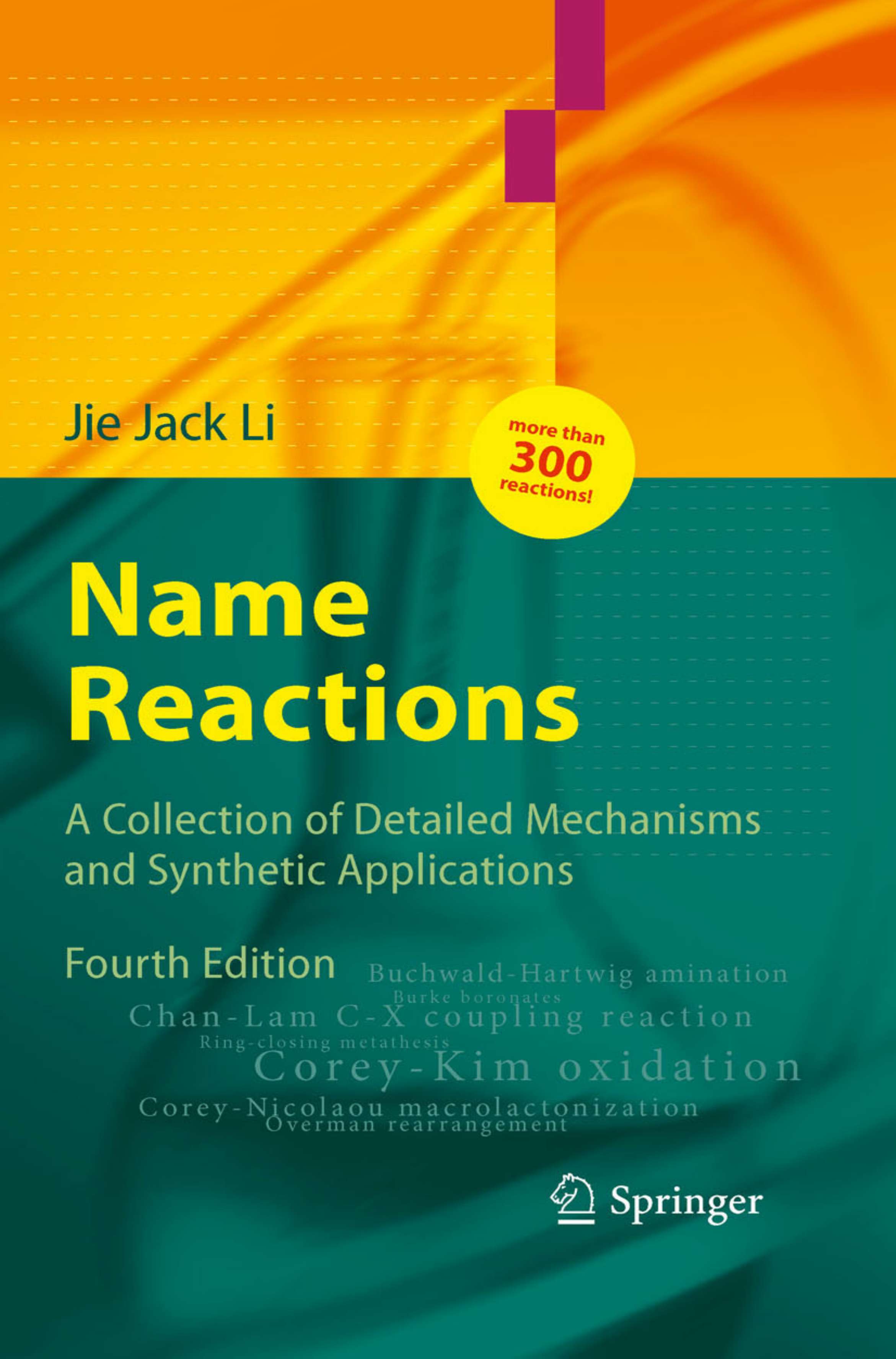

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Name Reactions

A Collection of Detailed Mechanisms and Synthetic Applications

Fourth Expanded Edition

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To Vivien

Foreword

I don't have my name on anything that I don't really do.
–Heidi Klum

Can the organic chemists associated with so-called "Named Reactions" make the same claim as supermodel Heidi Klum? Many scholars of chemistry do not hesitate to point out that the names associated with "name reactions" are often not the actual inventors. For instance, the Arndt–Eistert reaction has nothing to do with either Arndt or Eistert, Pummerer did not discover the "Pummerer" rearrangement, and even the famous Birch reduction owes its initial discovery to someone named Charles Wooster (first reported in a DuPont patent). The list goes on and on…

But does that mean we should ignore, boycott, or outlaw "named reactions"? Absolutely not. The above examples are merely exceptions to the rule. In fact, the chemists associated with name reactions are typically the original discoverers, contribute greatly to its general use, and/or are the first to popularize the transformation. Regardless of the controversial history underlying certain named reactions, it is the students of organic chemistry who benefit the most from the cataloging of reactions by name. Indeed, it is with **education** in mind that Dr. Jack Li has masterfully brought the chemical community the latest edition of *Name Reactions*.

It is clear why this beautiful treatise has rapidly become a bestseller within the chemical community. The quintessence of hundreds of named reactions is encapsulated in a concise format that is ideal for students and seasoned chemists alike. Detailed mechanistic and occasionally even historical details are given for hundreds of reactions along with key references. This "must-have" book will undoubtedly find a place on the bookshelves of all serious practitioners and students of the art and science of synthesis.

Phil S. Baran
May 2009
La Jolla, California

Preface

The first three editions of this book have been warmly embraced by the organic chemistry community. Many readers have indicated that while they like the detailed mechanisms, they prefer to have more real case applications in synthesis. For this edition, we have revolutionized the format, which finally liberated more space to accomodate many more synthetic examples. As a consequence, the subtitle of the book has been changed to *A Collection of Detailed Mechanisms and Synthetic Applications*. When putting together the 4th edition, I also strived to capture the latest references, up to 2009 whenever possible. Coincidentally, my daughter Vivien, a sophomore at the University of Michigan, will take soon Organic Chemistry. I hope she finds this book useful in preparing for her exams.

I am very much indebted to the readers who have kindly written to me with suggestions, which helped transform this book into a useful reference book for senior undergrate and graduate students around the world—the second edition was translated to both Chinese and Russian. I am grateful to my good friend Derek A. Pflum at Ash Stevens Inc. who kindly proofead the entire manuscript and provided many invaluable suggestions. Prof. Derrick L. J. Clive at University of Alberta also proofread the first half of the manuscript and offered helpful comments. I also wish to thank Prof. Phil S. Baran at Scripps Research Institute and his students, Tanja Gulder, Yoshi Ishihara, Chad A. Lewis, Jonathan Lockner, Jun Cindy Shi, and Ian B. Seiple for proofreading the final draft of the manuscript. Their knowledge and time have tremendously enhanced the quality of this book. Any remaining errors are, of course, solely my own responsibility.

As always, I welcome your critique!

Jie Jack Li
May 2009
Killingworth, Connecticut

Table of Contents

Abbreviations and Acronyms

●—	polymer support
3CC	three-component condensation
4CC	four-component condensation
9-BBN	9-borabicyclo[3.3.1]nonane
A	adenosine
Ac	acetyl
ADDP	1,1'-(azodicarbonyl)dipiperidine
AIBN	2,2′-azobisisobutyronitrile
Alpine-borane®	*B*-isopinocampheyl-9-borabicyclo[3.3.1]-nonane
AOM	*p*-Anisyloxymethyl = *p*-$MeOC_6H_4OCH_2$-
Ar	aryl
B**:**	generic base
[bimim]Cl•2AlCl$_3$	1-butyl-3-methylimidazolium chloroaluminuminate
BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
Bn	benzyl
Boc	*tert*-butyloxycarbonyl
BT	benzothiazole
Bz	benzoyl
Cbz	benzyloxycarbonyl
CuTC	copper thiophene-2-carboxylate
DABCO	1,4-diazabicyclo[2.2.2]octane
dba	dibenzylideneacetone
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCC	1,3-dicyclohexylcarbodiimide
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
de	diastereoselctive excess
DEAD	diethyl azodicarboxylate
(DHQ)$_2$-PHAL	1,4-bis(9-*O*-dihydroquinine)-phthalazine
(DHQD)$_2$-PHAL	1,4-bis(9-*O*-dihydroquinidine)-phthalazine
DIAD	diisopropyl azodidicarboxylate
DIBAL	diisobutylaluminum hydride
DIPEA	diisopropylethylamine
DMA	*N,N*-dimethylacetamide
DMAP	4-*N,N*-dimethylaminopyridine
DME	1,2-dimethoxyethane
DMF	*N,N*-dimethylformamide
DMFDMA	*N,N*-dimethylformamide dimethyl acetal
DMS	dimethylsulfide
DMSO	dimethylsulfoxide
DMSY	dimethylsulfoxonium methylide
DMT	dimethoxytrityl
DPPA	diphenylphosphoryl azide
dppb	1,4-bis(diphenylphosphino)butane

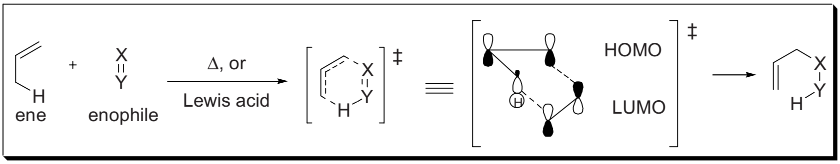
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1′-bis(diphenylphosphino)ferrocene
dppp	1,3-bis(diphenylphosphino)propane
dr	diastereoselctive ratio
DTBAD	di-*tert*-butylazodicarbonate
DTBMP	2,6-di-*tert*-butyl-4-methylpyridine
E1	unimolecular elimination
E1cB	2-step, base-induced β-elimination *via* carbanion
E2	bimolecular elimination
EAN	ethylammonium nitrate
EDDA	ethylenediamine diacetate
ee	enantiomeric excess
Ei	two groups leave at about the same time and bond to each other as they are doing so.
Eq	equivalent
Et	ethyl
EtOAc	ethyl acetate
HMDS	hexamethyldisilazane
HMPA	hexamethylphosphoramide
HMTTA	1,1,4,7,10,10-hexamethyltriethylenetetramine
IBX	*o*-iodoxybenzoic acid
Imd	imidazole
KHMDS	potassium hexamethyldisilazide
LAH	lithium aluminum hydride
LDA	lithium diisopropylamide
LHMDS	lithium hexamethyldisilazide
LTMP	lithium 2,2,6,6-tetramethylpiperidide
M	metal
m-CPBA	*m*-chloroperoxybenzoic acid
MCRs	multicomponent reactions
Mes	mesityl
MPS	morpholine-polysulfide
Ms	methanesulfonyl
MWI	microwave irradiation
MVK	methyl vinyl ketone
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
NIS	*N*-iodosuccinimide
NMP	1-methyl-2-pyrrolidinone
Nos	nosylate (4-nitrobenzenesulfonyl)
N-PSP	*N*-phenylselenophthalimide
N-PSS	*N*-phenylselenosuccinimide
Nu	nucleophile
PCC	pyridinium chlorochromate
PDC	pyridinium dichromate
Piv	pivaloyl

PMB	para-methoxybenzyl
PPA	polyphosphoric acid
PPTS	pyridinium *p*-toluenesulfonate
PT	phenyltetrazolyl
PyPh$_2$P	diphenyl 2-pyridylphosphine
Pyr	pyridine
Red-Al	sodium bis(methoxy-ethoxy)aluminum hydride
Red-Al (SMEAH)	sodium bis(methoxy-ethoxy)aluminum hydride
Salen	*N,N′*-disalicylidene-ethylenediamine
SET	single electron transfer
SIBX	Stabilized IBX
SM	starting material
SMEAH	sodium bis(methoxy-ethoxy)aluminum hydride
S$_N$1	unimolecular nucleophilic substitution
S$_N$2	bimolecular nucleophilic substitution
S$_N$Ar	nucleophilic substitution on an aromatic ring
TBABB	tetra-*n*-butylammonium bibenzoate
TBAF	tetra-*n*-butylammonium fluoride
TBAO	1,3,3-trimethyl-6-azabicyclo[3.2.1]octane
TBDMS	*tert*-butyldimethylsilyl
TBDPS	*tert*-butyldiphenylsilyl
TBS	*tert*-butyldimethylsilyl
t-Bu	*tert*-butyl
TDS	thexyldimethylsilyl
TEA	triethylamine
TEOC	trimethysilylethoxycarbonyl
Tf	trifluoromethanesulfonyl (triflyl)
TFA	trifluoroacetic acid
TFAA	trifluoroacetic anhydride
TFP	tri-2-furylphosphine
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TMEDA	*N,N,N′,N′*-tetramethylethylenediamine
TMG	1,1,3,3-tetramethylguanidine
TMP	tetramethylpiperidine
TMS	trimethylsilyl
TMSCl	trimethylsilyl chloride
TMSCN	trimethylsilyl cyanide
TMSI	trimethylsilyl iodide
TMSOTf	trimethylsilyl triflate
Tol	toluene or tolyl
Tol-BINAP	2,2′-bis(di-*p*-tolylphosphino)-1,1′-binaphthyl
TosMIC	(*p*-tolylsulfonyl)methyl isocyanide
Ts	tosyl
TsO	tosylate

UHP	urea-hydrogen peroxide
Δ	solvent heated under reflux

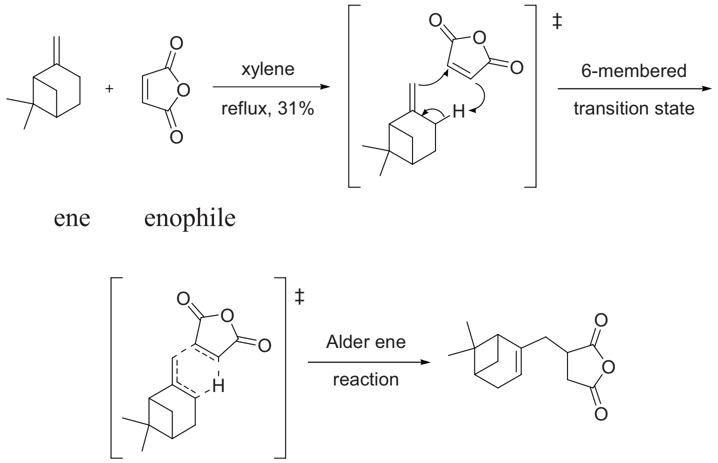
Alder ene reaction

The Alder ene reaction, also known as the hydro-allyl addition, is addition of an enophile to an alkene (ene) *via* allylic transposition. The four-electron system including an alkene π-bond and an allylic C–H σ-bond can participate in a pericyclic reaction in which the double bond shifts and new C–H and C–C σ-bonds are formed.



X=Y: C=C, C≡C, C=O, C=N, N=N, N=O, S=O, *etc*.

Example 1[5]



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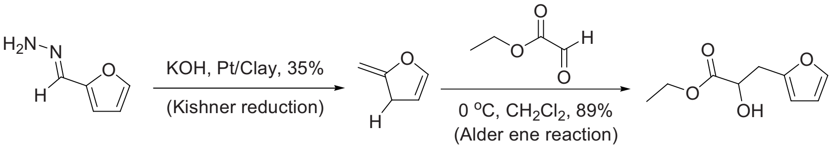
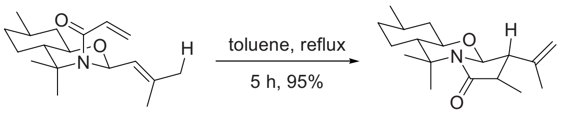


Example 3, Intramolecular Alder-ene reaction[8]



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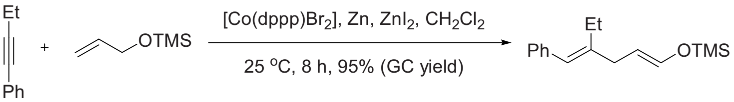
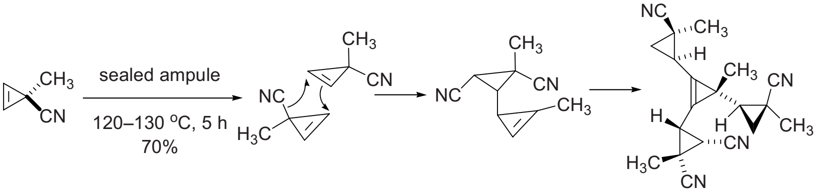
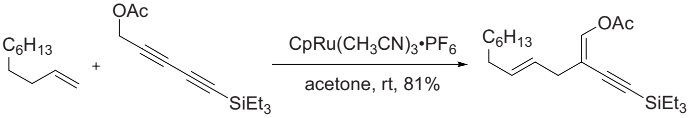
Example 4, Cobalt-catalyzed Alder-ene reaction[9]



Example 5, Nitrile-Alder-ene reaction[10]



Example 6[11]



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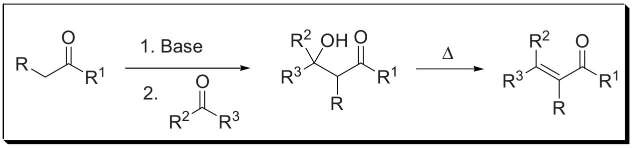
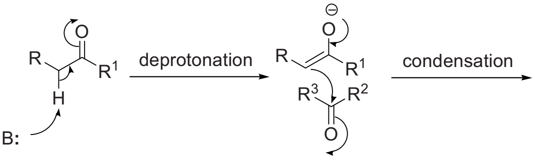
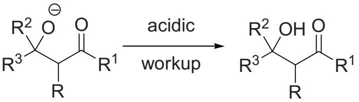
Aldol condensation

The Aldol condensation is the coupling of an enolate ion with a carbonyl compound to form a β-hydroxycarbonyl, and sometimes, followed by dehydration to give a conjugated enone. A simple case is addition of an enolate to an **ald**ehyde to afford an alcoh**ol**, thus the name **aldol**.







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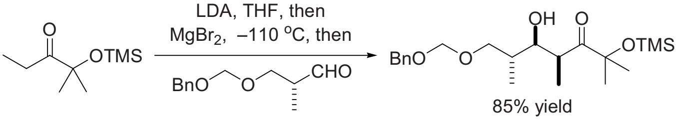

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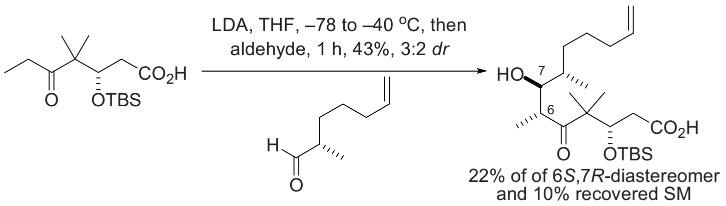

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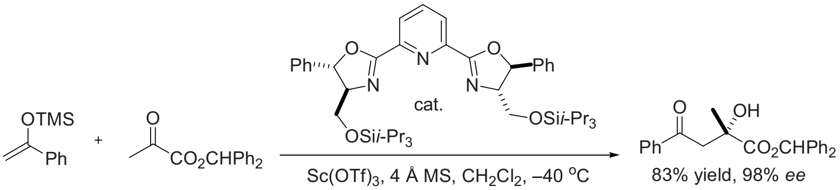
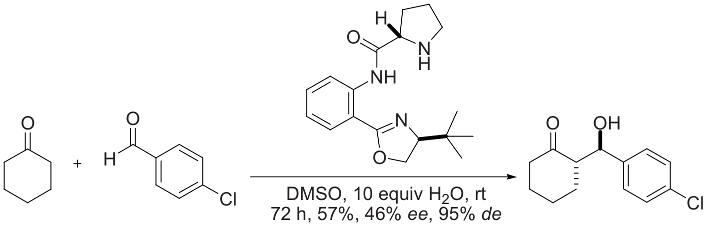
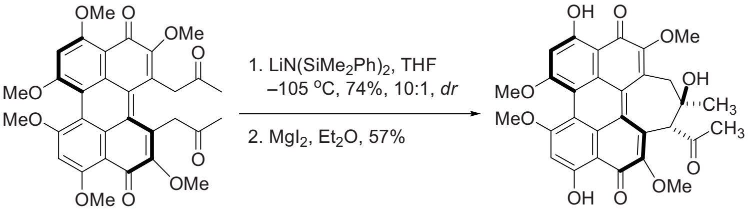
Example 3, Enantioselective Mukaiyama-aldol reaction[10]



Example 4, Intermolecular aldol reaction using organocatalyst[12]



Example 5, Transannular aldol reaction[13]



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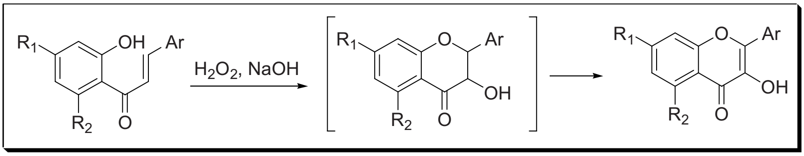
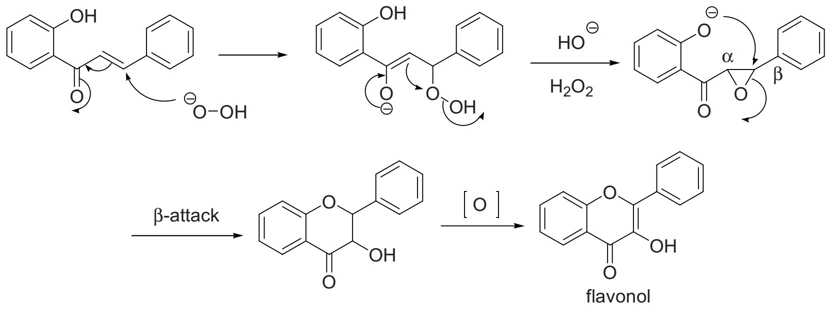
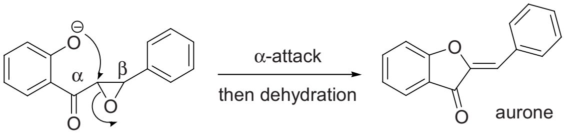
Algar–Flynn–Oyamada Reaction

Conversion of 2′-hydroxychalcones to 2-aryl-3-hydroxy-4*H*-1benzopyran-4-ones (flavonols) by an oxidative cyclization.

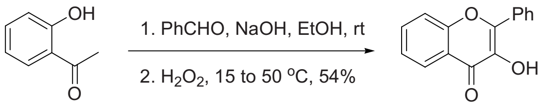




A side reaction:



Example 1[5]



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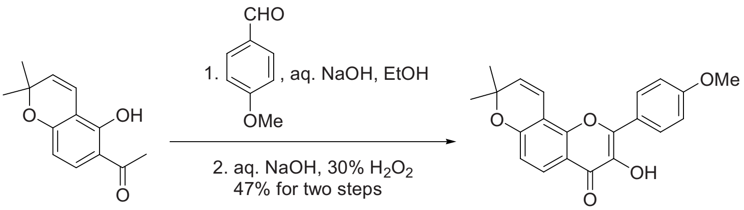
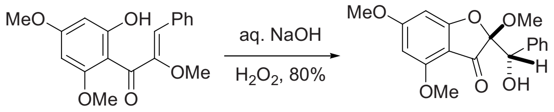
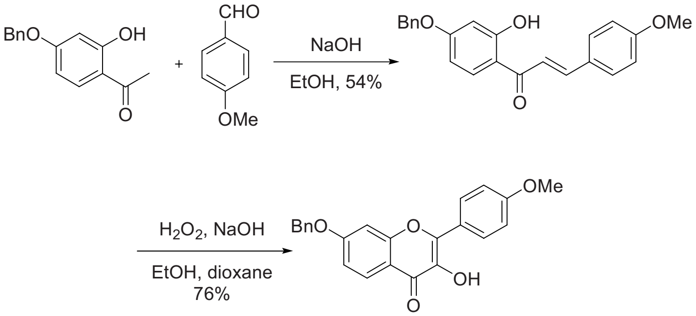


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_3,

Example 3, The side reaction dominated to give the aurone derivative:[9]



Example 4[12]



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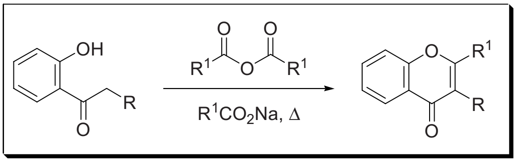
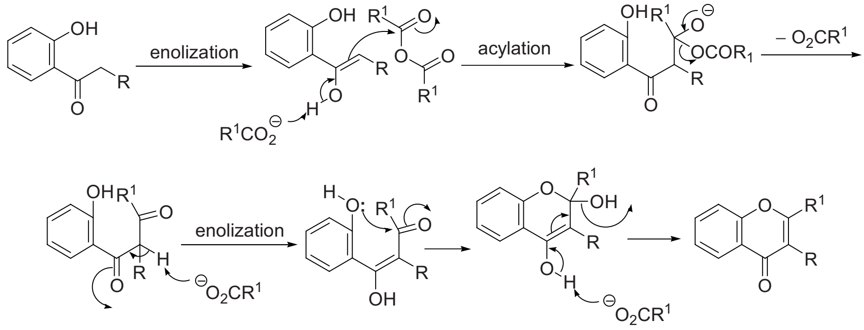
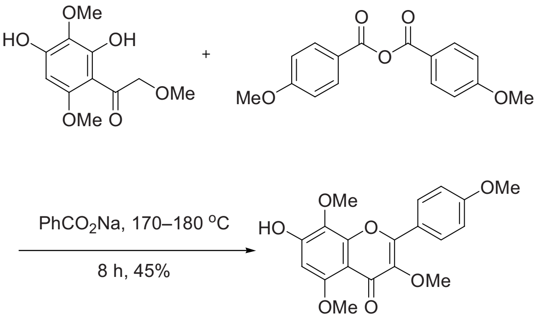
Allan–Robinson reaction

Synthesis of flavones or isoflavones by the treatment of of *o*-hydroxyaryl ketones with aromatic aldehydes. *Cf.* Kostanecki reaction on page 322.

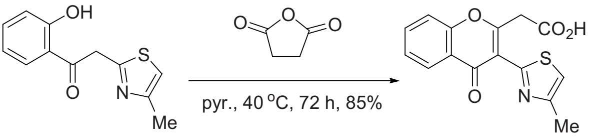




Example 1[6]



Example 2[9]



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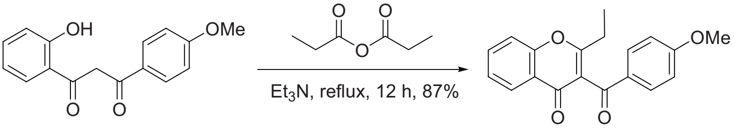
Example 3[10]



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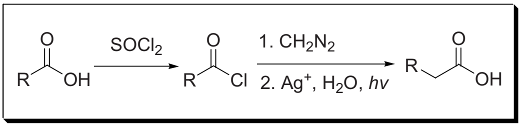
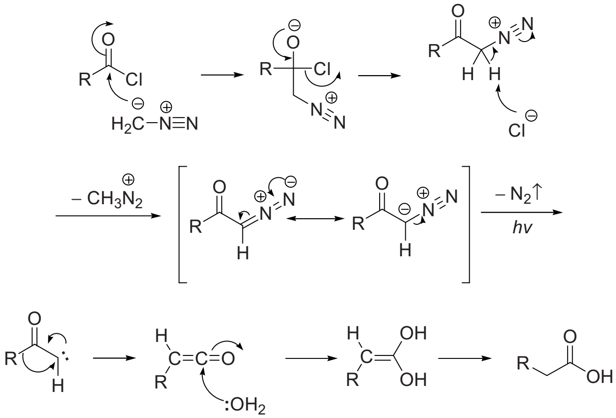
Arndt–Eistert homologation

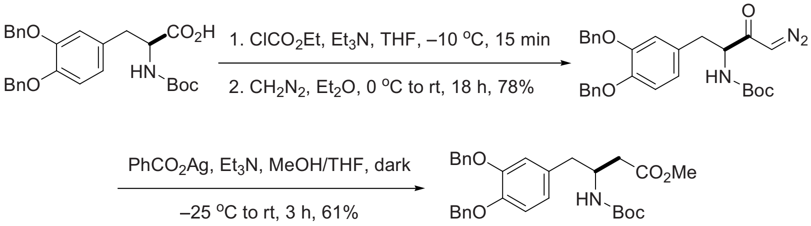
One-carbon homologation of carboxylic acids using diazomethane.



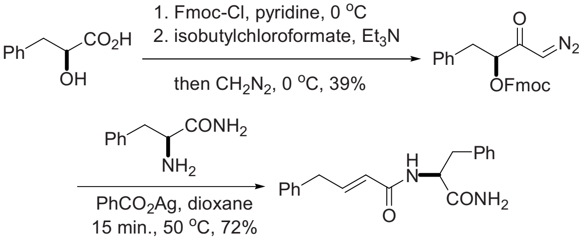


α-ketocarbene intermediate ketene intermediate

Example 1[7]



Example 2, An interesting variation[9]



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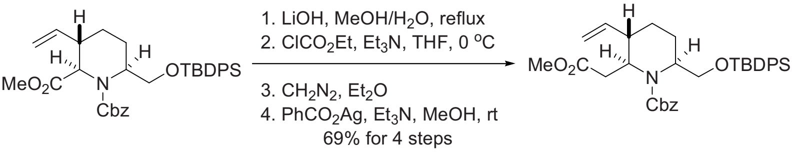
Example 3[10]



References

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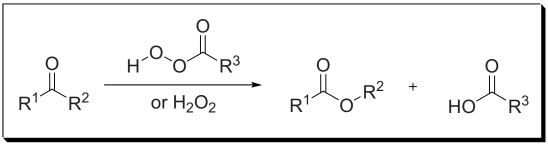
Baeyer–Villiger oxidation

General scheme:

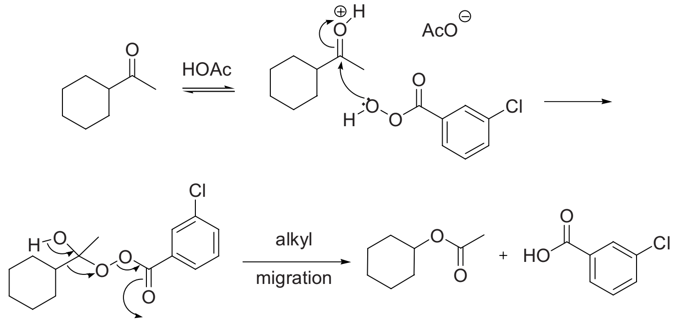


The most electron-rich alkyl group (more substituted carbon) migrates first. The general migration order: tertiary alkyl > cyclohexyl > secondary alkyl > benzyl > phenyl > primary alkyl > methyl >> H.

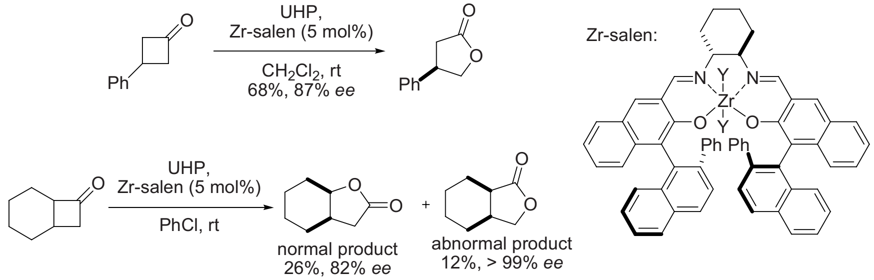
For substituted aryls:

p-MeO-Ar > *p*-Me-Ar > *p*-Cl-Ar > *p*-Br-Ar > *p*-MeOAr > *p*-O$_2$N-Ar

Example 1:

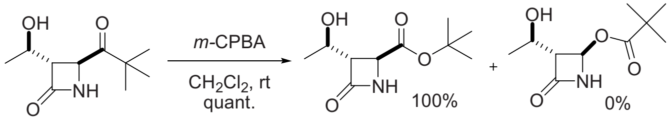


Example 2[4]



UHP = Urea-hydrogen peroxide complex

Example 3[5]



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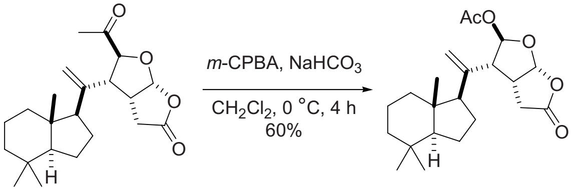
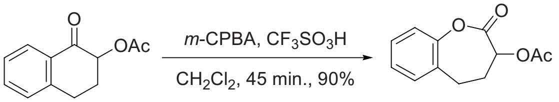
Example 4[6]



Example 5[8]



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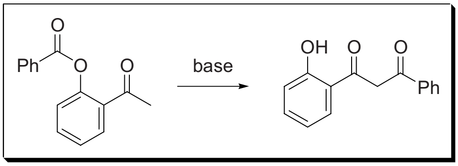
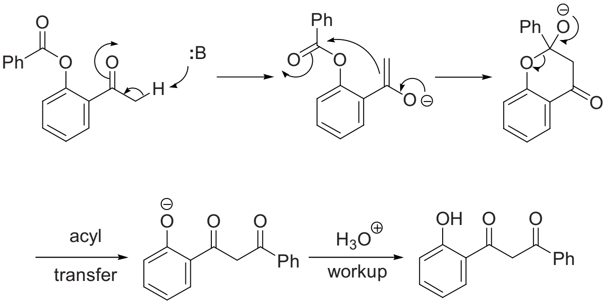
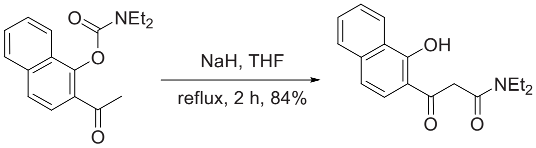
Baker–Venkataraman rearrangement

Base-catalyzed acyl transfer reaction that converts α-acyloxyketones to β-diketones.

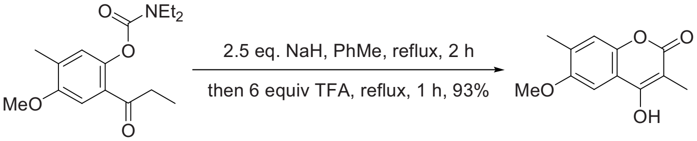




Example 1, Carbamoyl Baker–Venkataraman rearrangement[5]



Example 2, Carbamoyl Baker–Venkataraman rearrangement[6]



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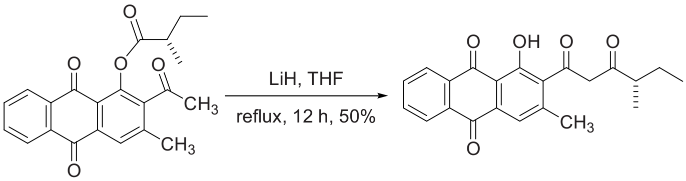
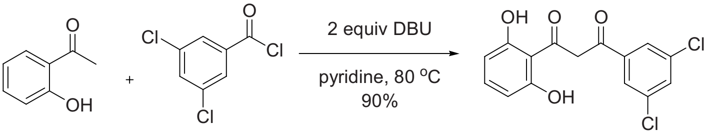
Example 3, Ester Baker–Venkataraman rearrangement[9]



Example 4, Ester Baker–Venkataraman rearrangement[10]



References

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2. Mahal, H. S.; Venkataraman, K. *J. Chem. Soc.* **1934**, 1767–1771. K. Venkataraman studied under Robert Robinson Manchester. He returned to India and later arose to be the Director of the National Chemical Laboratory at Poona.
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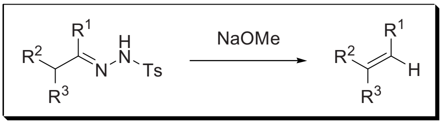
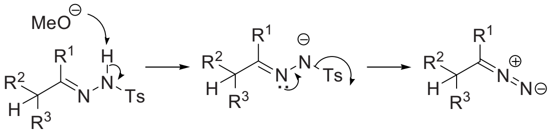
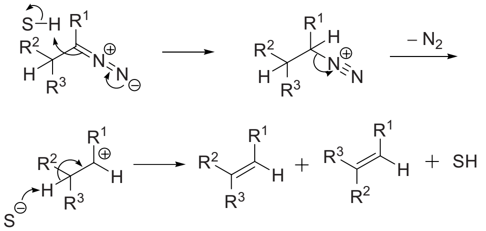
Bamford–Stevens reaction

The Bamford–Stevens reaction and the Shapiro reaction share a similar mechanistic pathway. The former uses a base such as Na, NaOMe, LiH, NaH, $NaNH_2$, heat, *etc.*, whereas the latter employs bases such as alkyllithiums and Grignard reagents. As a result, the Bamford–Stevens reaction furnishes more-substituted olefins as the thermodynamic products, while the Shapiro reaction generally affords less-substituted olefins as the kinetic products.

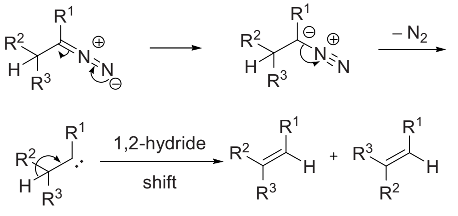




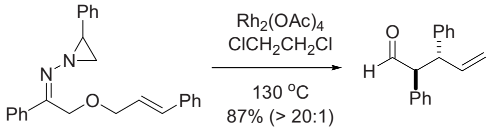
In protic solvent (S–H):



In aprotic solvent:



Example 1, Tandem Bamford–Stevens/thermal aliphatic Claisen rearrangement sequence[2]



The starting material *N*-aziridinyl imine is also known as Eschenmoser hydrazone.

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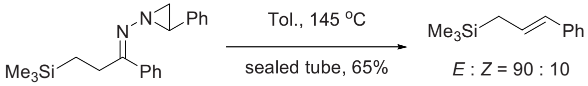
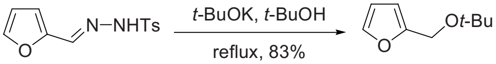
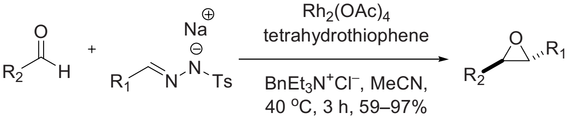
Example 2, Thermal Bamford–Stevens[6]



Example 3[7]



Example 4[8]



References

1. Bamford, W. R.; Stevens, T. S. M. *J. Chem. Soc.* **1952**, 4735–4740. Thomas Stevens (1900–2000), another chemist centenarian, was born in Renfrew, Scotland. He and his student W. R. Bamford published this paper at the University of Sheffield, UK. Stevens also contributed to another name reaction, the McFadyen–Stevens reaction (page 334).
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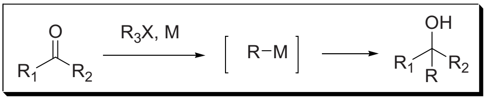
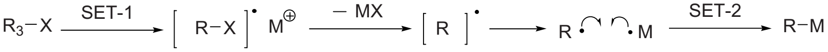
Barbier coupling reaction

In essence, the Barbier coupling reaction is a Grignard reaction carried out *in situ* although its discovery preceded that of the Grignard reaction by a year. *Cf.* Grignard reaction (Page 266).

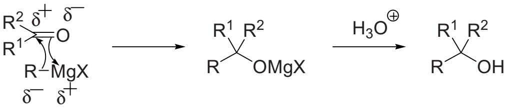


According to conventional wisdom,[3] the organometallic intermediate (M = Mg, Li, Sm, Zn, La, *etc.*) is generated *in situ*, which is intermediately trapped by the carbonyl compound. However, recent experimental and theoretical studies seem to suggest that the Barbier coupling reaction goes through a single electron transfer pathway.

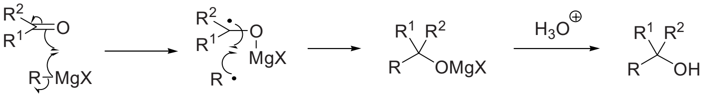
Generation of the Grignard reagent,



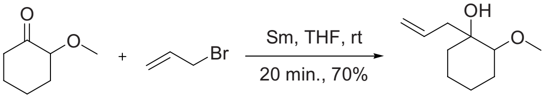
Ionic mechanism,



Single electron transfer mechanism,

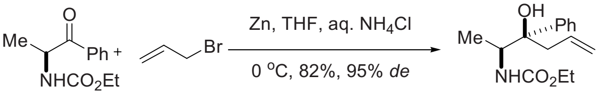


Example 1[6]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_9,

Example 2[9]



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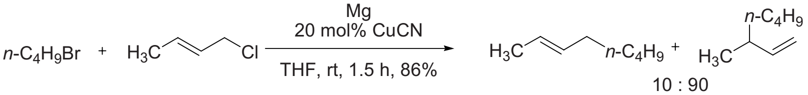

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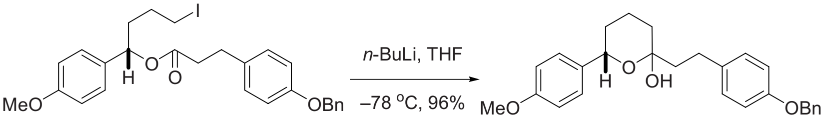

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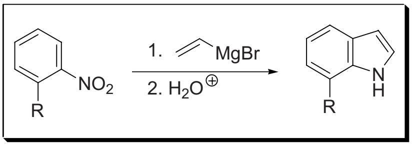
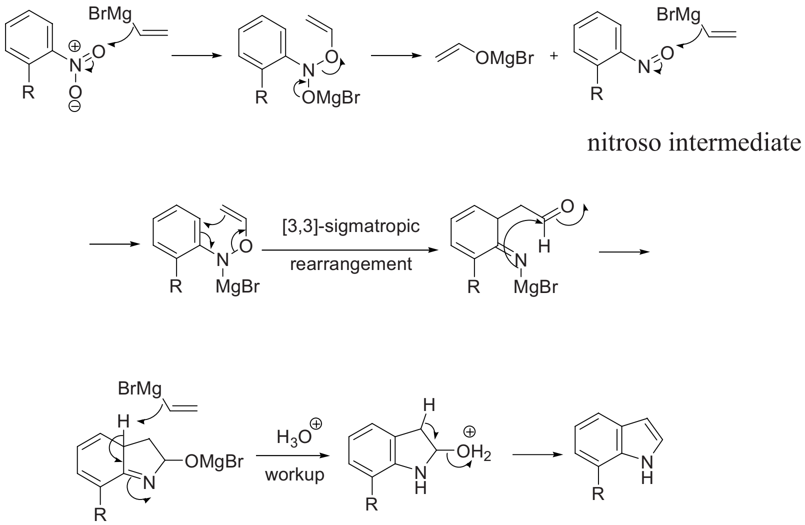
Bartoli indole synthesis

7-Substituted indoles from the reaction of *ortho*-substituted nitroarenes and vinyl Grignard reagents.





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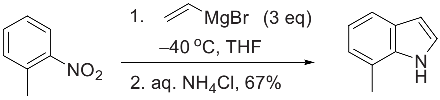

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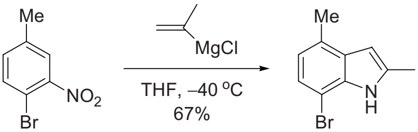

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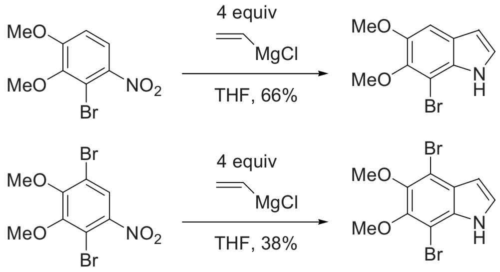

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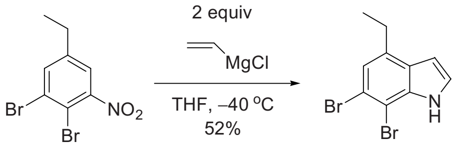

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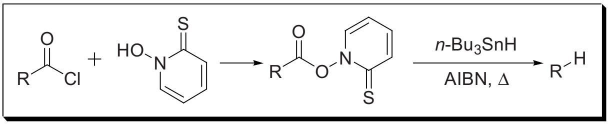
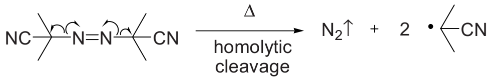
Barton radical decarboxylation

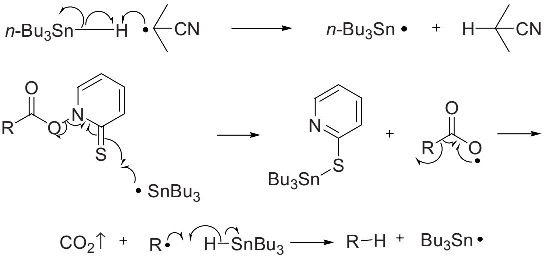
Radical decarboxylation *via* the corresponding thiocarbonyl derivatives of the carboxylic acids.



Barton ester



AIBN = 2,2′-azobisisobutyronitrile



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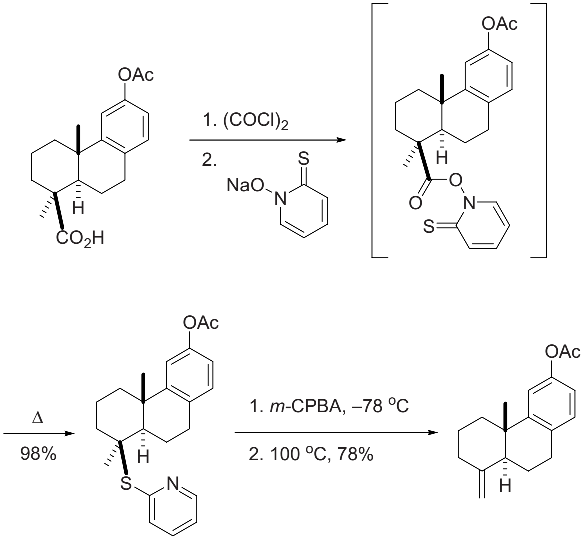

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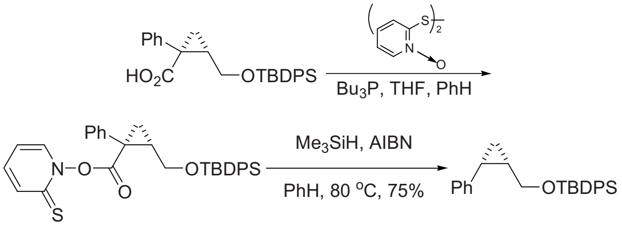
Example 2[6]



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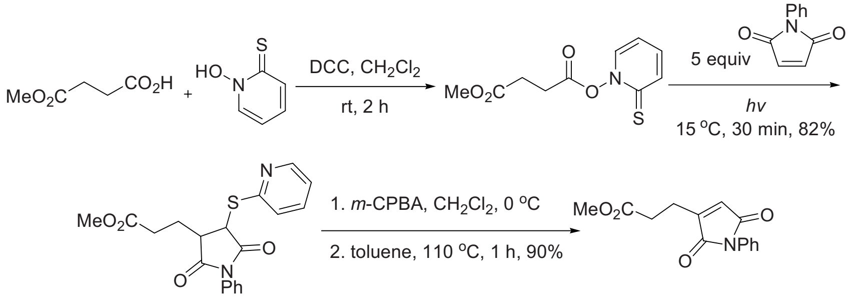

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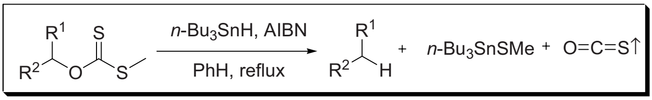
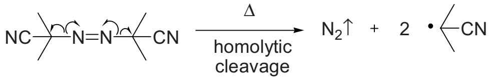
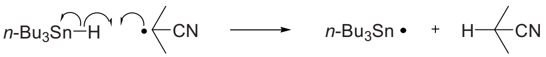
Barton–McCombie deoxygenation

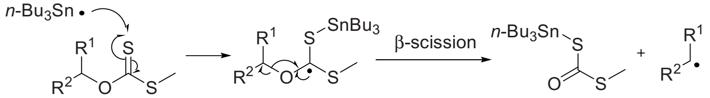
Deoxygenation of alcohols by means of radical scission of their corresponding thiocarbonyl derivatives.

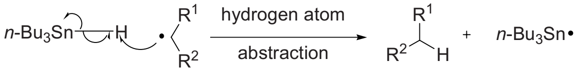


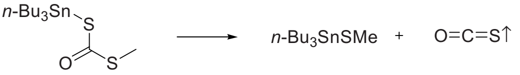


AIBN = 2,2′-azobisisobutyronitrile









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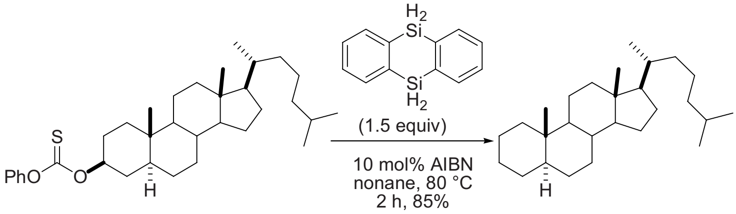

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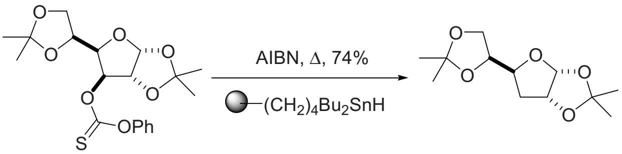
Example 2[6]



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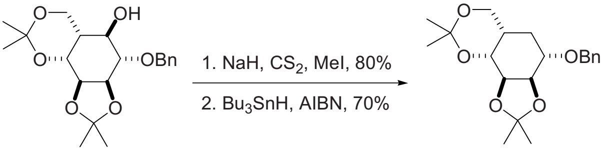

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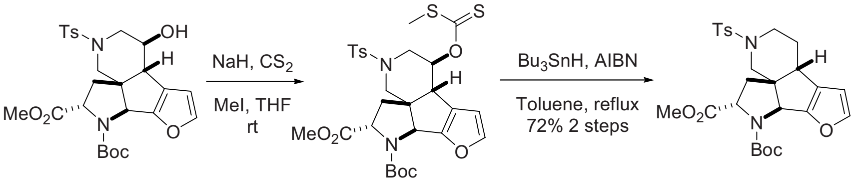

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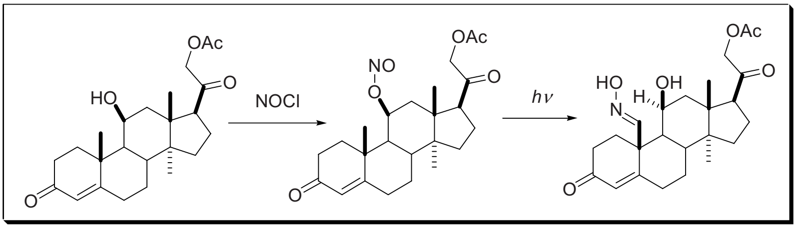
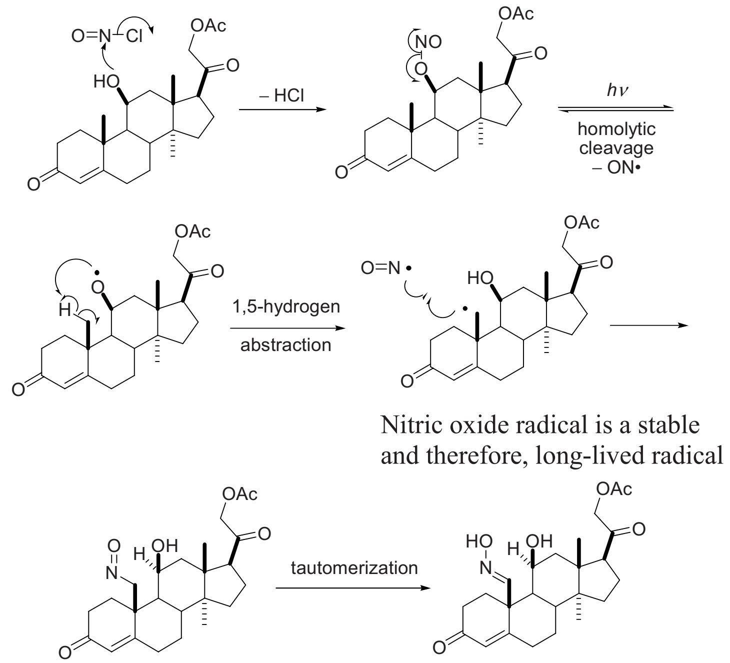
Barton nitrite photolysis

Photolysis of a nitrite ester to a γ-oximino alcohol.

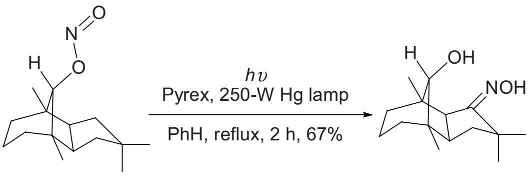




Nitric oxide radical is a stable and therefore, long-lived radical

nitroso intermediate

Example 1[2]



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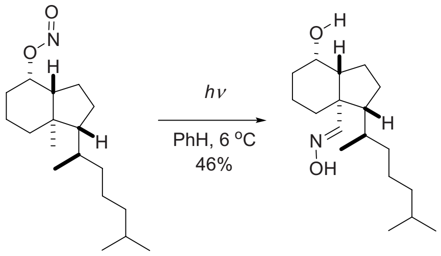
Example 2[6]



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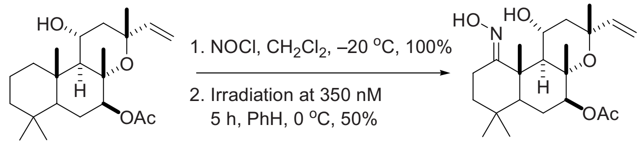

References

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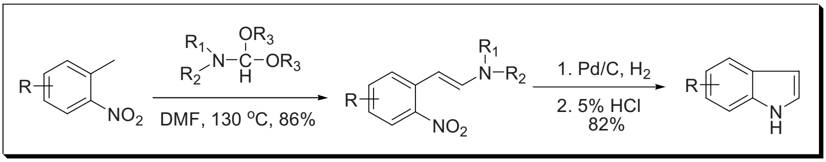
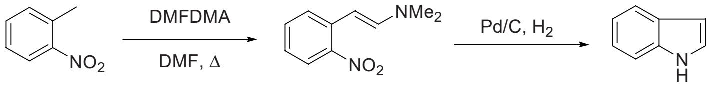
Batcho–Leimgruber indole synthesis

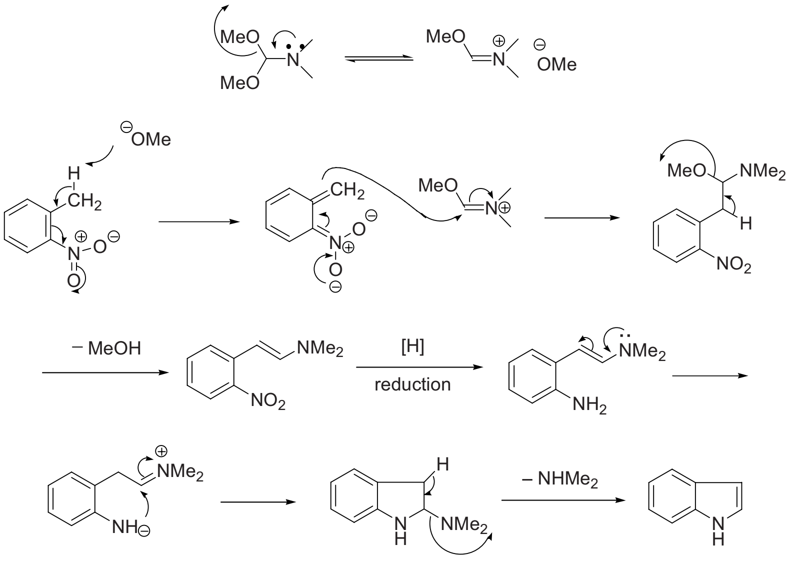
Condensation of *o*-nitrotoluene derivatives with formamide acetals, followed by reduction of the *trans*-β-dimethylamino-2-nitrostyrene to furnish indole derivatives.



Example 1[4]



DMFDMA = *N,N*-dimethylformamide dimethyl acetal, $Me_2NCH(OMe)_2$



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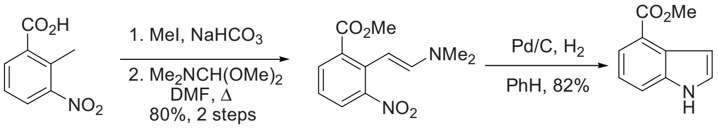

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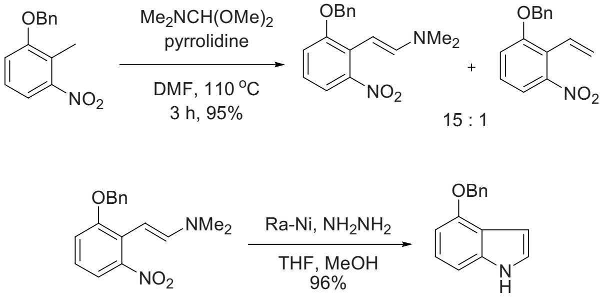
Example 3[5]



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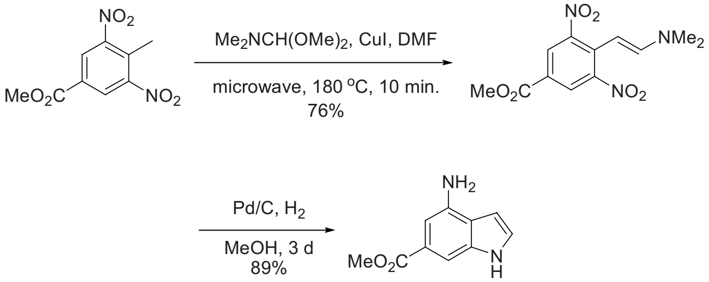

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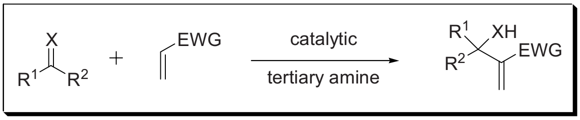
Baylis–Hillman reaction

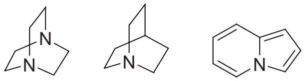
Also known as Morita–Baylis–Hillman reaction. It is a carbon–carbon bond-forming transformation of an electron-poor alkene with a carbon electrophile. Electron-poor alkenes include acrylic esters, acrylonitriles, vinyl ketones, vinyl sulfones, and acroleins. On the other hand, carbon electrophiles may be aldehydes, α-alkoxycarbonyl ketones, aldimines, and Michael acceptors.

General scheme:

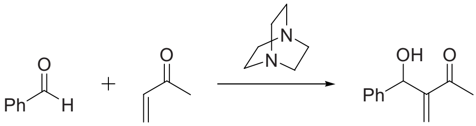


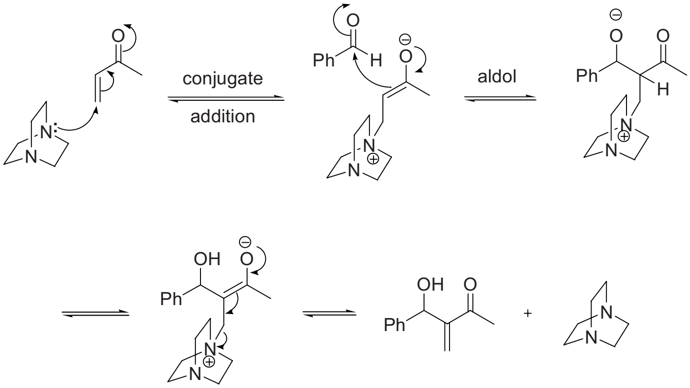
X = O, NR_2, EWG = CO_2R, COR, CHO, CN, SO_2R, SO_3R, $PO(OEt)_2$, $CONR_2$, $CH_2{=}CHCO_2Me$

Alternative catalytic tertiary amines:



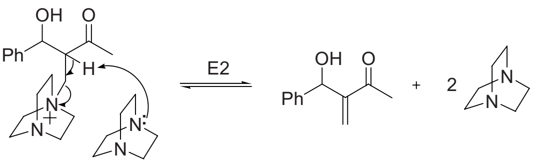
Example 1:



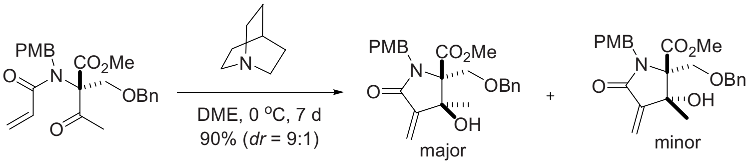


E2 (bimolecular elimination) mechanism is also operative here:

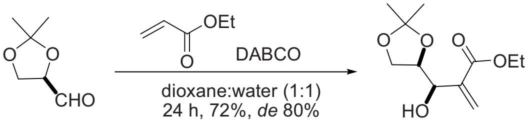
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_15,



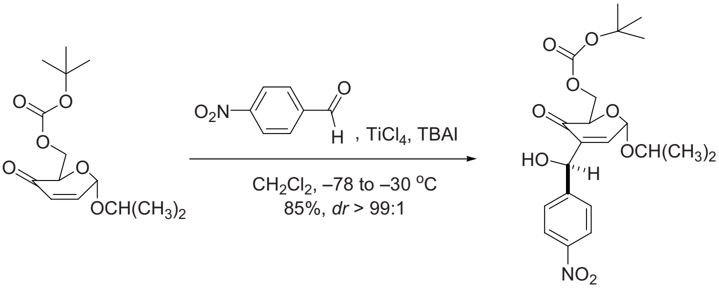
Example 2, Intramolecular Baylis–Hillman reaction[6]



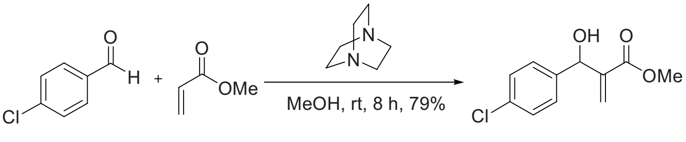
Example 3[7]



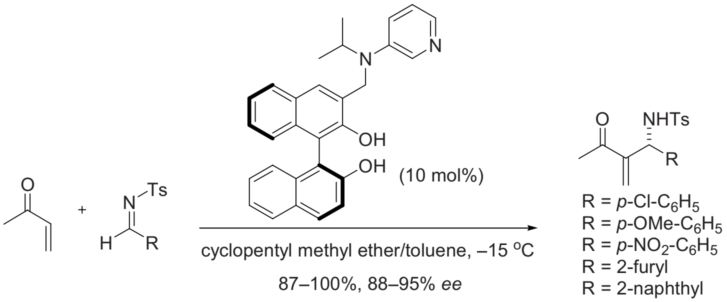
Example 4[8]



Example 5[9]



Example 6[10]



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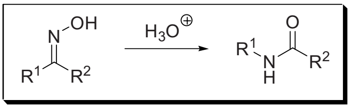
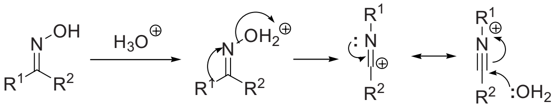
Beckmann rearrangement

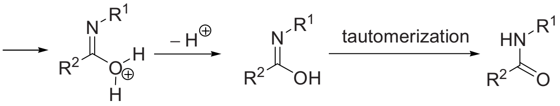
Acid-mediated isomerization of oximes to amides.

In protic acid:

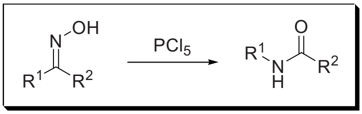


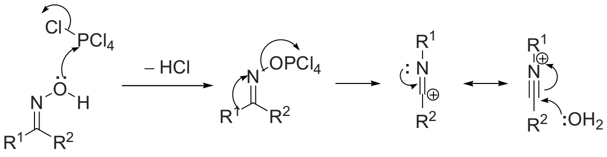


the substituent *trans* to the leaving group migrates

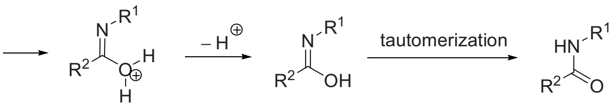


With PCl_5:

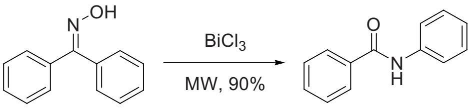




Again, the substituent *trans* to the leaving group migrates

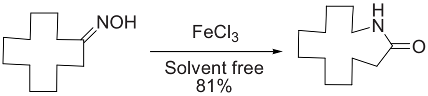


Example 1, Microwave (MW) reaction[3]

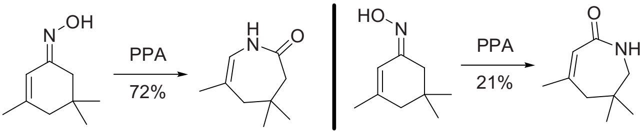


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_16,

Example 2[4]

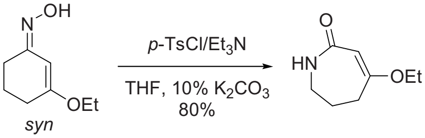


Example 3[6]

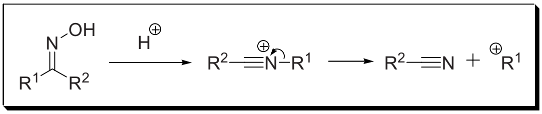


PPA = **p**oly**p**hosphoric **a**cid

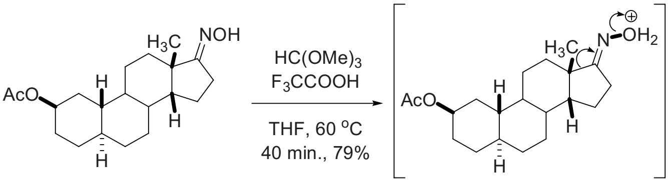
Example 4[8]

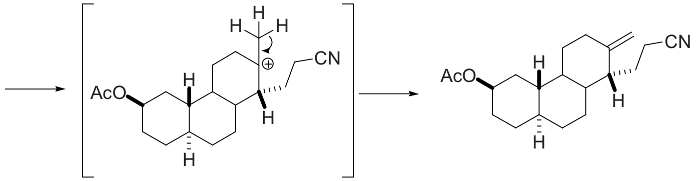


Abnormal Beckmann rearrangement is when the migrating substituent fragment (e.g., R^1) departs from the intermediate, leaving a nitrile as a stable product.



Example 1[9]





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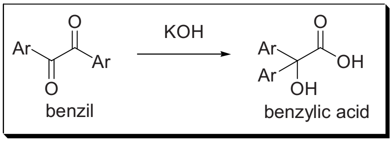
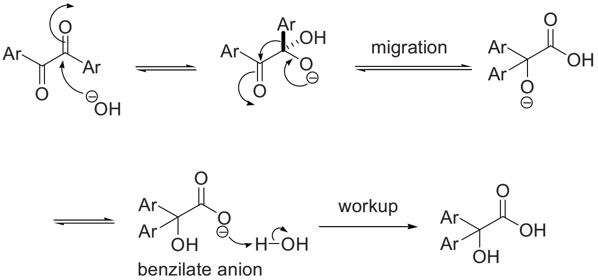
Benzilic acid rearrangement

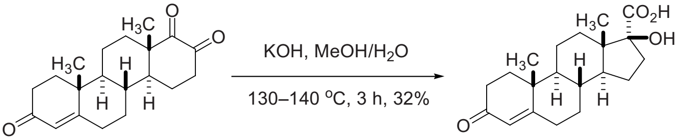
Rearrangement of benzil to benzylic acid *via* aryl migration.



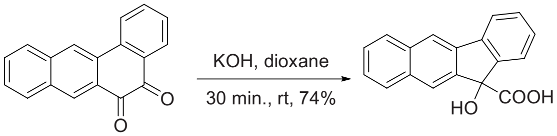


Final deprotonation of the carboxylic acid drives the reaction forward.

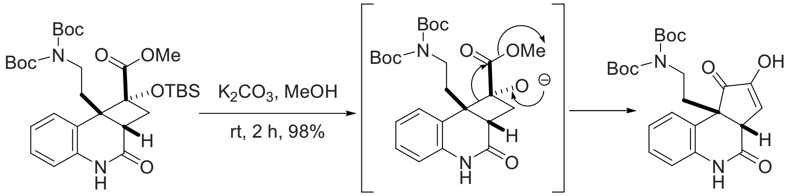
Example 1[3]



Example 2[6]



Example 3, Retro-benzilic acid rearrangement[7]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_17,

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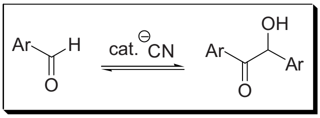
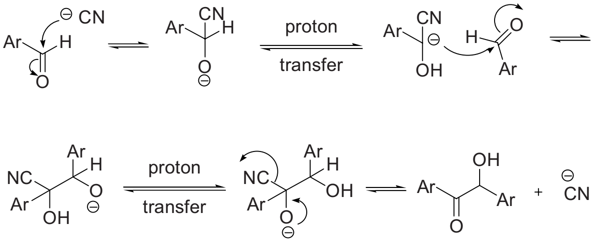
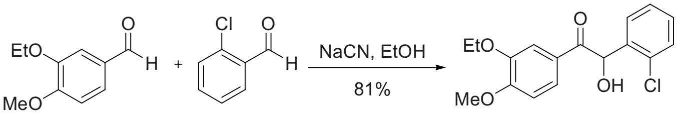
Benzoin condensation

Cyanide-catalyzed condensation of aryl aldehyde to benzoin. Now cyanide is mostly replaced by a thiazolium salt. *Cf.* Stetter reaction.





Example 1[2]



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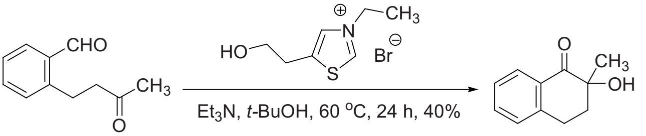

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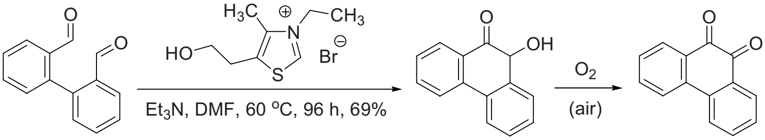
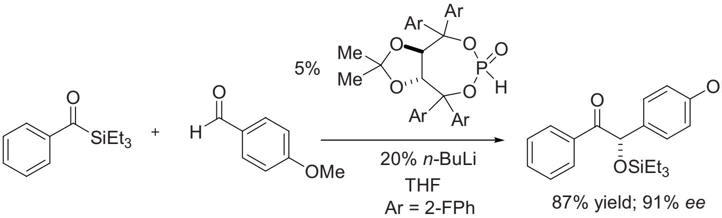
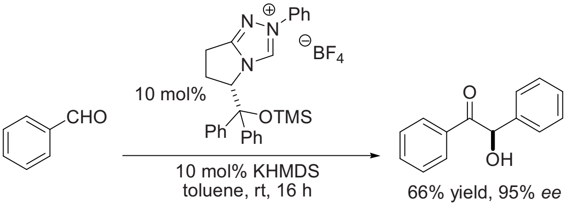


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_18,

Example 4[9]



Example 5[10]



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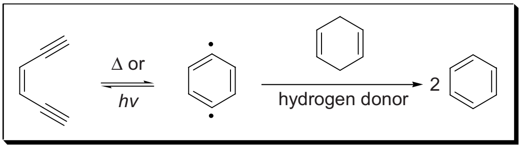
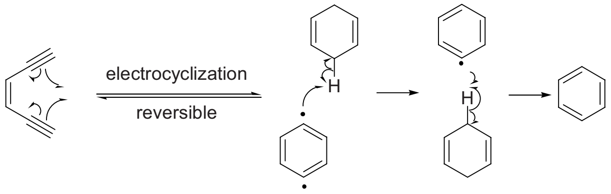
Bergman cyclization

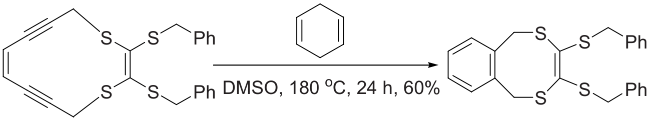
1,4-Benzenediyl diradical formation from enediyne *via* electrocyclization.





enediyne 1,4-benzenediyl diradical

Example 1[6]



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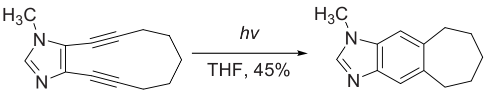
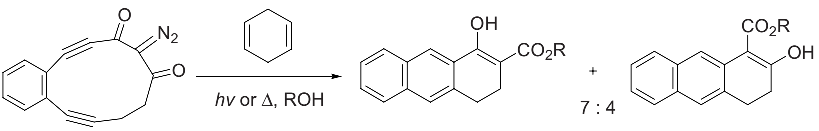
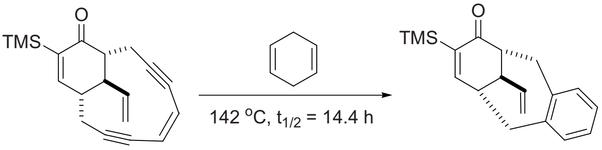


Example 3, Wolff rearrangement followed by the Bergman cyclization[8]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_19,

Example 4[10]



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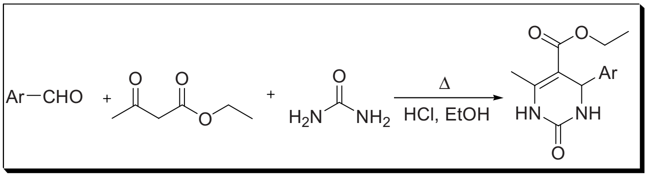
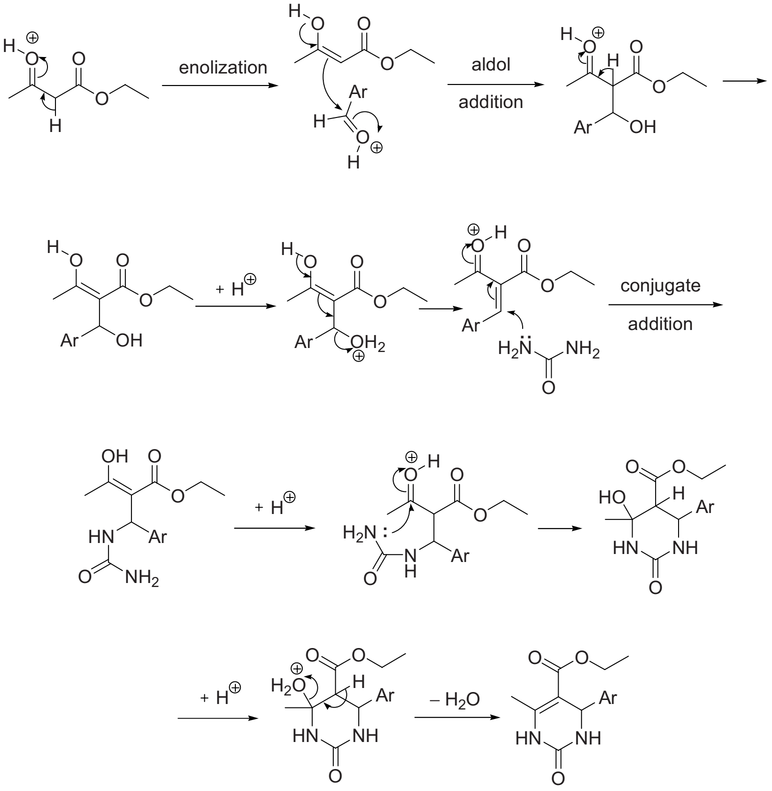
Biginelli pyrimidone synthesis

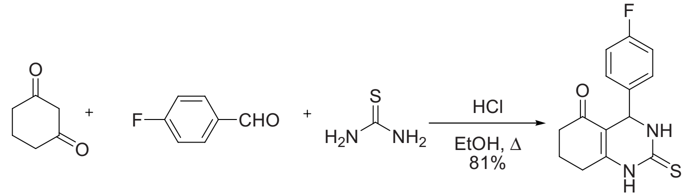
One-pot condensation of an aromatic aldehyde, urea, and β-dicarbonyl compound in the acidic ethanolic solution and expansion of such a condensation thereof. It belongs to a class of transformations called multicomponent reactions (MCRs).



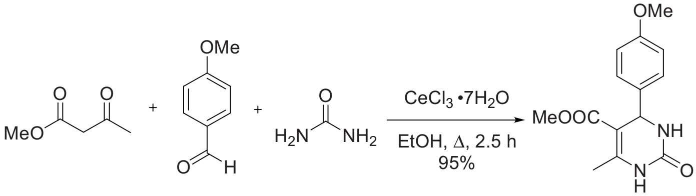


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_20,

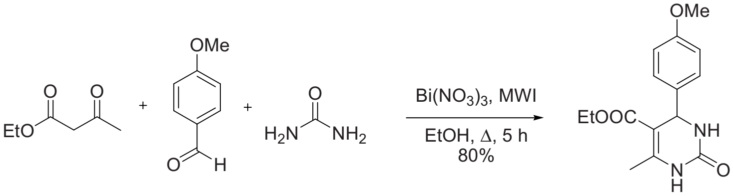
Example 1[4]



Example 2[5]



Example 3, Microwave-induced Biginelli condensation (MWI = microwave irradiation)[9]



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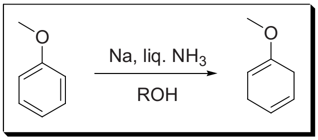
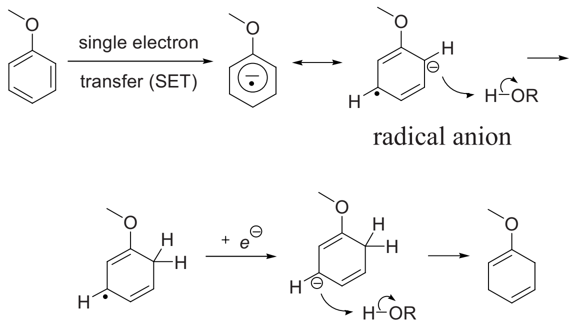
Birch reduction

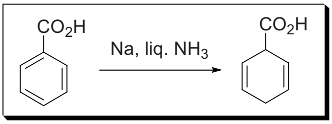
The Birch reduction is the 1,4-reduction of aromatics to their corresponding cyclohexadienes by alkali metals (Li, K, Na) dissolved in liquid ammonia in the presence of an alcohol.

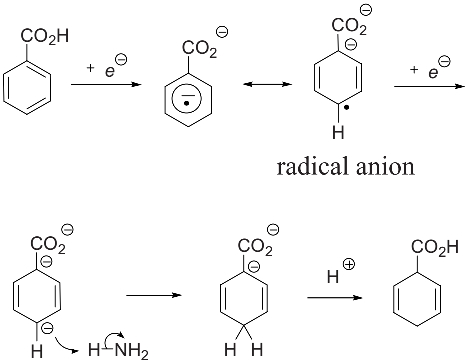
Benzene ring bearing an electron-donating substituent:





Benzene ring with an electron-withdrawing substituent:





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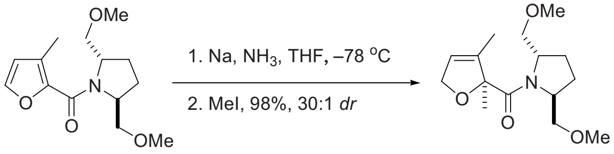
Example 1[4]



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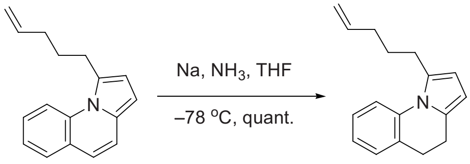

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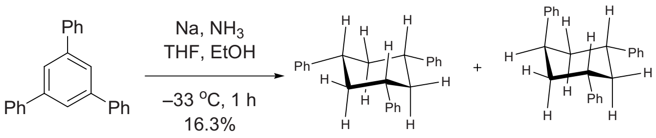

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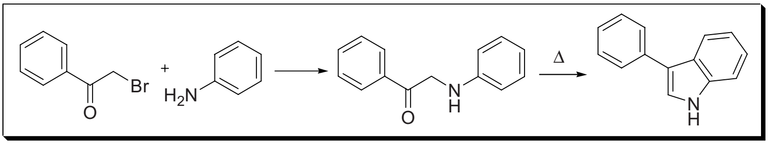
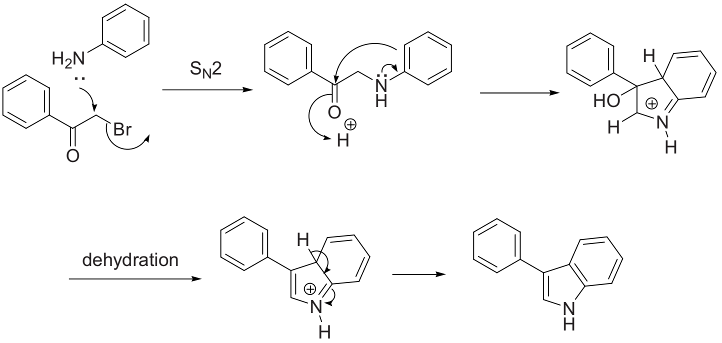
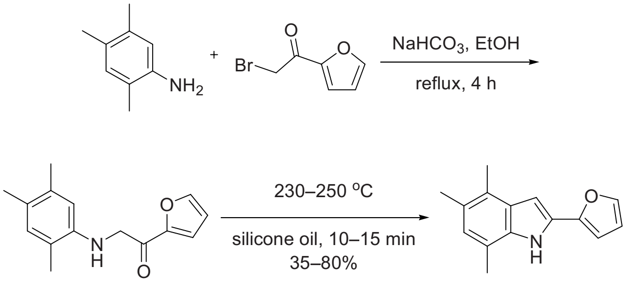
Bischler–Möhlau indole synthesis

The Bischler–Möhlau indole synthesis, also known as the Bischler indole synthesis, refers to the synthesis of 3-arylindoles from the cyclization of ω-arylamino-ketones and excess anilines.





Example 1[5]



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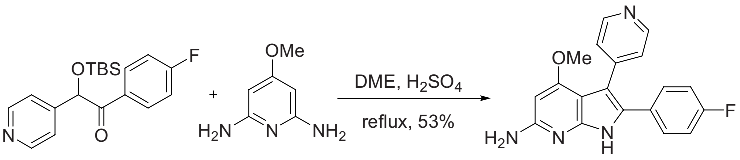

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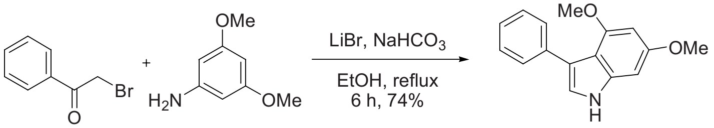
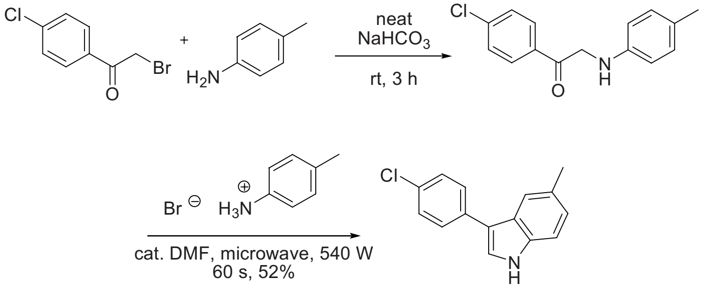
Example 3[10]



Example 4, Microwave-assisted, solvent-free Bischler indole synthesis[11]



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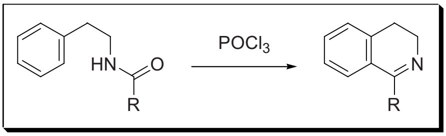
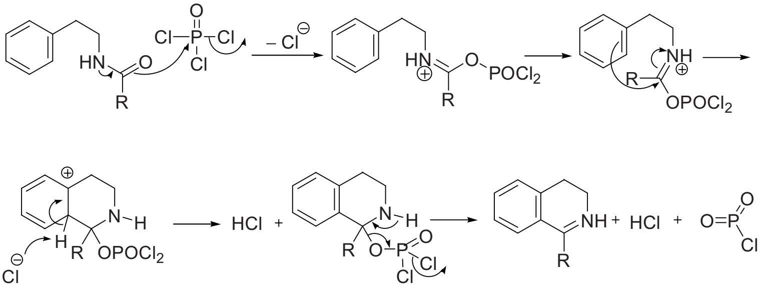
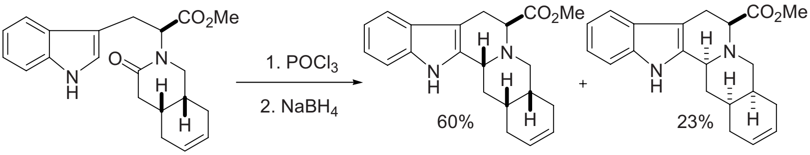
Bischler–Napieralski reaction

Dihydroisoquinolines from β-phenethylamides in refluxing phosphorus oxychloride.





Example 1[2]



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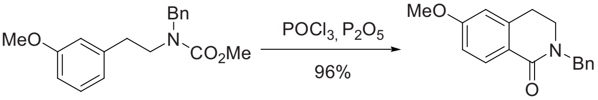

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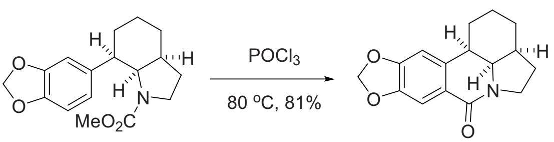

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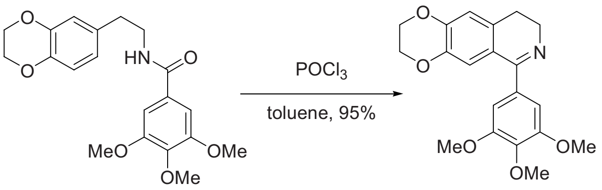
Example 4[7]



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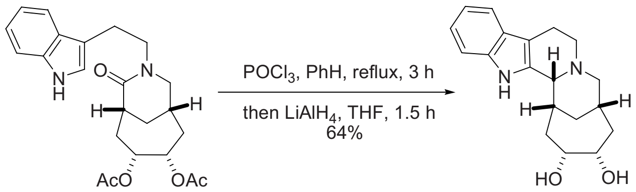

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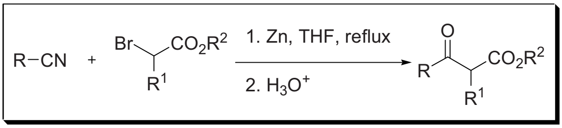
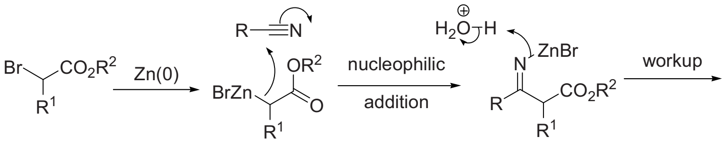
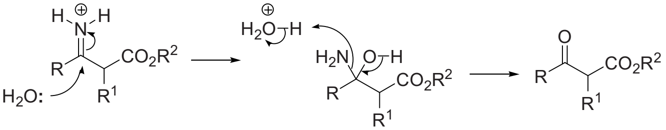
Blaise reaction

β-Ketoesters from nitriles, α-haloesters and Zn. *Cf*. Reformatsky reaction.

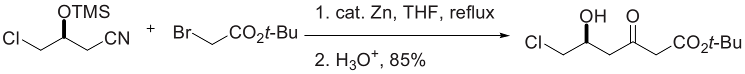




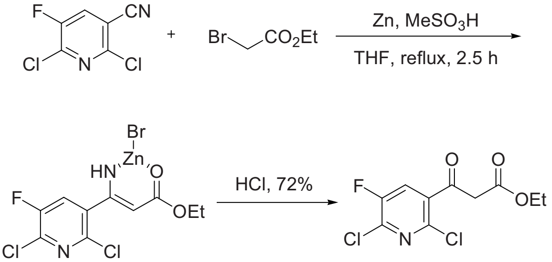
The Zn enolate itself is a *C*-enolate (in the crystal form), but for the reaction to occur, it equilibrates back into an *O*-enolate



Example 1, Preparation of the statin side chain[5]

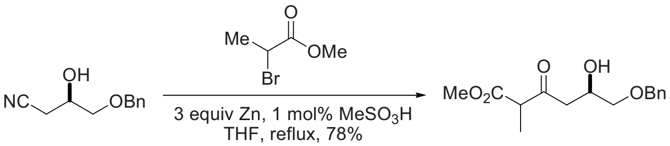


Example 2[6]

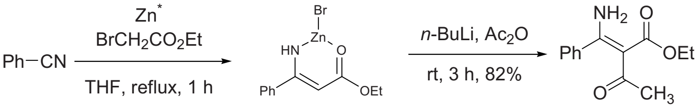


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_24,

Example 3[7]



Example 4, The first chemoselective tandem acylation of the Blaise reaction intermediate[9]



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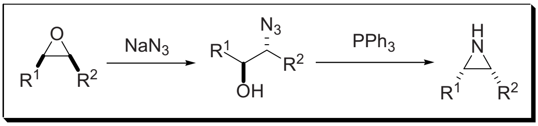
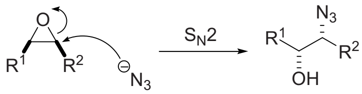
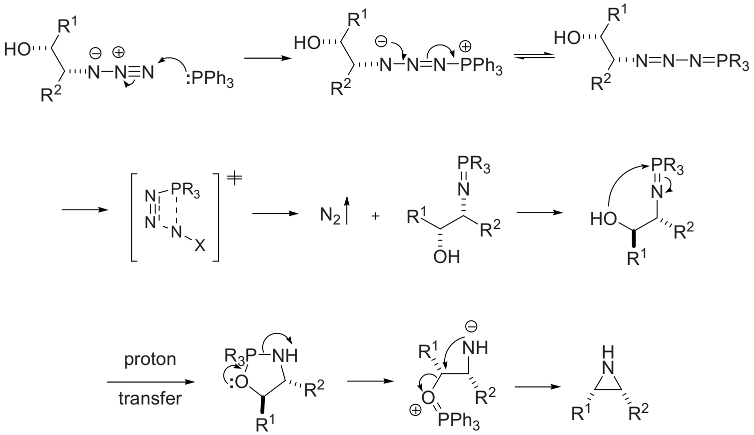
Blum–Ittah aziridine synthesis

Ring opening of oxiranes using azide followed by PPh_3-reduction of the intermediate azido-alcohol to give the corresponding aziridines.

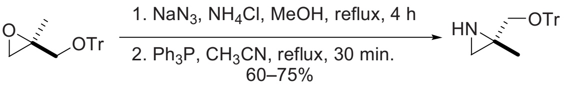




Regardless of the regioselectivity of the S_N2 reaction of the azide, the ultimate stereochemical outcome for the aziridine is the same.



Example 1[3]



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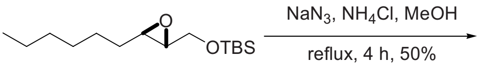
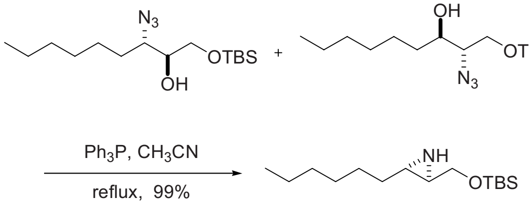


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_25,



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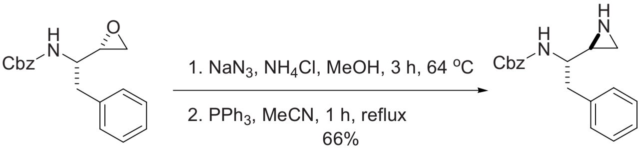

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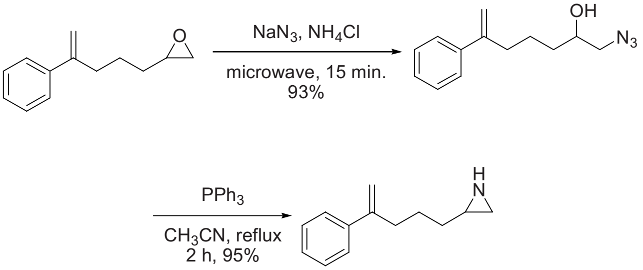

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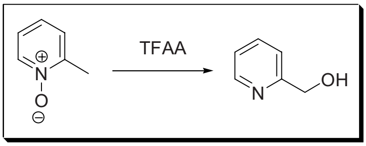
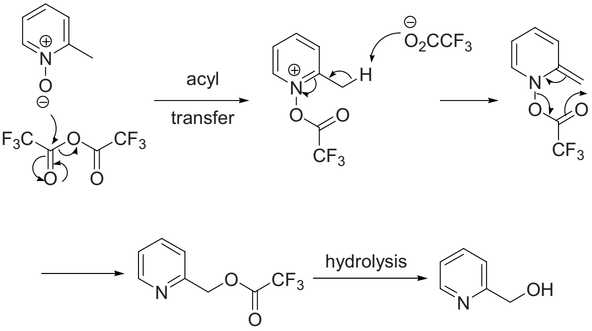
Boekelheide reaction

Treatment of 2-methylpyridine *N*-oxide with trifluoroacetic anhydride, or acetic, anhydride gives rise to 2-hydroxymethylpyridine.



TFAA, trifluoroacetic anhydride



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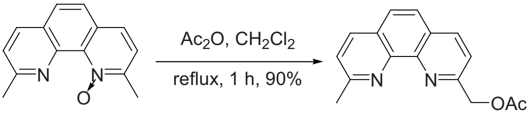

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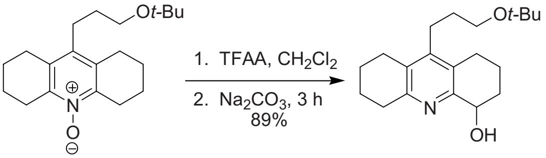

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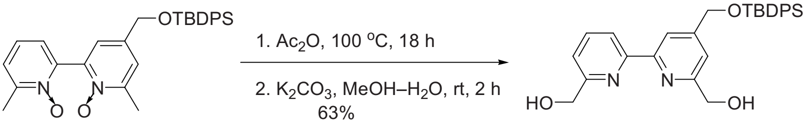

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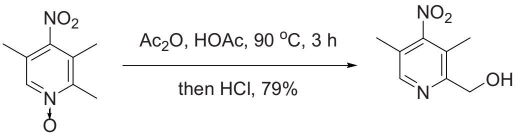
Example 4[9]



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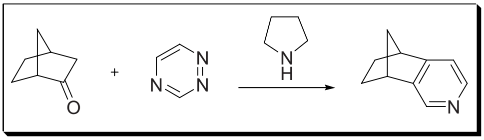
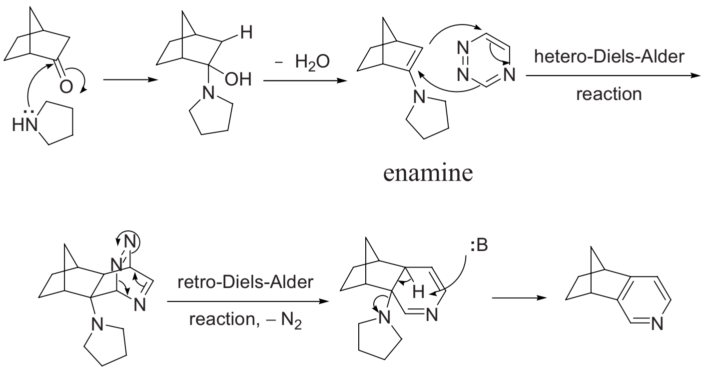
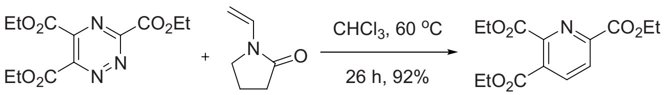
Boger pyridine synthesis

Pyridine synthesis *via* hetero-Diels–Alder reaction of 1,2,4-triazines and dienophiles (e.g., enamine) followed by extrusion of N_2.

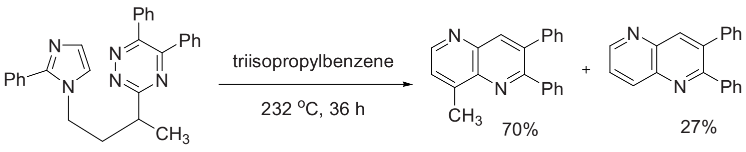




Example 1[3]



Example 2, Intramolecular Boger pyridine synthesis[8]



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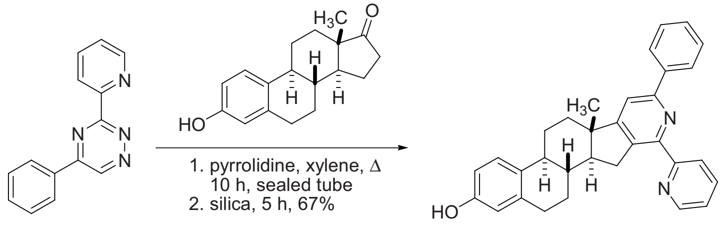
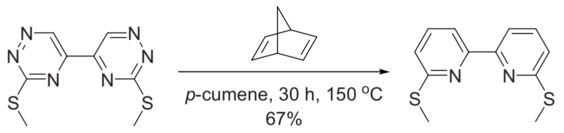
Example 3[10]



Example 4[11]



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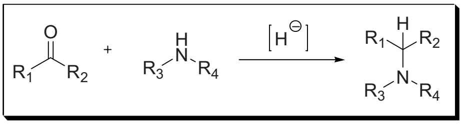
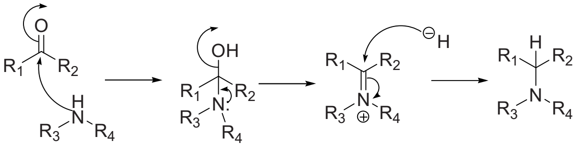
Borch reductive amination

Reduction (often using $NaCNBH_3$) of the imine, formed by an amine and a carbonyl, to afford the corresponding amine—basically, reductive amination.





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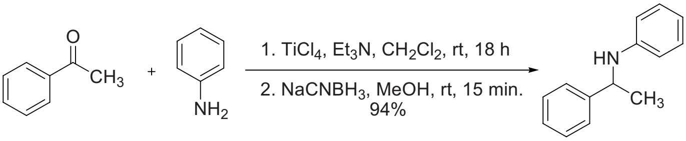
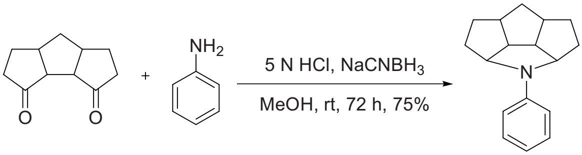


Example 2[5]



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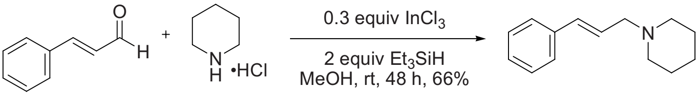

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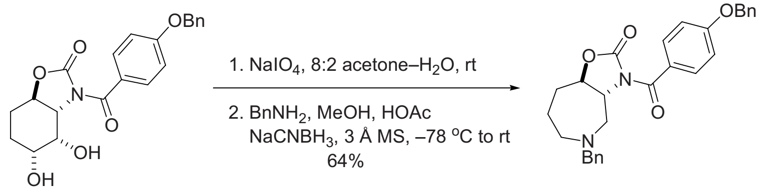
Example 4[9]



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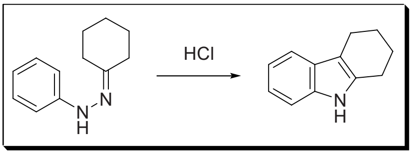
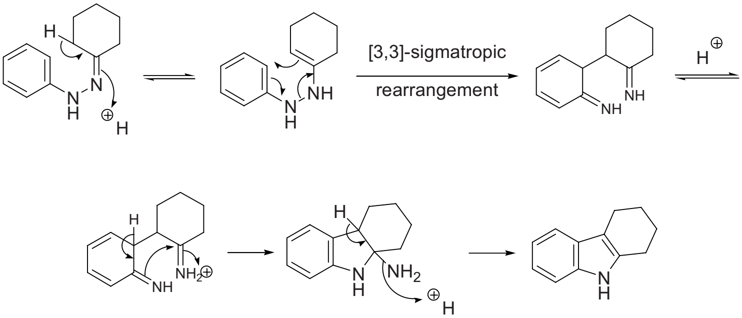
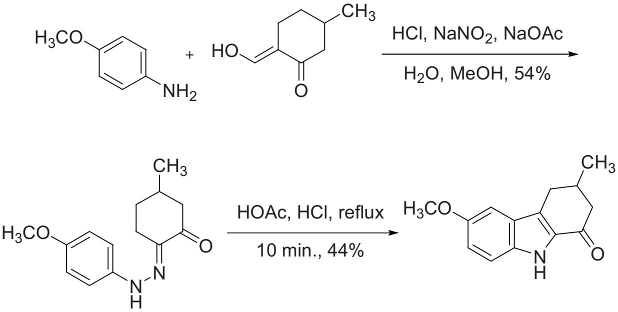
Borsche–Drechsel cyclization

Tetrahydrocarbazole synthesis from cyclohexanone phenylhydrazone. *Cf.* Fischer indole synthesis.

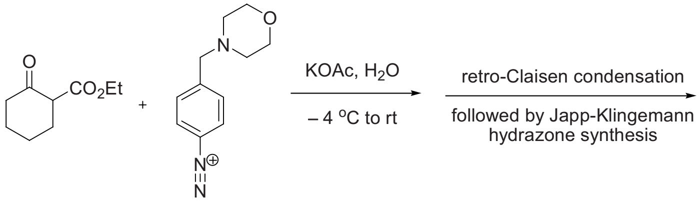




Example 1[6]



Example 2[10]



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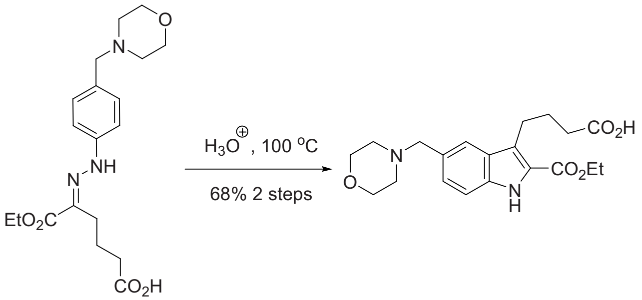
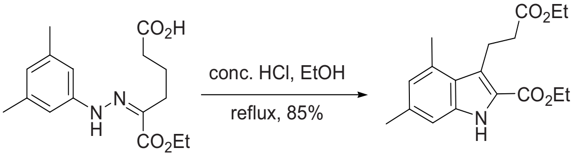


Example 3[10]



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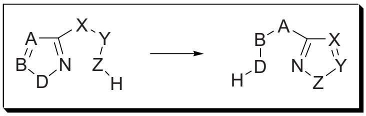
Boulton–Katritzky rearrangement

Rearrangement of one five-membered heterocycle into another under thermolysis.



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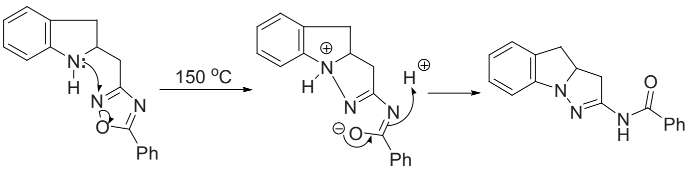
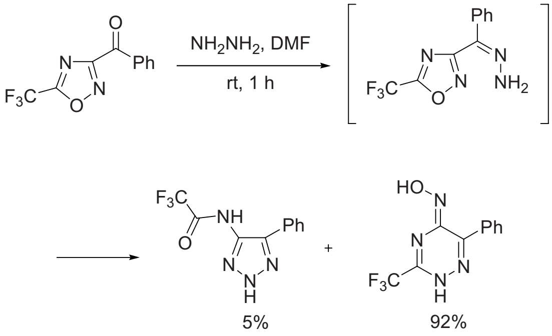
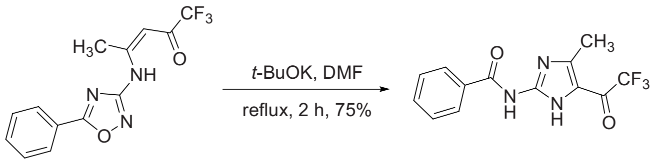


Example 2, Hydrazinolysis[7]



Example 4[3]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_30,

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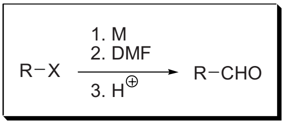
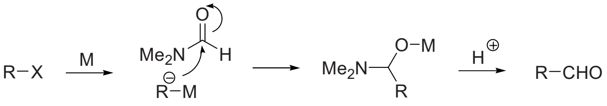
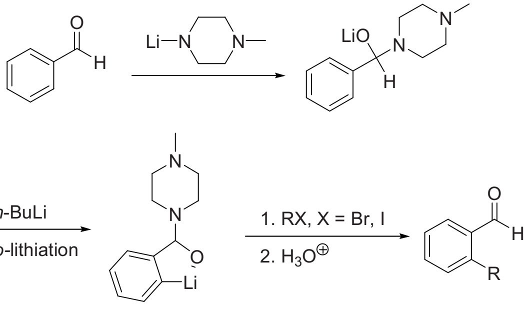
Bouveault aldehyde synthesis

Formylation of an alkyl or aryl halide to the homologous aldehyde by transformation to the corresponding organometallic reagent then addition of DMF (M = Li, Mg, Na, and K).





Comins modification:[4]



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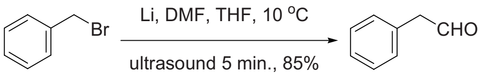

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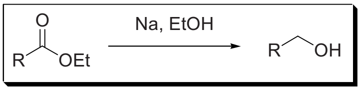
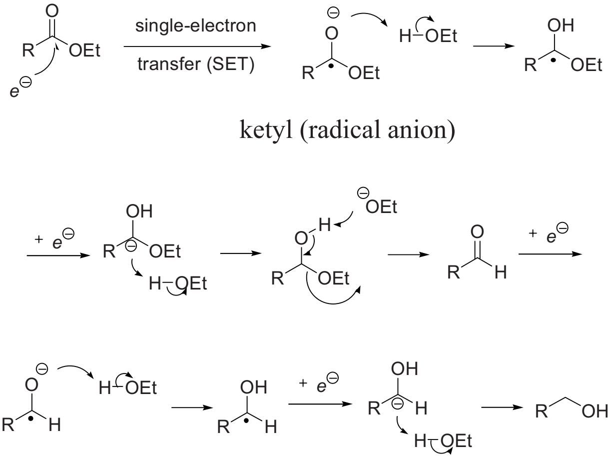
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_31,

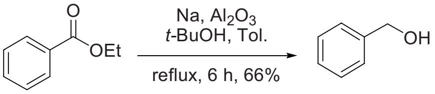
Bouveault–Blanc reduction

Reduction of esters to the corresponding alcohols using sodium in an alcoholic solvent.





Example[2]



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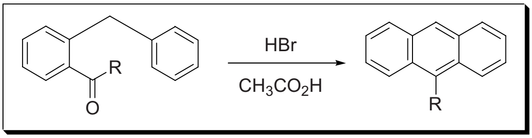
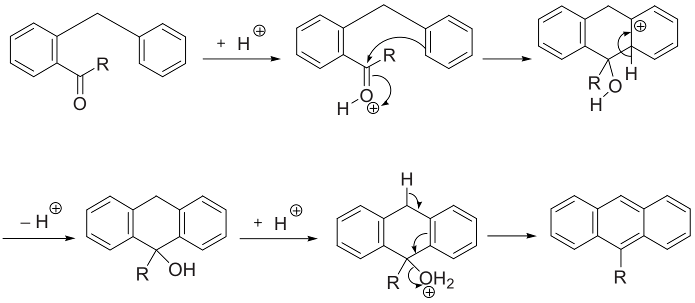
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_32,

Bradsher reaction

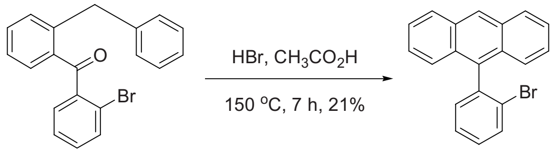
The intramolecular Bradsher cyclization refers to the acid-catalyzed aromatic cyclodehydration of *ortho*-acyl diarylmethanes to form anthracenes. On the other hand, the intermolecular Bradsher cycloaddition often involves the Diels–Alder reaction of a pyridium with a vinyl ether or vinyl sulfide.



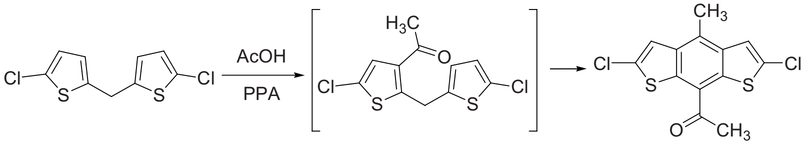
anthracene



Example 1, Intramolecular Bradsher reaction[2]

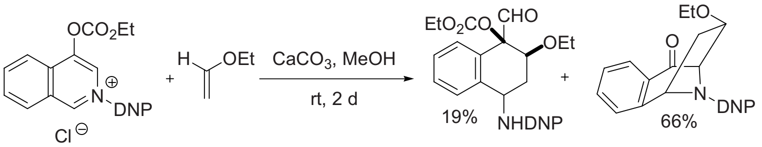


Example 2, Intramolecular Bradsher reaction[5]

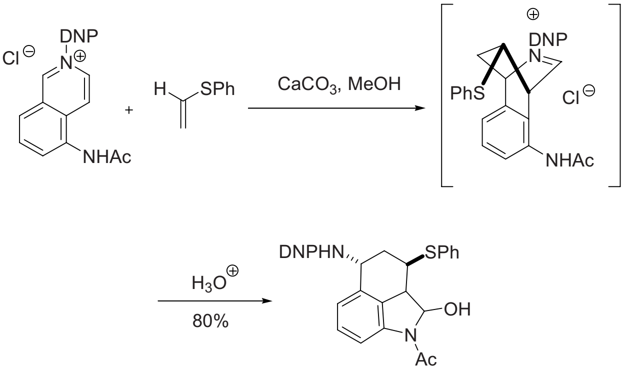


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_33,

Example 3, Intermolecular Bradsher cycloaddition (DNP = dinitrophenyl)[8]



Example 4, Intermolecular Bradsher cycloaddition[10]



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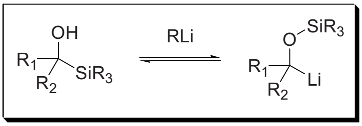
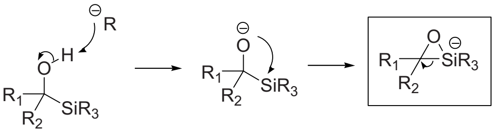
Brook rearrangement

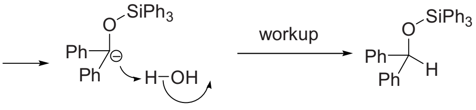
Rearrangement of α-silyl oxyanions to α-silyloxy carbanions *via* a reversible process involving a pentacoordinate silicon intermediate is known as the [1,2]-Brook rearrangement, or [1,2]-silyl migration.

[1,2]-Brook rearrangement

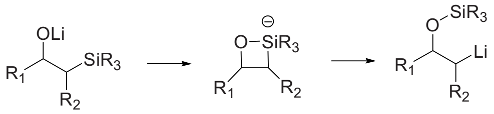




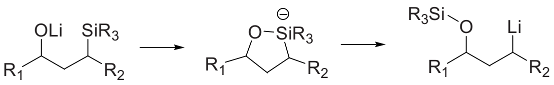
pentacoordinate silicon intermediate



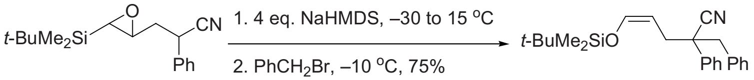
[1,3]-Brook rearrangement



[1,4]-Brook rearrangement



Example 1[6]



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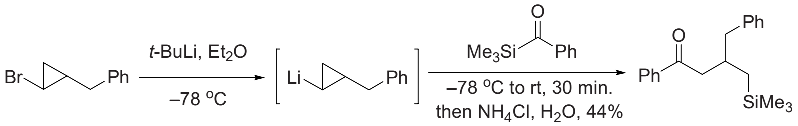
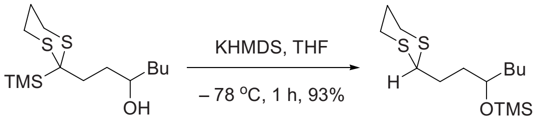
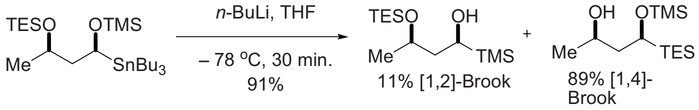
Example 2, [1,2]-Brook rearrangement followed by a retro-[1,5]-Brook rearrangement[8]



Example 3, [1,5]-Brook rearrangement[9]



Example 4, Retro-[1,4]-Brook rearrangement[10]



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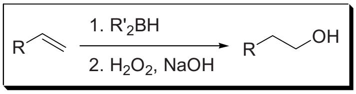
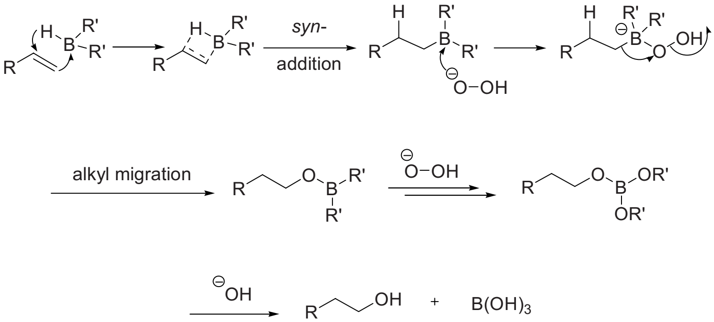
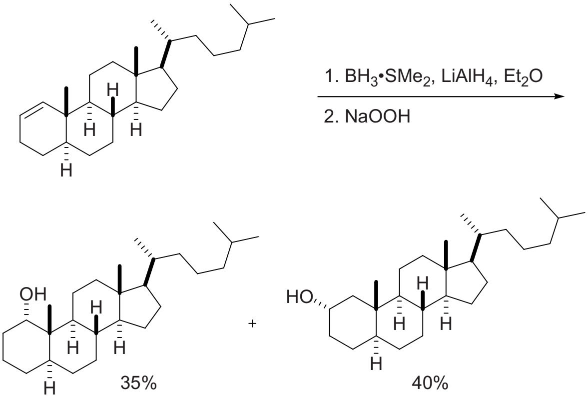
Brown hydroboration

Addition of boranes to olefins followed by alkalinic oxidation of the organoborane adducts to afford alcohols.

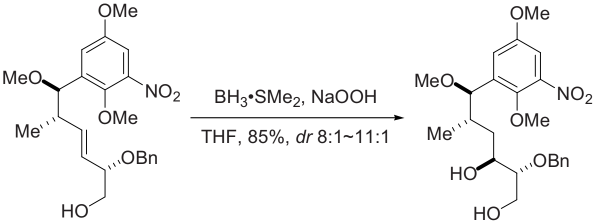




Example 1[2]



Example 2[7]



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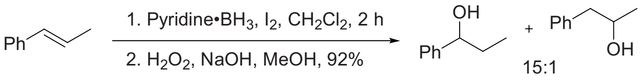
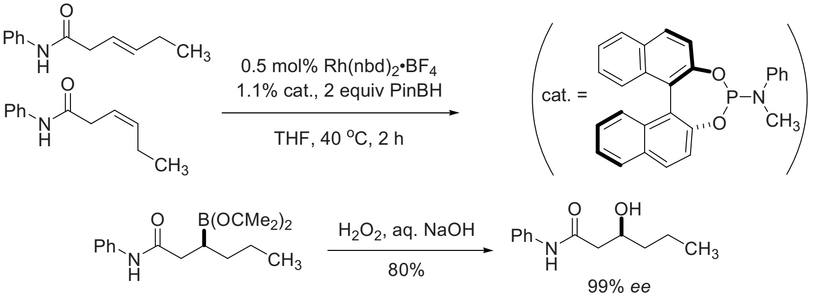
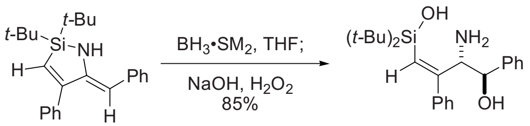
Example 3[8]



Example 4, Asymmetric hydroboration[10]



Example 5[11]



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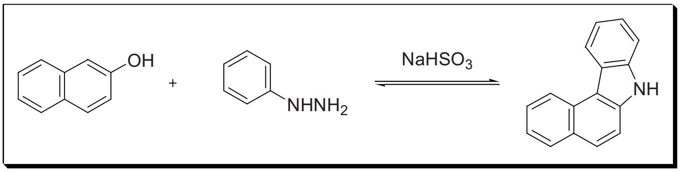
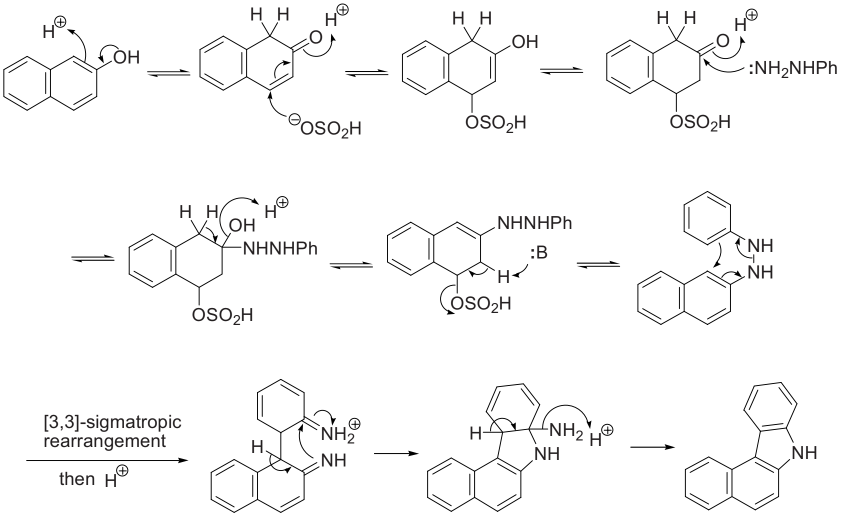
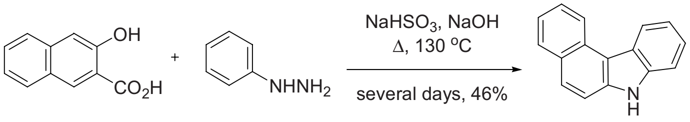
Bucherer carbazole synthesis

Carbazole formation from naphthols and aryl hydrazines promoted by sodium bisulfite. Another variant of the Fischer indole synthesis.

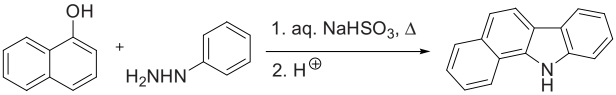




Example 1[2]



Example 2[3]



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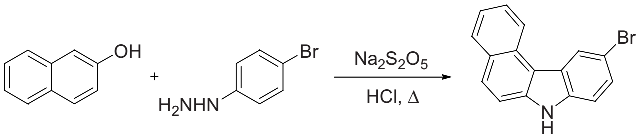
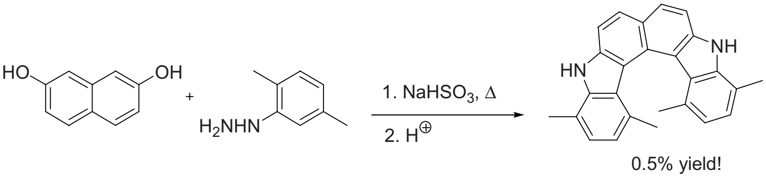
Example 3[7]



Example 3[4]



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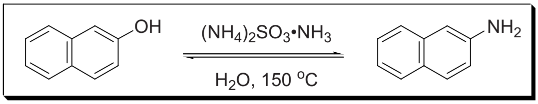
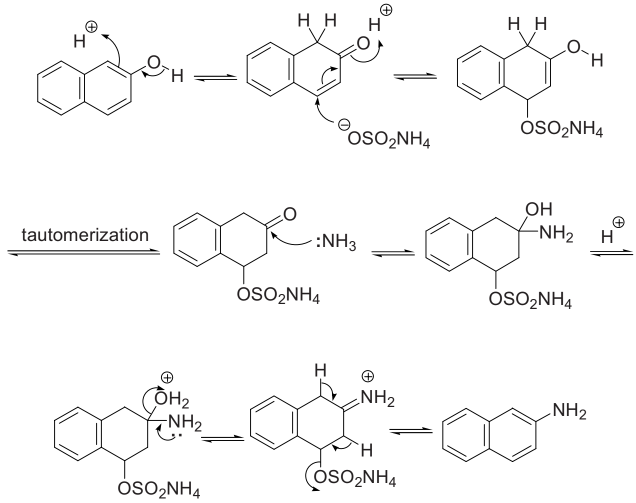
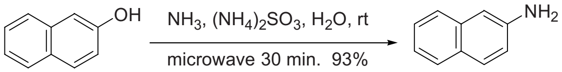
Bucherer reaction

Transformation of β-naphthols to β-naphthylamines using ammonium sulfite.

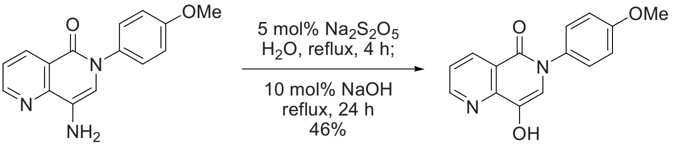




Example 1, Although the classic Bucherer reaction requires high temperatures, it may be carried out at room temperature with the aid of microwave (150 watts):[7]



Example 2, Retro-Bucherer reaction[7]



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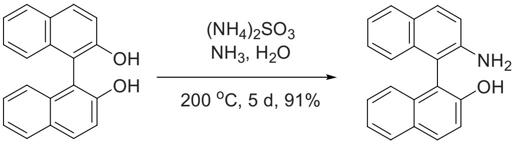
Example 3[8]



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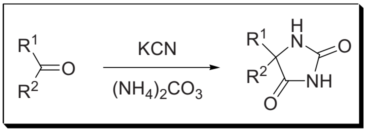
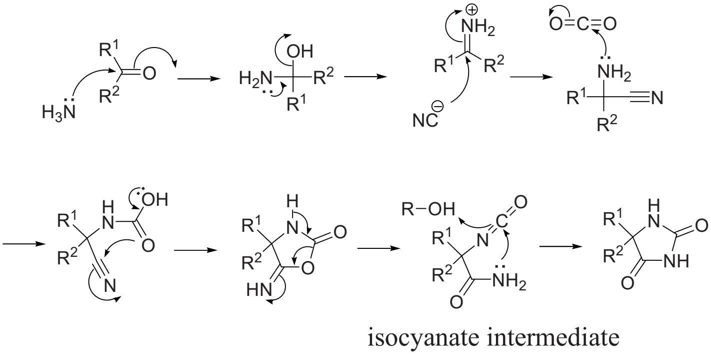
Bucherer–Bergs reaction

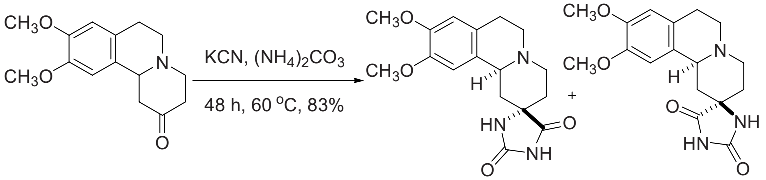
Formation of hydantoins from carbonyl compounds with potassium cyanide (KCN) and ammonium carbonate [$(NH_4)_2CO_3$] or from cyanohydrins and ammonium carbonate. It belongs to the category of multiple component reactions (MCRs).



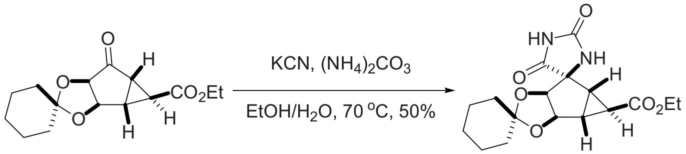
$$(NH_4)_2CO_3 = 2\ NH_3 + CO_2 + H_2O$$



Example 1[5]



Example 2[6]



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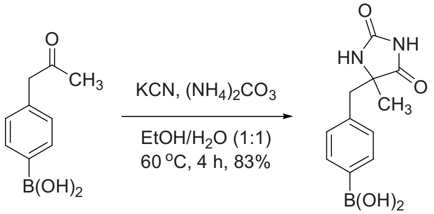
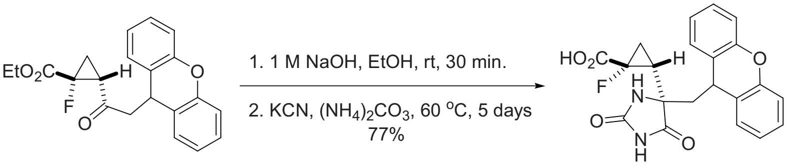
Example 3[7]



Example 4[9]



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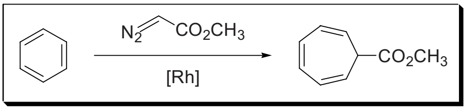
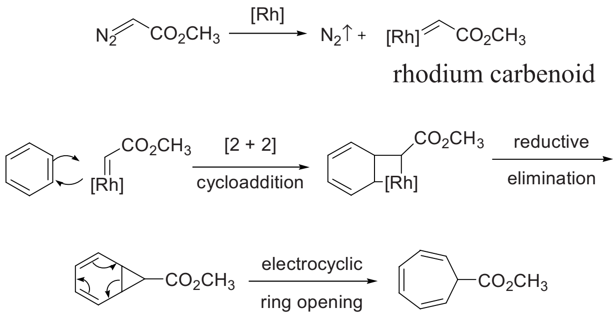
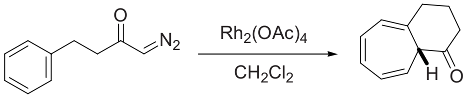
Büchner ring expansion

Reaction of a phenyl ring with diazoacetic esters to give cyclohepta-2,4,6-trienecarboxylic acid esters. Intramolecular Büchner reaction is more useful in synthesis. *Cf.* Pfau–Platter azulene synthesis.

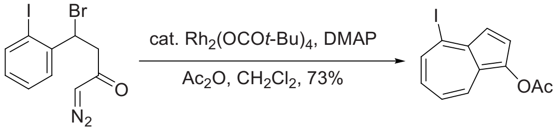




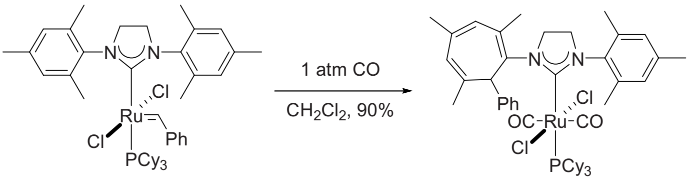
Example 1, Intramolecular Büchner reaction[7]



Example 2, Intramolecular Büchner reaction[8]

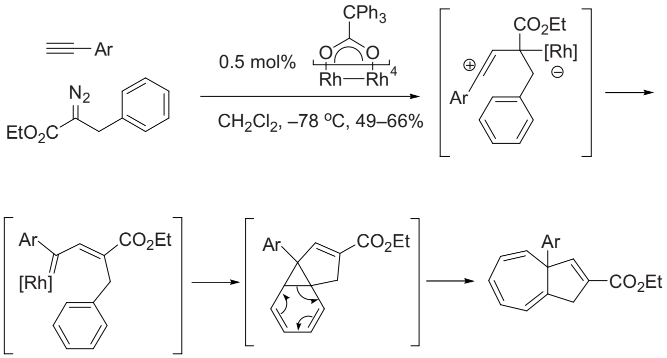


Example 3, An intramolecular Büchner reaction within the Grubbs' catalyst![9]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_39,

Example 4[10]



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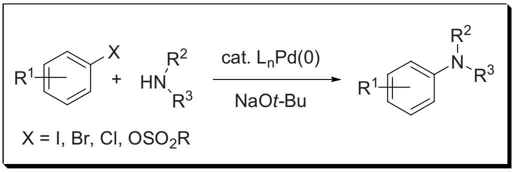
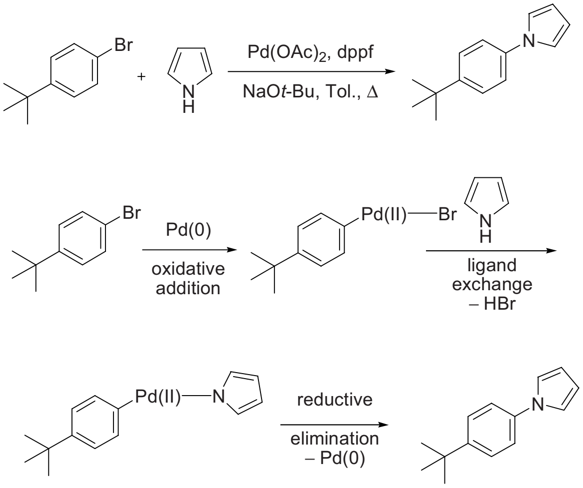
Buchwald–Hartwig amination

The Buchwald–Hartwig amination is an exceedingly general method for generating an aromatic amine from an aryl halide or an aryl sulfonates. The key feature of this methodology is the use of catalytic palladium modulated by various electron-rich ligands. Strong bases, such as sodium *tert*-butoxide, are essential for catalyst turnover.

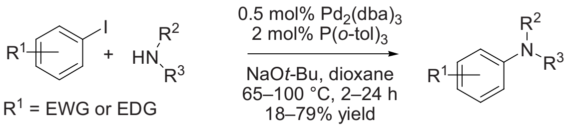


Mechanism:



The catalytic cycle is shown on the next page.

Example 1[3]



R^1 = EWG or EDG
amine = 2° cyclic or acyclic
amine = 1° aliphatic: low yield, unless R^1 *ortho*

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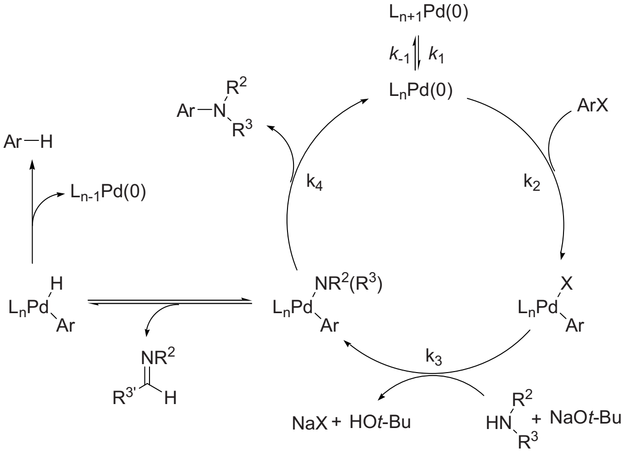
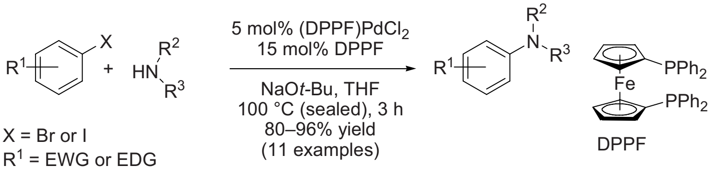
Catalytic cycle:



Pd(BINAP)$_2$ catalyzed

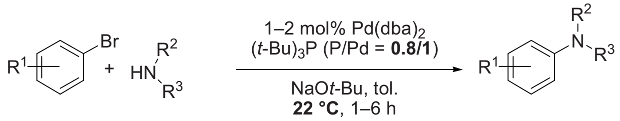
$$\boxed{\frac{-\mathrm{d}[\mathrm{ArX}]}{\mathrm{d}t} = \frac{k_1k_2}{k_{-1}[\mathrm{L}]}[\mathrm{ArX}][\mathrm{Pd}]}$$

Example 2[4]



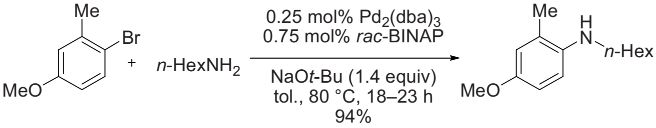
X = Br or I
R^1 = EWG or EDG
amine = 2° acyclic (one example)
amine = 1° aliphatic or aromatic

Example 3, Room temperature Buchwald–Hartwig amination[9]

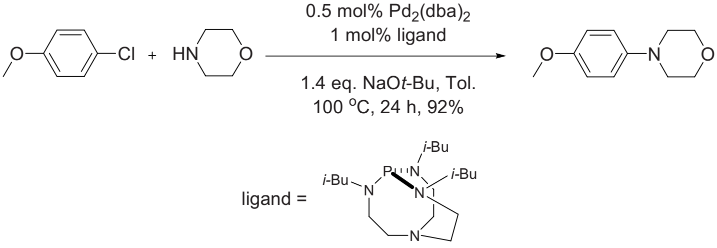


R^1 = EDG or EWG
amine = 2° cyclic or acyclic: aromatic, aliphatic, or azoles
amine = 1° anilines: **no aliphatic**

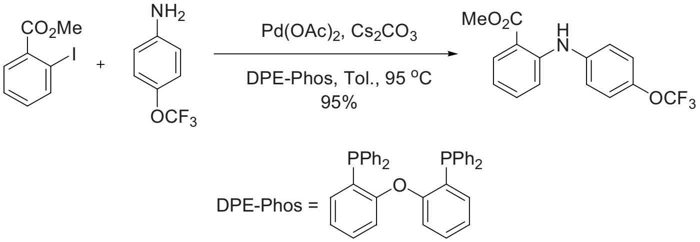
Example 4[10]



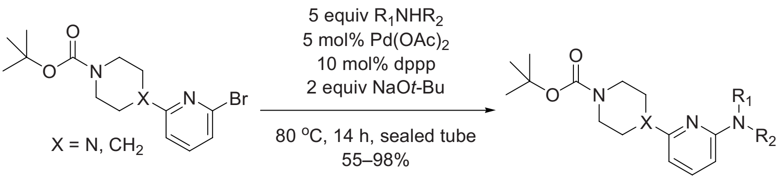
Example 5[11]



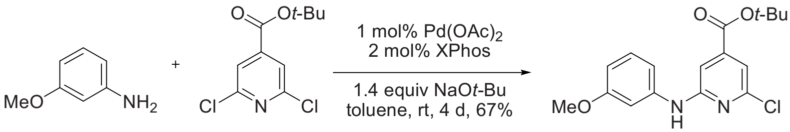
Example 6[12]



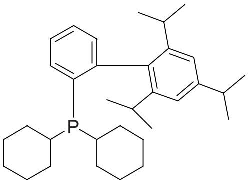
Example 7, Amination of volatile amines[14]



Example 8[15]



XPhos =



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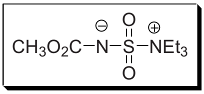
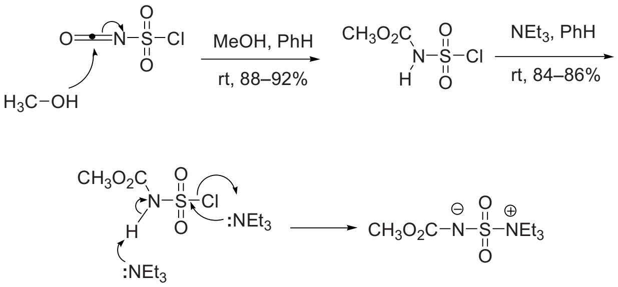
Burgess reagent



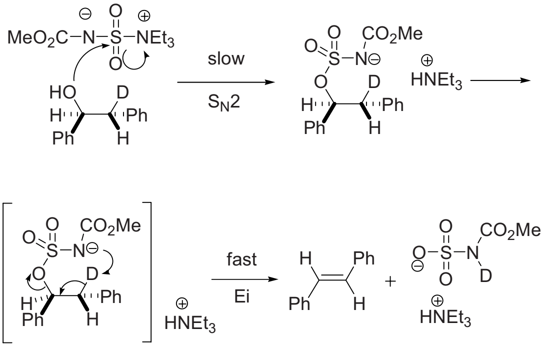
$$CH_3O_2C-\overset{\ominus}{N}-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-\overset{\oplus}{N}Et_3$$

The Burgess reagent [(methoxycarbonylsulfamoyl)triethylammonium hydroxide inner salt], a neutral, white crystalline solid, is efficient at generating olefins from secondary and tertiary alcohols where the first-order thermolytic Ei (during the elimination takes place—the two groups leave at about the same time and bond to each other concurrently) mechanism prevails.

Preparation[2]

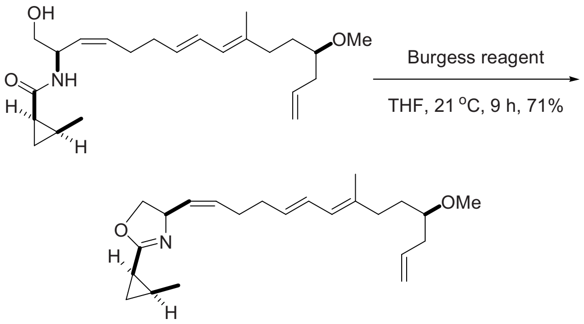


Mechanism[5]

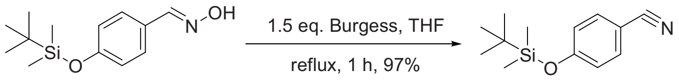


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_41,

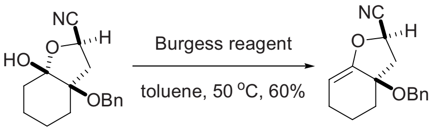
Example 1, On primary alcohols, the hydroxyl group does not eliminate but rather undergoes substitution[3]



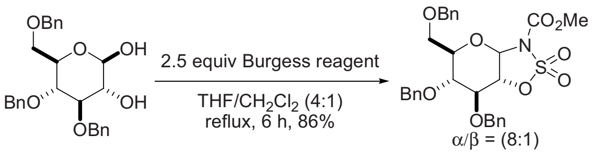
Example 2[6]



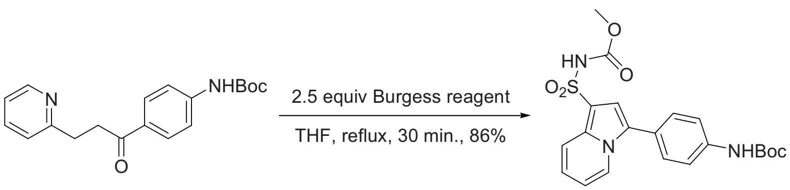
Example 3[7]



Example 4[8]



Example 5[10]



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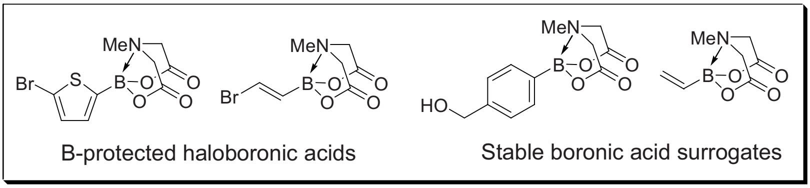
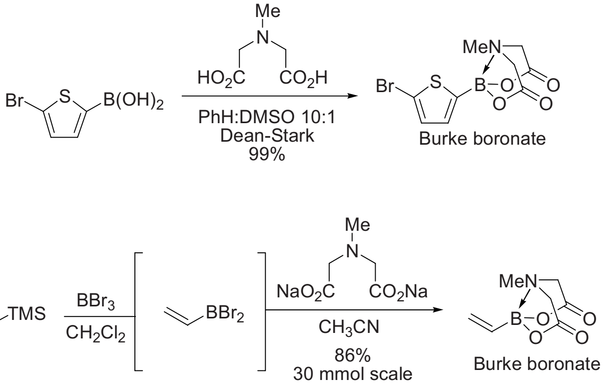
Burke boronates



Burke boronates can serve as B-protected haloboronic acids for a wide variety of applications in iterative cross-coupling.[1–6] The corresponding boronic acids can be liberated using mild aqueous bases such as NaOH or $NaHCO_3$.[1–4] Burke boronates are also compatible with many synthetic reagents, enabling the synthesis of complex boronic acids from simple B-containing starting materials.[3,6] They can also serve as stable building blocks for cross-coupling, i.e., under aqueous basic conditions, the corresponding boronic acid is released and coupled in situ.[2,3,7] Moreover, Burke boronates are highly crystalline, monomeric, free-flowing solids that are indefinitely stable to benchtop storage under air and compatible with silica gel chromatography.[1–3,6]

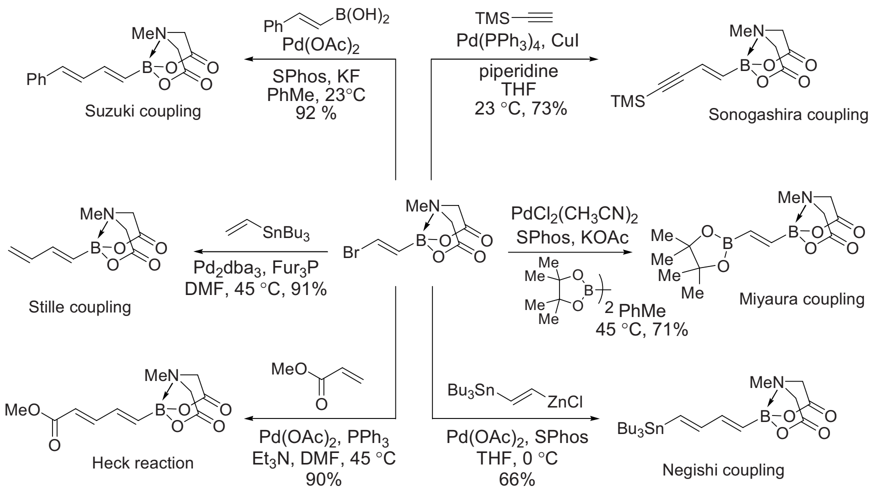
Preparation:[1,2,4,6]



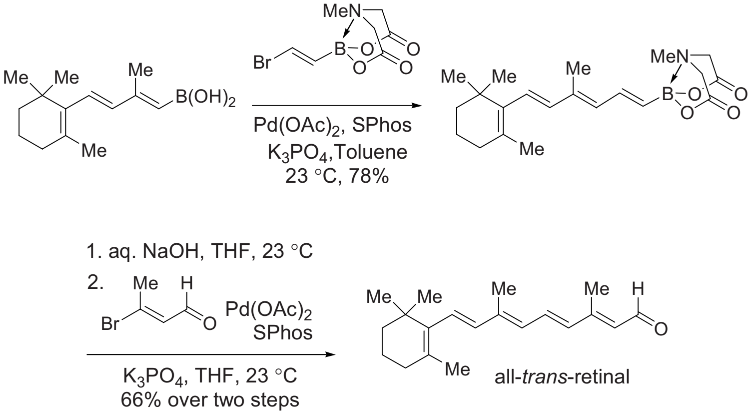
Burke boronates can be conveniently prepared from the corresponding boronic acids via complexation with *N*-methyliminodiacetic acid (MIDA)[1,4] or from dibromoboranes via complexation with $MIDA^{2-}Na^{+}_{2}$.[2,6] Alternatively, many of these building blocks are now commercially available.

J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_42,

Example 1[2]
A wide range of selective couplings can be performed at the halide terminus of a B-protected haloboronic acid.

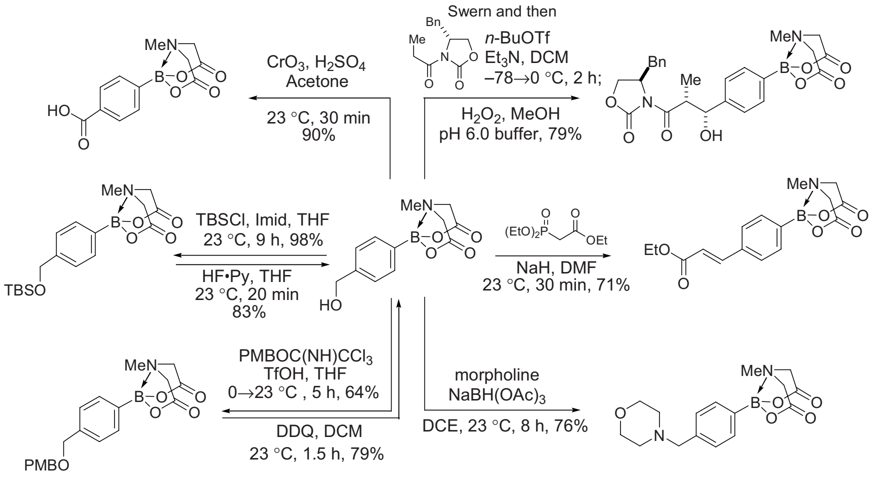


Example 2[2]
Small molecule natural products can be prepared via iterative cross-coupling with B-protected haloboronic acids.



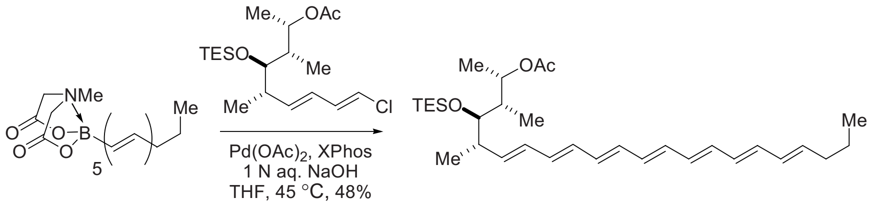
Example 3[3]

Burke boronates are stable to a wide range of synthetic reagents, including acids, non-aqueous bases, oxidants, reductants, electrophiles, and soft nucleophiles. This reagent compatibility enables multistep synthesis of complex boranes from simple boron-containing starting materials.



Example 4[2]

Burke boronates can be hydrolyzed *in situ* under aqueous basic coupling conditions, as evidenced by this synthesis of the complex polyene skeleton of amphotericin B.



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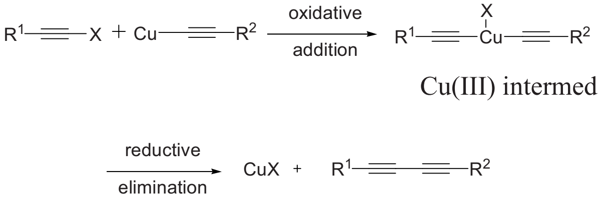
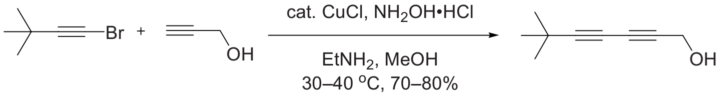
Cadiot–Chodkiewicz coupling

Bis-acetylene synthesis from alkynyl halides and alkynyl copper reagents. *Cf.* Castro–Stephens reaction.

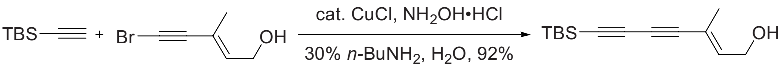


Cu(III) intermediate

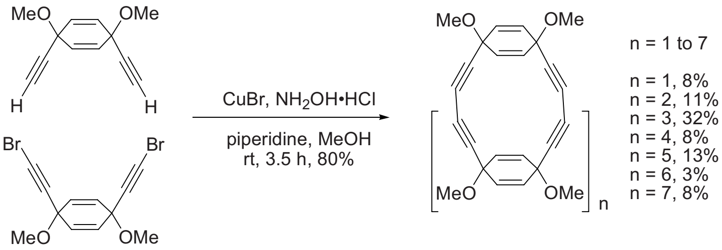
Example 1[3]



Example 2[7]



Example 3[9]



Example 4, Cadiot–Chodkiewicz active template synthesis of rotaxanes and switchable molecular shuttles with weak intercomponent interactions[10]

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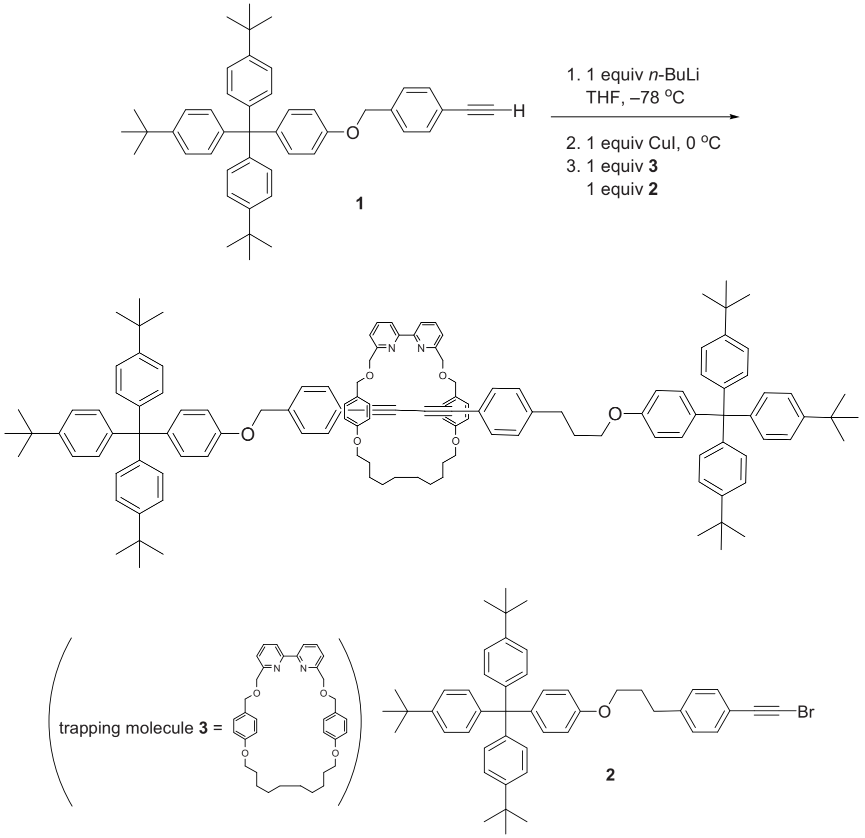

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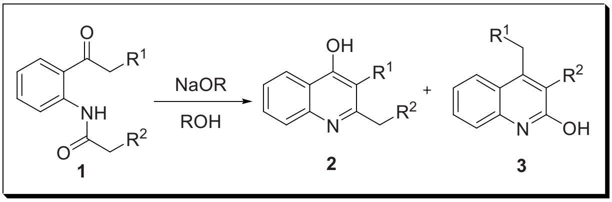
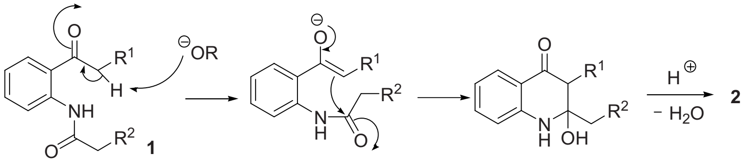
Camps quinoline synthesis

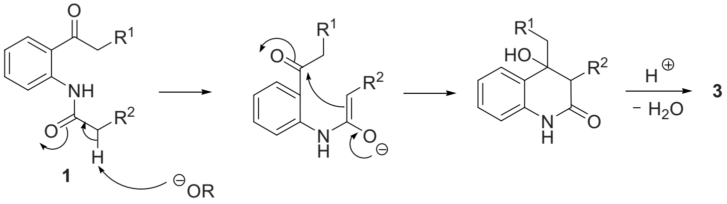
Base-catalyzed intramolecular condensation of a 2-acetamido acetophenone (**1**) to a 2-(and possibly 3)-substituted-quinolin-4-ol (**2**), a 4-(and possibly 3)-substituted-quinolin-2-ol (**3**), or a mixture.



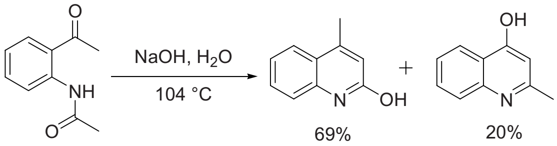
Pathway A:



Pathway B:

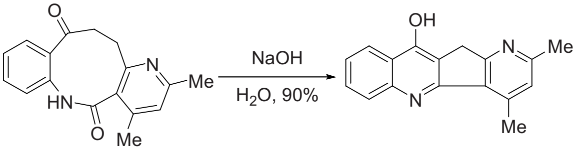


Example 1[1]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_44,

Example 2[6]



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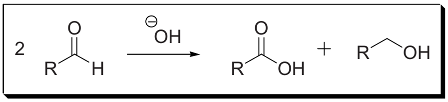
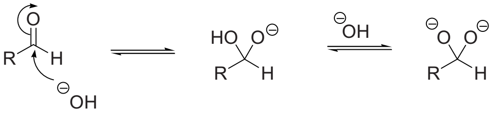
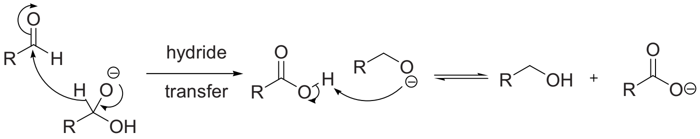
Cannizzaro reaction

Redox reaction between aromatic aldehydes, formaldehyde or other aliphatic aldehydes without α-hydrogen. Base is used to afford the corresponding alcohols and carboxylic acids.



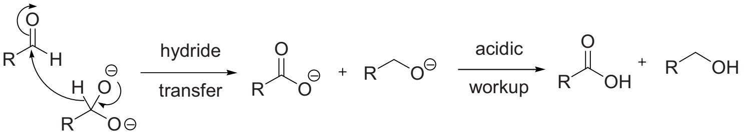


Pathway A:

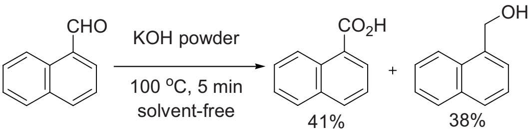


Final deprotonation of the carboxylic acid drives the reaction forward.

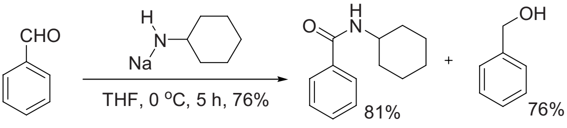
Pathway B:



Example 1[4]

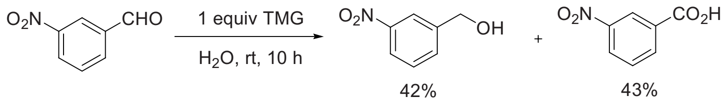


Example 2[6]



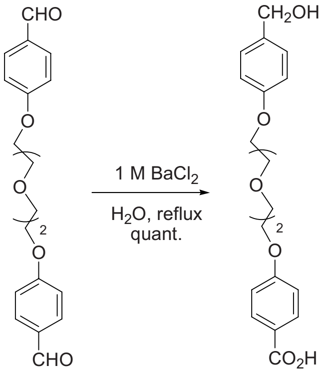
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_45,

Example 3[8]



TMG = 1,1,3,3-tetramethylguanidine

Example 4, Desymmetrization by intramolecular Cannizzaro reaction[9]



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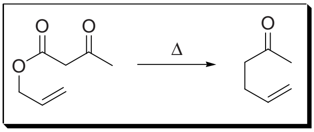
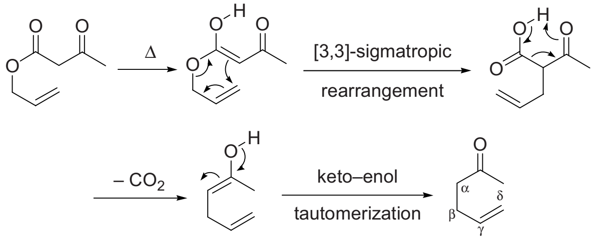
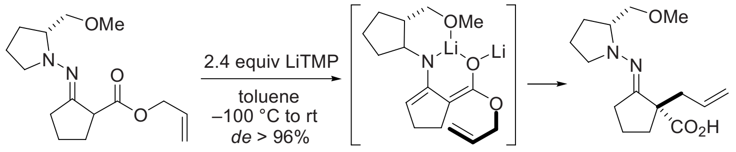
Carroll rearrangement

Thermal rearrangement of β-ketoesters followed by decarboxylation to yield γ-unsaturated ketones *via* anion-assisted Claisen rearrangement. It is a variant of the Claisen rearrangement (page 117).

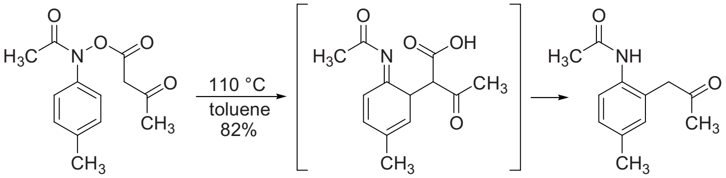




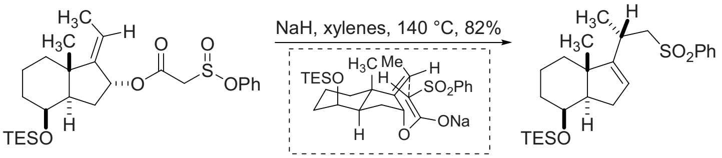
Example 1, Asymmetric Carroll rearrangement[4,5]



Example 2, Hetero-Carroll rearrangement[6]



Example 3[7]



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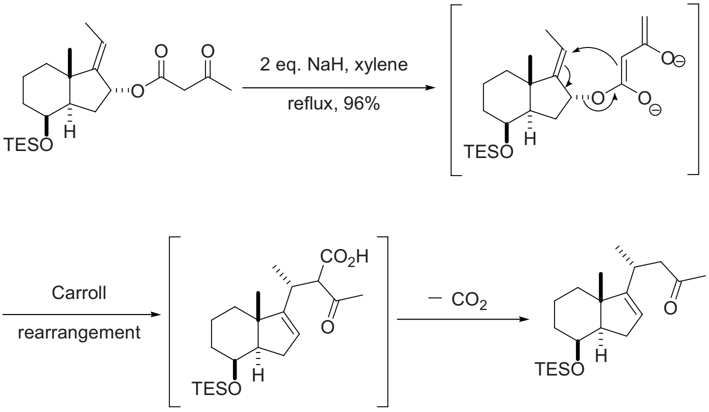
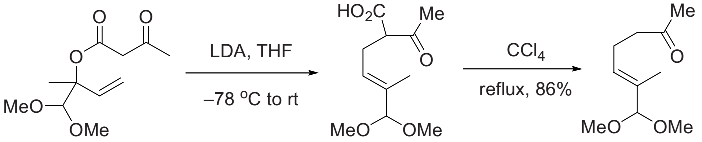
Example 4, Similar to Example 3[7]



Example 5[8]



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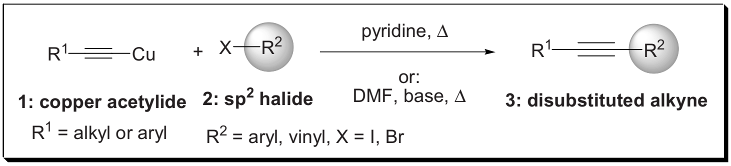
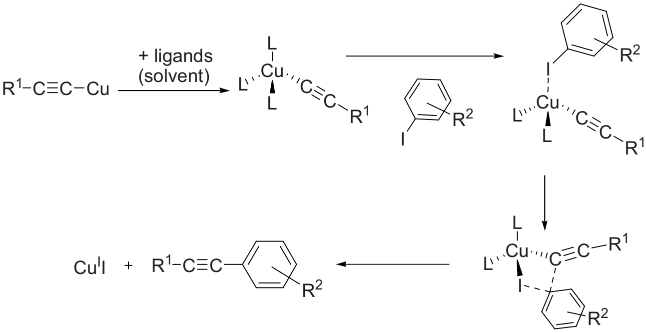
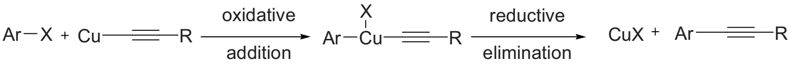
Castro–Stephens coupling

Aryl–acetylene synthesis, *Cf.* Cadiot–Chodkiewicz coupling and Sonogashira coupling. The Castro–Stephens coupling uses stoichiometric copper, whereas the Sonogashira variant uses catalytic palladium and copper.



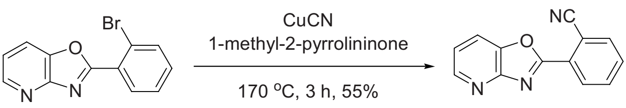


An alternative mechanism similar to that of the Cadiot–Chodkiewicz coupling:

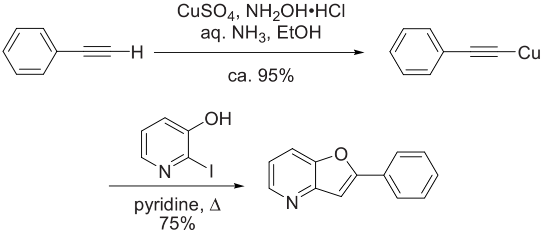


Cu(III) intermediate

Example 1, A variant, also known as the Rosenmund–von Braun synthesis of aryl nitriles[2]



Example 2[4]



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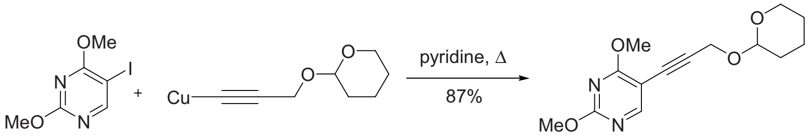
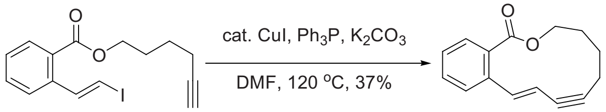
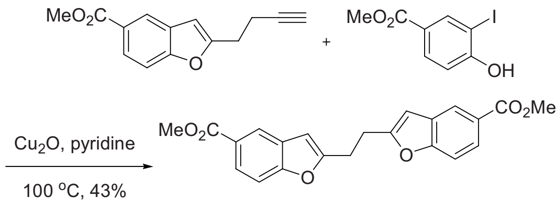
Example 3[5]



Example 4[8]



Example 5, *In situ* Castro–Stephens reaction[10]



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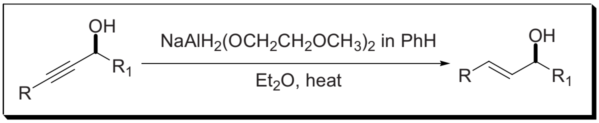
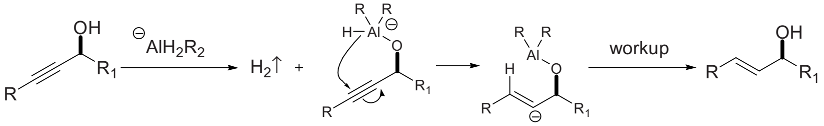
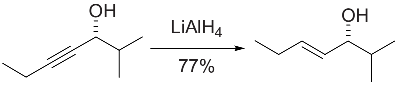
Chan alkyne reduction

Stereoselective reduction of acetylenic alcohols to *E*-allylic alcohols using **s**odium bis(2-**m**ethoxy**e**thoxy)**a**luminum **h**ydride (SMEAH, also known as Red-Al) or LiAlH$_4$.

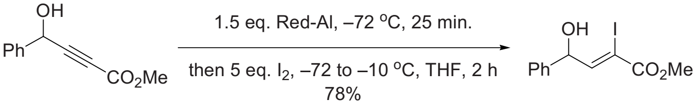




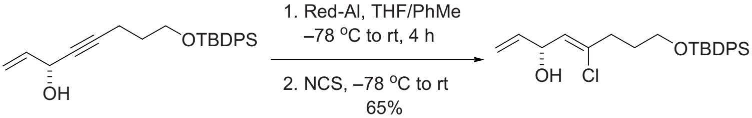
Example 1[3]



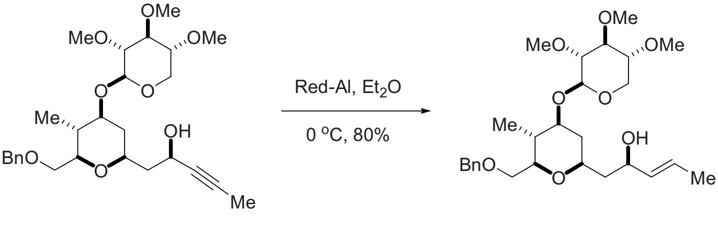
Example 2[4]



Example 3[6]



Example 4[7]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_48,

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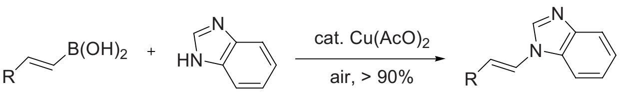
Chan–Lam C–X coupling reaction

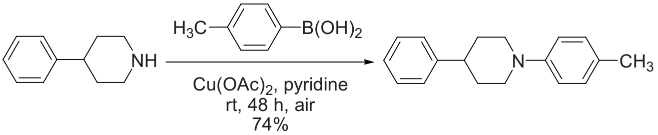
Arylation of a wide range of NH/OH/SH substrates by oxidative cross-coupling with boronic acids in the presence of catalytic cupric acetate and either triethylamine or pyridine at room temperature in air. The reaction works for amides, amines, anilines, azides, hydantoins, hydrazines, imides, imines, nitroso, pyrazinones, pyridones, purines, pyrimidines, sulfonamides, sulfinates, sulfoximines, ureas, alcohols, phenols, and thiols. It is also the mildest method for *N*/*O*-vinylation. The boronic acids can be replaced with siloxanes or stannanes. The mild condition of this reaction is an advantage over Buchwald–Hartwig's Pd-catalyzed cross-coupling. The Chan–Lam C–X bond cross-coupling reaction is complementary to Suzuki–Miyaura's C–C bond cross-coupling reaction.

$$\text{Ar—M} \quad + \quad \text{H—XR} \xrightarrow[\text{air}]{\text{cat. Cu(AcO)}_2} \text{Ar—XR}$$

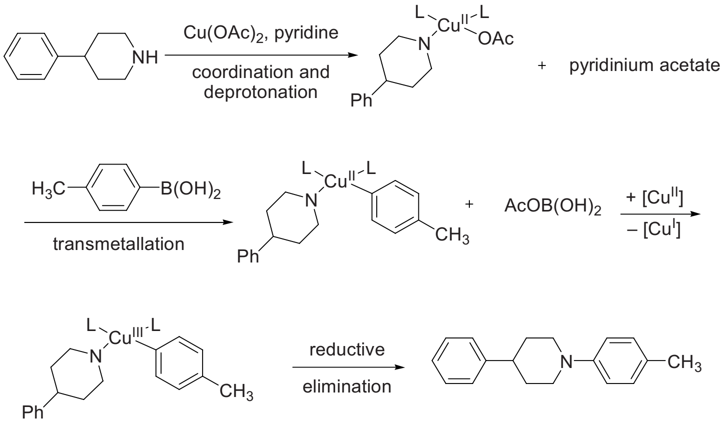
$M = B(OH)_2, B(OR)_2, B(OR)_3^-, BF_3^-, SnMe_3, Si(OMe)_3.$
$X = N, O, S, Se, Te.$



Example 1[1a,d]



Mechanism:[1c,d,17]



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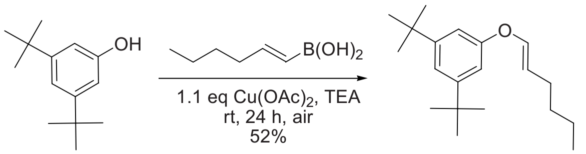
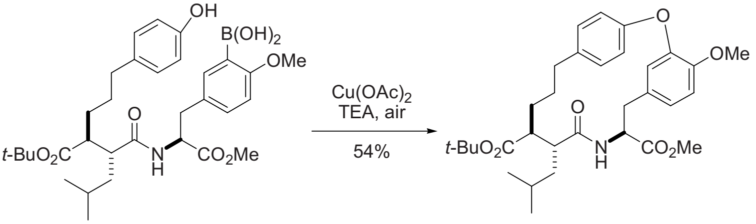
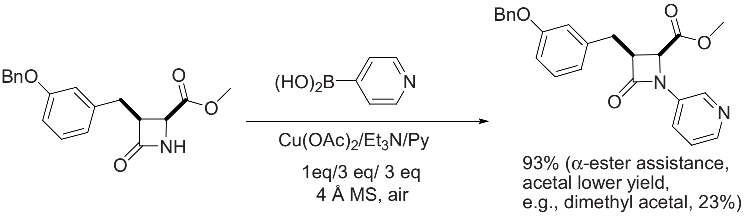
Example 2[4]



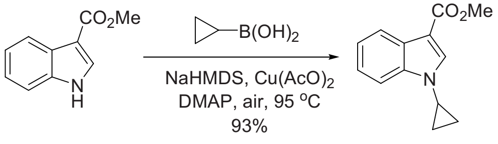
Example 3[5]



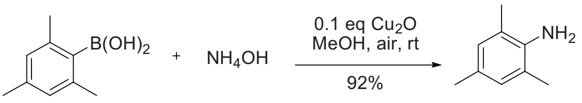
Example 4[13]



Example 5[14]



Example 6[15]



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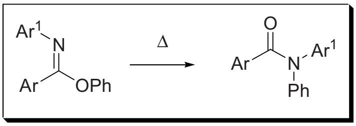
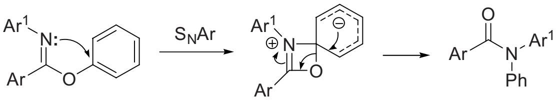
Chapman rearrangement

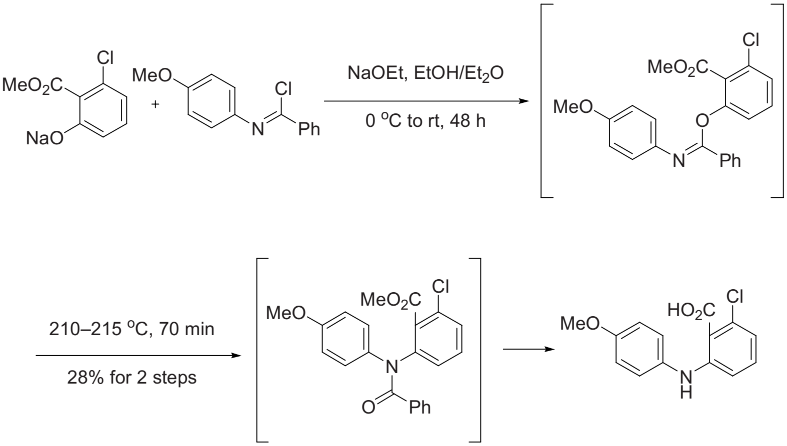
Thermal aryl rearrangement of *O*-aryliminoethers to amides.



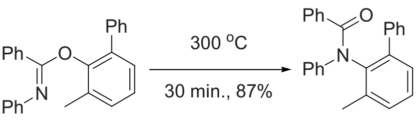


oxazete intermediate

Example 1[2]



Example 2[4]



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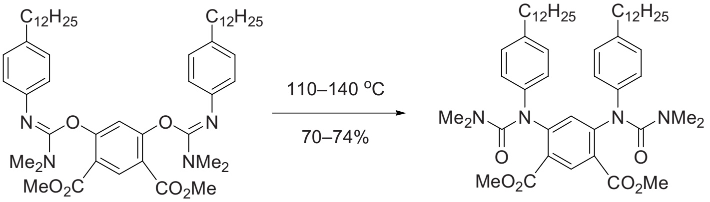
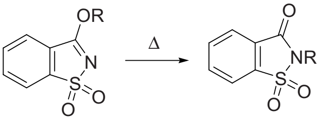
Example 3, Double Chapman rearrangement[10]



Example 4, Chapman-like thermal rearrangement[11]



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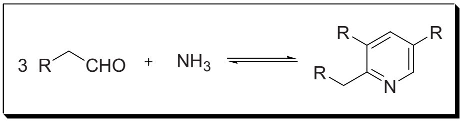
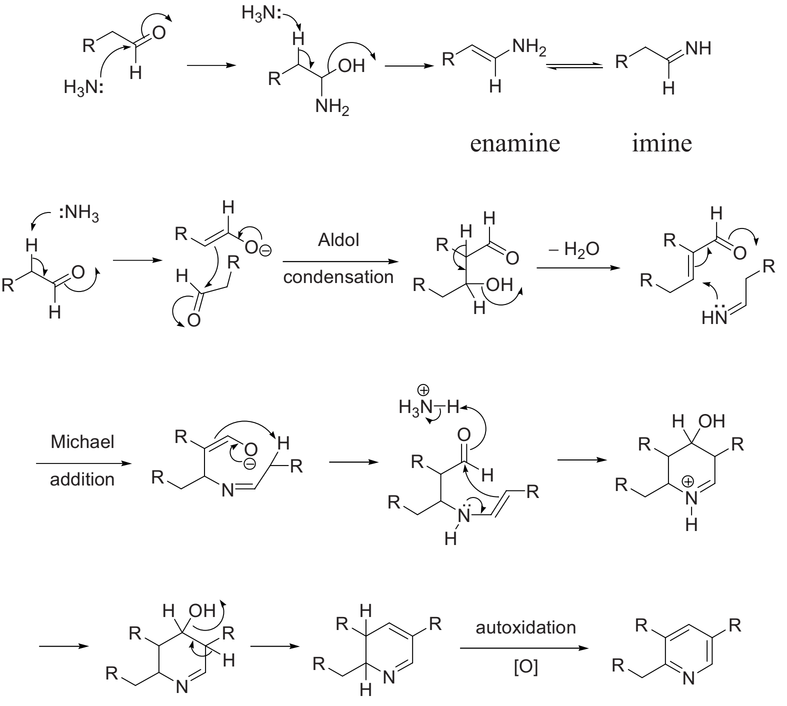
Chichibabin pyridine synthesis

Condensation of aldehydes with ammonia to afford pyridines.





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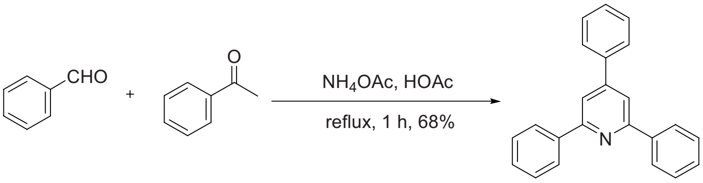

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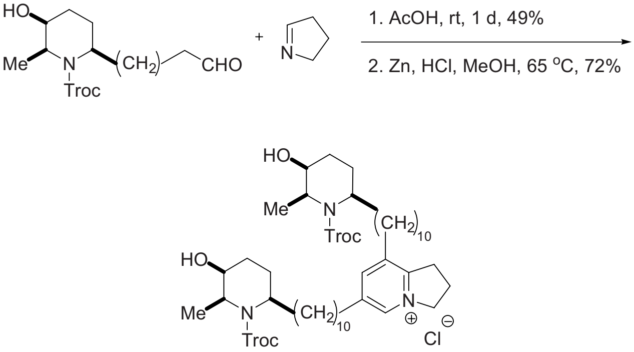
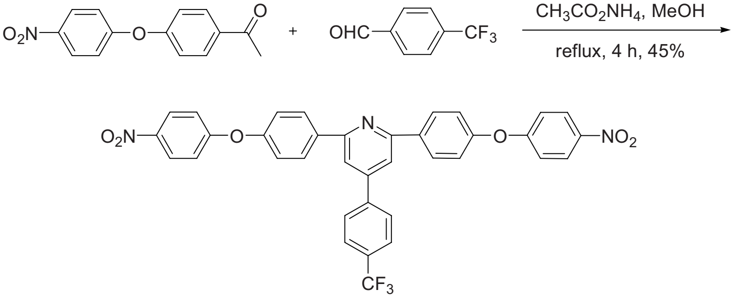
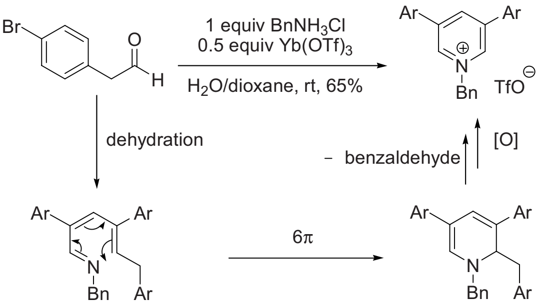
Example 2[8]



Example 3[9]



Example 4, An abnormal Chichibabin reaction[10]



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want to cooperate with the pupil and gave Chichibabin a negative judgment on his Ph.D. work, earning Chichibabin the nickname “the self-educated man.”

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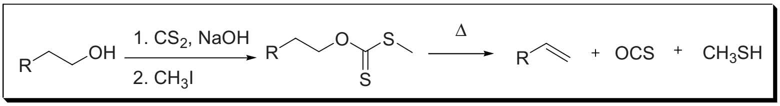
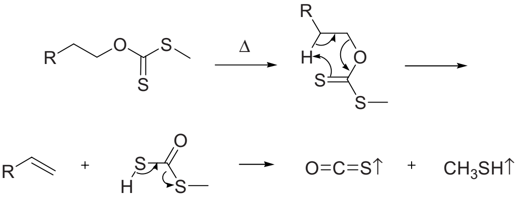
Chugaev elimination

Thermal elimination of xanthates to olefins.



xanthate



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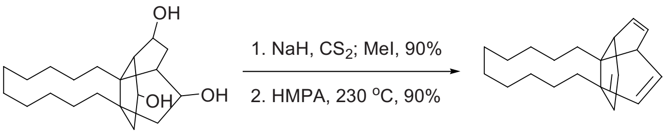
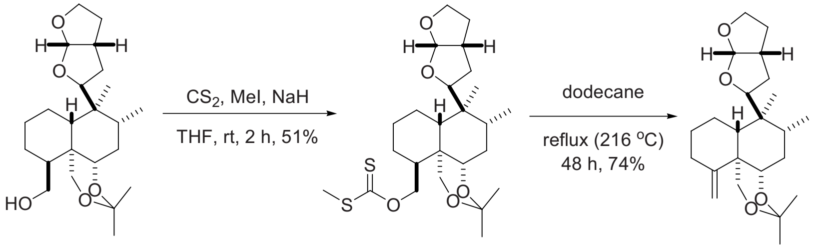
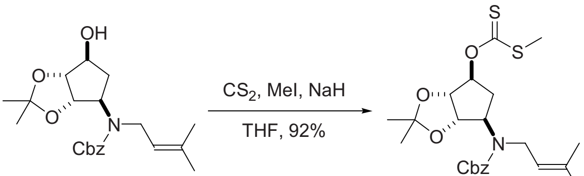


Example 2[5]



Example 3, Chugaev *syn*-elimination is followed by an intramolecular ene reaction[6]



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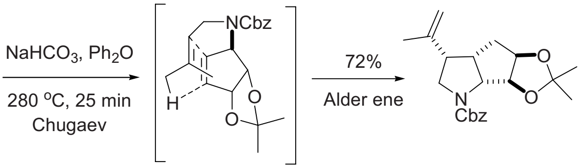

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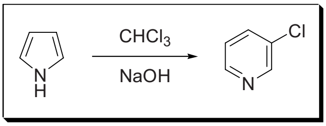
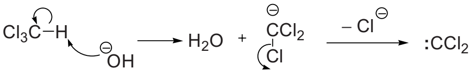
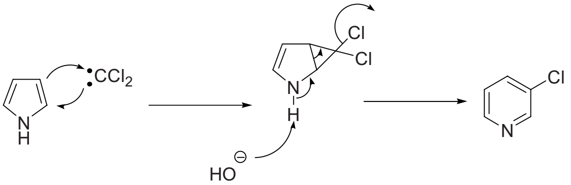
Ciamician–Dennsted rearrangement

Cyclopropanation of a pyrrole with dichlorocarbene generated from $CHCl_3$ and NaOH. Subsequent rearrangement takes place to give 3-chloropyridine.





carbene



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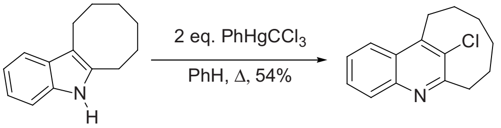

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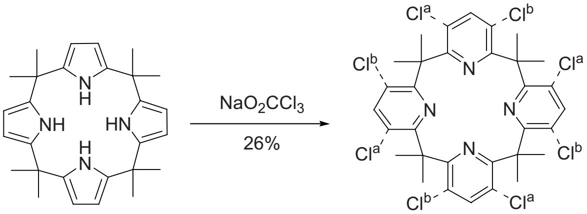

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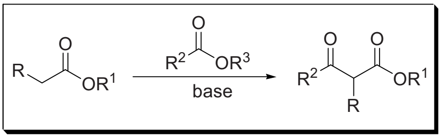
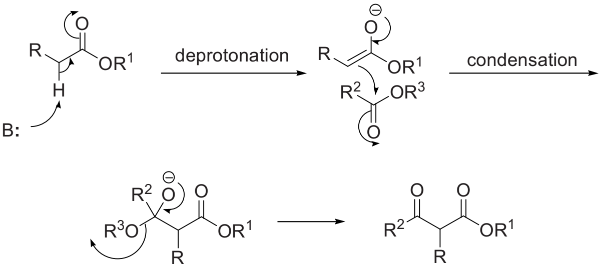
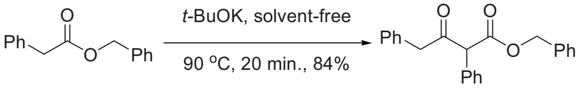
Claisen condensation

Base-catalyzed condensation of esters to afford β-keto esters.

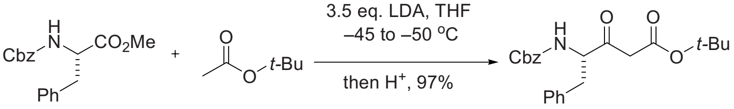




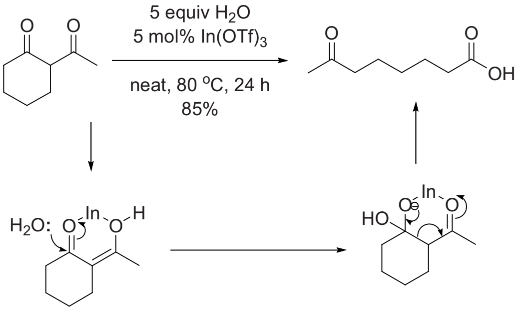
Example 1[4]



Example 2[6]



Example 3, Retro-Claisen condensation[9]



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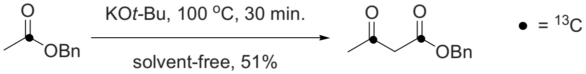
Example 4, Solvent-free Claisen condensation[10]



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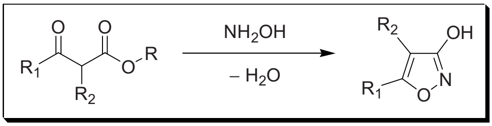
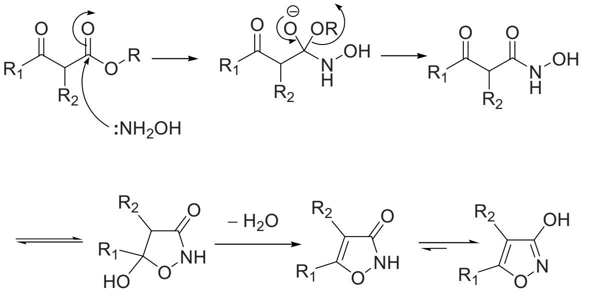
Claisen isoxazole synthesis

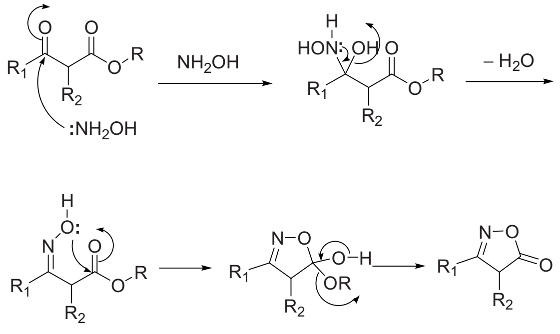
Cyclization of β-keto esters with hydroxylamine to provide 3-hydroxy-isoxazoles (3-isoxazolols).





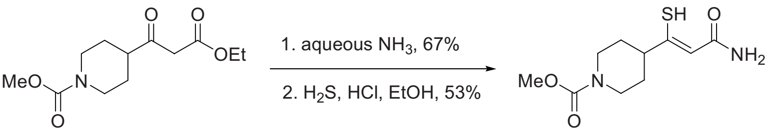
3-isoxazolol

A side reaction:

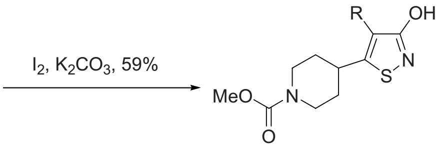


5-isoxazolone

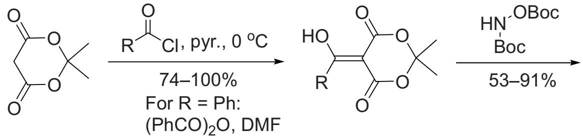
Example 1, A thio-analog[6]



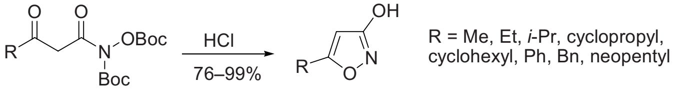
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_55,



Example 2[7]

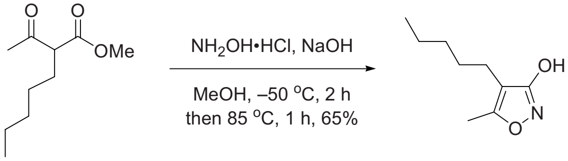


Meldrum's acid



R = Me, Et, *i*-Pr, cyclopropyl, cyclohexyl, Ph, Bn, neopentyl

Example 3[8]



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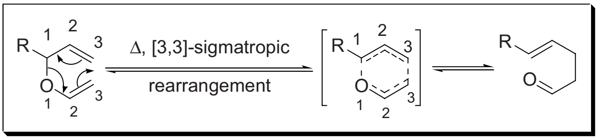
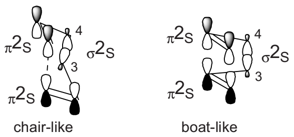
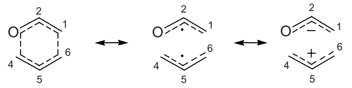
Claisen rearrangements

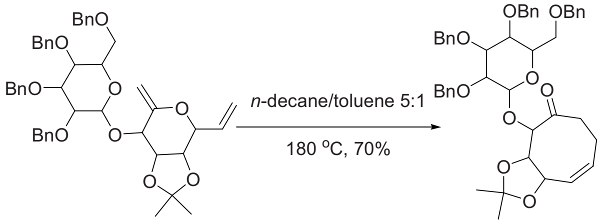
The Claisen, *para*-Claisen rearrangements, Belluš–Claisen rearrangement; Corey–Claisen, Eschenmoser–Claisen rearrangement, Ireland–Claisen, Kazmaier–Claisen, Saucy–Claisen; orthoester Johnson–Claisen, along with the Carroll rearrangement, belong to the category of *[3,3]-sigmatropic rearrangements*. The Claisen rearrangement is a concerted process and the arrow pushing here is merely illustrative.







Example 1[7]



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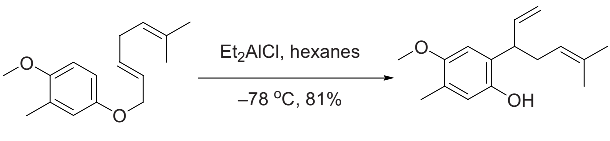
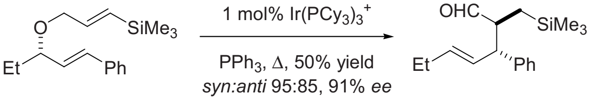


Example 3[9]



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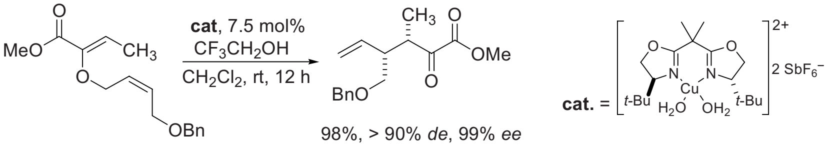
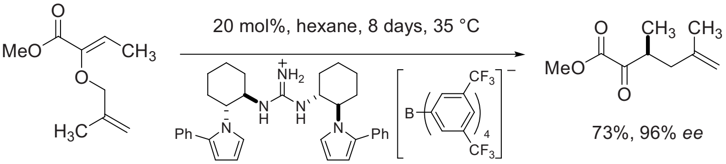
Example 4, Asymmetric Claisen rearrangement[10]



Example 5, Asymmetric Claisen rearrangement[11]



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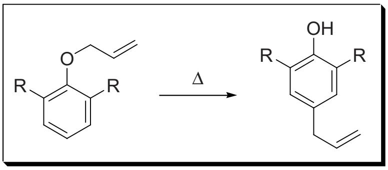
para-*Claisen rearrangement*

Further rearrangement of the normal *ortho*-Claisen rearrangement product gives the *para*-Claisen rearrangement product.



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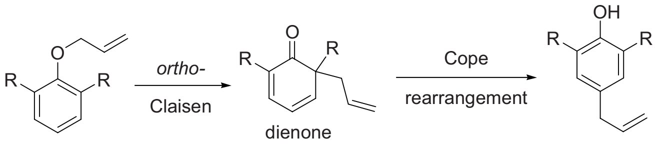

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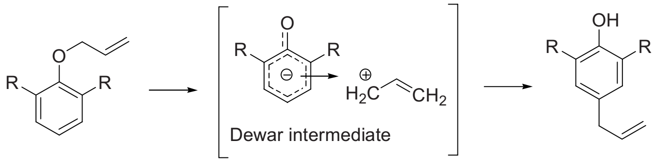

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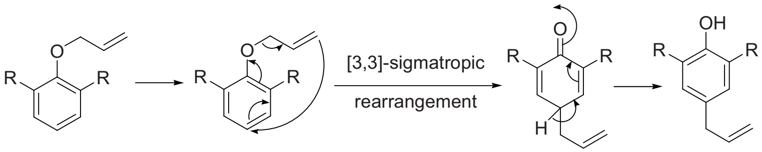

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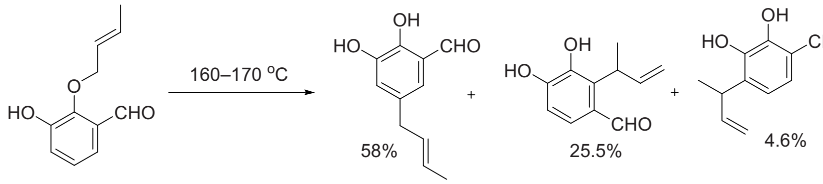

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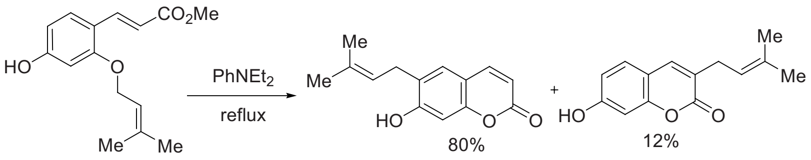

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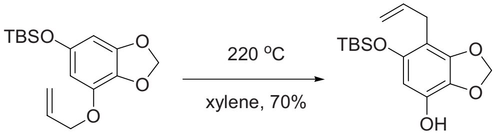

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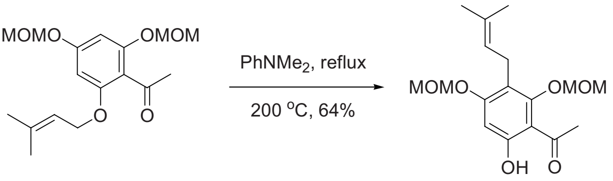

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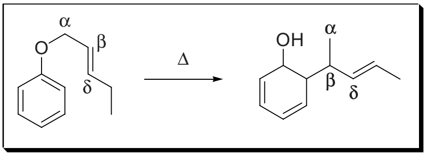
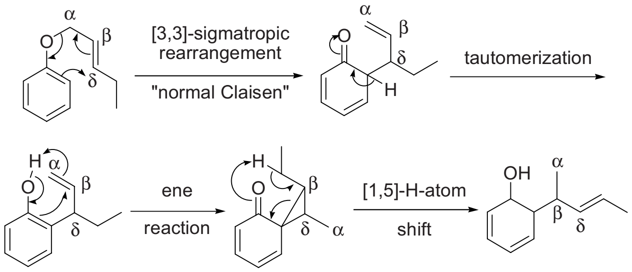
Abnormal Claisen rearrangement

Further rearrangement of the normal Claisen rearrangement product with the β-carbon becoming attached to the ring.





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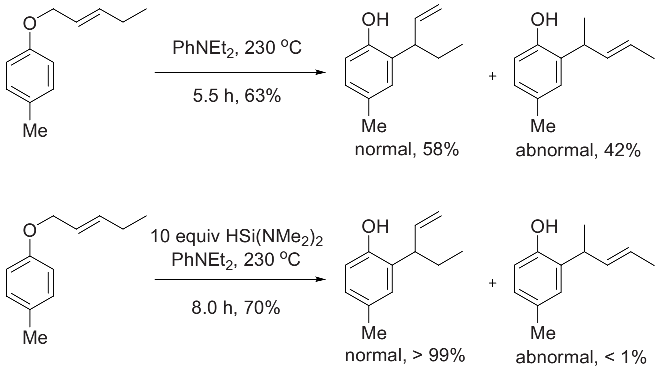
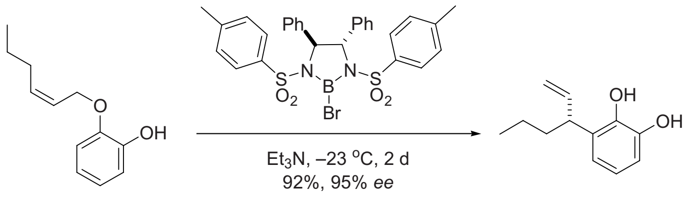


Example 2, Enantioselective aromatic Claisen rearrangement[4]



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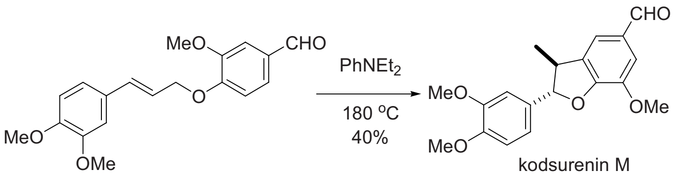
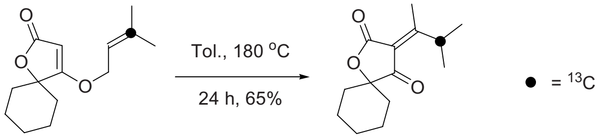
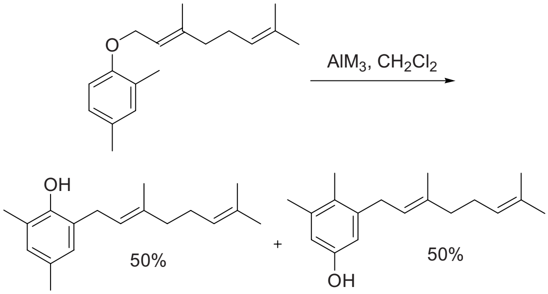


Example 4[6]



Example 5[7]



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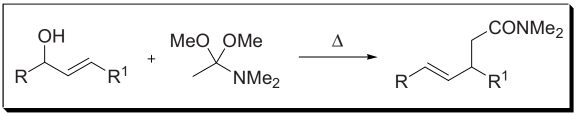
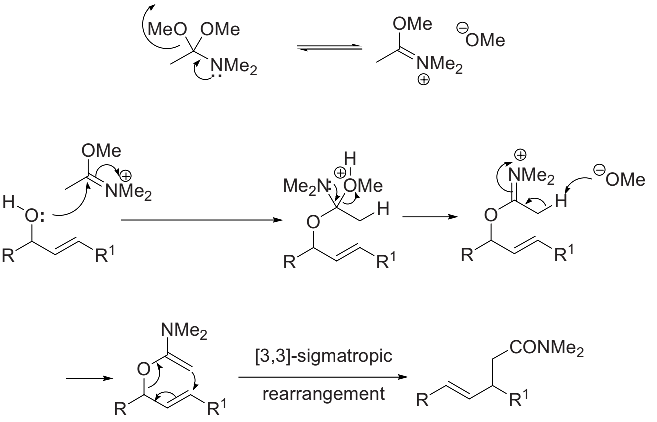
Eschenmoser–Claisen amide acetal rearrangement

[3,3]-Sigmatropic rearrangement of *N,O*-ketene acetals to yield γ,δ-unsaturated amides. Since Eschenmoser was inspired by Meerwein's observations on the interchange of amide, the Eschenmoser–Claisen rearrangement is sometimes known as the Meerwein–Eschenmoser–Claisen rearrangement.





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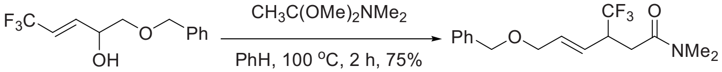

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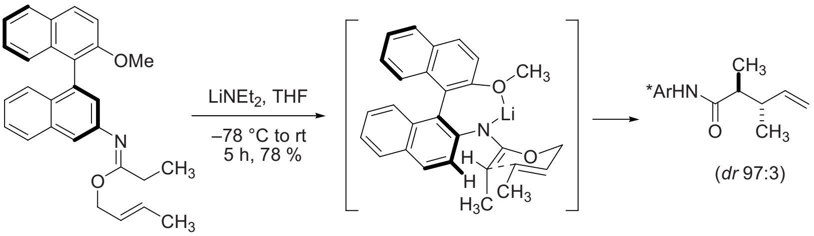

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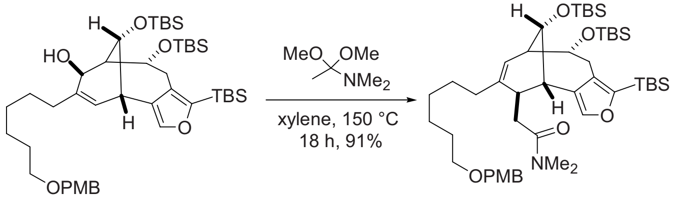

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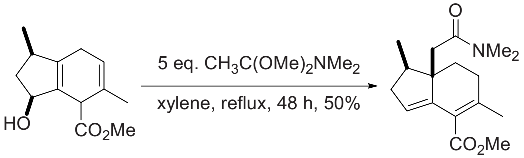

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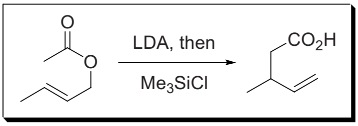
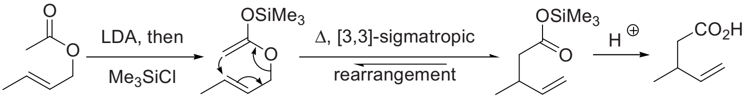
Ireland–Claisen (silyl ketene acetal) rearrangement

Rearrangement of allyl trimethylsilyl ketene acetal, prepared by reaction of allylic ester enolates with trimethylsilyl chloride, to yield γ,δ-unsaturated carboxylic acids. The Ireland–Claisen rearrangement seems to be advantageous to the other variants of the Claisen rearrangement in terms of *E/Z* geometry control and mild conditions.





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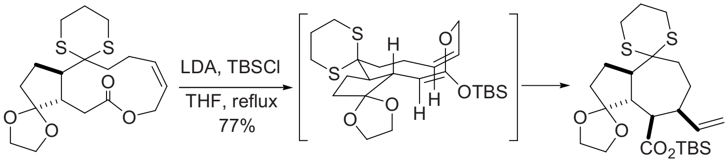

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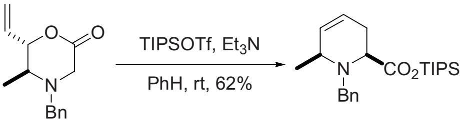
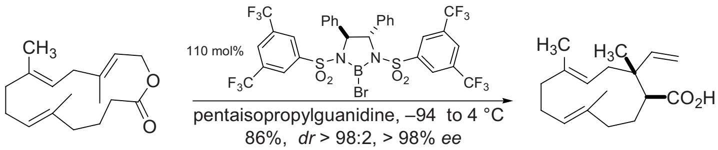
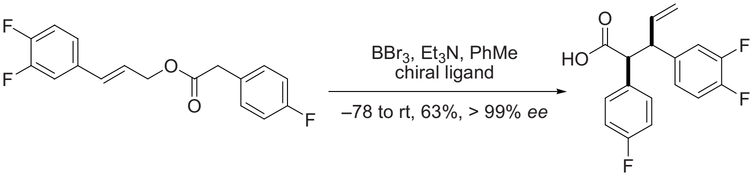


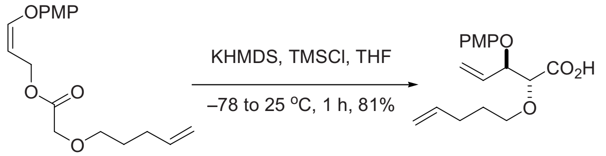
Example 3, Enantioselective ester enolate-Claisen Rearrangement[6]



Example 4, A modified Ireland–Claisen rearrangement[8]



Example 5[9]



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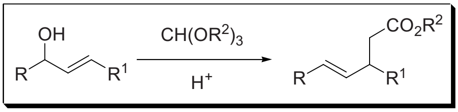
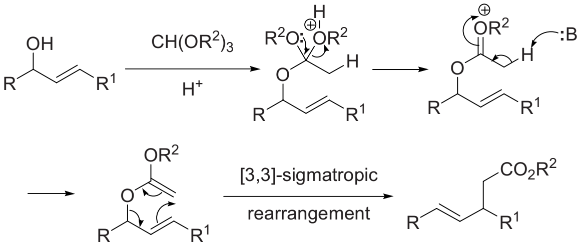
Johnson–Claisen orthoester rearrangement

Heating of an allylic alcohol with an excess of trialkyl orthoacetate in the presence of trace amounts of a weak acid gives a mixed orthoester. Mechanistically, the orthoester loses alcohol to generate the ketene acetal, which undergoes [3,3]-sigmatropic rearrangement to give a γ,δ-unsaturated ester.





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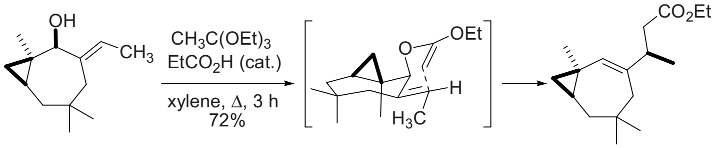

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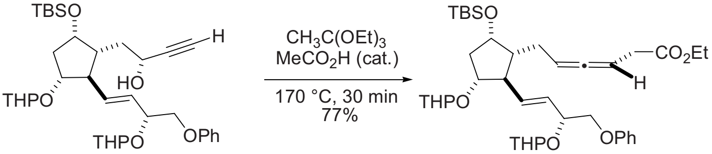
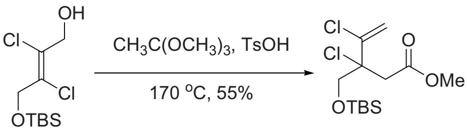
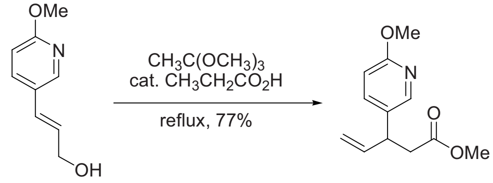


Example 3[4]



Example 4[9]



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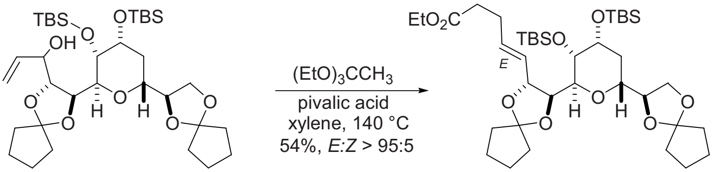

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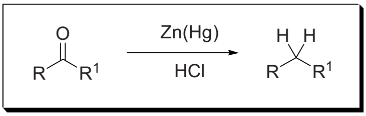
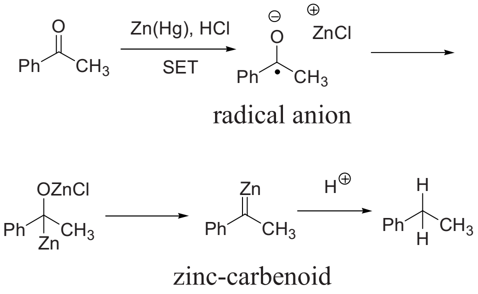
Clemmensen reduction

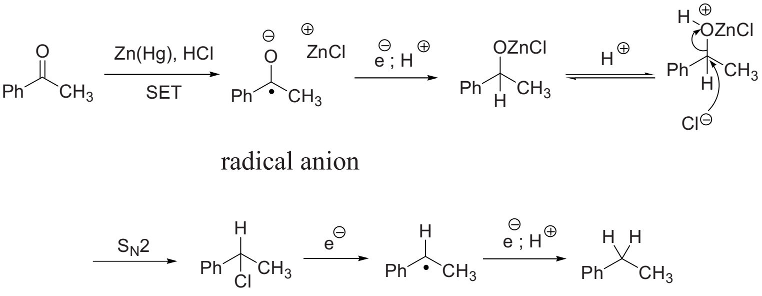
Reduction of aldehydes and ketones to the corresponding methylene compounds using amalgamated zinc in hydrochloric acid.



The zinc-carbenoid mechanism:[3]



The radical anion mechanism:



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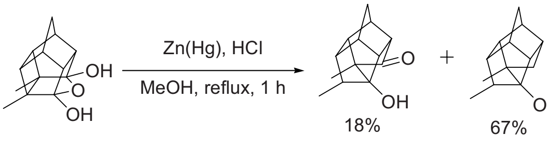
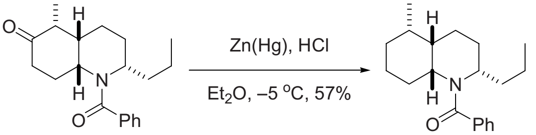


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_57,

Example 2[6]



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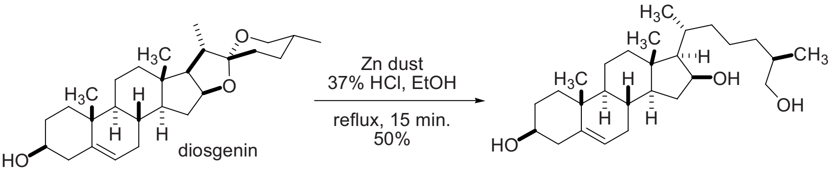

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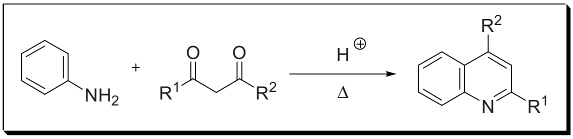
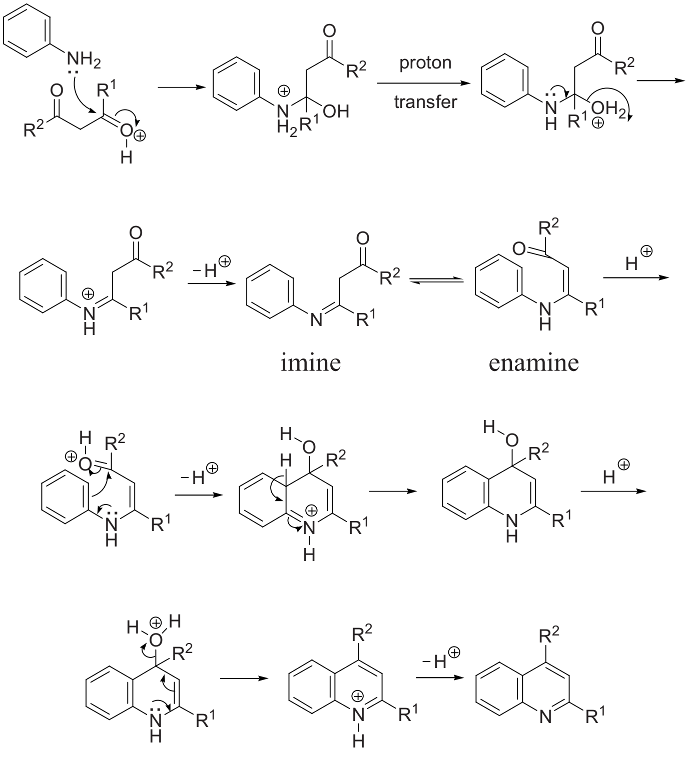
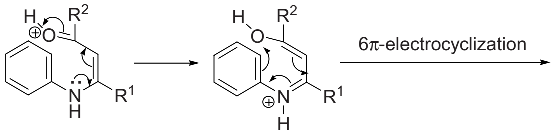
Combes quinoline synthesis

Acid-catalyzed condensation of anilines and β-diketones to assemble quinolines. *Cf.* Conrad–Limpach reaction.

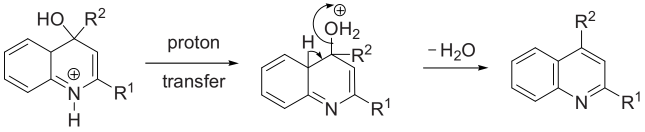




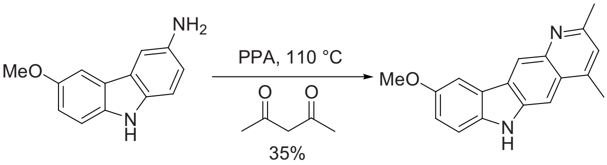
An electrocyclization mechanism is also possible:



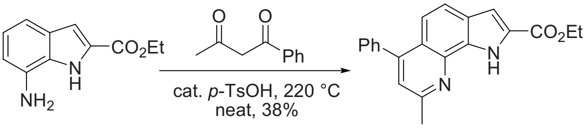
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_58,



Example 1[6]



Example 2[7]



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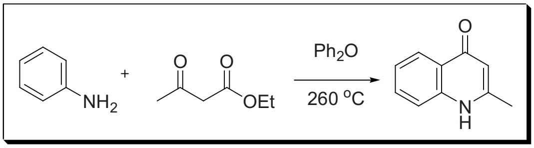
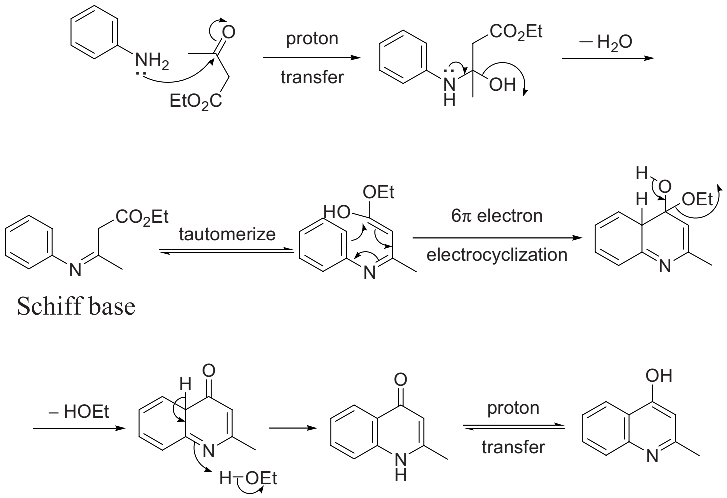
Conrad–Limpach reaction

Thermal or acid-catalyzed condensation of anilines with β-ketoesters leads to quinolin-4-ones. *Cf.* Combes quinoline synthesis.





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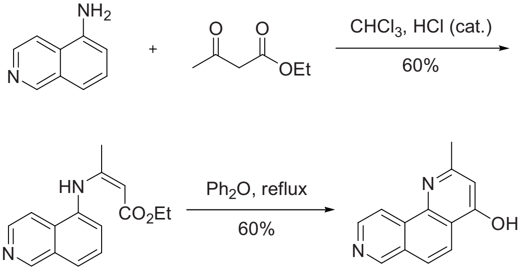
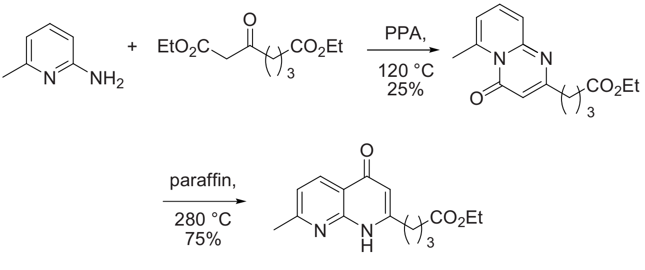
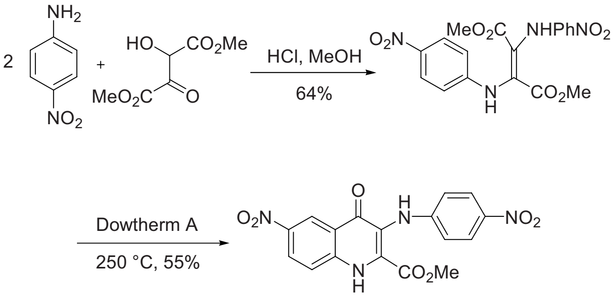


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_59,

Example 2[7]



Example 3[8]



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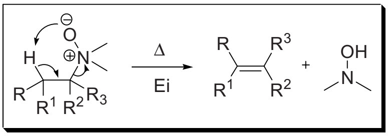
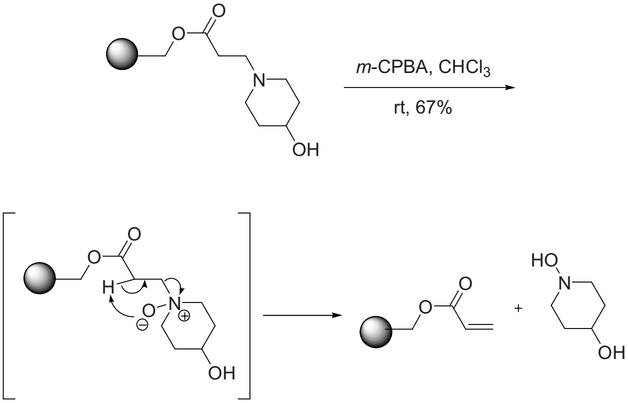
Cope elimination reaction

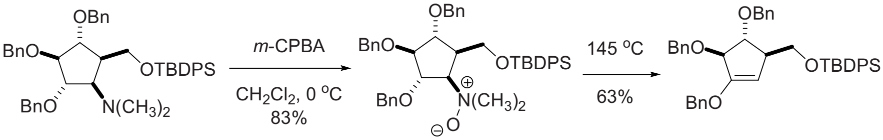
Thermal elimination of *N*-oxides to olefins and *N*-hydroxyl amines.



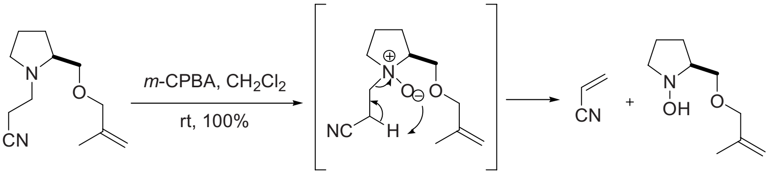
Example 1, Solid-phase Cope elimination[5]



Example 2[6]



Example 3[8]



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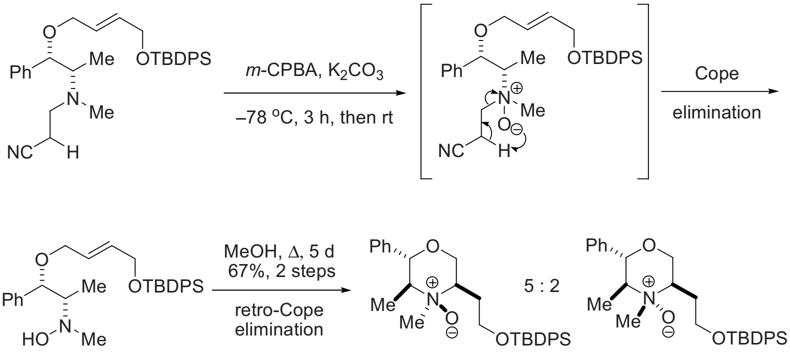
Example 4, Retro-Cope elimination[9]



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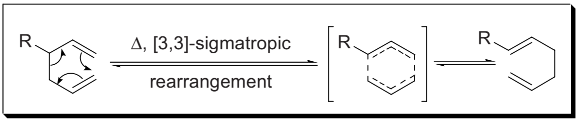
Cope rearrangement

The Cope, oxy-Cope, and anionic oxy-Cope rearrangements belong to the category of *[3,3]-sigmatropic rearrangements*. Since it is a concerted process, the arrow pushing here is only illustrative. This reaction is an equilibrium process. *Cf.* Claisen rearrangement.



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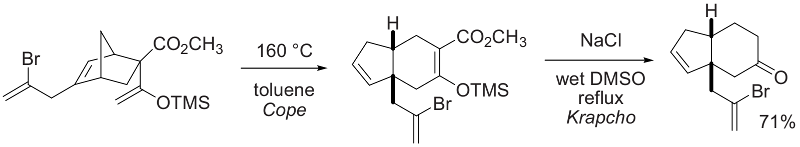

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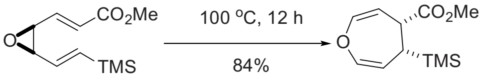

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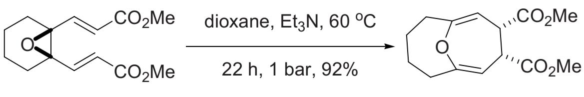

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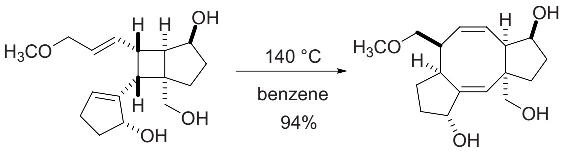

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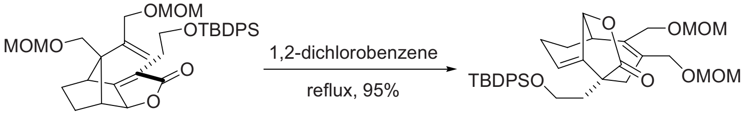

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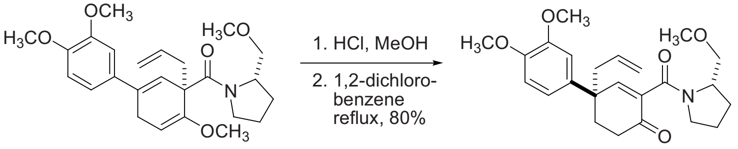
Example 6[12]



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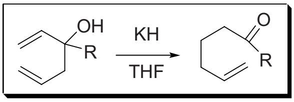
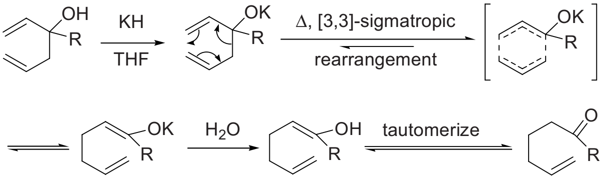
Anionic oxy-Cope rearrangement





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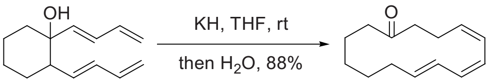

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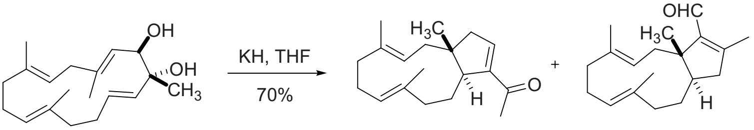

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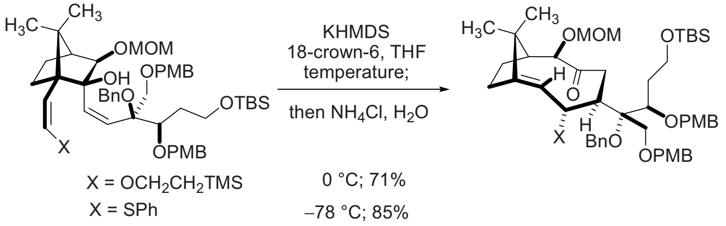

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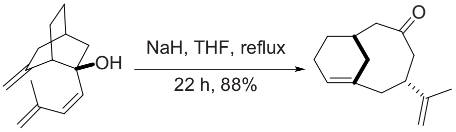

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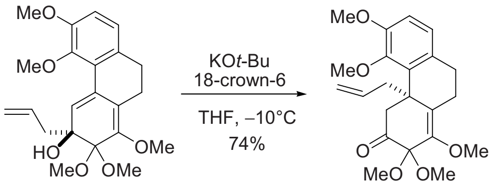

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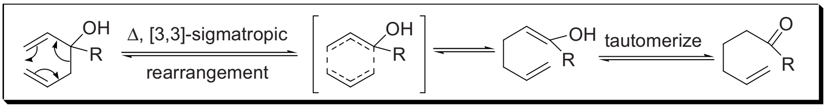
Oxy-Cope rearrangement

While the anionic oxy-Cope rearrangements work at low temperature, the oxy-Cope rearrangements require high temperature but provide a thermodynamic sink.



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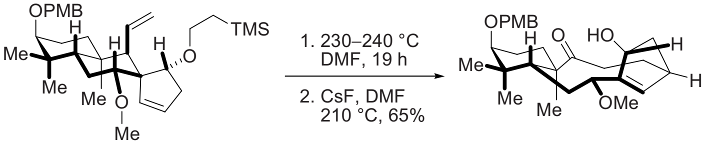

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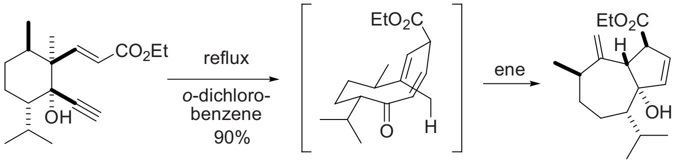

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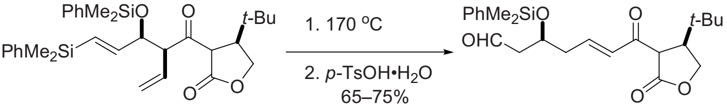

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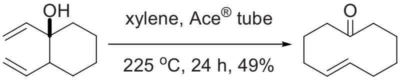

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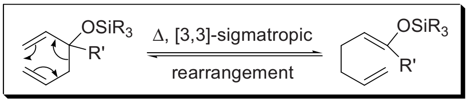
Siloxy-Cope rearrangement



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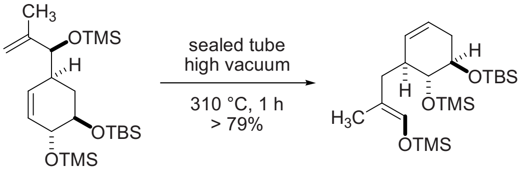
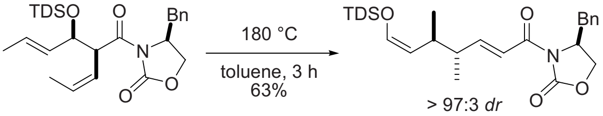
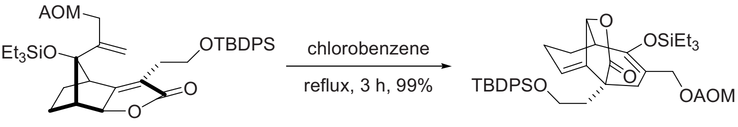


Example 2[2]



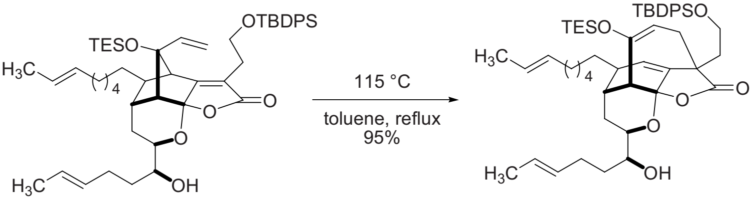
TDS = thexyldimethylsilyl

Example 3[3]



AOM = *p*-Anisyloxymethyl = *p*-$MeOC_6H_4OCH_2$-

Example 4[4]



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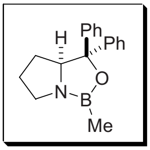
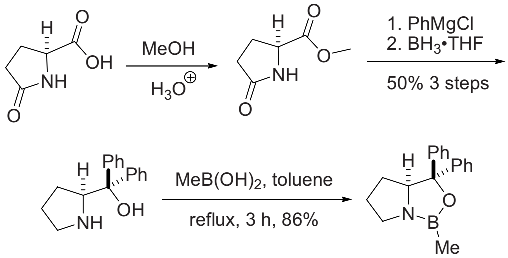
Corey–Bakshi–Shibata (CBS) reagent

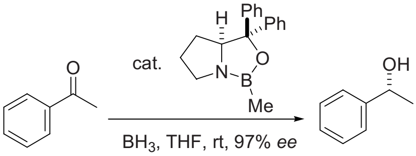


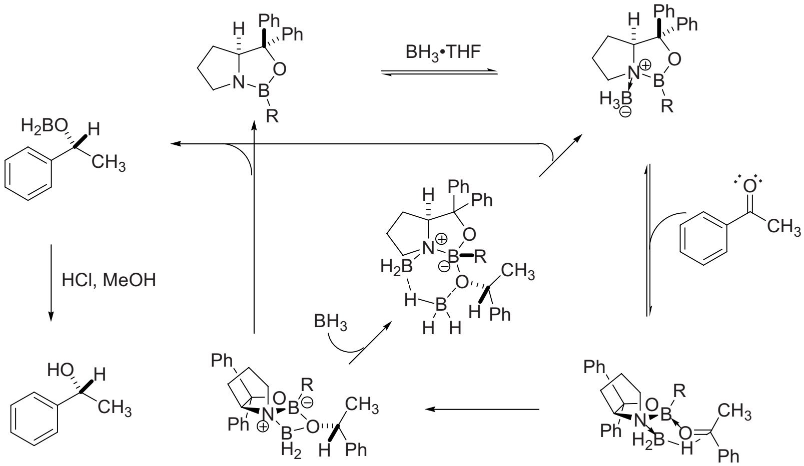
The CBS (Corey–Bakshi–Shibata) reagent is a chiral catalyst derived from proline. Also known as Corey's oxazaborolidine, it is used in enantioselective borane reduction of ketones, asymmetric Diels–Alder reactions and [3 + 2] cycloadditions.

Preparation[1,3]



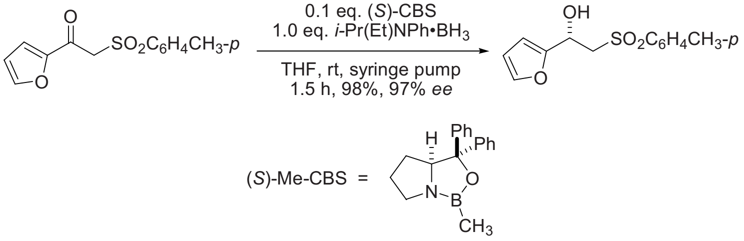
The mechanism and catalytic cycle:[1,3]



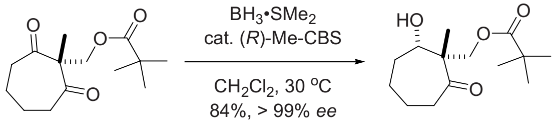


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_62,

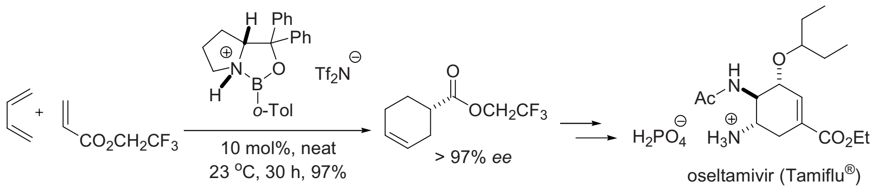
Example 1[6]



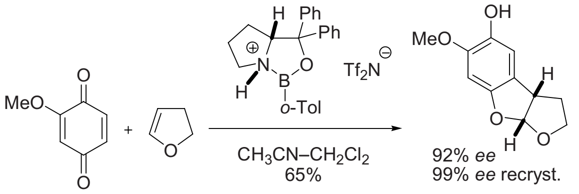
Example 2[9]



Example 3[11]



Example 4, Asymmetric [3 + 2]-cycloaddition[10]



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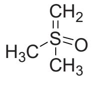
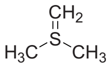
Corey–Chaykovsky reaction

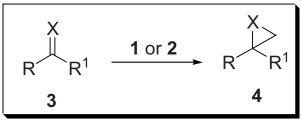
The Corey–Chaykovsky reaction entails the reaction of a sulfur ylide, either dimethylsulfoxonium methylide **1** (Corey's ylide) or dimethylsulfonium methylide **2**, with electrophile **3** such as carbonyl, olefin, imine, or thiocarbonyl, to offer **4** as the corresponding epoxide, cyclopropane, aziridine, or thiirane.



1

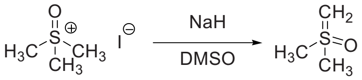


2

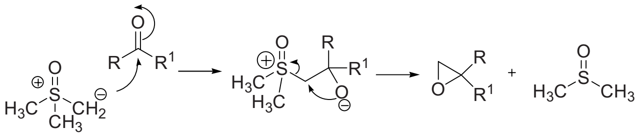


X = O, CH_2, NR^2, S, $CHCOR^3$, $CHCO_2R^3$, $CHCONR_2$, CHCN

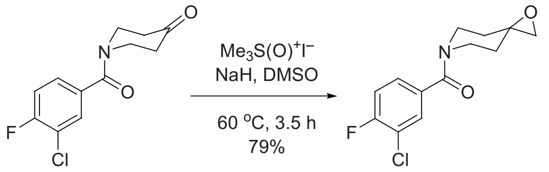
Preparation[1]



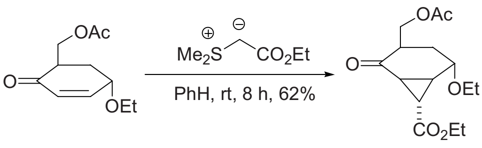
Mechanism[1]



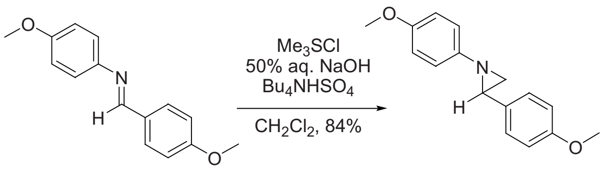
Example 1[11]



Example 2[9]

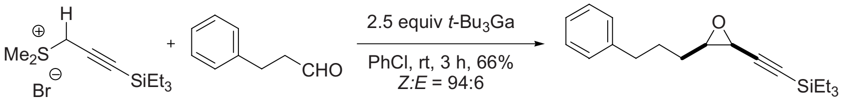


Example 3[10]

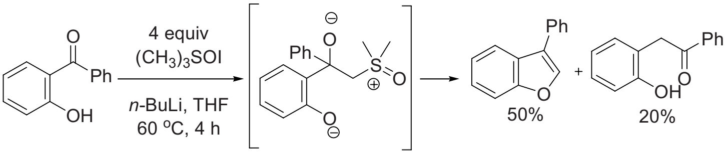


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_63,

Example 4[14]



Example 5[15]



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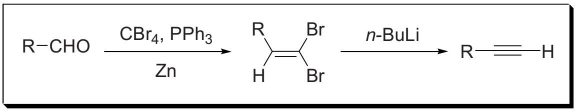
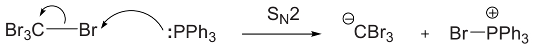
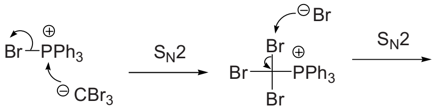
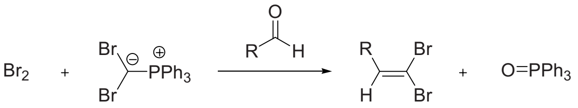
Corey–Fuchs reaction

One-carbon homologation of an aldehyde to dibromoolefin, which is then treated with *n*-BuLi to produce a terminal alkyne.



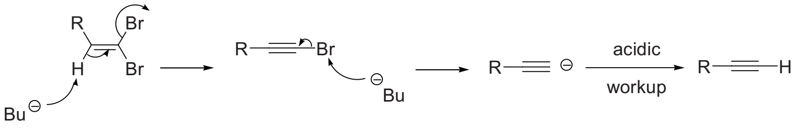




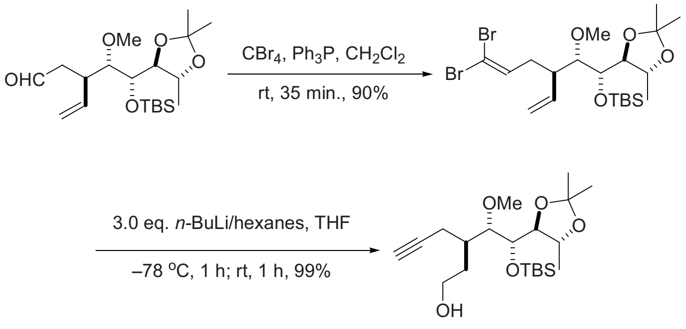


Wittig reaction (see page 578 for the mechanism)

$Br_2 + Zn \longrightarrow ZnBr_2$

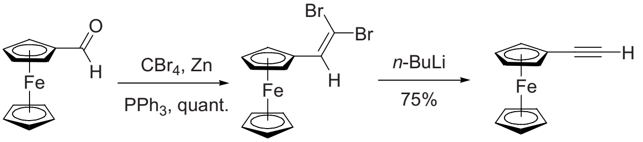


Example 1[3]

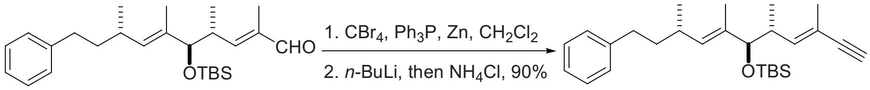


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_64,

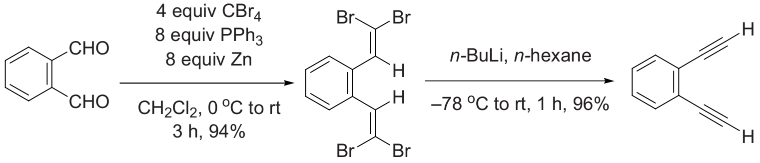
Example 2[7]



Example 3[8]



Example 4[10]



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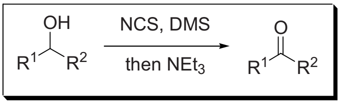
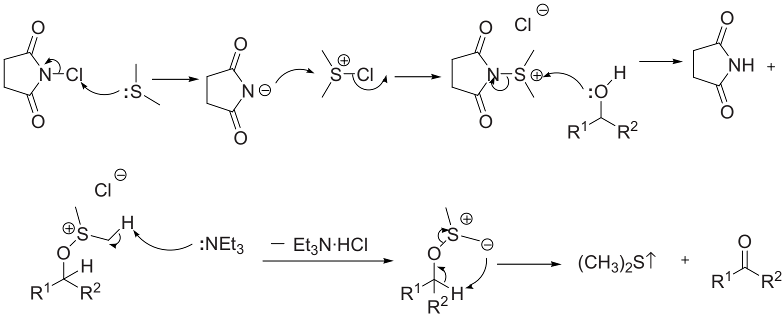
Corey–Kim oxidation

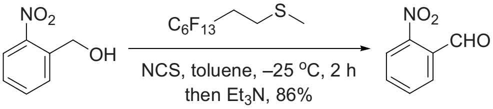
Oxidation of alcohol to the corresponding aldehyde or ketone using NCS/DMS, followed by treatment with a base. *Cf.* Swern oxidation.



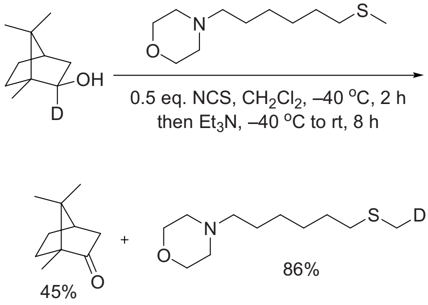
NCS = ***N*-C**hloro**s**uccinimide; DMS = **Dim**ethyl**s**ulfide.



Example 1, Fluorous Corey–Kim reaction[5]

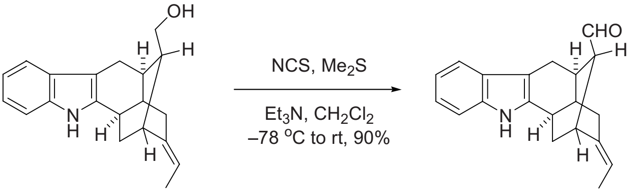


Example 2, Odorless Corey–Kim reaction[7]

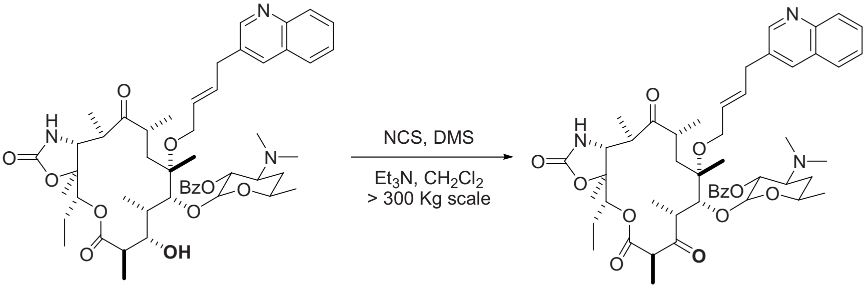


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_65,

Example 3[9]



Example 4[10]



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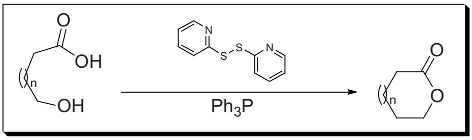
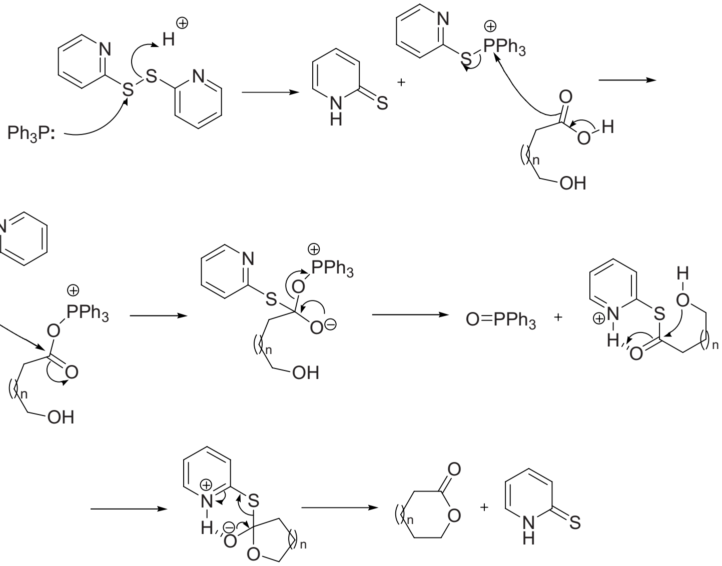
Corey–Nicolaou macrolactonization

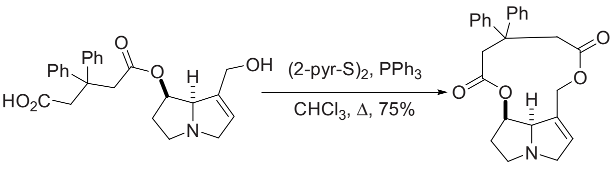
Macrolactonization of ω-hydroxyl-acid using 2,2′-dipyridyl disulfide. Also known as the Corey–Nicolaou double activation method.





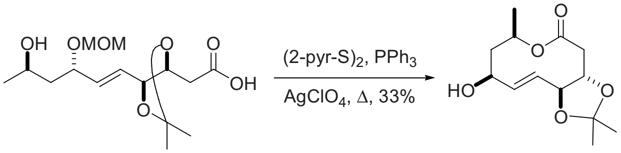
2-pyridinethione

Example 1[3]

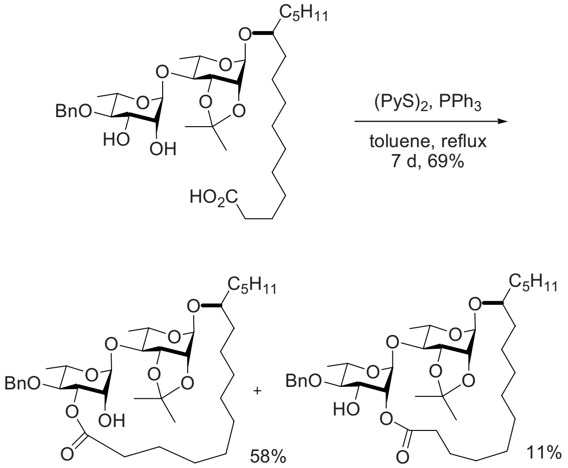


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_66,

Example 2[6]



Example 3[9]



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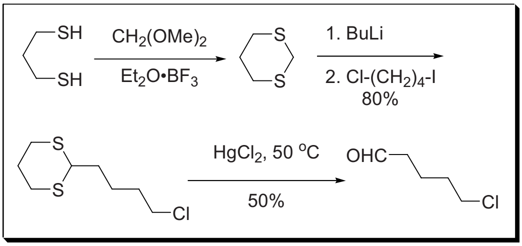
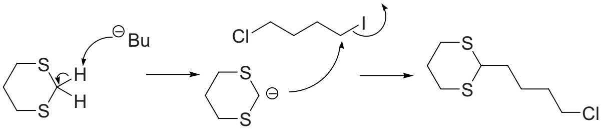
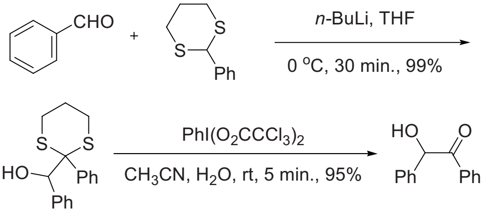
Corey–Seebach reaction

Dithiane as a nucleophile, serving as a masked carbonyl equivalent. This is an example of umpolung.

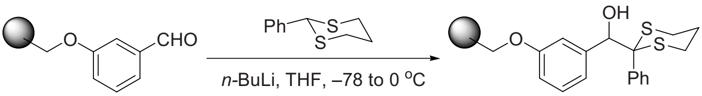




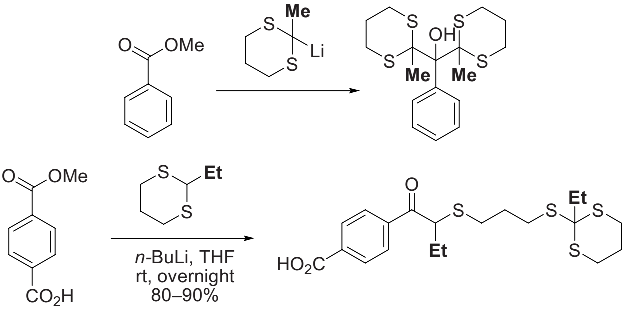
Example 1[2]



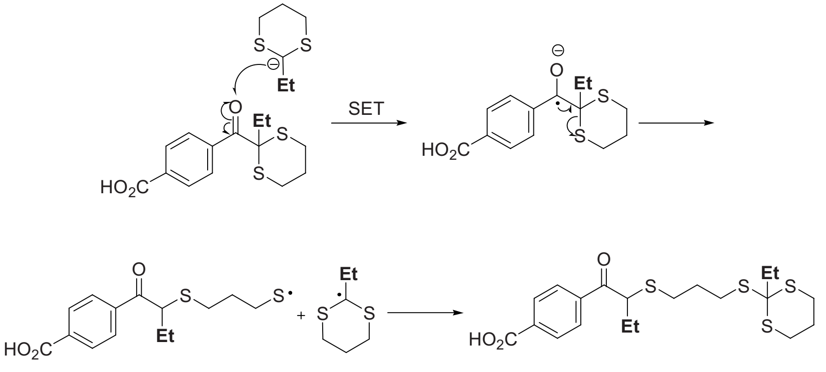
Example 2[4]



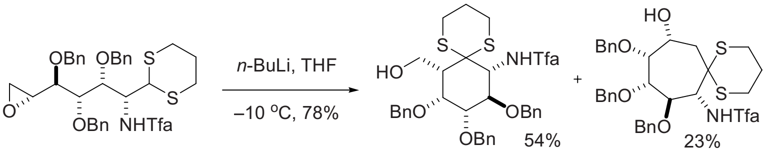
Example 3, Ethyl is infinitely different from methyl[6]



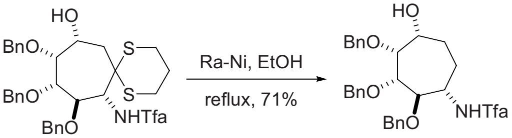
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_67,



Example 4[8]



Tfa = Trifluoroacetyl



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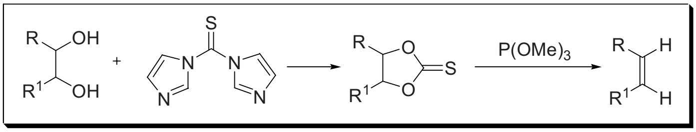
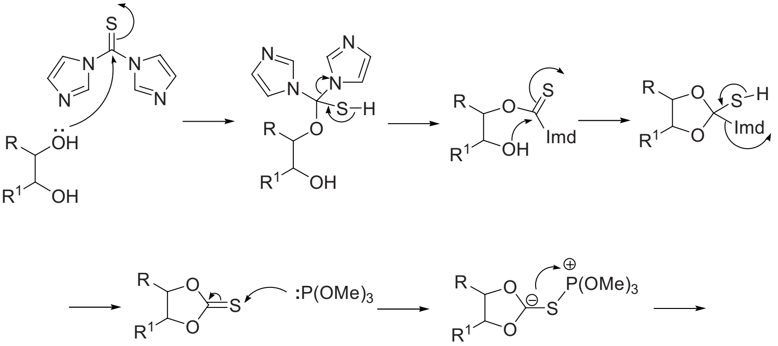
Corey–Winter olefin synthesis

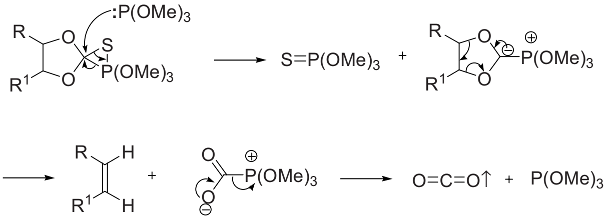
Transformation of diols to the corresponding olefins by sequential treatment with 1,1′-thiocarbonyldiimidazole (TCDI) and trimethylphosphite. Also known as Corey–Winter reductive elimination, or Corey–Winter reductive olefination.



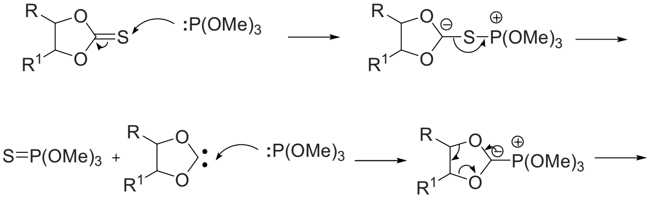
TCDI = Thiocarbonyldiimidazole



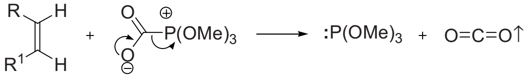
1,3-dioxolane-2-thione (cyclic thiocarbonate)



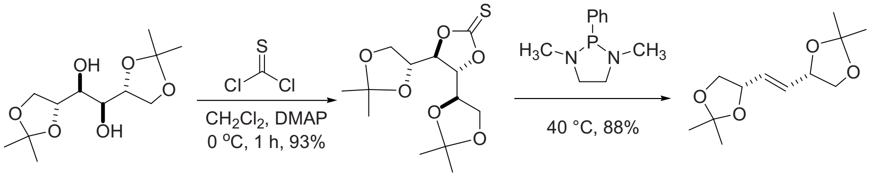
A mechanism involving a carbene intermediate can also be drawn and is supported by pyrolysis studies:



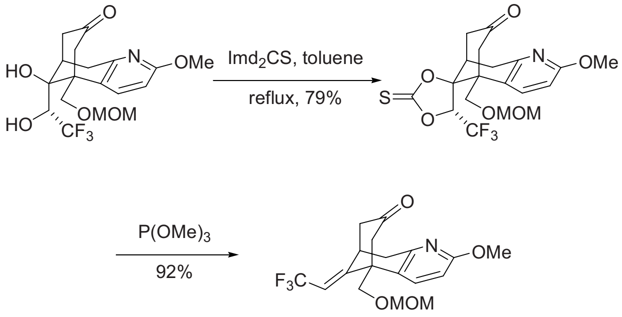
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_68,



Example 1[2]

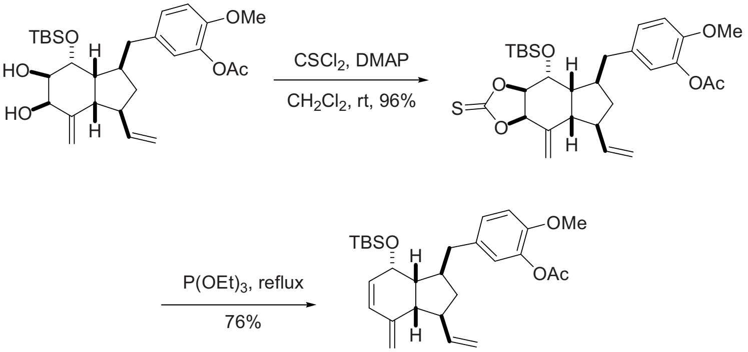


Example 2[4]

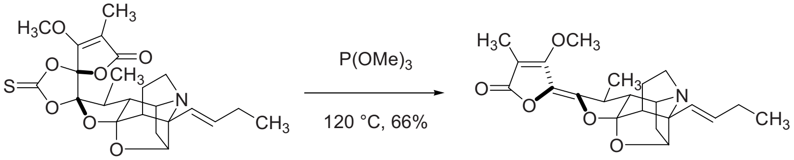


Single olefin isomer

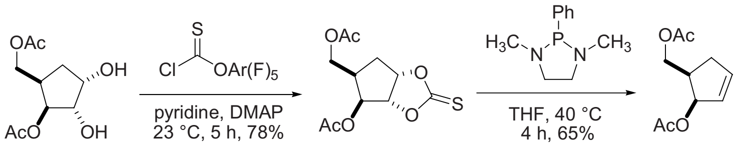
Example 3[8]



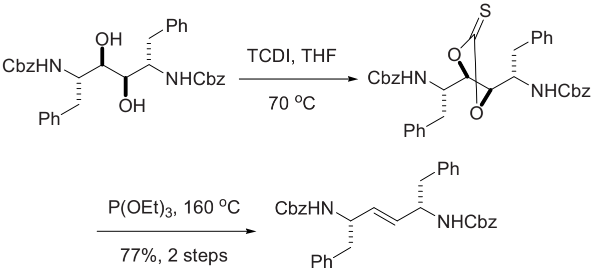
Example 4[9]



Example 5[10]



Example 6[11]



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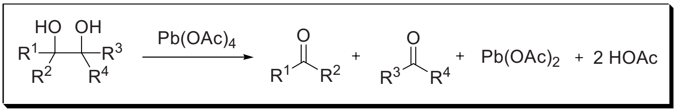
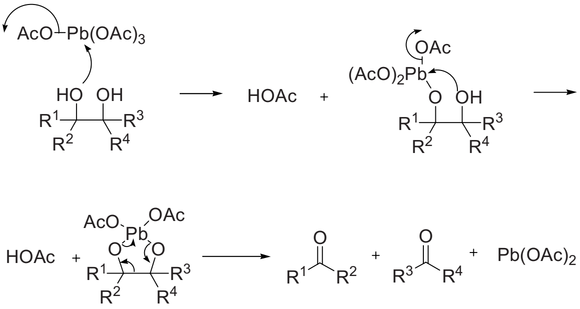
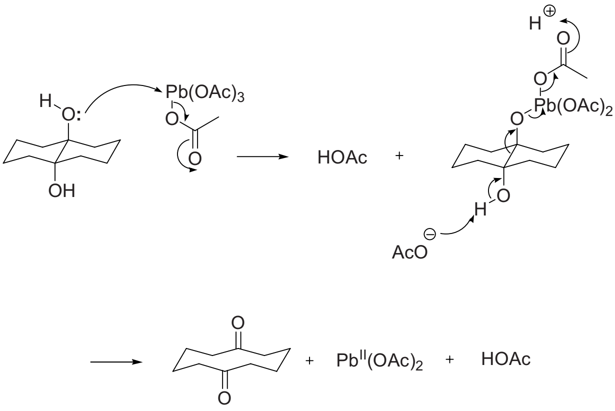
Criegee glycol cleavage

Vicinal diol is oxidized to the two corresponding carbonyl compounds using $Pb(OAc)_4$, (**l**ead **t**etra**a**cetate, LTA).

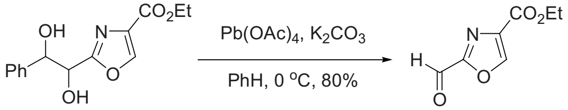




An acyclic mechanism is possible as well. It is much slower than the cyclic mechanism, but is operative when the cyclic intermediate can not form:[3]

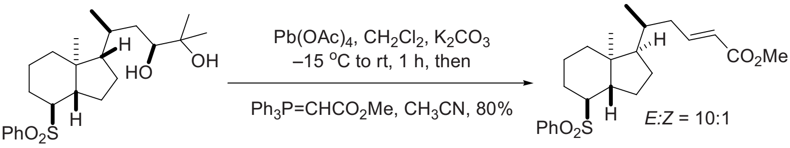


Example 1[7]

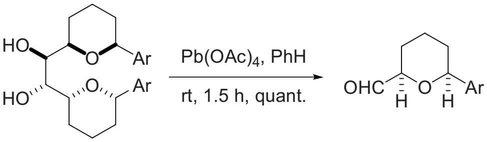


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_69,

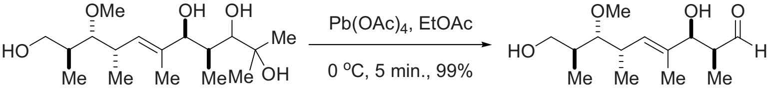
Example 2[9]



Example 3[10]



Example 4[11]



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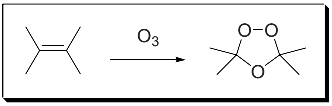
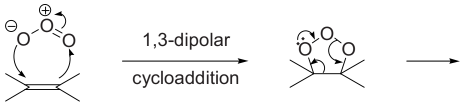
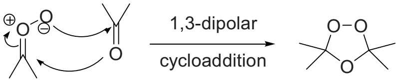
Criegee mechanism of ozonolysis





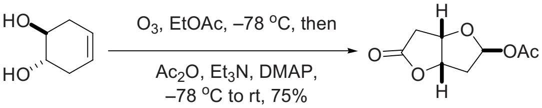
primary ozonide (1,2,3-trioxolane)



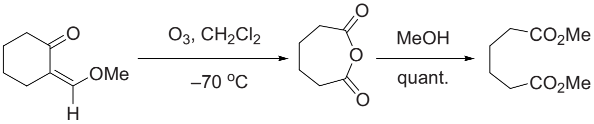
zwitterionic peroxide (Criegee zwitterion) also known as “carbonyl oxide”

secondary ozonide (1,2,4-trioxolane)

Example 1[7]



Example 2[8]



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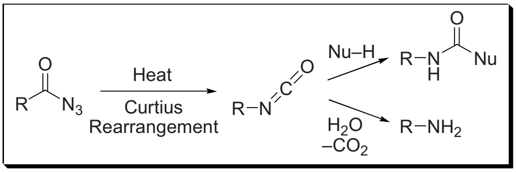
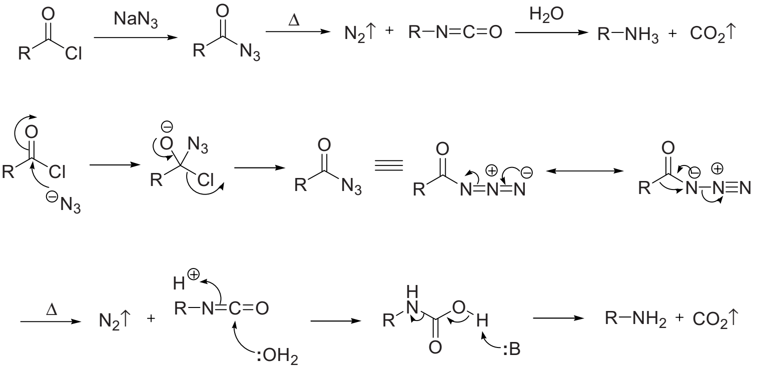
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_70,

Curtius rearrangement

Alkyl-, vinyl-, and aryl-substituted acyl azides undergo thermal 1,2-carbon-to-nitrogen migration with extrusion of dinitrogen — the Curtius rearrangement — producing isocyantes. Reaction of the isocyanate products with nucleophiles, often *in situ*, provides carbamates, ureas, and other *N*-acyl derivatives. Alternatively, hydrolysis of the isocyanates leads to primary amines.

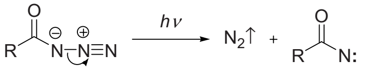


The thermal rearrangement:

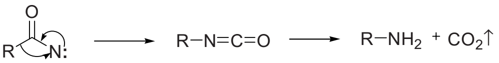


isocyanate intermediate

The photochemical rearrangement:

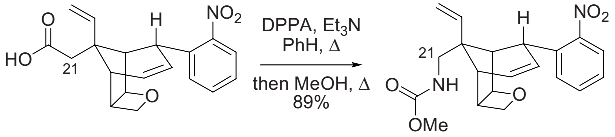


Nitrene



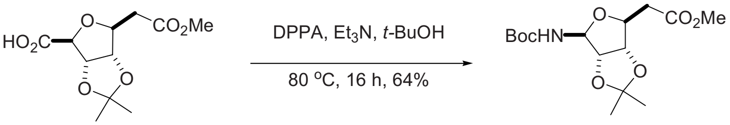
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_71,

Example 1, The Shioiri–Ninomiya–Yamada modification[2]

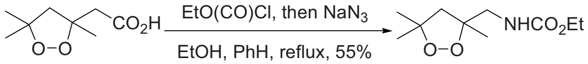


DPPA = diphenylphosphoryl azide

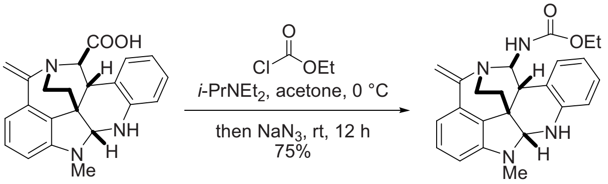
Example 2[3]



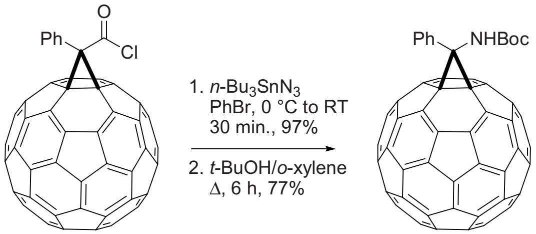
Example 3[4]



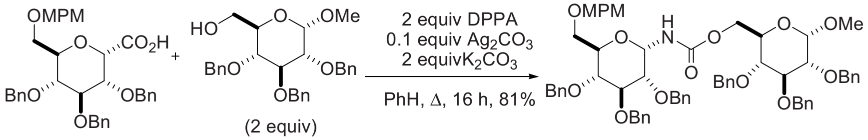
Example 4, The Weinstock variant of the Curtius rearrangement[6]



Example 5[7]



Example 6, The Lebel modification[8]



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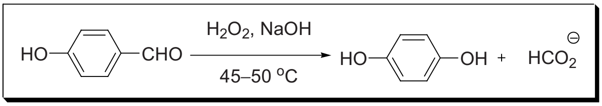
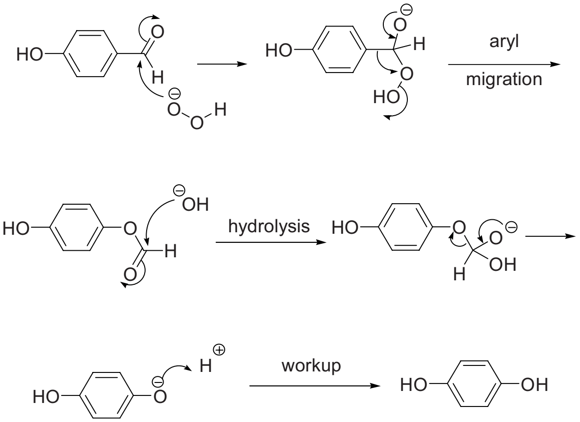
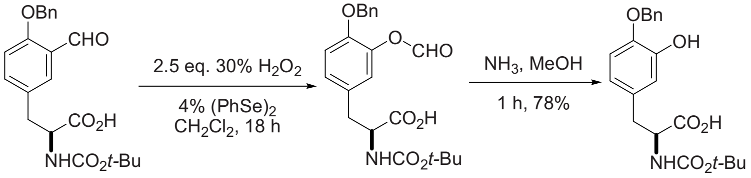
Dakin oxidation

Oxidation of aryl aldehydes or aryl ketones to phenols using basic hydrogen peroxide conditions. *Cf.* A variant of Baeyer–Villiger oxidation.





Example 1[6]



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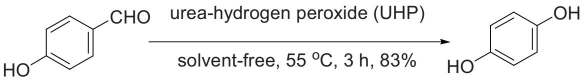
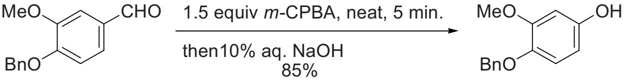


Example 3, Improved solvent-free Dakin oxidation protocol[9]



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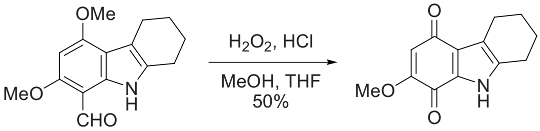
Example 4[10]



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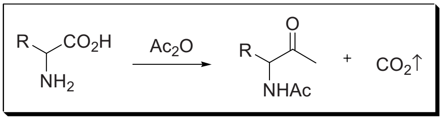
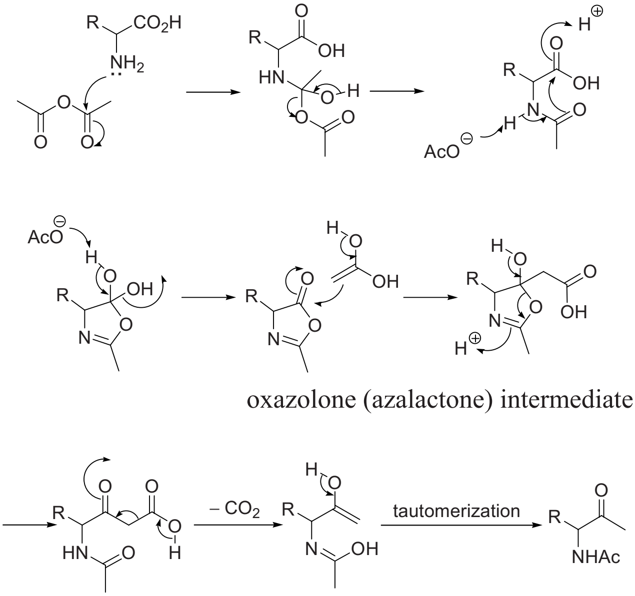
Dakin–West reaction

The direct conversion of an α-amino acid into the corresponding α-acetylamino-alkyl methyl ketone, *via* oxazoline (azalactone) intermediates. The reaction proceeds in the presence of acetic anhydride and a base, such as pyridine, with the evolution of CO_2.





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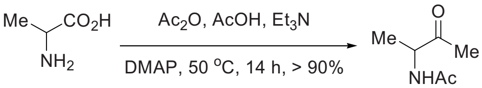

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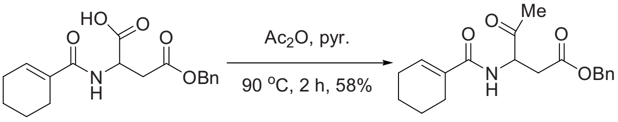

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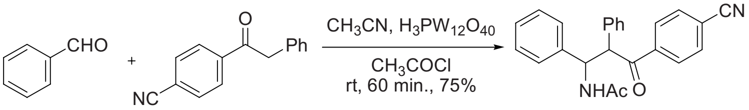
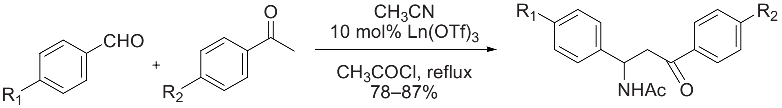
Example 3, Green Dakin–West reaction using the heteropoly acid catalyst, acetonitrile is a reactant[9]



Example 4, Acetonitrile is a reactant[10]



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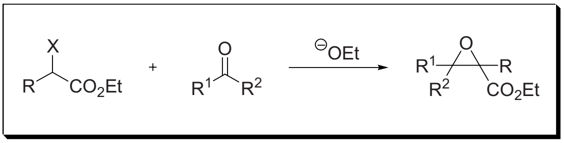
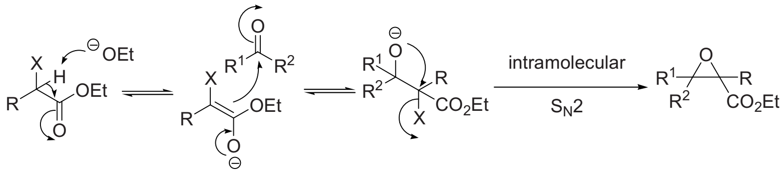
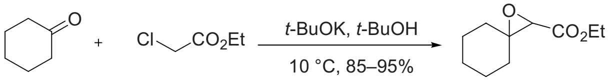
Darzens condensation

α,β-Epoxy esters (glycidic esters) from base-catalyzed condensation of α-haloesters with carbonyl compounds.





Example 1[4]



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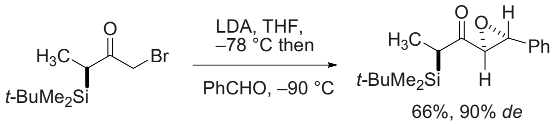
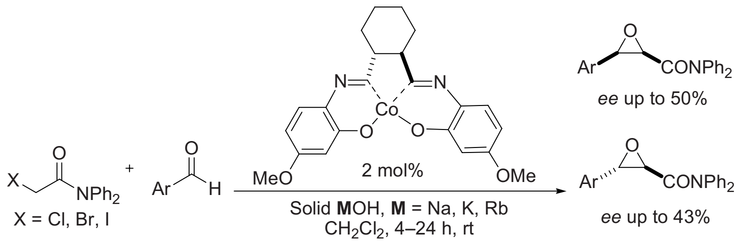


66%, 90% *de*

Example 3[9]



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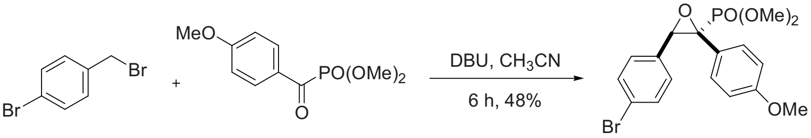
Example 4, the phenyl ring substituting for the carbonyl to acidify the protons[10]



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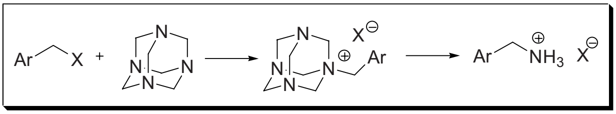
Delépine amine synthesis

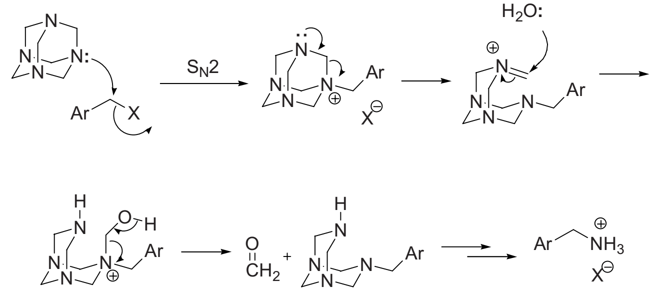
The reaction between alkyl halides and hexamethylenetetramine, followed by cleavage of the resulting salt with ethanolic HCl to yield primary amines.
Cf. Gabriel synthesis, where the product is also an amine and Sommelet reaction, where the product is an aldehyde. The Delépine works well for active halides such as benzyl, allyl halides, and α-halo-ketones.



hexamethylenetetramine

$$[ArCH_2C_6H_{12}N_4]^+X^- \quad + \quad 3\ HCl \quad + 6\ H_2O$$

$$\longrightarrow \ ArCH_2NH_2{\bullet}HX \quad + \quad 6\ CH_2O \quad + \quad 3\ NH_4Cl$$



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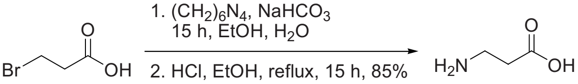

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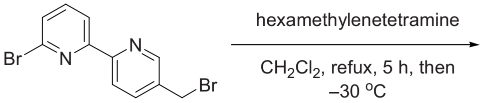

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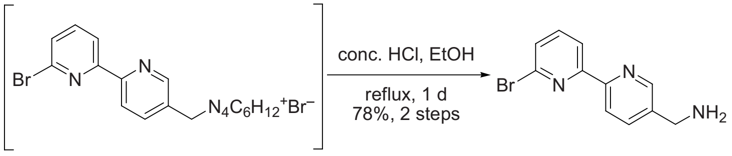
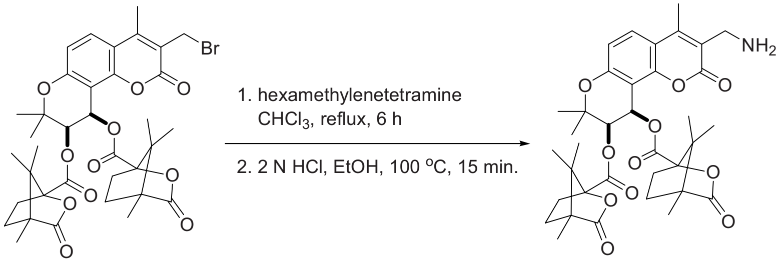


Example 3[8]



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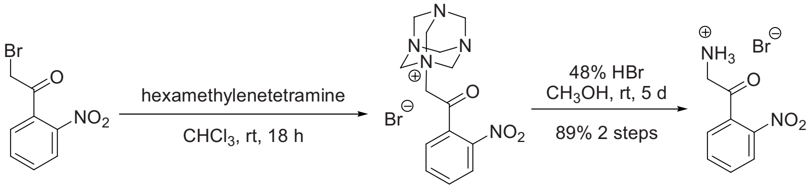

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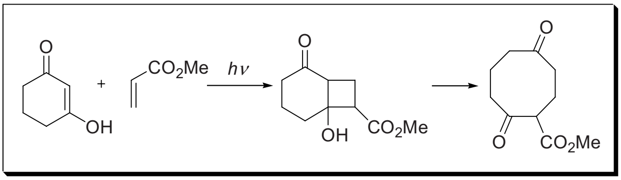
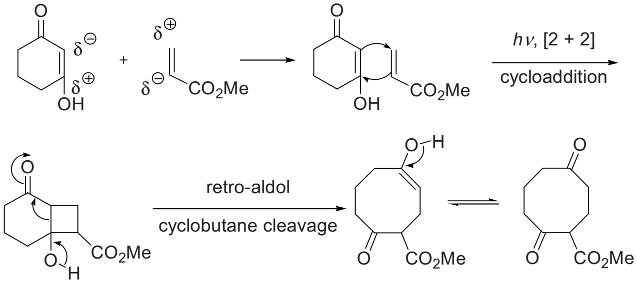
de Mayo reaction

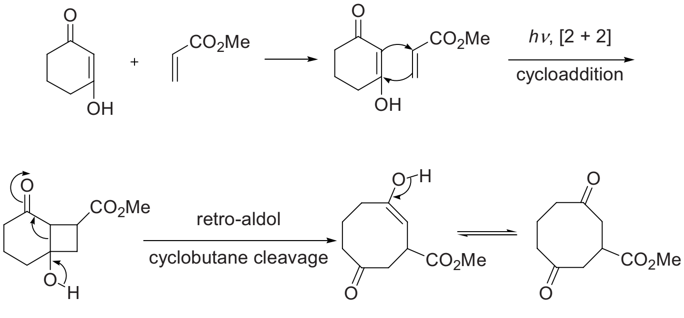
[2 + 2]-Photochemical cyclization of enones with olefins is followed by a retro-aldol reaction to give 1,5-diketones.



Head-to-tail alignment gives the major product:



Head-to-head alignment gives the minor regioisomer:



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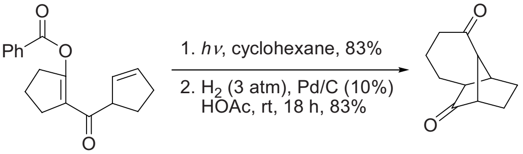

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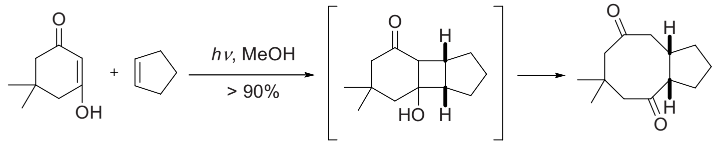
Example 2[6]



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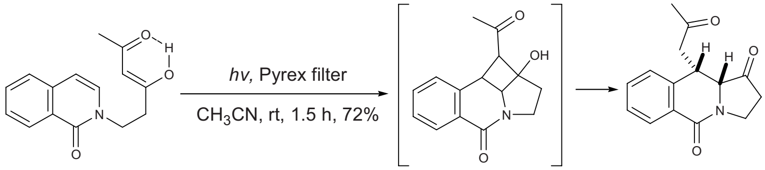

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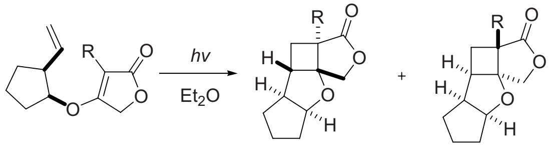

R = H	70%	100	:	0
R = Me	58%	50	:	50
R = *t*-Bu	72%	0	:	100

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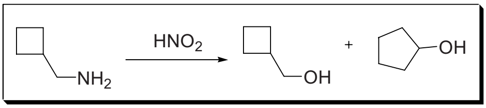
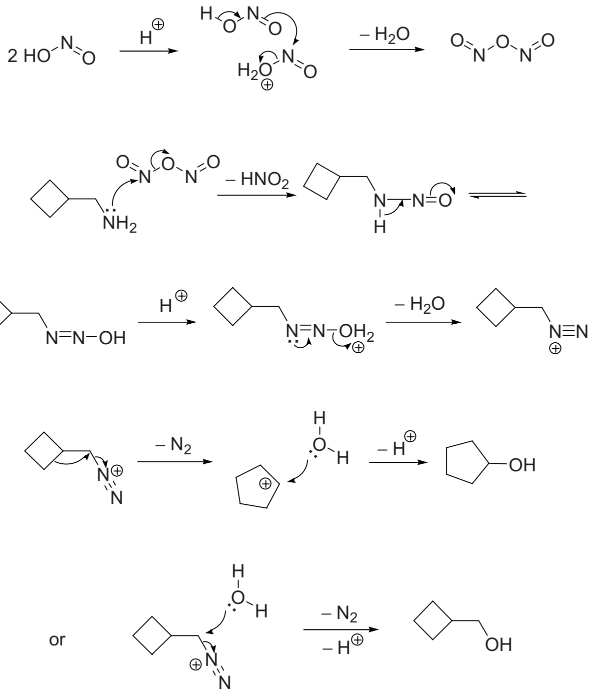
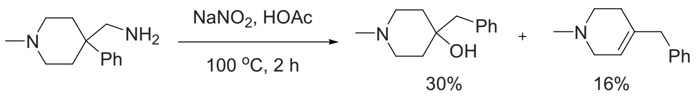
Demjanov rearrangement

Carbocation rearrangement of primary amines *via* diazotization to give alcohols through C–C bond migration.





Example 1[3]



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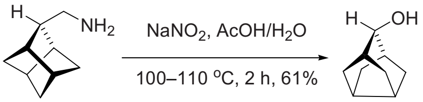

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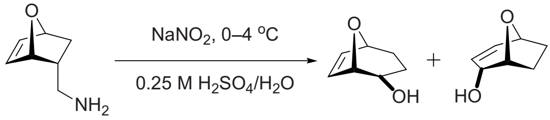
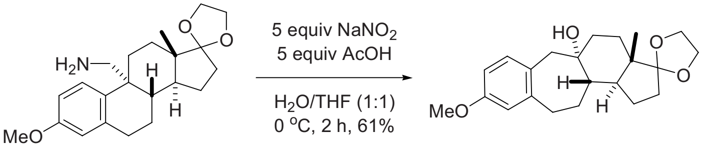
Example 3[7]



Example 4[8]



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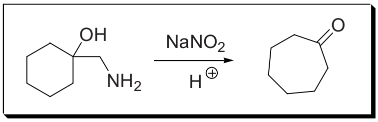
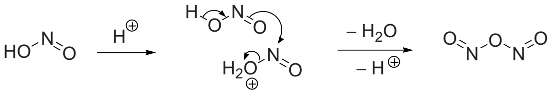
Tiffeneau–Demjanov rearrangement

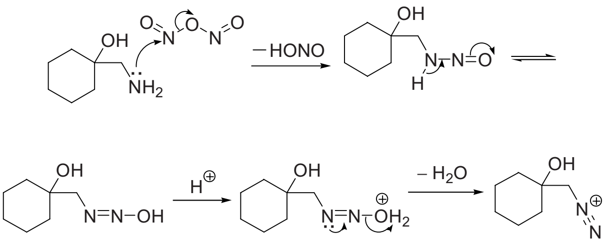
Carbocation rearrangement of β-aminoalcohols *via* diazotization to afford carbonyl compounds through C–C bond migration.



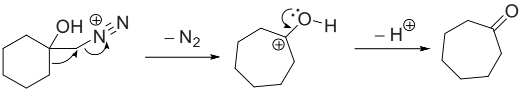
Step 1, Generation of N_2O_3



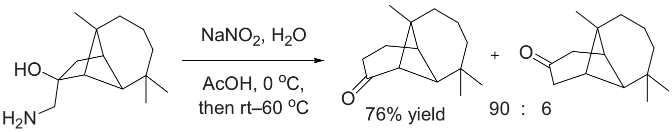
Step 2, Transformation of amine to diazonium salt



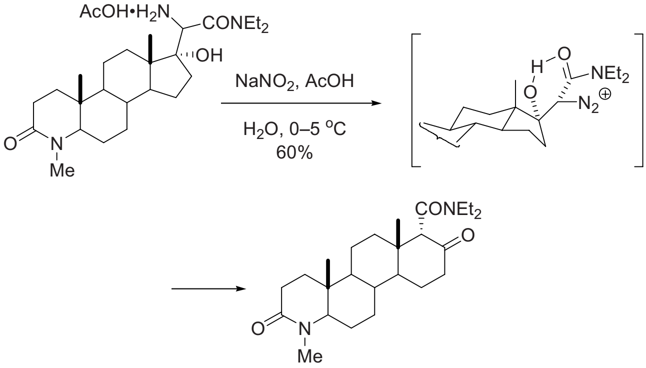
Step 3, Ring-expansion *via* rearrangement



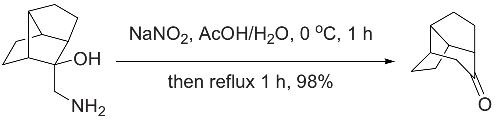
Example 1[5]



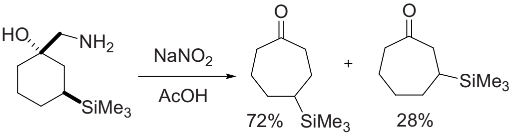
Example 2[6]



Example 3[7]



Example 4[9]



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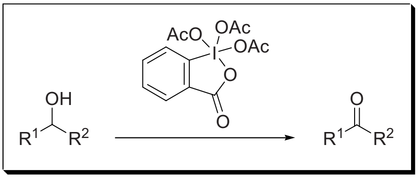
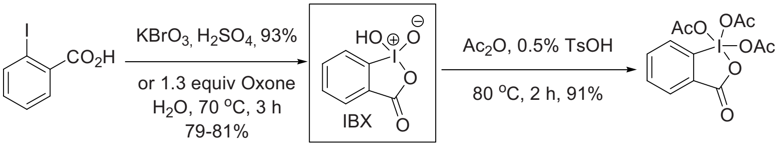
Dess–Martin periodinane oxidation

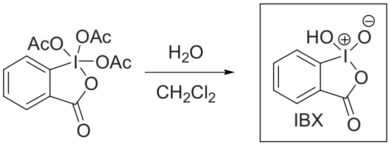
Oxidation of alcohols to the corresponding carbonyl compounds using triacetoxyperiodinane. The Dess–Martin periodinane, 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one, is one of the most useful oxidant for the conversion of primary and secondary alcohols to their corresponding aldehyde or ketone products, respectively.



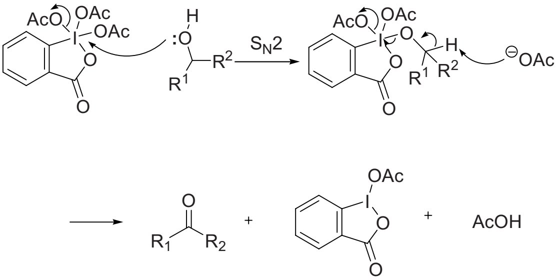
Preparation,[1,2] The oxone preparation is much safer and easier than $KBrO_3$. The IBX intermediate that comes out of it has proven to be far less explosive[12]



However, The Dess–Martin periodinane is hydrolyzed by moisture to *o*-iodoxybenzoic acid (IBX), which is a more powerful oxidating agent[3]



Mechanism[1]



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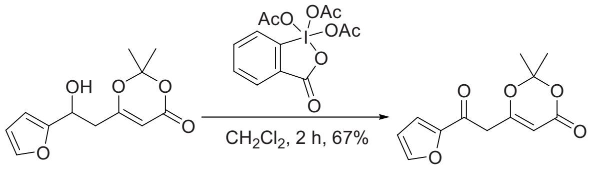
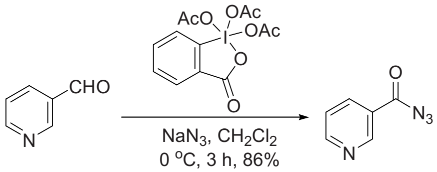
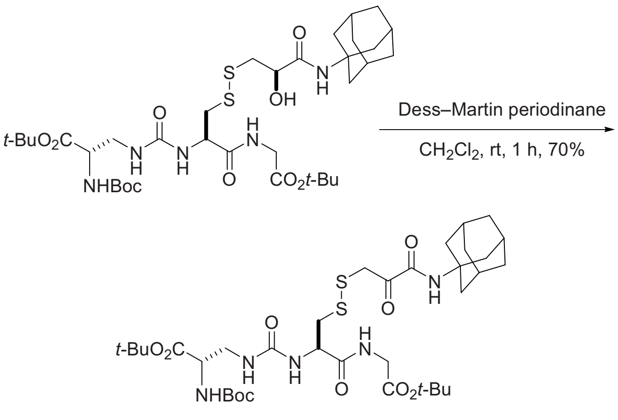
Example 1[6]



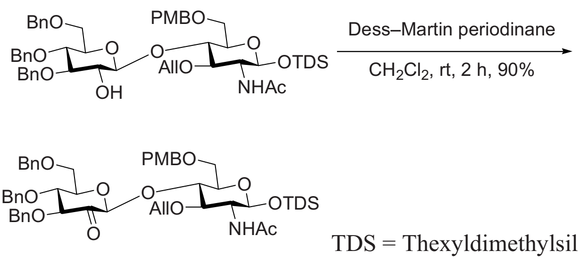
Example 2, An atypical Dess–Martin periodinane reactivity[7]



Example 3[10]



Example 4[11]



TDS = Thexyldimethylsilyl

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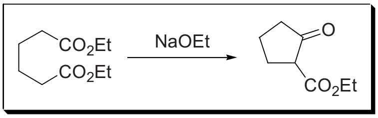
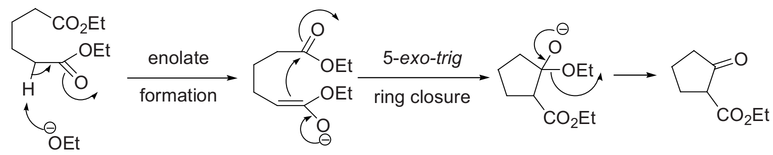
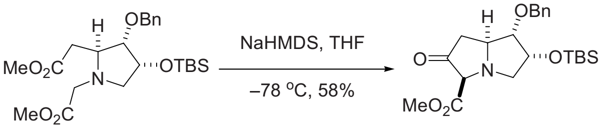
Dieckmann condensation

The Dieckmann condensation is the intramolecular version of the Claisen condensation.

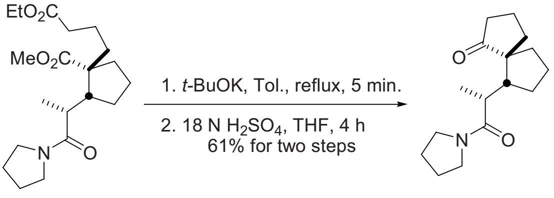




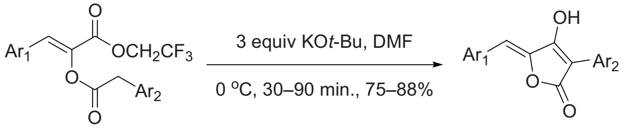
Example 1[6]



Example 2[8]



Example 3[9]



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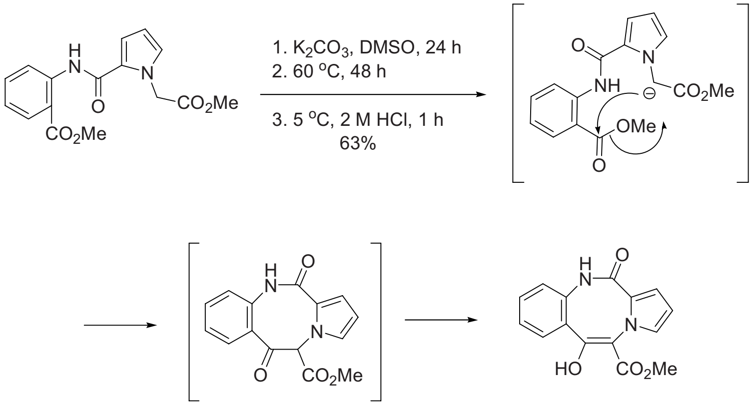
Example 4[10]



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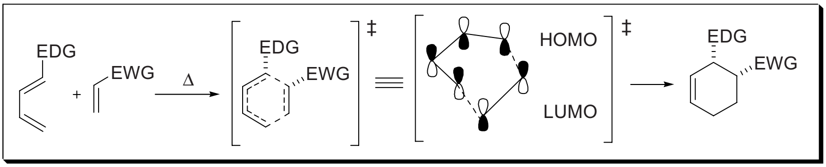
Diels–Alder reaction

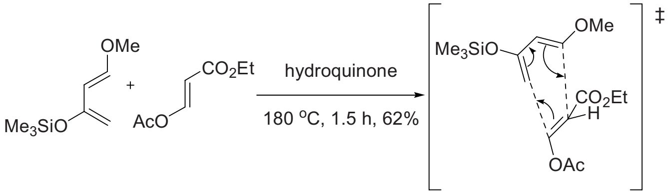
The Diels–Alder reaction, inverse electronic demand Diels–Alder reaction, as well as the hetero-Diels–Alder reaction, belong to the category of *[4+2]-cycloaddition reactions*, which are concerted processes. The arrow pushing here is merely illustrative.



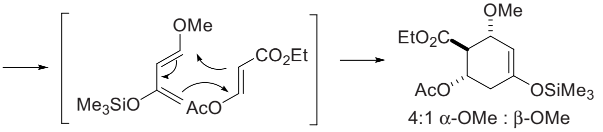
diene dienophile adduct

EDG = electron-donating group; EWG = electron-withdrawing group

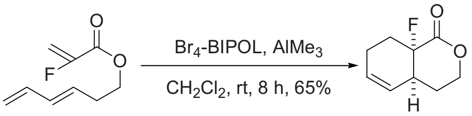
Example 1[6]



The Danishefsky diene Alder's *endo* rule



Example 2, Intramolecular Diels–Alder reaction[7]



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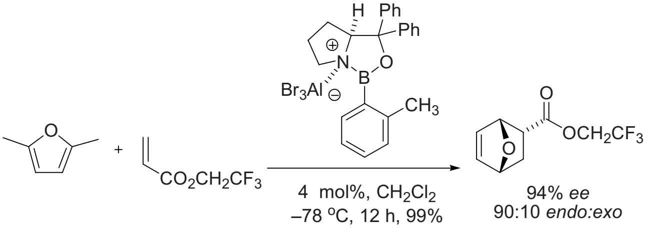
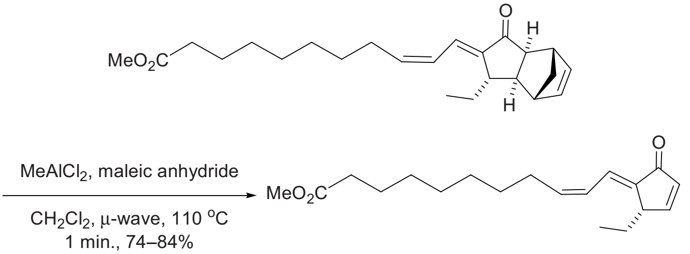
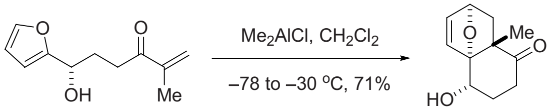
Example 3, Asymmetric Diels–Alder reaction[5,8]



Example 4, Retro-Diels–Alder reaction[4,9]



Example 5, Intramolecular Diels–Alder reaction[11]



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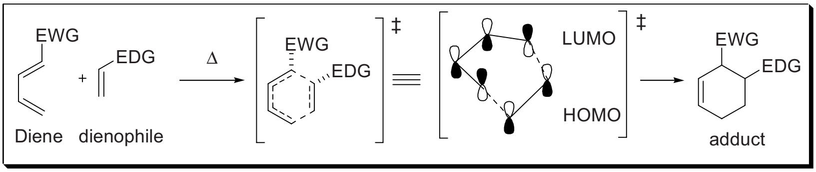
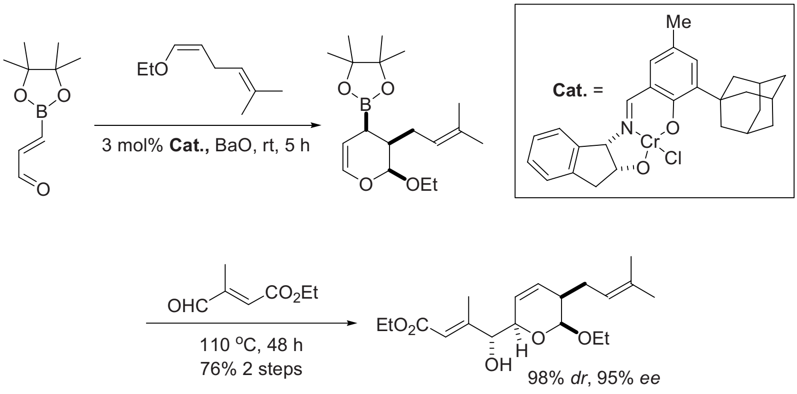
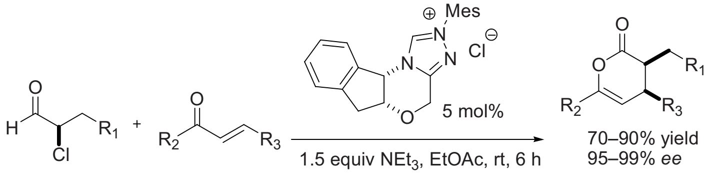
Inverse electronic demand Diels–Alder reaction



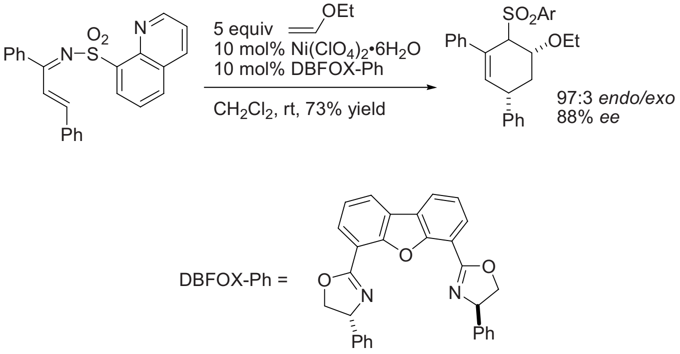
Example 1[2]



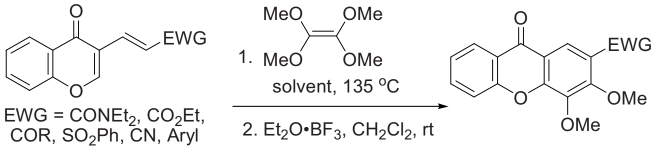
Example 2[3]

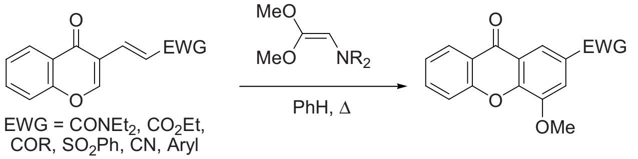


Example 3, Catalytic asymmetric inverse-electron-demand Diels–Alder reaction[4]



Example 4[5]





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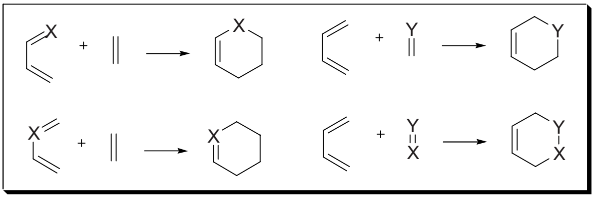
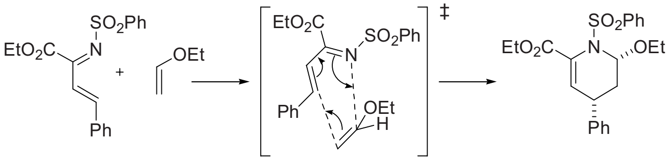
Hetero-Diels–Alder reaction

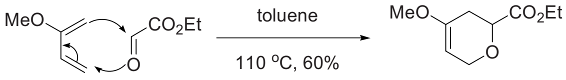
Heterodiene addition to dienophile or heterodienophile addition to diene. Typical hetero-Diels–Alder reactions are aza-Diels–Alder reaction and oxo-Diels–Alder reaction.



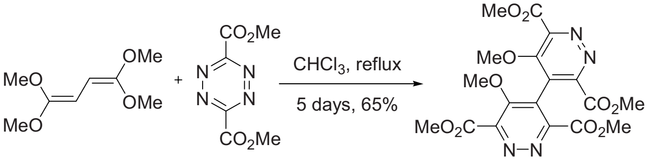
e.g.:



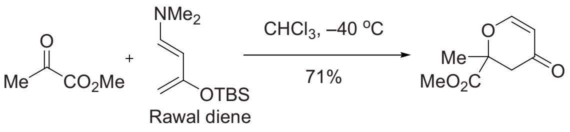
Example 1, Heterodienophile addition to diene[1]



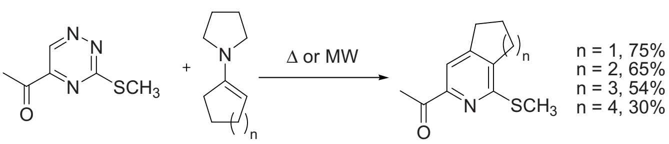
Example 2, Similar to the **Boger pyridine synthesis** (see page 59)[2]



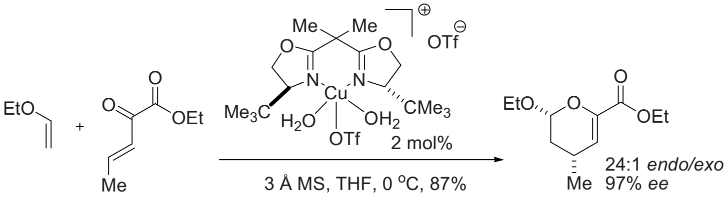
Example 3, Using **the Rawal diene**[4]



Example 4, Also similar to the Boger pyridine synthesis[6]



Example 5[7]



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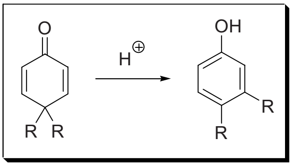
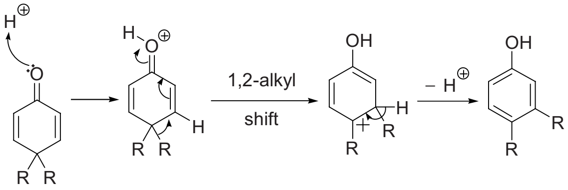
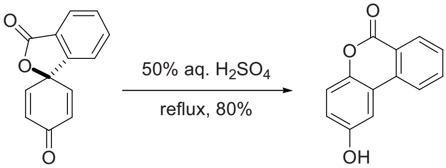
Dienone–phenol rearrangement

Acid-promoted rearrangement of 4,4-disubstituted cyclohexadienones to 3,4-disubstituted phenols.

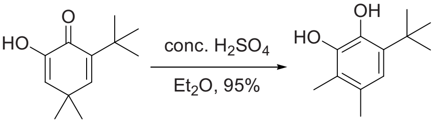




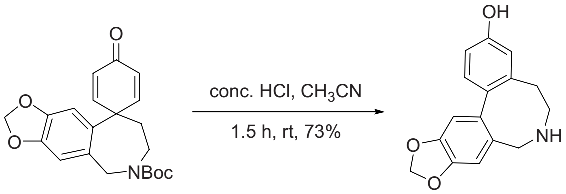
Example 1[4]



Example 2[5]



Example 3[9]



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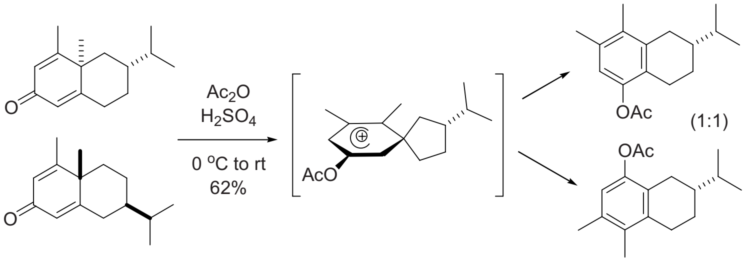
Example 4[10]



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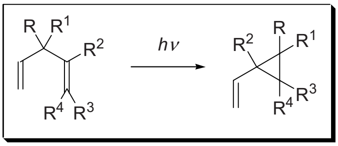
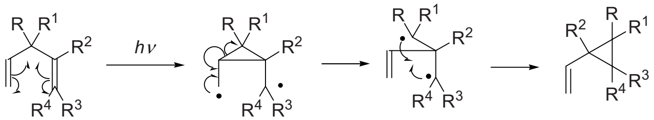
Di-π-methane rearrangement

Conversion of 1,4-dienes to vinylcyclopropanes under photolysis. Also known as the **Zimmerman rearrangement**.

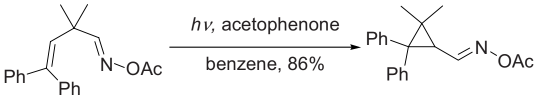


1,4-diene vinylcyclopropane

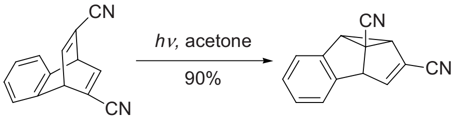


diradical diradical

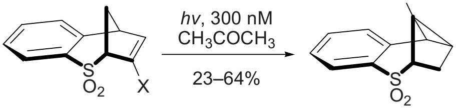
Example 1, Aza-π-methane rearrangement[2]



Example 2[4]



Example 3[8]



X = CH_3, CH_2Ph, $COCMe_3$, CO_2CH_2Ph
$SiMe_3$, $SnBu_3$, SePh, —≡—$(CH_2)_3CH_3$

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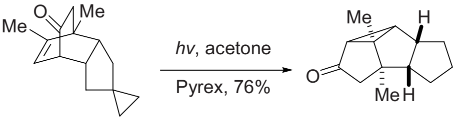
Example 4, Oxa-π-methane rearrangement[8]



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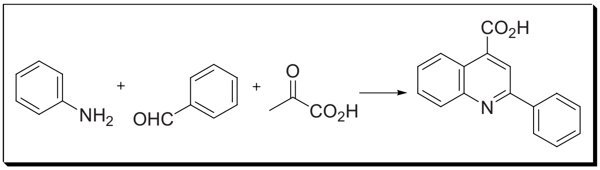
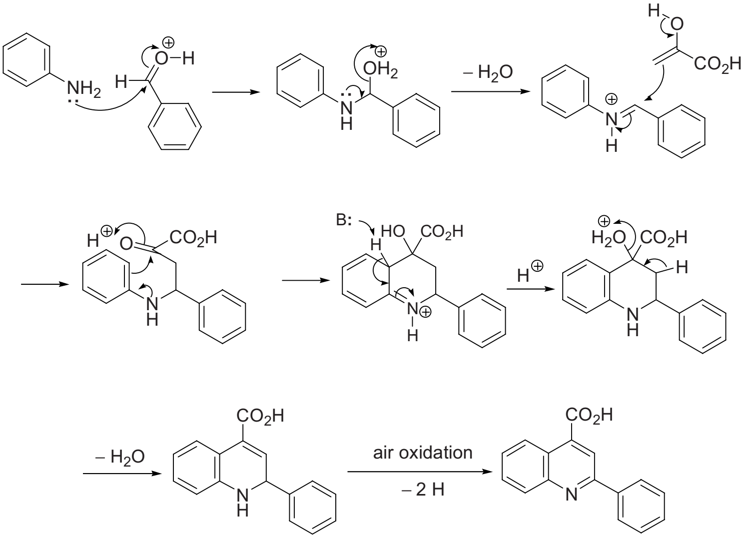
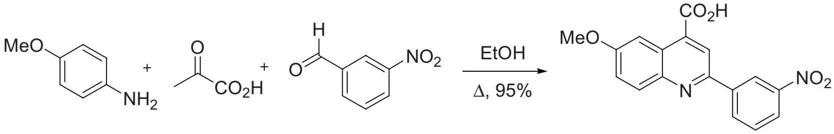
Doebner quinoline synthesis

Three-component coupling of an aniline, pyruvic acid, and an aldehyde to provide a quinoline-4-carboxylic acid.

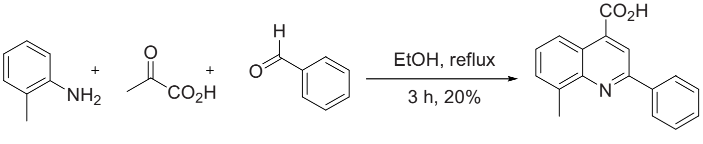




Example 1[2]



Example 2[6]



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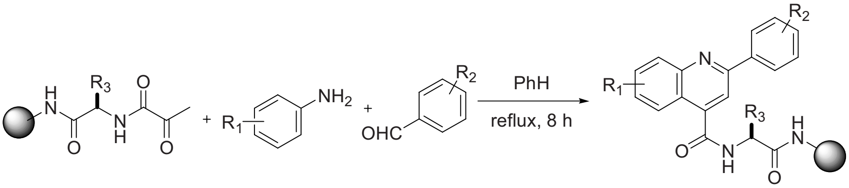
Example 3, Combinatorial Doebner reaction[7]



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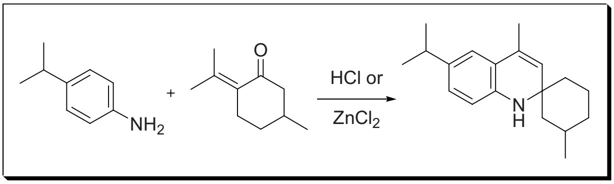
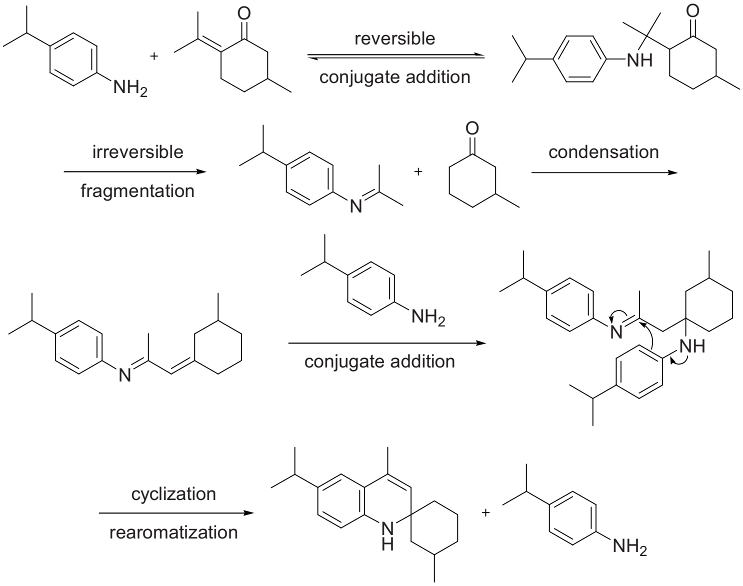
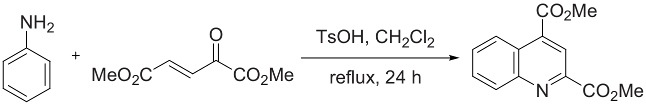
Doebner–von Miller reaction

Doebner–von Miller reaction is a variant of the Skraup quinoline synthesis (page 509). Therefore, the mechanism for the Skraup reaction is also operative for the Doebner–von Miller reaction. The following mechanism is favored by Denmark's mechnistic study using ^{13}C-labelled α,β-unsaturated ketones.[9]





Example 1[5]



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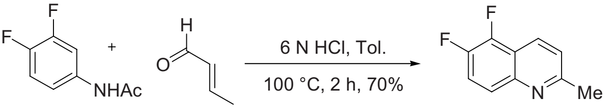
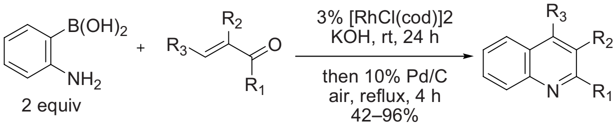


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_84,

Example 3, A novel variant[10]



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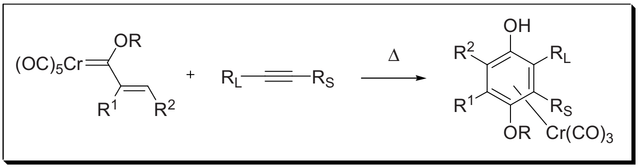
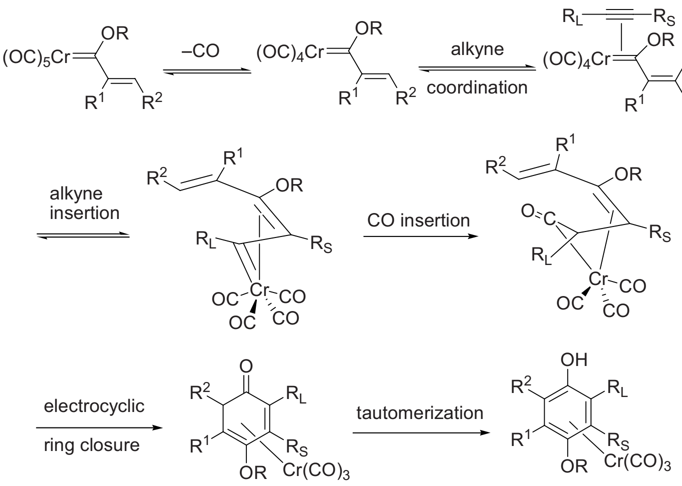
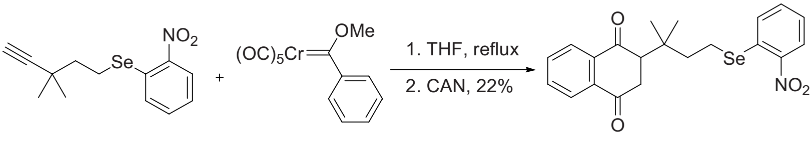
Dötz reaction

$Cr(CO)_3$-coordinated hydroquinone from vinylic alkoxy pentacarbonyl chromium carbene (Fischer carbene) complex and alkynes.

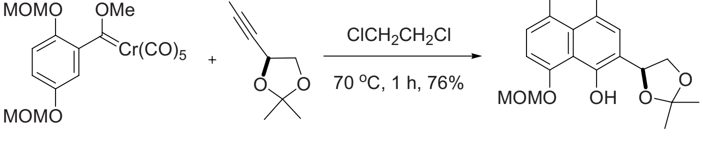




Example 1[5]



Example 3[8]



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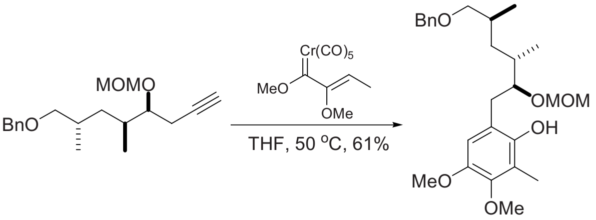
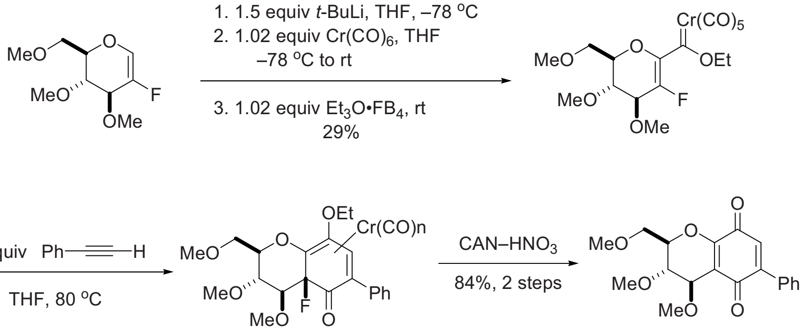
Example 3[8]



Example 3[9]



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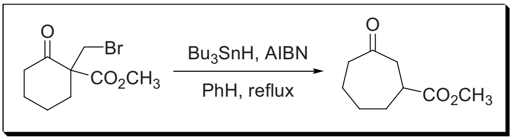
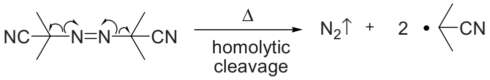
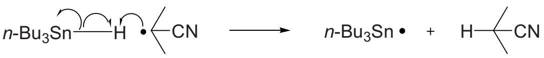
Dowd–Beckwith ring expansion

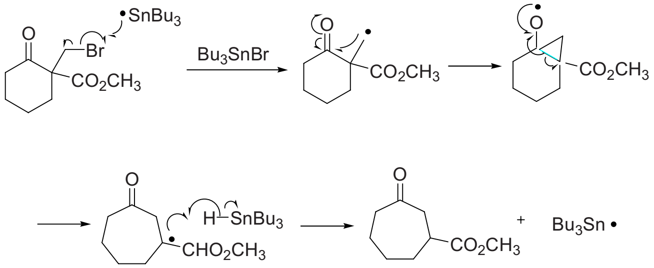
Radical-mediated ring expansion of 2-halomethyl cycloalkanones.



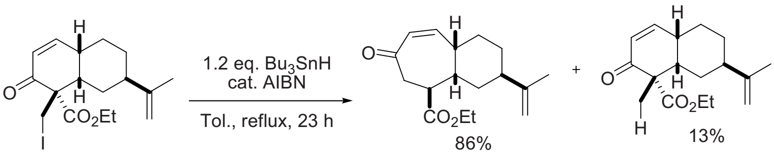


2,2′-azobisisobutyronitrile (AIBN)

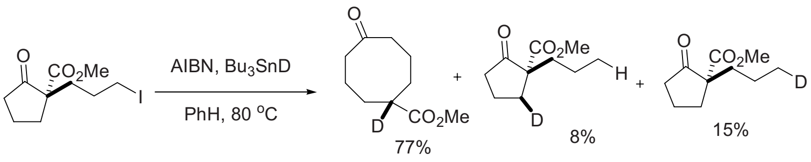




Example 1[4]



Example 2[9]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_86,

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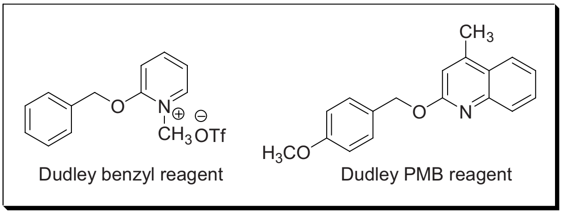
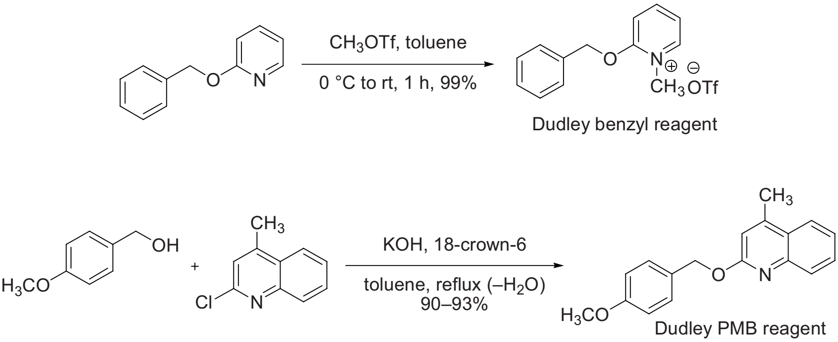
Dudley reagent



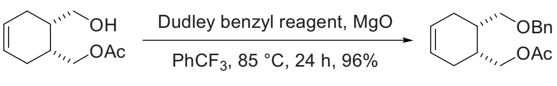
The Dudley reagents are employed for the protection of alcohols as benzyl[1] or PMB[2] ethers, respectively, under mild conditions. Carboxylic acids are readily protected as well.[3] Activation of the appropriate Dudley reagent in the presence of an alcohol furnishes the desired arylmethyl ether. The benzyl reagent is activated upon warming to approximately 80–85 °C, whereas activation of the PMB reagent occurs at room temperature upon treatment with methyl triflate (CH_3OTf) or protic acid.[4] Aromatic solvents, most commonly trifluorotoluene, often provide the best results. Magnesium oxide (MgO) is typically included in the reaction mixture as an acid scavenger.[5] For benzylation of carboxylic acids, triethylamine (Et_3N) is used in place of MgO.[3]

Preparation:[1–3]



The Dudley reagents are conveniently prepared from readily available starting materials and are indefinitely stable to storage and handling under standard laboratory conditions. Alternatively, both reagents are commercially available.

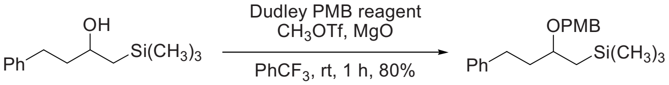
Example 1[6]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_87,

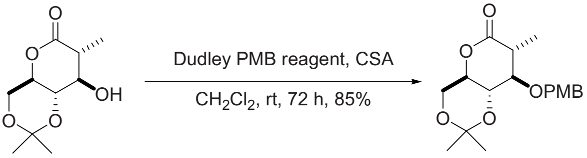
Benzylation of a monoacetylated diol is shown in Example 1.[6] The Dudley benzyl reagent was uniquely effective for protection of the free alcohol without loss and/or migration of the labile acetyl group.

Example 2[2]



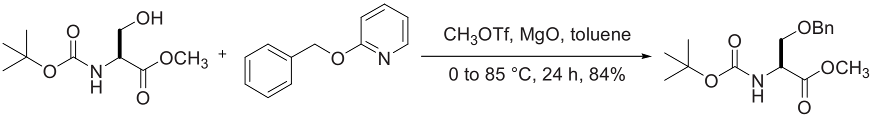
PMB-protection of a β-hydroxysilane can be accomplished without competition from the Peterson elimination (Example 2),[2] which would occur under the basic or acidic conditions required for many other alkylation reactions.

Example 3[4]



The Dudley PMB reagent can also be activated under mildly acidic conditions using catalytic camphorsulfonic acid (CSA) in lieu of CH_3OTf (Example 3).[4]

Example 4, *In situ*-formation of the Dudley benzyl reagent is achieved by treating a mixture of an alcohol and 2-benzyloxypyridine with CH_3OTf[7]



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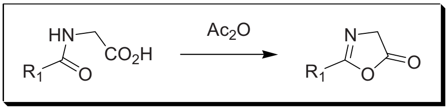
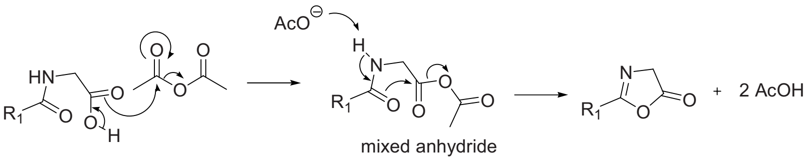
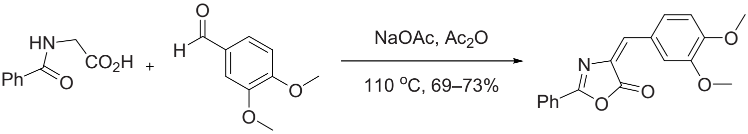
Erlenmeyer–Plöchl azlactone synthesis

Formation of 5-oxazolones (or “azlactones”) by intramolecular condensation of acylglycines in the presence of acetic anhydride.

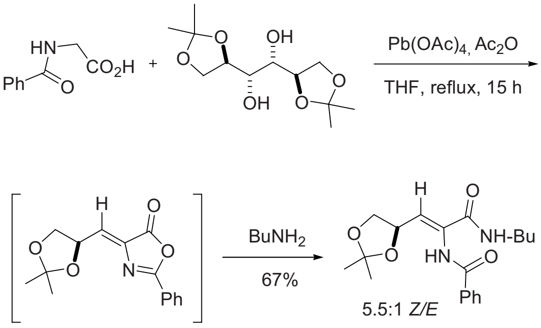




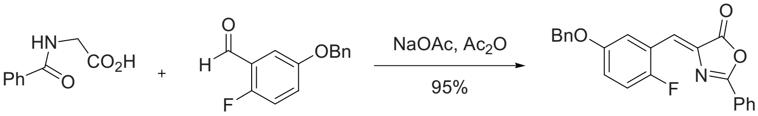
Example 1[2]



Example 2[8]



Example 3[9]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_88,

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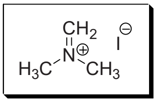
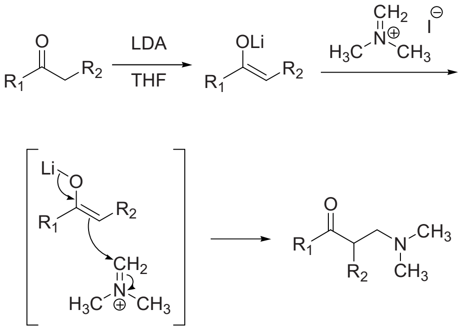
Eschenmoser's salt



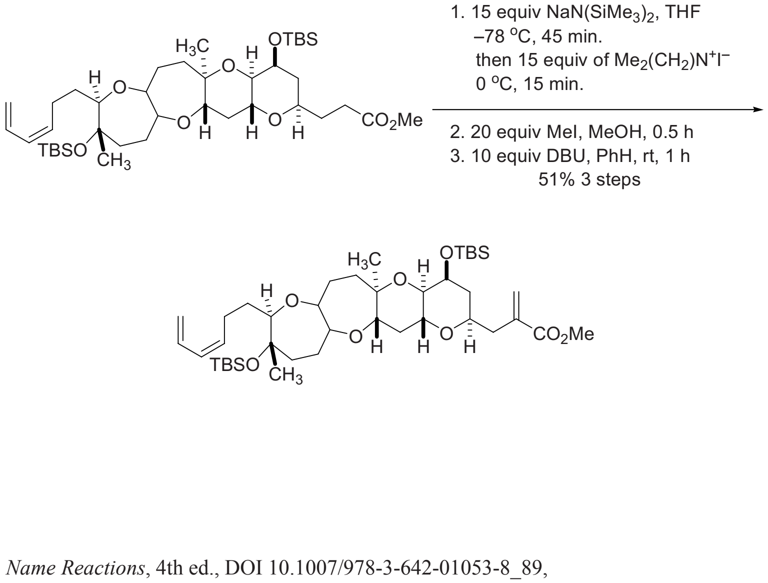
Eschenmoser's salt, dimethylmethylideneammonium iodide, is a strong dimethylaminomethylating agent, used to prepare derivatives of the type $RCH_2N(CH_3)_2$. Enolates, enolsilylethers, and even more acidic ketones undergo efficient dimethylaminomethylation—employed in the Mannich reaction.

Mechanism



Example 1[3]

Once prepared, the resulting tertiary amines can be further methylated and then subjected to base-induced elimination to afford methylenated ketones.



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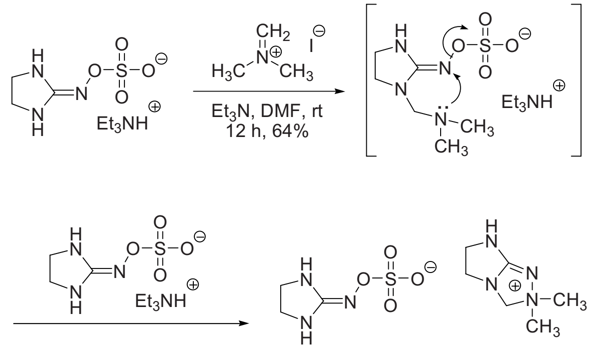
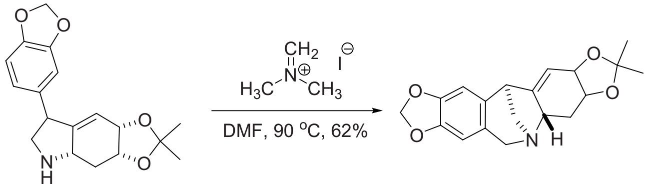
Example 2[4]



Example 3[5]



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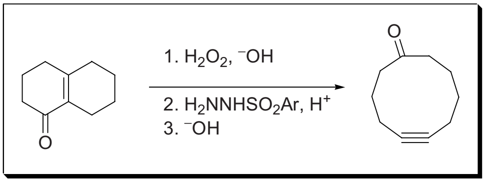
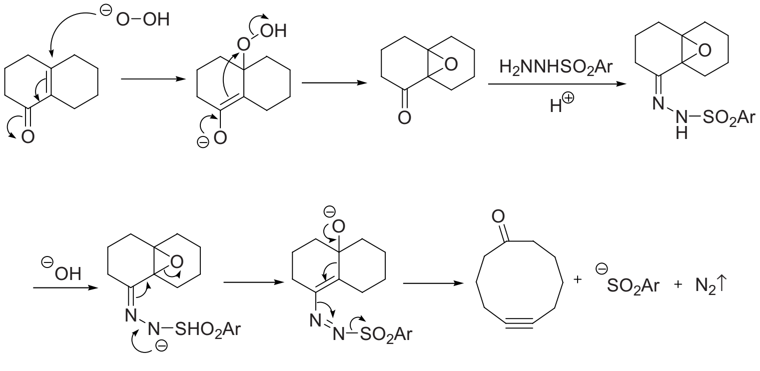
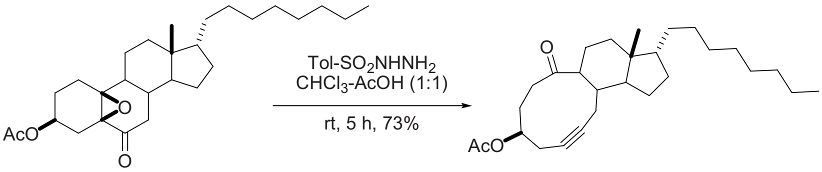
Eschenmoser–Tanabe fragmentation

Fragmentation of α,β-epoxyketones *via* the intermediacy of α,β-epoxy sulfonylhydrazones.





Example 1[4]



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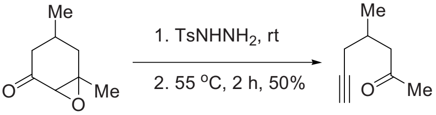

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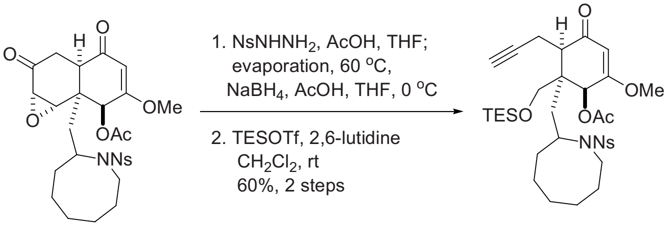
Example 3[9]



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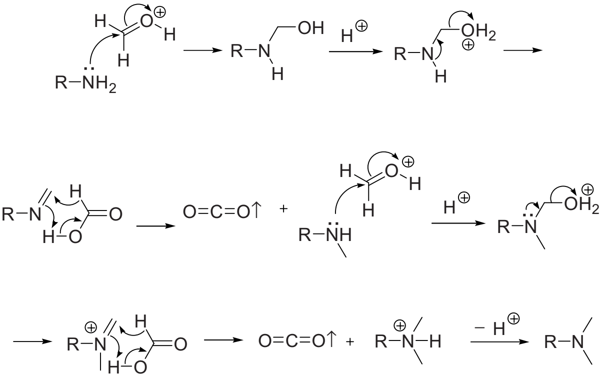
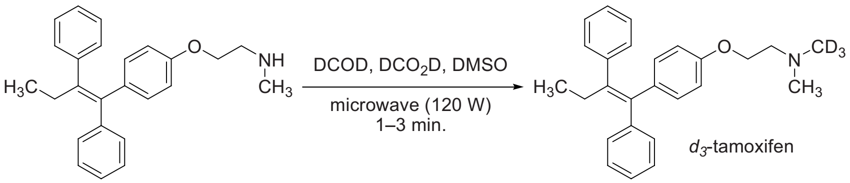
Eschweiler–Clarke reductive alkylation of amines

Reductive methylation of primary or secondary amines using formaldehyde and formic acid. *Cf.* Leuckart–Wallach reaction.

formic acid is the hydride source as a reducing agent



Example 1[7]



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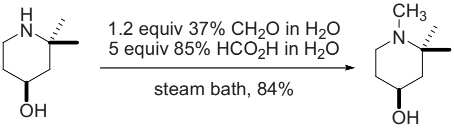

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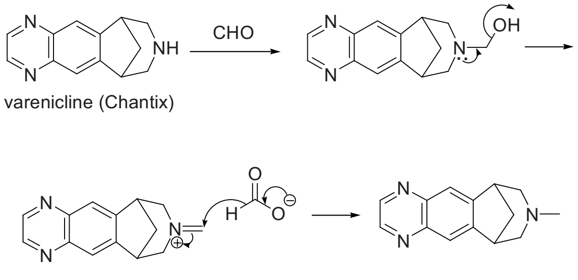
Example 3[10]



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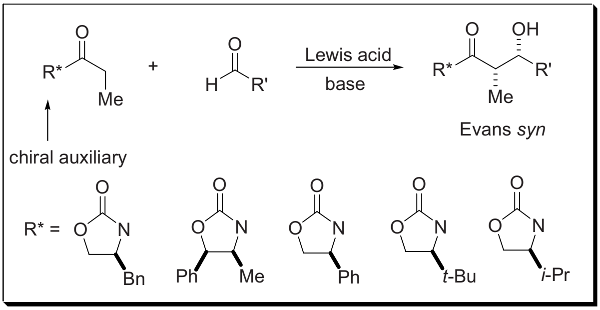
Evans aldol reaction

Asymmetric aldol condensation of aldehyde and chiral acyl oxazolidinone, the Evans chiral auxiliary.



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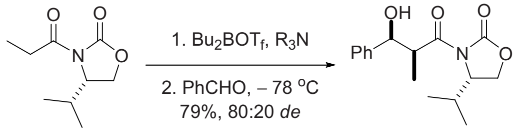

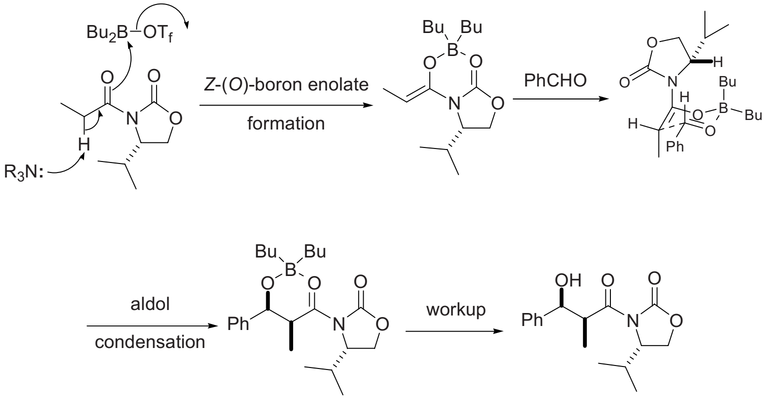

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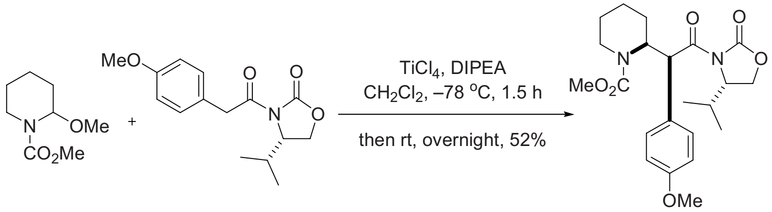

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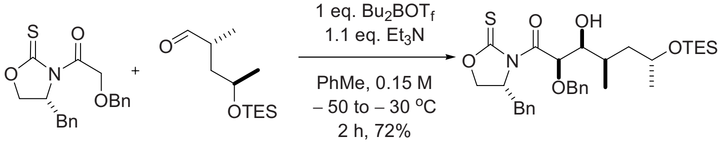
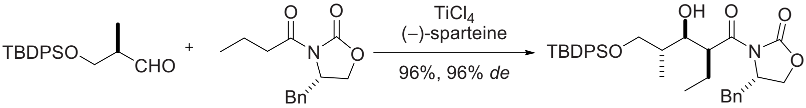
Example 3[9]



Example 4, Crimmins procedure[10]



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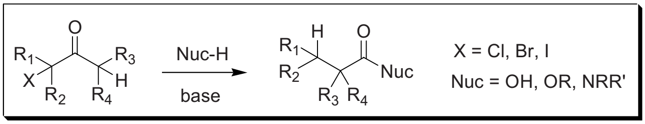
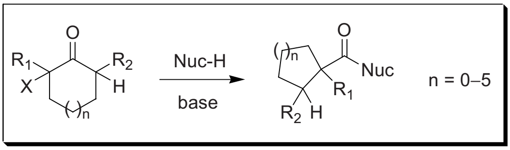
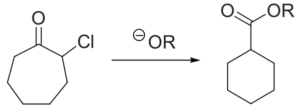
Favorskii rearrangement

Transformation of enolizable α-haloketones to esters, carboxylic acids, or amides *via* alkoxide-, hydroxide-, or amine-catalyzed rearrangements, respectively.

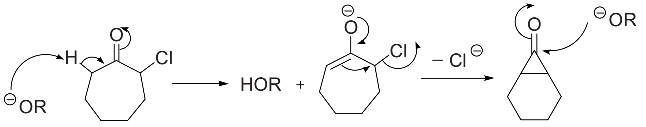


The intramolecular Favorskii Rearrangement:

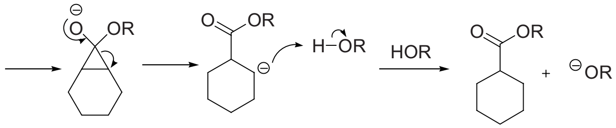




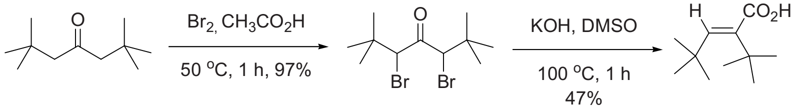
enolizable α-haloketone



cyclopropanone intermediate



Example 1[2]



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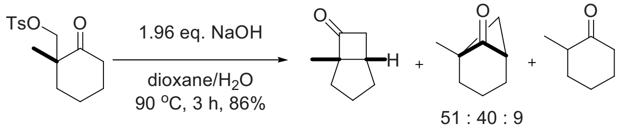
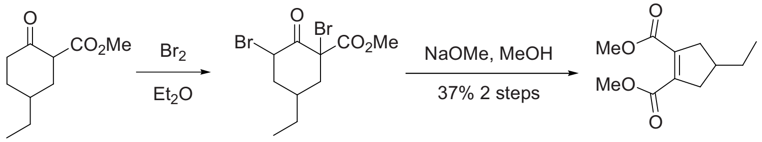
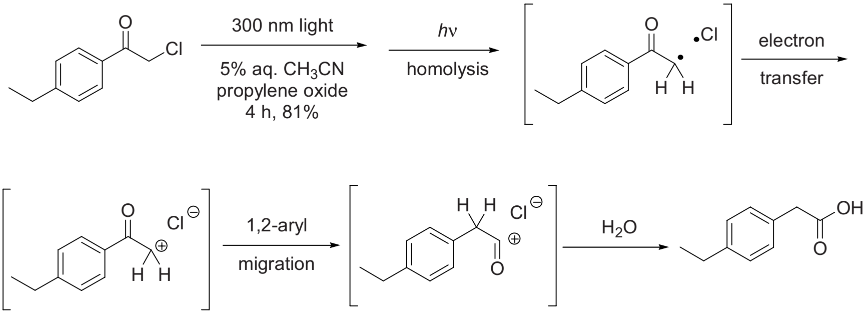
Example 2, Homo-Favorskii rearrangement[3]



Example 3[6]



Example 4, Photo-Favorskii Rearrangement[7]



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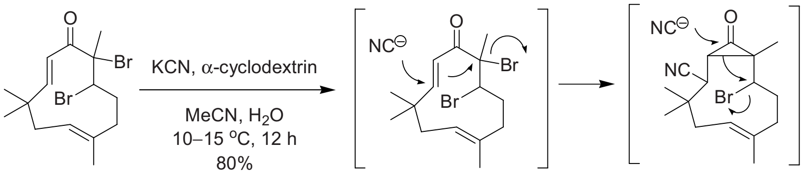
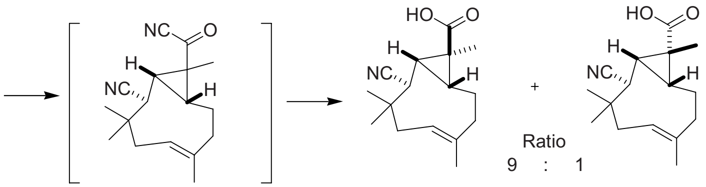
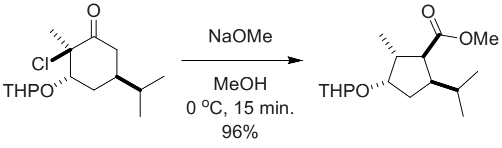




Example 6[10]



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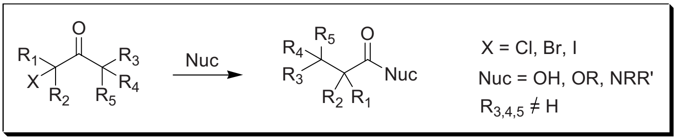
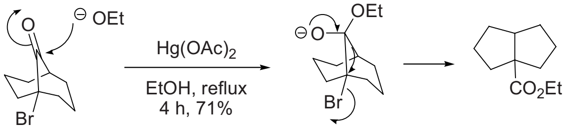
Quasi-Favorskii rearrangement

If there are no enolizable hydrogens present, the classical Favorskii rearrangement is not possible. Instead, a semi-benzylic mechanism can lead to a rearrangement referred to as quasi-Favorskii.

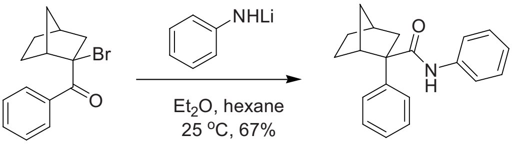


Example 1, Arthur C. Cope's initial discovery[1]

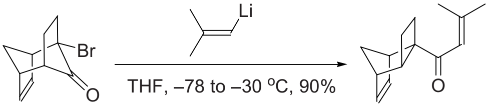


non-enolizable ketone

Example 2[5]



Example 3[6]



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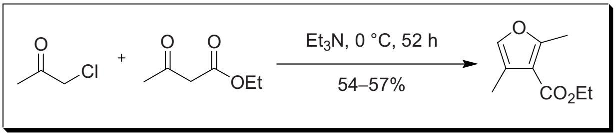
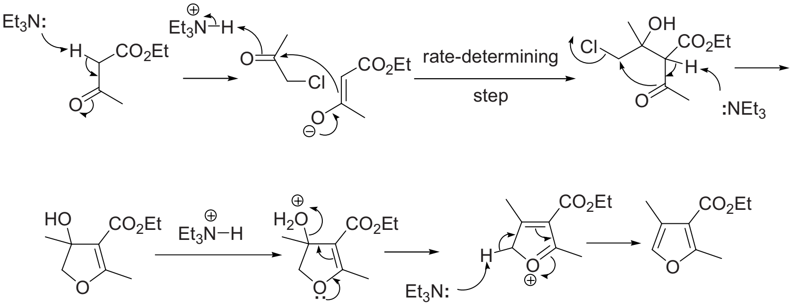
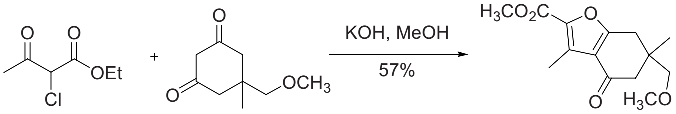
Feist–Bénary furan synthesis

α-Haloketones react with β-ketoesters in the presence of base to fashion furans.

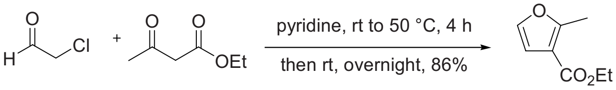




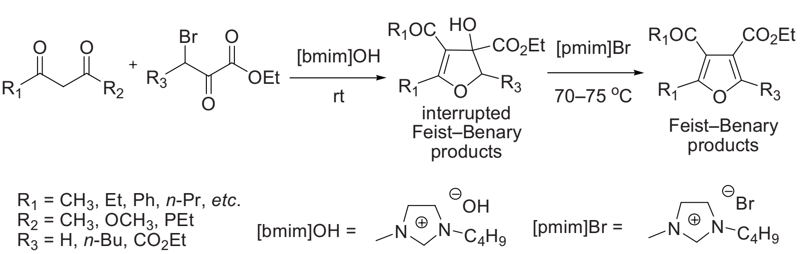
Example 1[2,3]



Example 2[4]



Example 3, Ionic liquid-promoted interrupted Feist–Benary reaction[10]



R$_1$ = CH$_3$, Et, Ph, *n*-Pr, *etc*.
R$_2$ = CH$_3$, OCH$_3$, PEt
R$_3$ = H, *n*-Bu, CO$_2$Et

J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_94,

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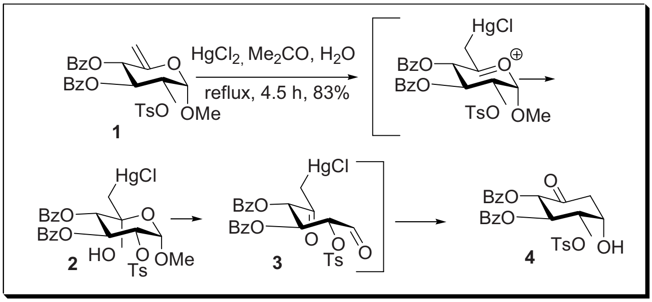
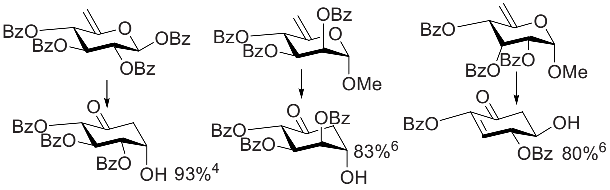
Ferrier carbocyclization

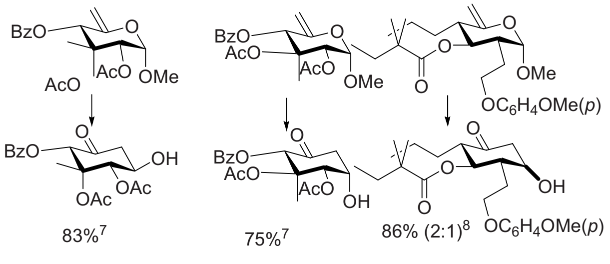
This process (also known as the "Ferrier II Reaction") has proved to be of considerable value for the efficient, one-step conversion of 5,6-unsaturated hexopyranose derivatives into functionalized cyclohexanones useful for the preparation of such enantiomerically pure compounds as inositols and their amino, deoxy, unsaturated and selectively *O*-substituted derivatives, notably phosphate esters. In addition, the products of the carbocyclization have been incorporated into many complex compounds of interest in biological and medicinal chemistry.[1,2]

General examples:[3]

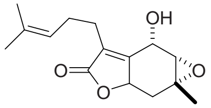




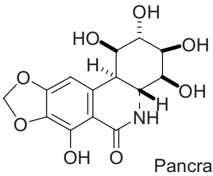
More complex products:



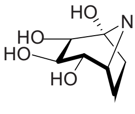
Complex bioactive compounds made following the application of the reaction:



Paniculide A[9]



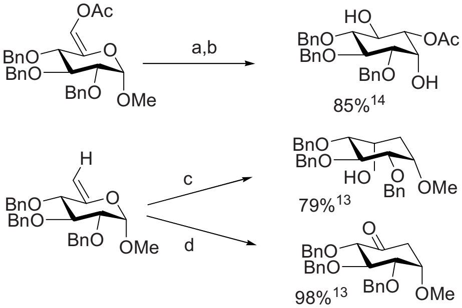
Pancratistatin[10]



Calystegine B_2[11]

J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_95,

Modified hex-5-enopyranosides and reactions



a, $Hg(OCOCF_3)_2$, Me_2CO, H_2O, 0 °C; b, $NaBH(OAc)_3$, AcOH, MeCN, rt; c, *i*-Bu_3Al, PhMe, 40 °C; d, Ti(O*i*-Pr)Cl_3, CH_2Cl_2, –78 °C, 15 min. (Note: The aglycon is retained in the Al- and Ti-induced reactions).

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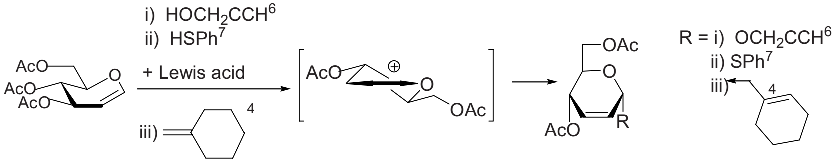
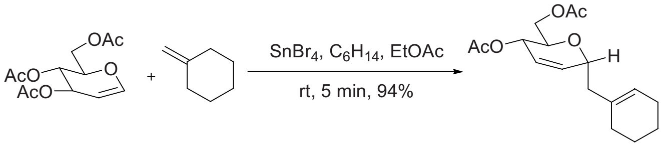
Ferrier glycal allylic rearrangement

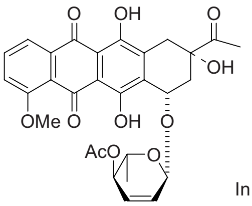
In the presence of Lewis acid catalysts *O*-substituted glycal derivatives can react with *O*-, *S*-, *C*- and, less frequently, *N*-, *P*- and halide nucleophiles to give 2,3-unsaturated glycosyl products.[1,2] This allylic transformation has been termed the "Ferrier Reaction" or, to avoid complications, the "Ferrier I Reaction" or the "Ferrier Rearrangement". However, the reaction was first noted by Emil Fischer when he heated tri-*O*-acetyl-*D*-glucal in water.[3] When carbon nucleophiles are involved, the term "Carbon Ferrier Reaction" has been used,[4] although the only contribution the Ferrier group made in this area was to find that tri-*O*-acetyl-*D*-glucal dimerizes under acid catalysis to give a *C*-glycosidic product.[5] The general reaction is illustrated by the separate conversions of tri-*O*-acetyl-*D*-glucal with *O*-, *S*- and *C*-nucleophiles to the corresponding 2,3-unsaturated glycosyl derivatives. Normally, Lewis acids are used as catalysts, boron trifluoride etherate being the most common. Allyloxycarbenium ions are involved as intermediates, high yields of products are obtained, and glycosidic compounds with quasi-axial bonds (as illustrated) predominate (commonly in the α,β-ratio of about 7:1). The examples illustrated[4,6,7] are typical of a very large number of literature reports.[1]



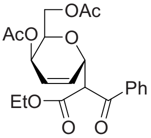
General examples[4]



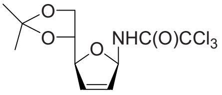
More complex products made directly from the corresponding glycols:



In benzene, BF_3•OEt_2, 5 °C, 10 min, (67%, α-anomer).[8]



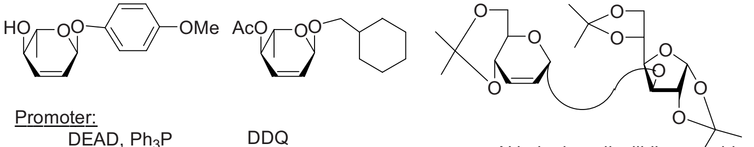
In $PhCOCH_2CO_2Et$, $BF_3.OEt_2$, rt, 15 min, (81% α-anomer).[9]



By spontaneous sigmatropic rearrangement of the glycal 3-trichloroacetimidate made with NaH, Cl_3CCN, (78% α-anomer).[10]

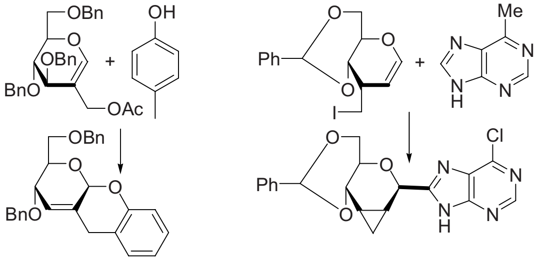
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_96,

Products formed without acid catalysts



Promoter:		
DEAD, Ph_3P (80%, α-anomer)[11]	DDQ (88%, mainly α)[12]	*N*-iodonium dicollidine perchlorate (65%, mainly α)[13]
C-3 leaving group of glycal:		
hydroxy	acetoxy	pent-4-enoyloxy

Modified glycals and their reactions:



$BF_3 \cdot OEt_2$, CH_2Cl_2, 0 °C (70%, mainly α)[14]

$AgNO_3$, Na_2CO_3, reflux $MeNO_2$, 6 h (58%, α,β 1:1).[15]

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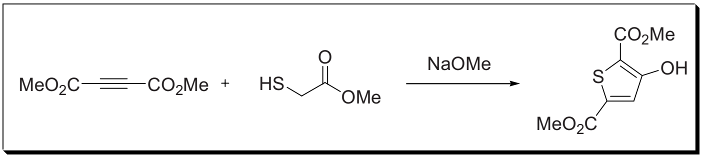
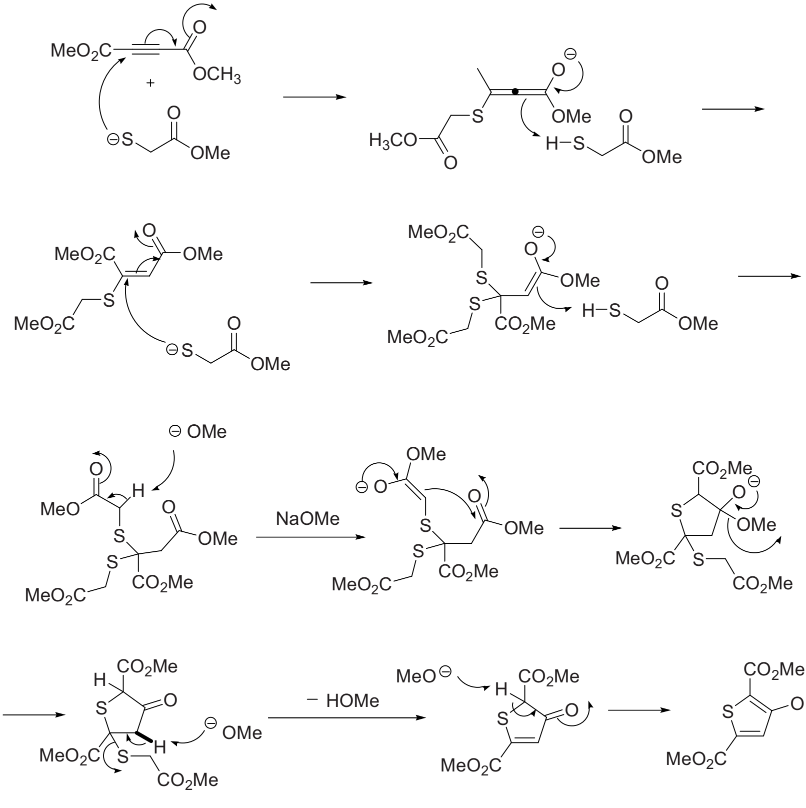
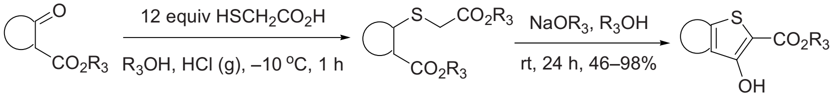
Fiesselmann thiophene synthesis

Condensation reaction of thioglycolic acid derivatives with α,β-acetylenic esters, which upon treatment with base result in the formation of 3-hydroxy-2-thiophenecarboxylic acid derivatives.



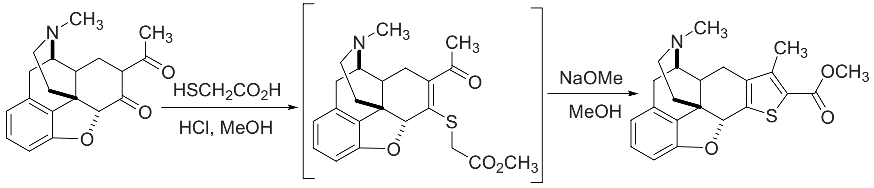


Example 1[5]

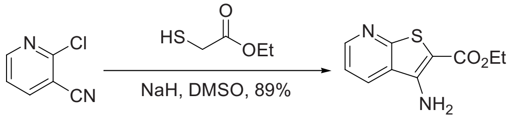


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_97,

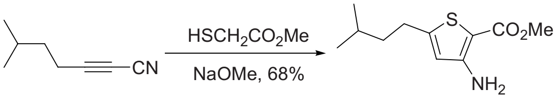
Example 2[6]



Example 3[7]



Example 4[9]



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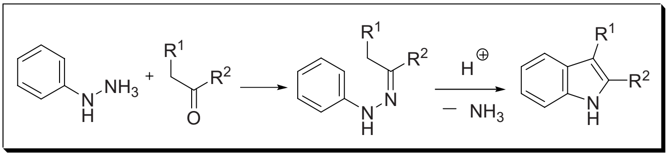
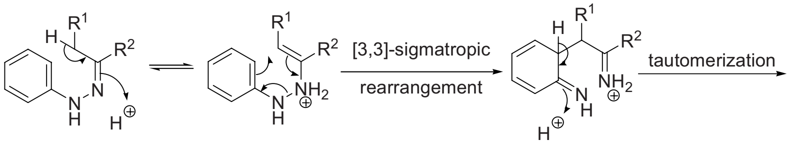
Fischer indole synthesis

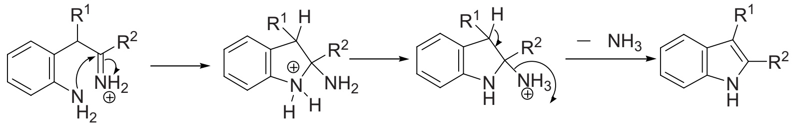
Cyclization of arylhydrazones to indoles.



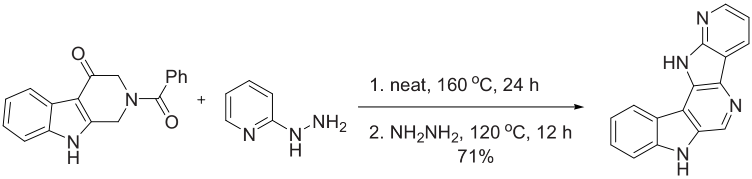
phenylhydrazine phenylhydrazone



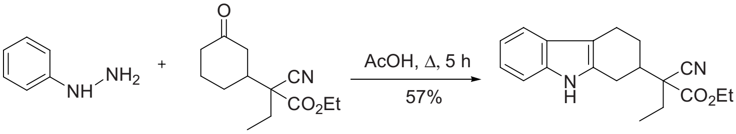
protonation ene-hydrazine double imine



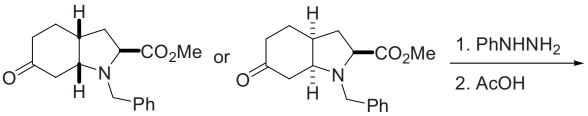
Example 1[3]



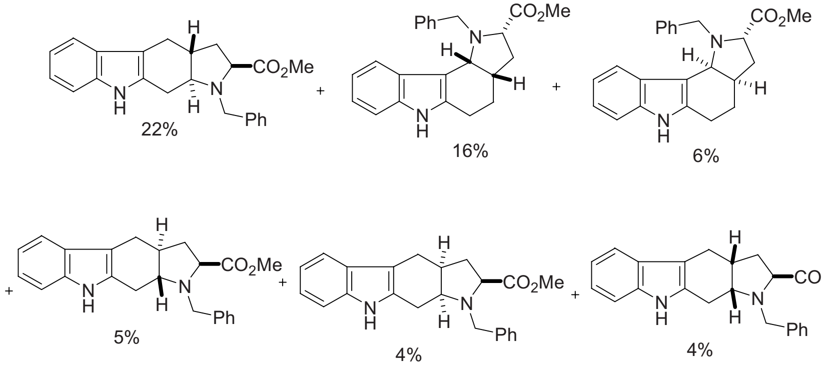
Example 2[13]



Example 4 (Severe racemization)[9]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_98,



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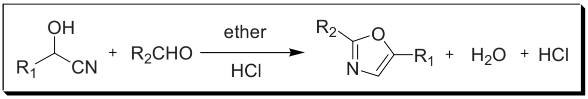
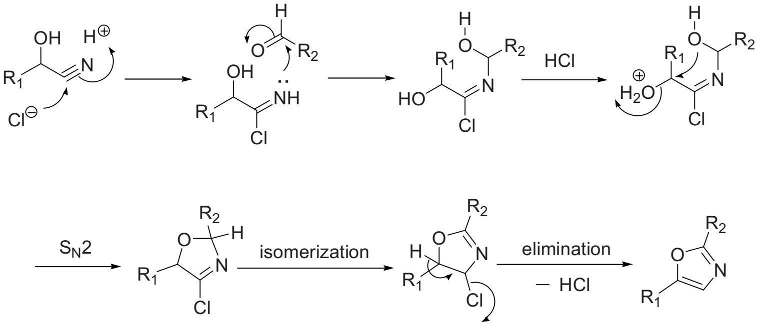
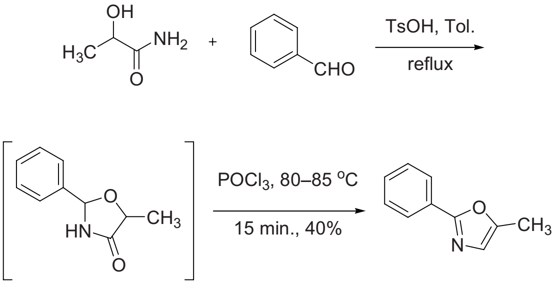
Fischer oxazole synthesis

Oxazoles from the condensation of equimolar amounts of aldehyde cyanohydrins and aromatic aldehydes in dry ether in the presence of dry hydrochloric acid.

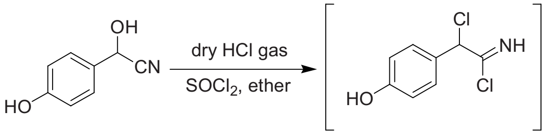




Example 1[4]



Example 2[8]



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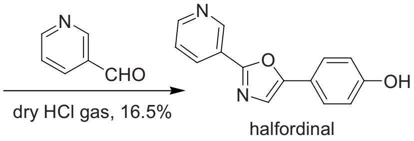

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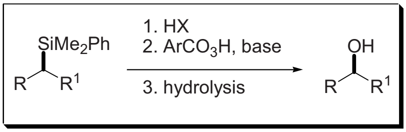
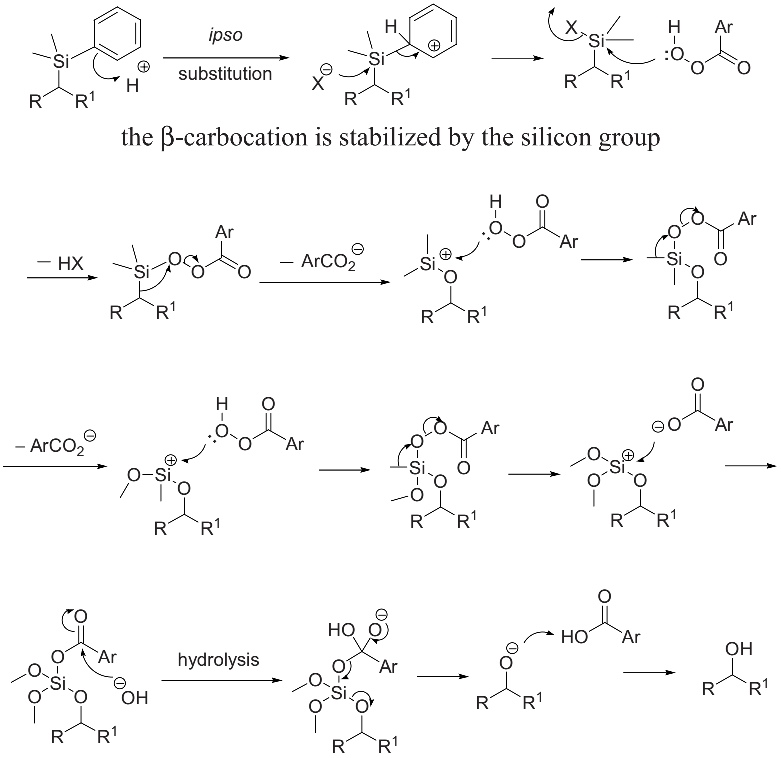
Fleming–Kumada oxidation

Stereoselective oxidation of alkyl-silanes into the corresponding alkyl-alcohols using peracids.

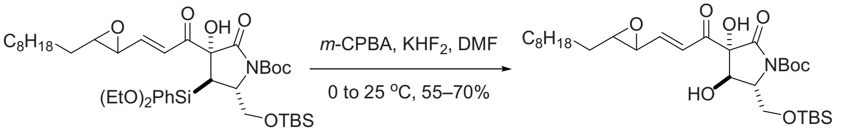


retention of configuration



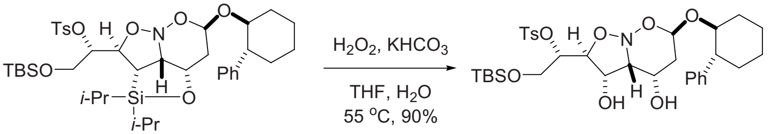
the β-carbocation is stabilized by the silicon group

Example 1[4]

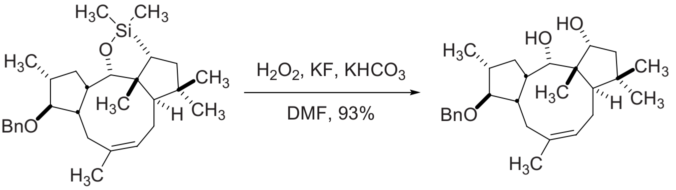


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_100,

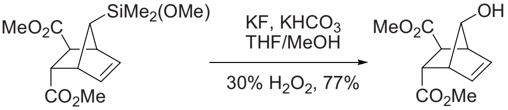
Example 2[5]



Example 3[8]



Example 4[9]



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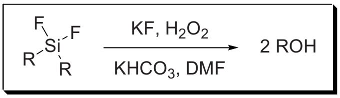
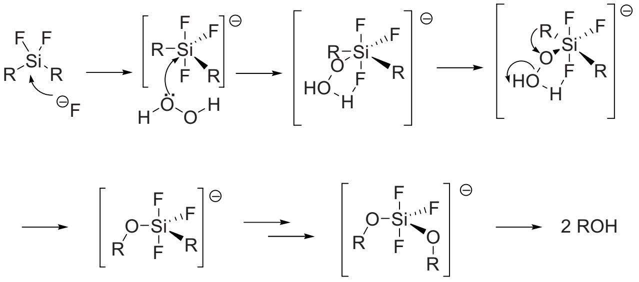
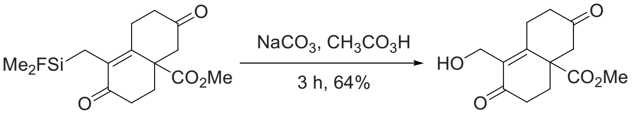
Tamao–Kumada oxidation

Oxidation of alkyl fluorosilanes to the corresponding alcohols. A variant of the Fleming–Kumada oxidation.

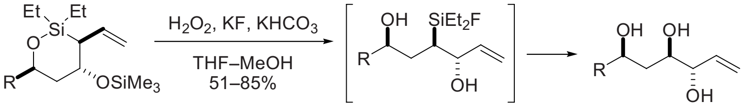




Example 1[3]



Example 2[4]



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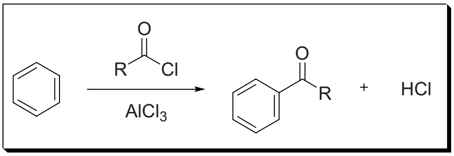
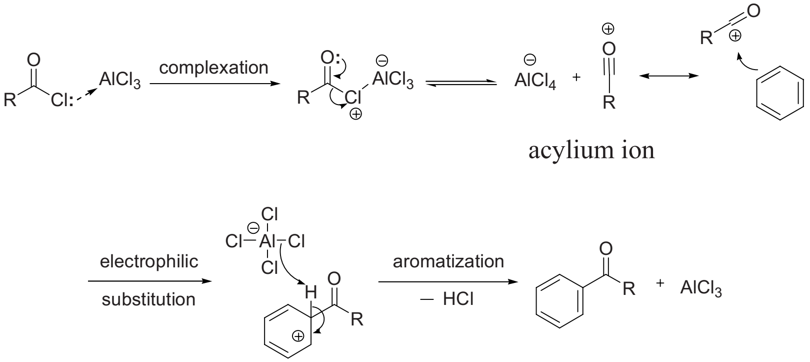
Friedel–Crafts reaction

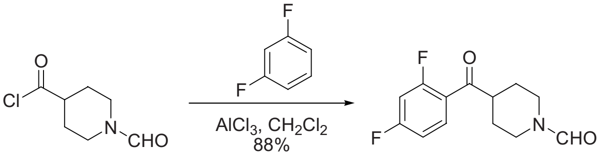
Friedel–Crafts acylation reaction

Introduction of an acyl group onto an aromatic substrate by treating the substrate with an acyl halide or anhydride in the presence of a Lewis acid.

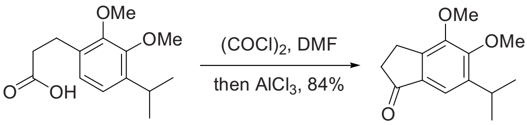




Example 1, Intermolecular Friedel–Crafts acylation[6]

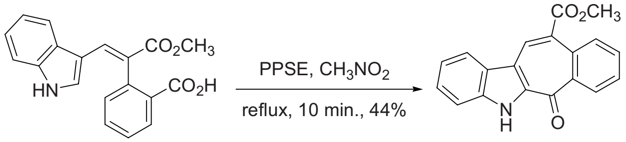


Example 2, Intramolecular Friedel–Crafts acylation[7]



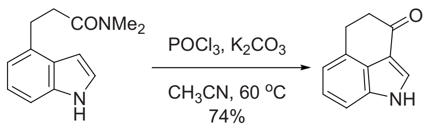
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_101,

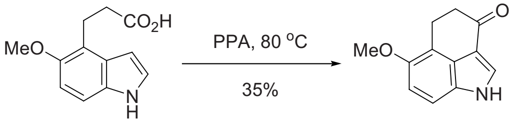
Example 3, Intramolecular Friedel–Crafts acylation[8]

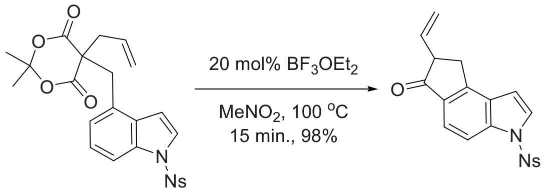


PPSE = Trimethylsilyl polyphosphate

Example 4, Intramolecular Friedel–Crafts acylation[9]







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the Lewis acid-catalyzed alkylations and acylations and published more than 50 papers and patents on the Friedel–Crafts reaction, which has become one of the most useful organic reactions.

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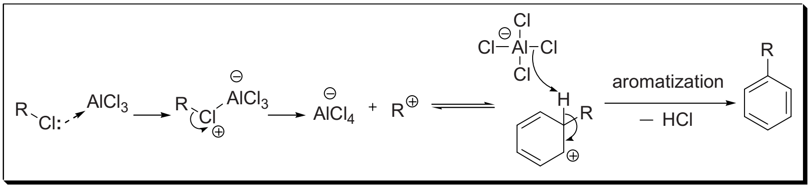
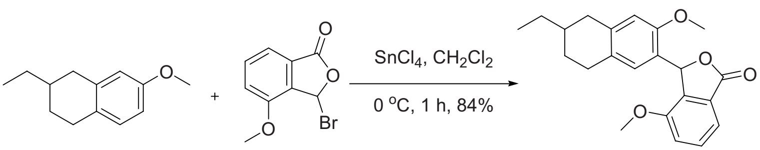
Friedel–Crafts alkylation reaction

Introduction of an alkyl group onto an aromatic substrate by treating the substrate with an alkylating agent such as alkyl halide, alkene, alkyne and alcohol in the presence of a Lewis acid.

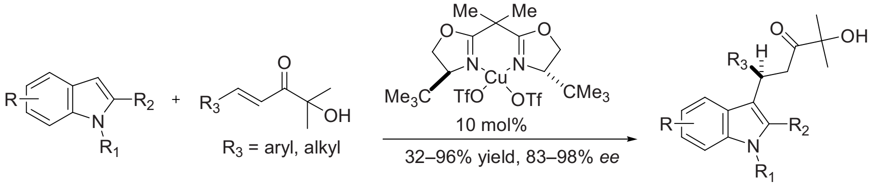


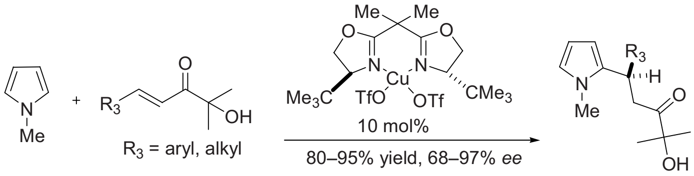
alkyl cation

Example 1[1]

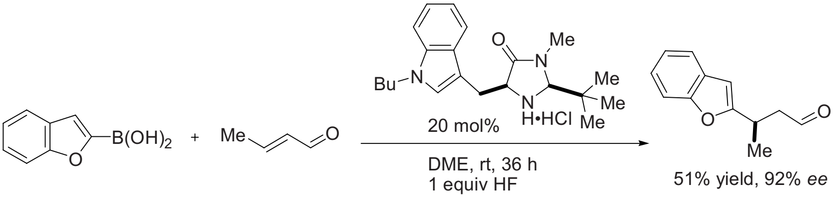


Example 2[4]





Example 3[5]



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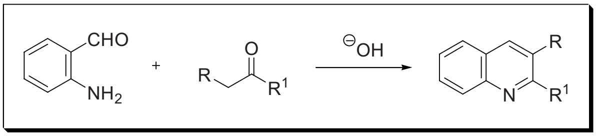
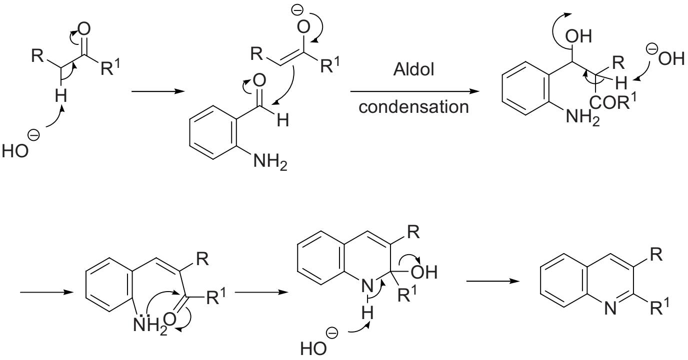
Friedländer quinoline synthesis

The Friedländer quinoline synthesis combines an α-amino aldehyde or ketone with another aldehyde or ketone with at least one methylene α adjacent to the carbonyl to furnish a substituted quinoline. The reaction can be promoted by acid, base, or heat.





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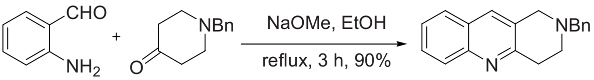

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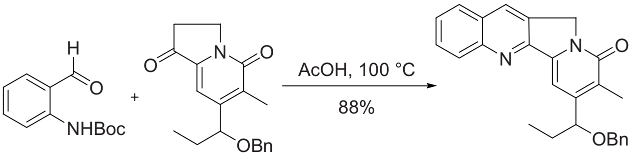
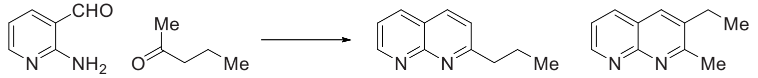


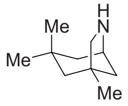
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_102,

Example 3[8]

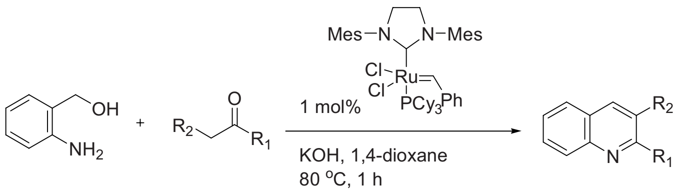


Conditions	Conversion	Ratio
NaOH, rt	> 99%	37:63
pyrrolidine, 5% H_2SO_4, rt	97%	86:14
TBAO, 5% H_2SO_4, rt	> 99%	87:13
TBAO, 5% H_2SO_4, slow addition, 65 °C	> 99%	94:6

TBAO = 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane



Example 4[10]



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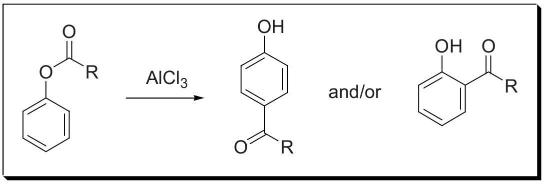
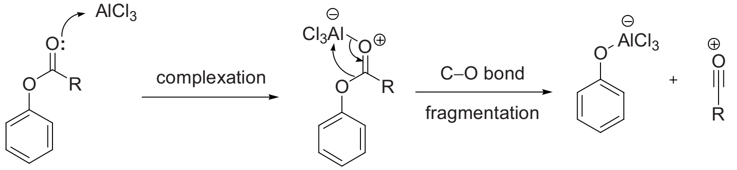
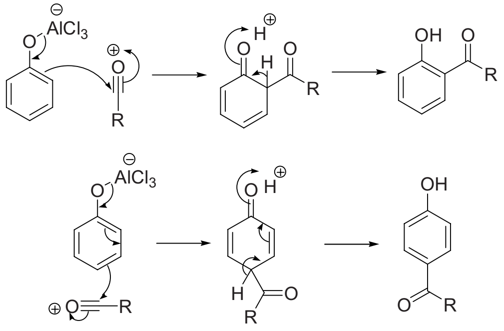
Fries rearrangement

Lewis acid-catalyzed rearrangement of phenol esters and lactams to 2- or 4-ketophenols. Also known as the Fries–Finck rearrangement.

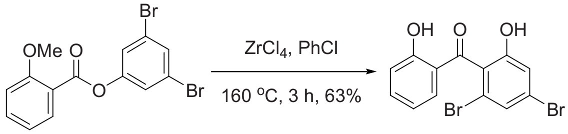




aluminum phenolate, acylium ion



Example 1[5]



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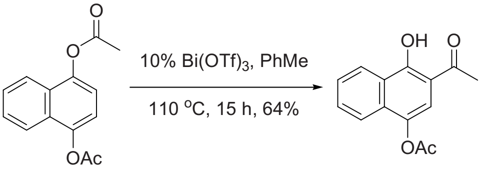
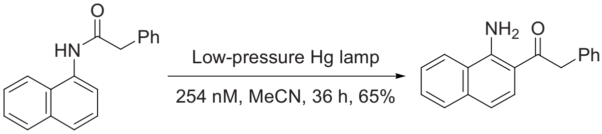
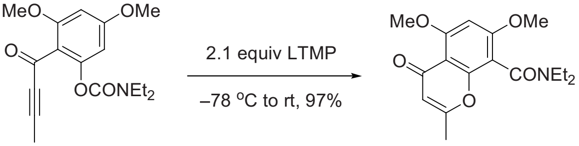
Example 2[6]



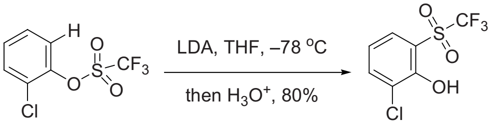
Example 3, Photo-Fries rearrangement[7]



Example 4, *ortho*-Fries rearrangement[8]



Example 5, Thia-Fries rearrangement[9]



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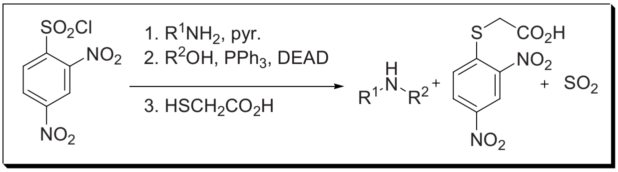
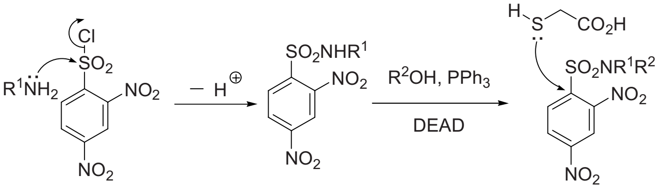
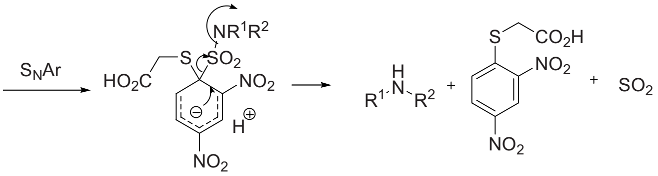
Fukuyama amine synthesis

Transformation of a primary amine to a secondary amine using 2,4-dinitrobenzenesulfonyl chloride and an alcohol. Also known as the Fukuyama–Mitsunobu procedure.



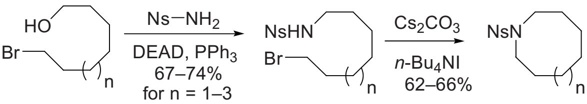


See page 365 for mechanism of the Mitsunobu reaction.

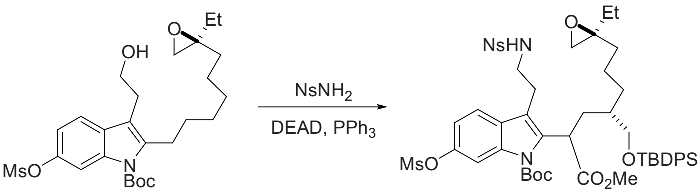


Meisenheimer complex

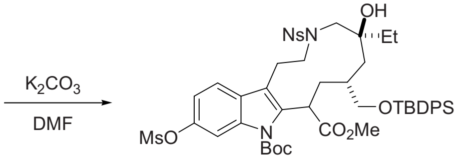
Example 1[6]



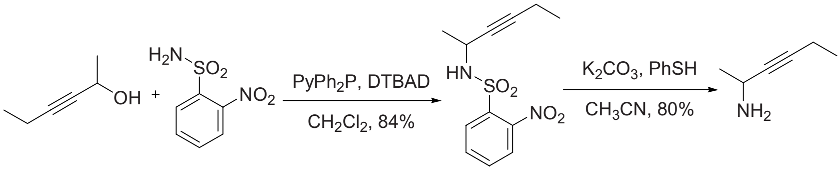
Example 2[7]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_104,



Example 3[8]



$PyPh_2P$ = diphenyl 2-pyridylphosphine; DTBAD = di-*tert*-butylazodicarbonate

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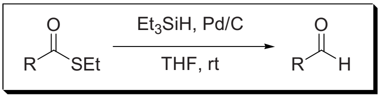
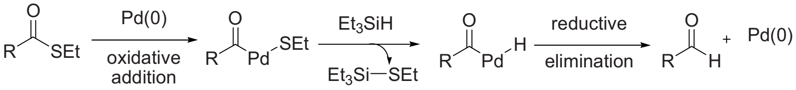
Fukuyama reduction

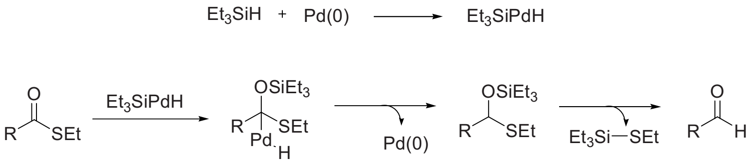
Aldehyde synthesis through reduction of thiol esters with Et_3SiH in the presence of Pd/C catalyst.



Path A:



Path B:



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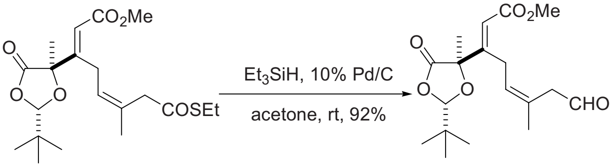

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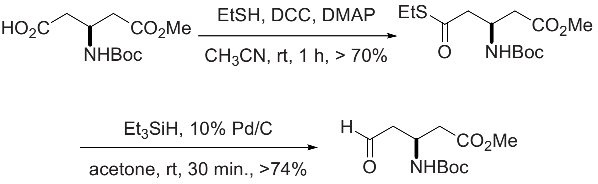
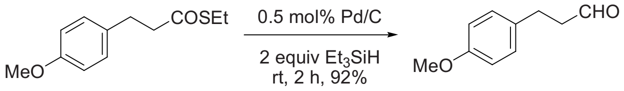


Example 3[8]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_105,

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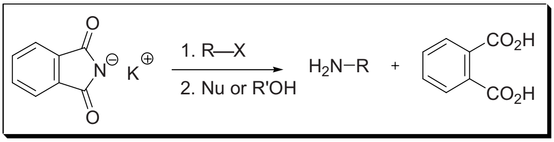
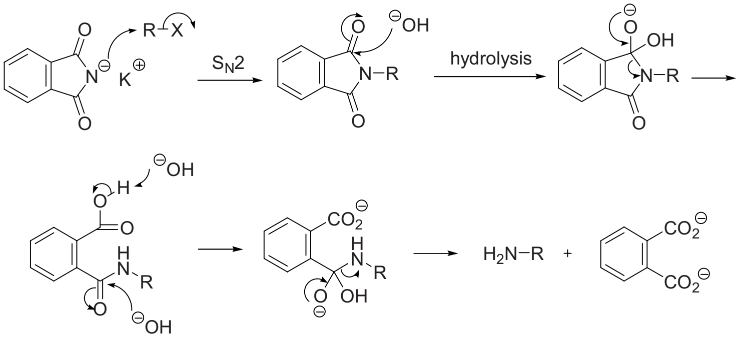
Gabriel synthesis

Synthesis of primary amines using potassium phthalimide and alkyl halides.





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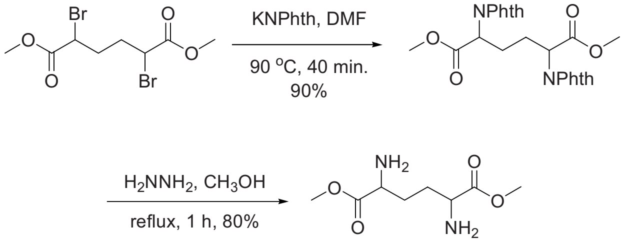
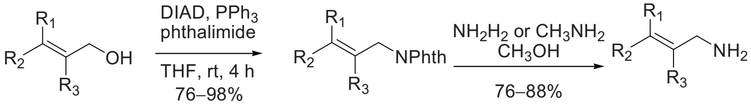
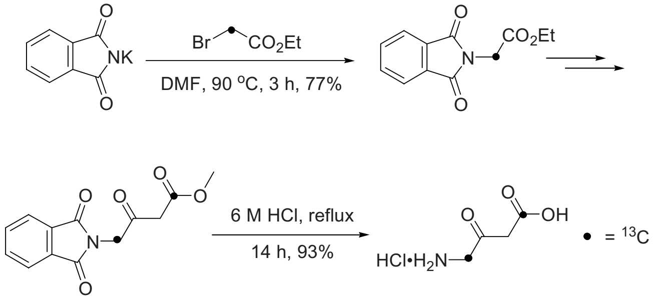


Example 2[6]

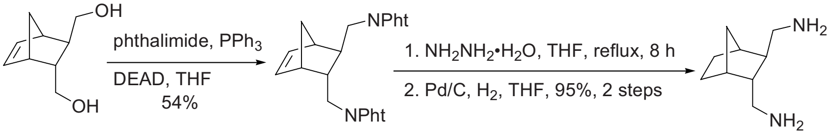


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_106,

Example 3[8]



Example 4[9]



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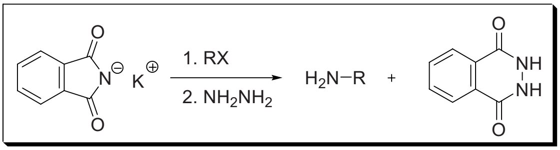
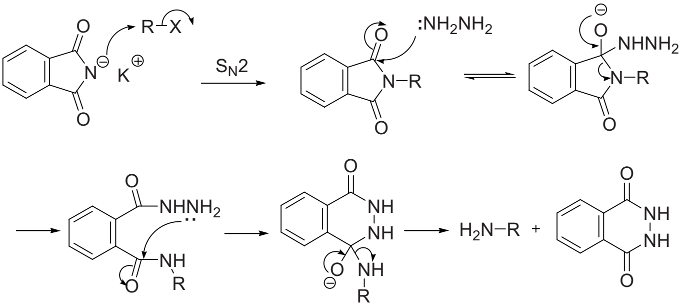
Ing–Manske procedure

A variant of Gabriel amine synthesis where hydrazine is used to release the amine from the corresponding phthalimide:





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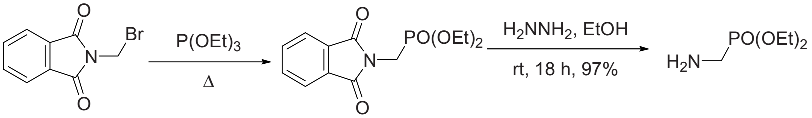

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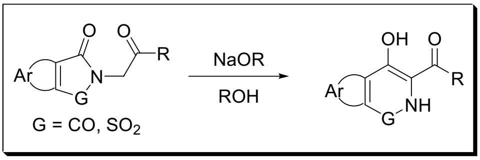
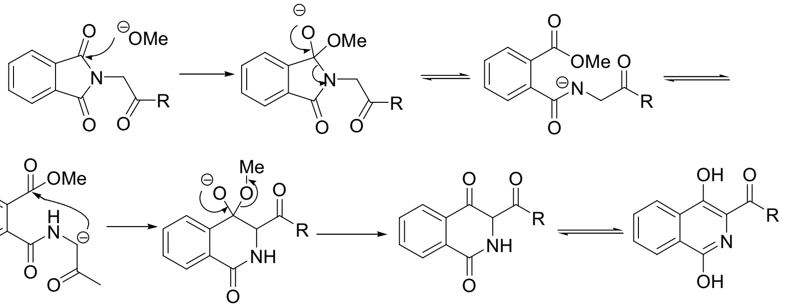
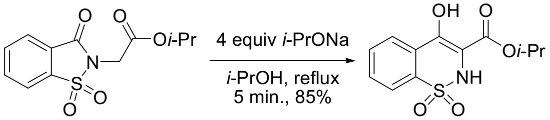
Gabriel–Colman rearrangement

Reaction of the enolate of a maleimidyl acetate to provide isoquinoline 1,4-diol.





Example 1[6]



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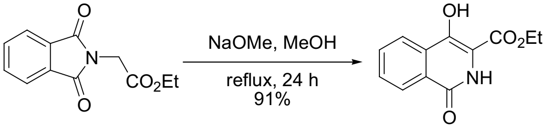

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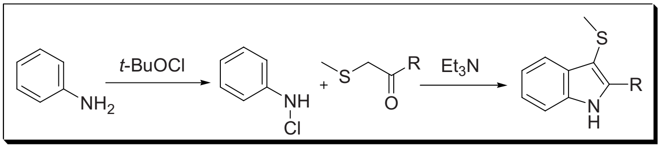
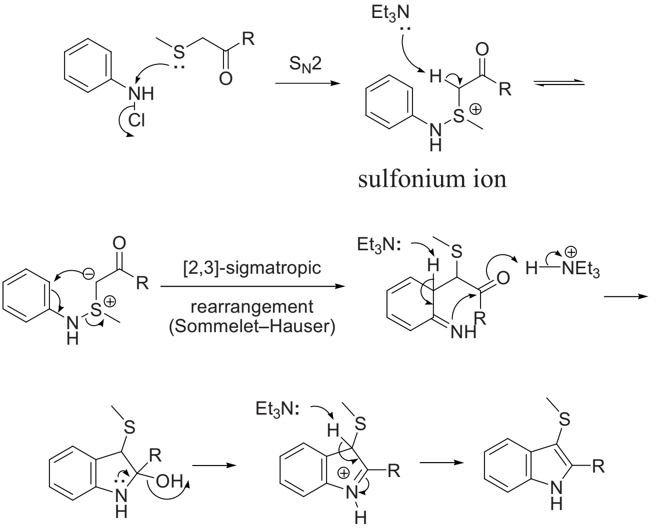
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_107,

Gassman indole synthesis

The Gassman indole synthesis involves a one-pot process in which a hypohalite, a β-carbonyl sulfide derivative, and a base are added sequentially to an aniline or a substituted aniline to provide 3-thioalkoxyindoles. The sulfur can be easily removed by hydrogenolysis or Raney nickel.





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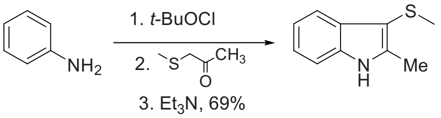

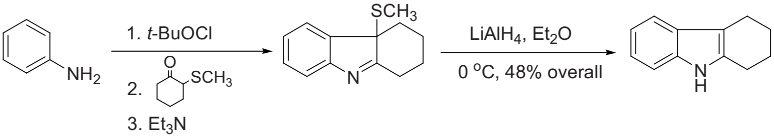

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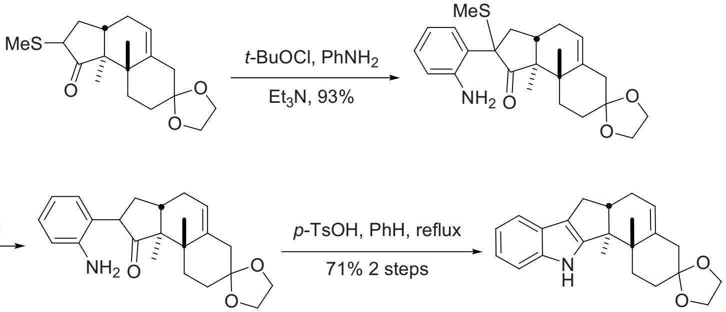
Example 2[2]



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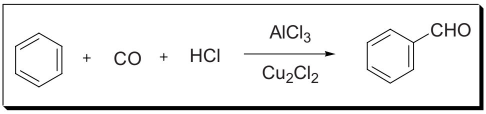
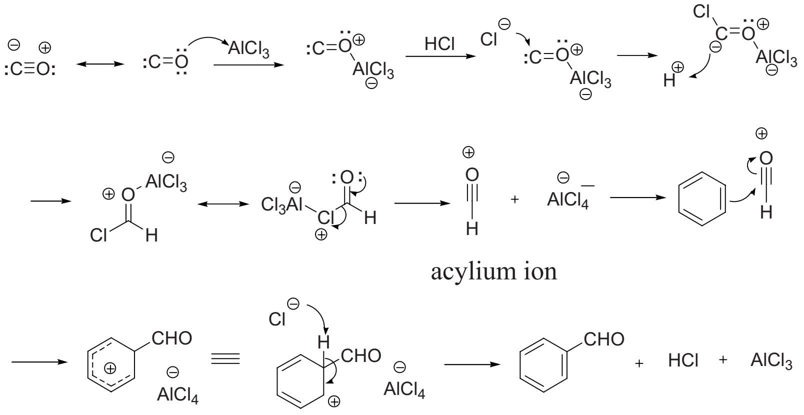
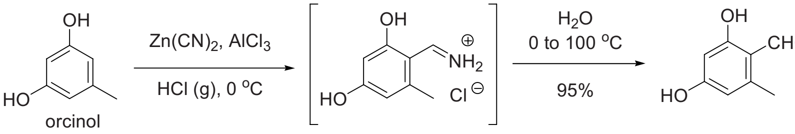
Gattermann–Koch reaction

Formylation of arenes using carbon monoxide and hydrogen chloride in the presence of aluminum chloride under high pressure.





Example, A more practical variant[4]



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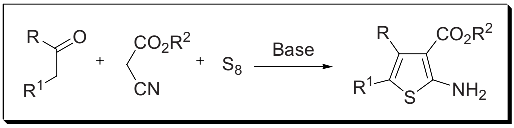
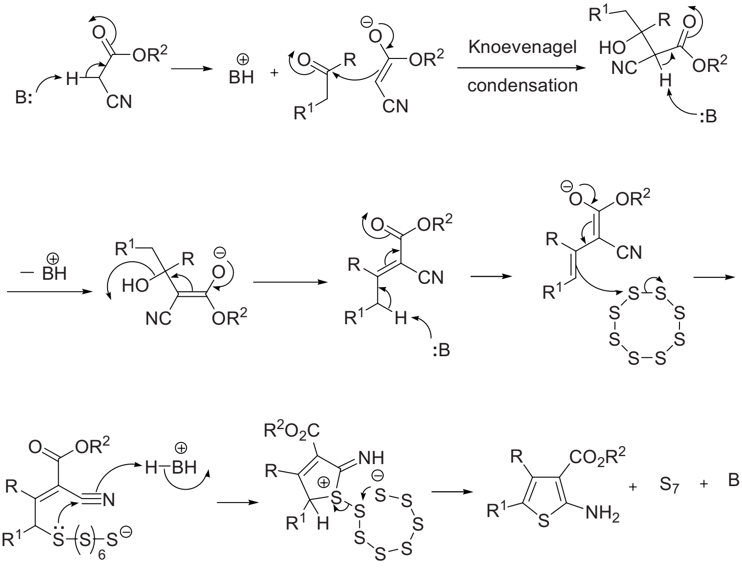
Gewald aminothiophene synthesis

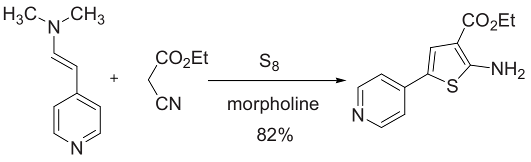
Base-promoted aminothiophene formation from ketone, α-active methylene nitrile and elemental sulfur.



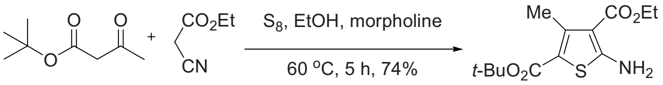


Ylidene-sulfur adduct

Example 1[4]



Example 2[7]



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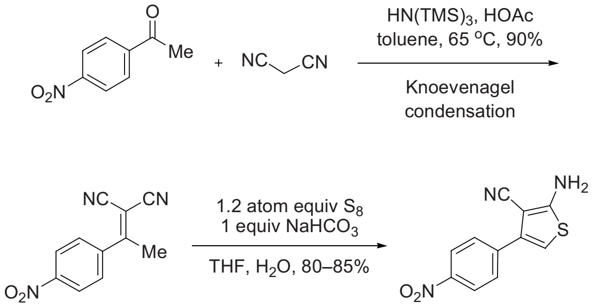
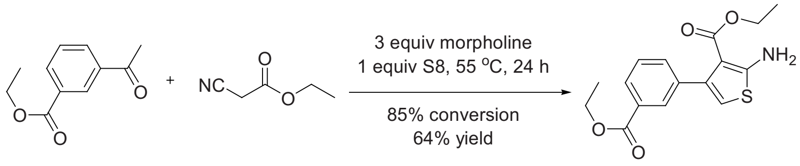
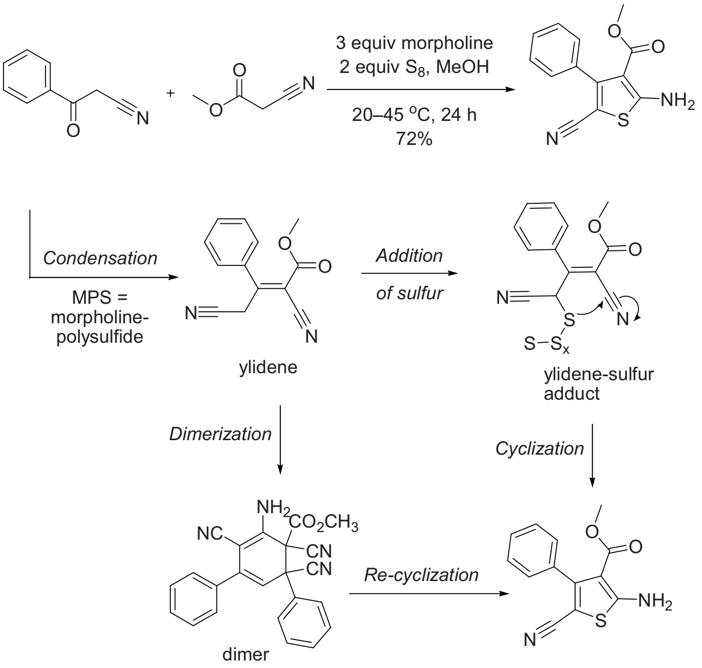
Example 3[9]



Example 4[10]



Example 5[11]



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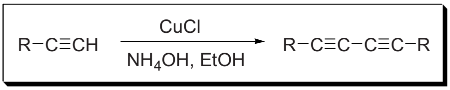
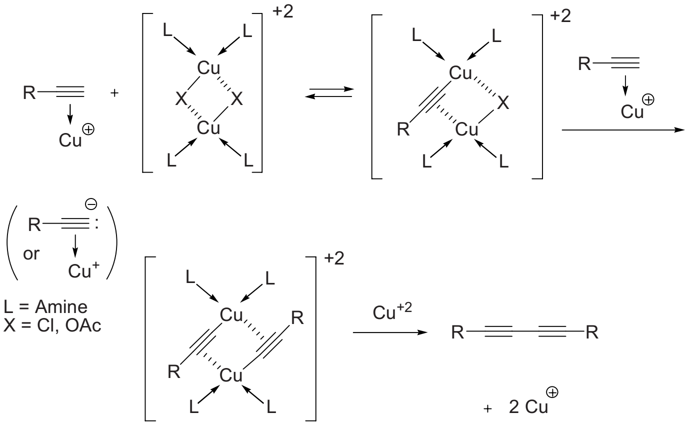
Glaser coupling

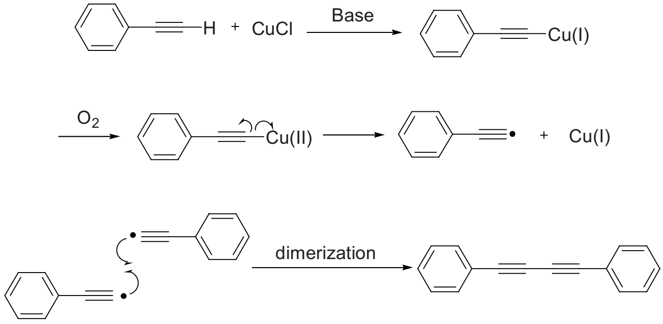
Oxidative homo-coupling of terminal alkynes using copper catalyst in the presence of oxygen.



$$R{-}C{\equiv}CH \xrightarrow[NH_4OH,\ EtOH]{CuCl} R{-}C{\equiv}C{-}C{\equiv}C{-}R$$



Alternatively, the radical mechanism is also operative:



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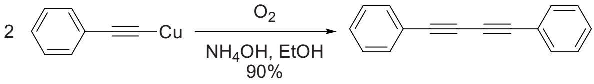

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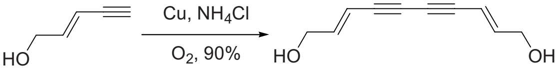
Example 2, Homo-coupling[2]



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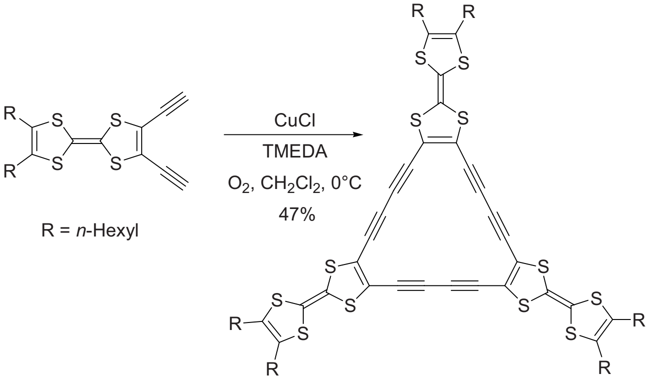

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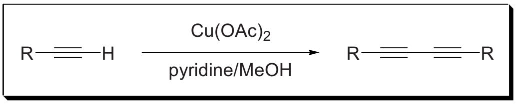
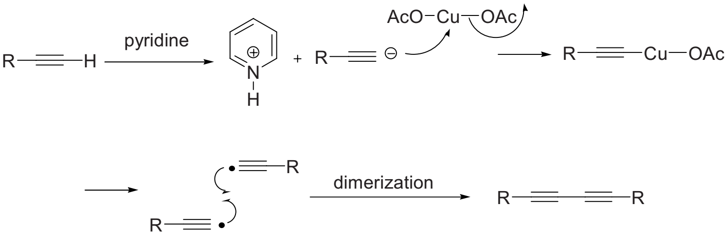
Eglinton coupling

Oxidative homo-coupling of terminal alkynes mediated by stoichiometric (or often excess) $Cu(OAc)_2$. A variant of the Glaser coupling reaction.





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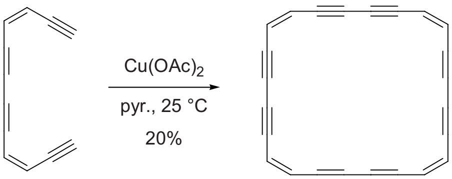
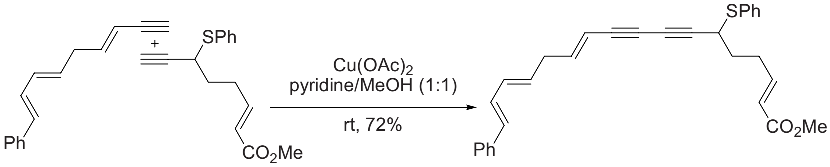
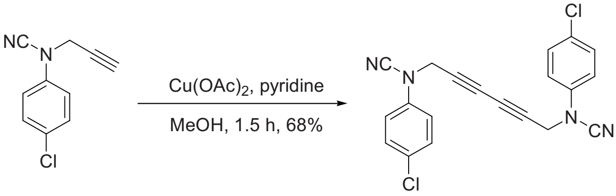


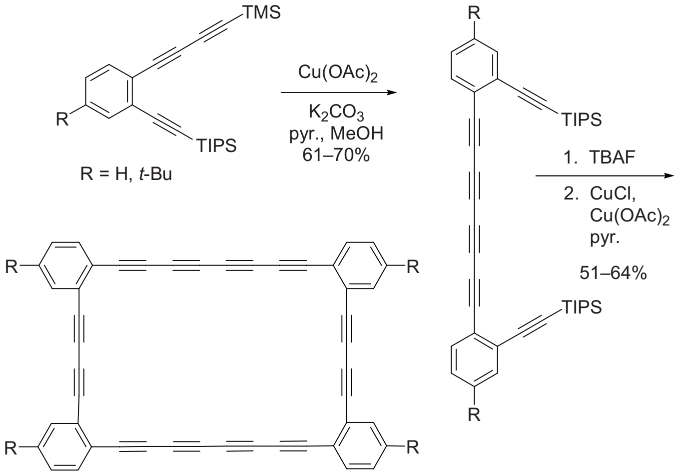
Example 2, Cross-coupling[3]



Example 3, Homo-coupling[4]



Example 4[5]



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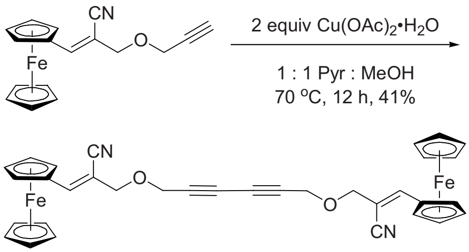
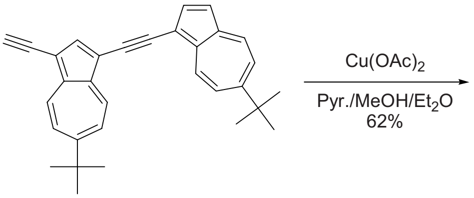
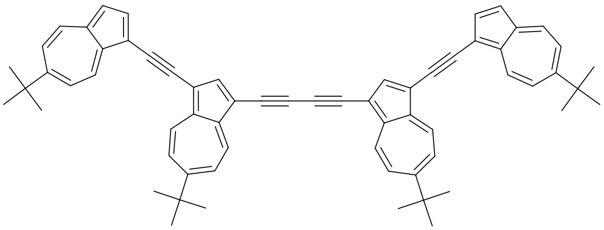


Example 6[12]





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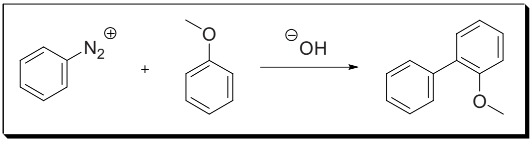
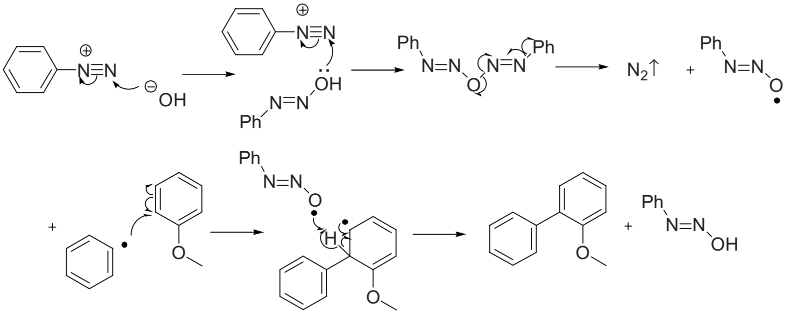
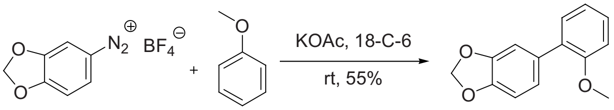
Gomberg–Bachmann reaction

Base-promoted radical coupling between an aryl diazonium salt and an arene to form a diaryl compound.





Example 1[4]



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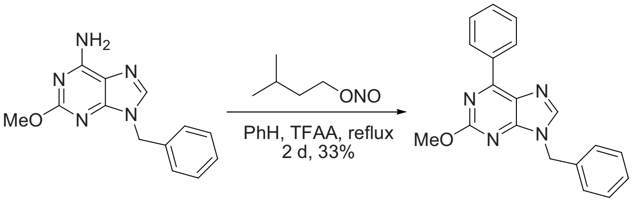

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Gould–Jacobs reaction

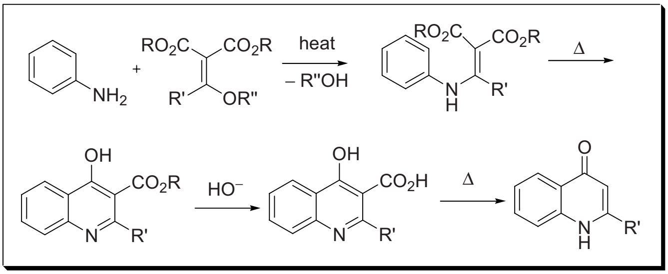
The Gould–Jacobs reaction is a sequence of the following reactions:

a. Substitution of an aniline with either alkoxy methylenemalonic ester or acyl malonic ester providing the anilinomethylenemalonic ester;

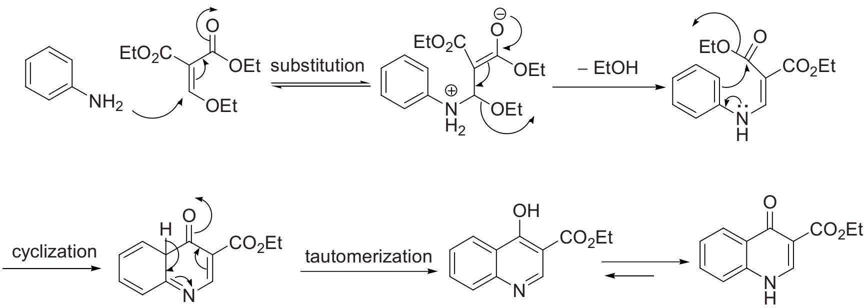
b. Cyclization of to the 4-hydroxy-3-carboalkoxyquinoline (4-hydroxyquinolines exist predominantly in 4-oxoform);

c. Saponification to form acid;

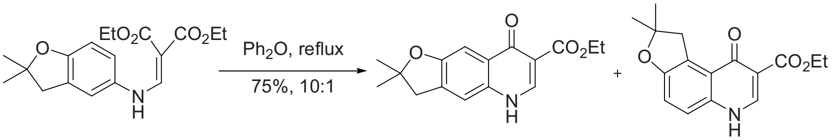
d. Decarboxylation to give the 4-hydroxyquinoline. Extension could lead to unsubstituted parent heterocycles with fused pyridine ring of Skraup type.



R = alkyl; R' = alkyl, aryl, or H; R'' = alkyl or H



Example 1[3]



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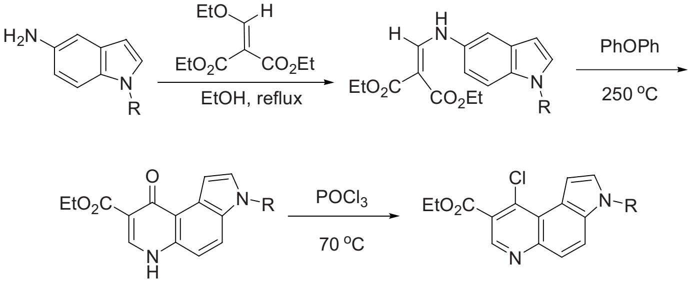
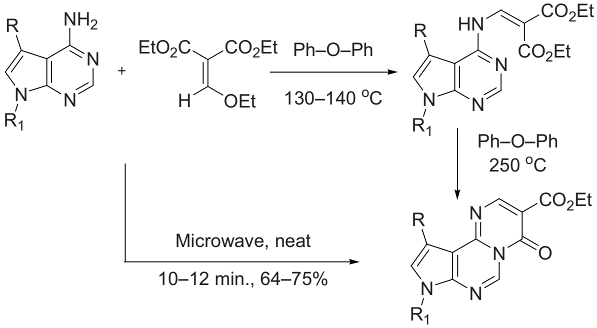
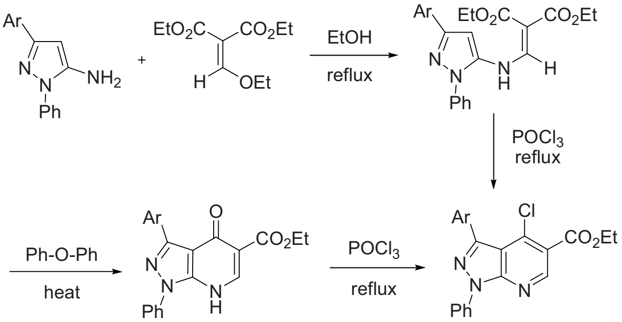
Example 2[8]



Example 3, Microwave-assisted Gould–Jacobs reaction[9]



Example 4[10]



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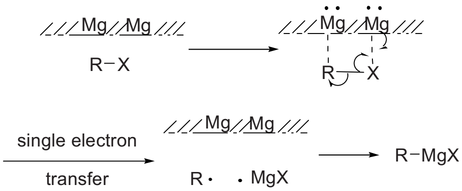
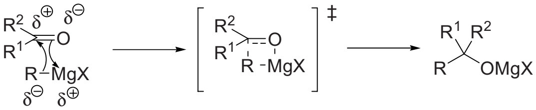
Grignard reaction

Addition of organomagnesium compounds (Grignard reagents), generated from organohalides and magnesium metal, to electrophiles.

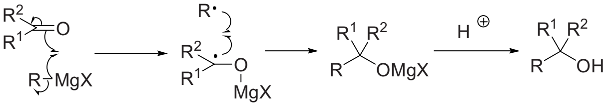
Formation of the Grignard reagent:



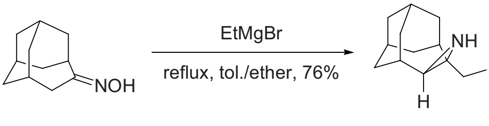
Grignard reaction, ionic mechanism:



Radical mechanism,



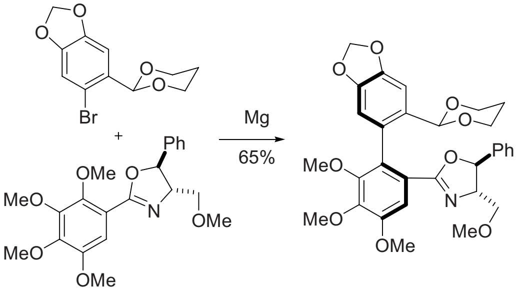
Example 1[4]



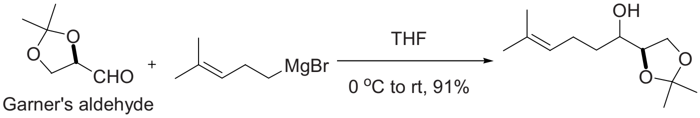
This reaction is known as the *Hoch–Campbell aziridine synthesis*, which entails treatment of ketoximes with excess Grignard reagents and subsequent hydrolysis of the organometallic complex to produce aziridines.

J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_114,

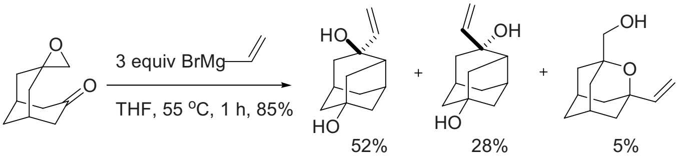
Example 2[5]



Example 5[10]



Example 6[11]



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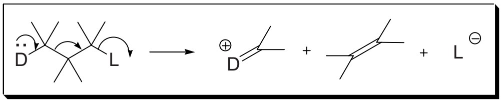
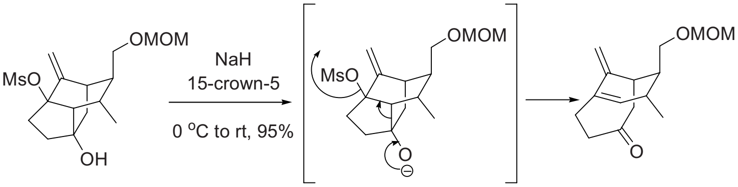
Grob fragmentation

The C–C bond cleavage primarily via a concerted process involving a five atom system. General scheme:

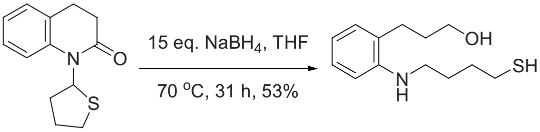


D = O$^-$, NR$_2$; L = OH$_2^+$, OTs, I, Br, Cl

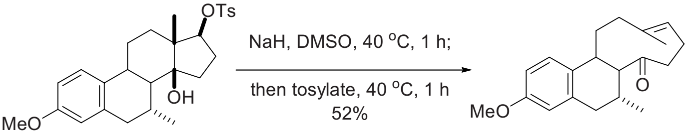
Example 1[2]



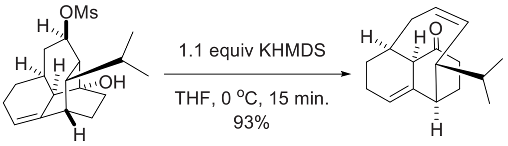
Example 2, Aza-Grob fragmentation[3]



Example 3[7]



Example 4[8]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_115,

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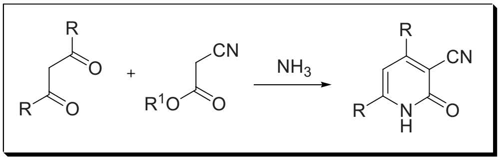
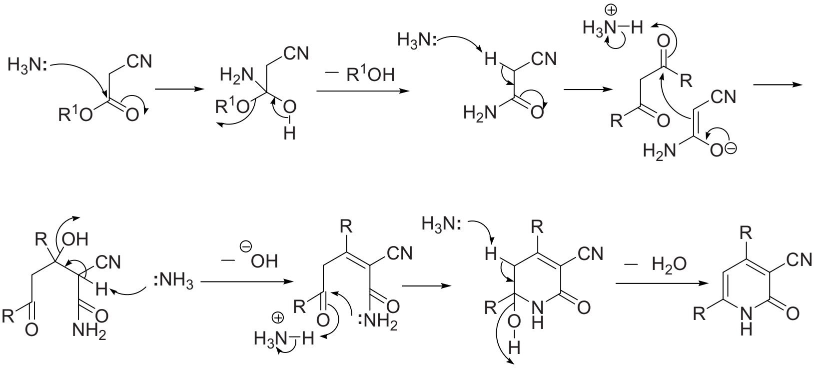
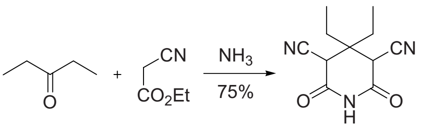
Guareschi–Thorpe condensation

2-Pyridone formation from the condensation of cyanoacetic ester with diketone in the presence of ammonia.





Example[6]



Guareschi imide

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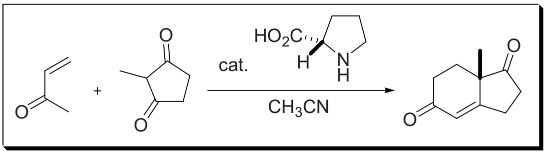
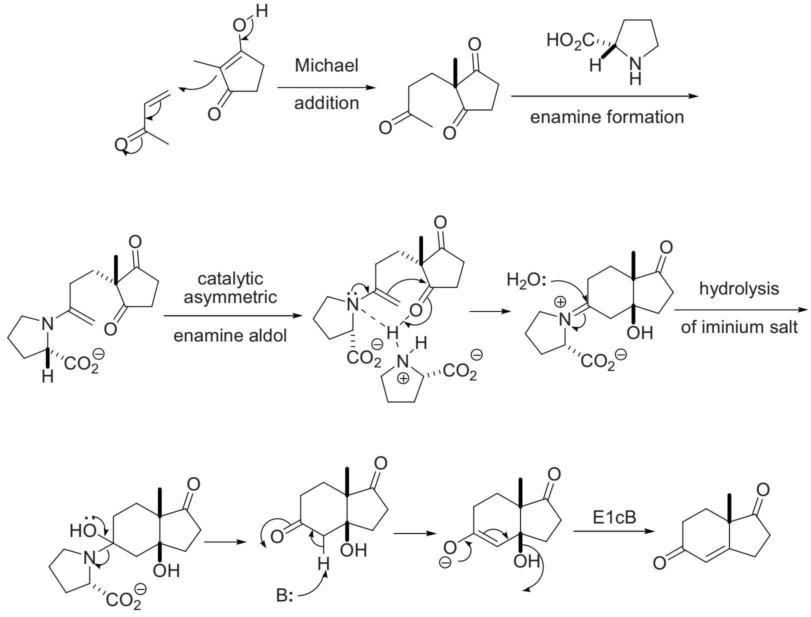
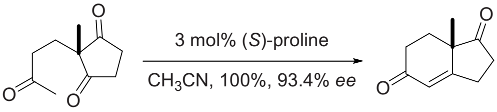
Hajos–Wiechert reaction

Asymmetric Robinson annulation catalyzed by (*S*)-(−)-proline.

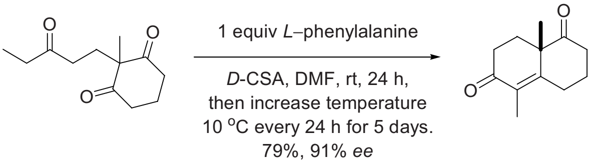




Example 1[1a]

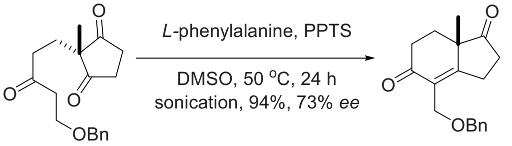


Example 2[3]

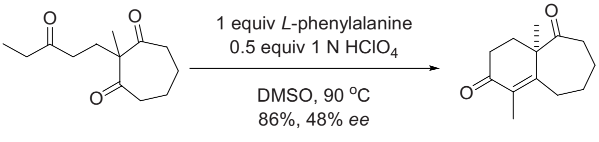


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_117,

Example 3[8]



Example 4[9]



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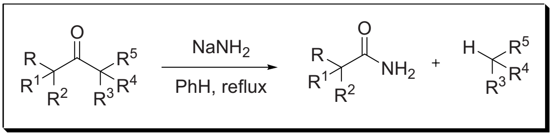
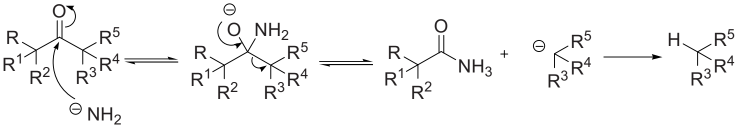
Haller–Bauer reaction

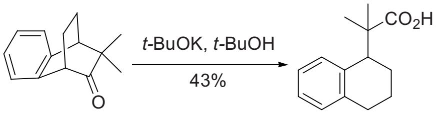
Base-induced cleavage of non-enolizable ketones leading to carboxylic amide derivative and a neutral fragment in which the carbonyl group is replaced by a hydrogen.



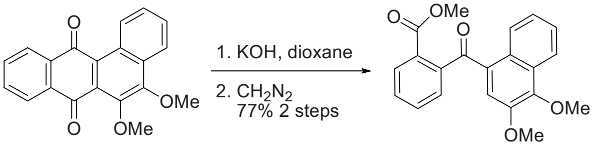
non-enolizable ketone



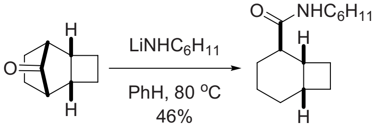
Example 1[4]



Example 2[9]



Example 3, Racemization[10]



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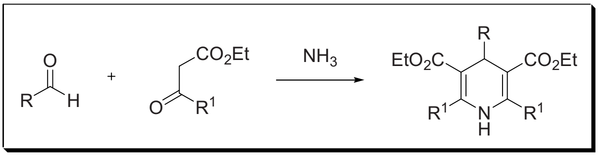
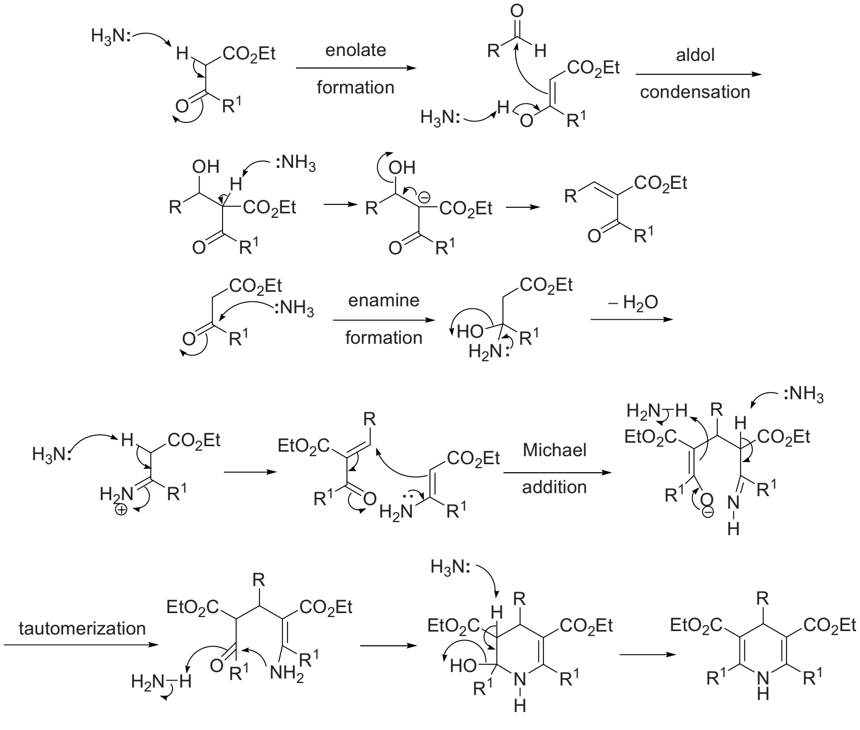
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_118,

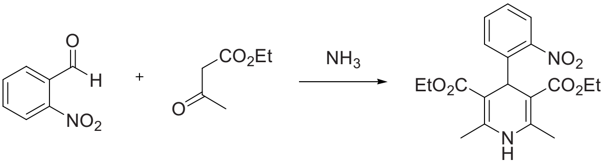
Hantzsch dihydropyridine synthesis

1,4-Dihydropyridine from the condensation of aldehyde, β-ketoester and ammonia. Hantzsch 1,4-dihydropyridines are popular reducing reagents in organocatalysis.





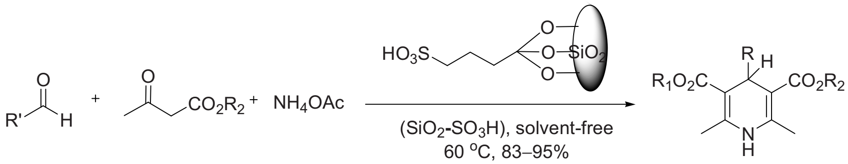
Example 1[2]



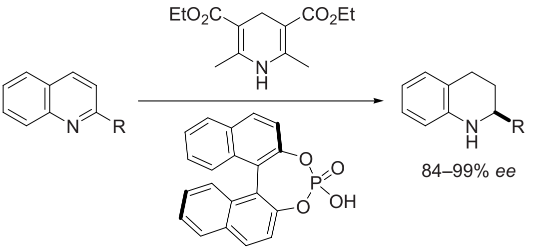
nifedipine

J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_119,

Example 2[9]



Example 3, Hantzsch 1,4-dihydropyridine as a hydrogen donor[10]



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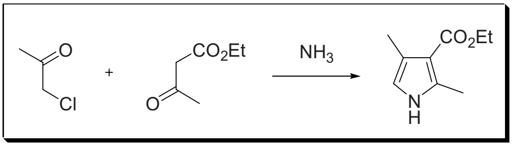
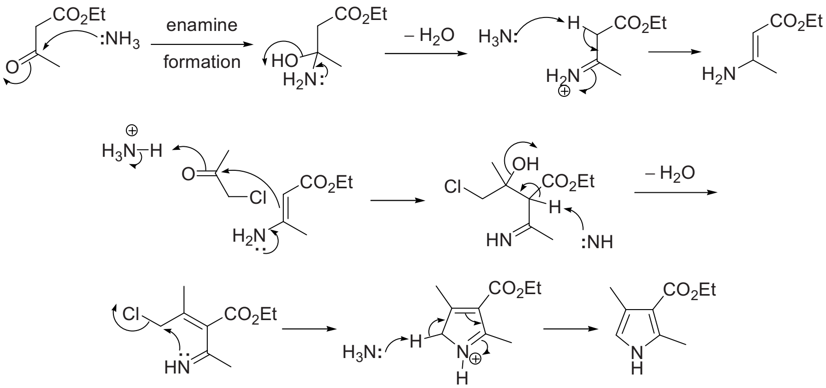
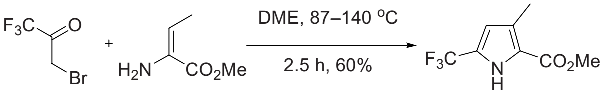
Hantzsch pyrrole synthesis

Reaction of α-chloromethyl ketones with β-ketoesters and ammonia to assemble pyrroles.

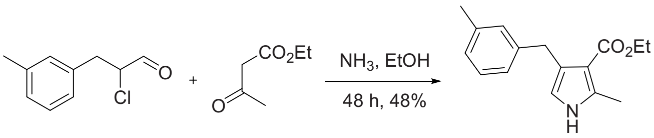




Example 1[4]



Example 2[7]



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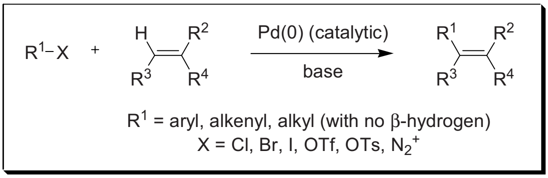
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_120,

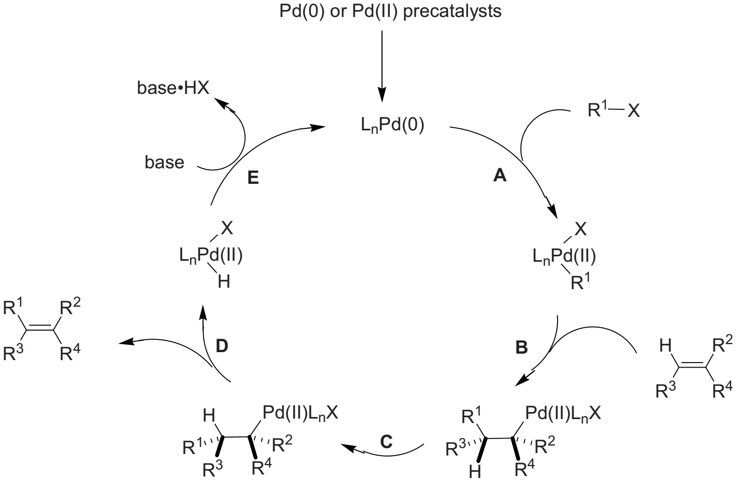
Heck reaction

The palladium-catalyzed alkenylation or arylation of olefins.



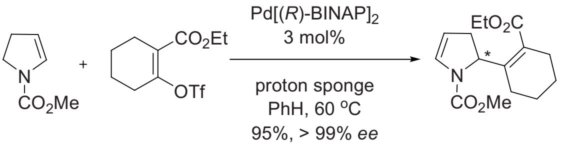
R^1 = aryl, alkenyl, alkyl (with no β-hydrogen)
X = Cl, Br, I, OTf, OTs, N_2^+

The catalytic cycle:



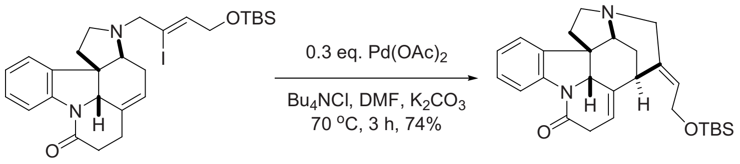
A: Oxidative addition
B: Migratory insertion (*syn*)
C: C–C bond rotation
D: *syn*-β-elimination
E: Reductive elimination

Example 1, Asymmetric intermolecular Heck reaction[6]

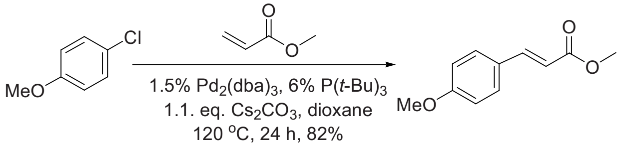


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_121,

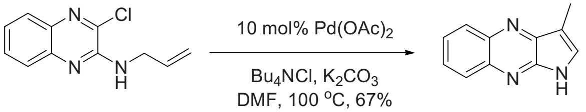
Example 2, Intramolecular Heck[7]



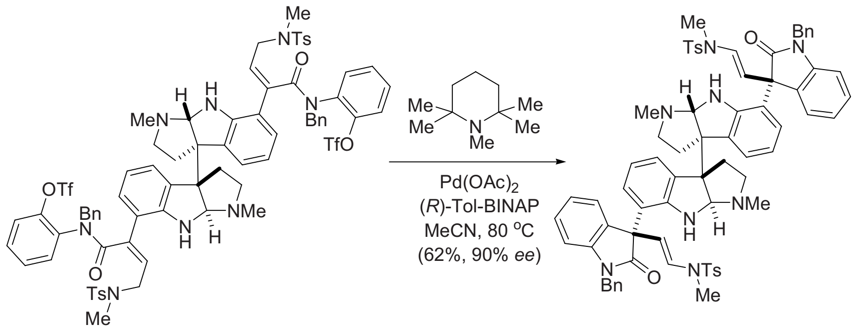
Example 3[8]



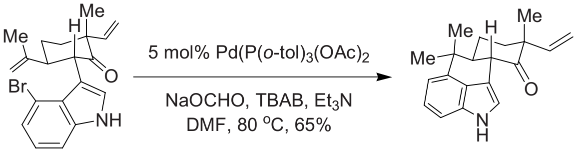
Example 4, Intramolecular Heck[9]



Example 5, Intramolecular Heck[13]



Example 6, Reductive Heck reaction[17]



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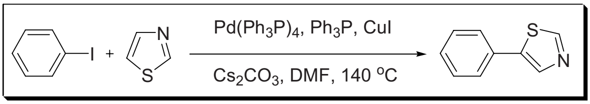
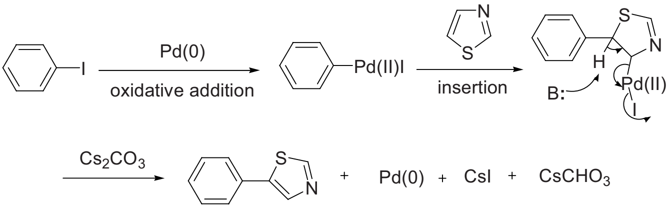
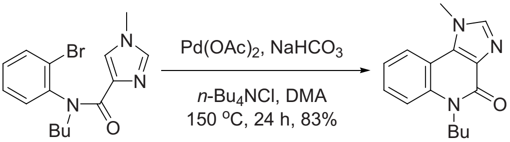
Heteroaryl Heck reaction

Intermolecular or intramolecular Heck reaction that occurs onto a heteroaryl recipient.

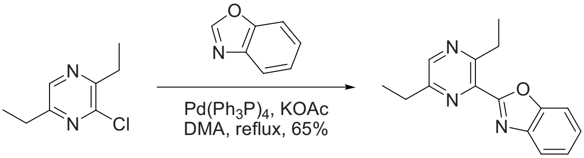




Example 1[2]



Example 2[3]



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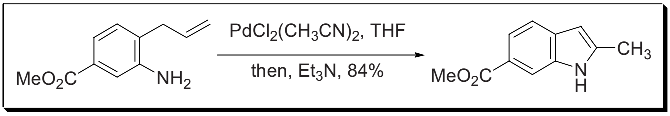
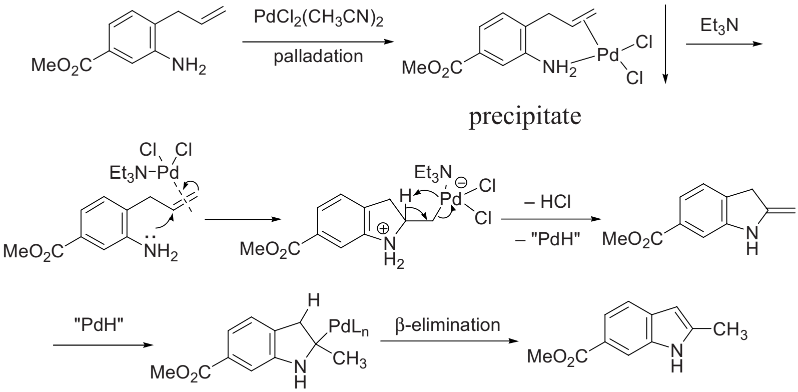
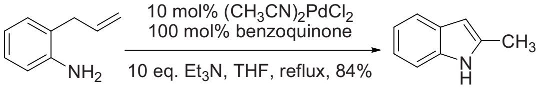
Hegedus indole synthesis

Stoichiometric Pd(II)-mediated oxidative cyclization of alkenyl anilines to indoles. *Cf.* Wacker oxidation.

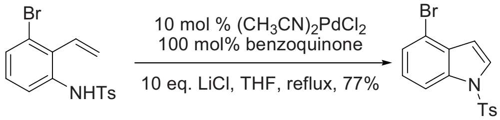




Example 1[1a]



Example 2[1d]



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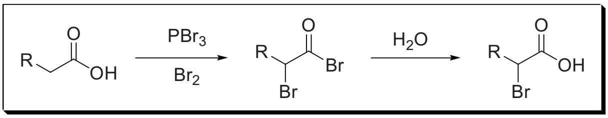
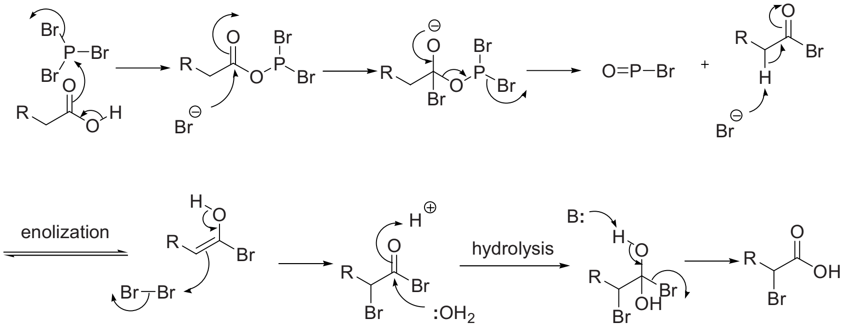
Hell–Volhard–Zelinsky reaction

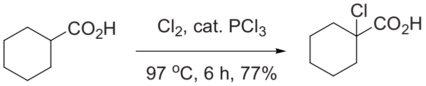
α-Halogenation of carboxylic acids using X_2/PBr_3.



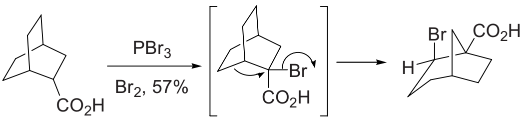
α-bromoacid



Example 1[5]



Example 2[6]



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J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_123,

Tyaspol, Russia. He studied at Göttingen under Victor Meyer, receiving his Ph.D. In 1889. Zelinsky returned to Russia and became a professor at the University of Moscow. On his ninetieth birthday in 1951, he was awarded the Order of Lenin.

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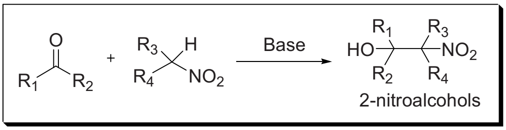
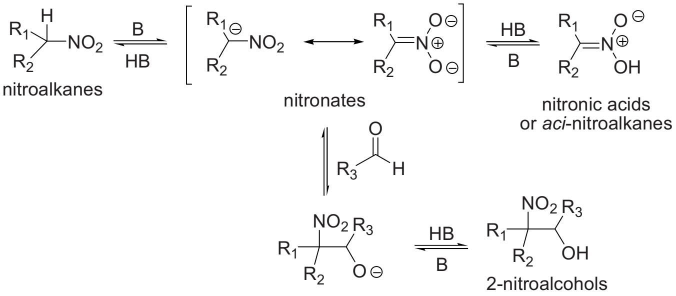
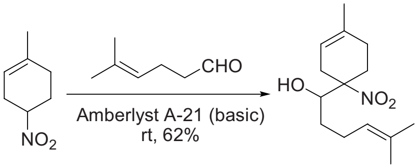
Henry nitroaldol reaction

The nitroaldol condensation reaction involving aldehydes and nitronates, derived from deprotonation of nitroalkanes by bases.

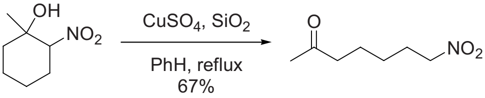




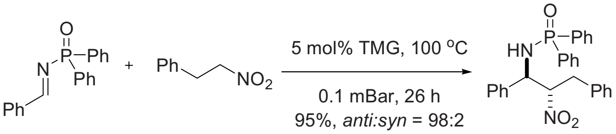
Example 1[4]



Example 2, Retro-Henry reaction[5]

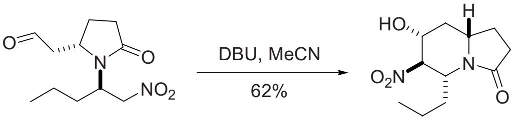


Example 3, Aza-Henry reaction[8]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_124,

Example 4, Intramolecular Henry reaction[10]



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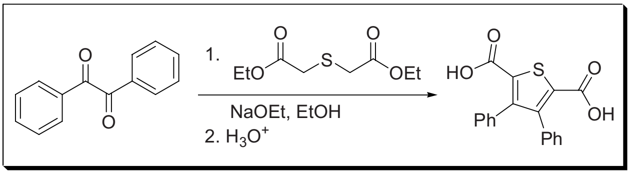
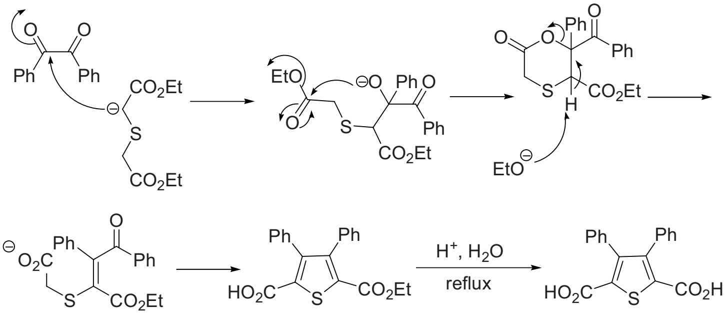
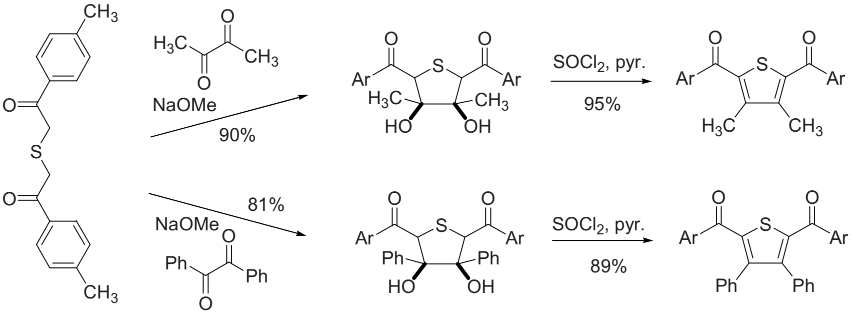
Hinsberg synthesis of thiophene derivatives

Condensation of diethyl thiodiglycolate and α-diketones under basic conditions, which provides 3,4-disubstituted thiophene-2,5-dicarbonyls upon hydrolysis of the crude ester product with aqueous acid.

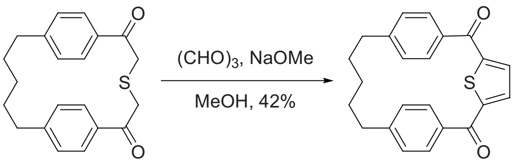




Example 1[2]

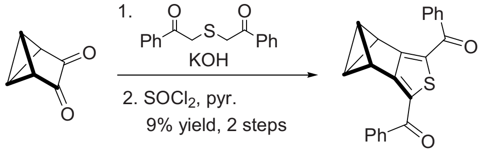


Example 2[4]

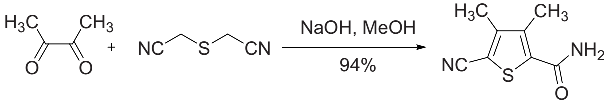


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_125,

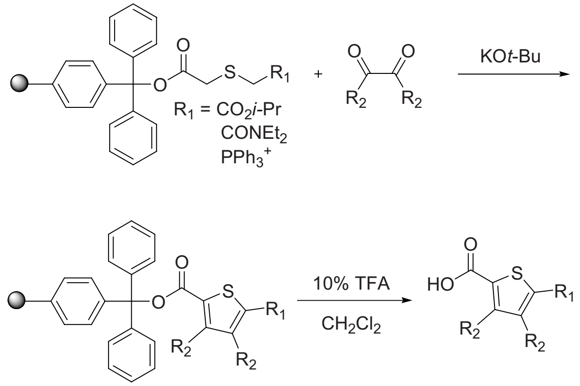
Example 3[5]



Example 4[6]



Example 5, Polymer-support Hinsberg thiophene synthesis[9]



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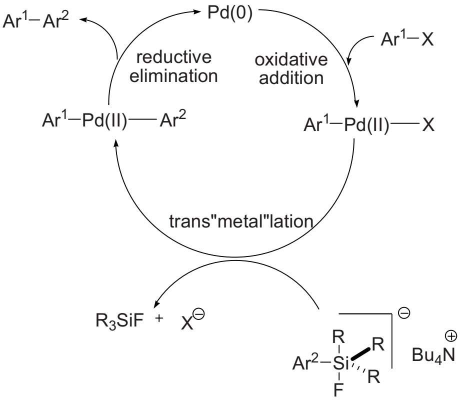
Hiyama cross-coupling reaction

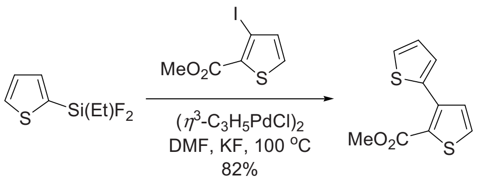
Palladium-catalyzed cross-coupling reaction of organosilicons with organic halides, triflates, *etc*. In the presence of an activating agent such as fluoride or hydroxide (transmetallation is reluctant to occur without the effect of an activating agent). For the catalytic cycle, see the Kumada coupling on page 325.

$$\boxed{R^1\text{–SiY} \ + \ R^2\text{–X} \xrightarrow[\text{activator}]{\text{Pd catalyst}} R^1\text{–}R^2}$$

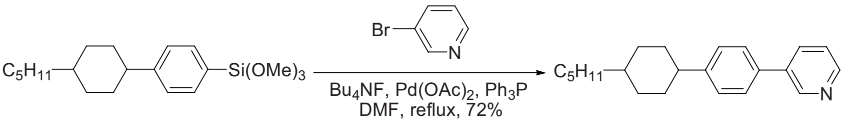
R^1 = alkenyl, aryl, alkynyl, alkyl
R^2 = aryl, alkyl, alkenyl
Y = $(OR)_3$, Me_3, Me_2OH, $Me_{(3\text{-}n)}F_{(n+3)}$
X = Cl, Br, I, OTf
activator = TBAF, base



Example 1[1a]

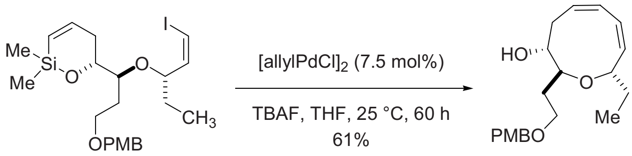


Example 2[2]

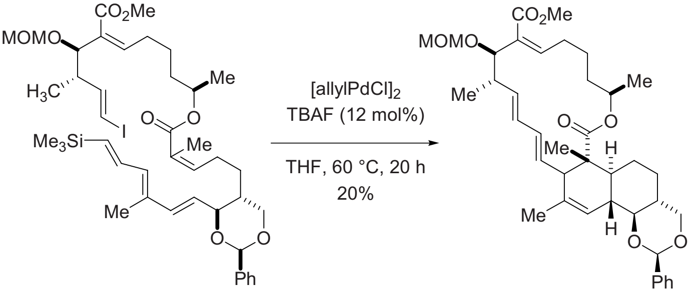


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_126,

Example 3[7]



Example 4[9]



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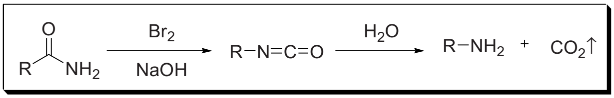
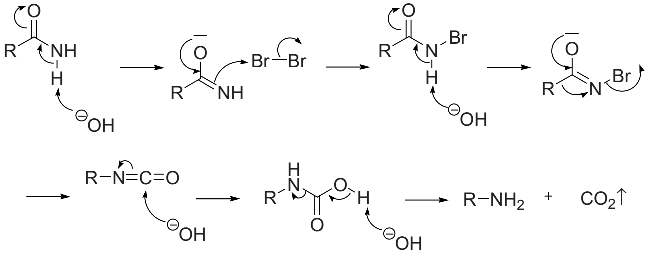
Hofmann rearrangement

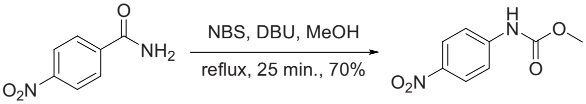
Upon treatment of primary amides with hypohalites, primary amines with one less carbon are obtained *via* the intermediacy of isocyanate. Also know as the Hofmann degradation reaction.



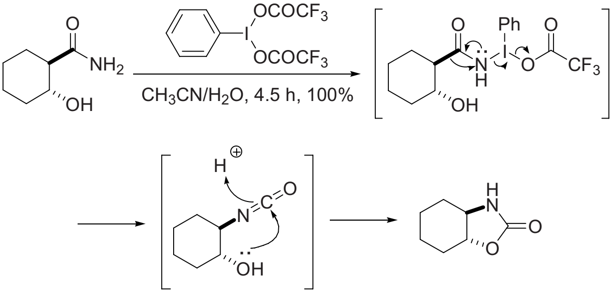


isocyanate intermediate

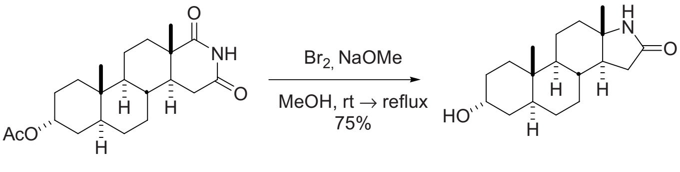
Example 1, NBS variant[2]



Example 2, Iodosobenzene diacetate[5]

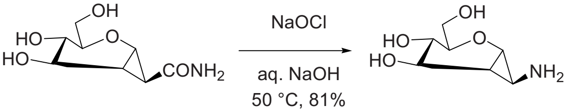


Example 3, Bromine and alkoxide[6]

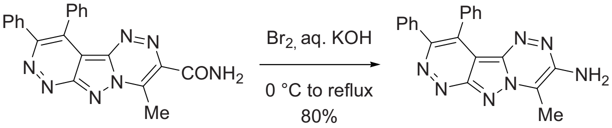


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_127,

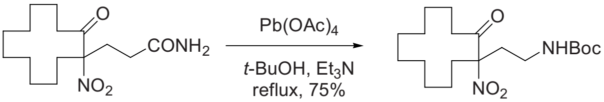
Example 4, Sodium hypochlorite[7]



Example 5, The original conditions, bromine and hydroxide[9]



Example 6, Lead tetraacetate[10]



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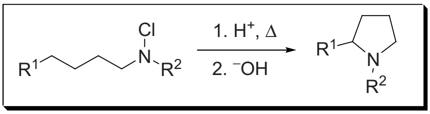
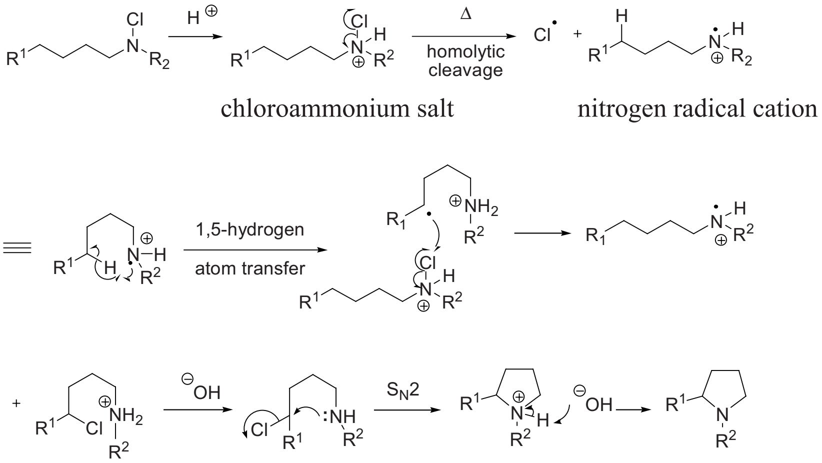
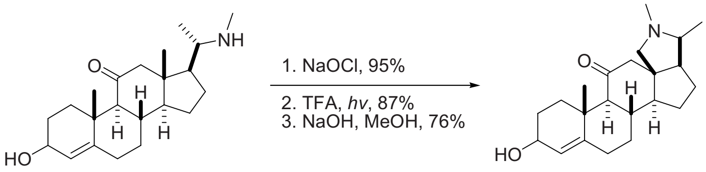
Hofmann–Löffler–Freytag reaction

Formation of pyrrolidines or piperidines by thermal or photochemical decomposition of protonated *N*-haloamines.

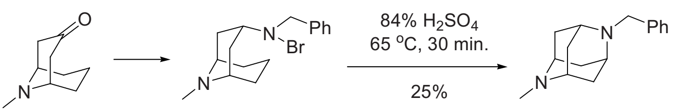




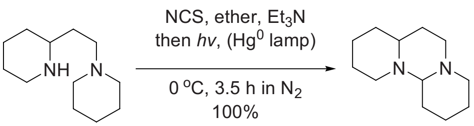
Example 1[2]



Example 2[4]



Example 3[5]



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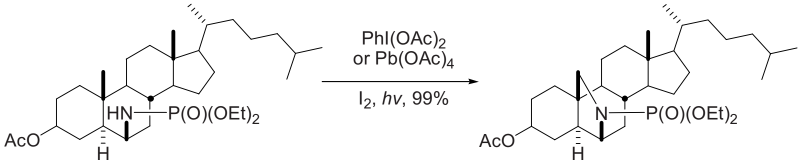
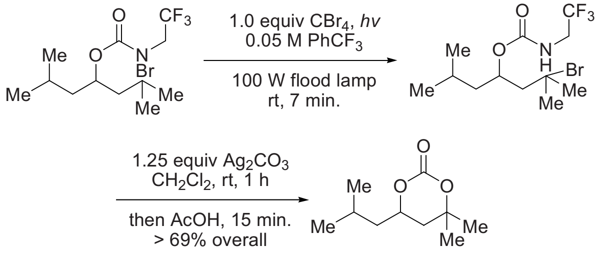
Example 4[7]



Example 5[12]



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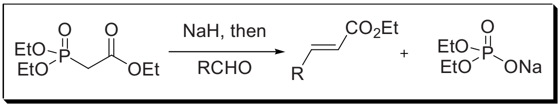
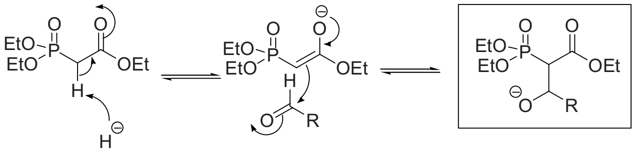
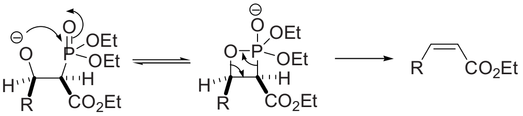
Horner–Wadsworth–Emmons reaction

Olefin formation from aldehydes and phosphonates. Workup is more advantageous than the corresponding Wittig reaction because the phosphate by-product can be washed away with water. Typically gives the *trans*- rather than the *cis*-olefins.

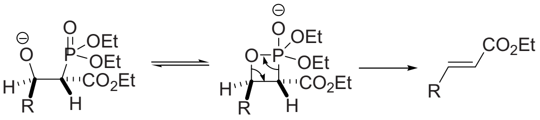




The stereochemical outcome: *erythro* (kinetic) or *threo* (thermodynamic)

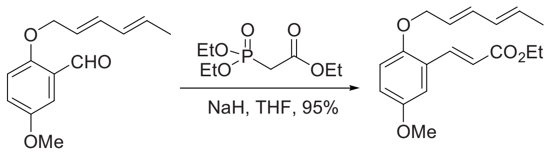


erythro, kinetic adduct

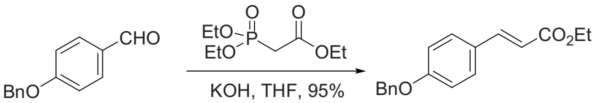


threo, thermodynamic adduct

Example 1[3]



Example 2[4]



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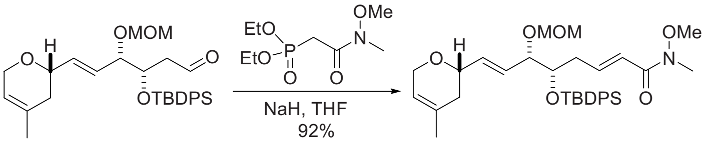

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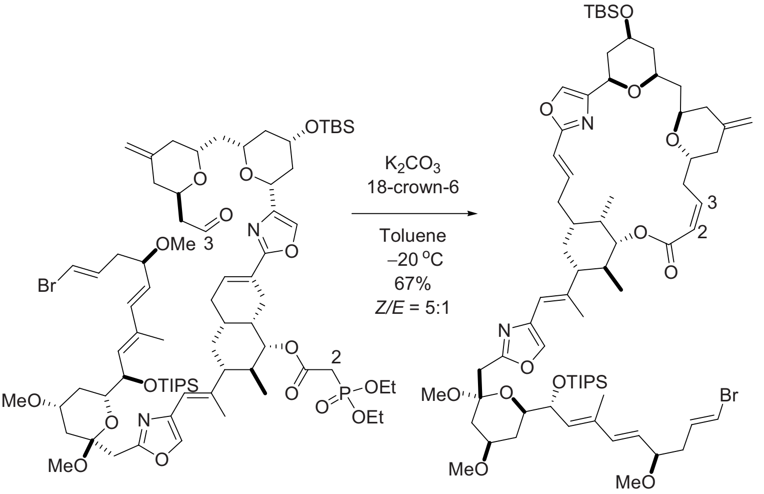
Example 4, Intramolecular Horner–Wadsworth–Emmons[9]



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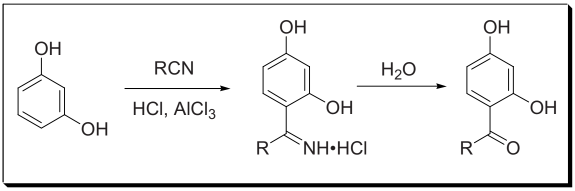
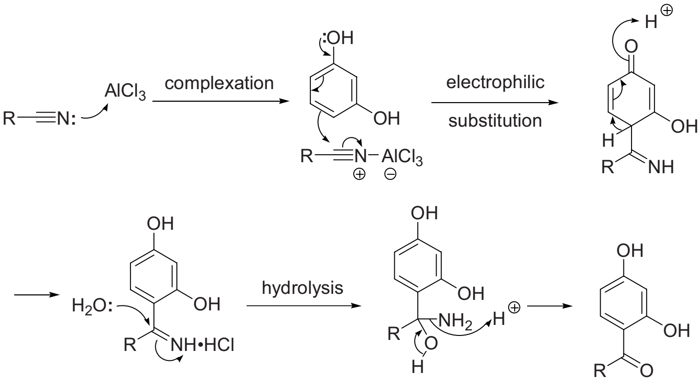
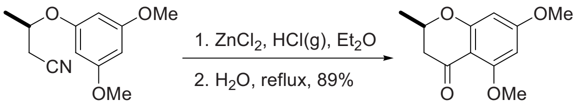
Houben–Hoesch reaction

Acid-catalyzed acylation of phenols as well as phenolic ethers using nitriles.

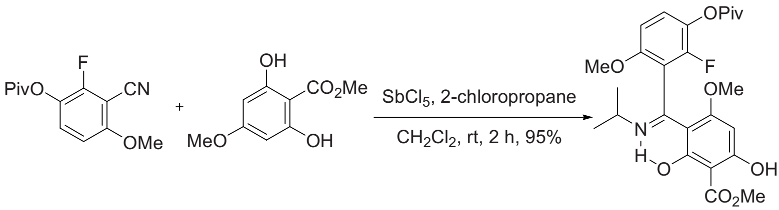




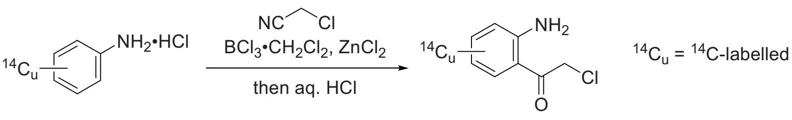
Example 1, Intramolecular Houben–Hoesch reaction[3]



Example 2[6]



Example 3[8]



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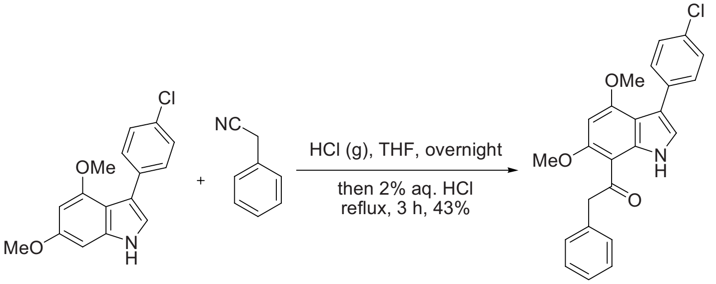
Example 4[9]



References

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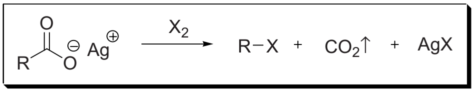
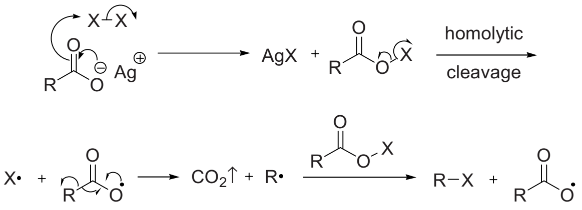
Hunsdiecker–Borodin reaction

Conversion of silver carboxylate to halide by treatment with halogen.





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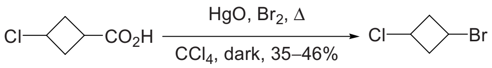
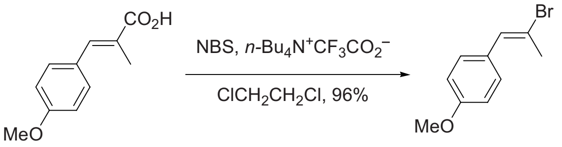
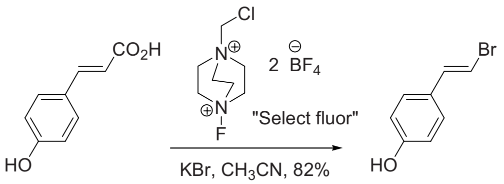


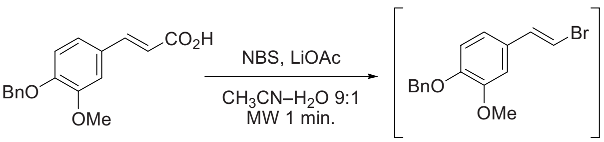
Example 2[6]



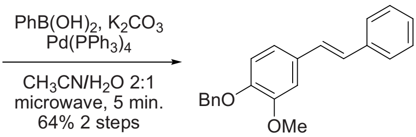
Example 3[8]



Example 4, One-pot microwave-Hunsdiecker–Borodin followed by Suzuki[10]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_131,



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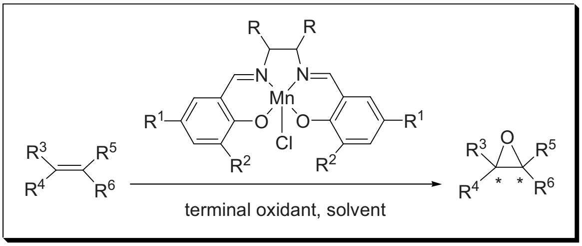
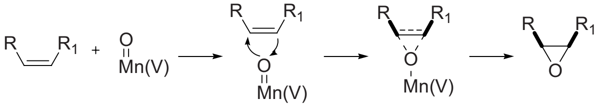
Jacobsen–Katsuki epoxidation

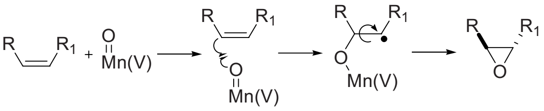
Mn(III)salen-catalyzed asymmetric epoxidation of (*Z*)-olefins.



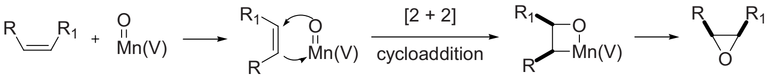
1. Concerted oxygen transfer (*cis*-epoxide):



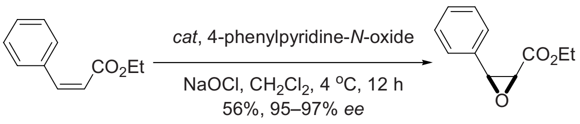
2. Oxygen transfer *via* radical intermediate (*trans*-epoxide):



3. Oxygen transfer *via* manganaoxetane intermediate (*cis*-epoxide):



Example 1[2]



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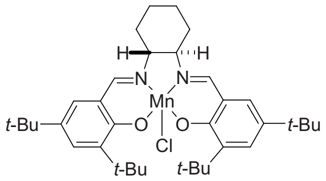
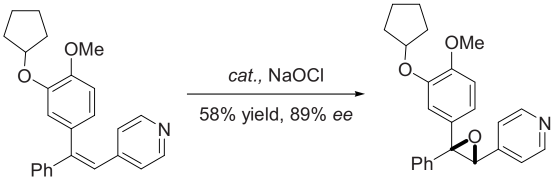
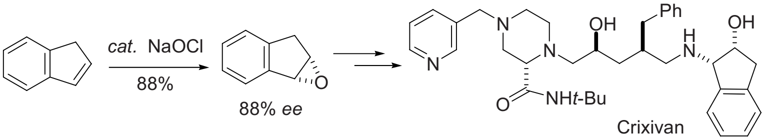


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_132,

Example 2[5]



Example 2[6]



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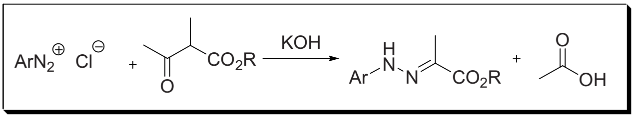
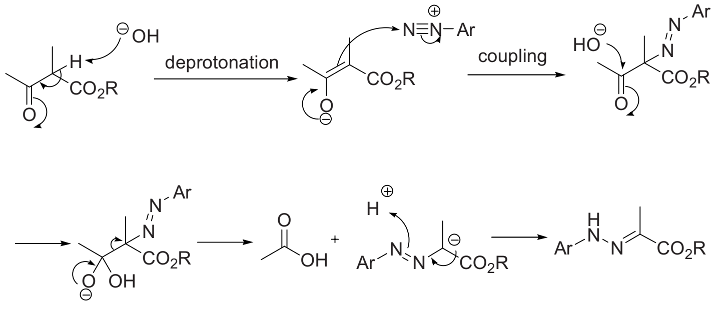
Japp–Klingemann hydrazone synthesis

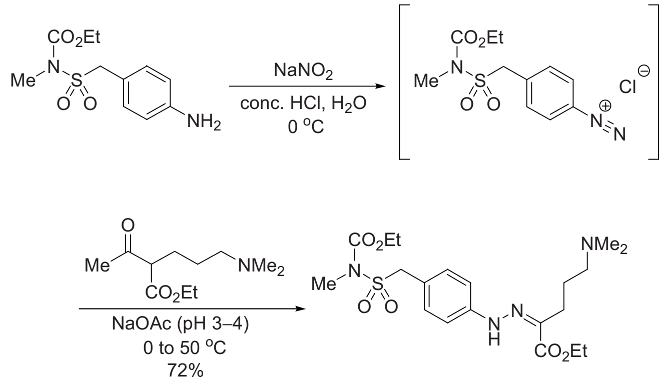
Hydrazones from β-ketoesters and diazonium salts with the acid or base.



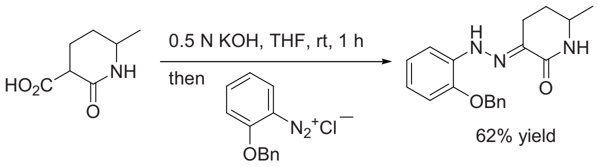
Diazonium salt β-keto-ester hydrazone



Example 1[4]



Example 2[6]



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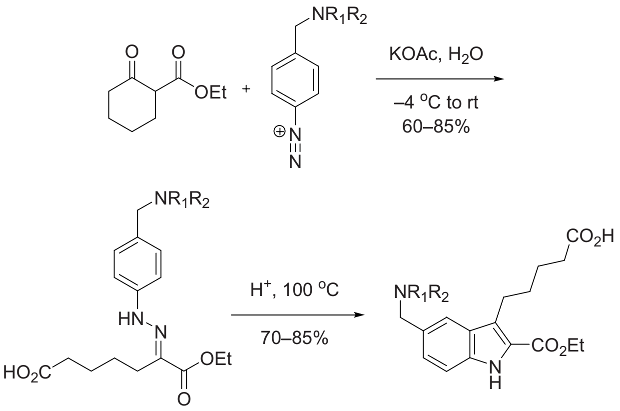
Example 3[10]



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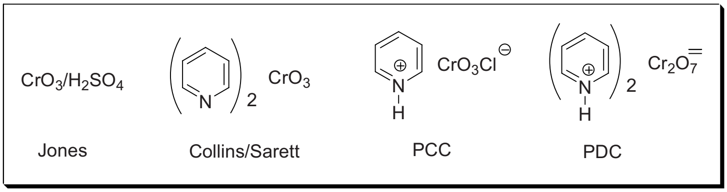
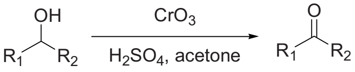
Jones oxidation

The **Collins/Sarett oxidation** (chromium trioxide-pyridine complex), and **Corey´s PCC** (pyridinium chlorochromate) and **PDC** (pyridinium dichromate) **oxidations** follow a similar pathway as the **Jones oxidation** (chromium trioxide and sulfuric acid in acetone). All these oxidants have a chromium (VI), normally black or yellow, which is reduced to Cr(IV), often green.

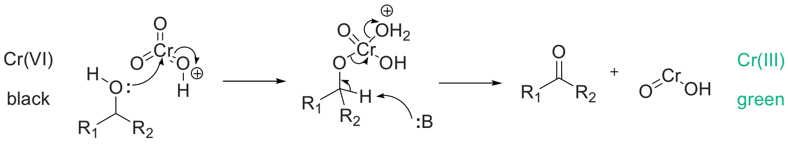


Jones oxidation

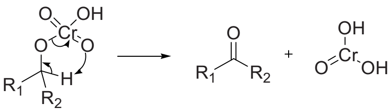
By the Jones oxidation, the primary alcohols are oxidized to the corresponding aldehyde or carboxylic acids, whereas the secondary alcohols are oxidized to the corresponding ketones.



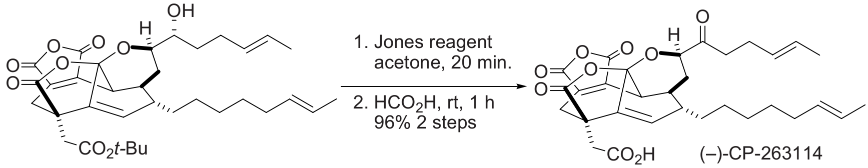
$$CrO_3 + H_2O \rightarrow H_2CrO_4$$



The intramolecular mechanism is also operative:



Example 1[6]



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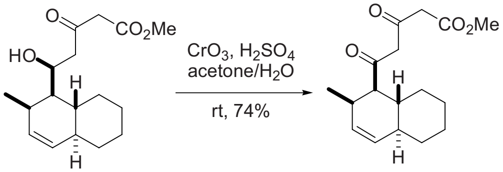
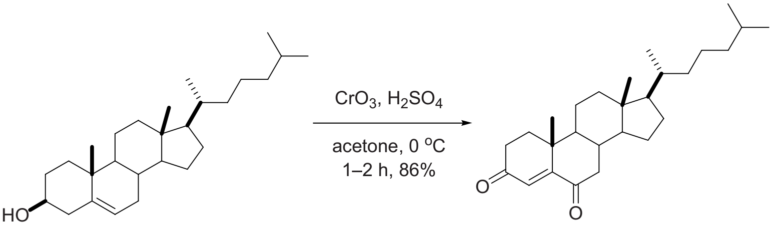
Example 2[7]



Example 3[19]



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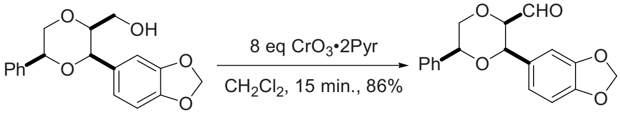
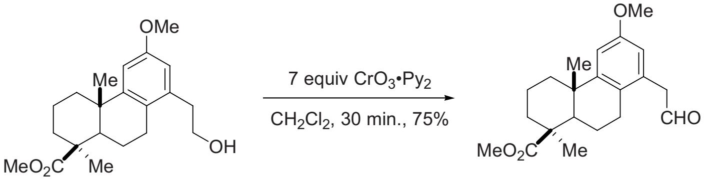
Collins–Sarett oxidation

Different from the Jones oxidation, the Collins–Sarett oxidation converts primary alcohols to the corresponding aldehydes.

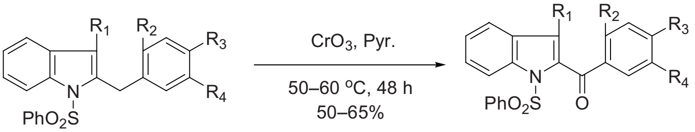
Example 1[5]



Example 2[7]



Example 3[9]



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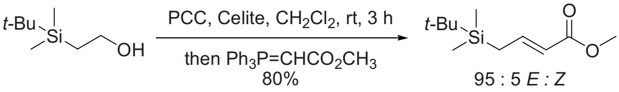
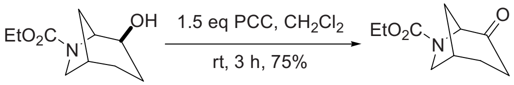
PCC oxidation

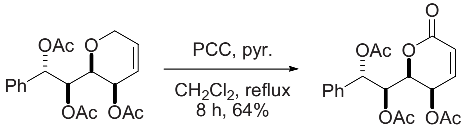
Example 1, One-pot PCC–Wittig reactions[2]



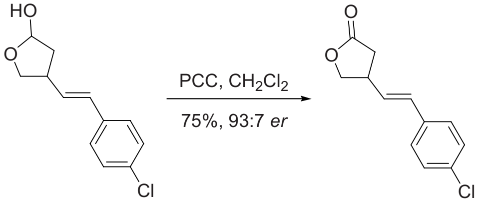
Example 2[3]



Example 3[4]



Example 4[5]



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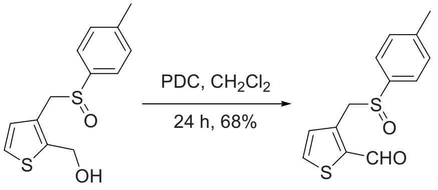
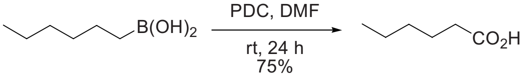
PDC oxidation

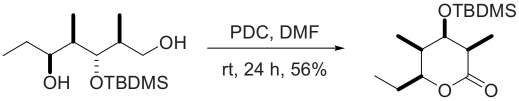
Example 1[2]



Example 2, Cleavage of primary carbon–boron bond[3]



Example 3[4]



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2 Terpstra, J. W.; Van Leusen, A. M. *J. Org. Chem.* **1986**, *51*, 230–208.

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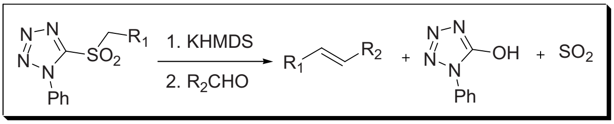
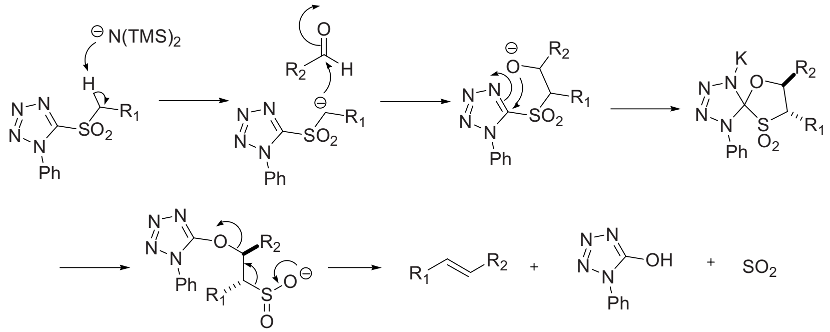
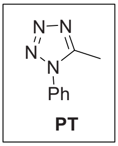
Julia–Kocienski olefination

Modified one-pot Julia olefination to give predominantly (*E*)-olefins from heteroarylsulfones and aldehydes. A sulfone reduction step is *not* required.

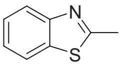




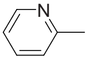
Alternatives to tetrazole:



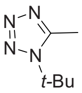
PT



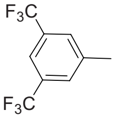
BT



PYR

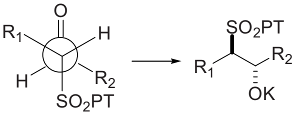


TBT

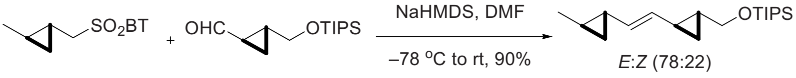


BTFP

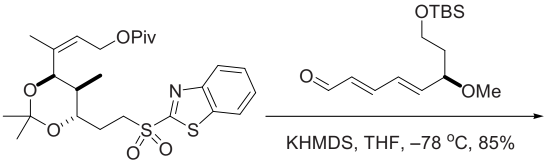
The use of larger counterion (such as K^+) and polar solvents (such as DME) favors an open transition state (PT = phenyltetrazolyl):



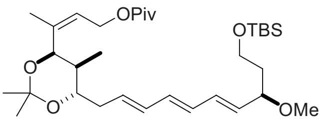
Example 1, (BT = benzothiazole)[2]



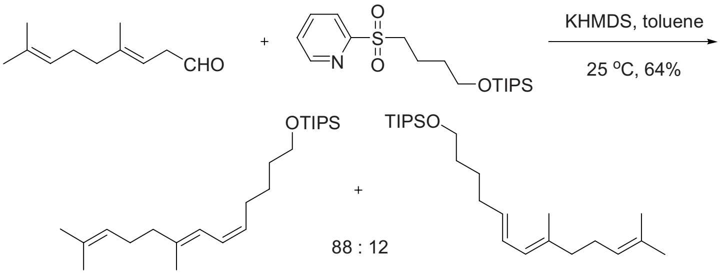
Example 2[3]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_135,



Example 3[7]



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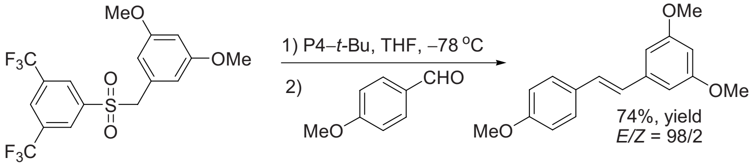

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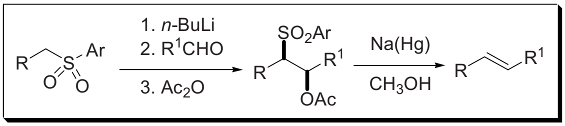
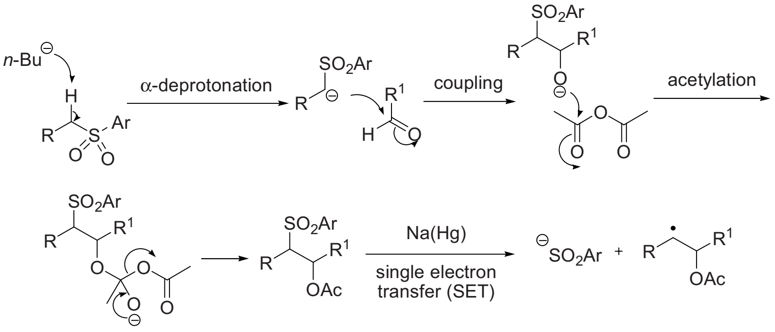
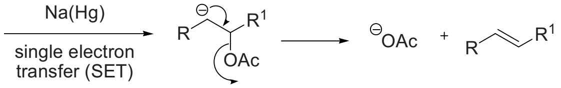
Julia–Lythgoe olefination

(*E*)-Olefins from sulfones and aldehydes.

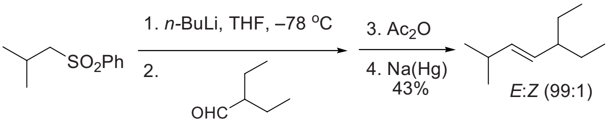




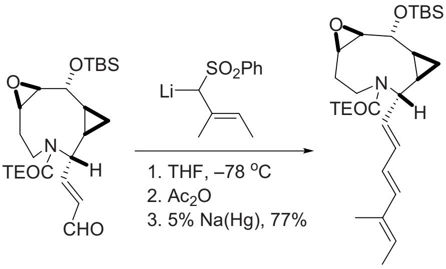
4 possible diastereomers



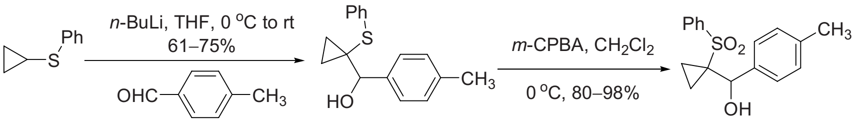
Example 1[2]



Example 2[3]



Example 3[7]



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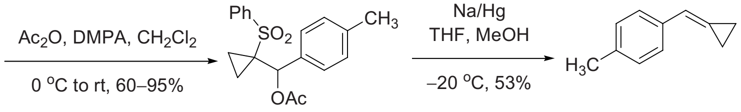
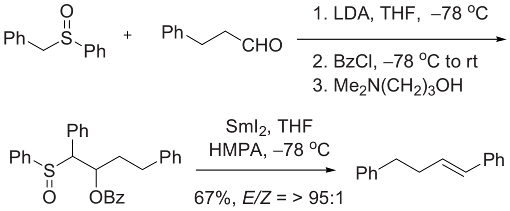


Example 4[8]



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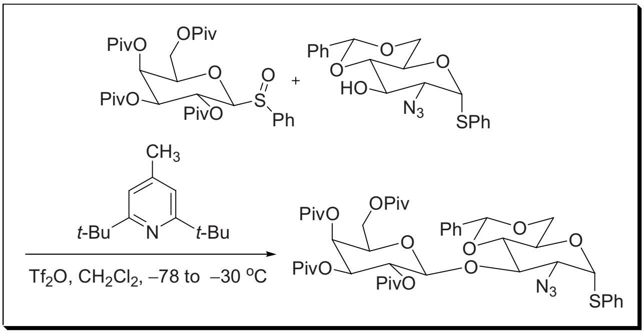
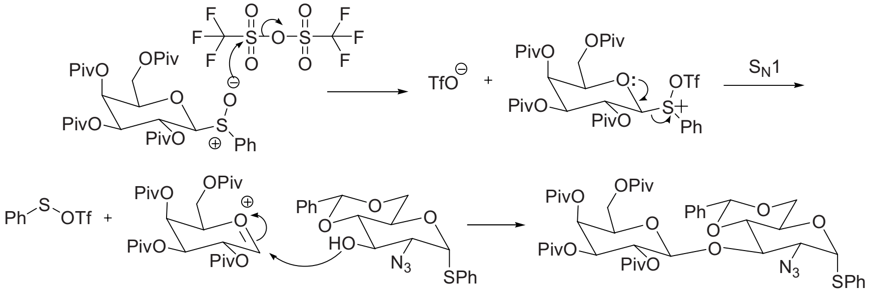
Kahne glycosidation

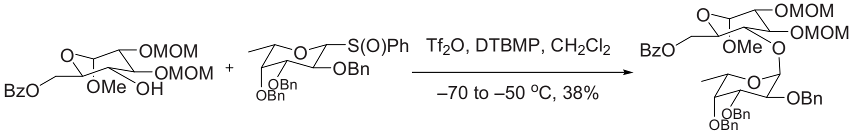
Diastereoselective glycosidation of a sulfoxide at the anomeric center as the glycosyl acceptor. The sulfoxide activation is achieved using Tf_2O.



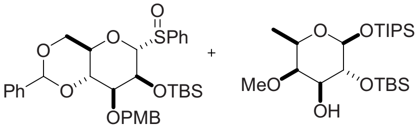


oxonium ion

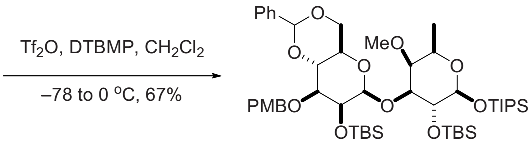
Example 1[1d]



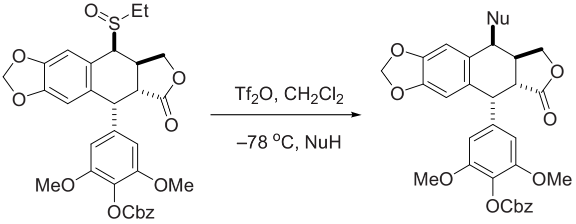
Example 2[4]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_137,



Example 3, Reverse Kahne-type glycosylation[6]



NuH = ROH, ArOH, $ArNH_2$, CH_2=$CHCH_2TMS$

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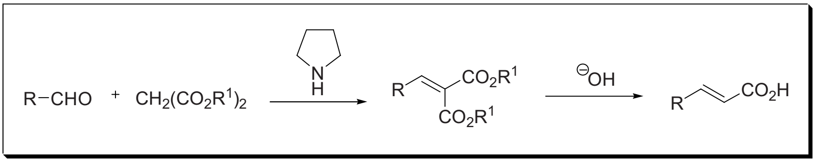
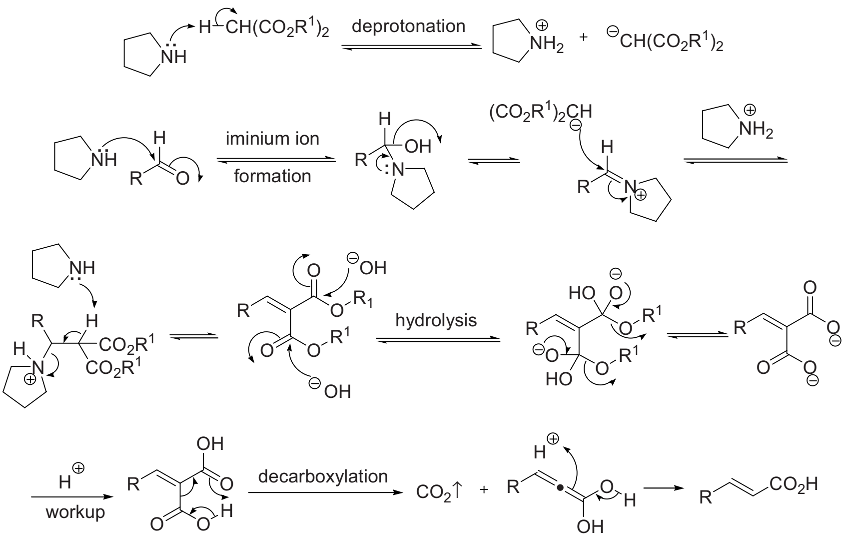
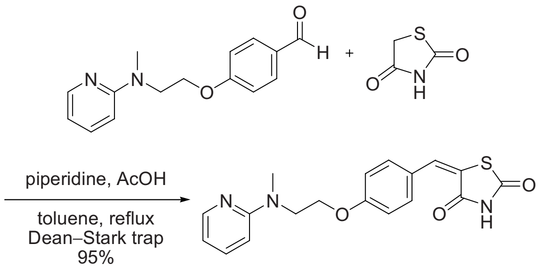
Knoevenagel condensation

Condensation between carbonyl compounds and activated methylene compounds catalyzed by amines.

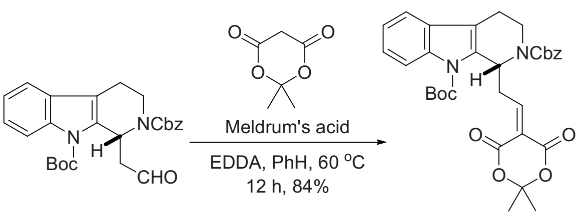




Example 1[3]



Example 2, EDDA = Ethylenediamine diacetate[5]



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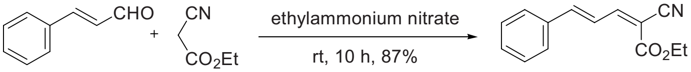
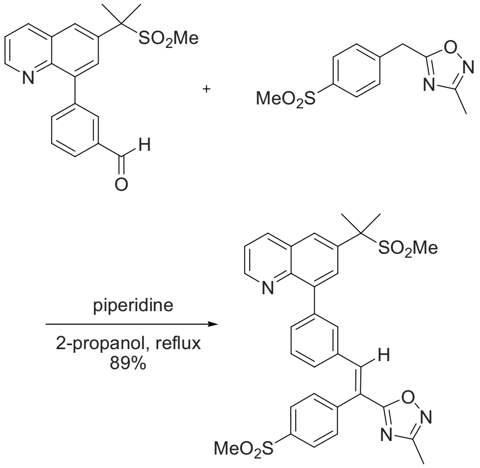
Example 3, Using ionic liquid ethylammonium nitrate (EAN) as solvent[8]



Example 4[9]



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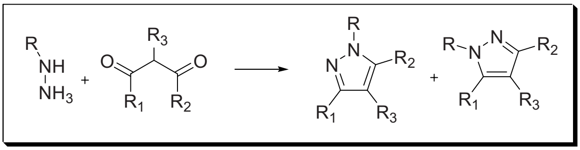
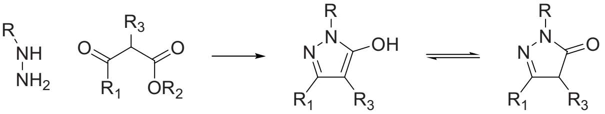
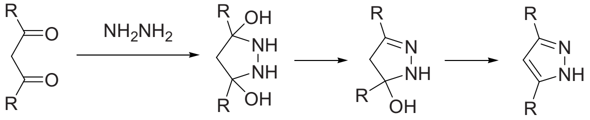
Knorr pyrazole synthesis

Reaction of hydrazine or substituted hydrazine with 1,3-dicarbonyl compounds to provide the pyrazole or pyrazolone ring system. *Cf.* Paal–Knorr pyrrole synthesis (page 411).

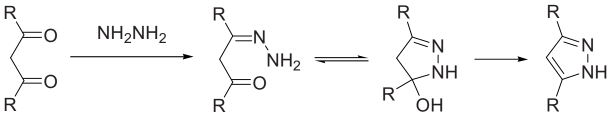


R = H, Alkyl, Aryl, Het-aryl, Acyl, *etc*.





Alternatively,



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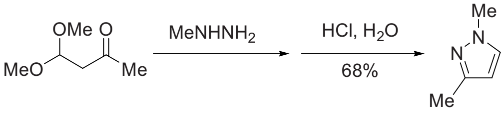
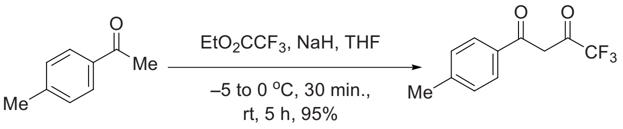
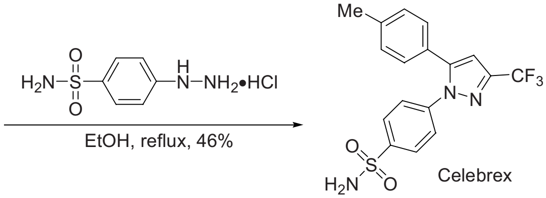


Example 2[8]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_139,



References

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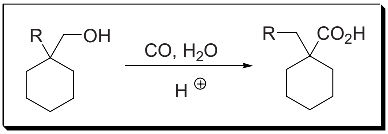
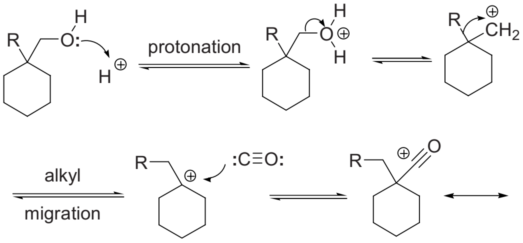
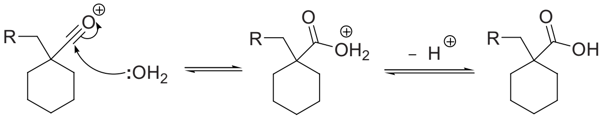
Koch–Haaf carbonylation

Strong acid-catalyzed tertiary carboxylic acid formation from alcohols or olefins and CO.



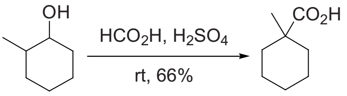


The tertiary carbocation is thermodynamically favored

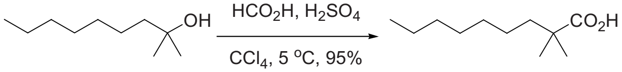


acylium ion

Example 1[3]



Example 2[5]



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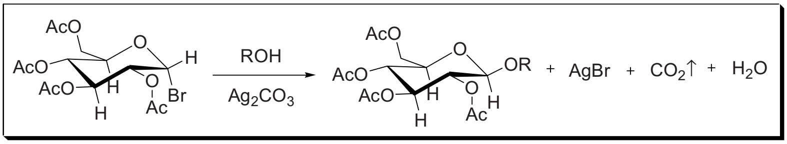
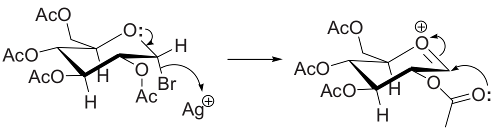
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_140,

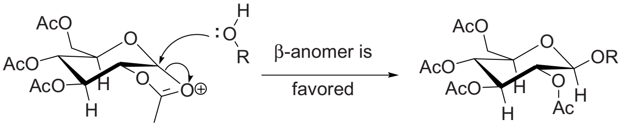
Koenig–Knorr glycosidation

Formation of the β-glycoside from α-halocarbohydrate under the influence of silver salt.



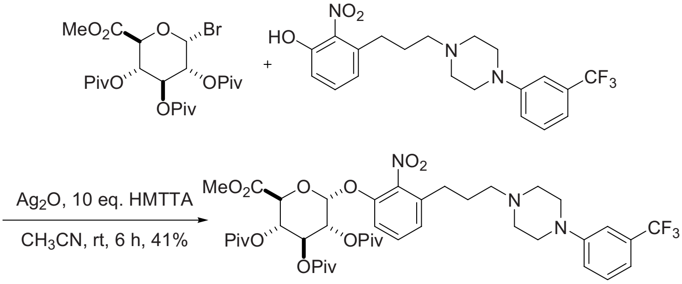


oxonium ion

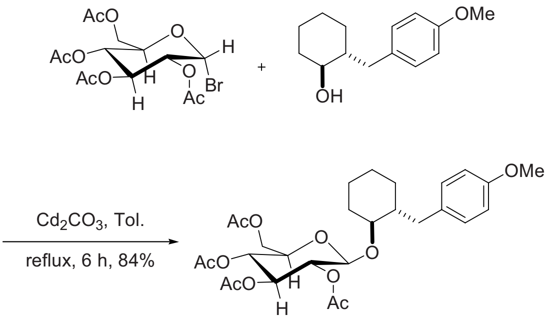


β-anomer

Example 1[7]

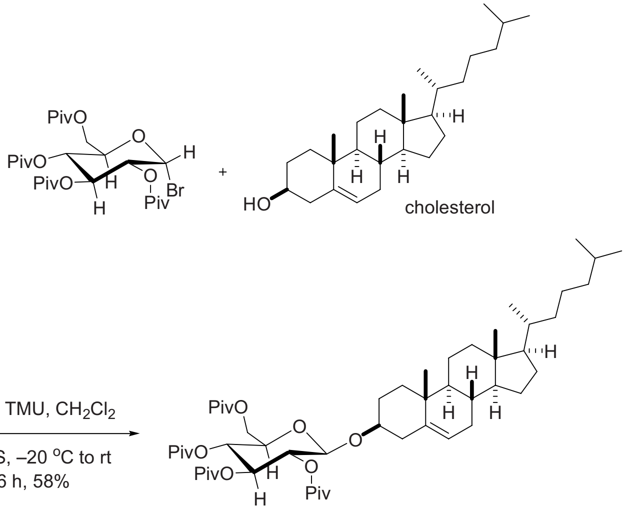


Example 2[8]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_141,

Example 3[9]



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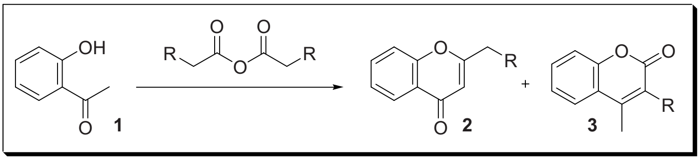
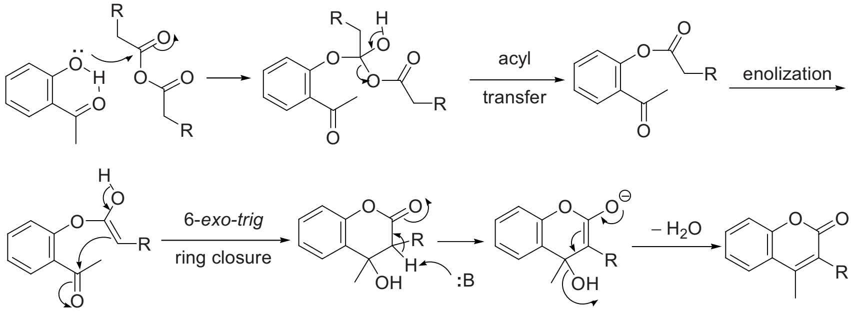
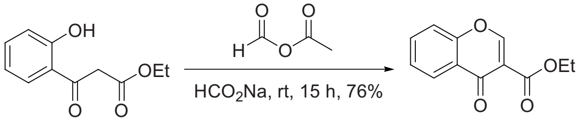
Kostanecki reaction

Also known as **Kostanecki–Robinson reaction**. Transformation **1**→**2** represents an **Allan–Robinson reaction** (see page 8), whereas **1**→**3** is a **Kostanecki (acylation) reaction**:

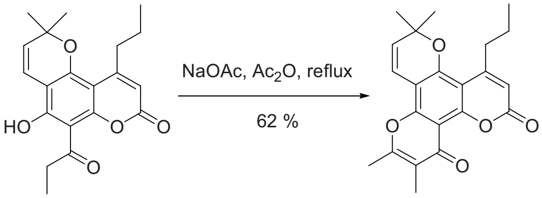




Example 1[2]



Example 2[3]



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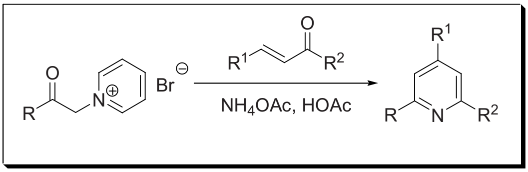
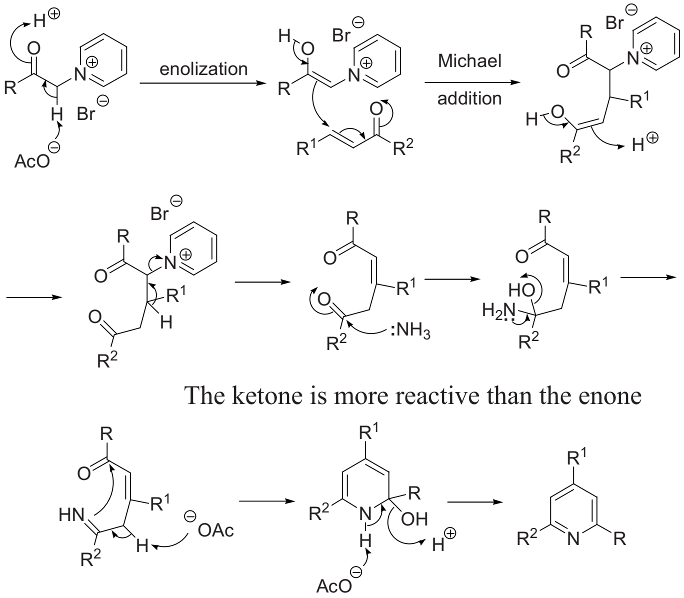
Kröhnke pyridine synthesis

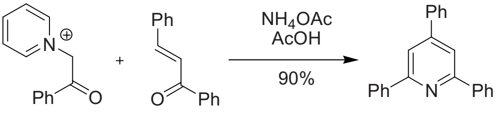
Pyridines from α-pyridinium methyl ketone salts and α,β-unsaturated ketones.



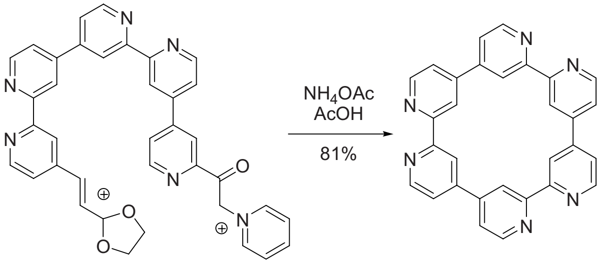


The ketone is more reactive than the enone

Example 1[1b]

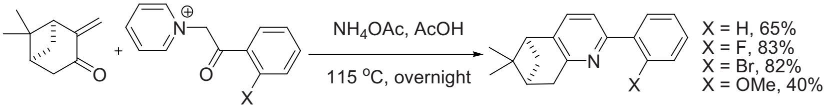


Example 2[4]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_143,

Example 3[6]



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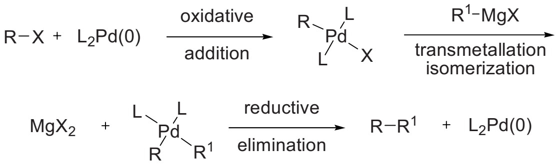
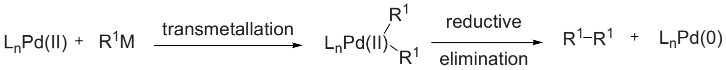
Kumada cross-coupling reaction

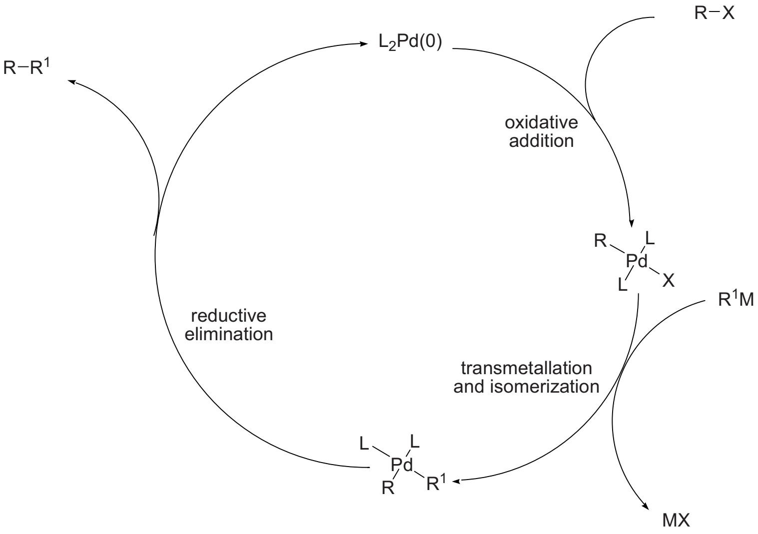
The Kumada cross-coupling reaction (also occasionally known as the Kharasch cross-coupling reaction) was originally reported as the nickel-catalyzed cross-coupling of Grignard reagents with aryl- or alkenyl halides. It has subsequently been developed to encompass the coupling of organolithium or organomagnesium compounds with aryl-, alkenyl or alkyl halides, catalyzed by nickel or palladium. The Kumada cross-coupling reaction, as well as the Negishi, Stille, Hiyama, and Suzuki cross-coupling reactions, belong to the same category of Pd-catalyzed cross-coupling reactions of organic halides, triflates and other electrophiles with organometallic reagents. These reactions follow a general mechanistic catalytic cycle as shown below. There are slight variations for the Hiyama and Suzuki reactions, for which an additional activation step is required for the transmetallation to occur.

$$\boxed{\text{R–X} + \text{R}^1\text{–MgX} \xrightarrow{\text{Pd(0)}} \text{R–R}^1 + \text{MgX}_2}$$



The catalytic cycle:





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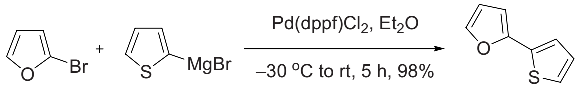
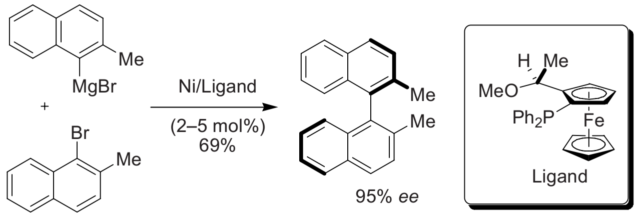
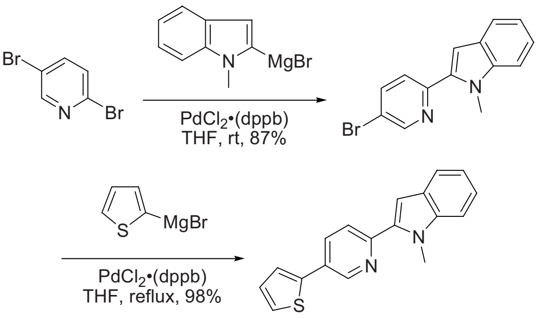
Example 1[2]



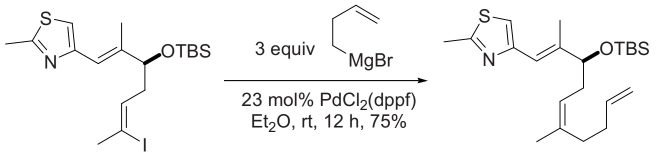
Example 2[3]



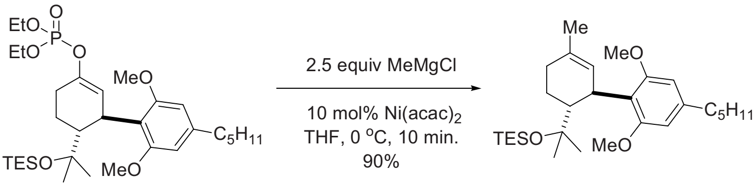
Example 3[5]



Example 4[8]



Example 5[9]



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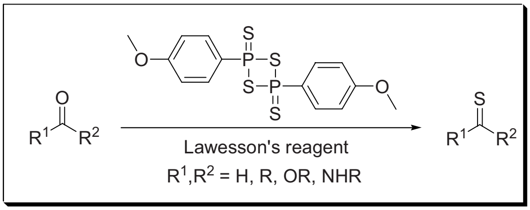
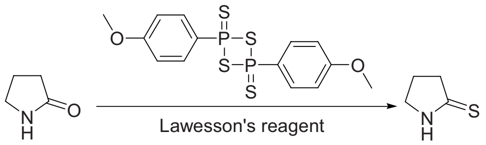
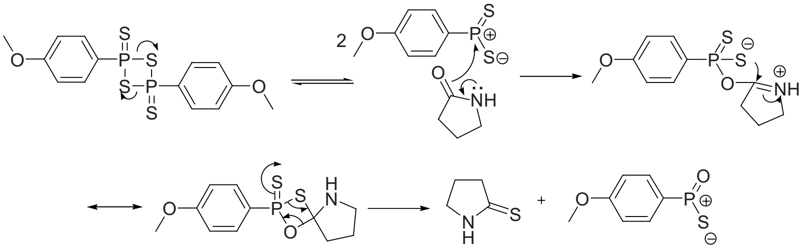
Lawesson's reagent

2,4-Bis(4-methoxyphenyl)-1,3-dithiadiphosphetane-2,4-disulfide transforms the carbonyl groups of aldehydes, ketones, amides, lactams, esters and lactones into the corresponding thiocarbonyl compounds. *Cf.* Knorr thiophene synthesis.







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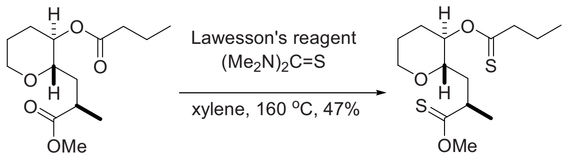

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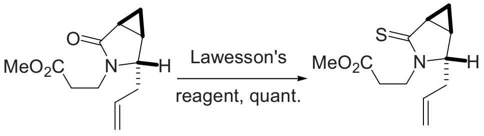
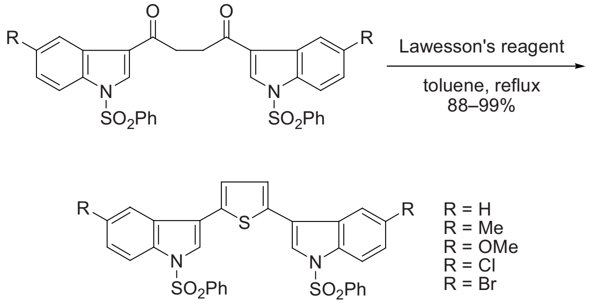
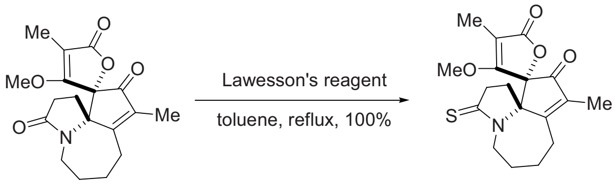


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_145,

Example 3, Thiophene from dione[8]



Example 4[10]



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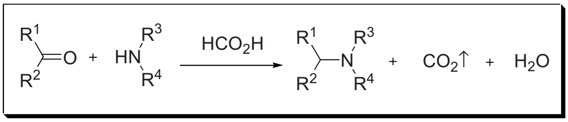
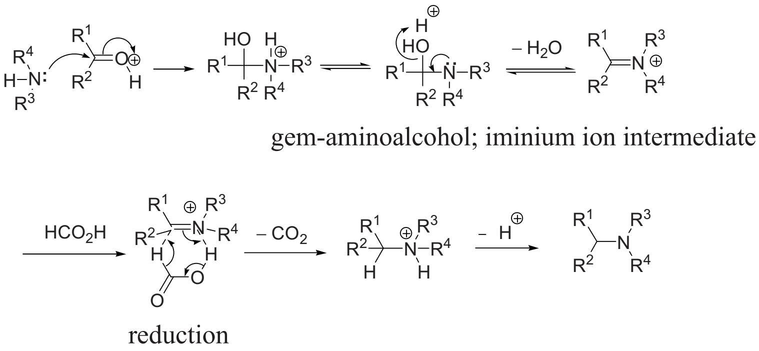
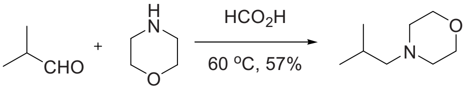
Leuckart–Wallach reaction

Amine synthesis from reductive amination of a ketone and an amine in the presence of excess formic acid, which serves as the reducing reagent by delivering a hydride. When the ketone is replaced by formaldehyde, it becomes the Eschweiler–Clarke reductive alkylation of amines on page 210.





Example 1[4]



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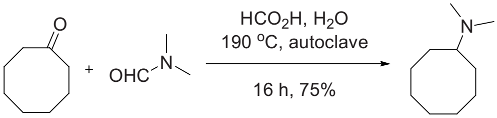
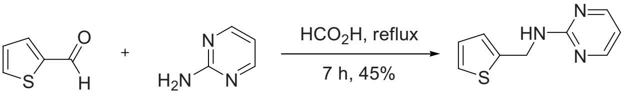
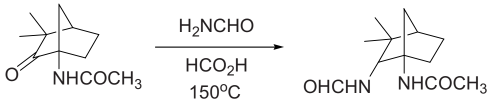


Example 3[7]

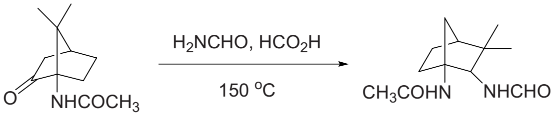


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_146,

Example 4[8]



An unexpected intramolecular transamidation *via* a Wagner–Meerwein shift after the Leuckart–Wallach reaction



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2. Wallach, O. *Ann.* **1892**, *272*, 99. Otto Wallach (1847–1931), born in Königsberg, Prussia, studied under Wöhler and Hofmann. He was the director of the Chemical Institute at Göttingen from 1889 to 1915. His book "Terpene und Kampfer" served as the foundation for future work in terpene chemistry. Wallach was awarded the Nobel Prize in Chemistry in 1910 for his work on alicyclic compounds.
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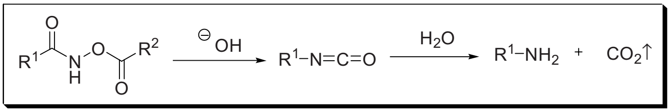
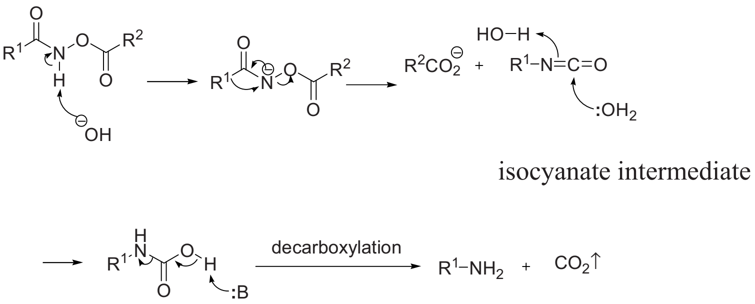
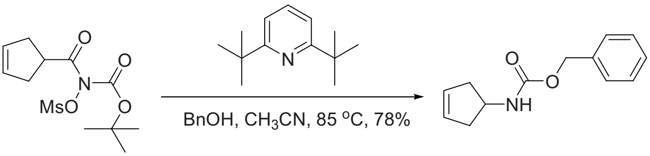
Lossen rearrangement

The Lossen rearrangement involves the generation of an isocyanate via thermal or base-mediated rearrangement of an activated hydroxamate which can be generated from the corresponding hydroxamic acid. Activation of the hydroxamic acid can be achieved through *O*-acylation, *O*-arylation, chlorination, or *O*-sulfonylation. Such hydroxamic acids can also be activated using polyphosphoric acid, carbodiimide, Mitsunobu conditions, or silyation. The product of the Lossen rearrangement, an isocyanate can be subsequently converted to an urea or an amine resulting in the net loss of one carbon atom relative to the starting hydroxamic acid.

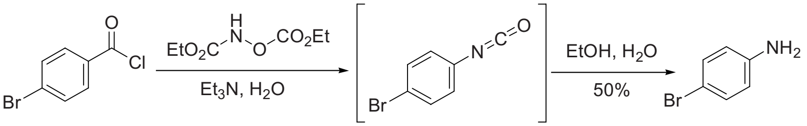




Example 1[6]



Example 2[7]



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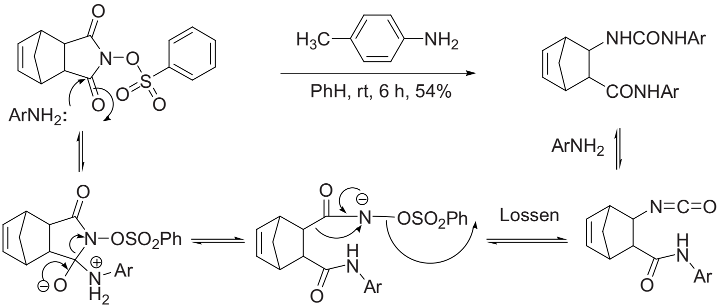
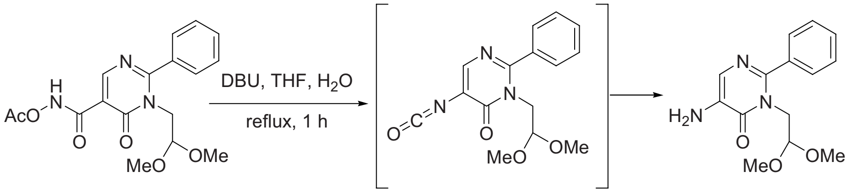
Example 3[8]



Example 4[9]



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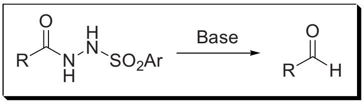
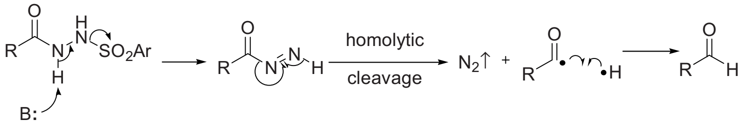
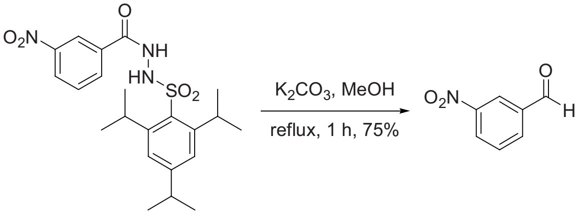
McFadyen–Stevens reduction

Treatment of acylbenzenesulfonylhydrazines with base delivers the corresponding aldehydes.

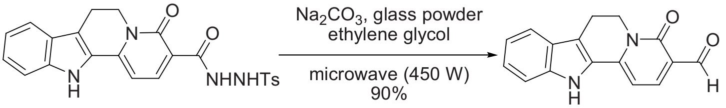




Example 1[8]



Example 2[10]



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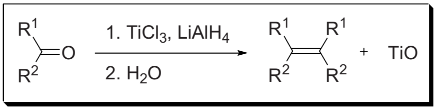
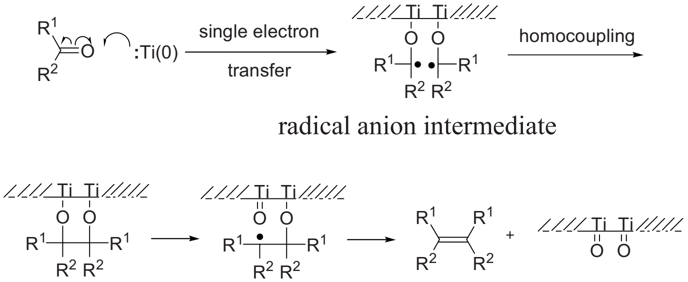
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_148,

McMurry coupling

Olefination of carbonyls with low-valent titanium such as Ti(0) derived from $TiCl_3/LiAlH_4$. A single-electron process.

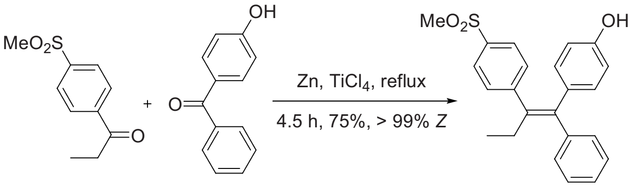


$$Ti(III)Cl_3 + LiAlH_4 \longrightarrow Ti(0)$$

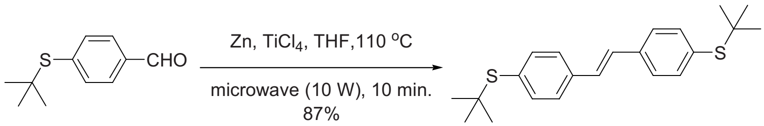


oxide-coated titanium surface

Example 1, Cross-McMurry coupling[7]

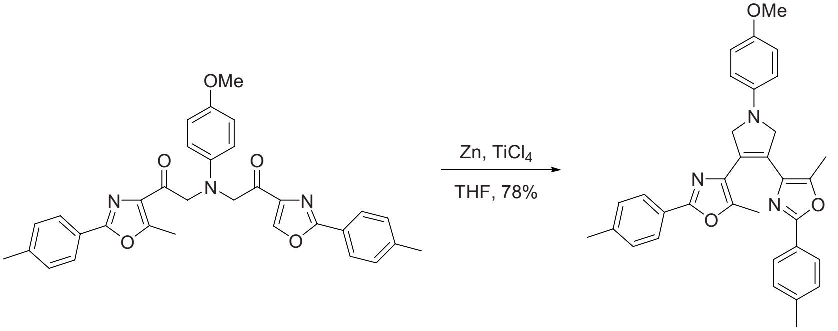


Example 2, Homo-McMurry coupling[8]

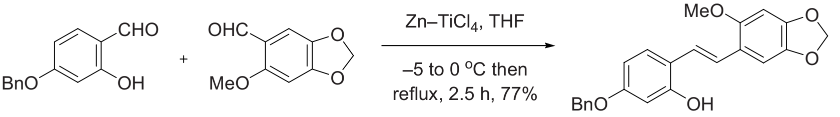


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_149,

Example 3, Cross-McMurry coupling[9]



Example 4, Cross-McMurry coupling[10]



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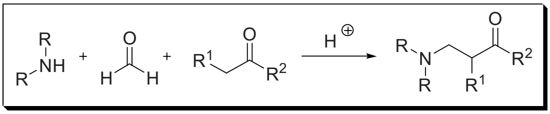
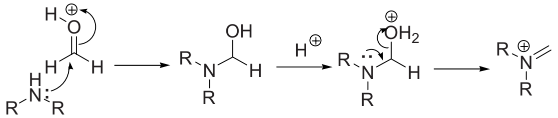
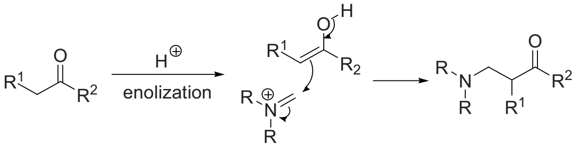
Mannich reaction

Three-component aminomethylation from amine, aldehyde and a compound with an acidic methylene moiety.

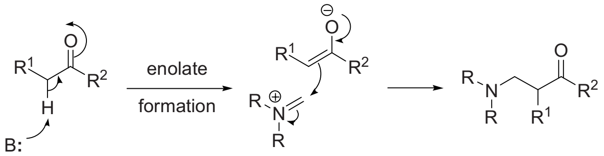




When R = Me, the $^{+}Me_2N{=}CH_2$ salt is known as *Eschenmoser's salt* (page 206)

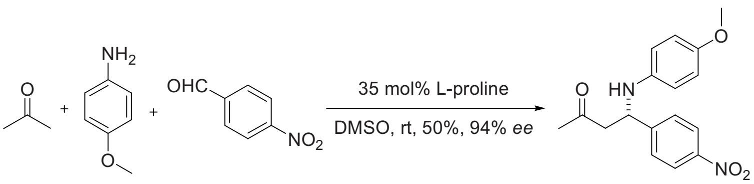


The Mannich reaction can also operate under basic conditions:

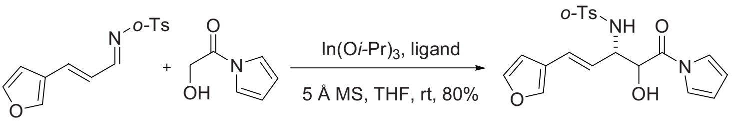


Mannich Base

Example 1, Asymmetric Mannich reaction[2]

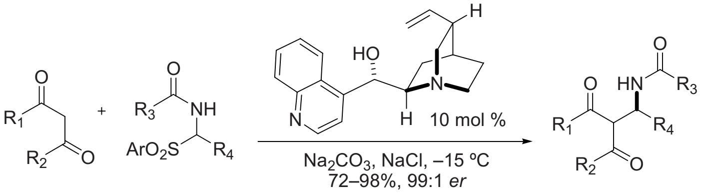


Example 2, Asymmetric Mannich-type reaction[9]

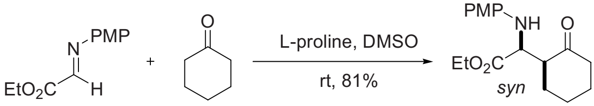


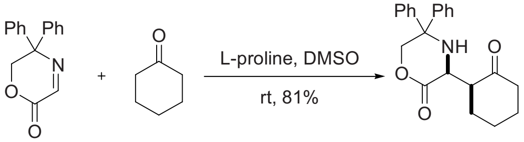
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_150,

Example 3, Asymmetric Mannich reaction[10]



Example 4[11]





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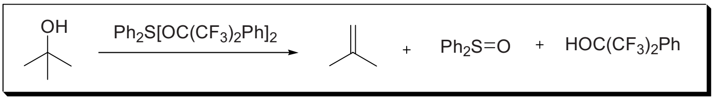
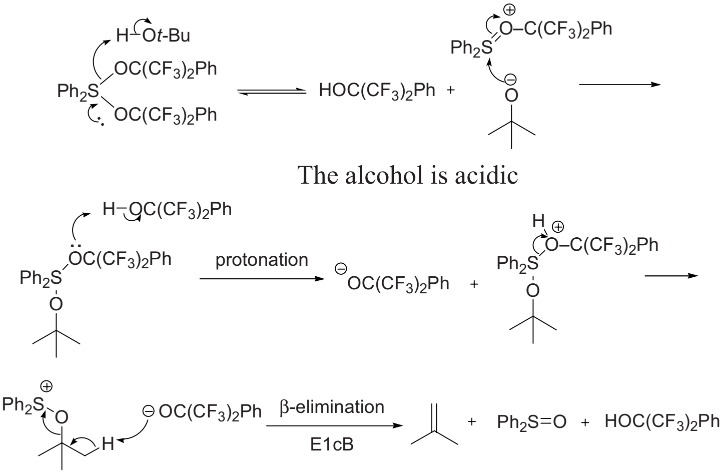
Martin's sulfurane dehydrating reagent

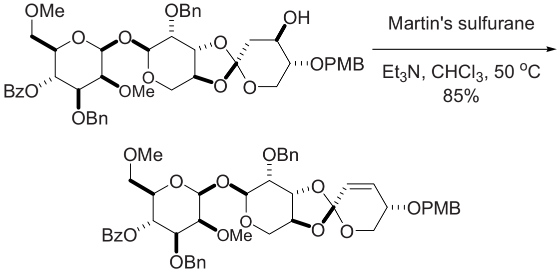
Dehydrates secondary and tertiary alcohols to give olefins, but forms ethers with primary alcohols. *Cf.* Burgess dehydrating reagent.



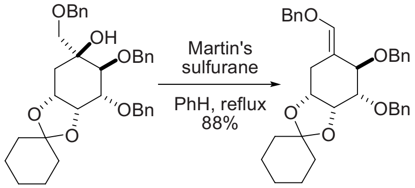


The alcohol is acidic

Example 1[5]

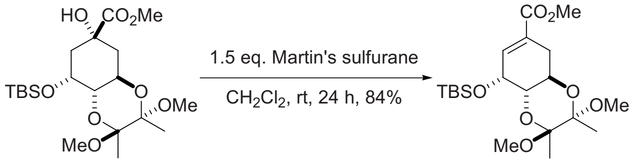


Example 2[6]

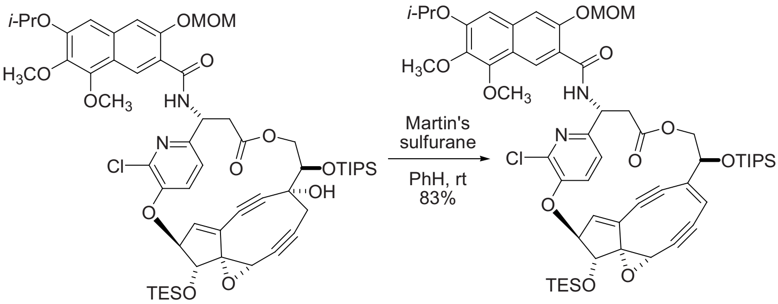


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_151,

Example 3[7]



Example 4[9]



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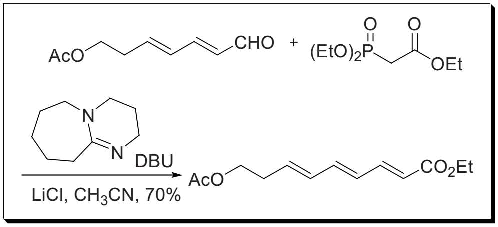
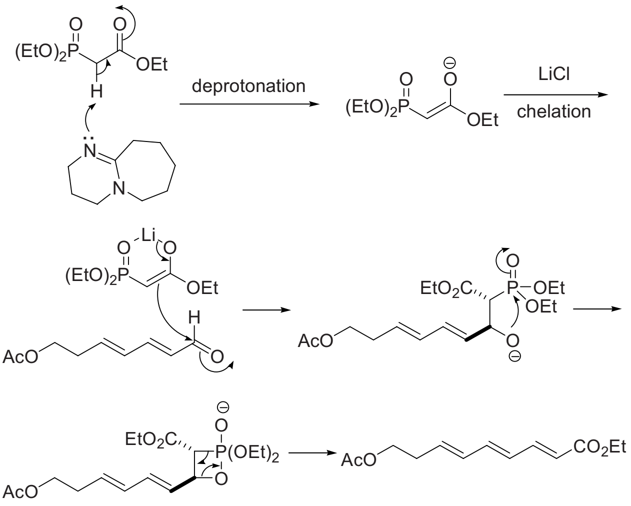
Masamune–Roush conditions for the Horner–Emmons reaction

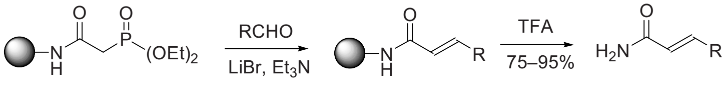
Applicable to base-sensitive aldehydes and phosphonates for the Horner–Wadsworth–Emmons reaction. α-Keto or α-alkoxycarbonyl phosphonate required.



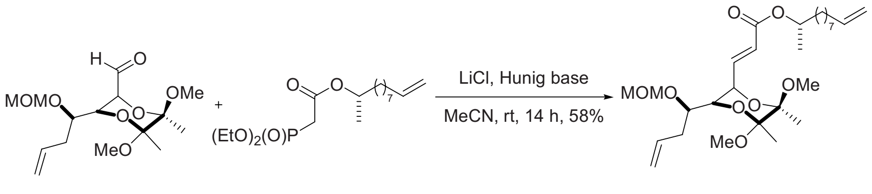
DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene



Example 1[5]

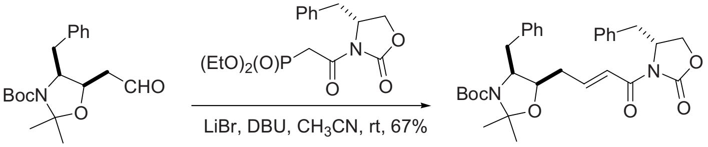


Example 2[6]

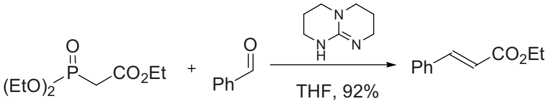


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_152,

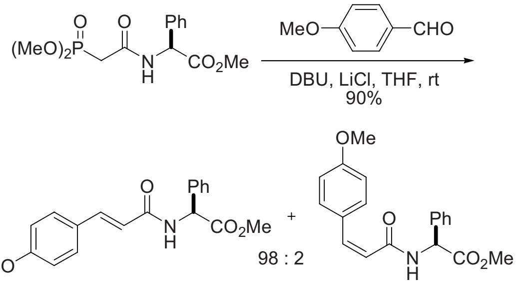
Example 3[7]



Example 4[8]



Example 5[10]



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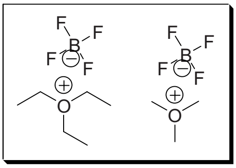
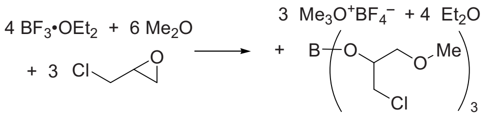
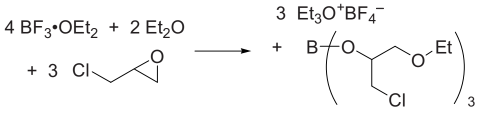
Meerwein's salt

Meerwein's salts, also known as the Meerwein reagent, refer to trimethyloxonium tetrafluoroborate ($Me_3O^+BF_4^-$) and triethyloxonium tetrafluoroborate ($Et_3O^+BF_4^-$). Named after the inventor Hans Meerwein,[1] these trialkyloxonium salts are powerful alkylating agents.

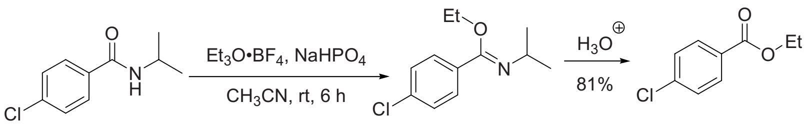


Preparation:[2]



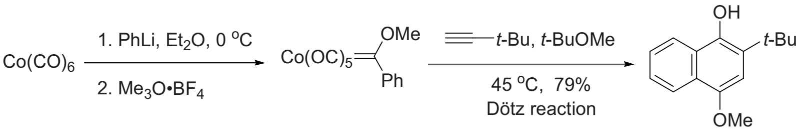


Example 1, The Meerwein reagent is an excellent *O*-alkylating agent:[5]

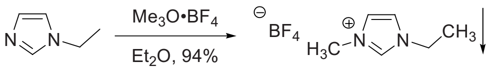


Transforming an amide into its corresponding ethyl or methyl esters

Example 2, *Metal*-methylation[4]



Example 3, *N*-Alkylation, the product is an ionic liquid[8]



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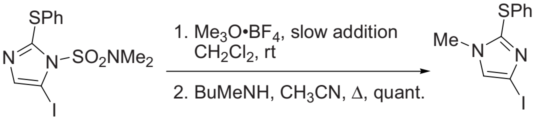
Example 4, *N*-Methylation[9]



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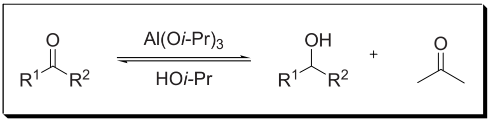
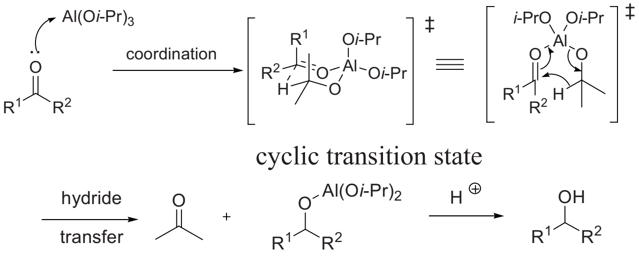
Meerwein–Ponndorf–Verley reduction

Reduction of ketones to the corresponding alcohols using Al(O*i*-Pr)$_3$ in isopropanol. Reverse of the Oppernauer oxidation.





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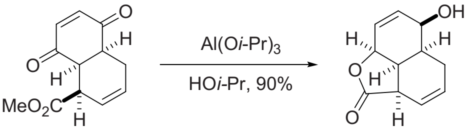

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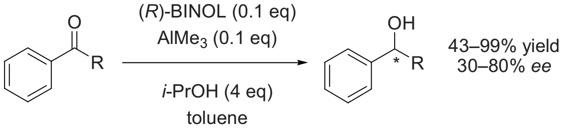
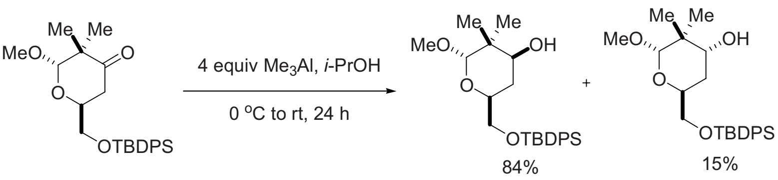
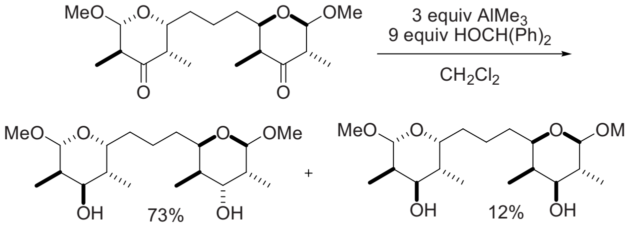


Example 3[7]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_154,

Example 4[9]



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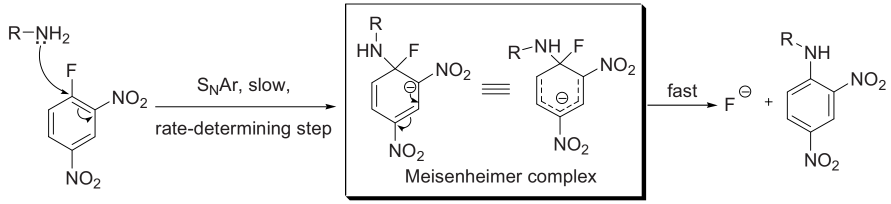
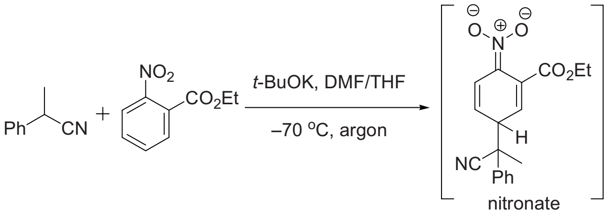
Meisenheimer complex

Also known as **the Meisenheimer–Jackson salt**, the stable intermediate for certain S_NAr reactions.

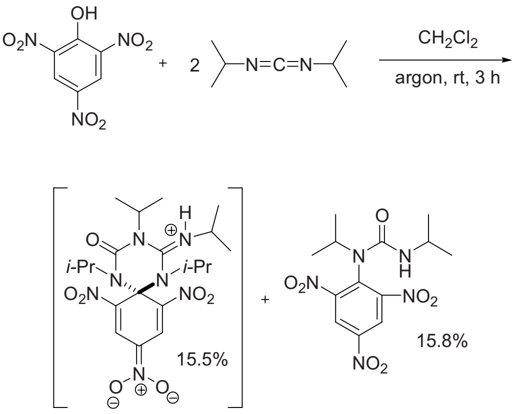


Sanger's reagent, *ipso* attack *ipso* substitution

Example 1[7]



Example 2[9]



The reaction using Sanger's reagent is faster than using the corresponding chloro-, bromo-, and iododinitrobenzene—the fluoro-Meisenheimer complex is the most stabilized because F is the most electron-withdrawing. The reaction rate does not depend upon the capacity of the leaving group.

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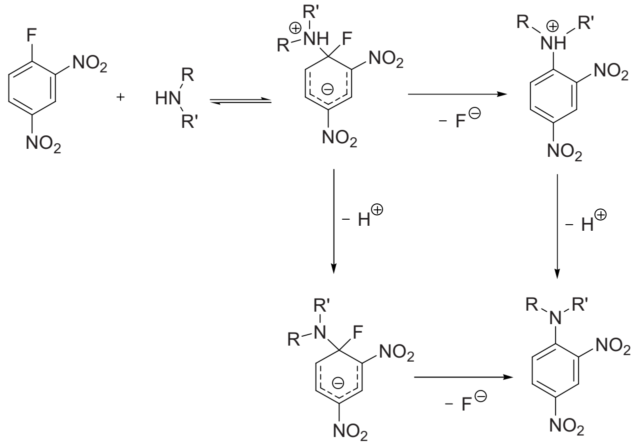
Example 3[10]



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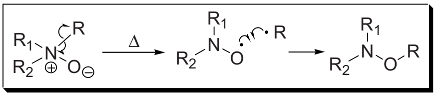
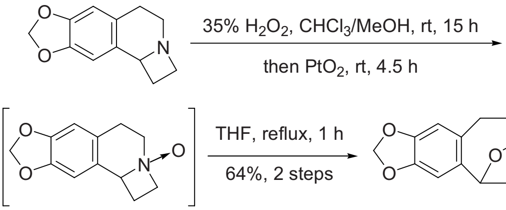
[1,2]-Meisenheimer rearrangement

[1,2]-Sigmatropic rearrangement of tertiary amine *N*-oxides to substituted hydroxylamines.



Example 1[7]



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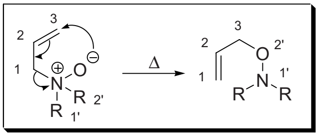
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_156,

[2,3]-Meisenheimer rearrangement

[2,3]-Sigmatropic rearrangement of allylic tertiary amine-*N*-oxides to give *O*-allyl hydroxylamines:



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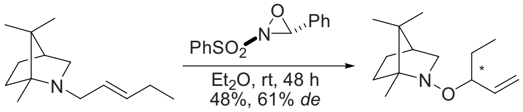

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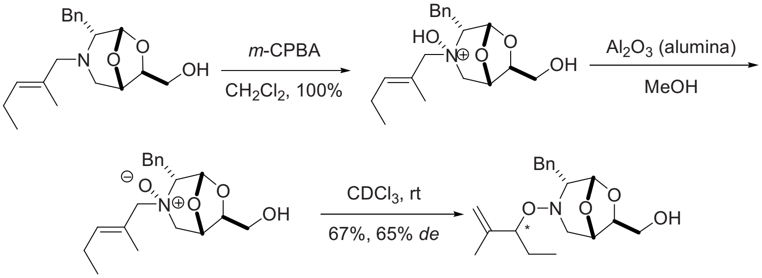

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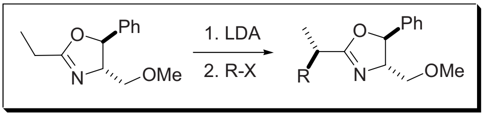
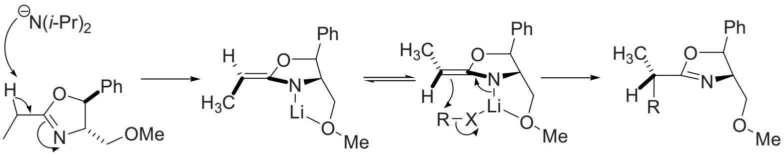
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_157,

Meyers oxazoline method

Chiral oxazolines employed as activating groups and/or chiral auxiliaries in nucleophilic addition and substitution reactions that lead to the asymmetric construction of carbon–carbon bonds.





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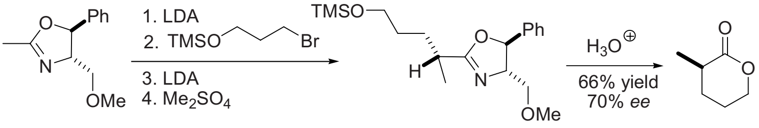

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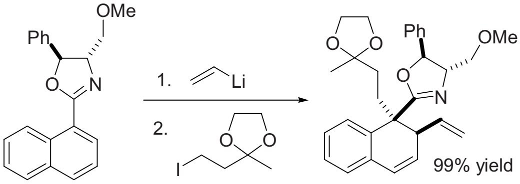
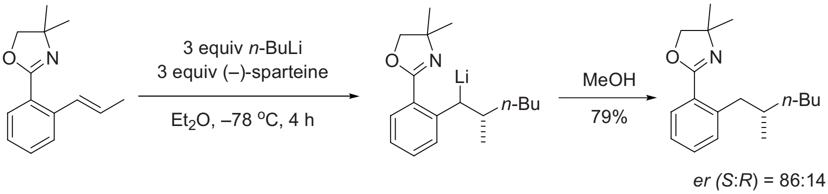


Example 3[9]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_158,

References

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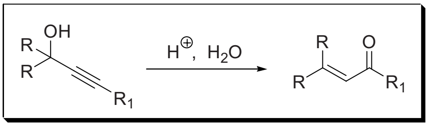
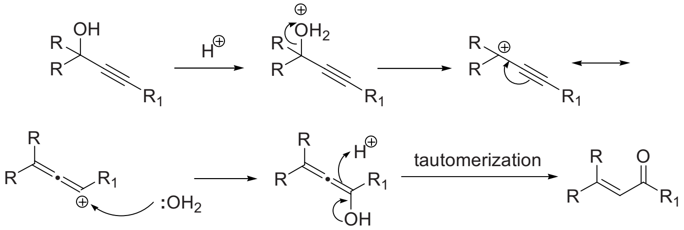
Meyer–Schuster rearrangement

The isomerization of secondary and tertiary α-acetylenic alcohols to α,β-unsaturated carbonyl compounds *via* 1,3-shift. When the acetylenic group is terminal, the products are aldehydes, whereas the internal acetylenes give ketones. *Cf.* Rupe rearrangement.





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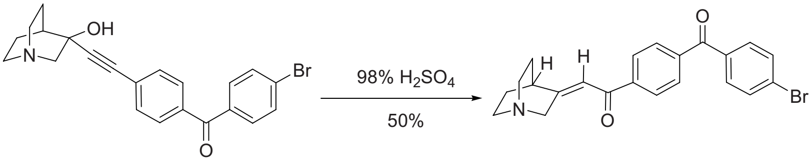

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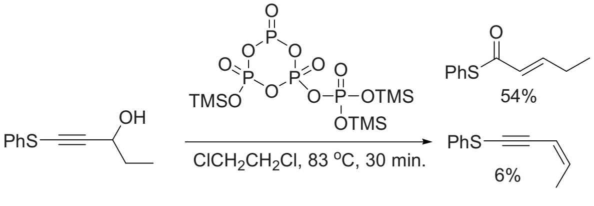
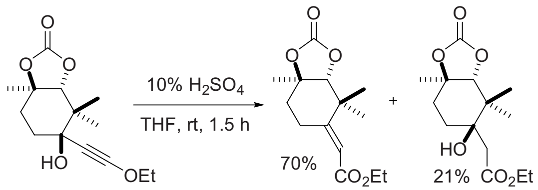


Example 3[8]



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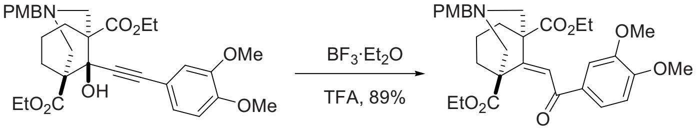
Example 4[9]



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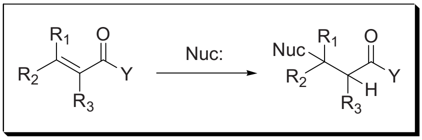
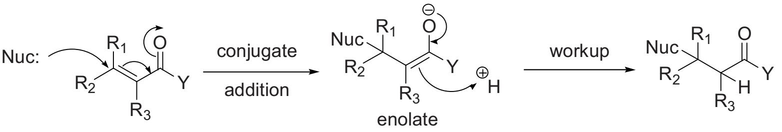
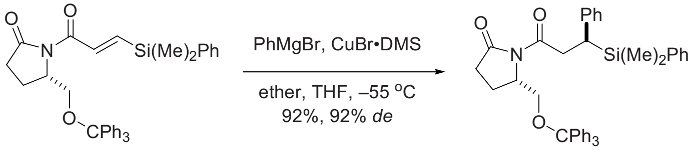
Michael addition

Also known as conjugate addition, Michael addition is the 1,4-addition of a nucleophile to an α,β-unsaturated system.

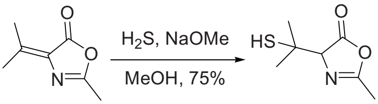




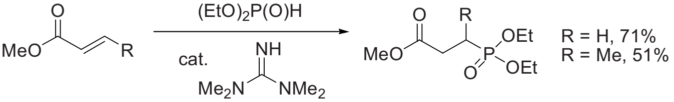
Example 1, Asymmetric Michael addition[2]



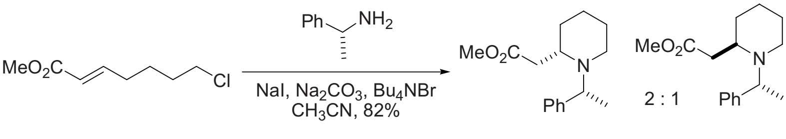
Example 2, Thia-Michael addition[3]



Example 3, Phospha-Michael addition[7]



Example 4, Asymmetric aza-Michael addition[9]



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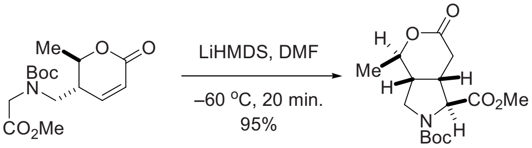
Example 5, Intramolecular Michael addition[10]



References

1. Michael, A. *J. Prakt. Chem*. **1887**, *35*, 349. Arthur Michael (1853−1942) was born in Buffalo, New York. He studied under Robert Bunsen, August Hofmann, Adolphe Wurtz, and Dimitri Mendeleev, but never bothered to take a degree. Back to the United States, Michael became a Professor of Chemistry at Tufts University, where he married one of his most brilliant students, Helen Abbott, one of the few female organic chemists in this period. Since he failed miserably as an administrator, Michael and his wife set up their own private laboratory at Newton Center, Massachusetts, where the Michael addition was discovered.
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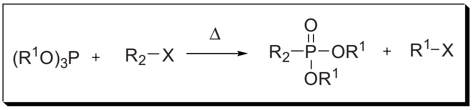
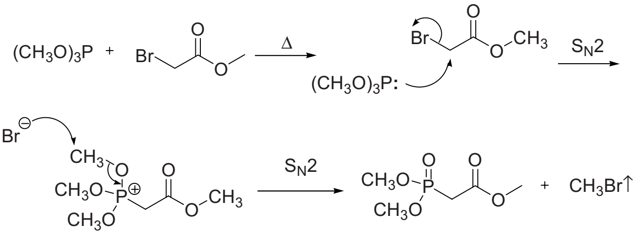
Michaelis–Arbuzov phosphonate synthesis

Phosphonate synthesis from the reaction of alkyl halides with phosphites.
General scheme:

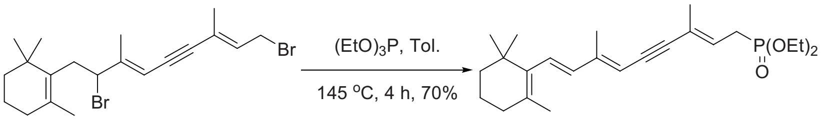


R^1 = alkyl, *etc*.; R_2 = alkyl, acyl, *etc*.; X = Cl, Br, I

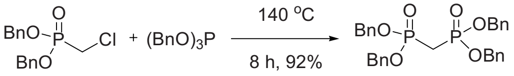
For instance:



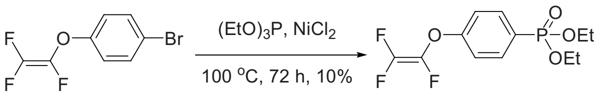
Example 1[2]



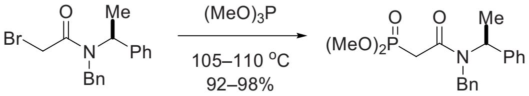
Example 2[6]



Example 3[7]

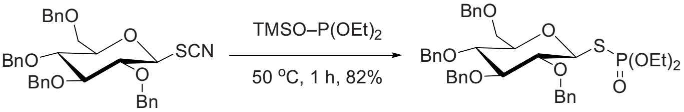


Example 4[9]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_161,

Example 5[10]



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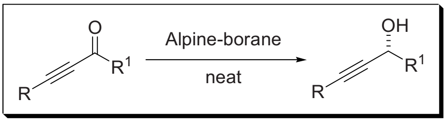
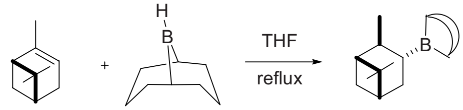
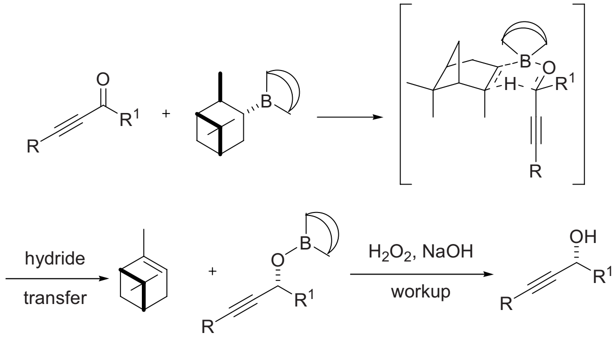
Midland reduction

Asymmetric reduction of ketones using Alpine-borane®.
Alpine-borane® = *B*-isopinocampheyl-9-borabicyclo[3.3.1]nonane.

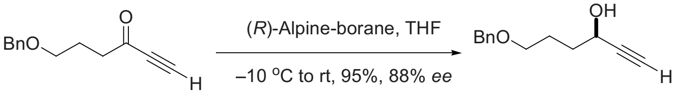




(1*R*)-(+)-α-pinene 9-BBN (*R*)-Alpine-borane
9-BBN = 9-borabicyclo[3.3.1]nonane



Example 1[6]



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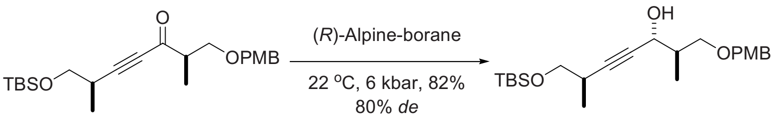
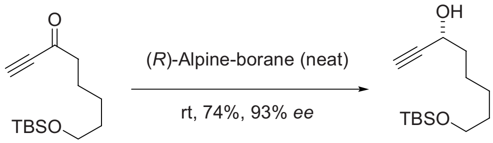


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_162,

Example 3[8]



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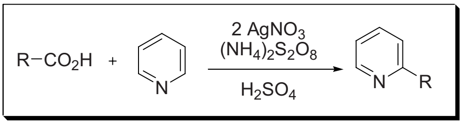
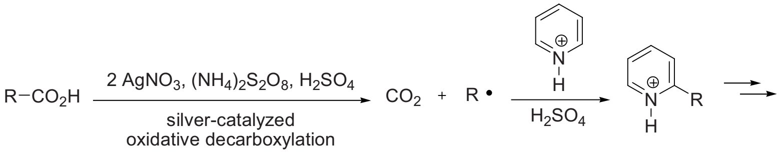
Minisci reaction

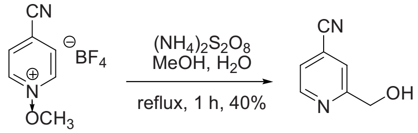
Radical-based carbon–carbon bond formation with electron-deficient heteroaromatics. The reaction entails an intermolecular addition of a nucleophilic radical to protonated heteroaromatic nucleus.



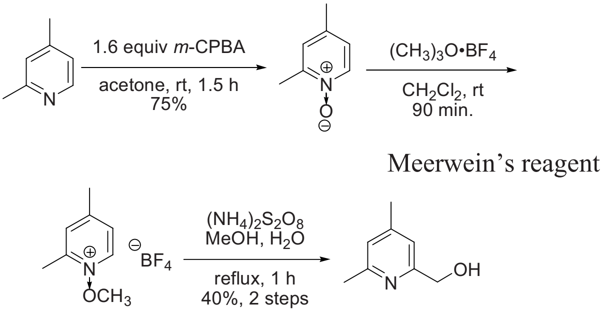


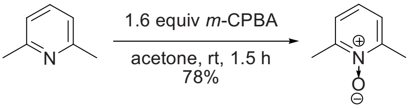
Example 1[4]

$$S_2O_8^{=} + CH_3OH \longrightarrow \bullet CH_2OH + H^+ + SO_4^{=} + SO_4^{\bullet -}$$

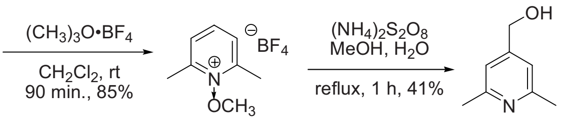


Example 2[5]

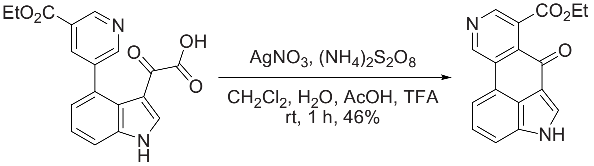




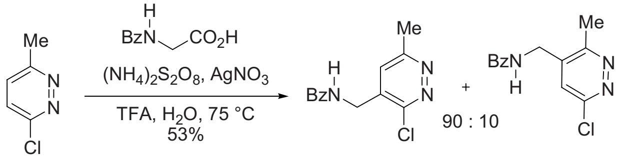
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_163,



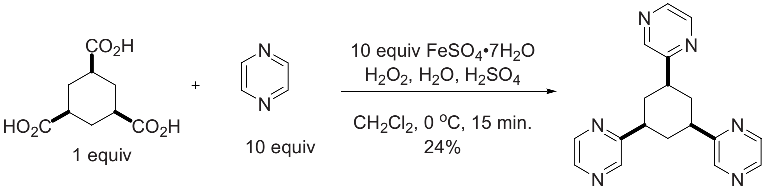
Example 3, Intramolecular Minisci reaction[6]



Example 4[7]



Example 5[10]



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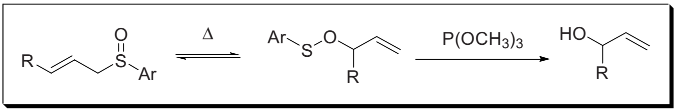
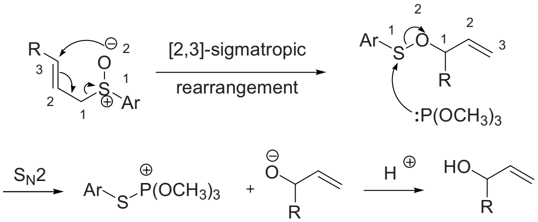
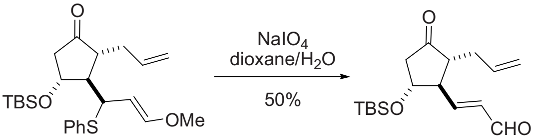
Mislow–Evans rearrangement

[2,3]-Sigmatropic rearrangement of allylic sulfoxide to allylic alcohol.

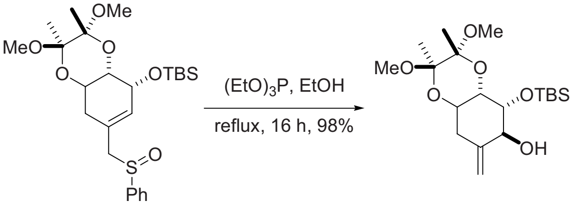




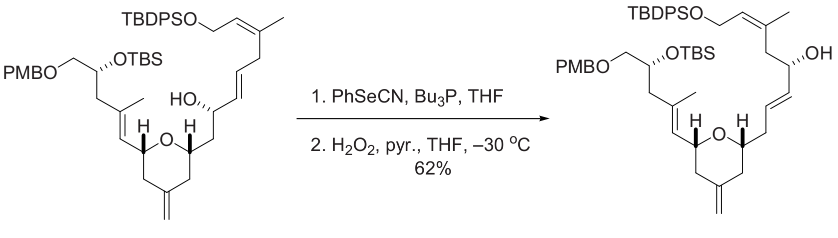
Example 1[2]



Example 2[7]



Example 3, Seleno-Mislow-Evans[8]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_164,

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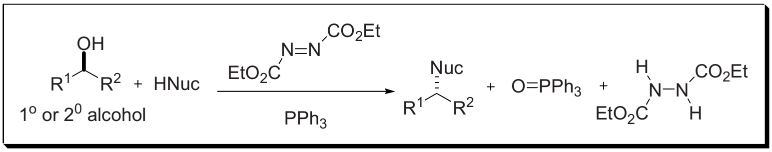
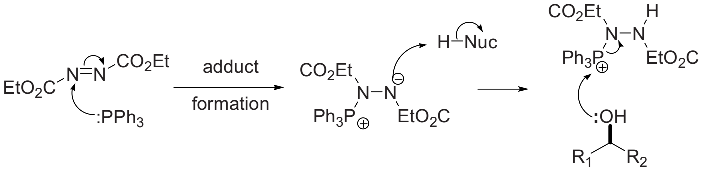
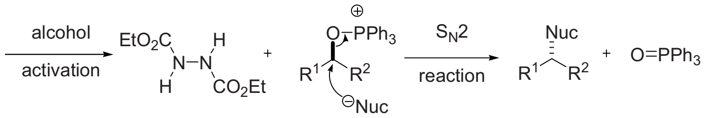
Mitsunobu reaction

S_N2 inversion of an alcohol by a nucleophile using disubstituted azodicarboxylates (originally, diethyl diazodicarboxylate, or DEAD) and trisubstituted phosphines (originally, triphenylphosphine).

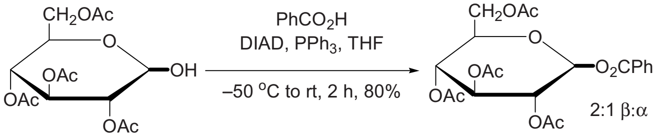




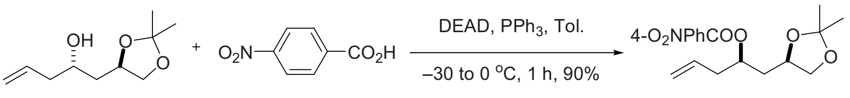
Diethyl azodicarboxylate (DEAD)



Example 1[2]



Example 2[3]



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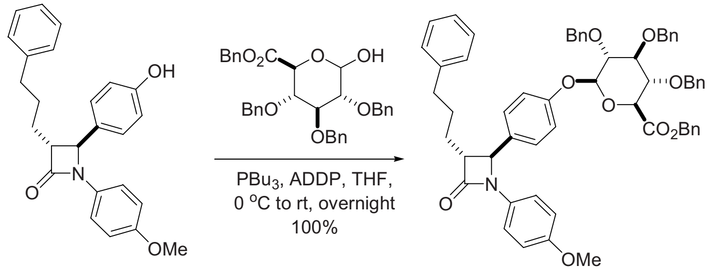
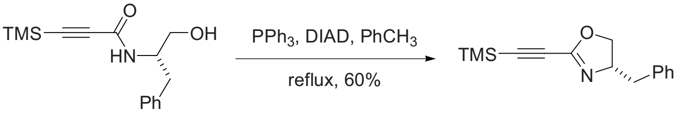
Example 3, Ether formation[6]

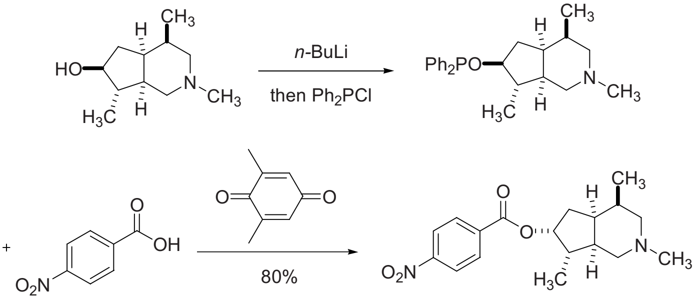


ADDP = 1,1'-(azodicarbonyl)dipiperidine

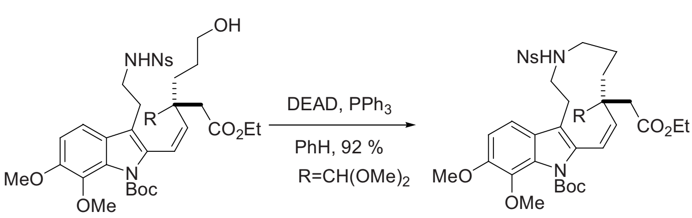
Example 4[7]



Example 5[8]



Example 6, Intramolecular Mitsunobu reaction[9]



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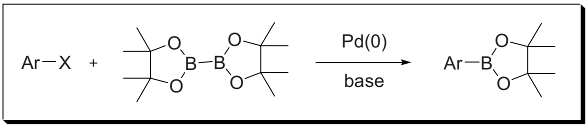
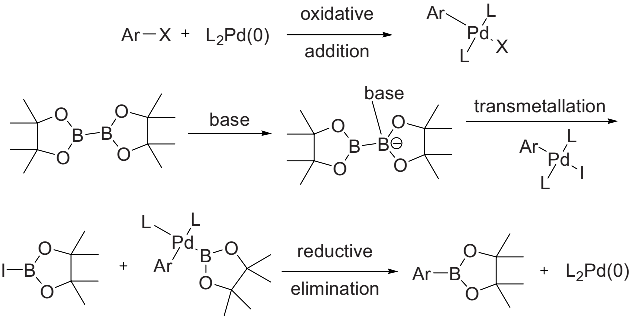
Miyaura borylation

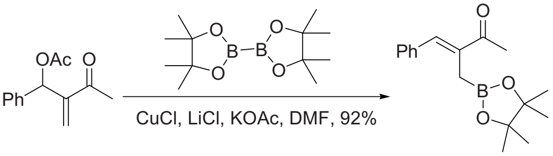
Palladium-catalyzed reaction of aryl halides with diboron reagents to produce arylboronates. Also known as Hosomi–Miyaura borylation.



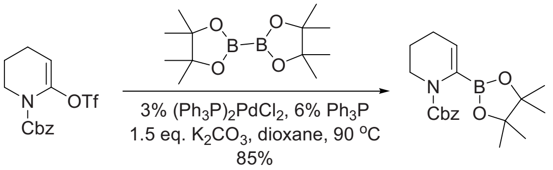
X = I, Br, Cl, OTf.



Example 1[7]

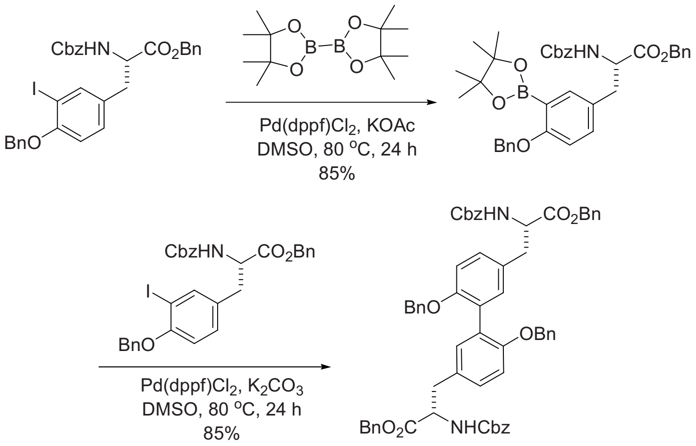


Example 2[8]

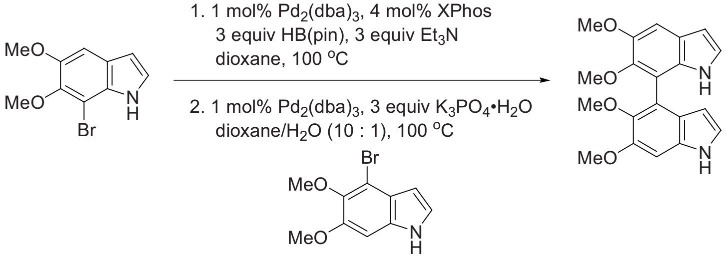


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_166,

Example 3[9]



Example 4, One-pot synthesis of biindolyl[10]



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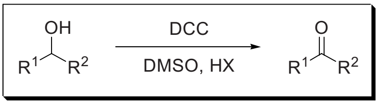
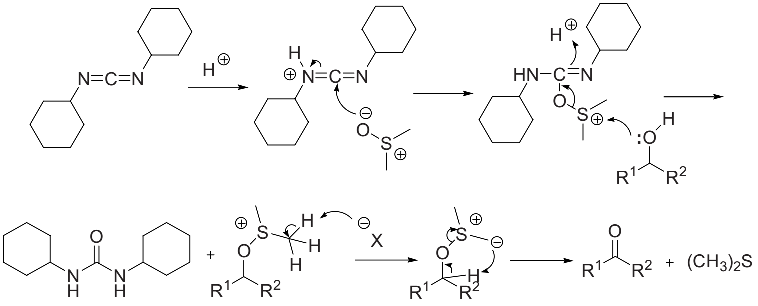
Moffatt oxidation

Oxidation of alcohols using DCC and DMSO, aka "Pfitzner–Moffatt oxidation".

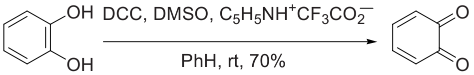


DCC, 1,3-dicyclohexylcarbodiimide

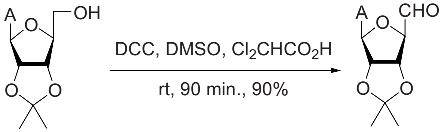


1,3-dicyclohexylurea

Example 1[2]



Example 2[8]



A = adenosine

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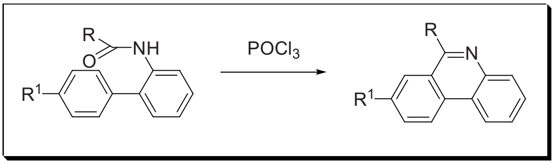
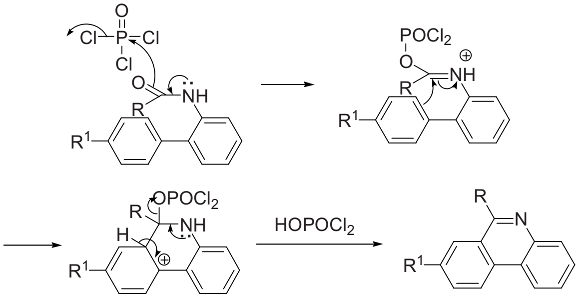
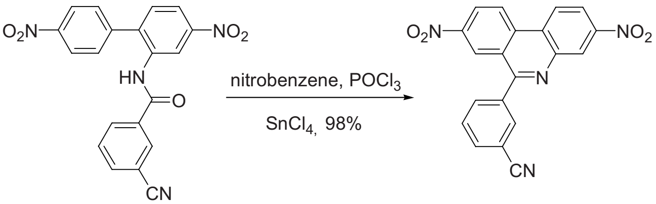
Morgan–Walls reaction

Phenanthridine cyclization by dehydrative ring closure of acyl-*o*-aminobiphenyls with phosphorus oxychloride in boiling nitrobenzene.



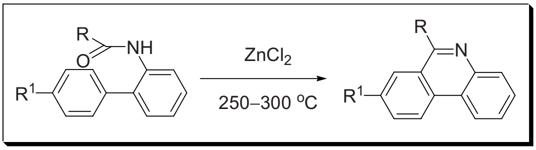


Example 1[6]

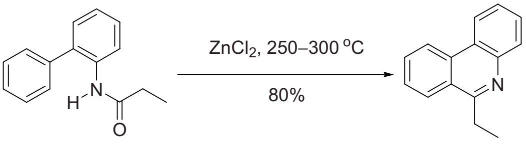


Pictet–Hubert reaction

The Morgan-Walls reaction is a variant of the Pictet-Hubert reaction where the phenanthridine cyclization was accomplished by dehydrative ring closure of acyl-*o*-aminobiphenyls on heating with zinc chloride at 250–300 °C.



Example 2[4]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_168,

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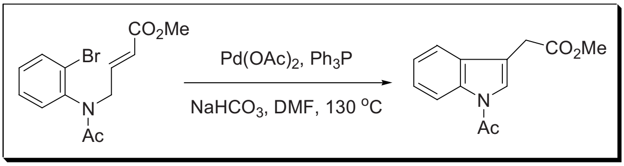
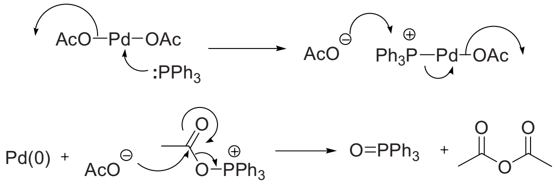
Mori–Ban indole synthesis

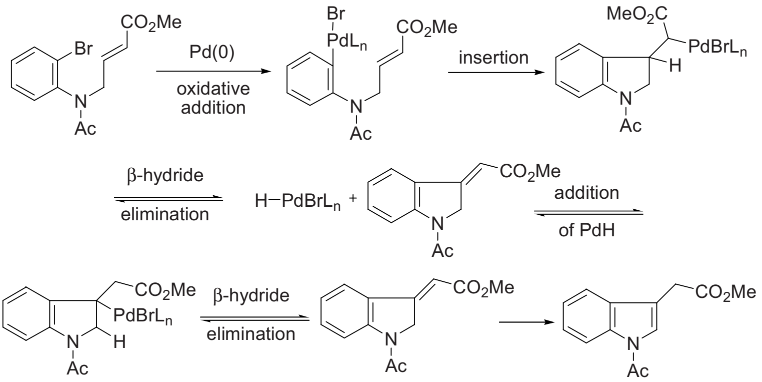
Intramolecular Heck reaction of *o*-halo-aniline with pendant olefin to prepare indole.



Reduction of Pd(OAc)$_2$ to Pd(0) using Ph$_3$P:



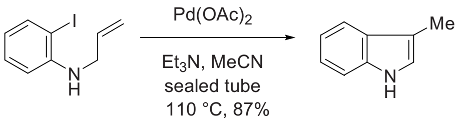
Mori–Ban indole synthesis:



Regeneration of Pd(0):

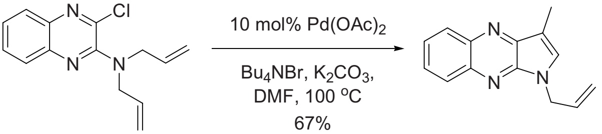
$$\text{H–PdBrL}_n + \text{NaHCO}_3 \longrightarrow \text{Pd(0)} + \text{NaBr} + \text{H}_2\text{O} + \text{CO}_2\uparrow$$

Example 1[1a]

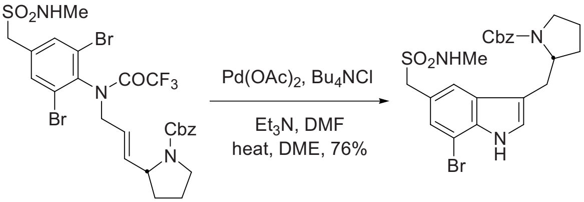


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_169,

Example 2[4]



Example 3[7]



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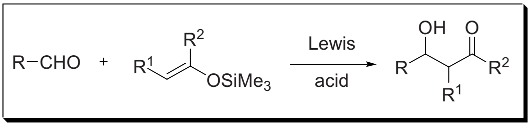
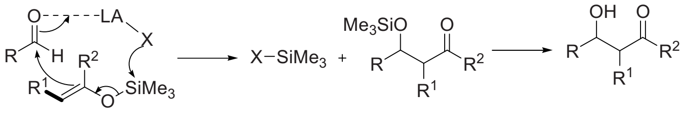
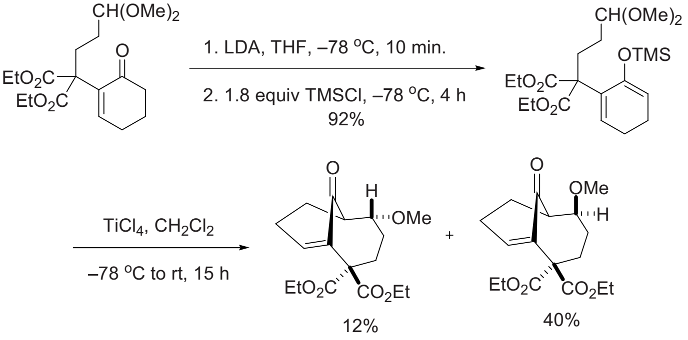
Mukaiyama aldol reaction

Lewis acid-catalyzed aldol condensation of aldehyde and silyl enol ether.

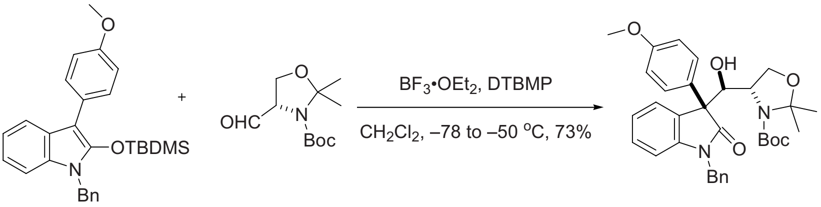




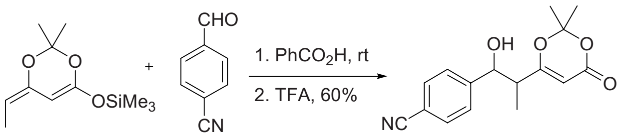
Example 1, Intramolecular Mukaiyama aldol reaction[3]



Example 2, Mukaiyama aldol reaction[7]



Example 3, Vinylogous Mukaiyama aldol reaction[8]



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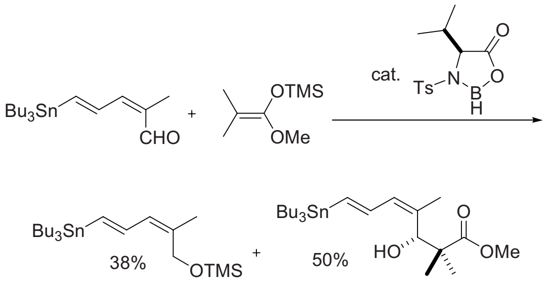
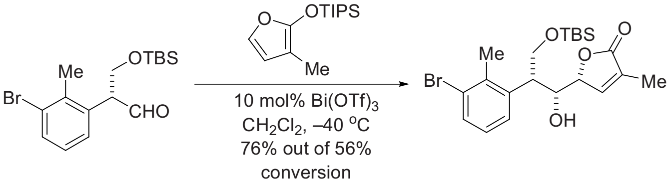
Example 4, Asymmetric Mukaiyama aldol reaction[10]



Example 5, Mukaiyama aldol reaction[12]



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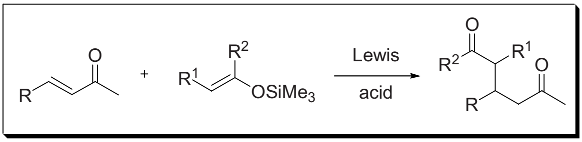
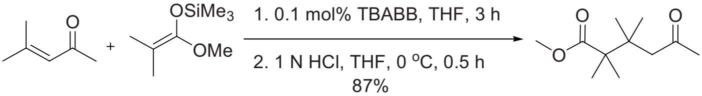
Mukaiyama Michael addition

Lewis acid-catalyzed Michael addition of silyl enol ether to an α,β-unsaturated system.

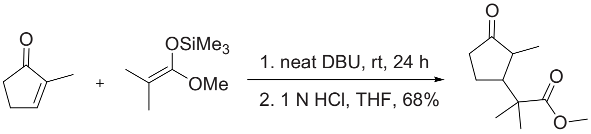


Example 1[2]

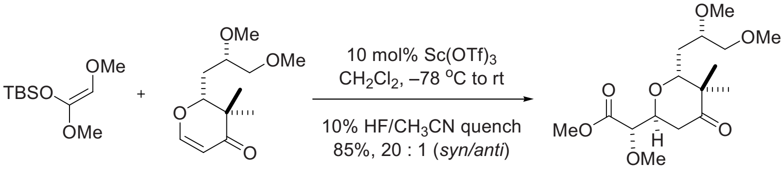


TBABB = tetra-*n*-butylammonium bibenzoate

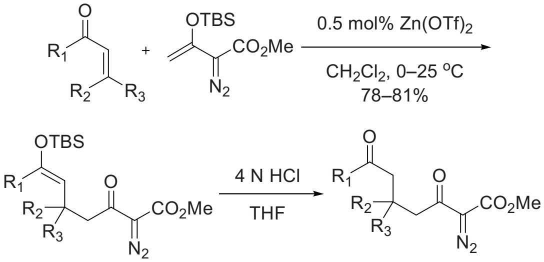
Example 2[5]



Example 3[8]



Example 4[9]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_171,

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1. (a) Mukaiyama, T.; Narasaka, K.; Banno, K. *Chem. Lett.* **1973**, 1011–1014. (b) Mukaiyama, T.; Narasaka, K.; Banno, K. *J. Am. Chem. Soc*. **1974**, *96*, 7503–7509. (c) Mukaiyama, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 5590–5614. (Review).
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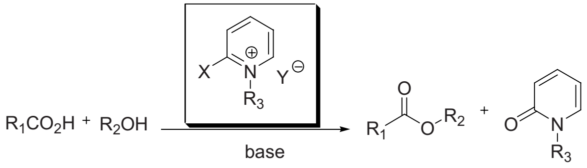
Mukaiyama reagent

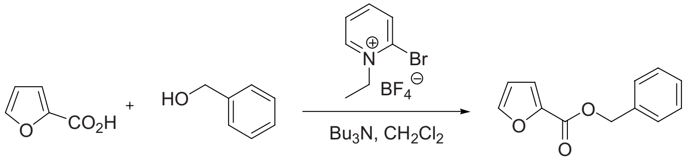
Mukaiyama reagent such as 2-chloro-1-methyl-pyridinium iodide for esterification or amide formation.

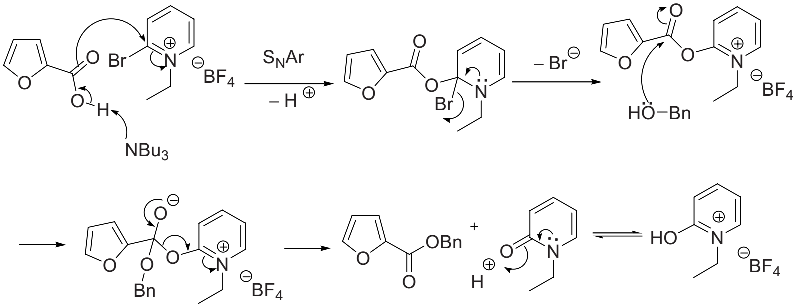
General scheme:



X = F, Cl, Br

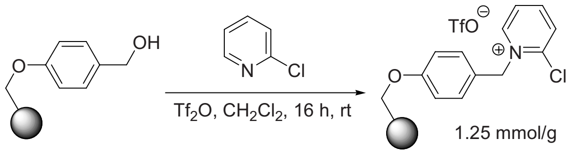
Example 1[1c]



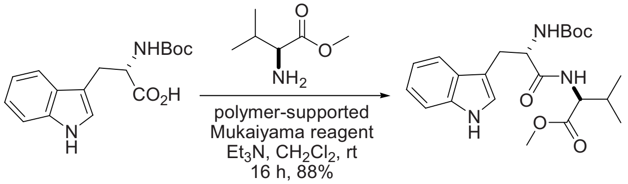


Amide formation using the Mukaiyama reagent follows a similar mechanistic pathway.[1d]

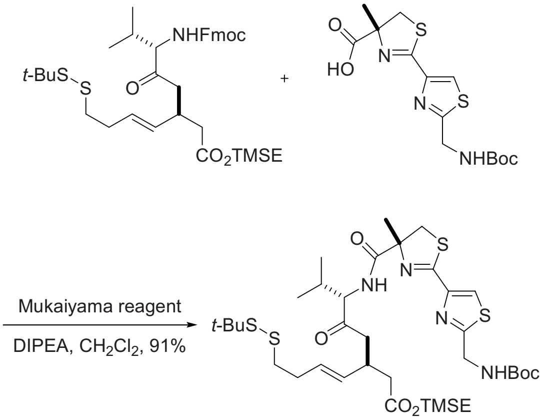
Example 2, Polymer-supported Mukaiyama reagent[5]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_172,



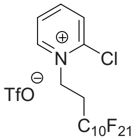
Example 3[9]



Example 4, Fluorous Mukaiyama reagent[10]

$$\mathrm{RCO_2H} \;+\; \mathrm{R^1NH_2 \text{ or } R^2OH} \xrightarrow[\text{2. } \mathrm{H_2O}\text{, rt, 5 min., 87–100\%}]{\substack{\text{1. Fluorous Mukaiyama reagent} \\ \text{1 equiv DMAP, 3 equiv } \mathrm{Et_3N} \\ \text{dry DMF, rt, 1h}}} \mathrm{RCONHR^1} \text{ or } \mathrm{RCO_2R^2}$$

Fluorous Mukaiyama reagent



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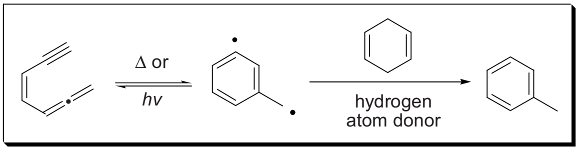
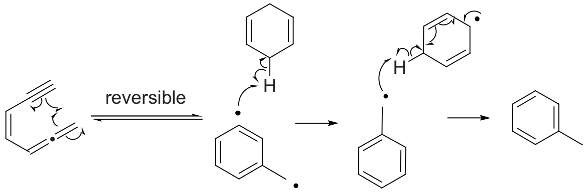
Myers–Saito cyclization

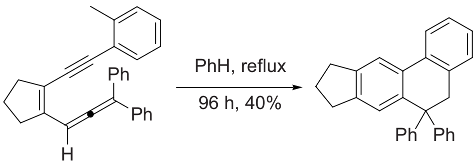
Cf. Bergman cyclization and Schmittel cyclization.



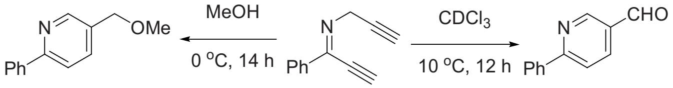


allenyl enyne diradical

Example 1[3]



Example 2, Aza-Myers–Saito reaction[8]



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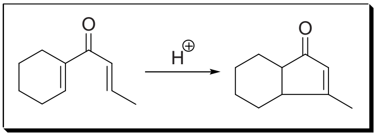
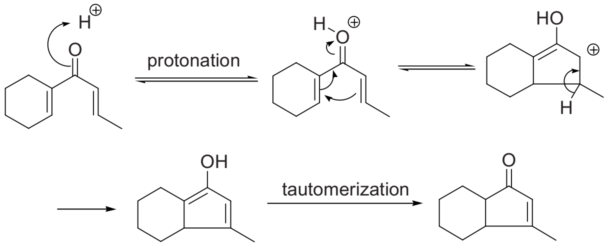
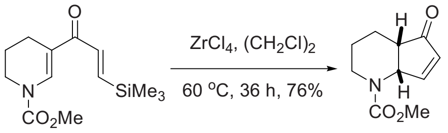
Nazarov cyclization

Acid-catalyzed electrocyclic formation of cyclopentenone from di-vinyl ketone.

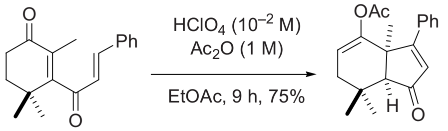




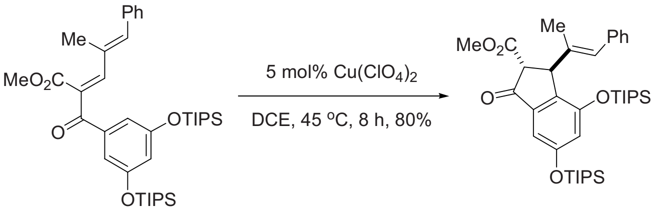
Example 1[2]



Example 2[6]



Example 3[9]



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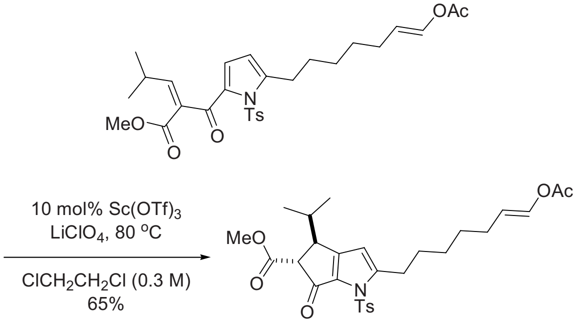
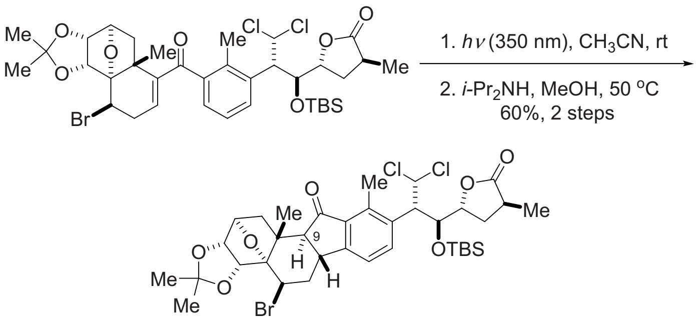
Example 4[10]



Example 5[11]



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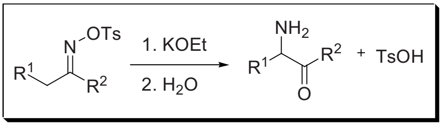
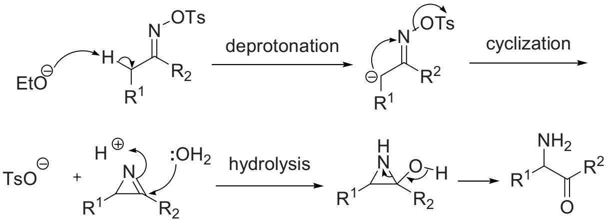
Neber rearrangement

α-Aminoketone from tosyl ketoxime and base. The net conversion of a ketone into an α-aminoketone *via* the oxime.

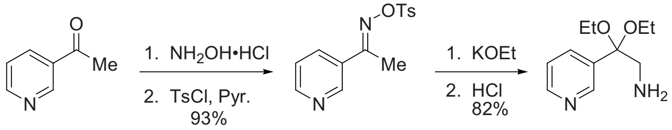


ketoxime α-aminoketone

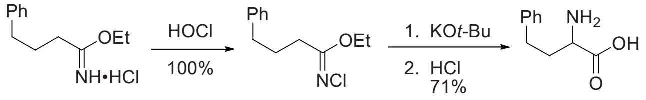


azirine intermediate

Example 1[3]



Example 2, A variant using iminochloride[5]



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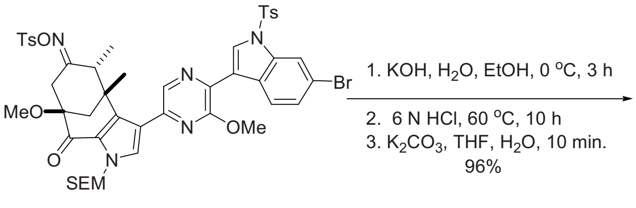
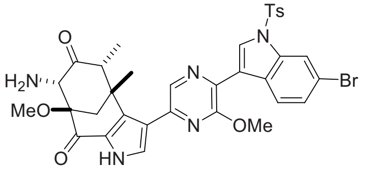


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_175,



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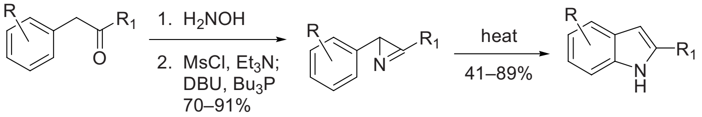

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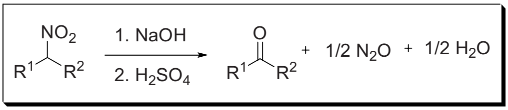
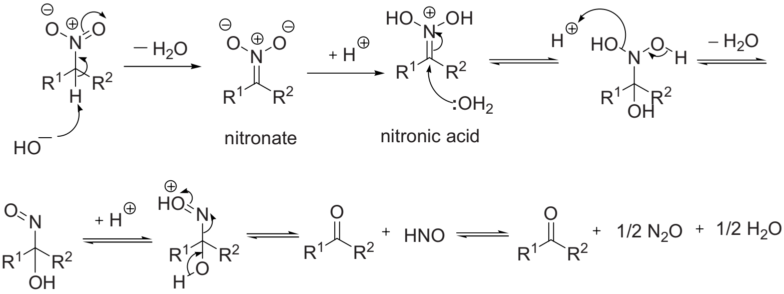
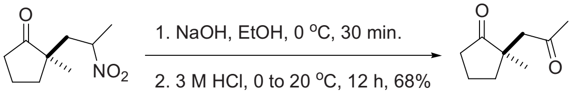
Nef reaction

Conversion of a primary or secondary nitroalkane into the corresponding carbonyl compound.





Example 1[4]



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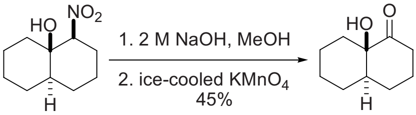
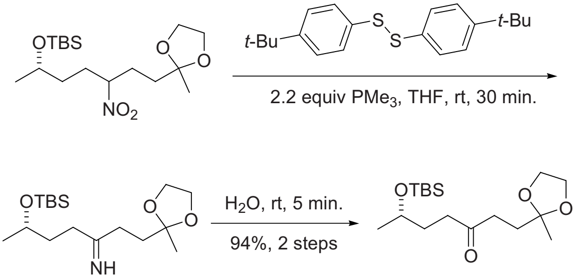


Example 3[9]



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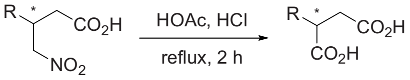
Example 4[10]



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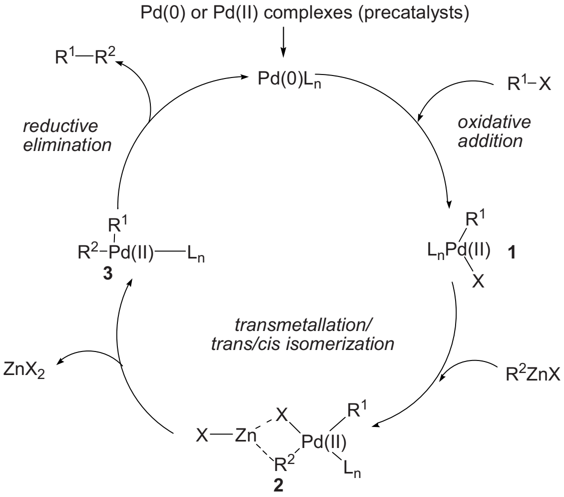
Negishi cross-coupling reaction

The Negishi cross-coupling reaction is the nickel- or palladium-catalyzed coupling of organozinc compounds with various halides or triflates (aryl, alkenyl, alkynyl, and acyl).

$$R^1{-}X \quad + \quad R^2Zn{-}Y \xrightarrow[\text{solvent}]{\text{NiL}_n \text{ or PdL}_n} R^1{-}R^2$$

R^1 = aryl, alkenyl, alkynyl, acyl
R^2 = aryl, heteroaryl, alkenyl, allyl, Bn, homoallyl, homopropargyl
X = Cl, Br, I, OTf
Y = Cl, Br, I
L_n = PPh_3, dba, dppe



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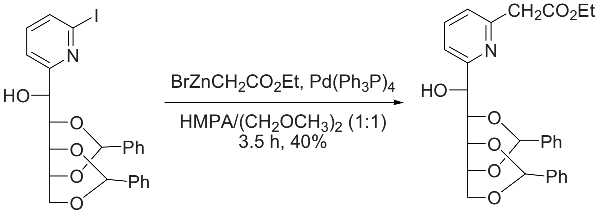
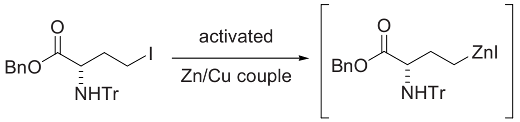
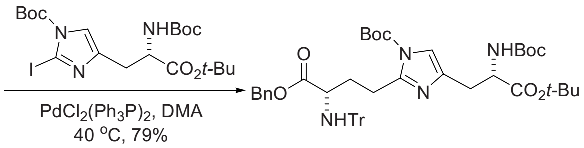


Example 2[4]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_177,



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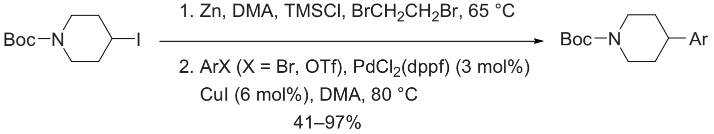
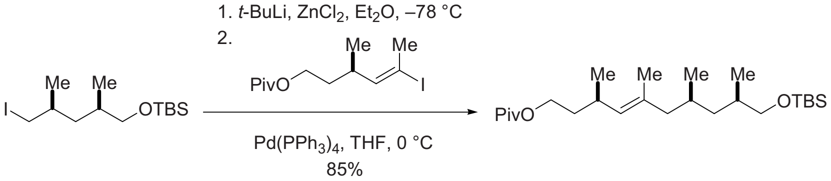


Example 4[9]



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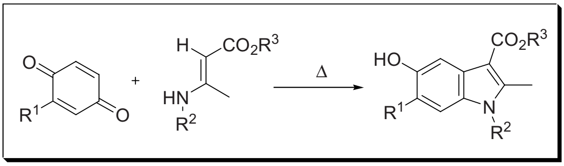
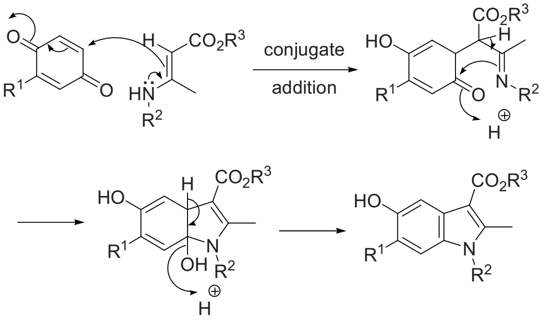
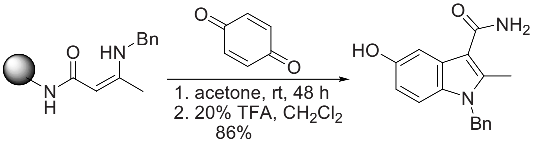
Nenitzescu indole synthesis

5-Hydroxylindole from condensation of *p*-benzoquinone and β-aminocrotonate.

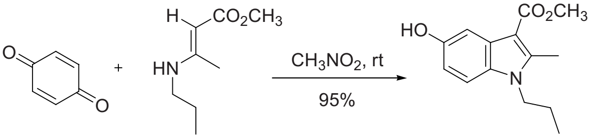




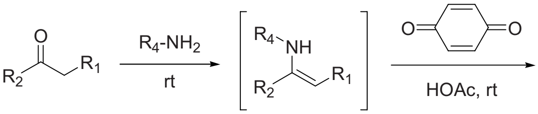
Example 1[5]



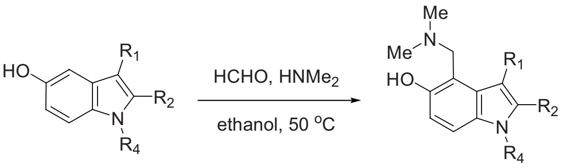
Example 2[6]



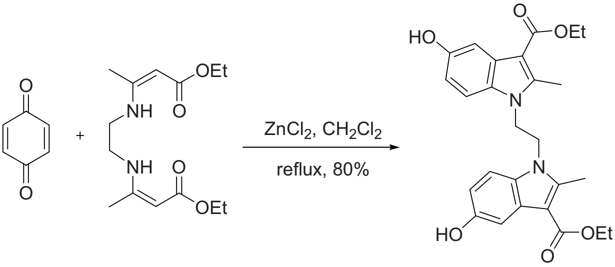
Example 3[7]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_178,



Example 4[10]



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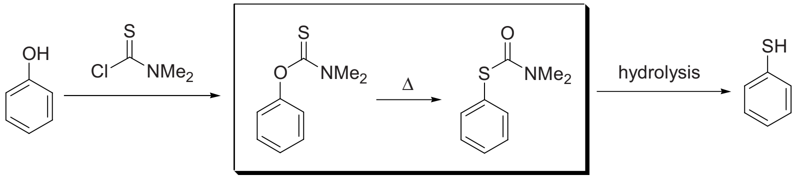
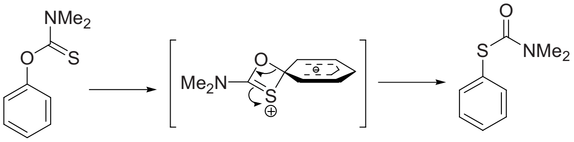
Newman–Kwart rearrangement

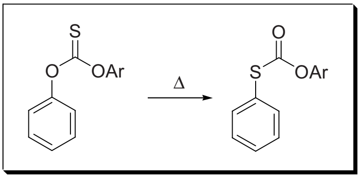
Transformation of phenol to the corresponding thiophenol, a variant of the Smile reaction (page 513).



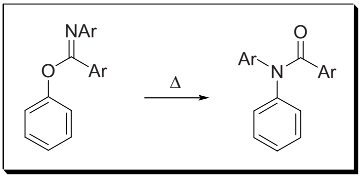


The Newman–Kwart rearrangement is a member of a series of related rearrangements, such as the **Schönberg rearrangement** and the **Chapman rearrangement** (page 105), in which aryl groups migrate intramolecularly between nonadjacent atoms. The Schönberg rearrangement is the most similar and involves the 1,3-migration of an aryl group from oxygen to sulfur in a diarylthioncarbonate. The Chapman rearrangement involves an analogous migration but to nitrogen.

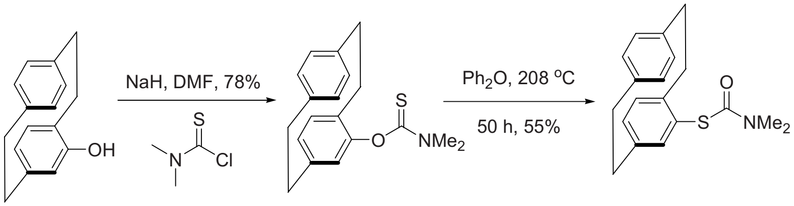
Schönberg rearrangement



Chapman rearrangement

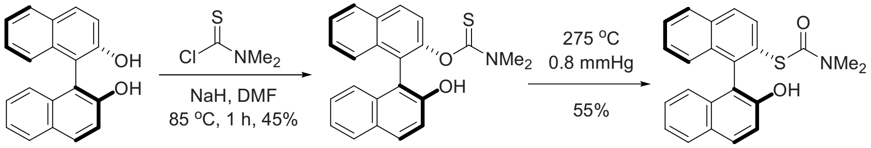


Example 1[5]

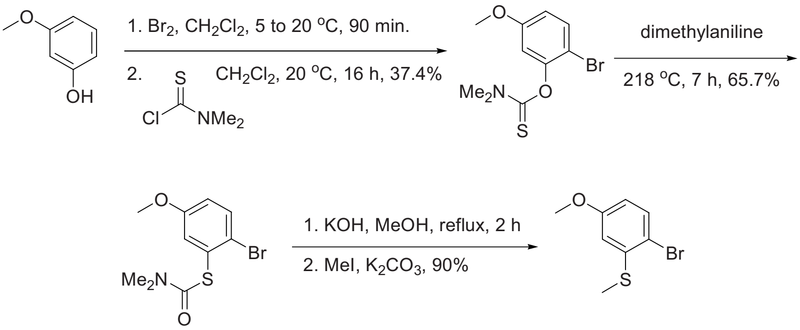


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_179,

Example 2[6]



Example 3[7]



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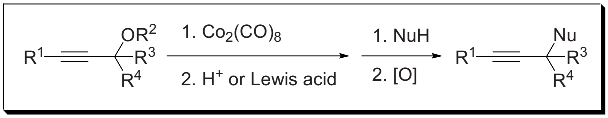
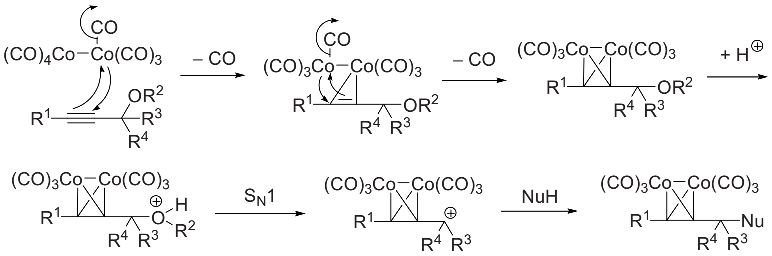
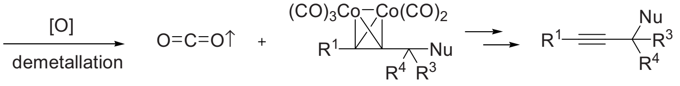
Nicholas reaction

Hexacarbonyldicobalt-stabilized propargyl cation is captured by a nucleophile. Subsequent oxidative demetallation then gives the propargylated product.

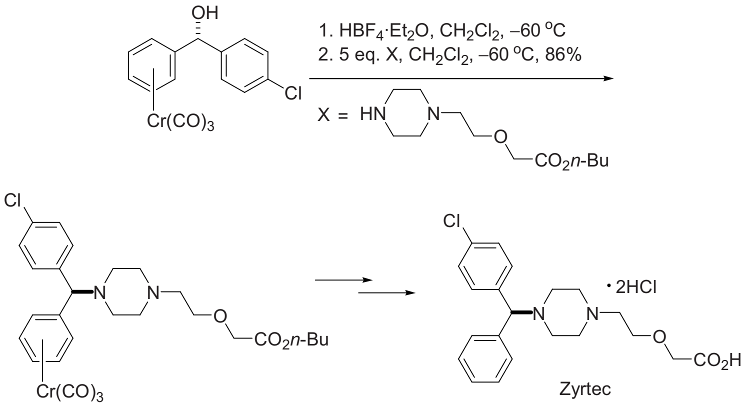




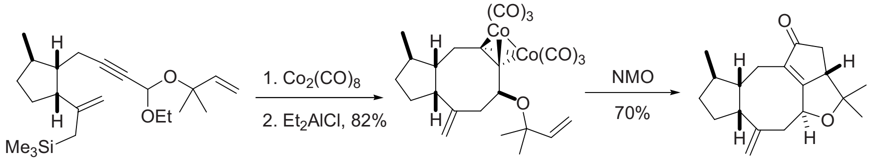
propargyl cation intermediate (stabilized by the hexacarbonyldicobalt complex).



Example 1, A chromium variant of the Nicholas reaction[3]

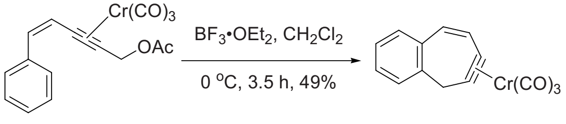


Example 2, A Nicholas-Pauson–Khand sequence[4]

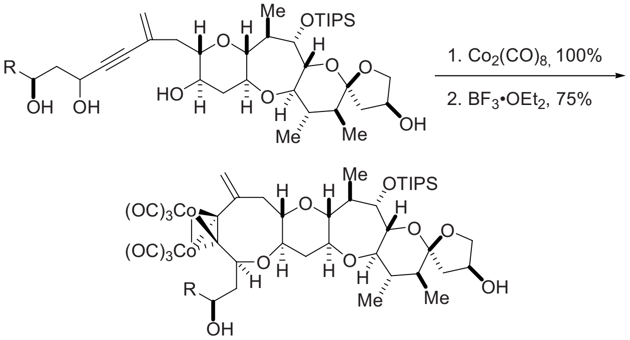


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_180,

Example 3, Intramolecular Nicholas reaction using chromium[7]



Example 4[9]



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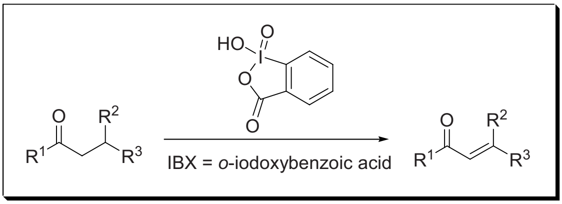
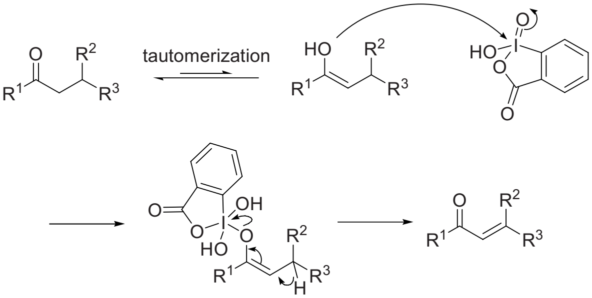
Nicolaou IBX dehydrogenation

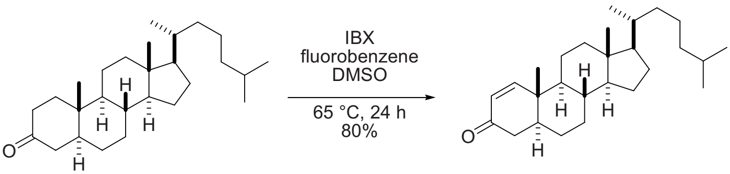
α,β-Unsaturation of aldehydes and ketones mediated by stoichiometric amounts of *o*-iodoxybenzoic acid (IBX), alternative to the Saegusa oxidation (page 482).



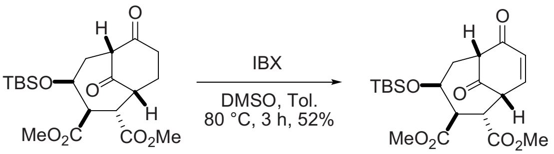
A SET mechanism has also been proposed. Additionally, silyl enol ethers are also viable substrates.



Example 1[1a]

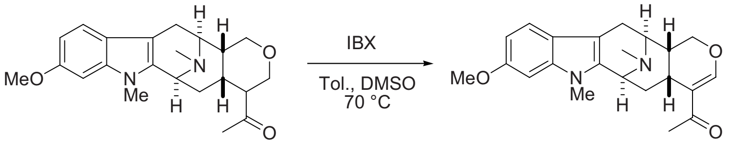


Example 2[3]

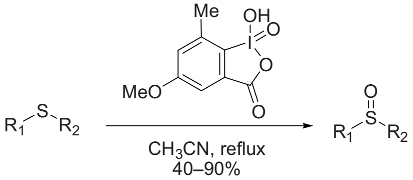


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_181,

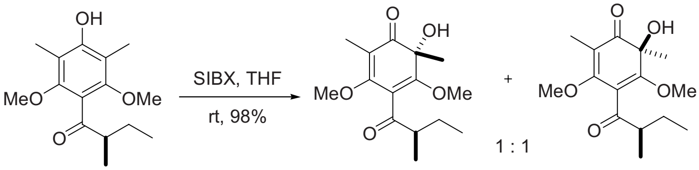
Example 3[7]



Example 4, *o*-Methyl-IBX (Me-IBX)[9]



Example 5, Stabilized IBX (SIBX)[10]



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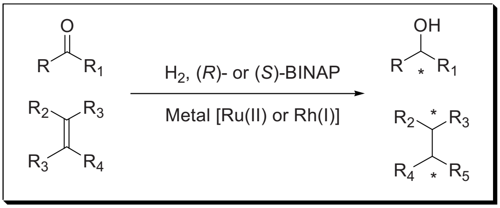
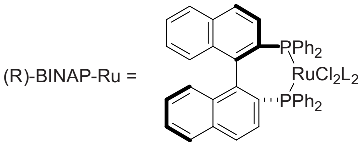
Noyori asymmetric hydrogenation

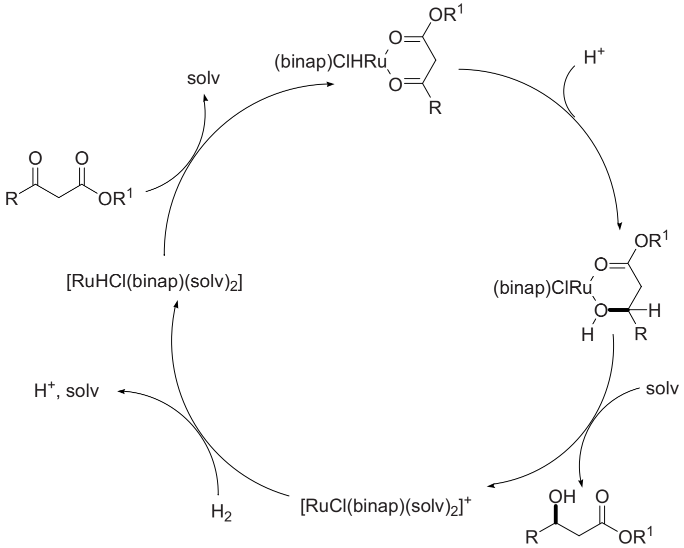
Asymmetric reduction of carbonyls and alkenes *via* hydrogenation, catalyzed by a ruthenium(II) BINAP complex.



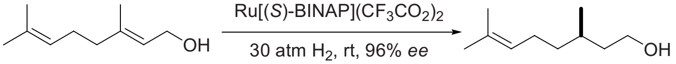


$$[RuCl_2(binap)(solv)_2] \xrightarrow[-\,HCl]{H_2} [RuHCl(binap)(solv)_2]$$

The catalytic cycle:

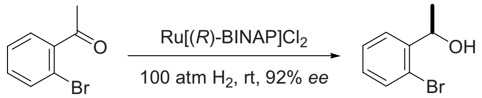


Example 1[1b]

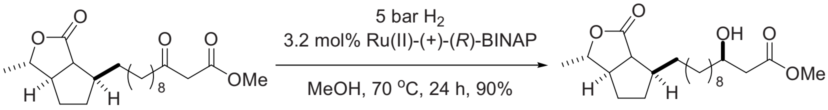


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_182,

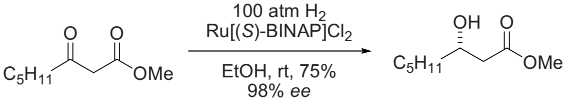
Example 2[1c]



Example 3[9]



Example 4[10]



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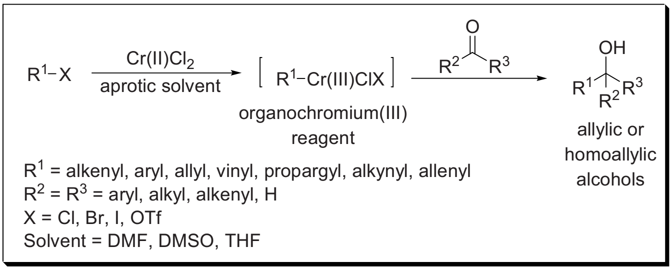
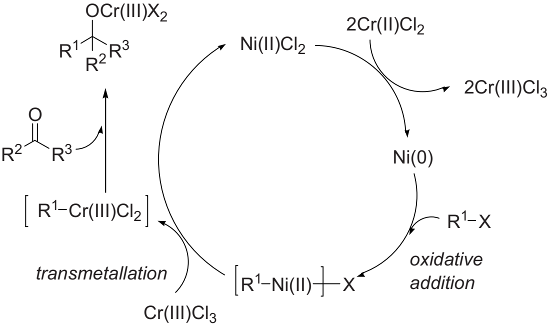
Nozaki–Hiyama–Kishi reaction

Cr–Ni bimetallic catalyst-promoted redox addition of vinyl halides to aldehydes.

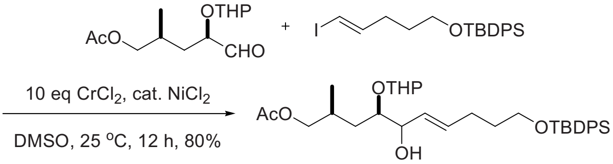


R^1 = alkenyl, aryl, allyl, vinyl, propargyl, alkynyl, allenyl
R^2 = R^3 = aryl, alkyl, alkenyl, H
X = Cl, Br, I, OTf
Solvent = DMF, DMSO, THF

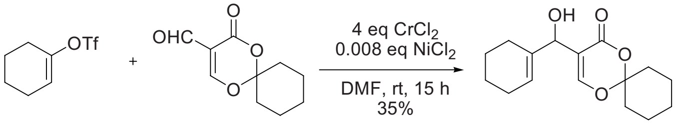
The catalytic cycle:[2]



Example 1[3]

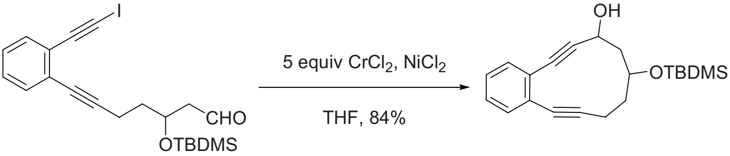


Example 2[5]

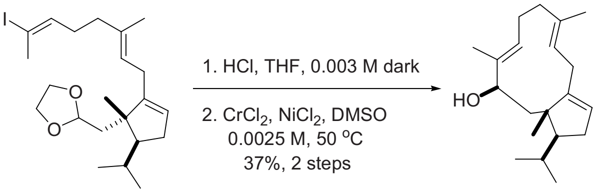


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_183,

Example 3, Intramolecular Nozaki–Hiyama–Kishi reaction[8]



Example 4, Intramolecular Nozaki–Hiyama–Kishi reaction[9]



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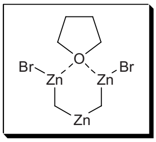
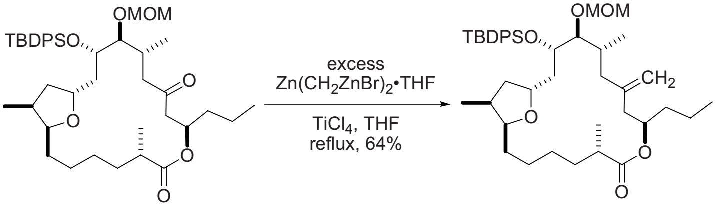
Nysted reagent

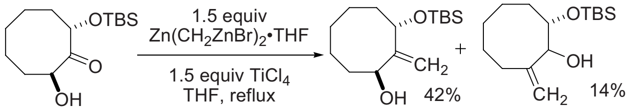
The Nysted reagent, cyclo-dibromodi-μ-methylene(μ-tetrahydrofuran)trizinc, is used for the olefination of ketones and aldehydes.



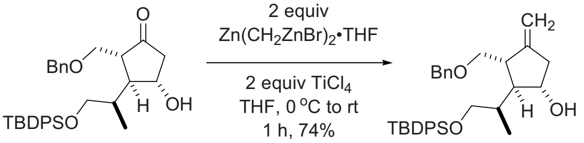
Example 1, The Wittig reagent opened the lactone:[6]



Example 2[8]



Example 3[9]



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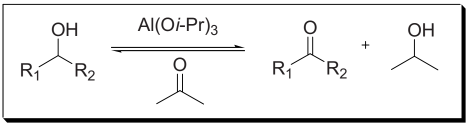
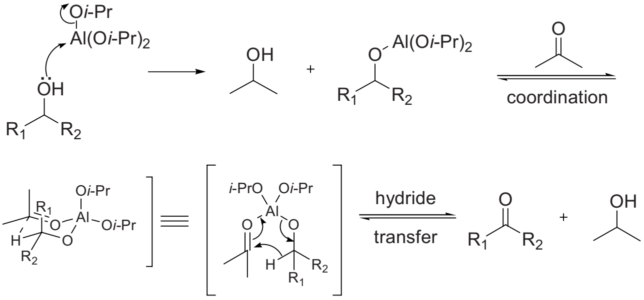
Oppenauer oxidation

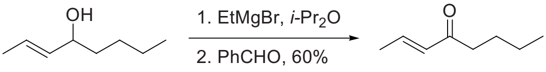
Alkoxide-catalyzed oxidation of secondary alcohols. Reverse of the Meerwein–Ponndorf–Verley reduction.



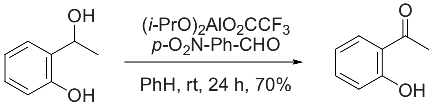


cyclic transition state

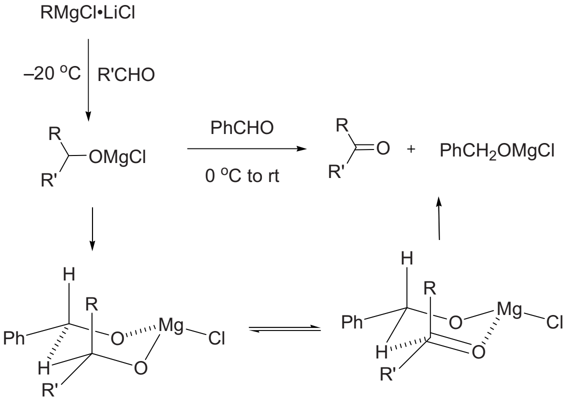
Example 1, Mg-Oppenauer oxidation[3]



Example 2[6]

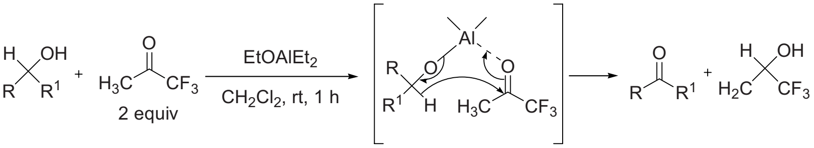


Example 3, Mg-Oppenauer oxidation[8]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_185,

Example 4[10]



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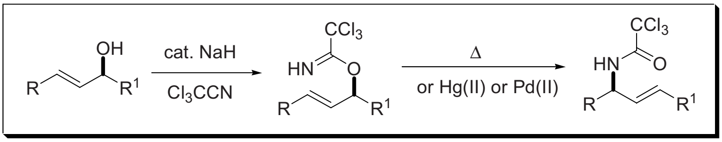
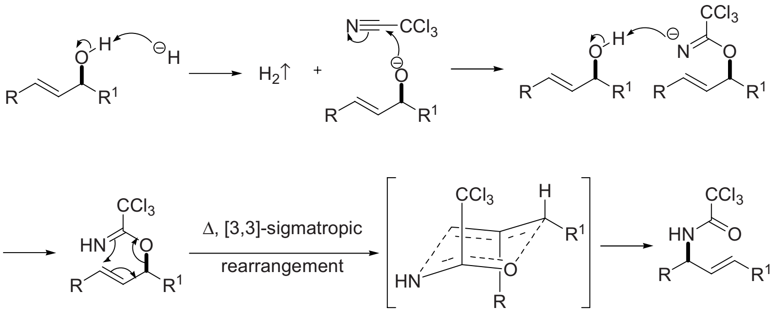
Overman rearrangement

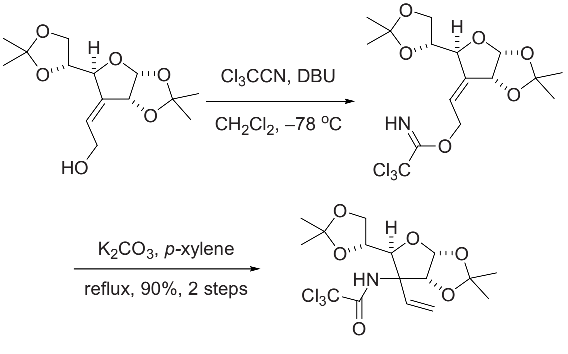
Stereoselective transformation of allylic alcohol to allylic trichloroacetamide *via* trichloroacetimidate intermediate.



trichloroacetimidate



Example 1[5]



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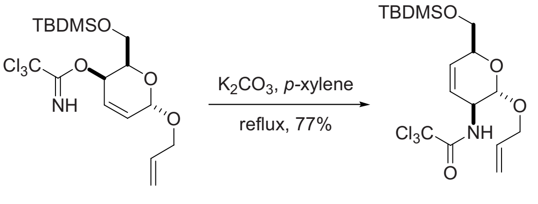

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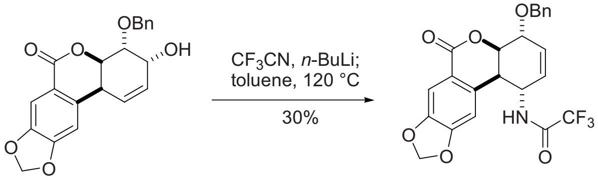
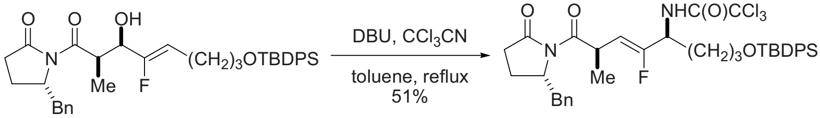
Example 3[7]



Example 4[9]



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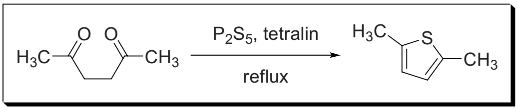
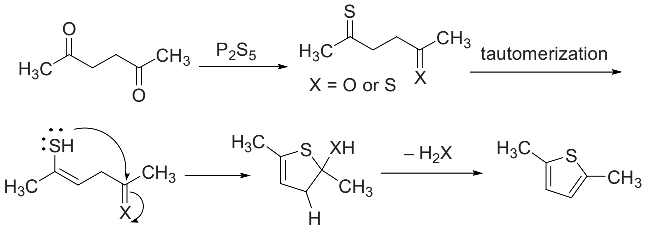
Paal thiophene synthesis

Thiophene synthesis from addition of a sulfur atom to 1,4-diketones and subsequent dehydration.



The reaction now is frequently carried out using the Lawesson's reagent. For the mechanism of carbonyl to thiocarbonyl transformation, see Lawesson's reagent on page 328.



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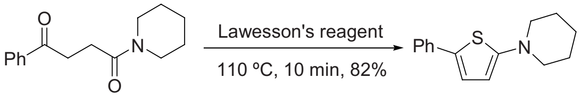
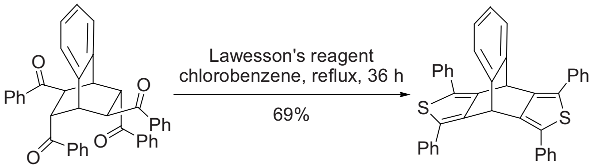


Example 2[3]



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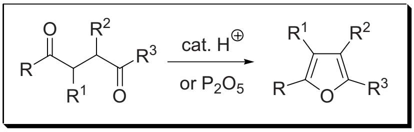
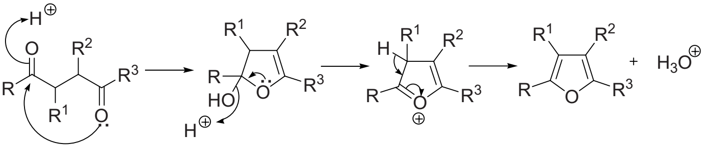
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_187,

Paal–Knorr furan synthesis

Acid-catalyzed cyclization of 1,4-diketones to form furans.





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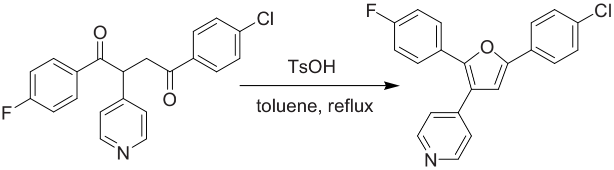

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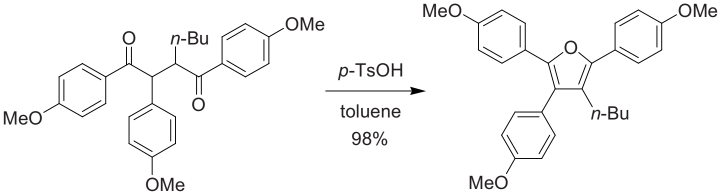

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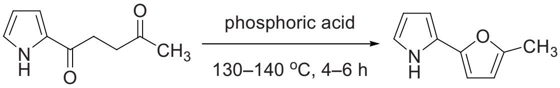
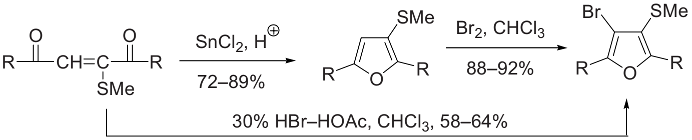


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_188,

Example 4[10]



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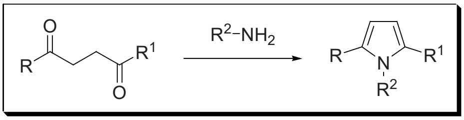
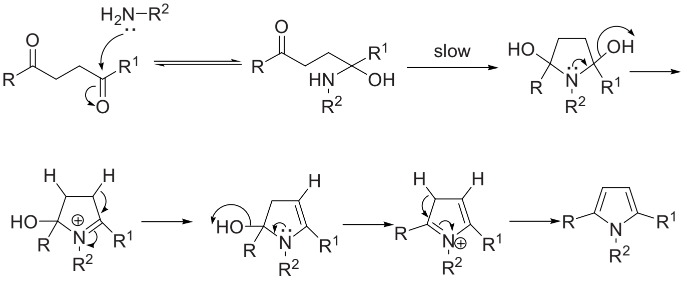
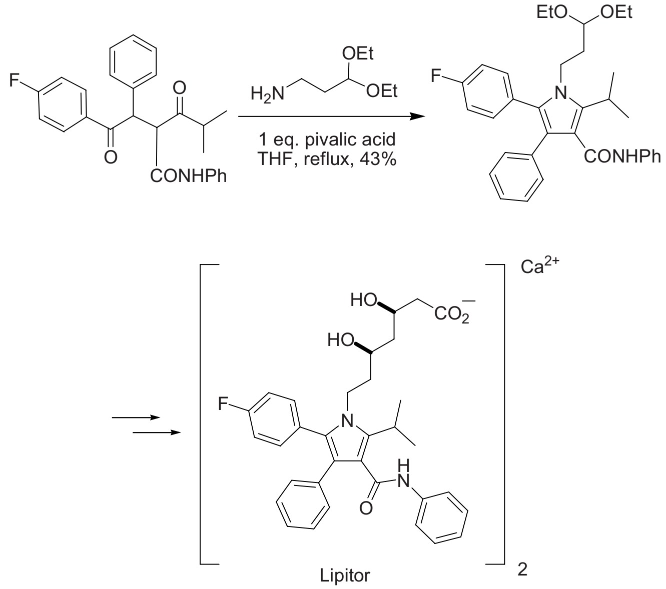
Paal–Knorr pyrrole synthesis

Reaction between 1,4-diketones and primary amines (or ammonia) to give pyrroles. A variation of the Knorr pyrazole synthesis (page 317).



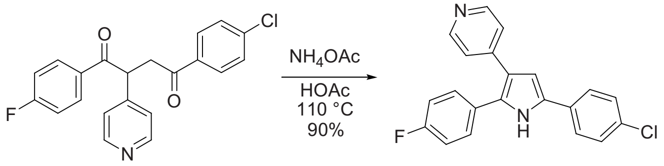


Example 1[4]

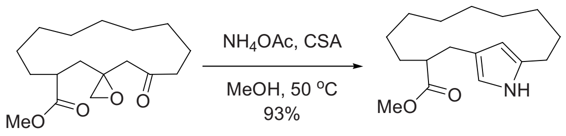


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_189,

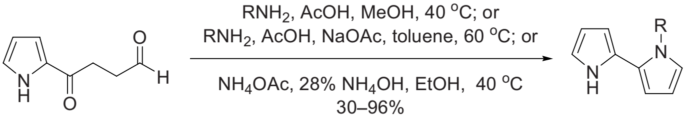
Example 2[5]



Example 3[9]



Example 4[10]



References

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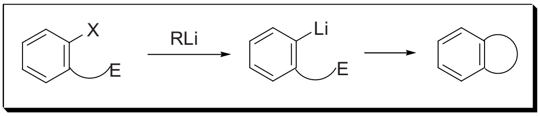
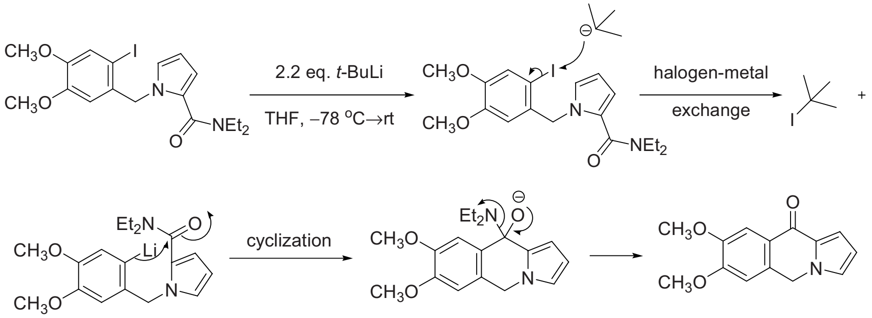
Parham cyclization

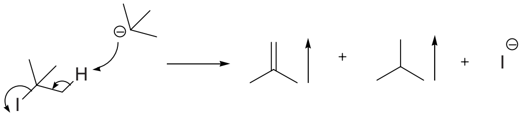
The Parham cyclization is the generation by halogen–lithium exchange of aryllithiums and heteroaryllithiums, and their subsequent intramolecular cyclization onto an electrophilic site.



E.g.



The fate of the second equivalent of *t*-BuLi:



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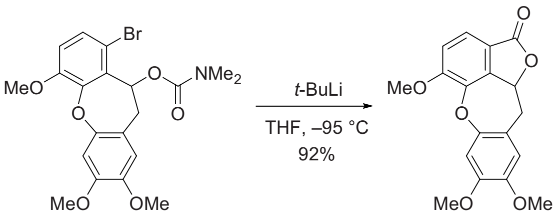

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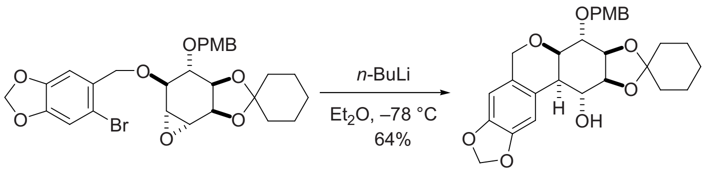

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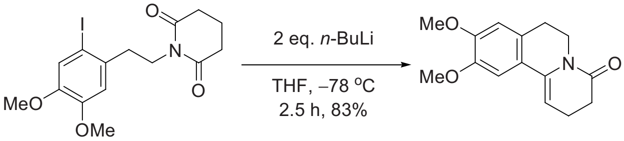
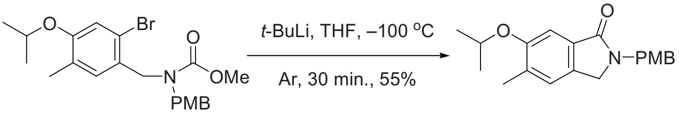
Example 3[5]



Example 4[9]



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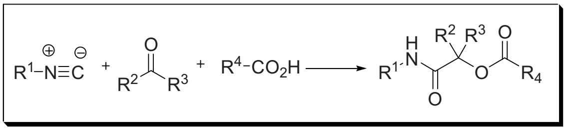
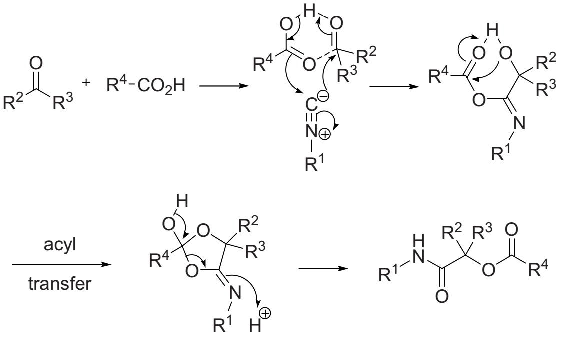
Passerini reaction

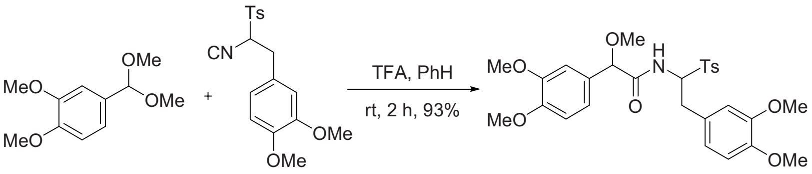
Three-component condensation (3CC) of carboxylic acids, *C*-isocyanides, and carbonyl compounds to afford α-acyloxycarboxamides. *Cf.* Ugi reaction.



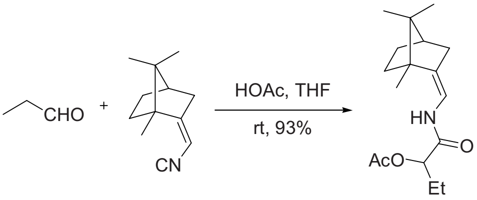
isocyanide



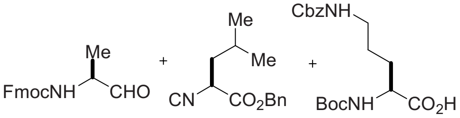
Example 1[3]



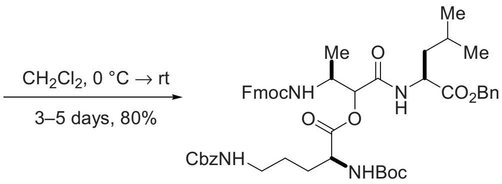
Example 2[5]



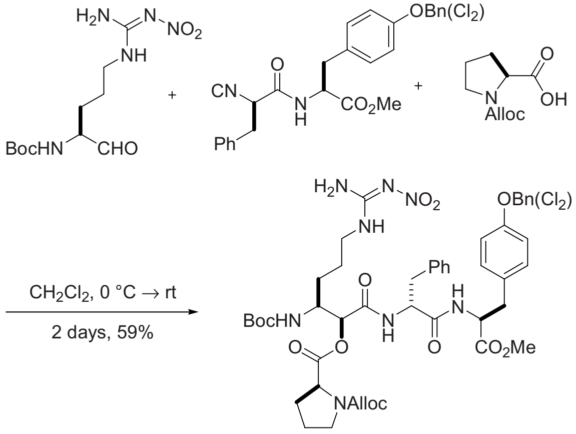
Example 3[6]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_191,



Example 4[7]



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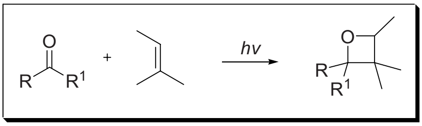
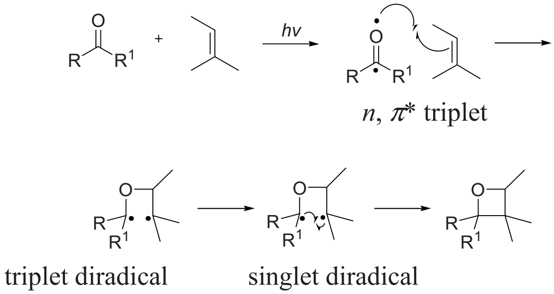
Paternó–Büchi reaction

Photoinduced electrocyclization of a carbonyl with an alkene to form polysubstituted oxetane ring systems



oxetane



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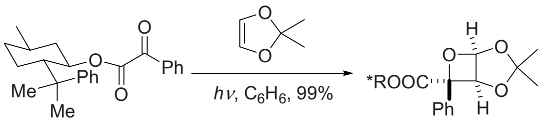
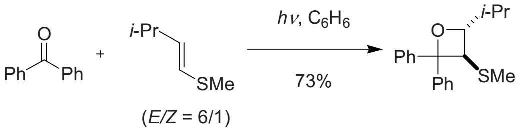
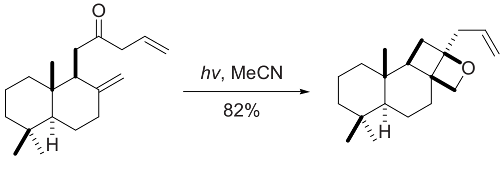


Example 2[4]

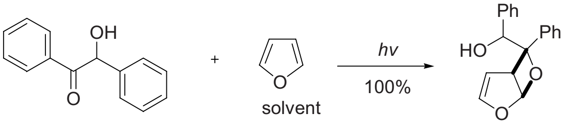


Example 3[6]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_192,

Example 4[8]



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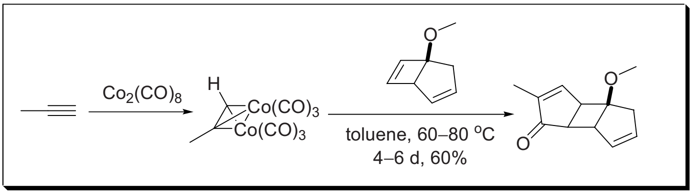
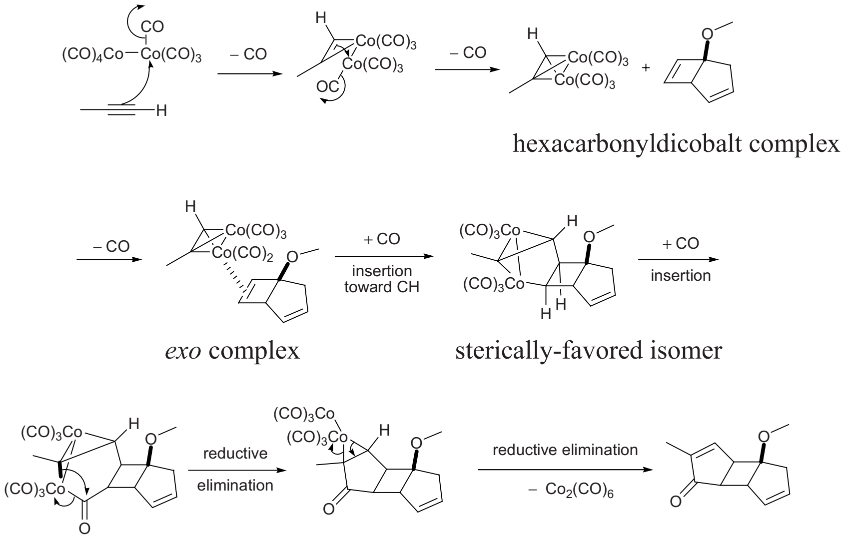
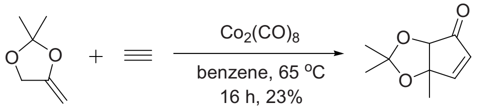
Pauson–Khand reaction

Formal [2 + 2 +1] cycloaddition of an alkene, alkyne, and carbon monoxide mediated by octacarbonyl dicobalt to form cyclopentenones.

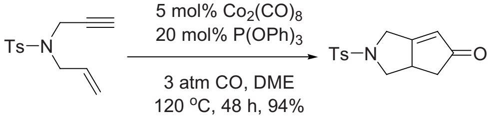




Example 1[3]



Example 2, A catalytic version[6]



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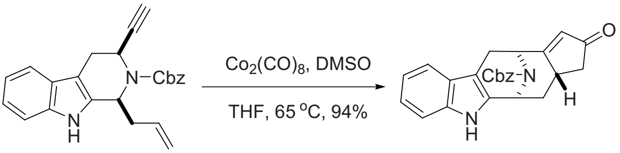
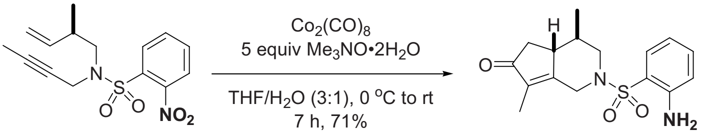
Example 3, Intramolecular Pauson–Khand reaction[9]



Example 4, Intramolecular Pauson–Khand reaction[10]



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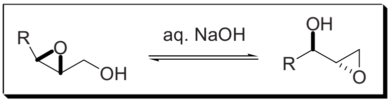
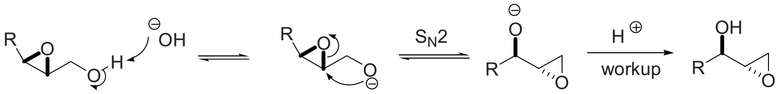
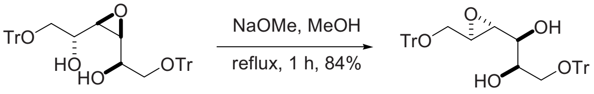
Payne rearrangement

The isomerization of 2,3-epoxy alcohol under the influence of a base to 1,2-epoxy-3-ol is referred to as the Payne rearrangement. Also known as epoxide migration.





Example 1[2]



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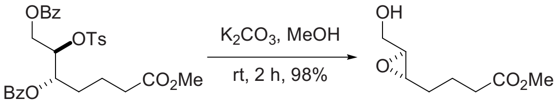
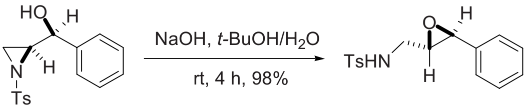
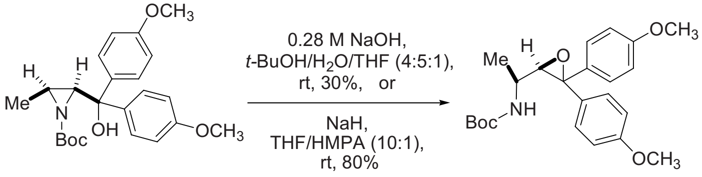


Example 3, Aza-Payne rearrangement[8]



Example 4, Aza-Payne rearrangement[9]



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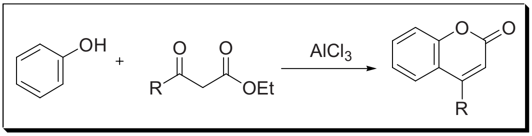
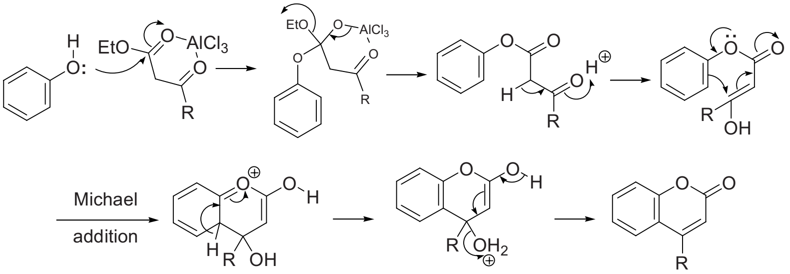
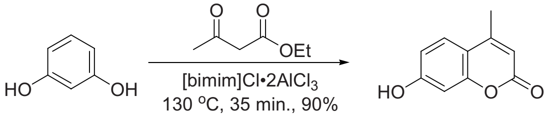
Pechmann coumarin synthesis

Lewis acid-mediated condensation of phenol with β-ketoester to produce coumarin.

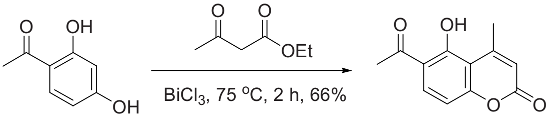




Example 1[6]



Example 2[8]



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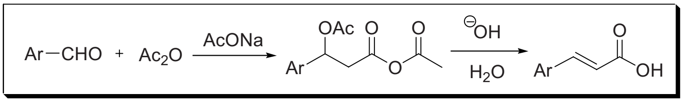
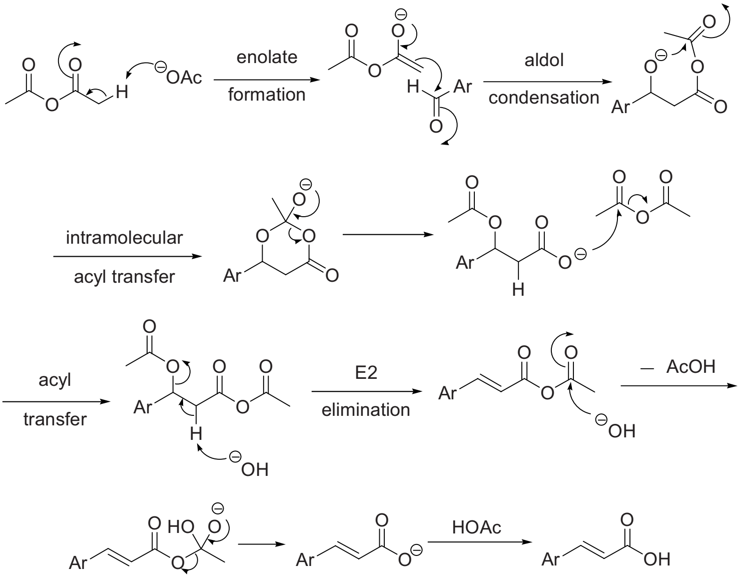
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_195,

Perkin reaction

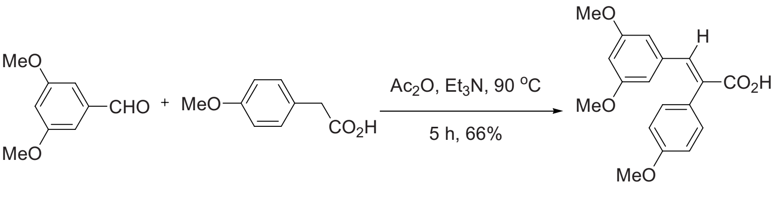
Cinnamic acid synthesis from aryl aldehyde and acetic anhydride.



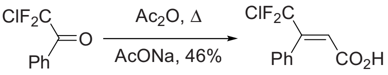
cinnamic acid



Example 1[7]



Example 2[9]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_196,

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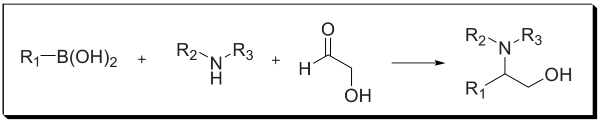
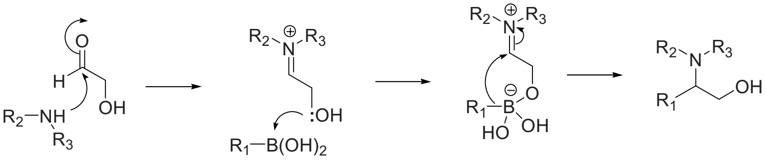
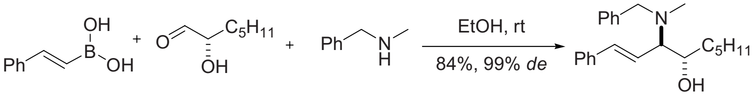
Petasis reaction

Allylic amine from the three-component reaction of a vinyl boronic acid, a carbonyl and an amine. Also known as boronic acid-Mannich or Petasis boronic acid-Mannich reaction. *Cf.* Mannich reaction.





Example 1[2]



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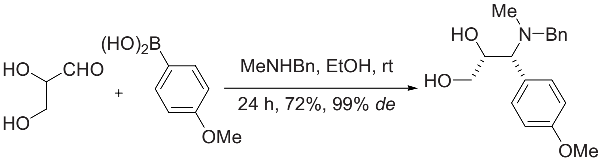
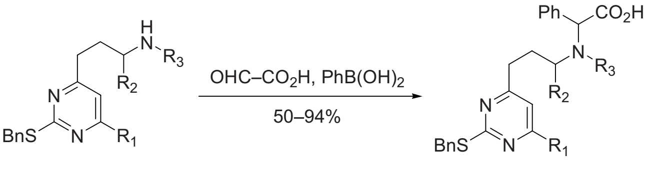
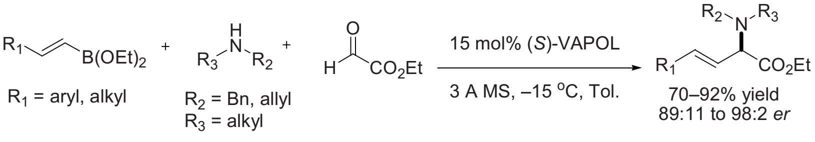


Example 3[9]



Example 4, Asymmetric Petasis reaction[10]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_197,

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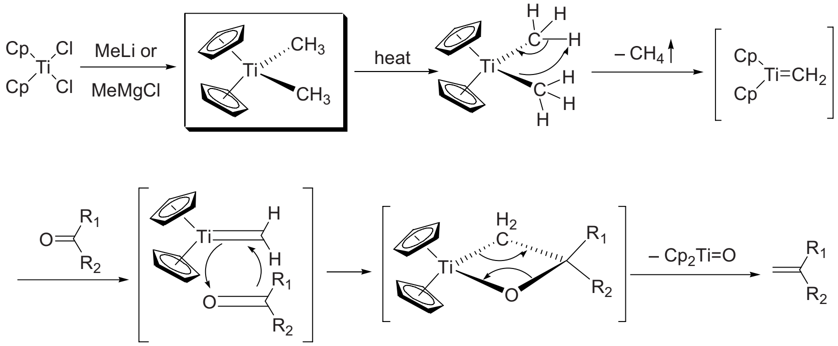
Petasis reagent

The Petasis reagent (Cp_2TiMe_2, dimethyltitanocene) undergoes similar olefination reactions with ketones and aldehydes as does the Tebbe's reagent. The originally proposed mechanism[5] was very different from that of Tebbe olefination. However, later experimental data seem to suggest that both Petasis and Tebbe olefination share the same mechanism, i.e., the carbene mechanism involving a four-membered titanium oxide ring intermediate.[9] Petasis reagent is easier to make than the Tebbe reagent.



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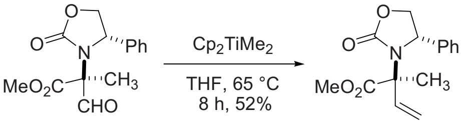

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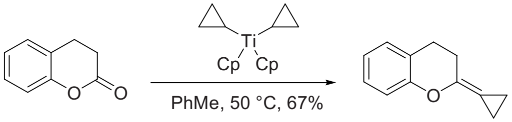
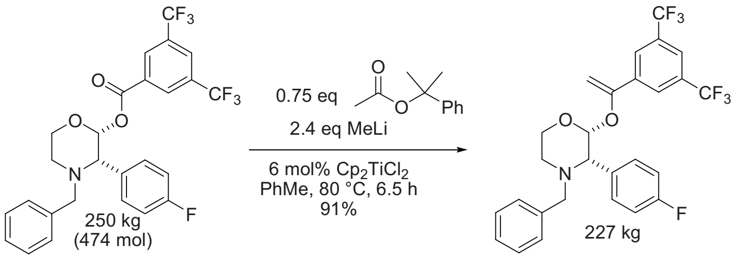
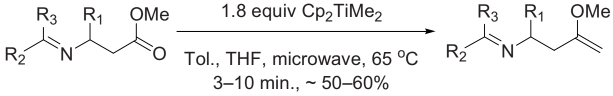


Example 3[5]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_198,

Example 4[8]



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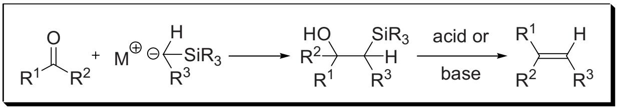
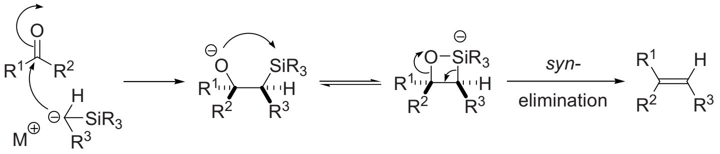
Peterson olefination

Alkenes from α-silyl carbanions and carbonyl compounds. Also known as the sila-Wittig reaction.

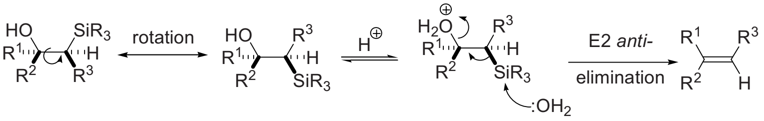


Basic conditions:



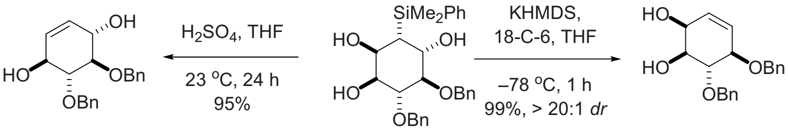
β-silylalkoxide intermediate

Acidic conditions:

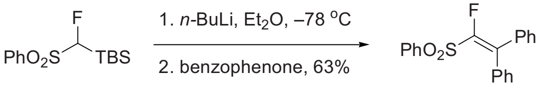


β-hydroxysilane

Example 1[6]



Example 2[7]



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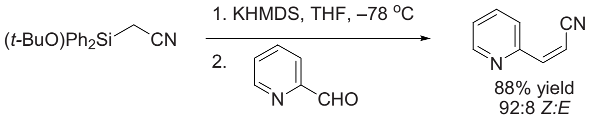
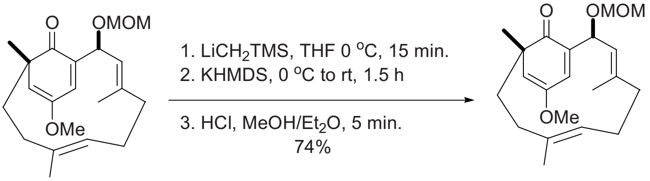


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_199,

Example 4[10]



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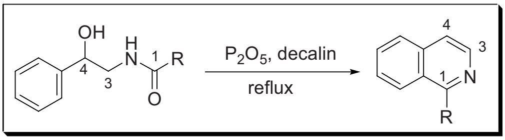
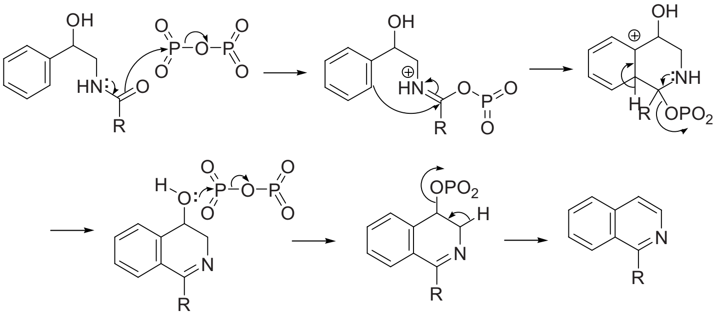
Pictet–Gams isoquinoline synthesis

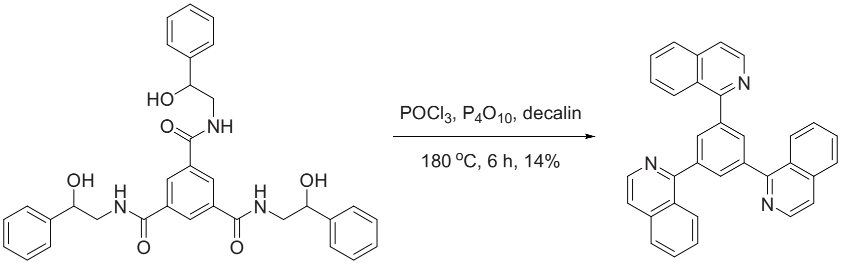
The isoquinoline framework is derived from the corresponding acyl derivatives of β-hydroxy-β-phenylethylamines. Upon exposure to a dehydrating agent such as phosphorus pentoxide, or phosphorus oxychloride, under reflux and in an inert solvent such as decalin, isoquinoline frameworks are formed.



P_2O_5 actually exists as P_4O_{10}, an adamantane-like structure.



Example 1[4]



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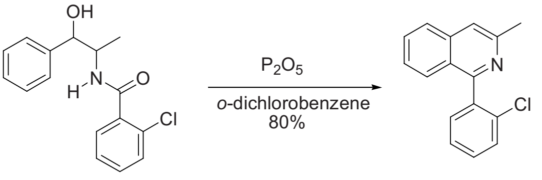

J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_200,

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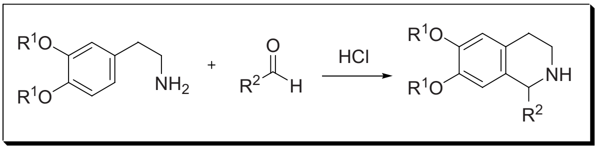
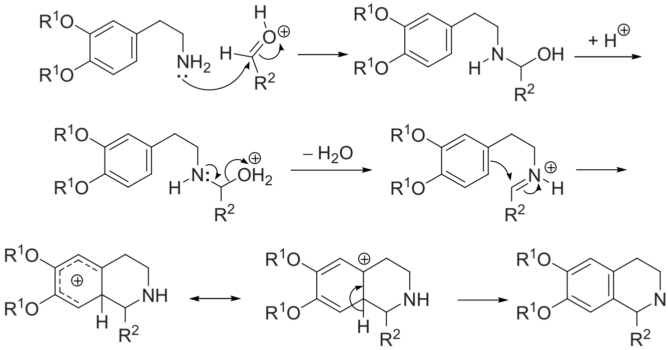
Pictet–Spengler tetrahydroisoquinoline synthesis

Tetrahydroisoquinolines from condensation of β-arylethylamines and carbonyl compounds followed by cyclization.





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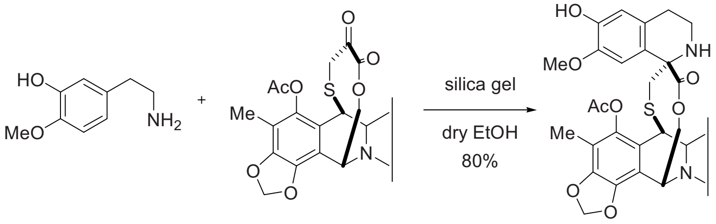

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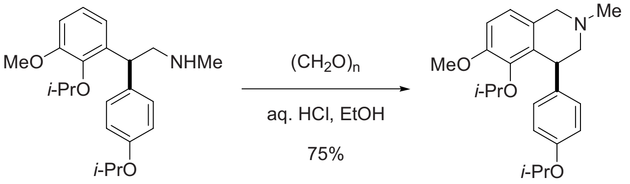
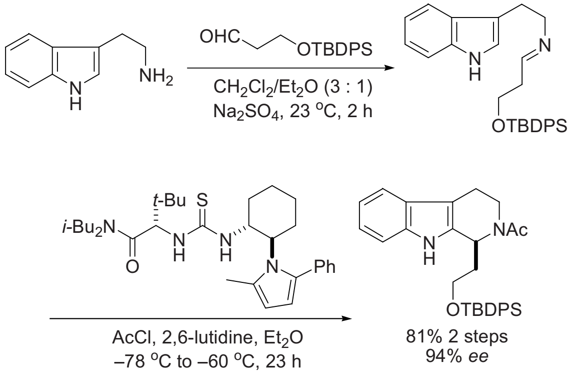
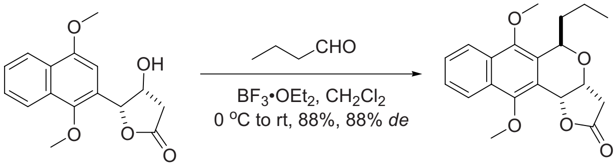


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_201,

Example 3, Asymmetric acyl Pictet–Spengler[9]



Example 4, Oxa-Pictet–Spengler[10]



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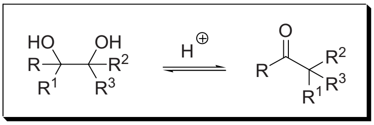
Pinacol rearrangement

Acid-catalyzed rearrangement of vicinal diols (pinacols) to carbonyl compounds.

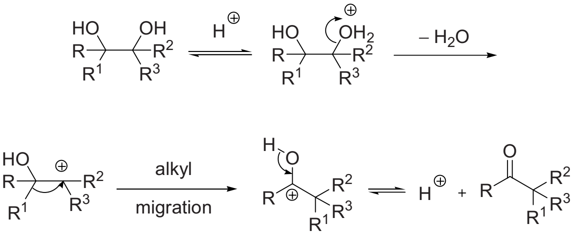


The most electron-rich alkyl group (more substituted carbon) migrates first. The general migration order:

tertiary alkyl > cyclohexyl > secondary alkyl > benzyl > phenyl > primary alkyl > methyl >> H.

For substituted aryls:

p-MeO-Ar > *p*-Me-Ar > *p*-Cl-Ar > *p*-Br-Ar > *p*-MeOAr > *p*-O_2N-Ar



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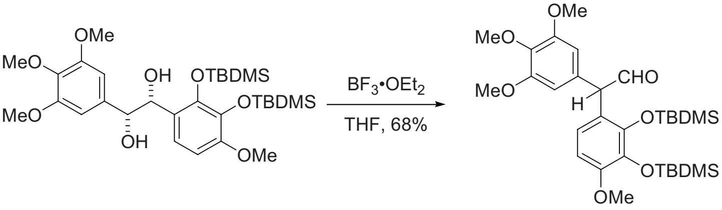

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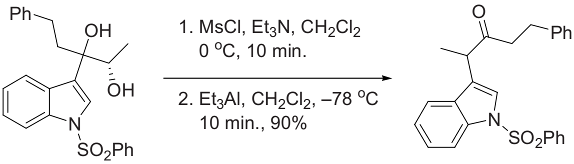
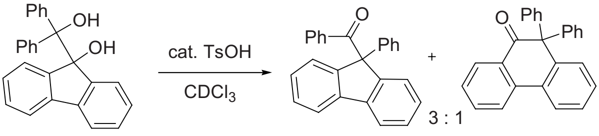
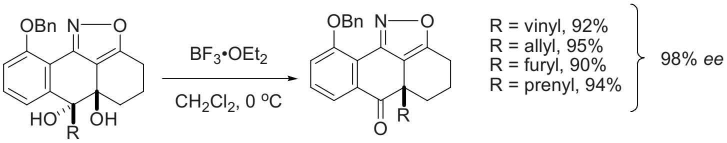


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_202,

Example 3[7]



Example 4[9]



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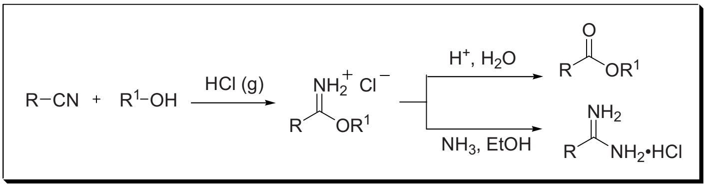
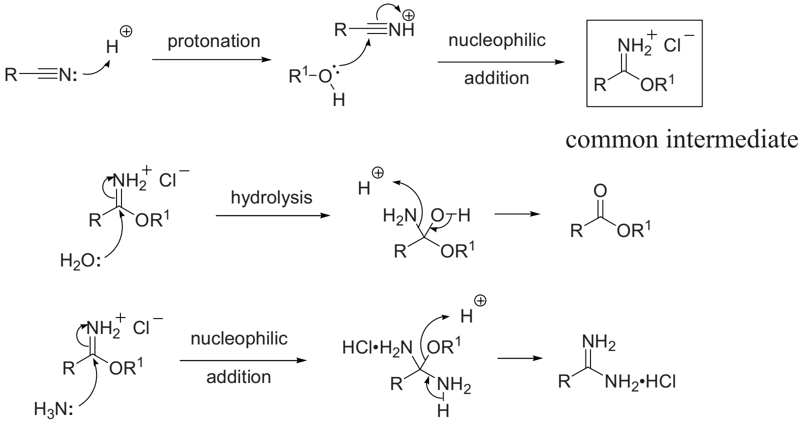
Pinner reaction

Transformation of a nitrile into an imino ether, which can be converted to either an ester or an amidine.





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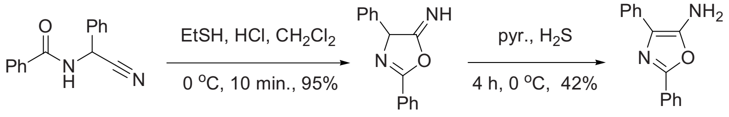

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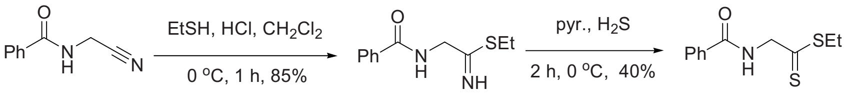

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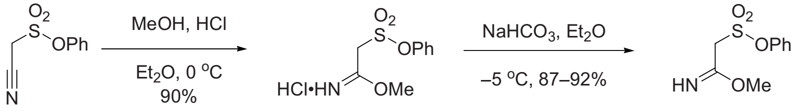

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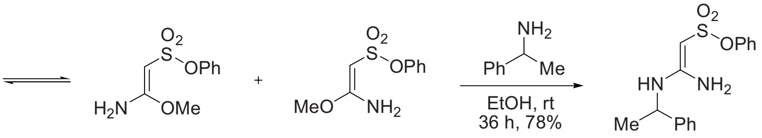
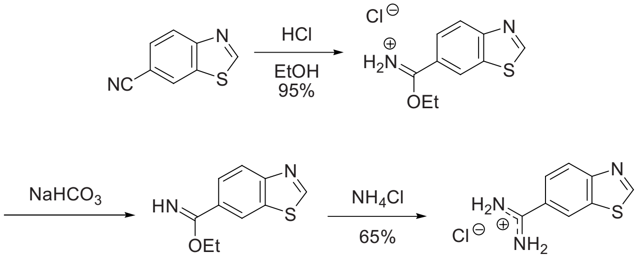


Example 4[10]



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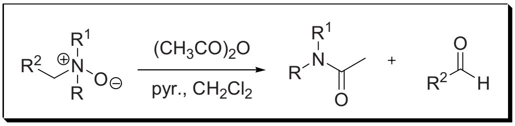
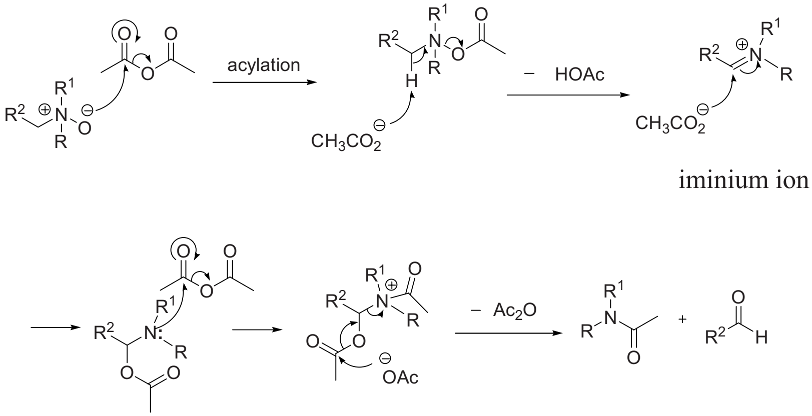
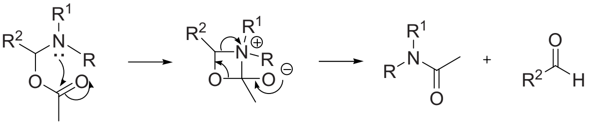
Polonovski reaction

Treatment of a tertiary *N*-oxide with an activating agent such as acetic anhydride, resulting in rearrangement where an *N,N*-disubstituted acetamide and an aldehyde are generated.

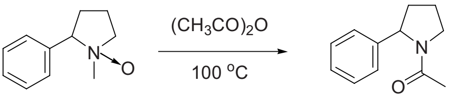




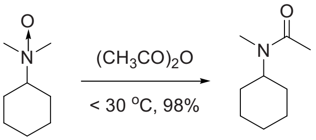
The intramolecular pathway is also operative:



Example 1[1]



Example 2[2]



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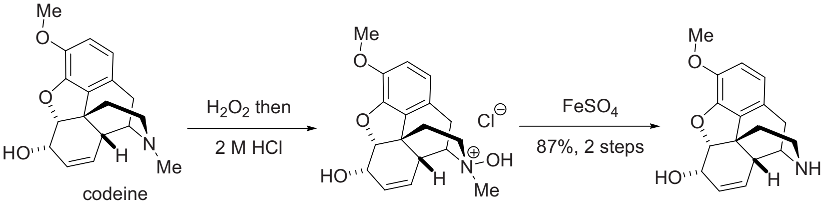
Example 3, Iron salt-mediated Polonovski reaction[9]



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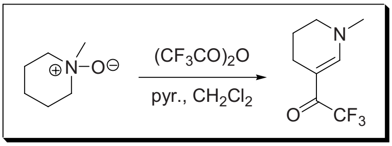
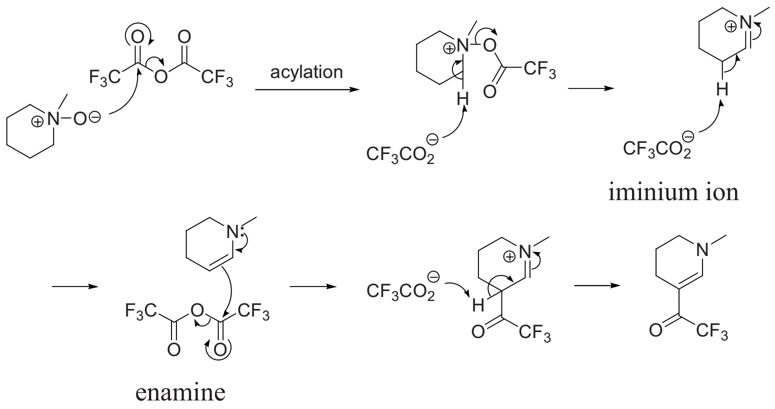
Polonovski–Potier reaction

A modification of the Polonovski reaction where trifluoroacetic anhydride is used in place of acetic anhydride. Because the reaction conditions for the Polonovski–Potier reaction are mild, it has largely replaced the Polonovski reaction.



tertiary *N*-oxide



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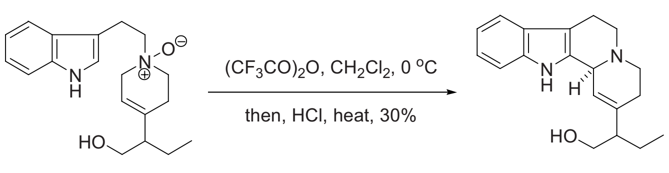
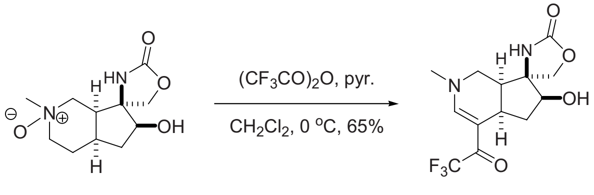


Example 2[5]



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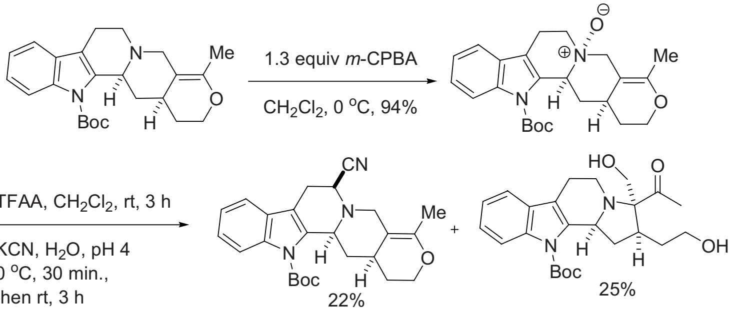
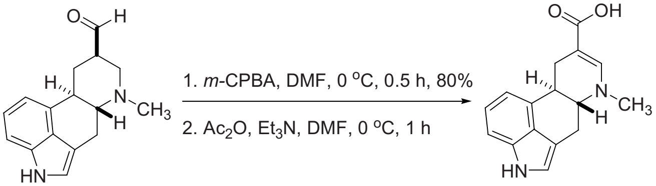
Example 3[8]



Example 4[10]



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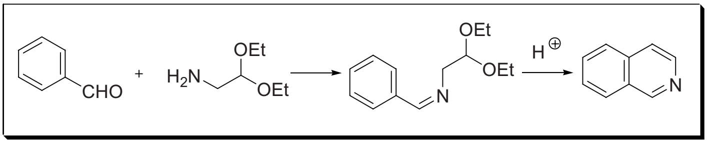
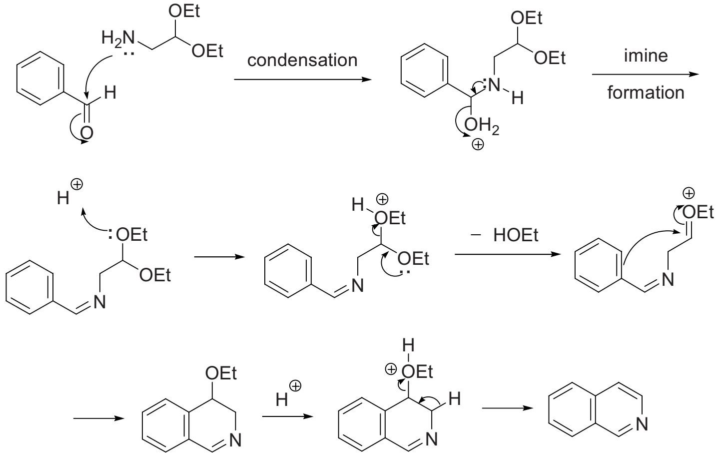
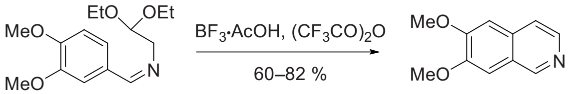
Pomeranz–Fritsch reaction

Isoquinoline synthesis *via* acid-mediated cyclization of the appropriate aminoacetal intermediate.





Example 1[3]



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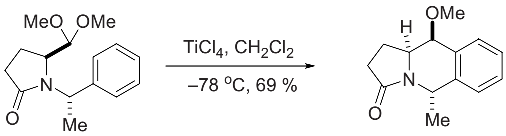

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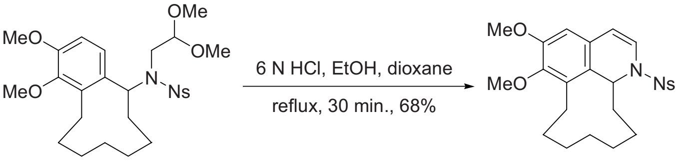
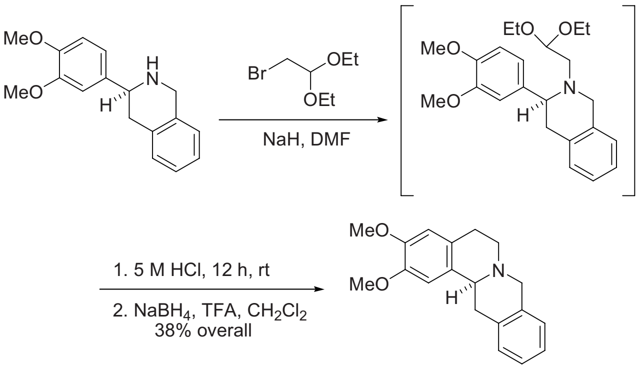
Example 3[9]



Example 4, **Bobbitt modification**[10]



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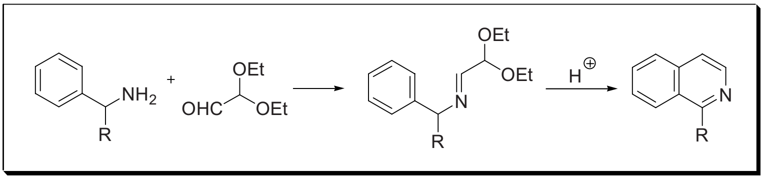
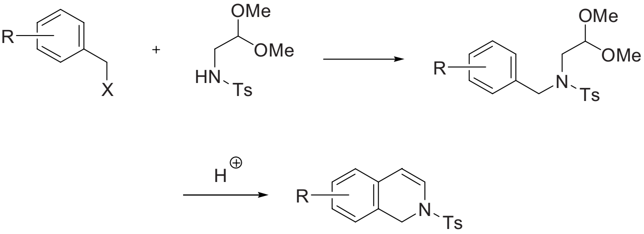
Schlittler–Müller modification

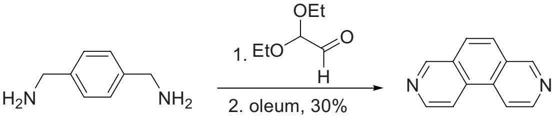
Simple permutation where the amine and the aldehyde switch places for the two reactants in comparison to the Pomeranz–Fritsch reaction.



Example 1[3]



Example 2[4]



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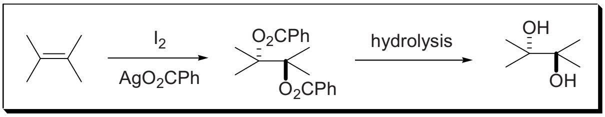
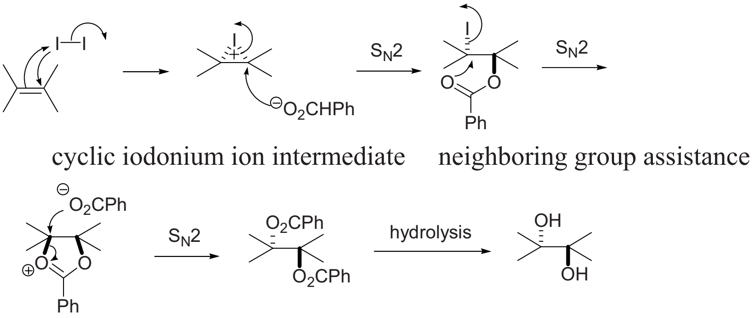
Prévost *trans*-dihydroxylation

Cf. Woodward *cis*-dihydroxylation.





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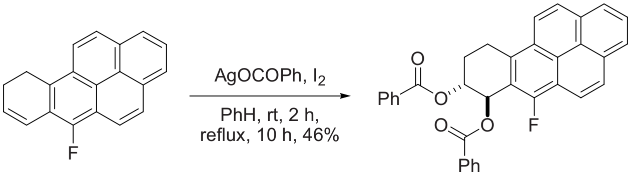

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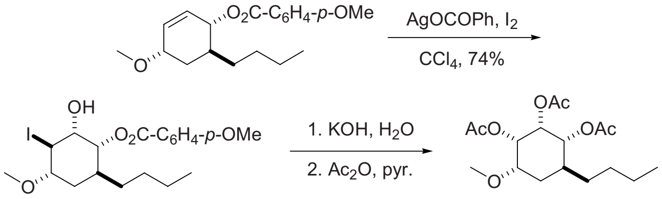

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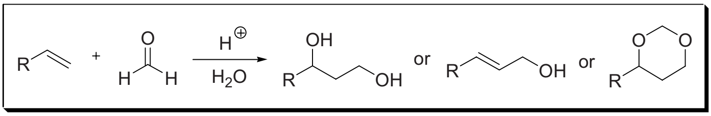
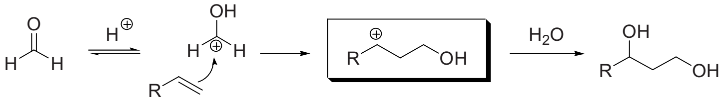
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_207,

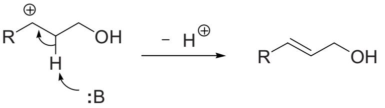
Prins reaction

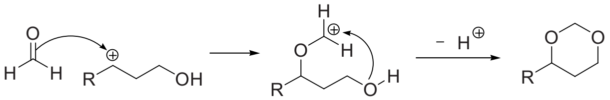
The Prins reaction is the acid-catalyzed addition of aldehydes to alkenes and gives different products depending on the reaction conditions.



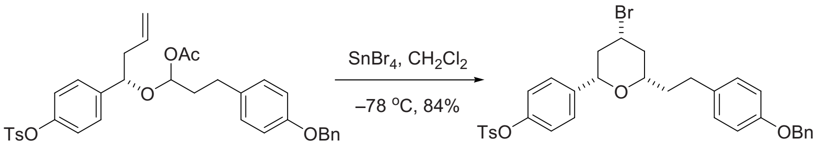


the common intermediate

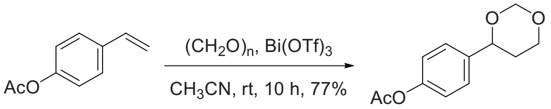




Example 1[5]



Example 2[7]



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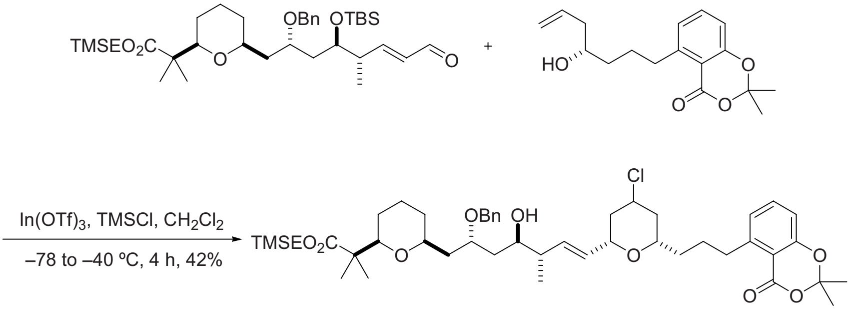
Example 3[9]



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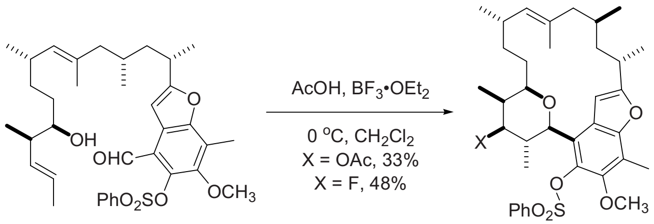

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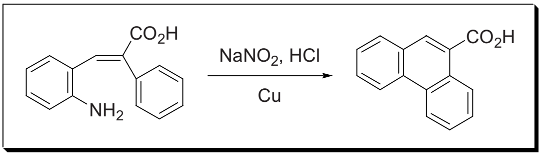
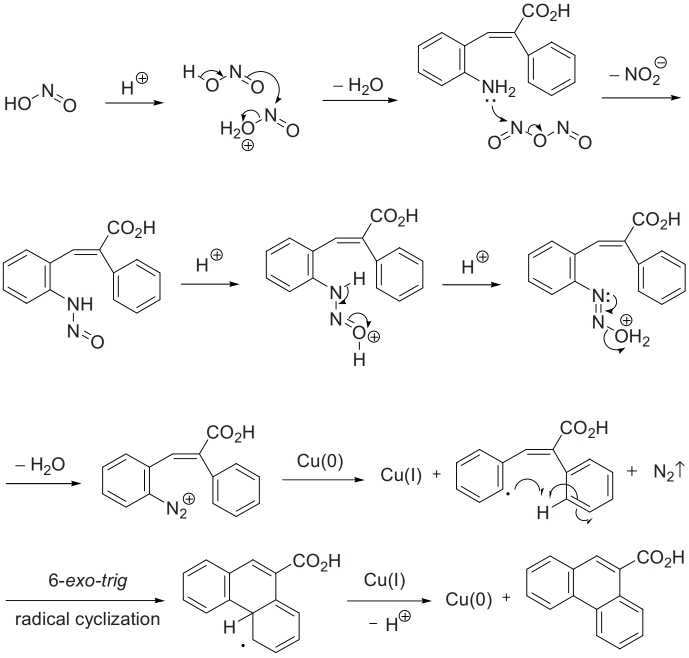
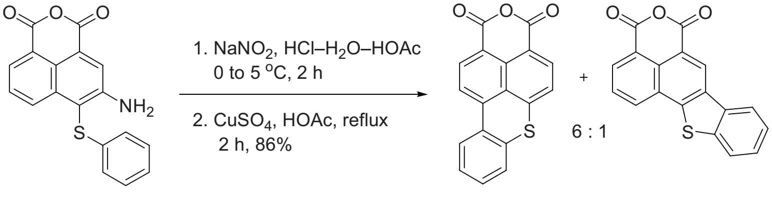
Pschorr cyclization

The intramolecular version of the Gomberg–Bachmann reaction.





Example 1[7]



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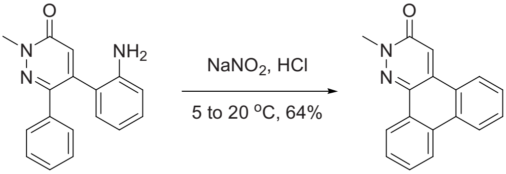
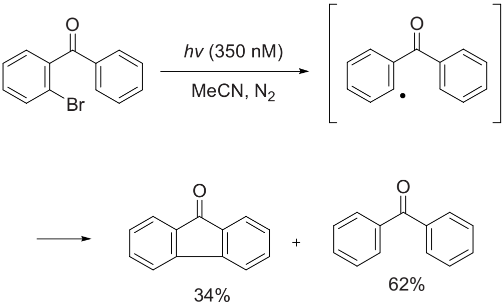
Example 2[8]



Example 3[10]



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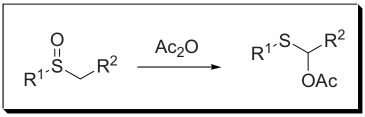
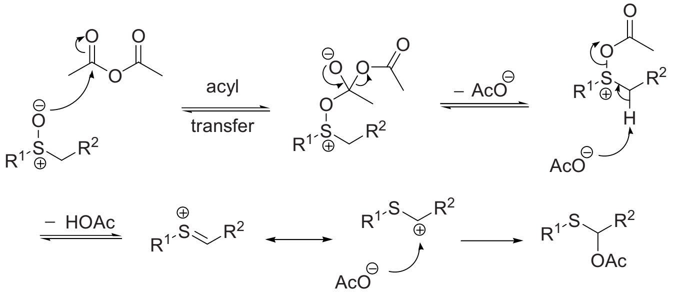
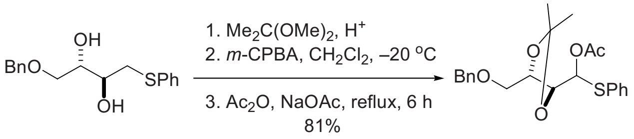
Pummerer rearrangement

The transformation of sulfoxides into α-acyloxythioethers using acetic anhydride.

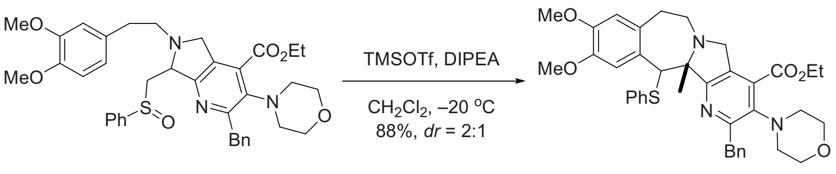




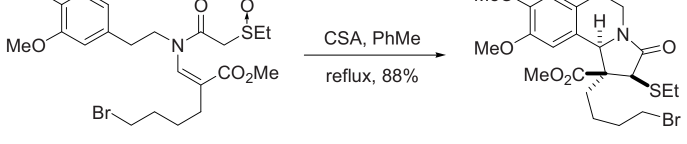
Example 1[2]



Example 2[7]



Example 3[8]



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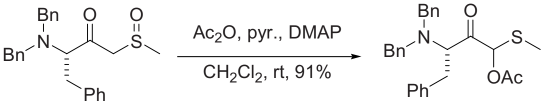
Example 4[9]



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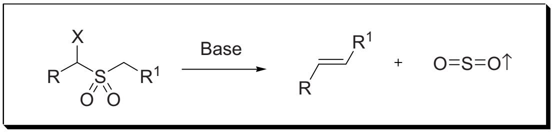
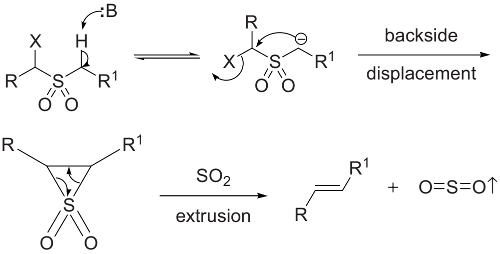
Ramberg–Bäcklund reaction

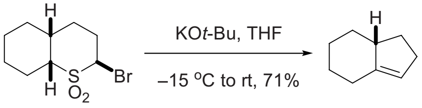
Olefin synthesis *via* α-halosulfone extrusion.



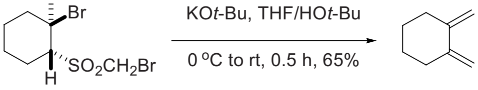


episulfone intermediate

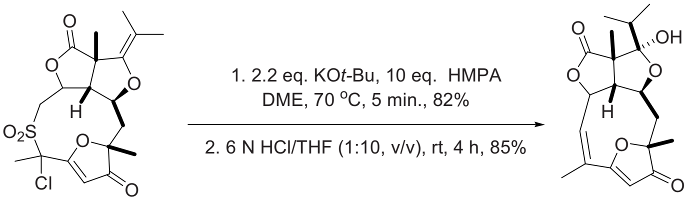
Example 1[4]



Example 2[5]



Example 3[6]



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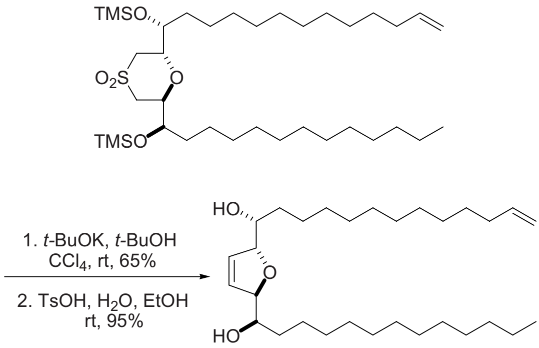
Example 4, *in situ* chlorination[7]



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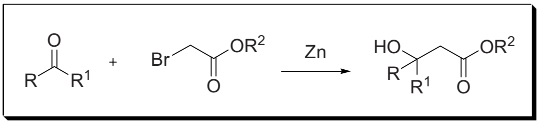
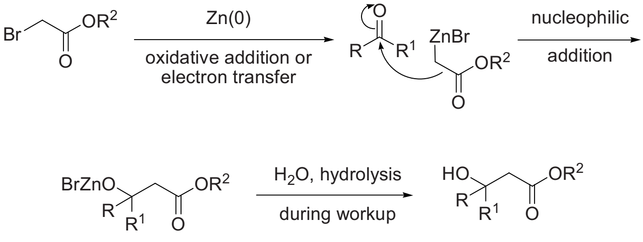
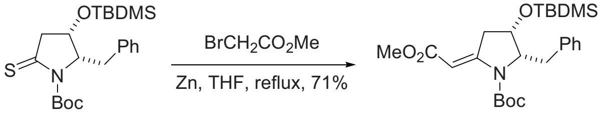
Reformatsky reaction

Nucleophilic addition of organozinc reagents generated from α-haloesters to carbonyls.

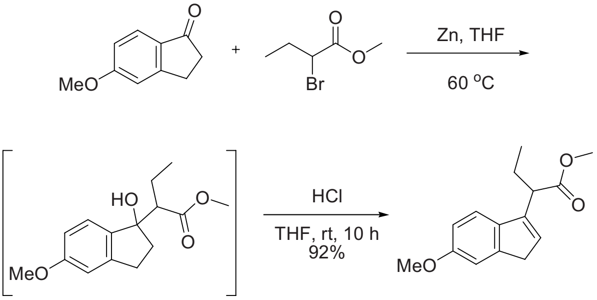




Example 1[4]



Example 2[6]



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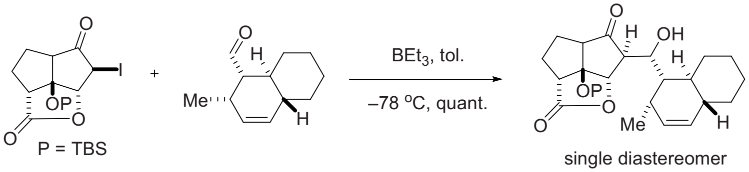
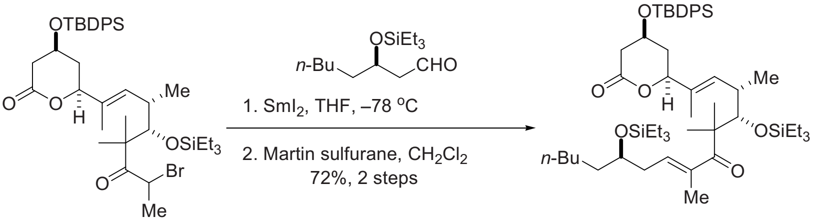
Example 3, Boron-mediated Reformatsky reaction[8]



Example 4, SmI_2-mediated Reformatsky reaction[9]



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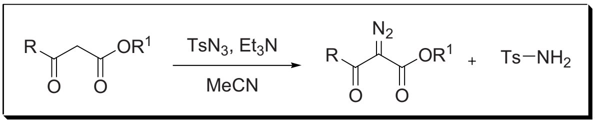
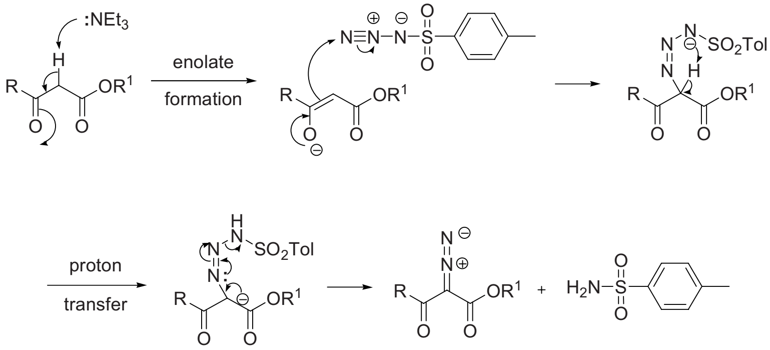
Regitz diazo synthesis

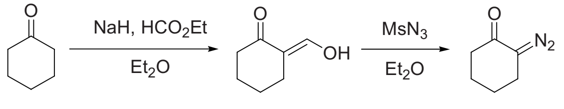
Synthesis of 2-diazo-1,3-diketones or 2-diazo-3-oxoesters using sulfonyl azides.

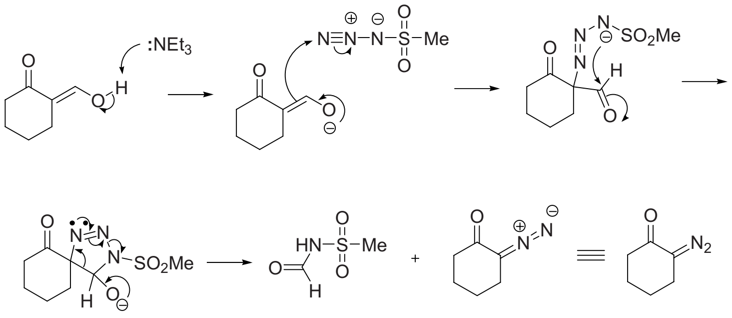




tosyl amide is the by-product

When only one carbonyl is present, ethylformate can be used as an activating auxiliary:[6–9]





Alternatively, the triazole intermediate may be assembled *via* a 1,3-dipolar cycloaddition of the enol and mesyl azide:

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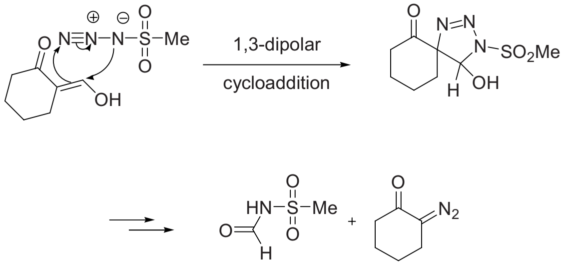
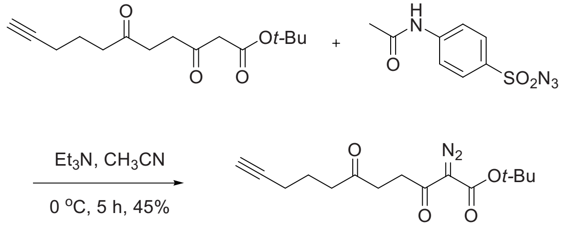
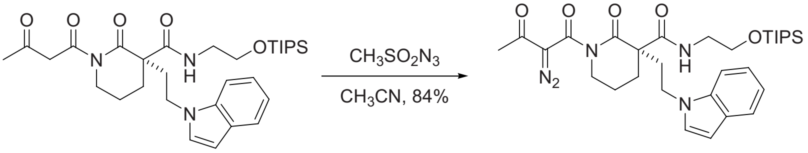


Example 1[5]



Example 2[10]



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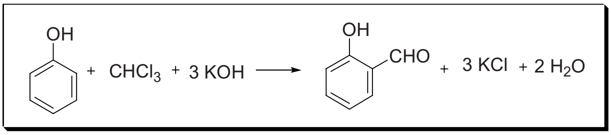
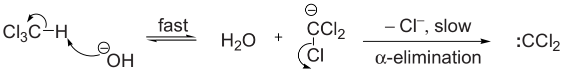
Reimer–Tiemann reaction

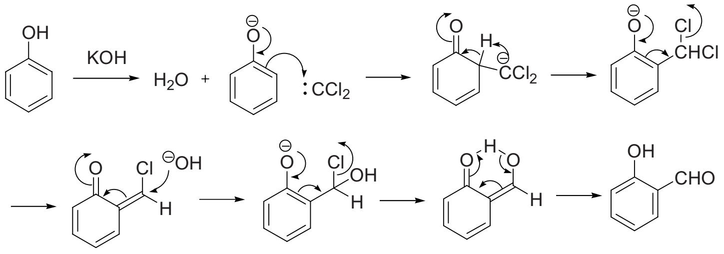
Synthesis of *o*-formylphenol from phenols and chloroform in alkaline medium.



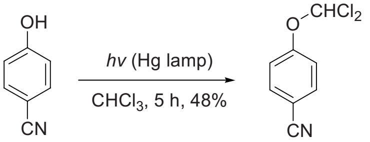
a. Carbene generation:



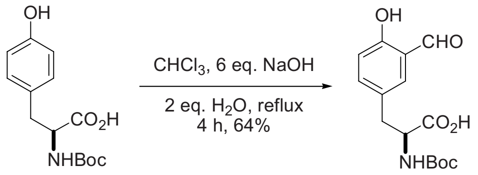
b. Addition of dichlorocarbene and hydrolysis:



Example 1, Photo-Reimer–Tiemann reaction without base[7]



Example 2[8]



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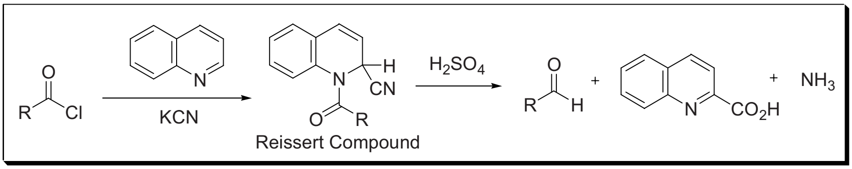
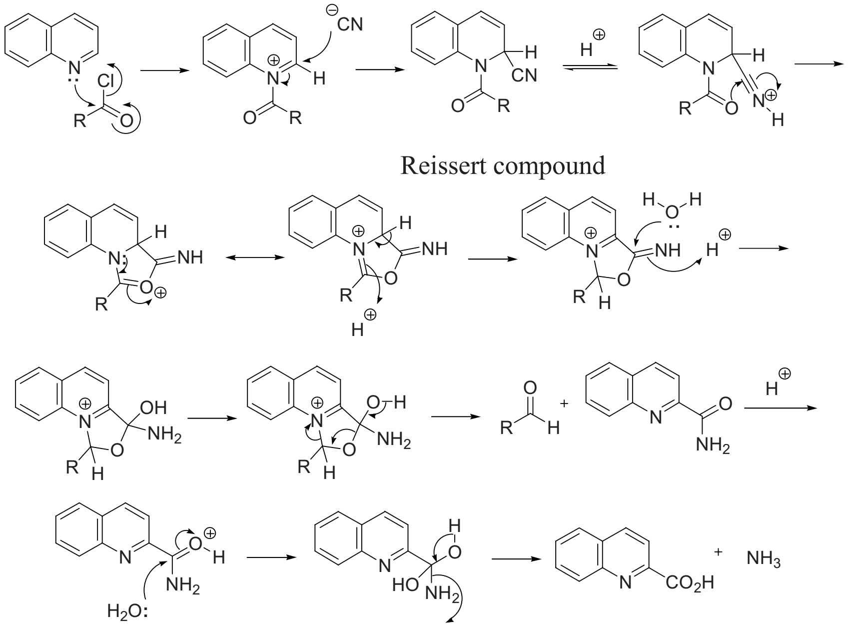
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_214,

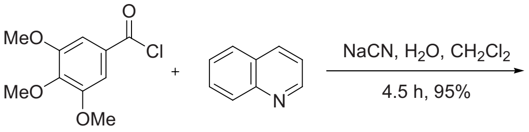
Reissert reaction

Treatment of quinoline or isoquinoline with acid chloride and KCN gives quinaldic acid, aldehyde, and KCN.

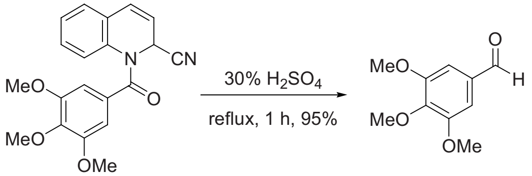




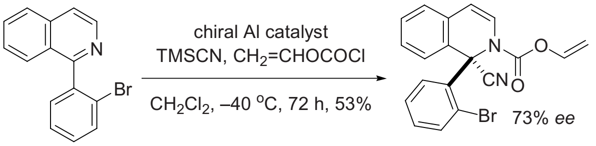
Example 1[3]



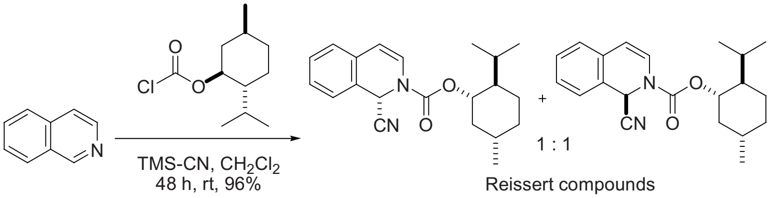
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_215,



Example 2, Reissert compound from isoquinoline[7]



Example 3, Reissert compound fron isoquinoline[10]



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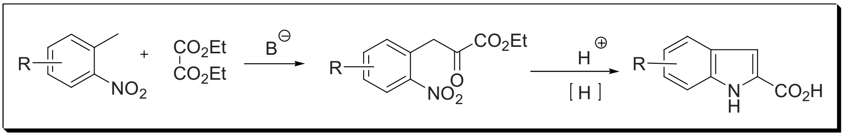
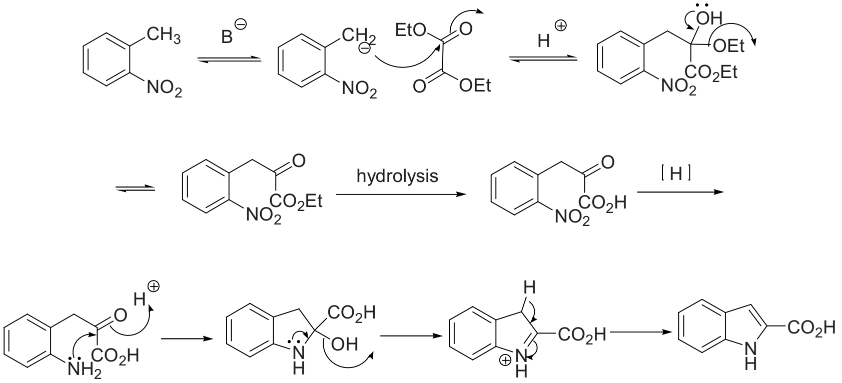
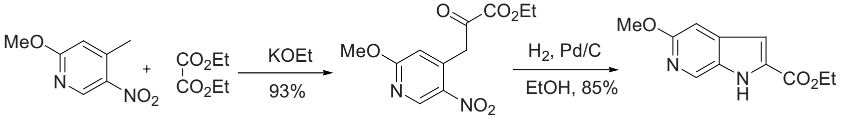
Reissert indole synthesis

The Reissert indole synthesis involves base-catalyzed condensation of an *o*-nitrotoluene derivative with an ethyl oxalate, which is followed by reductive cyclization to an indole-2-carboxylic acid derivative.

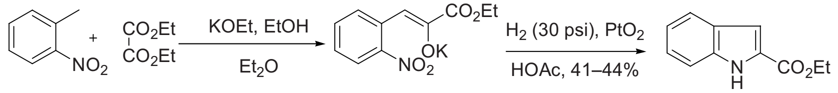




Example 1[2]



Example 2[3]



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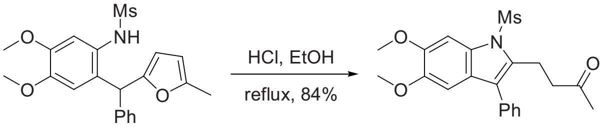
Example 3, Furan ring as the masked carbonyl[10]



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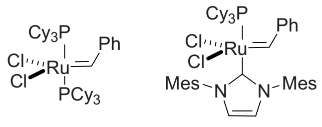
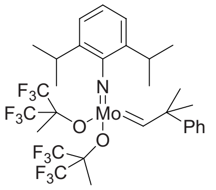
Ring-closing metathesis (RCM)



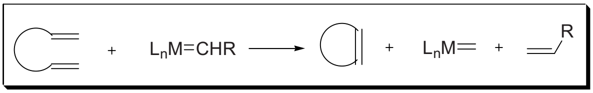


Grubbs’ catalysts
Mes = mesityl

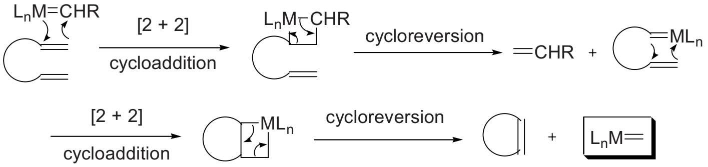
Schrock’s catalyst

All three catalysts are illustrated as “L_nM=CHR” in the mechanism below.

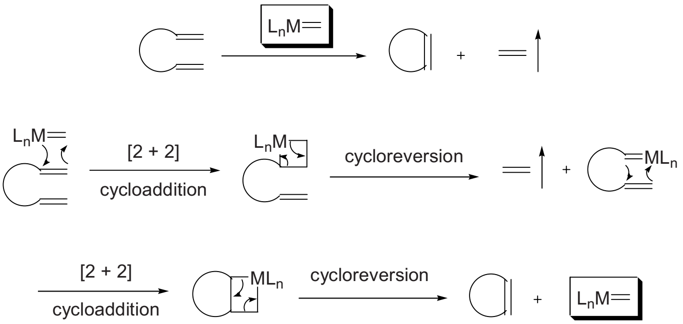
Generation of the real catalyst from the precatalysts:



the active catalyst

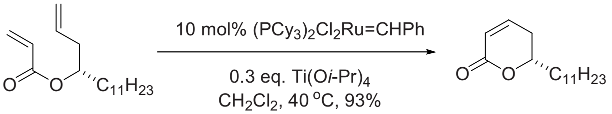


Catalytic cycle:

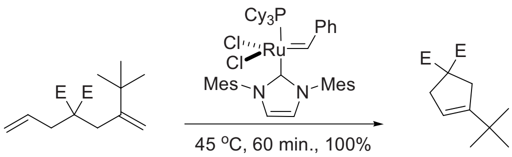


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_217,

Example 1[3]

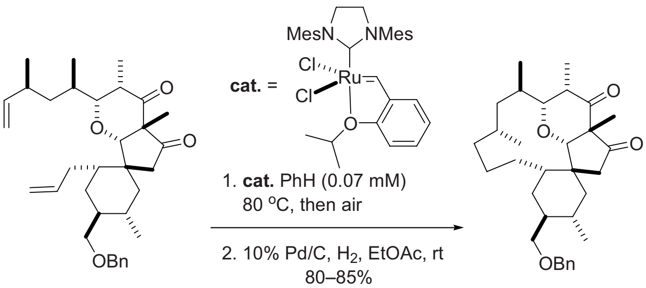


Example 2[5]

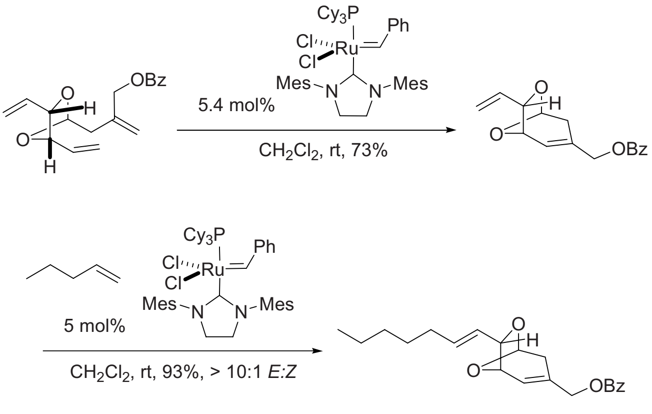


$E = CO_2Et$

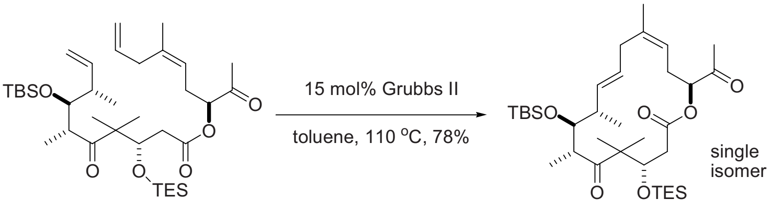
Example 3[7]



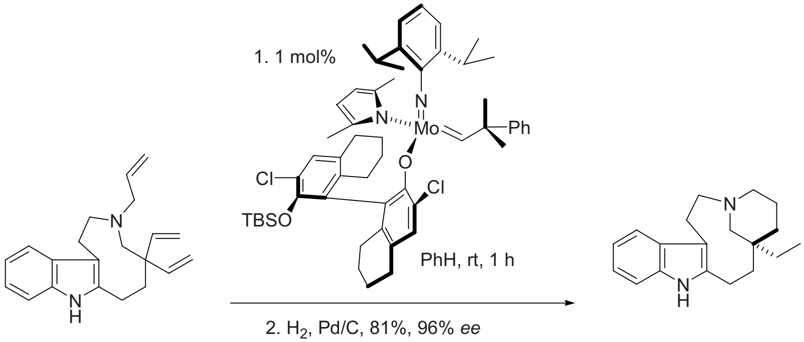
Example 4[9]



Example 5[10]



Example 6[12]



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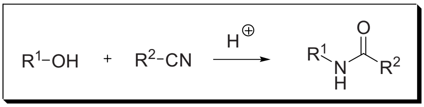
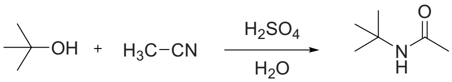
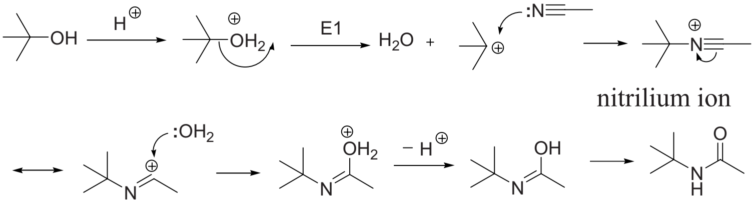
Ritter reaction

Amides from nitriles and alcohols in strong acids.
General scheme:

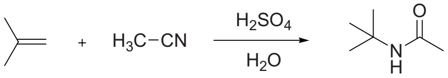


e.g.:

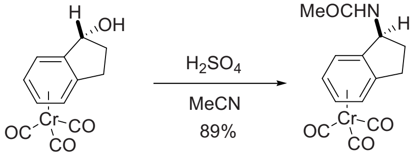




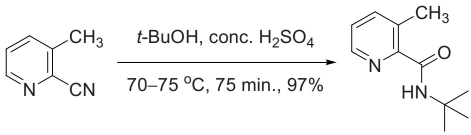
Similarly:



Example 1[3]



Example 2[4]



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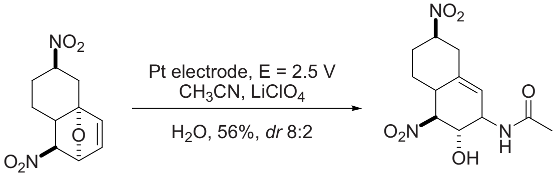
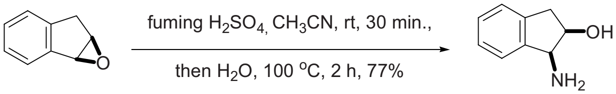
Example 3[5]



Example 4[6]



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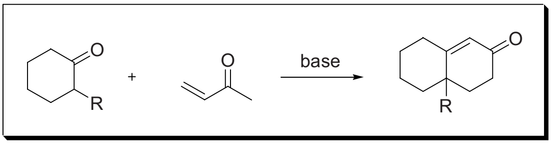
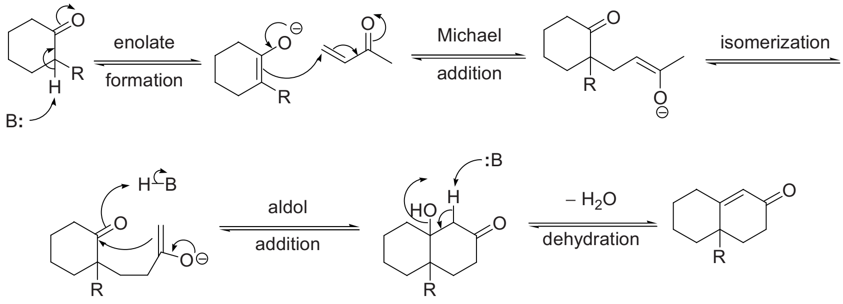
Robinson annulation

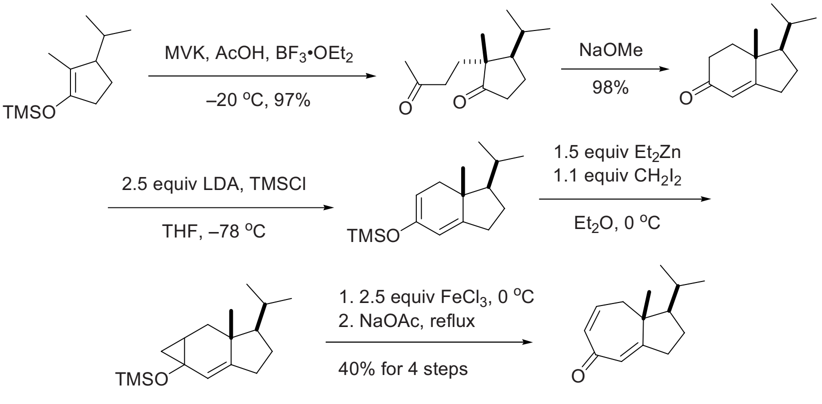
Michael addition of cyclohexanones to methyl vinyl ketone followed by intramolecular aldol condensation to afford six-membered α,β-unsaturated ketones.



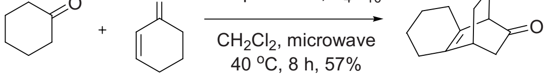
methyl vinyl ketone (MVK)



Example 1, Homo-Robinson[7]



Example 2[8]



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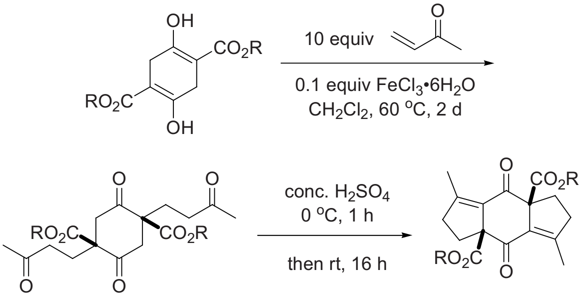
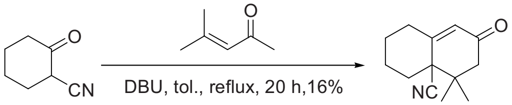
Example 3, Double Robinson-type cyclopentene annulation[9]



Example 4[10]



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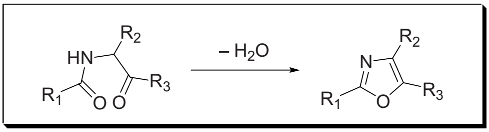
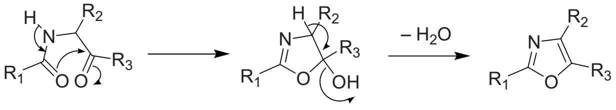
Robinson–Gabriel synthesis

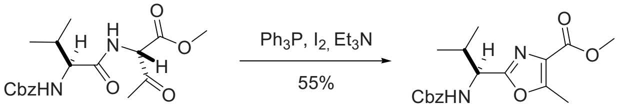
Cyclodehydration of 2-acylamidoketones to give 2,5-di- and 2,4,5-trialkyl, aryl, heteroaryl-, and aralkyloxazoles.



R_1, R_2, R_3 = alkyl, aryl, heteroaryl



Example 1[3]



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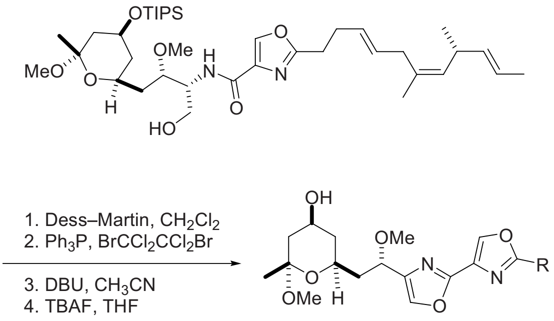
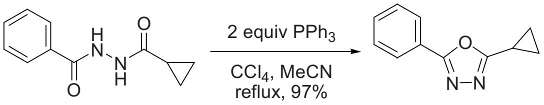
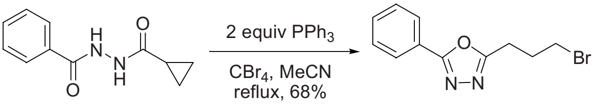


(+)-hennoxazole A

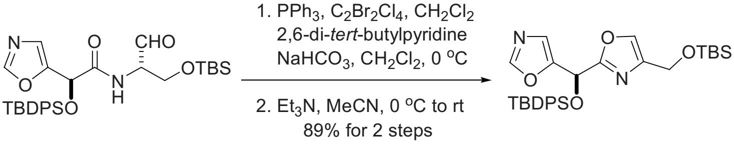
Example 3, Halogen effect[9]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_220,



Example 4[10]



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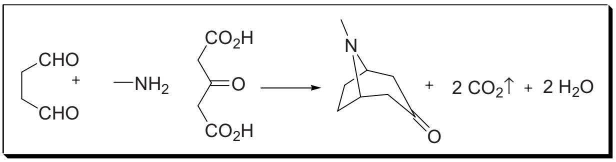
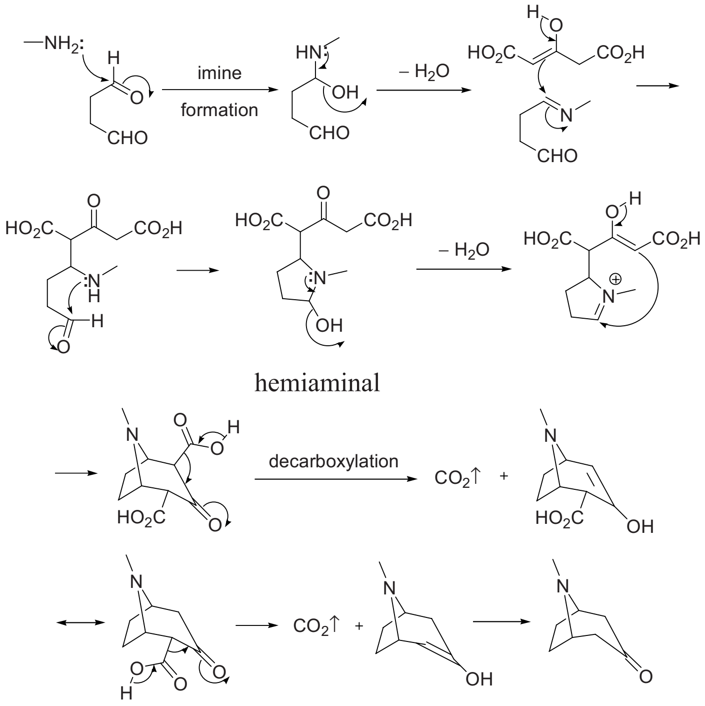
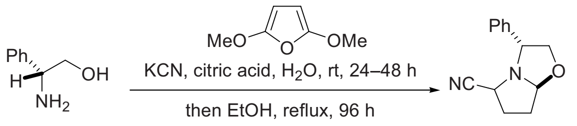
Robinson–Schöpf reaction

1,4-Diketone condensations with primary amines to give tropinones.



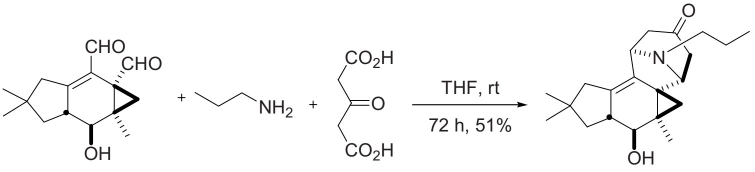


Example 1[5]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_221,

Example 2[9]



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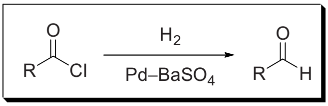
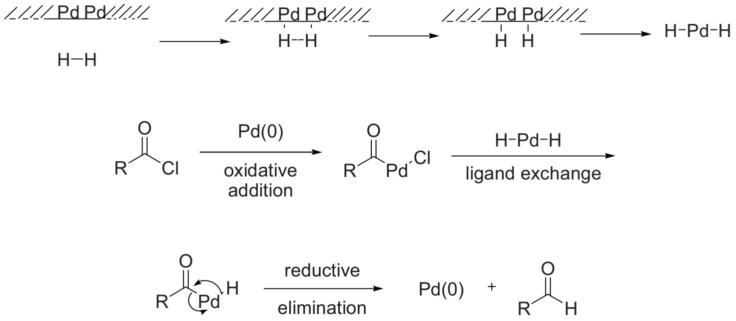
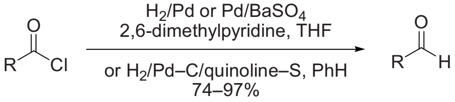
Rosenmund reduction

Hydrogenation reduction of acid chloride to aldehyde using $BaSO_4$-poisoned palladium catalyst. Without this poisoning, the resulting aldehyde may be further reduced to the corresponding alcohol.

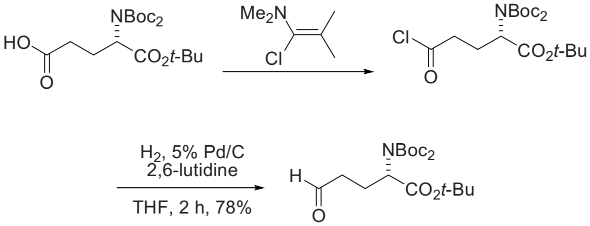




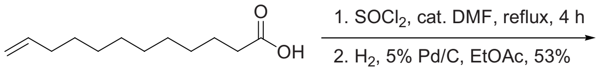
Example 1[4]



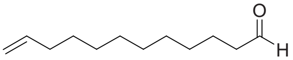
Example 2[6]



Example 3[9]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_222,



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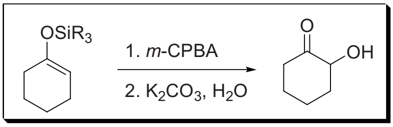
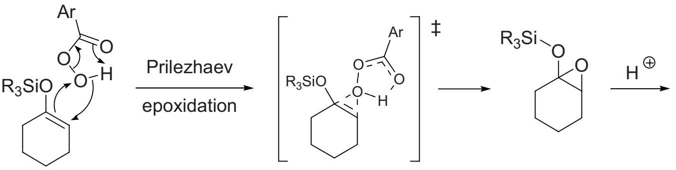
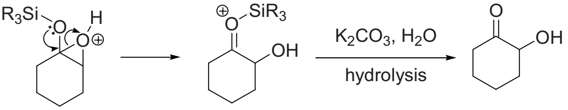
Rubottom oxidation

α-Hydroxylation of enolsilanes.

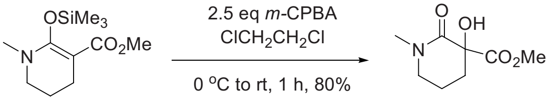




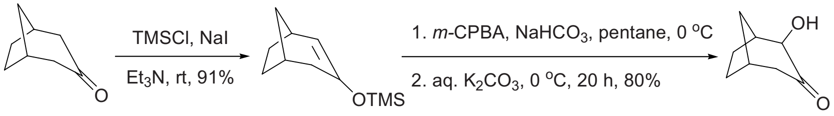
The "butterfly" transition state



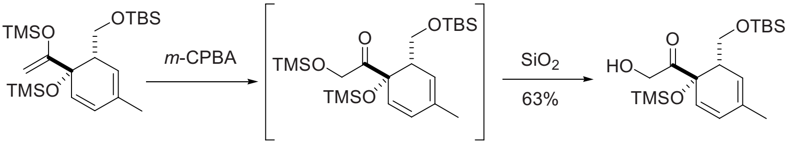
Example 1[2]



Example 2[3]



Example 3[4]



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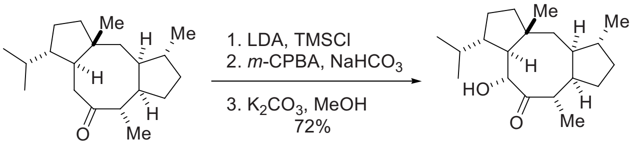
Example 4[5]



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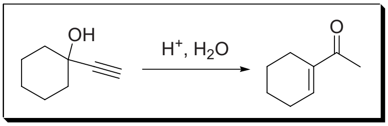
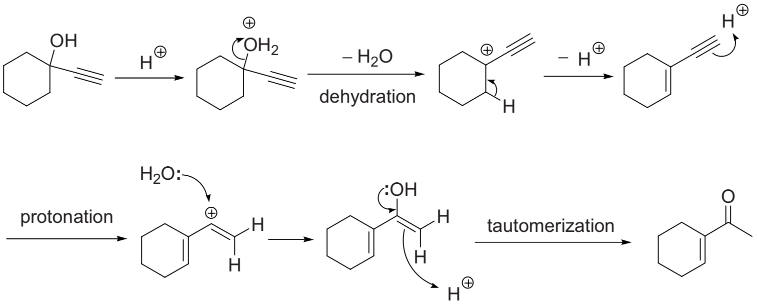
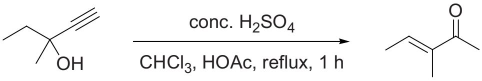
Rupe rearrangement

Acid-catalyzed rearrangement of tertiary α-acetylenic (terminal) alcohols, leading to the formation of α,β-unsaturated ketones rather than the corresponding α,β-unsaturated aldehydes. *Cf.* Meyer–Schuster rearrangement.

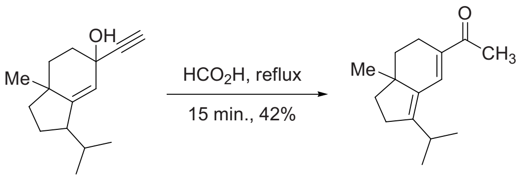




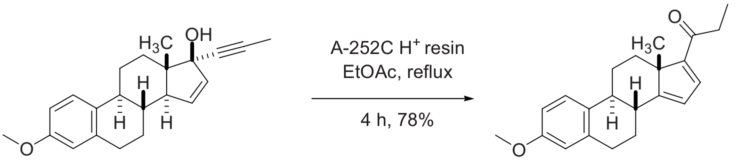
Example 1[4]



Example 2[8]



Example 3[9]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_224,

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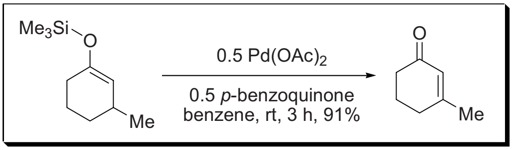
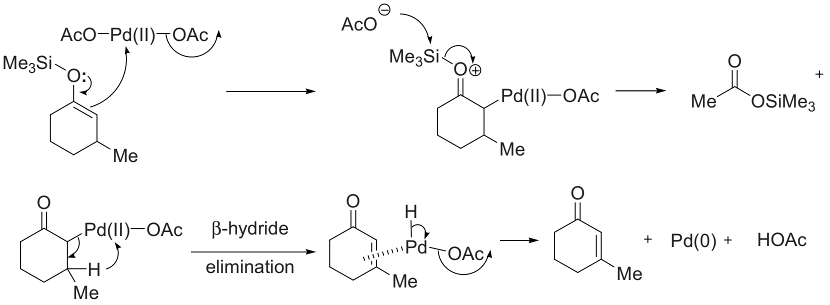
Saegusa oxidation

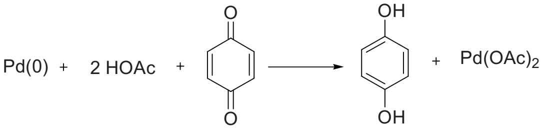
Palladium-catalyzed conversion of enol silanes to enones, also known as the Saegusa enone synthesis.



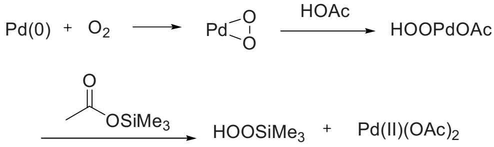
The mechanism is similar to that of the Wacker oxidation (page 564).



Regenerating the Pd(II) oxidant:



Larock reported regeneration of the Pd(II) oxidant using oxygen:[4]



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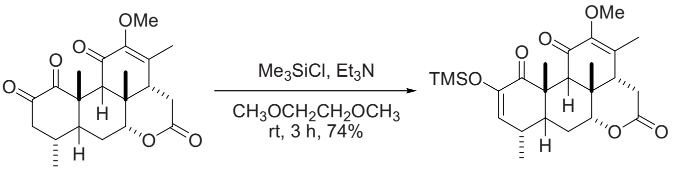
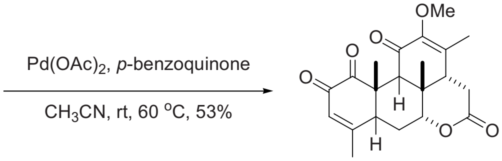
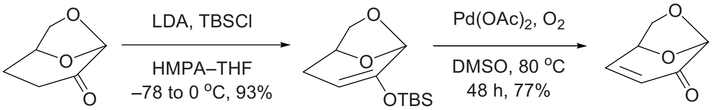


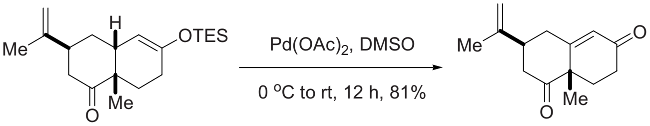
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_225,



Example 2[8]



Example 3[10]



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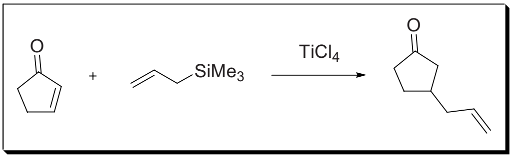
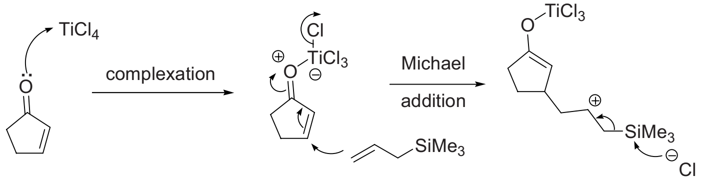
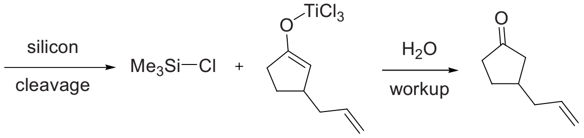
Sakurai allylation reaction

Lewis acid-mediated addition of allylsilanes to carbon nucleophiles. Also known as the Hosomi–Sakurai reaction. The allylsilane will add to the carbonyl compound directly if the electrophile (carbonyl group) is not part of an α,β-unsaturated system (Example 2), giving rise to an alcohol.

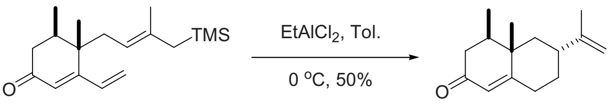




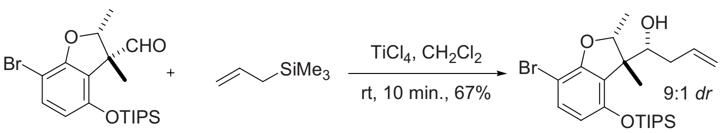
The β-carbocation is stabilized by the β-silicon effect



Example 1[2]



Example 2[6]



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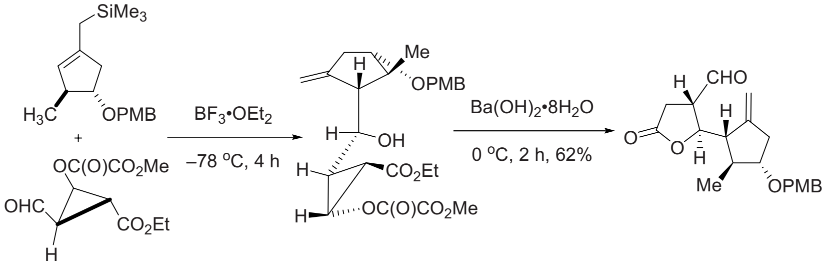
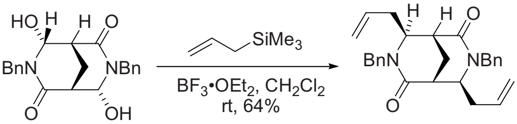
Example 3[9]



Example 4[10]



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Sandmeyer reaction

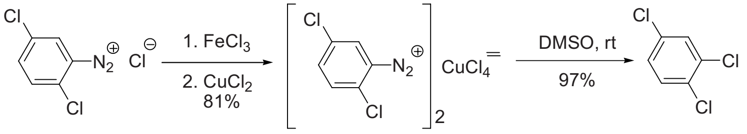
Haloarenes from the reaction of a diazonium salt with CuX.

$$\boxed{\begin{array}{c} \mathrm{ArN_2^{\oplus}}\ \mathrm{Y^{\ominus}} \xrightarrow{\mathrm{CuX}} \mathrm{Ar{-}X} \\ \mathrm{X = Cl, Br, CN} \end{array}}$$

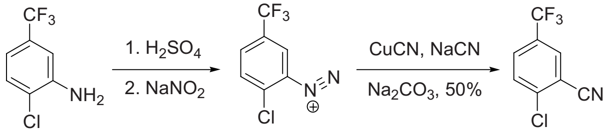
e.g.:

$$\mathrm{ArN_2^{\oplus}}\ \mathrm{Cl^{\ominus}} \xrightarrow{\mathrm{CuCl}} \mathrm{N_2}\uparrow + \mathrm{Ar}\bullet + \mathrm{CuCl_2} \longrightarrow \mathrm{Ar{-}Cl} + \mathrm{CuCl}$$

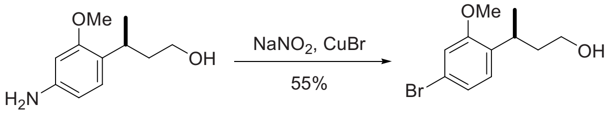
Example 1[4]



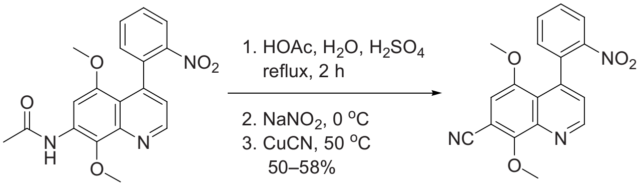
Example 2[7]



Example 3[8]



Example 4[9]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_227,

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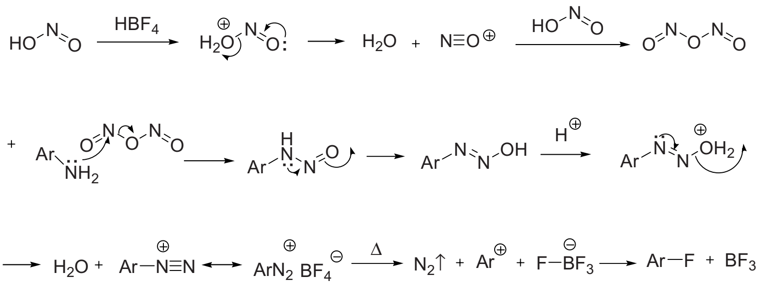
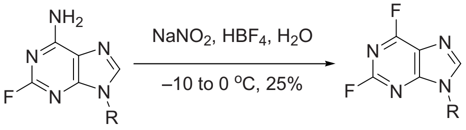
Schiemann reaction

Fluoroarene formation from arylamines. Also known as the Balz–Schiemann reaction.

$$\boxed{\begin{array}{c} Ar{-}NH_2 + HNO_2 + HBF_4 \longrightarrow \\ ArN_2^{\oplus}\ BF_4^{\ominus} \xrightarrow{\Delta} Ar{-}F + N_2\uparrow + BF_3 \end{array}}$$

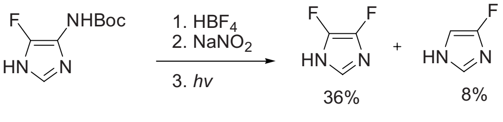


Example 1[4]

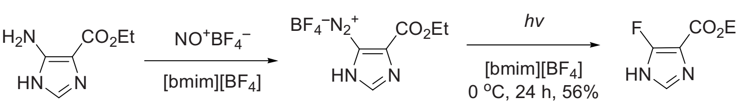


R = 2,3-5-tri-*O*-acetyl-β-*D*-ribofuranose

Example 2, Photo-Schiemann reaction[6]

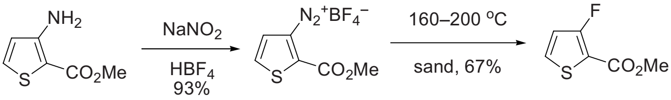


Example 3, Photo-Schiemann reaction[8]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_228,

Example 4[10]



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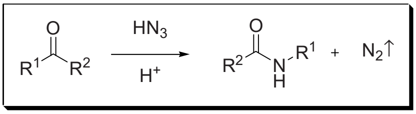
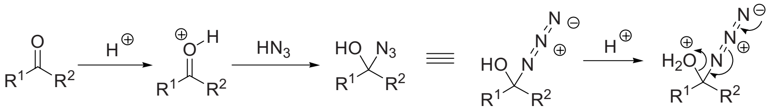
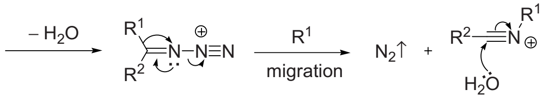
Schmidt rearrangement

The Schmidt reactions refer to the acid-catalyzed reactions of hydrazoic acid with electrophiles, such as carbonyl compounds, tertiary alcohols and alkenes. These substrates undergo rearrangement and extrusion of nitrogen to furnish amines, nitriles, amides or imines.

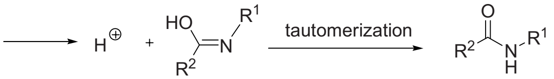




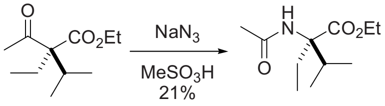
azido-alcohol



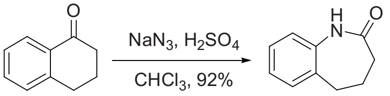
nitrilium ion intermediate (*Cf.* Ritter intermediate)



Example 1, A classic example[3]

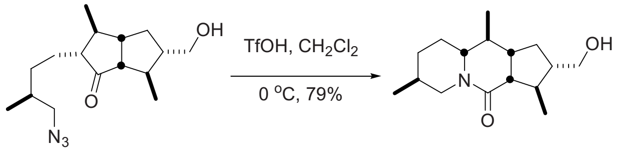


Example 2[5]

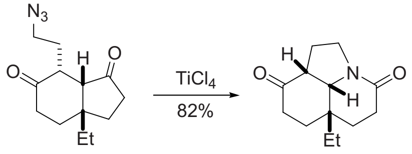


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_229,

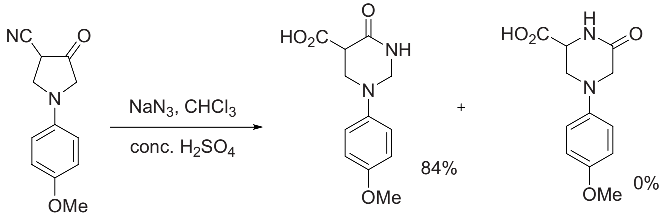
Example 3, Intramolecular Schmidt rearrangement[6]



Example 4, Intramolecular Schmidt rearrangement[8]



Example 5, Intermolecular Schmidt rearrangement[9]



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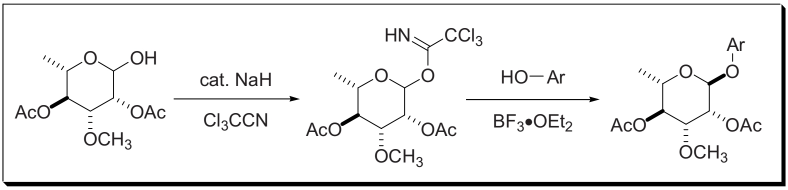
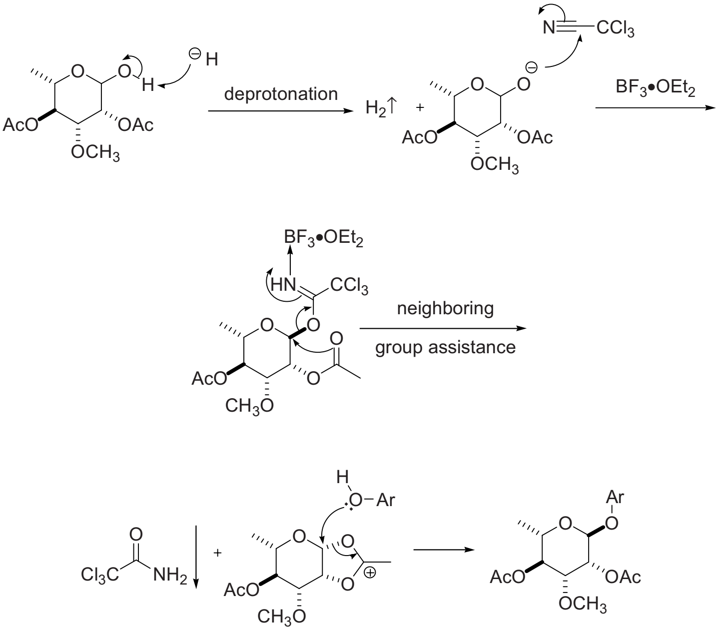
Schmidt's trichloroacetimidate glycosidation reaction

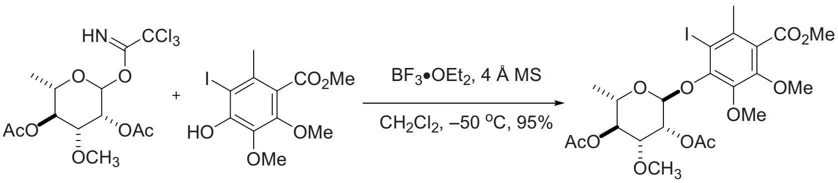
Lewis acid-promoted glycosidation of trichloroacetimidates with alcohols or phenols.



trichloroacetimidate



Example 1[5]



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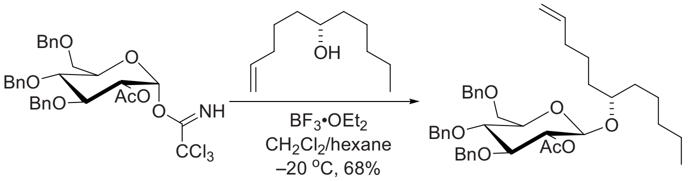
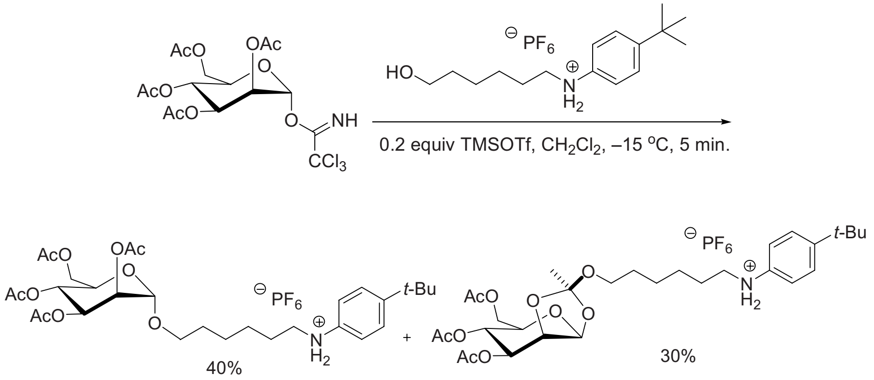
Example 2[7]



Example 3[9]



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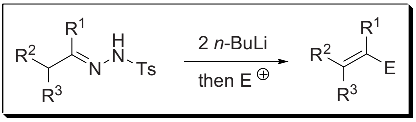
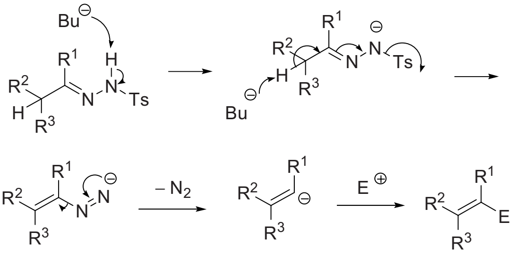
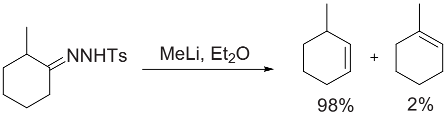
Shapiro reaction

The Shapiro reaction is a variant of the Bamford–Stevens reaction. The former uses bases such as alkyl lithium and Grignard reagents whereas the latter employs bases such as Na, NaOMe, LiH, NaH, $NaNH_2$, *etc*. Consequently, the Shapiro reaction generally affords the less-substituted olefins (the kinetic products), while the Bamford–Stevens reaction delivers the more-substituted olefins (the thermodynamic products).

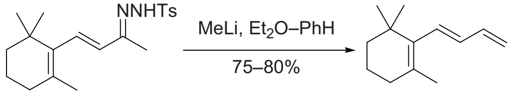




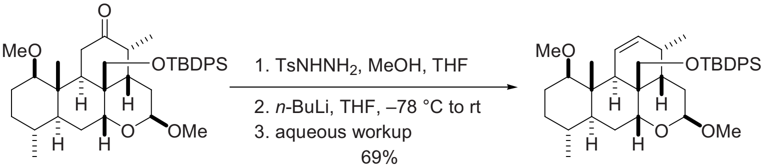
Example 1[2]



Example 2[3]

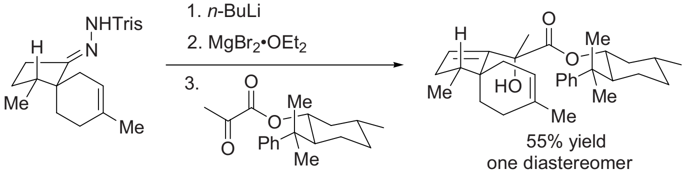


Example 3[7]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_231,

Example 4[8]



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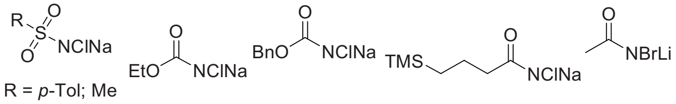
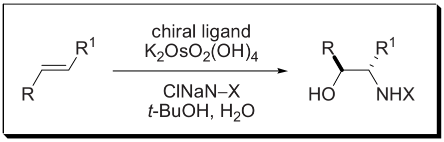
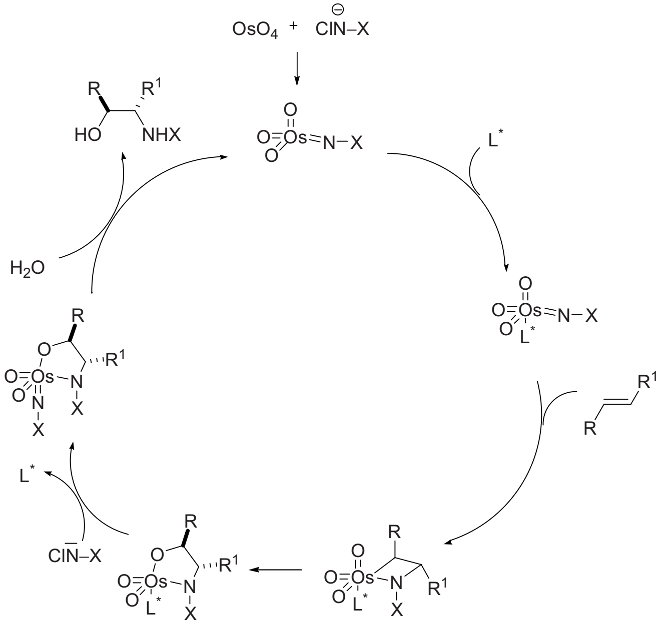
Sharpless asymmetric amino-hydroxylation

Osmium-mediated *cis*-addition of nitrogen and oxygen to olefins. Regioselectivity may be controlled by ligand. Nitrogen sources (X–NClNa) include:

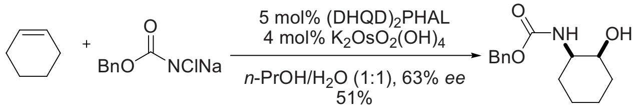




The catalytic cycle:



Example 1[1b]



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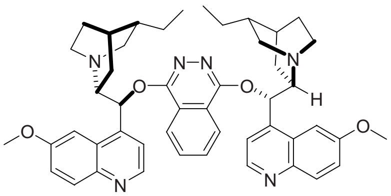
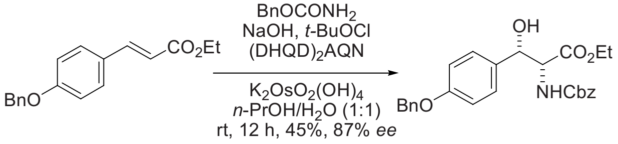
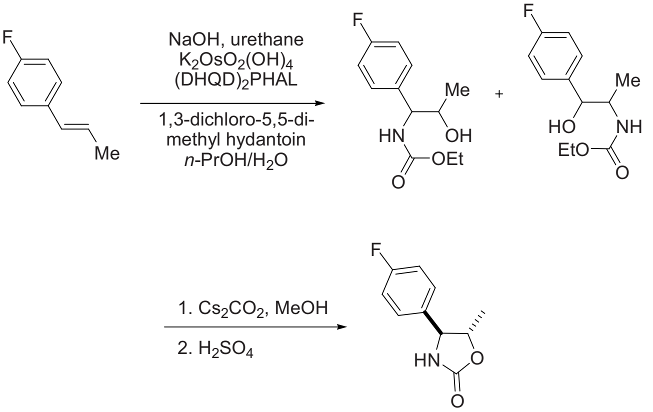
$(DHQD)_2$-PHAL = 1,4-bis(9-*O*-dihydroquinidine)phthalazine:



Example 2[2]



Example 3[6]



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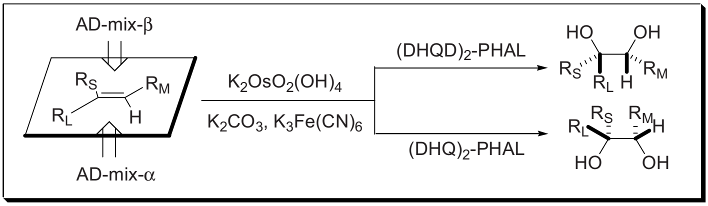
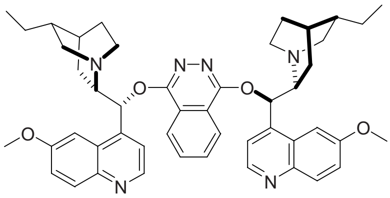
Sharpless asymmetric dihydroxylation

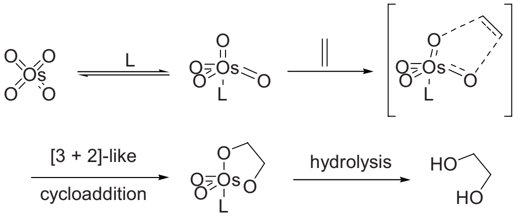
Enantioselective *cis*-dihydroxylation of olefins using osmium catalyst in the presence of cinchona alkaloid ligands.



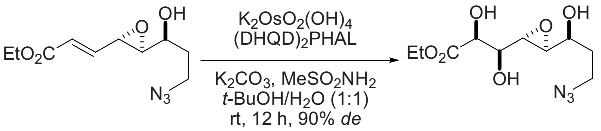
$(DHQ)_2$-PHAL = 1,4-bis(9-*O*-dihydroquinine)phthalazine:



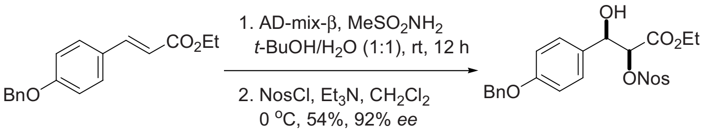
The concerted [3 + 2] cycloaddition mechanism:[5]



Example 1[2]



Example 2[4]



Nos = nosylate = 4-nitrobenzenesulfonyl

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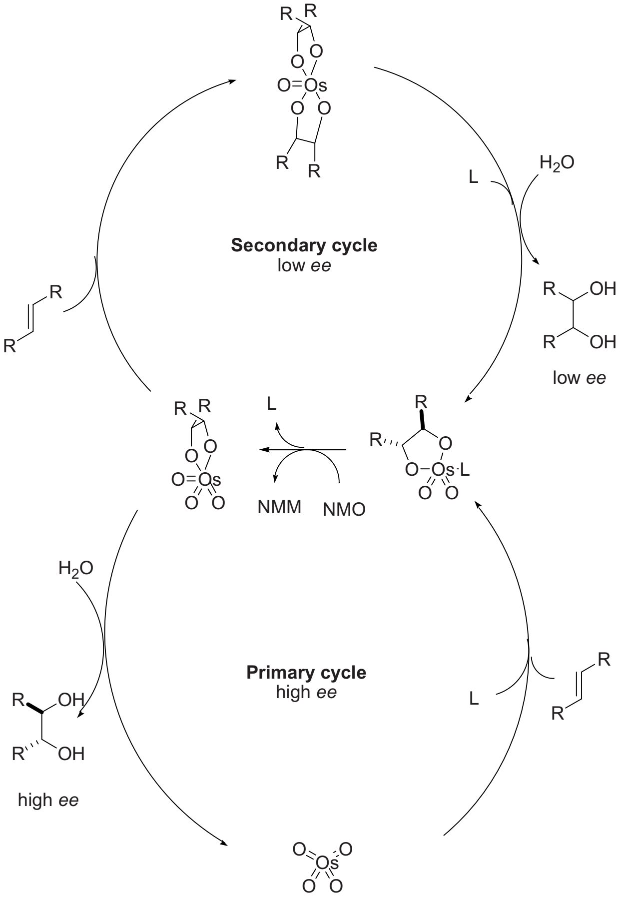
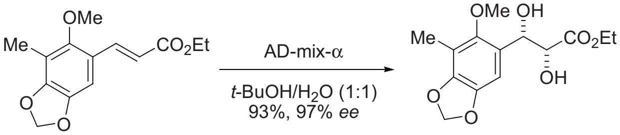
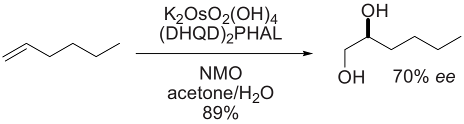
The catalytic cycle: (the secondary cycle is shut off by maintaining a low concentration of olefin):



Example 3[9]



Example 4[10]



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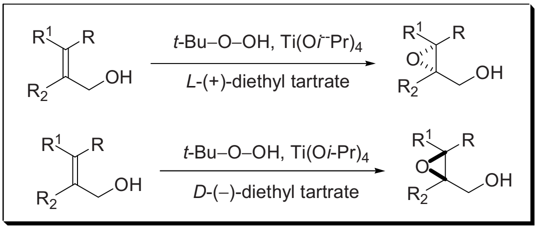
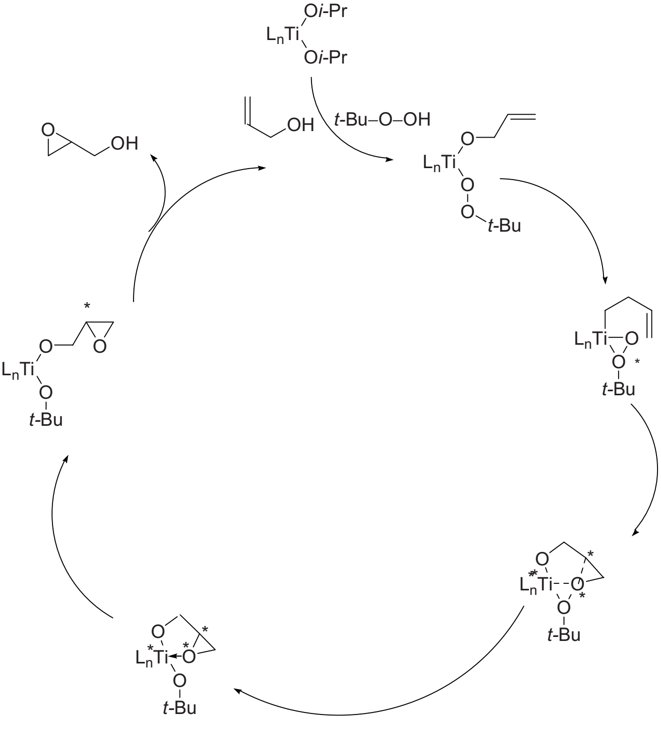
Sharpless asymmetric epoxidation

Enantioselective epoxidation of allylic alcohols using *t*-butyl peroxide, titanium tetra-*iso*-propoxide, and optically pure diethyl tartrate.

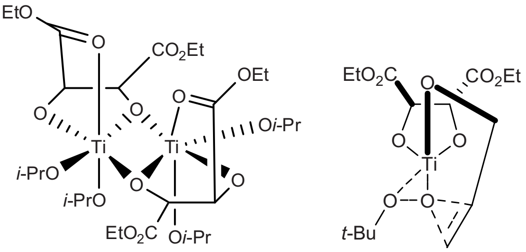


The catalytic cycle:

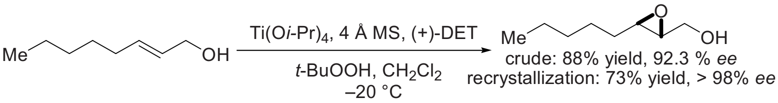


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_234,

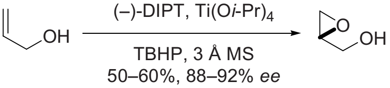
The putative active catalyst and the transition state:



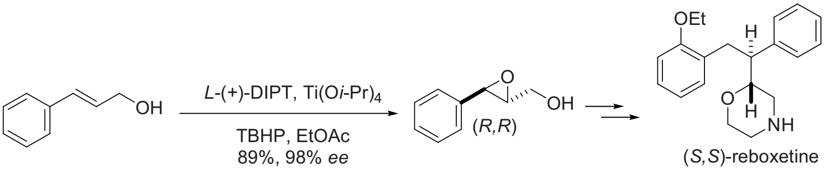
Example 1[3]



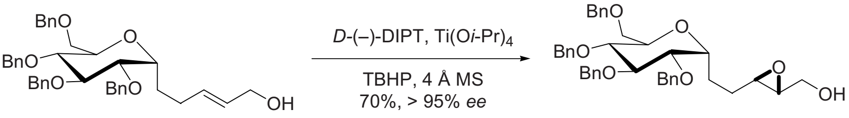
Example 2[3]



Example 3[11]



Example 4[12]



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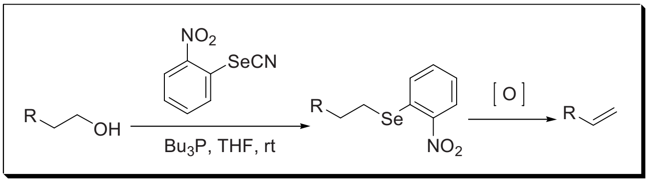
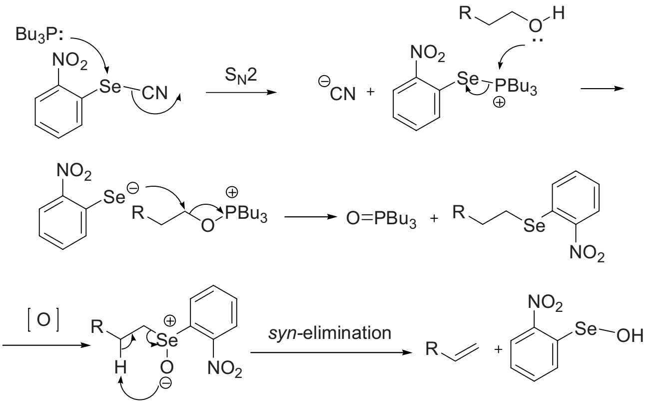
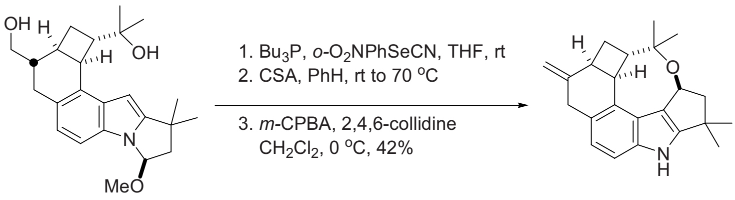
Sharpless olefin synthesis

Olefin synthesis from the *syn*-oxidative elimination of *o*-nitrophenyl selenides, which may be prepared using *o*-nitrophenyl selenocyanate and Bu_3P, among other methods.

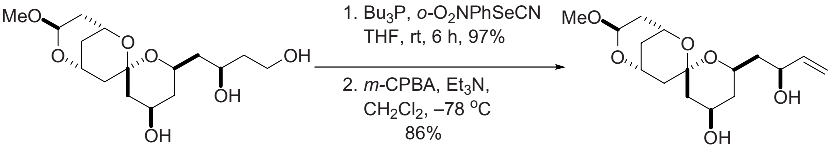




Example 1[3]



Example 2[6]



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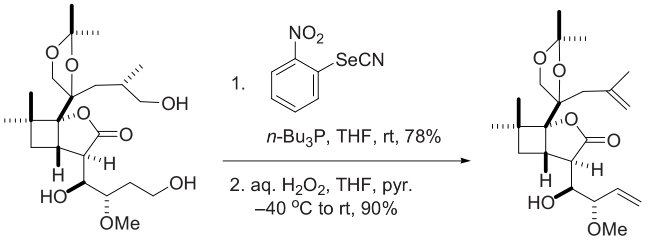
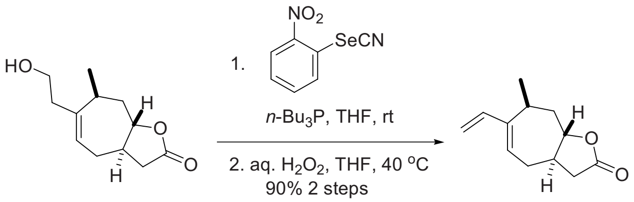
Example 3[9]



Example 4[10]



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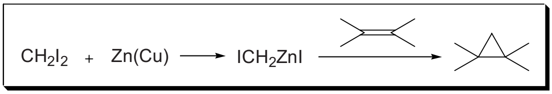
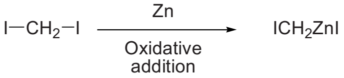
Simmons–Smith reaction

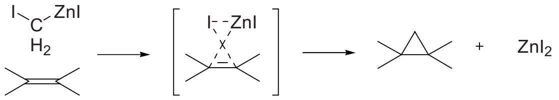
Cyclopropanation of olefins using CH_2I_2 and Zn(Cu).



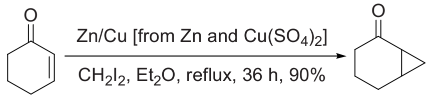


Simmons–Smith reagent

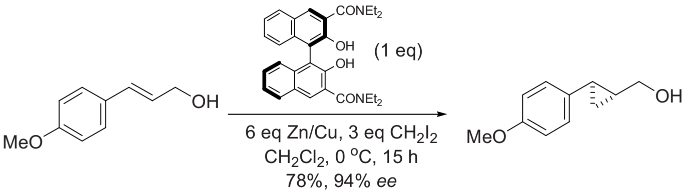
$$2\ ICH_2ZnI \rightleftharpoons (ICH_2)_2Zn + ZnI_2$$



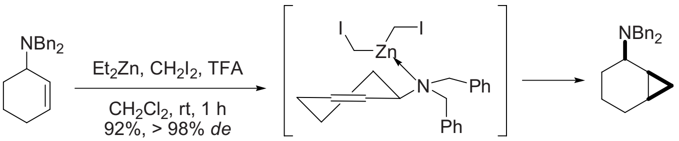
Example 1[2]



Example 2, An asymmetric version[3]



Example 3, Diastereoselective Simmons–Smith cyclopropanations of allylic amines and carbamates[9]



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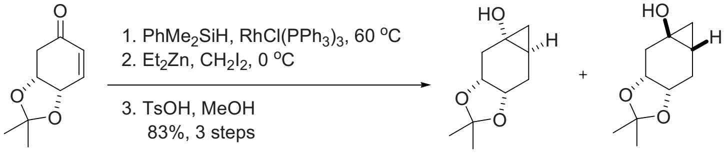
Example 4[10]



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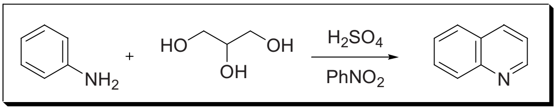
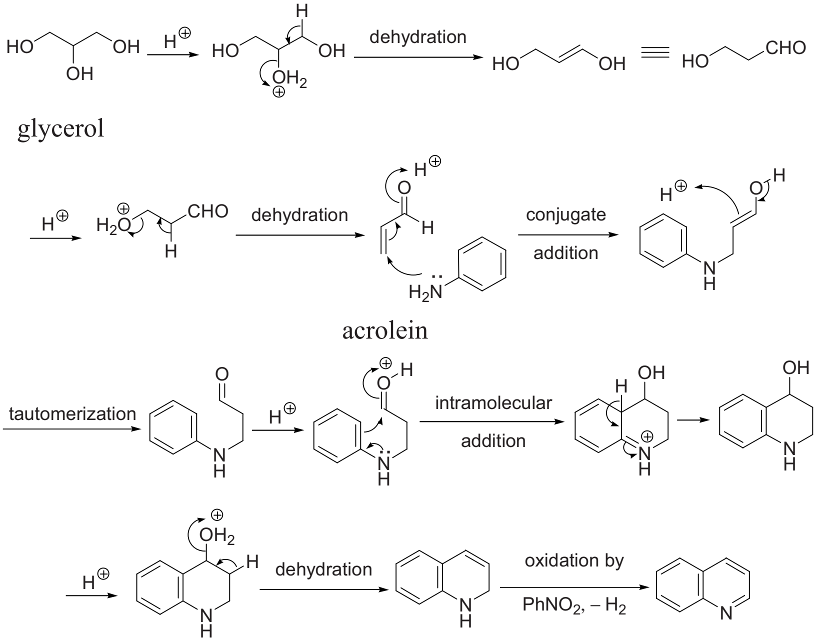
Skraup quinoline synthesis

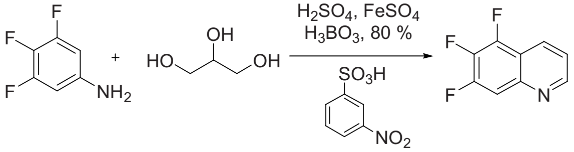
Quinoline from aniline, glycerol, sulfuric acid and oxidizing agent (e.g. $PhNO_2$).





For an alternative mechanism, see that of the Doebner–von Miller reaction (page 196).

Example 1[5]



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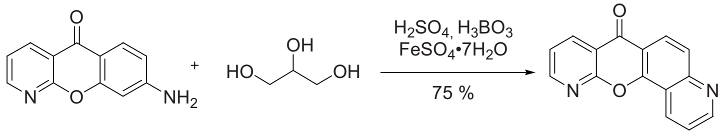
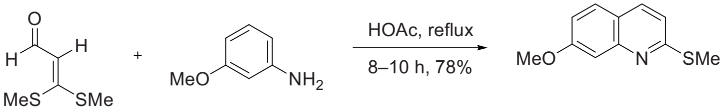
Example 2[6]



Example 3, A modified Skraup quinoline synthesis[8]



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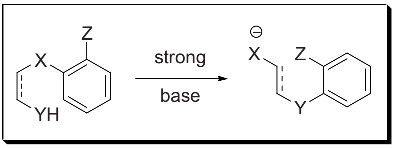
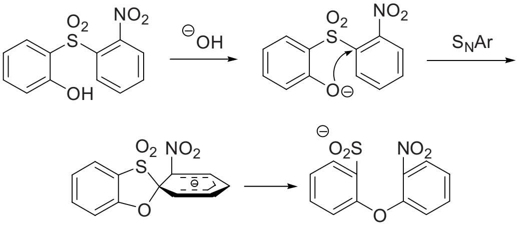
Smiles rearrangement

Intramolecular nucleophilic aromatic rearrangement. General scheme:



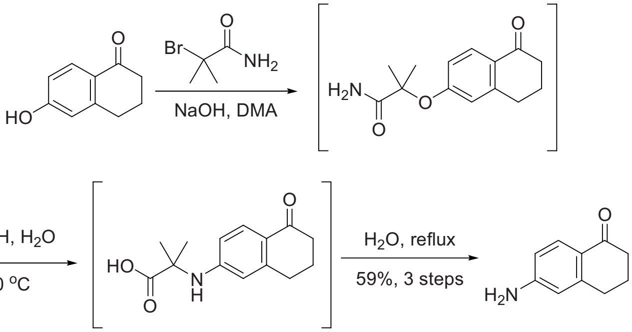
X = S, SO, SO_2, O, CO_2
YH = OH, NHR, SH, CH_2R, CONHR
Z = NO_2, SO_2R

e.g.:

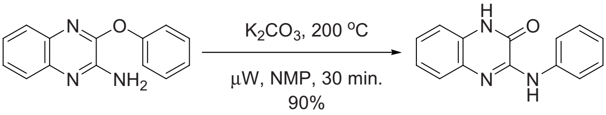


spirocyclic anion intermediate (Meisenheimer complex)

Example 1[7]



Example 2, Microwave Smiles rearrangement[9]



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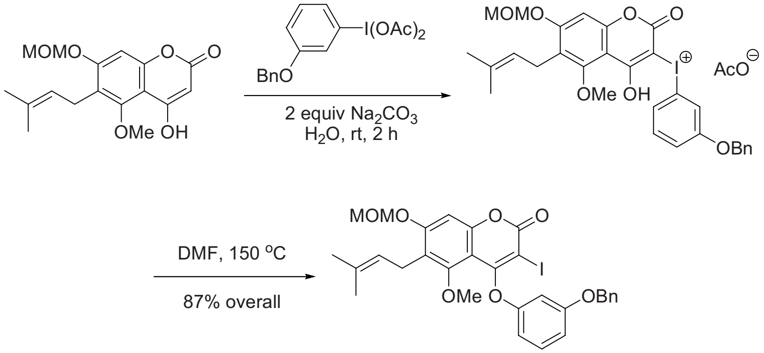
Example 3[10]



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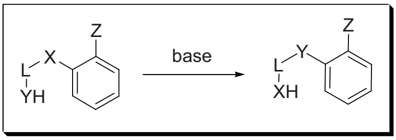
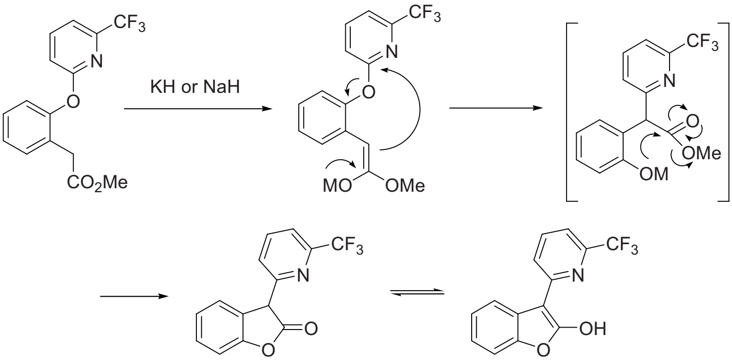
Truce–Smile rearrangement

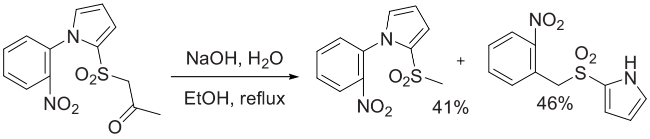
A variant of the Smiles rearrangement where Y is carbon:



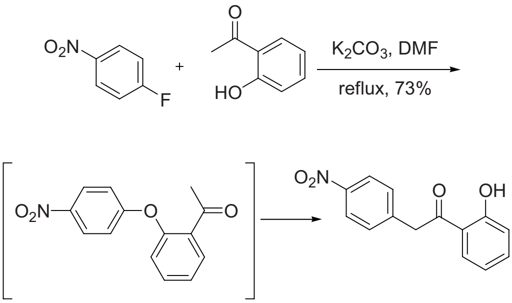
Example 1[6]



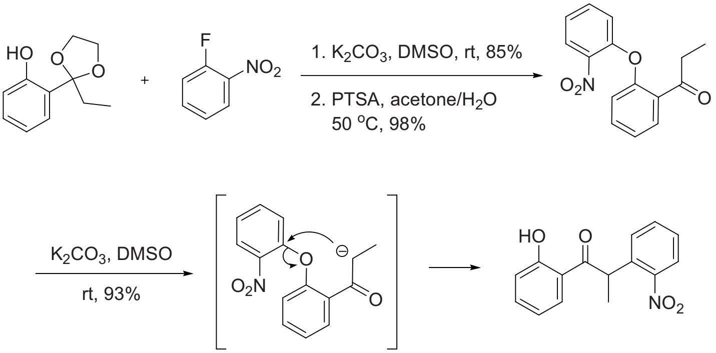
Example 2[7]



Example 3[8]



Example 4[10]



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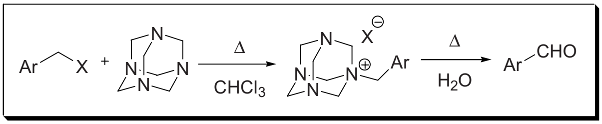
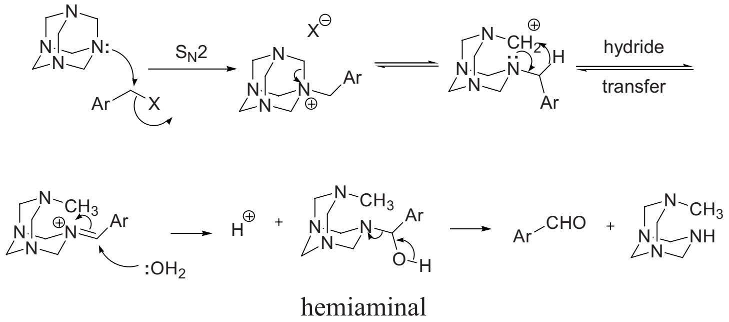
Sommelet reaction

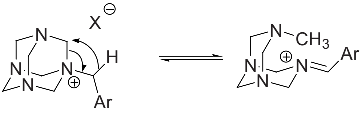
Transformation of benzyl halides to the corresponding benzaldehydes with the aide of hexamethylenetetramine. *Cf.* Delépine amine synthesis (page 171).



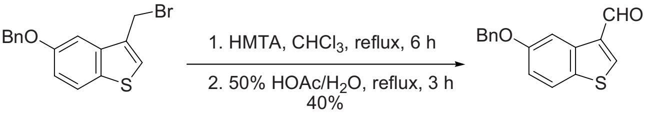
hexamethylenetetramine



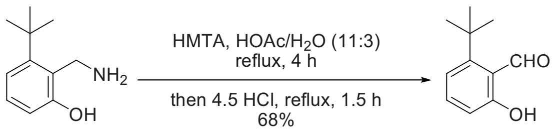
The hydride transfer and the ring-opening of hexamethylenetetramine may occur in a synchronized fashion:



Example 1[3]

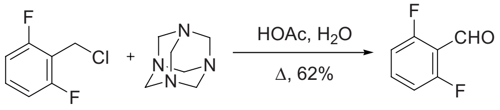


Example 2[4]

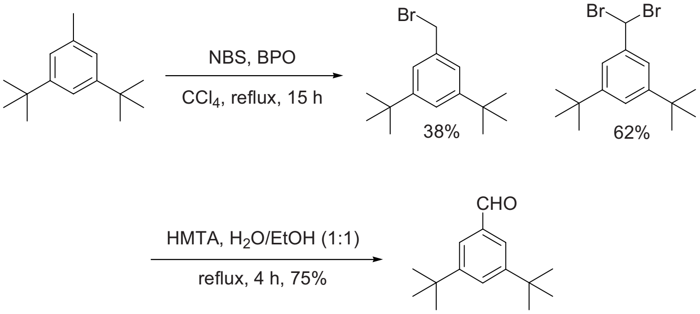


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_239,

Example 3[7]



Example 4[8]



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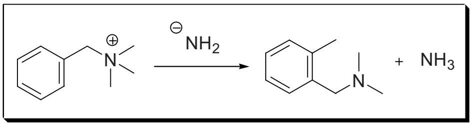
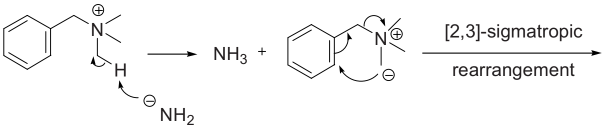
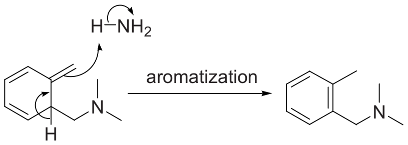
Sommelet–Hauser rearrangement

[2,3]-Wittig rearrangement of benzylic quaternary ammonium salts upon treatment with alkali metal amides *via* the ammonium ylide intermediates.





ammonium ylide



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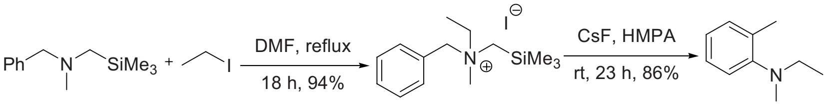

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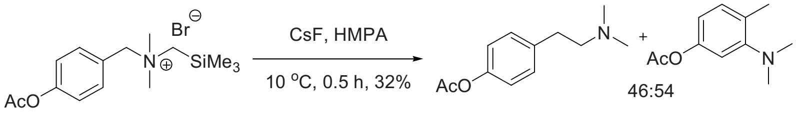

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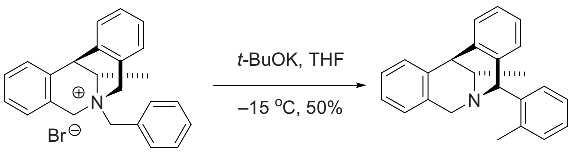

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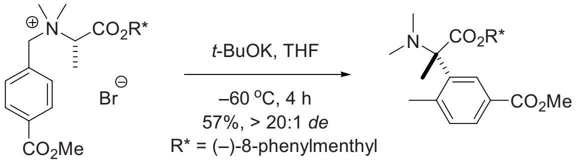
Example 4[10]



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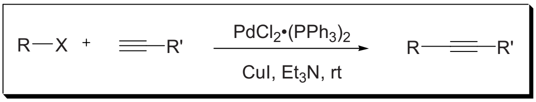
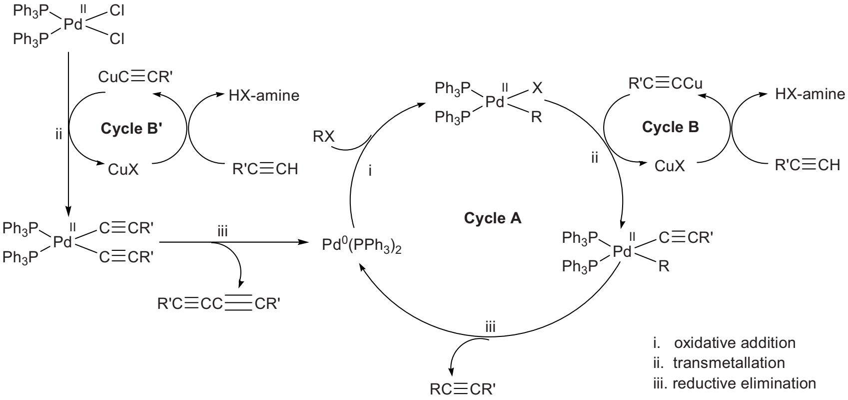
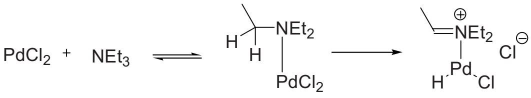
Sonogashira reaction

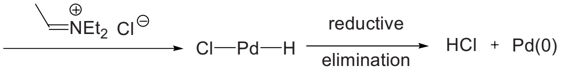
Pd/Cu-catalyzed cross-coupling of organohalides with terminal alkynes. *Cf.* Cadiot–Chodkiewicz coupling and Castro–Stephens reaction. The Castro–Stephens coupling uses stoichiometric copper, whereas the Sonogashira variant uses catalytic palladium and copper.





Note that Et_3N may reduce Pd(II) to Pd(0) as well, where Et_3N is oxidized to the iminium ion at the same time:





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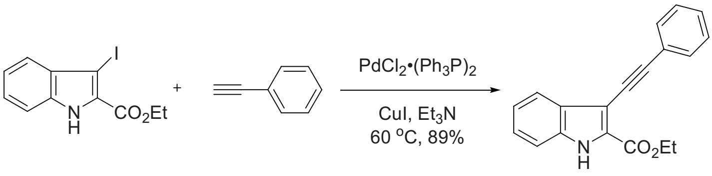

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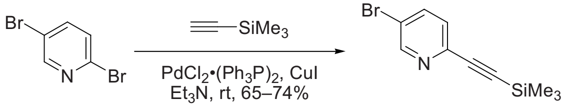
Example 2[3]



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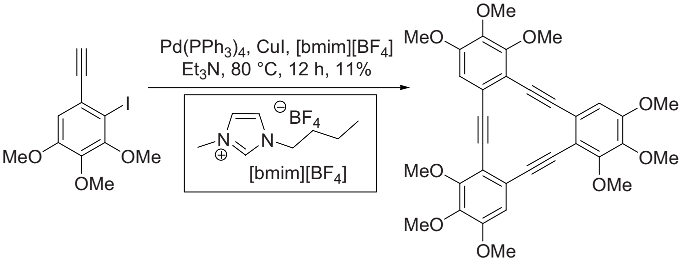

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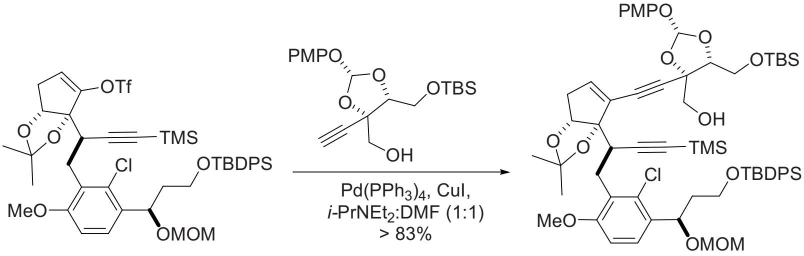

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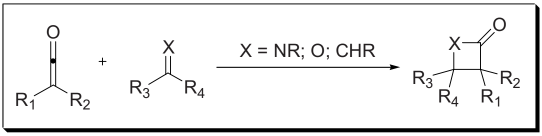
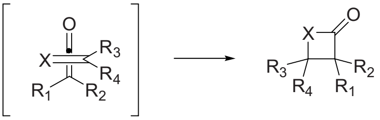
Staudinger ketene cycloaddition

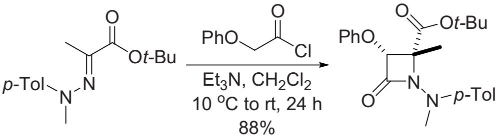
[2 + 2]-Cycloaddition of ketene and imine to form β-lactam. Other coupling partners for ketenes include: olefin to give cyclobutanone and carbonyl to give β-lactone.





puckered transition state:

Example 1[6]



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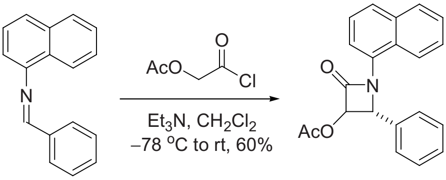

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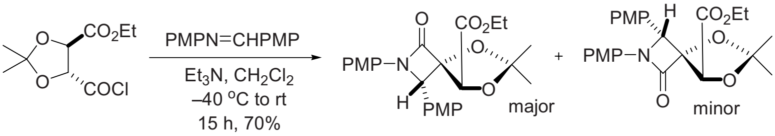

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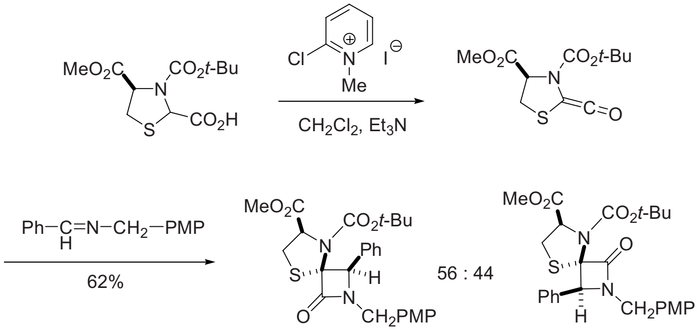

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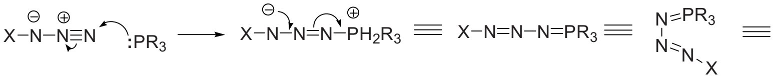
Staudinger reduction

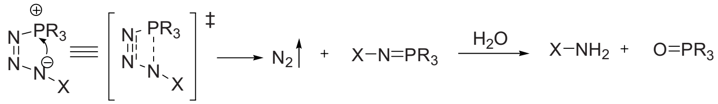
Phosphazo compounds (e.g., iminophosphoranes) from the reaction of tertiary phosphine (e.g., Ph_3P) with organic azides.

$$\boxed{X{-}N_3 \xrightarrow{PR_3} X{-}N{=}N{-}N{=}PR_3 \xrightarrow{-\ N_2} X{-}N{=}PR_3}$$

phosphazide

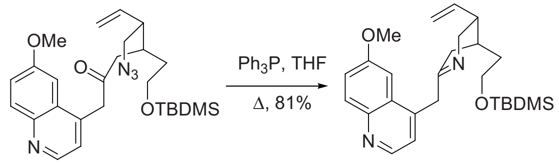


phosphazide



4-membered ring transition state

Example 1[2]



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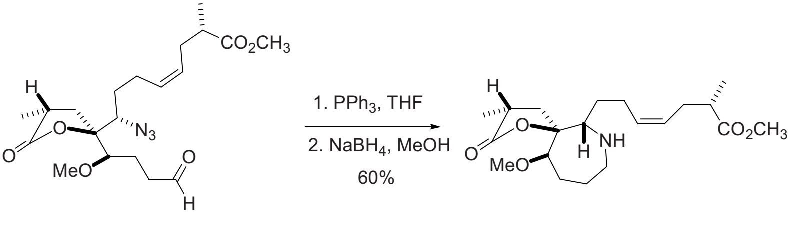

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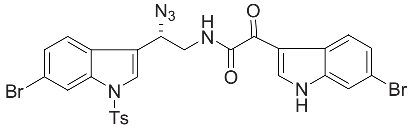
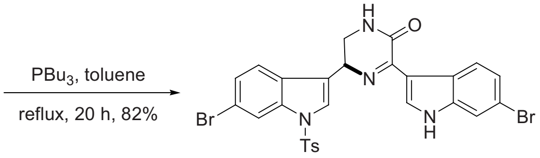


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_243,



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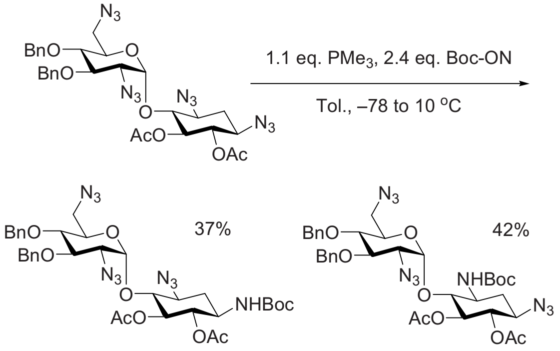

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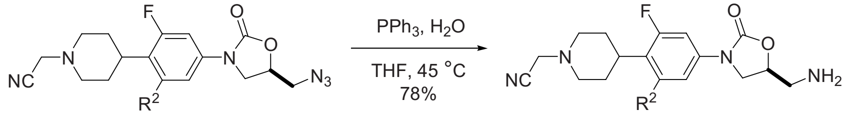

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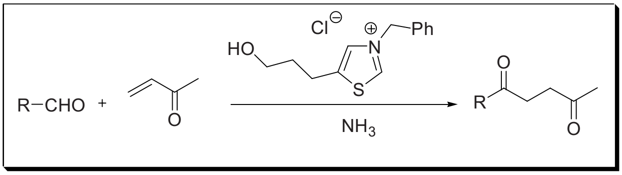
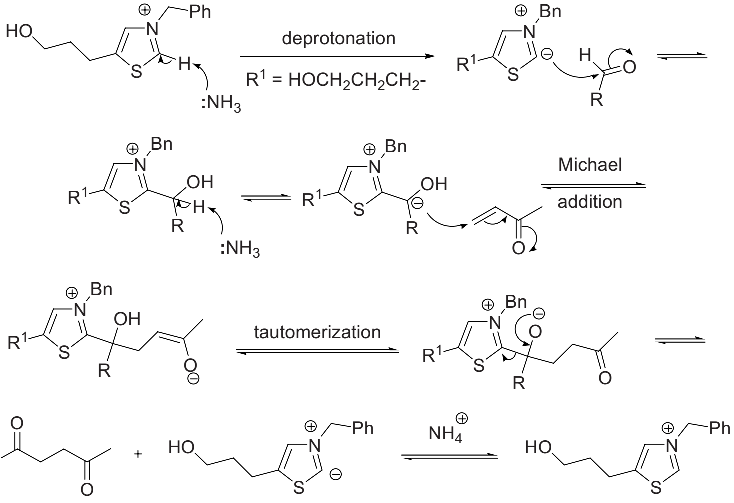
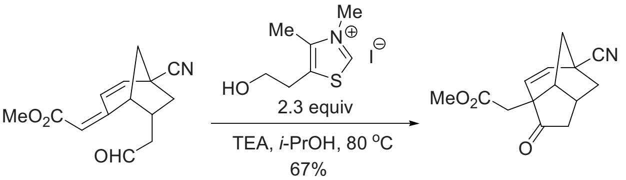
Stetter reaction

1,4-Dicarbonyl derivatives from aldehydes and α,β-unsaturated ketones and esters. The thiazolium catalyst serves as a safe surrogate for $^{-}$CN. Also known as the Michael–Stetter reaction. *Cf.* Benzoin condensation.

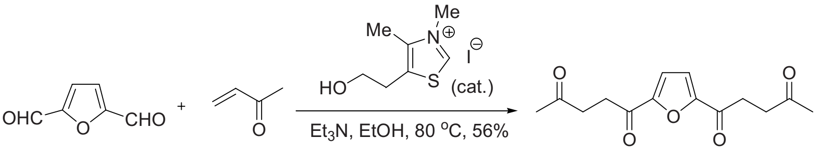




Example 1, Intramolecular Stetter reaction[2]



Example 2[3]



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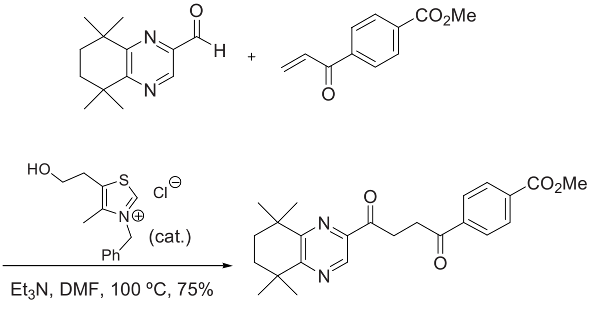
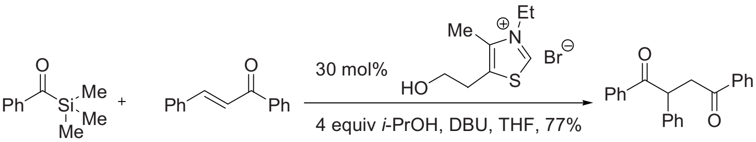
Example 3[5]



Example 4, Sila-Stetter reaction[9]



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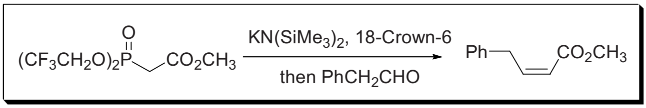
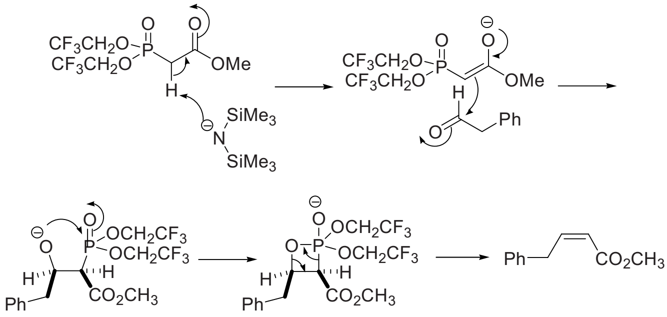
Still–Gennari phosphonate reaction

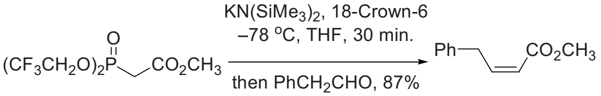
A variant of the Horner–Emmons reaction using bis(trifluoroethyl)phosphonate to give *Z*-olefins.





erythro isomer, kinetic adduct

Example 1[2]



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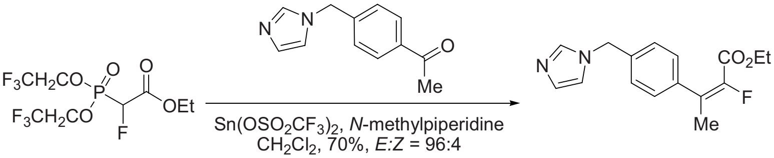
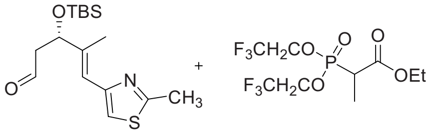
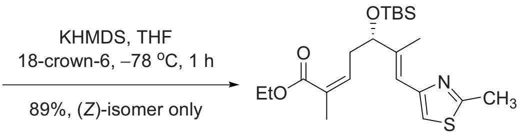


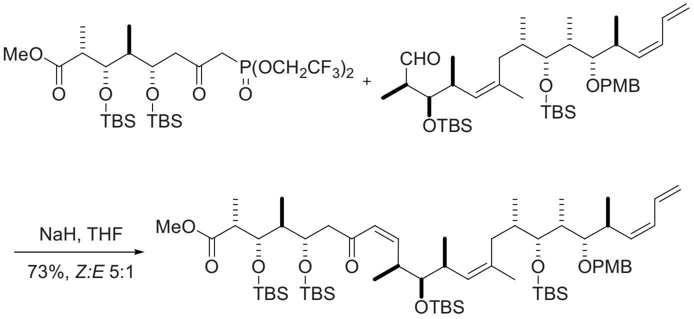
Example 3[4]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_245,



Example 4[9]



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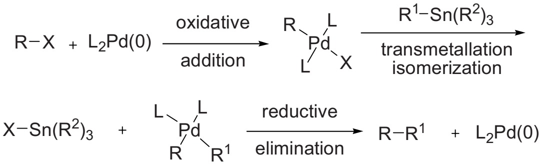
Stille coupling

Palladium-catalyzed cross-coupling reaction of organostannanes with organic halides, triflates, *etc*. For the catalytic cycle, see Kumada coupling on page 325.

$$\boxed{R{-}X \quad + \quad R^1{-}Sn(R^2)_3 \xrightarrow{Pd(0)} R{-}R^1 \quad + \quad X{-}Sn(R^2)_3}$$



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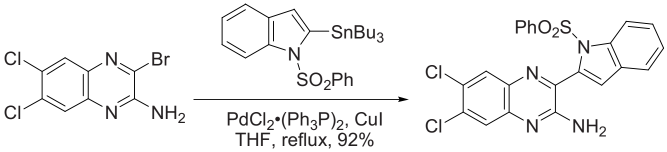

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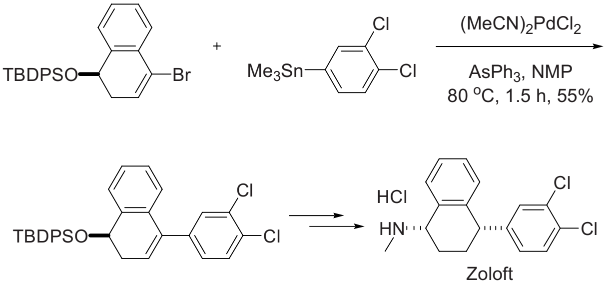
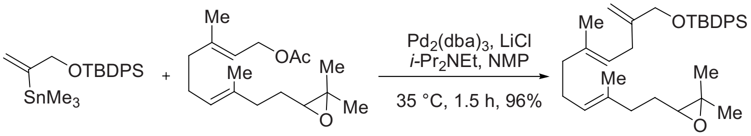


Example 3, π-Allyl Stille coupling[8]



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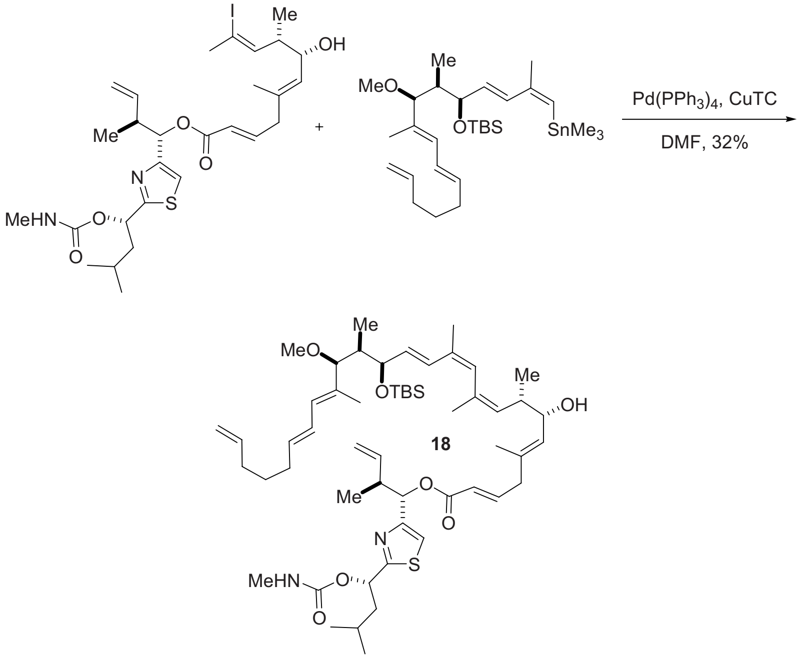
Example 4[9]



18

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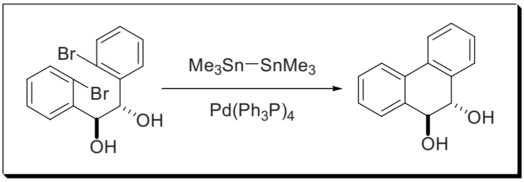
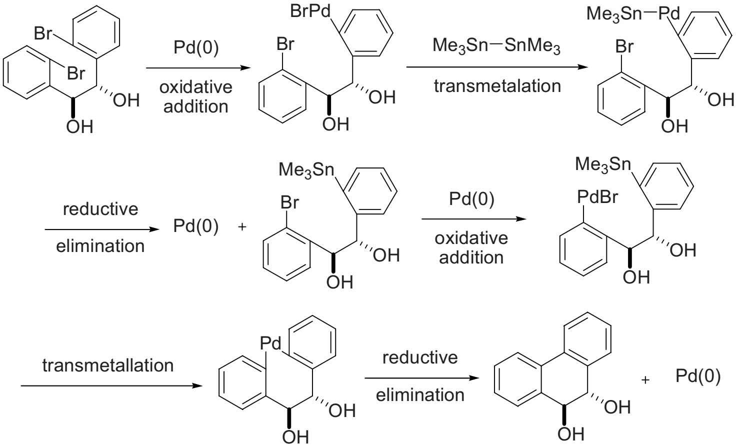
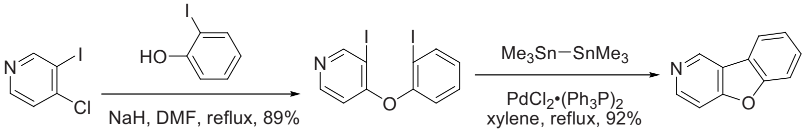
Stille−Kelly reaction

Palladium-catalyzed intramolecular cross-coupling reaction of bis-aryl halides using ditin reagents.





Example 1[6]



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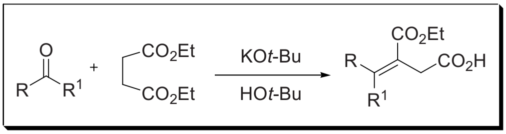
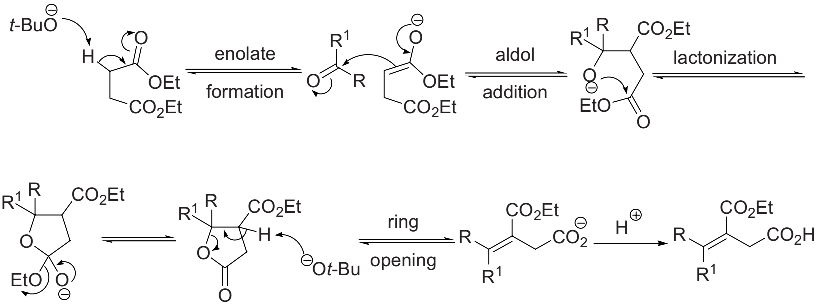
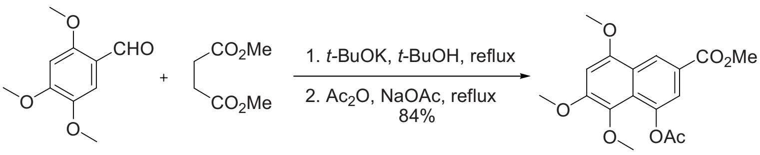
Stobbe condensation

Condensation of diethyl succinate and its derivatives with carbonyl compounds in the presence of bases.

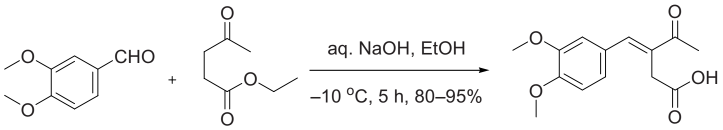




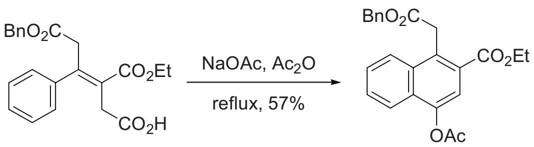
Example 1, Stobbe condensation and cyclization[5]



Example 2, Stobbe condensation[6]



Example 3, Cyclization of the Stobbe product[7]



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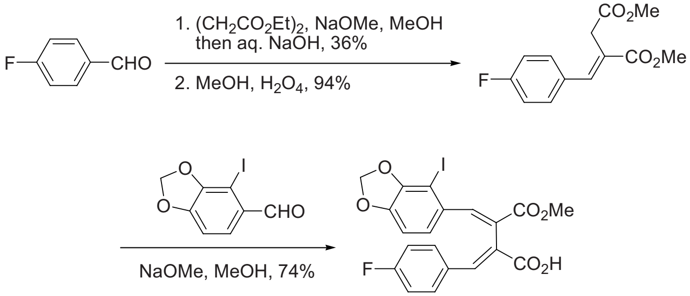
Example 4, Two sequential Stobbe condensations[9]



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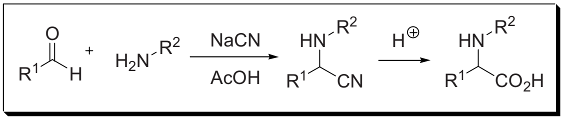
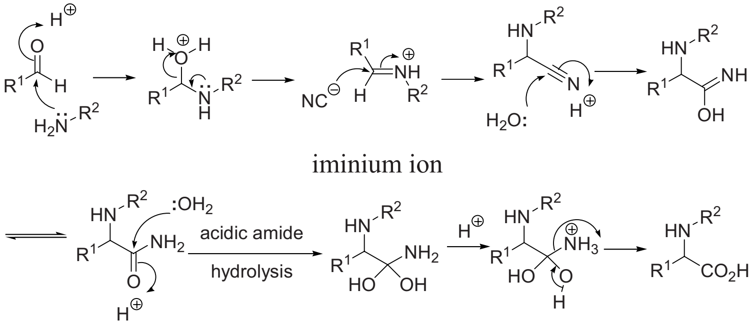
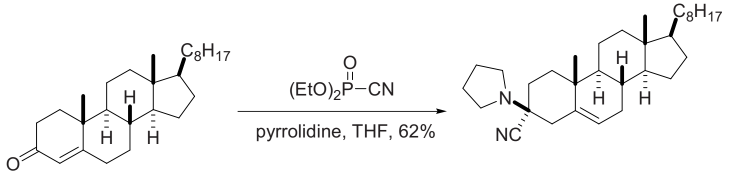
Strecker amino acid synthesis

Sodium cyanide-promoted condensation of aldehyde, or ketone, with amine to afford α-amino nitrile, which may be hydrolyzed to α-amino acid.

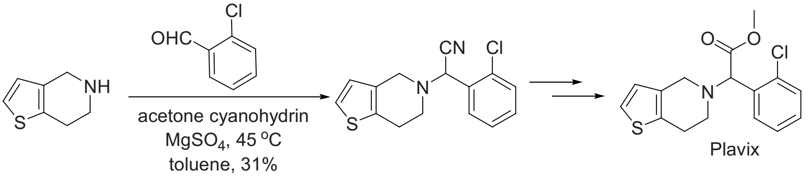




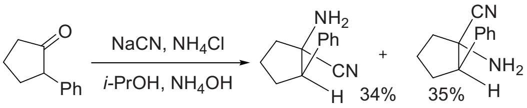
Example 1, Soluble cyanide source[2]



Example 2[3]



Example 3[8]



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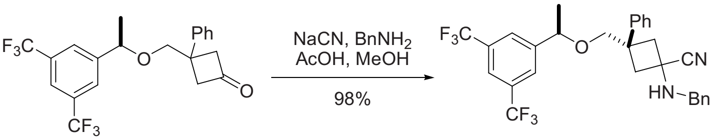
Example 4[9]



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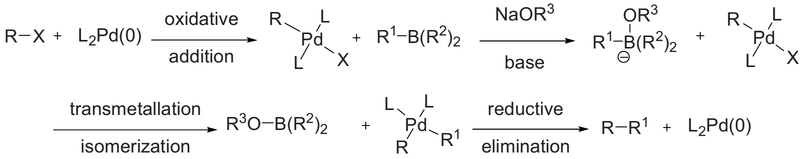
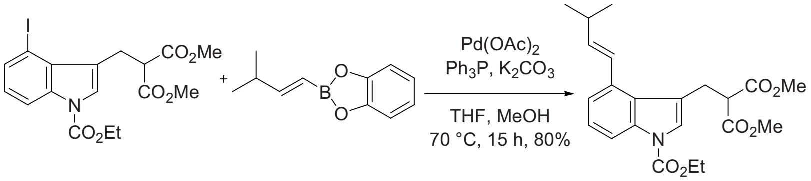
Suzuki–Miyaura coupling

Palladium-catalyzed cross-coupling reaction of organoboranes with organic halides, triflates, *etc*. In the presence of a base (transmetallation is reluctant to occur without the activating effect of a base). For the catalytic cycle, see Kumada coupling on page 325.

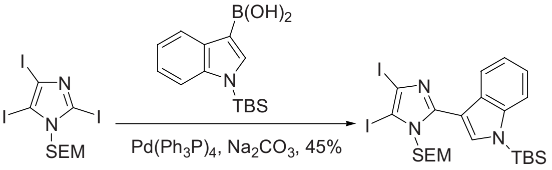
$$\boxed{R{-}X \; + \; R^1{-}B(R^2)_2 \xrightarrow[\text{NaOR}^3]{L_2Pd(0)} R{-}R^1}$$



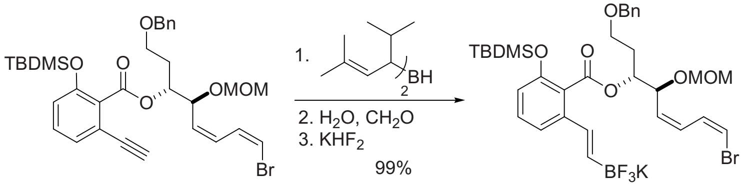
Example 1[2]



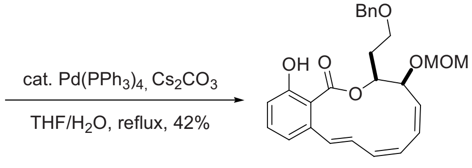
Example 2[4]



Example 3, Intramolecular Suzuki–Miyaura coupling[8]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_250,



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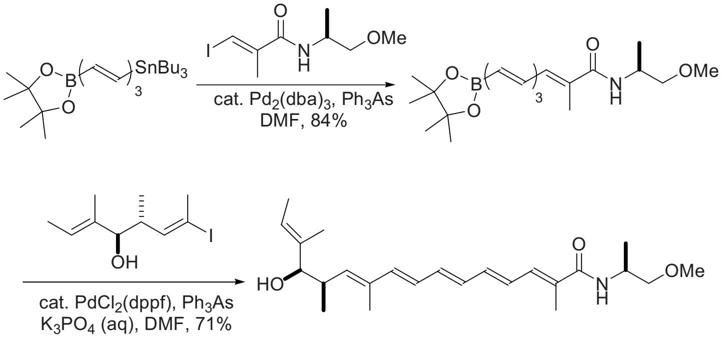

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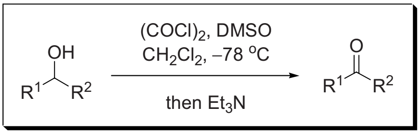
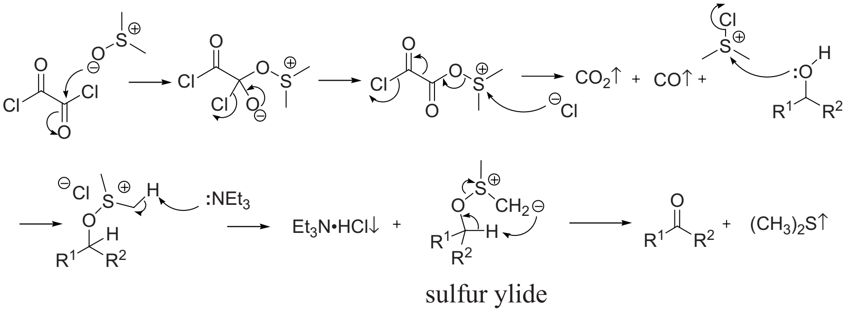
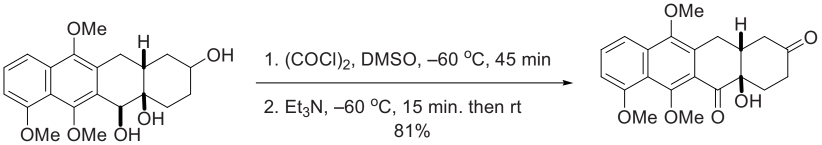
Swern oxidation

Oxidation of alcohols to the corresponding carbonyl compounds using $(COCl)_2$, DMSO, and quenching with Et_3N.

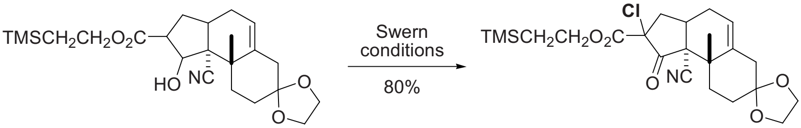




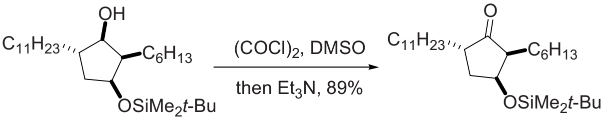
Example 1[2]



Example 2[3]



Example 3[5]



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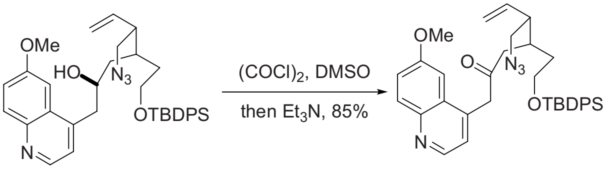
Example 4[7]



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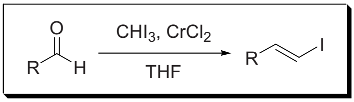
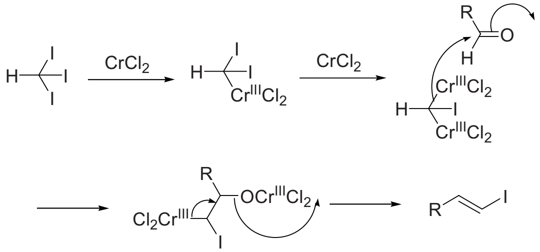
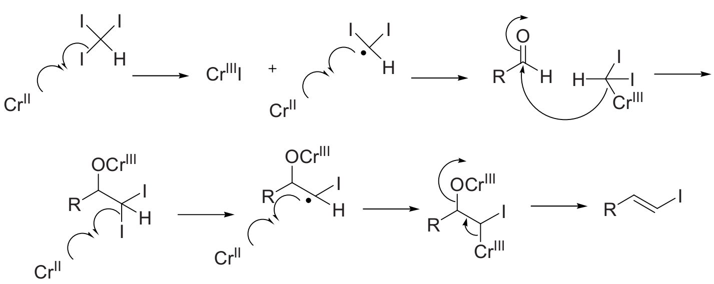
Takai reaction

Stereoselective conversion of an aldehyde to the corresponding *E*-vinyl iodide using CHI_3 and $CrCl_2$.

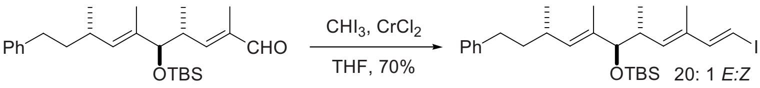




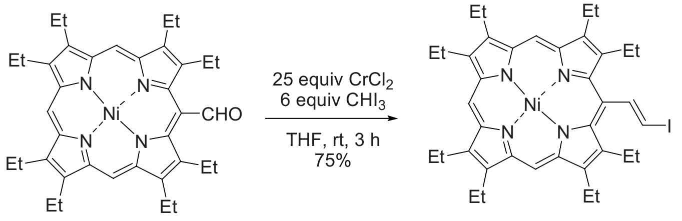
A radical mechanism was recently proposed[10]



Example 1[2]

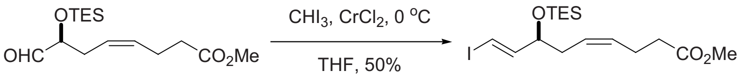


Example 2[3]

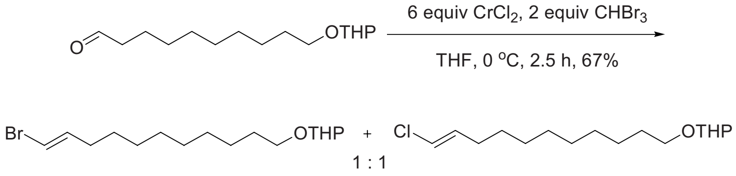


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_252,

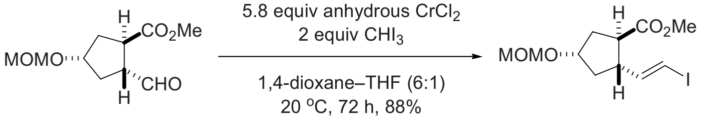
Example 3[4]



Example 4, A Br/Cl variant[9]



Example 5[10]



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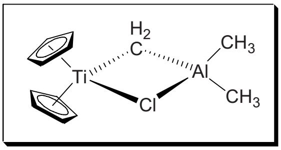
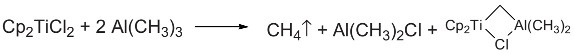
Tebbe's reagent

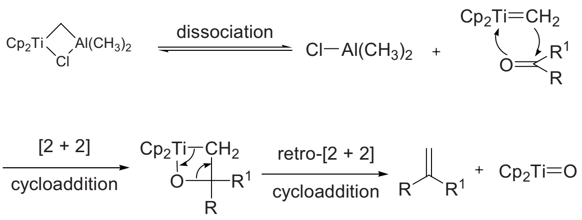
The Tebbe's reagent, μ-chlorobis(cyclopentadienyl)(dimethylaluminium)-μ-methylenetitanium, transforms a carbonyl compound to the corresponding *exo*-olefin.



Preparation:[2,6]



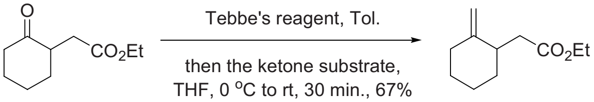
Mechanism:[3]



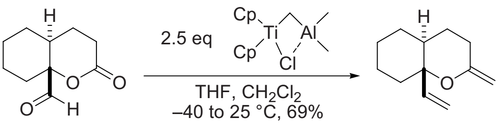
oxatitanacyclobutane

formation of the strong Ti=O is the driving force.

Example 1, Ketone[2]

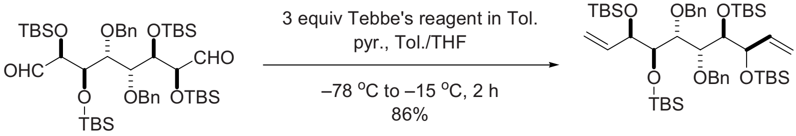


Example 2, Double Tebbe[4]

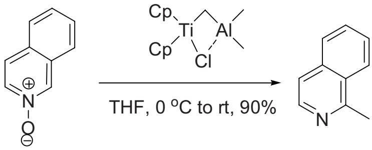


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_253,

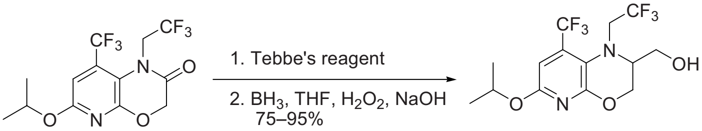
Example 3, Double Tebbe[5]



Example 4, *N*-Oxide[6]



Example 5, Amide[11]



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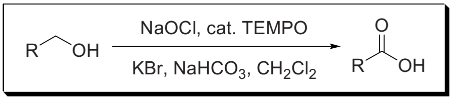
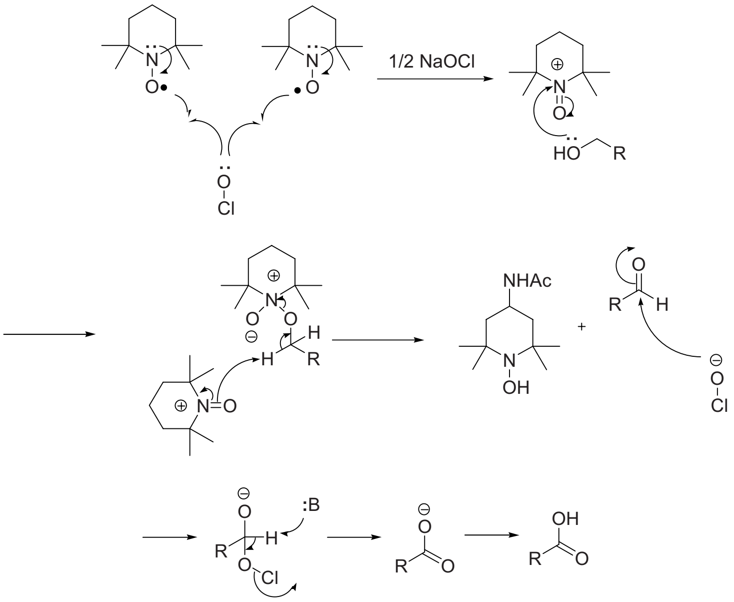
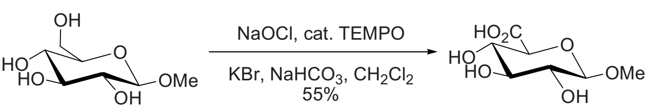
TEMPO oxidation

TEMPO = **Te**tra**m**ethyl **p**entahydropyridine **o**xide. 2,2,6,6-Tetramethylpiperidinyloxy is a stable nitroxyl radical, which serves in oxidations as catalyst





Example 1[4]



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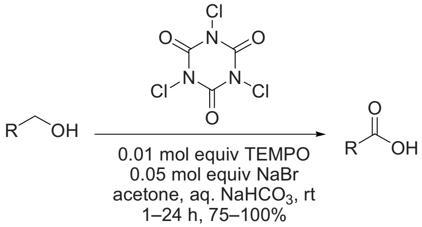
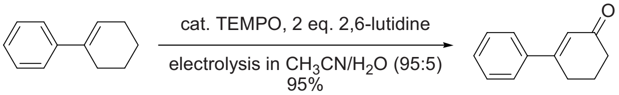
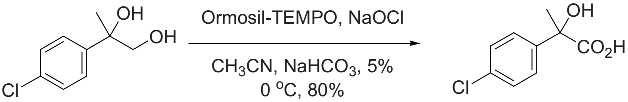
Example 2, Trichloroisocyanuric/TEMPO Oxidation[5]



Example 3[8]



Example 4[10]



"Ormosil-TEMPO" is a sol-gel hydrophobized nanostructured silica matrix doped with TEMPO

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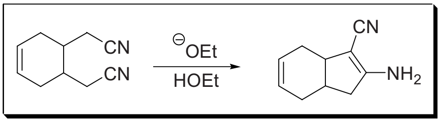
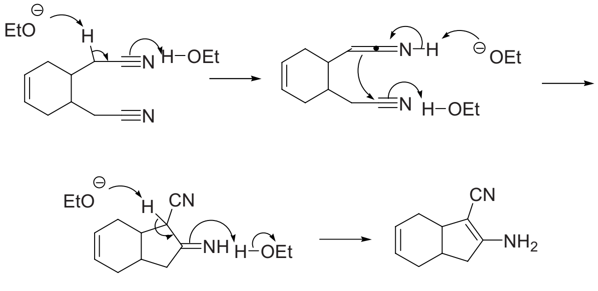
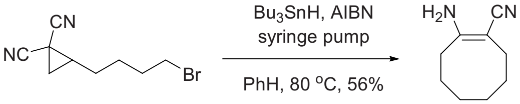
Thorpe–Ziegler reaction

The intramolecular version of the Thorpe reaction, which is base-catalyzed self-condensation of nitriles to yield imines that tautomerize to enamine.

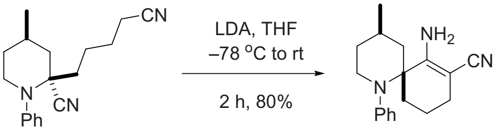




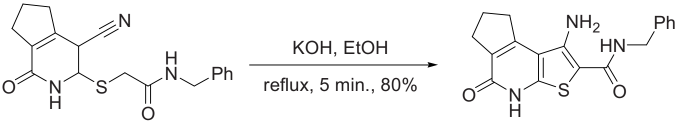
Example 1, A radical Thorpe–Ziegler reaction[2]



Example 2[5]

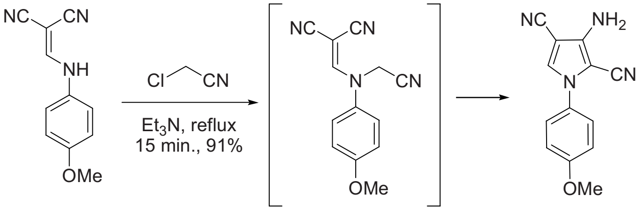


Example 3[8]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_255,

Example 4[9]



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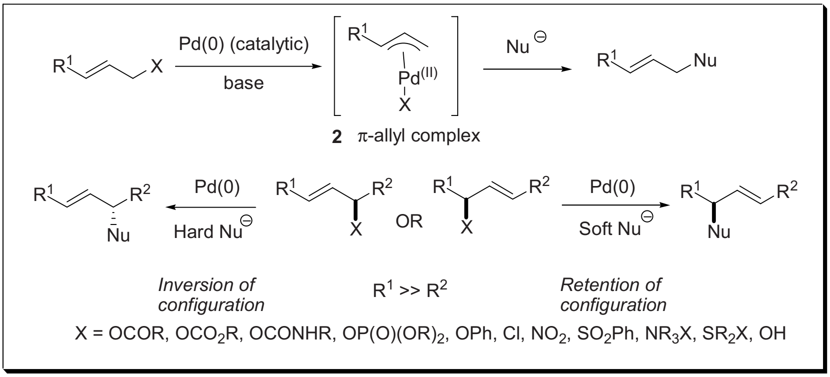
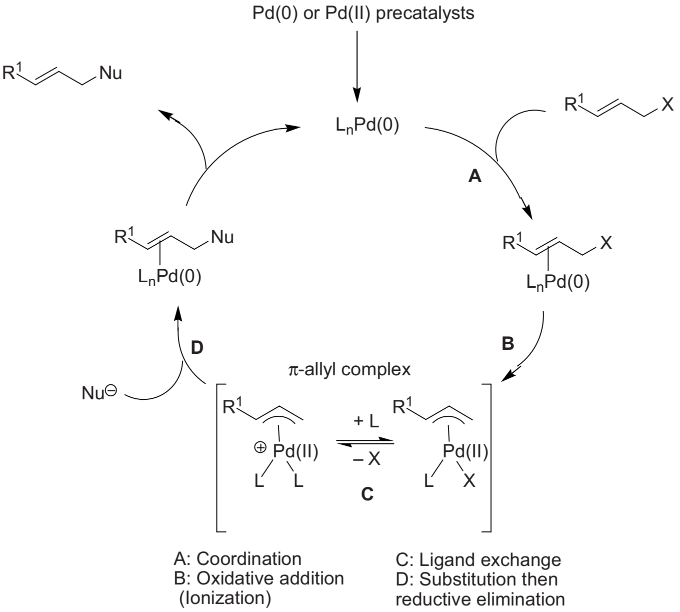
Tsuji–Trost reaction

The Tsuji–Trost reaction is the palladium-catalyzed substitution of allylic leaving groups by carbon nucleophiles. These reactions proceed via π-allylpalladium intermediates.

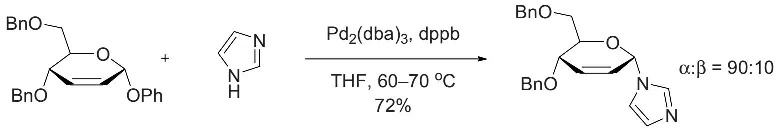


The catalytic cycle:

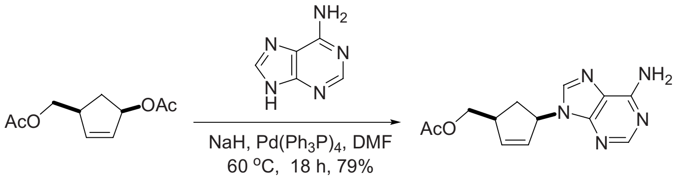


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_256,

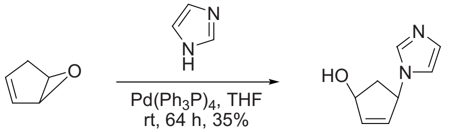
Example 1, Allylic ether[3]



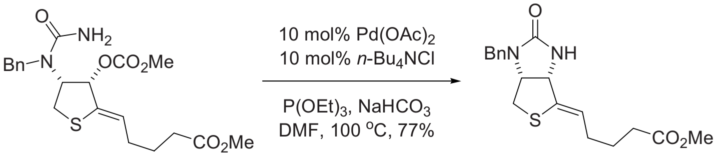
Example 2, Allylic acetate[3]



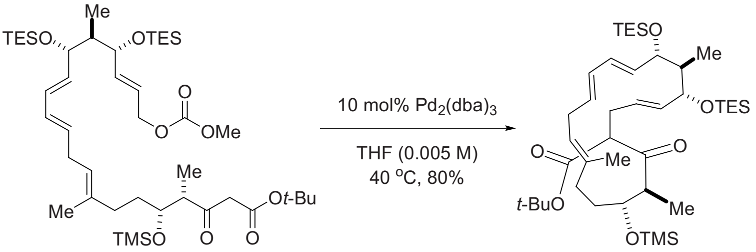
Example 3, Allylic epoxide[5]



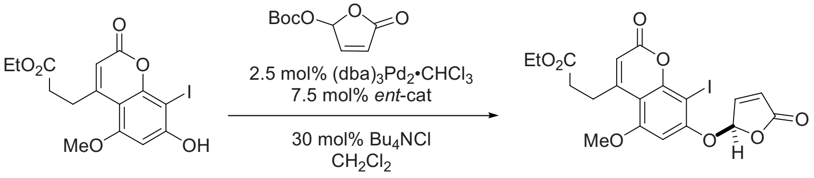
Example 4, Intramolecular Tsuji–Trost reaction[6]



Example 5, Intramolecular Tsuji–Trost reaction[7]

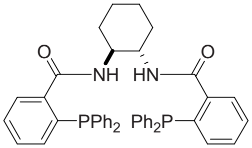


Example 6, Asymmetric Tsuji–Trost reaction[8]



89% yield, 95% *ee*

ent-cat =



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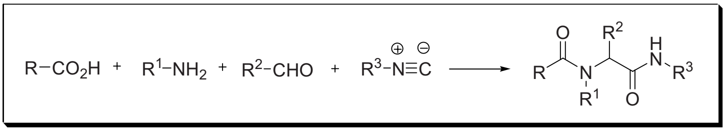
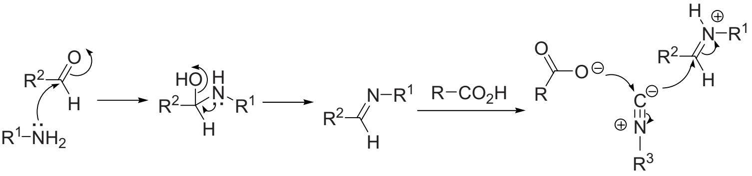
Ugi reaction

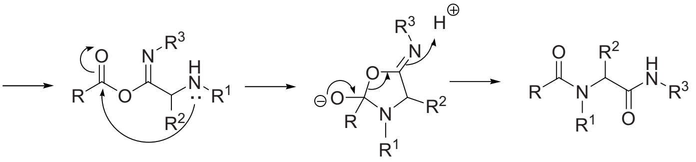
Four-component condensation (4CC) of carboxylic acids, *C*-isocyanides, amines, and carbonyl compounds to afford diamides. *Cf.* Passerini reaction.



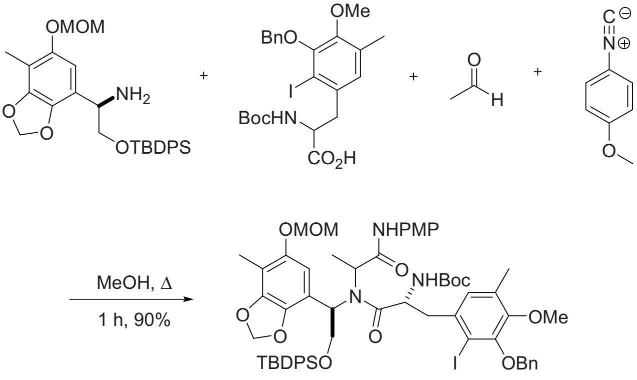
isocyanide



imine

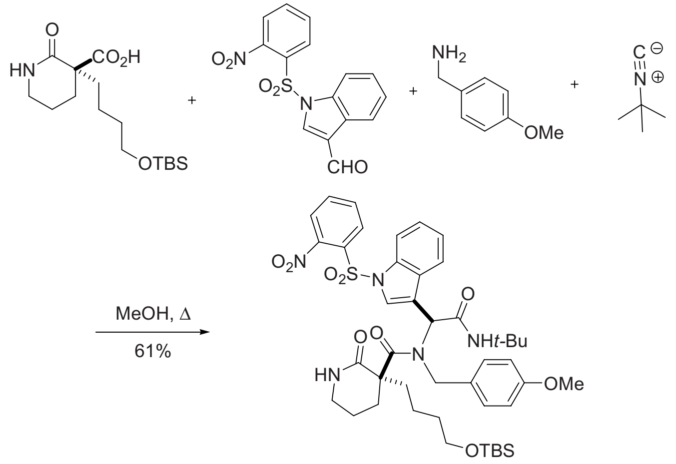


Example 1[2]

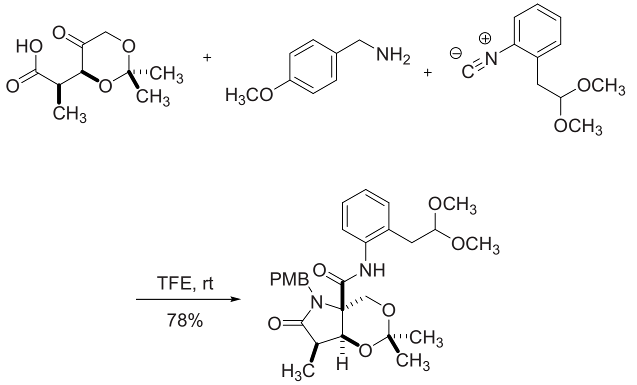


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_257,

Example 2[5]



Example 3[7]



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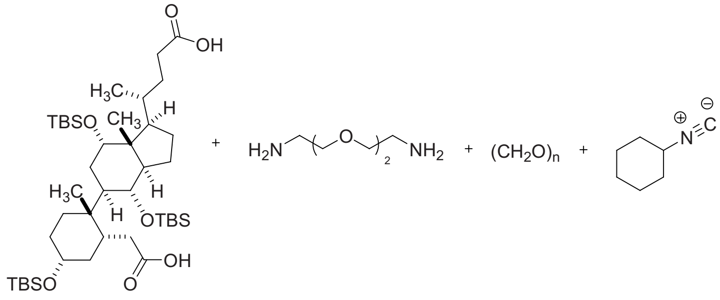

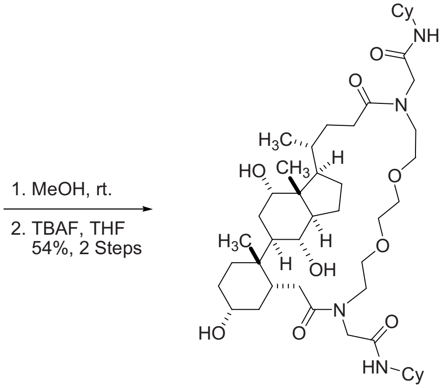

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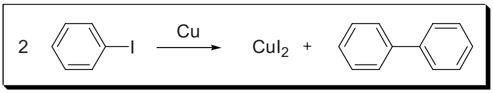
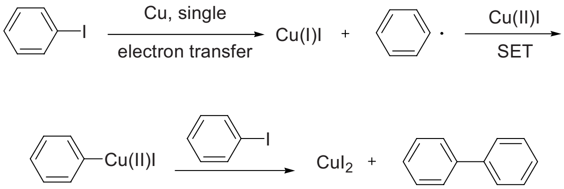
Ullmann coupling

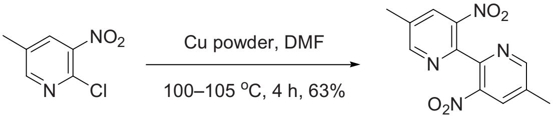
Homocoupling of aryl halides in the presence of Cu or Ni or Pd to afford biaryls.



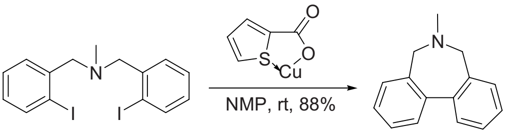


The overall transformation of PhI to PhCuI is an oxidative addition process.

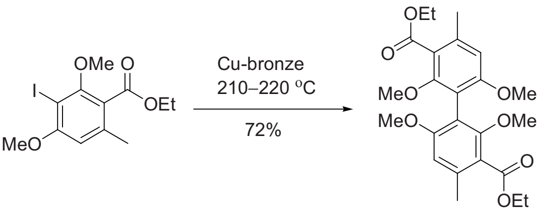
Example 1[3]



Example 2, CuTC-catalyzed Ullmann coupling[4]



Example 3[5]



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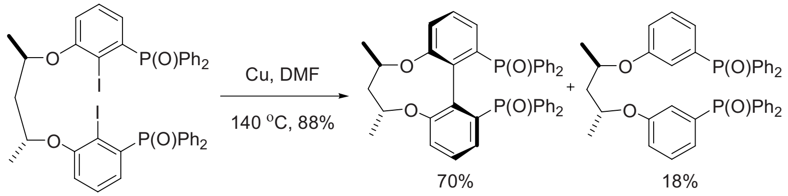
Example 4[8]



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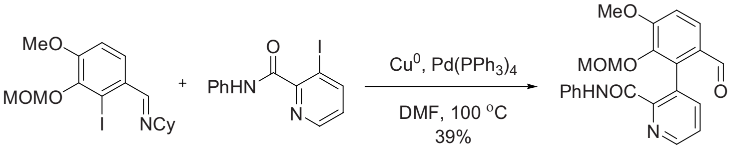

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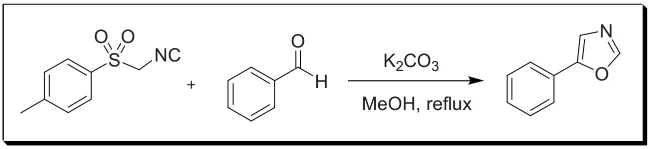
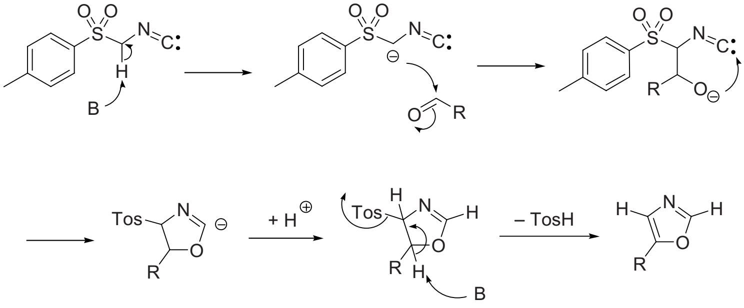
van Leusen oxazole synthesis

5-Substituted oxazoles through the reaction of *p*-tolylsulfonylmethyl isocyanide (TosMIC, also known as the van Leusen reagent) with aldehydes in protic solvents at refluxing temperatures.





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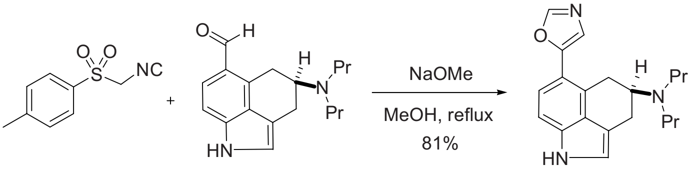

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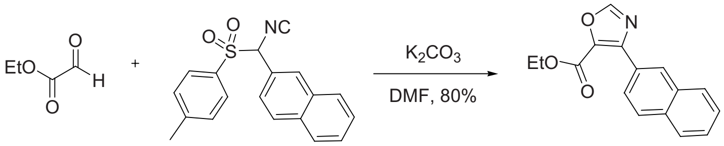

J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_259,

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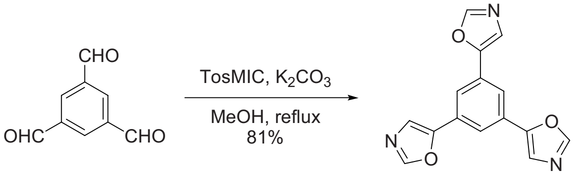

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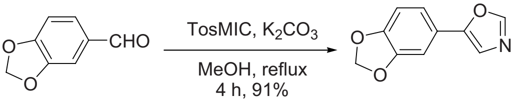

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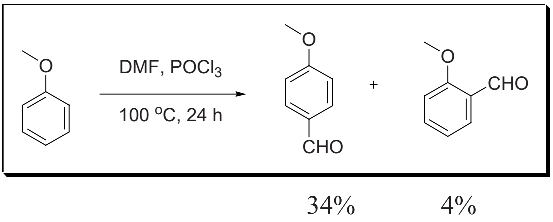
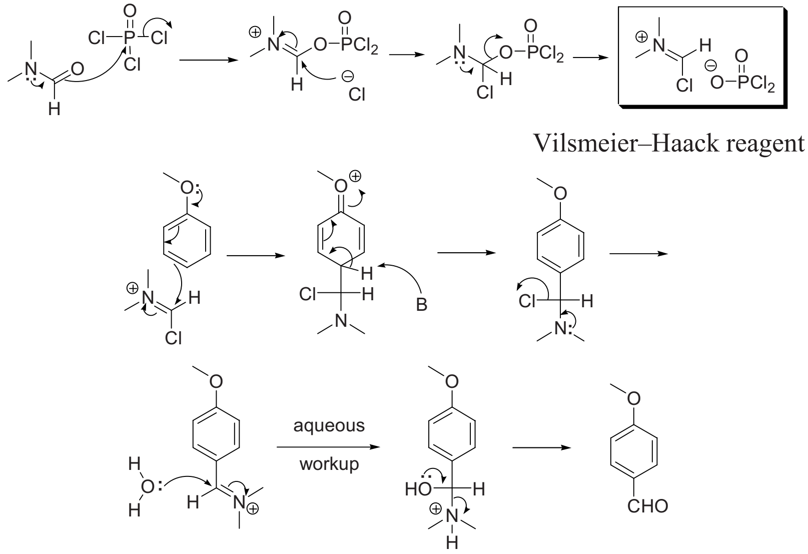
Vilsmeier–Haack reaction

The Vilsmeier–Haack reagent, a chloroiminium salt, is a weak electrophile. Therefore, the Vilsmeier–Haack reaction works better with electron-rich carbocycles and heterocycles.





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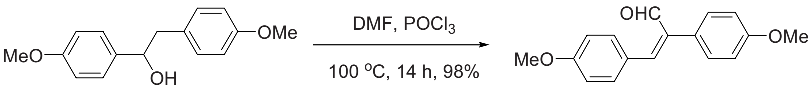

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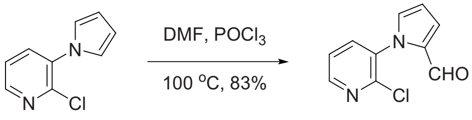

J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_260,

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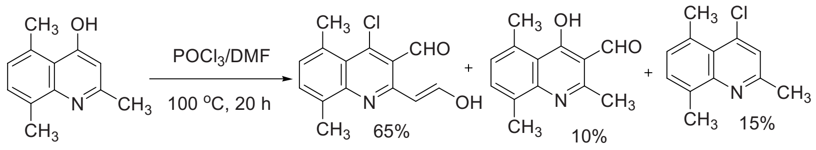

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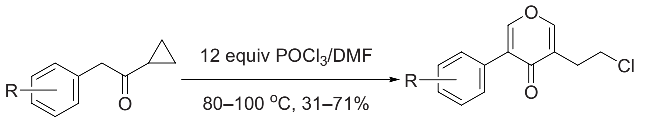

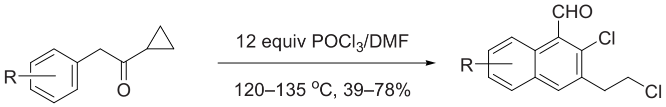

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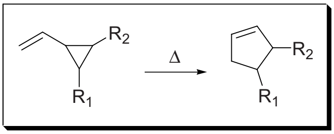
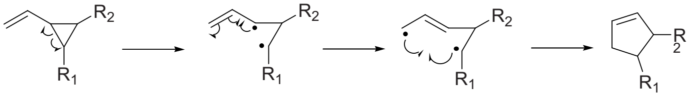
Vinylcyclopropane–cyclopentene rearrangement

Transformation of vinylcyclopropane to cyclopentene *via* a diradical intermediate.





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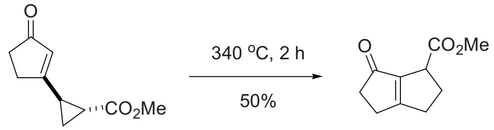

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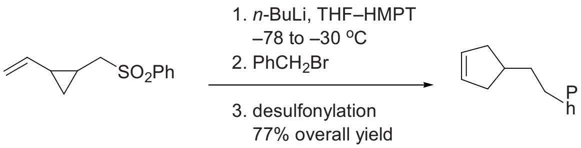

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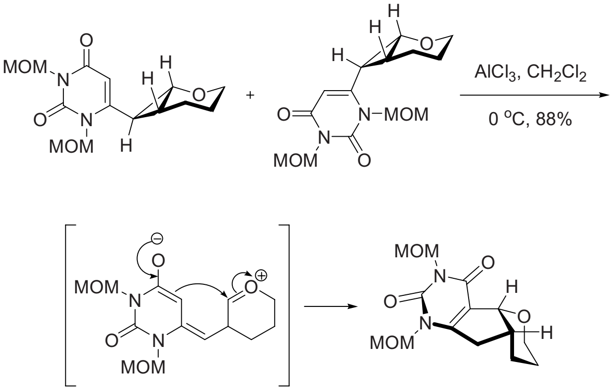
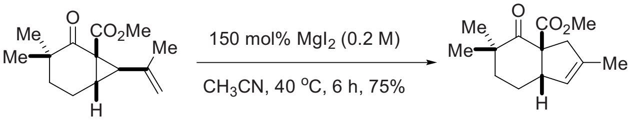


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_261,

Example 4[10]



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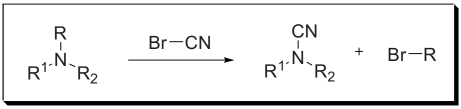
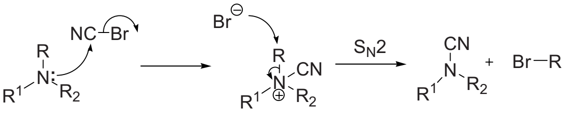
von Braun reaction

Different from the von Braun degradation reaction (amide to nitrile), the von Braun reaction refers to the treatment of tertiary amines with cyanogen bromide, resulting in a substituted cyanamide.





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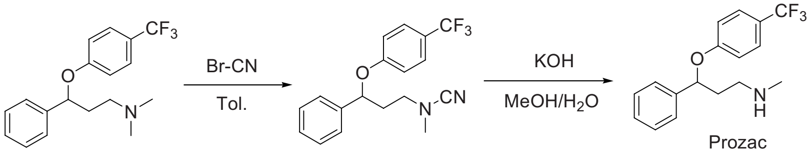

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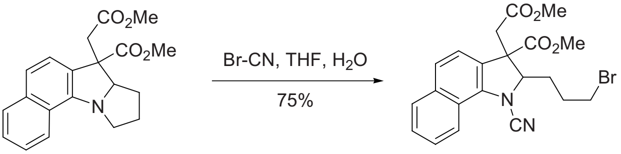

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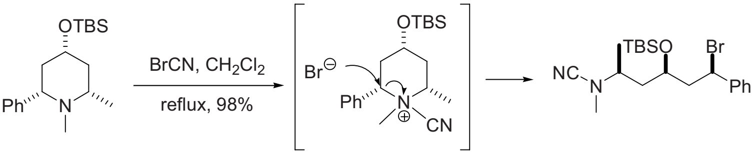

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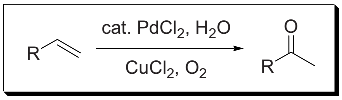
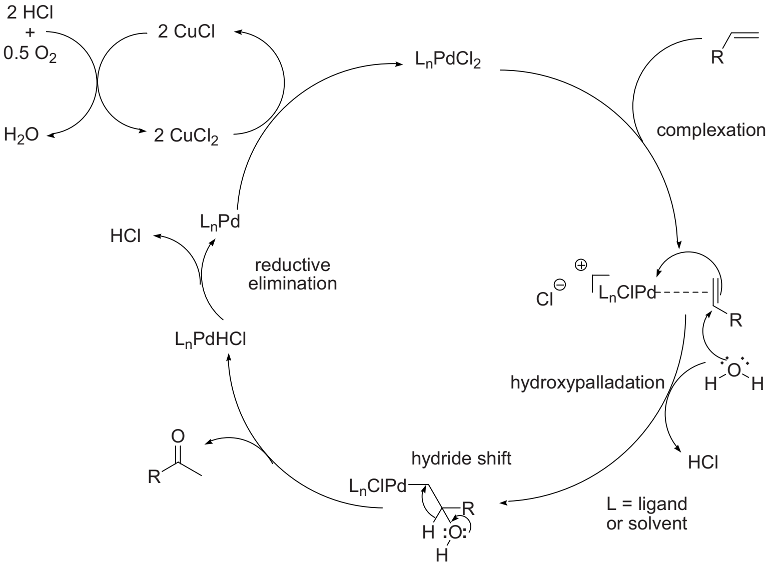
Wacker oxidation

Palladium-catalyzed oxidation of olefins to ketones, and aldehydes in certain cases.





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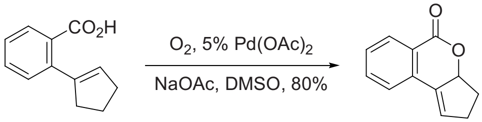

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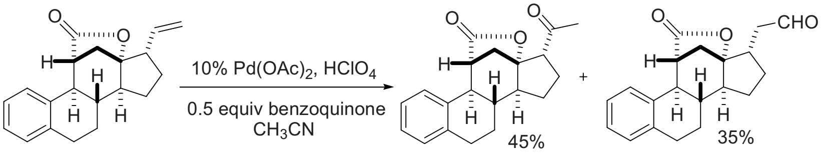

J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_263,

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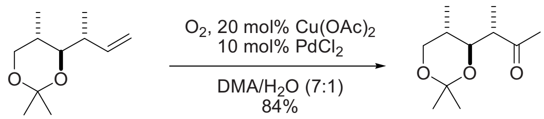

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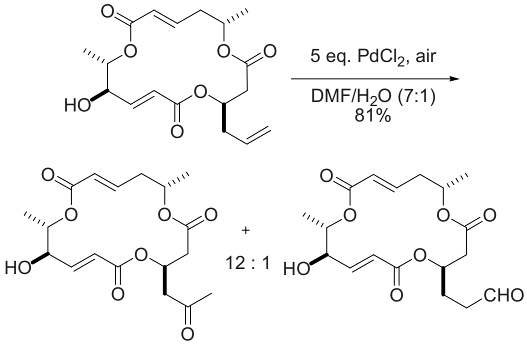

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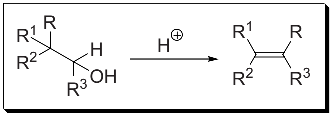
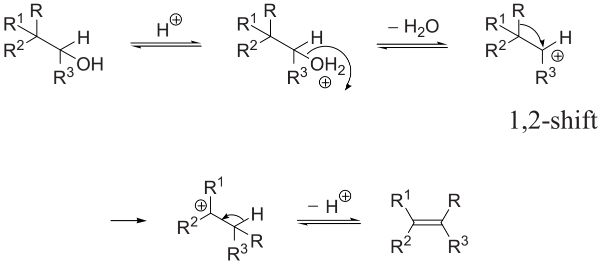
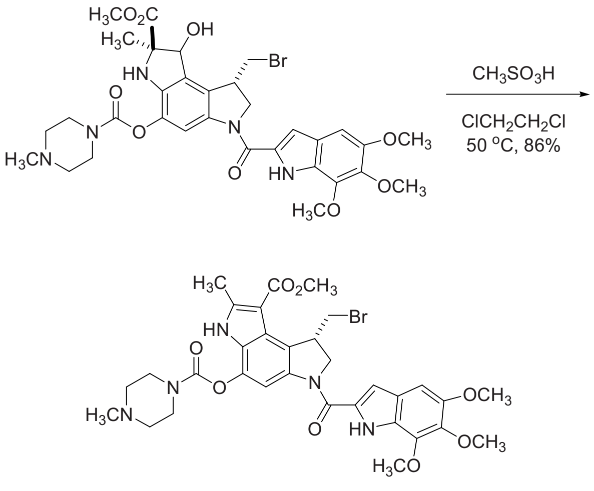
Wagner–Meerwein rearrangement

Acid-catalyzed alkyl group migration of alcohols to give more substituted olefins.

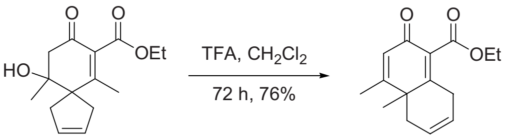




Example 1[3]



Example 2, Double Wagner–Meerwein rearrangement[6]



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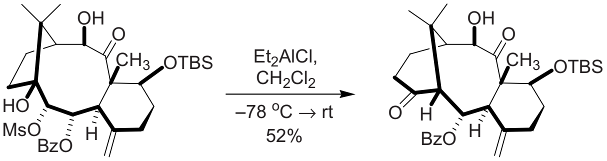
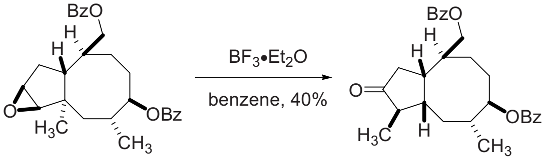
Example 3[7]



Example 4[9]



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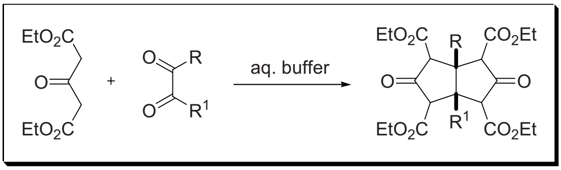
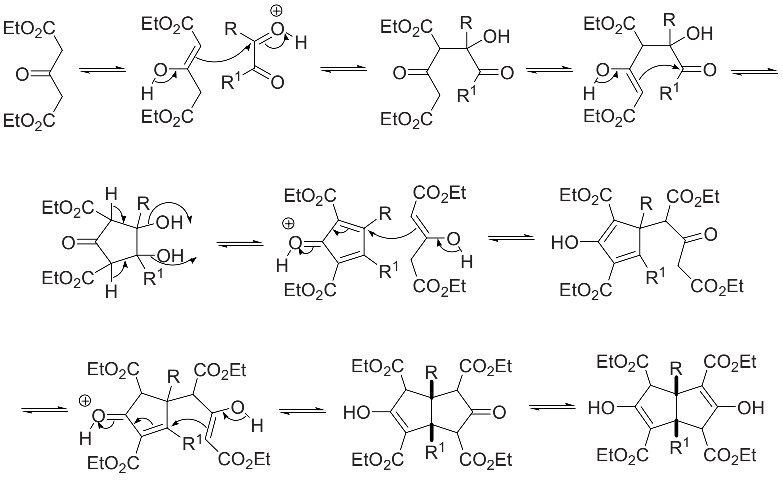
Weiss–Cook reaction

Synthesis of *cis*-bicyclo[3.3.0]octane-3,7-dione. The product is frequently decarboxylated.





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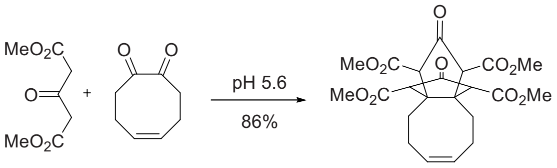
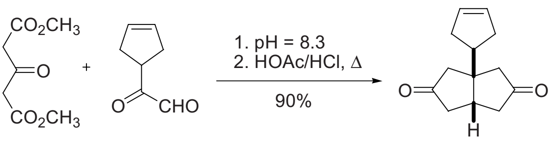


Example 2[3]



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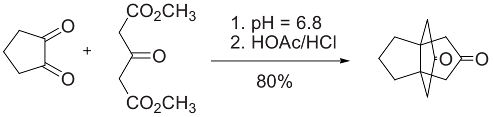
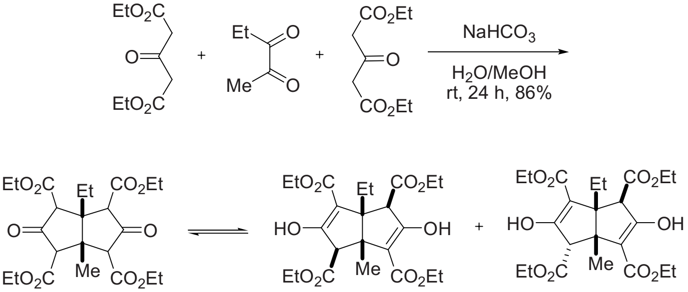
Example 3[4]



Example 4[9]



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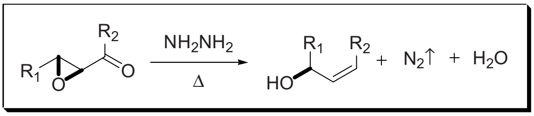
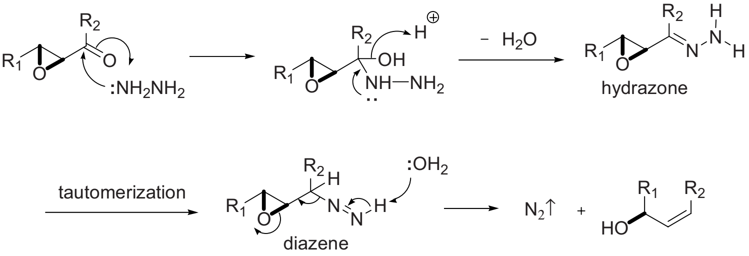
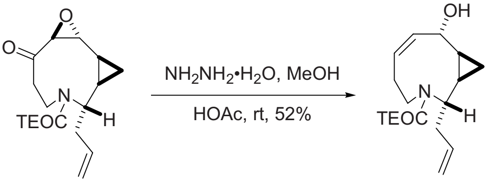
Wharton reaction

Reduction of α,β-epoxy ketones by hydrazine to allylic alcohols.

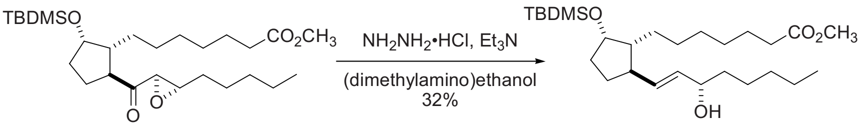




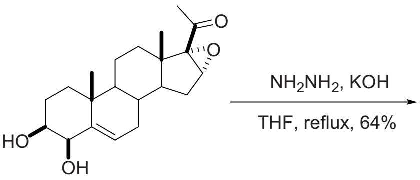
Example 1[5]



Example 2[6]



Example 3[7]



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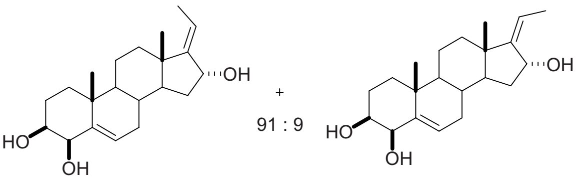
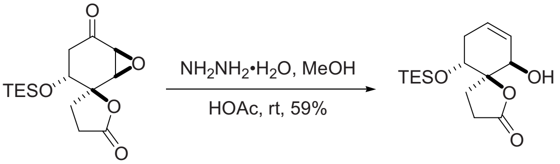


Example 4[8]



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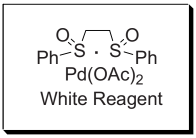
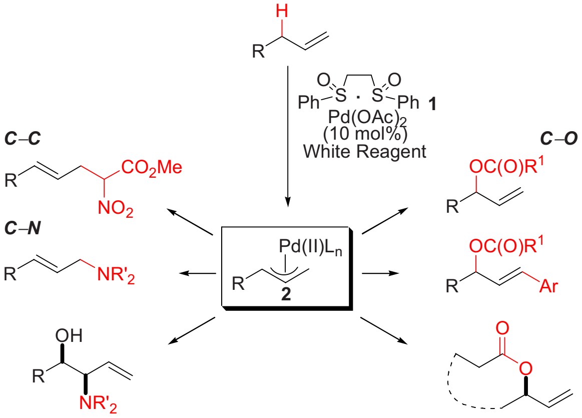
White Reagent



The White Reagent **1** is a highly versatile, commercially-available catalyst for allylic C–H oxidation which allows for the construction of useful C–O, C–N, and C–C bonds directly from relatively inert allylic C–H bonds (Figure 1).[1–11] The White Reagent enables novel and predictable disconnections for the synthesis of complex molecules which can streamline their synthesis.[2,4,7,8] Widely available α-olefins undergo intra- and intermolecular C–H oxidation with remarkably high levels of chemo-, regio-, and stereoselectivity. Mechanistic studies provide evidence that the White Reagent promotes allylic C–H cleavage to generate π-allylpalladium intermediate **2** which can then be functionalized with an oxygen, nitrogen or carbon nucleophile (Figure 1).[3]

Figure 1



Common organic functionality such as Lewis basic phenol **3**,[3] acid-labile acetal **4**,[8] highly reactive aryl triflate **6**,[11] and depsipeptide **5**[5] are well-tolerated under the mild reaction conditions (Figure 2). In all cases the products are isolated as one regioisomer and olefin isomer after column purification.

Current state-of-the-art methods for constructing C–N bonds rely on functional group interconversions or C–C bond forming reactions using preoxidized materials. Allylic amination using the White Reagent can streamline the synthesis of nitrogen-containing molecules by reducing the functional group manipulations necessary for working with oxygenated intermediates. Allylic C–H amination was used to synthesize (–)-**8**, an intermediate in the synthesis of *L*-acosamine derivative **9** (Figure 3A).[7] The C–H amination route to (–)-**8** proceeded in half the total number of steps, no functional group manipulations, and

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comparable overall yield to the alternative C–O to C–N bond-forming route. Intermolecular C–H amination has also led to the construction of (+)-deoxynegamycin analogue **12** in five less steps and improved overall yield compared to the alternative route relying on C–O substitution (Figure 3B).[8]

Figure 2

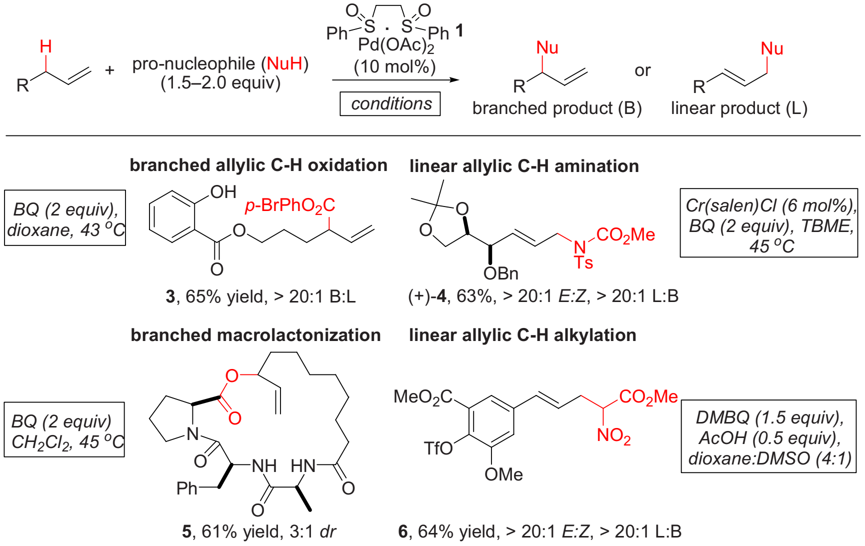
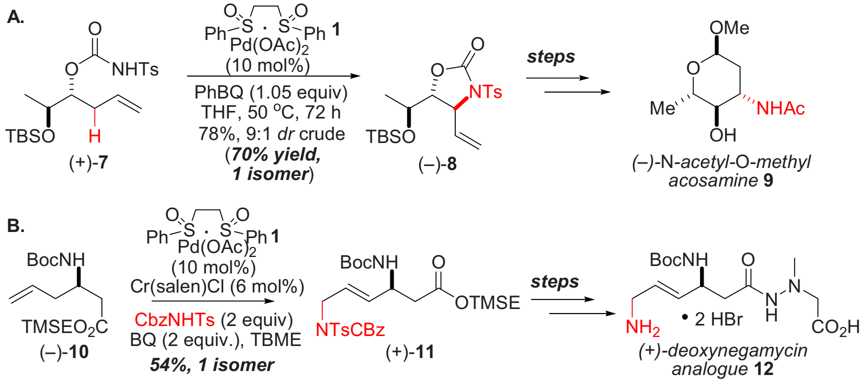
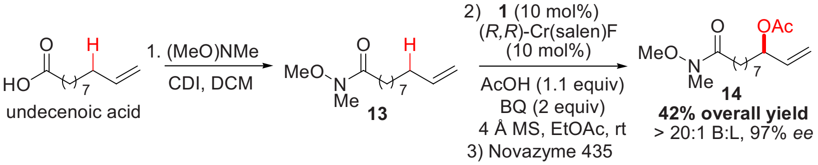


Figure 3



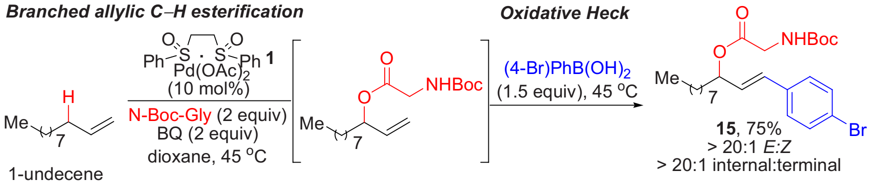
Similarly, allylic C–H oxidation can streamline the construction of oxygenated compounds by reducing functional group manipulations necessary for working with bisoxygenated intermediates. For example, a chiral allylic C–H oxidation/enzymatic resolution sequence furnished bisoxygenated compound **14** in 97% *ee* and in 42% overall yield in just 3 steps from a commercially available monooxygenated precursor, 11-undecenoic acid (Figure 4).[10] Alternative routes to similar molecules require protection/deprotection sequences and use a kinetic resolution giving a maximum of 50% yield.

Figure 4



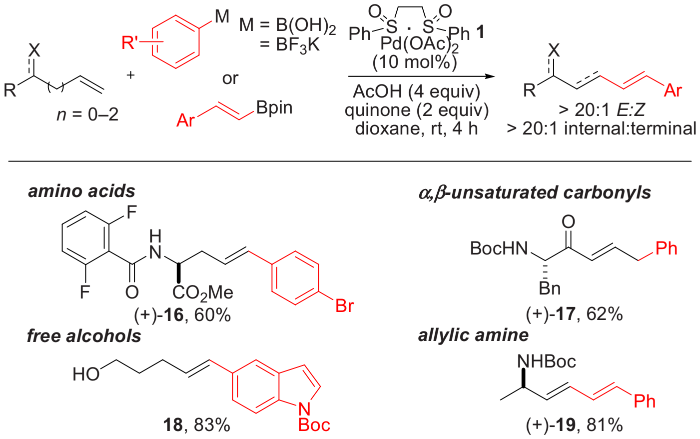
In addition to allylic C–H oxidation, the White Reagent also catalyzes intermolecular Heck arylations.[6] Notably, the arylation uses electronically *unbiased* α-olefins and aryl boronic acids and occurs under acidic, oxidative conditions. A one-pot allylic C–H oxidation/vinylic C–H arylation reaction furnishes *E*-arylated allylic esters with high regio- and stereoselectivities (Figure 5). This three-component coupling can be used to rapidly synthesize densely functionalized products from inexpensive hydrocarbon feedstocks. *N*-Boc glylcine allylic ester **9** was synthesized in one step using commercially available olefin, amino acid, and boronic acid reagents. Compounds similar to **15** have been transformed into medicinally relevant dipeptidyl peptidase IV inhibitors.[6]

Figure 5



Besides the one-pot process described above, the White Reagent catalyzes a chelate-controlled oxidative Heck arylation between a wide range of α-olefins and organoborane compounds in good yields and with excellent regio- and stereoselectivities (Figure 6).[9] Unlike other Heck arylation methods, no Pd–H isomerization is observed under the mild reaction conditions. Aryl boronic acids, styrenylpinacol boronic esters, and aryl potassium trifluoroborates (activated with boric acid) are all compatible with the general reaction conditions.

Figure 6



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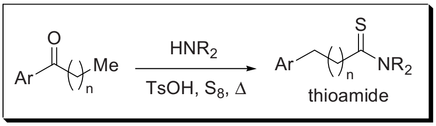
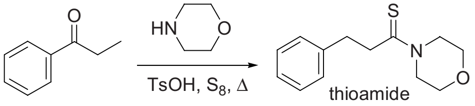
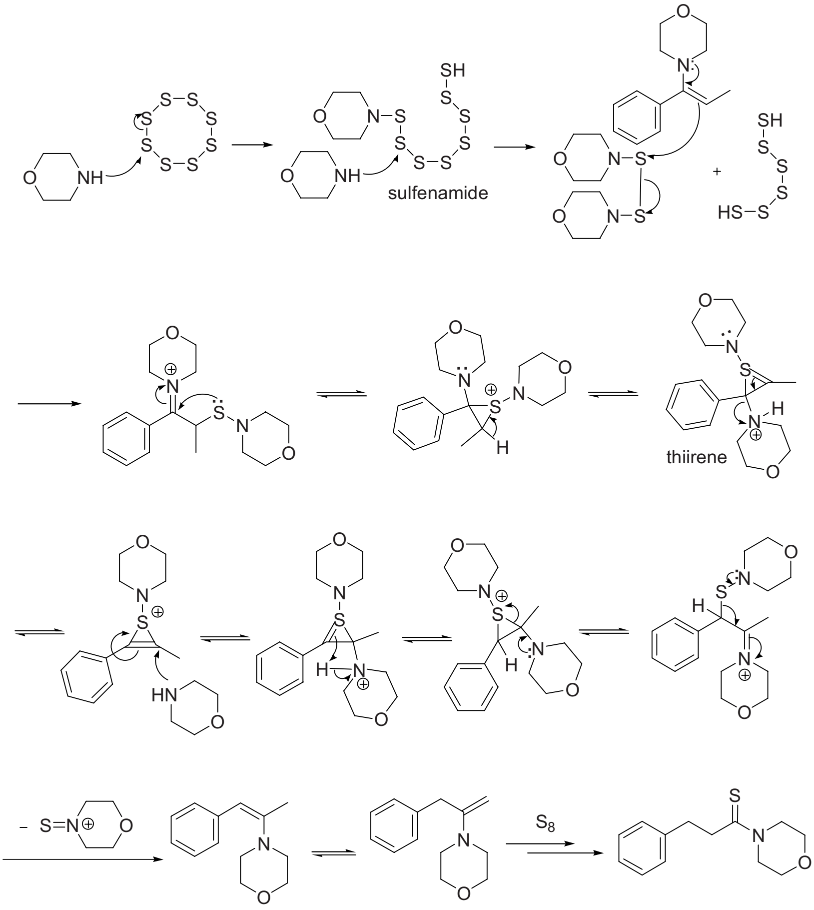
Willgerodt–Kindler reaction

Conversion of a ketone to thioamide, with functional group migration.



In Carmack's mechanism,[2] the most unusual movement of a carbonyl group from methylene carbon to methylene carbon was proposed to go through an intricate pathway *via* a highly reactive intermediate with a sulfur-containing heterocyclic ring. The sulfenamide serves as the isomerization catalyst. e.g.:





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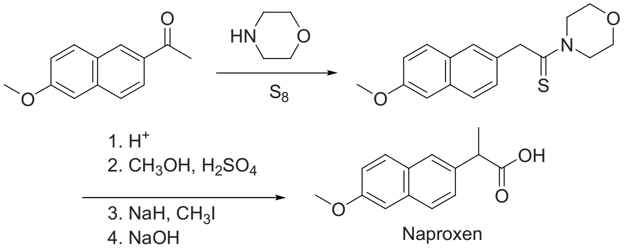
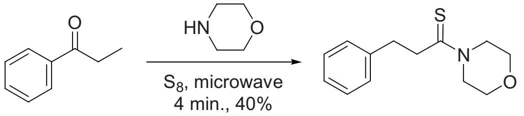
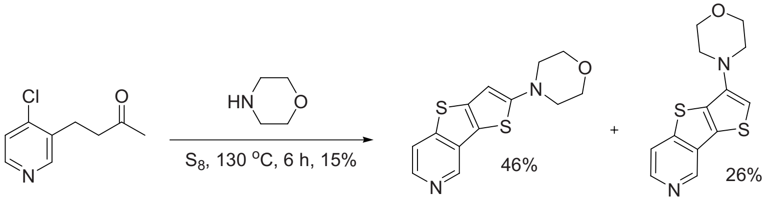
Example 1, The Willgerodt–Kindler reaction was a key operation in the initial synthesis of racemic Naproxen:[3]



Example 2[5]



Example 3, A domino annulation reaction under Willgerodt–Kindler conditions:[10]



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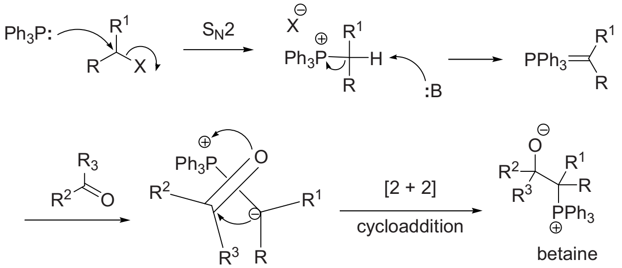
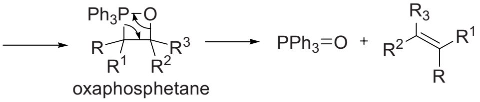
Wittig reaction

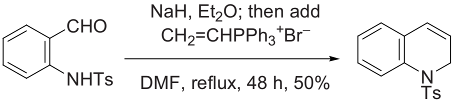
Olefination of carbonyls using phosphorus ylides, typically the *Z*-olefin is obtained.



“puckered” transition state, irreversible and concerted



Example 1[3]



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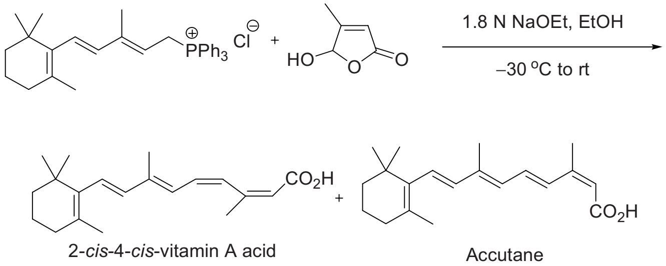

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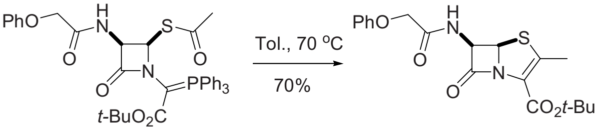
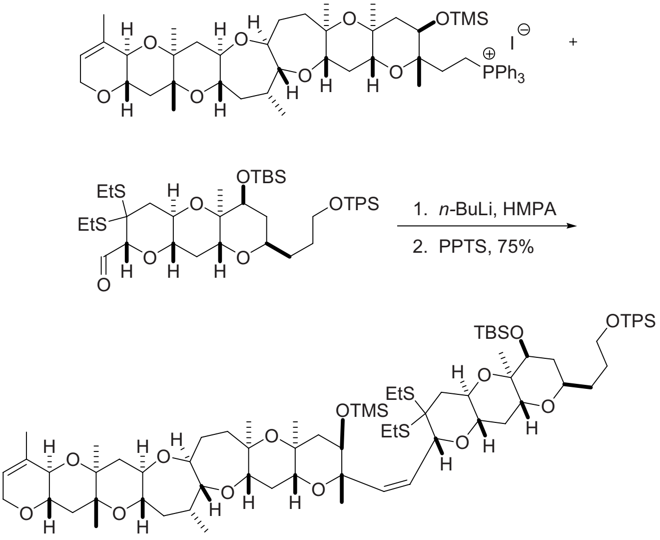
Example 3[5]



Example 4[9]



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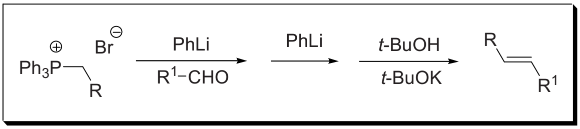
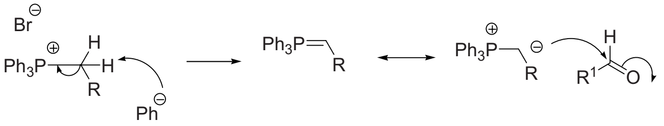
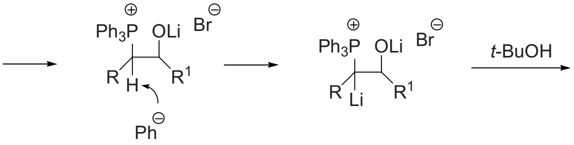
Schlosser modification of the Wittig reaction

The normal Wittig reaction of nonstabilized ylides with aldehydes gives *Z*-olefins. The Schlosser modification of the Wittig reaction of nonstabilized ylides furnishes *E*-olefins instead.



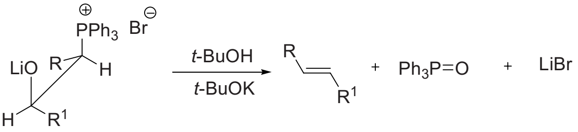


phosphorus ylide



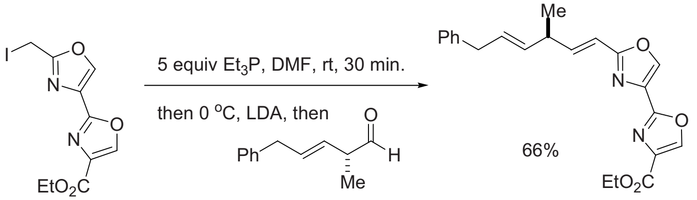
LiBr complex of β-oxo ylide

These conditions allow for the *erythreo* betaine to interconvert to the *threo* betaine

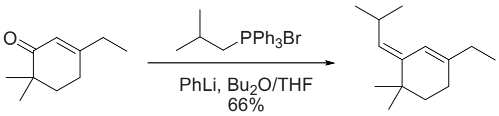


LiBr complex of *threo* betaine

Example 1[6]



Example 2[10]



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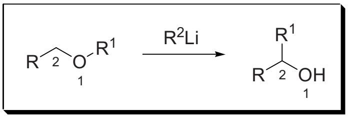
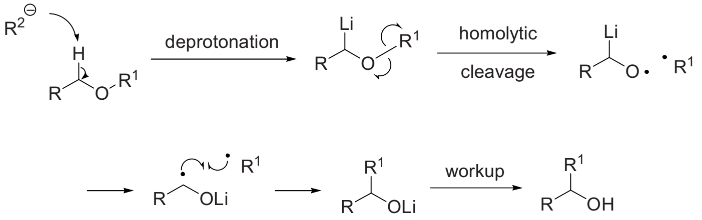
[1,2]-Wittig rearrangement

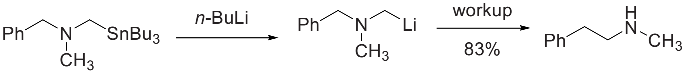
Treatment of ethers with bases, such as alkyl lithium, results in alcohols.



The [1,2]-Wittig rearrangement is believed to proceed via a radical mechanism:



Example 1, Aza [1,2]-Wittig rearrangement[2]



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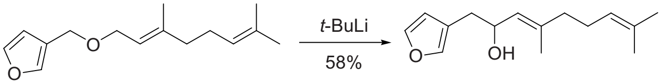

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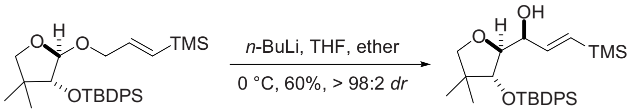

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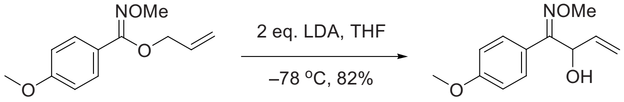

Example 5[8]

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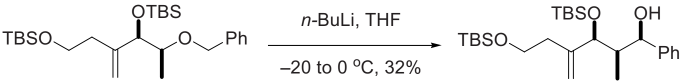

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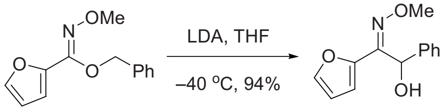

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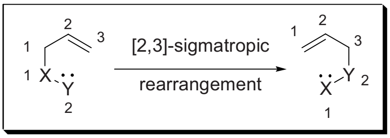
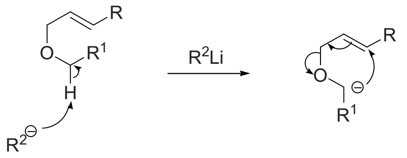
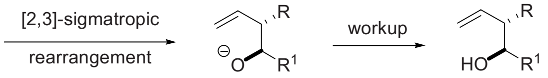
[2,3]-Wittig rearrangement

Transformation of allyl ethers into homoallylic alcohols by treatment with base. Also known as the Still–Wittig rearrangement. *Cf.* Sommelet–Hauser rearrangement.





R^1 = alkynyl, alkenyl, Ph, COR, CN.



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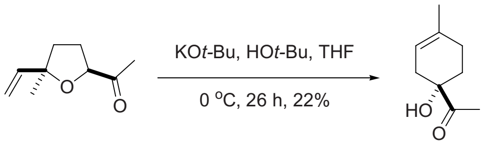

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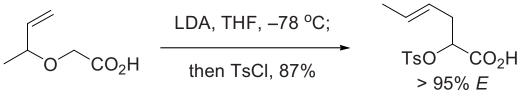

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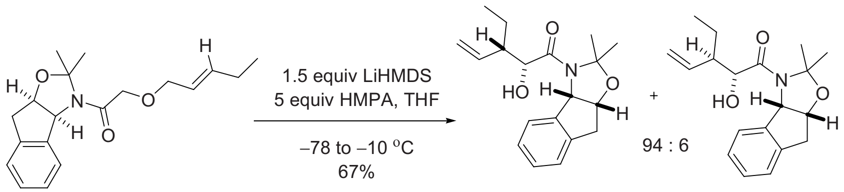
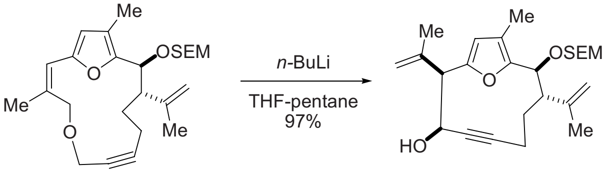


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_271,

Example 4[6]



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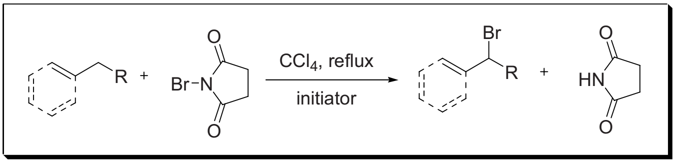
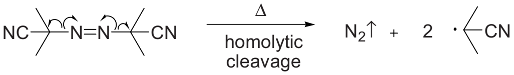
Wohl–Ziegler reaction

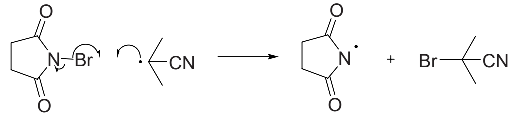
The Wohl–Ziegler reaction is the reaction of an allylic or benzylic substrate with *N*-bromosuccinimide (NBS) under radical initiating conditions to provide the corresponding allylic or benzylic bromide. Conditions used to promote the radical reaction are typically radical initiators, light and/or heat; carbon tetrachloride (CCl_4) is typically utilized as the solvent.



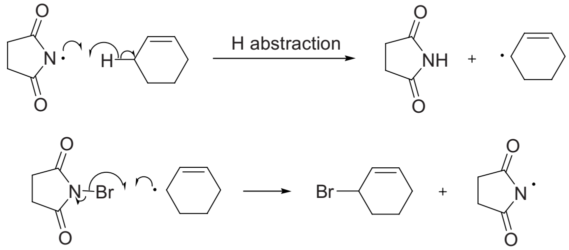
Initiation:



2,2′-azobisisobutyronitrile (AIBN)

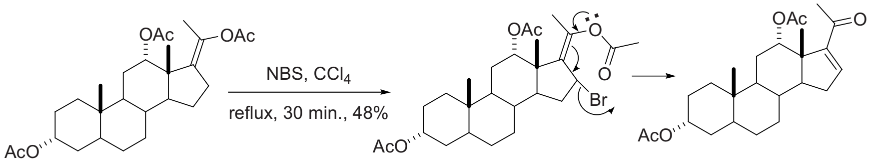


Propagation:



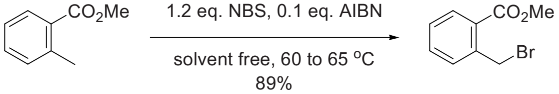
The succinimidyl radical is now available for the next cycle of the radical chain reaction.

Example 1[3]

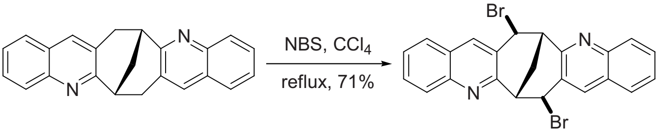


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_272,

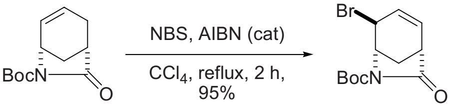
Example 2[7]



Example 3[8]



Example 4[9]



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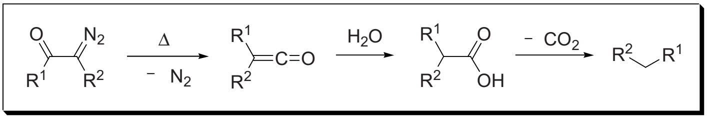
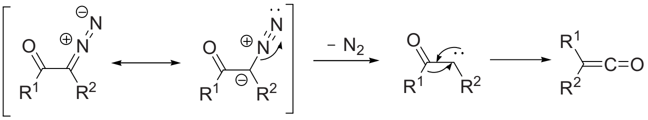
Wolff rearrangement

Conversion of an α-diazoketone into a ketene.



α-diazoketone ketene intermediate

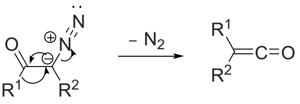
Step-wise mechanism:



α-ketocarbene

Treatment of the ketene with water would give the corresponding homologated carboxylic acid.

Concerted mechanism:



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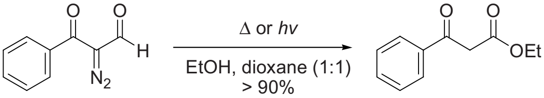

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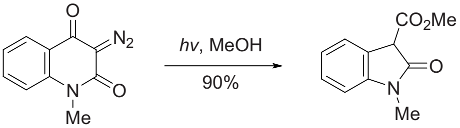

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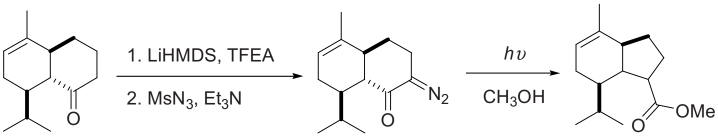
Example 3[4]



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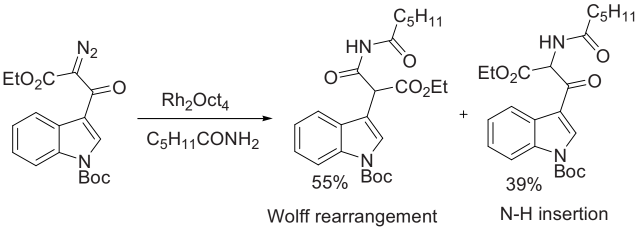

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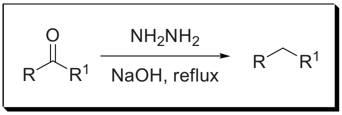
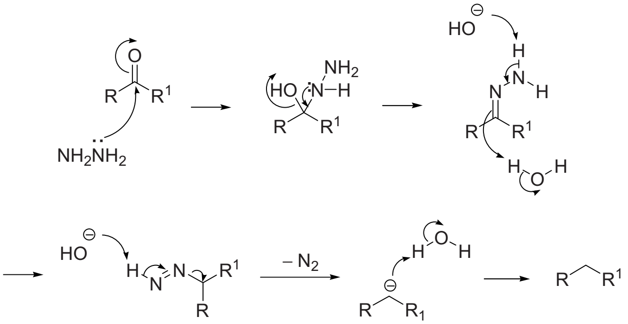
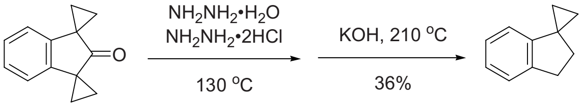
Wolff–Kishner reduction

Carbonyl reduction to methylene using basic hydrazine.

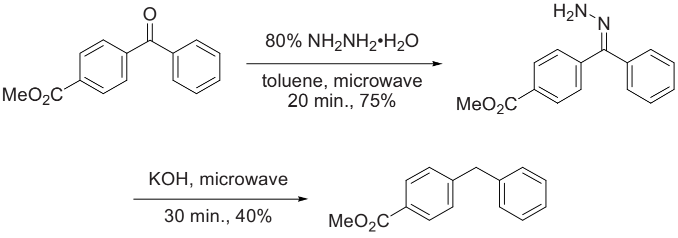




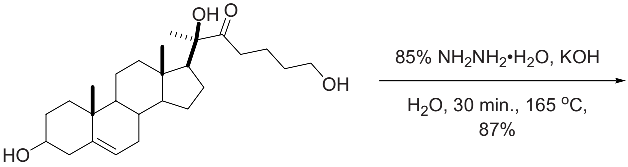
Example 1, Huang Minlon modification, with loss of ethylene here[5]



Example 2[7]



Example 3[8]



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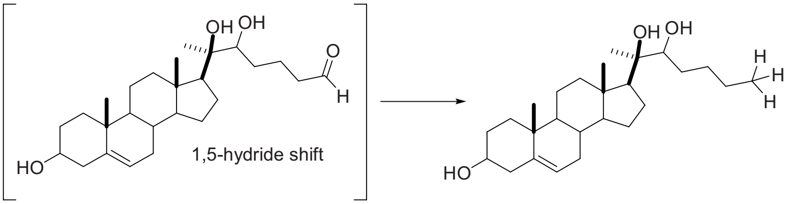
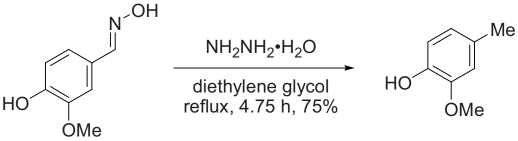


Example 4, Huang Minlon modification[10]



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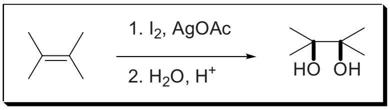
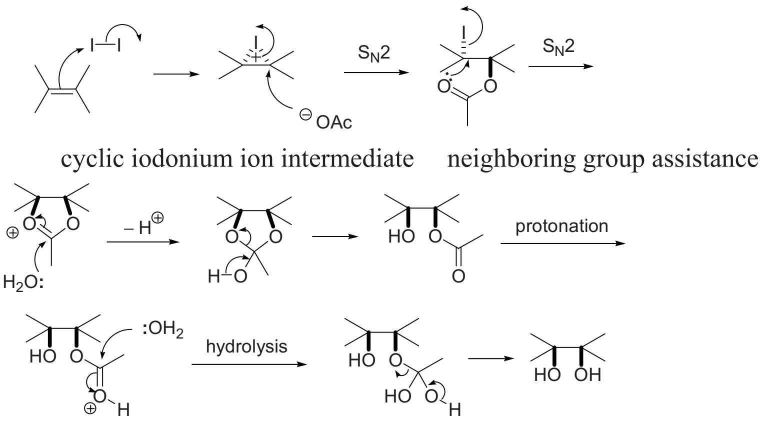
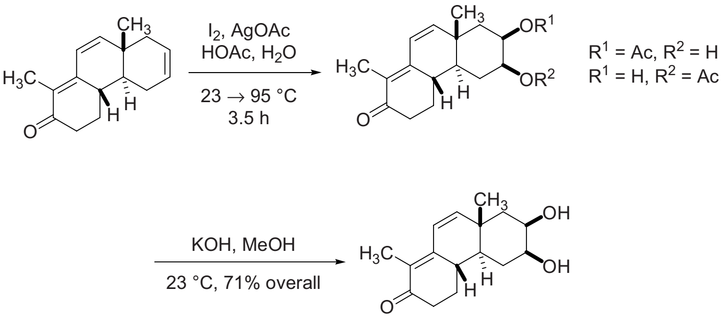
Woodward *cis*-dihydroxylation

Cf. Prévost *trans*-dihydroxylation.

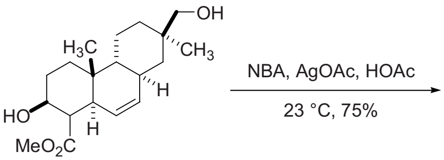




Example 1[1]



Example 2[6]



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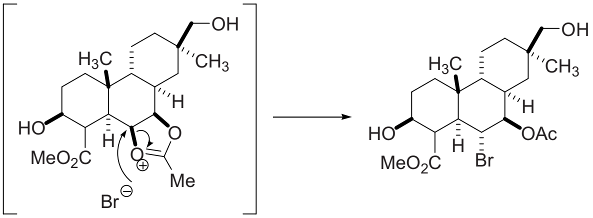

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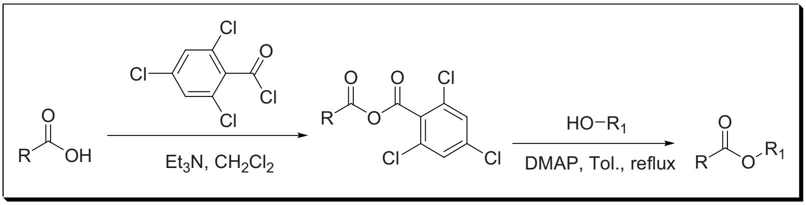
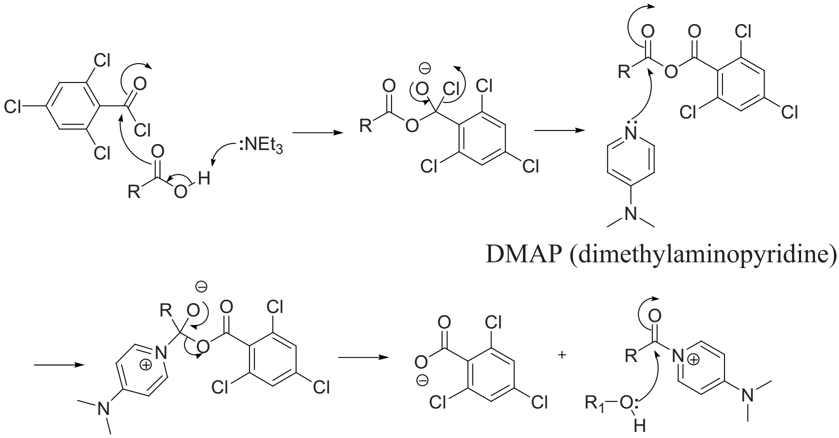
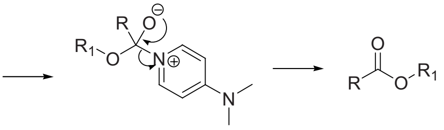
Yamaguchi esterification

Esterification using 2,4,6-trichlorobenzoyl chloride (the Yamaguchi reagent).

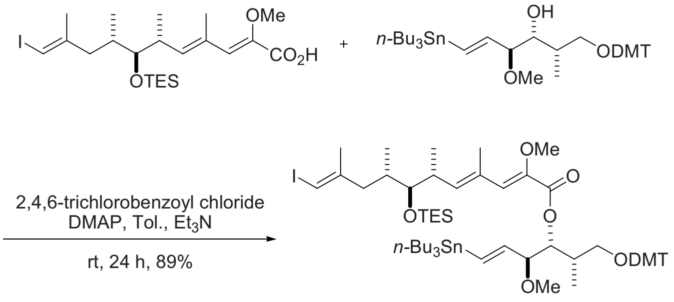




Steric hindrance of the chloro substituents blocks attack of the other carbonyl of the mixed anhydride intermediate.



Example 1, Intermolecular coupling[5]



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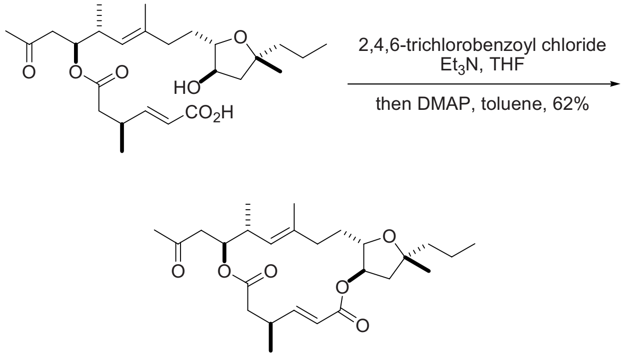
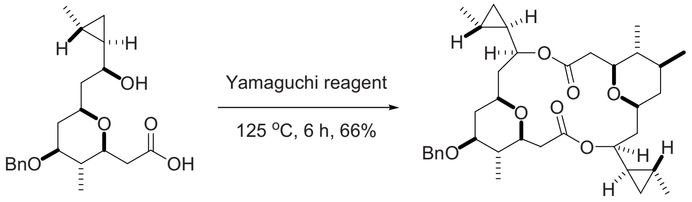
Example 2, Intramolecular coupling[7]



Example 3, Dimerization[8]



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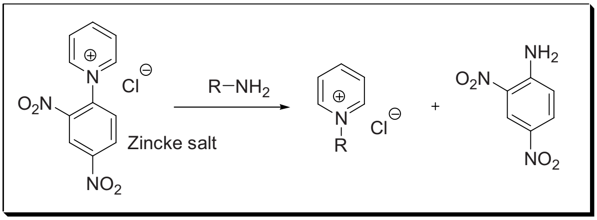
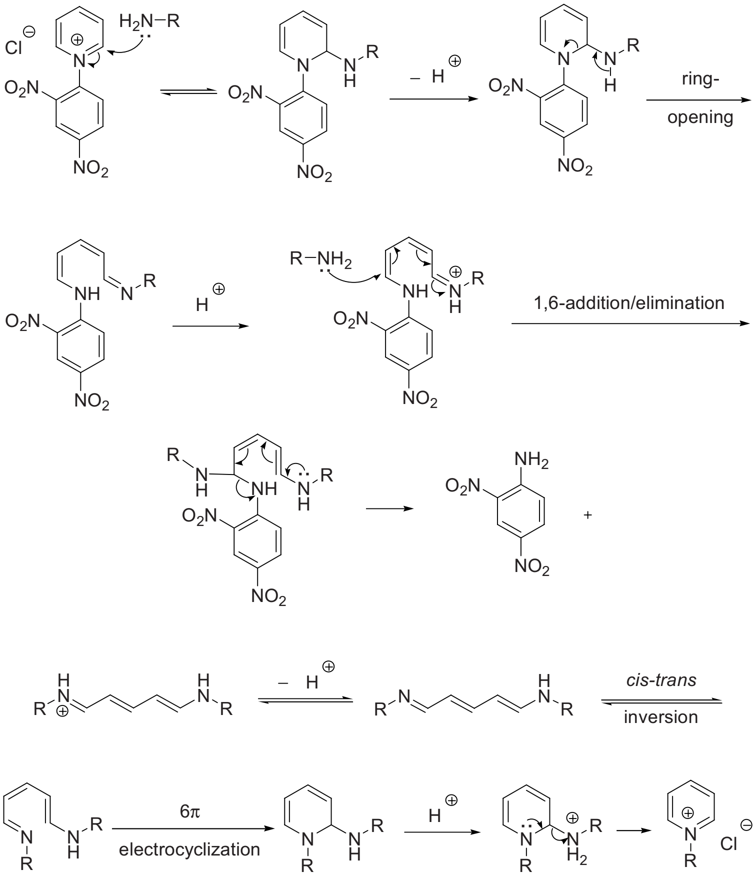
Zincke reaction

The Zincke reaction is an overall amine exchange process that converts *N*-(2,4-dinitrophenyl)pyridinium salts, known as Zincke salts, to *N*-aryl or *N*-alkyl pyridiniums upon treatment with the appropriate aniline or alkyl amine.





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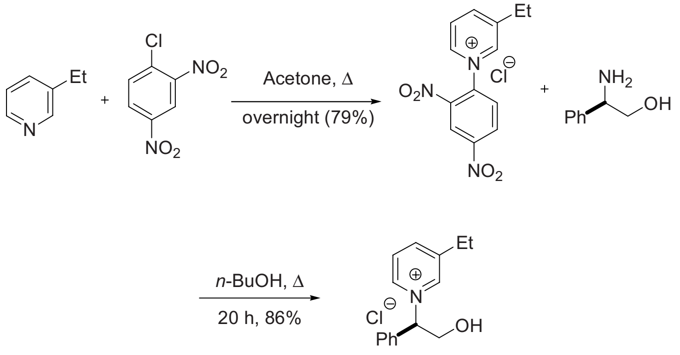
Example 1[5]



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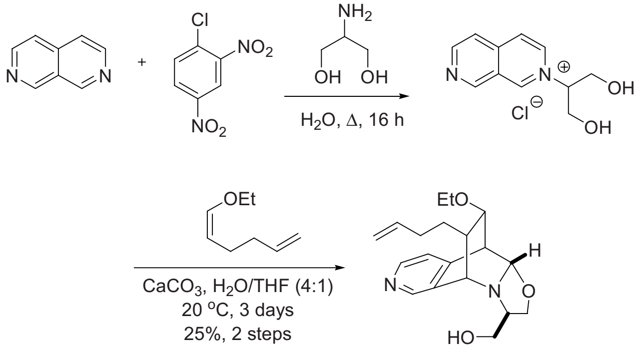

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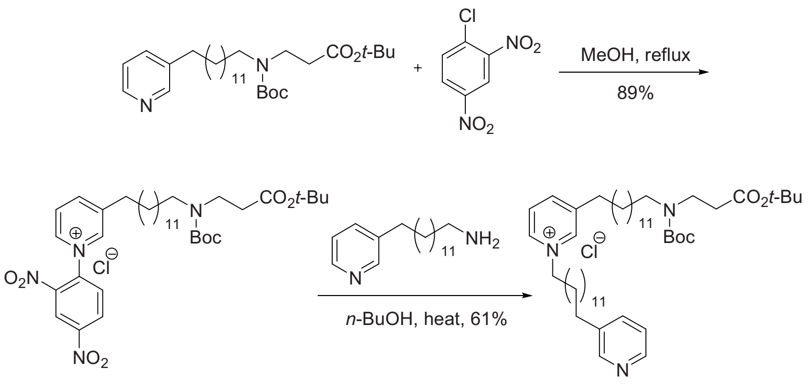
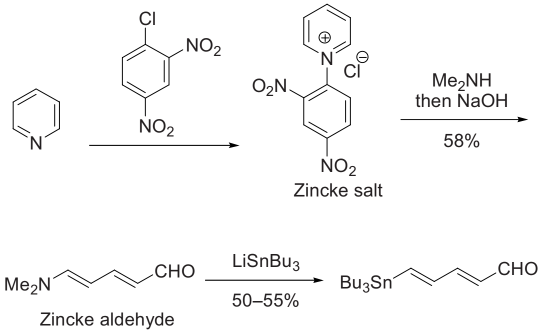


Example 4[10]



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Subject Index

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