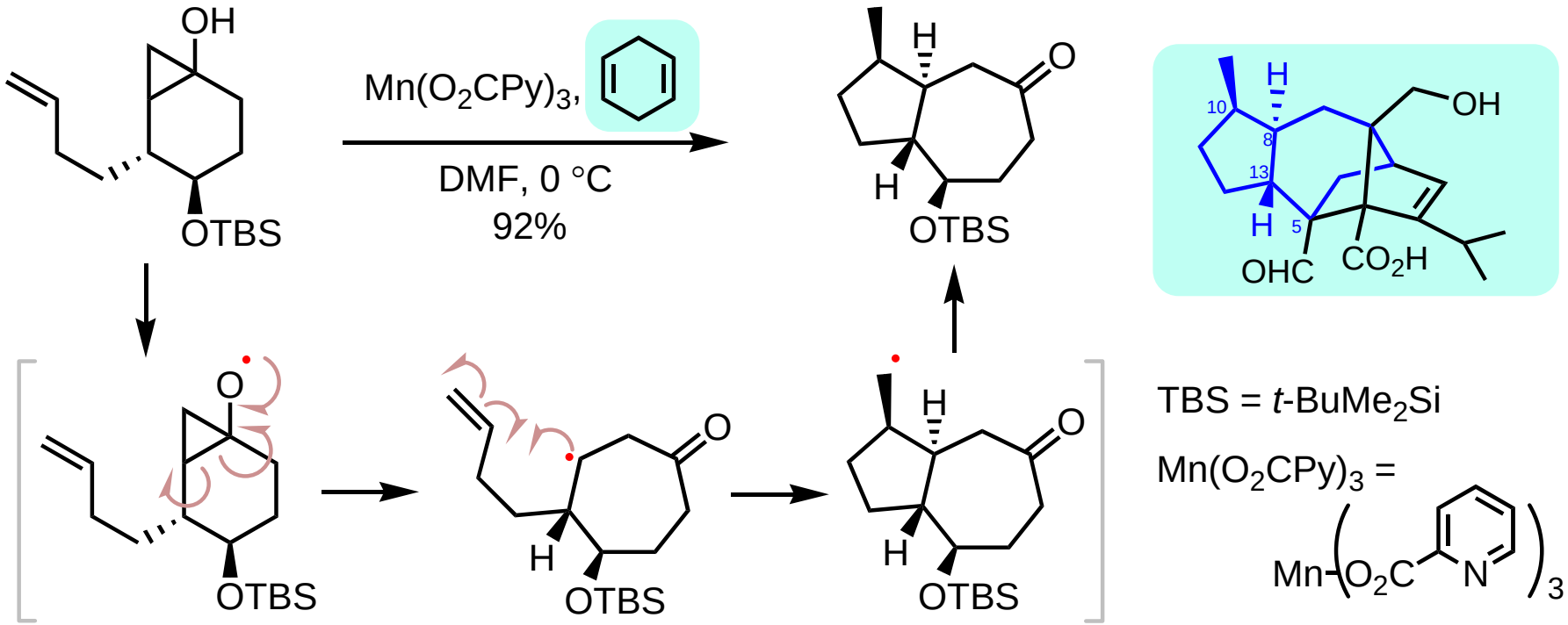
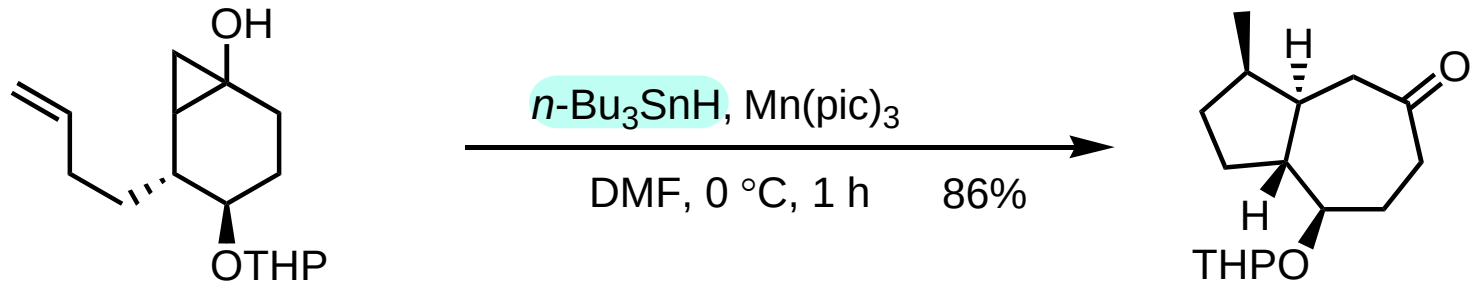


Preparation of Bicyclo[5.3.0]decan-3-one Derivative





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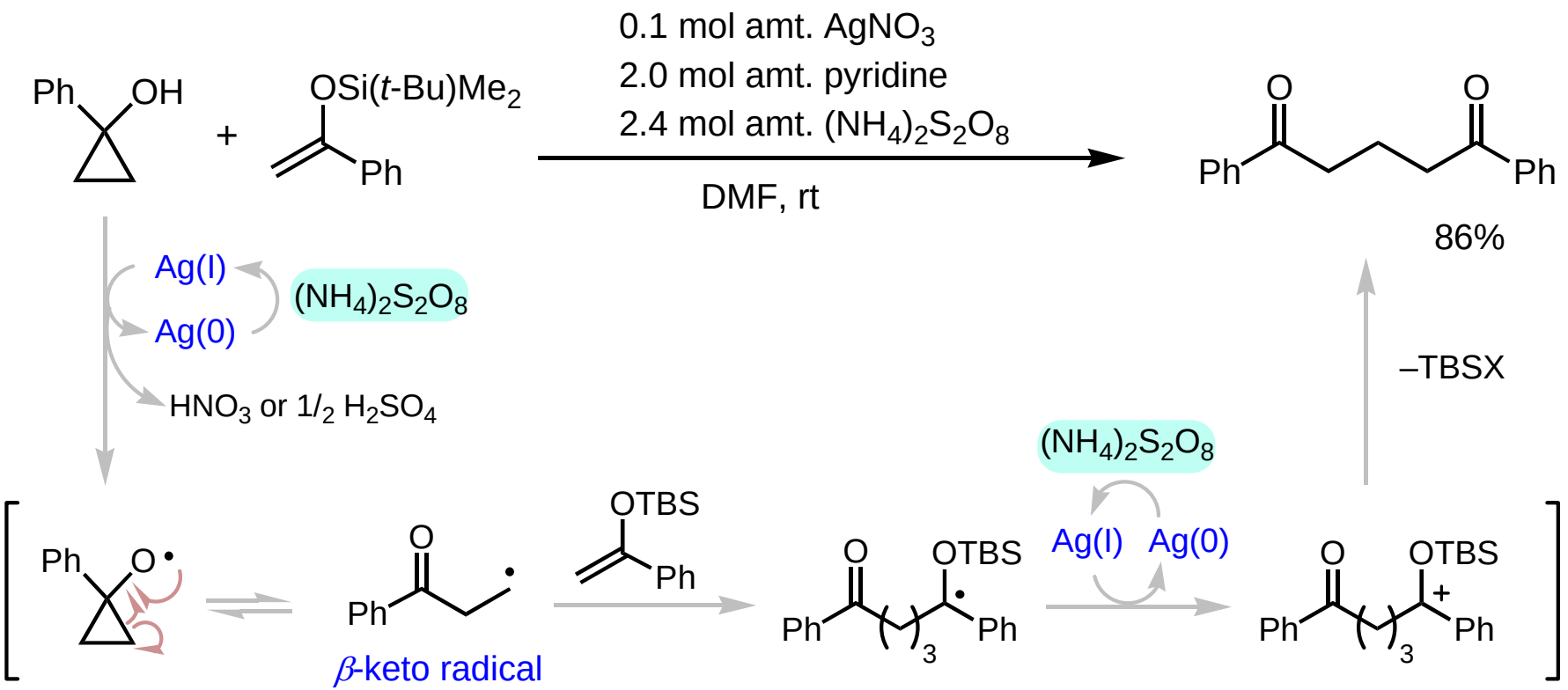
Ag(I)-Pyridine Catalytic System



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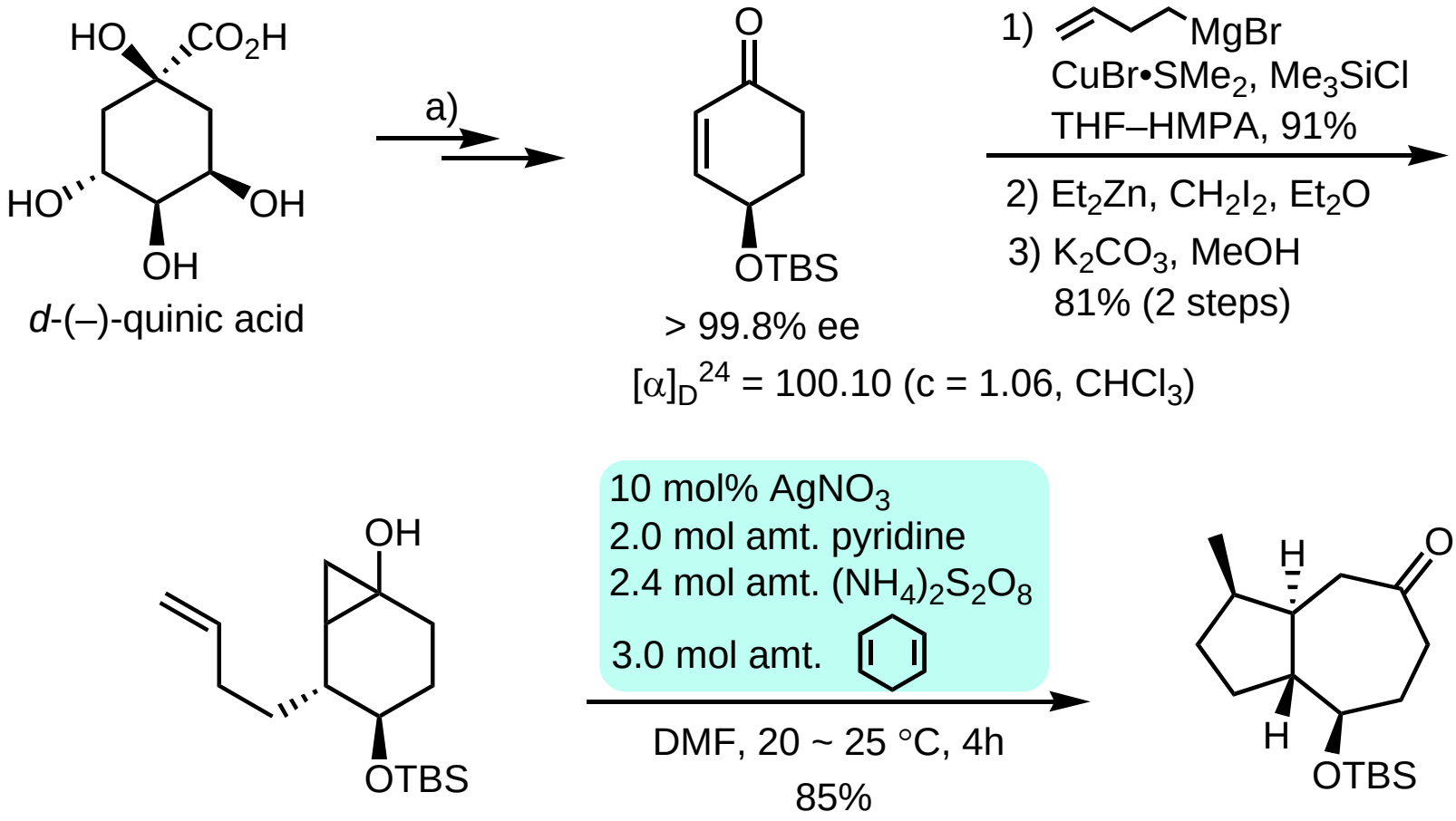

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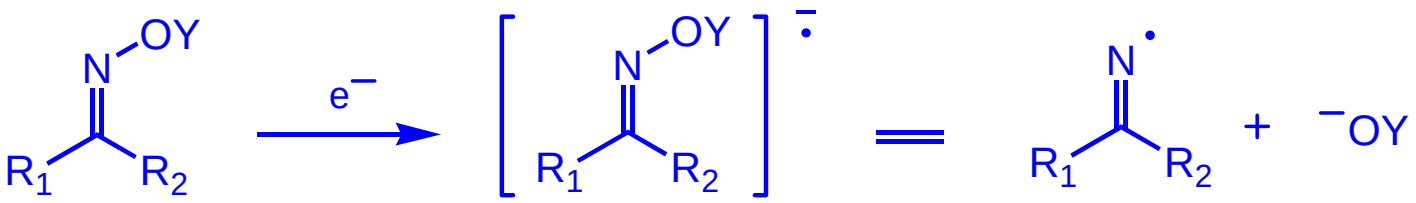
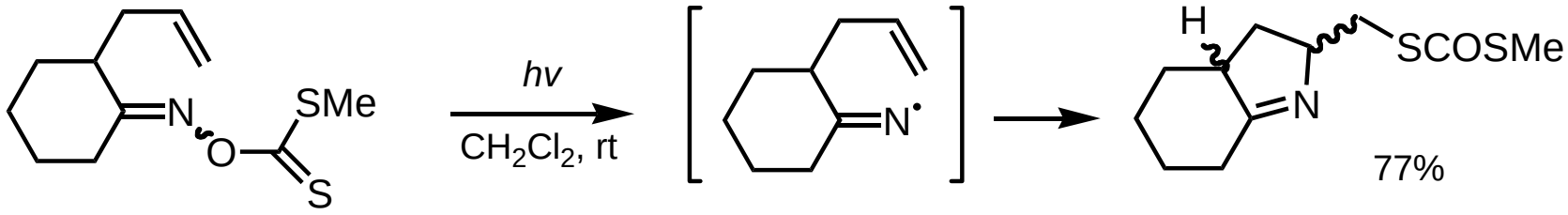


Anion Radical of Oxime Alkylidne Aminyl Radical



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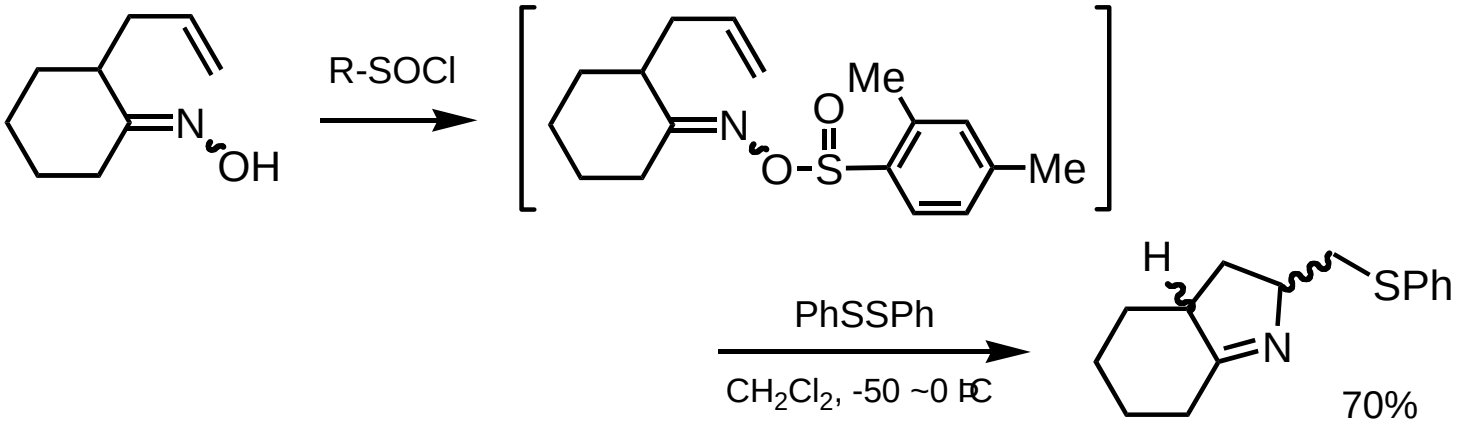

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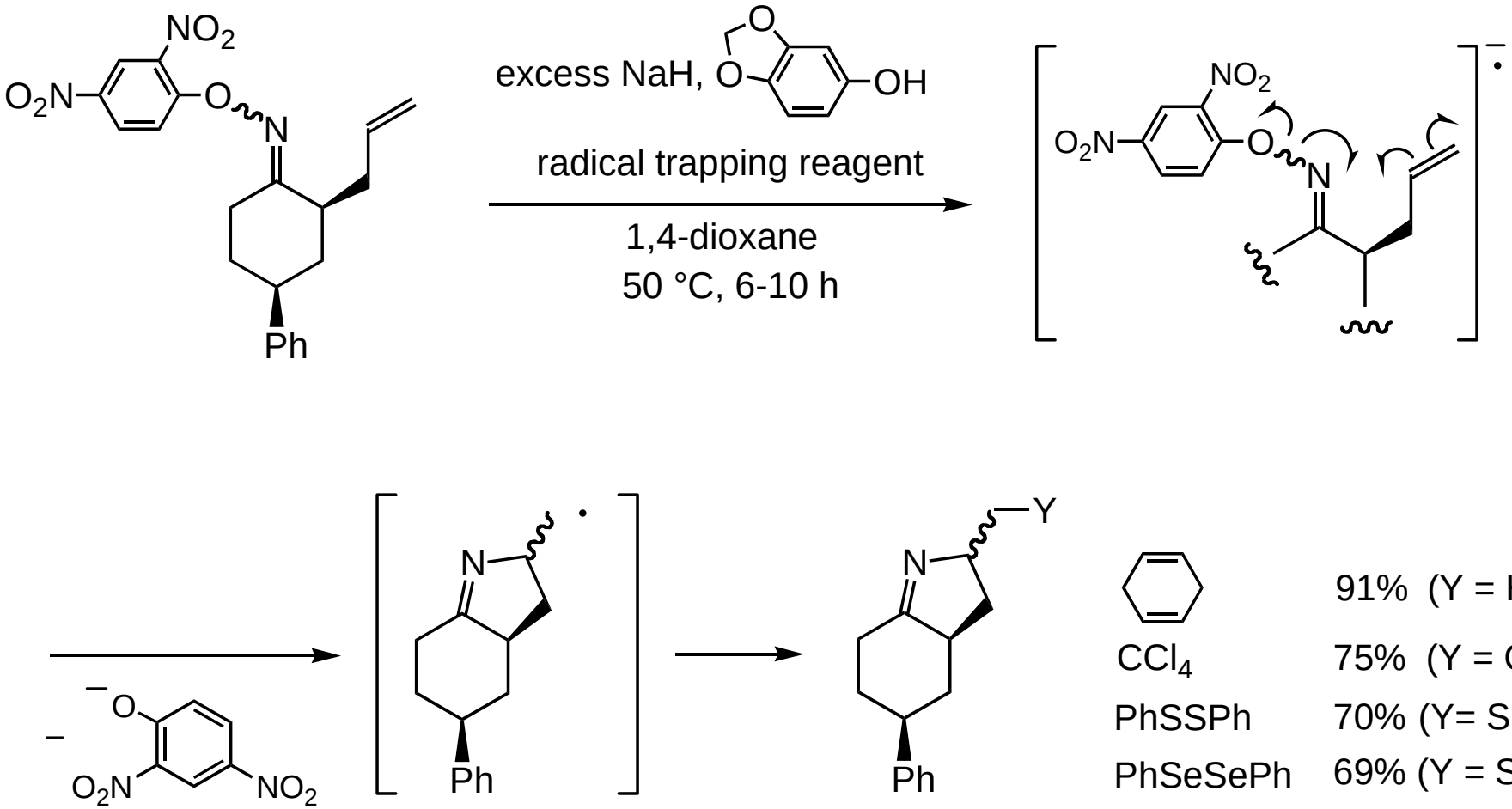

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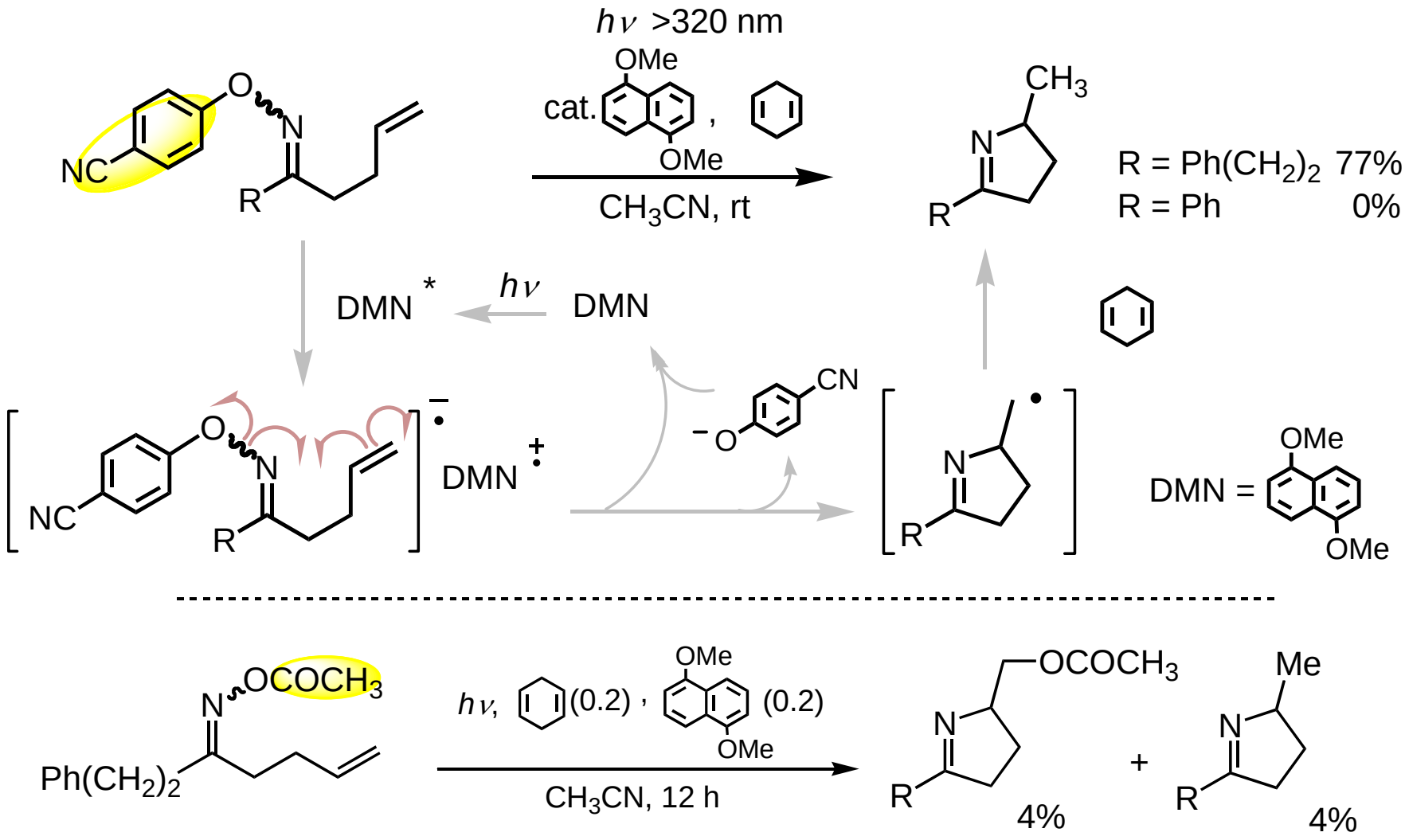
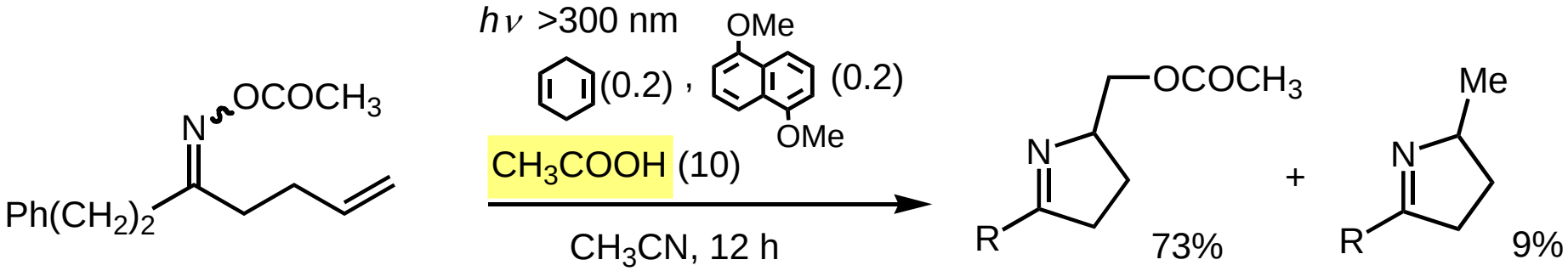
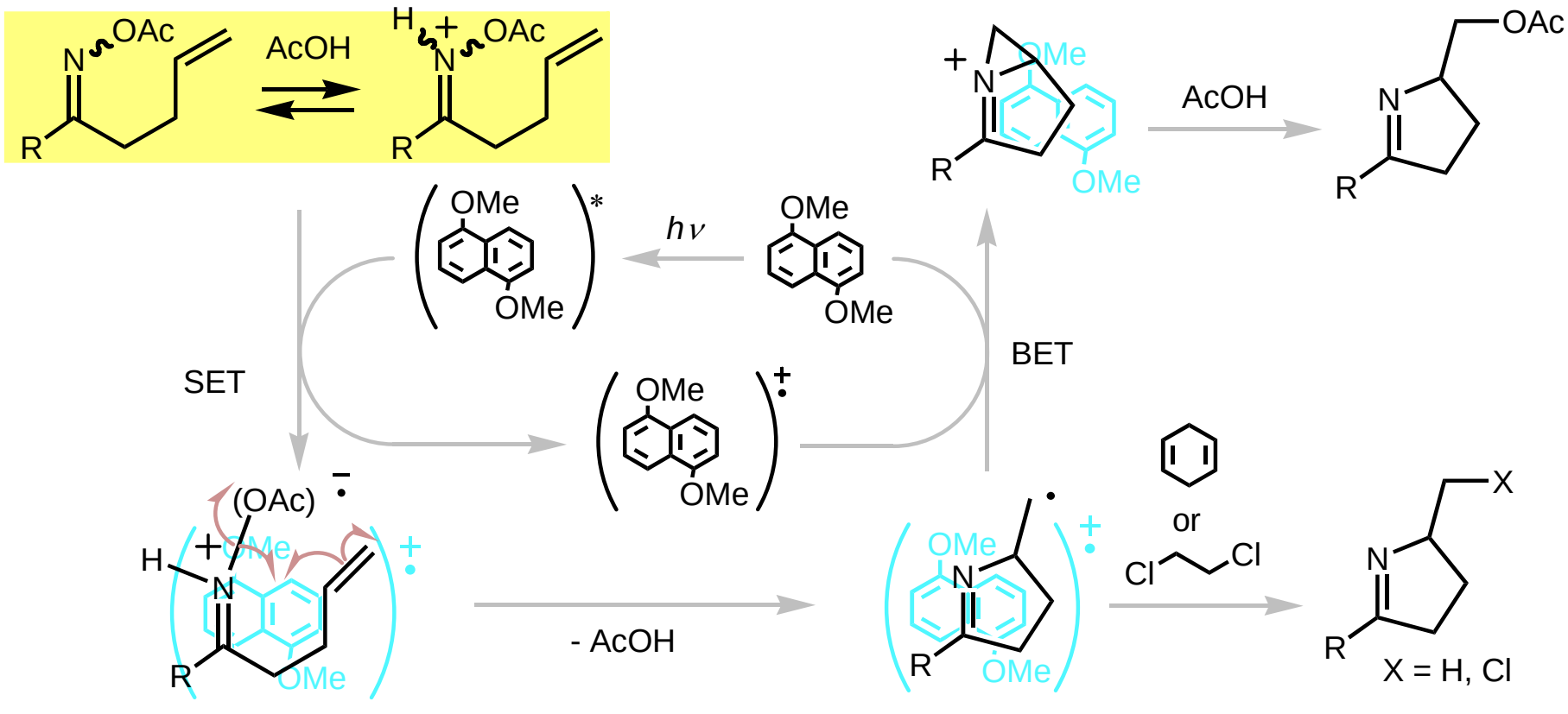
Photochemical Electron Transfer

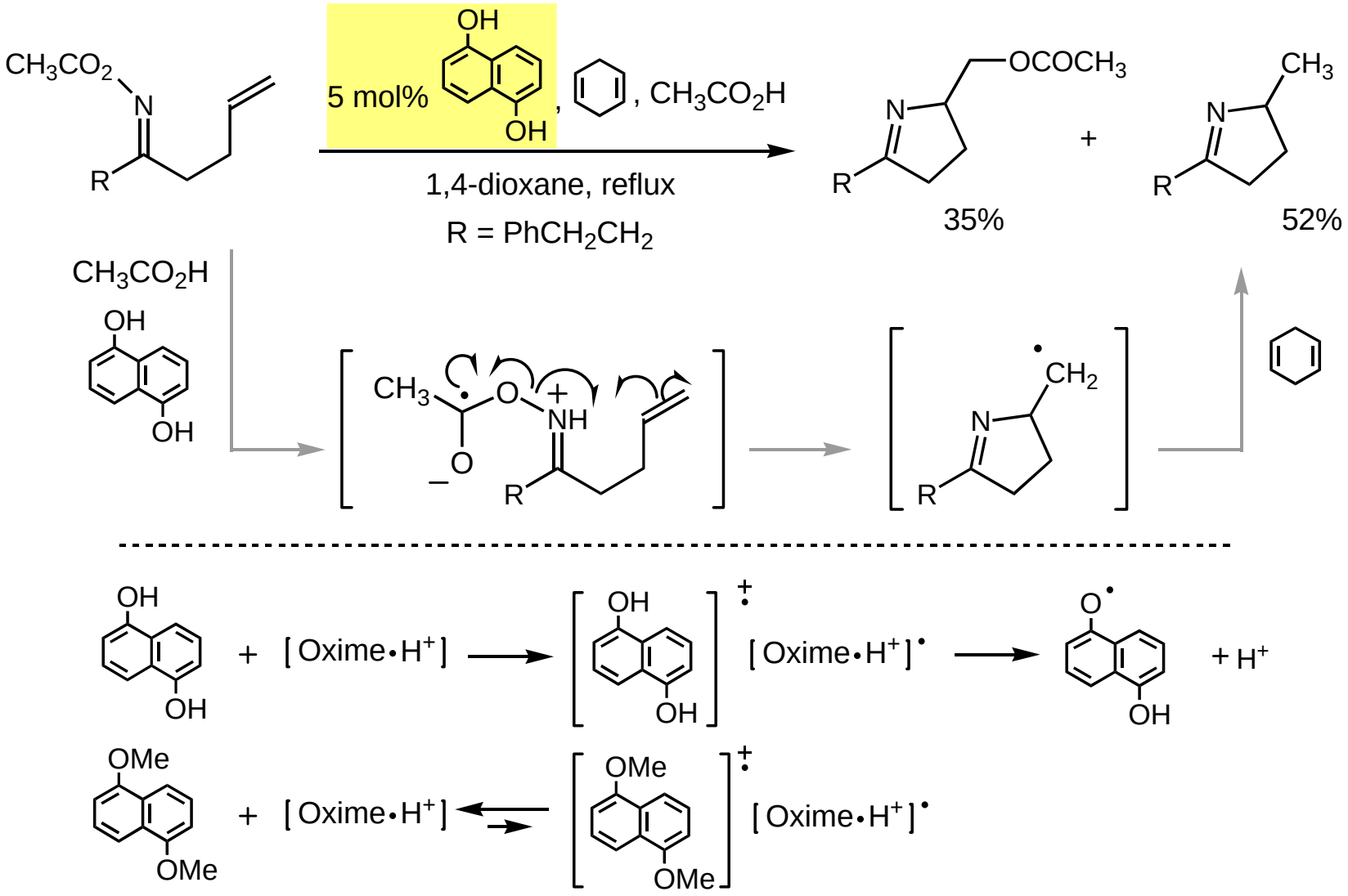


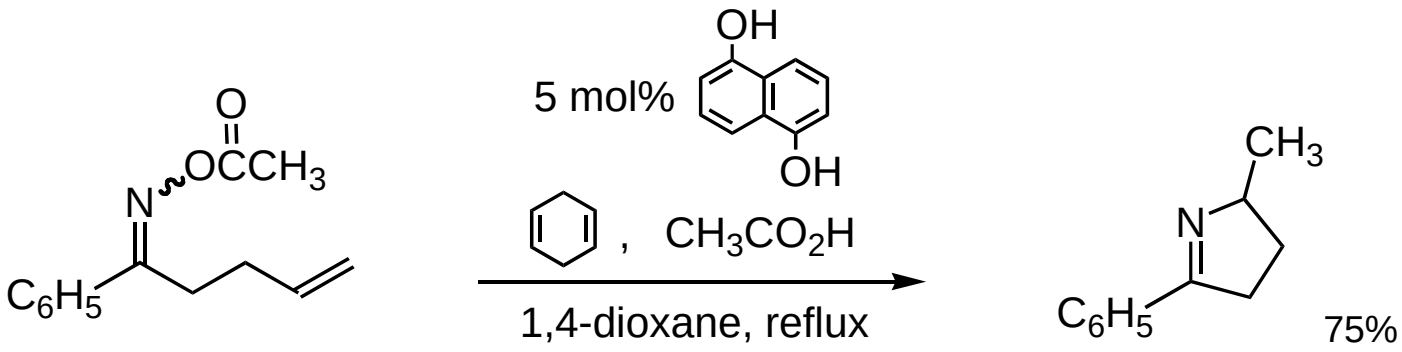


Tetrahedron Lett., **46**, 2373 (2005).

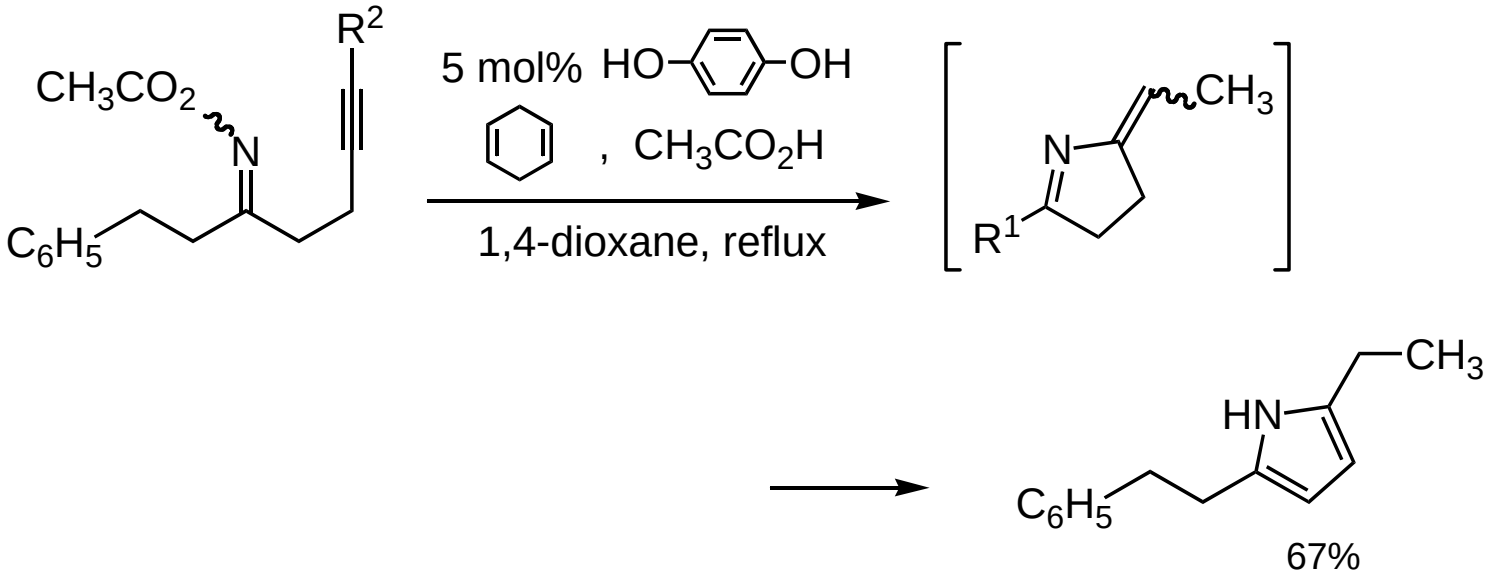


Non-Photochemical Electron Transfer Catalysts





Chem. Lett., **2002**, 144.



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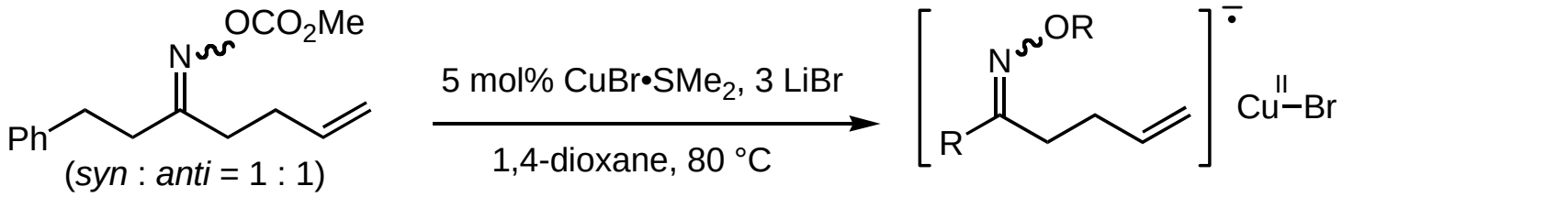
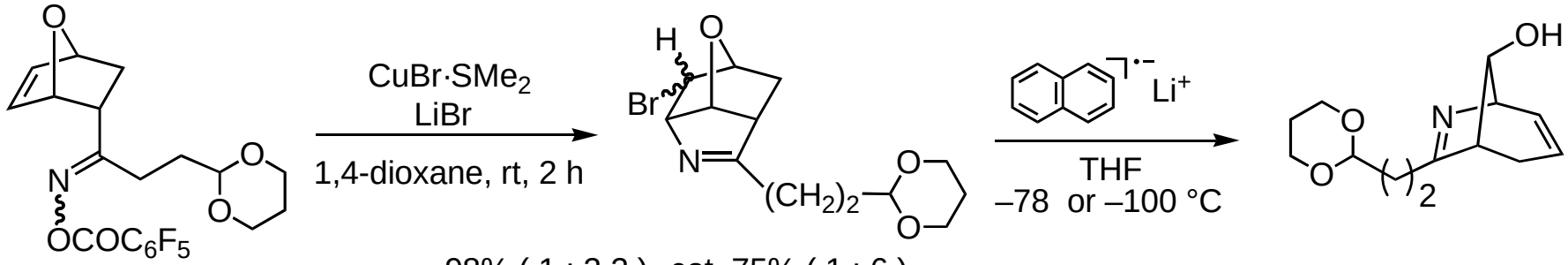
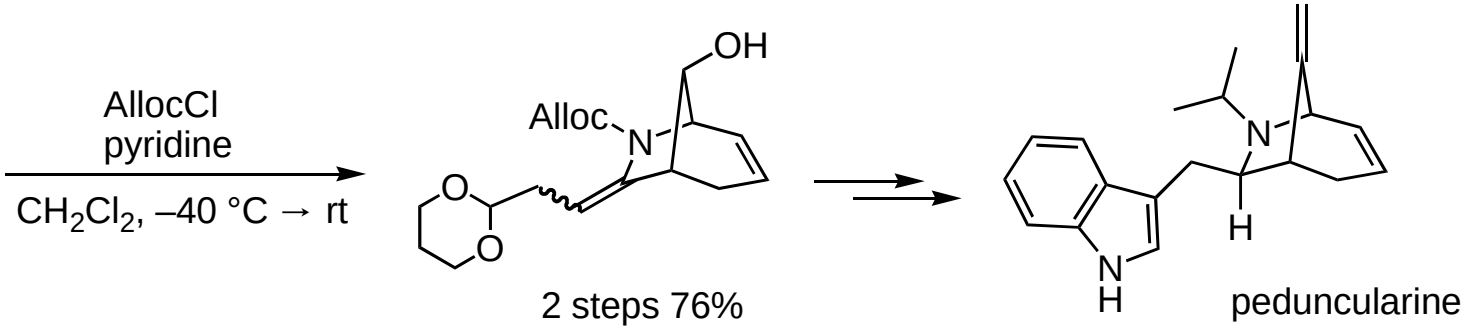
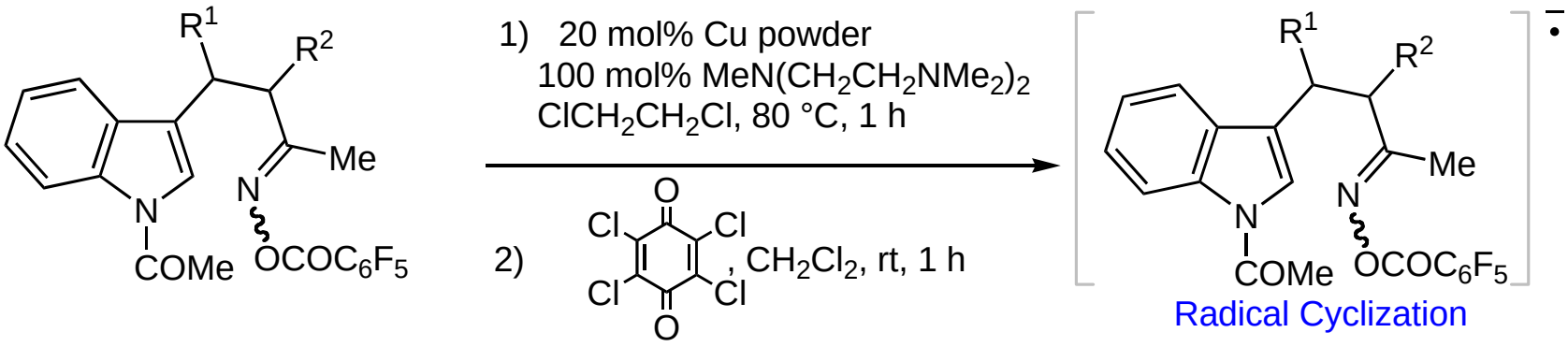
Preparation of 3,4-Dihydro-2*H*-pyrroles with Cu(I)-Catalyst





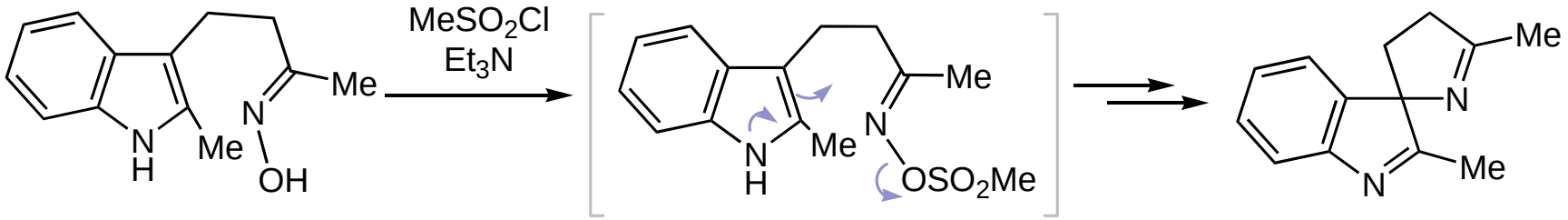


Bull. Chem. Soc. Jpn., **79**, 1552 (2006).



R^1	R^2	Yield / %
H	H	75
t-BuO_2C	H	68
H	Me	83

Bull. Chem. Soc. Jpn., **78**, 1659 (2005).



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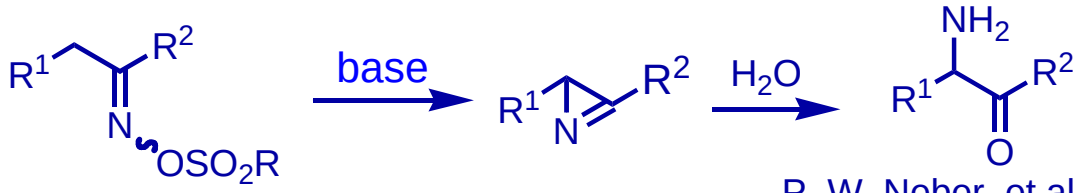
Oxime ⟶ 2*H*-Azirine



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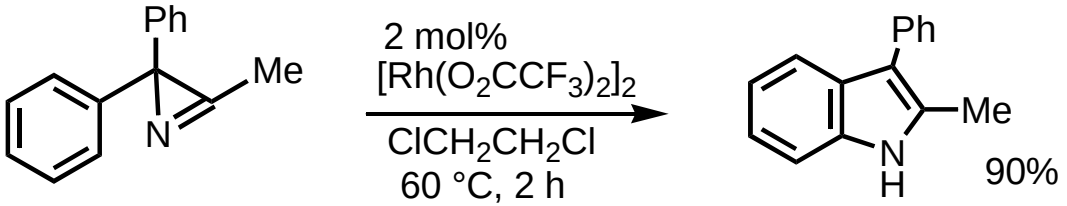

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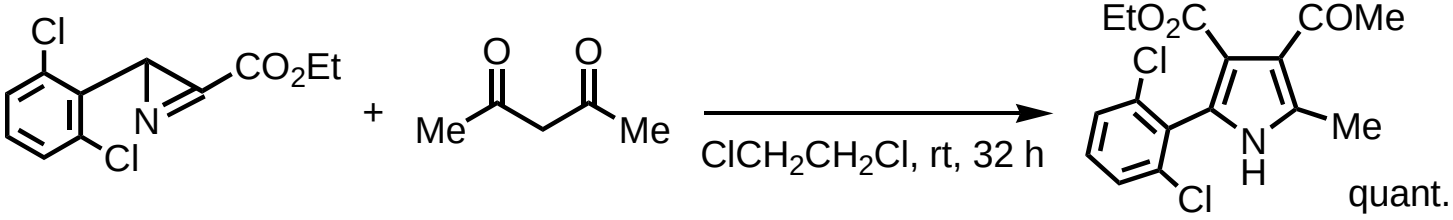
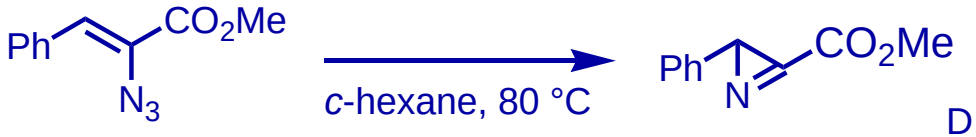


2*H*-Azirine ⟶ Vinyl Azide



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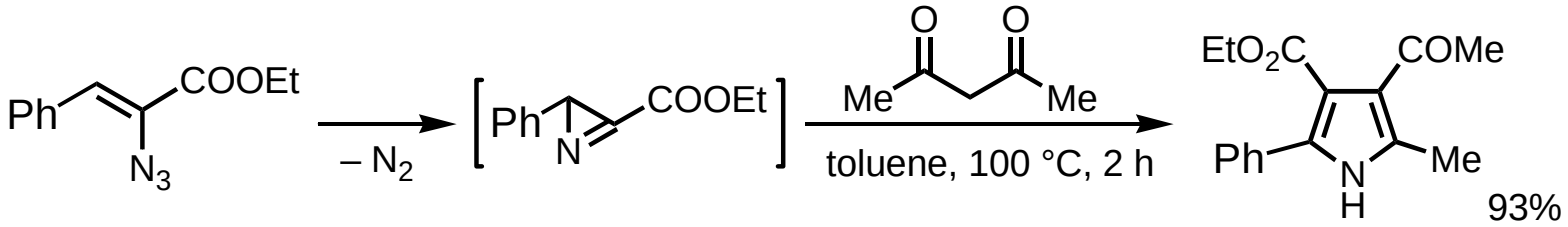
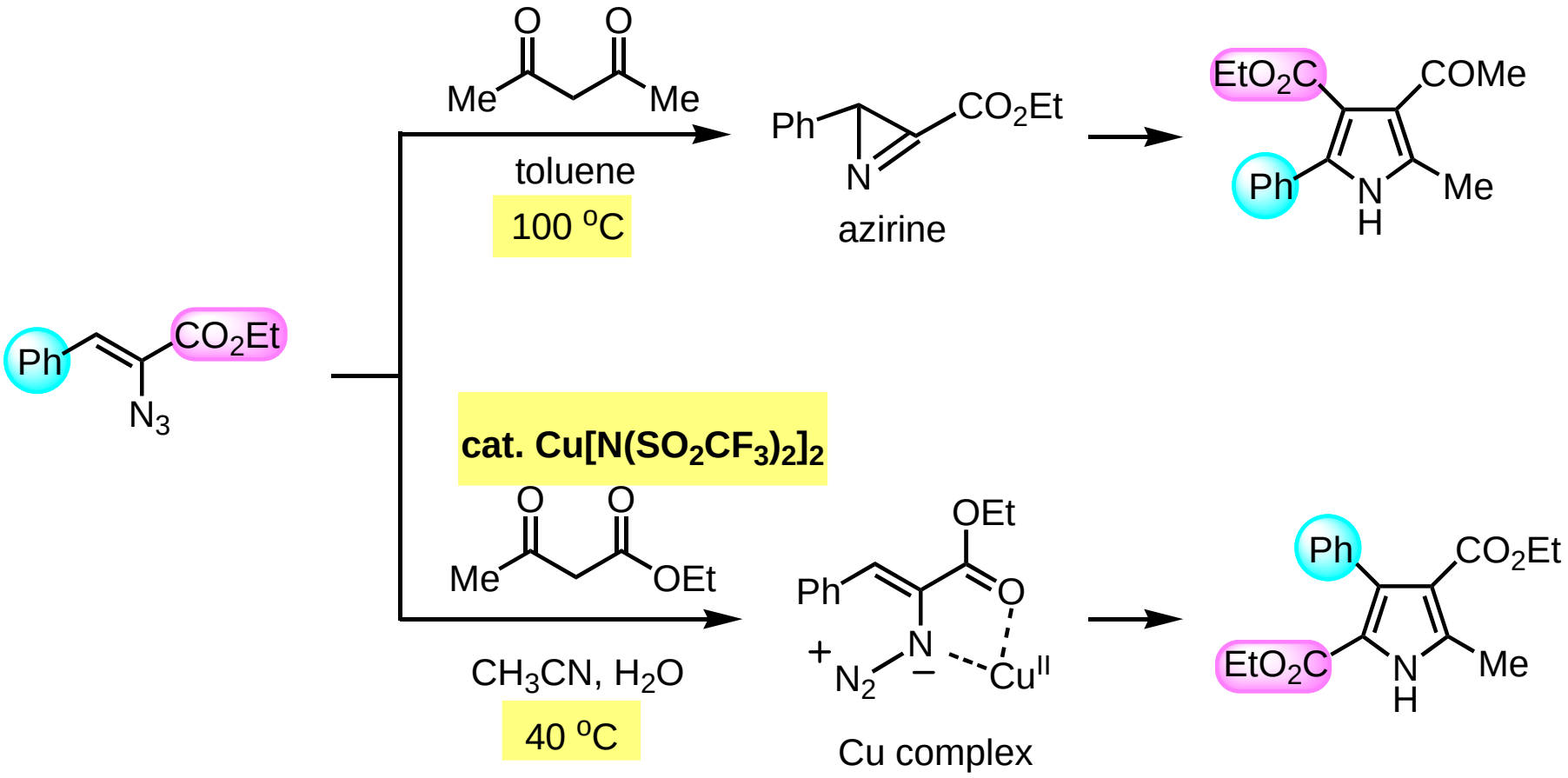


Synthesis of Pyrroles from Vinyl Azides



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from May, 2007

Catalytic C-C and C-N Bond Formation

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