药明康德经典译丛

原著（美）Jie Jack Li
荣国斌 译
朱士正 校

超过
300
个反应!

有机人名反应——机理及应用（原书第四版）

Name Reactions

A Collection of Detailed Mechanisms and Synthetic Applications

Fourth Edition

科学出版社

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内 容 简 介

国内外涉及有机人名反应的著作也有一些，但本书是颇有特色的一种。它并不追求齐全，但富有时代感，着眼于反应是否创新及有否应用价值。全书精选了300多个有机人名反应，每个反应均给出一步一步详尽的电子转移机理过程。新版本进一步增加了相关人名反应在合成中的应用，并增补了最新的参考文献，其中有相当部分是综述类论文，以帮助读者更好地理解和认识有机反应，同时为深入应用有机反应提供了方便。这样的编写方式极富参考价值。因此，该书在2002年初版发行后深受市场欢迎，故近年来不断修订补充。本书是根据其2009年7月出版的第4版翻译而成。

本书适合高等院校化学类专业本科生、研究生以及有机化学及相关学科的研发人员参考使用。

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《药明康德经典译丛》丛书序

新药研发中，引入先进的知识和经验比单纯购买先进的仪器设备更有意义。经典仍需研读，《药明康德经典译丛》丛书是药明康德的高级管理人员凭借数十年的制药企业研发经验，精选了国外新药研发的优秀书籍，组织具有专业知识背景的团队，引进版权、翻译并出版的一系列学习教材和科研资料。

药明康德新药开发有限公司自2000年成立以来，一直以“变革新药研发、造福人类健康”为使命，专注于新药研发服务、逐步成长为一家能“提供一站式药物研发服务，以提高新药研究成功率、并缩短新药研发时间”的企业。公司目前拥有四千多名员工，相继荣获德勤“亚太地区高科技高成长500强”和亚洲地区“Red Herring 100强”等称号，已经发展成为亚洲规模最大、全球发展最快的新药研发服务企业，成为国际知名的新药研发服务公司。药明康德（NYSE: WX）于2007年8月9日成功地在纽约证券交易所上市。2008年初药明康德成功收购了美国AppTec实验室服务公司。2009年药明康德在苏州建成亚洲最大的药物安全评价中心。2011年4月，药明康德累计营业额突破10亿美元。

人才是药明康德最宝贵的财富。为了让公司保持强劲的国际竞争力，药明康德实施人才全球化战略。在不断从海外吸收高层次国际化人才的同时，也在全国范围内全力吸纳最优秀的科技精英，提供广阔的专业舞台和世界一流的科研环境。在推动人才团队为世界药物研发领域作出杰出贡献的同时，公司也培育扶持他们逐步成为顶尖的药物研发专家。在企业高速发展中，我们清楚地感觉到一份企业的社会责任感。公司意识到：企业不应该一味地向社会索取人才，更应该适时回报社会，为人才的培养和成长贡献力量。为企业本身和所处的社会营造一个“和谐—健康—稳定—可持续发展”的人才生态系统。这样才有利于避免短期行为，谋求长效发展，形成百年基业。

药明康德一直在为不断地提高公司科学研究的水平而追踪世界新成果，同时也努力把国际先进知识和经验介绍给国内的同行，以共同提高中国小分子药物研发的整体水平。近年来，药明康德凭借众多优秀的青年科研人员和先进的科研设备，研发实力已在国际药物研发服务领域得到公认，也保证了《药明康德经典译丛》丛书的内在质量。

我们希望《药明康德经典译丛》丛书的出版能够为国内新药研究专业人才的培养，为国内药物化学的发展有所贡献。目前已经出版的译著：

2006年	《有机化合物的波谱解析》	华东理工大学出版社
2008年	《新药合成艺术》	华东理工大学出版社
2008年	《有机成名反应、试剂和缩略词》	华东理工大学出版社
2010年	《有机合成——切断法》	科学出版社

译校者的话

有机化学是一门富有个人特色和高度竞争性的学科。化学家已发现了难以计数的各类有机反应，其中有相当数量的是以一个或多个化学家的姓名来归类和命名的。许多有机人名反应的发现者获得过诺贝尔化学奖。

有机人名反应是有机化学的一大特色而占有有机反应的核心地位。毫无疑义的是，要学好有机化学，熟悉有机人名反应是基本要求；要做好有机化学的研究工作，掌握更多的有机人名反应是素质要求。

国内外涉及有机人名反应的著作也有一些，由Jie Jack Li编著的“Name Reactions”则是颇有特色的一种。它并不追求齐全，但能从广大读者对反应的基本需求出发，强调时代感，着眼于基础性、应用性和新颖性；每个反应均通过图式给出详尽而又完整的一步步电子转移的过程，故既适于学生理解这些有机反应的过程，又为科研工作者了解相关进展提供了随手可得的众多资料和参考文献。本书第二版的中文译本《有机人名反应及机理》是2003年由我们翻译、华东理工大学出版社出版的。该书上市后受到读者的欢迎，已多次重印。事隔几年，Li再次编写了本书第四版。诚如他在新版“前言”中所表明的，新版提供了更多的合成实例，副标题也已改为《详尽的机理和合成应用集成》，使新版更为实用并更能反映当代进展。

新版共给出了302个最重要的一直在普遍应用的有机反应或试剂，每个反应或试剂都有扩展，有些是最近几年才刚发现的新反应或试剂；此外还有2 900多篇直至2009年度以综述或应用为主的参考文献。新版的另一个亮点则是提供了不少有机人名反应发现者的简历，他们栩栩如生的为人风格跃然纸上，令人更生崇敬之感。

我们有幸再次将本书新版（第四版）译成中文。译校工作中对原著的一些差错做了改正；一些英文人名、单位名未作翻译；一些读者都能理解的如Example、Figure 、or、reflux、yield及*anti*、*cis*-、*dr*、*ee*、*etc.*、*syn*、*trans*-等常见英文单词和商标名也未作翻译。希望新版中文本能继续为我国的有机化学工作者和学习者所欢迎而成为一种常用和不可或缺的参考工具书。

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2011年1月于上海

序

我不会把我的名字放到与我不相干的任何事上。

——Heidi Klum

和被称为“人名反应”联系在一起的有机化学家是如超级名模Heidi Klum所声称的那样吗？许多化学家会马上指出，与“人名反应”联系在一起的人常常并不是发现者。如，Arndt-Eistert反应与Arndt或Eistert毫无关联，Pummerer没有发现Pummerer重排反应，即使是著名的Birch还原反应也应该归于Charles Wooster(第一个在DuPont专利中报道)。还可以列出许多。

但是因为如此我们就可以忽视、抵制或宣布“人名反应”是无效的吗？上述这些例子实际上只是惯例的例外。事实上，与“人名反应”联系在一起的化学家们就是原始反应的代表，也是对反应的普遍应用和/或推广、扩展做出重要贡献的第一个人。尽管一些人名反应有历史争议，学习有机化学的学生们通过一览人名反应还是会受益良多。Jack Li博士正是基于教育这一点向化学界奉献了最新版本的“人名反应”一书。

这本漂亮的著作成为畅销书是理所当然的事。几百个人名反应的精髓被压缩进一个简明的对学生和有经验的化学家都能适用的样式。几百个人名反应的详尽机理及一些历史渊源和关键的参考文献都已给出。这本“必备书”无疑将能出现在从事合成艺术和科学的学生及所有从业者的书架上。

Phil S. Baran

2009年5月于La Jolla, California

前　言

本书前三版一直在有机化学界受到欢迎和好评。许多读者反映，他们希望得知确切的详尽机理以用于实际合成工作。本版为此作了较大变革，更多的篇幅提供给合成实例，故本书的副标题也已改为《详尽的机理和合成应用集成》。在整理本版时，我力求能查到最近可能得到的直至2009年度的文献。我的女儿，Vivien，一个在密歇根大学（University of Michigan）上二年级的大学生将很快上"有机化学"课程了。我希望她能感到本书对她进行复习备考是有用的。

很多读者写信给我提出建议并使本书能成为世界各地的高年级本科生、研究生的有用参考书，这些都使我受益匪浅。本书第二版已译成汉语和俄语。我要感谢在Ash Stevens Inc.工作的好朋友Derek A. Pflum，他仔细地全文阅读了本版的初稿并提出了许多无价的建议。在阿尔贝特大学（University of Alberta.）工作的Derrick L. J. Clive 教授预审了原稿的前半部分并给出有益的评注。我还要感谢在Scripps Research Institute工作的Phil S. Baran教授和他的学生Tanja Gulder、Yoshi Ishihara、Chard A. Lewis、Jonathan Lockner、Jun Cindy Shi和ShiIan B. Seiple为本书最终定稿所做的校阅。他们的知识和所花费的时间大大提升了本书的质量。而余留的错误则应由我本人负责。

一如既往，我欢迎你的评论！

Jie Jack Li

2009年5月于 Killingworth，Connection

缩略词和首字母缩略词

	聚合物载体
3CC	three-component condensation 三组分缩合
4CC	four-component condensation 四组分缩合
9-BBN	9-borabicyclo[3.3.1]nonane 9-硼双环[3.3.1]壬烷
A	adenosine 腺苷
Ac	acetyl 乙酰基
ADDP	1,1'-(azodicarbonyl)dipiperidine 1,1'-(偶氮二羰基)二哌啶
AIBN	2,2'-azobisisobutyronitrile 2,2'-偶氮二异丁腈
Alpine-borane	*β*-isopinocamphenyl-9-borabicyclo[3.3.1]-nonane *β*-3α-蒎烯-9-硼杂双环[3.3.1]壬烷
AOM	*p*-anisyloxymethyl 对甲氧基苯氧甲基
aq	aqueous 水相
Ar	aryl 芳基
atm	atmosphere 大气压
B	generic base 普通碱
[bimim]Cl · 2AlCl$_3$	1-butyl-3-methylimidazolium chloroaluminuminate 1-丁基-3-甲基咪唑鎓氯化铝
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl 2,2'-双（二苯基膦）-1,1'-联萘
Bn	benzyl 苄基
Boc	*t*-butoxycarbonyl 叔丁氧羰基
BT	benzotriazol 苯并噻唑
Bz	benzoyl 苯甲酰基
cat	catalysis or catalyst 催化(剂)
Cbz	benzyloxycarbonyl 苄氧羰基
CuTC	Copper(I) thiophene-2-carboxylate 2-噻吩甲酸铜
d	day 天
DABCO	1,4-diazabicyclo[2.2.2]octane 三亚乙基二胺
Dba	dibenzylideneacetone 二亚苄基丙酮
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene 1,5-二氮杂双环[5.4.0]十一碳-7-烯
DCC	dicyclohexylcarbodiimide 二环己基碳二亚胺
DDQ	2,3-dichloro-5,6-dicyano-*p*-benzoquinone 2,3-二氯-5,6-二氰基苯醌
de	diastereomeric excess 非对映体过量
DEAD	diethyl azodicarboxylate 偶氮二甲酸二乙酯
(DHQ)$_2$-PHAL	1,4-bis(9-*O*-dihydroquinine)phthalazine 1,4-双(9-*O*-二氢喹宁)-2,3-二氮杂萘
(DHQ)$_2$PHAL	1,4-bis(9-*O*-dihydroquinidine)phthalazine 1,4-双(9-*O*-二氢奎尼定基)-2,3-二氮杂萘
DIAD	diisopropyl azodicarboxylate 偶氮二甲酸二异丙酯
DIBAL	diisobutylaluminium hydride 二异丁基氢化铝
DIPEA	diisopropylethylamine 二异丙基乙基胺
DMA	*N,N*-dimethylacetamide *N,N*-二甲基乙酰胺
DMAP	4-dimethylaminopyridine 4-二甲氨基吡啶

DME	1,2-dimethoxyethane 1,2-二甲氧基乙烷
DMF	*N,N*-dimethylformamide *N,N*-二甲基甲酰胺
DMFDMA	dimethylformamide dimethyl acetal 二甲基甲酰胺二甲缩醛
DMS	dimethylsulfide 二甲硫醚
DMSO	dimethyl sulfoxide 二甲亚砜
DMSY	dimethylsulfoxonium methylide 二甲基氧化锍亚甲基
DMT	4,4'-dimethoxytrityl 4,4'-二甲氧基三苯甲基
DNP	dinitrophenyl 二硝基苯基
DPPA	diphenoxyphosphinyl azide 二苯氧基磷酰叠氮化物
dppb	1,4-bis(diphenylphosphino)butane 1,4-二(二苯基膦基)丁烷
dppe	1,2-bis(diphenylphosphino)ethane 1,2-二(二苯基膦基)乙烷
dppf	1,1'-bis(diphenylphosphino)ferrocene 1,1'-二(二苯基膦基)二茂铁
dppp	1,3-bis(diphenylphosphino)propane 1,3-二(二苯基膦基)丙烷
dr	diastereomeric ratio 非对映异构体比例
DTBAD	di-*tert*-butylazodicarboxylate 偶氮二甲酸二叔丁酯
DTBMP	2,6-di-*tert*-butyl-4-methylpyridine 2,6-二叔丁基一4-甲基吡啶
E	Entgegen *E*式
E1	unimolecular elimination 单分子消除
E1cb	unimolecular elimination via carbanion 经负碳离子单分子消除
E2	bimolecular elimination 双分子消除
EAN	ethylammonium nitrate 硝酸乙铵
EDDA	ethylenediamine-*N,N'*-diacetic acid *N,N'*-乙二胺二乙酸
ee	enantiomeric excess 对映体过量
Ei	intramolecular elimination 分子内消除
eq(ui)	equivalent 当量
Et	ethyl 乙基
EtOAc	ethyl acetate 乙酸乙酯
g gas	气体
h hour	小时
HMDS	1,1,1,3,3,3-hexamethyldisilazane 六甲基二硅胺
HMPA	hexamethylphosphoric triamide (hexamethylphosphoramide) 六甲基磷酰(三)胺
HMTTA	1,1,4,7,10,10-hexamethyltriethylenetetramine 1,1,4,7,10,10-六甲基三亚乙基四胺
IBX	*o*-iodoxybenzoic acid 邻碘酰基苯甲酸
imd	imidazole 咪唑
KHMDS	potassium hexamethyldisilazide 六甲基二硅胺钾
LAH	lithium aluminium hydride 四氢锂铝
LDA	lithium diisopropylamide 二异丙基胺基锂
LHMDS	lithium hexamethyldisilazide 六甲基二硅烷基胺基锂
Liq	liquid 液体
LTMP	lithium 2,2,6,6-tetramethylpiperidide 2,2,6,6-四甲基哌

	啶锂
Me	methyl 甲基
***m*-CPBA**	*m*-chloroperbenzoic acid 间氯过氧苯甲酸
MCRs	multicomponent reaction 多组分反应
Mes	mesityl 2,4,6-三甲基苯基
min	minute 分(钟)
MWI	microwave irradiation 微波激发
MVK	methyl vinyl ketone 甲基乙烯基酮
NBS	*N*-bromosuccinimide *N*-溴代琥珀酰亚胺
NCS	*N*-chlorosuccinimide *N*-氯代琥珀酰亚胺
NIS	*N*-iodosuccinimide *N*-碘代琥珀酰亚胺
NMP	*N*-methyl-2-pyrrolidinone *N*-甲基-2-吡咯酮
Nos	2- or 4-nitrobenzenesulfonyl 2-或4-硝基苯磺酰基
***N*-PSP**	*N*-phenylselenophthalimide *N*-苯硒基邻苯二甲酰亚胺
***N*-PSS**	*N*-phenylselenosuccinimide *N*-苯硒基丁二甲酰亚胺
Nu	nucleophile 亲核试剂
PCC	pyridinium chlorochromate 氯铬酸吡啶盐
PDC	pyridinium dichromate 重铬酸吡啶盐
Ph	phenyl 苯基
Piv	pivaloyl 特戊酰基
PMB	*p*-methoxybenzyl 对甲氧基苄基
PPA	polyphosphoric acid 多聚磷酸
PPTS	pyridinium *p*-toluenesulfonate 对甲苯磺酸吡啶盐
PT	phenyl tetrazolyl 苯基四唑基
$PyPh_2P$	diphenyl 2-pyridylphosphine 二苯基2-吡啶基膦
pyr	pyridine 吡啶
quant	quantitative 定量
Red-Al	sodium bis(2-methoxyethoxy)aluminum hydride 二(2-甲氧基乙基)氢化铝钠
rt	room temperature 室温
Salen	*N,N'*-disalicylidene ethylenediamine *N,N'*-亚乙基双水杨基亚胺
SET	single electron transfer 单电子转移
SIBX	stabilized IBX 稳定的IBX
SM	starting material 起始原料
SMEAH	sodium bis(2-methoxyethoxy)aluminum hydride 二(2-甲氧基乙氧基)氢化铝钠
S_N1	unimolecular nucleophilic substitution 单分子亲核取代反应
S_N2	bimolecular nucleophilic substitution 双分子亲核取代反应
S_NAr	nucleophilic substitution on an aromatic ring 芳环上的亲核取代反应
solv	solvent 溶剂
TBABB	tetra-*n*-butylammonium bibenzoate 联苯酸四丁基铵盐
TBAF	tetra-*n*-butylammonium fluoride 四丁基氟化胺
TBAO	1,3,3-trimethyl-6-azabicyclo[3.2.1]octane 1,3,3-三甲基-6-氮杂双环[3.2.1]辛烷
TBDMS	*tert*-butyldimethylsilyl 叔丁基二甲基硅基
TBDPS	*tert*-butyldiphenylsilyl 叔丁基二苯基硅基

TBS	*tert*-butyldimethylsilyl 叔丁基二甲基硅基
***t*-Bu**	*tert*-butyl 叔丁基
TDS	thexyl dimethyl silyl 二甲基(叔丁基乙基)硅基
TEA	triethylamine 三乙胺
TEOC	2-(trimethylsilyl)ethoxycarbonyl 2-三甲基硅基乙氧羰基
Tf	trifluoromethanesulfonyl 三氟甲磺酰基
TFA	trifluoroacetic acid 三氟乙酸
TFAA	trifluoroacetic anhydride 三氟乙酸酐
TFP	tris(2-furyl)phosphine 三(2-呋喃基)膦
THF	tetrahydrofuran 四氢呋喃
TIPS	triisopropylsilyl 三异丙基硅基
TMEDA	*N,N,N',N'*-tetramethyl 1,2-ethanediamine *N,N,N',N'*-四甲基乙二胺
TMG	1,1,3,3-tetramethylguanidine 1,1,3,3-四甲基胍
TMP	2,2,6,6-tetramethylpiperidine 2,2,6,6-四甲基哌啶
TMS	trimethylsilyl 三甲基硅基
TMSCl	trimethylsilyl chrolide 三甲基氯硅烷
TMSCN	trimethylsilyl cyanide 三甲基氰硅烷
TMSI	trimethylsilyl iodide 三甲基碘硅烷
TMSOTf	trimethylsilyl triflate 三甲基三氟甲磺酰基硅烷
Tol	toluene or *p*-tolyl 甲苯或对甲苯基
Tol-BINAP	2,2'-bis(di-*p*-tolylphosphino)-1,1'-binaphthyl 2,2'-二(对甲苯基膦)-1,1'-联萘
TosMIC	(*p*-tolylsulfonyl)methyl isocyanide 对甲苯磺酰基甲基异氰
Ts	tosyl 对甲苯磺酰基
TsO	tosylate 对甲苯磺酸酯(盐)
UHP	urea hydrogen peroxide complex 脲素过氧化氢络合物
Z	Zusammen Z式
Δ	Solvent heated under reflux 加热回流的溶剂

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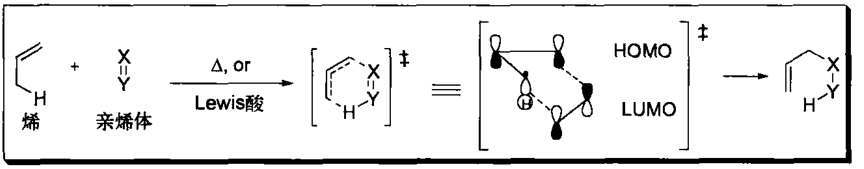
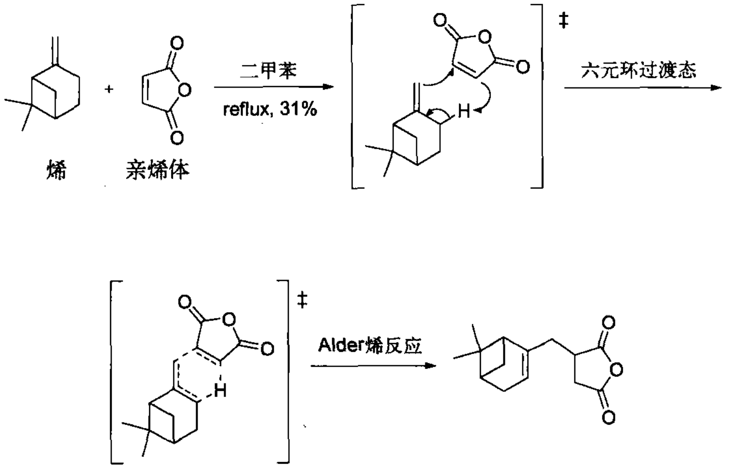
Alder烯反应

Alder烯反应，又常称氢-烯丙基加成反应，是一个亲烯体经过烯丙基转移加成到一个烯烃上的反应。包括一个烯烃 π 键和烯丙基 C—Hσ 键的四电子体系参与的一个周环反应，双键发生迁移并形成新的 C—Hσ 键和 C—Cσ 键。

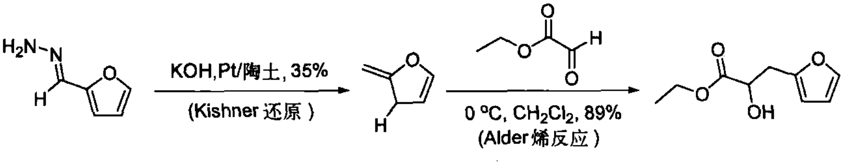


X=Y: C=C, C≡C, C=O, C=N, N=N, N=O, S=O, *etc.*

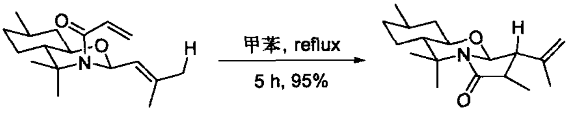
Example 1[5]



Example 2[7]

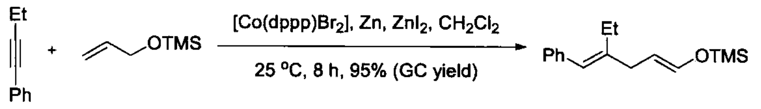


Example 3, 分子内 Alder-烯反应[8]

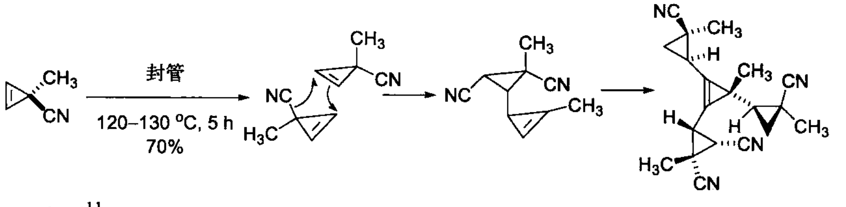


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_1,

Example 4, Co催化的 Alder 烯反应[9]



Example 5, 腈的 Alder-烯反应[10]



Example 6[11]

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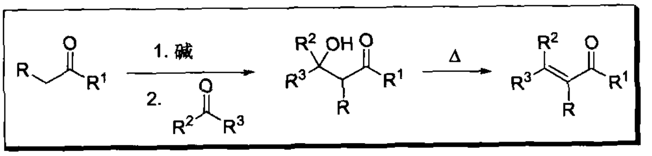
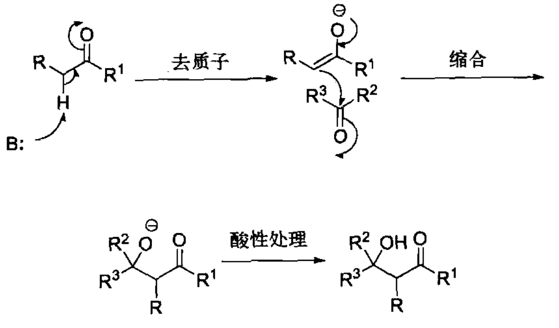
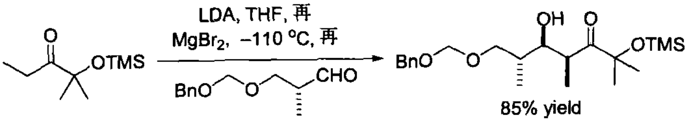
Aldol缩合反应

Aldol反应亦称醇醛缩合反应，是一个烯醇离子和羰基化合物缩合而形成一个β-羟基羰基化合物，有时又接着脱水给出一个共轭烯酮的反应。一个简单的实例是一个烯醇化物对一个醛（**Ald**ehyde）加成而给出一个醇（alcoh**ol**），故名为Aldol。

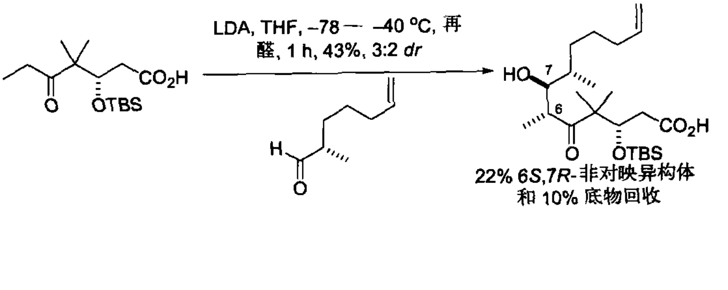




Example 1[3]

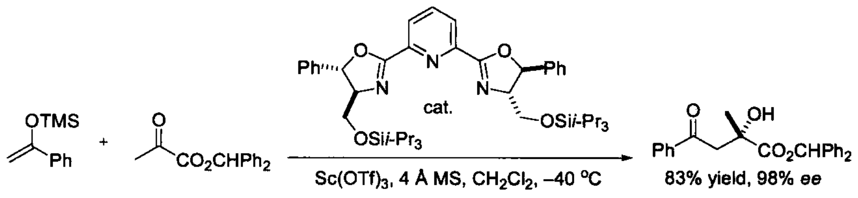


Example 2[8]

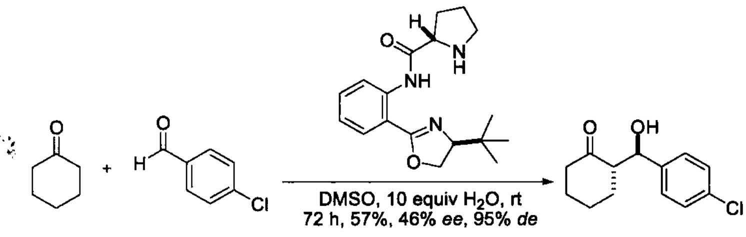


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_2,

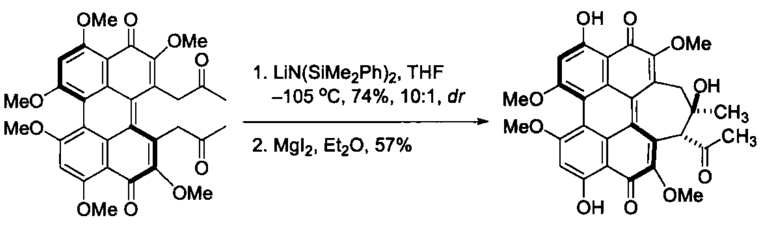
Example 3, 对映选择性 Mukaiyama-aldol 反应[10]



Example 4,有机催化的 aldol 反应[12]



Example 5, 跨环的 aldol 反应[13]



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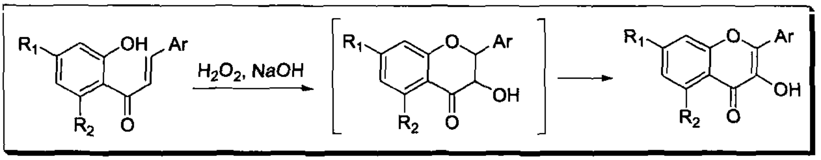
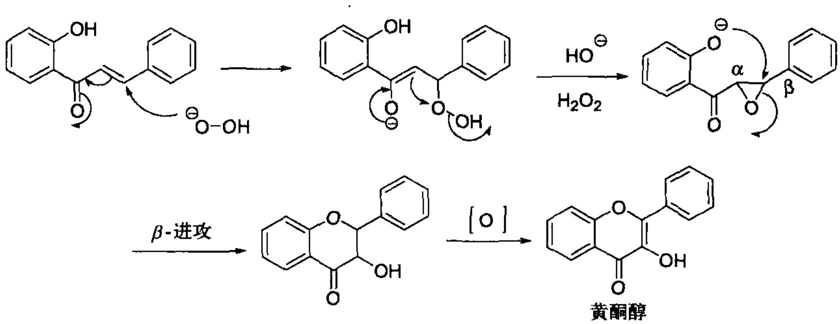
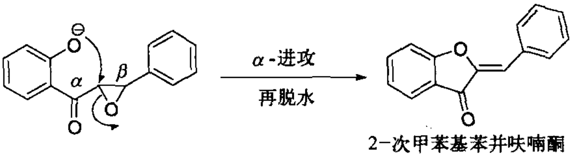
Algar-Flynn-Oyamada反应

2'-羟基查尔酮经氧化环化转化为2-芳基-3-羟基-4*H*-苯并吡喃(黄酮醇)。

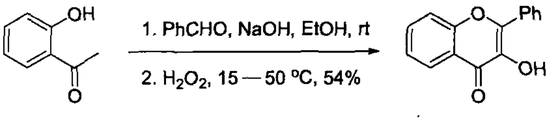




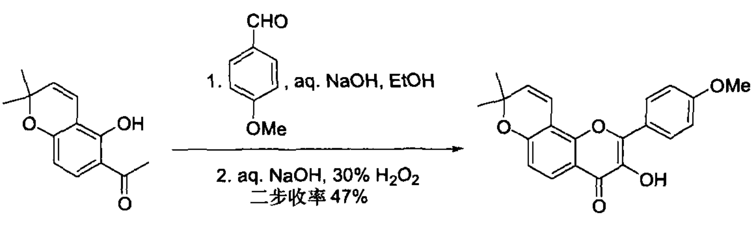
副反应:



Example 1[5]

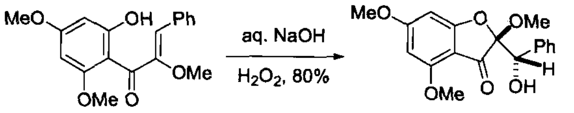


Example 2[5]

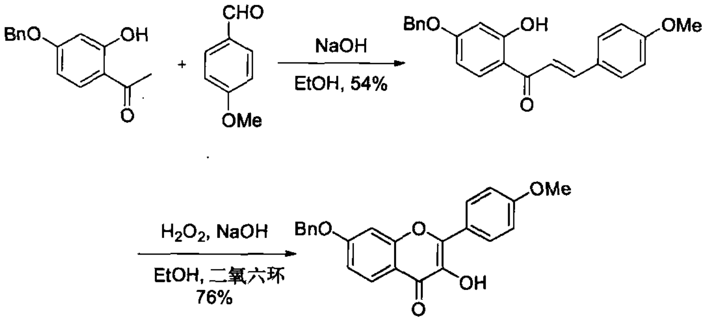


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_3,

Example 3, 副反应给出苯并呋喃酮类衍生物：[9]



Example 4[12]



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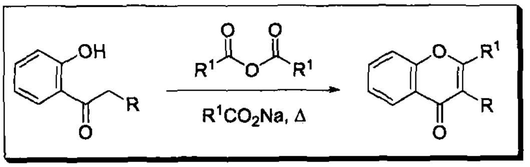
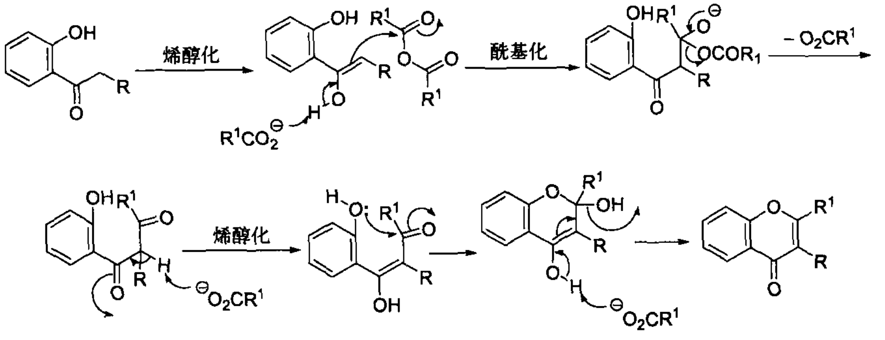
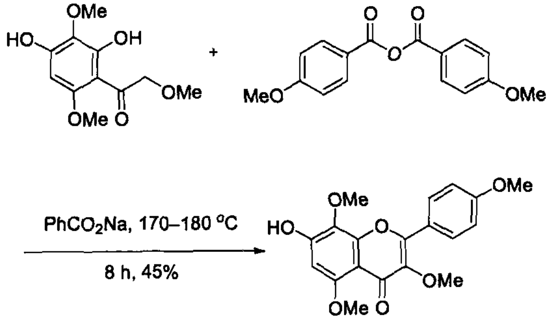
Allan-Robinson反应

邻羟基芳基酮用酸酐处理合成黄酮或异黄酮。(参见第322页上的Kostanecki反应)

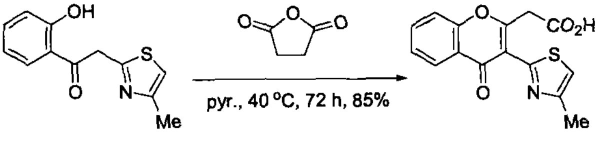




Example 1[6]



Example 2[9]



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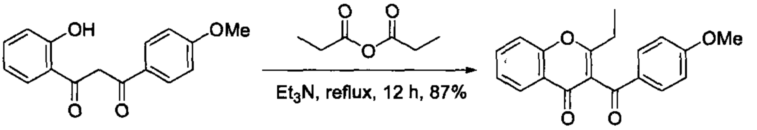
Example 3[10]



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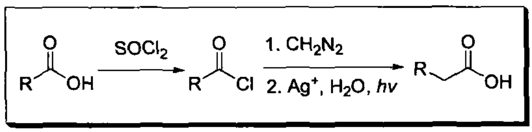
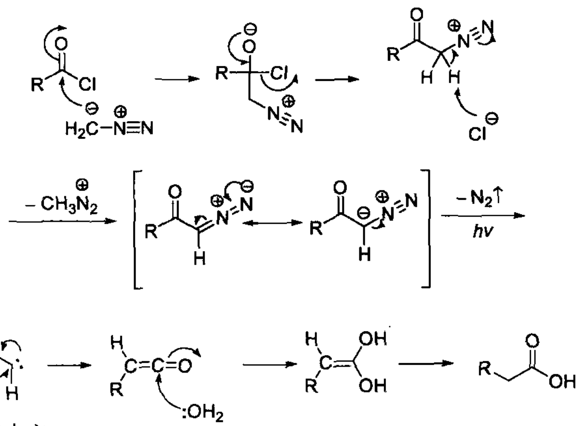
Arndt-Eistert 同系增碳反应

羧酸经重氮甲烷处理增加一个同系碳。

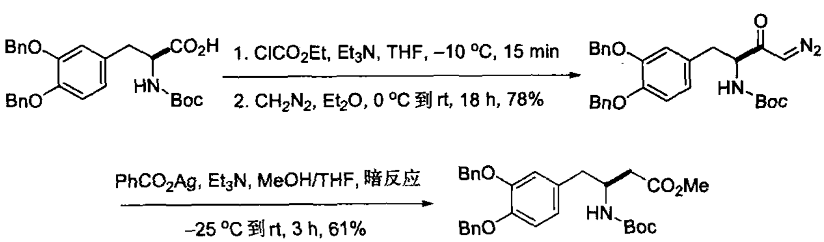




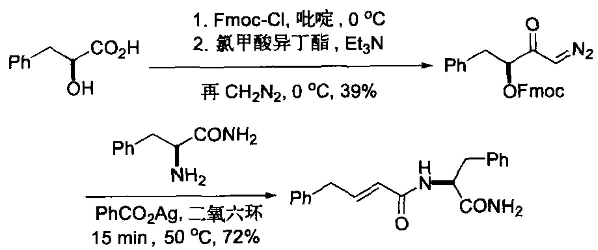
α-羰基卡宾中间体

烯酮中间体

Example 1[7]

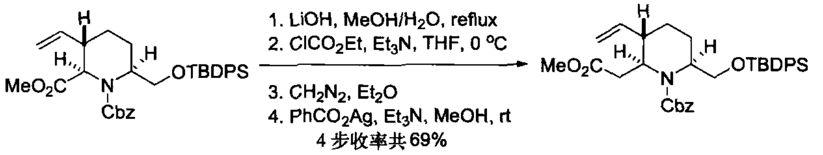


Example 2, 一个有意义的变异[9]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_5,

Example 3[10]



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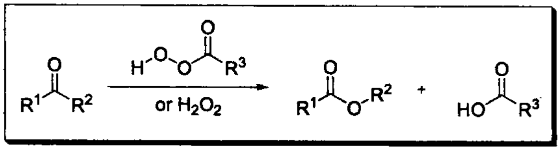
Baeyer-Villiger氧化反应

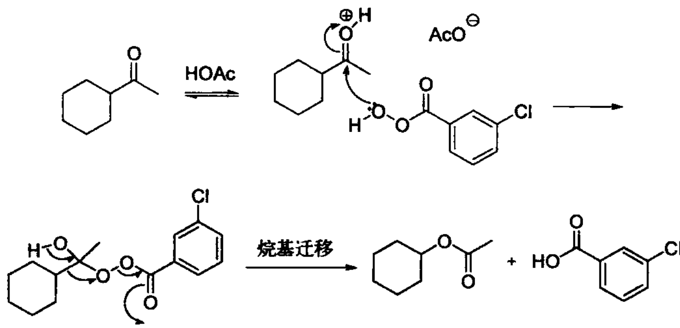
通式



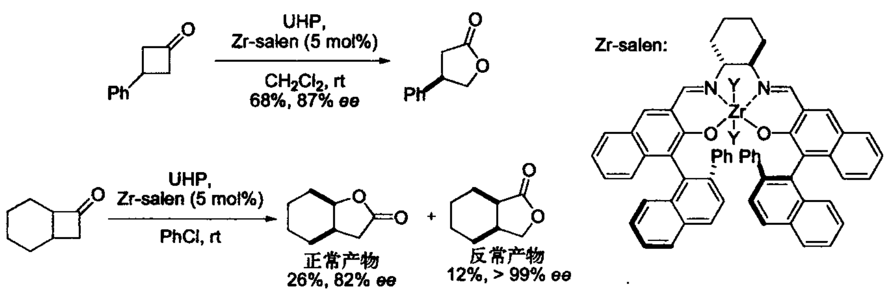
富电子的烷基（多取代碳原子）先迁移。迁移能力为叔烷基＞环己基＞仲烷基＞苄基＞苯基＞伯烷基＞甲基＞氢。

取代苯基的迁移能力为*p*-MeO-Ar＞*p*-Me-Ar＞*p*-Cl-Ar＞*p*-Br-Ar＞*p*-NO_2-Ar

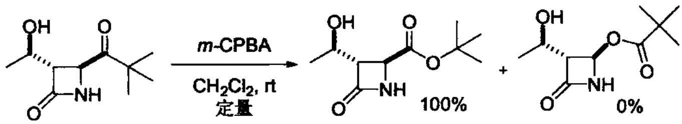
Example 1:



Example 2[4]

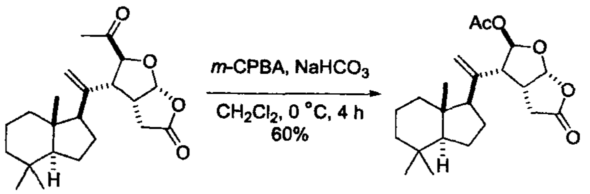


Example 3[5]

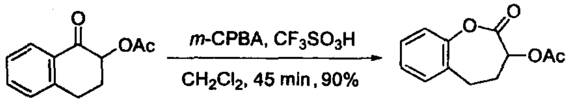


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_6,

Example 4[6]



Example 5[8]



References

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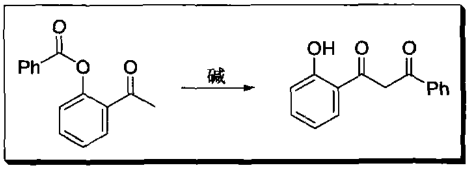
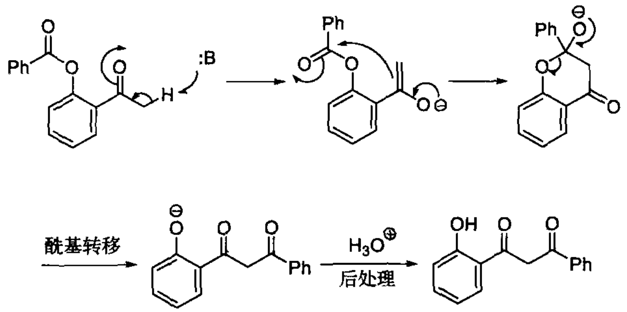
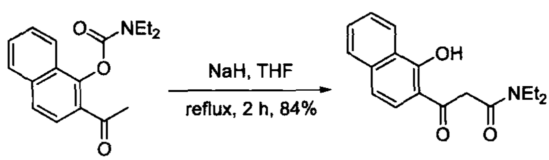
Baker-Venkataraman重排反应

碱催化下转变 α-酰氧酮为 β-二酮的重排反应。

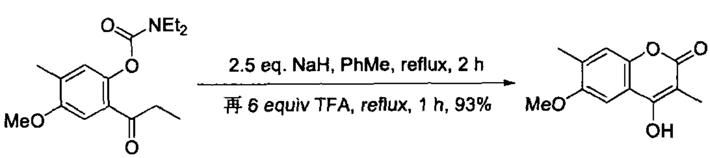




Example 1, 氨基甲酰基 Baker–Venkataraman 重排[5]



Example 2, 氨基甲酰基 Baker–Venkataraman 重排[6]



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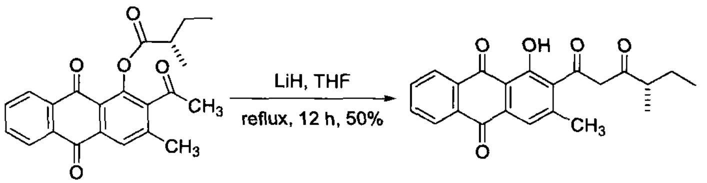
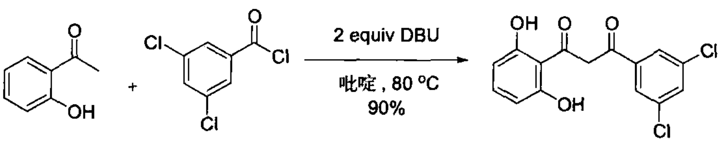
Example 3, 酯基 Baker–Venkataraman 重排[9]



Example 4, 酯基 Baker–Venkataraman 重排[10]



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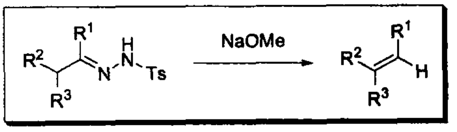
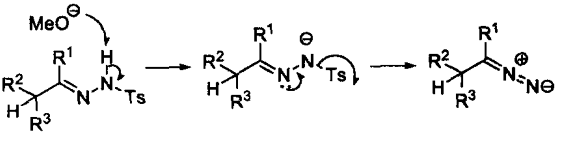
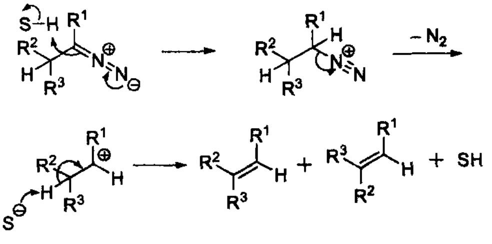
Bamford-Stevens反应

Bamford-Stevens反应和Shapiro反应有相同的机理。前者使用如Na、NaOMe、LiH、NaH、$NaNH_2$为碱和加热等条件，后者使用烷基锂和格氏试剂为碱。结果是Bamford-Stevens反应得到多取代的热力学稳定的烯，后者一般得到少取代的动力学产物烯。

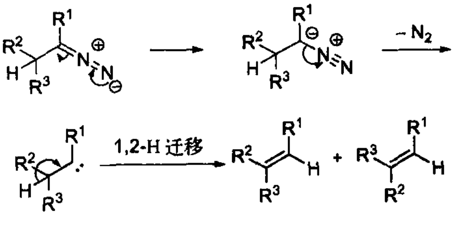




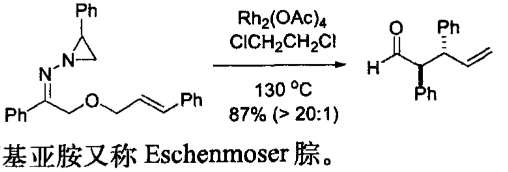
质子性溶剂中(S–H):



非质子性溶剂中:



Example 1, 串联Bamford–Stevens 热脂肪族 Claisen重排[2]



底物 N- 氮杂环丙基亚胺又称 Eschenmoser 腙。

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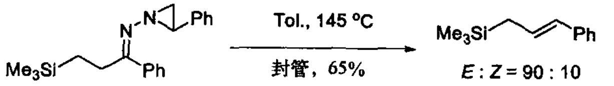
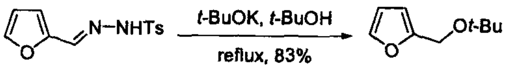
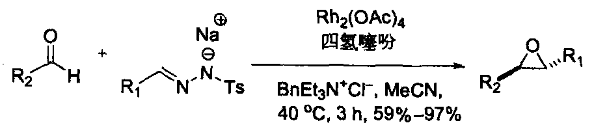
Example 2, 热 Bamford–Stevens反应[6]



Example 3[7]



Example 4[8]



References

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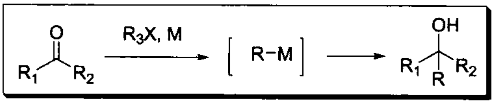
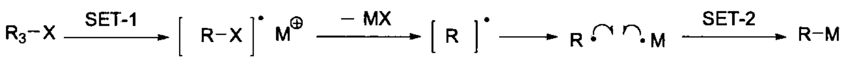
Barbier偶联反应

Barbier偶联加成反应虽然比格氏反应(见第266页)要早一年操作，但实际上和格氏反应是同时成功的。

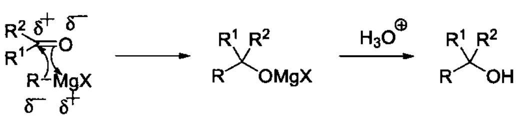


基于通用的常识，就地生成的Mg、Li、Sm、Zn、La等有机金属中间体立即被羰基化合物捕获。但最近的实验和理论研究都表明，Barbier偶联反应是通过单电子转移路径而实现的。

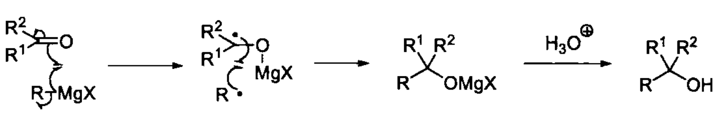
Grignard试剂制备，



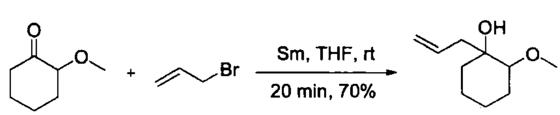
离子机理，



单电子转移机理，



Example 1[6]



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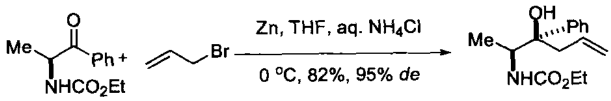
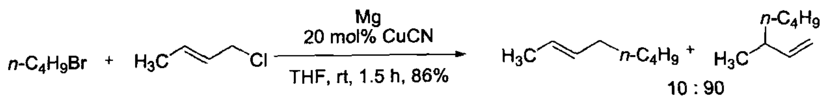
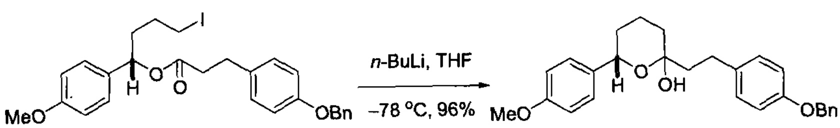
Example 2[9]



Example 3[10]



Example 4[11]



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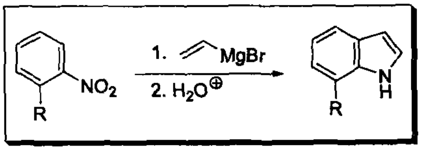
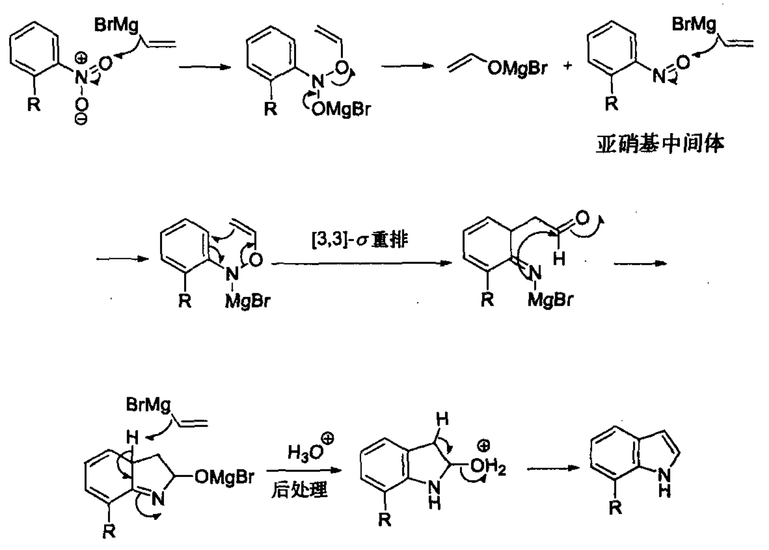
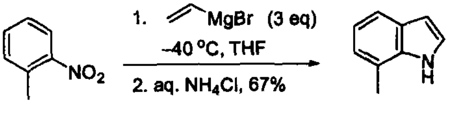
Bartoli吲哚合成反应

邻取代硝基芳烃和烯基格氏试剂反应生成7-取代吲哚。

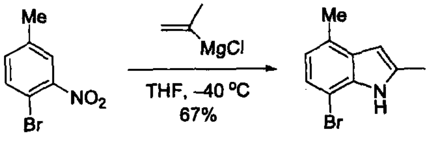




Example 1[3]



Example 2[6]



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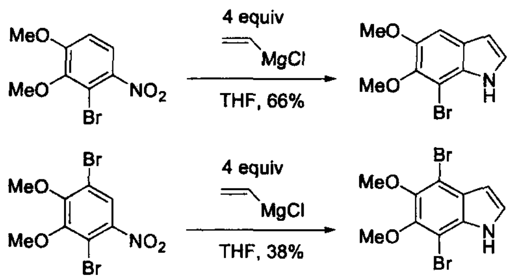
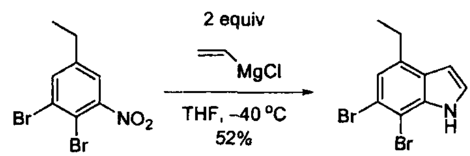
Example 3[10]



Example 4[11]



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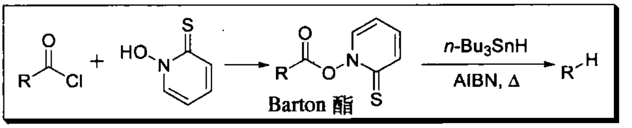
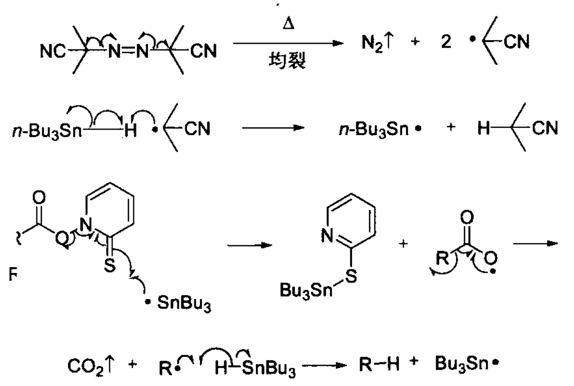
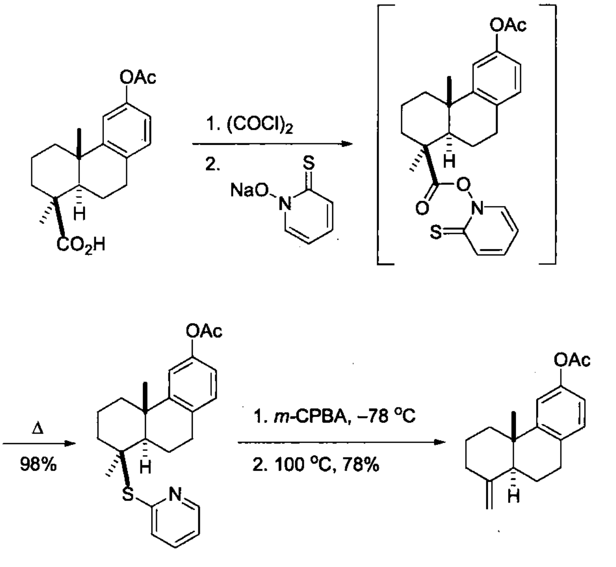
Barton自由基脱羧反应

羧酸的硫羰基衍生物可发生自由基脱羧反应。



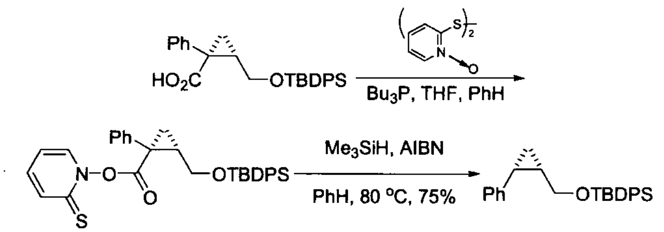


Example 1[3]

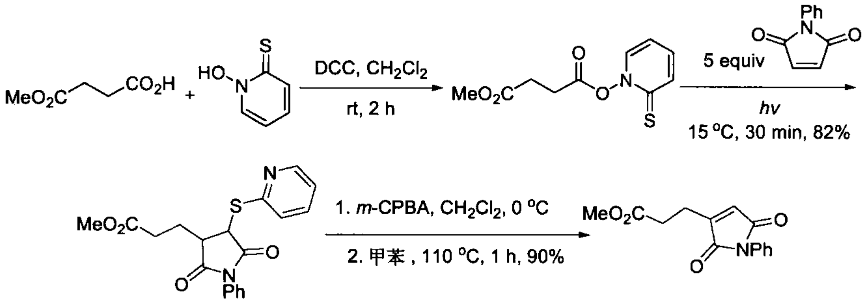


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_11,

Example 2[6]



Example 3[9]



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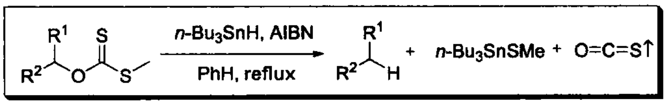
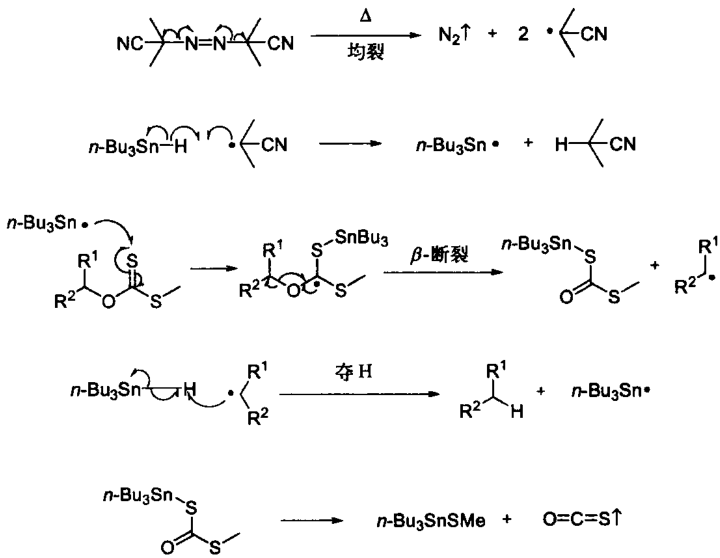
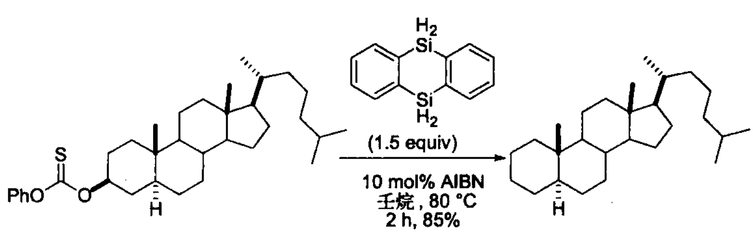
Barton- McCombie去氧反应

醇的硫羰基衍生物可发生自由基裂解脱氧反应。



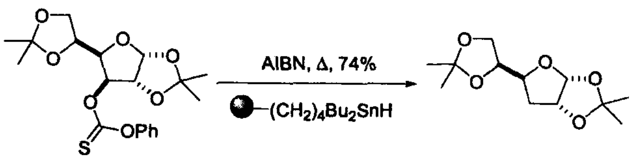


Example 1[2]

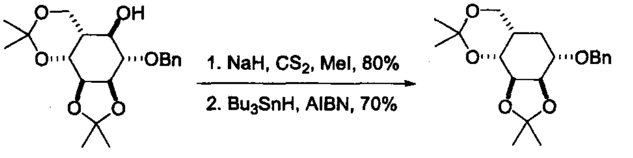


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_12,

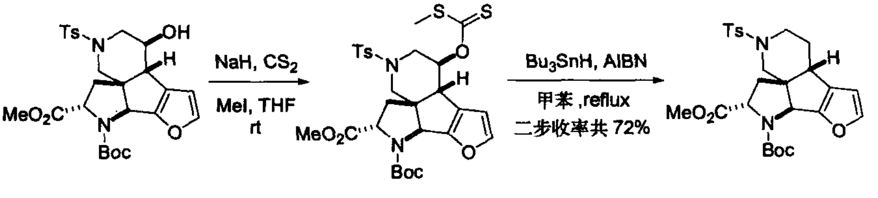
Example 2[6]



Example 3[10]



Example 4[11]



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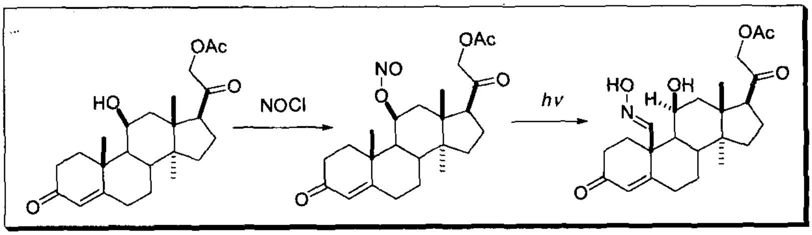
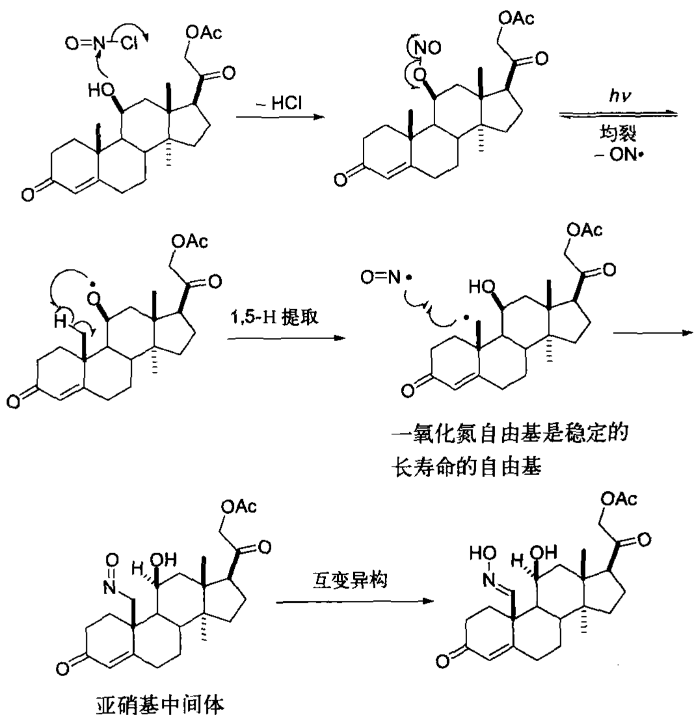
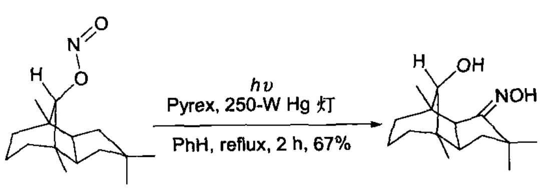
Barton亚硝酸酯光解反应

亚硝酸酯光解反应生成 γ-肟醇。



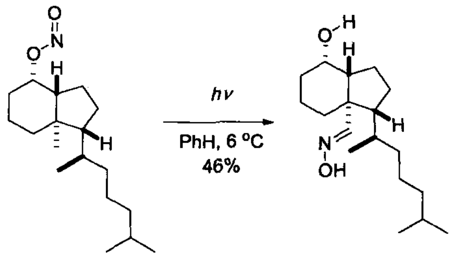


Example 1[2]

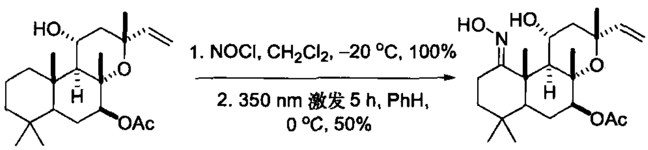


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_13,

Example 2[6]



Example 3[7]



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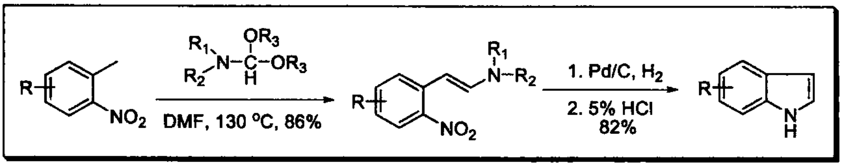
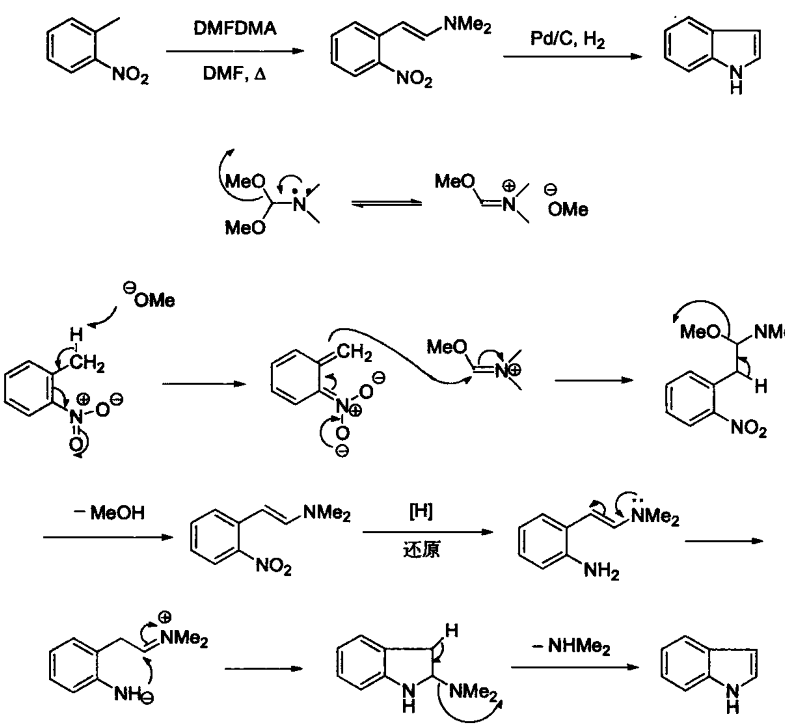
Batcho-Leimgruber 吲哚合成反应

邻硝基甲苯衍生物和甲酰胺缩酮反应得到的*trans*-β-二甲氨基-2-硝基甲苯衍生物还原后生成取代吲哚衍生物。



Example 1[4]



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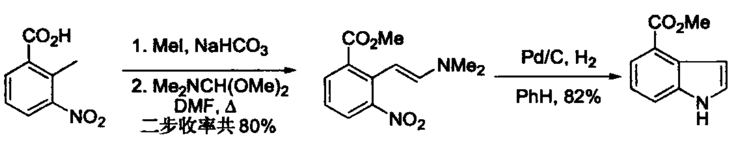
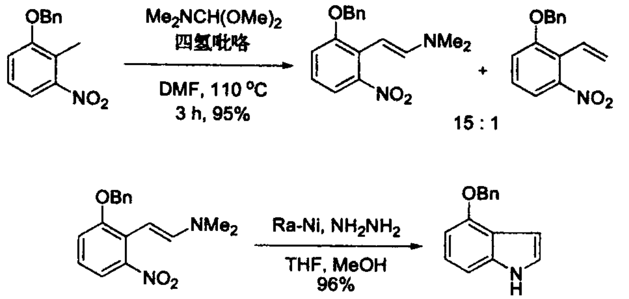
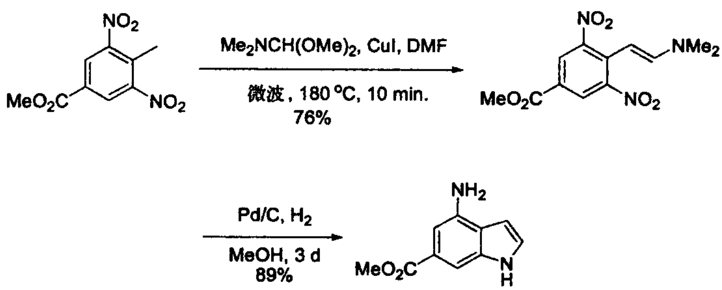


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_14,

Example 3[5]



Example 4[10]



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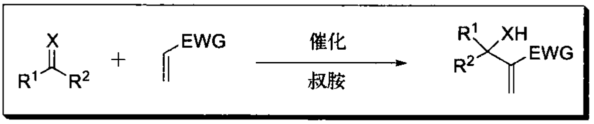
Baylis-Hillman 反应

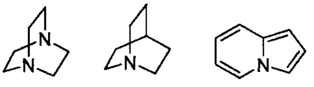
本反应亦称Morita-Baylis-Hillman 反应，是一个缺电子烯烃和一个亲电的碳物种间的C—C成键反应。缺电子烯烃包括丙烯酸酯、丙烯腈、乙烯基酮、乙烯基砜和丙烯醛。另一个亲电的碳物种则可以是醛、α-烷氧羰基酮、醛亚胺和Michael受体。

通式：

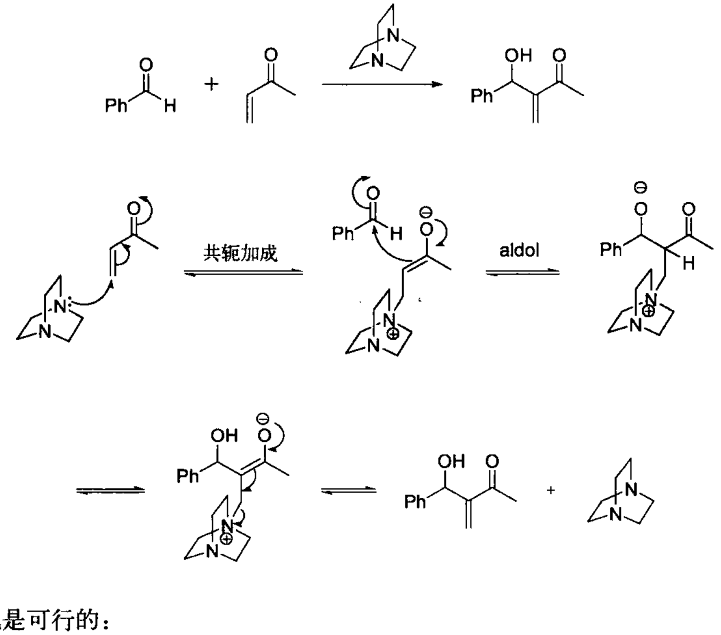


$X = O, NR_2$, $EWG = CO_2R, COR, CHO, CN, SO_2R, SO_3R, PO(OEt)_2, CONR_2, CH_2{=}CHCO_2Me$

其他催化用叔胺：



Example 1:



E2 机理也是可行的：

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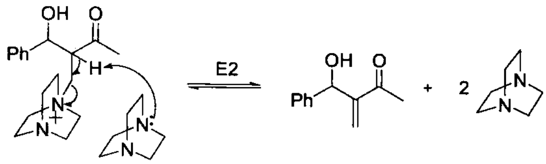
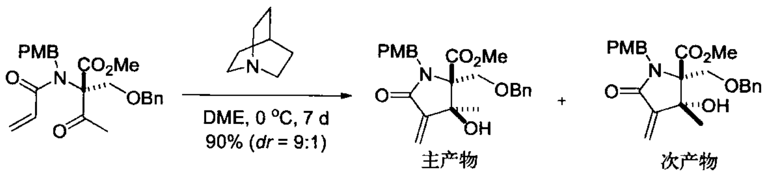
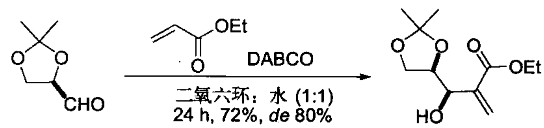


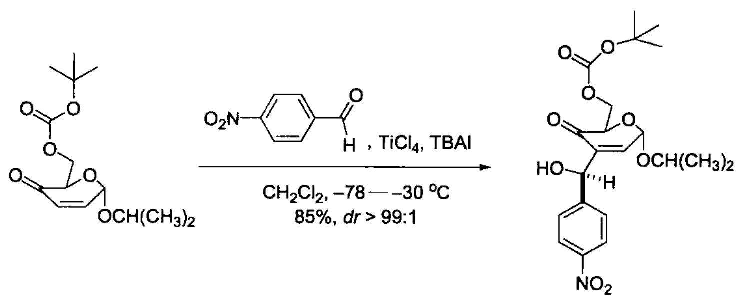
Example 2, 分子内 Baylis–Hillman 反应[6]



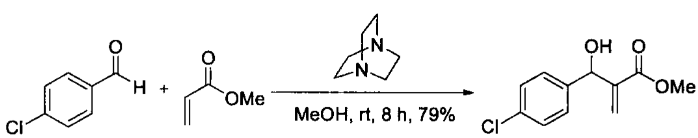
Example 3[7]



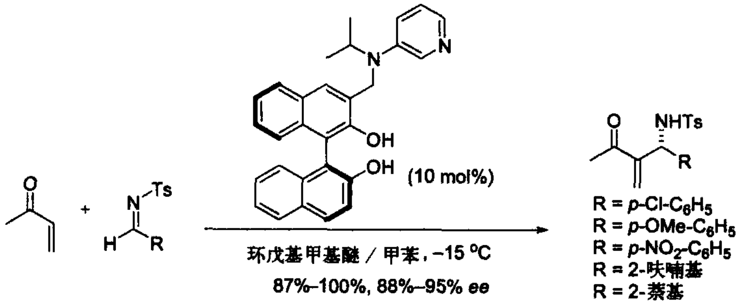
Example 4[8]



Example 5[9]



Example 6[10]



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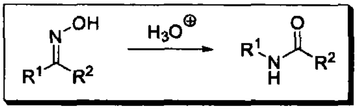
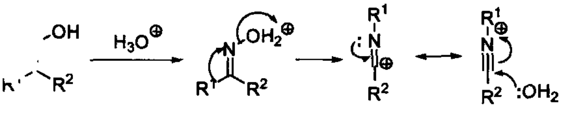
Beckman重排反应

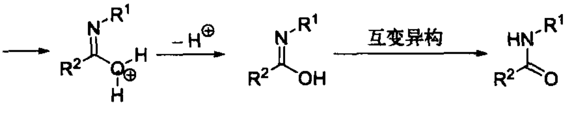
肟在酸介质中异构化为酰胺。

质子酸中：

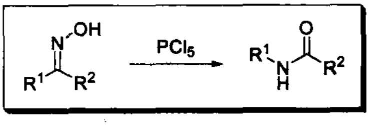


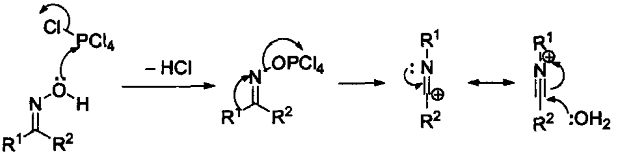


与离去基团处于反式的取代基迁移

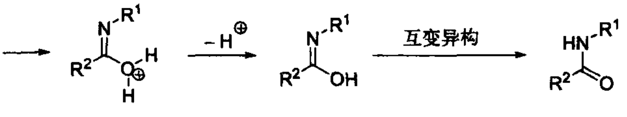


用PCl_5:

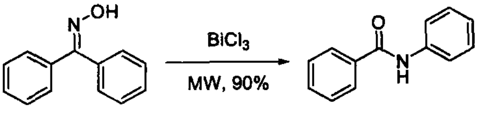




还是与离去基团处于反式的取代基迁移

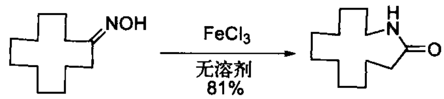


Example 1, 微波反应[3]

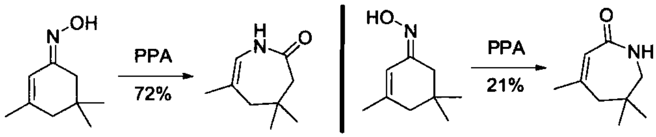


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_16,

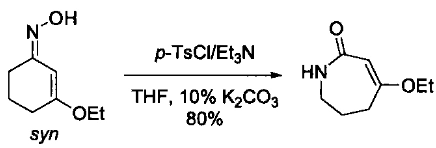
Example 2[4]



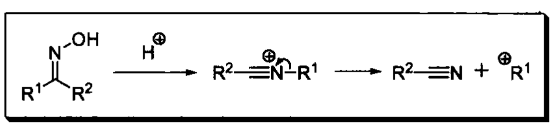
Example 3[6]



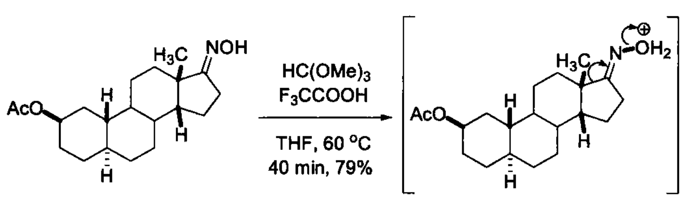
Example 4[8]

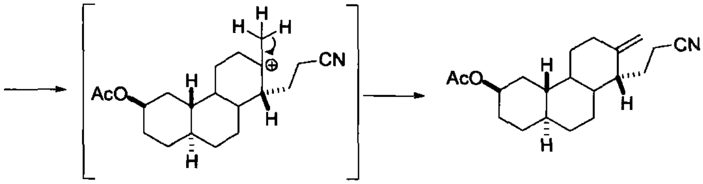


当迁移的取代基团（R^1）从中间体上消除而留下一个稳定的腈产物时会发生**反常的Beckman重排反应**。



Example 1[9]





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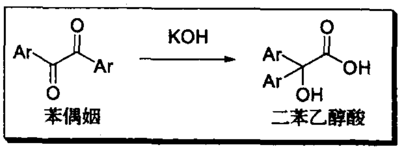
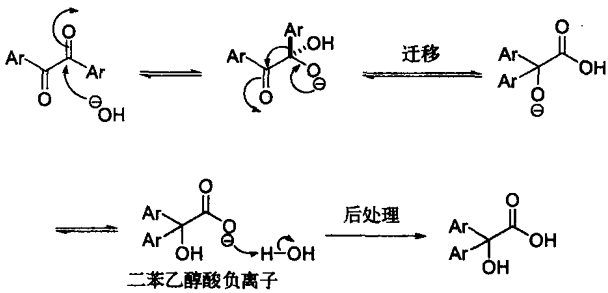
Benzilic（二苯乙醇酸）重排

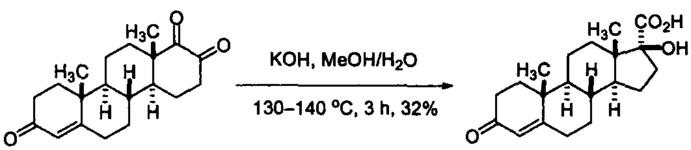
二苯乙二酮由芳基迁移重排为二苯乙醇酸



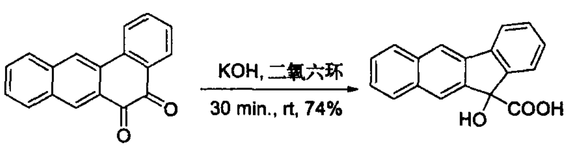


最后一步酸的去质子反应推动反应正向进行。

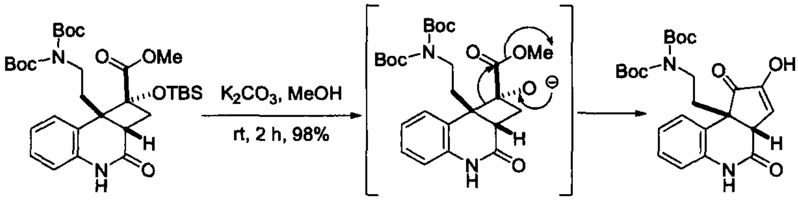
Example 1[3]



Example 2[6]



Example 3, 逆二苯乙醇酸重排[7]



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

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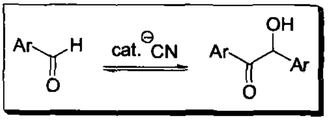
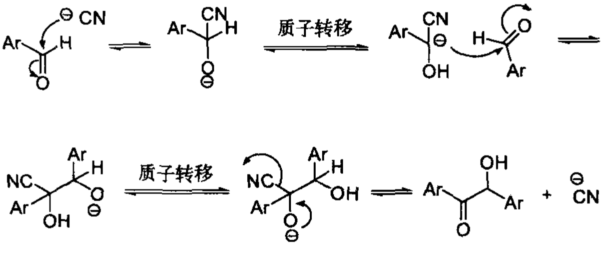
Benzoin（苯偶姻）缩合反应

氰根离子催化下芳香醛缩合为苯偶姻的反应。现在氰根离子已为噻唑鎓盐所代替。参见第525页上的Stetter反应。





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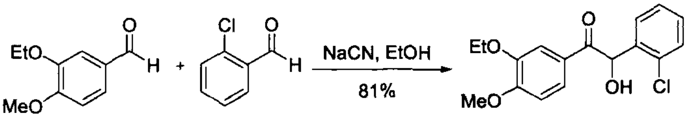

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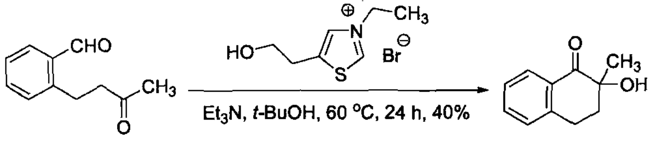

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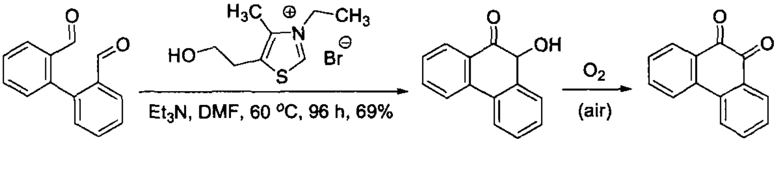
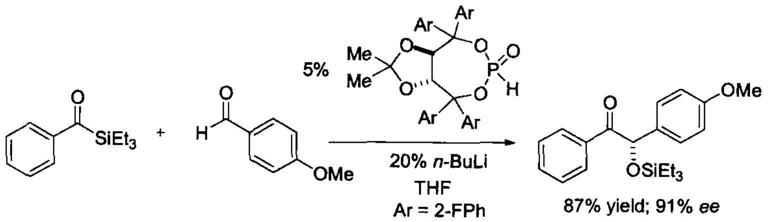
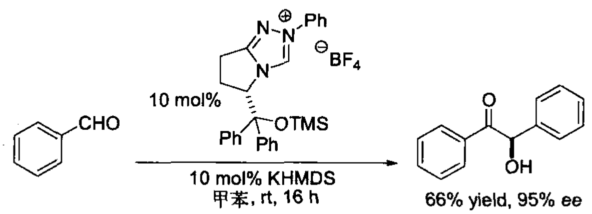


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_18,

Example 4[9]



Example 5[10]



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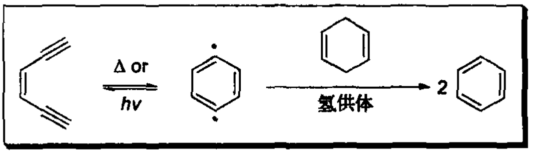
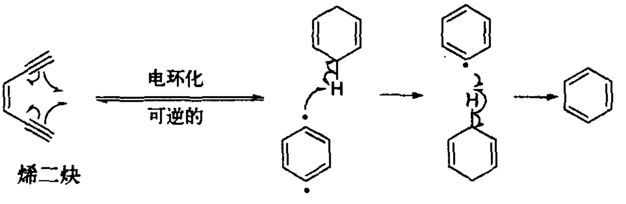
Bergman环化反应

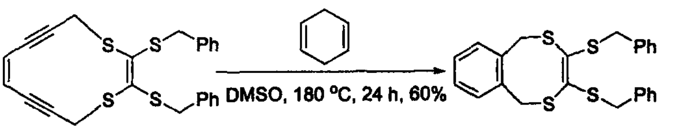
从烯二炔经电环化反应生成1,4-苯基双自由基。





1,4-苯基双自由基

Example 1[6]



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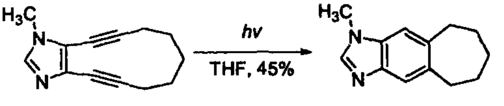
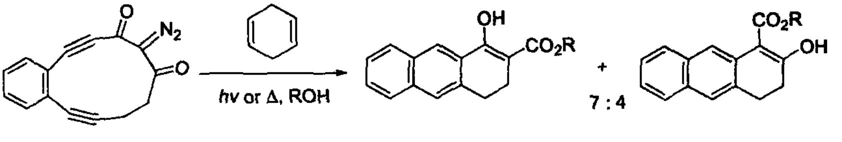
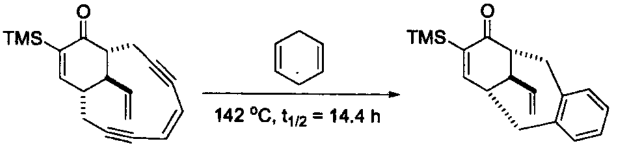


Example 3, Wolff重排后再Bergman环化[8]



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

Example 4[10]



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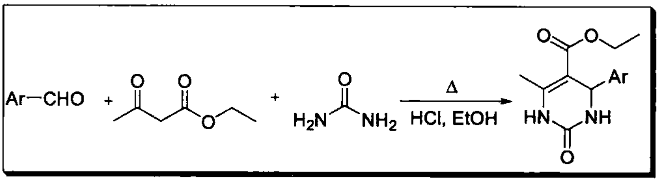
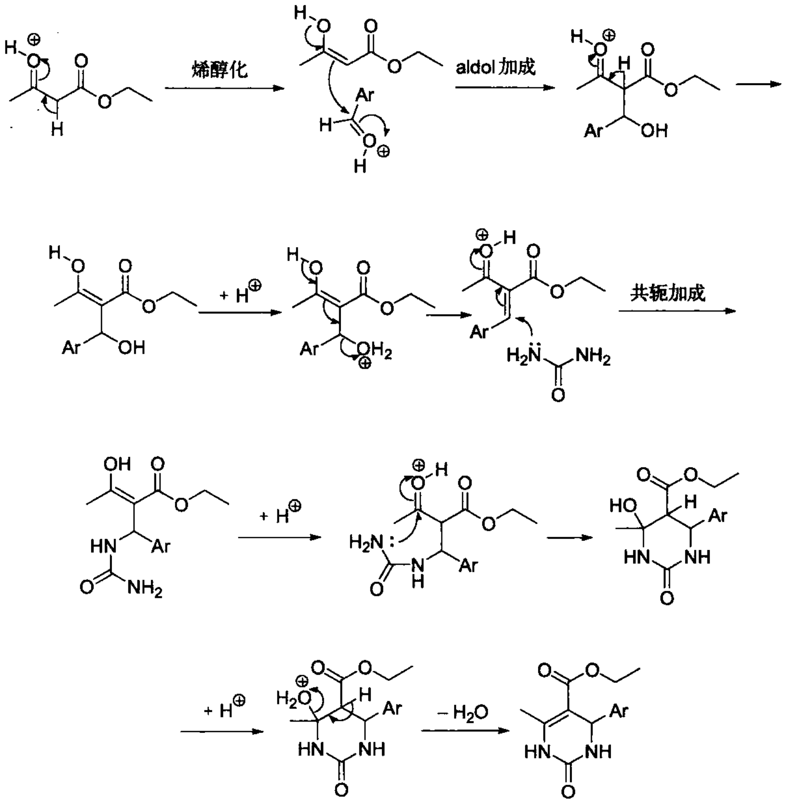
Biginelli嘧啶酮合成反应

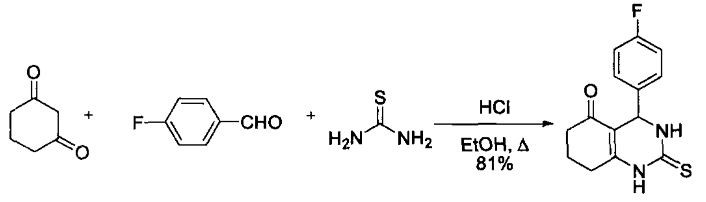
芳香醛、尿素和β-二羰基化合物在酸性醇溶液中一锅煮的缩合反应。此类缩合反应已得到扩展，属于多组分反应（MCRs）的一例。



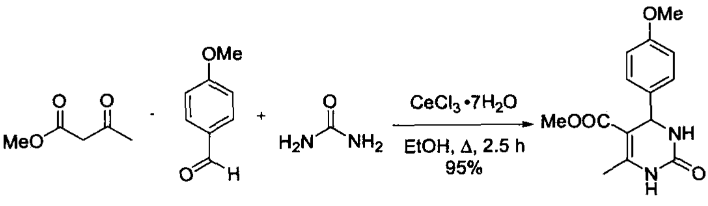


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_20,

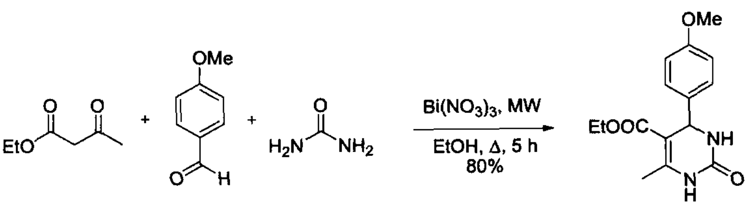
Example 1[4]



Example 2[5]



Example 3, 微波促进的Biginelli 缩合反应[9]



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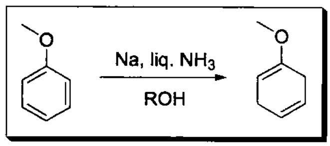
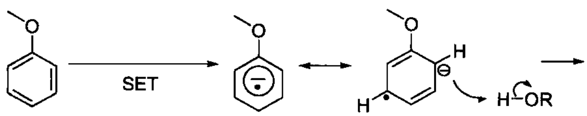
Birch 还原反应

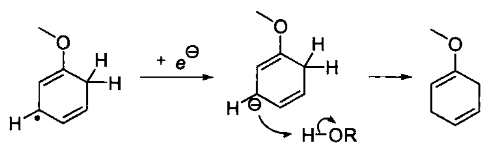
Birch还原反应是用溶于液氨的碱金属Li、Na、K在醇存在下将一个芳环经1,4-还原为相应的环已二烯的反应。

带供电子取代基的苯环：

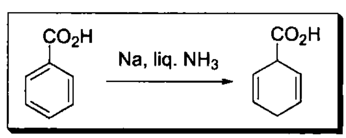


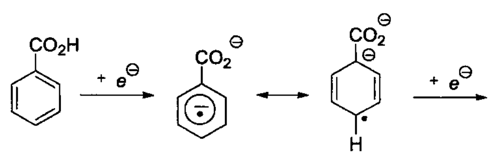


自由基负离子



带吸电子取代基的苯环：





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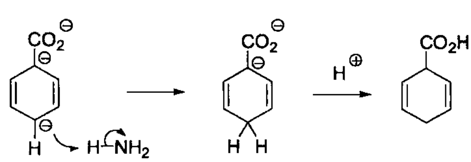

J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_21,

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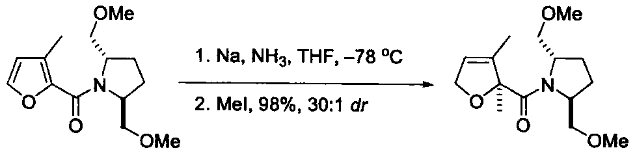

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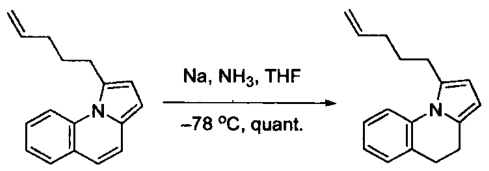

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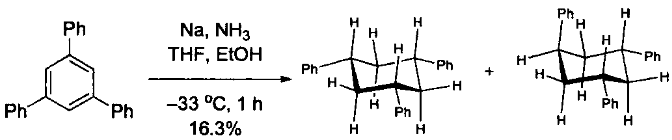

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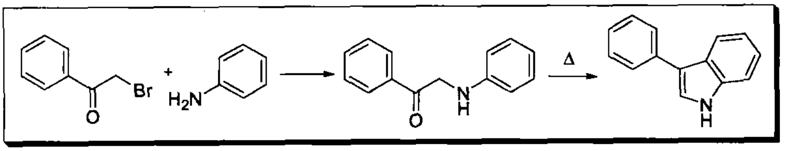
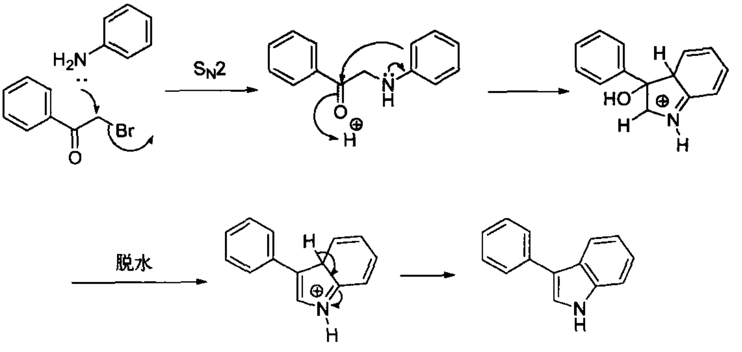
Bischler-Mohlau吲哚合成反应

Bischler-Mohlau吲哚合成反应亦称Bischler吲哚合成反应。从 α - 卤代芳香酮和过量的苯胺环化生成3-芳基吲哚。





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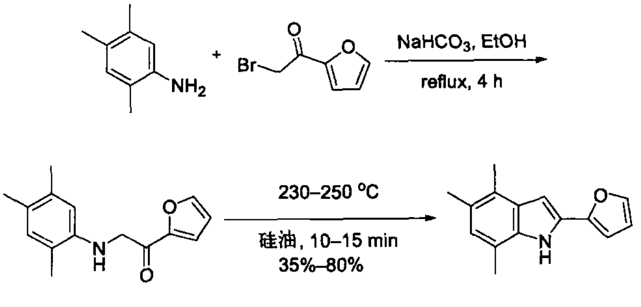

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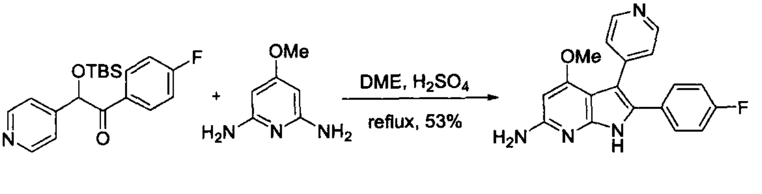
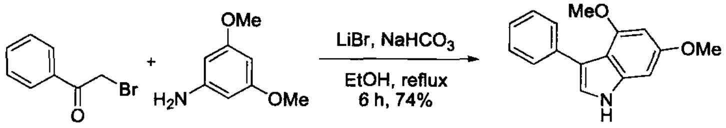
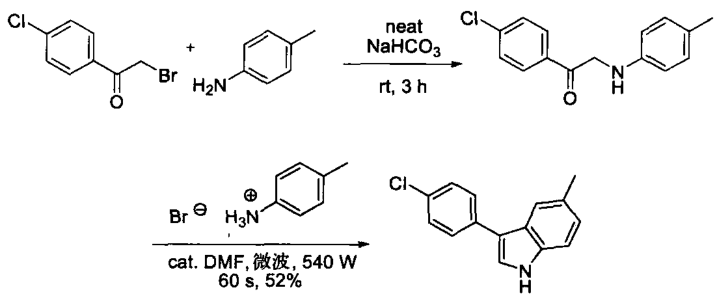


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_22,

Example 3[10]



Example 4, 微波促进的无溶剂 Bischler 吲哚合成[11]



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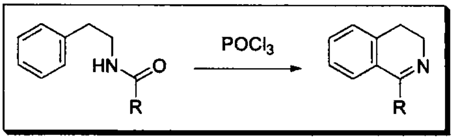
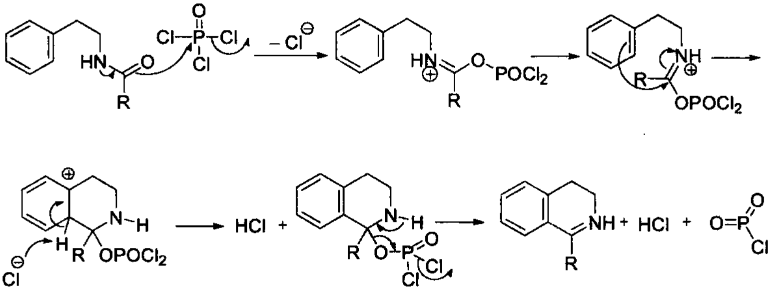
Bischler-Napieralski反应

β-苯乙基酰胺在回流的氧氯化磷作用下转化为二氢异喹啉的合成反应。





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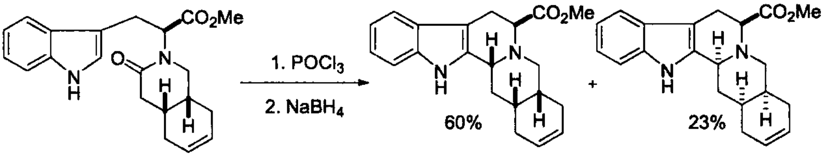

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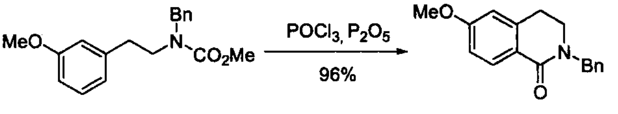

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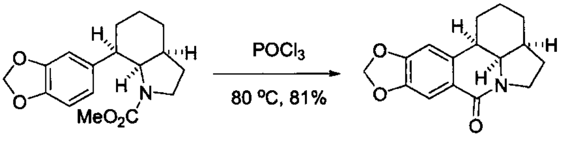
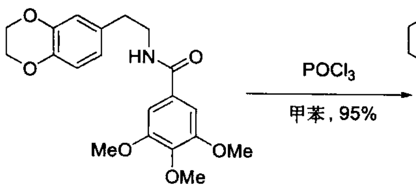
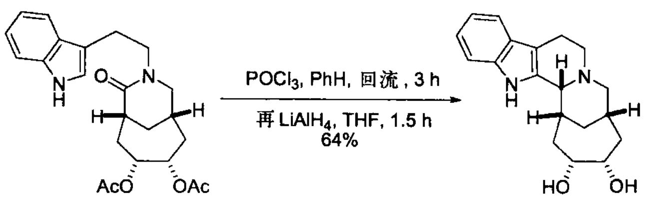


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_23,

Example 4[7]



Example 5[9]



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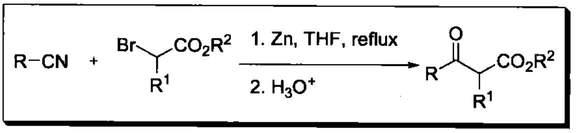
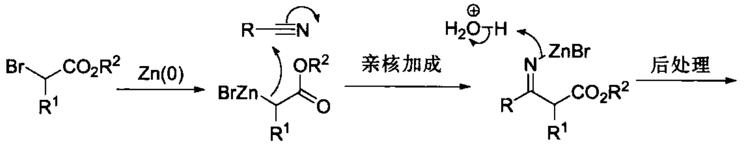
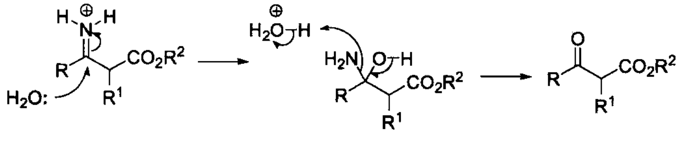
Blaise反应

腈与α-卤代酯在Zn作用下生成β-酮酯的加成反应。(参见第456页上的Reformatsky反应)

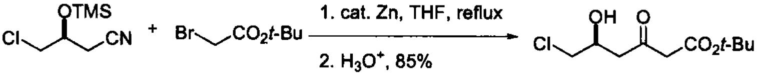




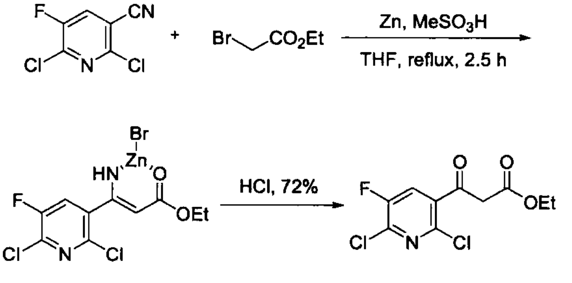
Zn的烯醇化物在晶态中是一个*C*-烯醇化物，但反应发生时平衡转为*O*-烯醇化物。



Example 1[5]

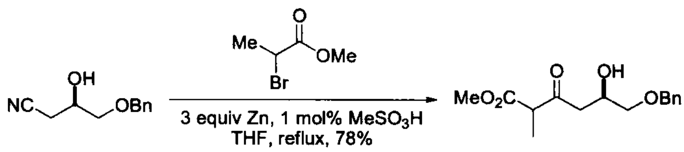


Example 2[6]

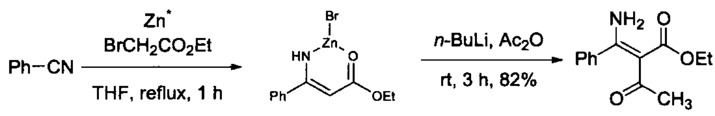


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_24,

Example 3[7]



Example 4,第一个Blaise反应中间体进行化学选择性的串联酰基化反应[9]。



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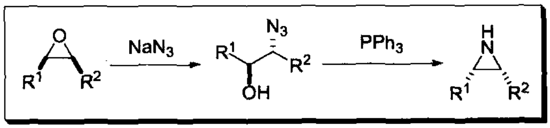
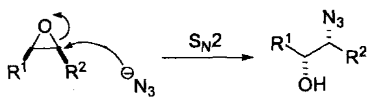
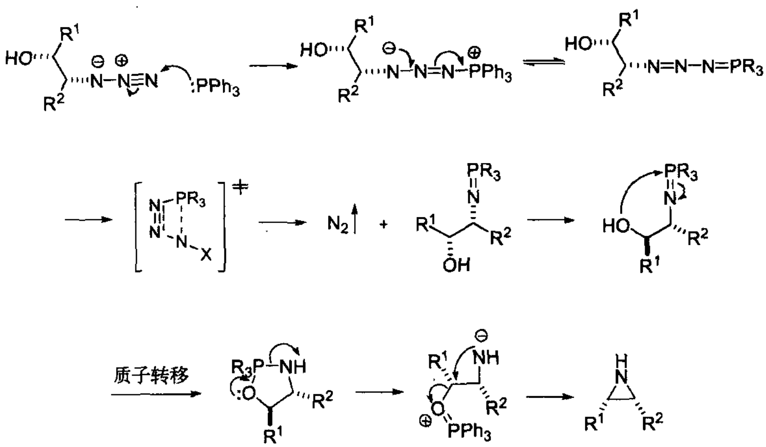
Blum-Ittah 氮丙啶合成反应

环氧化物用叠氮化物开环后得到的叠氮醇中间体再经 PPh_3 还原为相应的氮丙啶化合物。

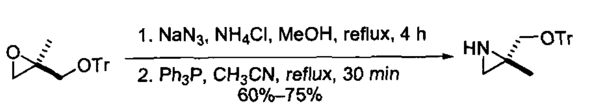




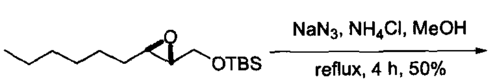
无论一个叠氮化物进行 S_N2 反应的位置选择性如何，最终氮丙啶产物的立体化学结果都是一样的。



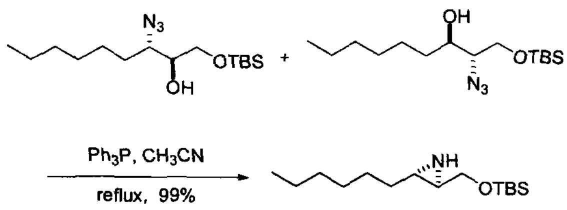
Example 1[3]



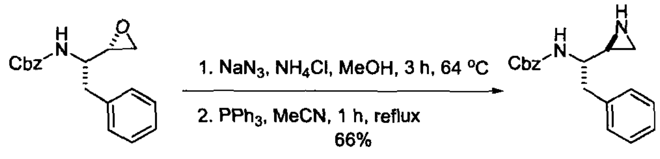
Example 2[5]



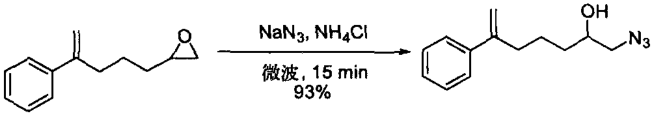
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_25,

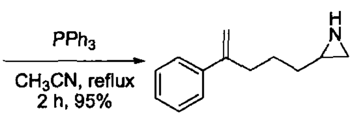


Example 3[7]



Example 4[8]





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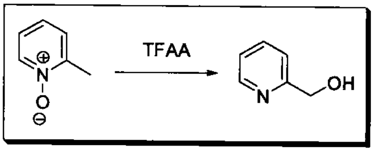
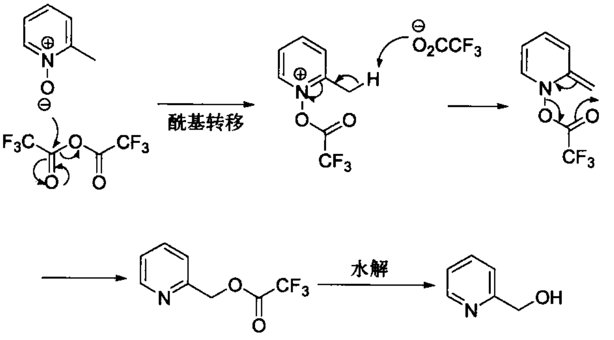
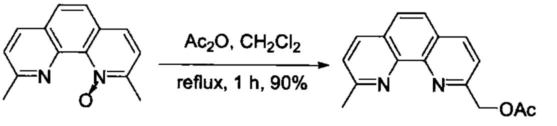
Boekelheide 反应

甲基吡啶的氮氧化物经三氟乙酸酐或乙酸酐处理给出2-羟甲基吡啶的重排反应。

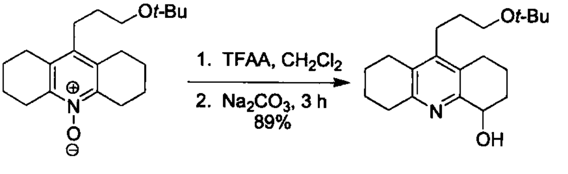




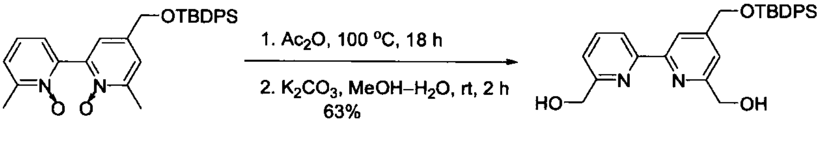
Example 1[4]



Example 2[6]

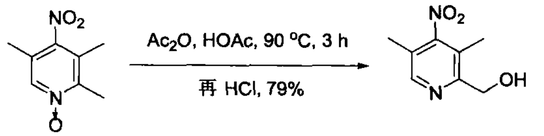


Example 3[8]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_26,

Example 4[9]



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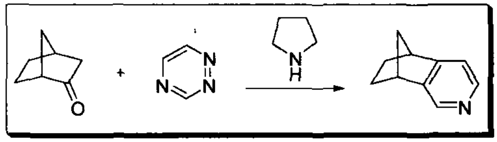
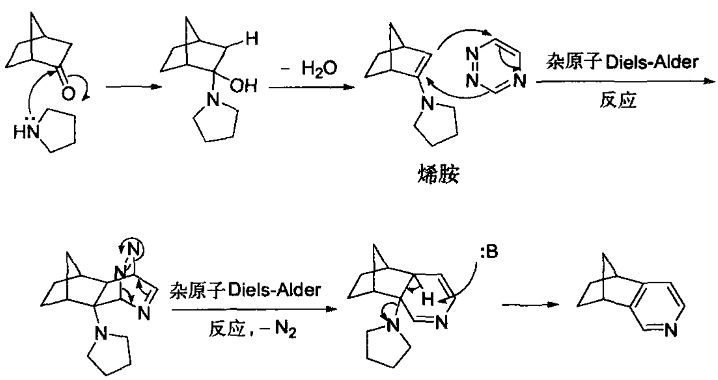
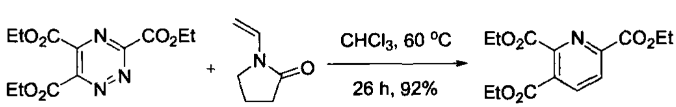
Boger 吡啶合成反应

1,2,4-三唑和亲双烯体（如烯胺）经杂原子Diels-Alder反应再脱氮生成吡啶的反应。

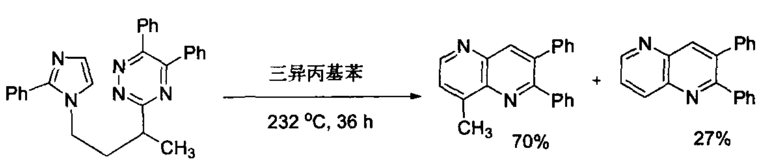




Example 1[3]

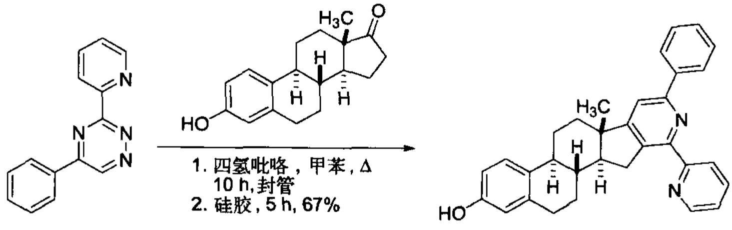


Example 2, 分子内Boger 吡啶合成[8]

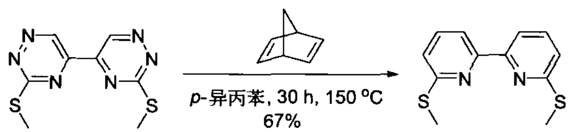


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_27,

Example 3[10]



Example 4[11]



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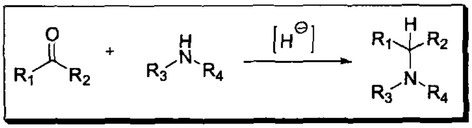
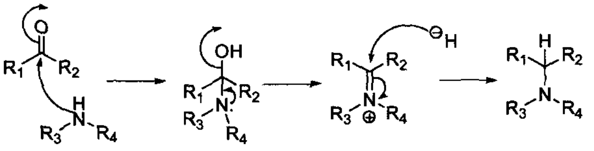
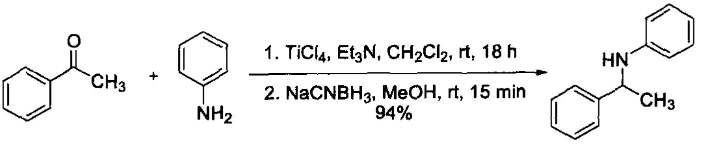
Borch还原氨化反应

由胺和羰基化合物而来的亚胺还原（常用$NaCNBH_3$）给出相应胺的还原氨化反应。

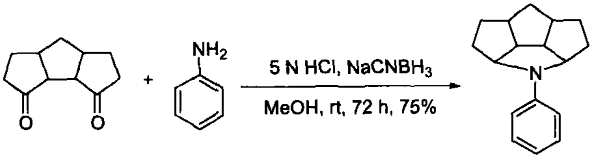




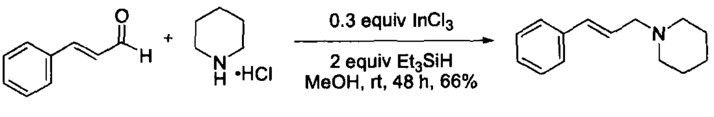
Example 1[4]



Example 2[5]

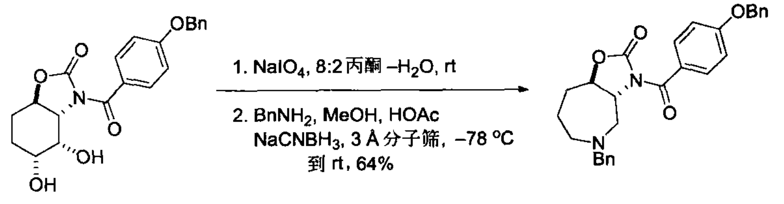


Example 3[8]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_28,

Example 4[9]



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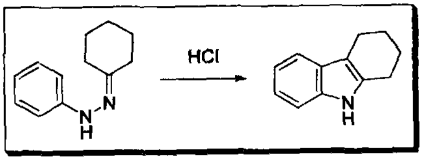
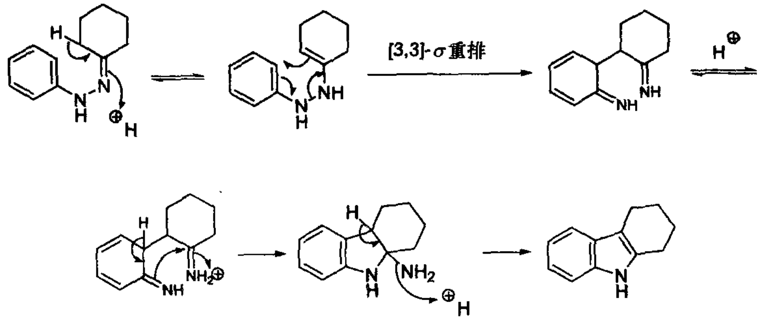
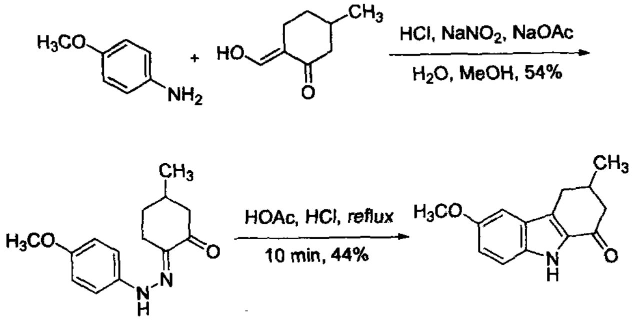
Borsche-Drechsel环化反应

从环己酮苯腙合成四氢咔唑（9-氮杂芴）的环化反应。参见第227页上的Fischer吲哚合成反应。

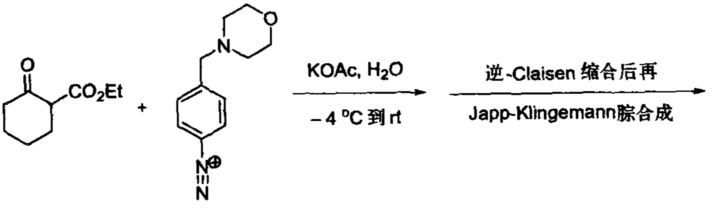




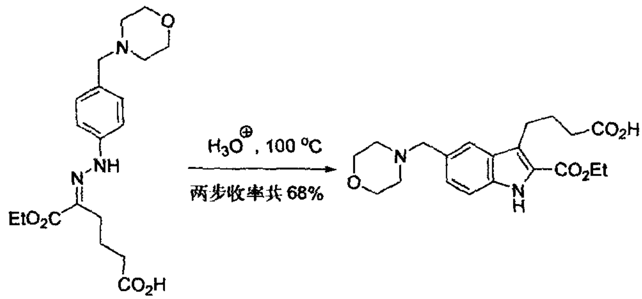
Example 1[6]



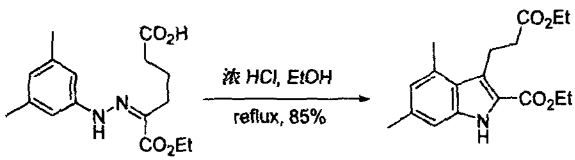
Example 2[10]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_29,



Example 3[10]



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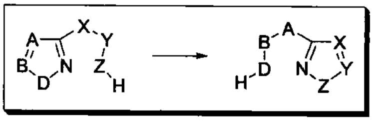
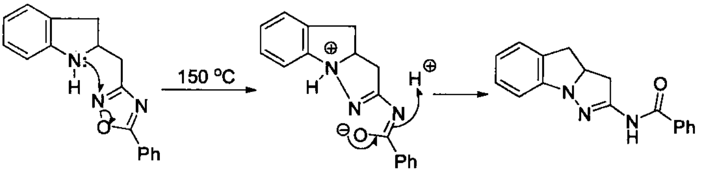
Boulton-Katritzky重排反应

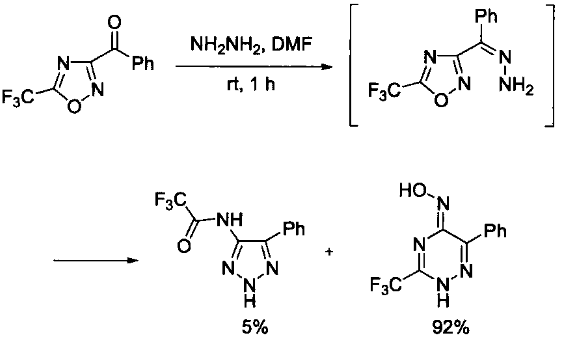
一个五元杂环热解下重排为另一个五元杂环的反应。



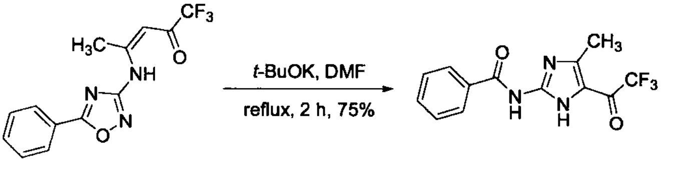
Example 1[4]



Example 2, 肼解[7]



Example 4[3]



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

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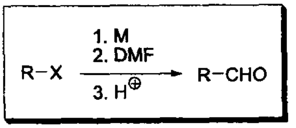
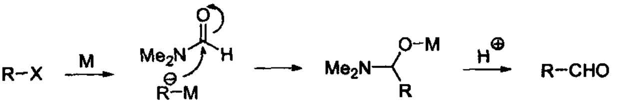
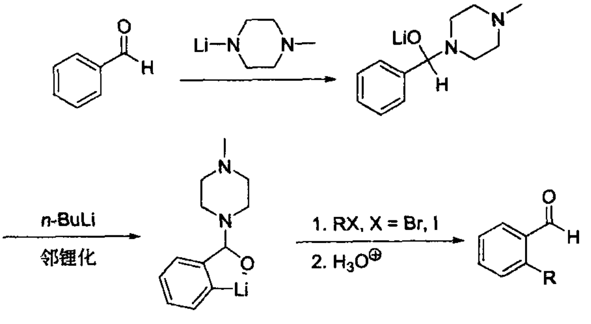
Bouveault醛合成反应

烷基或芳基卤代烃转化为相应的Li、Mg、Na、K等金属有机试剂后与DMF反应经甲酰化而成为同系醛的反应。

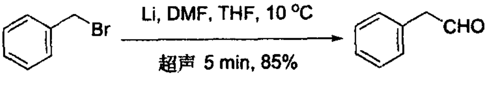




Comins 修正法:[4]



Example[3]



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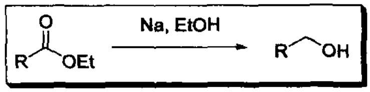
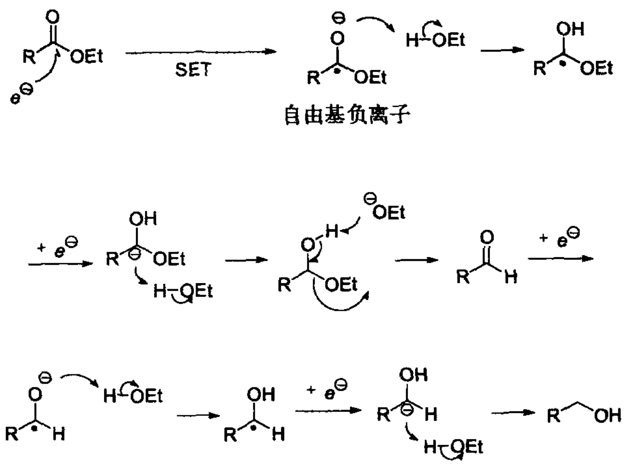
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_31,

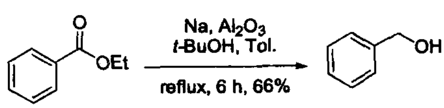
Bouveault-Blanc还原反应

用钠在醇溶剂中将酯还原为醇的反应。





Example[2]



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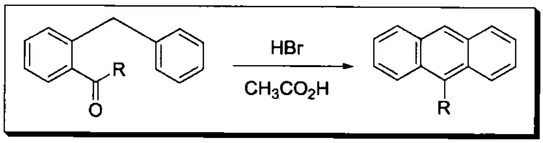
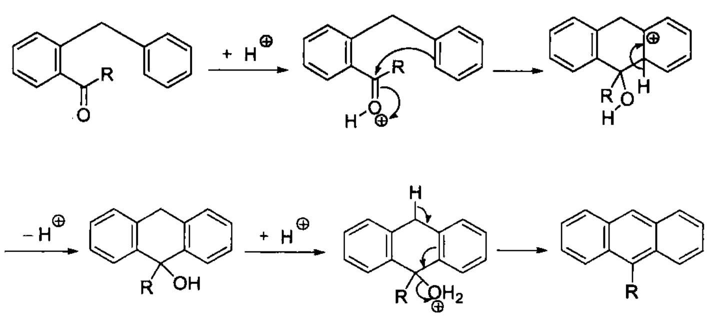
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_32,

Bradsher反应

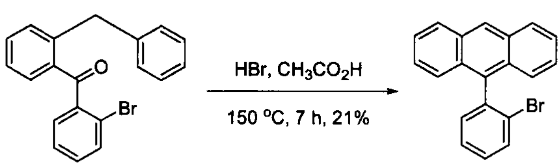
酸催化下邻酰基二芳基甲烷发生分子内Bradsher环化反应经脱水而环合生成蒽的反应。另一方面，分子间Bradsher环化反应常常包含一个吡啶和烯基醚或烯基硫化物的Diels-Alder反应。



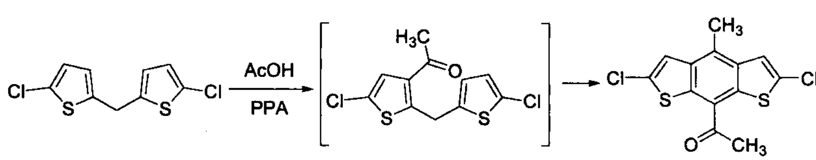
蒽



Example 1, 分子内 Bradsher 反应[2]

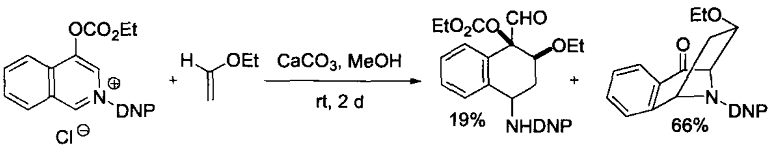


Example 2, 分子内 Bradsher 反应[5]

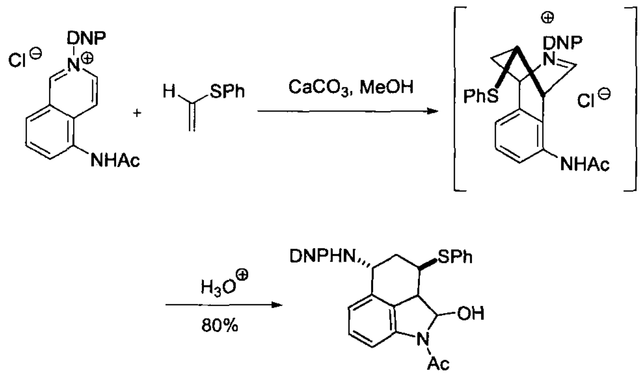


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_33,

Example 3, 分子间 Bradsher 环加成反应[8]



Example 4, 分子间 Bradsher 环加成反应[10]



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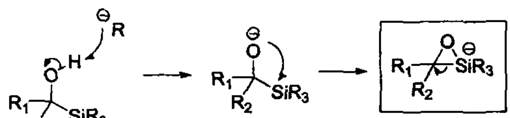
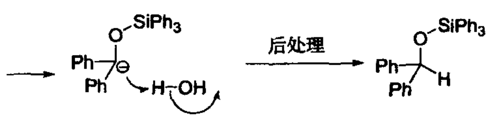
Brook重排反应

α-硅基氧负离子经一个五配位的硅中间体通过可逆过程重排为 α-硅氧基碳负离子的反应。该反应又称[1,2]-Brook重排反应或[1,2]-硅基迁移反应。

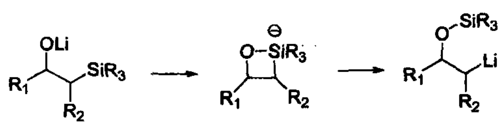
[1,2]-Brook 重排



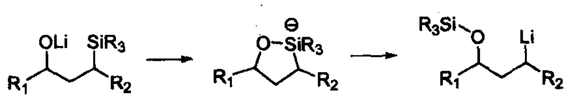
五配位硅中间体



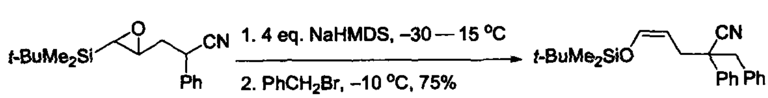
[1,3]-Brook 重排



[1,4]-Brook 重排

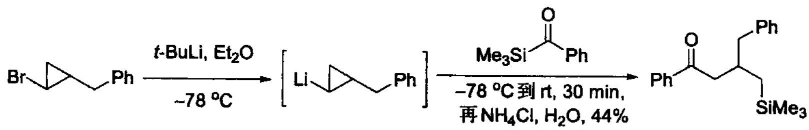


Example 1[6]

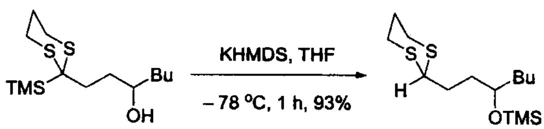


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_34,

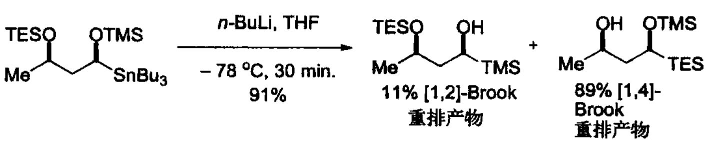
Example 2, [1,2]-Brook 重排再逆-[1,5]-Brook 重排[8]



Example 3, [1,5]-Brook 重排[9]



Example 4, 逆 -[1,4]-Brook 重排[10]



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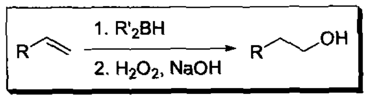
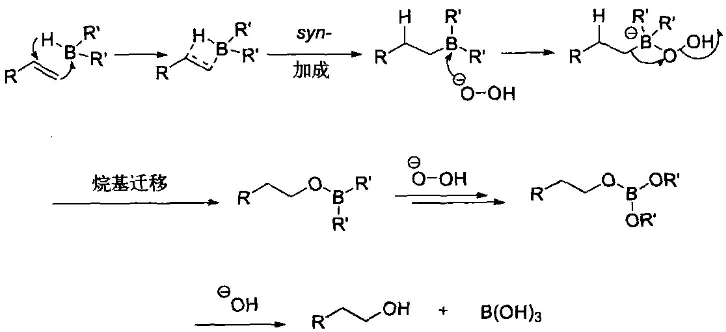
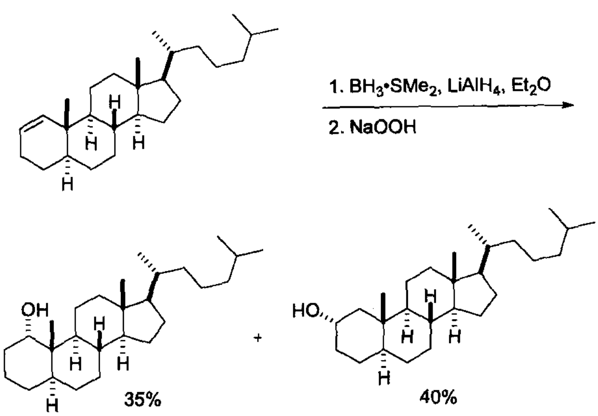
Brown硼氢化反应

硼烷与烯烃加成生成的有机硼烷经碱性氧化给出醇的反应。

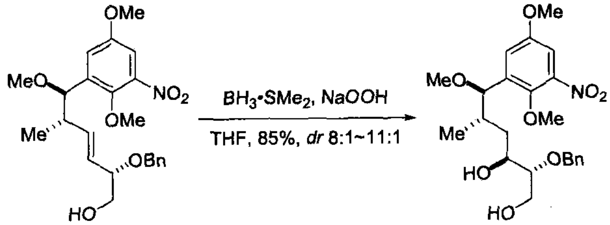




Example 1[2]

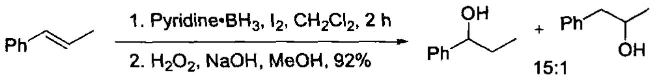


Example 2[7]

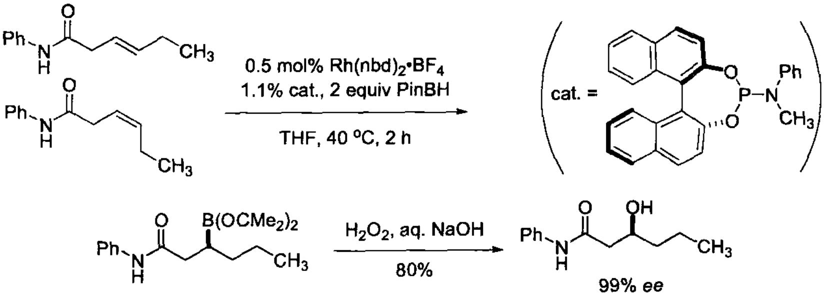


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_35,

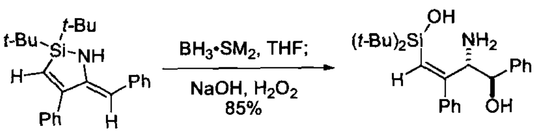
Example 3[8]



Example 4, 不对称硼氢化[10]



Example 5[11]



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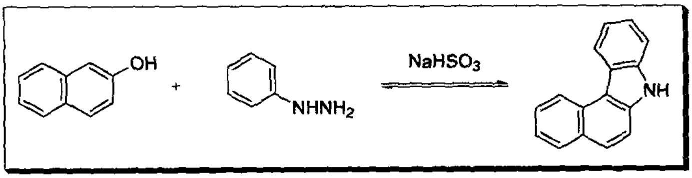
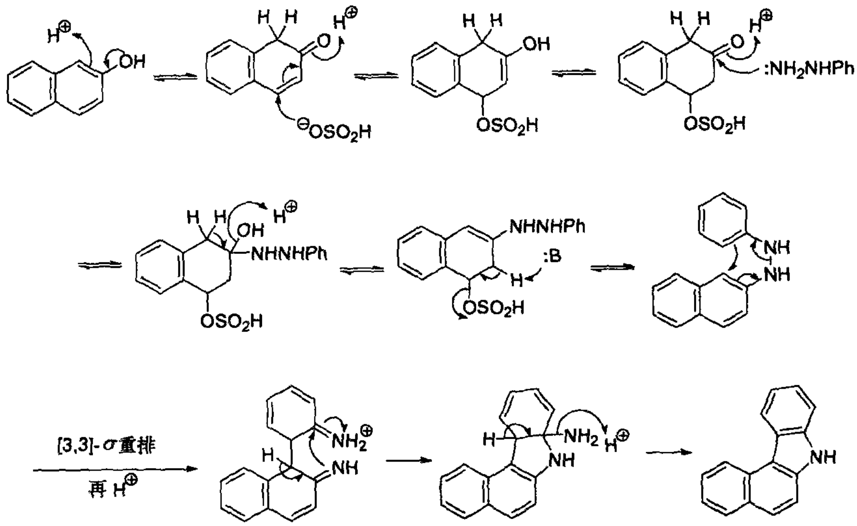
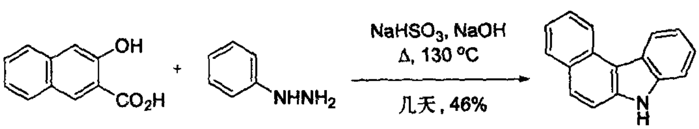
Bucherer咔唑合成反应

萘酚和芳香肼在$NaHSO_3$促进下生成咔唑的反应。

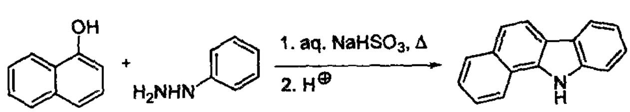




Example 1[2]

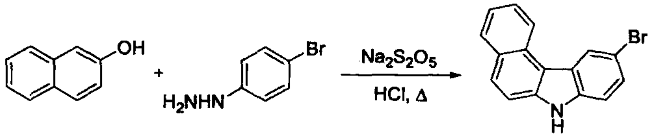


Example 2[3]

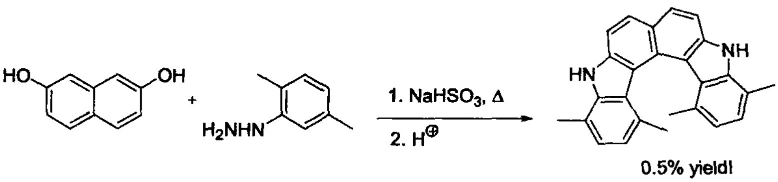


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_36,

Example 3[7]



Example 3[4]



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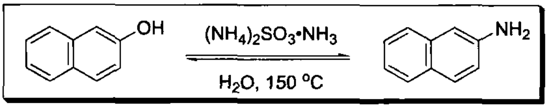
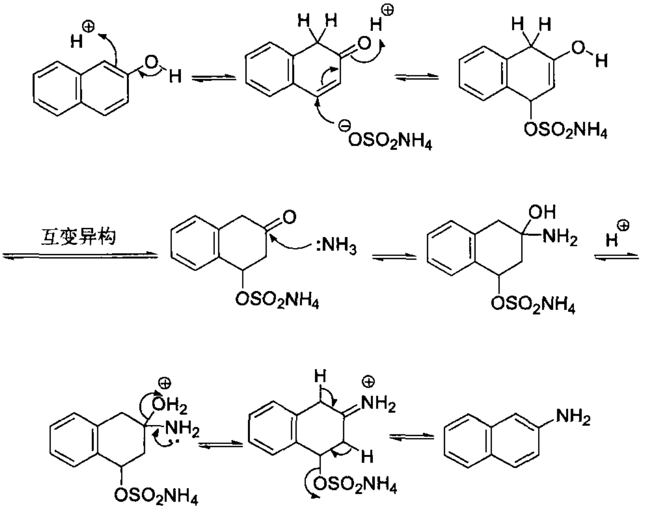
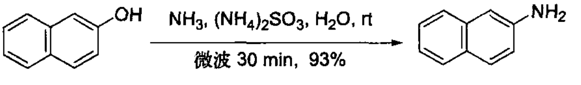
Bucherer反应

β-萘酚在$(NH_4)_2SO_3$作用下生成β-萘胺的反应。

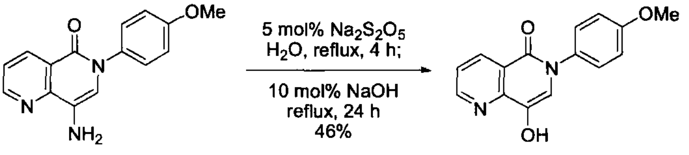




Example 1　虽然经典的Bucherer反应需在高温下进行，但在微波（150W）促进下室温时也能进行[7]。



Example 2　逆 Bucherer 反应[7]



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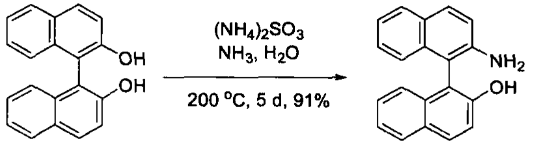
Example 3[8]



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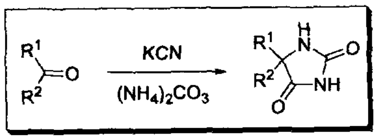
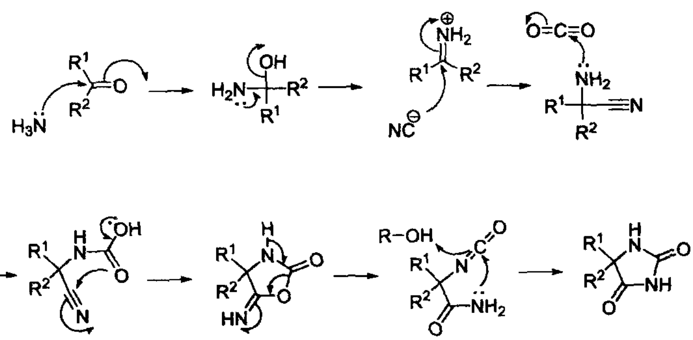
Bucherer-Bergs反应

羰基化合物和KCN及$(NH_4)_2CO_3$反应，或羟氰化合物和$(NH_4)_2CO_3$反应生成乙内酰脲的合成反应。该反应也是一个多组分反应（MCRs）。

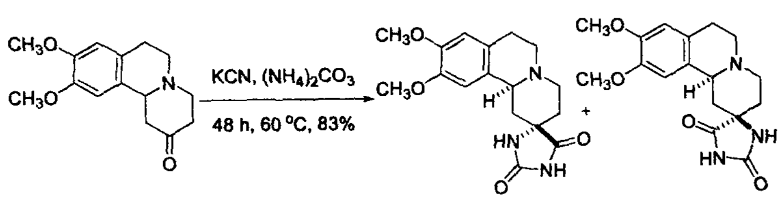


$$(NH_4)_2CO_3 = 2\,NH_3 + CO_2 + H_2O$$

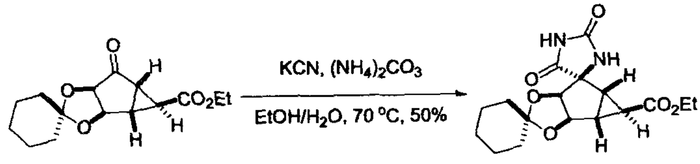


异氰酸酯中间体

Example 1[5]

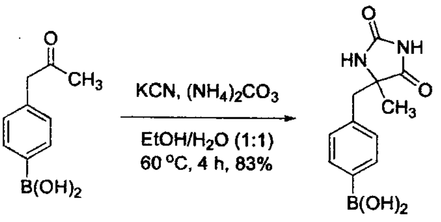


Example 2[6]

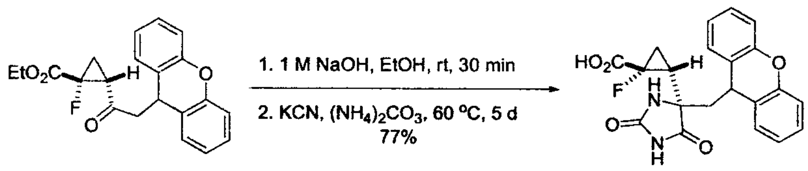


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_38,

Example 3[7]



Example 4[9]



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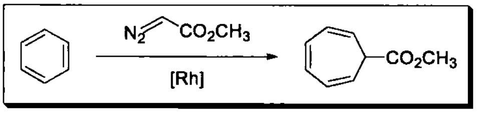
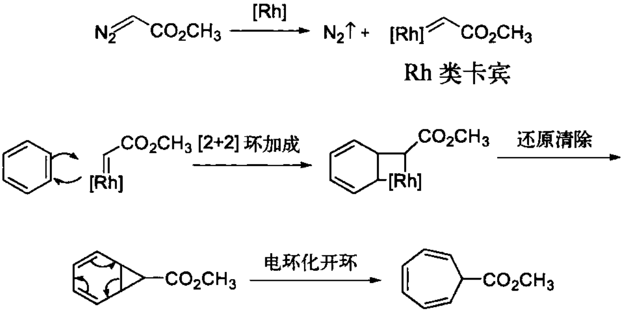
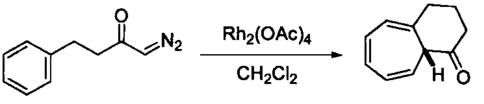
Büchner 扩环反应

苯环在重氮乙酸酯作用下生成2,4,6-环庚三烯酸酯的反应。分子内的Buchner反应用途更广。(参见Pfau-Platter反应)

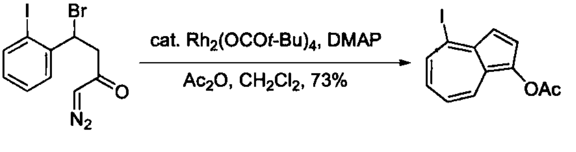




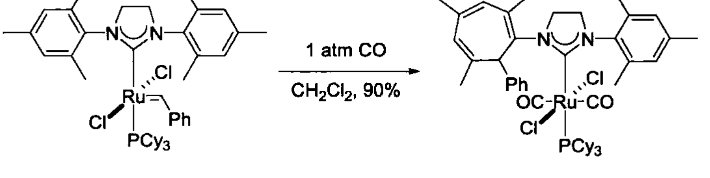
Example 1, 分子内Büchner 反应[7]



Example 2, 分子内Büchner 反应[8]

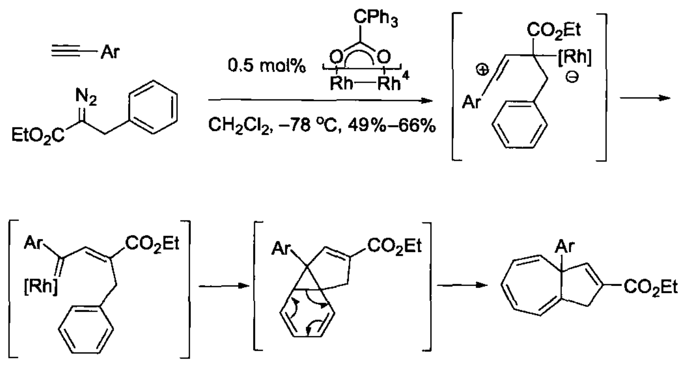


Example 3, 用Grubbs 催化剂进行的分子内 Büchner反应 [9]!



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

Example 4[10]



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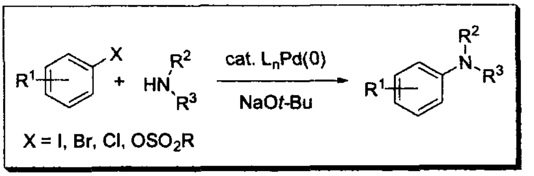
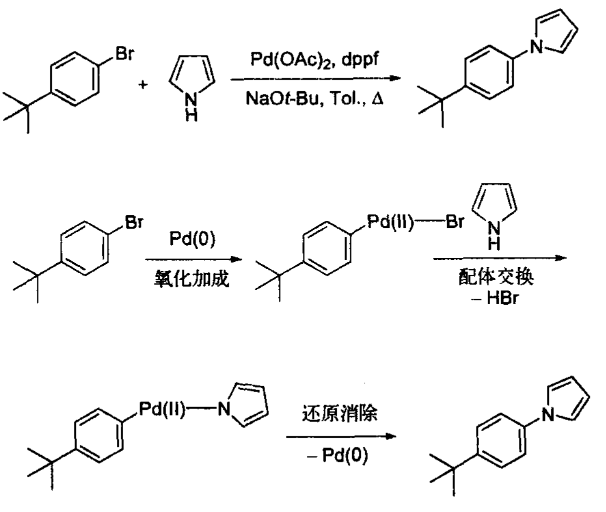
Buchwald-Hartwig 氨基化反应

本反应是从芳基卤代物或芳基磺酸酯出发生成芳香胺的通用方法。运用该反应的关键点是要用到催化量的由各种亲电子配体配位的钯。催化剂的再生必须有如叔丁氧钠一类强碱的存在。

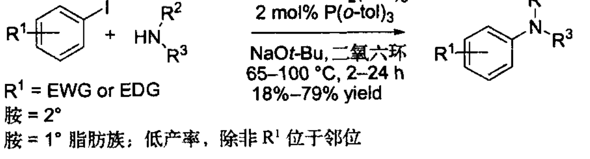


机理：



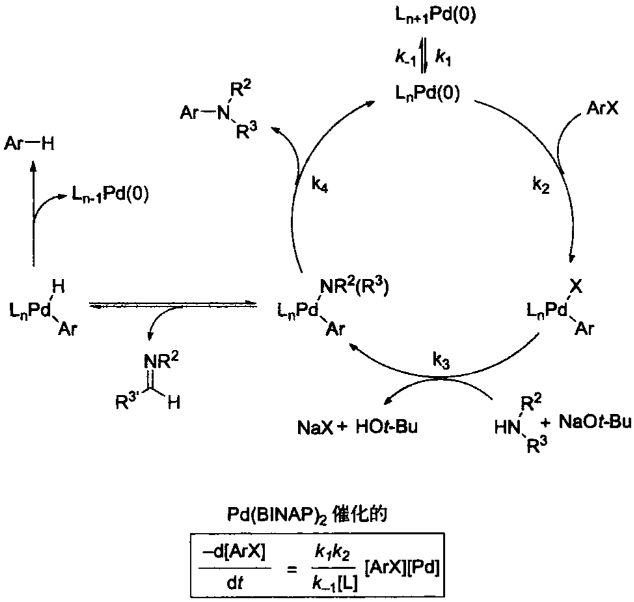
催化循环见第 81 页

Example 1[3]

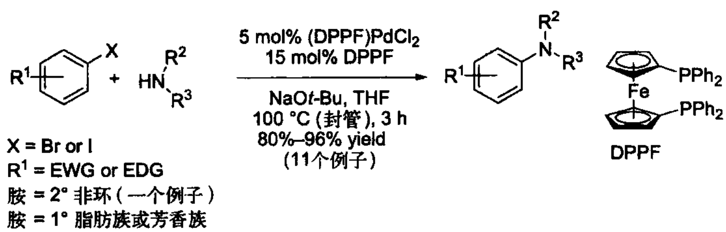


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_40,

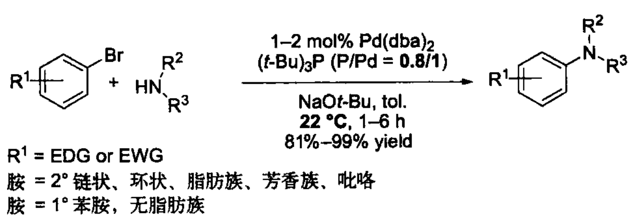
催化循环：



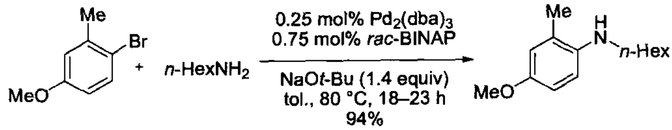
Example 2[4]



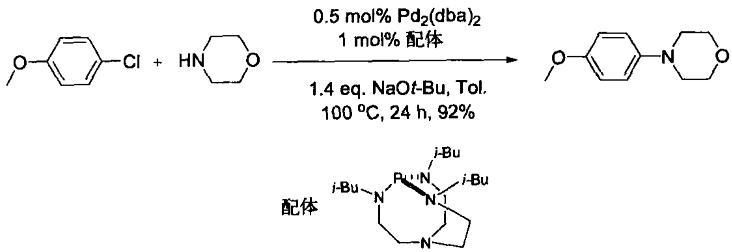
Example 3, 室温下的 Buchwald–Hartwig 氨基化反应[9]



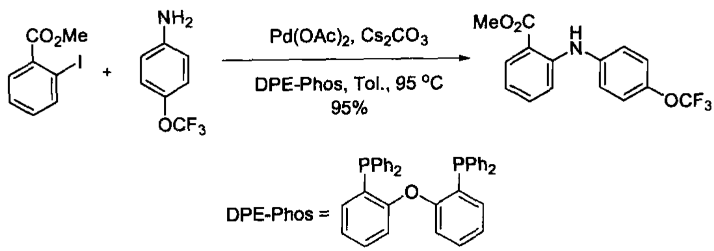
Example 4[10]



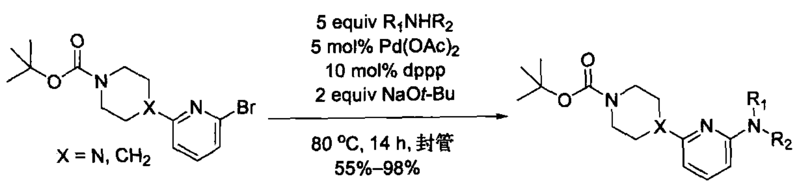
Example 5[11]



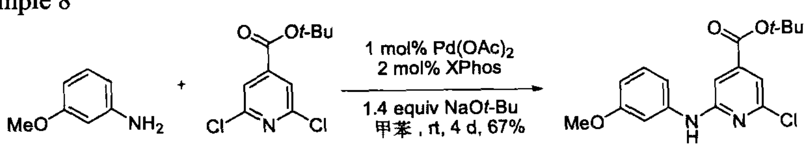
Example 6[12]

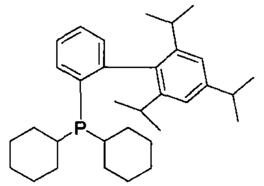


Example 7 挥发胺的胺基化[14]



Example 8[15]



XPhos = 

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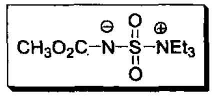
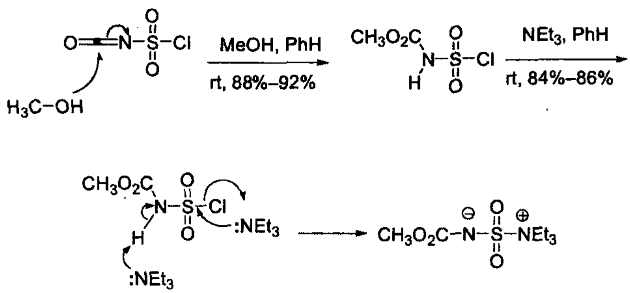
Burgess脱水剂

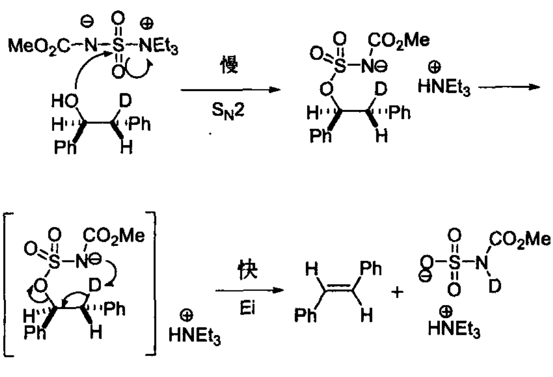


Burgess试剂，一个中性的晶体盐，三乙基铵乙氧羰基磺酰胺[$C_2H_5O_2CN^- SO_2N^+(C_2H_5)_3$]，能有效地将仲醇或叔醇转化为烯烃。反应经过一个Ei机理，两个基团几乎同时从底物消除下来并协同成键。

制备[2]

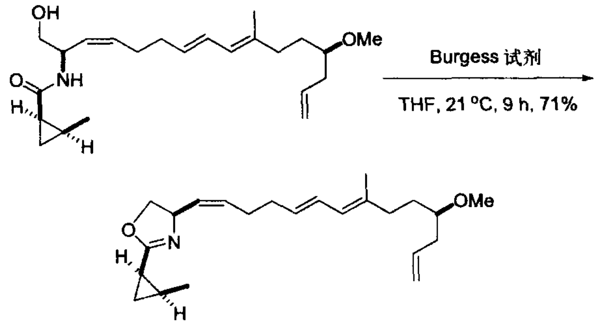


机理[5]

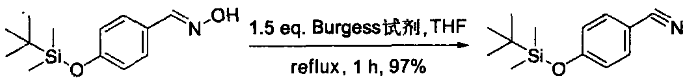


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_41,

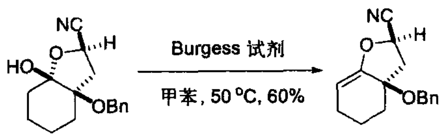
Example 1, 伯醇在此反应中无消除而发生取代 [3]



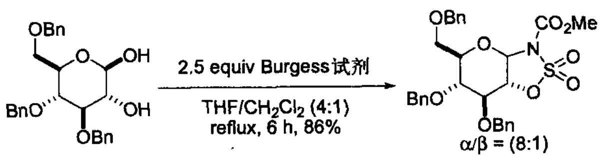
Example 2[6]



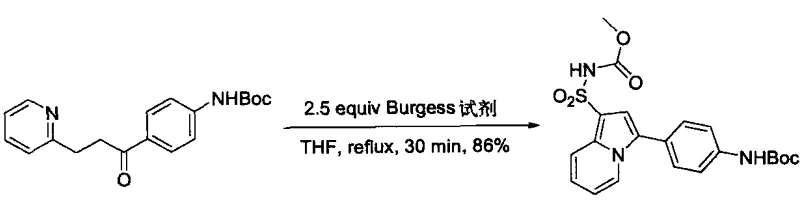
Example 3[7]



Example 4[8]



Example 5[10]



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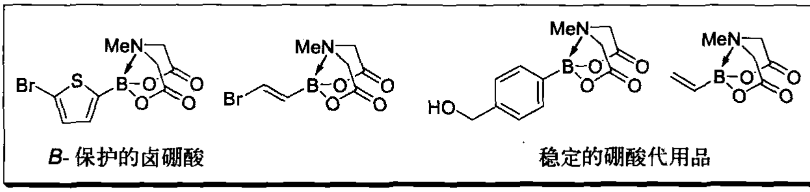
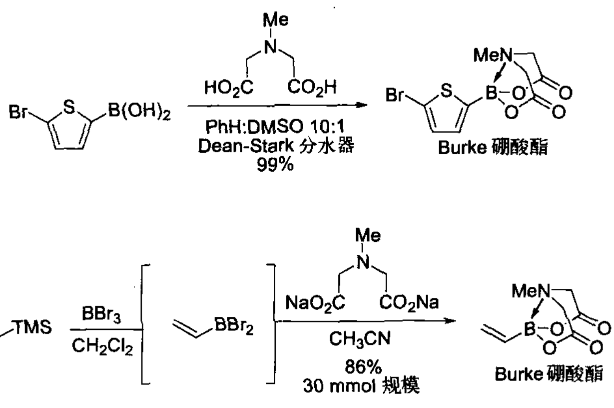
Burke 硼酸酯



Burke硼酸酯可起到与*B*-保护的卤硼酸一样的作用而用于各种多重交叉偶联反应[1-6]。使用温和的水相NaOH、$NaHCO_3$为碱时可释放出相应的硼酸。[1-4]Burke硼酸酯可兼容许多合成试剂，能用于将简单的含硼起始原料转化为硼酸的配合物[3,6]。它们也可作为稳定的合成砌块用于交叉偶联反应，如在温和的碱性水相中释放出相应的硼酸并就地参与偶联反应。[2,3,7] Burke硼酸酯还是一个高度成晶的单体。作为不会流动的固体，空气中保存在实验台上都很稳定，还可在硅胶色谱中使用[1-3,6]。

制备 [1,2,4,6]

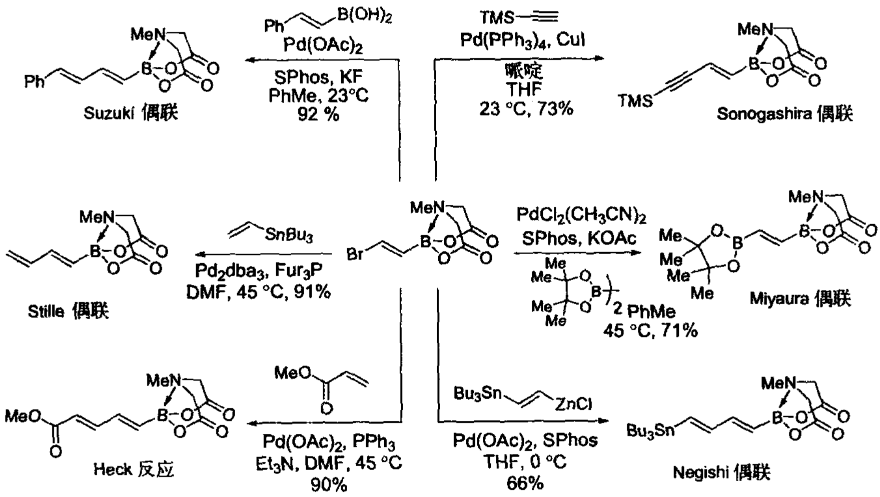


Burke硼酸酯可方便地从相应的硼酸和*N*-甲基-*N*, *N*-二乙酸（MIDA[1,4]）配位后制得，或用二溴硼烷和MIDA的二钠盐配位后制得[2,6]。许多用于合成砌块的Burke硼酸酯已有商业供应。

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

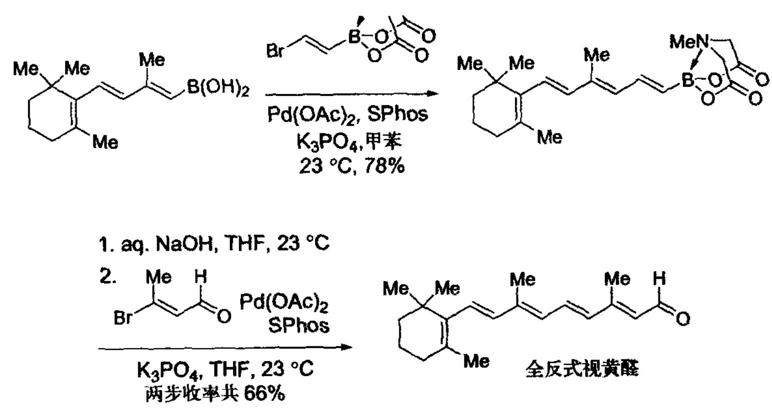
Example 1[2]

各种类型的选择性偶联反应在*B*-保护的卤硼酸上卤原子所在的一端进行。



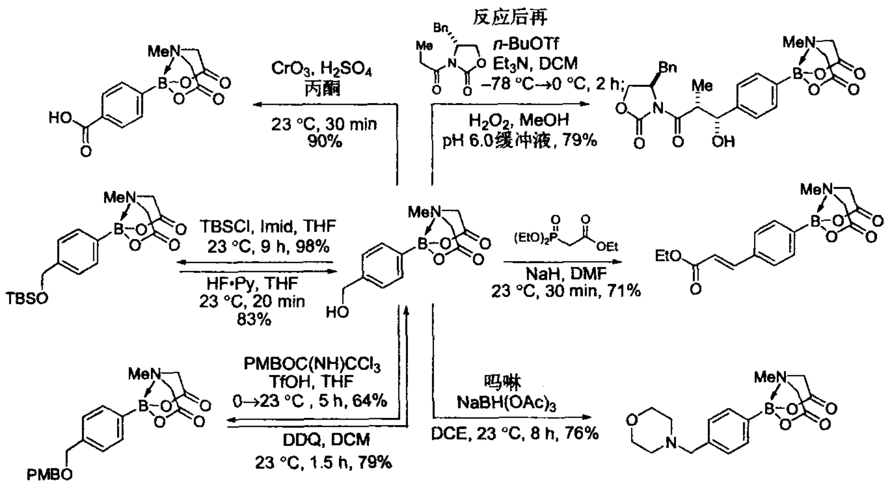
Example 2[2]

小分子天然产物也可由*B*-保护的卤硼酸经多重交叉偶联反应来制备。



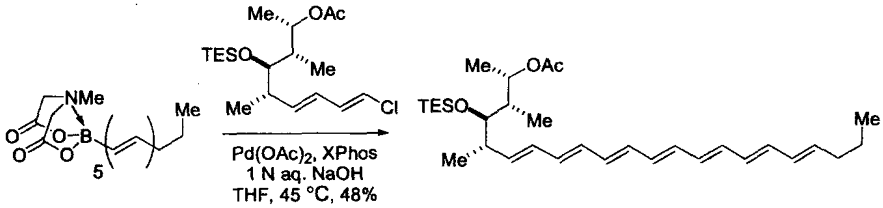
Example 3[3]

Burke硼酸酯可兼容包括酸、非水相碱、氧化剂、还原剂、亲电物种和软的亲核物种在内的许多合成试剂。该兼容性使其可以用于从简单的含硼起始原料转化为硼酸配合物的多步骤合成中。



Example 4[2]

Burke硼酸酯在水相碱性偶联的条件下能被就地水解，amphoericin B的多烯骨架的合成可以说明这一点。



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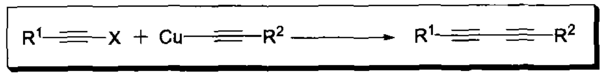
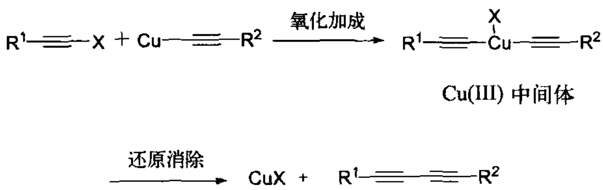
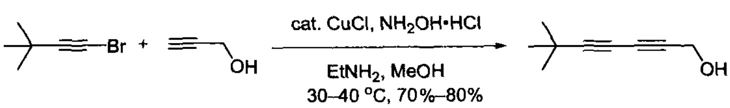
Cadiot-Chodkiewitz偶联反应

从炔基卤代烃和炔基铜合成双炔基化合物。(参见第98页上的**Castro-Stephens**反应)

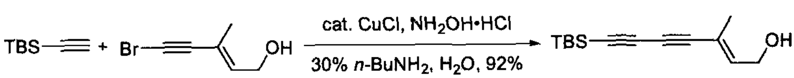




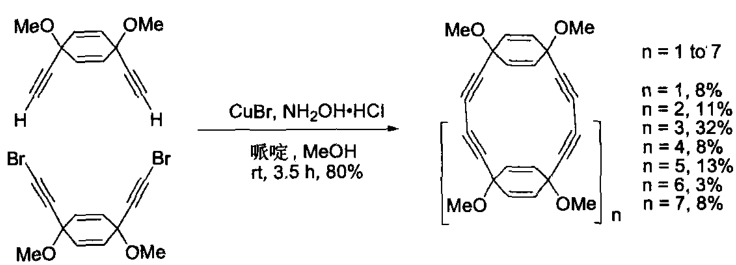
Example 1[3]



Example 2[7]

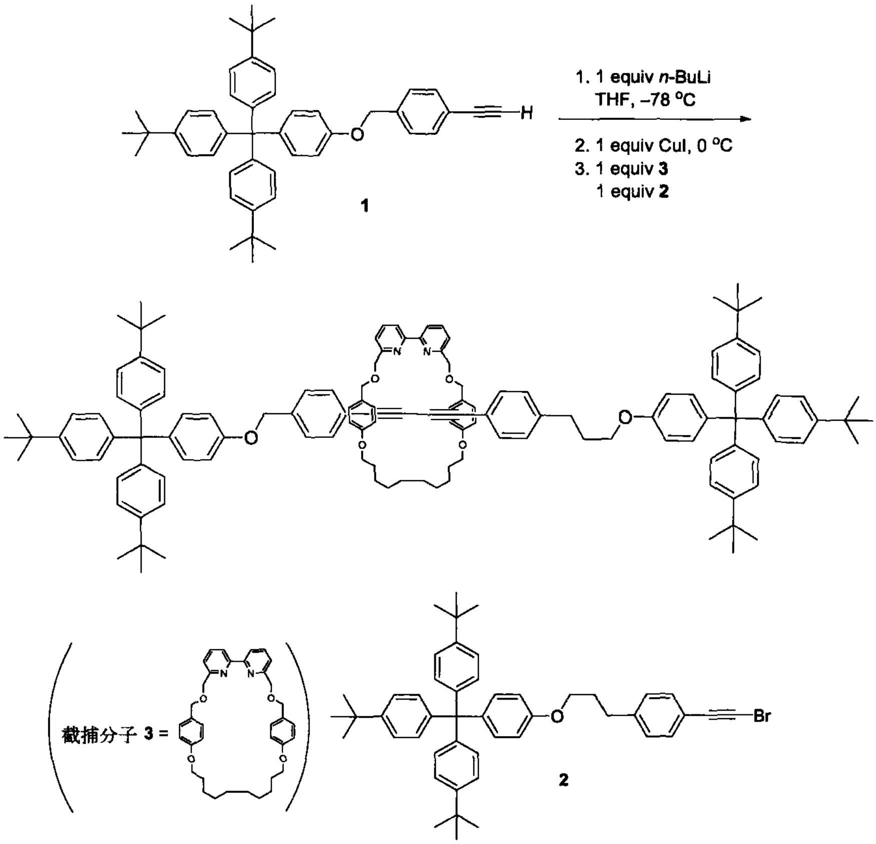


Example 3[9]



Example4, rotaxane 和因组分间弱的相互作用而能穿梭般来回移动的开关分子的合成可通过Cadiot-Chodkiewitz反应得到活性模块。[10]

J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_43,



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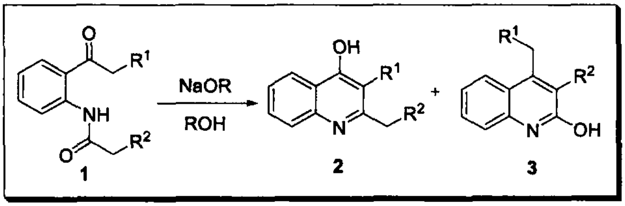
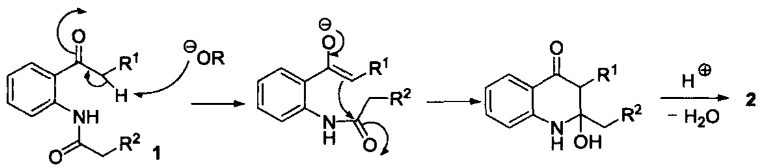
Camps喹啉合成反应

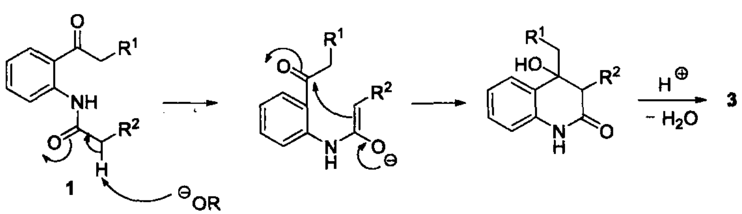
2-乙酰氨基酰基苯（1）在碱催化下缩合为2-（也可3-）取代喹啉-4-醇（2）和4-（也可3-）取代喹啉-2-醇（3）或它们的混合物。



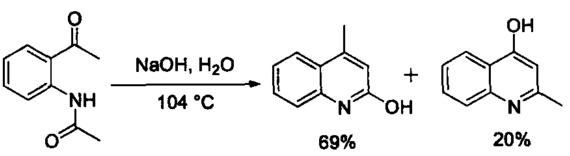
途径A:



途径B:

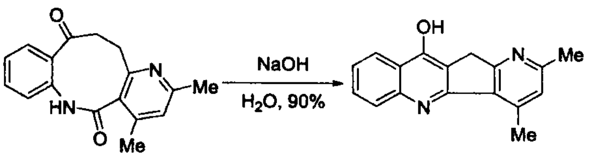


Example 1[1]



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

Example 2[6]



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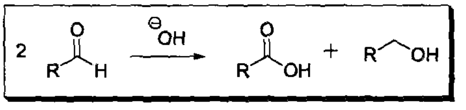
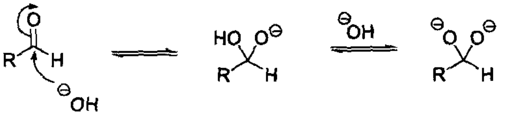
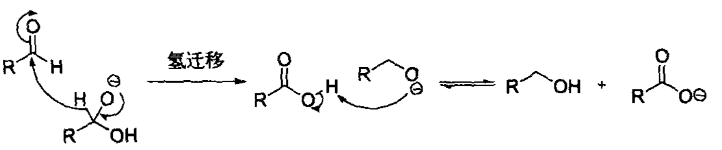
Cannizarro反应

在芳香醛、甲醛或其他无α-H的脂肪醛之间发生的氧化还原反应。碱用于产生相应的醇和酸产物。



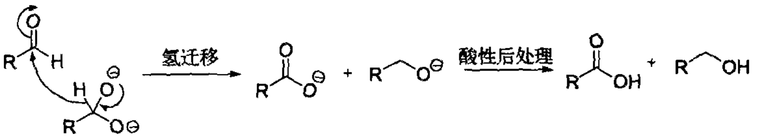


途径A:

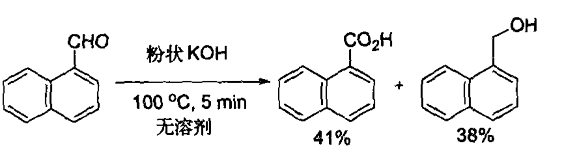


最后一步酸的去质子化推动反应正向进行。

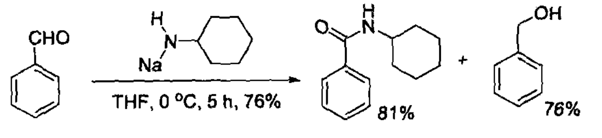
途径B:



Example 1[4]

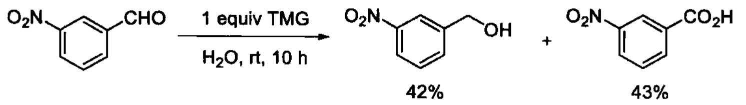


Example 2[6]

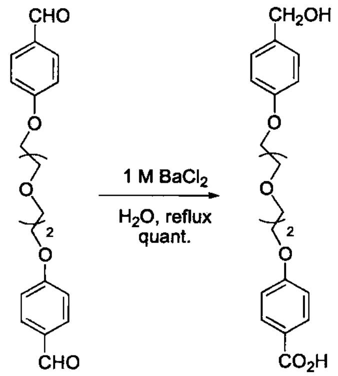


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_45,

Example 3[8]



Example 4, 去对称化的分子内Cannizzaro 反应[9]



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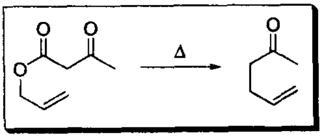
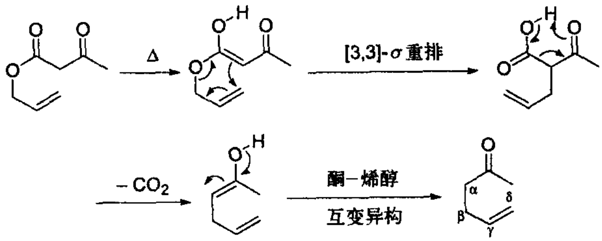
Carroll重排反应

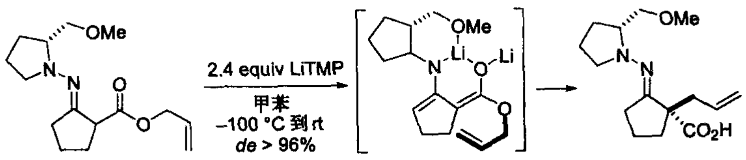
β-酮酯热重排后接着脱羧经负离子促进的Claisen重排反应生成γ-不饱和酮。这是Claisen重排反应（参见第117页）的一种变异反应。

参见第117页

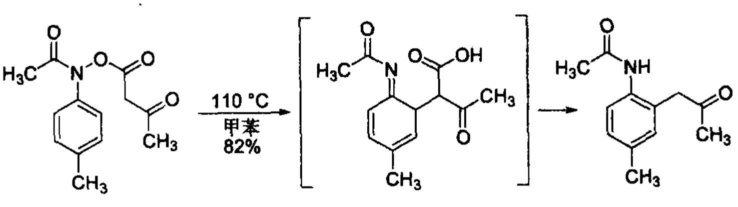




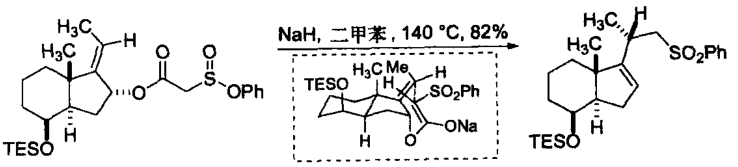
Example 1,不对称Carroll重排[4,5]



Example 2,杂原子Carroll重排[6]

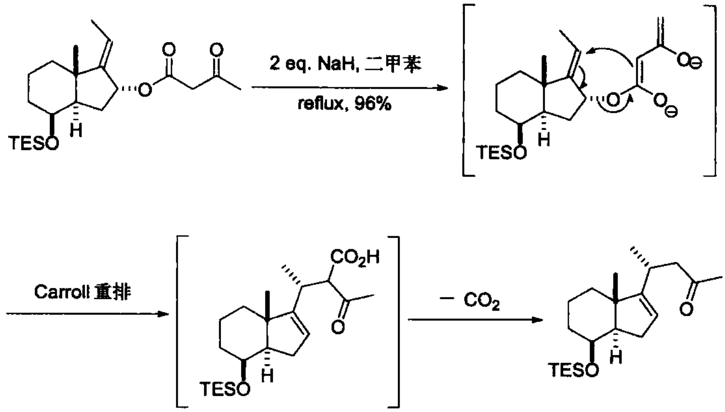


Example 3[7]

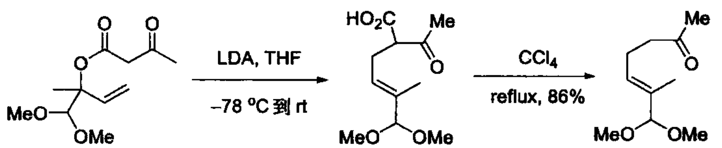


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_46,

Example 4, 与例子相似[7]



Example 5[8]



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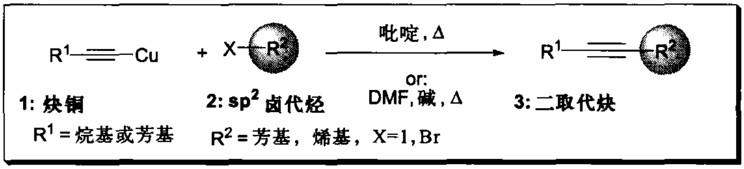
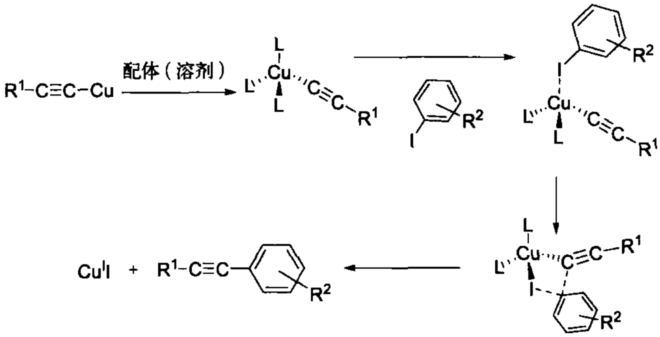
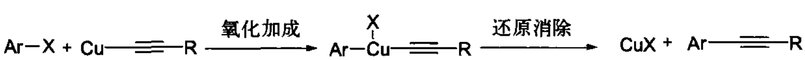
Castro-Stephens偶联反应

芳基炔烃的合成反应，参见第90页上的Cadiot-Chodkiewitz偶联反应和第519页上的Sonogashira偶联反应。本反应需用化学计量的铜，而Sonogashira偶联反应改进后只需催化量钯和铜。



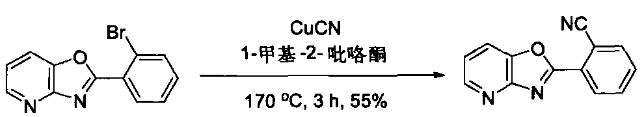


另一个机理与Cadiot–Chodkiewicz偶联反应相似：

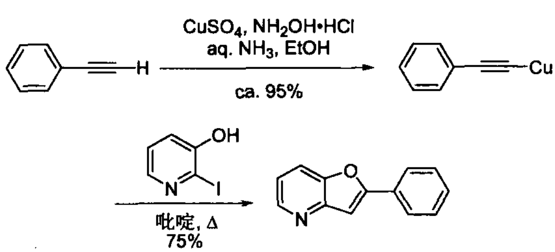


Cu(III)中间体

Example 1，一个变异反应，亦称 Rosenmund–von Braun 芳香腈合成[2]



Example 2[4]



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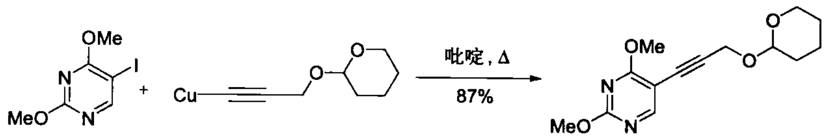
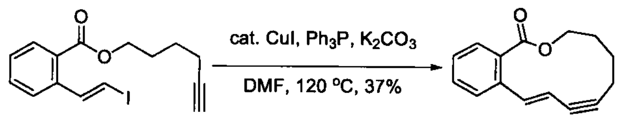
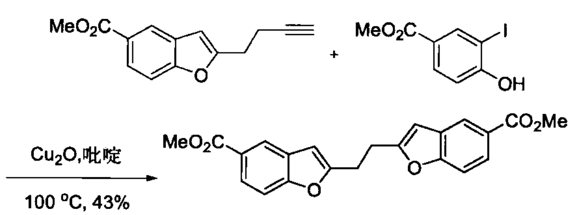
Example 3[5]



Example 4[8]



Example 5, 就地进行的 Castro–Stephens 反应[10]



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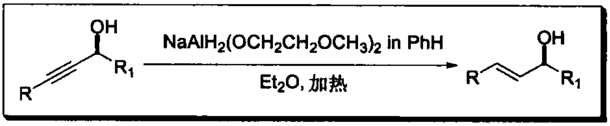
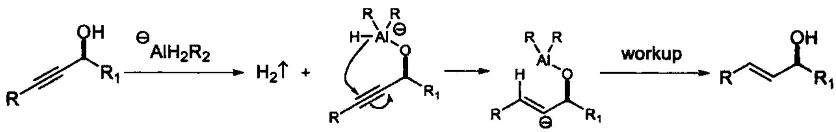
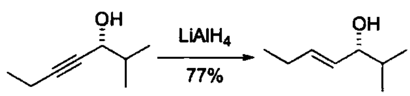
Chan 还原反应

用双(2-甲氧基乙氧基)氢化铝(SMEAH,又常称红铝)或锂铝氢立体选择性地还原炔基醇为*E*-烯丙基醇的反应。

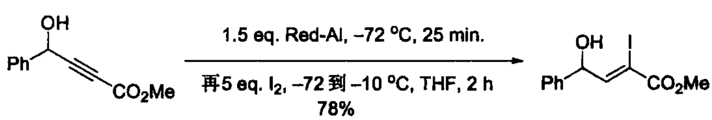




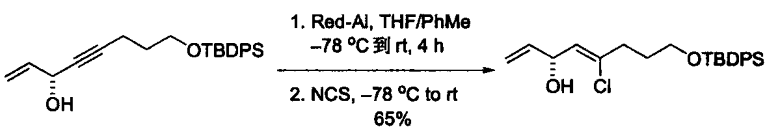
Example 1[3]



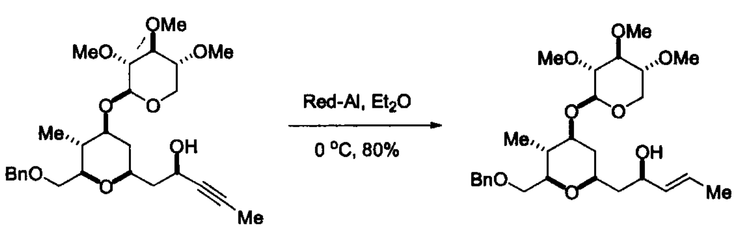
Example 2[4]



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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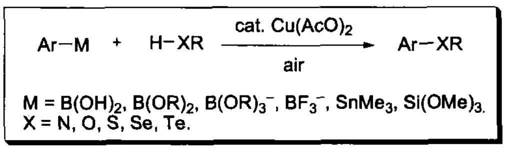
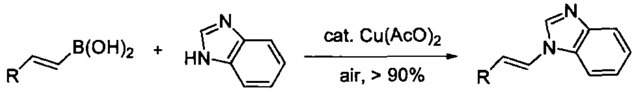
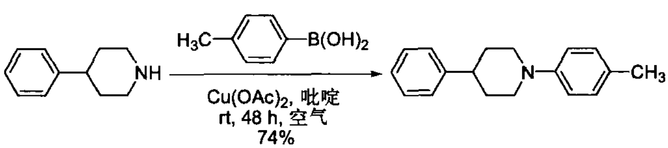
Chan-Lam C — X键偶联反应

各种带NH/OH/SH的底物于室温、空气中与硼酸在催化量乙酸铜及三乙胺（或吡啶）存在下经氧化交叉偶联发生芳基化反应。反应可适用于酰胺、胺、苯胺、叠氮化物、乙内酰脲、肼、酰亚胺、亚胺、亚硝基化物、吡嗪酮、吡啶酮、嘌呤、嘧啶、氨磺酰、亚磺酸盐、亚磺酰胺、脲、醇、酚和硫酚。本反应也是一个在N/O上发生烯基化的温和方法。硼酸可以用硅氧烷或锡烷替代。温和的反应条件使其优于Buchwald-Hartwig钯催化的交叉偶联反应。本反应也是对Suzuki-Miyaura C—C键交叉偶联反应的一个补充。

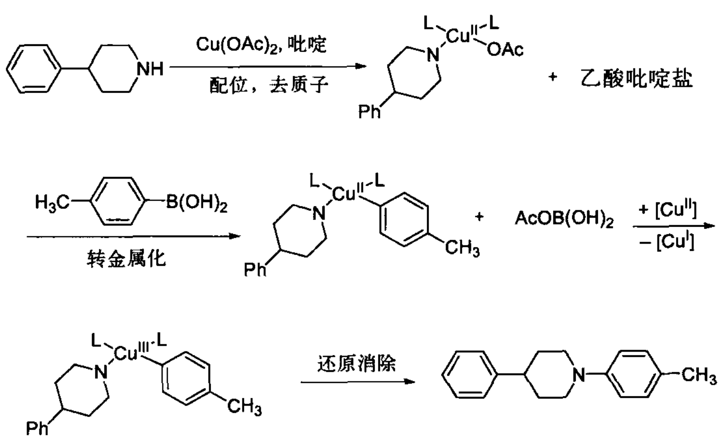




Example 1[1a,d]



Mechanism:[1c,d,17]



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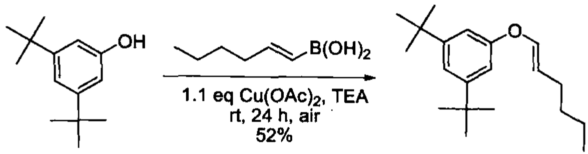
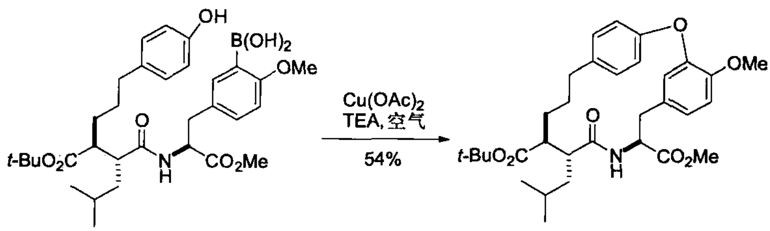
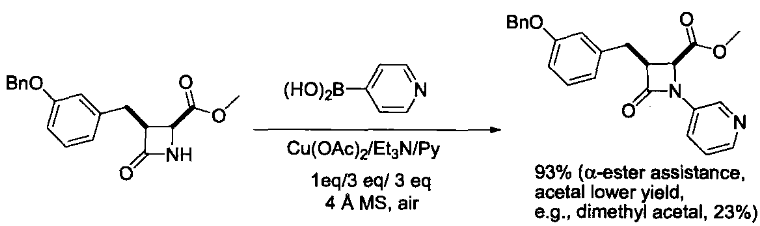
Example 2[4]



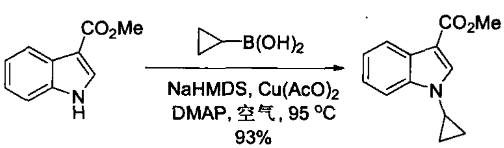
Example 3[5]



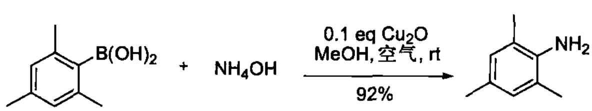
Example 4[13]



Example 5[14]



Example 6[15]



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Company 工作过。他跟罗切斯特大学（University of Rochester）Louis Friedrich 教授进行 Ph.D 研究工作，跟 Michael Jung 教授从事博士后研究工作，后来又跟加利福尼亚大学洛杉矶分校（UCLA）的克拉姆（Donald Cram）教授从事博士后研究工作。(c) Evans, D. A.; Katz, J. L.; West, T. R. *Tetrahedron Lett.* **1998**, *39*, 2937–2940. Evans 小组因长期从事万古霉素 (vancomycin) 全合成的研究而对 O– 芳构化反应非常重视。(d) Lam, P. Y. S.; Clark, C. G.; Saubern, S.; Adams, J.; Averill, K. M.; Chan, D. M. T.; Combs, A. *Synlett* **2000**, 674–676. (e) Lam, P. Y. S.; Bonne, D.; Vincent, G.; Clark, C. G.; Combs, A. P. *Tetrahedron Lett.* **2003**, *44*, 1691–1694.

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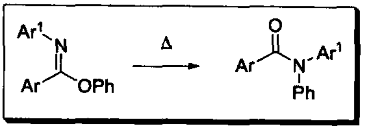
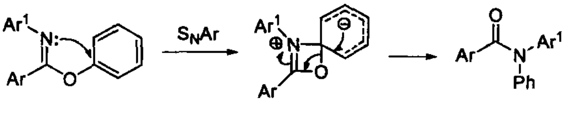
Chapman重排反应

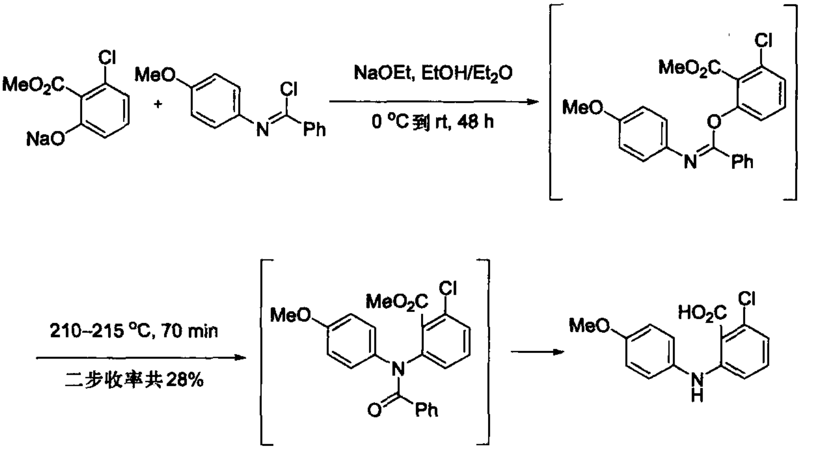
O-芳基亚胺醚热重排为酰胺。



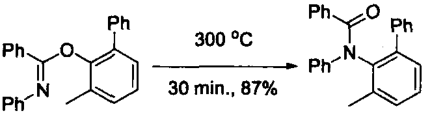


1,3-氧氮杂环丁烷中间体

Example 1[2]

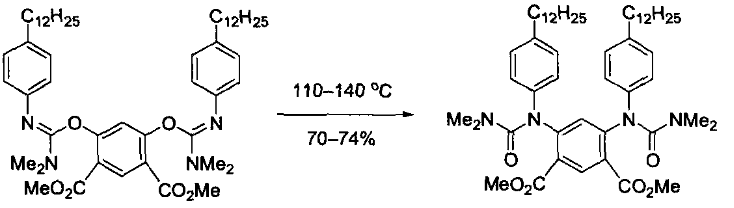


Example 2[4]

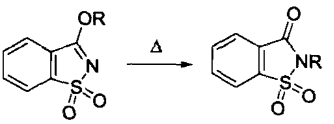


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_50,

Example 3, 二重 Chapman 重排[10]



Example 4类, Chapman热重排[11]



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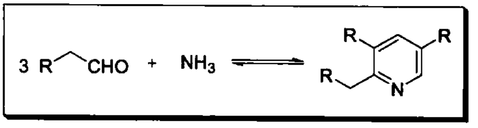
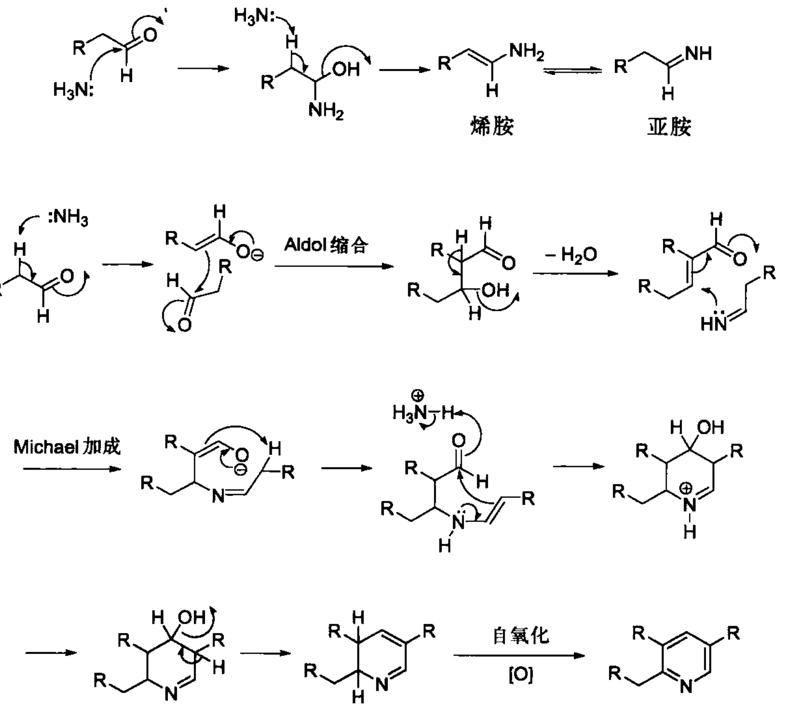
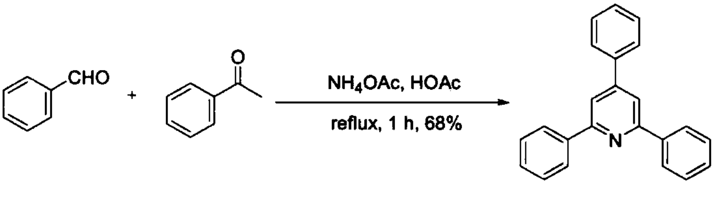
Chichibabin 吡啶合成反应

醛和氨缩合生成吡啶。



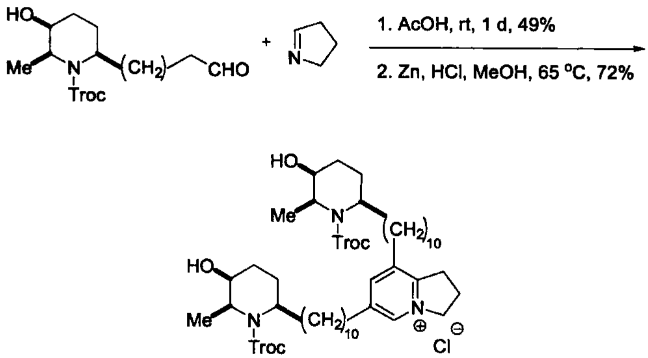


Example 1[4]

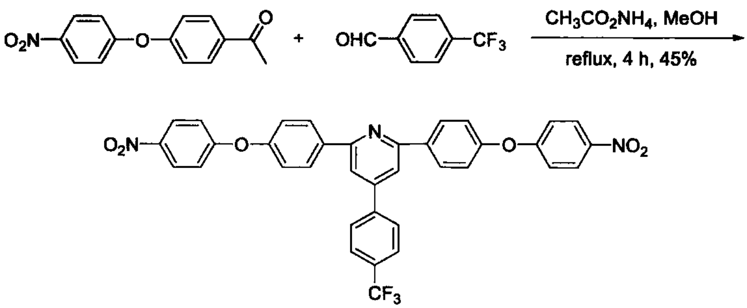


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_51,

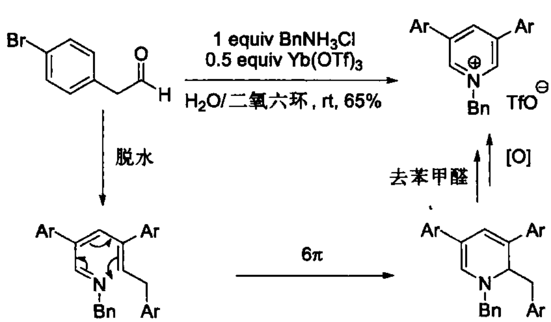
Example 2[8]



Example 3[9]



Example 4, 一个反常的Chichibabin 反应[10]



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Volhard-Zelinsky反应的发现者之一）不愿与这个学生合作共事，对齐齐巴宾的Ph.D论文也颇多微词，反使齐齐巴宾有一个“自学成才者”的昵称。

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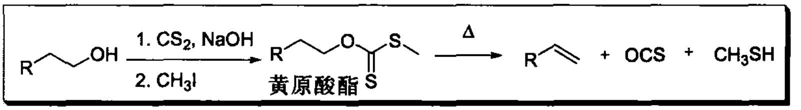
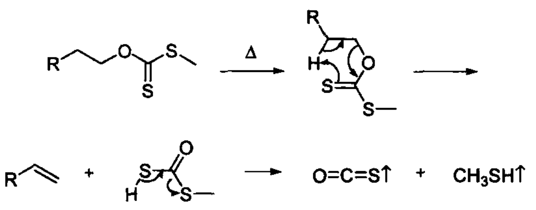
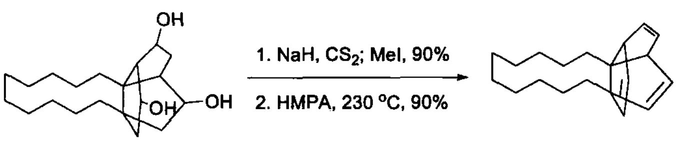
Chugaev 反应

黄原酸酯热解消除为烯烃。

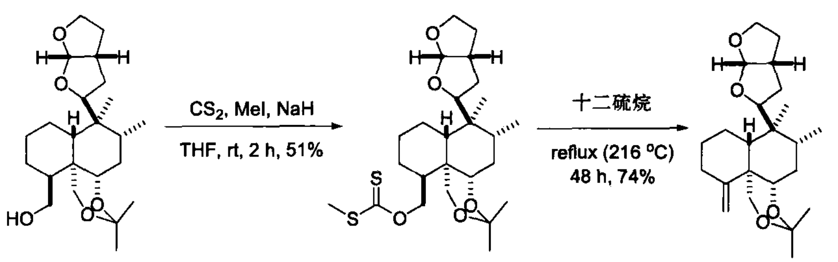




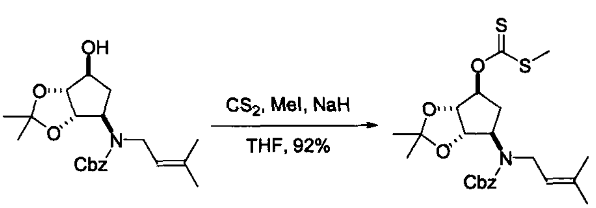
Example 1[4]



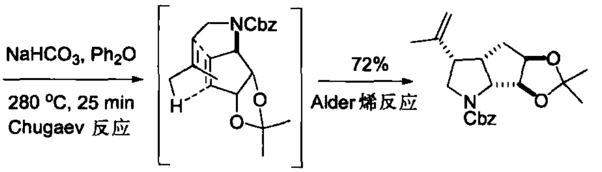
Example 2[5]



Example 3, Chugaev *syn*-消除反应后再分子内烯反应[6]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_52,



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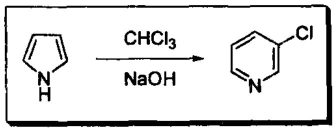
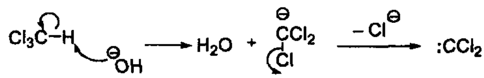
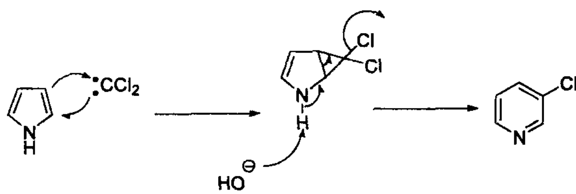
Ciamician-Dennstedt重排反应

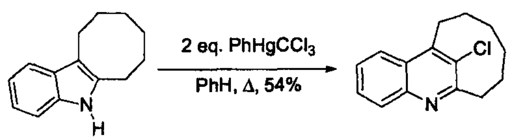
吡咯用从氯仿和NaOH反应而来的二氯卡宾处理发生环丙烷化，接着重排生成3-氯吡啶。



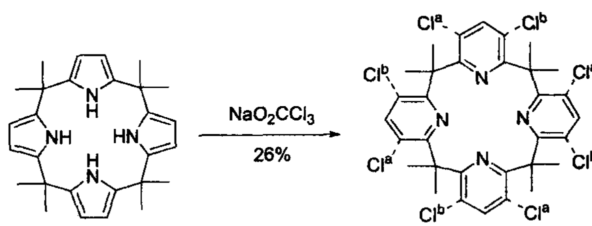




Example 1[4]



Example 2[5]



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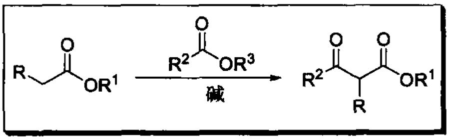
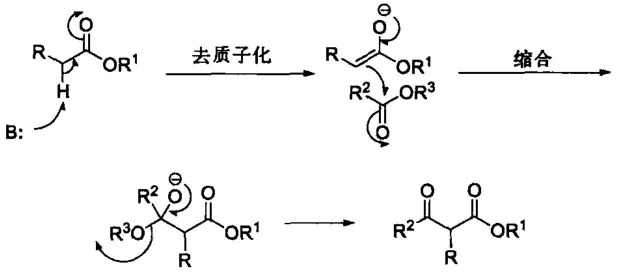
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_53,

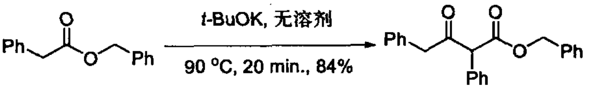
Claisen缩合反应

碱催化下酯缩合为 β-酮酯。

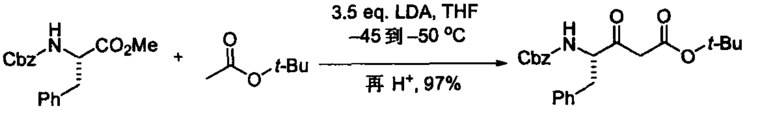




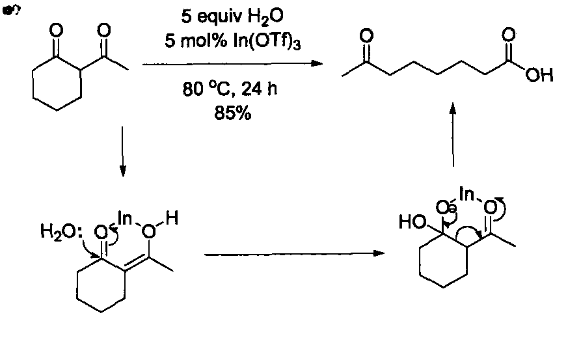
Example 1[4]



Example 2[6]

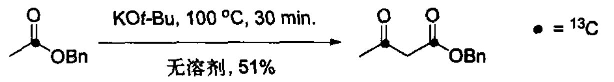


Example 3, 逆 Claisen 缩合[9]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_54,

Example 4, 无溶剂 Claisen缩合[10]



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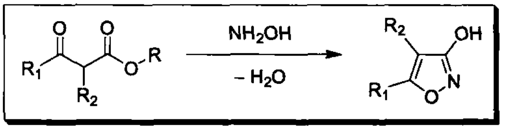
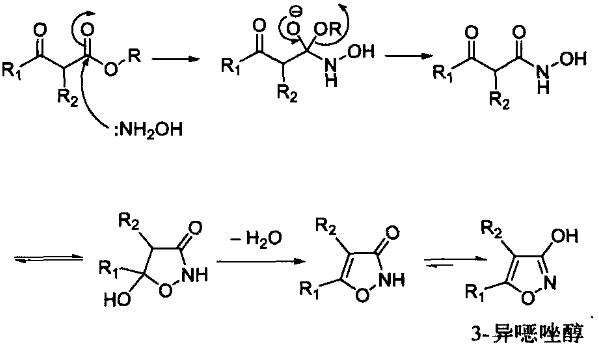
Claisen异噁唑合成

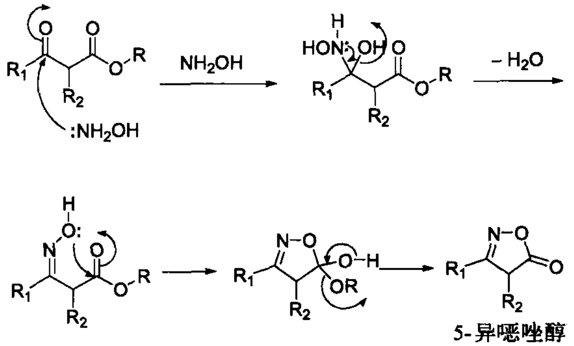
β-酮酯用羟氨处理环化为3-羟基异噁唑。





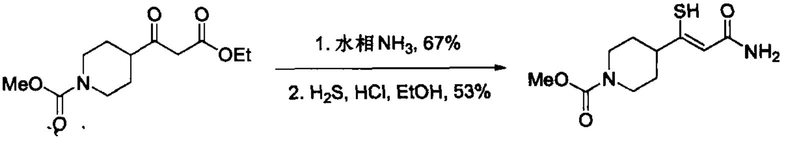
3-异噁唑醇

副反应:

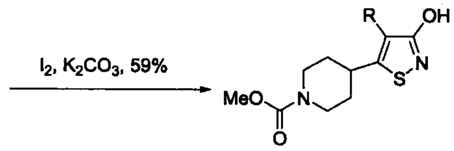


5-异噁唑醇

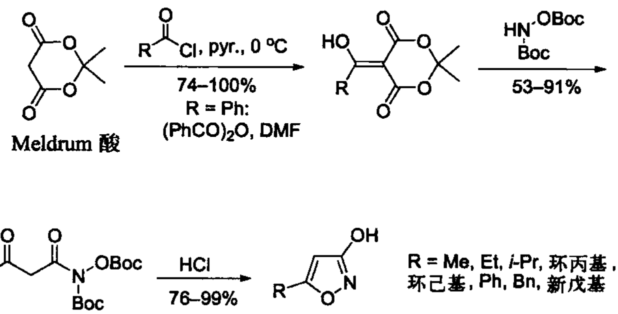
Example 1,硫同系物[6]



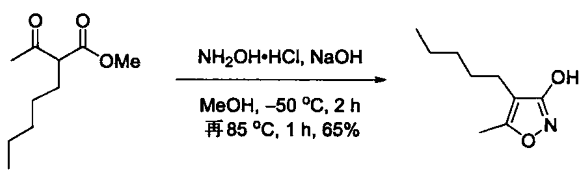
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_55,



Example 2[7]



Example 3[8]



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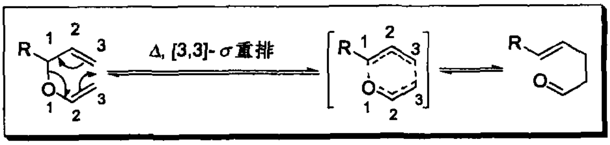
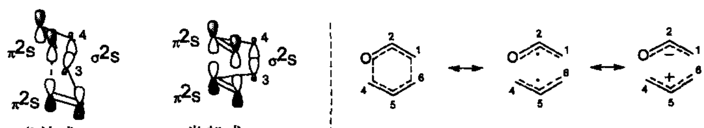
Claisen重排反应

Claisen重排反应、对位Claisen重排反应、Bellus-Claiso重排反应、 Corey-Claisen重排反应、Eschenmoser-Claisen重排反应、Ireland-Claisen重排反应、Kazmaier-Claisen重排反应、Saucy-Claisen重排反应、Johnson-Claisen原酸酯重排反应和Carroll重排反应都同属于[3,3]-σ重排反应。Claisen重排反应经过一个协同过程，此处显示的箭头推动只是为了方便说明。





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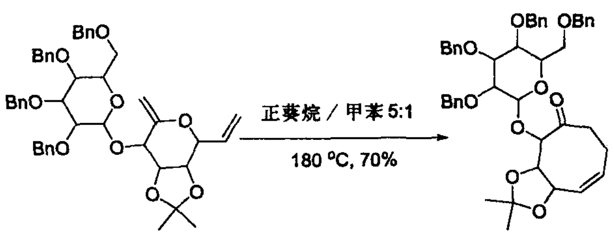
Example 1[7]



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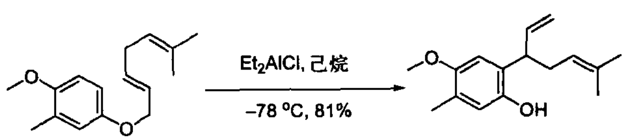
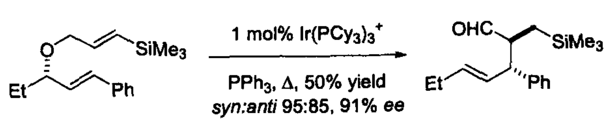
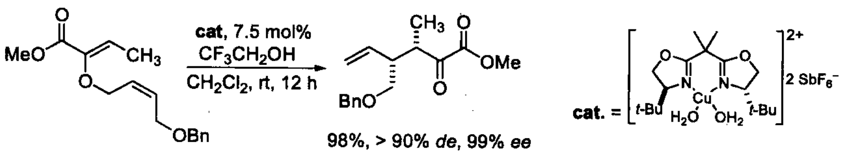


Example 3[9]

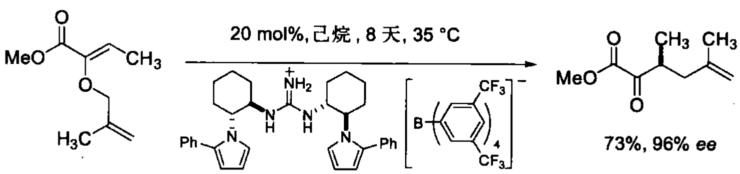


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_56,

Example 4, 不对称 Claisen 重排[10]



Example 5, 不对称 Claisen 重排[11]



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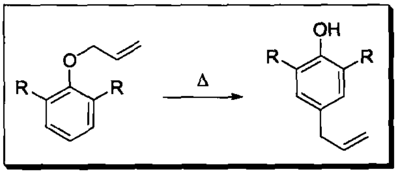
对位Claisen重排反应

邻位Claison重排反应后继续重排给出对位Claison重排反应产物。



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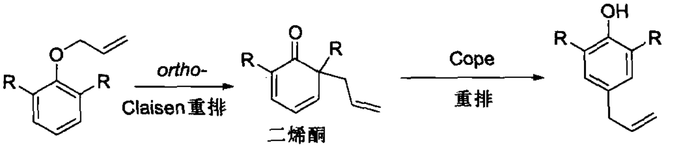
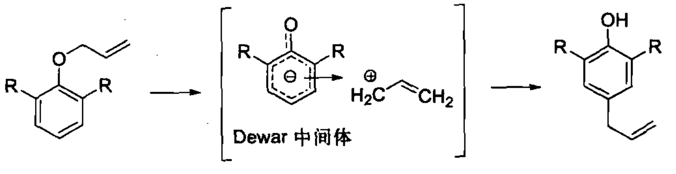
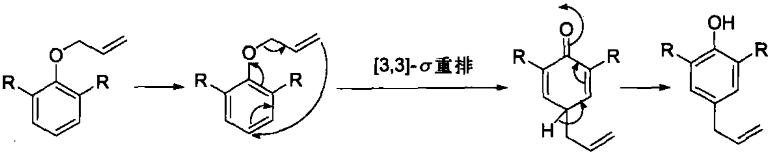


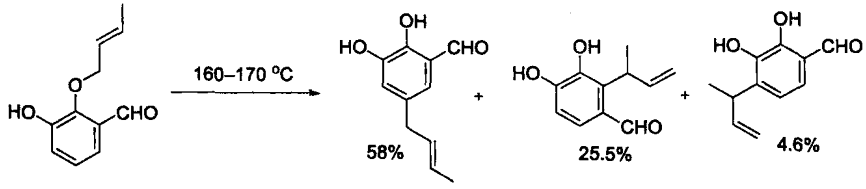
机理2:



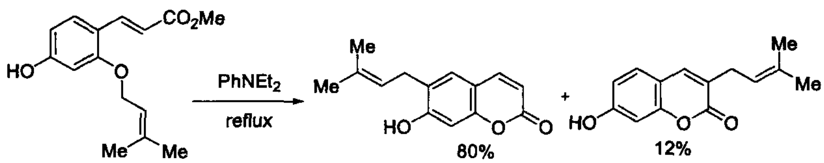
机理3:



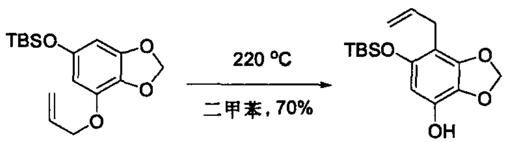
Example 1[6]



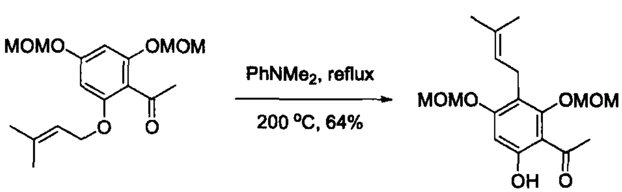
Example 2[7]



Example 3[8]



Example 4[10]



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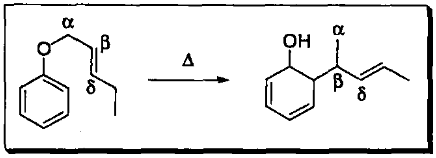
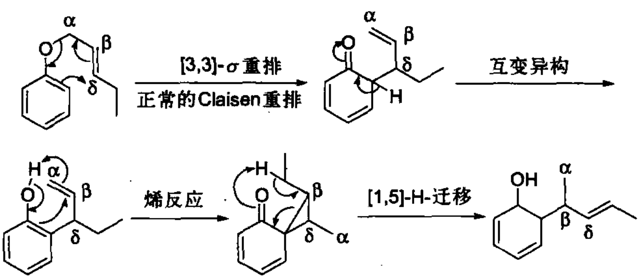
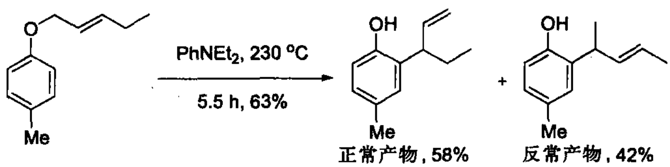
反常 Claisen 重排反应

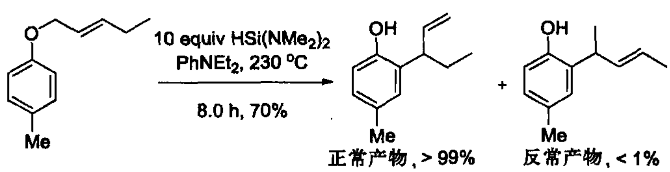
正常 Claisen 重排反应产物继续重排给出 β-碳接到环上的产物。



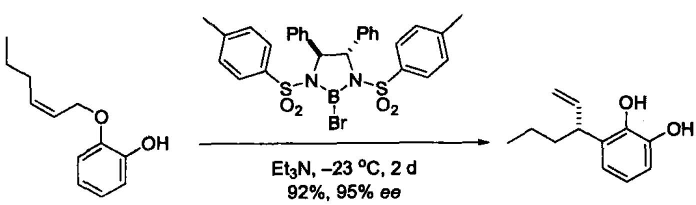


Example 1[3]

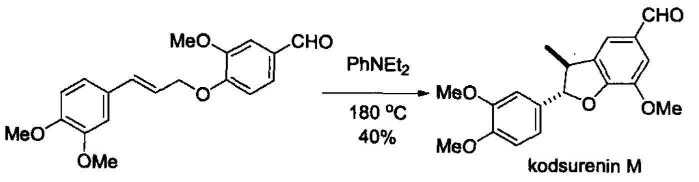




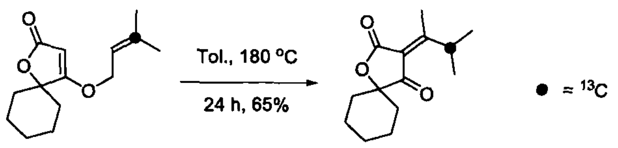
Example 2, 对映选择性芳香族 Claisen 重排[4]



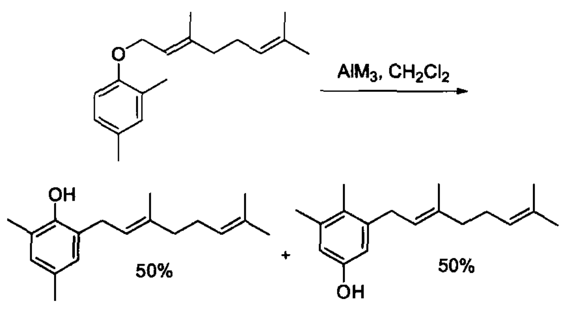
Example 3[5]



Example 4[6]



Example 5[7]



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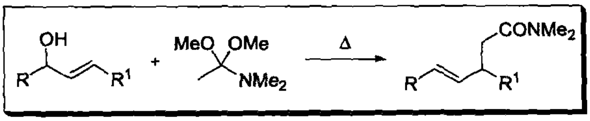
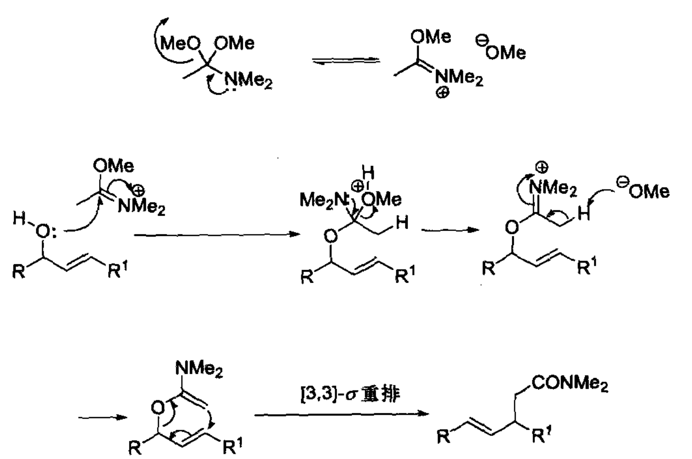
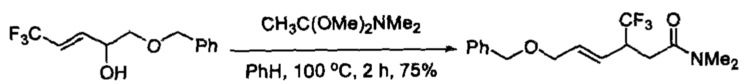
Eschenmoser-Claisen（酰胺缩酮）重排反应

N,O-烯酮缩酮进行[3,3]-σ 重排反应后生成γ,δ-不饱和酰胺。受益于Meerwein对酰胺交换研究的成果，Eschenmoser-Claisen重排反应又称Meerwein- Eschenmoser-Claisen重排反应。

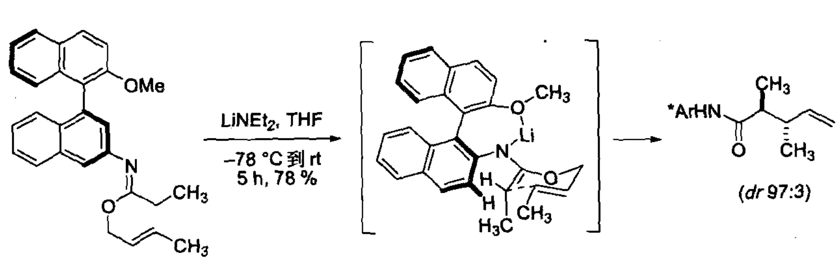




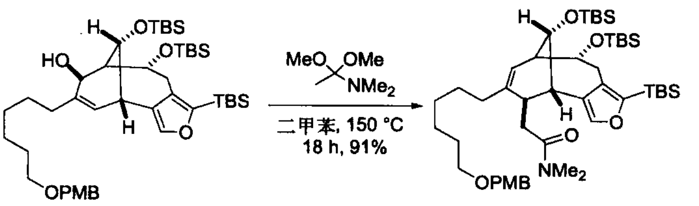
Example 1[4]



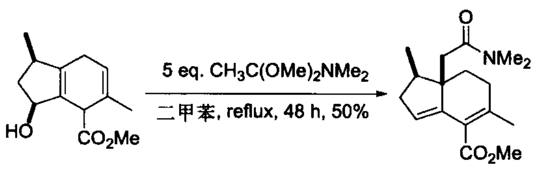
Example 2[5]



Example 3[6]



Example 4[8]



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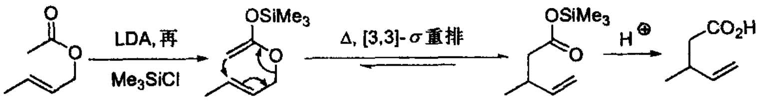
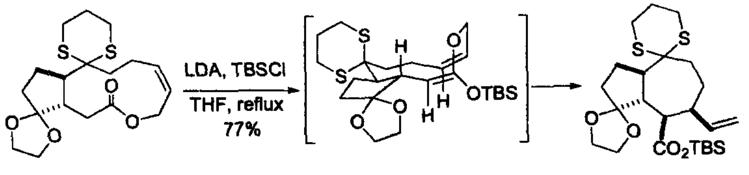
Ireland-Claisen（硅烯酮缩酮）重排反应

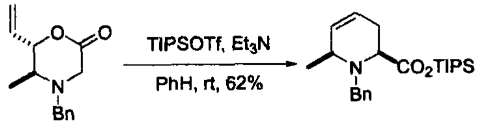
由烯丙基烯醇酯和三甲基氯硅烷而来的烯丙基三甲基硅基烯酮缩酮重排反应后生成 γ,δ-不饱和酸。在*E*/*Z*构型的控制及温和的反应条件方面，Ireland-Claisen重排反应比其他类型的Claisen重排反应要好。



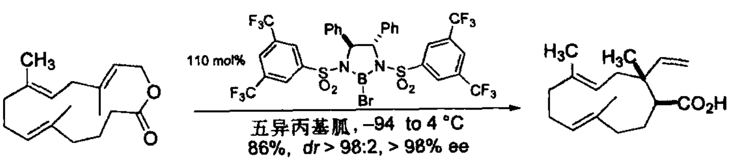
Example 1[2]



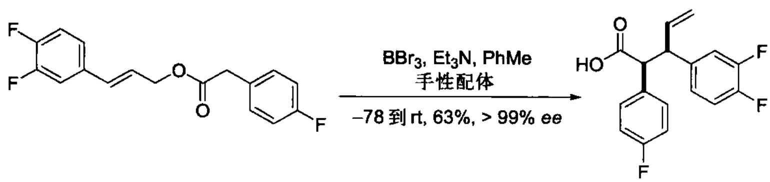
Example 2[3]



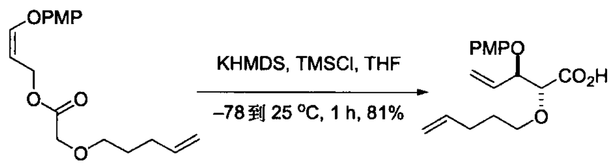
Example 3, 对映选择性Claisen 烯醇酯重排[6]



Example 4, 修正的Ireland–Claisen 重排[8]



Example 5[9]



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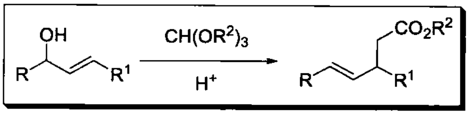
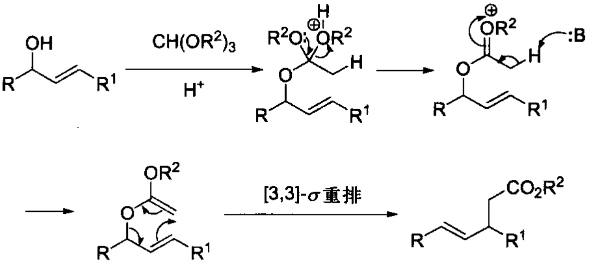
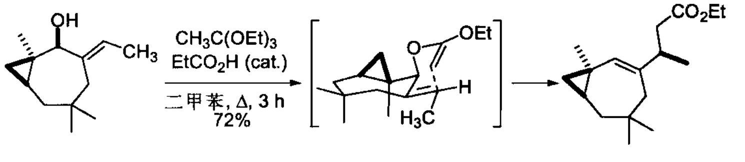
Johnson-Claisen (原酸酯) 重排反应

烯丙基醇和过量的三烷基原酸酯在微量的弱酸存在下加热给出一个混合的原酸酯。从机理上看，原酸酯失去醇生成烯酮缩酮后发生 [3,3]-σ 重排反应而生成 γ,δ-不饱和酯。

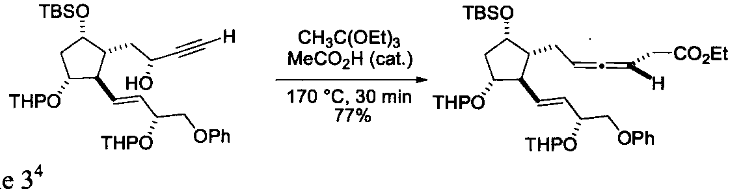




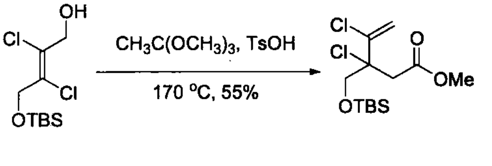
Example 1[2]



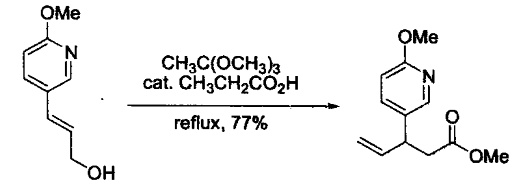
Example 2[3]



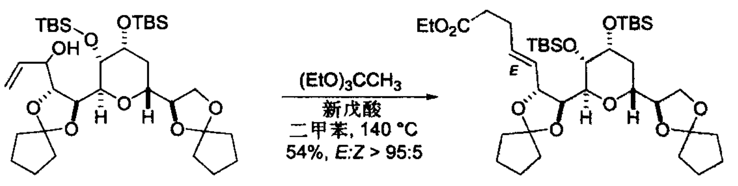
Example 3[4]



Example 4[9]



Example 5[10]



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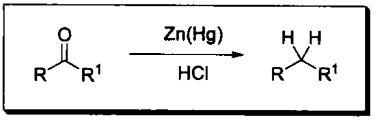
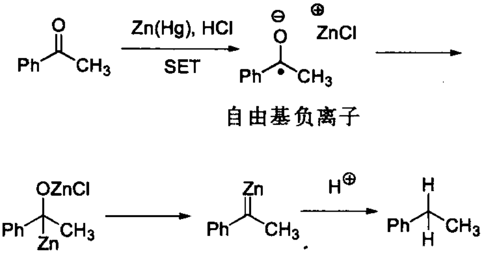
Clemmensen还原反应

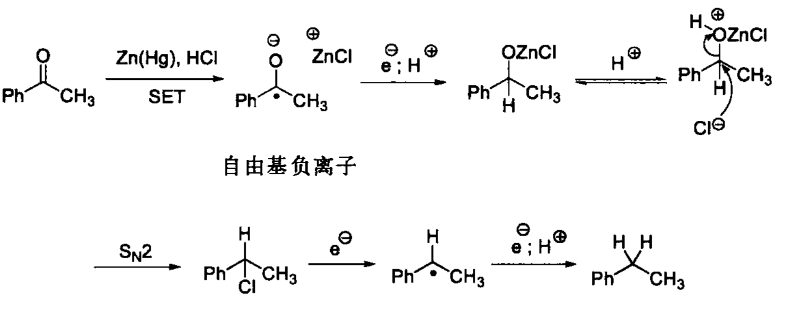
醛酮羰基在Zn/Hg作用下还原成亚甲基的反应。



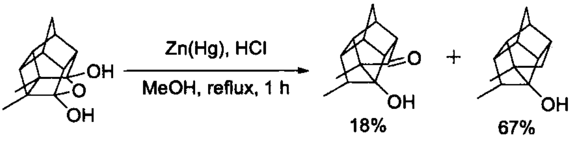
Zn 类卡宾机理:[3]



自由基负离子机理:

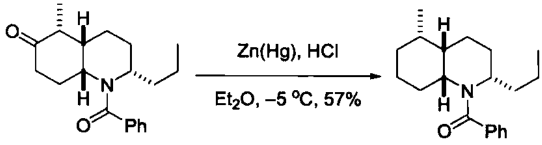


Example 1[5]

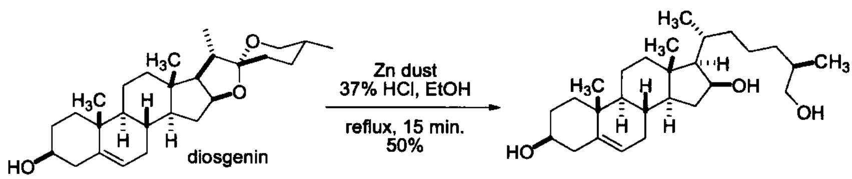


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_57,

Example 2[6]



Example 3[8]



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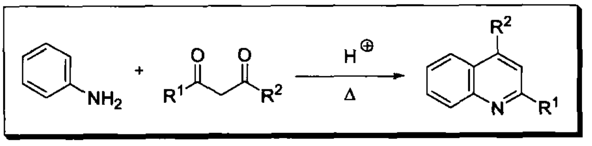
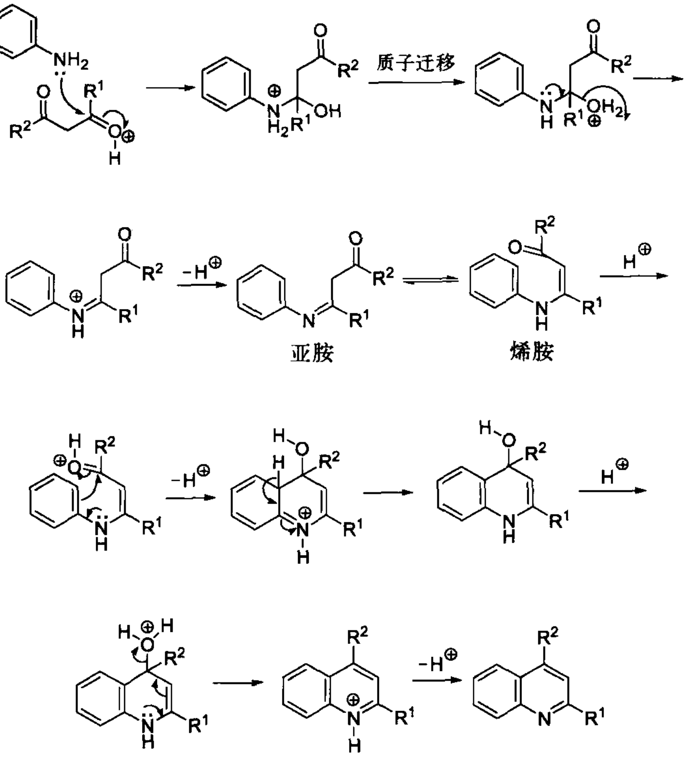
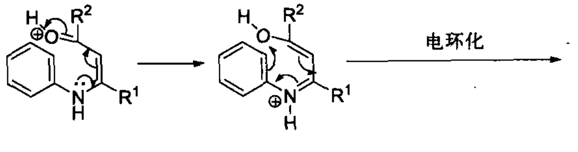
Combes喹啉合成反应

苯胺和β-二酮在酸催化下组合成喹啉。参见Conrad-Limpach反应（第133页）。

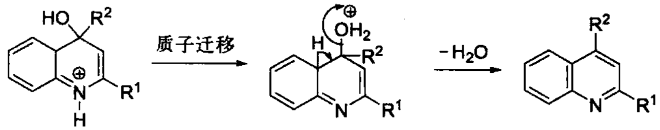




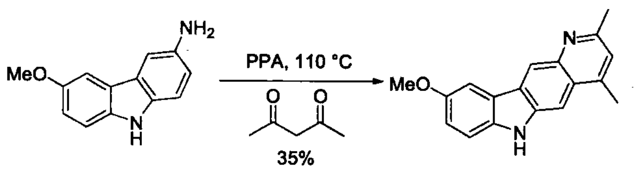
一个电环化机理也是可能的：



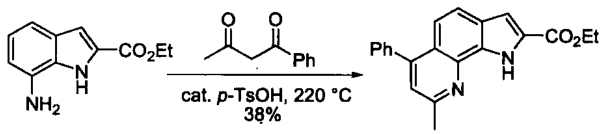
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_58,



Example 1[6]



Example 2[7]



References

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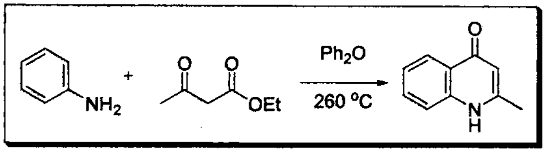
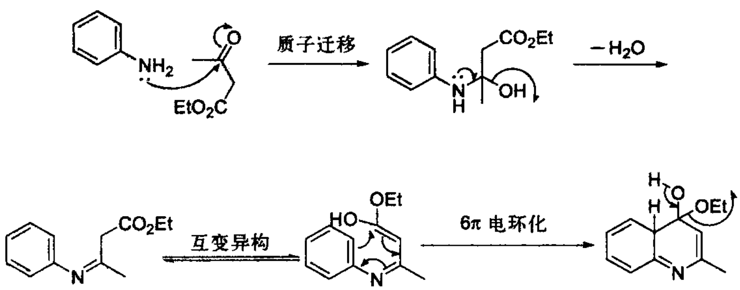
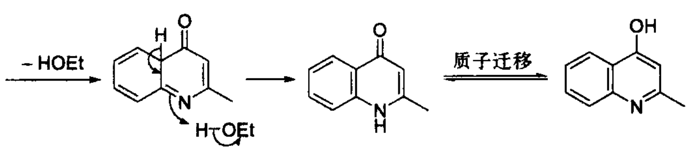
Conrad-Limpach反应

苯胺和β-酮酯在酸催化下或受热后给出4-喹啉酮。参见第131页上的Combes反应

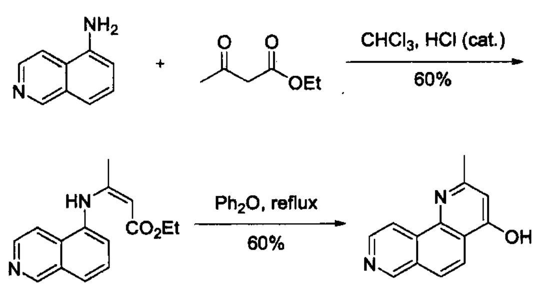




Schiff 碱

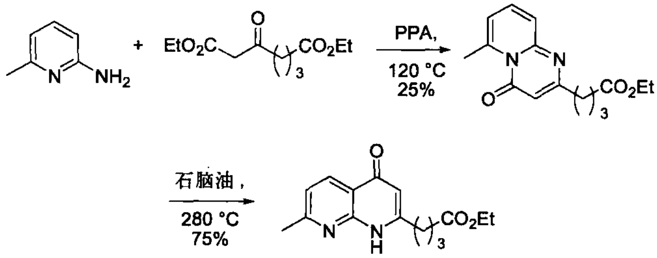


Example 1[3]

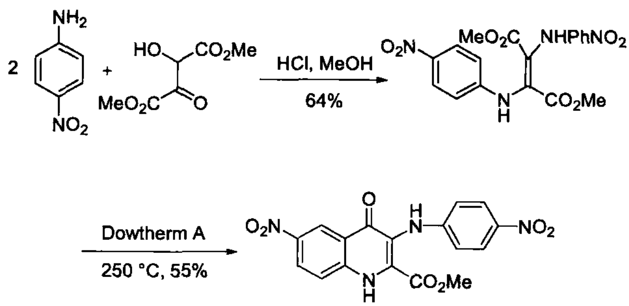


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_59,

Example 2[7]



Example 3[8]



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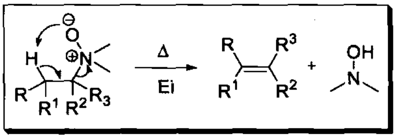
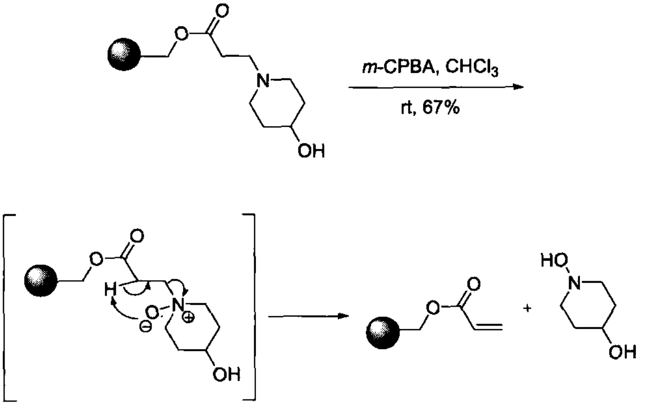
Cope 消除反应

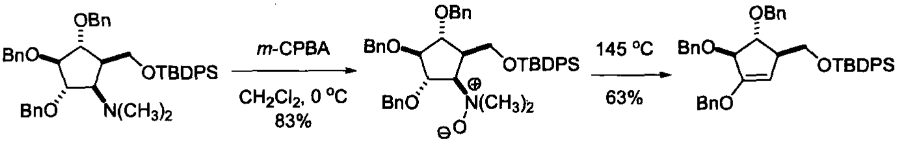
N-氧化物热消除为烯烃和*N*-羟基胺。



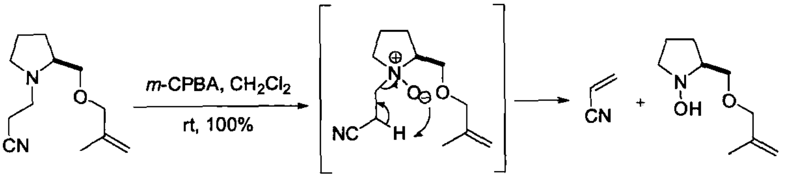
Example 1, 固相 Cope 消除[5]



Example 2[6]

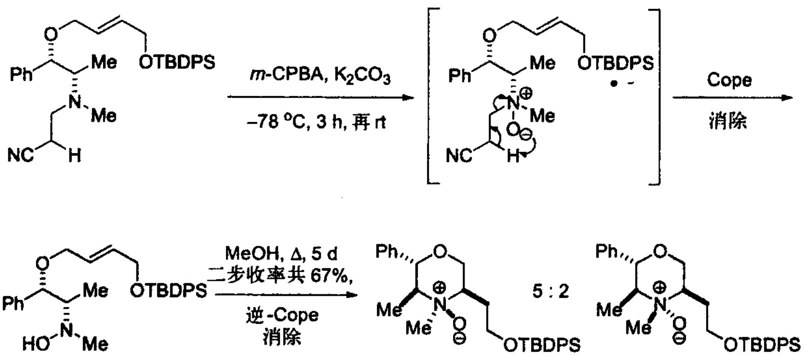


Example 3[8]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_60,

Example 4, Retro-Cope 消除[9]



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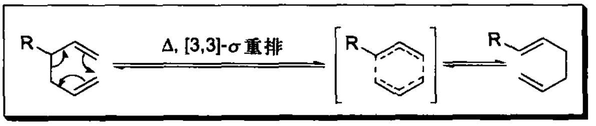
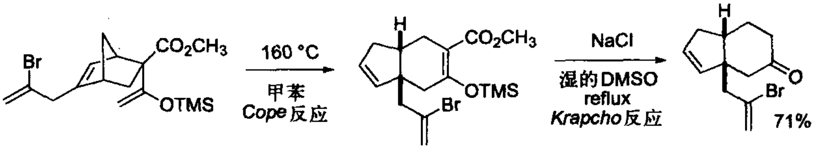
Cope重排反应

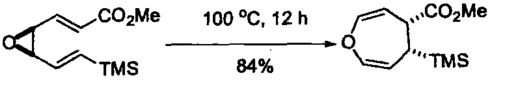
Cope重排反应、含氧Cope重排反应和负离子含氧Cope重排反应都同属[3,3]-σ 重排反应。这是一个协同过程，此处的箭头推动只是为了方便说明。本反应是个平衡反应。参见第117页上的Claison重排反应。



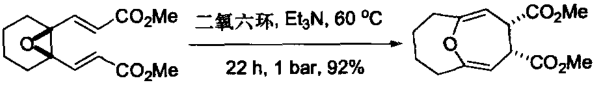
Example 1[4]



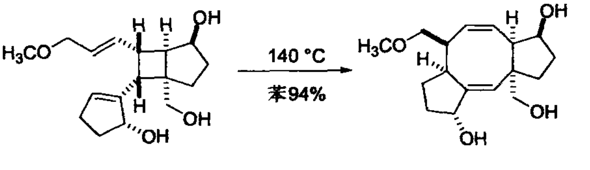
Example 2[6]



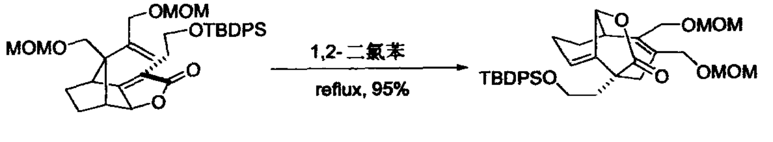
Example 3[9]



Example 4[10]

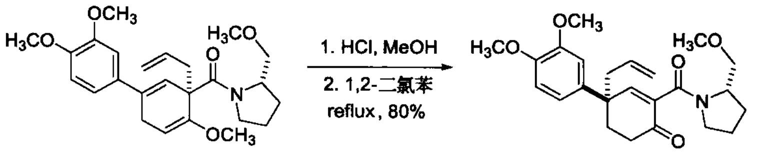


Example 5[11]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_61,

Example 6[12]



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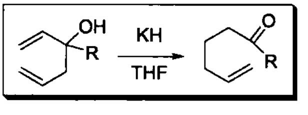
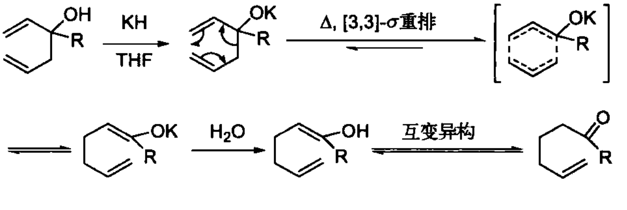
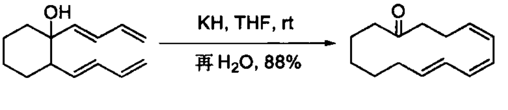
氧负离子Cope重排反应

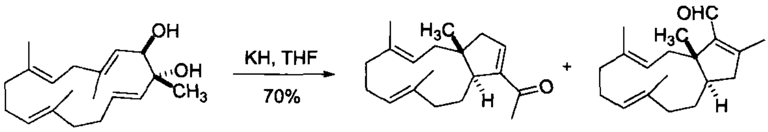




Example 1[1]



Example 2[4]



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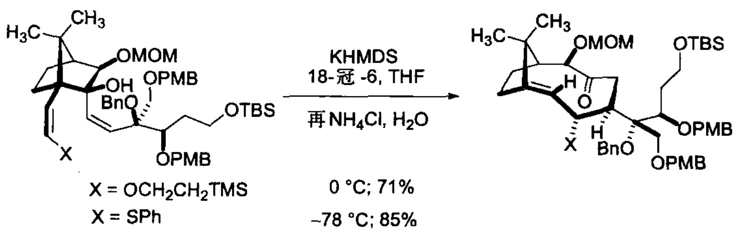

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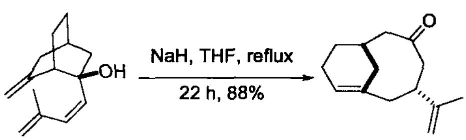
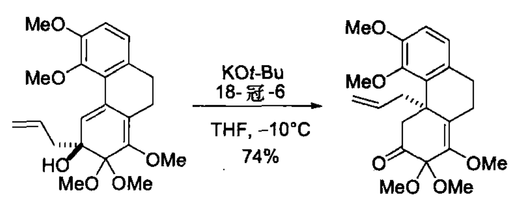


Example 5[9]



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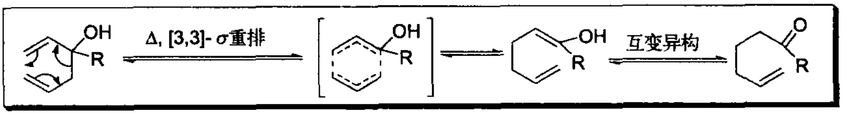
含氧Cope重排反应

负离子含氧Cope重排反应可在低温下发生，含氧Cope重排反应则需在高温低温下发生，但生成热力学稳定的产物。



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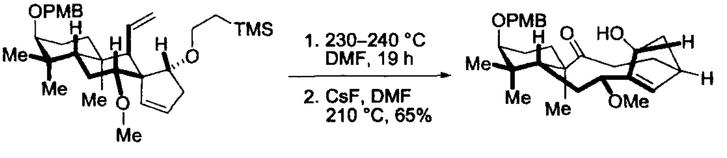

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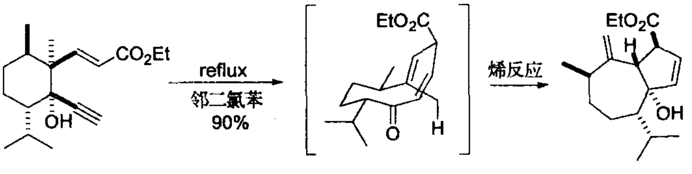
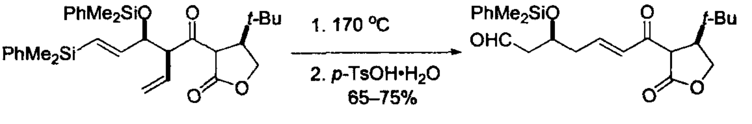
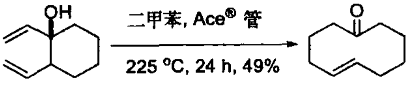


Example 3[4]



Example 4[6]



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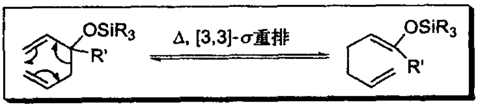
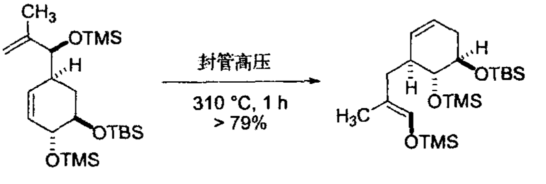
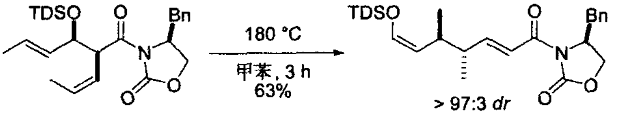
硅氧基Cope重排反应



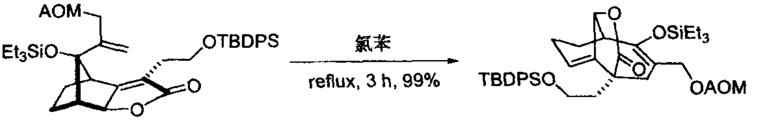
Example 1[1]



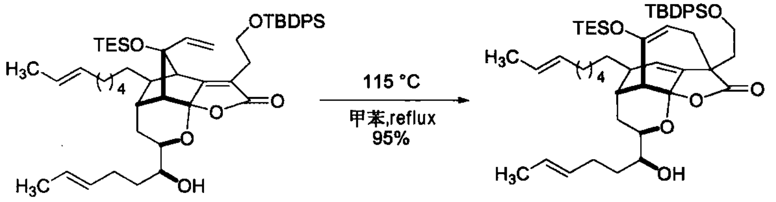
Example 2[2]



Example 3[3]



Example 4[4]



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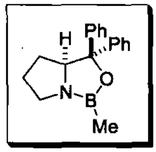
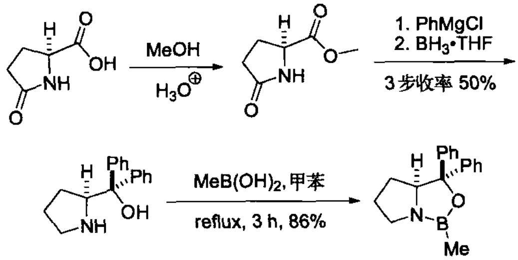
Corey-Bakshi-Shibata （CBS）试剂

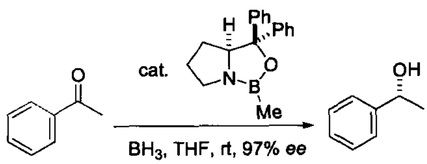


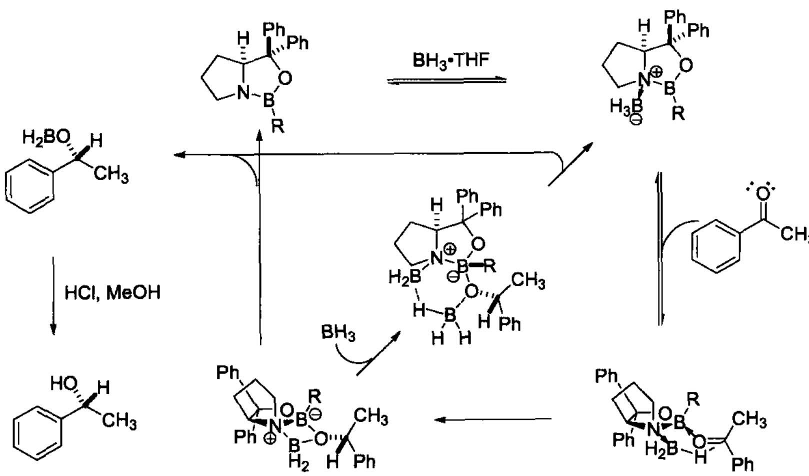
Corey-Bakshi-Shibata （CBS） 试剂是一个来自脯氨酸的手性催化剂。如同熟知的Corey试剂噁唑硼啉那样，本试剂用于酮的对映选择性还原、不对称的Diels-Alder反应和[3+2]环加成反应。

制备[1,3]



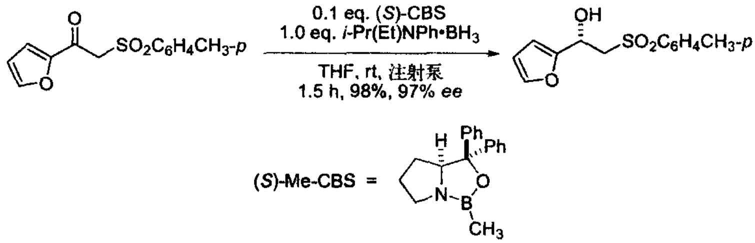
机理和催化循环:[1,3]



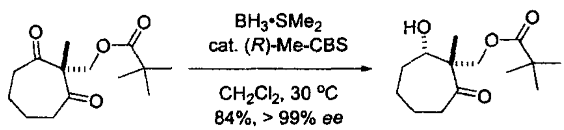


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_62,

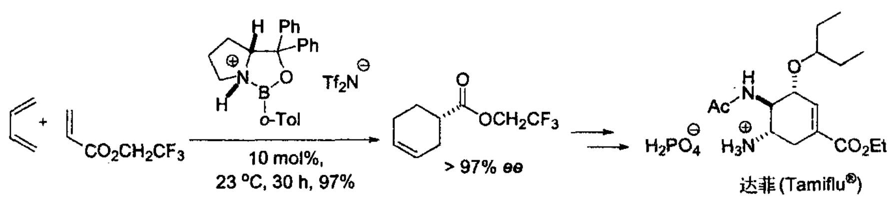
Example 1[6]



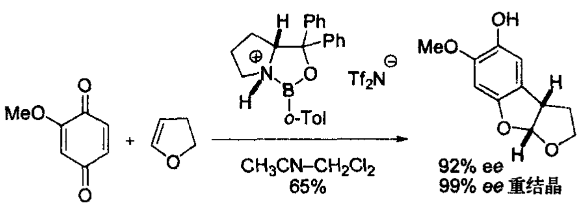
Example 2[9]



Example 3[11]



Example 4, 不对称 [3 + 2]-环加成[10]



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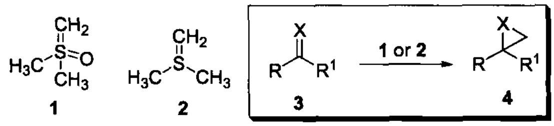
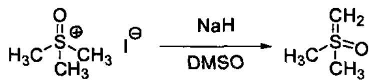
Corey-Chaykovsky反应

Corey-Chaykovsky反应是利用二甲基氧化锍亚甲基(**1**)、二甲基锍亚甲基(**2**)一类硫叶立德和羰基、烯烃、亚胺或硫羰基一类亲电物种(**3**)反应后给出**4**那样的环氧化物、环丙烷、氮杂环丙烷和硫杂环丙烷的反应。

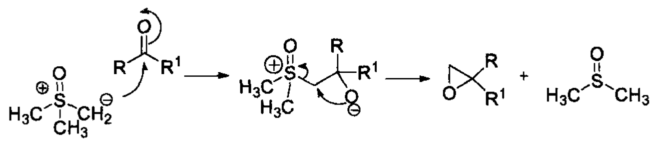


X = O, CH_2, NR^2, S, $CHCOR^3$, $CHCO_2R^3$, $CHCONR_2$, CHCN

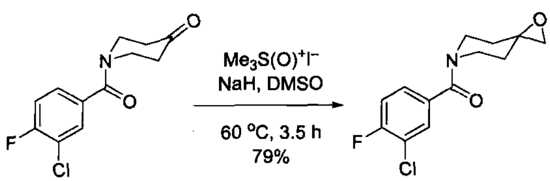
制备[1]



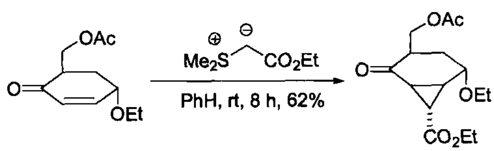
机理[1]



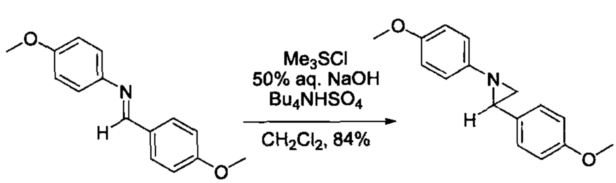
Example 1[11]



Example 2[9]



Example 3[10]



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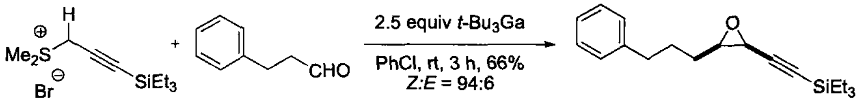
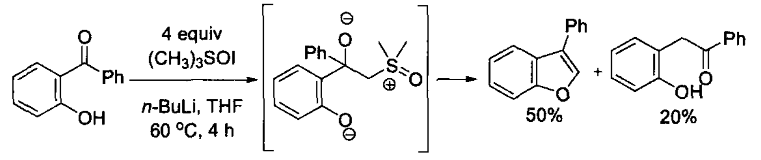
Example 4[14]



Example 5[15]



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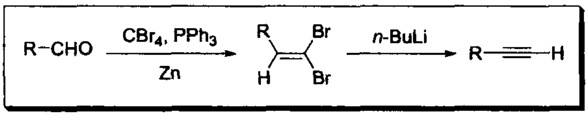
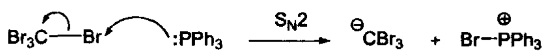
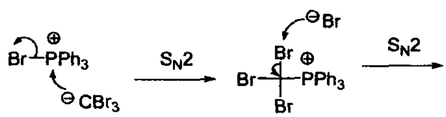
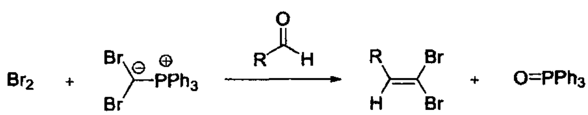
Corey-Fuchs反应

将醛先在链上增一碳为二溴烯烃，再用丁基锂处理后生成端基炔烃的合成反应。

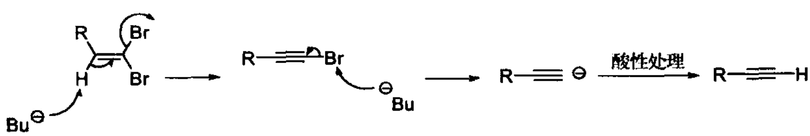




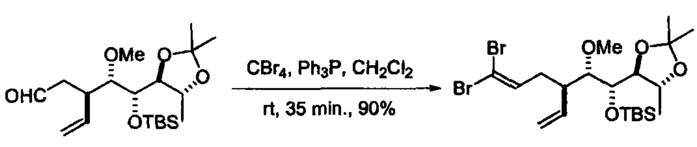


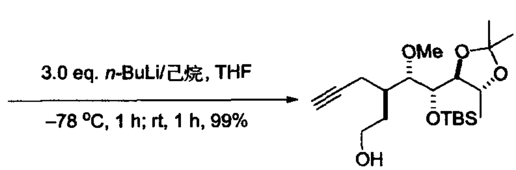


Wittig反应(见第578页上的机理)



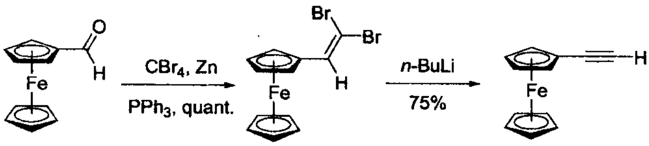
Example 1[3]



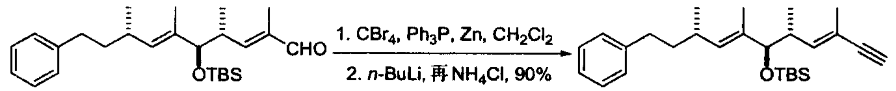


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_64,

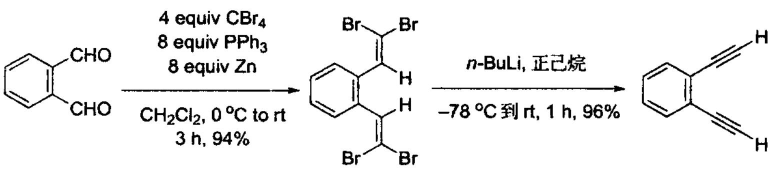
Example 2[7]



Example 3[8]



Example 4[10]



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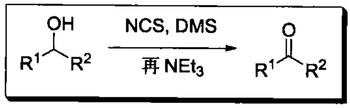
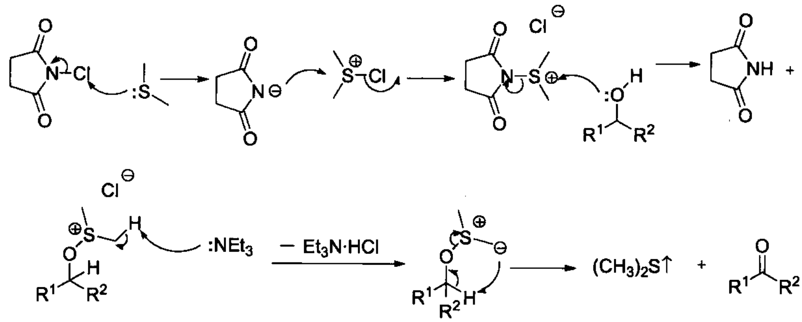
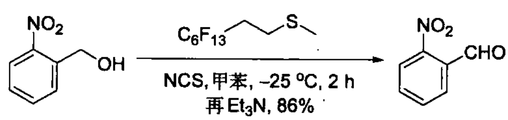
Corey-Kim氧化反应

醇用NCS/DMS氧化后再经碱处理为相应的醛酮。参见第538页上的Swern氧化反应。

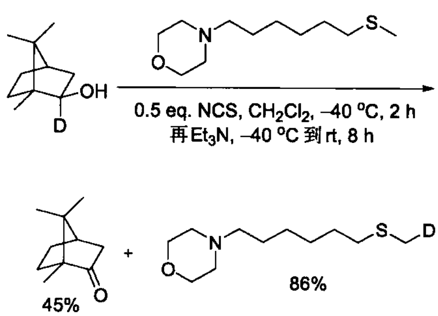




Example 1, 含氟的Corey–Kim 反应[5]

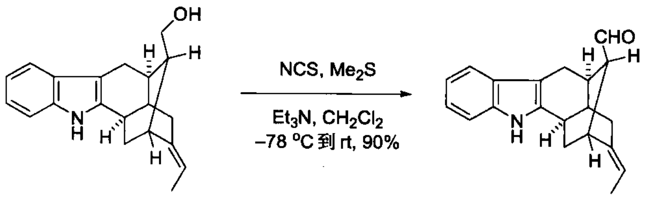


Example 2, 无嗅味的 Corey–Kim 反应[7]

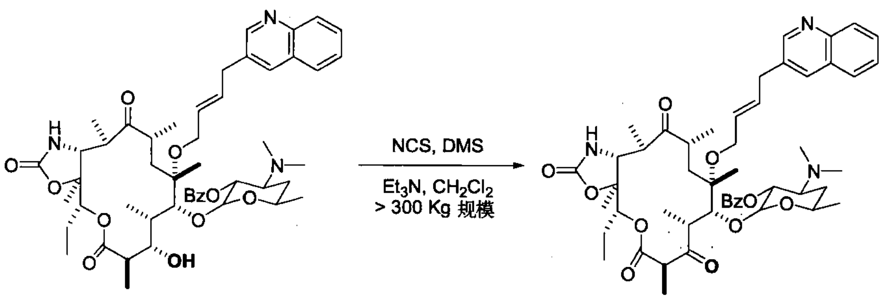


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_65,

Example 3[9]



Example 4[10]



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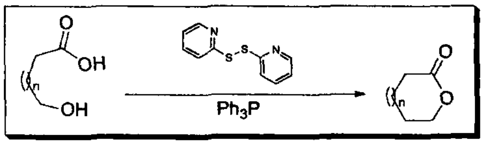
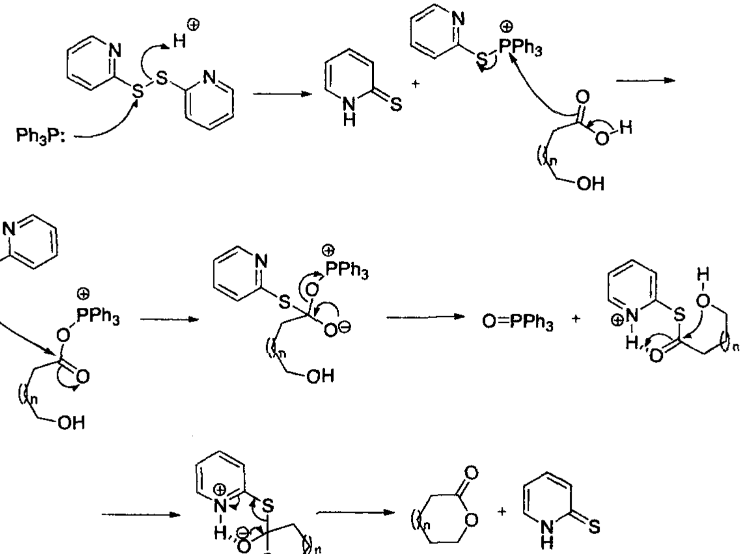
Corey-Nicolaou大环内酯化反应

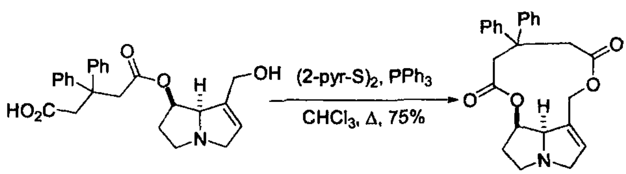
ω-羟基酸用2,2'-二吡啶基二硫化物进行大环内酯化反应。亦称Corey-Nicolaou二重活化法。





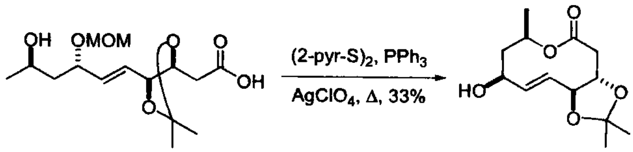
2-吡啶硫酮

Example 1[3]

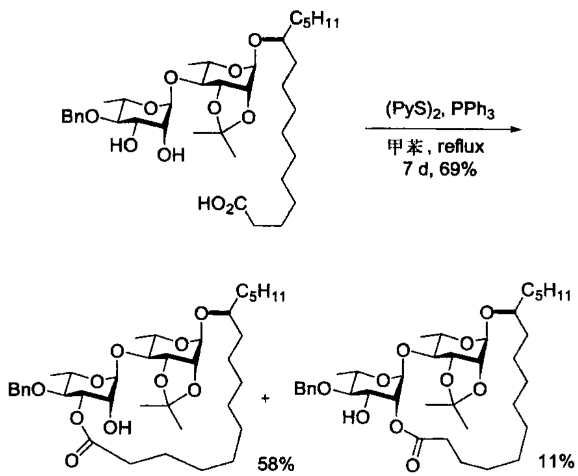


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_66,

Example 2[6]



Example 3[9]



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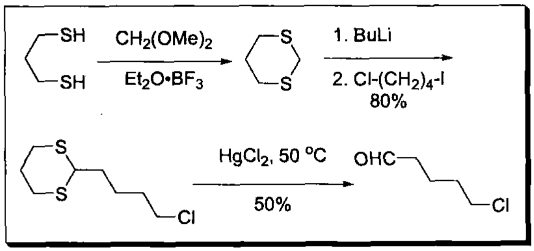
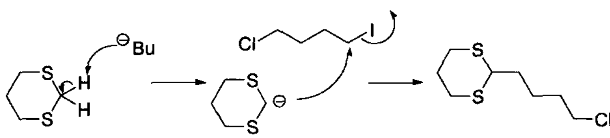
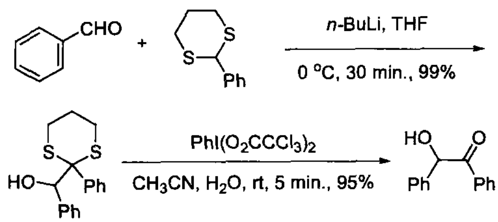
Corey-Seebach反应

二噻烷作为亲核物种，是一个被掩蔽的羰基等价物。这是一个极性反转的例子。

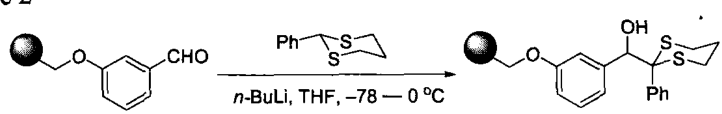




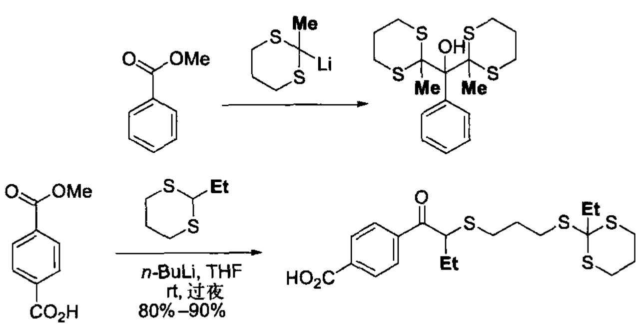
Example 1[2]



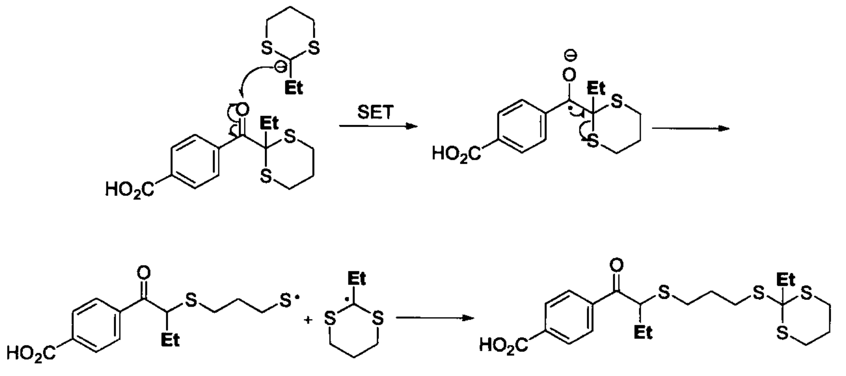
Example 2[4]



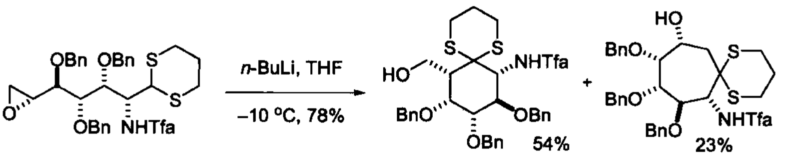
Example 3, 乙基确与甲基有很大不同[6]



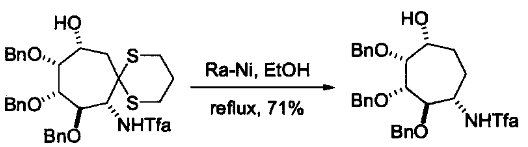
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_67,



Example 4[8]



Tfa：三氟乙酰基



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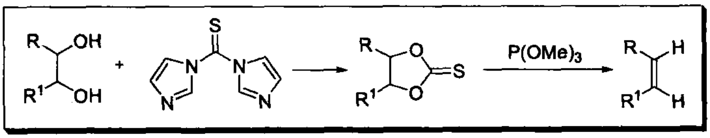
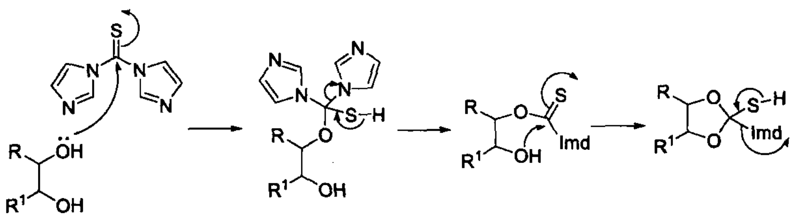
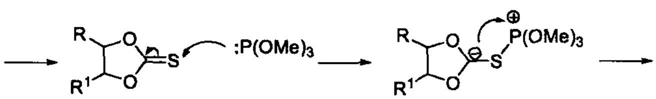
Corey-Winter烯烃合成反应

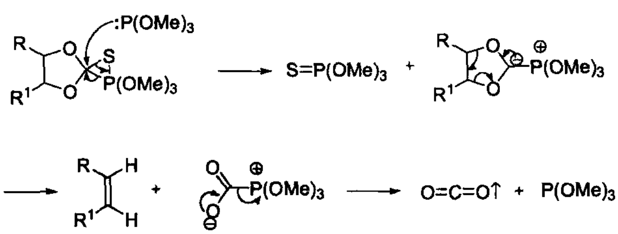
二醇用1,1'-硫羰基二咪唑（TCDI）和亚磷酸三甲酯先后处理后给出相应的烯烃。亦称Corey—Winter还原消除反应或Corey—Winter还原成烯反应。



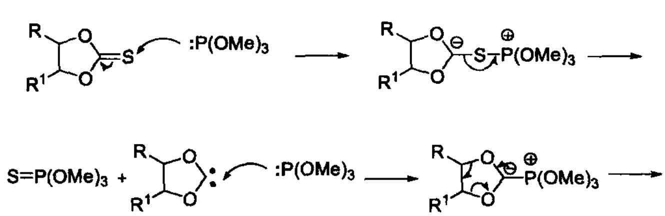




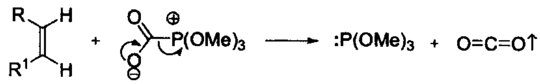
1,3-氧杂-2-硫酮
(环硫碳酸酯)



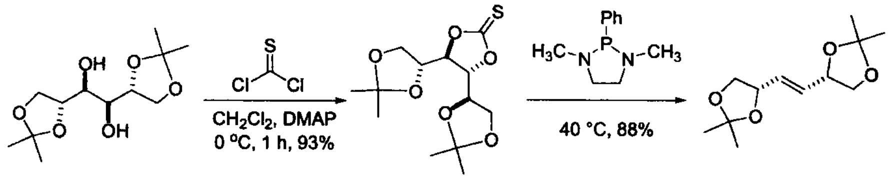
也可给出一个包括卡宾中间体的机理，并得到热解研究的支持。



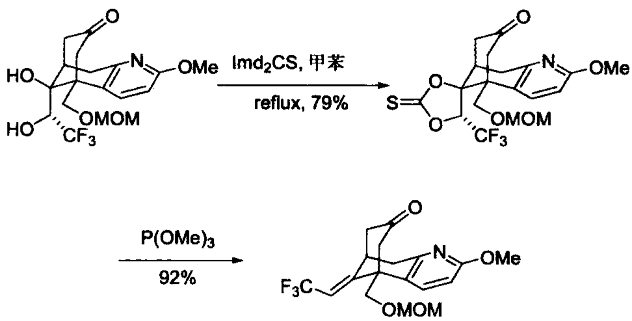
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_68,



Example 1[2]

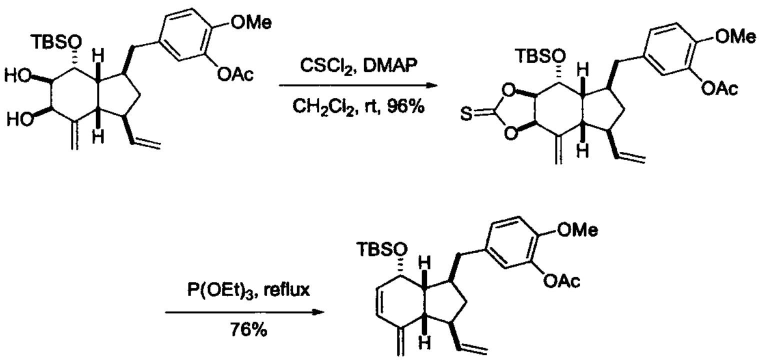


Example 2[4]

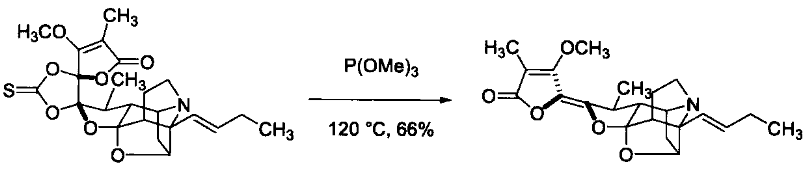


单一烯烃异构体

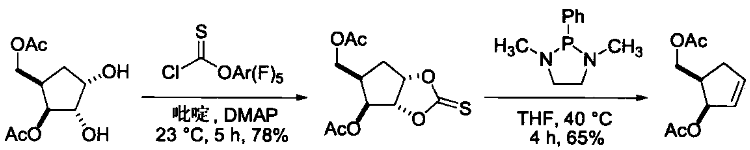
Example 3[8]



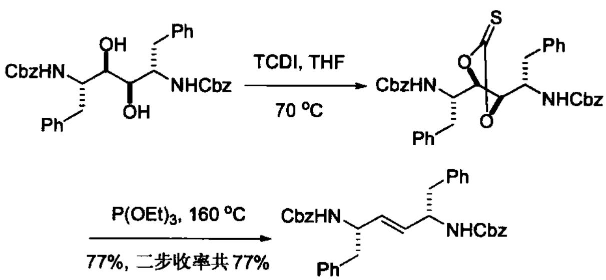
Example 4[9]



Example 5[10]



Example 6[11]



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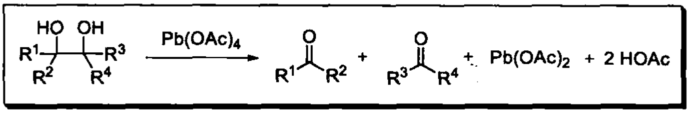
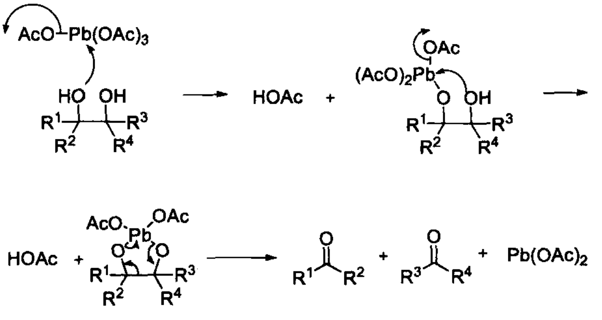
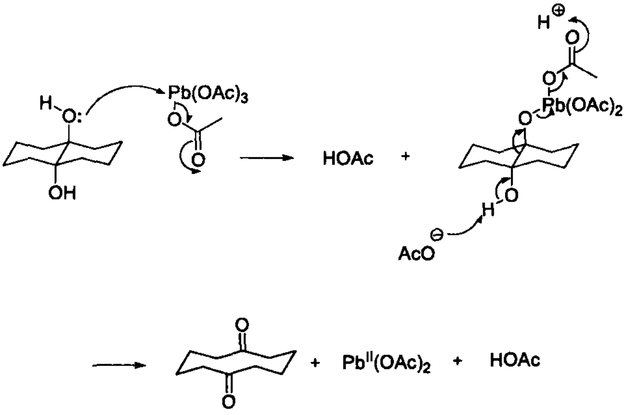
Criegee邻二醇裂解反应

邻二醇用$PbAc_4$（Lead tetraacetate, LTA）氧化为相应的二羰基化合物。

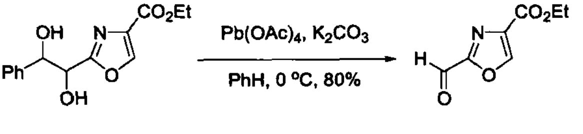




当不能形成一个环状中间体时，非环机理也有可能，但比环状机理的速率慢。[3]

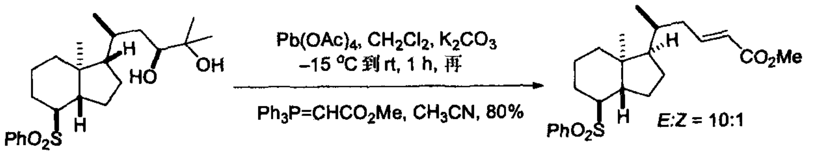


Example 1[7]

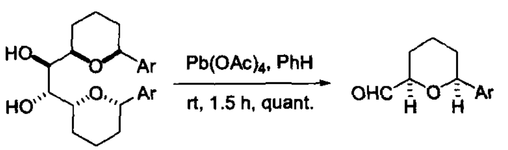


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_69,

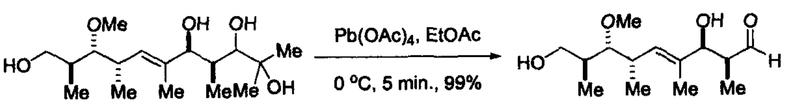
Example 2[9]



Example 3[10]



Example 4[11]



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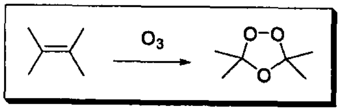
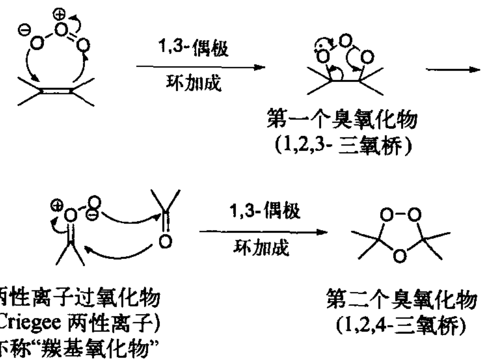
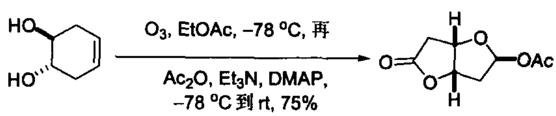
Criegee 臭氧化反应机理

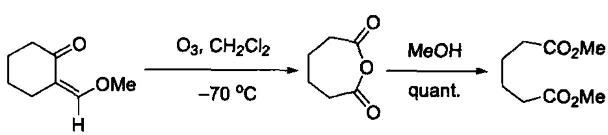




Example 1[7]



Example 2[8]



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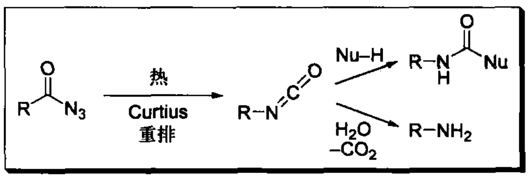
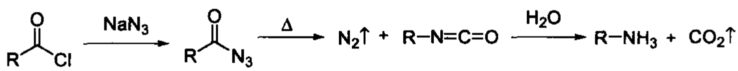
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_70,

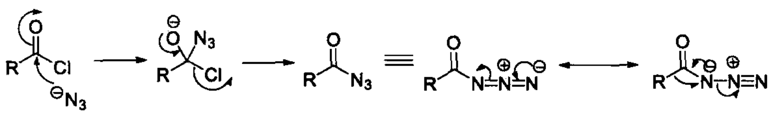
Curtius重排反应

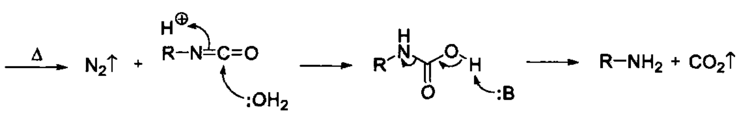
受热条件下，烷基、芳基和烯基取代的叠氮化物发生1,2-碳到氮的迁移并放出氮气而生成异氰酸酯。异氰酸酯产物常就地和亲核物种反应给出氨基甲酸酯、脲和其他的*N*-酰基衍生物或水解生成胺。



热重排：

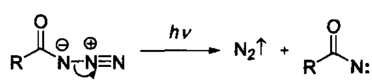




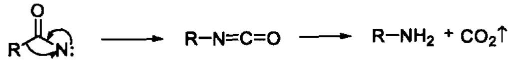


异氰酸酯中间体

光重排：

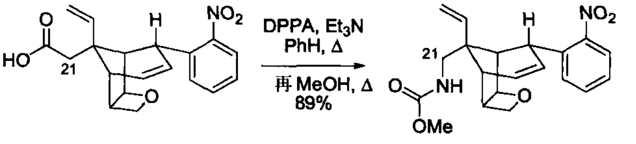


氮宾

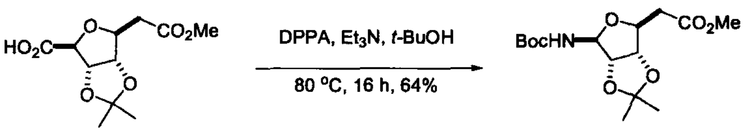


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_71,

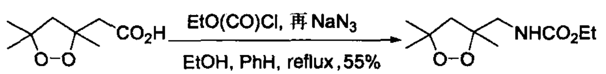
Example 1, Shioiri–Ninomiya–Yamada 修正法[2]



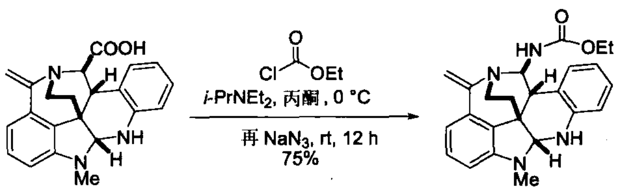
Example 2[3]



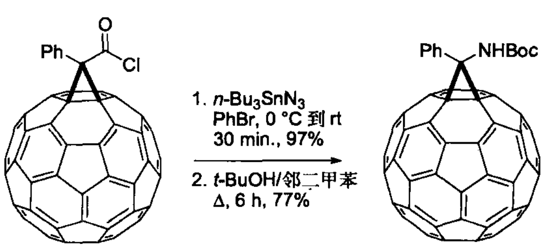
Example 3[4]



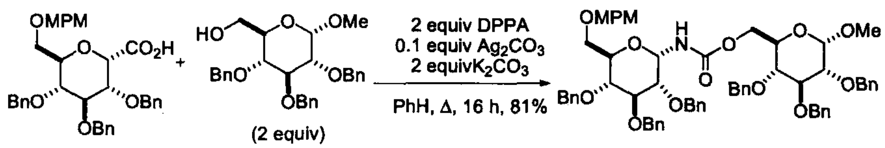
Example 4, Curtius 重排的 Weinstock 变异反应[6]



Example 5[7]



Example 6, Lebel 修正[8]



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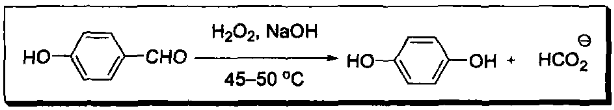
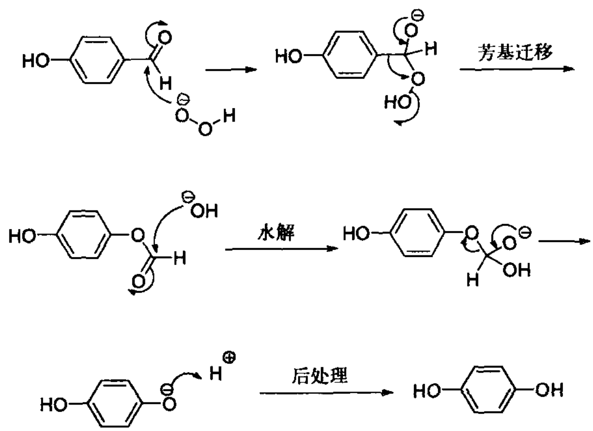
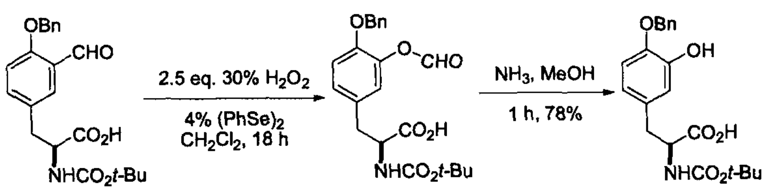
Dakin氧化反应

芳香醛酮用碱性过氧化氢氧化为酚。参见第12页上变异的Baeyer-Villiger氧化反应。

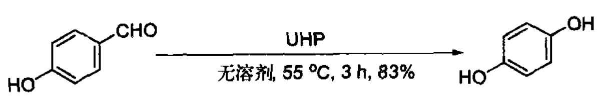




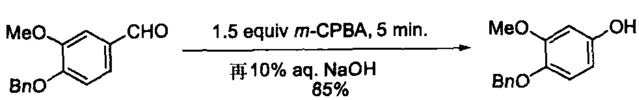
Example 1[6]



Example 2[7]



Example 3, 改进的无溶剂Dakin氧化方案[9]



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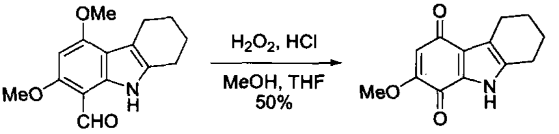
Example 4[10]



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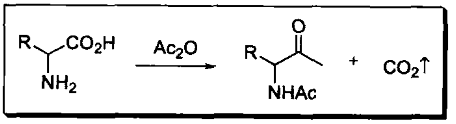
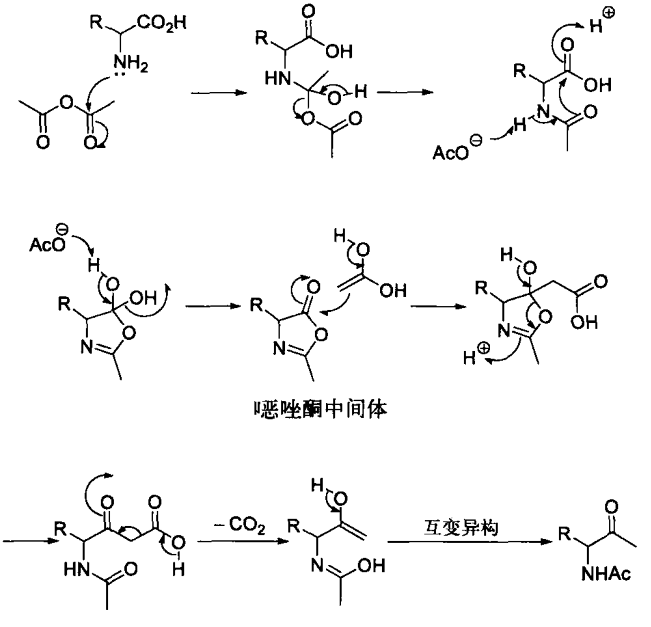
Dakin-West反应

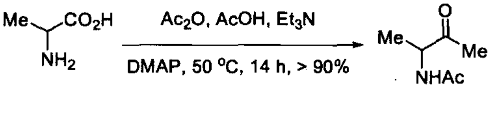
α-氨基酸经噁唑啉中间体直接转化为相应的α-酰氨基烷基甲基酮。反应在乙酐和吡啶一类碱存在下进行并放出CO_2。



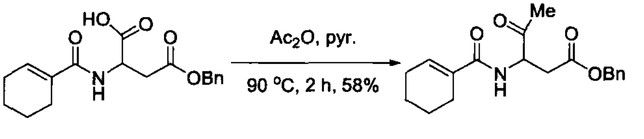


噁唑酮中间体

Example 1[6]

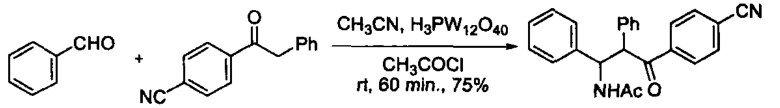


Example 2[7]

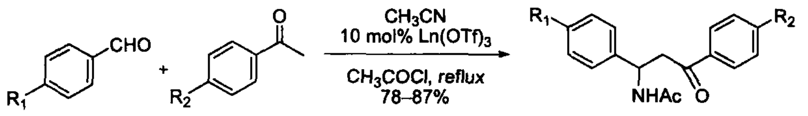


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_73,

Example 3，用杂多酸为催化剂，腈为反应底物进行的绿色Dakin-West反应。[9]



Example 4, 乙腈作为反应物[10]



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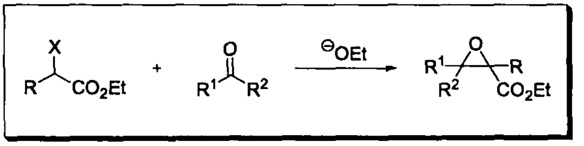
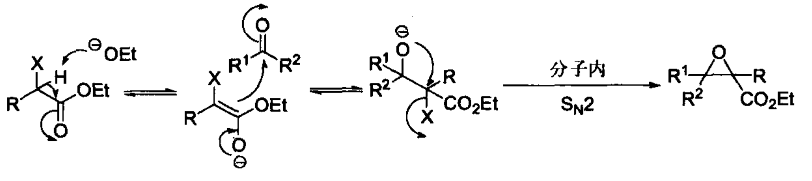
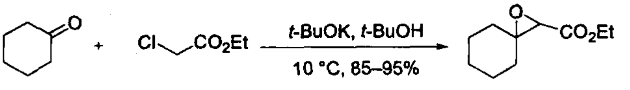
Darzens缩合反应

α-卤代酯和羰基化合物在碱催化下生成α,β-环氧酯(缩水甘油酸酯)。

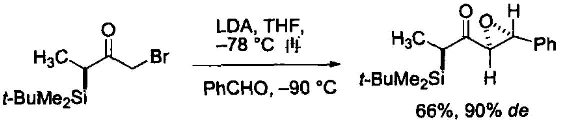




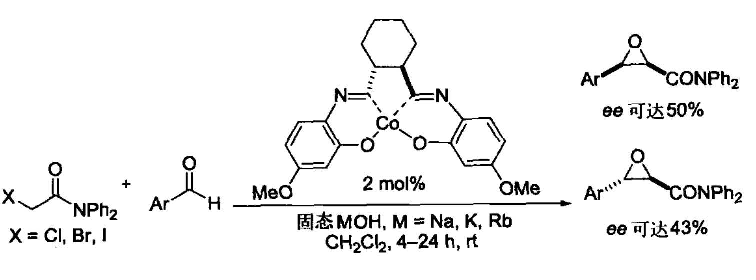
Example 1[4]



Example 2[6]



Example 3[9]



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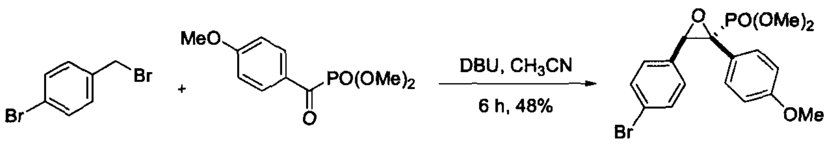
Example 4, 苯环取代使质子酸化[10]



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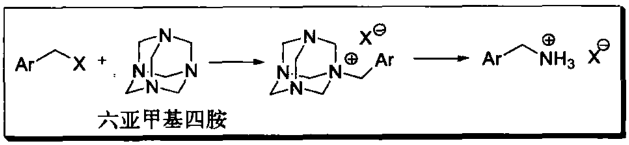
Delepine胺合成反应

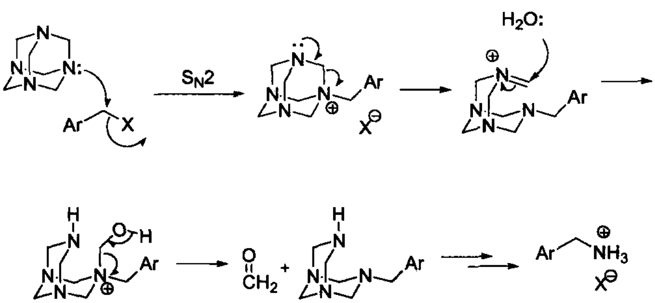
用HCl的醇溶液裂解由烷基卤和六次甲基四胺反应生成的盐给出伯胺。

参见第247页上同样生成胺的Gabrial反应和第515页上生成醛的Sommelet反应。Delepine反应对活泼的卤代烃，如苄卤、烯丙基卤和α-卤代酯特别有效。

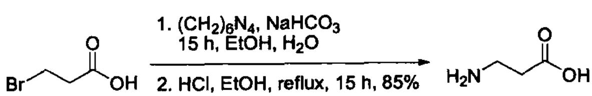


$$[ArCH_2C_6H_{12}N_4]^+X^- \quad + \quad 3\,HCl \quad + 6\,H_2O$$

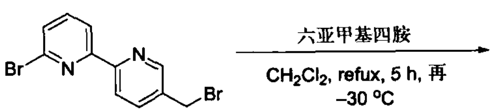
$$\longrightarrow \; ArCH_2NH_2{\cdot}HX \quad + \quad 6\,CH_2O \quad + \quad 3\,NH_4Cl$$



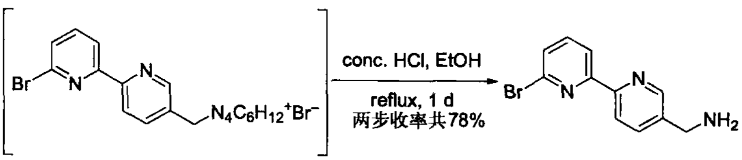
Example 1[3]



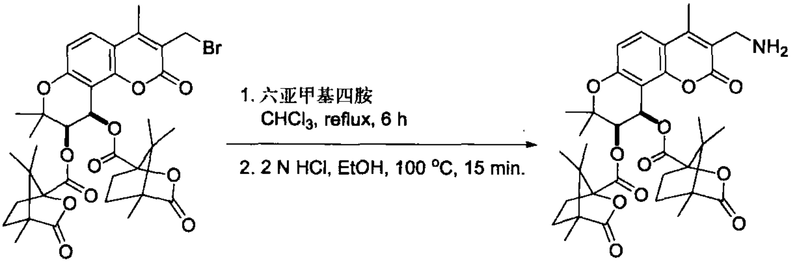
Example 2[7]



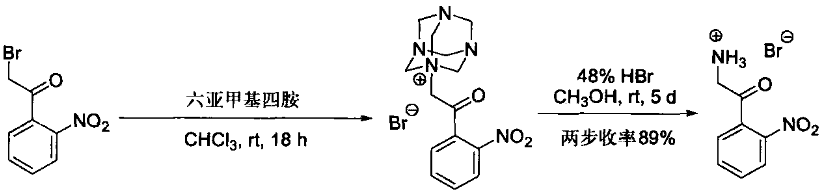
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_75,



Example 3[8]



Example 4[9]



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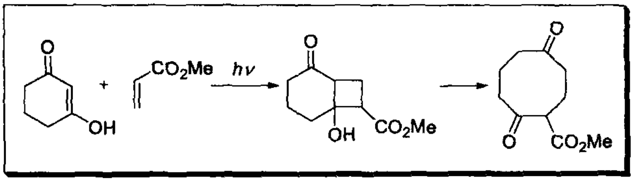
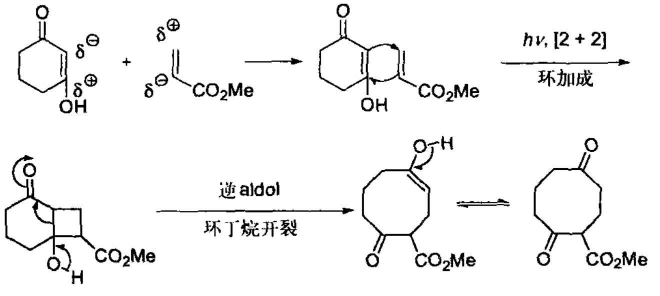
De Mayo反应

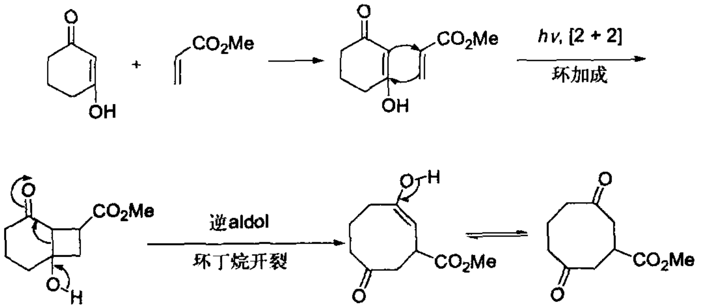
烯酮和烯烃在光促下进行[2+2]环加成反应后接着一个逆Aldol反应给出1,5-二酮。



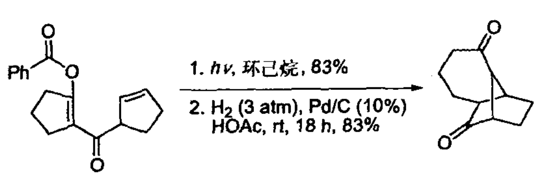
头尾排列给出主产物：



头头排列给出次产物：



Example 1[3]



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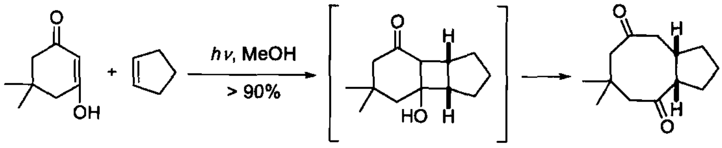
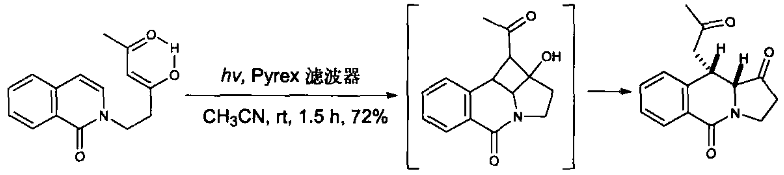
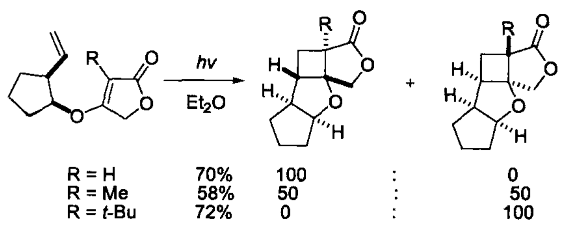
Example 2[6]



Example 3[9]



Example 4[10]



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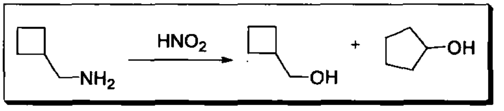
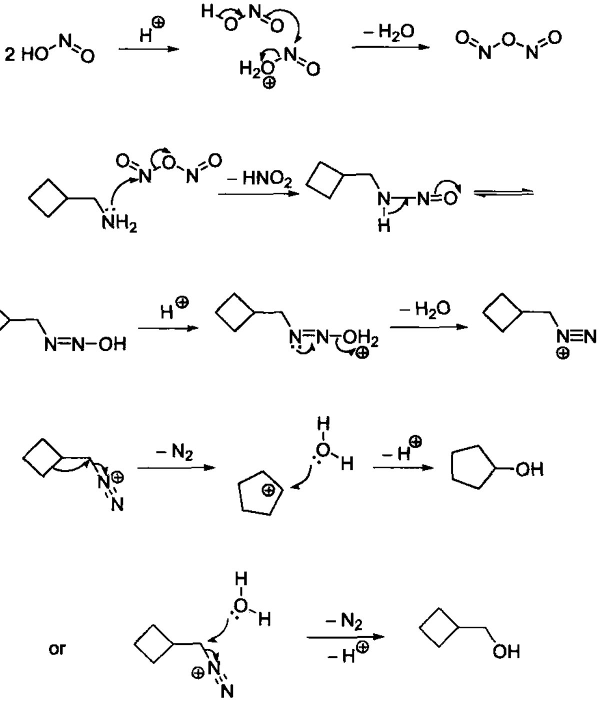
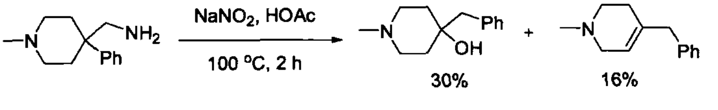
Demyanov重排反应

伯胺重氮化生成碳正离子后经C－C键迁移而重排为醇。

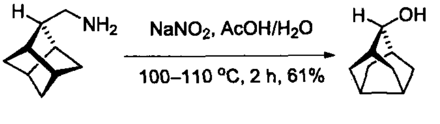




Example 1[3]

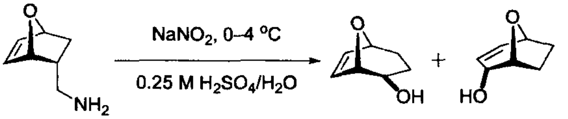


Example 2[6]

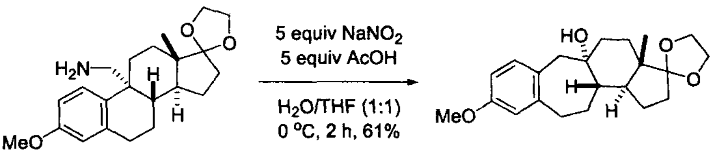


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_77,

Example 3[7]



Example 4[8]



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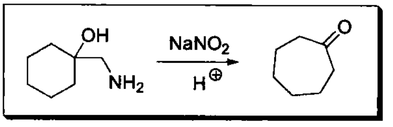
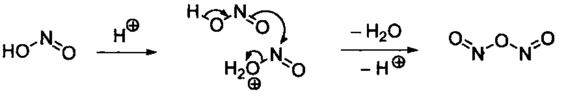
Tiffeneau- Demyanov重排反应

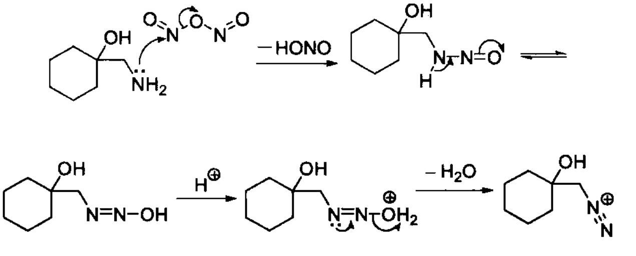
β-氨基醇重氮化生成碳正离子后经C－C键迁移而重排为羰基化合物。



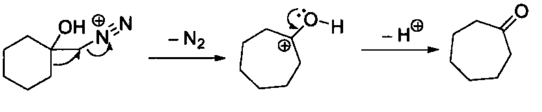
1, N_2O_3的产生



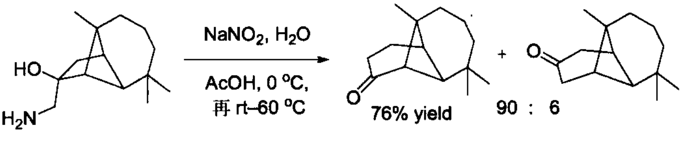
2, 胺转移为重氮盐



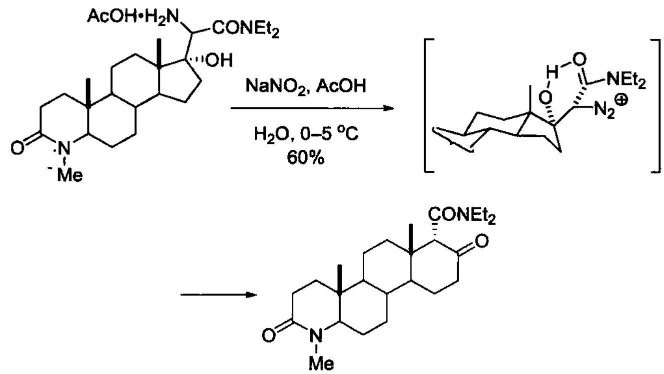
3, 重排扩环



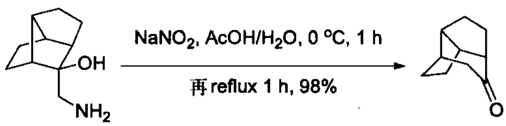
Example 1[5]



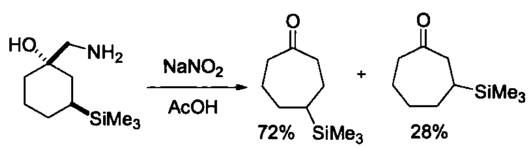
Example 2[6]



Example 3[7]



Example 4[9]



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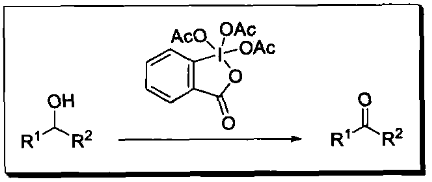
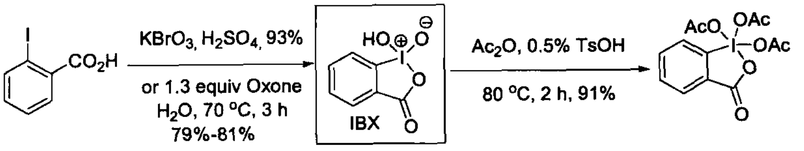
Dess-Martin超碘酸酯氧化反应

醇用Dess-Martin试剂氧化为相应的羰基化合物。Dess-Martin超碘酸酯试剂，即1,1,1-三乙酰氧-1,1-二氢-1,2-苯并碘酰-3(1*H*)-酮，是最有用的将伯醇、仲醇转变到相应的醛、酮化合物的氧化剂之一。

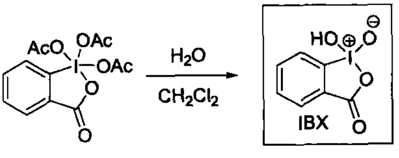


制备[1,2]：该试剂的制备要比$KBrO_3$的制备简单和安全，但该试剂中间体(IBX)也已证明很少爆炸性。[12]

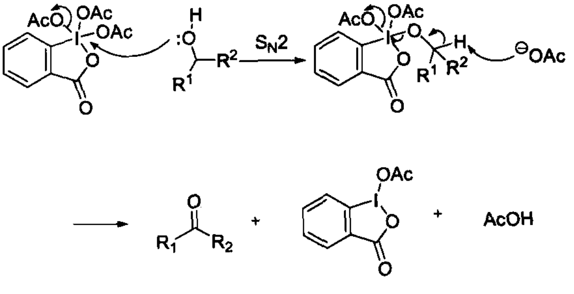


Oxone：过硫酸氢钾制剂

但该试剂易被水汽水解为氧化性更强的邻碘酰基苯甲酸(IBX)。[3]

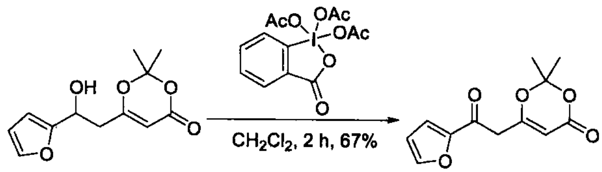


机理[1]

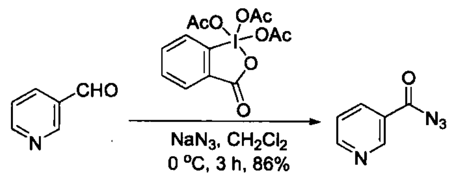


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_78,

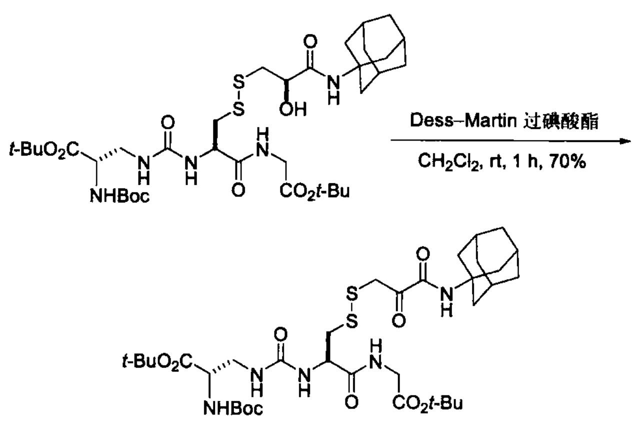
Example 1[6]



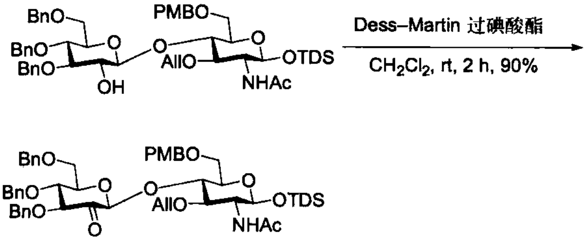
Example 2, 一个非典型 Dess–Martin 过碘酸酯的反应性[7]



Example 3[10]



Example 4[11]



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1. (a) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155–4156. 马 丁(James Cullen Martin, 1928-1999)在位于Urbana-Champaign的伊利诺依大学(University of Illinois)和University of Vanderbilt的36年间度过了出色的研究生涯。他分别在University of Vanderbilt和哈佛大学跟Don Person及P. D. Bartlett教授接受物理有机化学的训练,故早期的研究工作集中于碳正离子和双自由基化学上。但他的兴趣还是在探索化学键的极限方面,特别是有关主族元素的超价化合物。马丁小组在20多年中成功地制备出结构前所未知的S、P、Si、Br等元素的新型化合物,并最终得到难以置信的被誉为"圣杯"的稳定的五配位碳。尽管这些研究主要因马丁个人对成键模式的迷恋所推动,但并不是没有实用价值的。两个超价化合物,Martin硫烷(参见第339页,用于脱水)和Dess-Martin超碘酸酯已经在合成有机化学中得到广泛应用。马丁和他的学生戴斯(Dess)在位于Urbana-Champaign的伊利诺依大学(University of Illinois)发展了这一方法。(Martin的传略由Scott E.Denmark教 授 友 好 提 供)(b) Dess, D. B.; Martin, J. C. *J.Am. Chem Soc.* **1991**,*113, 727*–7287.
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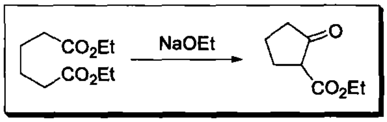
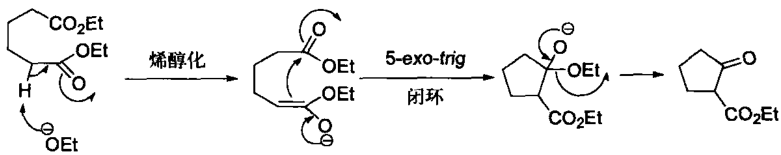
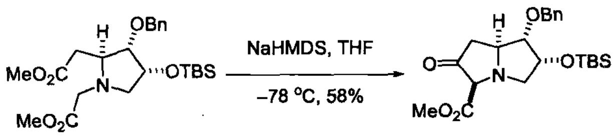
Dieckmann缩合反应

Dieckmann 酯缩合反应是Claison酯缩合反应在分子内进行的变异。

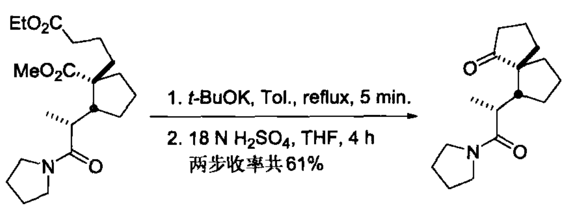




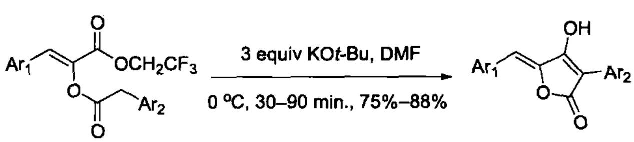
Example 1[6]



Example 2[8]

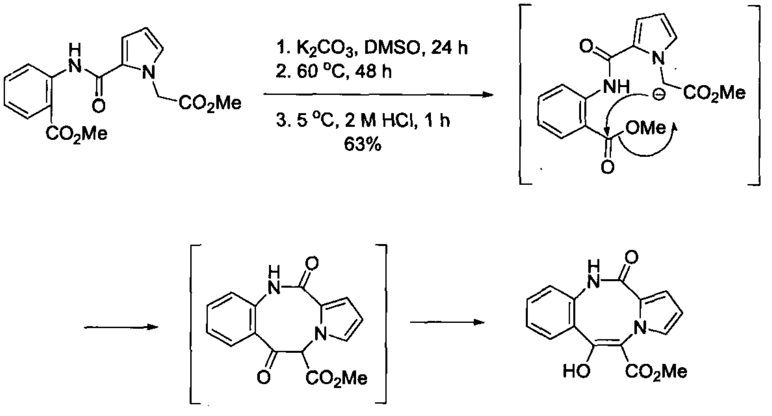


Example 3[9]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_79,

Example 4[10]



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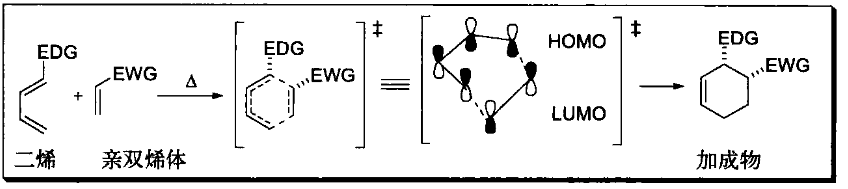
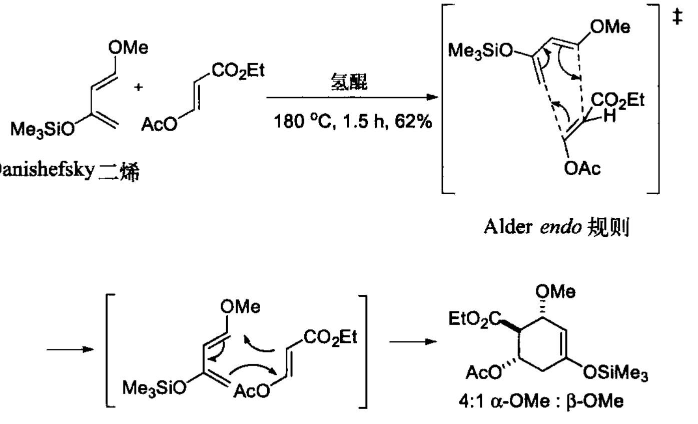
Diels-Alder反应

Diels-Alder反应，逆电子要求的Diels-Alder反应及杂原子Diels-Alder反应都属于经过协同过程的[4+2]-环加成反应。此处显示的箭头推动只是为了方便说明。

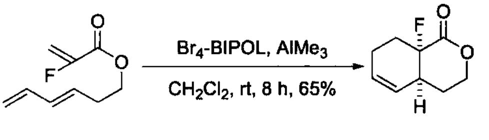


EDG = 供电子基团; EWG = 吸电子基团

Example 1[6]

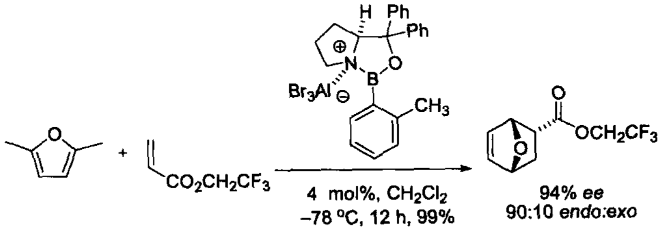


Example 2, 分子内Diels–Alder反应[7]

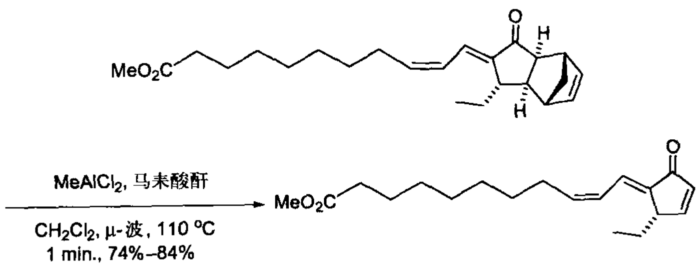


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_80,

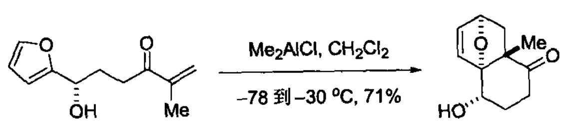
Example 3, 不对称 Diels–Alder 反应[5,8]



Example 4, 逆Diels–Alder 反应[4,9]



Example 5, 分子内Diels–Alder 反应[11]



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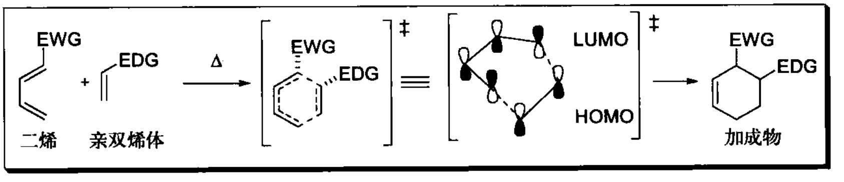
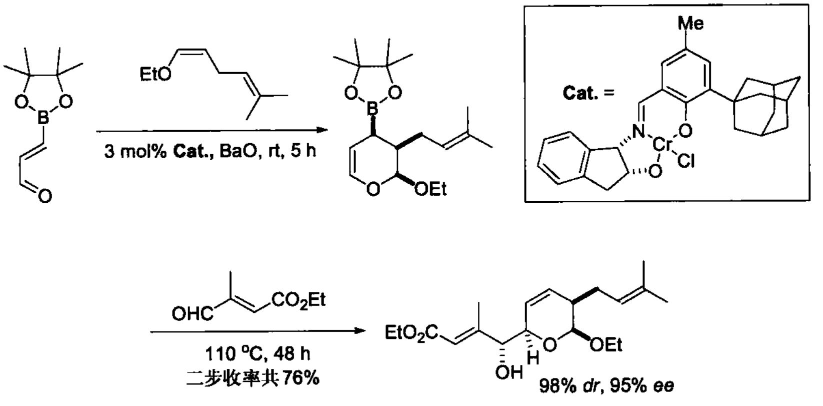
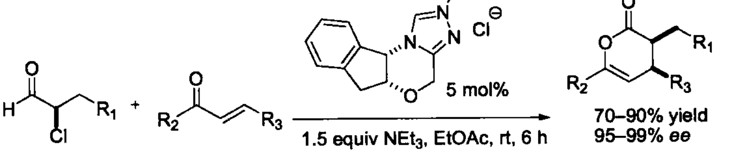
反转电子要求的Diels-Alder反应



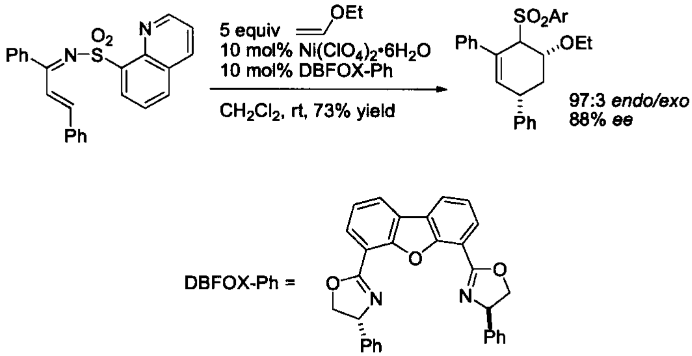
Example 1[2]



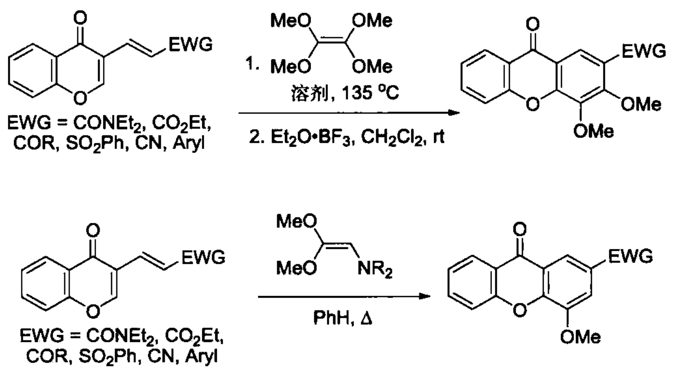
Example 2[3]



Example 3, 催化的不对称反转电子要求的Diels–Alder 反应[4]



Example 4[5]



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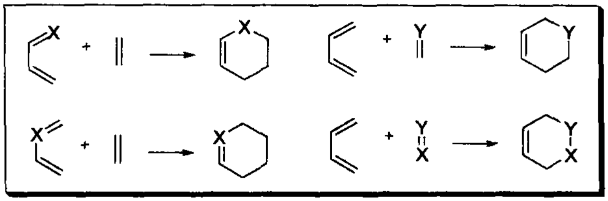
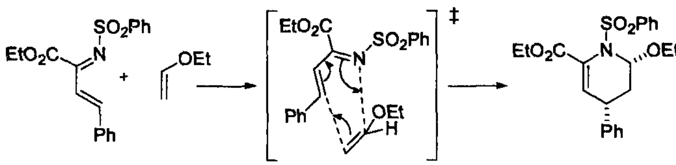
杂原子Diels-Alder反应

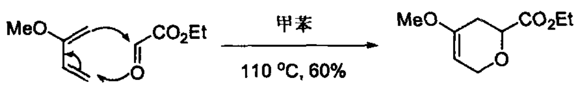
杂原子二烯或杂原子亲双烯参与的Diels-Alder反应。典型的有氮原子参与的和氧原子参与的Diels-Alder反应。



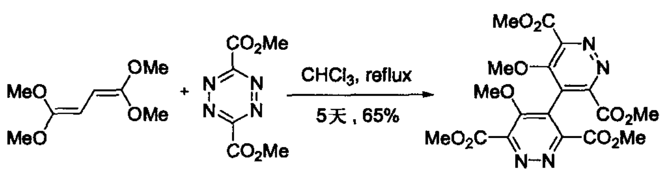
e.g.:



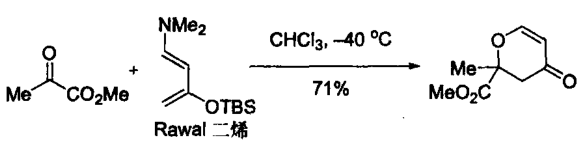
Example 1, 杂原子亲双烯体对二烯的加成[1]



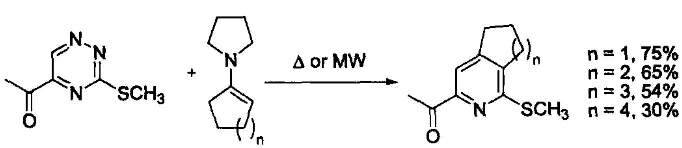
Example 2, 与第59页上的 Boger 吡啶合成相似[2]



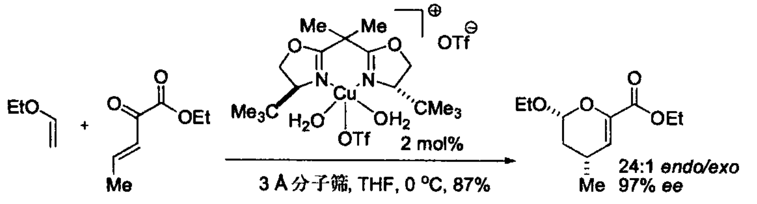
Example 3, 用Rawal 二烯的反应[4]



Example 4, 又一个与Boger 吡啶合成相似的反应[6]



Example 5[7]



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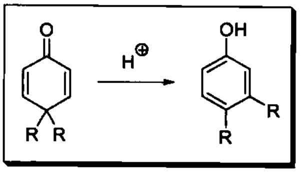
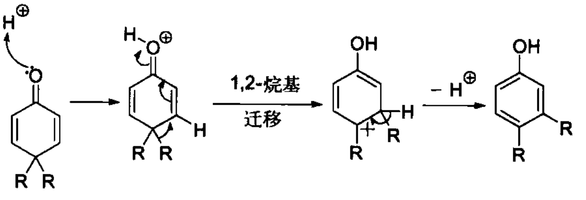
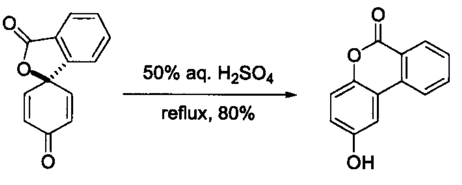
Dienone-Phenol （二烯酮-酚）重排反应

酸促进下4,4-二取代环己二烯酮重排为3,4-二取代酚。

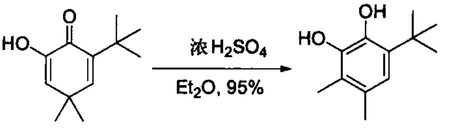




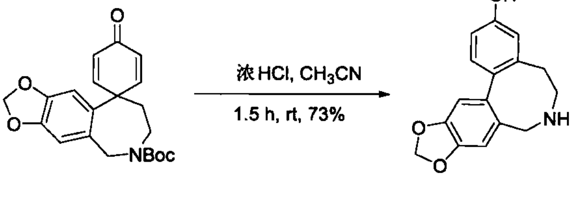
Example 1[4]



Example 2[5]



Example 3[9]



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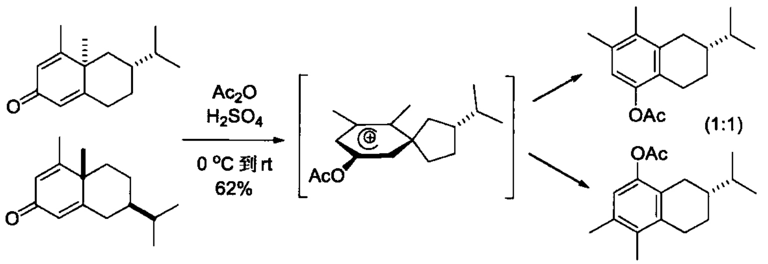
Example 4[10]



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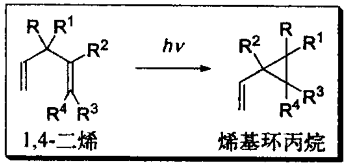
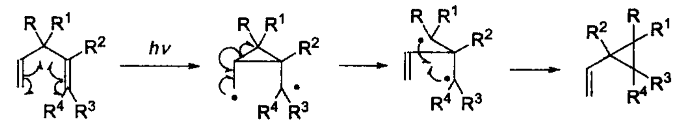
Di-π-（二-π-）甲烷重排反应

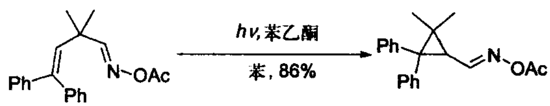
1,4-二烯光促狭转化为烯基环丙烷的反应，亦称Zimmerman重排反应。



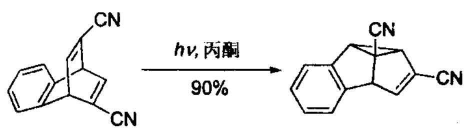


双自由基 双自由基

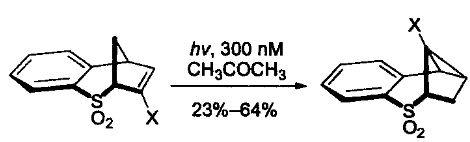
Example 1, 氮杂二-π-甲烷重排[2]



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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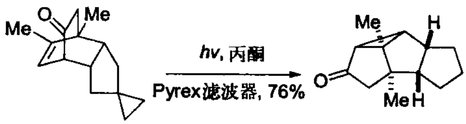
Example 4, 氧杂二-π-甲烷重排[8]



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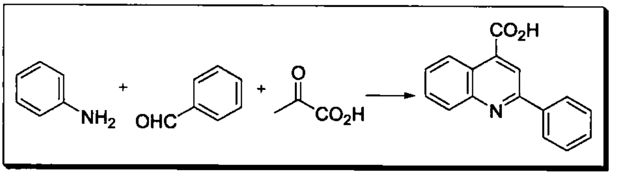
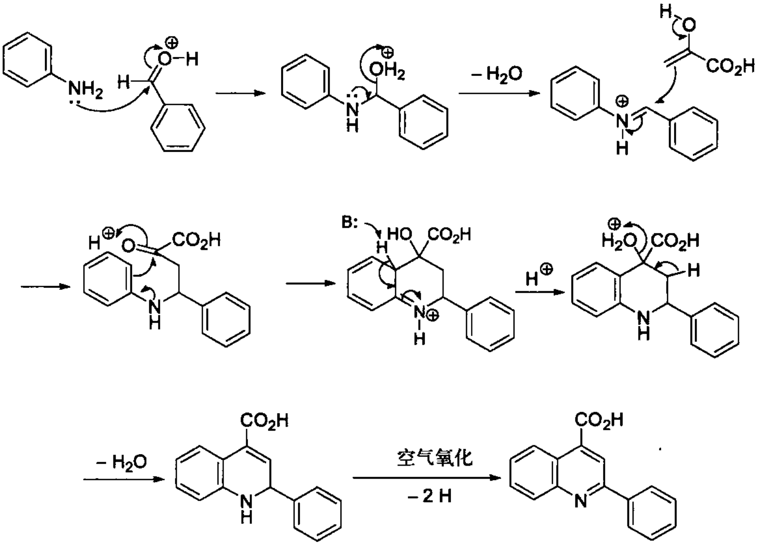
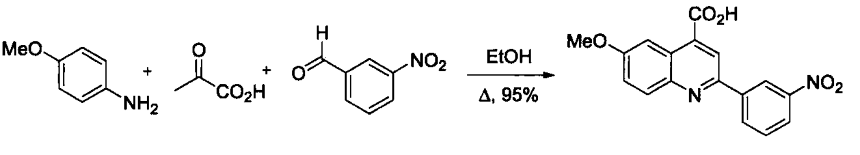
Doebner 喹啉合成反应

苯胺、醛和丙酮酸的三组分偶联给出 4-喹啉甲酸。

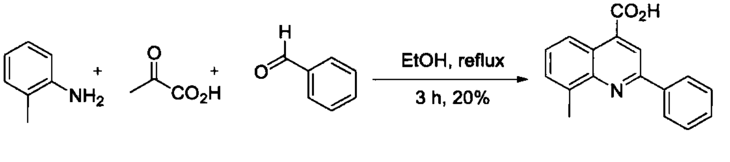




Example 1[2]



Example 2[6]



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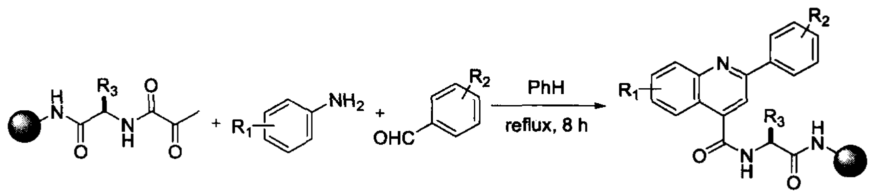
Example 3, 组合的 Doebner 反应[7]



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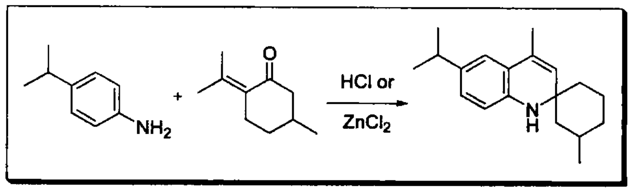
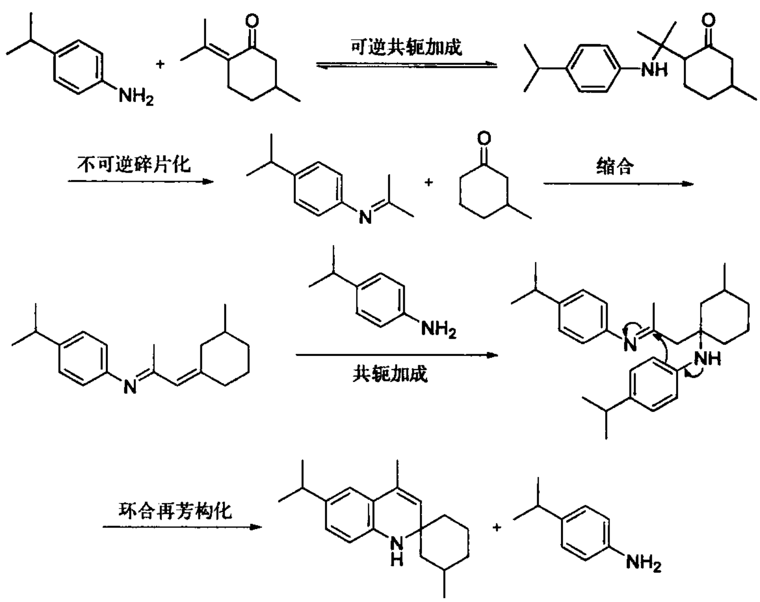
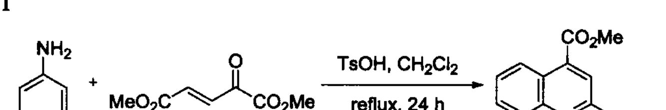
Doebner-von Miller 反应

Doebner-von Miller反应是Skraup喹啉合成反应（参见第509页）的变异。故Skraup反应机理也适用于Doebner-von Miller反应。下述机理是由Denmark利用^{13}C标记对α，β-不饱和酮进行研究所得出的。[9]

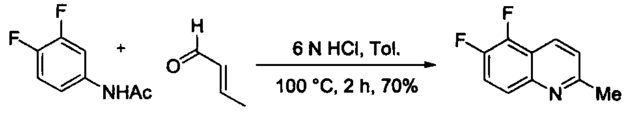




Example 1[5]

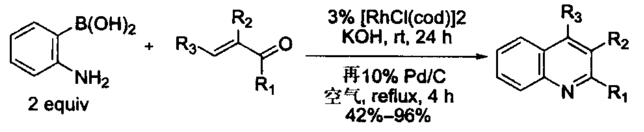


Example 2[6]



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

Example 3, 一个新的变异反应[10]



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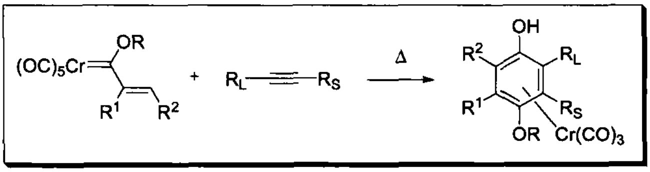
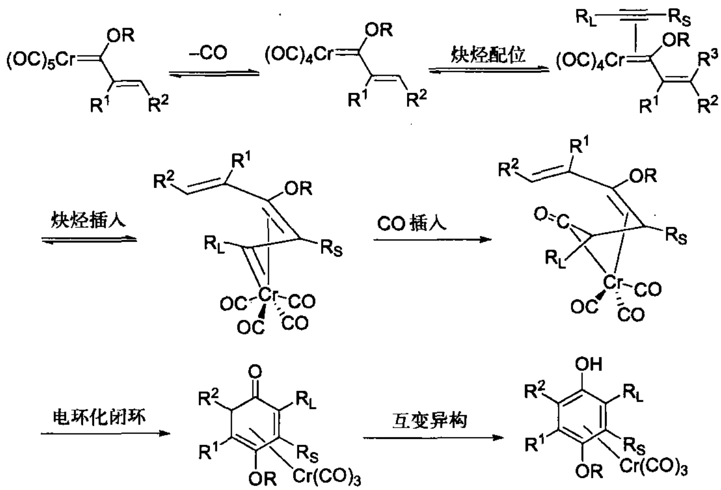
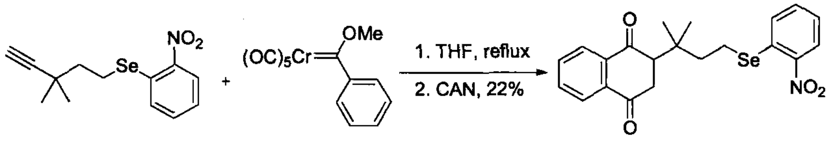
Dorz 反应

从烯基烷氧基五配位的铬卡宾配合物和炔烃合成$Cr(CO)_3$配位的氢醌。

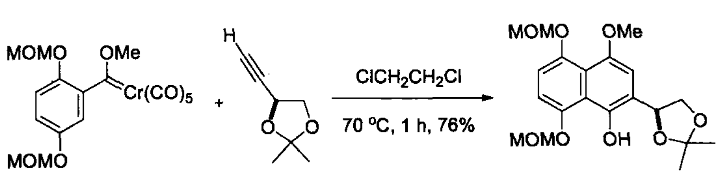




Example 1[5]

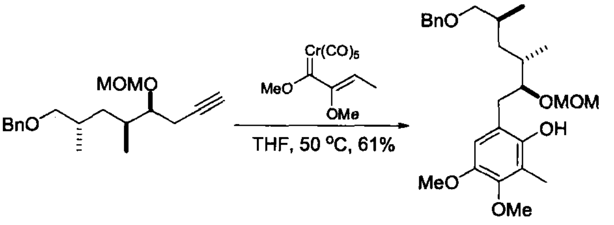


Example 3[8]

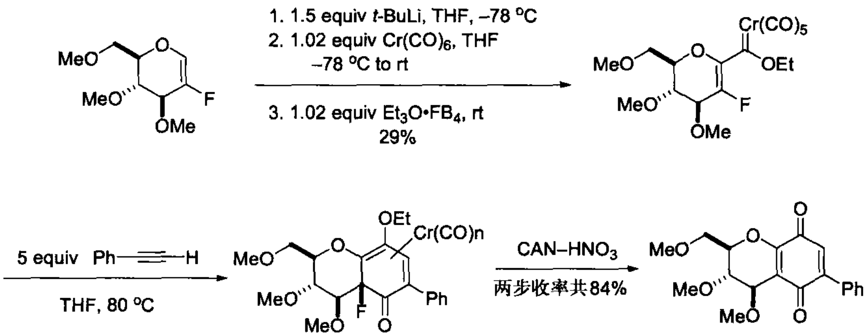


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_85,

Example 3[8]



Example 3[9]



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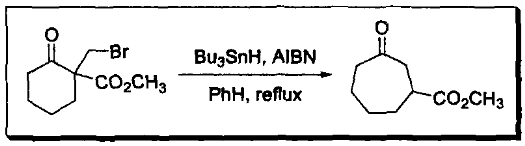
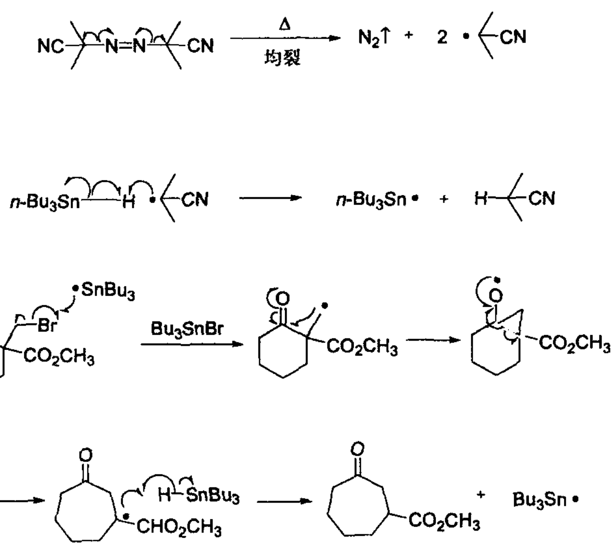
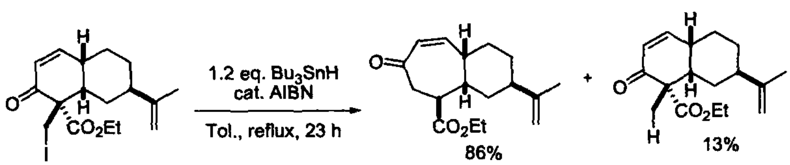
Dowd-Beckwith 扩环反应

2-卤甲基环烷酮经自由基过程的扩环反应。

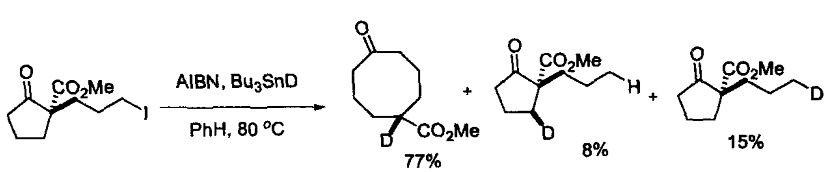




Example 1[4]



Example 2[9]



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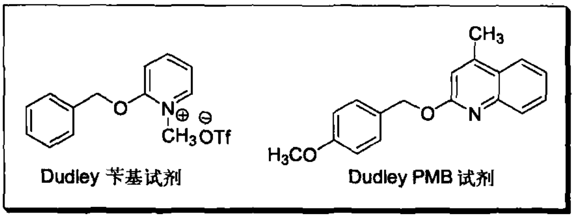
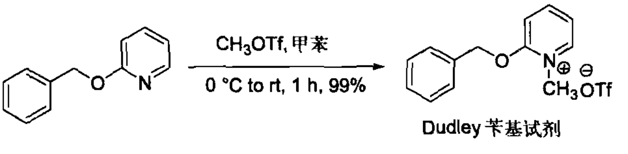
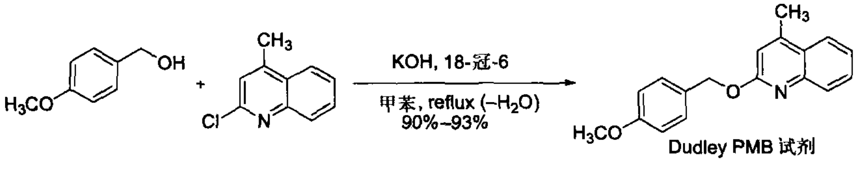
Dudley 试剂



Dudley试剂用于在温和的条件下保护醇为苄基醚[1]或PMB醚[2]。羧酸也很容易保护。[3]Dudley试剂经适当活化后即可将醇转化为所设计的苄基醚，苄基试剂的活化需加热到80~85℃，PMB试剂用三氟乙酸甲酯（CH_3OTf）或质子酸在室温就可活化。[4]芳香性溶剂（三氟甲苯最常用）常给出最佳结果。MgO作为一个酸清除剂是常见于反应混合物中的。[5]在羧酸苄基化时，Et_3N用来替代MgO。[3]

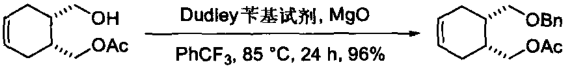
制备:[1-3]





Dudley试剂很易制备并在一般标准的实验室条件下就可保存和处理，而且也已有商业供应。

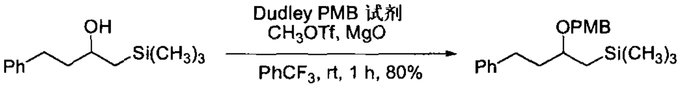
Example 1[6]



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

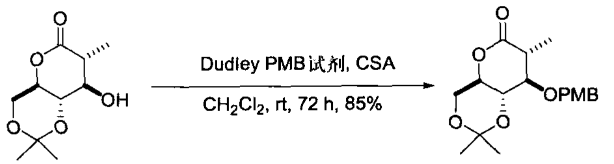
例1是单乙酰基化二醇的苄基化反应。[6] Dudley苄基化试剂对保护自由的醇有独特的优势且不会引起乙酰基的迁移和/或失去。

Example 2[2]



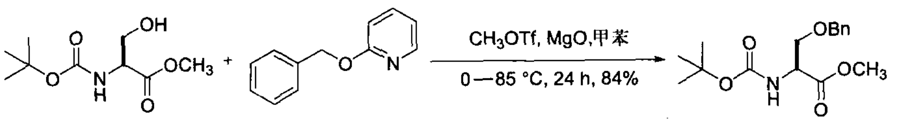
β-羟基硅烷进行PMB保护并不会引起在许多烷基化反应所需的酸性或碱性条件下会发生的Peterson消除反应（例2）。[2]

Example 3[4]



Dudley PMB试剂也可以在温和的酸性条件下来活化，只要使用催化量的樟脑磺酸即可替代三氟乙酸甲酯（例3）。[4]

例4，醇和2-苄氧吡啶所得混合物用三氟乙酸甲酯处理即可就地产生Dudley苄基化试剂。[7]



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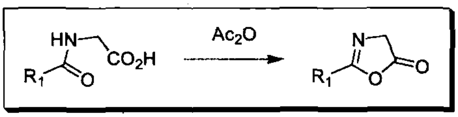
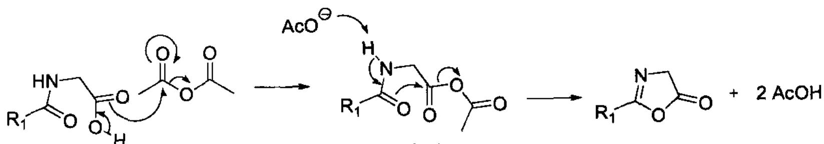
Erlenmeyer-Plochl 噁唑酮合成反应

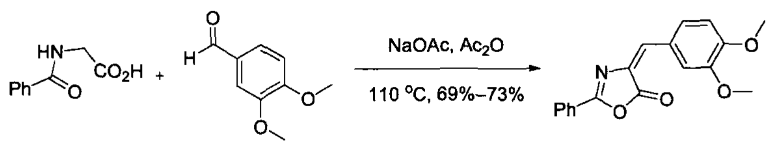
5-噁唑酮（或二氢唑酮）可以由酰胺基乙酸在乙酐存在下通过分子内缩和来得到。



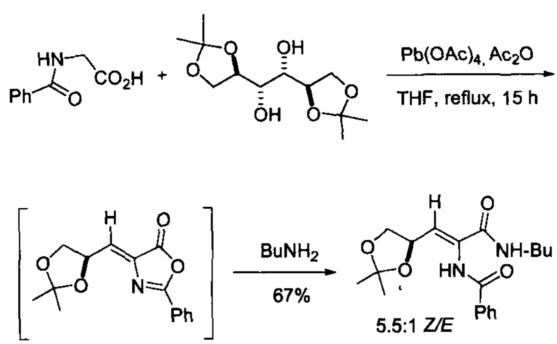


混酐

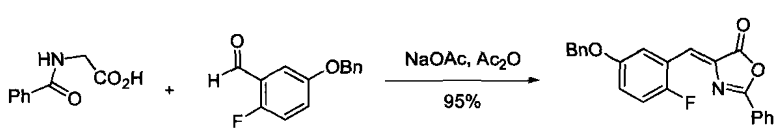
Example 1[2]



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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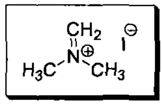
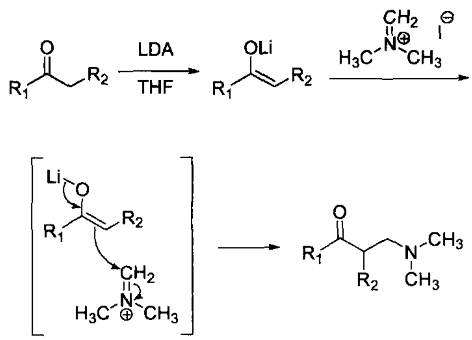
Eschenmoser 盐



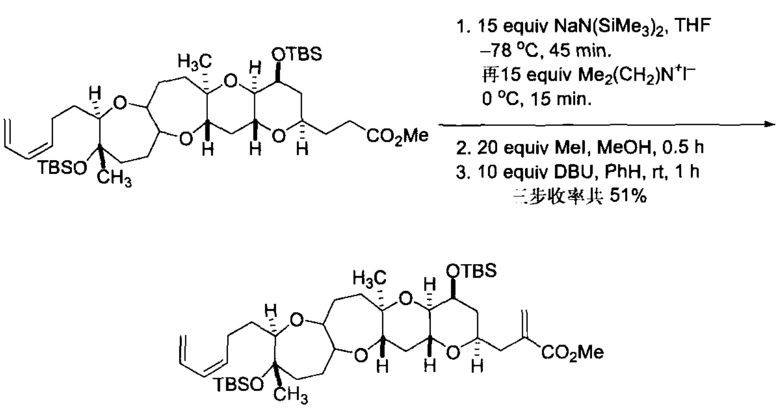
Eschenmoser 盐，二甲基亚甲基碘化铵是一个很强的二甲氨基甲基化试剂，用于制备$RCH_2N(CH_3)_2$一类化合物。烯醇化物、烯醇硅醚及更酸性的酮都可有效地进行二甲氨基甲基化用于Mannich反应。

机理



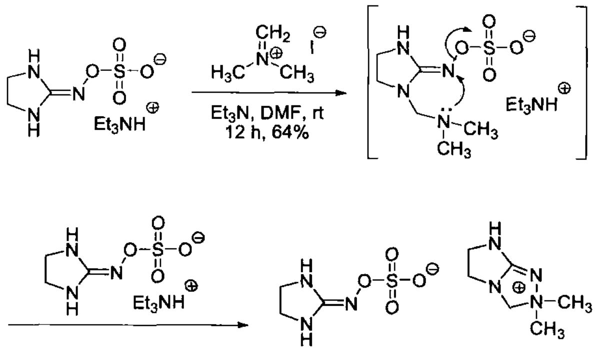
Example 1[3]

一旦制备后，得到的叔胺可进一步甲基化，随后在碱诱导下消除给出甲基化酮。

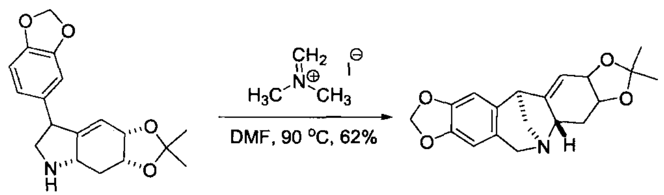


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_89,

Example 2[4]



Example 3[5]



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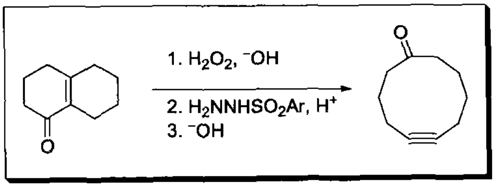
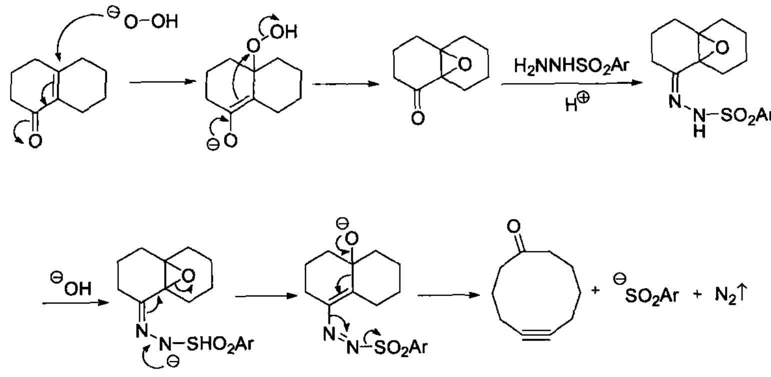
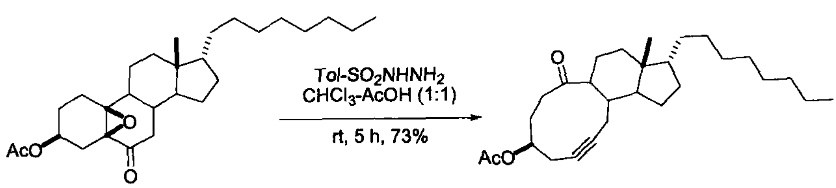
Eschenmoser-Tanabe 碎片化反应

α，β-环氧酮经 α，β-环氧砜基磺酰腙中间体而进行的碎片化反应。

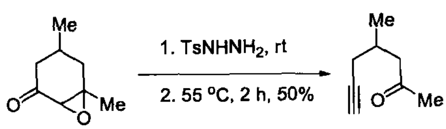




Example 1[4]



Example 2[7]



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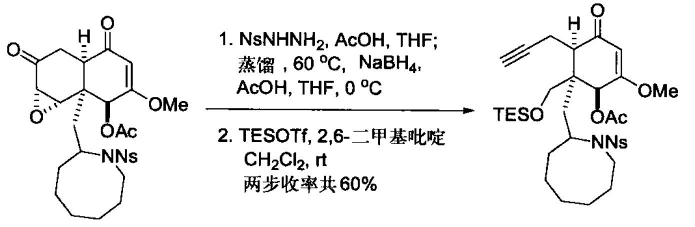
Example 3[9]



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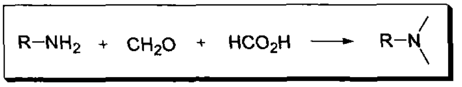
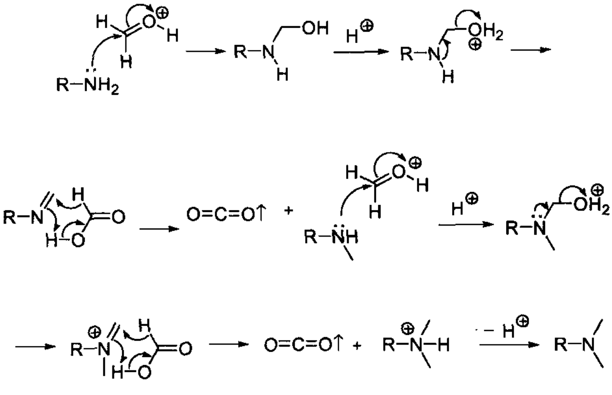
Eschweiler-Clarke 胺还原烷基化反应

伯胺或仲胺用甲醛和甲酸发生还原甲基化反应。

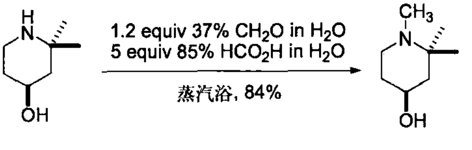


还原剂甲酸是负氢的来源



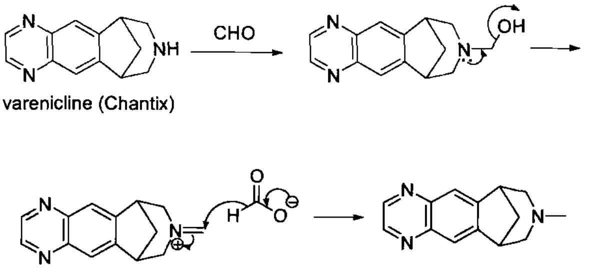
Example 1[7]

Example 2[9]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_91,

Example 3[10]



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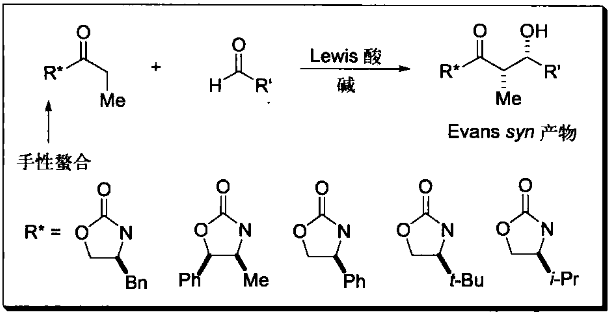
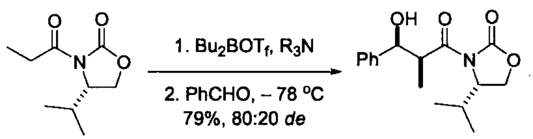
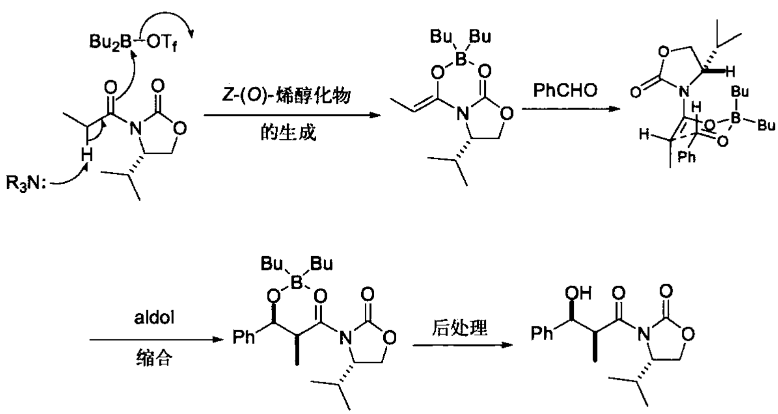
Evans aldol 反应

醛和被称为Evans手性螯合剂的手性酰基噁唑酮发生不对称aldol反应。



Example 1[2]





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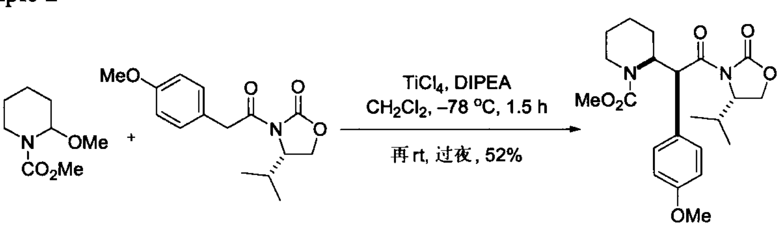
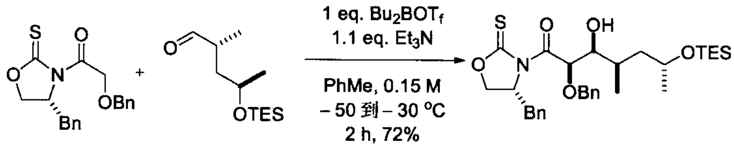
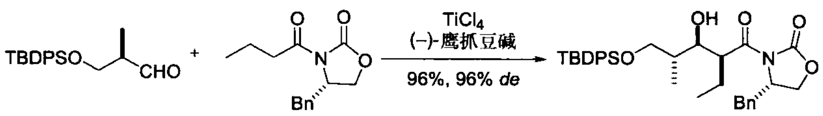


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_92,

Example 3[9]



Example 4, Crimmins 程序[10]



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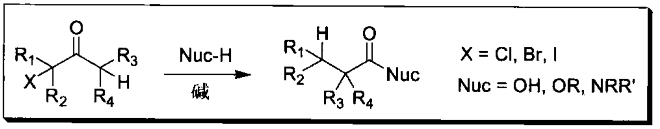
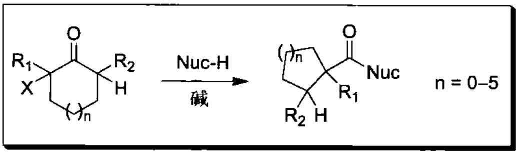
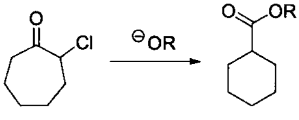
Favorskii 重排反应

可烯醇化的 α - 卤代酮经烷氧基、羟基或胺催化分别转化为酯、酸或酰胺。

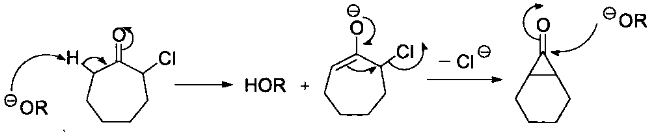


分子内Favorskii 重排:

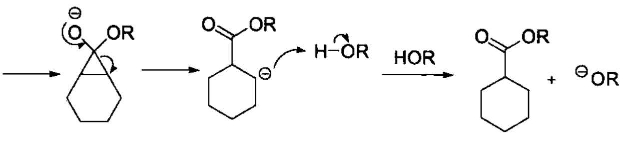




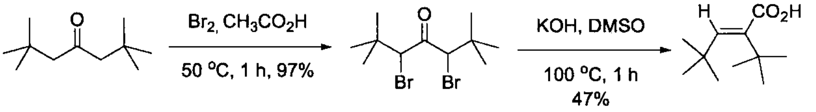
烯醇化α-卤代酮



环丙酮中间体



Example 1[2]



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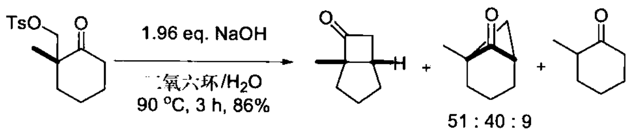
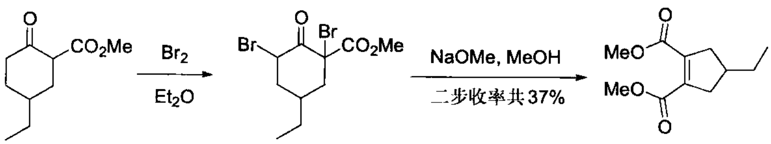
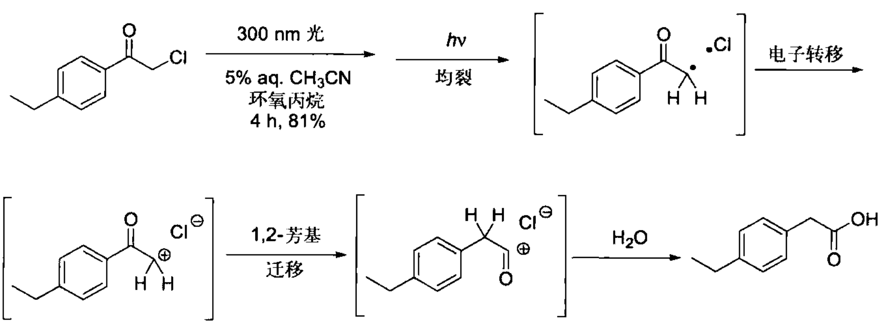
Example 2, 同Favorskii 重排[3]



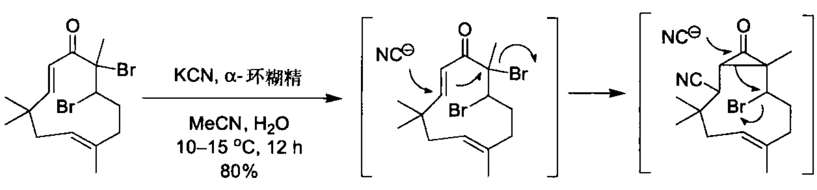
Example 3[6]

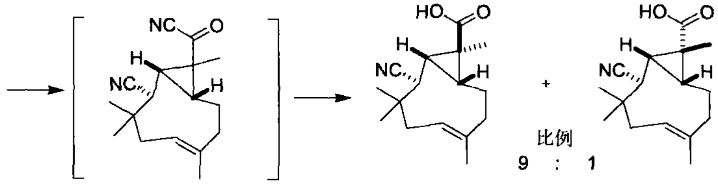


Example 4, 光促-Favorskii 重排[7]

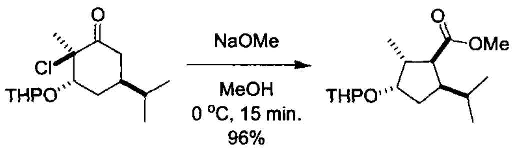


Example 5[8]





Example 6[10]



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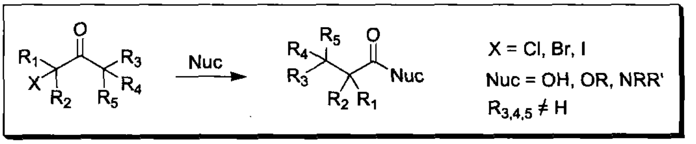
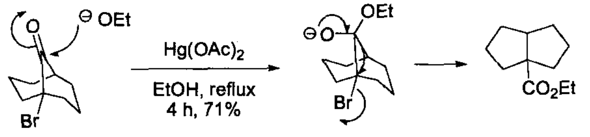
似Favorskii重排反应

若没有可烯醇化的氢存在，经典的Favorskii重排反应就不能发生。取而代之的是发生一个半苯偶酰过程导致重排，可认为是似Favorskii重排反应。

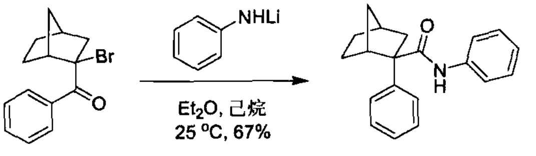


Example 1, Arthur C. Cope最初的发现[1]

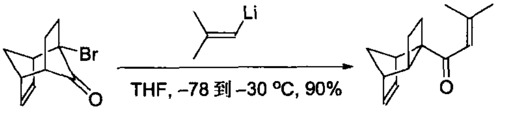


无烯醇化的酮

Example 2[5]



Example 3[6]



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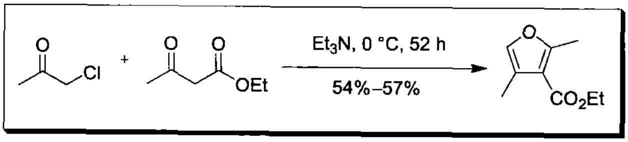
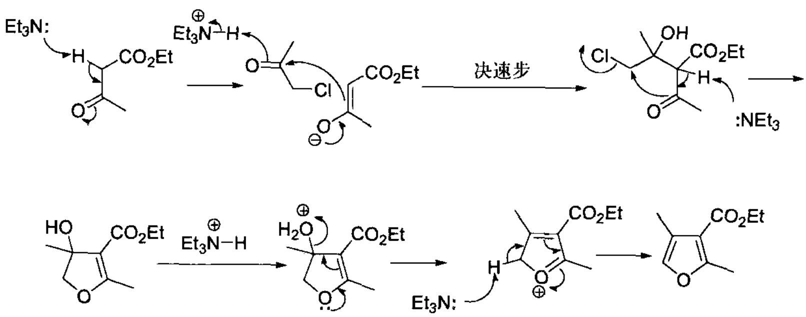
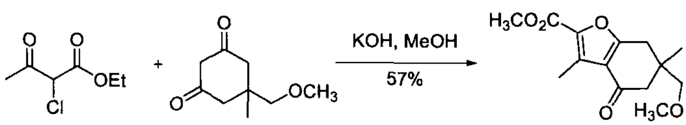
Feist-Benary 呋喃合成反应

α-卤代酮和 β-酮酯在碱存在下生成呋喃。

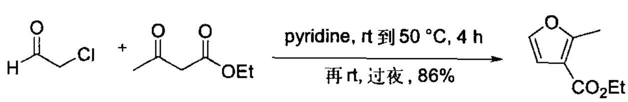




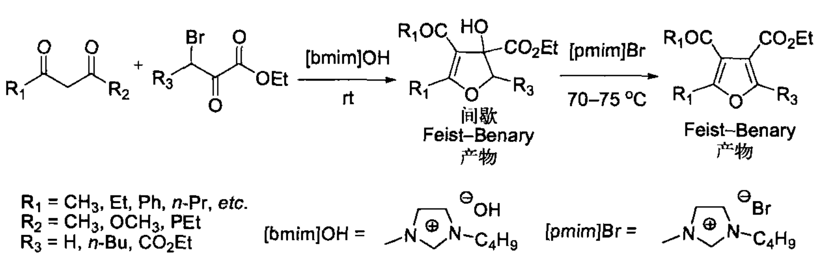
Example 1[2,3]



Example 2[4]



Example 3, 离子液体促进的间歇Feist–Benary 反应[10]



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

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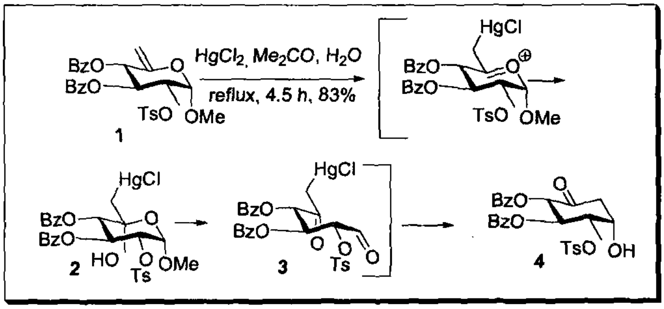
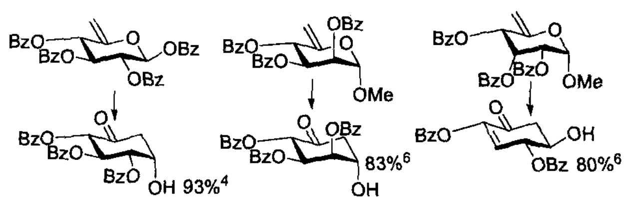
Ferrier 碳环化反应

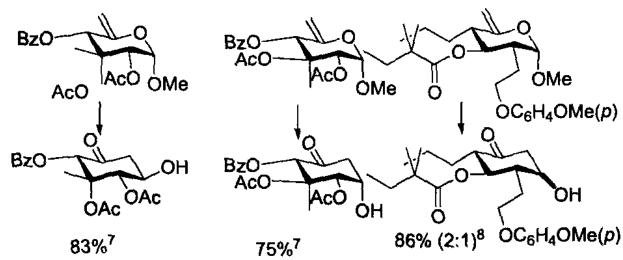
该反应亦称“Ferrier Ⅱ反应”，已证明可一步有效地将5,6-不饱和吡喃糖衍生物转化为官能团化的环己酮，这对于制备那些如肌醇一类对映纯的化合物及它们的氨基的、去氧的、不饱和的和选择性*O*-取代的衍生物，特别是磷酸酯是非常有价值的。此外，这类碳环化产物已被结合进许多有生物和药学意义的复杂化合物。[1,2]

通例:[3]

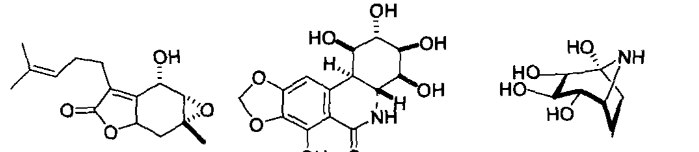




更复杂的产物:



反应可应用于下列各复杂的生理活性化合物:



Paniculide A[9] Pancratistatin[10] Calystegine B_2[11]

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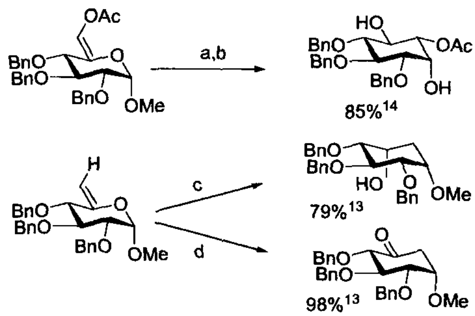
修正的己-5-烯酮吡喃糖苷及反应



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.（注：糖苷配基在 Al-和Ti-诱导的反应中得以保留）

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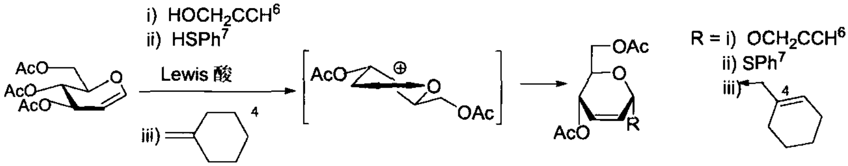
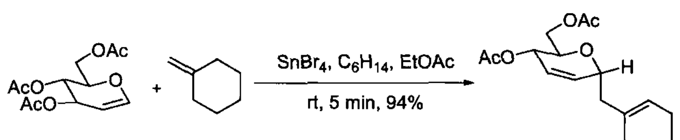
Ferrier 烯糖烯丙基重排反应

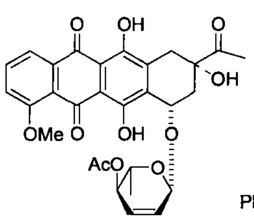
在Lewis酸存在下，*O*-取代的烯糖衍生物可与*O*-、*S*-、*C*-或较少见到的*N*-、*P*-和卤化物等亲核物种反应给出2,3-不饱和糖基产物。[1,2]这个烯丙基转移已被称为Ferrier反应，或为避免混乱而称"Ferrier Ⅰ反应"或"Ferrier重排反应"。但该反应实际上是费歇尔在水相中加热三*O*-乙酰基-D-己烯糖时所发现的。[3]当反应涉及碳亲核物种时已俗称"碳Ferrier反应"，[4]尽管Ferrier小组在这个领域只是发现了三*O*-乙酰基-D-己烯糖在酸催化下二聚给出*C*-配糖产物的反应。[5]通用的反应可以用*O*-乙酰基-D-己烯糖分别与*O*-、*S*-、*C*-亲核物种反应给出相应的2,3-不饱和糖基产物来表示。Lewis酸通常被用作催化剂，BF_3是最常用的。中间体产物是烯丙氧基碳负离子，配糖产物的产率很高且以假a-键为主（通常，α，β-之比为7:1）。给出的实例[4,6,7]是大量文献报道[1]中的典型。



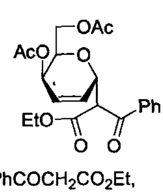
通例[4]



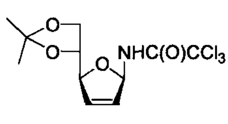
更复杂的产物可直接从相应的乙二醇制得：



苯，BF_3•OEt_2,
5 °C, 10 min, (67%, α-异头物).[8]



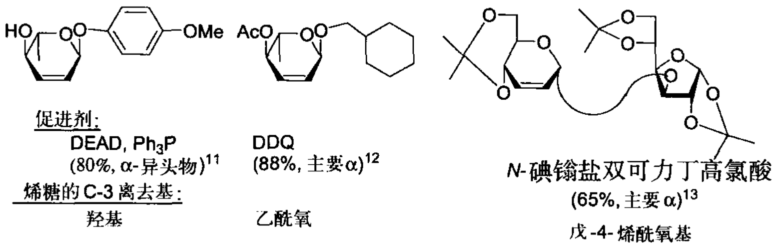
$PhCOCH_2CO_2Et$,
BF_3.OEt_2,
rt, 15 min,
(81% α-异头物).[9]



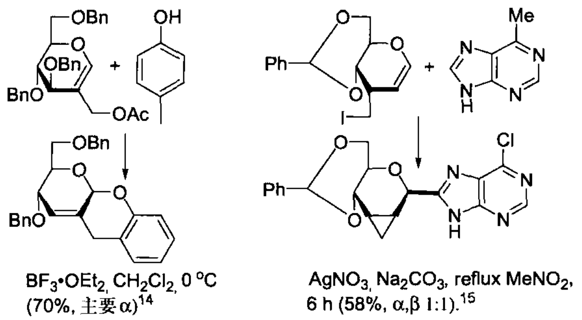
经自发的3-三氯乙酰亚氨烯糖用NaH, Cl_3CCN进行的σ重排。
(78% α-异头物).[10]

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

无酸催化剂下生成的产物：



修正的烯糖及它们的反应：



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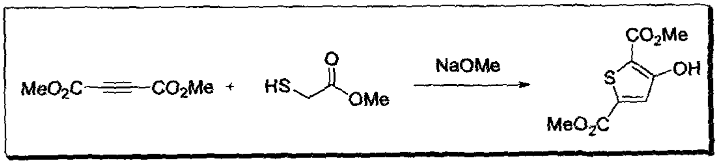
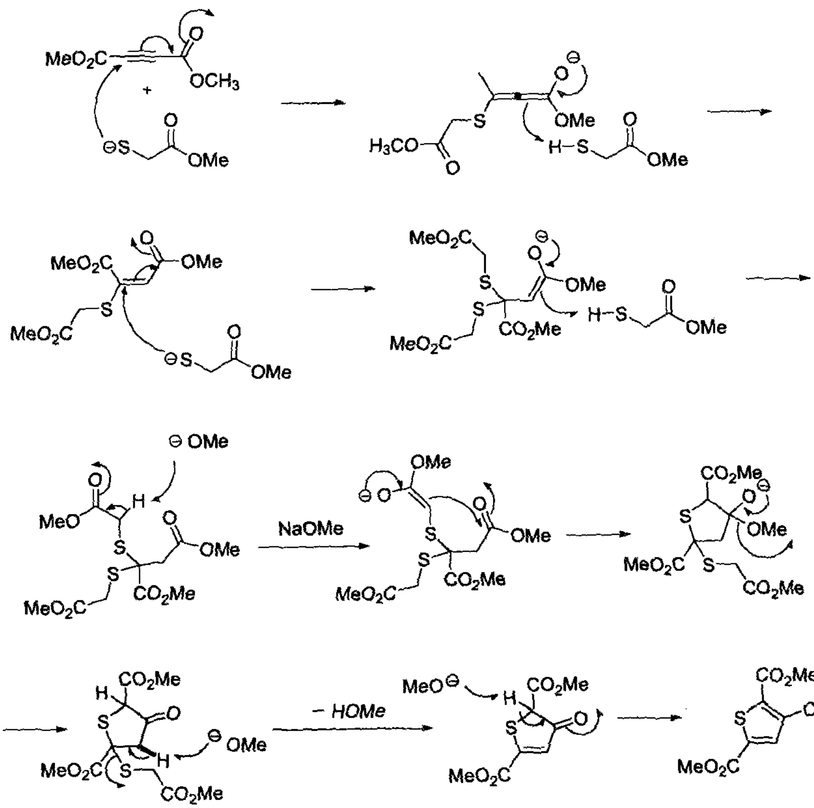
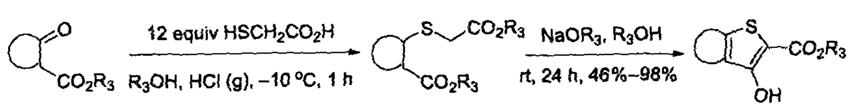
Fiesselman 噻吩合成反应

巯基乙酸衍生物和 α,β-丙炔酸酯用碱处理发生缩合反应生成3-羟基-2-噻吩甲酸的衍生物。





Example 1[5]



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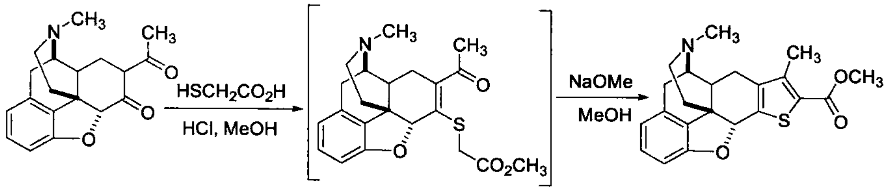
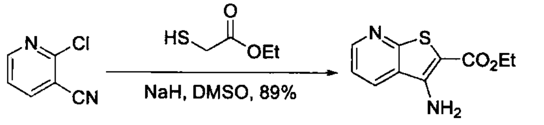
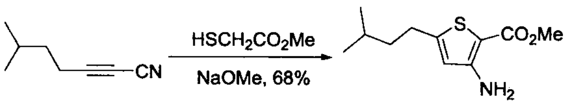
Example 2[6]



Example 3[7]



Example 4[9]



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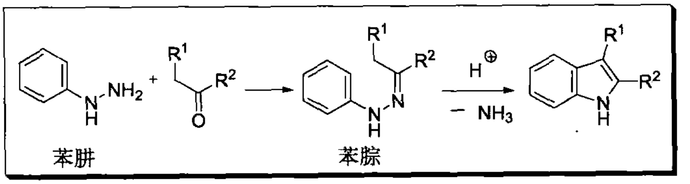
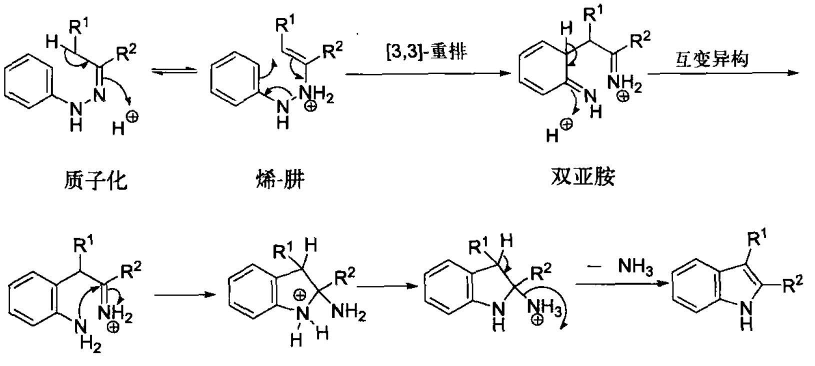
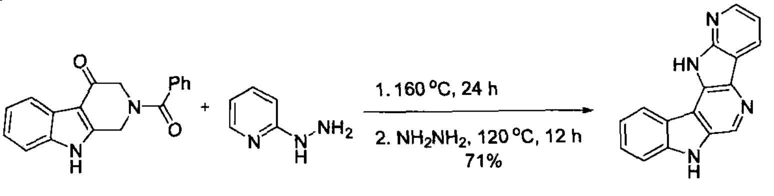
Fischer 吲哚合成反应

芳基腙环合生成吲哚。

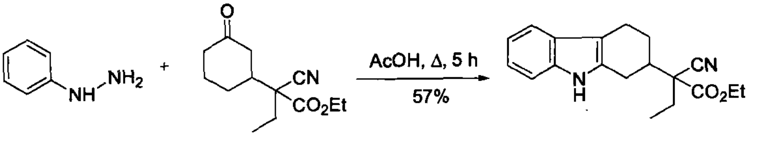




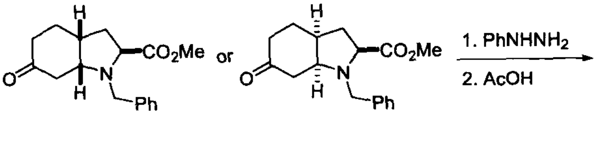
Example 1[3]



Example 2[13]



Example 4 (严重外消旋化)[9]



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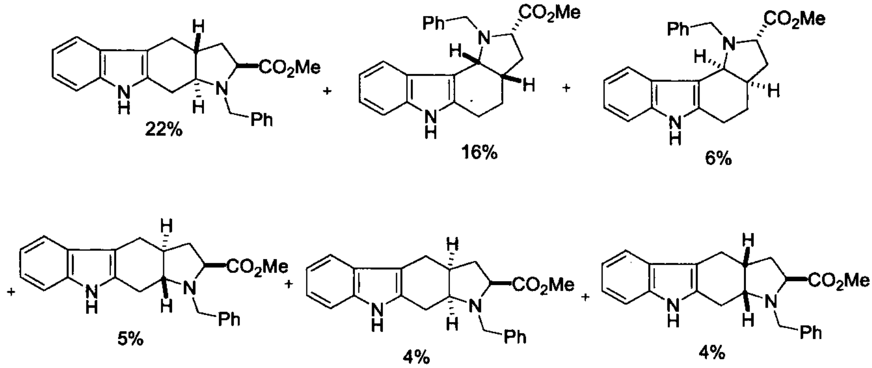

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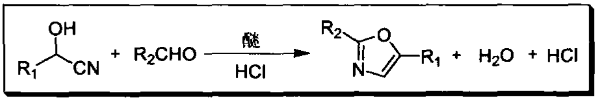
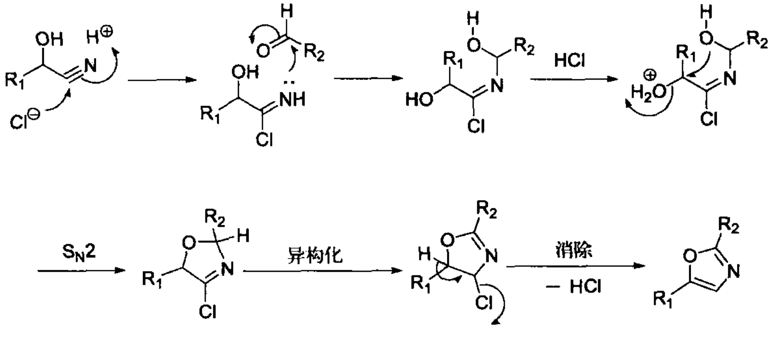
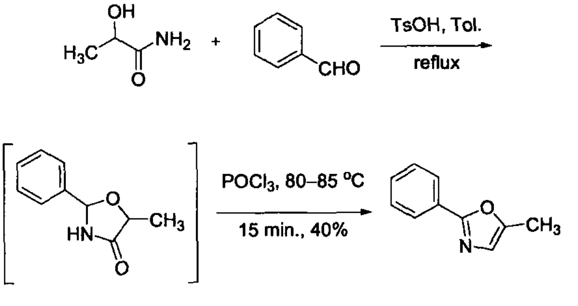
Fischer 噁唑合成反应

等量的由醛得来的羟氰化物和芳香醛在无水醚溶液中于干燥HCl存在下缩合成噁唑。

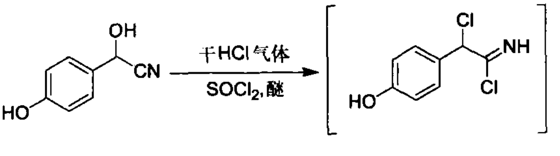




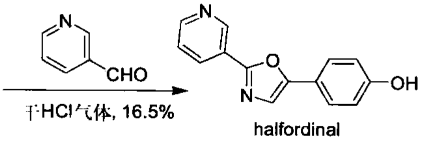
Example 1[4]



Example 2[8]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_99,



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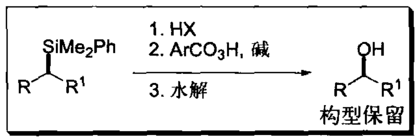
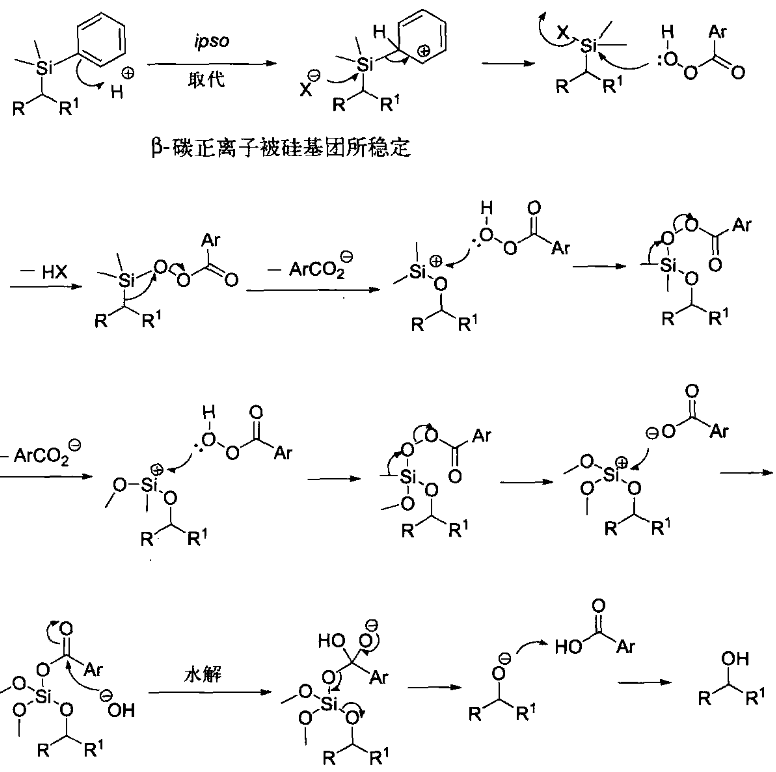
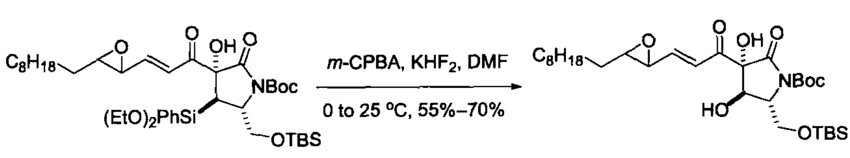
Fleming-Kumada 氧化反应

烷基硅烷用过氧酸被立体选择性地氧化为相应的烷基醇。



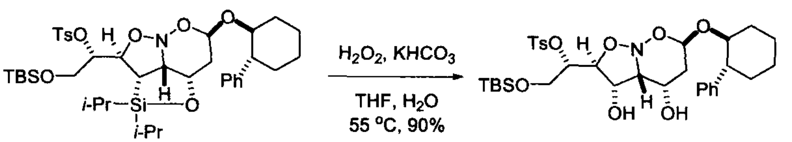


Example 1[4]

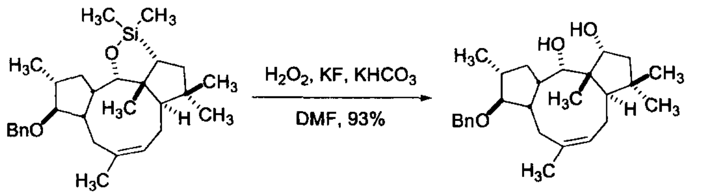


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_100,

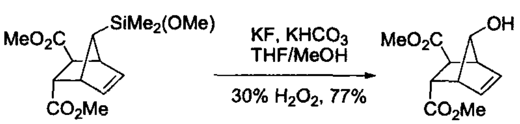
Example 2[5]



Example 3[8]



Example 4[9]



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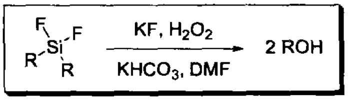
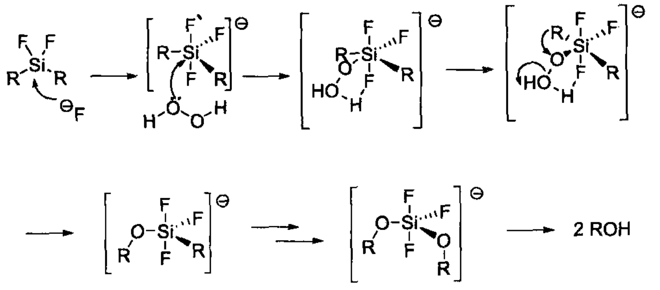
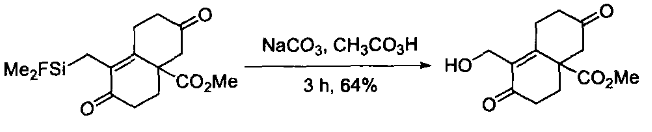
Tamao-Kumada 氧化反应

烷基氟硅烷被氧化为相应的烷基醇。是Fleming-Kumada氧化反应的变异。

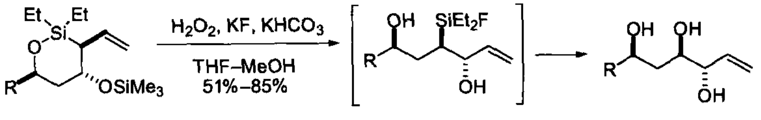




Example 1[3]



Example 2[4]



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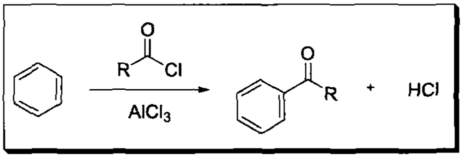
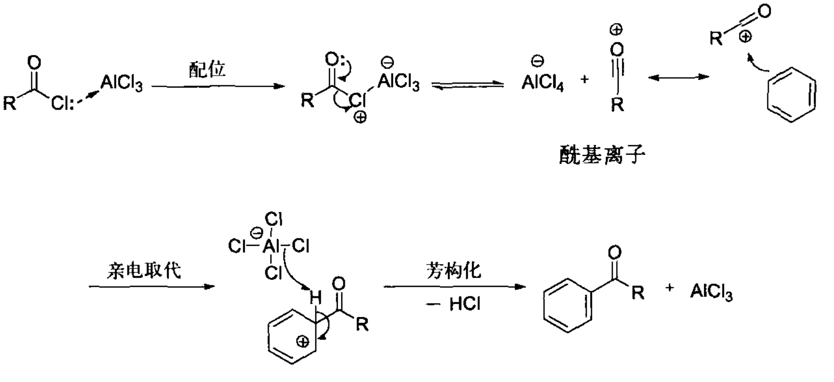
Friedel-Crafts 反应

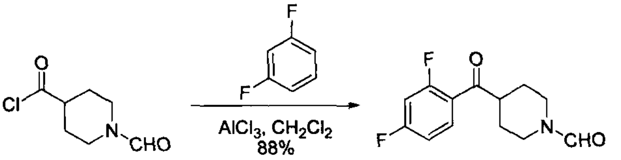
Friedel-Crafts 酰基化反应

在Lewis酸存在下芳香族底物与酰氯或酸酐反应生成酰基化芳香族产物。

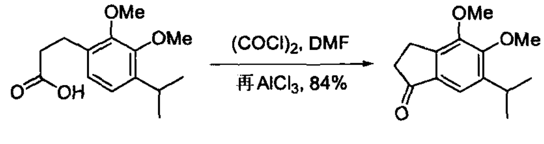




Example 1, 分子间Friedel–Crafts酰基化[6]

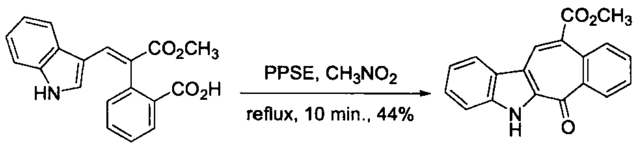


Example 2, 分子内Friedel–Crafts酰基化[7]



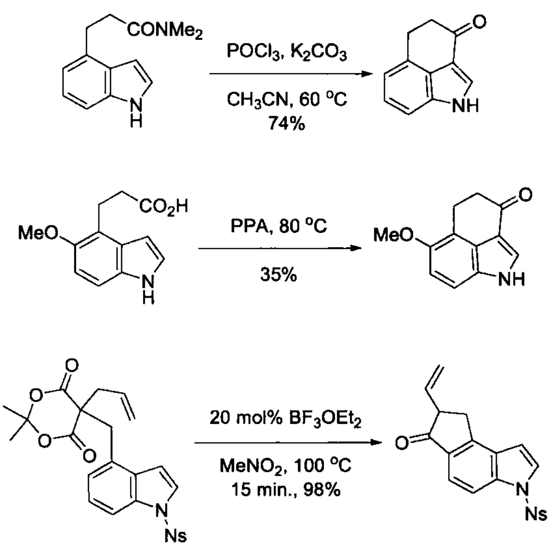
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_101,

Example 3, 分子内Friedel–Crafts 酰基化[8]



PPSE =三甲硅基聚磷酸酯

Example 4, 分子内Friedel–Crafts 酰基化[9]



References

1. Friedel, C.; Crafts, J. M. *Compt. Rend.* **1877**, *84*, 1392–1395.傅瑞德尔(Charles Friedel, 1832-1899)出生于法国的斯特拉斯堡并获得Ph.D学位。1869年，他在Sobonne跟武慈学习，随后成为有机化学教授并于1884年任主席。他也是法国化学会的发起者，担任过4届主席。克拉夫茨(James Mason Crafts, 1839-1917)出生于麻省的波士顿，年轻时跟本生和武慈学习，随后成为康奈尔大学和MIT的有机化学教授。从1874年到1891年，他在巴黎的Ecole de Mines和傅瑞德尔合作并一起发现了Friedel-Crafts反应。克拉夫兹于1892年回到MIT并在后来担任校长一职。Friedel-Crafts反应是机遇和明锐观测力的结果。1877年，他们都在武慈实验室工作，为了制备戊基碘，他们将戊基氯、铝和碘以苯为溶剂进行处理。结果并未生成戊基碘，却得到了戊基苯！不像简单地将反应倾倒了事的前人，他们仔细探究了该反应。发表了50多篇有关Lewis酸催化的烷基化和酰基化反应的论文及专利。 Friedel-Crafts反应也成为最有用的有机合成反应之一。

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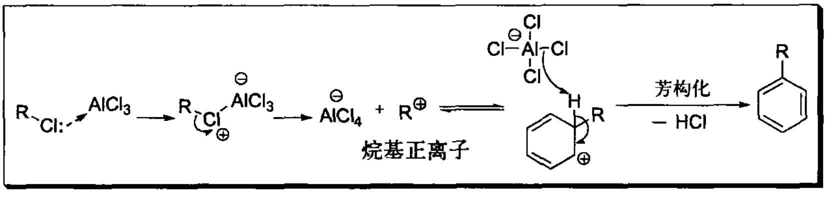
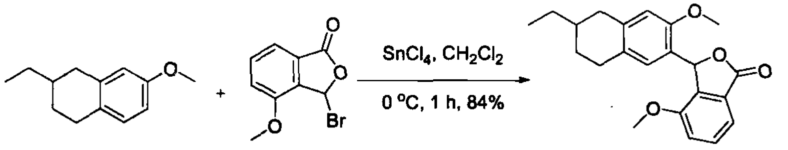
Friedel-Crafts 烷基化反应

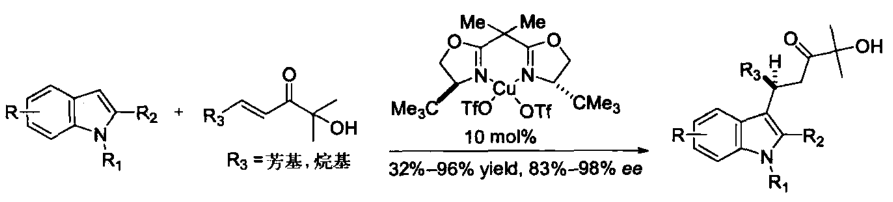
在Lewis酸存在下芳香族底物与烷基卤、烯烃、炔烃和醇等烷基化试剂反应生成烷基化芳香族产物。

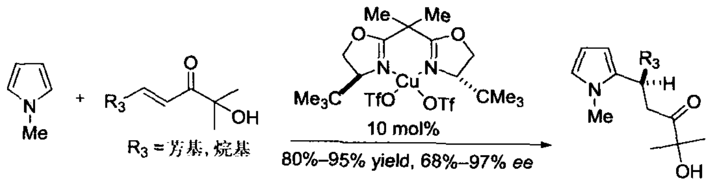


Example 1[1]

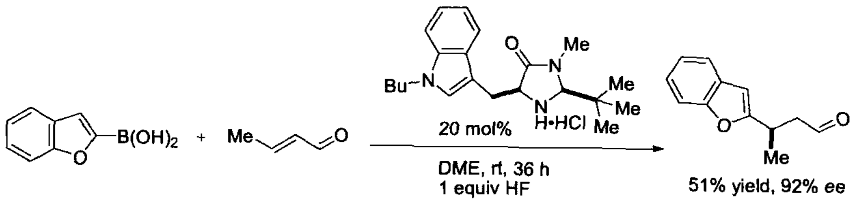


Example 2[4]





Example 3[5]



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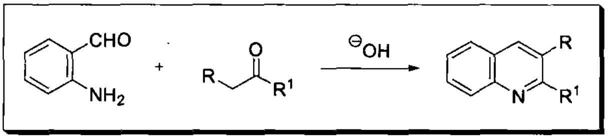
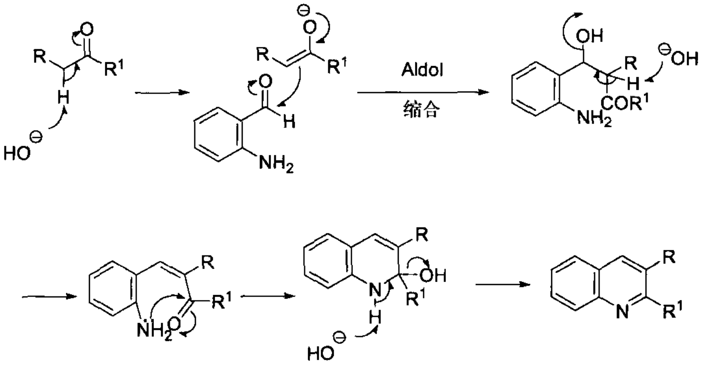
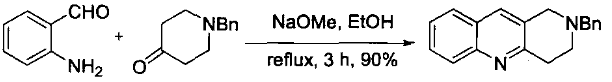
Friedlander 喹啉合成反应

α-氨基醛或 α-氨基酮和另一个醛或酮与至少一个羰基的 α-亚甲基缩合生成一个取代的喹啉。反应可被酸、碱或热促进。

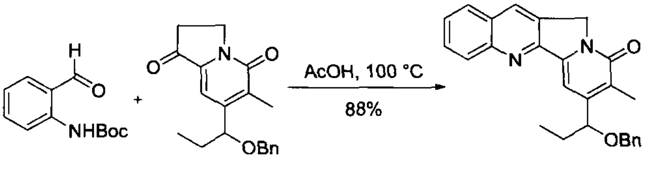




Example 1[5]

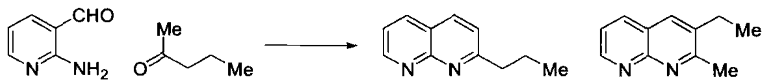


Example 2[7]



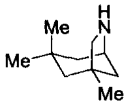
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_102,

Example 3[8]

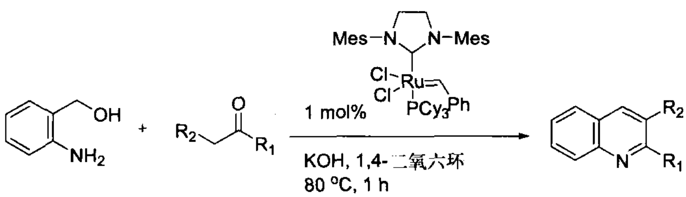


反应条件	转化率	比例
NaOH, rt	> 99%	37:63
四氢吡啶, 5% H_2SO_4, rt	97%	86:14
TBAO, 5% H_2SO_4, rt	> 99%	87:13
TBAO, 5% H_2SO_4, 慢慢加入, 65 °C	> 99%	94:6

TBAO =



Example 4[10]



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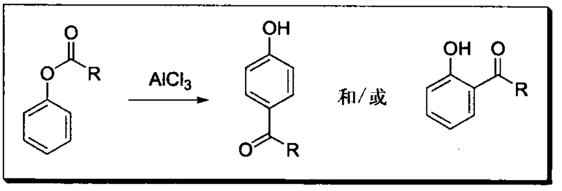
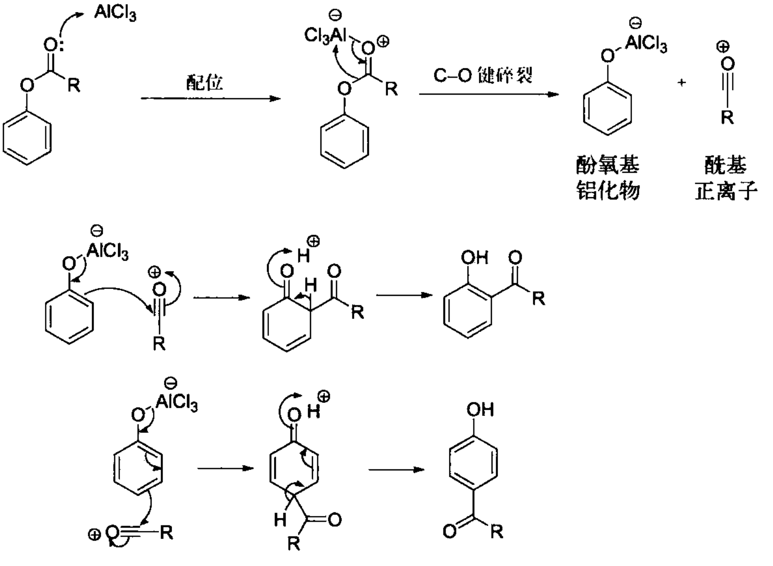
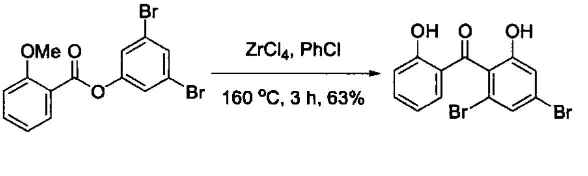
Fries 重排反应

Lewis酸催化的酚酯和内酰胺重排为2-或4-羰基酚的反应，亦称Fries-Finck重排反应。



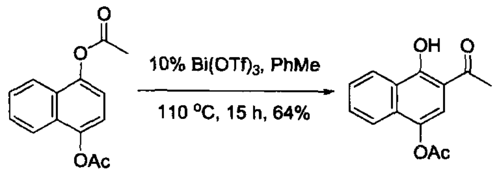


Example 1[5]

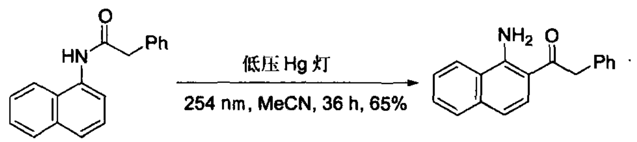


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_103,

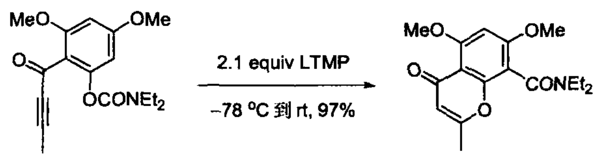
Example 2[6]



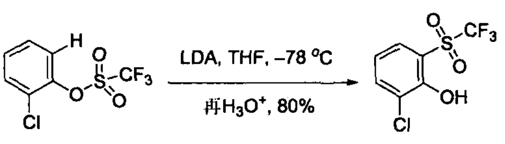
Example 3, 光促 Fries 重排[7]



Example 4, *ortho*-Fries 重排[8]



Example 5, 硫杂的-Fries重排[9]



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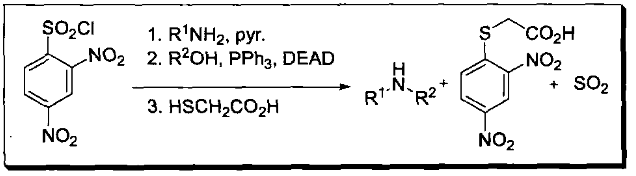
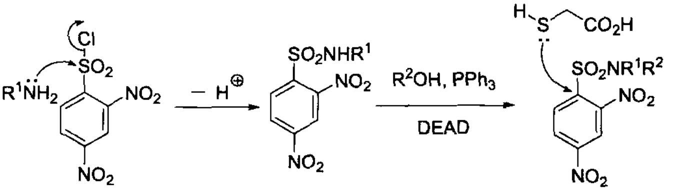
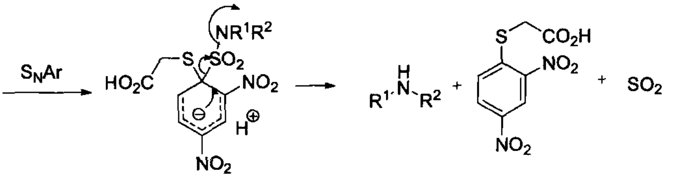
Fukuyama 胺合成反应

用2,4-二硝基苯磺酰氯和醇将伯胺转化为仲醇的反应，亦称Fukuyama-Mitsunobu 程序。



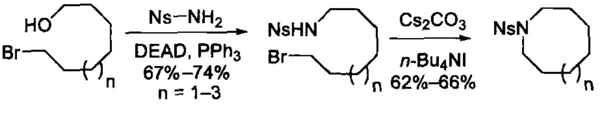


参见第365页上的Mitsunobu 反应机理。

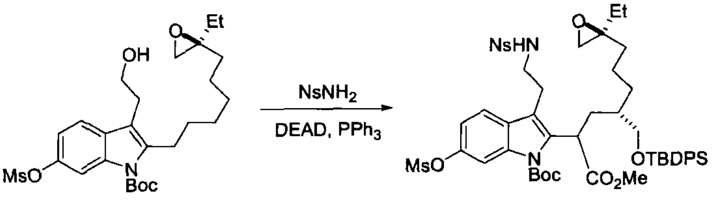


Meisenheimer 配合物

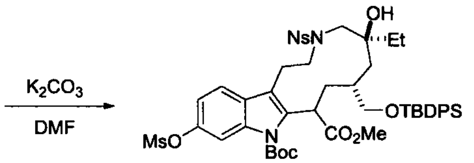
Example 1[6]



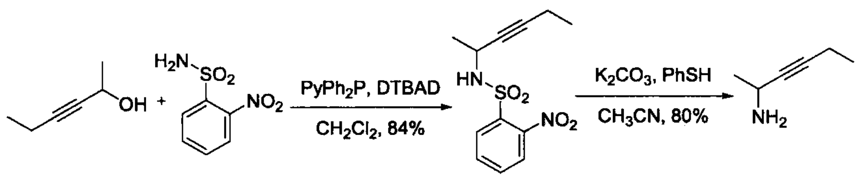
Example 2[7]



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



Example 3[8]



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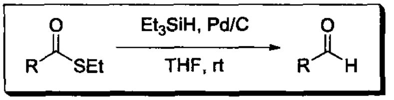
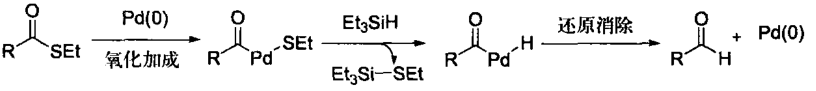
Fukuyama 还原反应

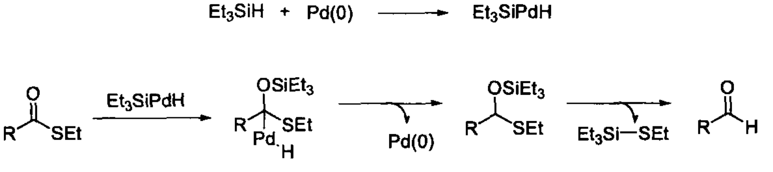
硫酯用Et_3SiH在Pd/C催化剂存在下被还原为醛。



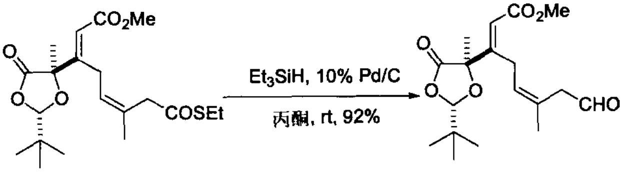
途径A:



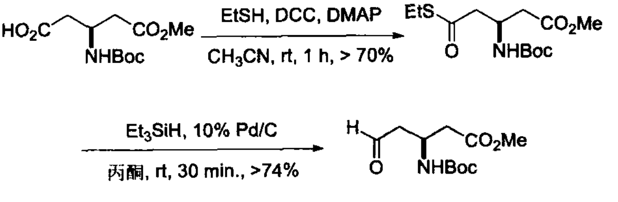
途径B:



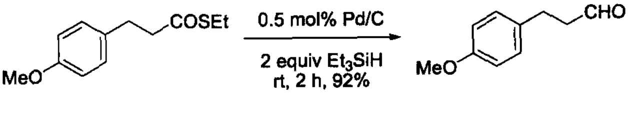
Example 1[1]



Example 2[3]



Example 3[8]



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

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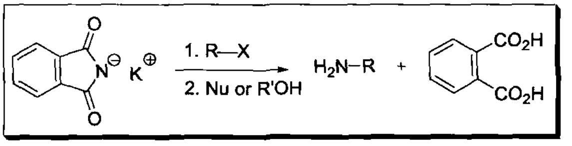
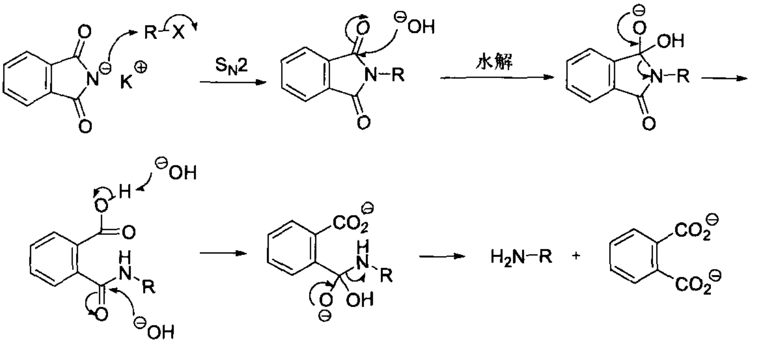
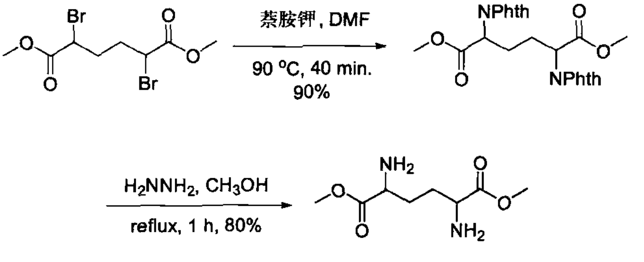
Gabriel 反应

邻苯二甲酰亚胺的钾盐和烷基卤反应制备伯胺。

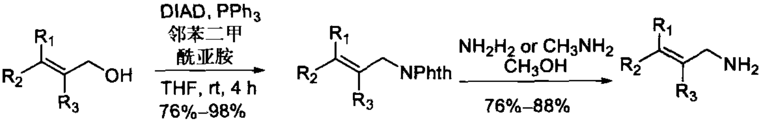




Example 1[2]

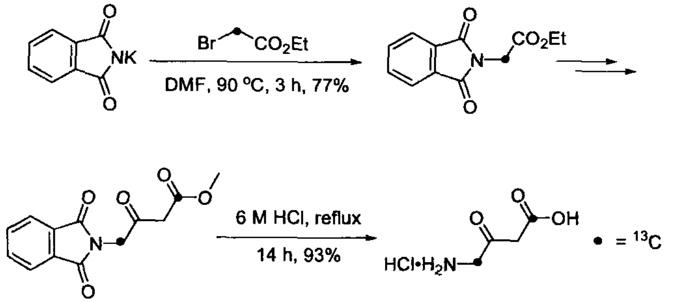


Example 2[6]

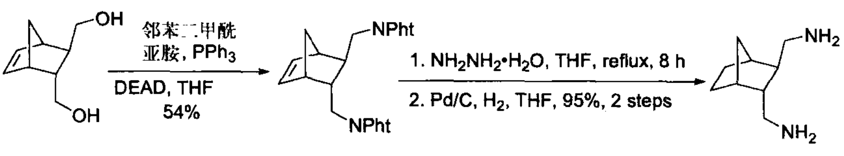


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_106,

Example 3[8]



Example 4[9]



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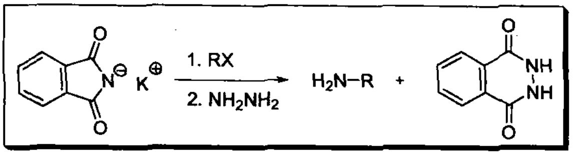
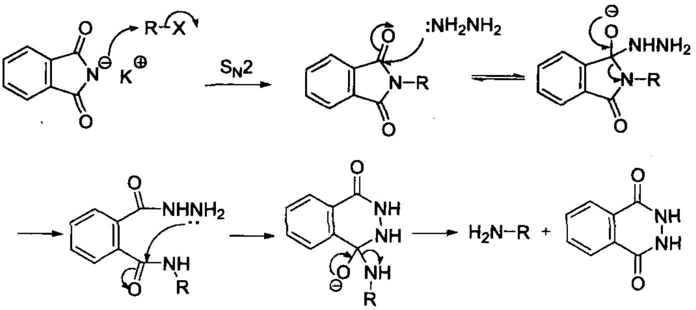
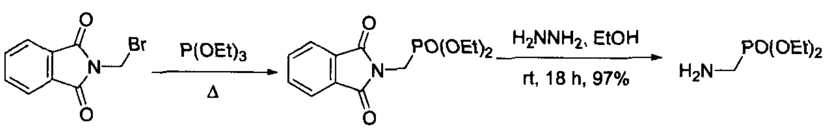
Ing-Monske 程序

Gabriel反应的一个变异。肼与相应的邻苯二甲酰亚胺化物反应后给出伯胺。





Example 1[6]



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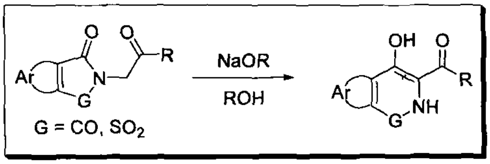
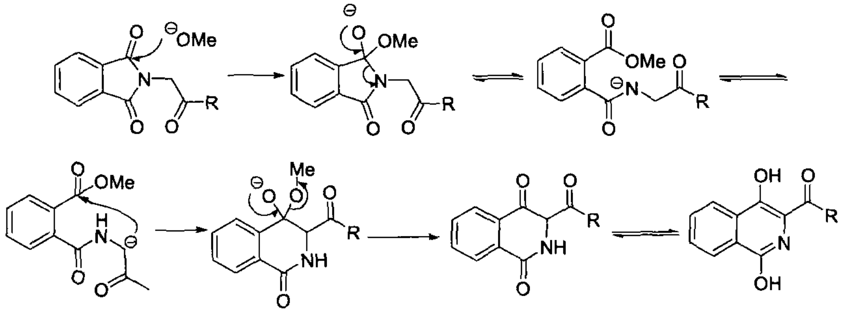
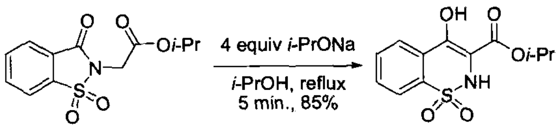
Gabriel-Colman 重排反应

N-酰基马来酰亚胺的烯醇盐反应给出 1,4-异喹啉二醇。

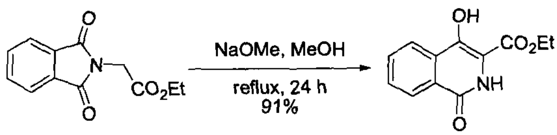




Example 1[6]



Example 2[9]



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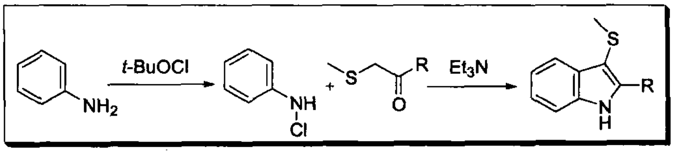
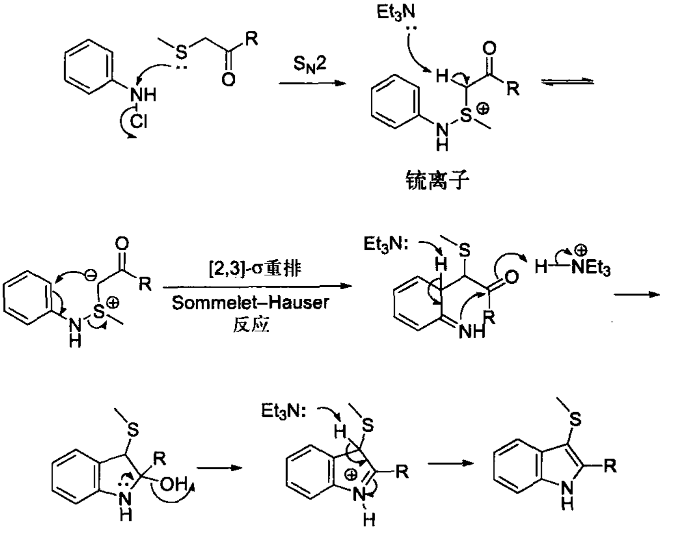
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_107,

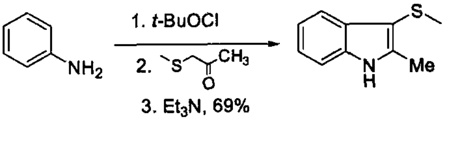
Gassman 吲哚合成反应

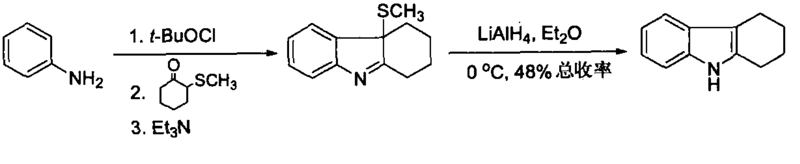
次氯酸盐、β-羰基硫醚衍生物和碱先后加到苯胺或取代的苯胺中去，一锅煮反应给出 3-硫烷基吲哚。硫很易由 Raney Ni 或氢解除去。





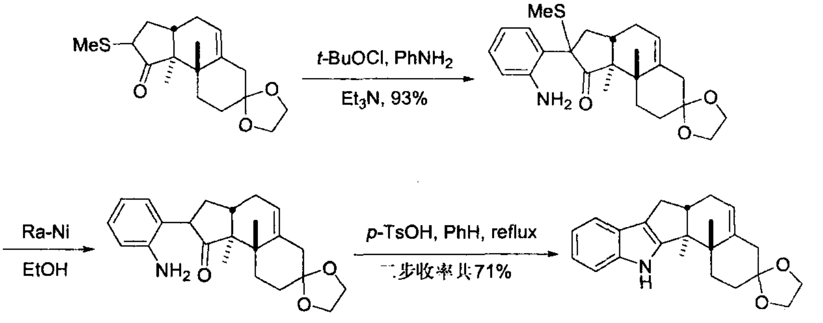
Example 1[1]





J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_108,

Example 2[2]



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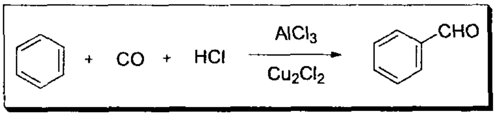
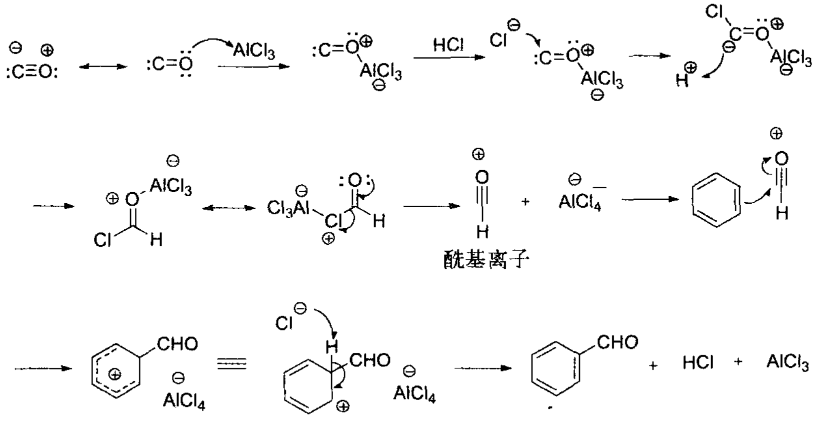
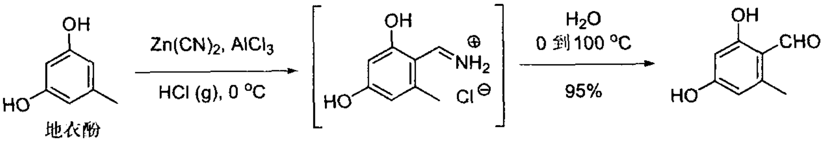
Gatermann-Koch 反应

芳烃用CO和HCl在$AlCl_3$存在下高压反应发生甲酰化。





Example, 更实用的变异[4]



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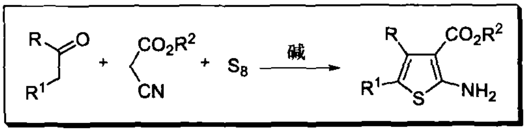
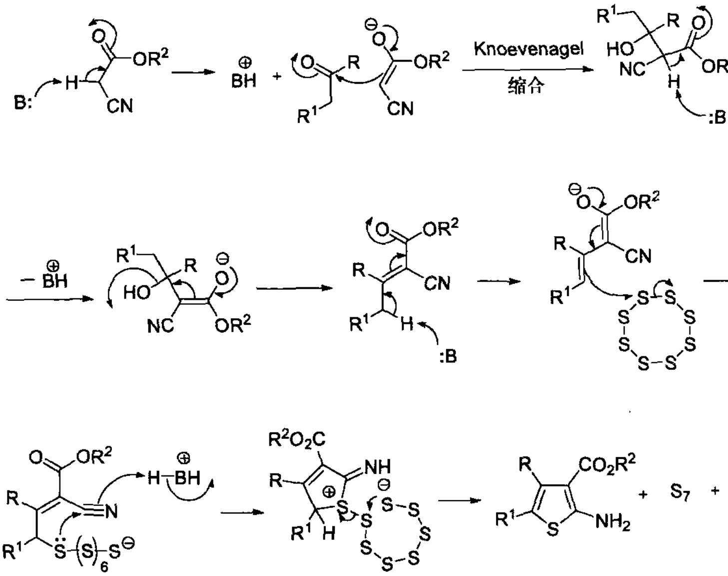
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_109,

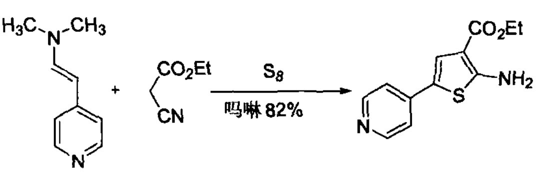
Gewald 氨基噻吩合成

酮、腈的 α -活泼亚甲基和硫在碱性促进下生成氨基噻吩的反应。

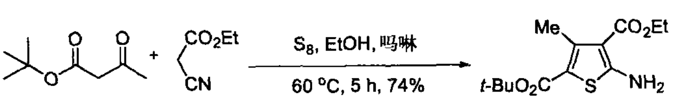




Example 1[4]

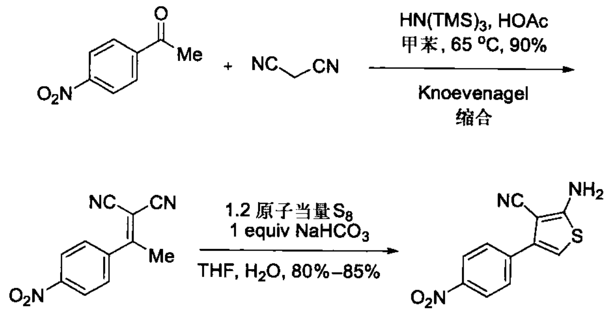


Example 2[7]

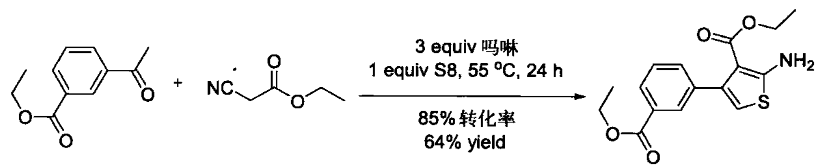


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_110,

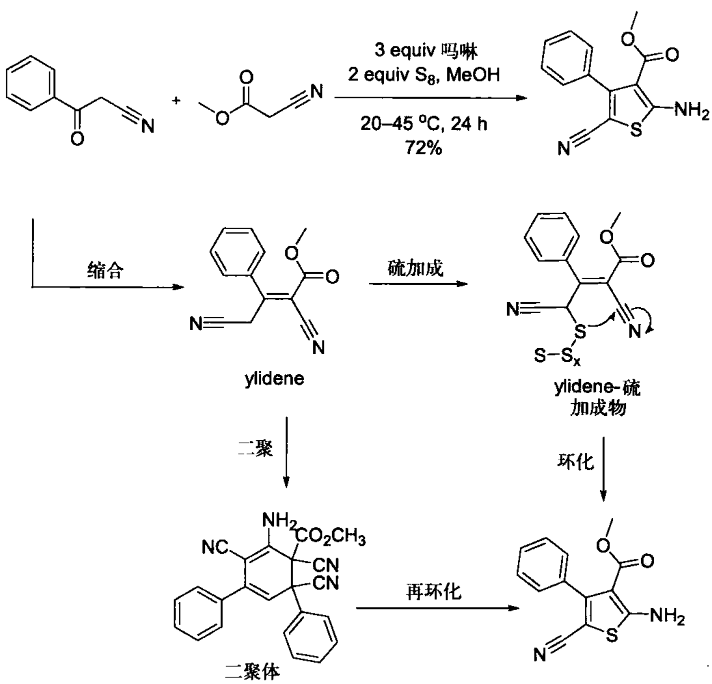
Example 3[9]



Example 4[10]



Example 5[11]



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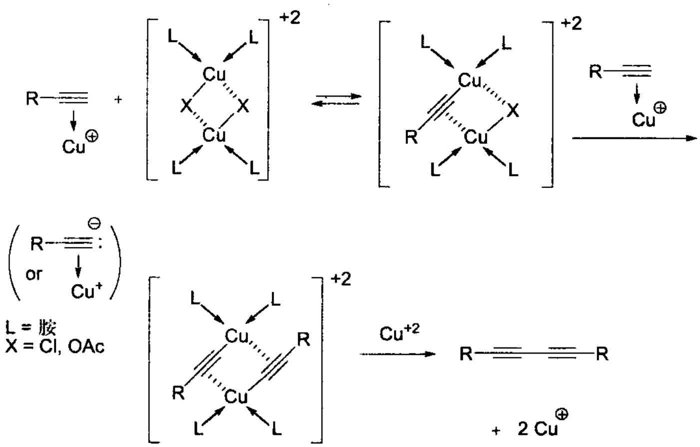
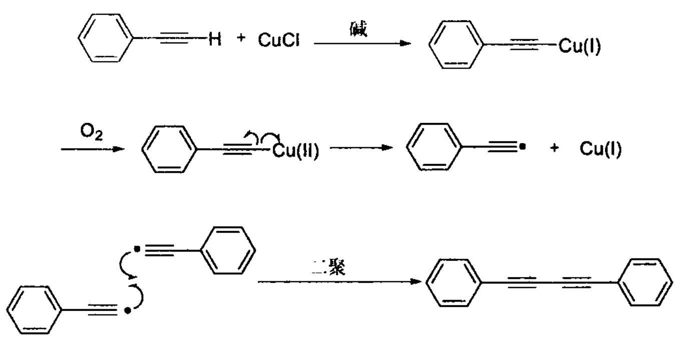
Glaser 偶联反应

端基炔烃在氧气氛中由铜催化发生氧化偶联反应。

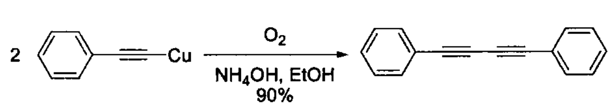
$$R-C\equiv CH \xrightarrow[NH_4OH,\ EtOH]{CuCl} R-C\equiv C-C\equiv C-R$$



经自由基机理也是可以的:

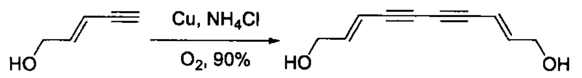


Example 1[1]

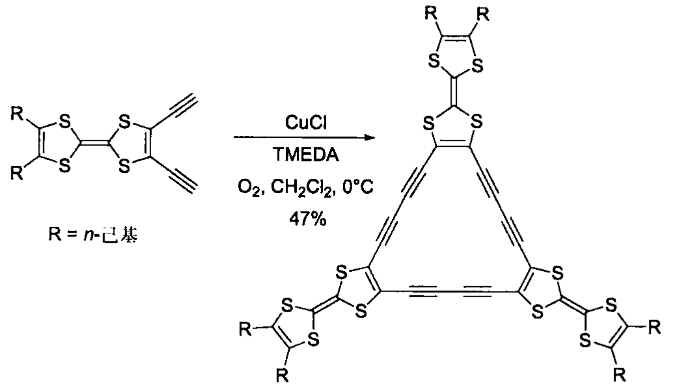


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_111,

Example 2, 同偶联[2]



Example 3[7]



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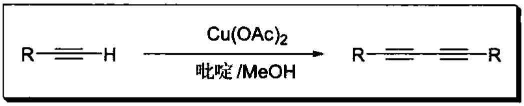
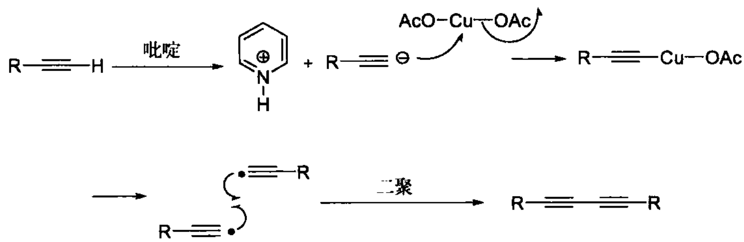
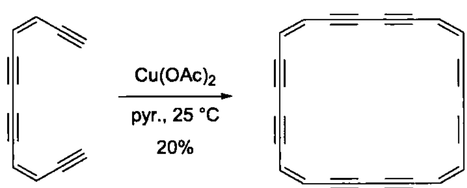
Eglinton 偶联反应

端基炔烃在氧气氛中由化学剂量或过量的**Cu(OAc)$_2$**促进发生氧化偶联反应，是Glaser 偶联反应的变异。

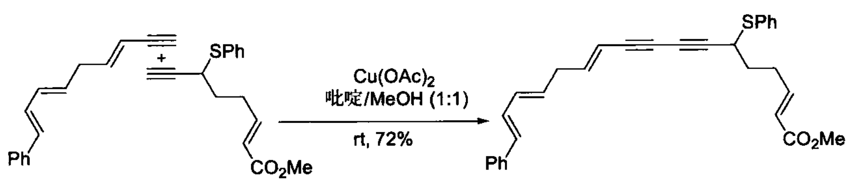




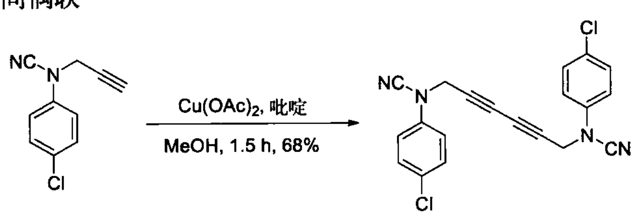
Example 1[2]



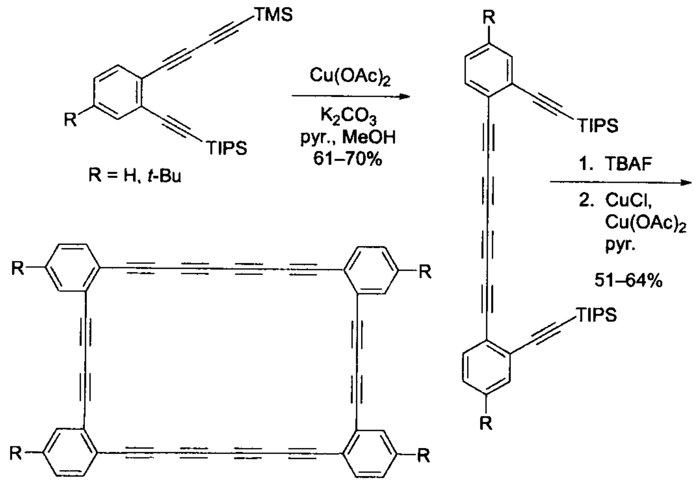
Example 2, 交叉偶联[3]



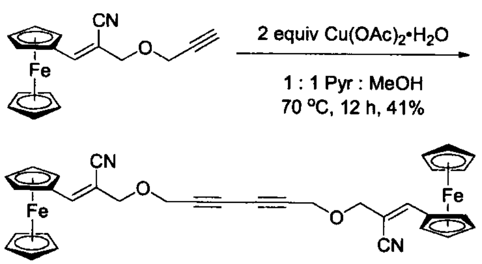
Example 3, 同偶联[4]



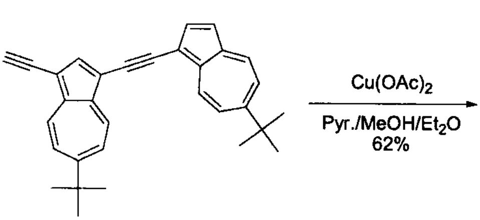
Example 4[5]

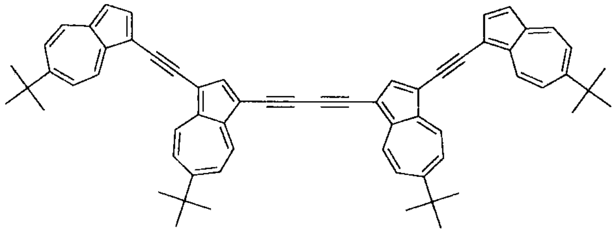


Example 5[11]



Example 6[12]





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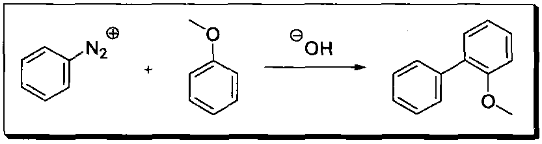
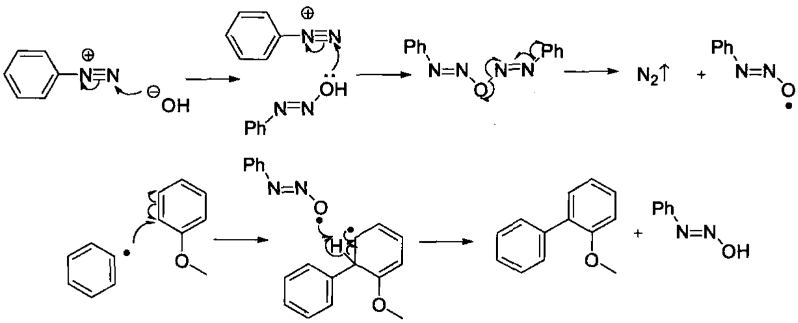
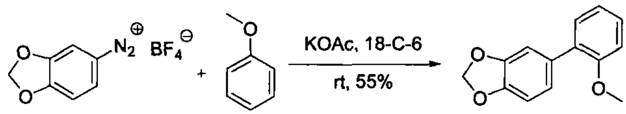
Gomberg-Bachmann 反应

芳基重氮盐和芳烃在碱促进下发生二芳基化合物的自由基偶联反应。

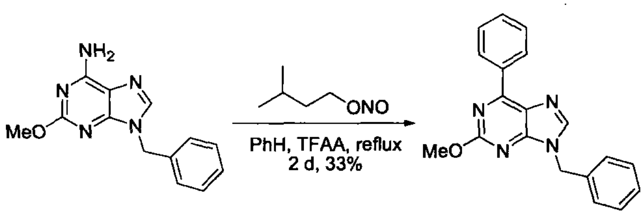




Example 1[4]



Example 2[5]



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J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_112,

Gould-Jacobs 反应

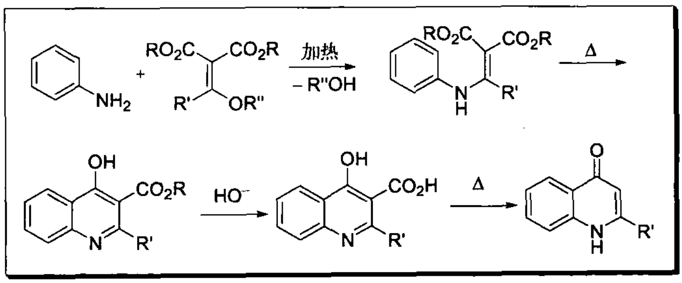
Gould-Jacobs反应涉及如下顺序反应：

a. 苯胺用烷氧基亚甲基丙二酸酯或酰基丙二酸酯取代生成苯胺基亚甲基丙二酸酯；

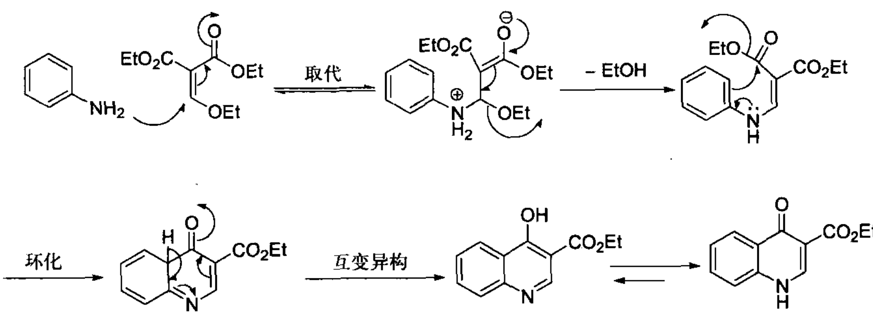
b. 环化为4-羟基-3-烷氧羰基喹啉（4-羟基主要以羰基形式存在）；

c. 皂化为酸；

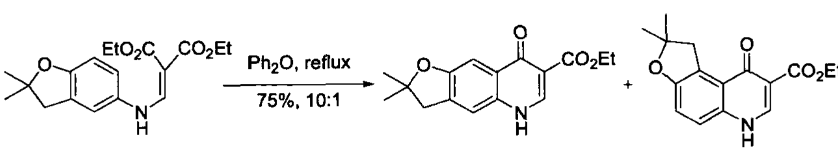
d. 脱羧给出4-羟基喹啉。反应可扩展为Skraup一类无取代的带吡啶稠合的杂环化合物。



R = 烷基; R' = 烷基,芳基, or H; R" = 烷基 or H

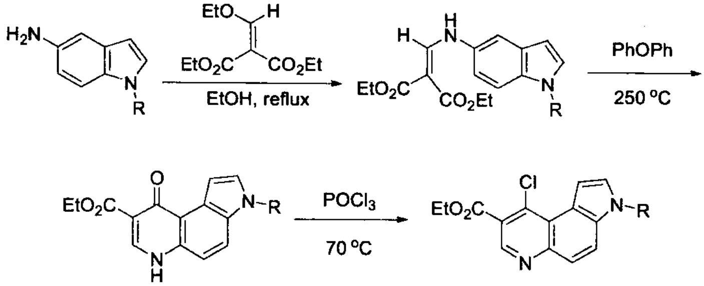


Example 1[3]

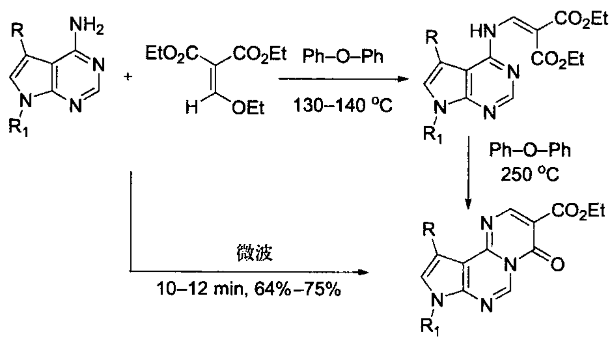


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_113,

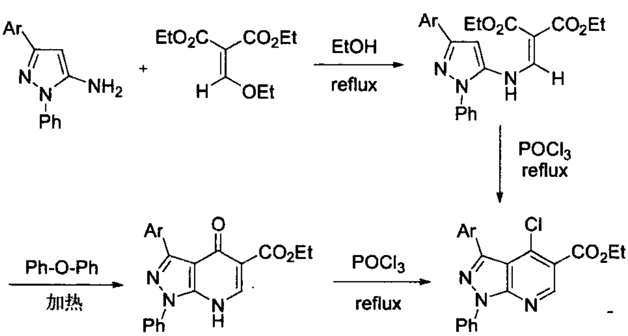
Example 2[8]



Example 3, 微波辅助的Gould–Jacobs 反应[9]



Example 4[10]



References

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工作并在该研究所与其同事杰卡布（Walter A.Jacobs）共同发现了Gould-Jacobs反应。

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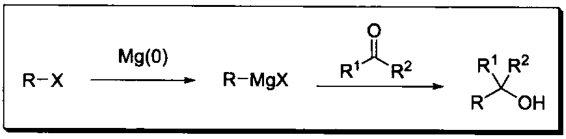
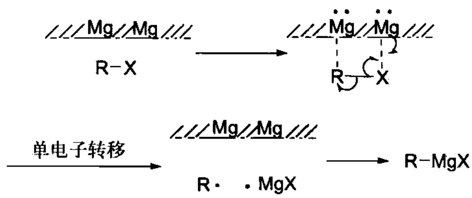
Grignard 反应

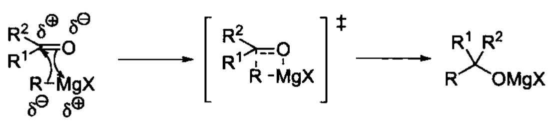
由有机卤代烃和镁金属制得的有机镁化合物(格氏试剂)对亲电物种的反应。



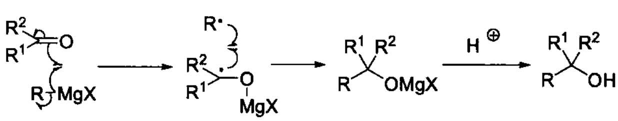
格氏试剂的生成:



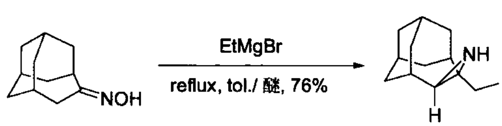
格氏反应，离子机理:



自由基机理



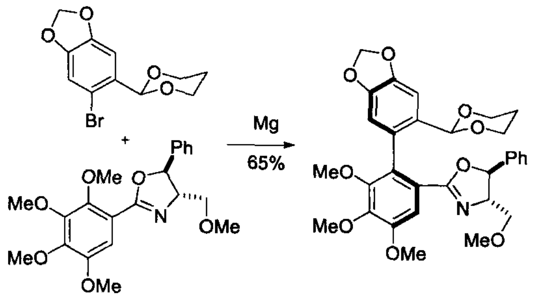
Example 1[4]



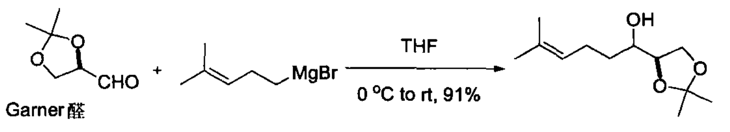
反应又称Hoch-Cambell氮杂环丙烷合成反应，酮肟与过量格氏试剂反应接着水解生成氮杂环丙烷。

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

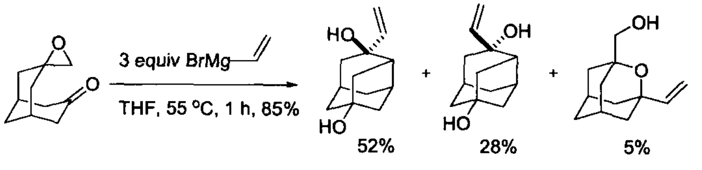
Example 2[5]



Example 5[10]



Example 6[11]



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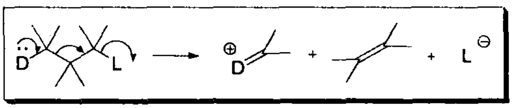
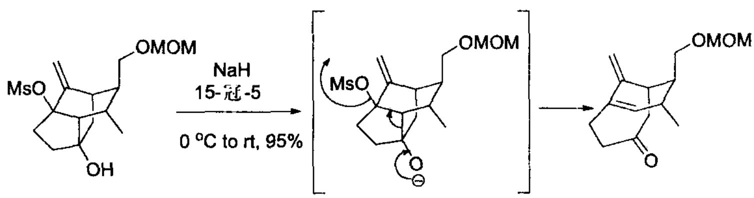
Grob 碎片化反应

主要包括一个涉及五原子体系协同过程的C—C键裂解反应。

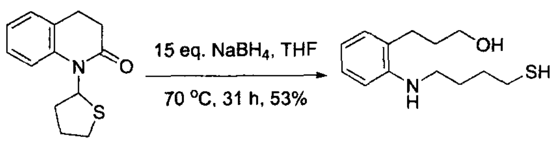


D = O⁻, NR_2; L = OH_2^+, OTs, I, Br, Cl

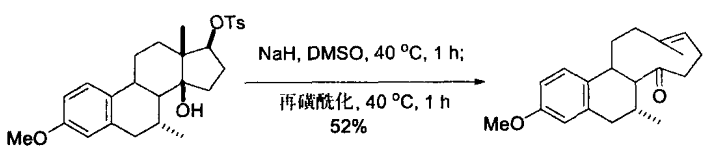
Example 1[2]



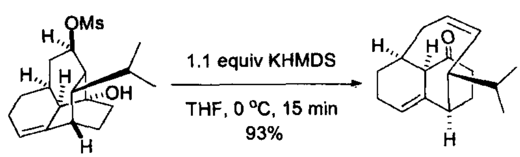
Example 2, 含氮的-Grob碎片化[3]



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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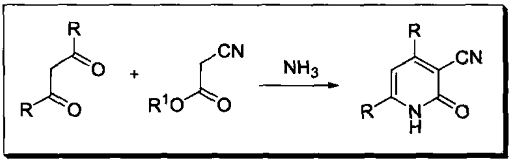
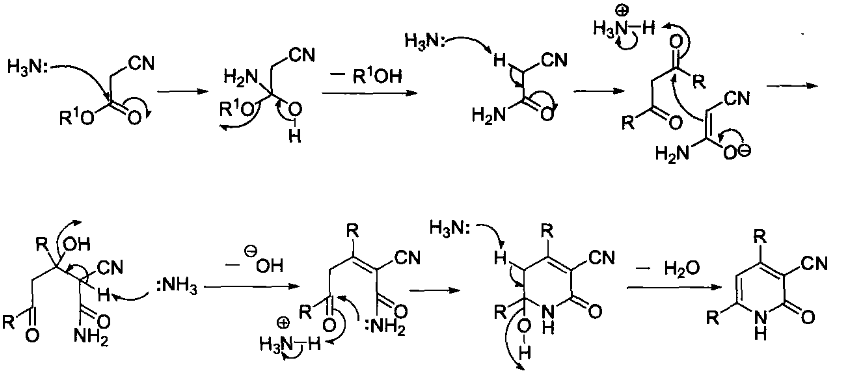
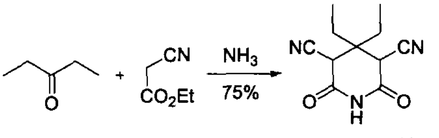
Guareschi-Thorpe 缩合反应

氰基乙酸和 β-二酮在氨存在下缩合生成2-吡啶酮。





Example[6]



Guareschi 亚胺

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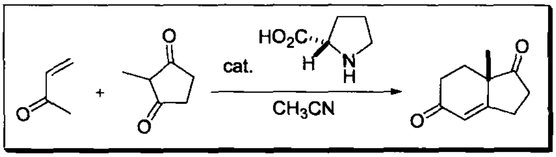
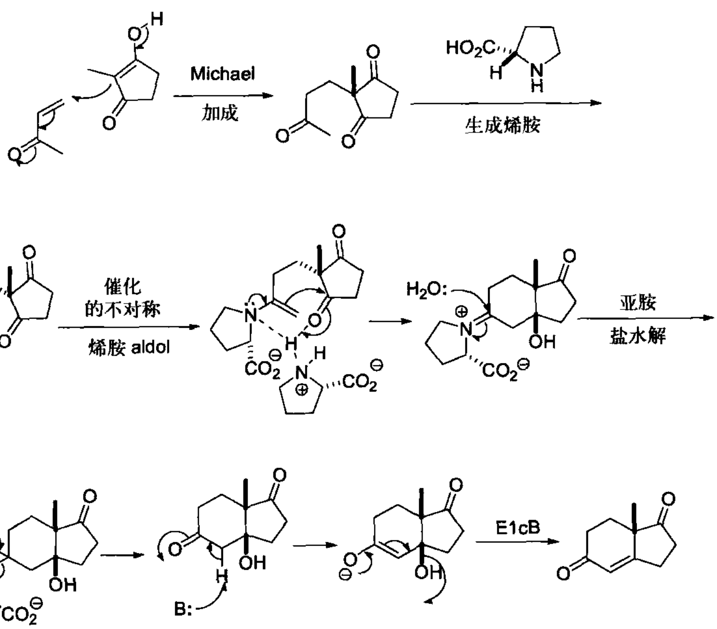
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_116,

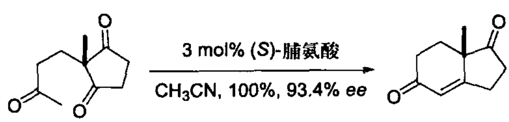
Hajos-Weichert 反应

(*S*)-(–)-脯氨酸催化的不对称Robinson增环反应。

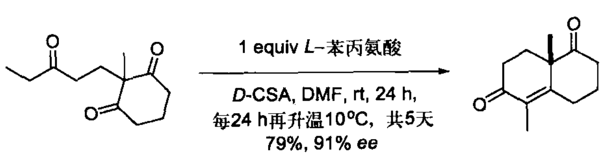




Example 1[1a]

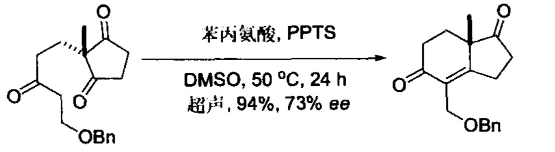


Example 2[3]

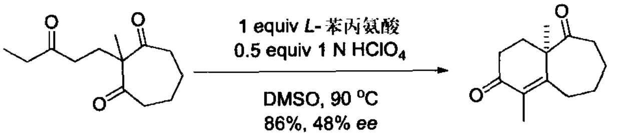


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_117,

Example 3[8]



Example 4[9]



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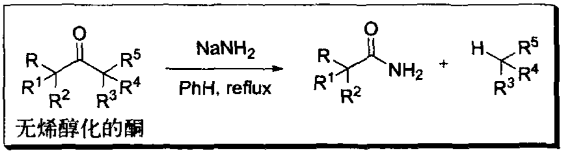
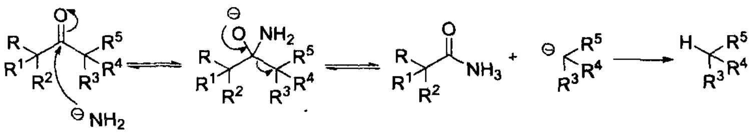
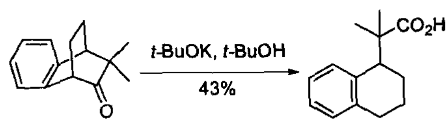
Haller-Bauer 反应

碱诱导裂解无烯醇化的酮生成酰胺衍生物和一个羰基被氢取代后的中性碎片。

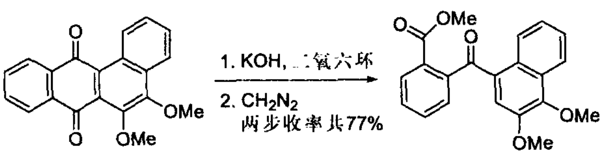




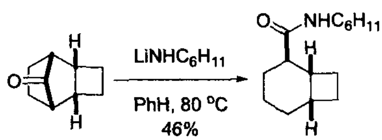
Example 1[4]



Example 2[9]



Example 3, 外消旋化[10]



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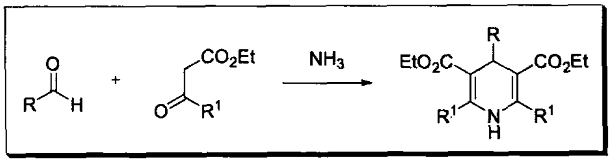
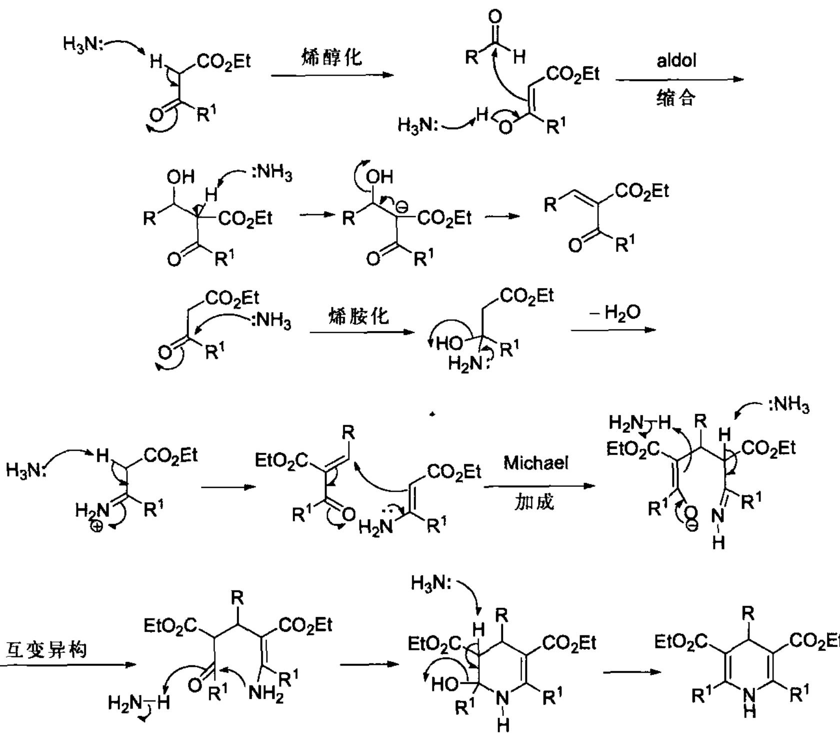
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_118,

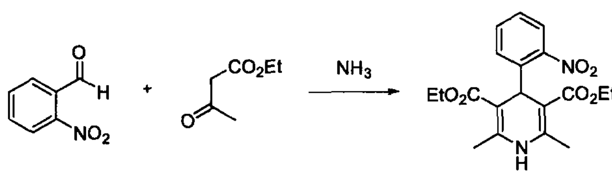
Hantzsch 二氢吡啶合成反应

醛、β-酮酯和氨缩合成1,4-二氢吡啶。Hantzsch二氢吡啶在有机催化反应中是个通用试剂。





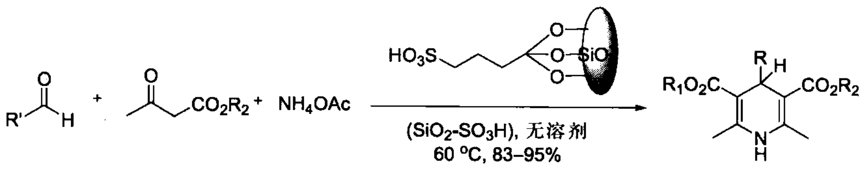
Example 1[2]



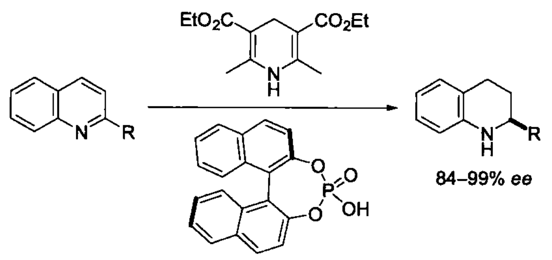
nifedipine

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

Example 2[9]



Example 3, Hantzsch 1,4-二氢吡啶作为氢的供体[10]



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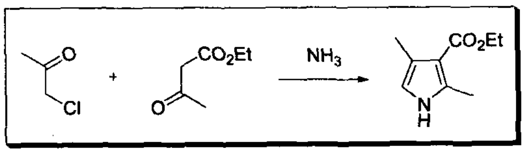
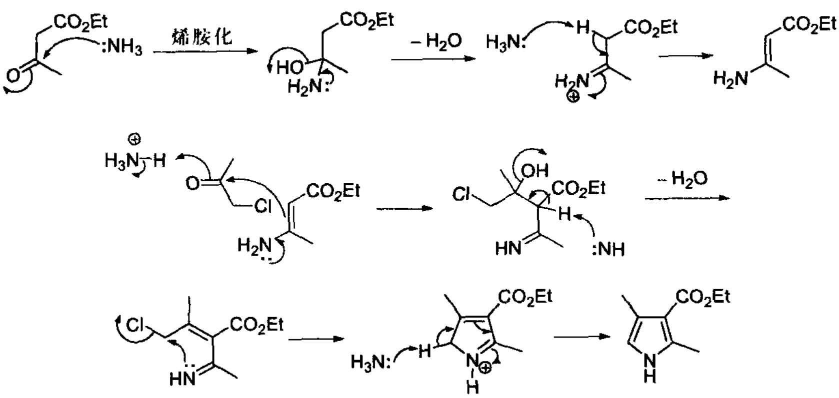
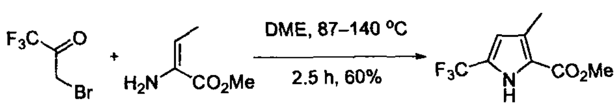
Hantzsch 吡咯合成反应

α-氯甲基酮、β-酮酯和氨缩合成吡咯的反应。

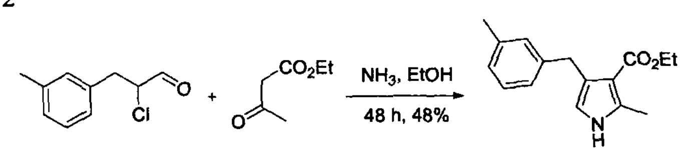




Example 1[4]



Example 2[7]



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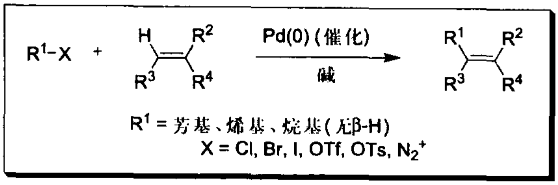
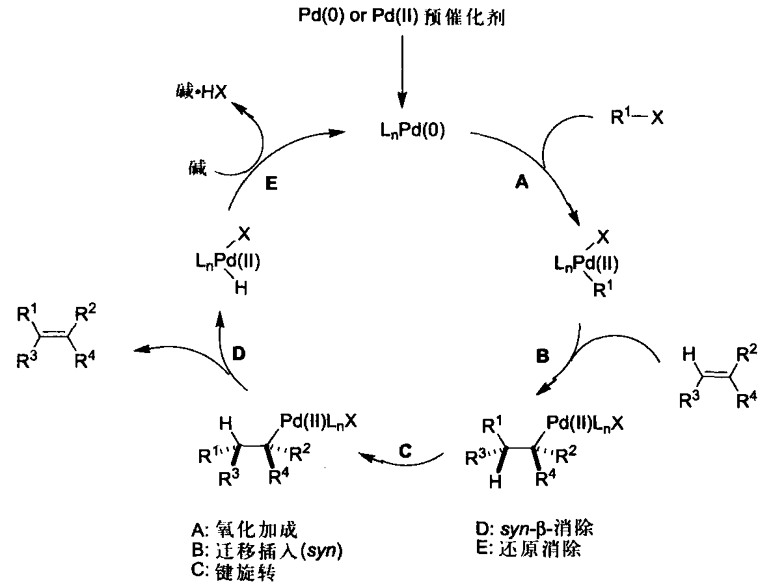
Heck 反应

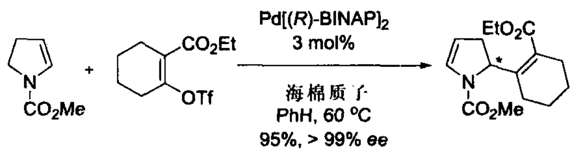
Pd-催化的烯烃烯基化或芳基化反应。



催化循环:

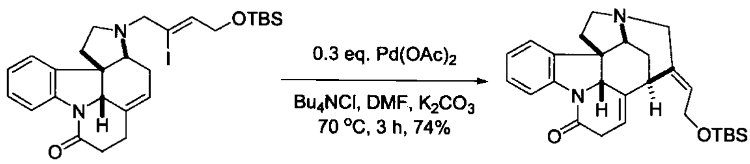


Example 1, 不对称分子间Heck反应[6]

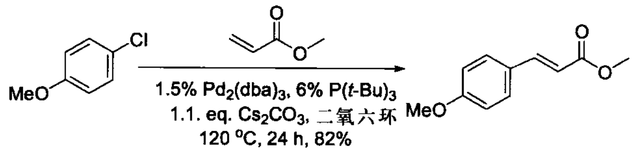


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_121,

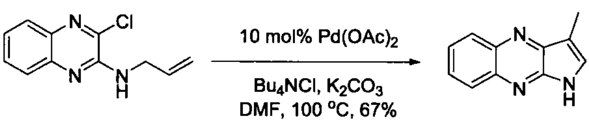
Example 2, 分子内Heck反应[7]



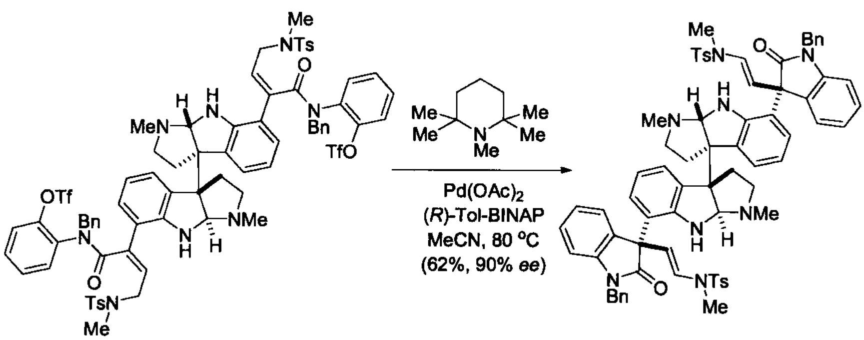
Example 3[8]



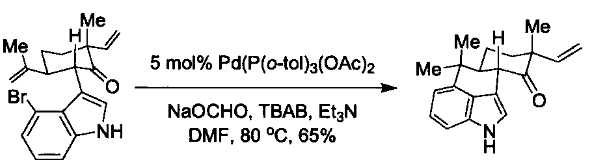
Example 4, 分子内Heck反应[9]



Example 5, 分子内Heck反应[13]



Example 6, 还原Heck反应[17]



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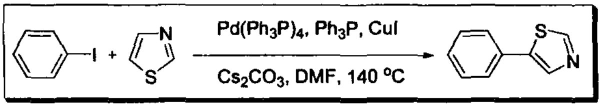
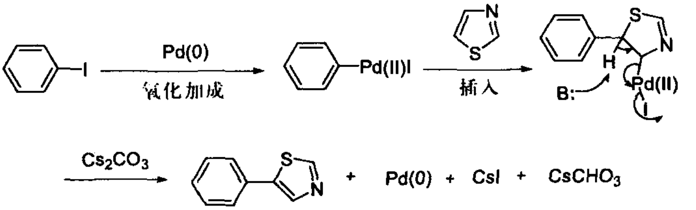
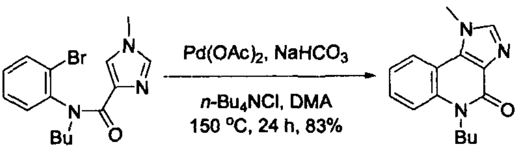
杂芳基Heck反应

分子内或分子间发生在杂芳基上的Heck反应。

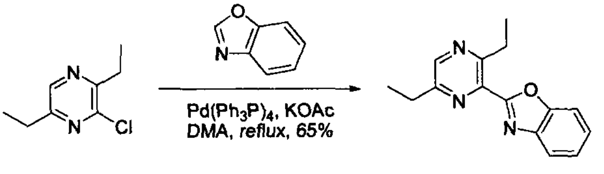




Example 1[2]



Example 2[3]



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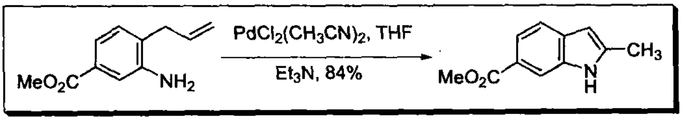
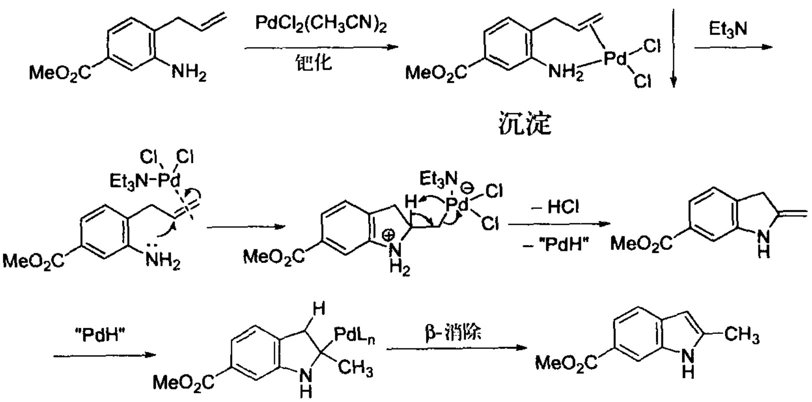
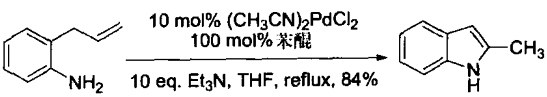
Hegedus 吲哚合成反应

化学计量的Pd(Ⅱ)促进的烯基苯胺发生氧化环合生成吲哚的反应。参见第564页上的Wacker氧化反应。

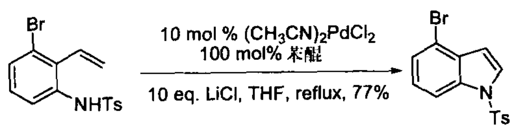




Example 1[1a]



Example 2[1d]



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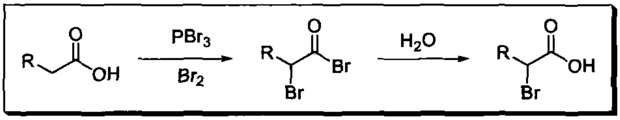
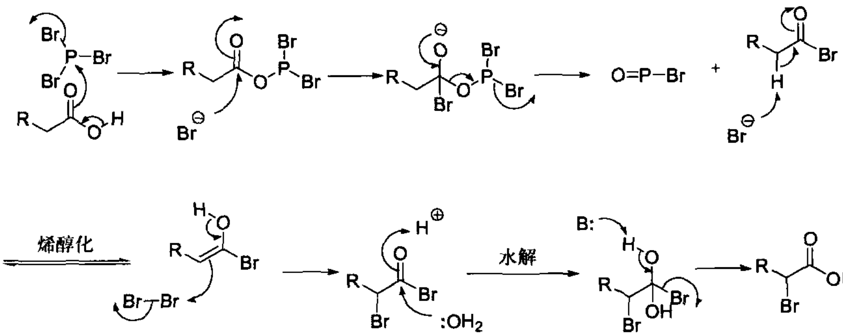
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_122,

Hell-Volhard-Zelinsky 反应

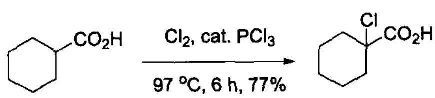
羧酸用X_2/PX_3进行 α - 卤代反应。



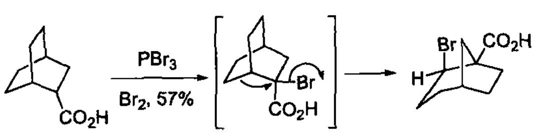
α-溴代酸



Example 1[5]



Example 2[6]



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(c) Zelinsky, N. D. *Ber.* **1887**, *20*, 2026. 泽林斯基(Nikolai D. Zelinsky，1861−1953)出生于俄罗斯的Tyaspol，在哥廷根跟迈耶尔(Victor Meyer)学习并获得Ph.D学位后

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

回到俄罗斯，而后成为莫斯科大学教授，1951年在他90岁生日那天被授予列宁勋章 (order of Lenin)。

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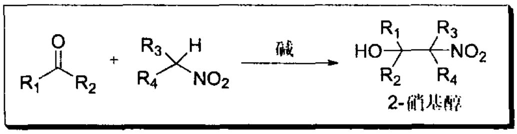
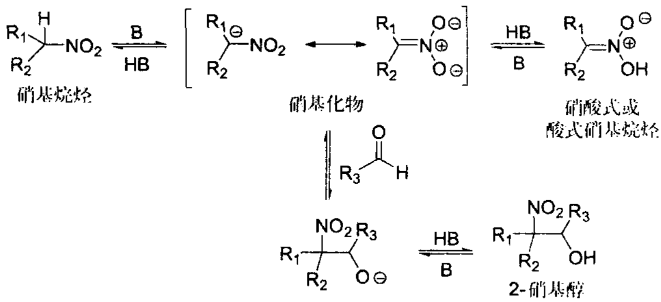
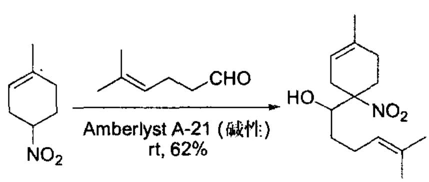
Henry 硝基化合物的 aldol 反应

醛和硝基烷烃经碱去质子后生成的硝基化物发生 aldol 反应。

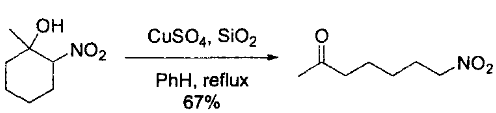




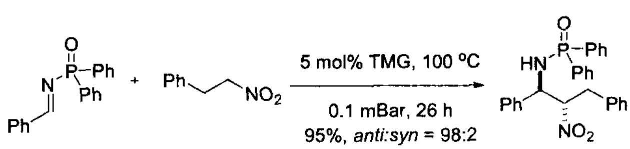
Example 1[4]



Example 2, 逆-Henry 反应[5]



Example 3, 含氮的 Henry 反应[8]



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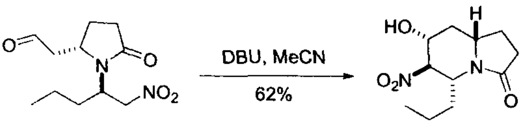
Example 4, 分子内Henry 反应[10]



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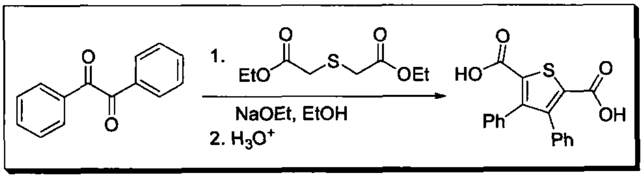
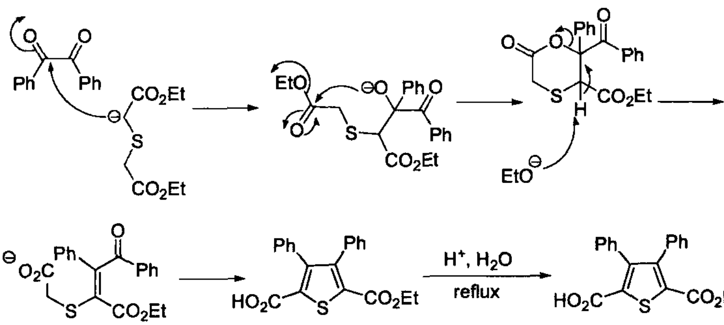
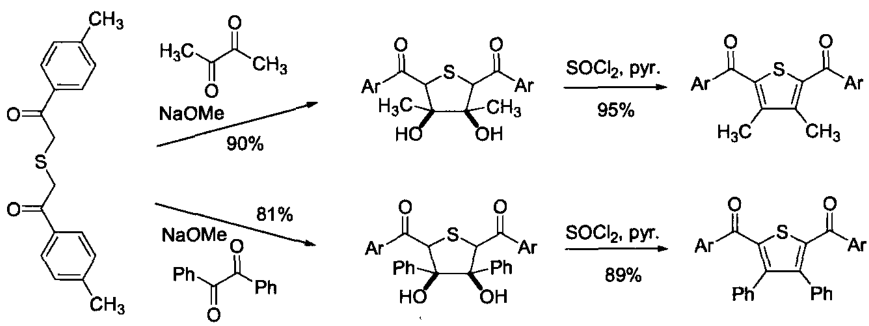
Hinsberg 噻吩衍生物合成反应

3-硫杂戊二酸二乙酯和 α-二酮在碱性条件下缩合后得到的酯产物经酸性水解给出 3,4-二取代噻吩-2,5-二羰基化合物。

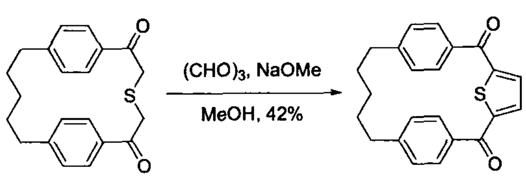




Example 1[2]

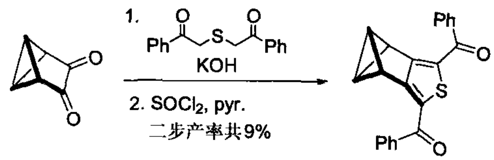


Example 2[4]

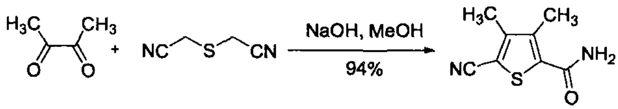


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_125,

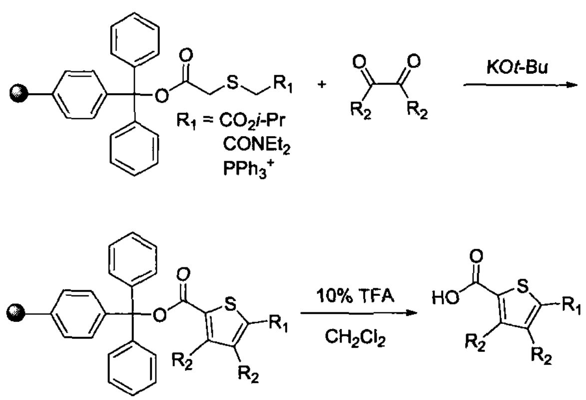
Example 3[5]



Example 4[6]



Example 5, 聚合物负载的Hinsberg 噻吩合成[9]



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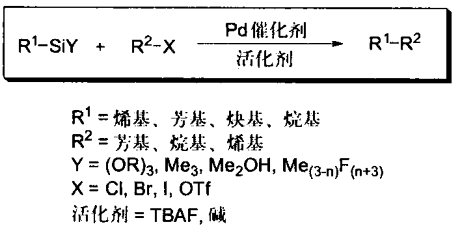
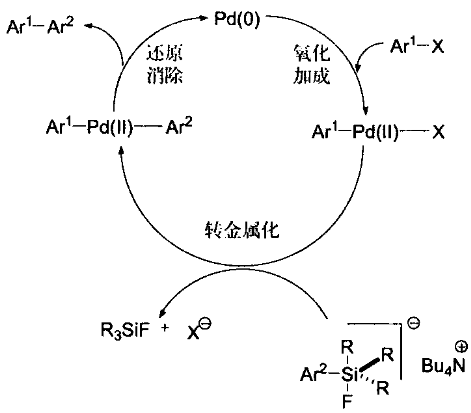
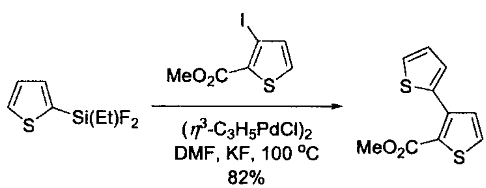
Hiyama 交叉偶联反应

Pd催化的卤代烃和有机硅烷、三氟磺酸酯间的交叉偶联反应。反应需F⁻、OH⁻等活化剂存在。若无此类活化剂参与，转金属化不易进行。催化循环参见第325页上的**Kumada**偶联反应。

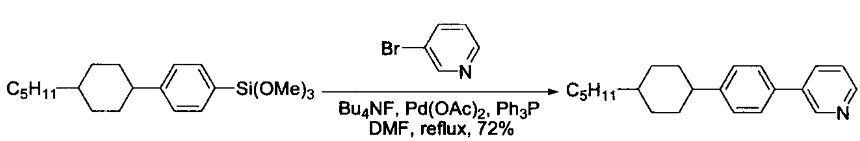




Example 1[1a]



Example 2[2]



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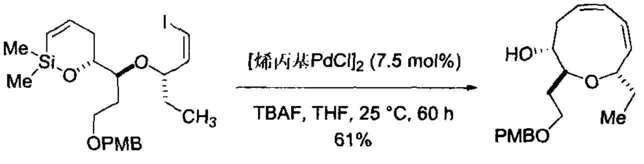
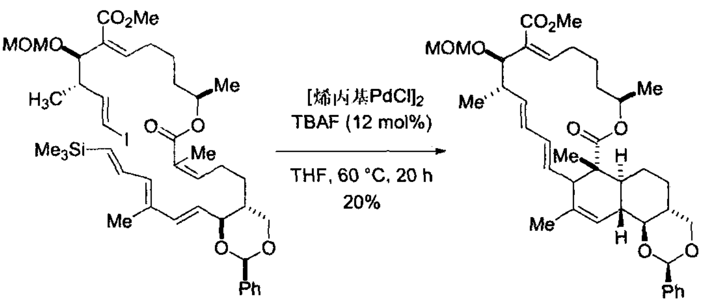
Example 3[7]



Example 4[9]



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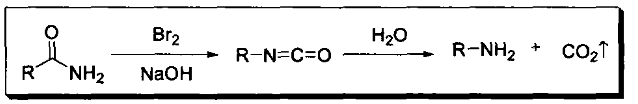
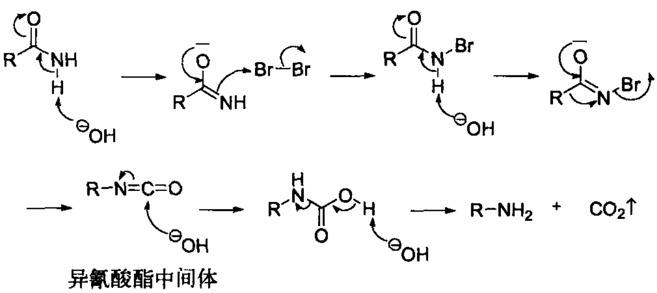
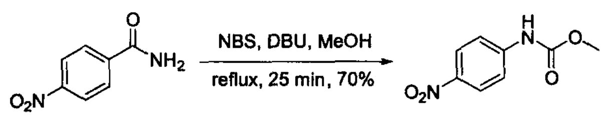
Hofmann 重排反应

伯酰胺用次卤酸盐处理经异氰酸酯中间体而生成少一个碳原子的伯胺。亦称**Hofmann**降解反应。

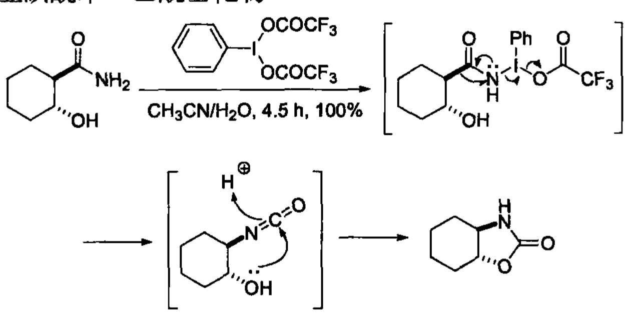




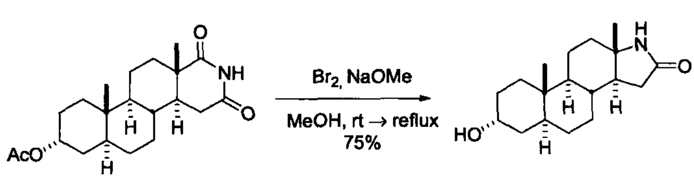
Example 1, NBS 变异[2]



Example 2, 亚碘酰苯二乙酰基化物[5]



Example 3, 溴和烷氧化物[6]



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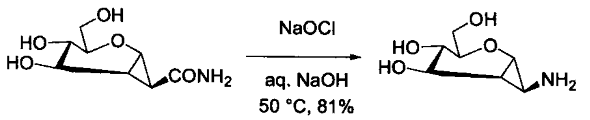
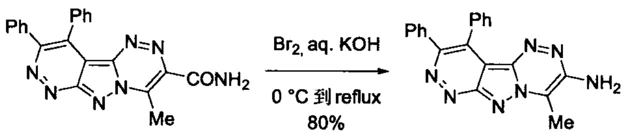
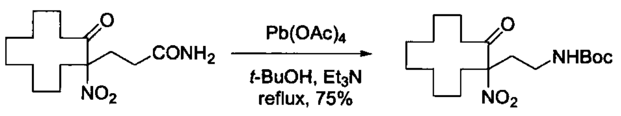
Example 4, 次氯酸钠[7]



Example 5, 原始的条件：Br_2/OH^-[9]



Example 6, 四乙酸铅[10]



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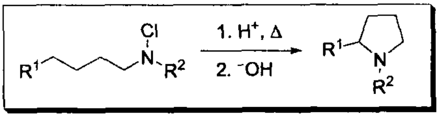
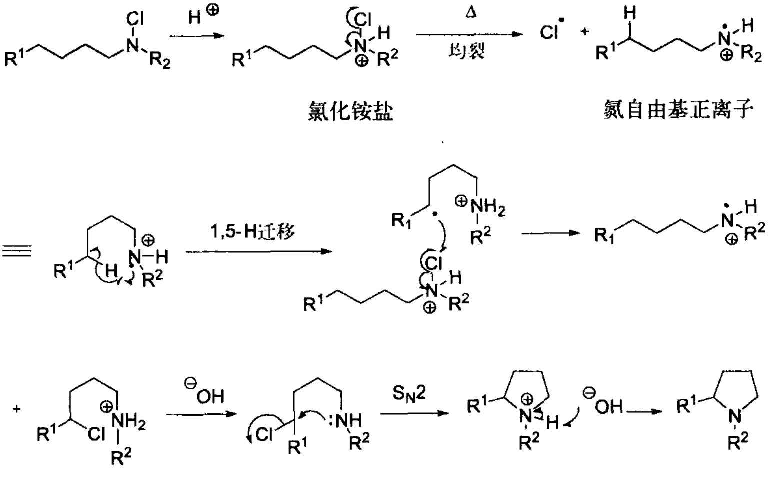
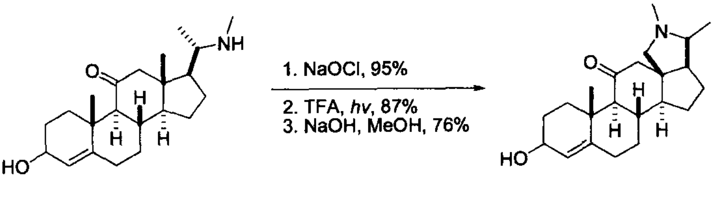
Hofmann-Loeffler-Freytag 反应

质子化的 *N*-卤代胺经热或光化学分解为四氢吡咯或哌啶。

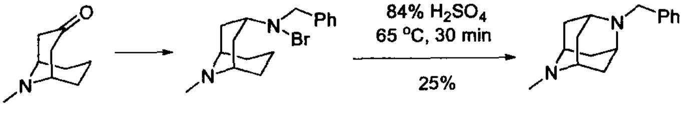




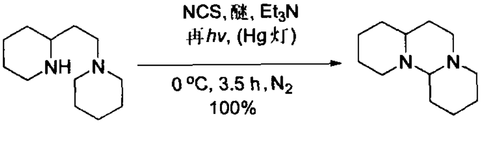
Example 1[2]



Example 2[4]



Example 3[5]



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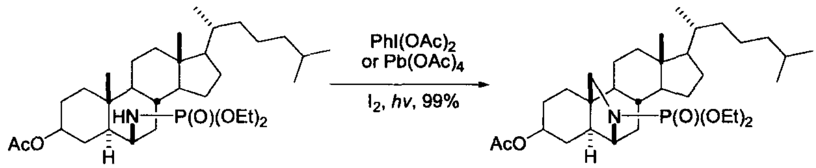
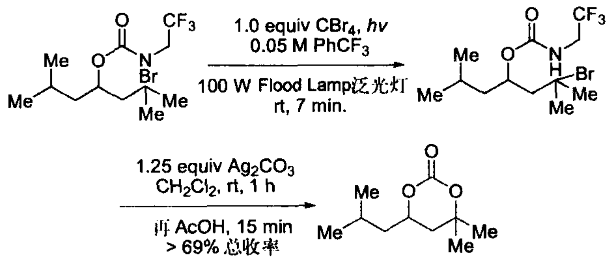
Example 4[7]



Example 5[12]



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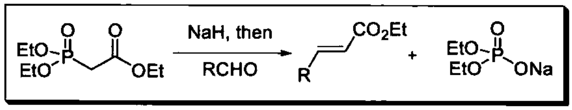
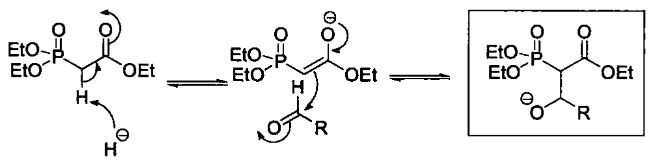
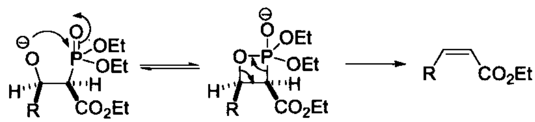
Horner-Wadsworth-Emmons 反应

从醛和磷酸酯得到烯烃。该反应的副产物是水溶性的，故反应操作比相应的Wittig反应方便。通常得到的烯烃产物中*trans*-构型比*cis*-构型多。

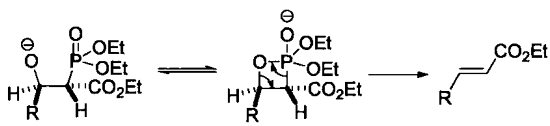




立体化学产出: 赤式(动力学)或苏式(热力学)

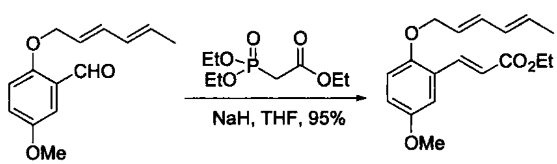


赤式，动力学加成物

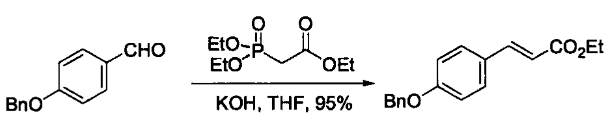


苏式，热力学加成物

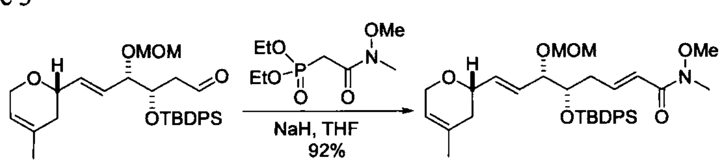
Example 1[3]



Example 2[4]



Example 3[7]



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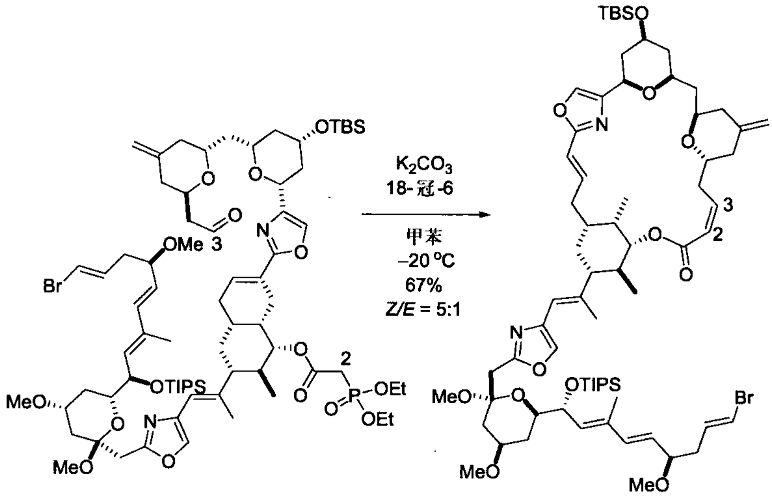
Example 4, 分子内Horner–Wadsworth–Emmons反应[9]



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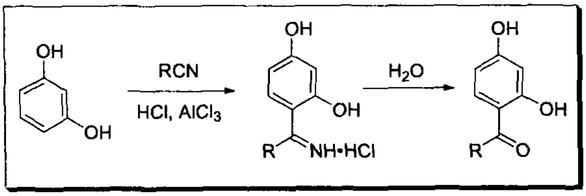
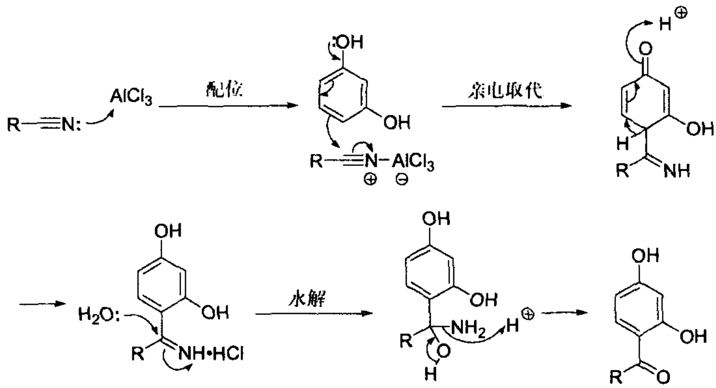
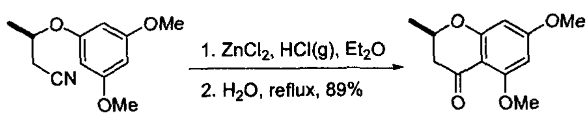
Houben-Hoesch 反应

酚及酚醚与腈在酸催化下发生酰基化反应。

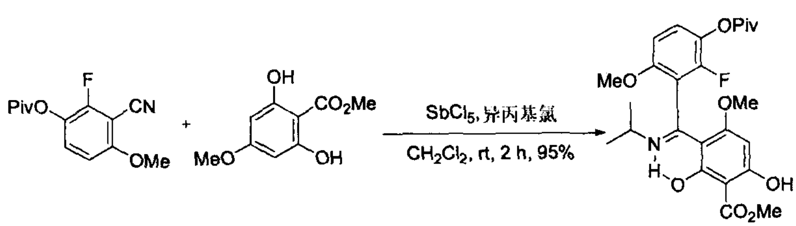




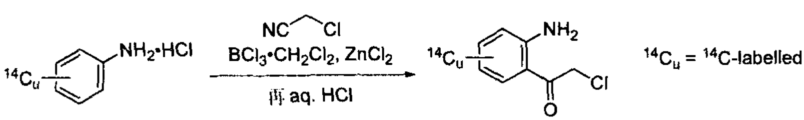
Example 1, 分子内Houben–Hoesch 反应[3]



Example 2[6]



Example 3[8]



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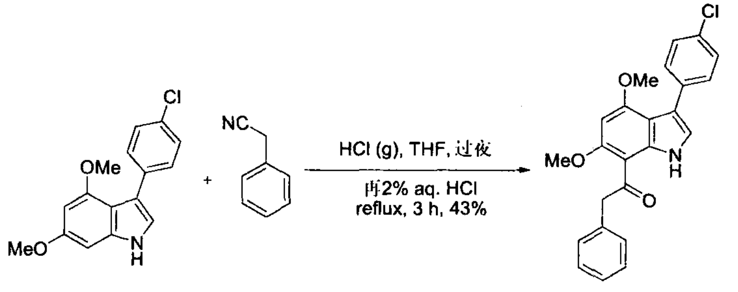
Example 4[9]



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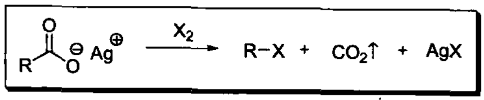
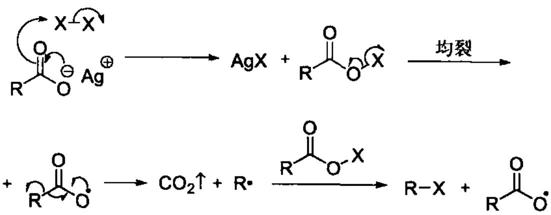
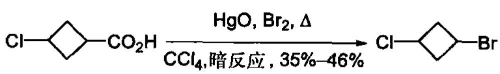
Hunsdiecker-Borodin 反应

羧酸银用卤素处理生成卤代烃。

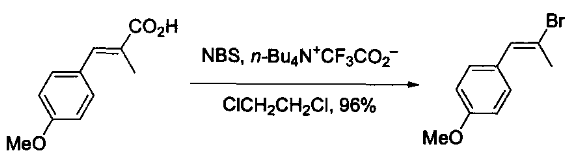




Example 1[5]



Example 2[6]



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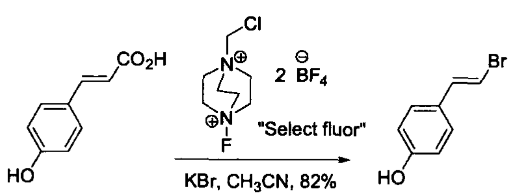
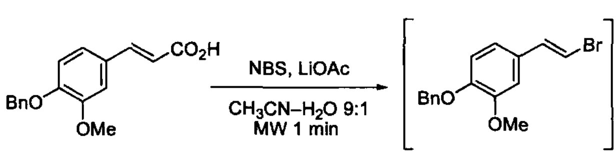
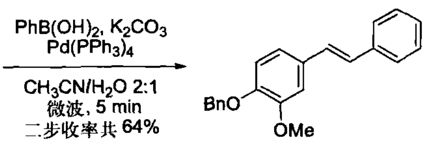


Example 4, 一锅煮微波促进的Hunsdiecker–Borodin再Suzuki反应[10]



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



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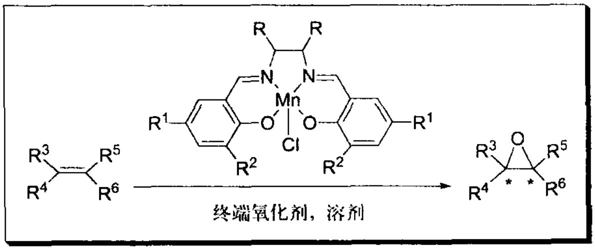
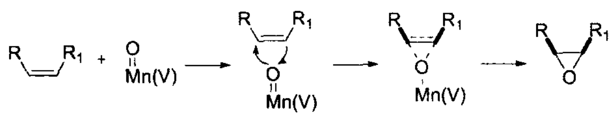
Jacobsen-Katsuki 环氧化反应

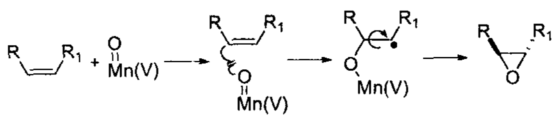
Z-烯烃在Mn(Ⅲ)-salen催化下的不对称环氧化反应。



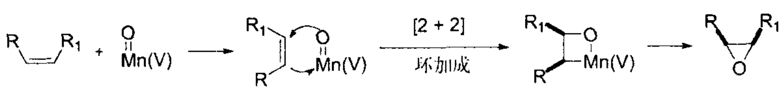
1. 协同的氧转移(*cis*-环氧化物):



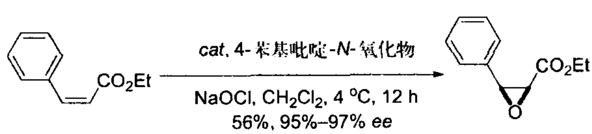
2. 经自由基中间体的氧转移(*trans*-环氧化物):

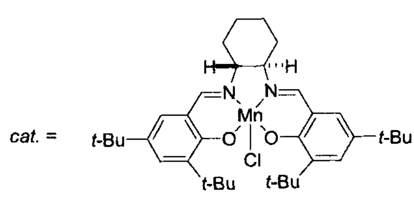


3. 经锰的氧化物中间体的氧转移(*cis*-环氧化物):



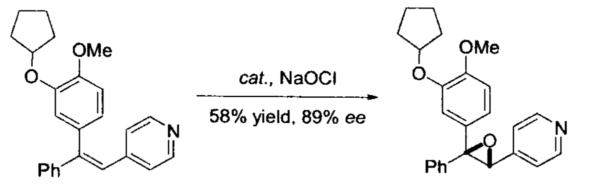
Example 1[2]



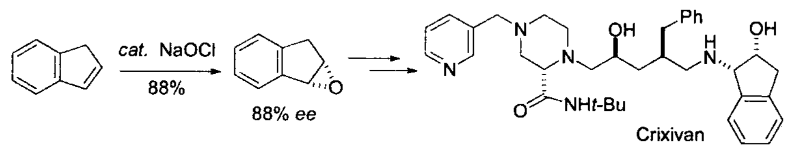


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_132,

Example 2[5]



Example 2[6]



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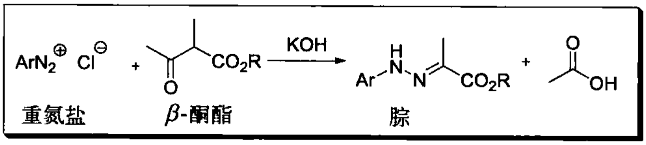
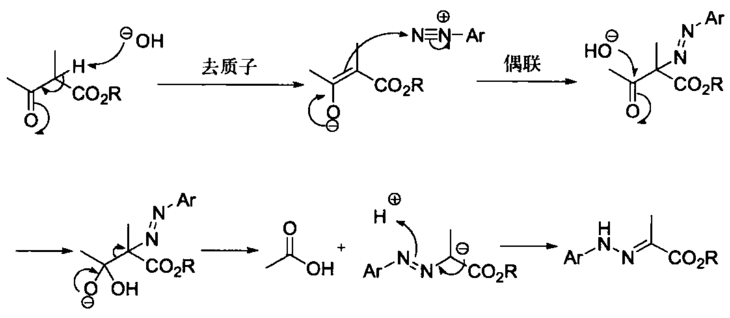
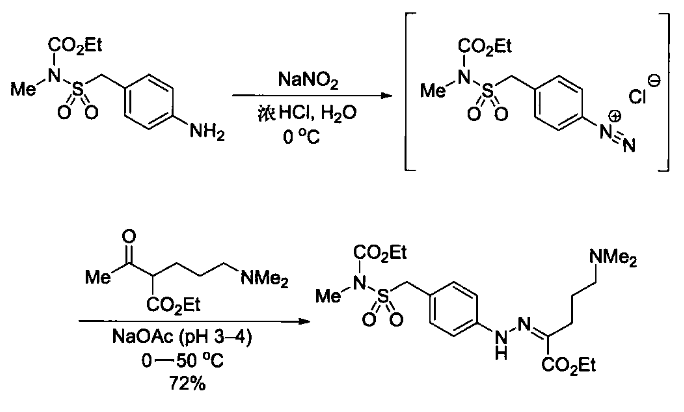
Japp-Klingemann 腙合成反应

β-酮酯和重氮盐在酸或碱存在下生成腙的合成反应。

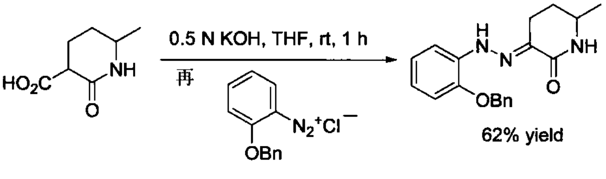




Example 1[4]

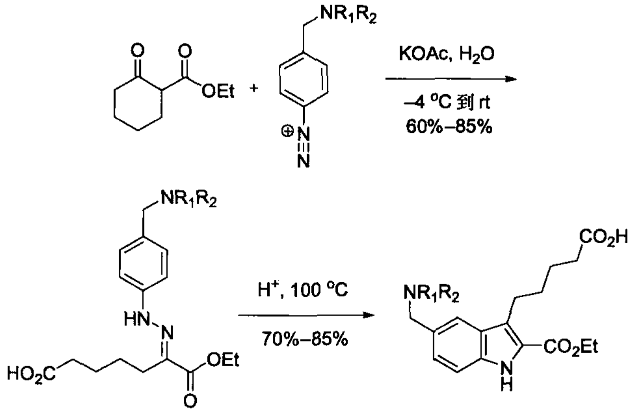


Example 2[6]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_133,

Example 3[10]



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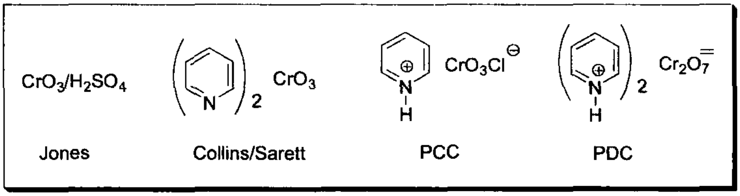
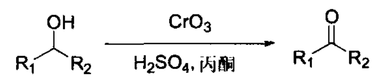
Jones 氧化反应

Collin-Sarett氧化剂（CrO_3-吡啶配合物）、Corey PCC氧化剂（吡啶-氯铬酸盐）、PDC氧化剂（吡啶-重铬酸盐）和Jones氧化剂（CrO_3-H_2SO_4-Me_2CO）氧化醇的反应都经过相同的过程。这些氧化剂都含有一个一般呈黑色或黄色的Cr（Ⅵ），还原后转为绿色的Cr（Ⅳ）。

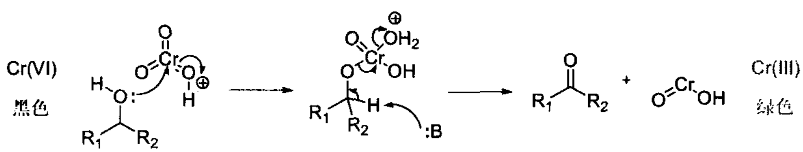


Jones 氧化反应

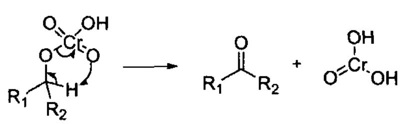
Jones氧化反应后伯醇被氧化为相应的醛或羧酸，仲醇被氧化为相应的酮。



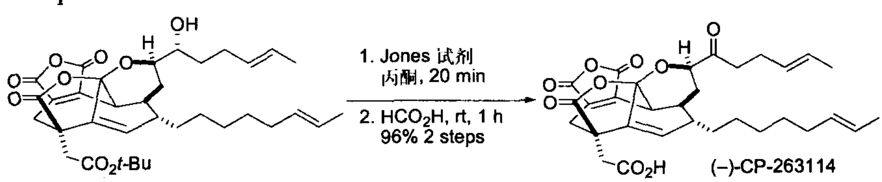
$$CrO_3 + H_2O \rightarrow H_2CrO_4$$



分子内机理也可发生:

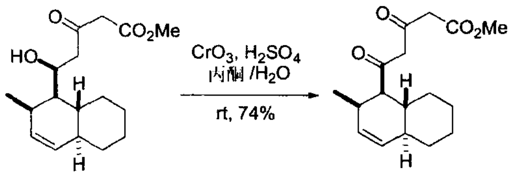


Example 1[6]

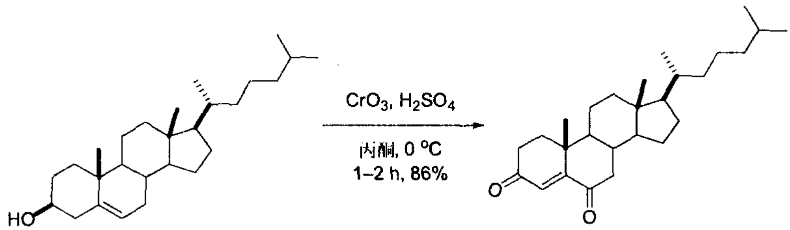


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_134,

Example 2[7]



Example 3[19]



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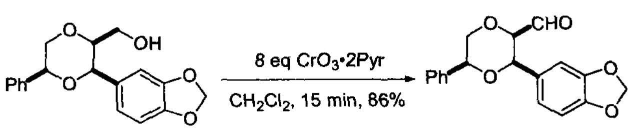
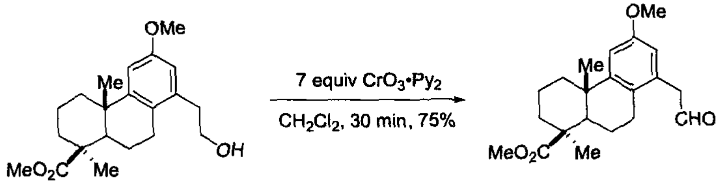
Collin-Sarett 氧化反应

与Jones氧化反应不同，Collin-Sarett氧化反应后伯醇被氧化为相应的醛。

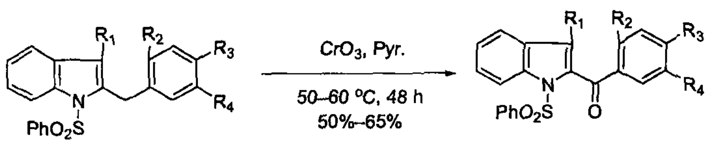
Example 1[5]



Example 2[7]



Example 3[9]



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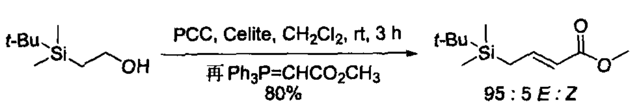
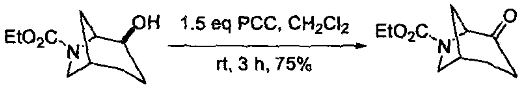
PCC 氧化反应

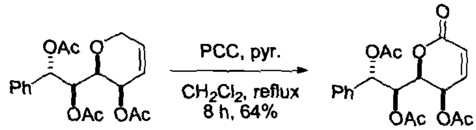
Example 1, 一锅煮 PCC–Wittig 反应[2]



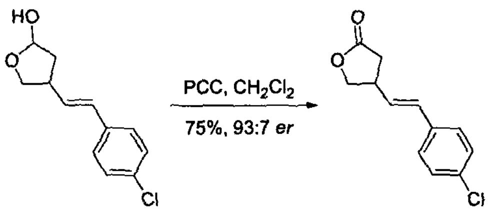
Example 2[3]



Example 3[4]



Example 4[5]



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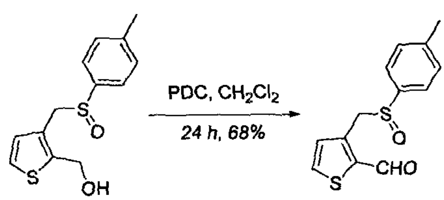
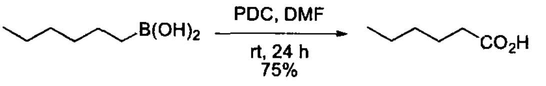
PDC 氧化反应

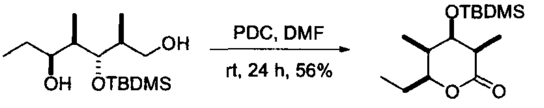
Example 1[2]



Example 2, 伯碳-硼键裂解[3]



Example 3[4]



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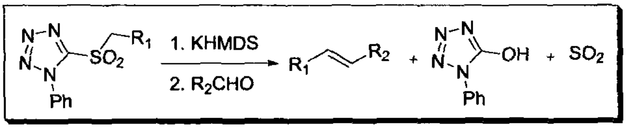
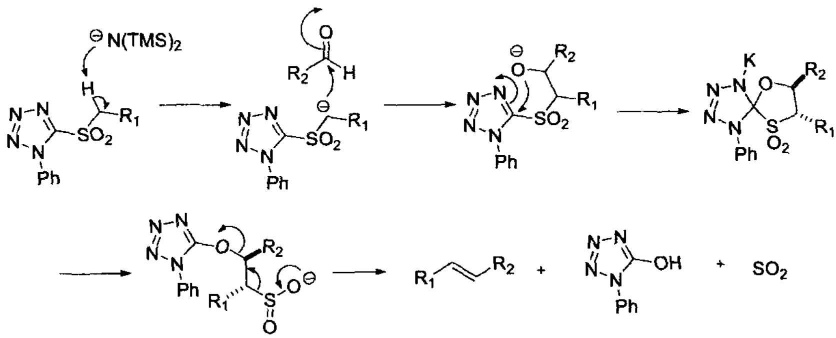
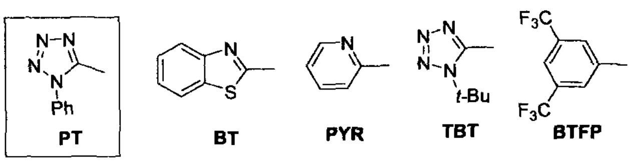
Julia-Kocieneski 烯基化反应

修正的一锅法Julia烯基化反应，将杂芳基砜和醛转变为相应的*E*-烯烃。砜的还原步在该反应中是不需要的。

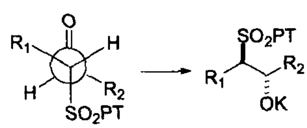




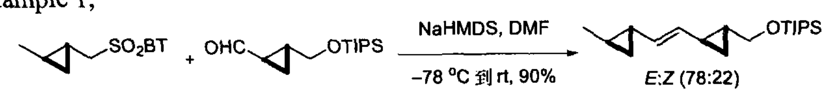
四唑的替代物:



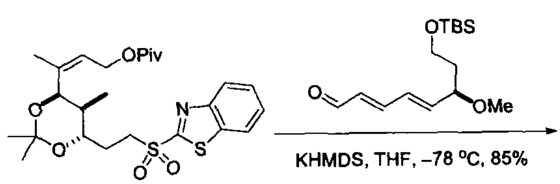
应用类似K⁺那样较大的配对离子和DME那样的极性溶剂有利于一个开放过渡态的形成（PT是苯基四唑）：



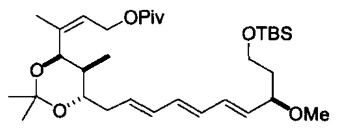
Example 1,[2]



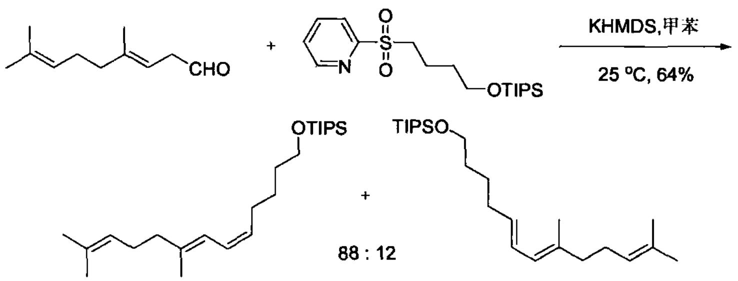
Example 2[3]



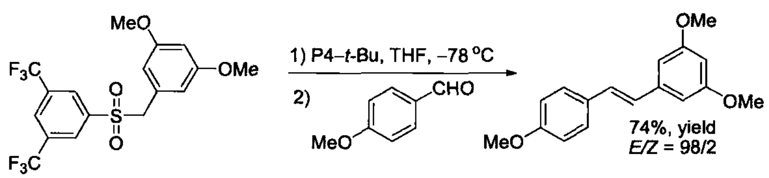
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_135,



Example 3[7]



Example 4[8]



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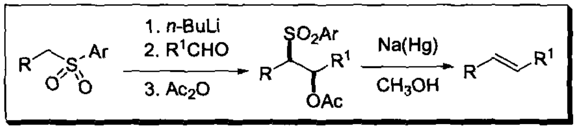
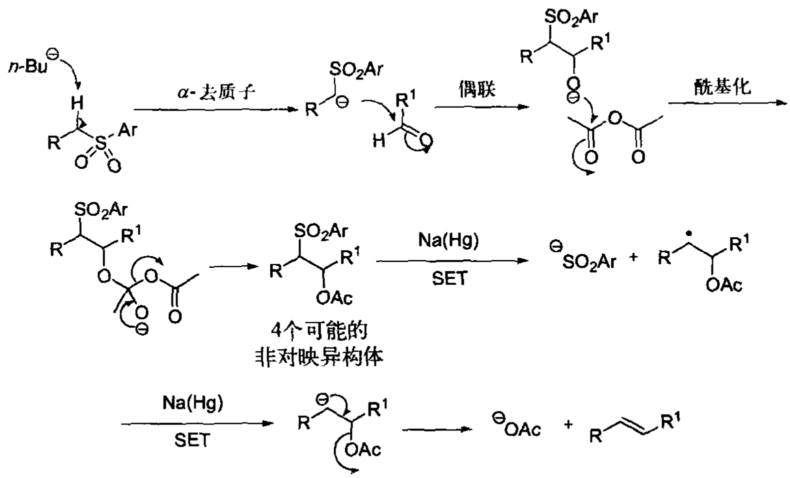
Julia-Lythgoe 烯基化反应

从砜和醛转变为相应的Z-烯烃。





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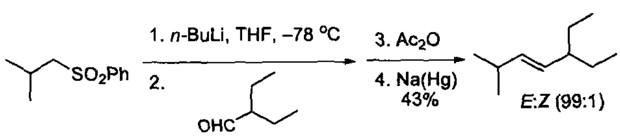

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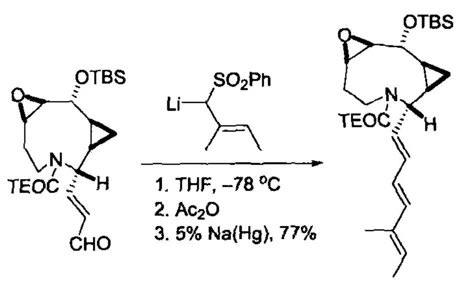
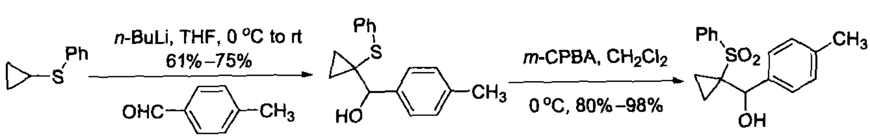
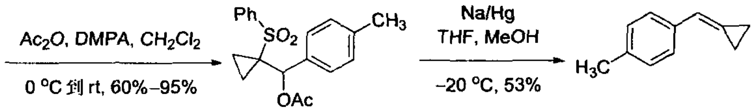


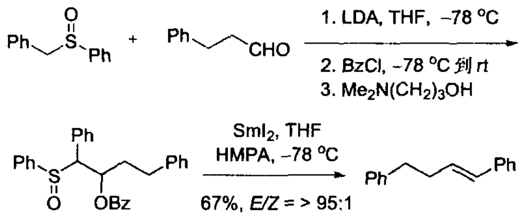
Example 3[7]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_136,



Example 4[8]



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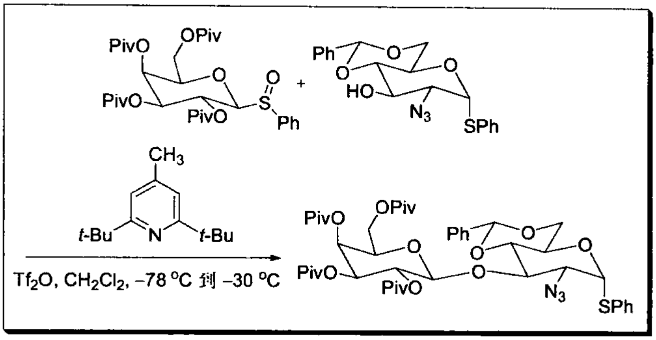
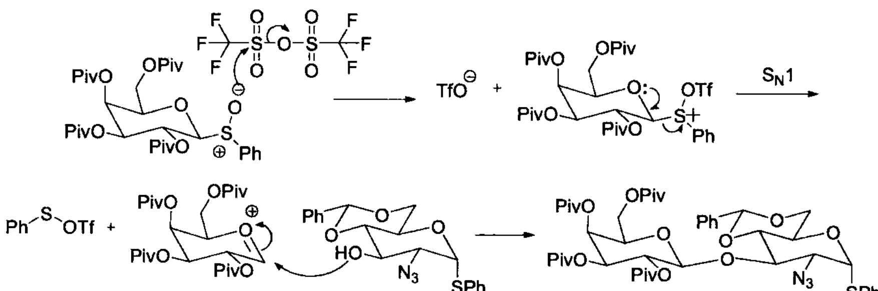
Kahne 苷化反应

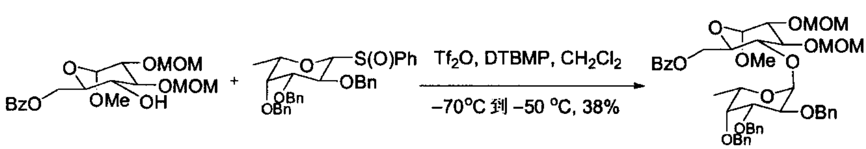
在异头中心上的亚砜作为苷化受体发生非对映选择性的苷化反应。砜的活化可用Tf_2O来实现。



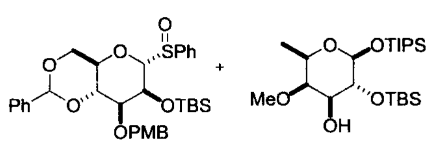


氧鎓离子

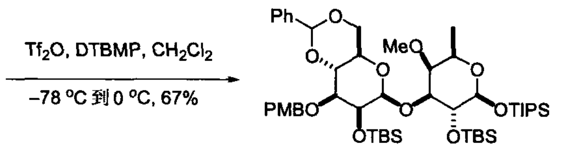
Example 1[1d]



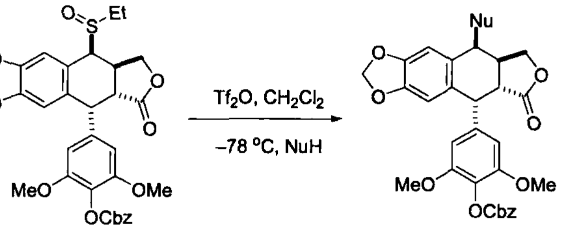
Example 2[4]



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



Example 3, 反Kahne类苷化反应[6]



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

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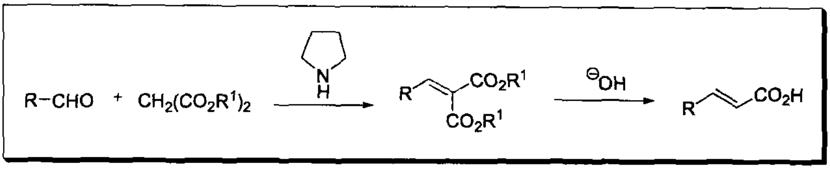
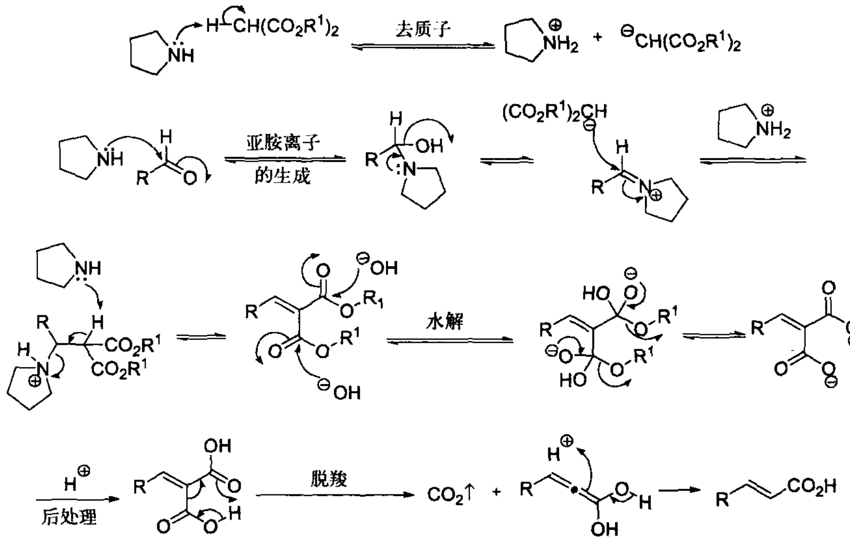
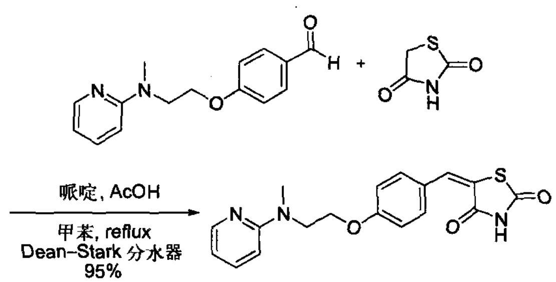
Knoevenagel 缩合反应

羰基化合物和活泼亚甲基化合物之间由胺催化的缩合反应。

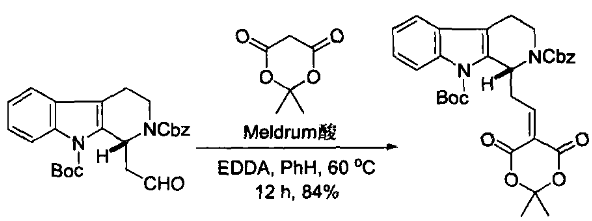




Example 1[3]

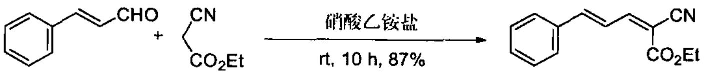


Example 2,[5]

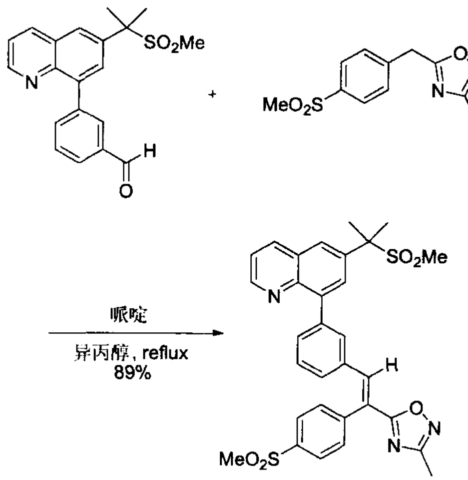


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_138,

Example 3, 用离子液体硝酸乙铵盐为溶剂[8]



Example 4[9]



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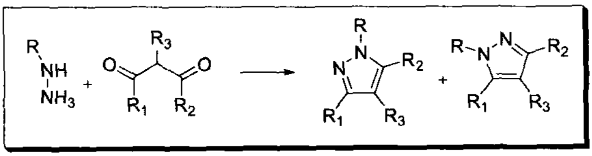
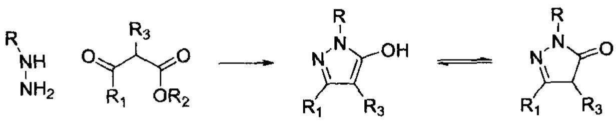
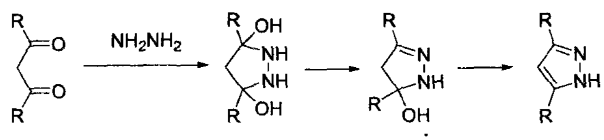
Knorr 吡唑合成反应

肼或取代肼与 β-二羰基化合物反应生成吡唑或吡唑酮环体系。参见第411页上的Paal-Knorr吡咯合成反应。



R = H，烷基，芳基，杂芳基，酰基等





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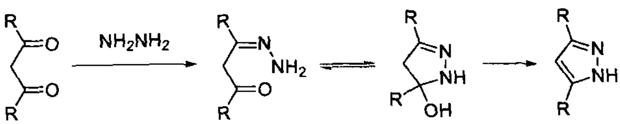
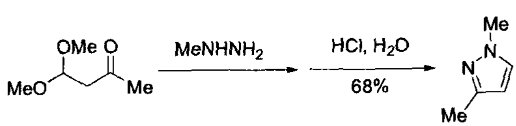
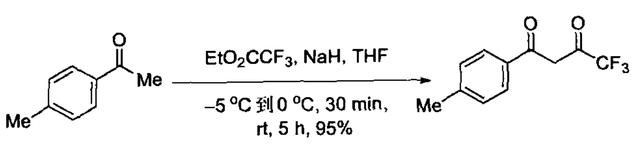


Example 1[2]



Example 2[8]



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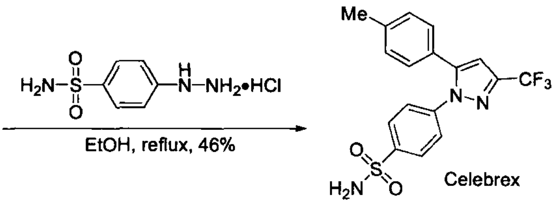

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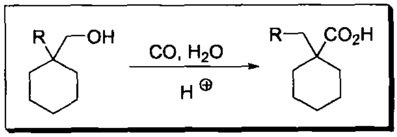
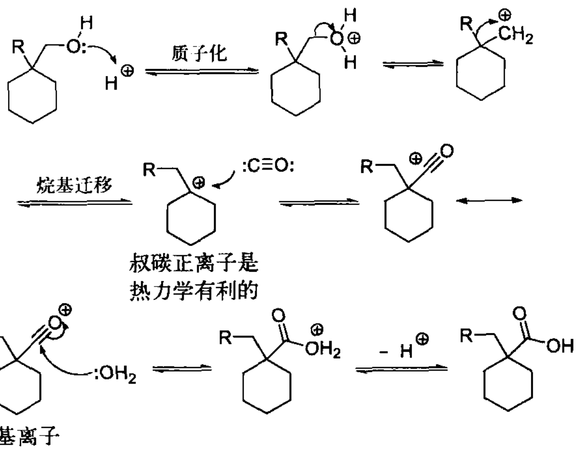
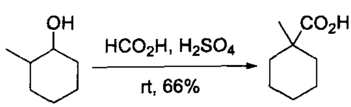
Koch-Haaf 羰基化反应

醇或烯烃和CO在强酸催化下生成叔取代羧酸的反应。

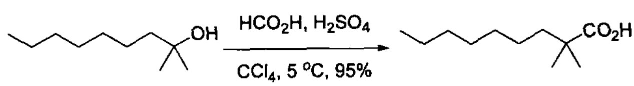




Example 1[3]



Example 2[5]



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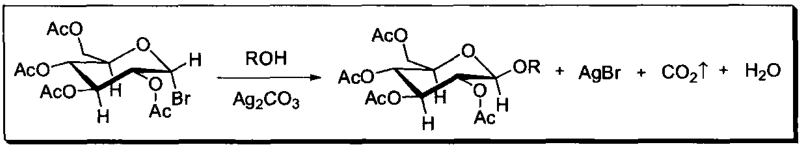
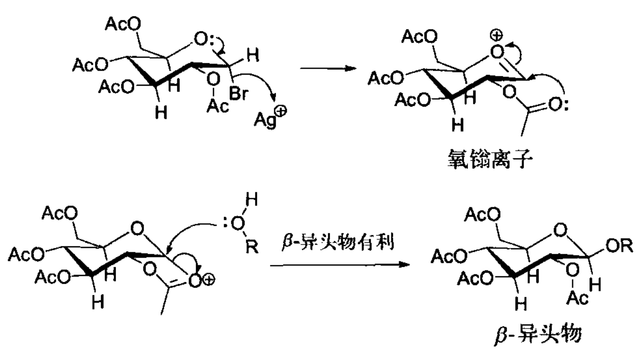
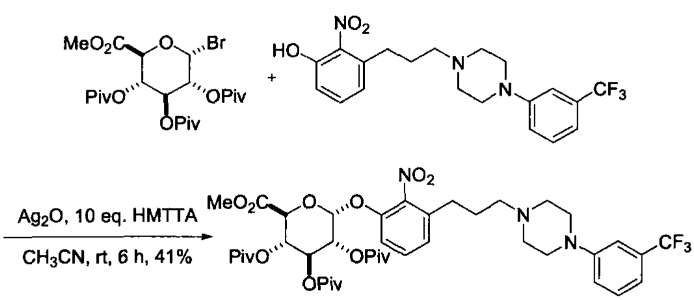
Koenig-Knorr 苷化反应

α-卤代糖在银盐影响下生成 *β*-苷的反应。

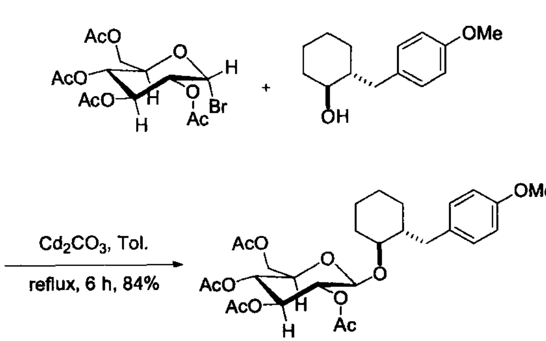




Example 1[7]

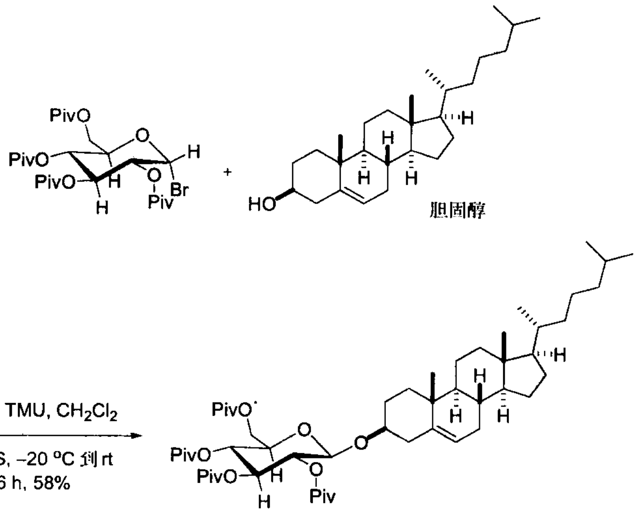


Example 2[8]



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

Example 3[9]



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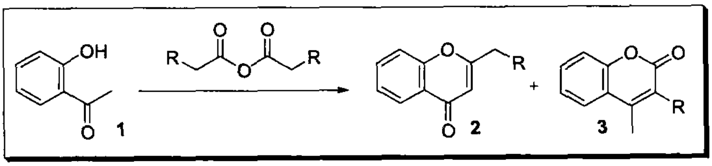
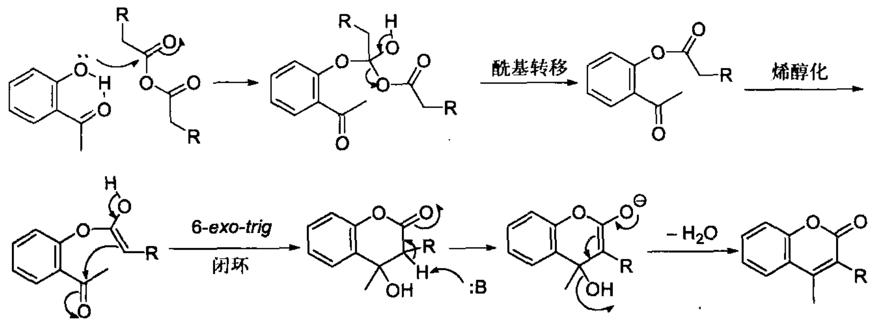
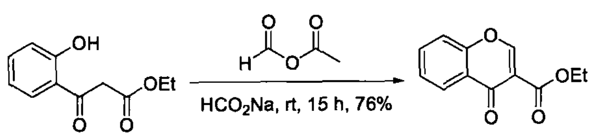
Kostanecki 反应

亦称Kostanecki-Robinson反应。**1**→**2**是Allan-Robinson反应(参见第8页),**1**→**3**是Kostanecki(酰基化)反应。

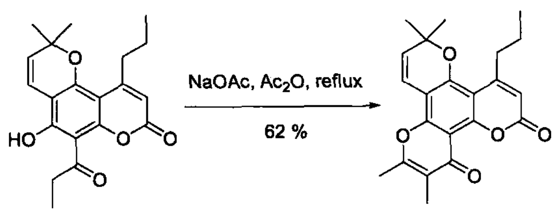




Example 1[2]



Example 2[3]



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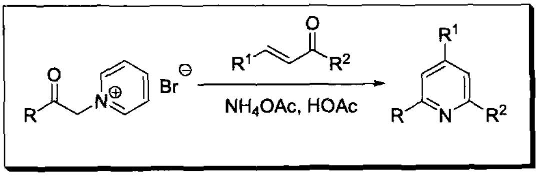
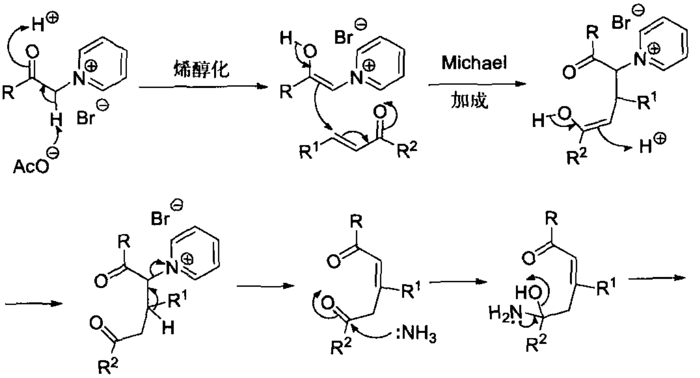
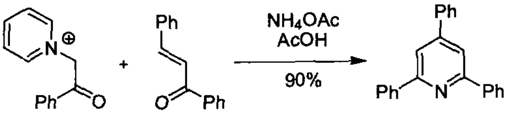
Krohnke 吡啶合成反应

α-吡啶甲基酮盐和 α, β-不饱和酮反应得到吡啶的反应。

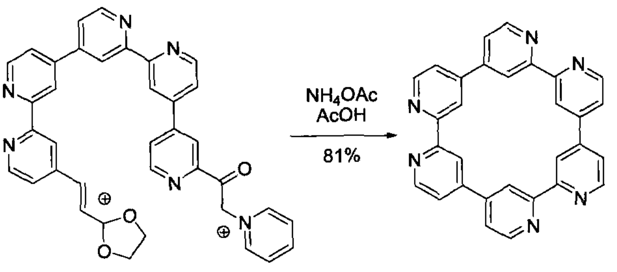




Example 1[1b]

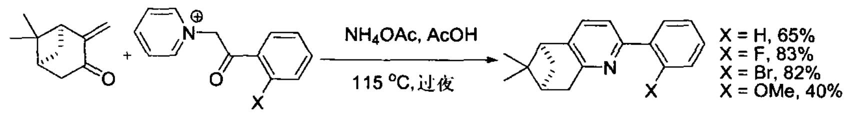


Example 2[4]



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

Example 3[6]



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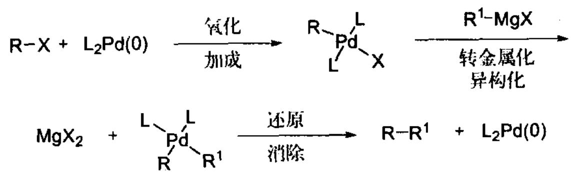
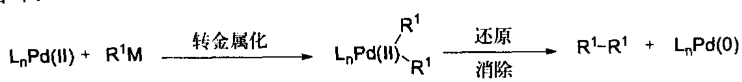
Kumada 交叉偶联反应

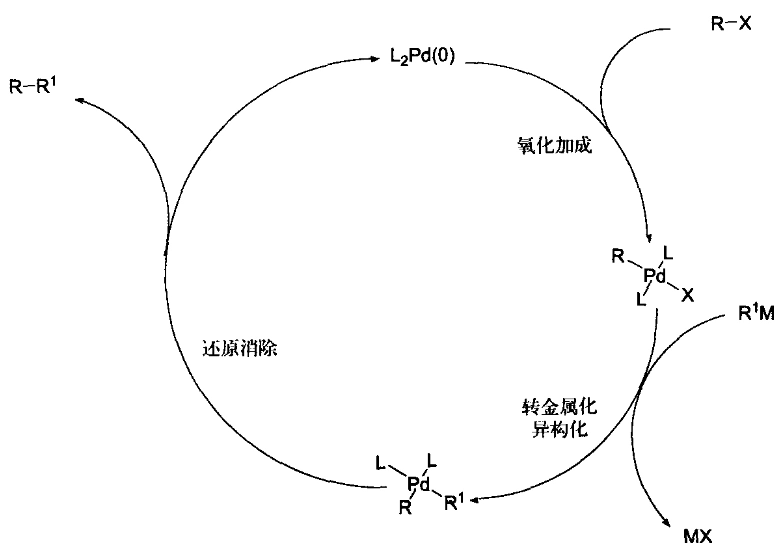
Kumada 交叉偶联反应（亦称Kharasch交叉偶联反应）原来是格氏试剂与芳基卤代烃或烯基卤代烃在Ni催化下的交叉偶联反应。后来逐渐发展成有机锂或有机镁与芳基卤代烃、烯基卤代烃或烷基卤代烃在Ni或Pd催化下的交叉偶联反应。Kumada交叉偶联反应与Negishi交叉偶联反应、Stille交叉偶联反应、Hiyama交叉偶联反应和Suzuki交叉偶联反应都属于同一个Pd催化的有机卤代烃、三氟磺酸酯和其他亲电物种与金属有机试剂之间的交叉偶联反应范畴。这些反应有如下所示的通用催化循环过程。Hiyama交叉偶联反应和Suzuki交叉偶联反应的机理和其他反应稍有不同，需要一步额外的转金属化反应的活化步骤。

$$\boxed{R\text{–}X + R^1\text{–}MgX \xrightarrow{Pd(0)} R\text{–}R^1 + MgX_2}$$



催化循环:





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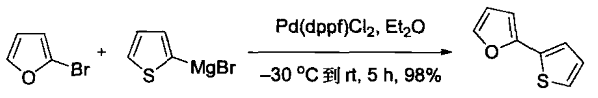
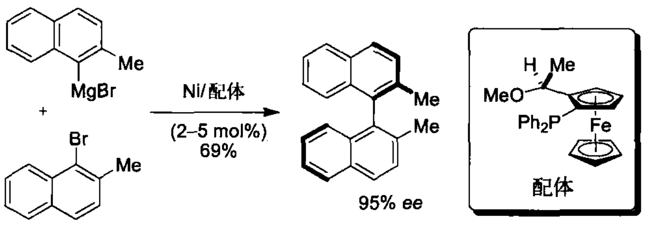
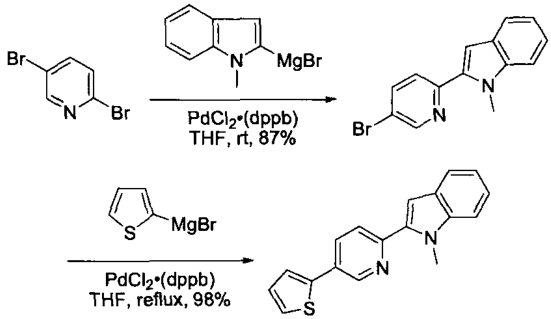
Example 1[2]



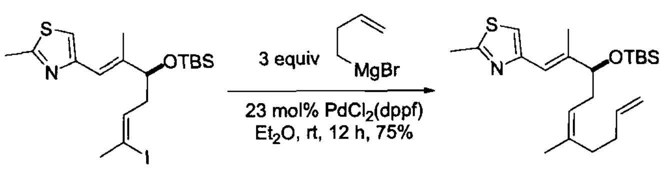
Example 2[3]



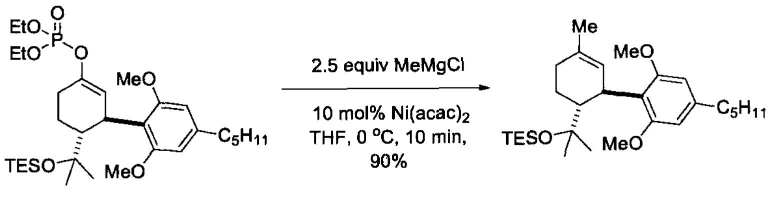
Example 3[5]



Example 4[8]



Example 5[9]



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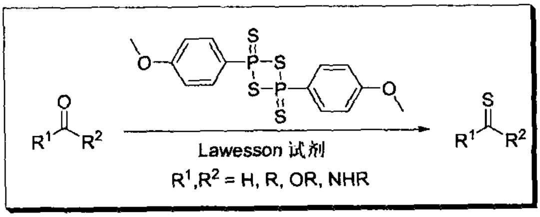
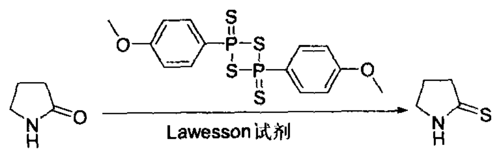
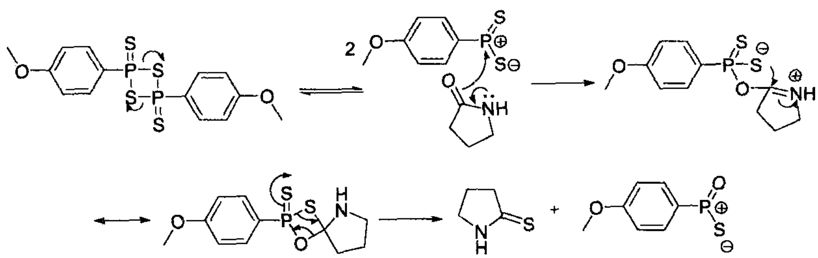
Lawesson 试剂

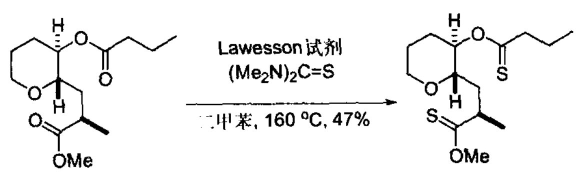
2,4-双(4-甲氧基苯基)-1,3-二硫-2,4-二硫代膦杂环丁烷可将醛、酮、酰胺、内酰胺、酯和内酯转化为相应的硫羰基化合物。



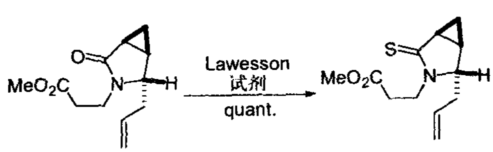




Example 1[4]



Example 2[5]



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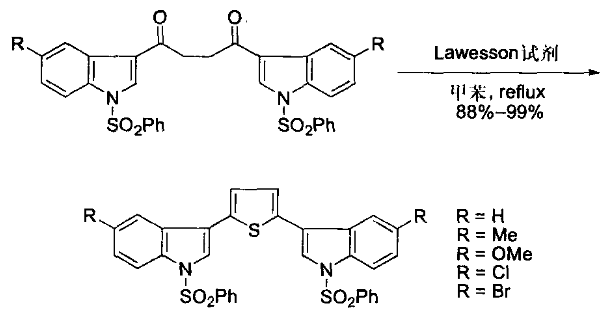
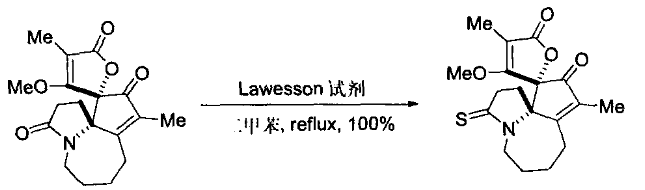
Example 3, 从二酮得到噻吩。[8]



Example 4[10]



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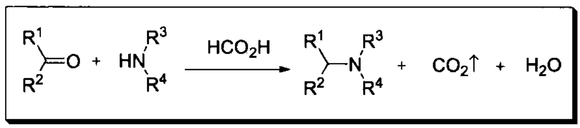
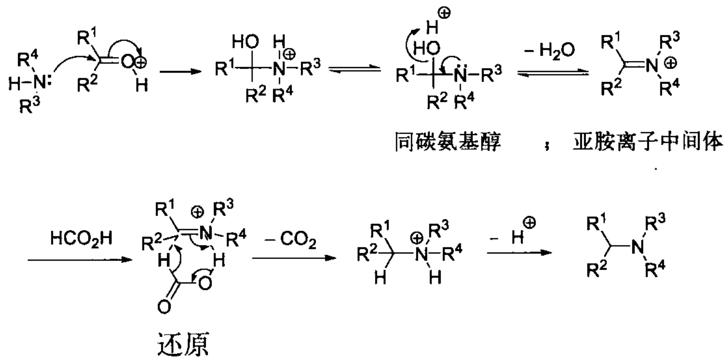
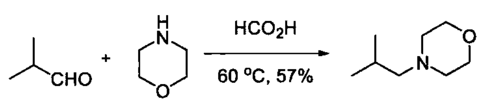
Leuckart-Wallach 反应

酮和胺在过量的相当于提供了一个负氢的还原剂甲酸存在下发生还原氨基化反应生成胺。用醛代替酮时，就是Eschweiler-Clarke还原氨基化反应（参见第210页）。

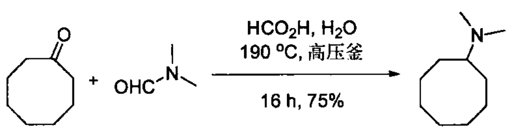




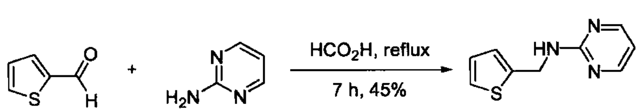
Example 1[4]



Example 2[6]

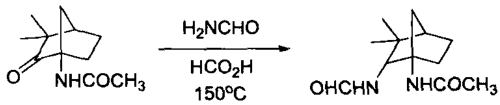


Example 3[7]

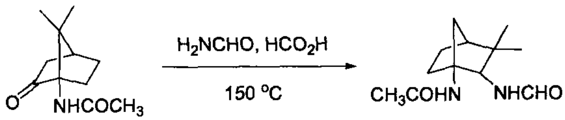


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_146,

Example 4[8]



一个新的经Leuckart-Wallach 反应再经 Wagner-Meerwein 迁移的转化反应



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2. 瓦拉赫生于普鲁士的柯尼斯堡，曾在武勒和霍夫曼指导下学习。在1889至1915年任哥廷根化学所主任，他写的一本书"萜烯和莰烯"乃是萜类化学研究的基础。瓦拉赫由于在脂环化学研究的贡献而获得1910年诺贝尔化学奖。
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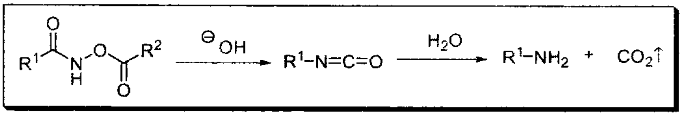
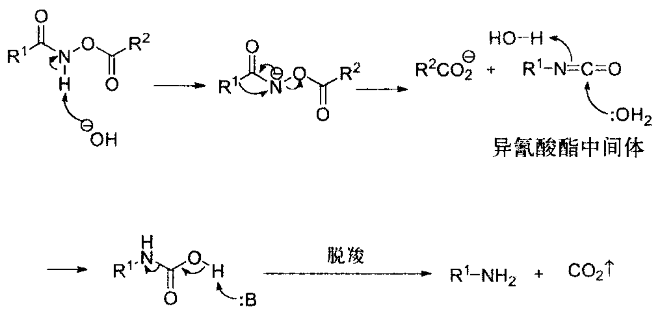
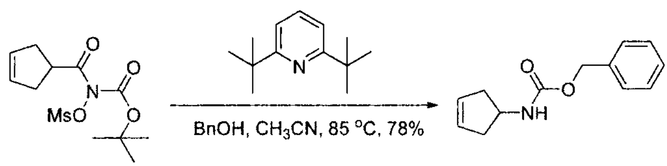
Lossen 重排反应

Lossen重排反应包括通过热或碱性环境下一个从异羟肟酸而得来的活化异羟肟酸酯重排而生成异氰酸酯的反应。异羟肟酸的活化可由*O*-酰基化、*O*-芳基化、*O*-磺酰化和氯化来实现。还有一些异羟肟酸可以由聚磷酸、碳二亚胺、硅基化和Mitsunobu反应条件来活化。Lossen重排反应的产物异氰酸酯可通过失去起始原料异羟肟酸中的一碳而进一步转化为脲或胺。

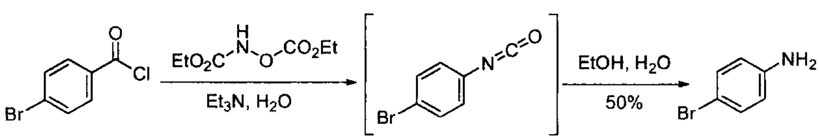




Example 1[6]

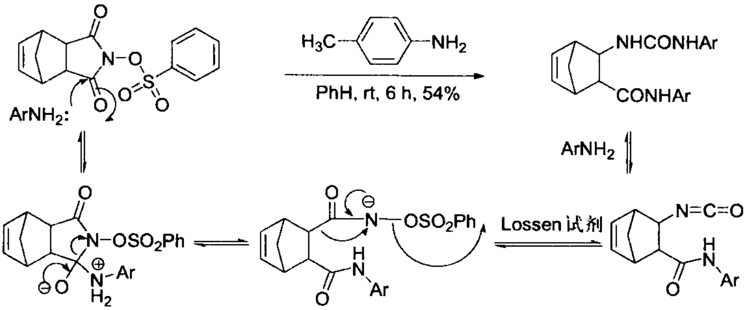


Example 2[7]

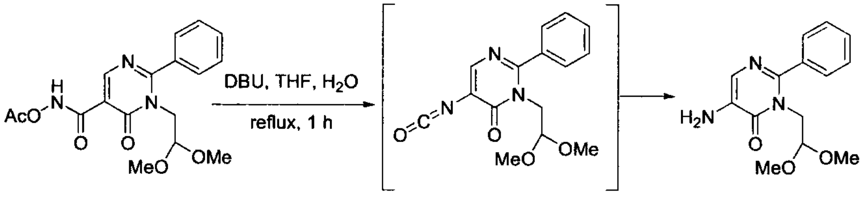


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_147,

Example 3[8]



Example 4[9]



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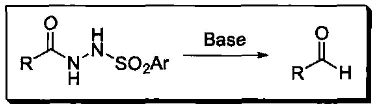
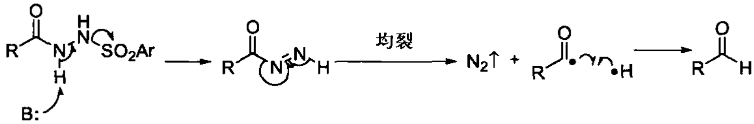
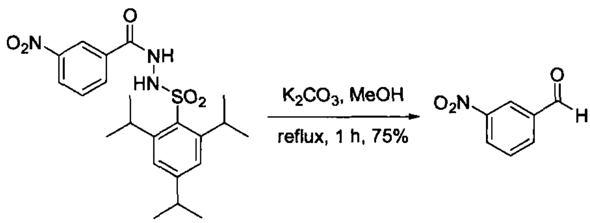
McFadyen-Stevens 反应

酰基苯磺酰肼用碱处理给出相应的醛。

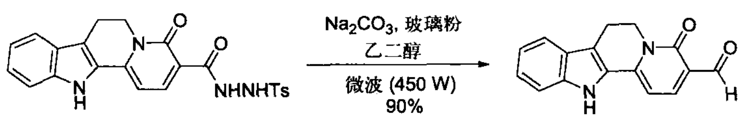




Example 1[8]



Example 2[10]



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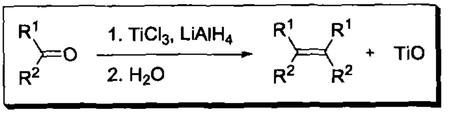
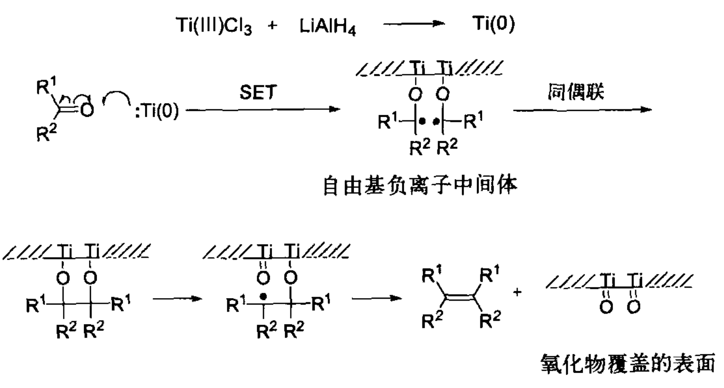
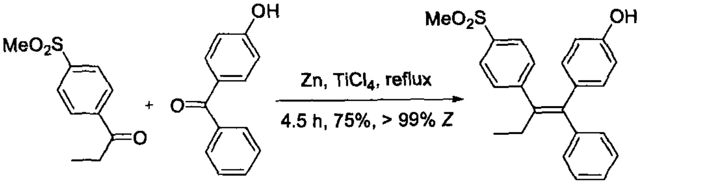
McMurry 偶联反应

羰基用得自$TiCl_3$-$LiAlH_4$的如Ti(0)一类低价钛进行单电子机理的烯基化反应。

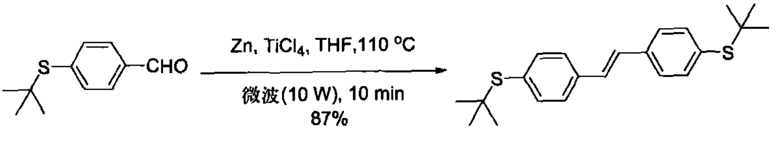




Example 1, 交叉-McMurry 偶联[7]

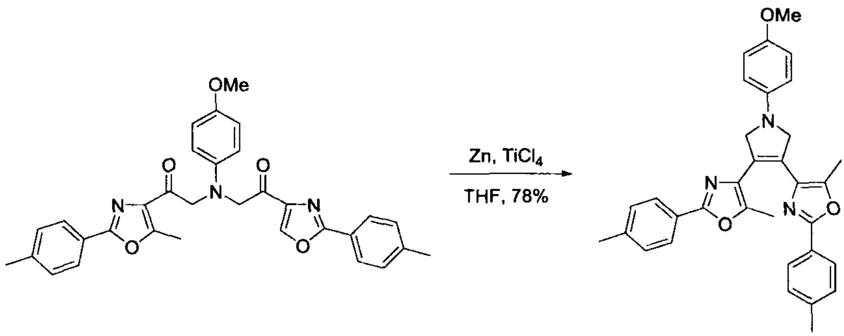


Example 2, 同-McMurry 偶联[8]

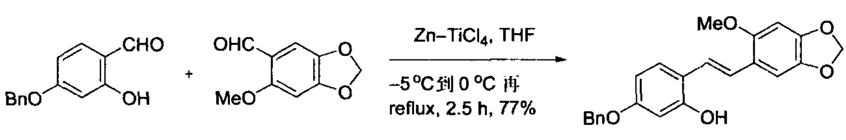


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_149,

Example 3, 交叉-McMurry 偶联[9]



Example 4, 交叉-McMurry 偶联[10]



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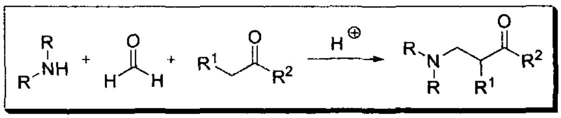
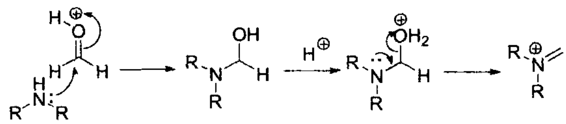
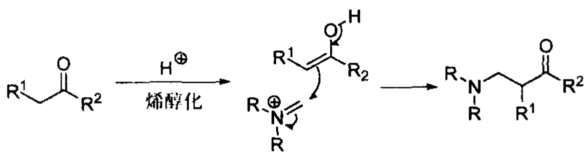
Mannich 反应

由胺、醛和带有酸性亚甲基成分的化合物形成的三组分发生的氨甲基化反应。

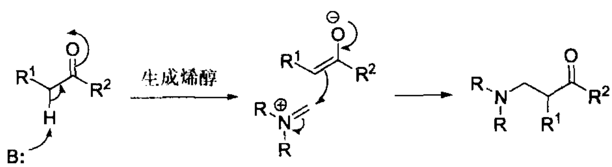




当 R = Me, $^{+}Me_2N{=}CH_2$ 盐称 *Eschenmoser's* 盐(参见第206页)

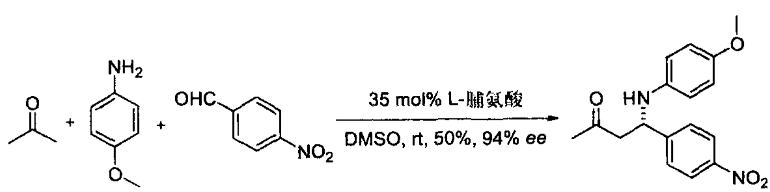


Mannich 反应也可在碱性条件下进行:

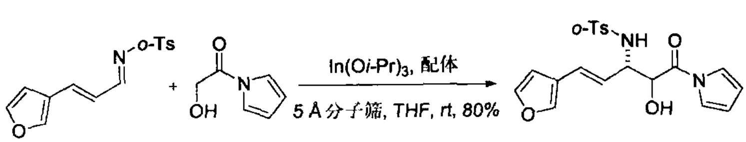


Mannich 碱

Example 1, 不对称Mannich 反应[2]



Example 2, 不对称 Mannich类反应[9]



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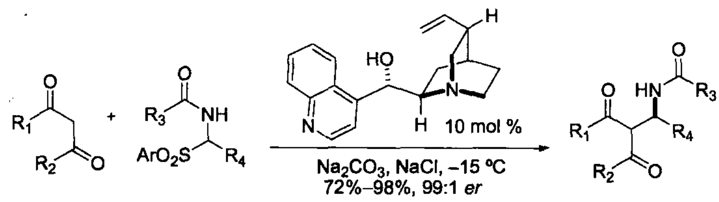
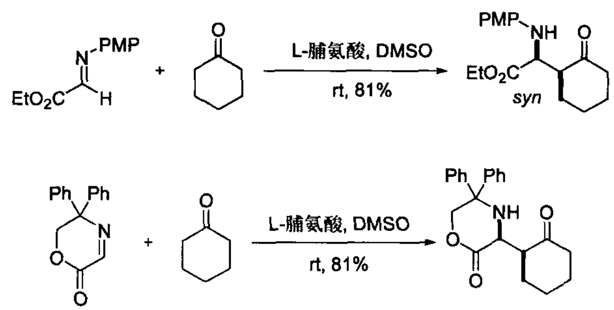
Example 3, 不对称 Mannich 反应[10]



Example 4[11]



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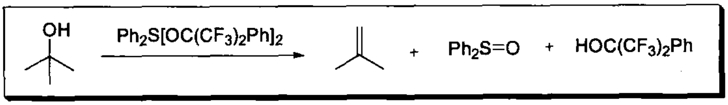
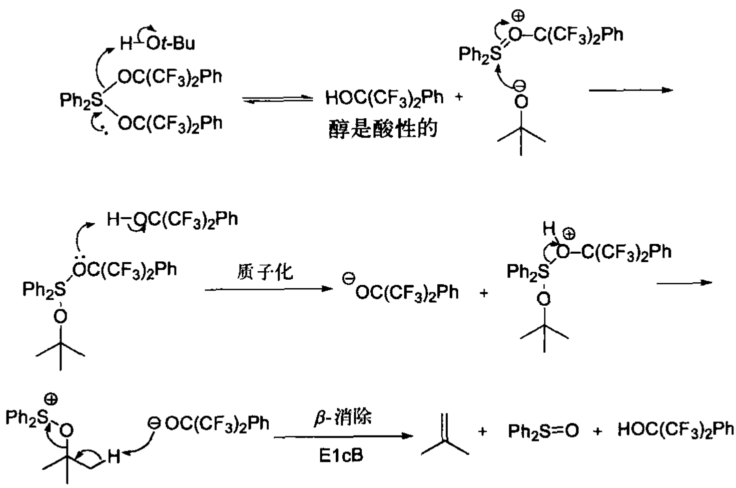
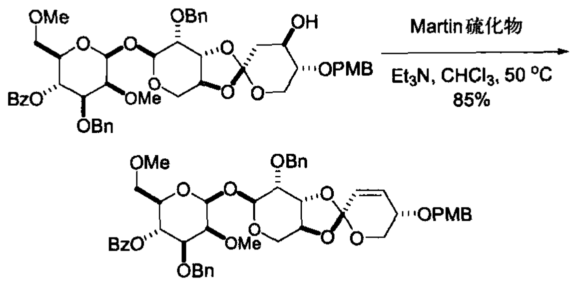
Martin 硫烷脱水剂

仲醇和叔醇脱水给出烯烃，而伯醇脱水后生成醚。参见第84页上的Burgess脱水剂。

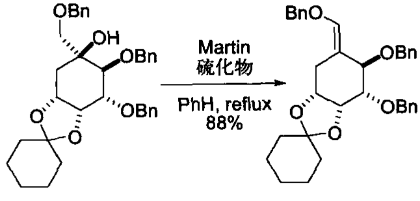




Example 1[5]

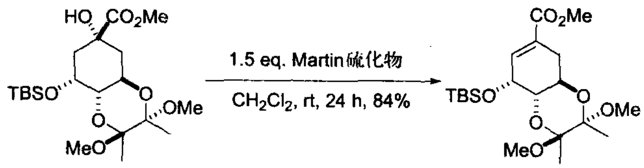


Example 2[6]

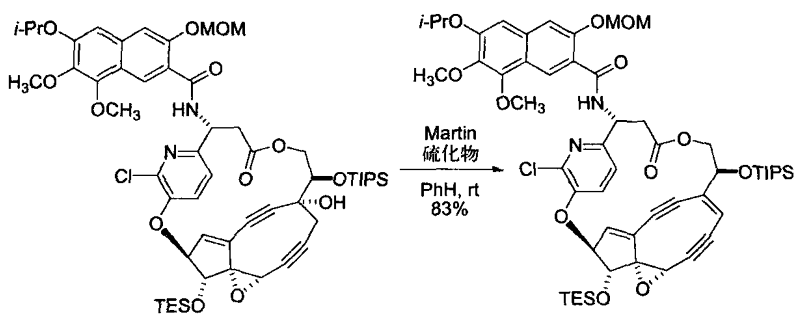


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_151,

Example 3[7]



Example 4[9]



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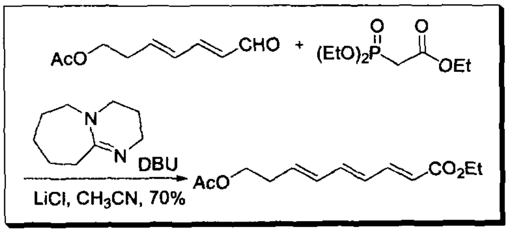
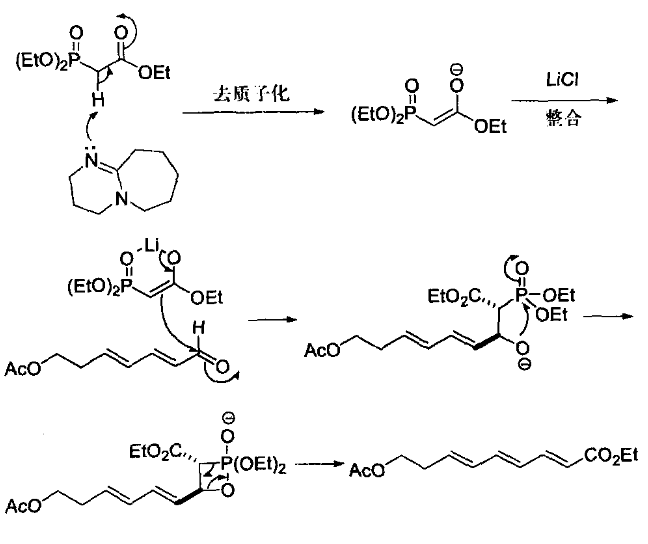
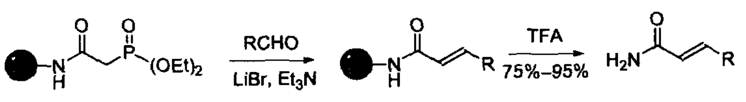
Masamune-Roush 反应

适于在Horner-Emmons反应中对碱敏感的醛和磷酸酯。反应需用到 α -酮基或 α -烷氧羰基磷酸酯。

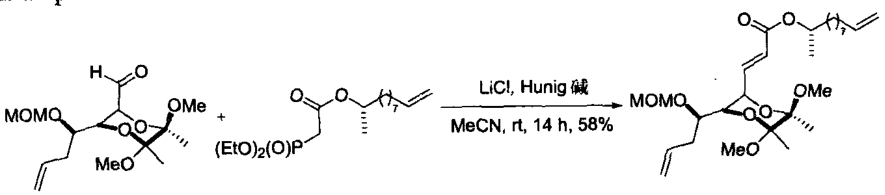




Example 1[5]

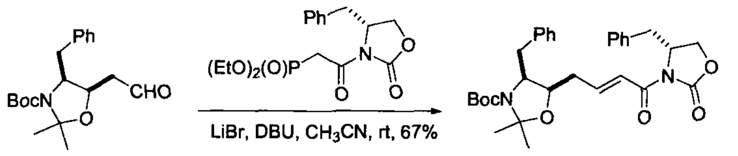


Example 2[6]

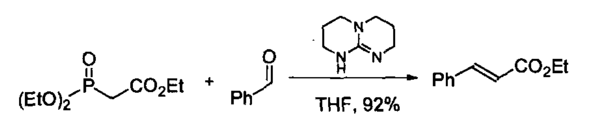


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_152,

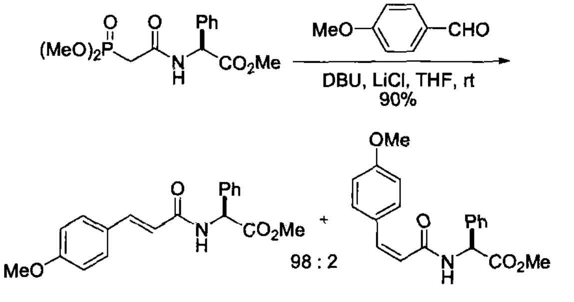
Example 3[7]



Example 4[8]



Example 5[10]



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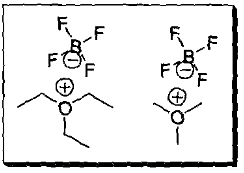
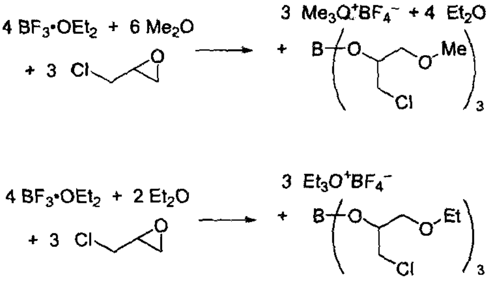
Meerwein 盐

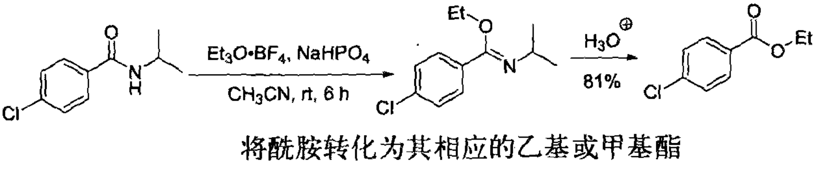
亦称Meerwein试剂，即三甲基氧鎓离子四氟化硼或三乙基氧鎓离子四氟化硼。命名来自其发现者Hans Meerwein。[1]这些三烷基氧鎓离子盐是强烷基化试剂。



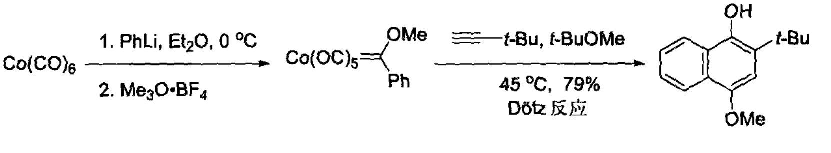
制备:[2]



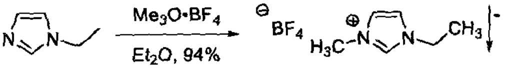
Example 1, Meerwein试剂是一种非常好的O-烷基化试剂:[5]



Example 2, 金属-甲基化[4]

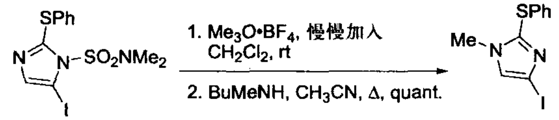


Example 3, N-烷基化，产物是离子液体[8]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_153,

Example 4, *N*-甲基化 [9]



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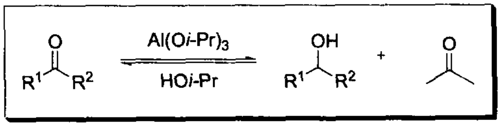
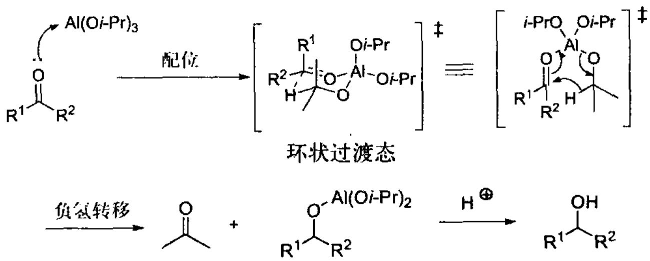
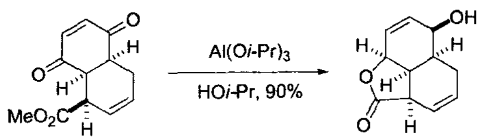
Meerwein-Ponndorf-Verley 还原反应

在^{i}PrOH溶液中用Al(O*i*-Pr)$_3$将酮还原为相应的醇。逆反应称Oppernauer氧化反应。

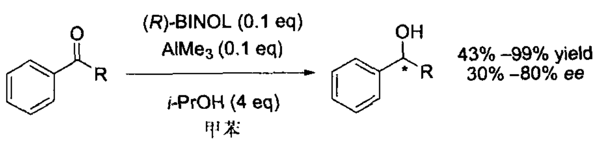




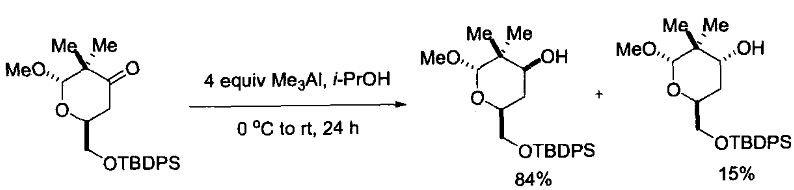
Example 1[2]



Example 2[4]

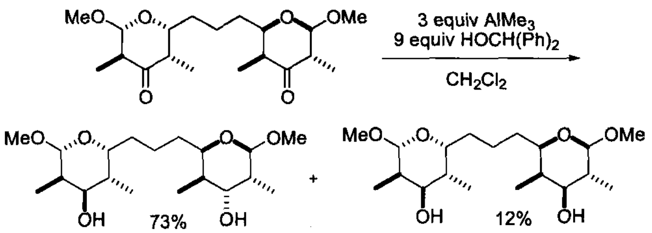


Example 3[7]



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

Example 4[9]



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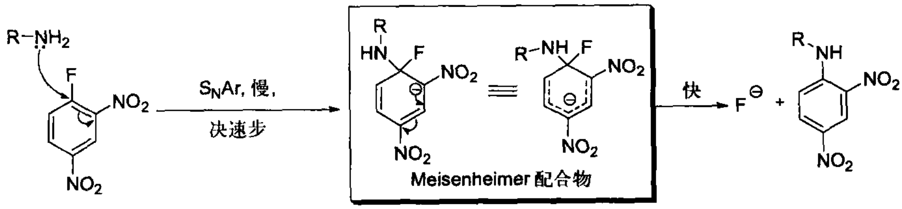
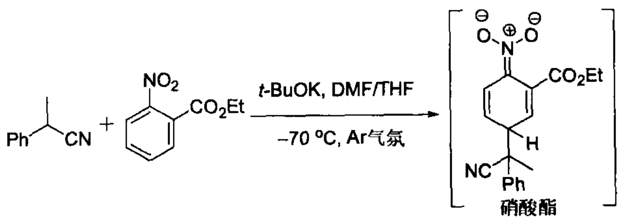
Meisenheimer 配合物

亦称Meisenheimer-Jackson盐，是一些S_NAr反应过程中稳定的中间体。

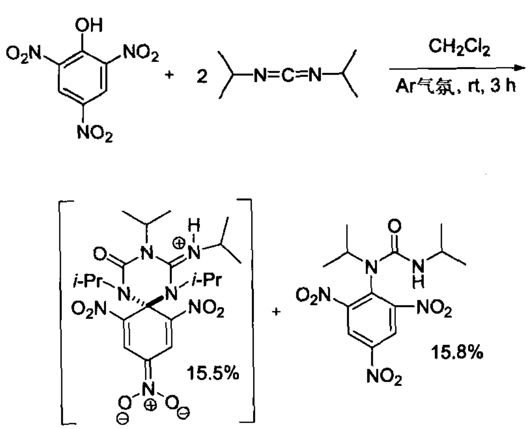


Sanger试剂, *ipso* 进攻 *ipso* 取代

Example 1[7]



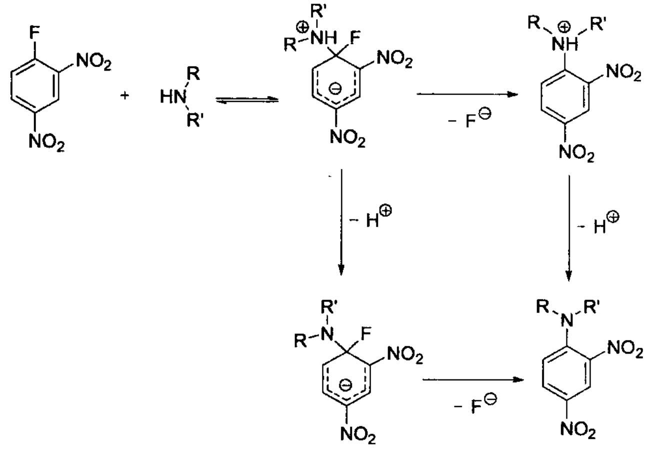
Example 2[9]



用Sanger试剂的反应比用其它相应的氯代、溴代或碘代二硝基苯为试剂的反应快。氟是最强的吸电子取代基，含氟的Meisenheimer配合物是非常稳定的。反应速率与离去基无关。

J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_155,

Example 3[10]



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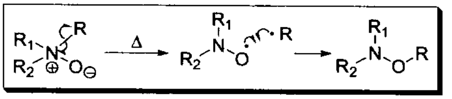
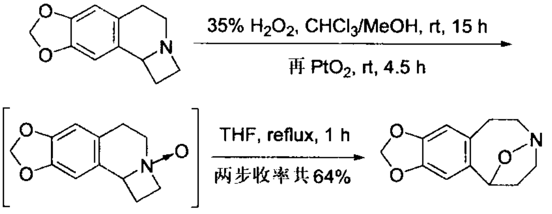
[1,2]-Meisenheimer 重排反应

叔胺的*N*-氧化物经[1,2]-σ 重排反应转化为取代羟胺。



Example 1[7]



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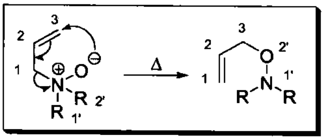
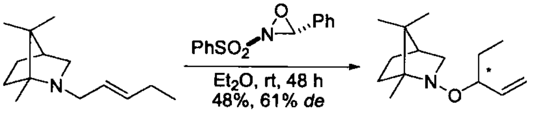
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_156,

[2,3]-Meisenheimer 重排反应

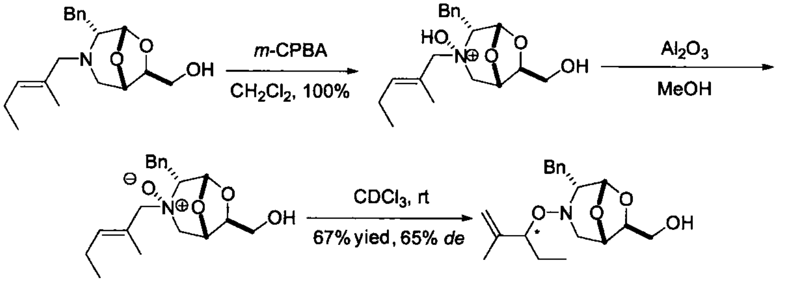
烯丙基叔胺的*N*-氧化物经[2,3]-σ 重排反应转化为*O*-烯丙基羟胺。



Example 1[7]



Example 2[8]



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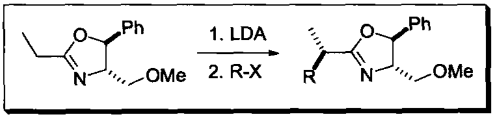
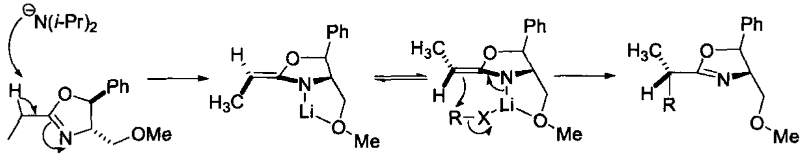
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_157,

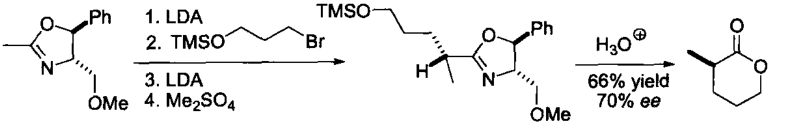
Meyers 噁唑啉方法

在亲核加成和取代反应中作为活化基团和/或螯合剂的手性噁唑啉可用于构筑不对称C—C键。

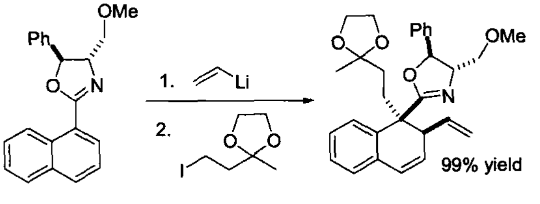




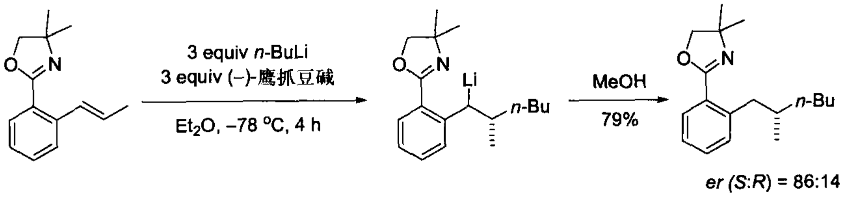
Example 1[2]



Example 2[5]



Example 3[9]



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

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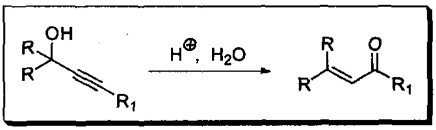
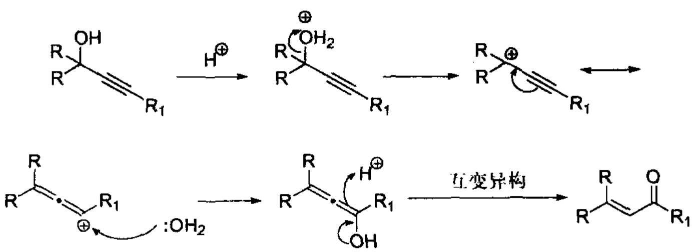
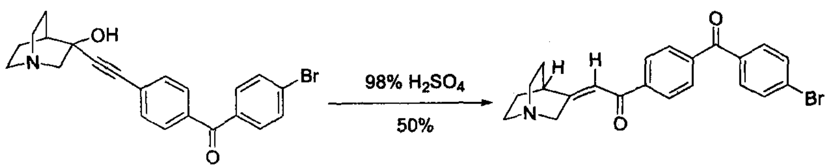
Meyers-Schuster 重排反应

α-炔基仲醇或叔醇经1,3-迁移异构为α，β-不饱和羰基化合物。端基炔基导致醛，链间炔基导致酮。参见第480页上的Rupe重排反应。

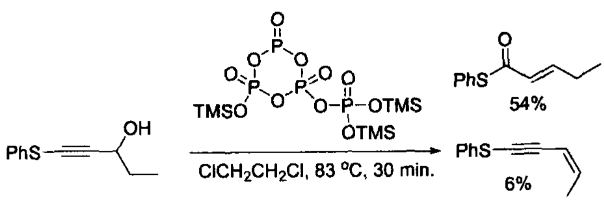




Example 1[6]



Example 2[7]



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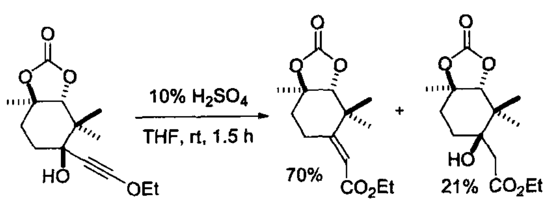

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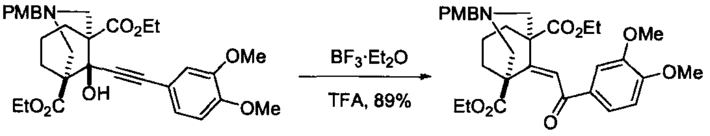
Example 4[9]



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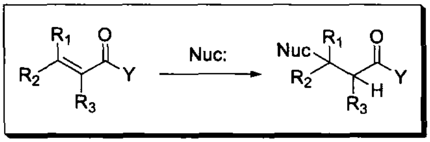
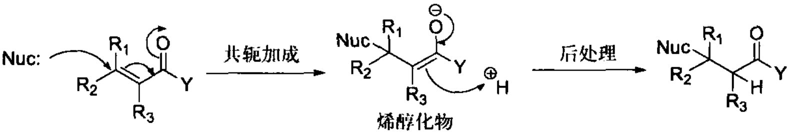
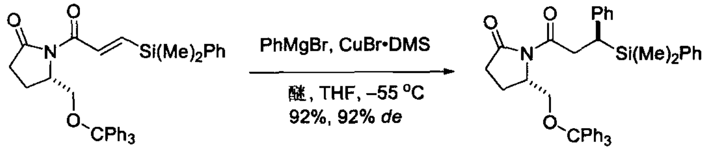
Michael 加成反应

亦称共轭加成反应，是亲核物种对 α，β-不饱和体系进行的1,4-加成反应。

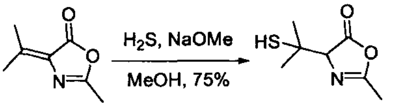




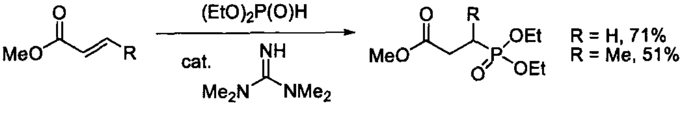
Example 1, 不对称 Michael 加成[2]



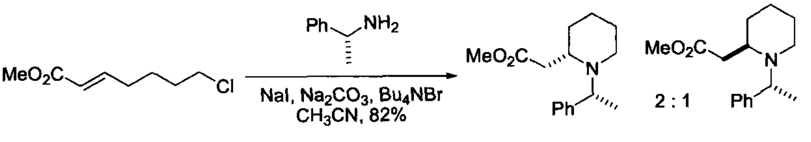
Example 2, 含硫的 Michael 加成[3]



Example 3, 含磷的 Michael 加成[7]



Example 4, 不对称含氮的 Michael 加成[9]



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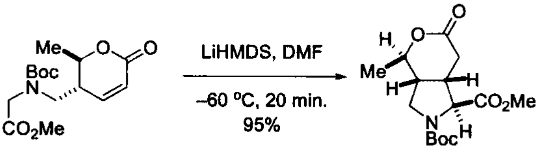
Example 5, 分子内 Michael 加成[10]



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1. Michael, A. *J. Prakt. Chem.* **1887**, *35*, 349. 迈克尔（Arthur Michael, 1853-1942）出生于纽约州的布法罗，跟过本生、 霍夫曼、武慈和门捷列夫搞研究，但从未去追求学位。回到美国后任塔夫茨大学（Tufts University）的化学教授并在那儿与他最出色的学生及那个时期少有的女性有机化学家Helen Abbott喜结良缘。迈克尔夫妇在马萨诸塞州的牛顿中心建立了私人实验室并在该实验室发现了Michael加成反应。
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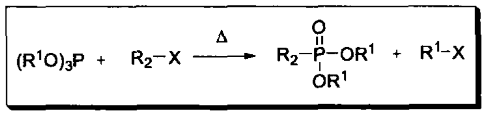
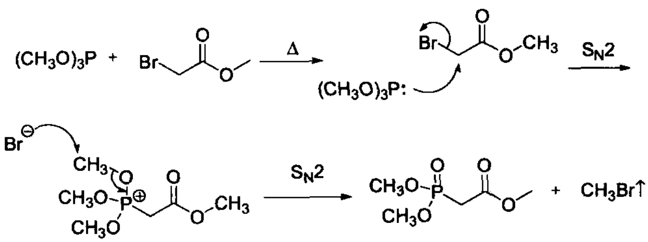
Michaelis-Arbuzov 膦酸酯合成反应

烷基卤和亚磷酸酯反应生成磷酸酯。



R^1 = 烷基, *etc.*; R_2 = 烷基, 酰基, *etc.*; X = Cl, Br, I

如:



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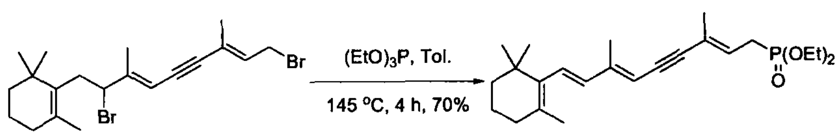

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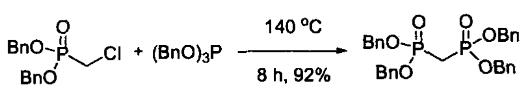
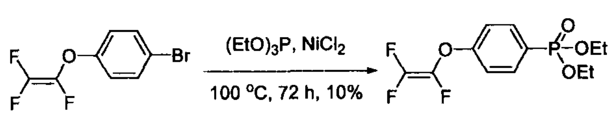
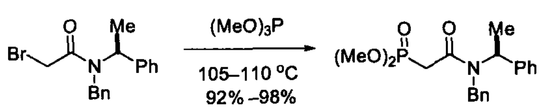


Example 3[7]

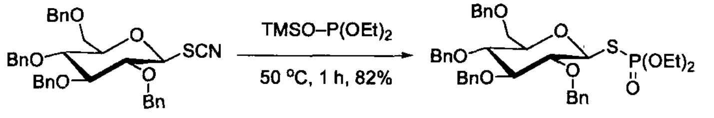


Example 4[9]



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

Example 5[10]



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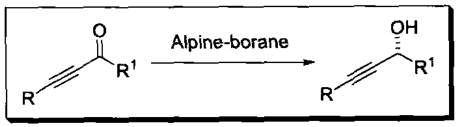
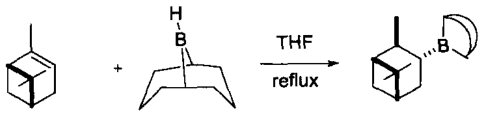
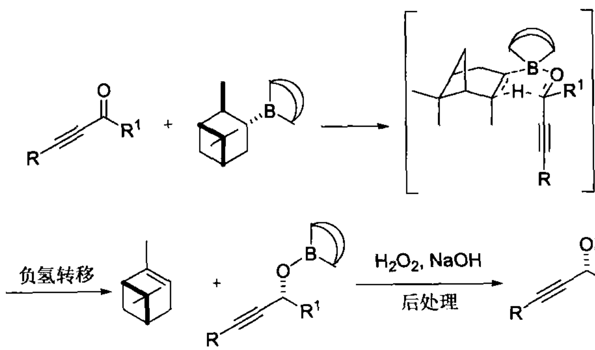
Midland 还原反应

用蒎基硼烷（Alpine-borane®）对酮进行的不对称还原。

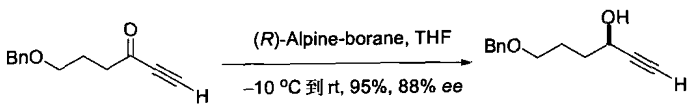




(1*R*)-(+)-α-蒎烯　　9-BBN　　(*R*)-Alpine-borane



Example 1[6]



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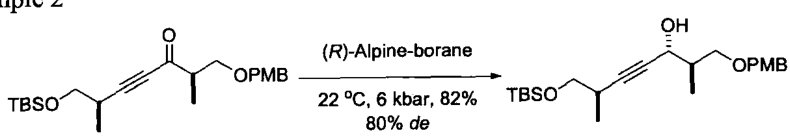
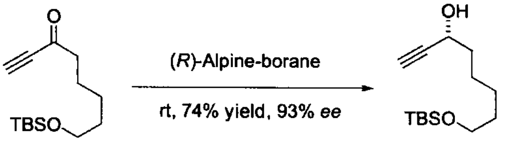


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_162,

Example 3[8]



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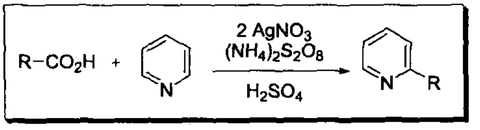
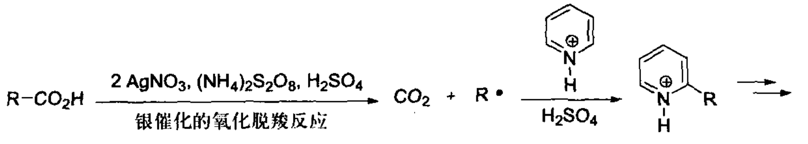
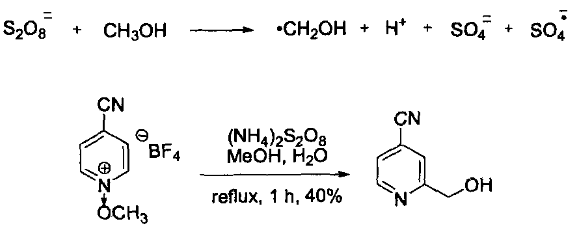
Minisci 反应

缺电子杂芳香族化合物进行自由基C－C键的构筑反应。反应需要一个亲核自由基对质子化杂芳香核的分子间加成。

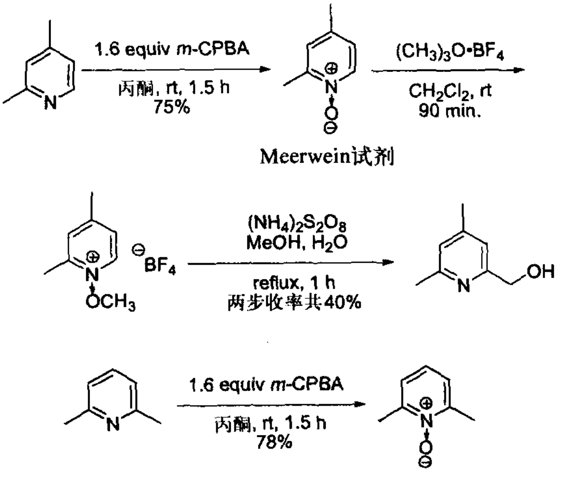




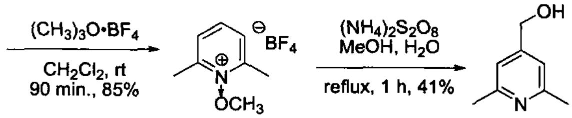
Example 1[4]



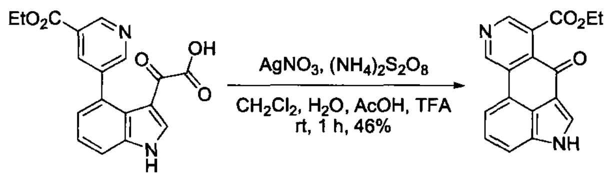
Example 2[5]



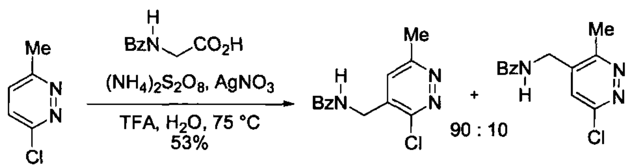
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_163,



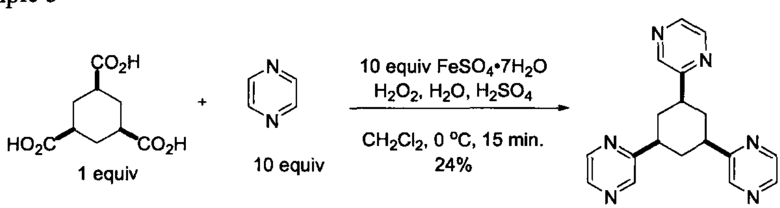
Example 3, 分子内 Minisci 反应[6]



Example 4[7]



Example 5[10]



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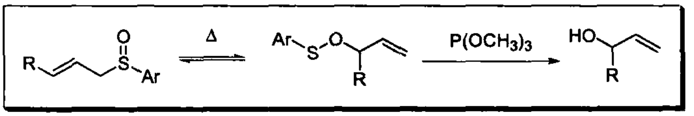
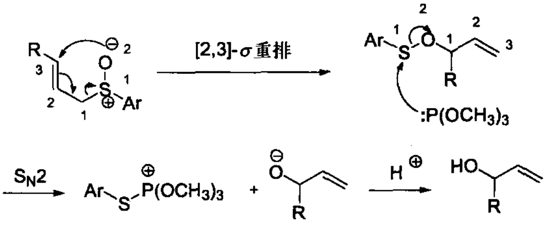
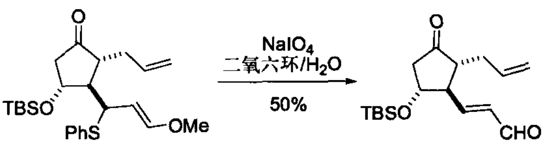
Mislow-Evans 重排反应

烯丙基亚砜经[2,3]-σ 重排反应转化为烯丙基醇。

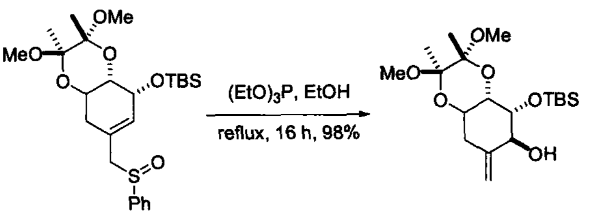




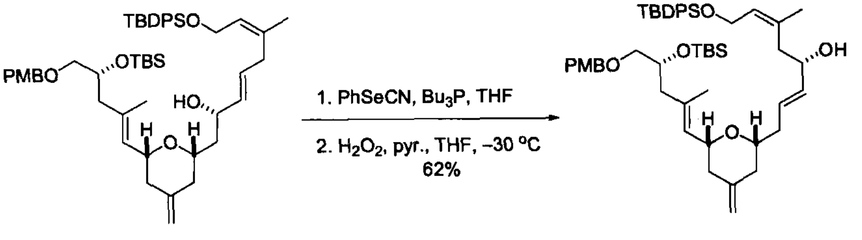
Example 1[2]



Example 2[7]



Example 3, Seleno-Mislow-Evans反应[8]



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

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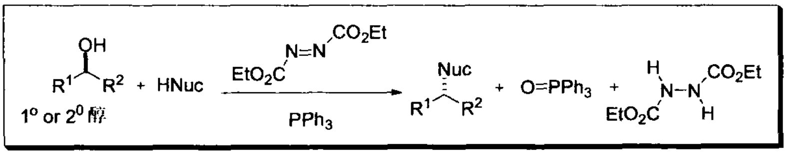
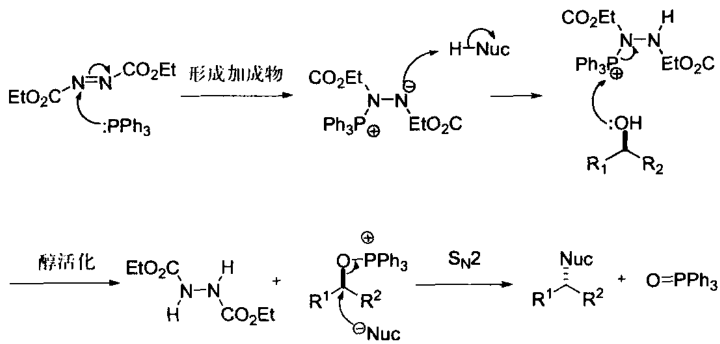
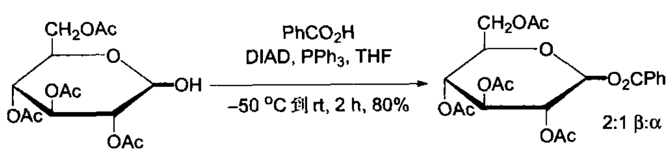
Mitsnobu 反应

用二取代的偶氮二羧酸酯（起自偶氮二羧酸二乙酯，DEAD）和三取代膦（起自 PPh_3）使醇在进行 S_N2.反应时发生构型反转。

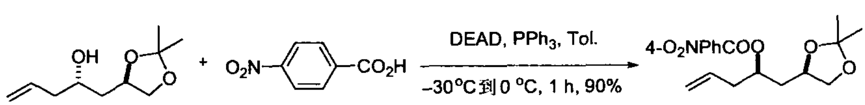




Example 1[2]



Example 2[3]



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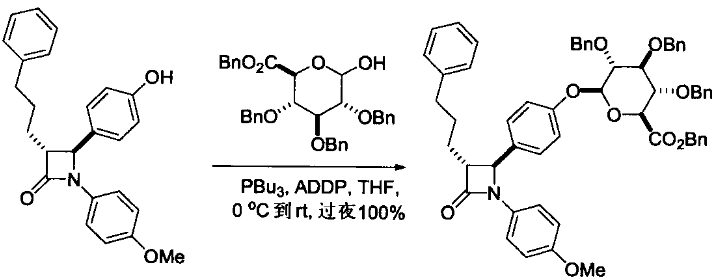
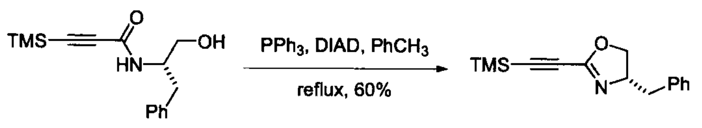
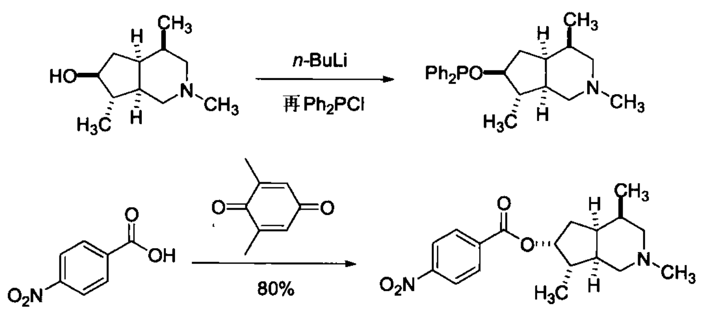
Example 3, 醚的生成[6]



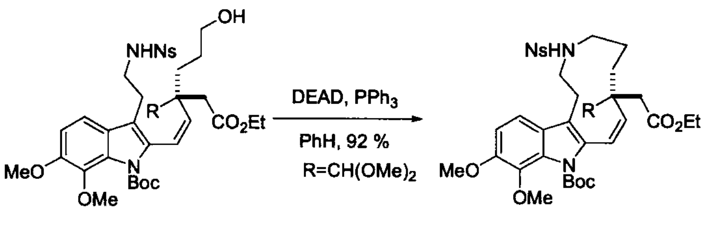
Example 4[7]



Example 5[8]



Example 6, 分子内 Mitsunobu 反应[9]



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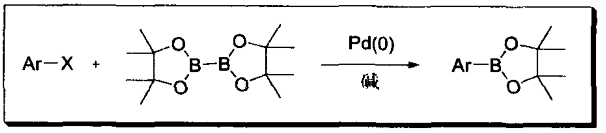
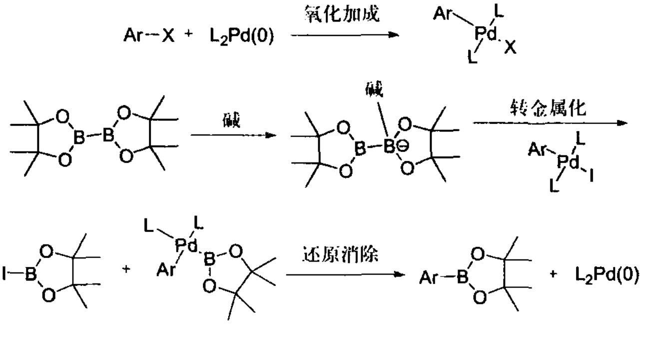
Miyaura 硼基化反应

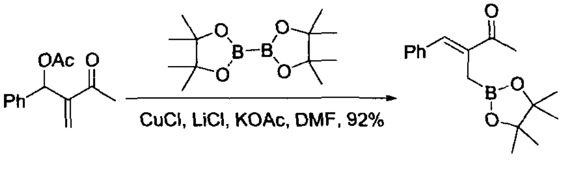
Pd催化的芳基卤和双硼试剂反应生成芳基硼酸酯。亦称Hosomi-Miyaura硼基化反应。



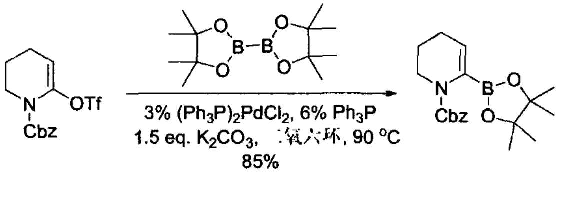
X = I, Br, Cl, OTf.



Example 1[7]



Example 2[8]



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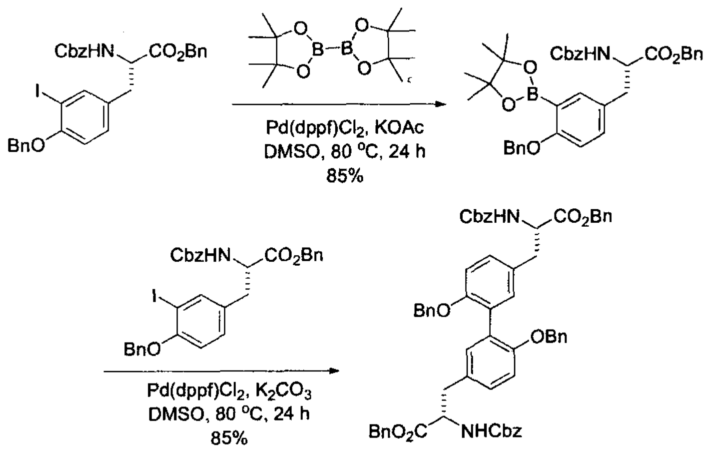
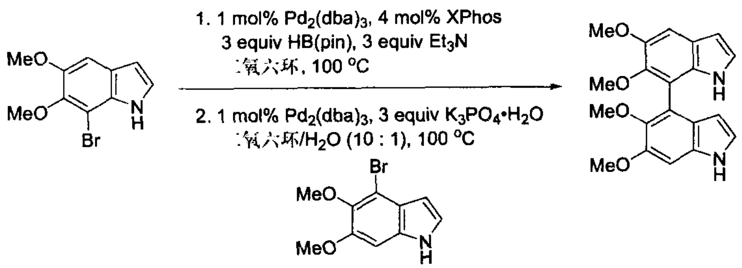
Example 3[9]



Example 4，一锅煮合成联吲哚[10]



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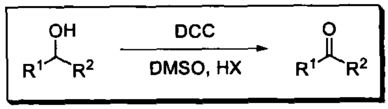
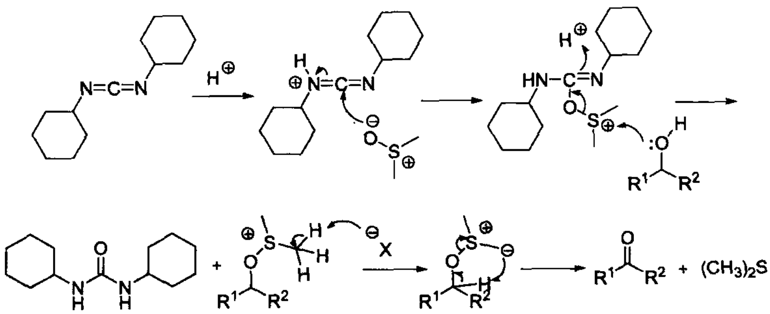
Moffatt 氧化反应

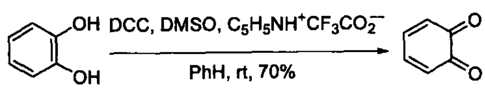
用DCC和DMSO对醇进行氧化反应。又名Pfitzener-Moffatt氧化反应。



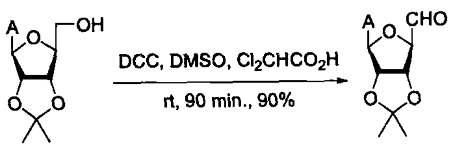


1,3-二环己基脲

Example 1[2]



Example 2[8]



A=腺苷

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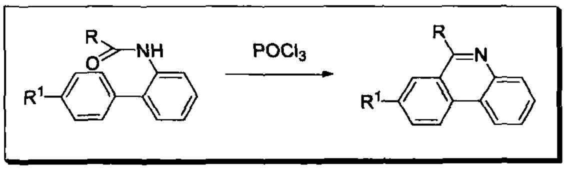
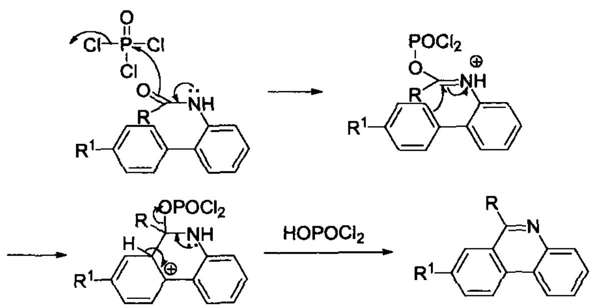
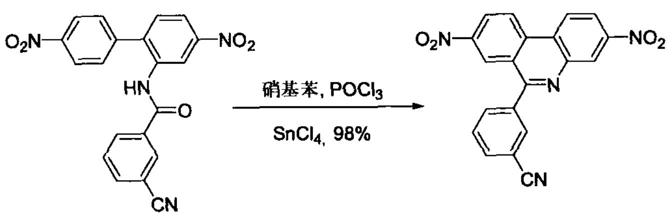
Morgan-Walls 反应

N-酰基邻氨基联苯用$POCl_3$在硝基苯中回流发生闭环脱水而环合成菲啶。



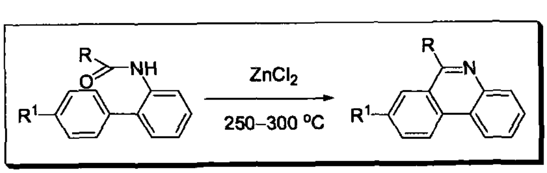


Example 1[6]

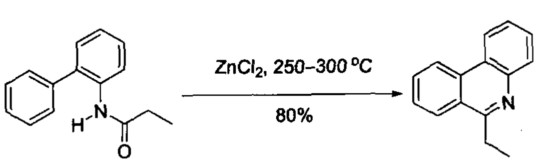


Pictet-Hubert 反应

Morgan-Walls反应是Pictet-Hubert反应的变异，后者的菲啶是由*N*-酰基邻氨基联苯用$ZnCl_2$加热到250 ~ 300℃发生闭环脱水而环合成的。



Example 2[4]



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

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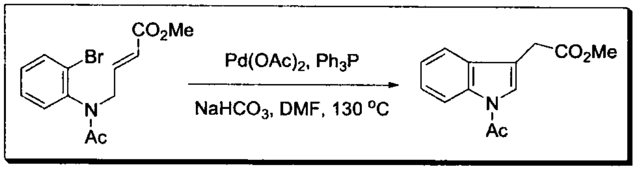
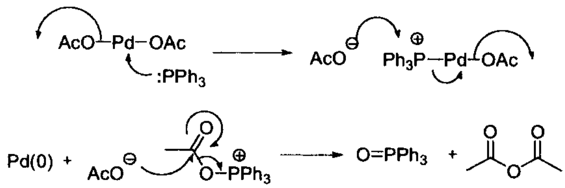
Mori-Ban 吲哚合成反应

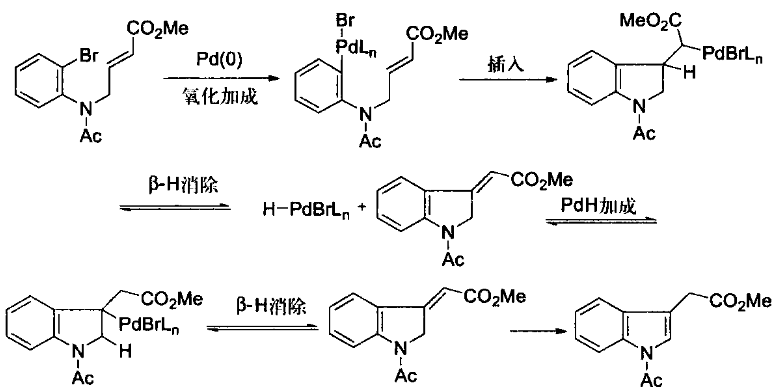
通过带侧基烯烃的邻氯苯胺进行的分子内Heck反应合成吲哚。



用Ph_3P还原 $Pd(OAc)_2$ 为 Pd(0)：



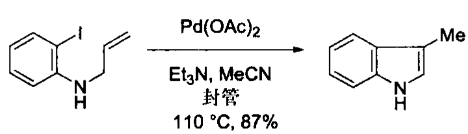
Mori–Ban 吲哚合成：



Pd(0)的产生：

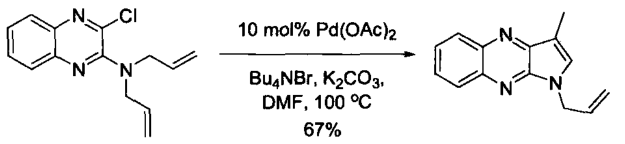
$$H\text{–}PdBrL_n + NaHCO_3 \longrightarrow Pd(0) + NaBr + H_2O + CO_2\uparrow$$

Example 1[1a]

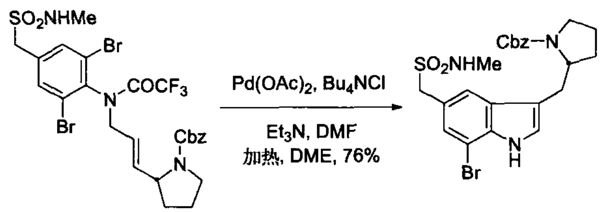


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_169,

Example 2[4]



Example 3[7]



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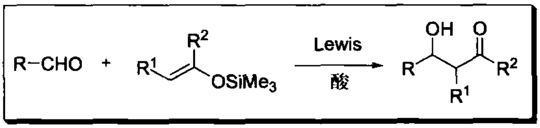
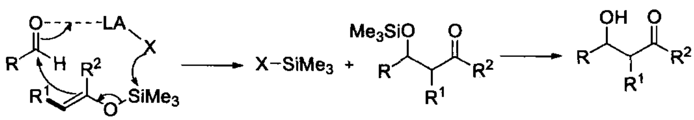
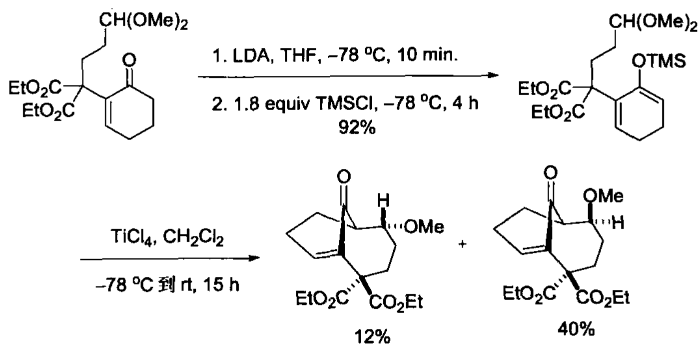
Mukaiyama aldol 反应

Lewis 酸催化的醛和硅基烯醇醚间进行的 aldol 反应。

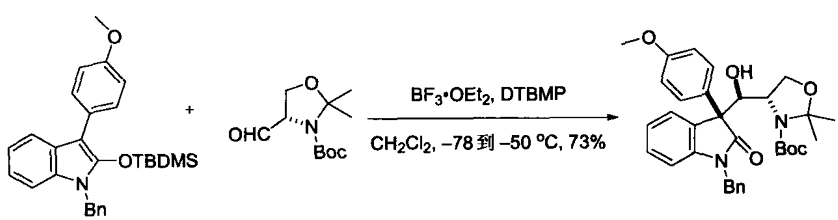




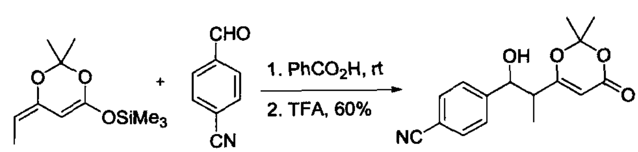
Example 1, 分子内 Mukaiyama aldol 反应[3]



Example 2, Mukaiyama aldol 反应[7]

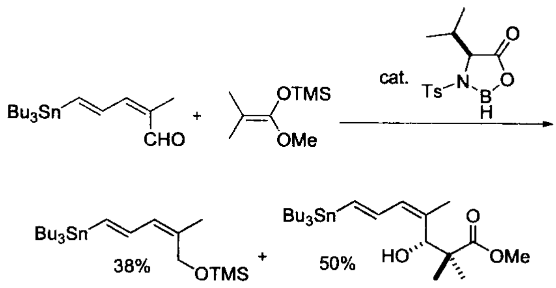


Example 3, 烯基化的 Mukaiyama aldol 反应[8]

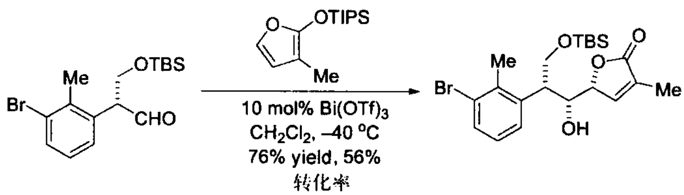


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_170,

Example 4, 不对称 Mukaiyama aldol 反应[10]



Example 5, Mukaiyama aldol 反应[12]



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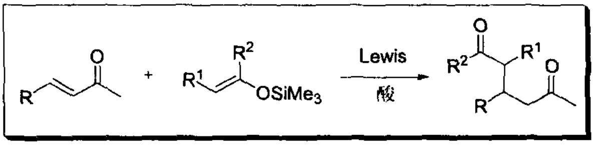
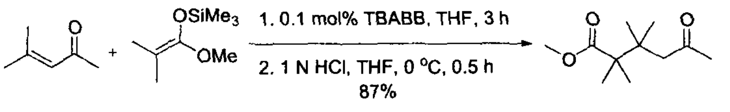
Mukaiyama Michael 加成反应

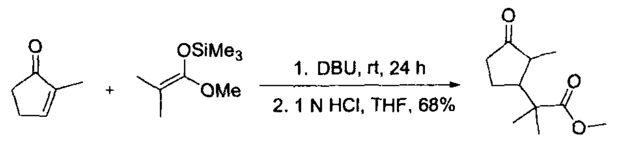
Lewis酸催化的硅基烯醇醚对 α , β -不饱和体系进行的Michael加成反应。



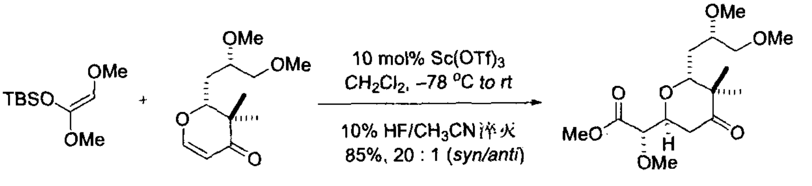
Example 1[2]



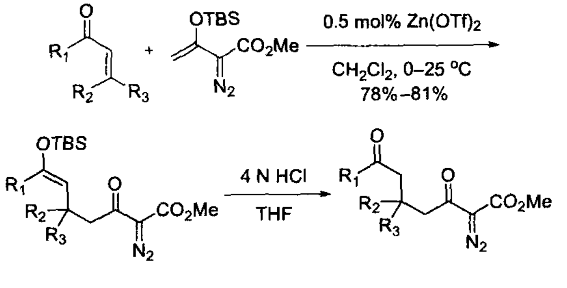
Example 2[5]



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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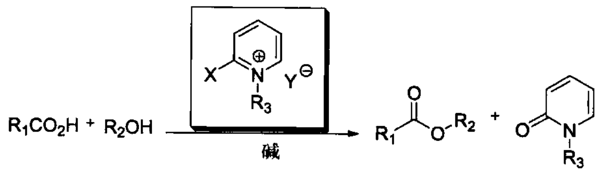
Mukaiyama 试剂

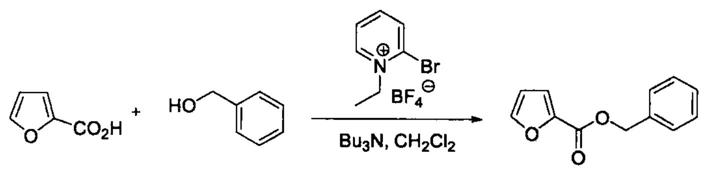
Mukaiyama试剂，即2-氯-1-甲基吡啶鎓碘盐一类试剂，用于酯化或酰胺的生成。

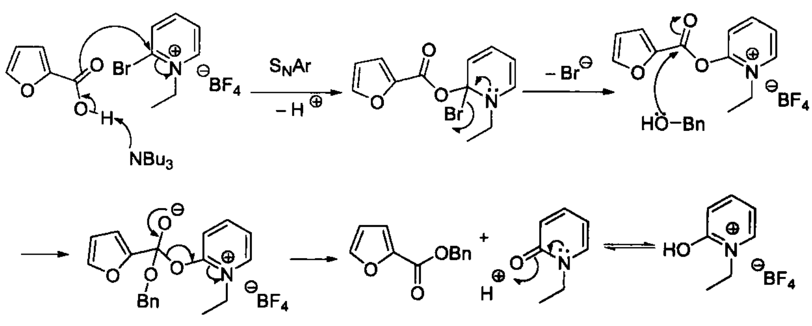
通式：



X = F, Cl, Br

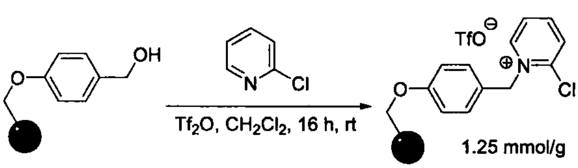
Example 1[1c]



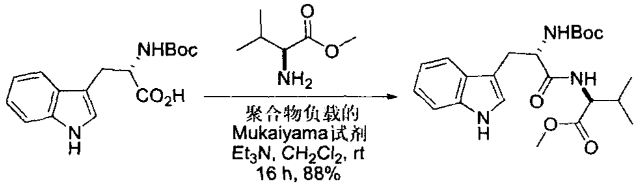


用Mukaiyama试剂来合成酰胺有相似的机理。[1d]

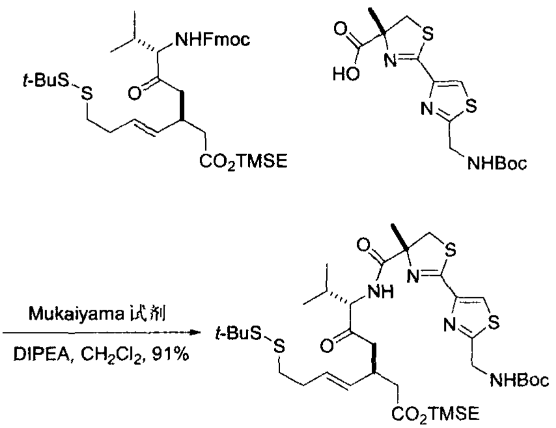
Example 2, 聚合物负载的Mukaiyama试剂[5]



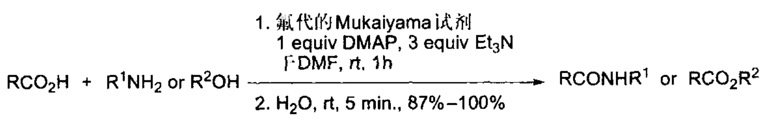
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_172,

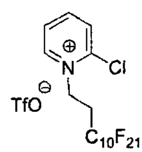


Example 3[9]



Example 4, 氟代的Mukaiyama试剂[10]



氟代的 Mukaiyama试剂 

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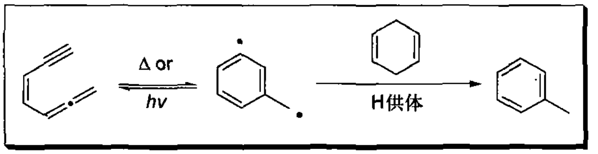
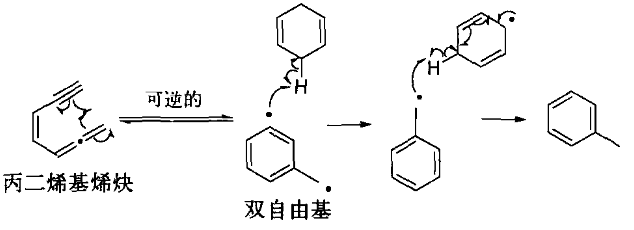
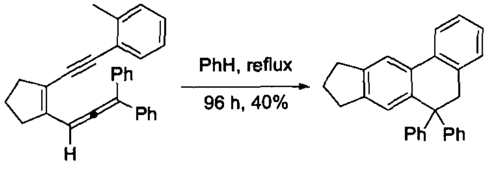
Myers-Saito 环化反应

参见第40页上的Bergman环化反应和Schmittel环化反应。

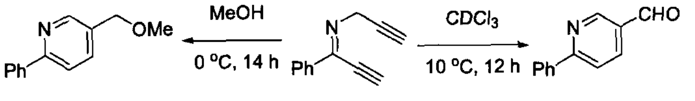




Example 1[3]



Example 2, 含氮的-Myers–Saito反应[8]



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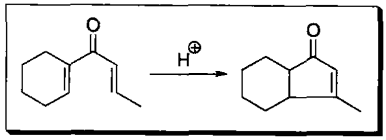
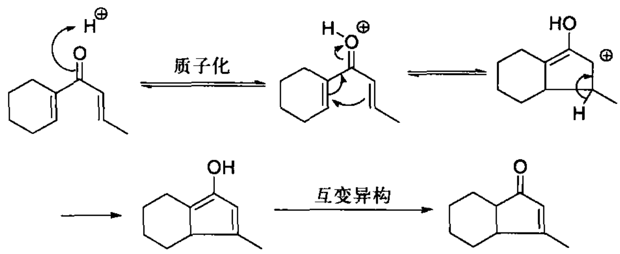
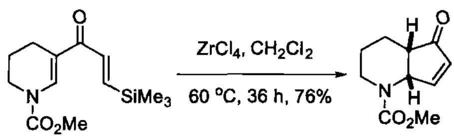
Nazarov 环化反应

酸催化下二烯基酮经电环化反应生成环戊烯酮。

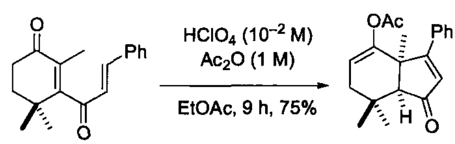




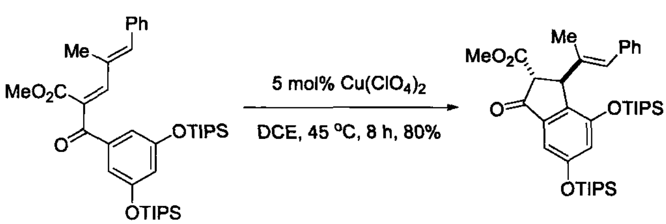
Example 1[2]



Example 2[6]

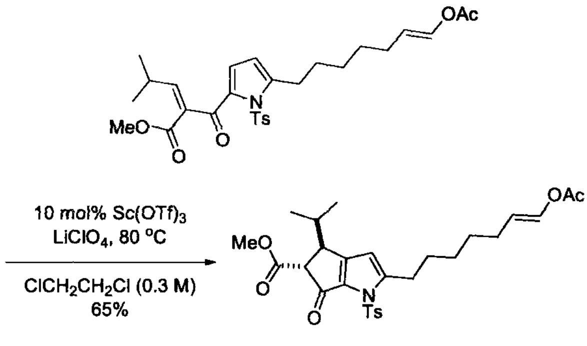


Example 3[9]

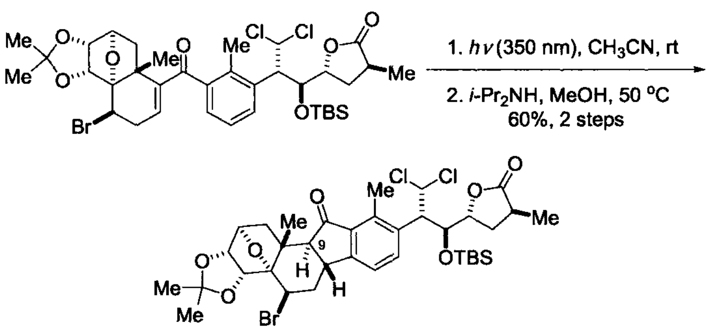


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_174,

Example 4[10]



Example 5[11]



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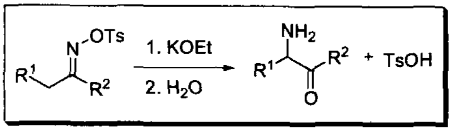
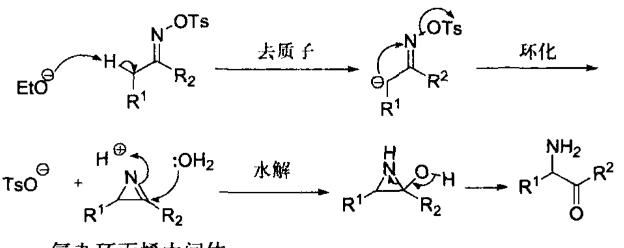
Neber 重排反应

由磺酰基酮肟和碱反应可得到 α - 氨基酮。净转化是从酮经肟转化为 α - 氨基酮。

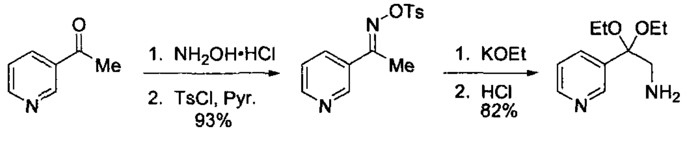


酮肟　　α-氨基酮

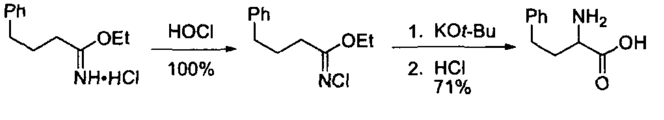


氮杂环丙烯中间体

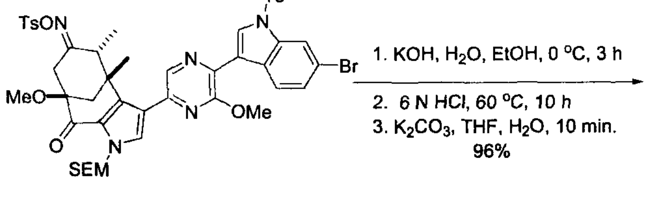
Example 1[3]



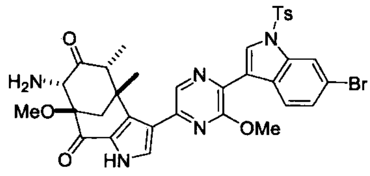
Example 2, 用亚胺基氯化物的变异[5]



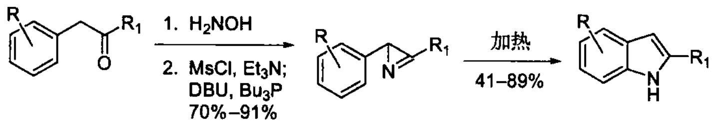
Example 3[8]



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



Example 4[9]



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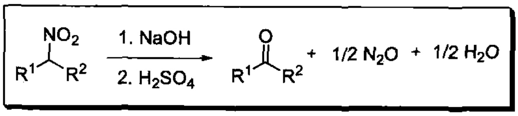
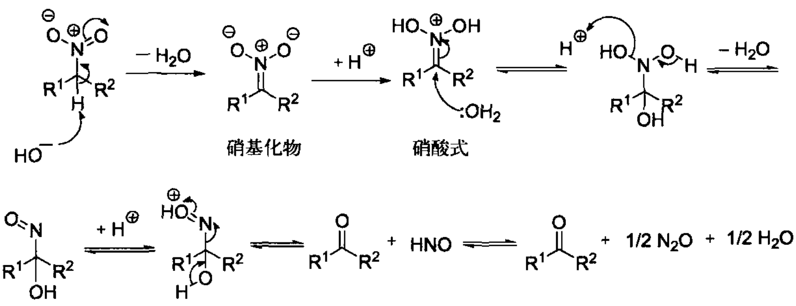
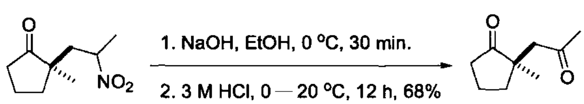
Nef 反应

伯或仲硝基烷烃转化为相应的羰基化合物。

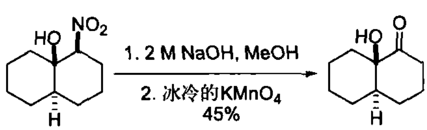




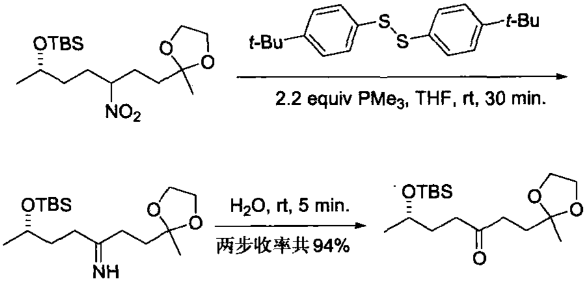
Example 1[4]



Example 2[7]

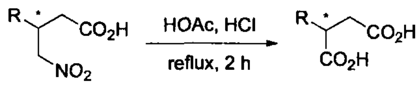


Example 3[9]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_176,

Example 4[10]



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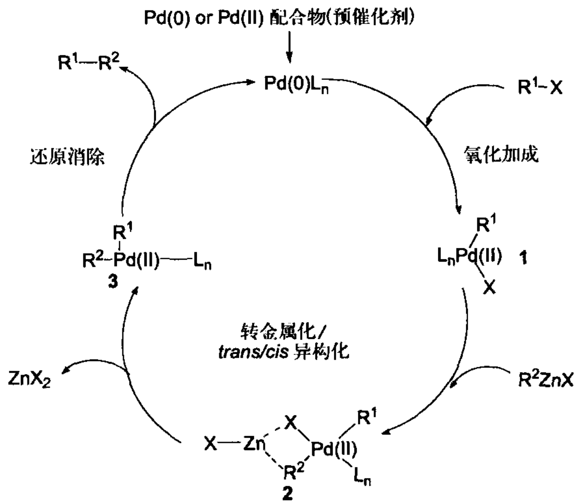
Negishi 交叉偶联反应

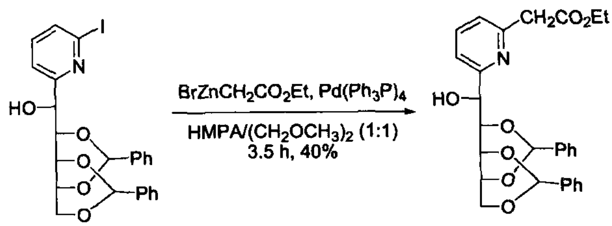
Negishi交叉偶联反应是在Ni或Pd催化下的有机锌化合物和各种卤代烃或三氟甲磺酸酯（芳基、烯基、炔基和酰基）之间的偶联反应。

$$R^1{-}X \;+\; R^2Zn{-}Y \xrightarrow[\text{溶剂}]{NiL_n \text{ or } PdL_n} R^1{-}R^2$$

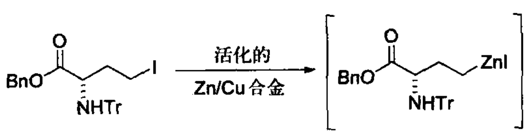
R^1 = 芳基、烯基、炔基、酰基
R^2 = 芳基、杂芳基、烯基、烯丙基、Bn、同烯丙基、同丙炔基
X = Cl, Br, I, OTf
Y = Cl, Br, I
L_n = PPh_3, dba, dppe



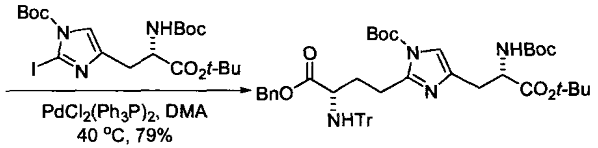
Example 1[3]



Example 2[4]



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



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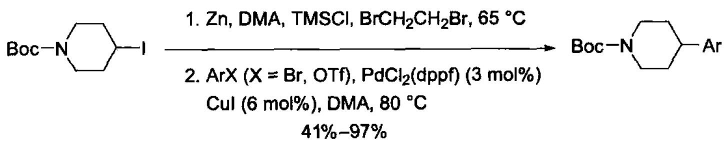
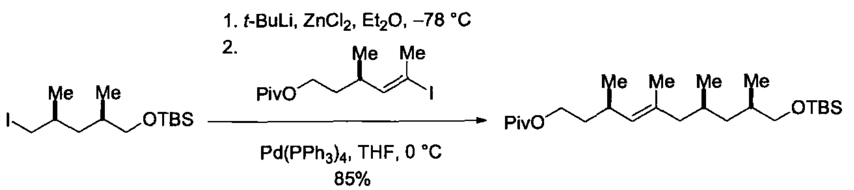


Example 4[9]



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译者注：E.Negishi（根岸英一）于2010年和R.F.Heck、A.Suzuki共享诺贝尔化学奖。

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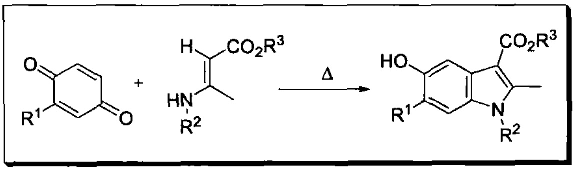
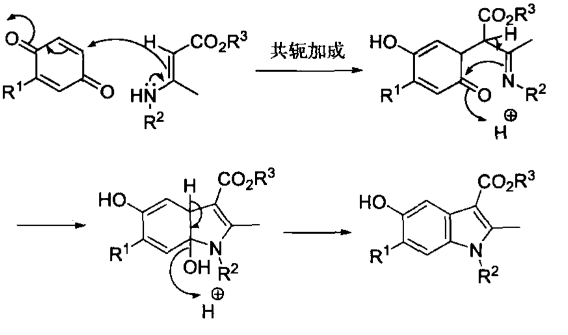
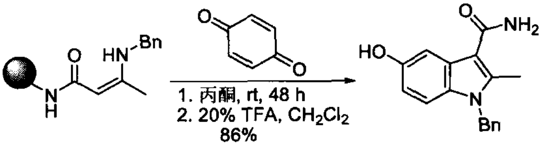
Nenitzescu 吲哚合成反应

对苯醌和 β-氨基丙烯酸酯缩合生成5-羟基吲哚。

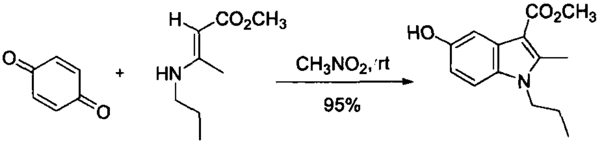




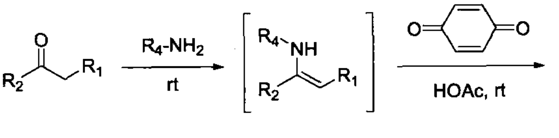
Example 1[5]



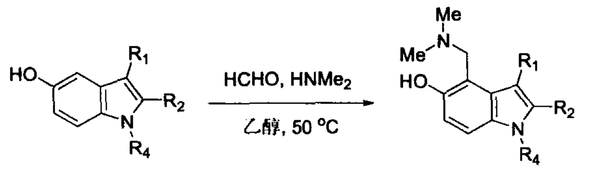
Example 2[6]



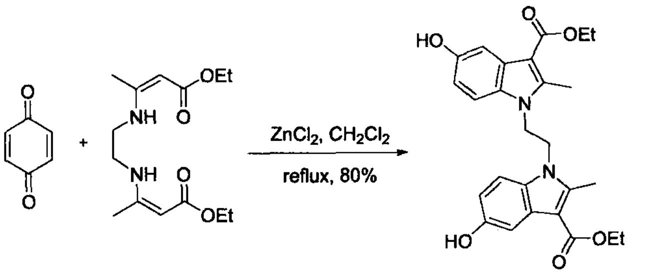
Example 3[7]



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



Example 4[10]



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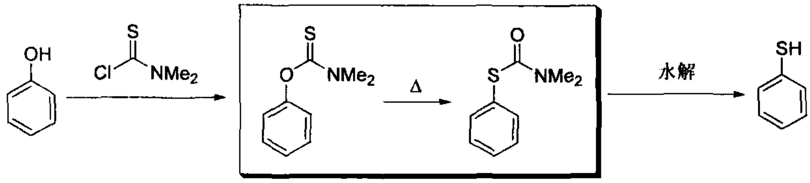
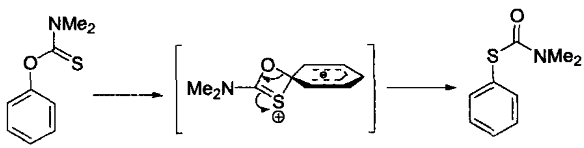
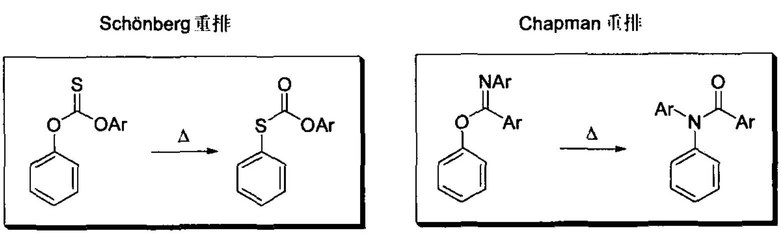
Newman-Kwart 反应

将酚转化为硫酚的反应。是第513页上的Smile反应的变异。

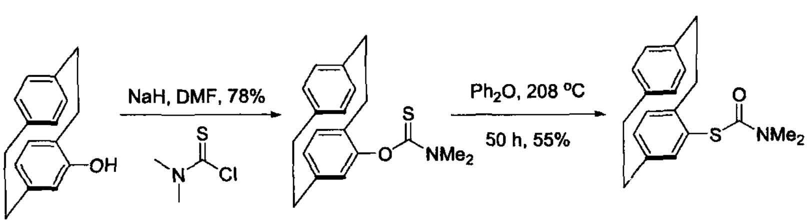




Newman-Kwart重排反应和Schonberg重排反应及第105页上的芳基在非相邻原子间发生的分子内Chapman重排反应同属一个系列。Schonberg重排反应与该反应最为相似，包括在二芳基硫代碳酸酯中的芳基从氧原子经1,3-迁移到硫原子的过程。Chapman重排反应也有类似的迁移，只不过是一个迁移到氮原子的过程。

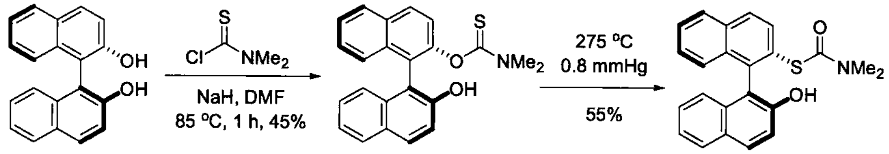


Example 1[5]

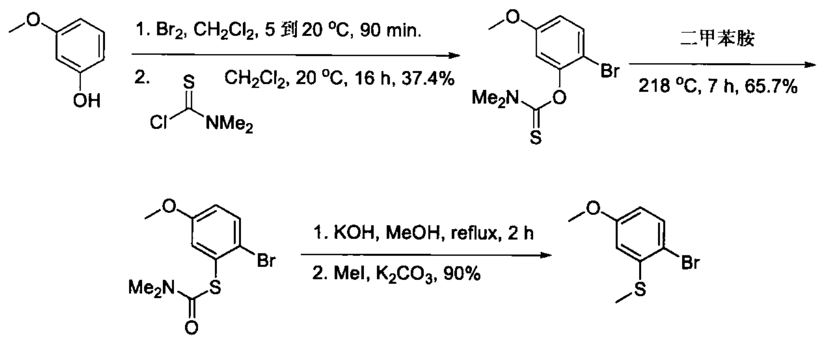


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_179,

Example 2[6]



Example 3[7]



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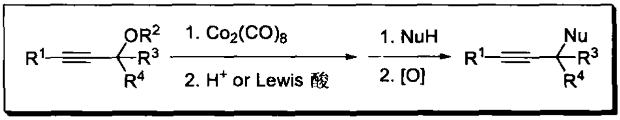
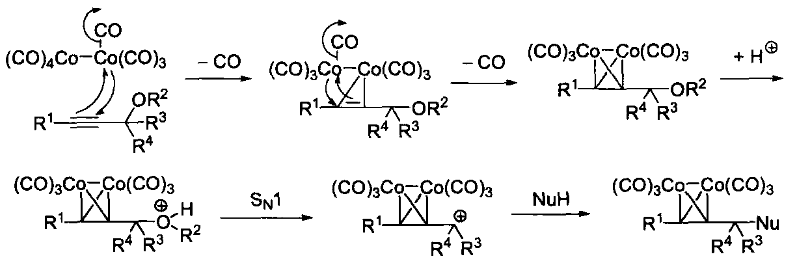
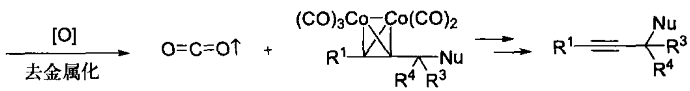
Nicholas 反应

六羰基二钴稳定的炔丙基正离子被一个亲核物种捕获，接着氧化去金属化给出炔丙基化的产物。

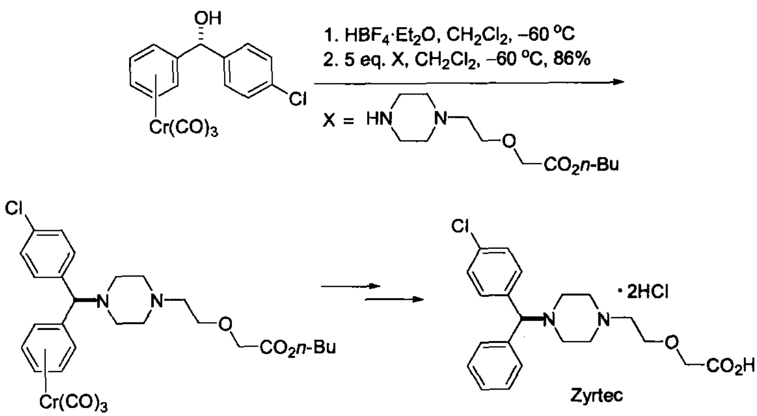




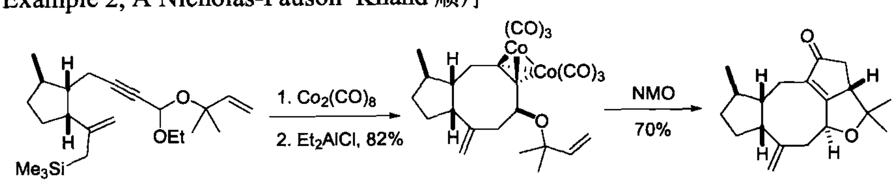
丙炔基正离子中间体(由六羰基二钴配合物稳定)



Example 1, Nicholas 反应的变异[3]

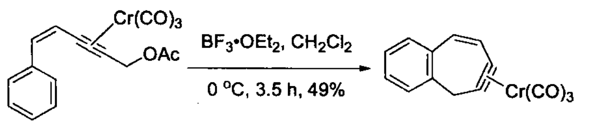


Example 2, A Nicholas-Pauson–Khand 顺序[4]

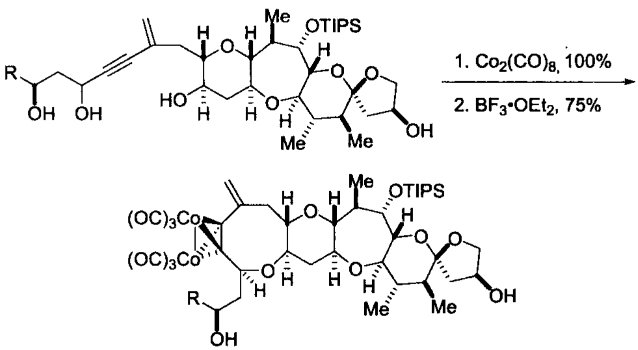


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_180,

Example 3, 分子内 Nicholas反应[7]



Example 4[9]



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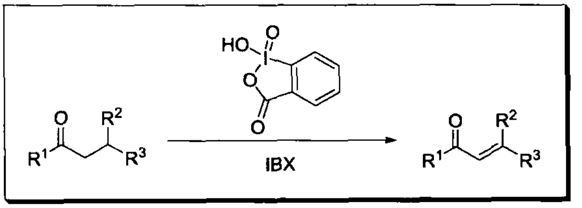
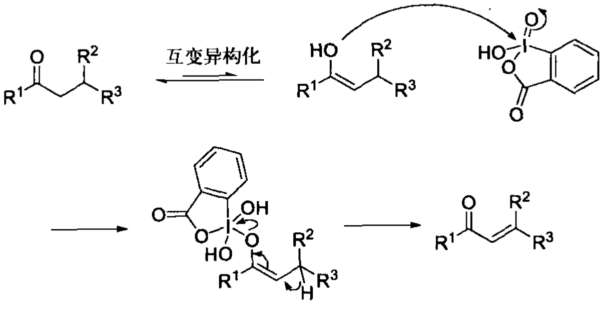
Nicholas IBX 脱氢反应

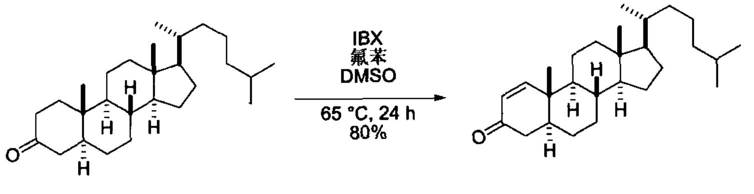
醛和酮的 α，β-不饱和化可由化学计量的邻碘酰基苯甲酸（IBX）或第482页上的Saegusa反应来实现。



反应被认为是SET机理，硅基烯醇醚也是可用的底物。



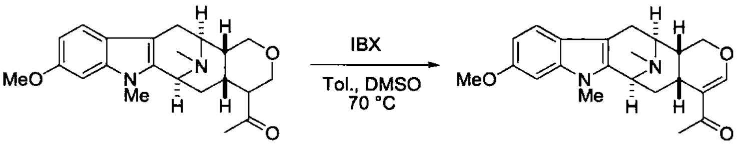
Example 1[1a]



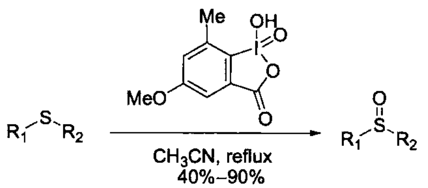
Example 2[3]

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

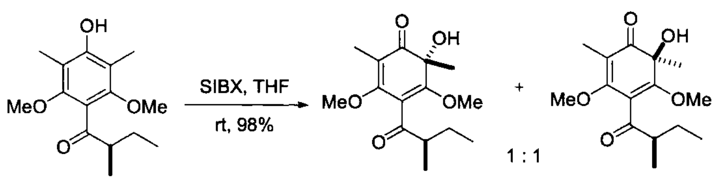
Example 3[7]



Example 4, o-甲基IBX (Me-IBX)[9]



Example 5, 稳定的IBX (SIBX)[10]



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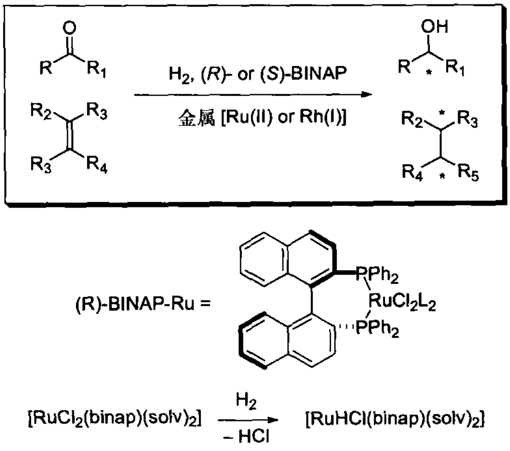
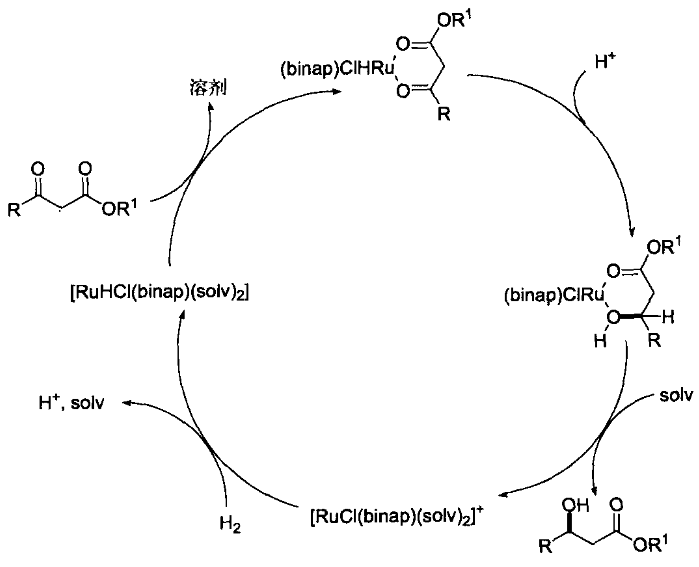
Noyori 不对称氢化反应

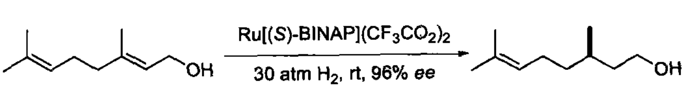
羰基和烯基经Rh(Ⅱ)-BINAP配合物催化进行的不对称氢化还原反应。



催化循环:

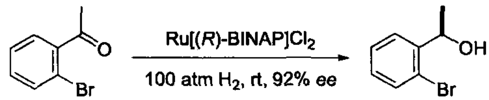


Example 1[1b]

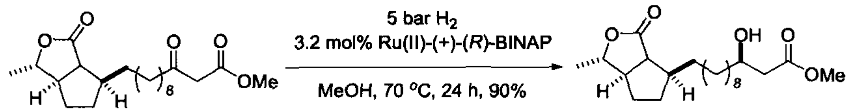


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_182,

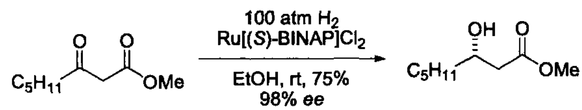
Example 2[1c]



Example 3[9]



Example 4[10]



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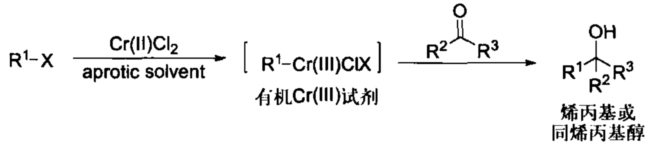
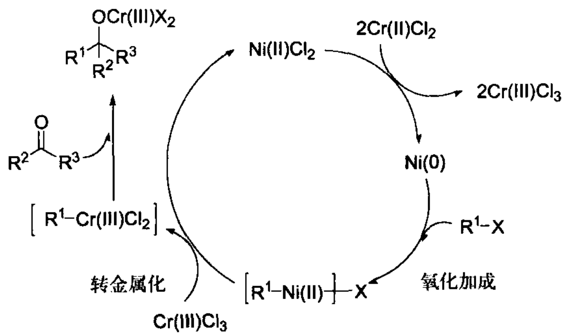
Nozaki-Hiyama-Kishi 反应

Cr-Ni 双金属催化剂促进的烯基卤代烃对醛的氧化还原反应。

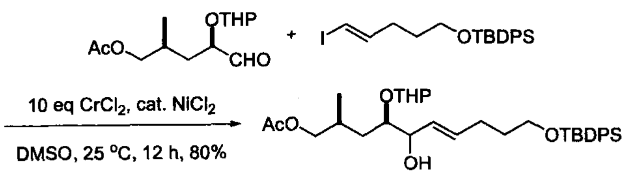


R^1 = 烯基、芳基、烯丙基、乙烯基、丙炔基、炔基、联烯基
R^2 = R^3 = 芳基、烷基、烯基、H
X = Cl, Br, I, OTf
溶剂= DMF, DMSO, THF

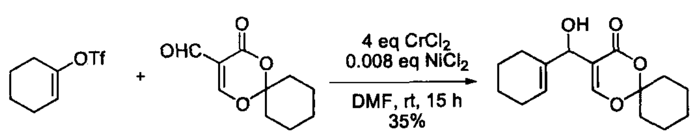
催化循环:[2]



Example 1[3]

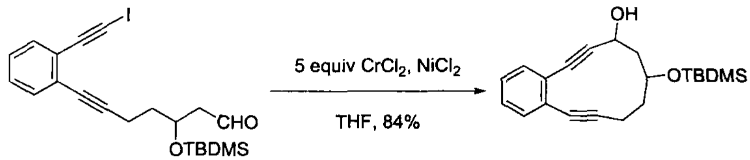


Example 2[5]

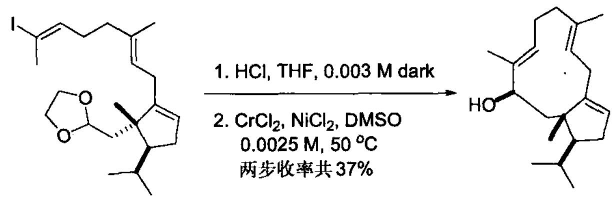


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_183,

Example 3, 分子内 Nozaki–Hiyama–Kishi 反应[8]



Example 4, 分子内 Nozaki–Hiyama–Kishi 反应[9]



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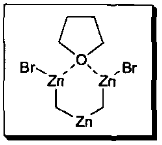
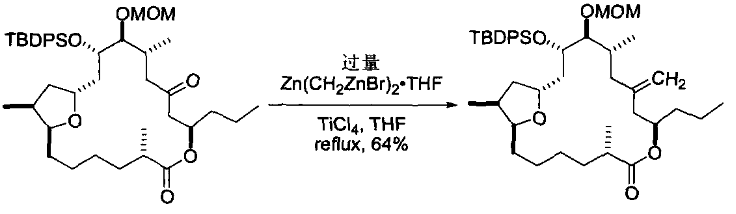
Nysted 试剂

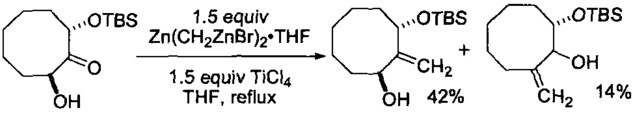
Nysted试剂，即环二溴二-μ-亚甲基(μ-四氢呋喃)三锌化物可用于醛酮的烯基化反应。



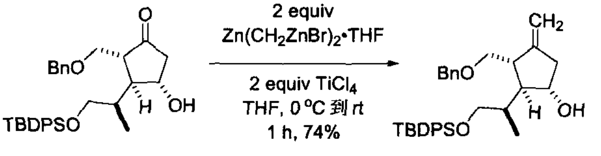
Example 1, Wittig 试剂打开内酯：[6]



Example 2[8]



Example 3[9]



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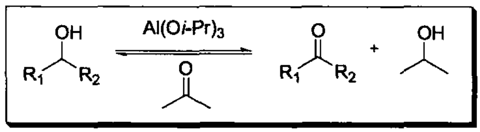
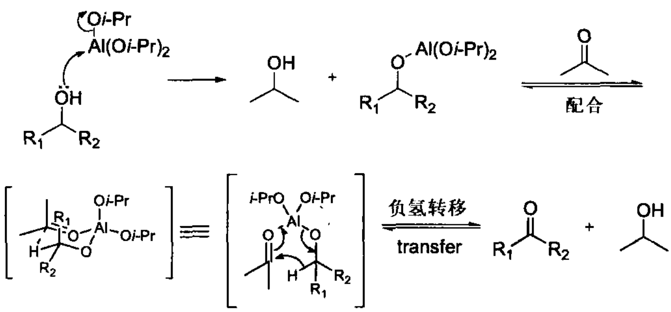
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_184,

Oppenauer 氧化反应

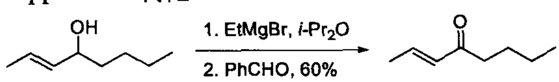
烷氧基催化的仲醇的氧化反应。是Meerwein-Poundorf-Vorley反应的逆反应。



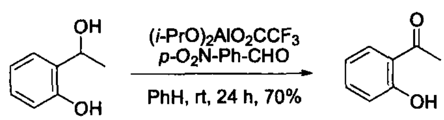


环状过渡态

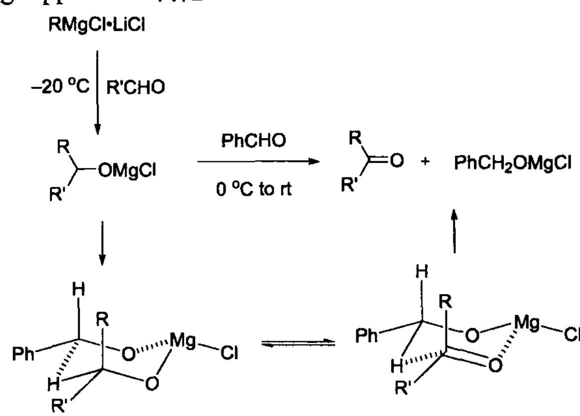
Example 1, Mg-Oppenauer 氧化[3]



Example 2[6]

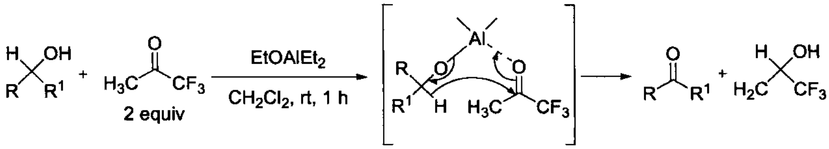


Example 3, Mg-Oppenauer 氧化[8]



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

Example 4[10]



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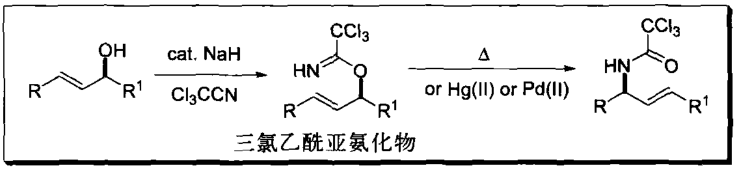
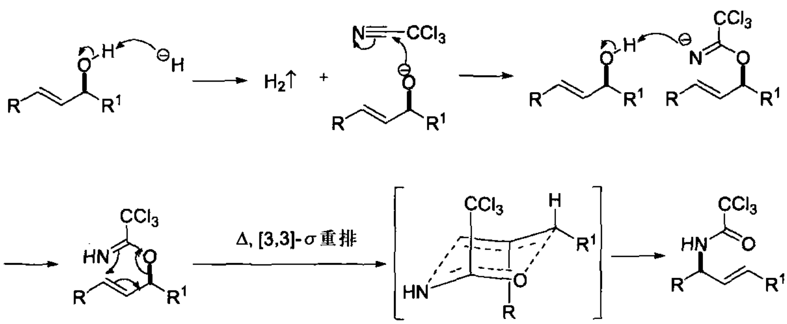
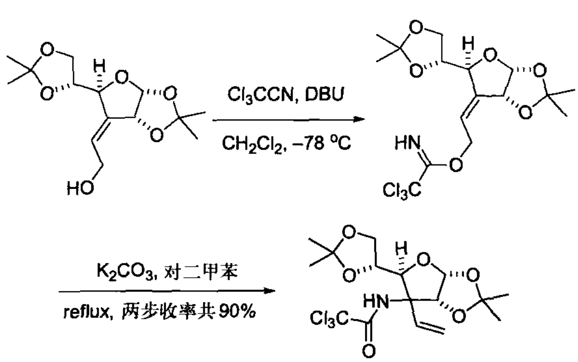
Overman 重排反应

烯丙基醇立体选择性地经三氯亚胺酯中间体转化为烯丙基三氯乙酰胺。

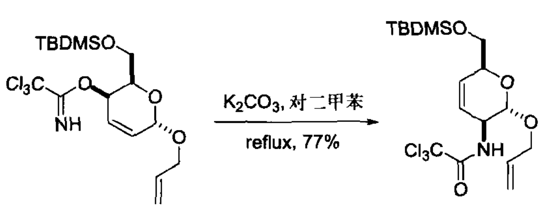




Example 1[5]

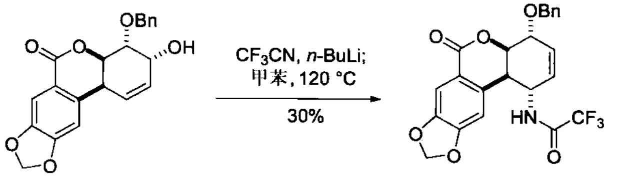


Example 2[6]

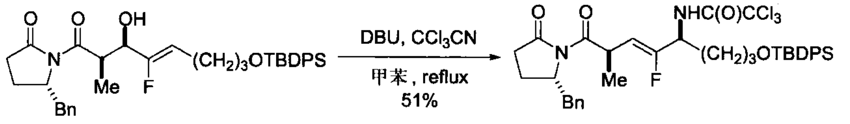


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_186,

Example 3[7]



Example 4[9]



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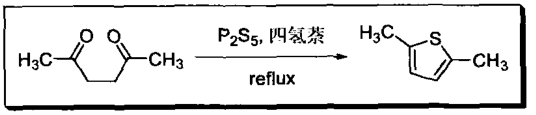
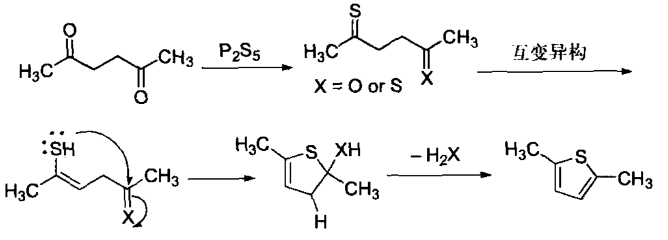
Paal 噻吩合成反应

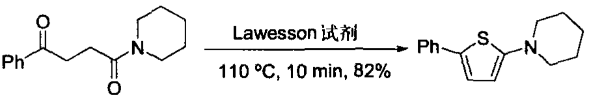
加一个硫原子到1,4-二酮后随之脱水生成噻酚的合成反应。



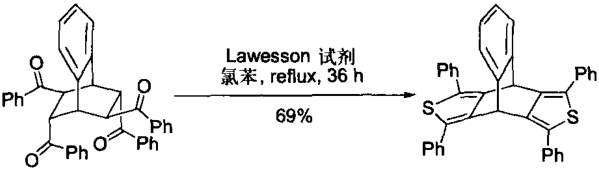
反应现在常用Lawesson试剂来操作。羰基转化为硫羰基的反应机理可见第328页上的Lawesson试剂。



Example 1[2]



Example 2[3]



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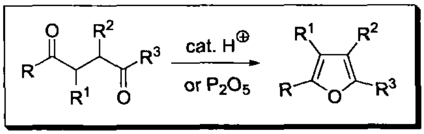
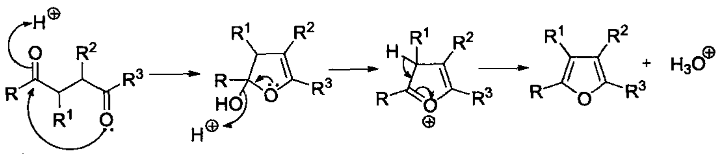
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_187,

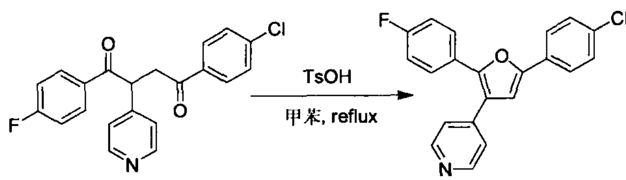
Paal-Knorr 呋喃合成反应

1,4-二酮酸催化下的环化反应给出呋喃的合成反应。

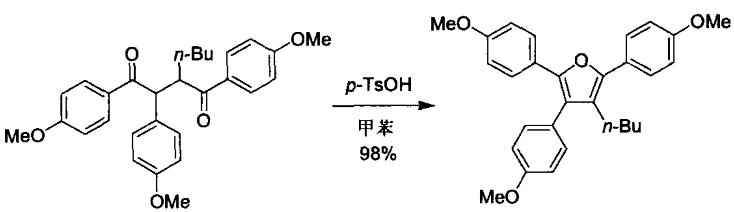




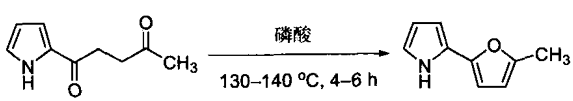
Example 1[3]



Example 2[6]

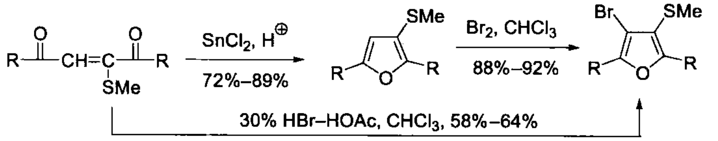


Example 3[9]



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

Example 4[10]



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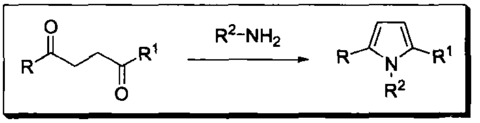
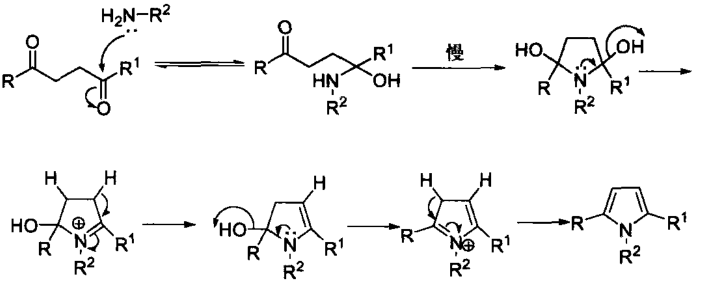
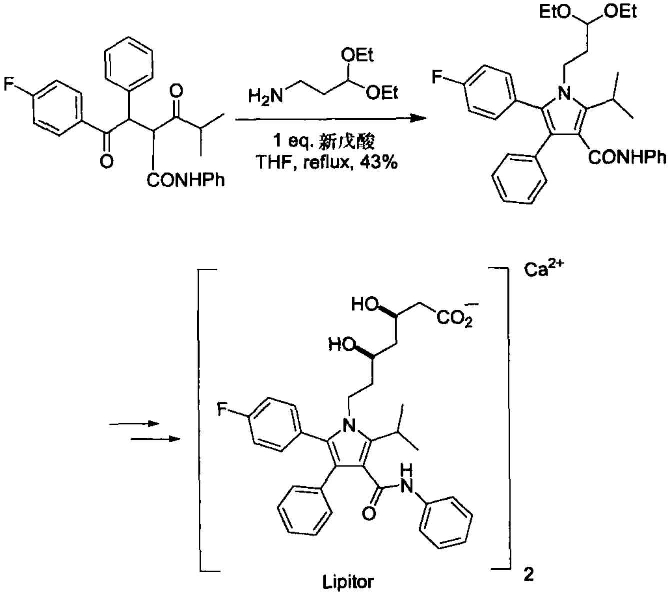
Paal-Knorr 吡咯合成反应

1,4-二酮和伯胺或氨反应给出吡咯的合成反应。是第317页上Knorr吡唑合成反应的变异。



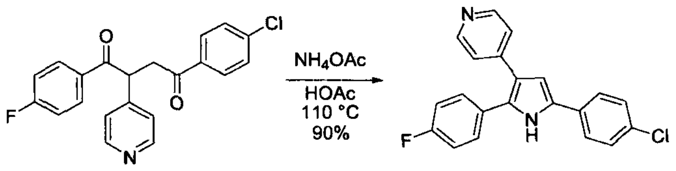


Example 1[4]

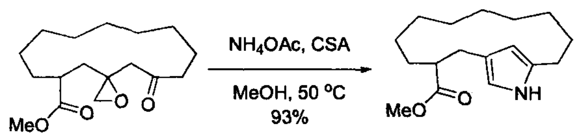


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_189,

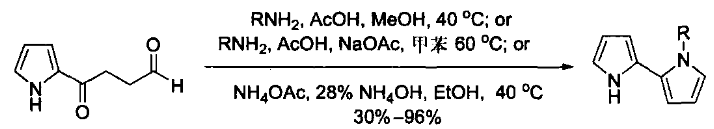
Example 2[5]



Example 3[9]



Example 4[10]



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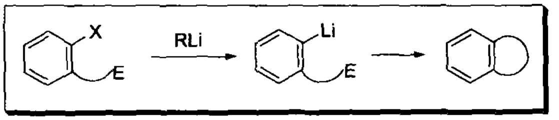
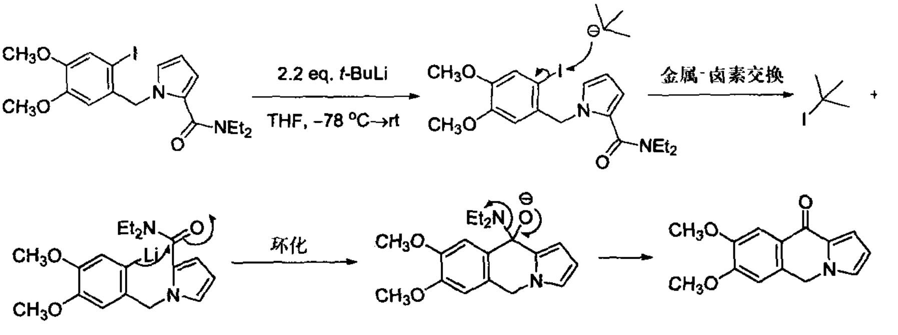
Parham 环化反应

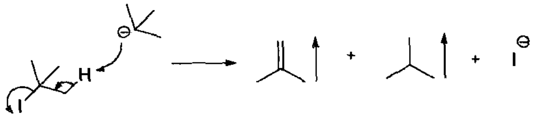
本反应起自芳基锂和杂芳基锂的锂卤交换反应和随后在亲电位上进行的分子内环化反应。



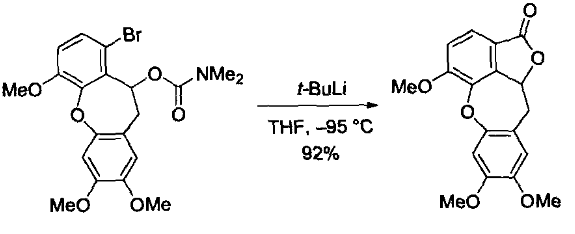
E.g.



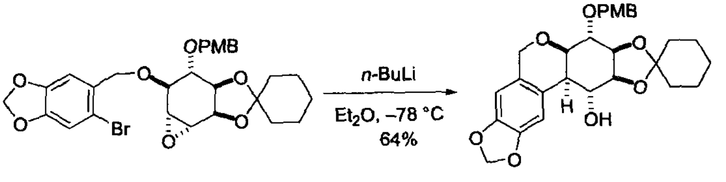
第二当量 ᵗBuLi 的作用：



Example 1[2]

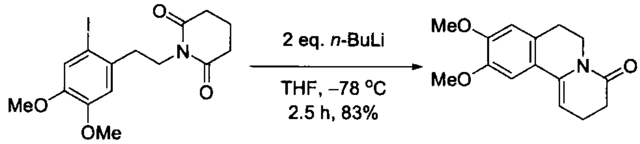


Example 2[4]

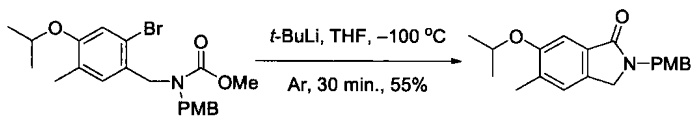


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_190,

Example 3[5]



Example 4[9]



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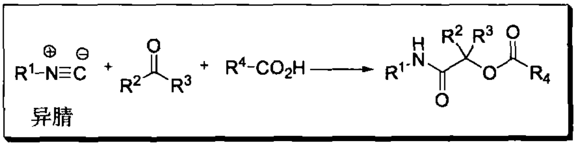
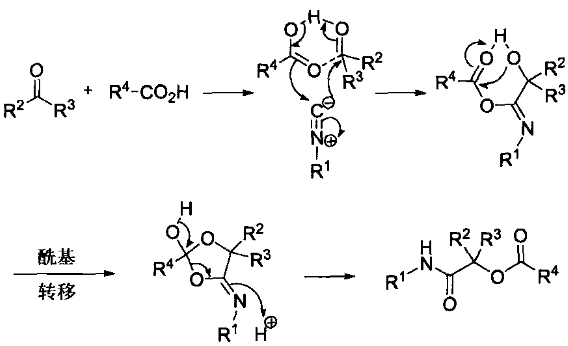
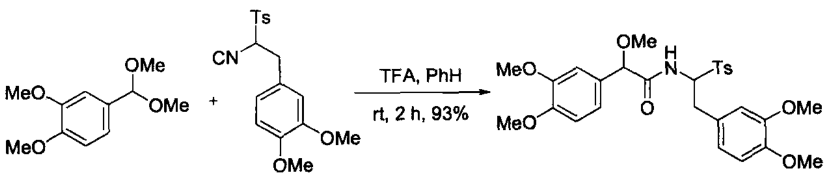
Passerini 反应

羧酸、*C*-异氰化酯和羰基化合物的三组分缩合反应（3CC）给出 α-酰氧基酰胺化物。参见第551页上的Ugi反应。

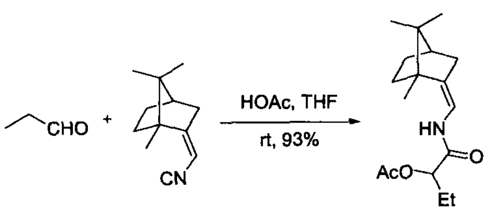




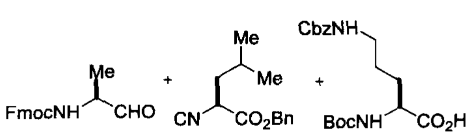
Example 1[3]



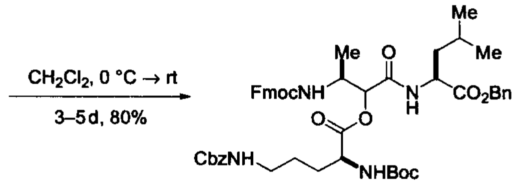
Example 2[5]



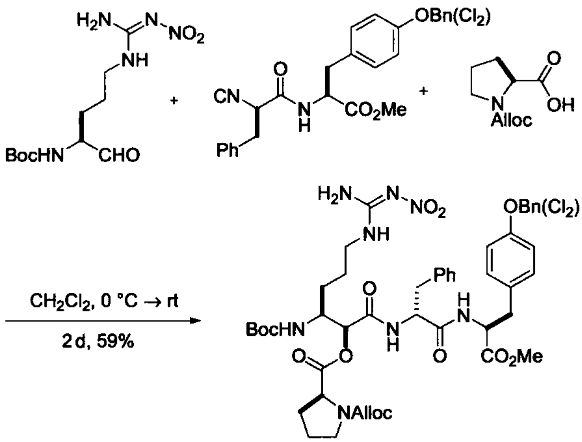
Example 3[6]



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



Example 4[7]



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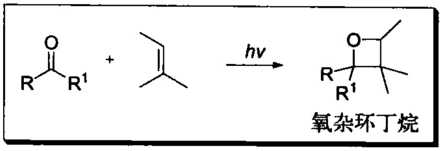
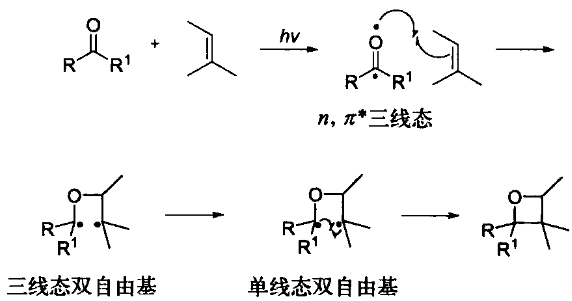
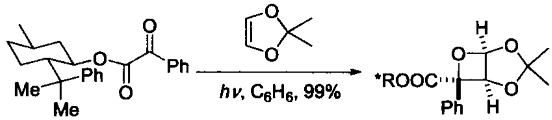
Paterno-Buchi 反应

光促的羰基和烯基发生电环化反应生成多取代氧杂环丁烷体系。

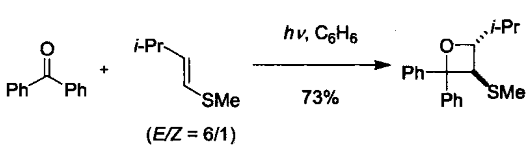




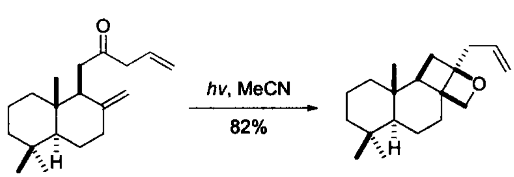
Example 1[2]



Example 2[4]

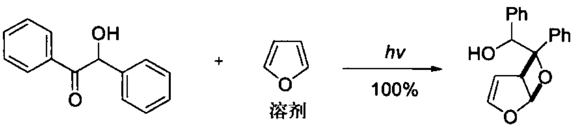


Example 3[6]



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

Example 4[8]



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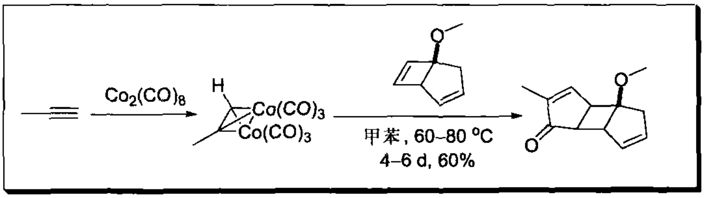
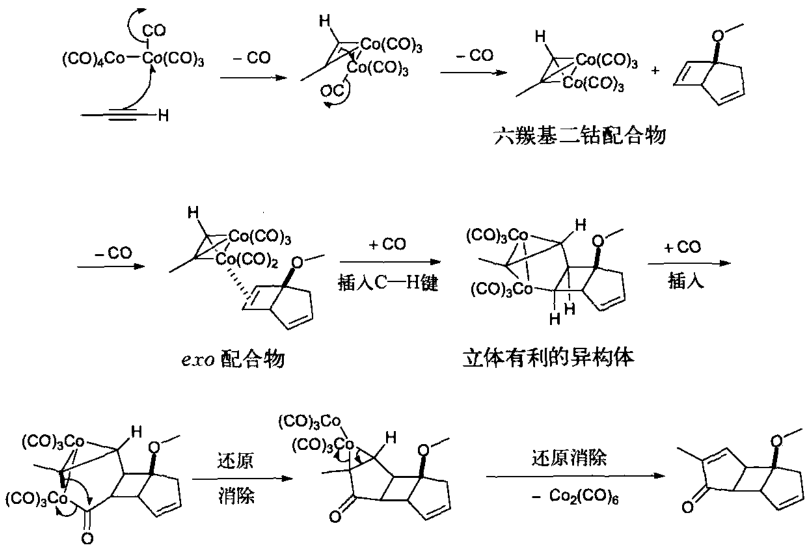
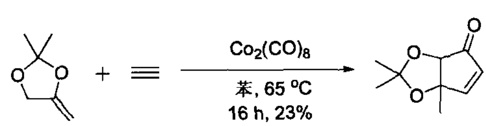
Pauson-Khand 反应

烯烃、炔烃和CO在八羰基二钴合物促进下发生形式上的[2+2+1]环加成反应生成环戊烯酮。

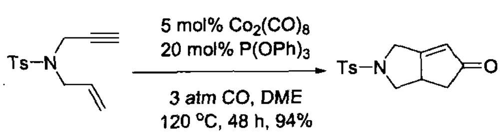




Example 1[3]

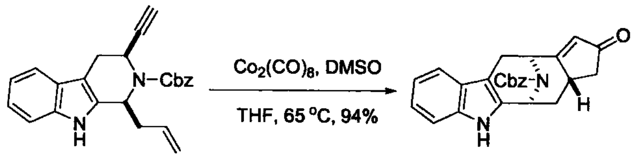


Example 2, 一个催化模式[6]

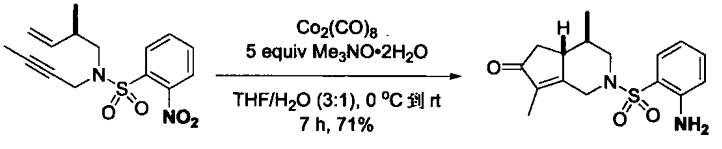


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_193,

Example 3, 分子内 Pauson–Khand 反应[9]



Example 4, 分子内 Pauson–Khand 反应[10]



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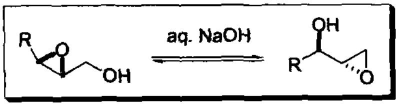
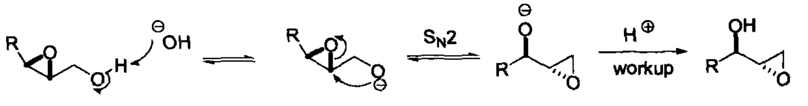
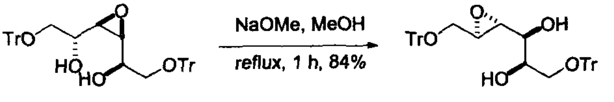
Payne 重排反应

Payne重排是2,3-环氧醇在碱影响下异构化为1,2-环氧-3-醇的反应。也是熟知的一个环氧基迁移的反应。

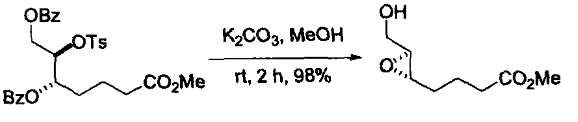




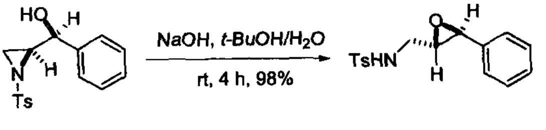
Example 1[2]



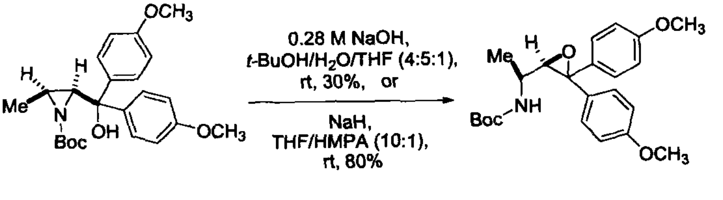
Example 2[3]



Example 3, 含氮的-Payne 重排[8]



Example 4, 含氮的-Payne 重排[9]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_194,

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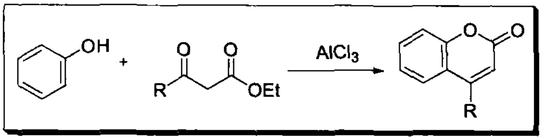
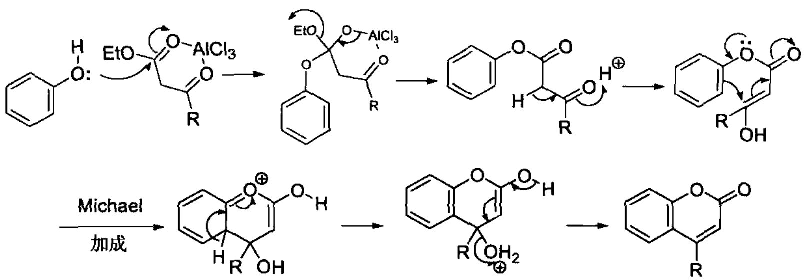
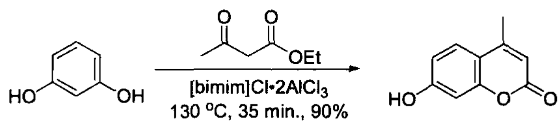
Pechmann 香豆素合成反应

酚和 β-酮酯在Lewis酸促进下缩合成香豆素的反应。

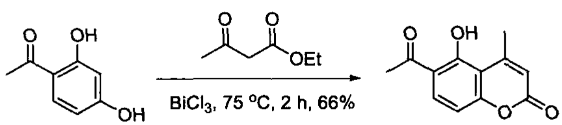




Example 1[6]



Example 2[8]



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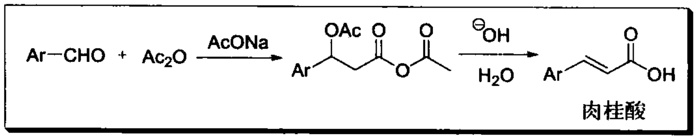
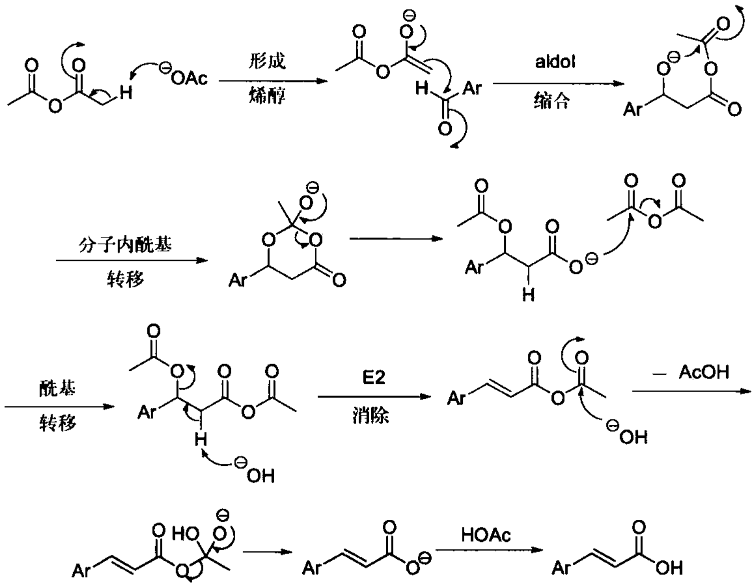
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_195,

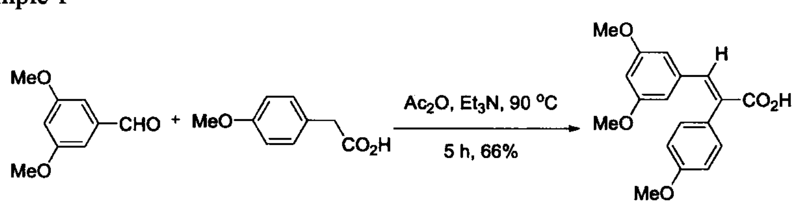
Perkin 反应

从芳香醛和乙酸酐合成肉桂酸。

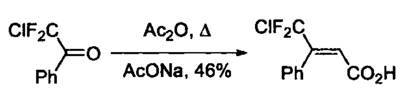




Example 1[7]



Example 2[9]



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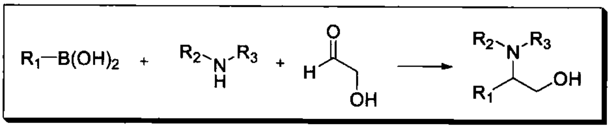
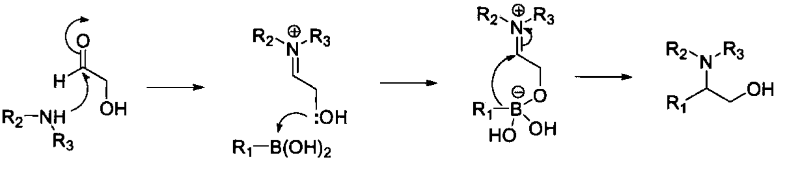
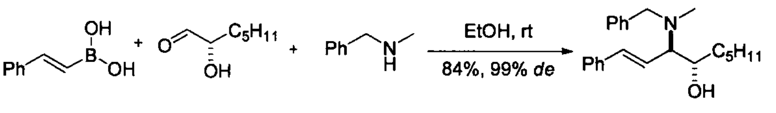
Petasis反应

烯基硼酸、羰基和胺的三组分反应给出烯丙基胺。亦称硼化物参与的Mannich-反应或Petasis 硼化物参与的Mannich反应。参见第337页上的Mannich反应。

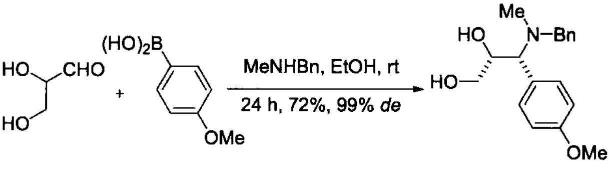




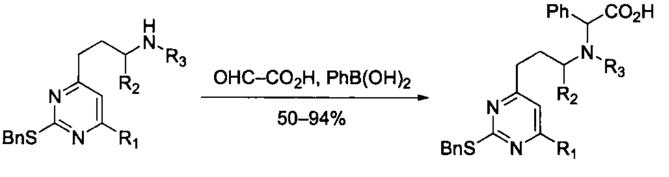
Example 1[2]



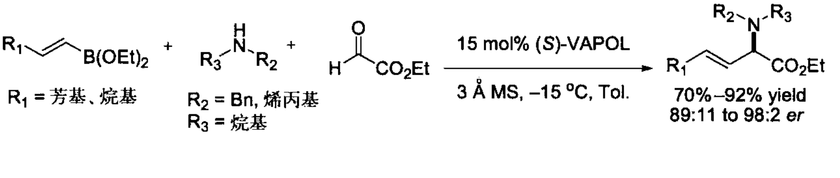
Example 2[4]



Example 3[9]



Example 4, 不对称 Petasis 反应[10]



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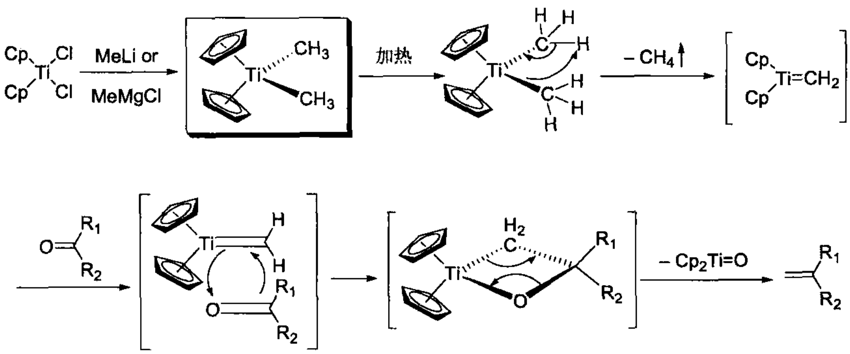
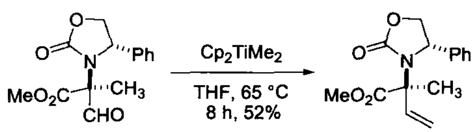
Petasis 试剂

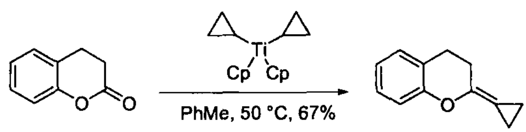
与Tebbe试剂相似，Petasis试剂，即二甲基二茂基钛[$(CH_3)_2TiCp_2$]也可对醛酮化合物进行烯基化反应。其机理在刚提出时认为与Tebbe烯基化反应有很大差异。[5] 但后来的实验数据表明，这两个烯基化反应经过同一过程，都包括一个钛氧杂四元环中间体的卡宾机理。[9] Petasis试剂的制备比Tebbe试剂方便。



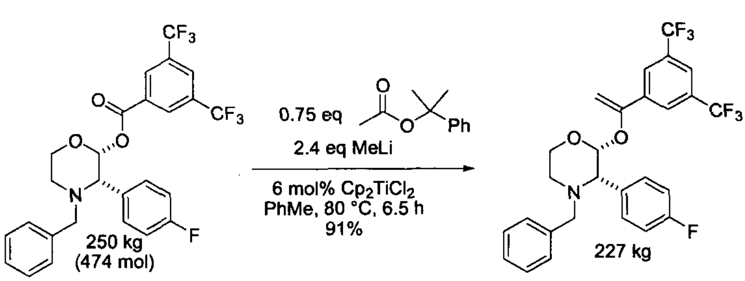
Example 1[2]



Example 2[3]

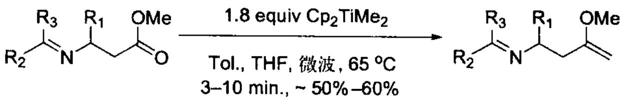


Example 3[5]



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

Example 4[8]



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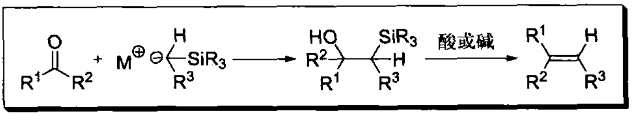
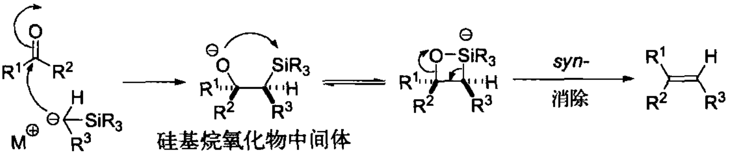
Peterson 烯基化反应

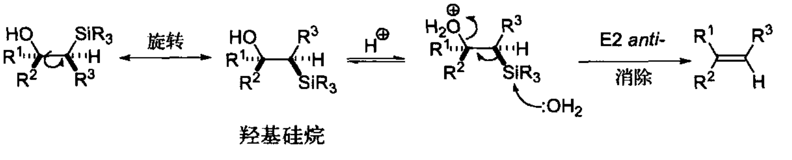
α-硅基碳负离子和羰基化合物反应生成烯烃。亦称Si-Wittig反应。



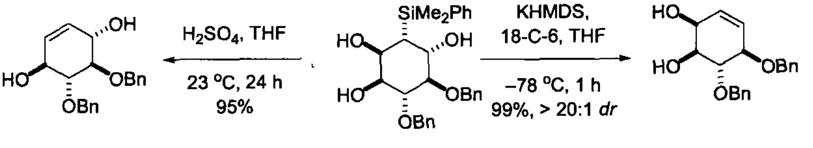
碱性条件：



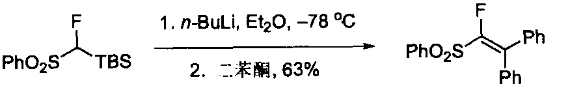
酸性条件：



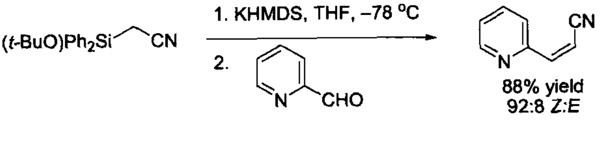
Example 1[6]



Example 2[7]

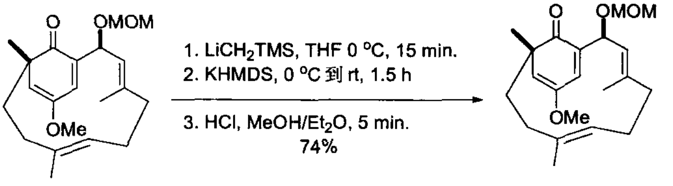


Example 3[8]



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

Example 4[10]



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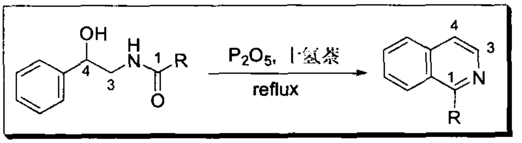
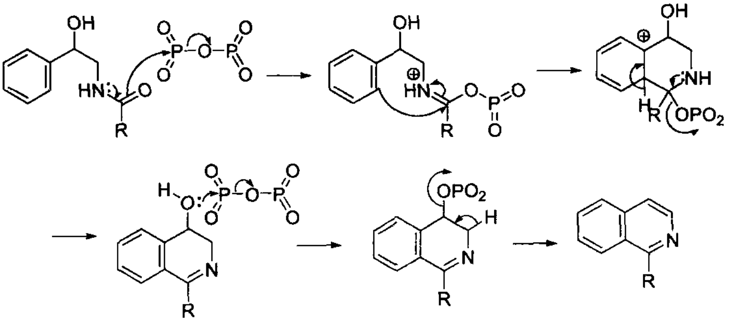
Pictet-Gams 异喹啉合成反应

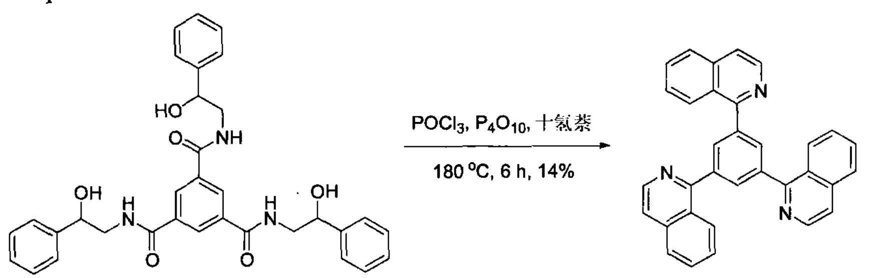
异喹啉骨架可由相应的 β-羟基-β-苯乙胺酰基衍生物经P_2O_5或$POCl_3$一类脱水剂在萘烷等惰性溶剂中回流处理来构筑。



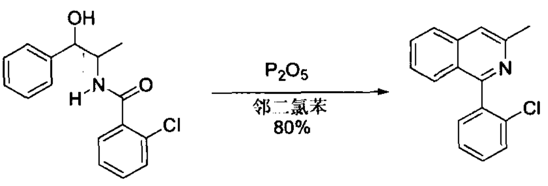
P_2O_5 实际上以 P_4O_{10} 存在，有金刚烷类结构。



Example 1[4]



Example 2[7]



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

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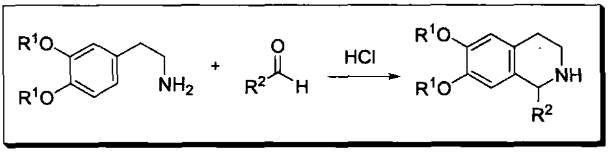
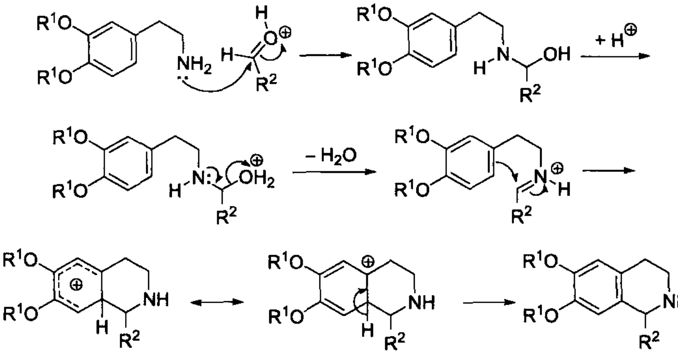
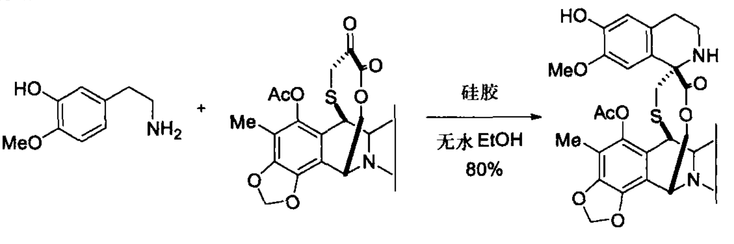
Pictet-Spengler 四氢异喹啉合成反应

四氢异喹啉骨架可由相应的 β-苯乙胺和羰基化合物缩合后环化得到。

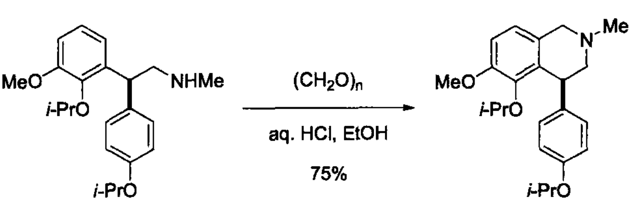




Example 1[4]

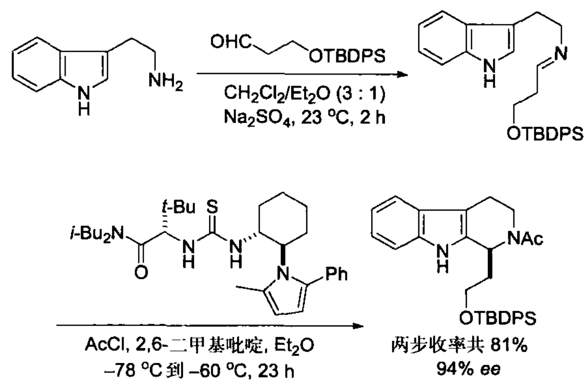


Example 2[7]

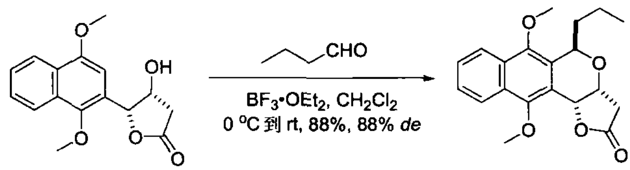


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_201,

Example 3, 不对称的酰基 Pictet–Spengler 反应[9]



Example 4, 含氧的Pictet–Spengler反应[10]



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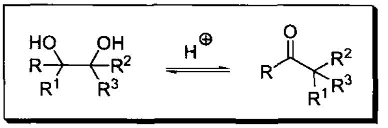
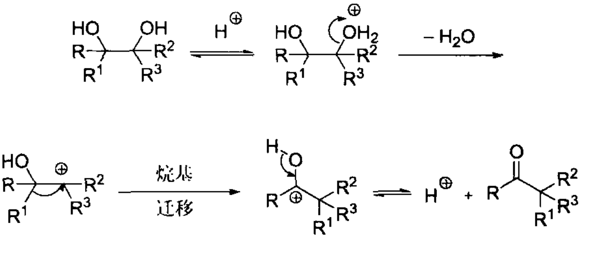
Pinacol（频哪醇）重排

酸催化下邻二醇（Pinacol，频哪醇）重排为羰基化合物。

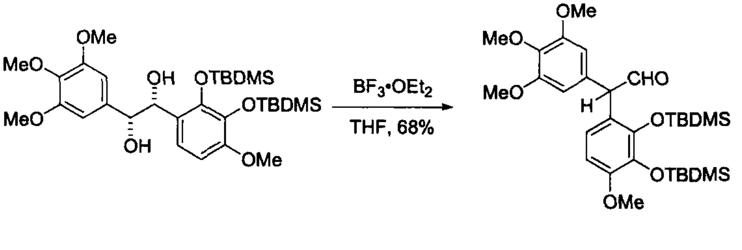


富电子烷基（多取代烷基）更易迁移，迁移能力大小一般为：
叔烷基＞环己基＞仲烷基＞苄基＞苯基＞伯烷基＞甲基＞H。

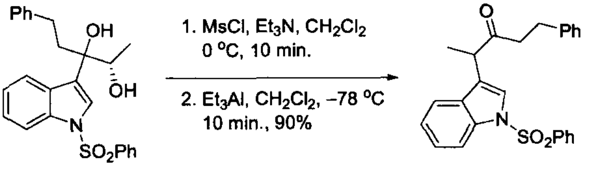
取代芳基的迁移能力大小一般为：
p-MeOAr＞*p*-MeAr＞*p*-ClAr＞*p*-BrAr＞*p*-NO_2Ar。



Example 1[4]

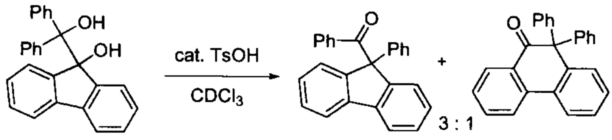


Example 2[5]

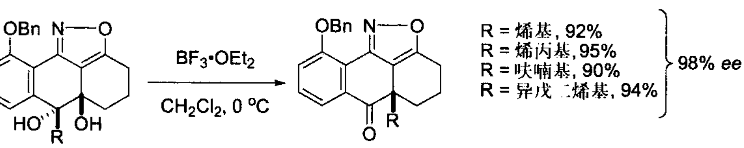


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_202,

Example 3[7]



Example 4[9]



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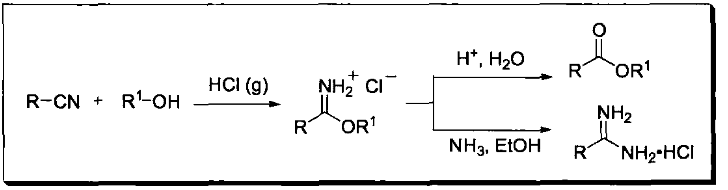
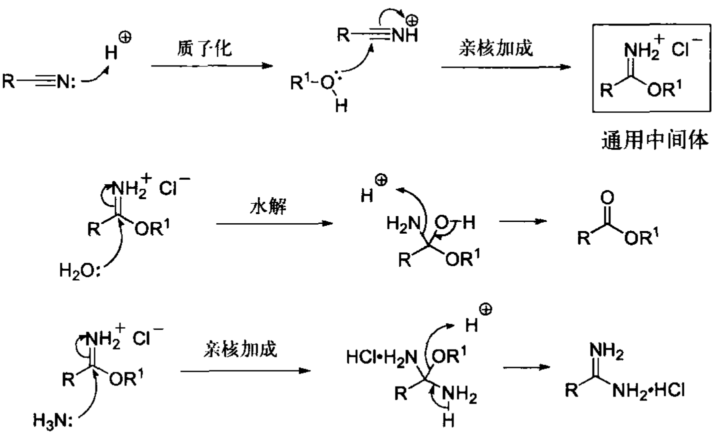
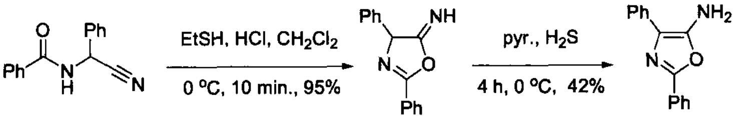
Pinner 反应

腈转化为亚胺醚,后者可进一步转化为酯或酰胺。

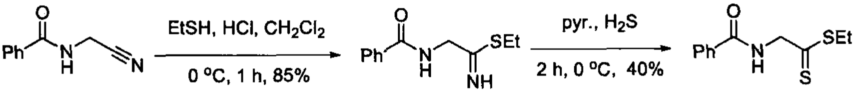




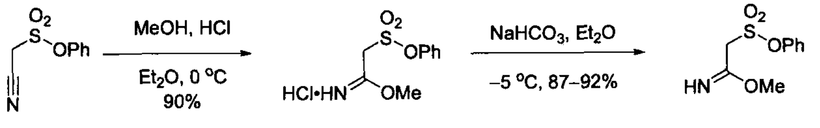
Example 1[2]



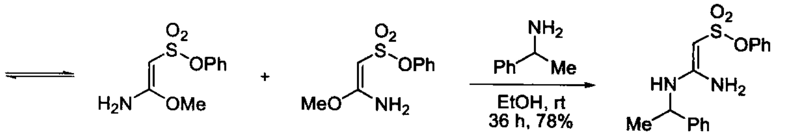
Example 2[2]



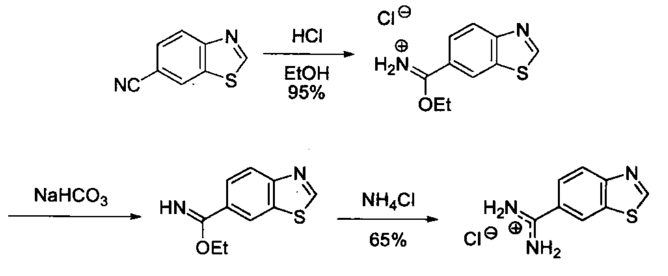
Example 3[6]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_203,



Example 4[10]



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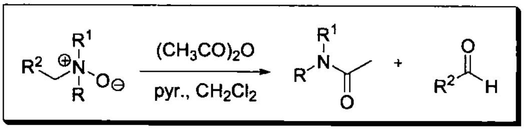
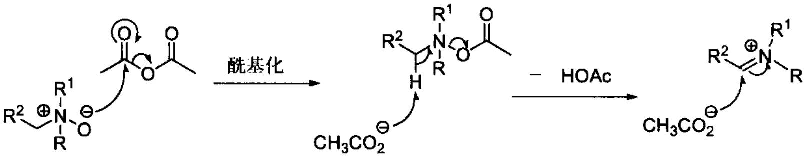
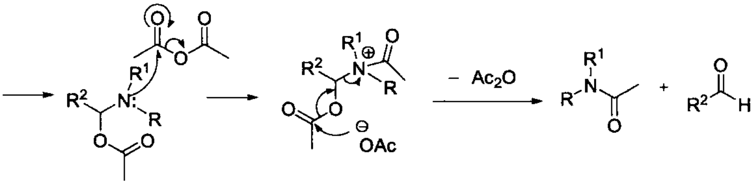
Polonovski 反应

N-氧化胺用一个如乙酸酐那样的活化剂处理，重排产生*N*, *N*-二取代酰胺和醛。

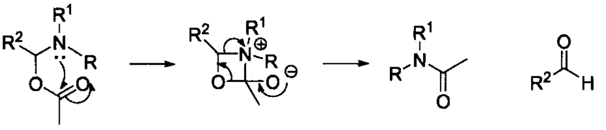




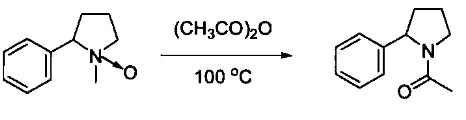
亚胺离子



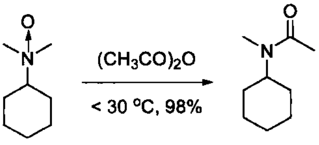
分子内路径也有可能：



Example 1[1]

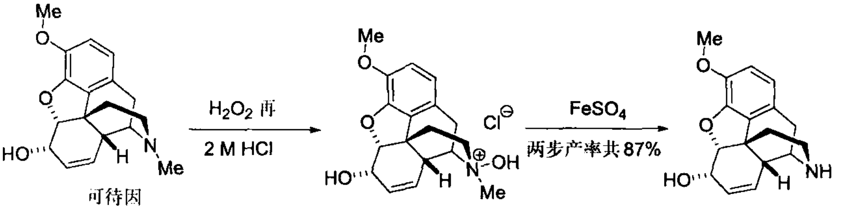


Example 2[2]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_204,

Example 3, 铁盐介质中的 Polonovski 反应[9]



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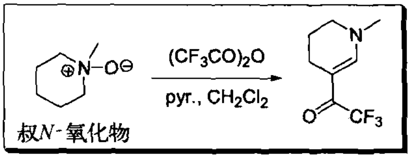
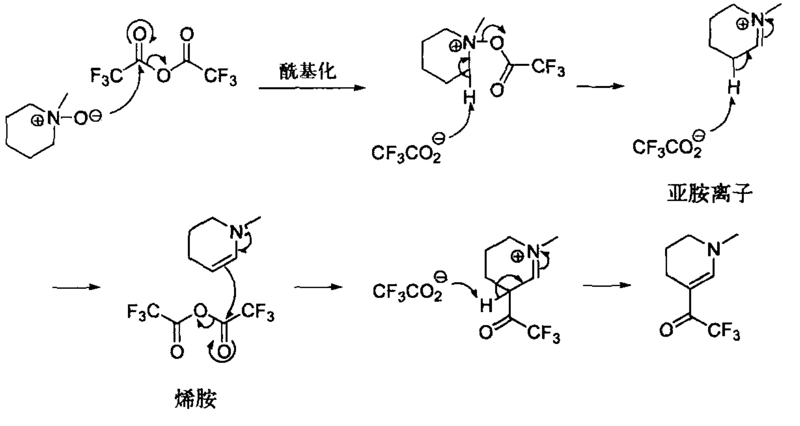
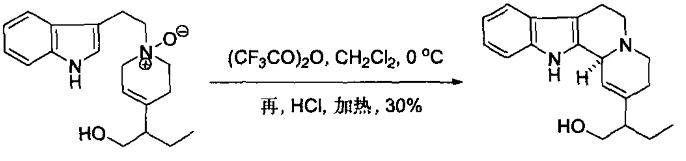
Polonovski-Potier 重排反应

用三氟乙酸酐替代乙酸酐进行的Polonovski反应。由于Polonovski反应条件更温和，本反应已基本为Polonovski反应所替代。

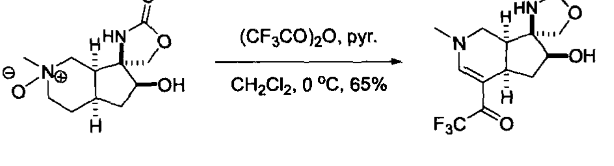




Example 1[2]

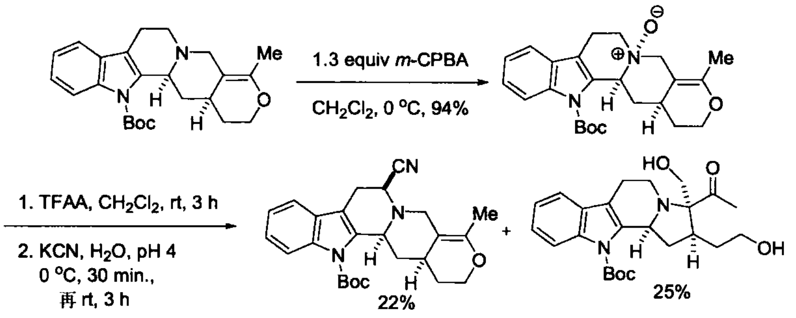


Example 2[5]

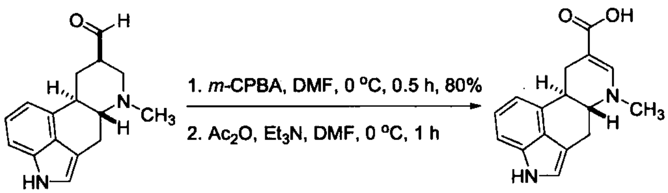


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_205,

Example 3[8]



Example 4[10]



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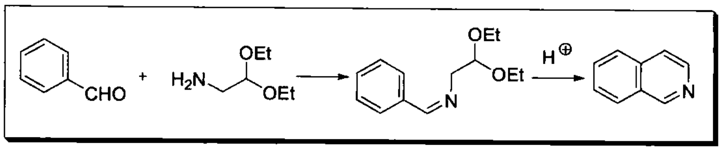
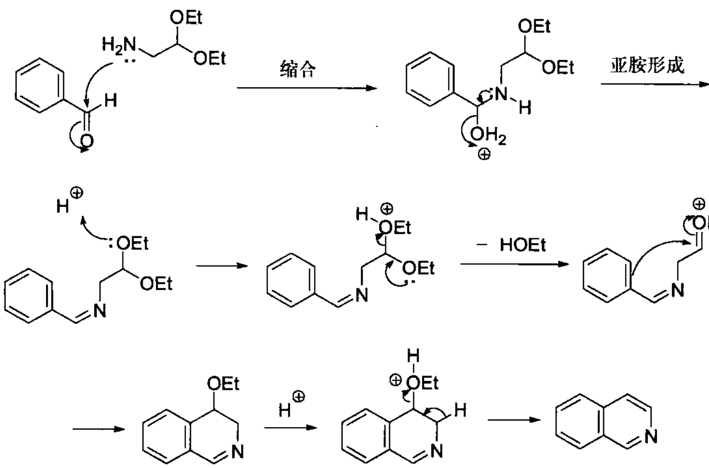
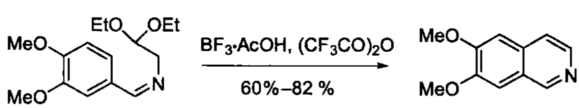
Pomeranz-Fritsch 反应

异喹啉可通过酸促进下氨基缩醛中间体的环化反应来制备。

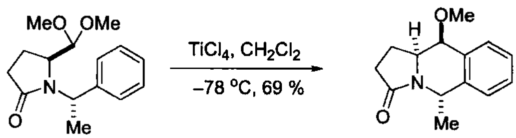




Example 1[3]

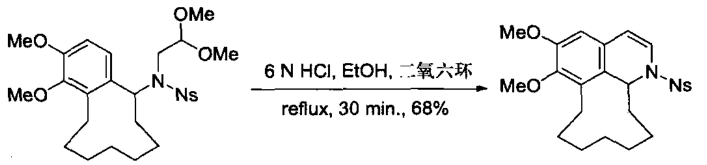


Example 2[4]

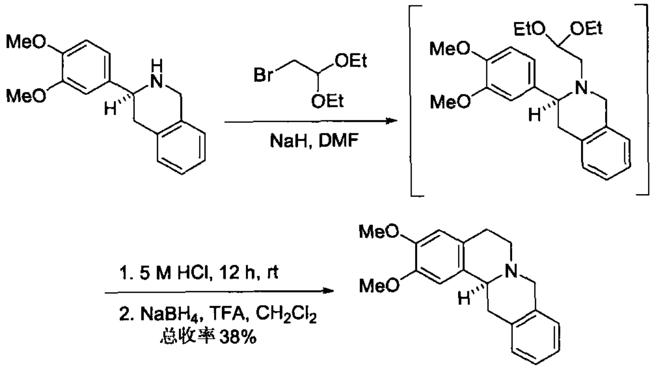


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_206,

Example 3[9]



Example 4, Bobbitt修正法[10]



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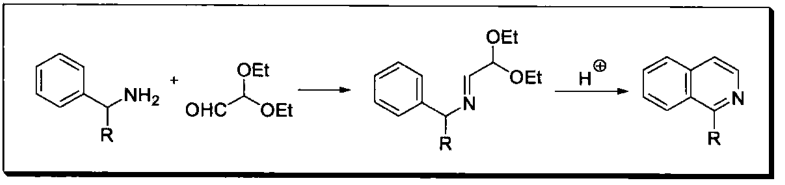
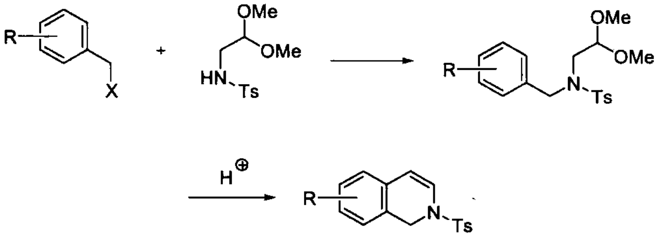
Schlittler-Muller 修正

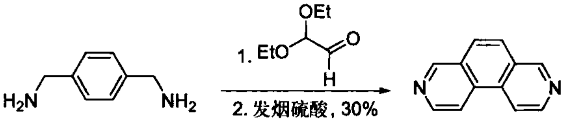
Pomeranz-Fritsch反应中两个底物的氨基和醛基简单地予以交换的反应。



Example 1[3]



Example 2[4]



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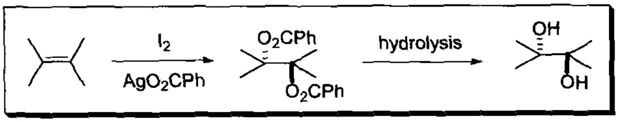
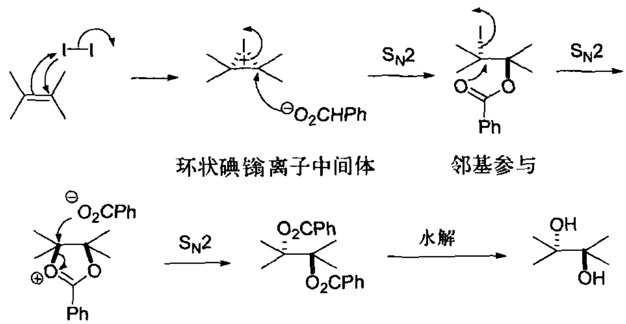
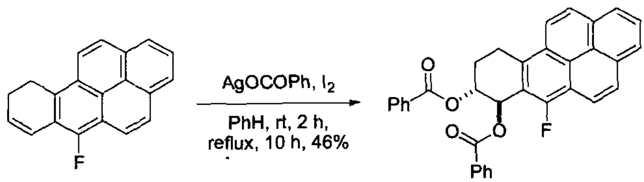
Prevost *trans*-双羟化反应

参见第592页上的Woodward *cis*-二羟基化反应。

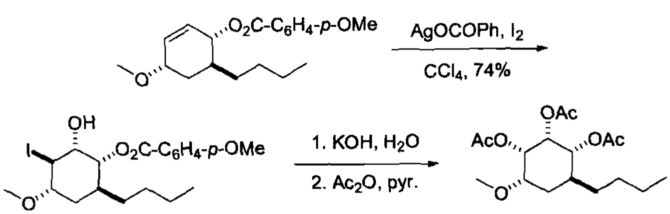




Example 1[5]



Example 2[9]



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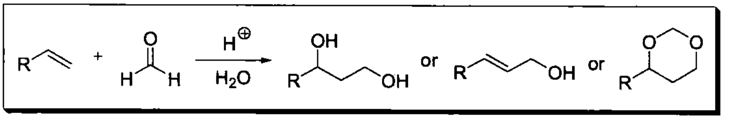
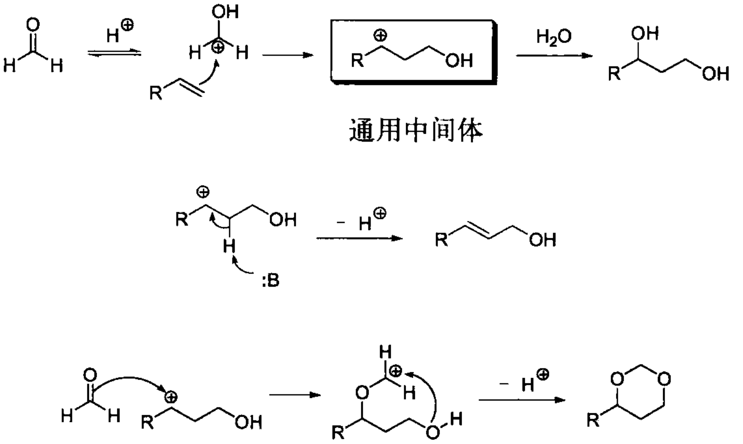
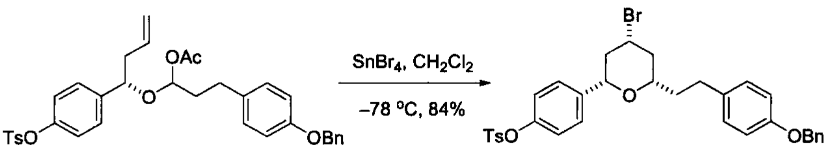
Prins 反应

Prins 反应是酸催化下醛基对烯烃加成后通过改变反应条件而给出各种不同产物的反应。

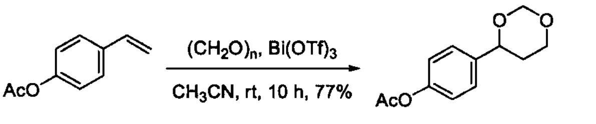




Example 1[5]

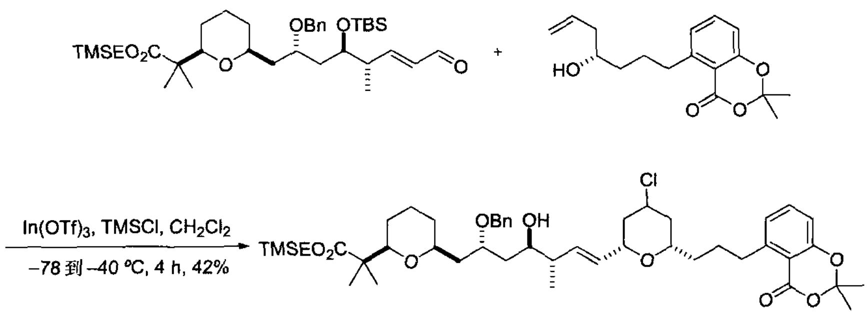


Example 2[7]

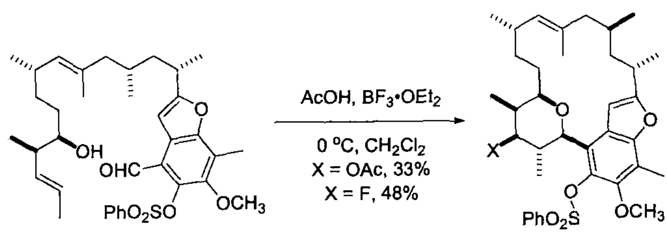


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_208,

Example 3[9]



Example 4[10]



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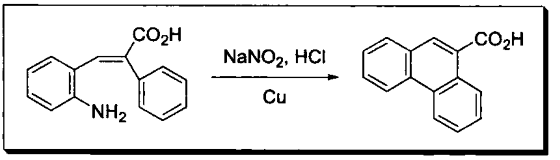
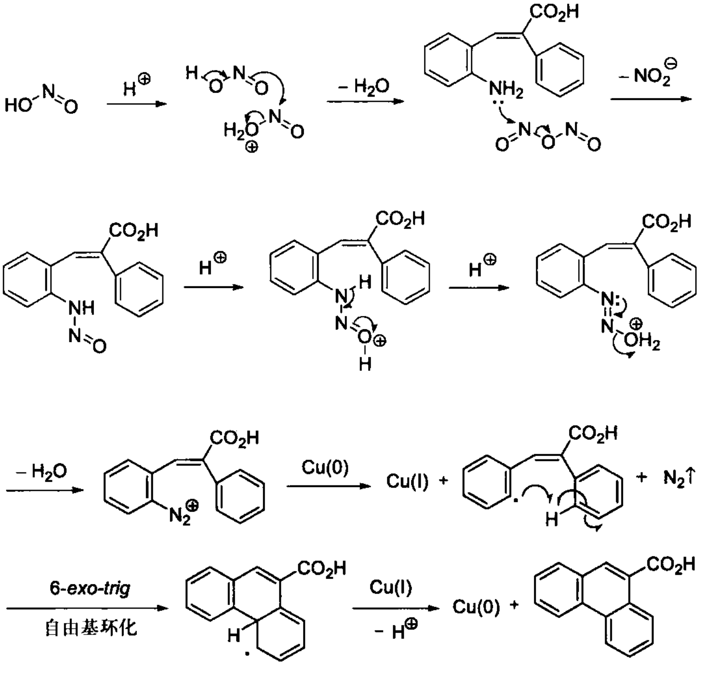
Pschorr 环化反应

应用于分子内的Gomberg-Bachmann反应。





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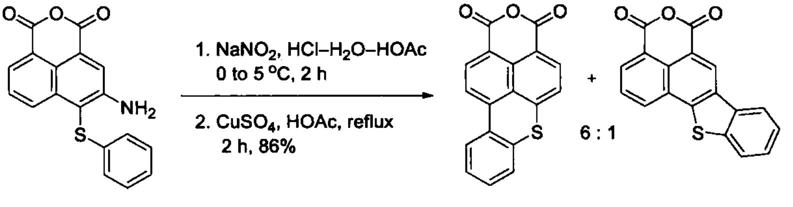
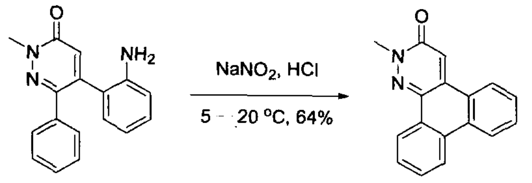
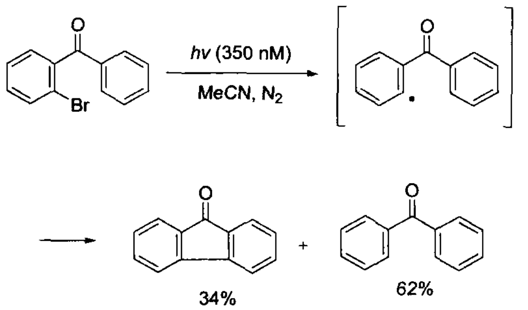


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_209,

Example 2[8]



Example 3[10]



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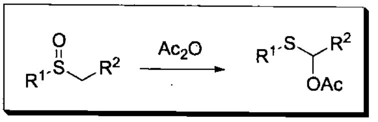
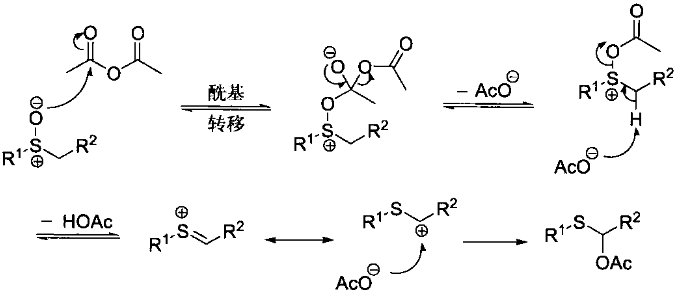
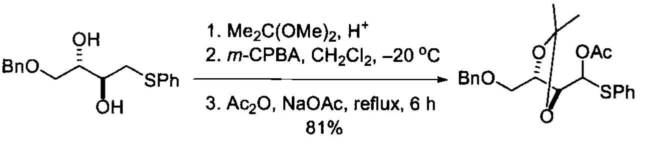
Pummerer 重排反应

亚砜用乙酸酐转化为 α -酰氧基硫醚的反应。





Example 1[2]



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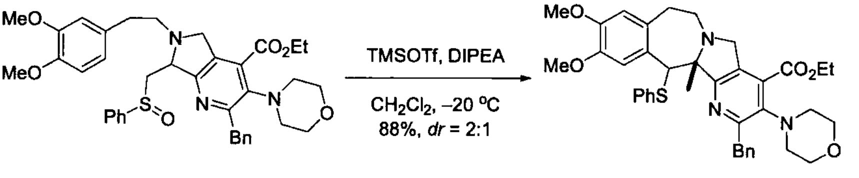

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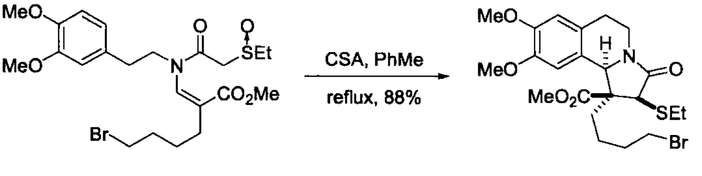
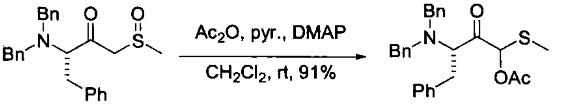


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_210,

Example 4[9]



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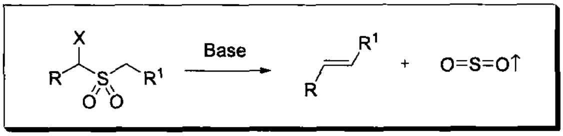
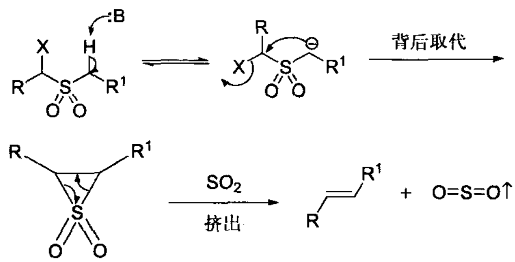
Ramburg-Backlund 反应

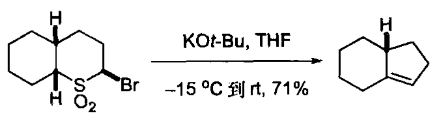
α - 卤代砜经挤出反应生成烯烃。



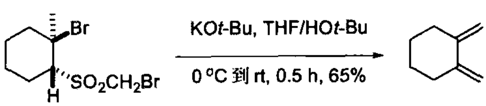


环砜中间体

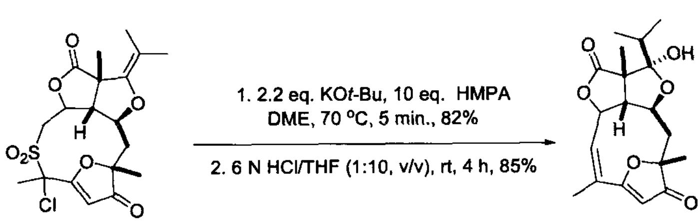
Example 1[4]



Example 2[5]

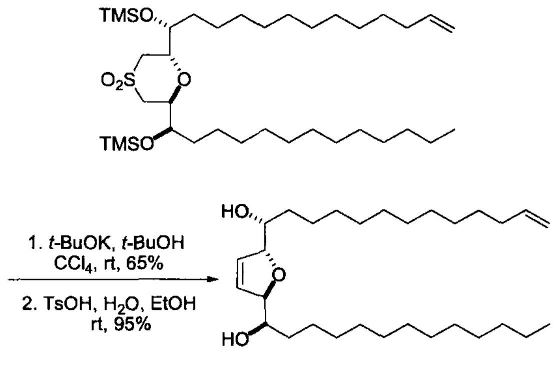


Example 3[6]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_211,

Example 4, 就地氯化[7]



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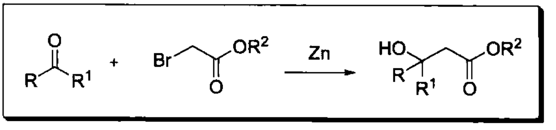
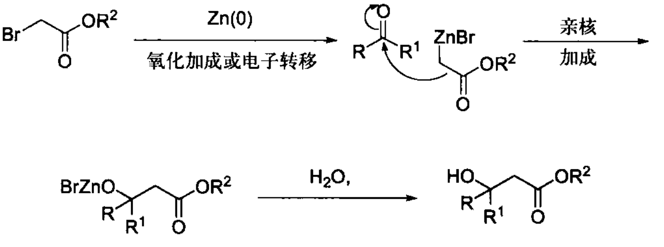
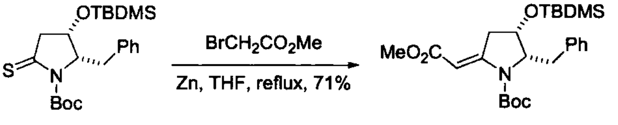
Reformatsky 反应

由 α - 卤代酯得来的有机锌化物对羰基的亲核加成反应。

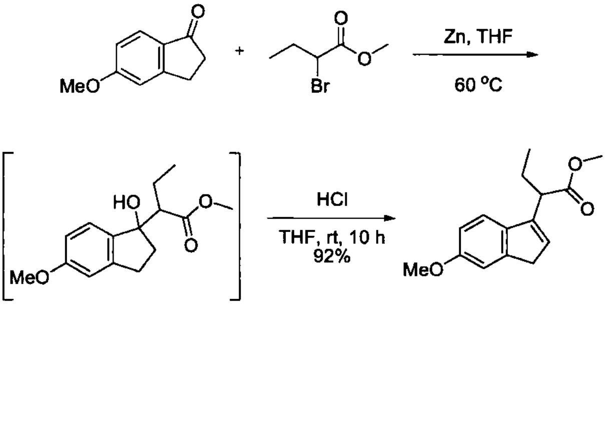




Example 1[4]

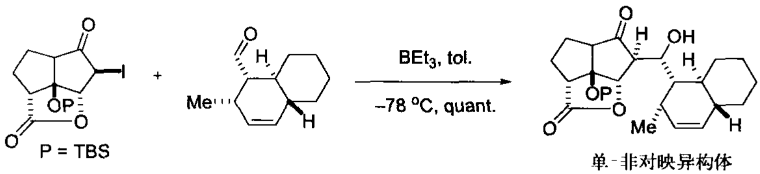


Example 2[6]

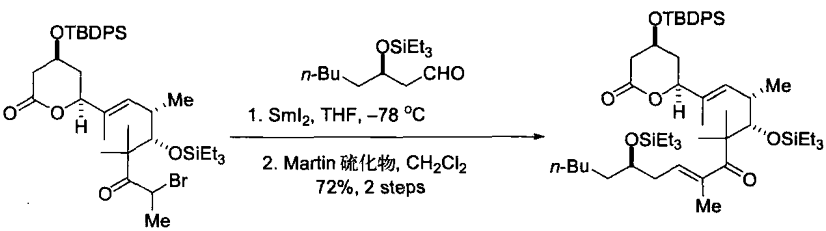


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_212,

Example 3, 含硼介质下的 Reformatsky 反应[8]



Example 4, SmI_2-促进的 Reformatsky 反应[9]



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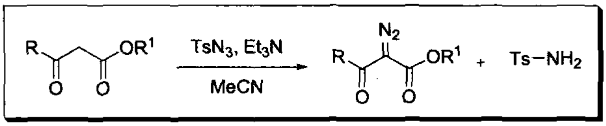
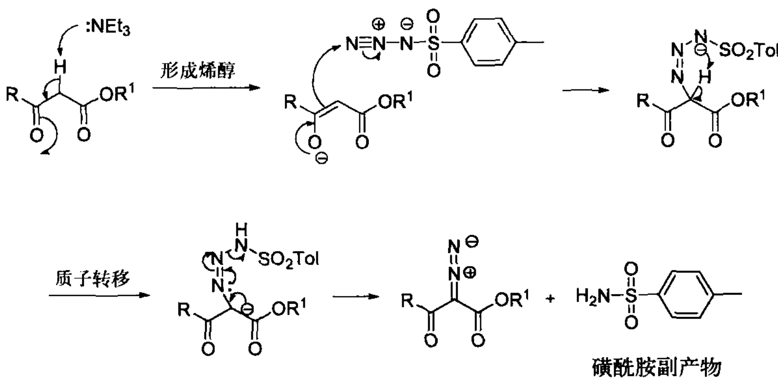
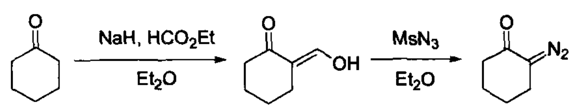
Regitz 重氮化物合成反应

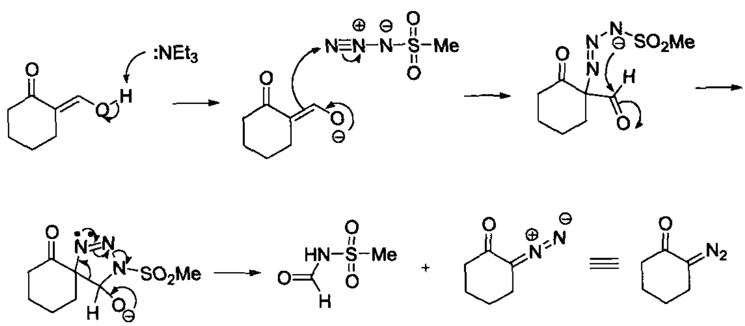
用磺酰重氮化物来合成2-重氮-1,3-二酮或2-重氮-3-氧代酯的反应。





只有一个羰基存在时，甲酸乙酯可用作活泼螯合剂。[6-9]





还有一种情况是，三唑中间体也可通过一个烯醇和甲磺酰重氮化物的1,3-环加成反应来达成：

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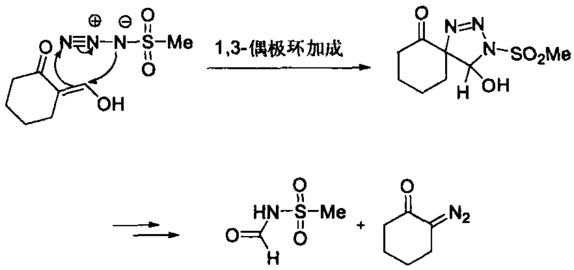
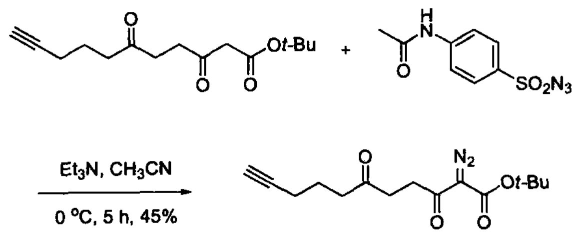
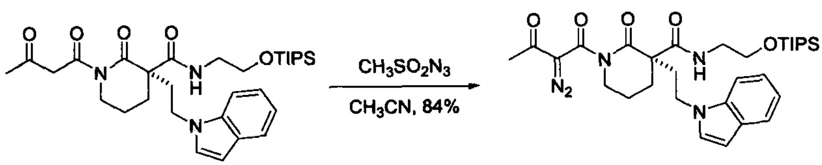


Example 1[5]



Example 2[10]



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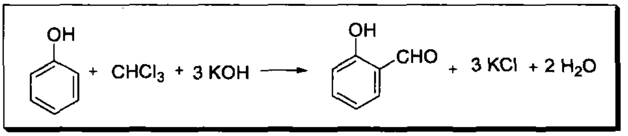
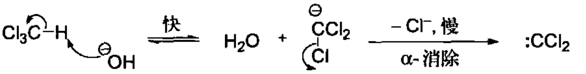
Reimer-Tiemann 反应

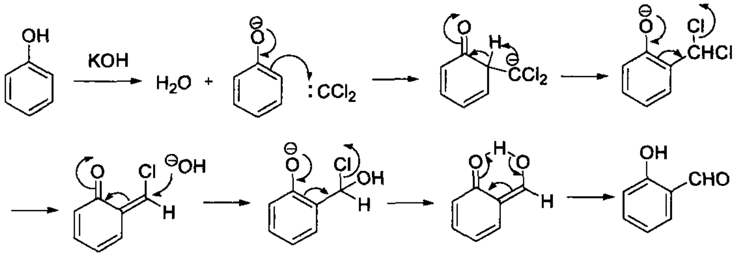
邻甲酰基酚可从酚和氯仿在碱性条件下的反应来合成。



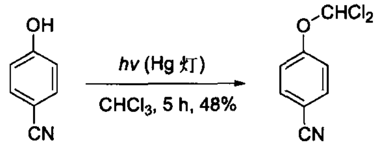
a. 产生卡宾：



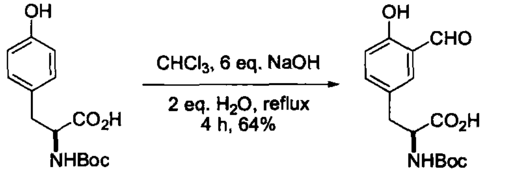
b. 二氯卡宾加成及水解：



Example 1, 光促的无碱下 Reimer–Tiemann 反应[7]



Example 2[8]



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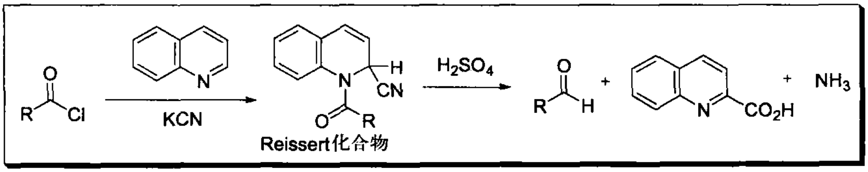
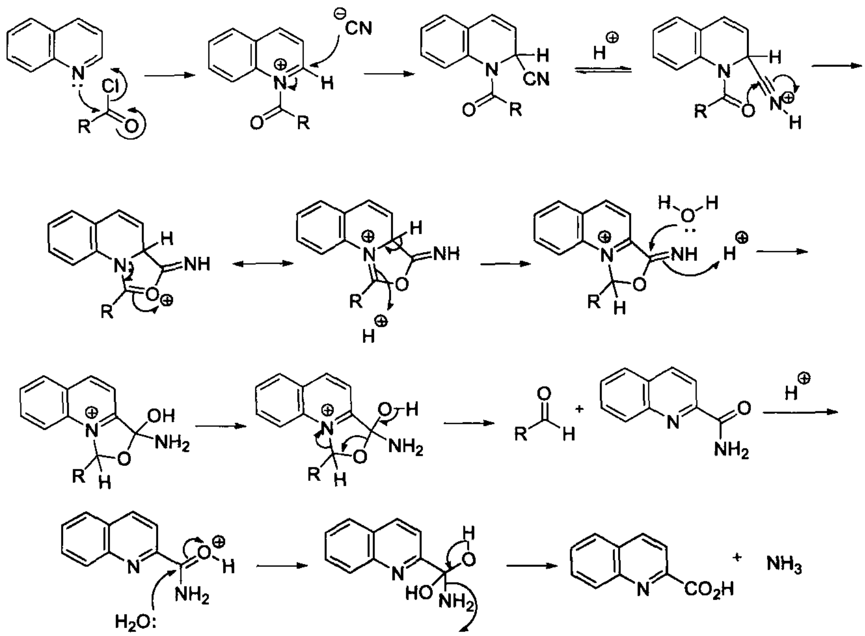
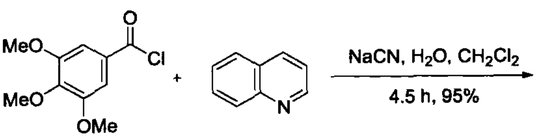
Reissert 反应

喹啉和异喹啉用酰氯和KCN反应给出喹啉酸、醛和氨。

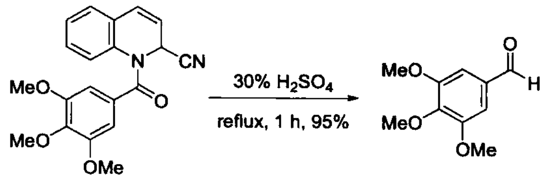




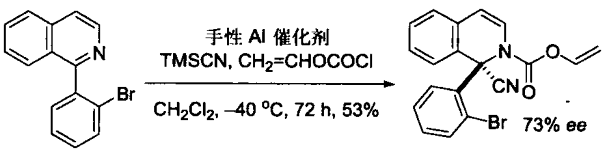
Example 1[3]



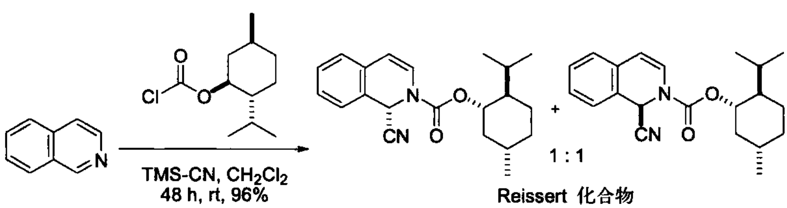
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_215,



Example 2, 从异喹啉而来的Reissert化合物[7]



Example 3, 从异喹啉而来的Reissert化合物[10]



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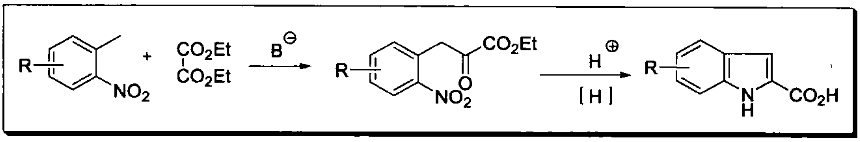
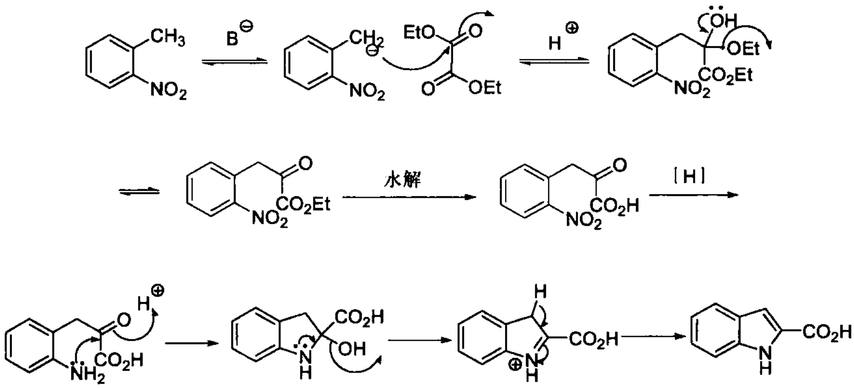
Reissert 吲哚合成反应

邻硝基甲苯衍生物和草酸乙酯在碱催化下缩合后再还原环合生成吲哚-2-羧酸衍生物的反应。





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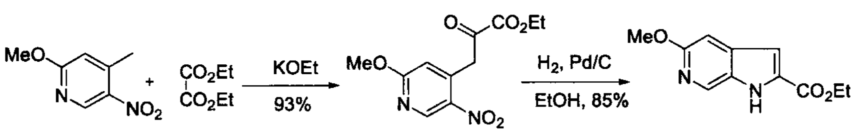
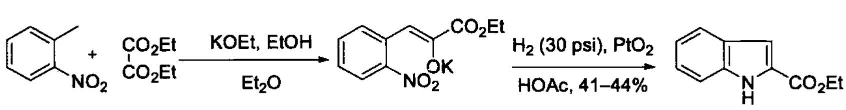
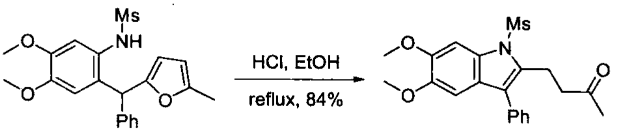


Example 2[3]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_216,

Example 3, 呋喃环是羰基的掩蔽体[10]



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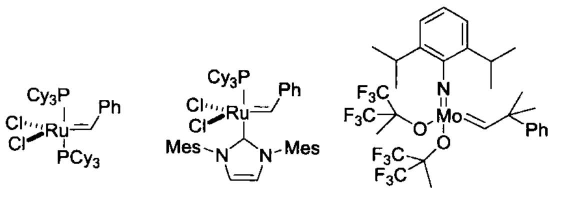
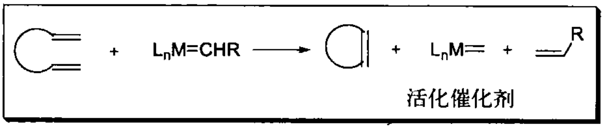
Ring-closing metathesis （RCM,闭环复分解反应）

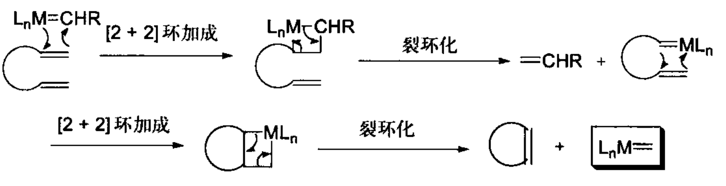


Grubbs催化剂　　　　Schrock催化剂

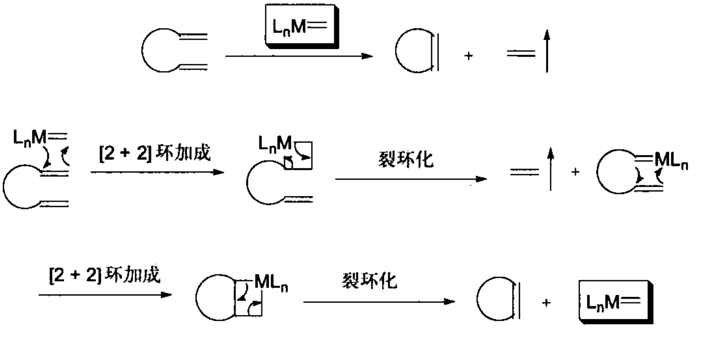
这三个催化剂在下面的机理中都用“LnM＝CHR”表示。

真正的催化剂有下面的预催化剂而来：



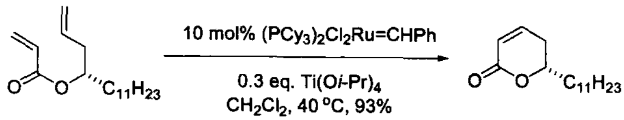


催化循环：

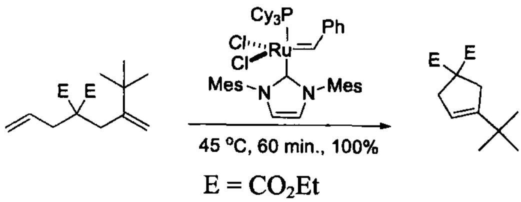


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_217,

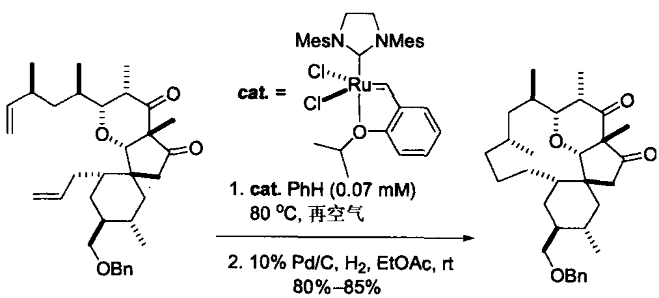
Example 1[3]



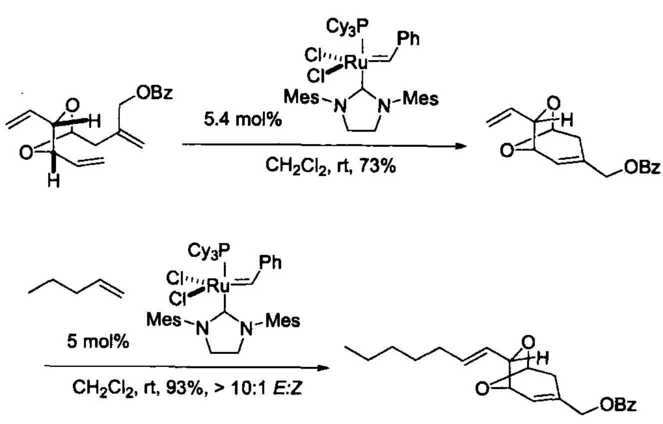
Example 2[5]



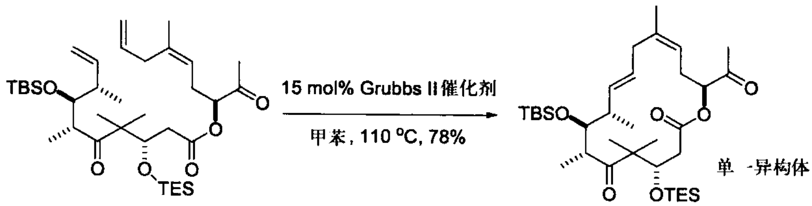
Example 3[7]



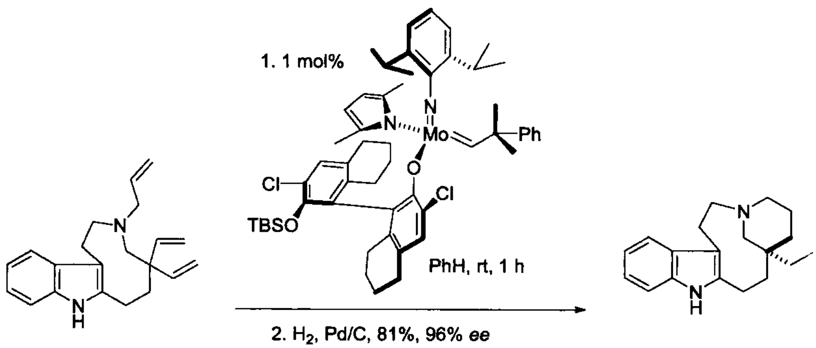
Example 4[9]



Example 5[10]



Example 6[12]



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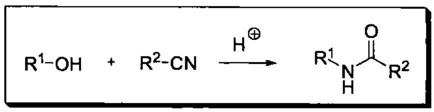
Ritter 反应

腈和醇在强酸参与下生成酰胺的反应。

通式：



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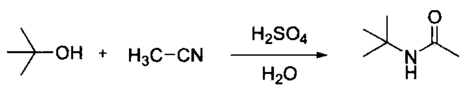

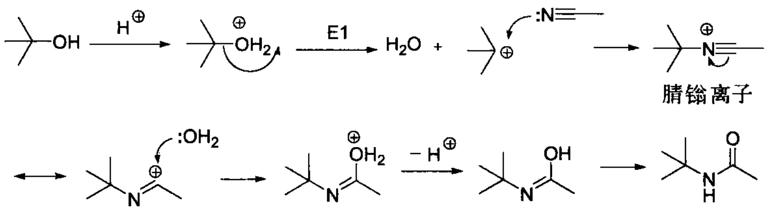

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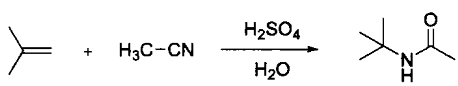
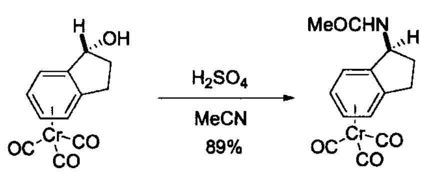
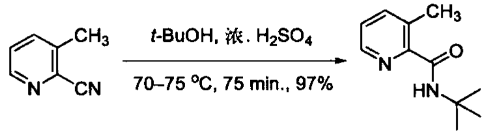


Example 1[3]



Example 2[4]



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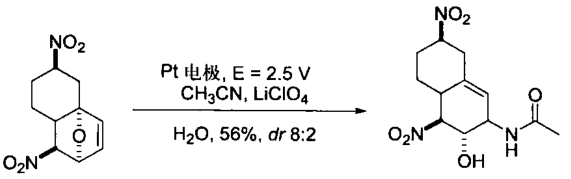
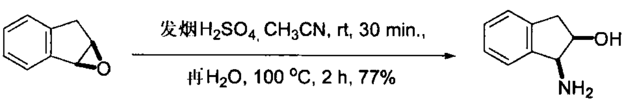
Example 3[5]



Example 4[6]



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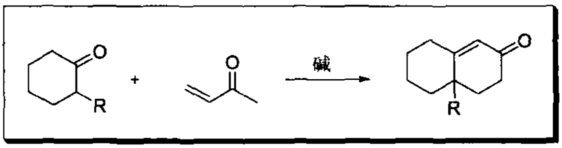
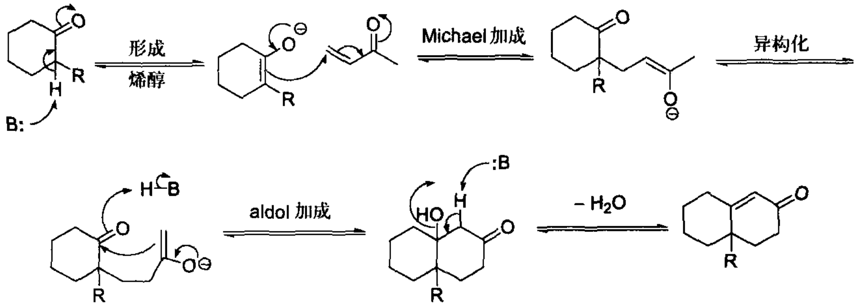
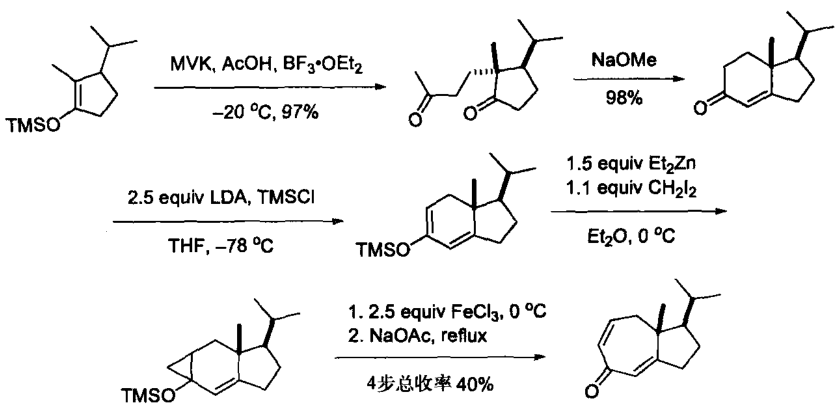
Robinson 增环反应

环己酮和甲基烯基酮发生Michael加成反应后再进行分子内aldol缩合反应给出六元环的 α , β -不饱和酮。

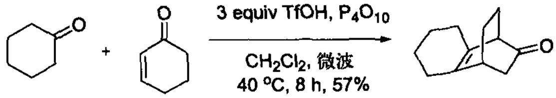




Example 1, 同Robinson反应[7]



Example 2[8]



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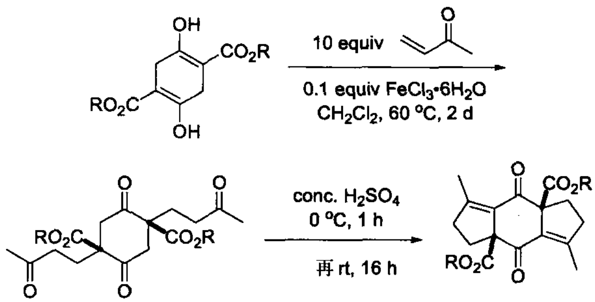
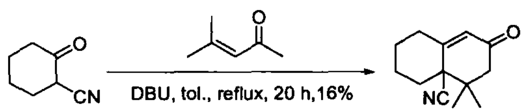
Example 3, 二重Robinson-类环戊烯增环反应[9]



Example 4[10]



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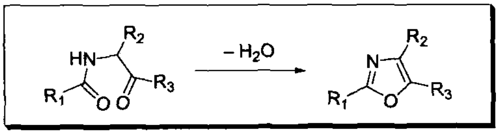
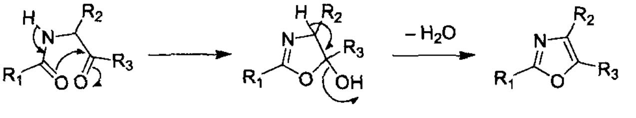
Robinson-Gabriel 合成反应

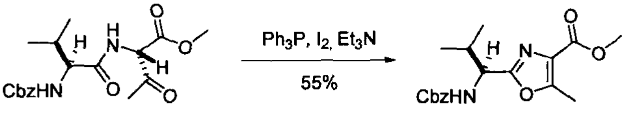
2-酰胺基酮环合脱水给出2,5-二和2,4,5-三烷基、芳基、杂芳基和芳烷基噁唑。



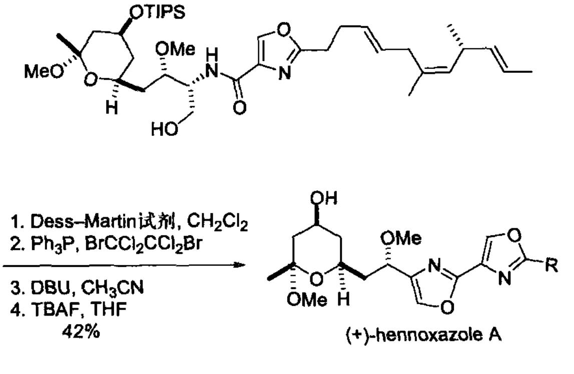
R_1, R_2, R_3 = 烷基、芳基、杂芳基



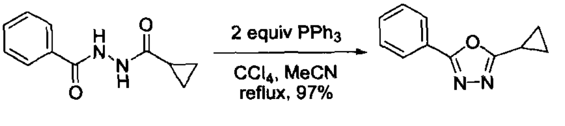
Example 1[3]



Example 2[4]



Example 3, 卤素效应[9]



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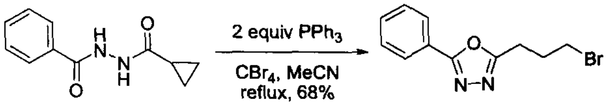
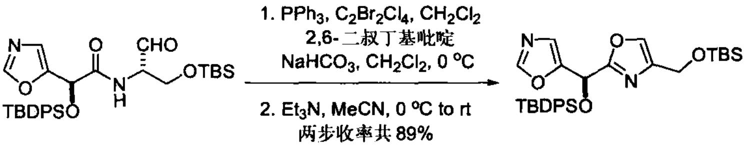


Example 4[10]



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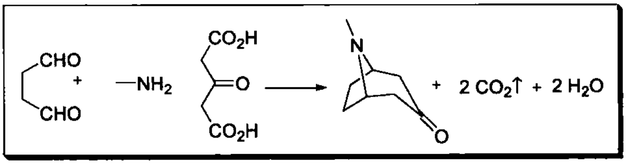
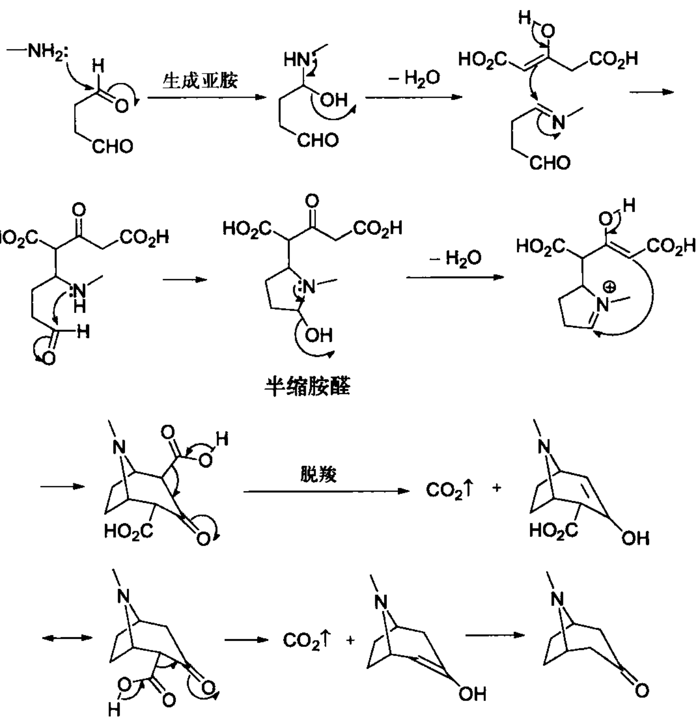
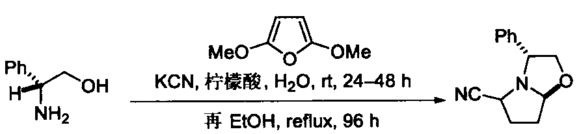
Robinson-Schopf 反应

1,4-二酮和伯胺经缩合反应后给出托品酮。



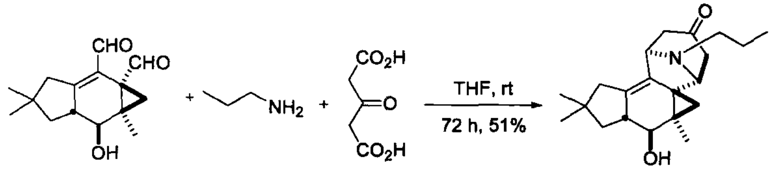


Example 1[5]



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

Example 2[9]



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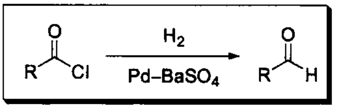
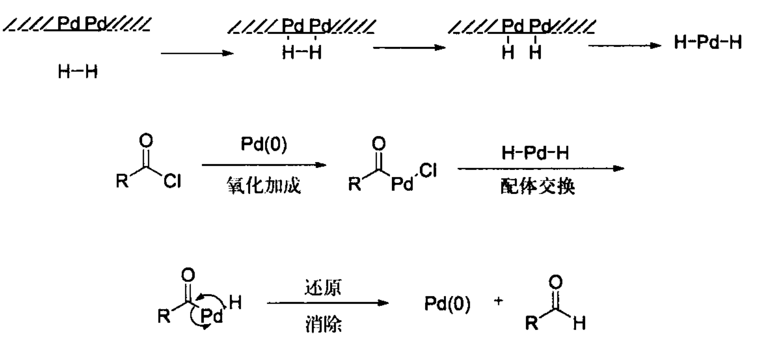
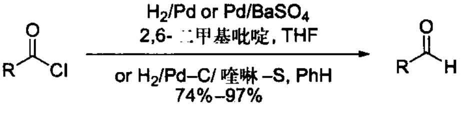
Rosenmund 还原反应

用$BaSO_4$处理的Pd催化剂将酰氯氢化还原为醛的反应。若Pd催化剂未经处理,醛会继续进行被还原为醇的反应。

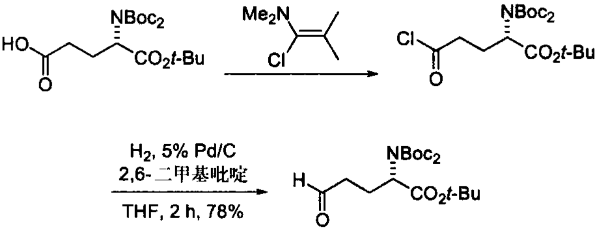




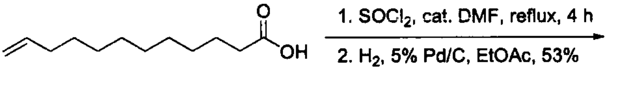
Example 1[4]



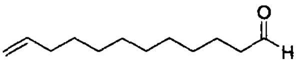
Example 2[6]



Example 3[9]



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



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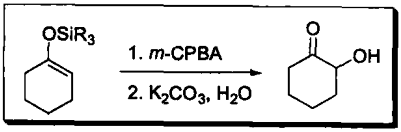
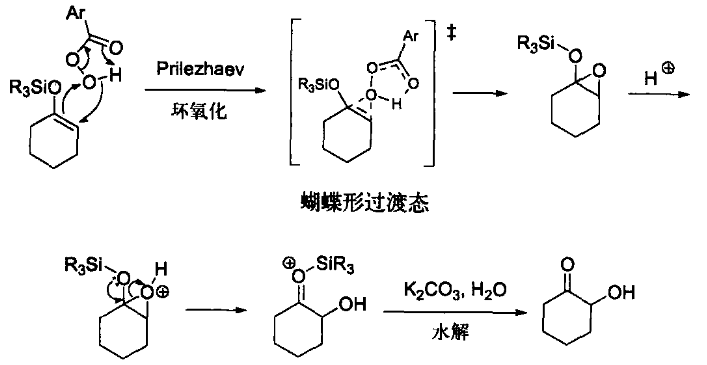
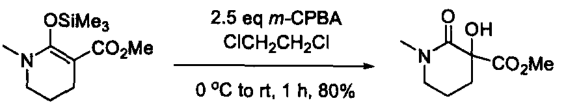
Rubottom 氧化反应

烯醇硅烷的 α -羟基化反应。

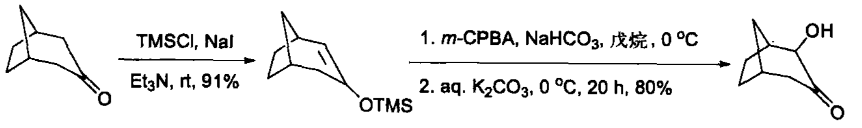




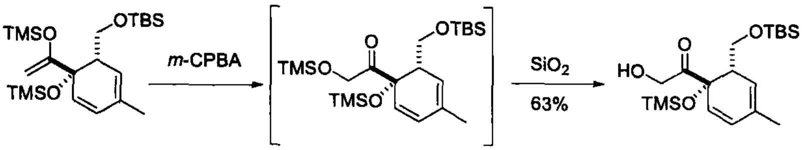
Example 1[2]



Example 2[3]

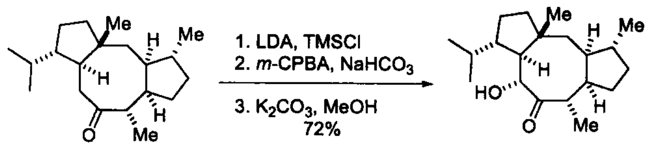


Example 3[4]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_223,

Example 4[5]



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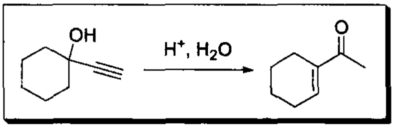
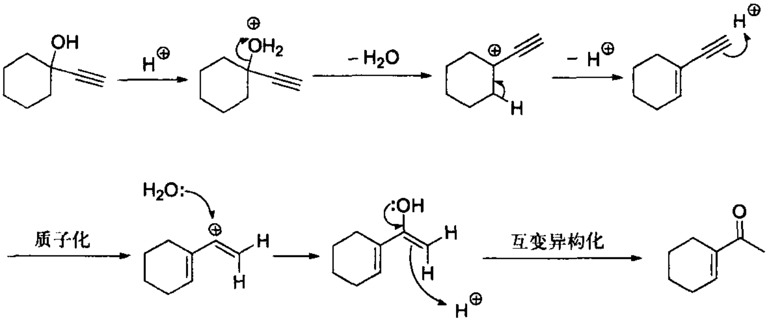
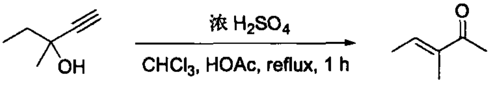
Rupe 重排反应

α-端基炔基叔醇在酸催化下重排生成 α,β-不饱和酮而非相应的 α,β-不饱和醛。参见第353页上的Meyer-Schuster重排反应。

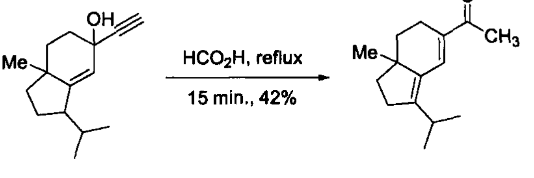




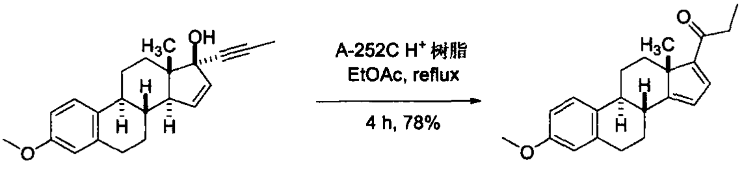
Example 1[4]



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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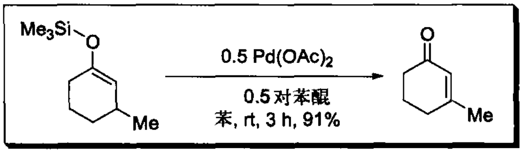
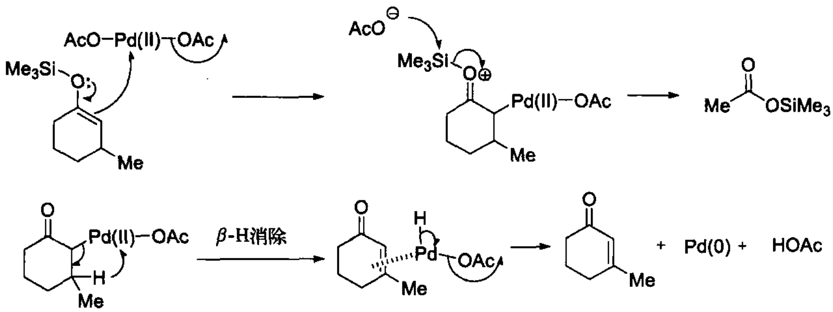
Saegusa 氧化反应

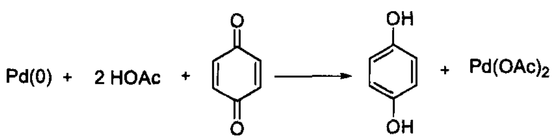
Pd催化的转化烯醇硅烷为烯酮的反应，亦称Saegusa烯酮合成反应。



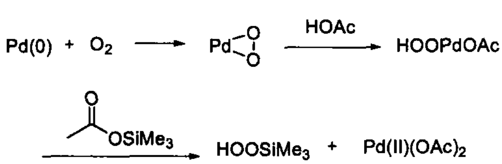
反应机理与第564页上的Wacker氧化反应相似。



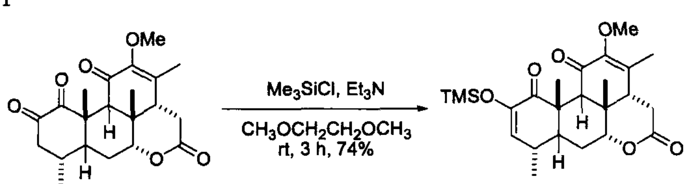
Pd(II)氧化物的生成：



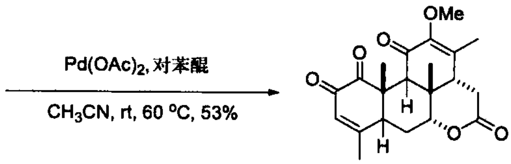
Larock 报告用氧来生成Pd(Ⅱ)氧化物：[4]



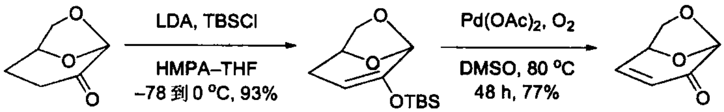
Example 1[3]



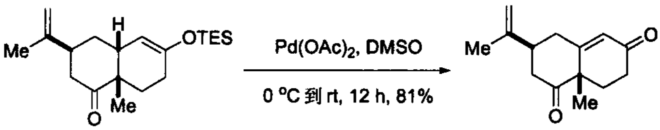
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_225,



Example 2[8]



Example 3[10]



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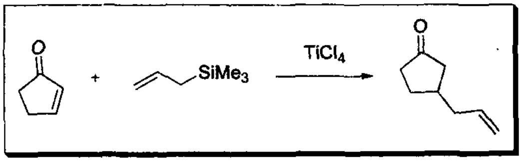
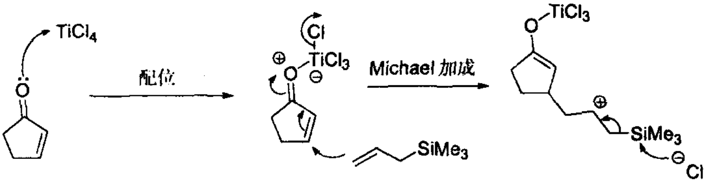
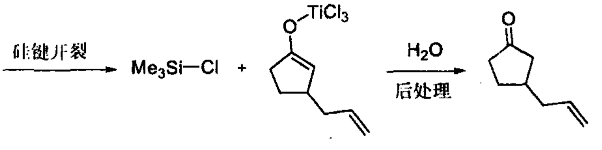
Sakurai 烯丙基化反应

Lewis酸促进的烯丙基硅烷对碳亲核物种的加成反应，亦称Hosomi-Sakurai反应。烯丙基硅烷可直接加到羰基化合物上，若羰基亲电体非 α,β-不饱和体系中的一部分时，反应可给出醇产物。

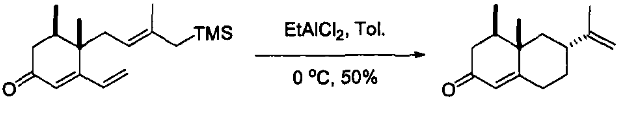




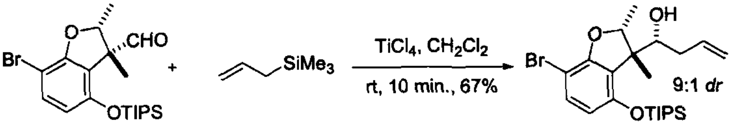
β-碳正离子被硅所稳定



Example 1[2]

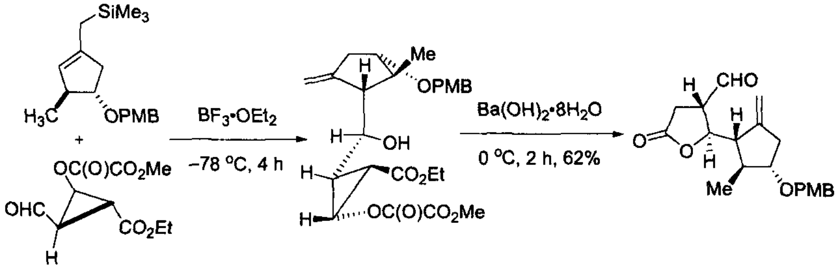


Example 2[6]

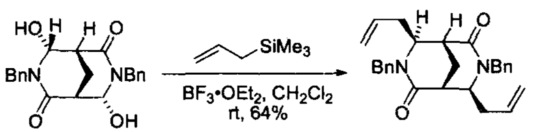


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_226,

Example 3[9]



Example 4[10]



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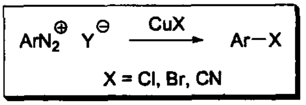
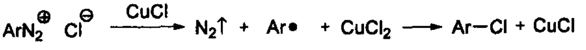
Sandmeyer 反应

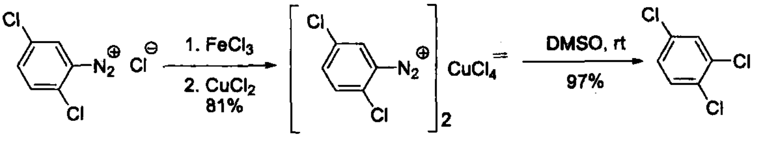
芳基卤可由重氮盐和CuX反应得到。



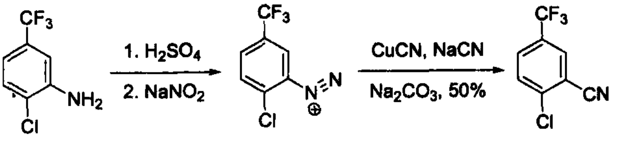
e.g.:



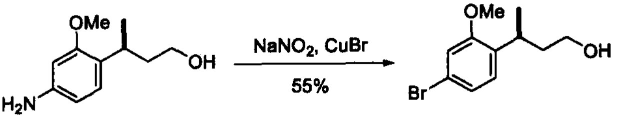
Example 1[4]



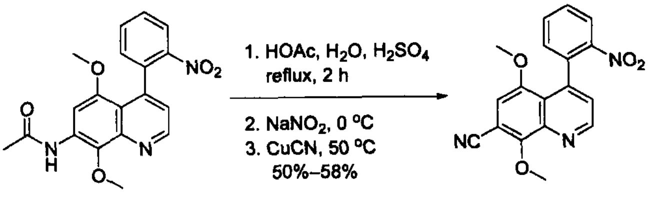
Example 2[7]



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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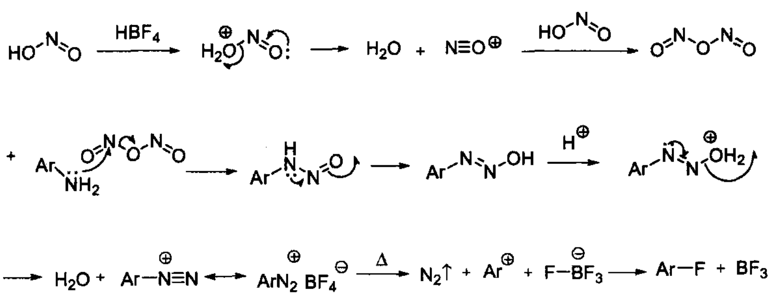
Schiemann 反应

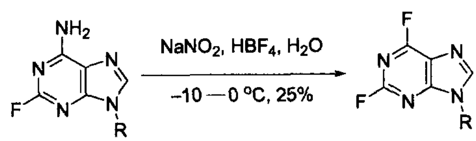
从芳香胺得到芳基氟化物，亦称Balz-Schiemann反应。

$$Ar{-}NH_2 + HNO_2 + HBF_4 \longrightarrow$$

$$ArN_2^{\oplus}\ BF_4^{\ominus} \xrightarrow{\Delta} Ar{-}F + N_2\uparrow + BF_3$$

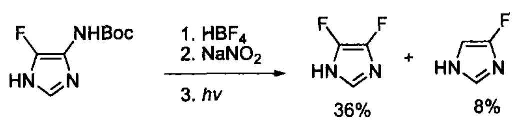


Example 1[4]

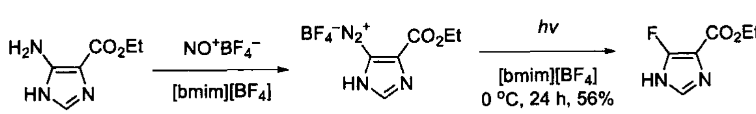


R = 2,3-5-三-O-乙酰基-β-*D*-呋喃核糖

Example 2，光促Schiemann反应[6]

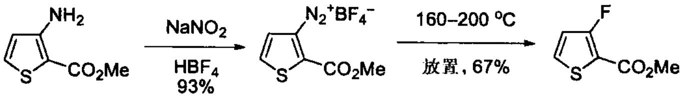


Example 3，光促Schiemann反应[8]



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

Example 4[10]



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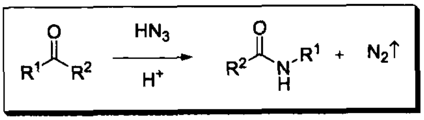
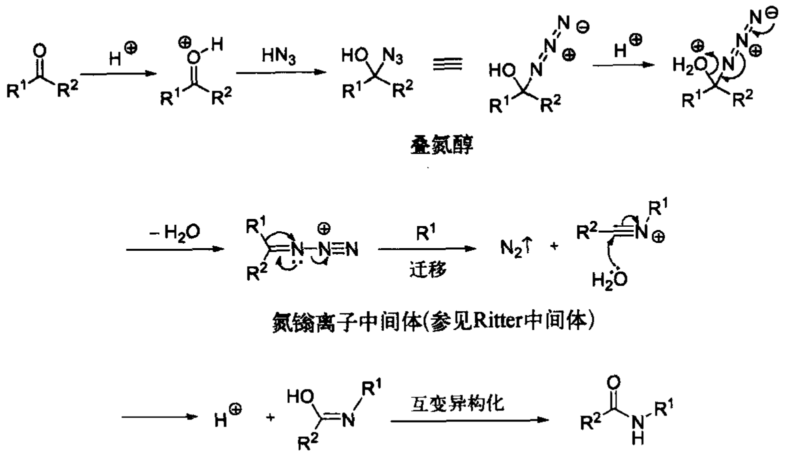
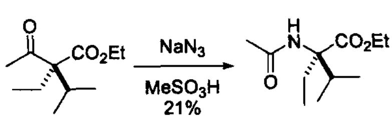
Schmidt 重排反应

Schmidt重排反应是酸促进的叠氮酸对羰基化合物、叔醇和烯烃等亲电体的反应。这些底物反应后发生重排，挤出一分子氮气生成胺、腈、酰胺或亚胺。

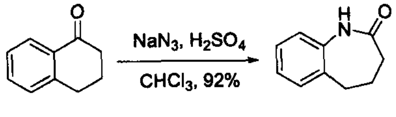




Example 1, 一个经典实例[3]

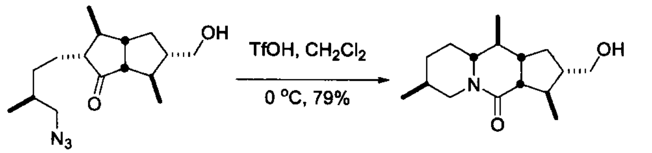


Example 2[5]

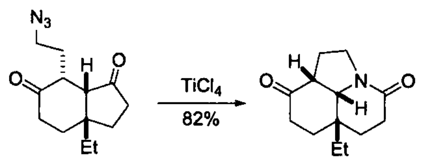


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_229,

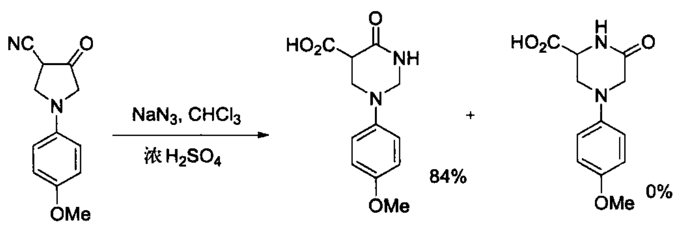
Example 3, 分子内 Schmidt 重排[6]



Example 4, 分子内 Schmidt 重排[8]



Example 5, 分子间 Schmidt 重排[9]



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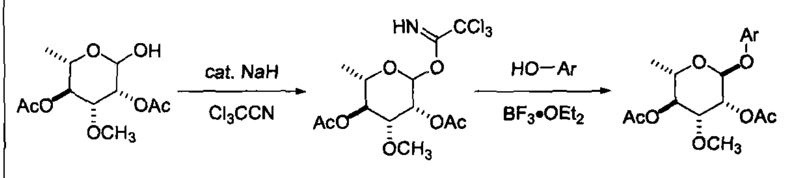
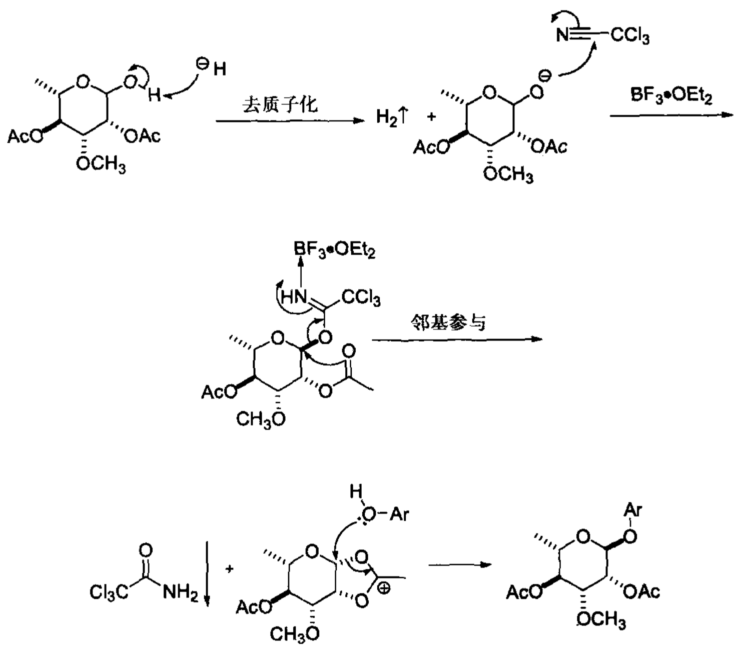
Schmidt 三氯酰亚胺苷化反应

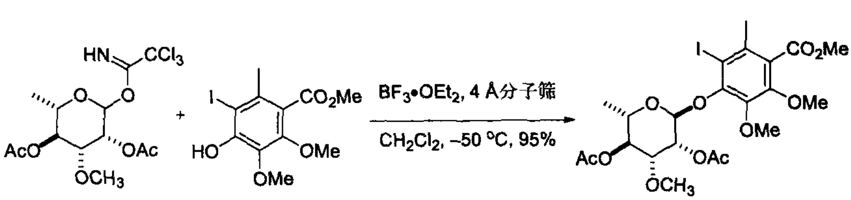
Lewis 酸促进的三氯酰亚胺和醇或酚的苷化反应。



三氯乙酰亚氨化物

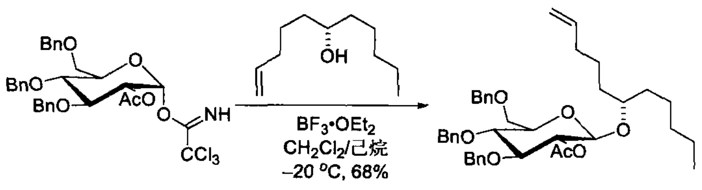


Example 1[5]

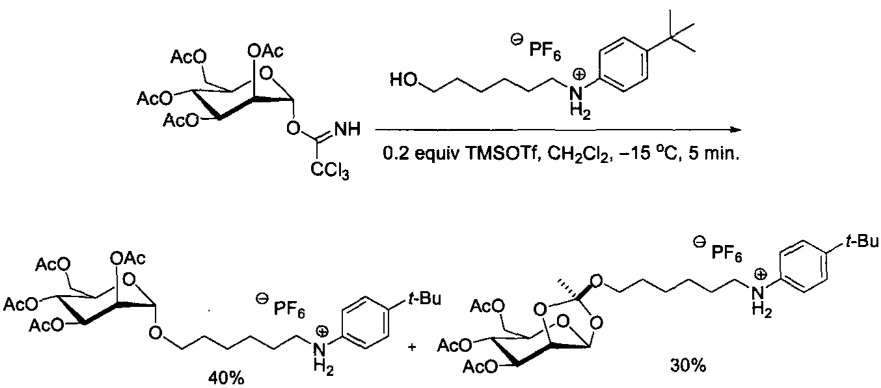


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_230,

Example 2[7]



Example 3[9]



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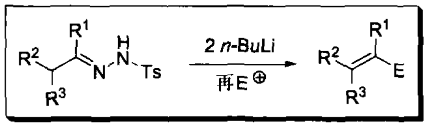
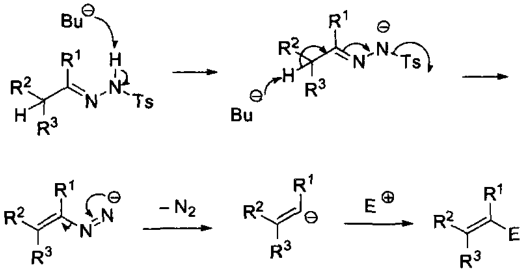
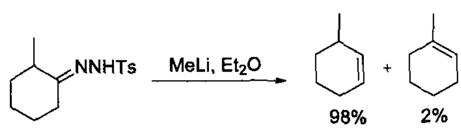
Shapiro反应

Shapiro反应是Bamford-Stevens反应的变异。前者用RLi和RMgX为碱，给出少取代烯烃产物(动力学产物)；后者用Na、NaOMe、LiH、NaH和$NaNH_2$等为碱，但给出多取代烯烃产物(热力学产物)。

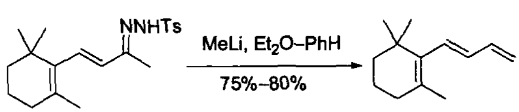




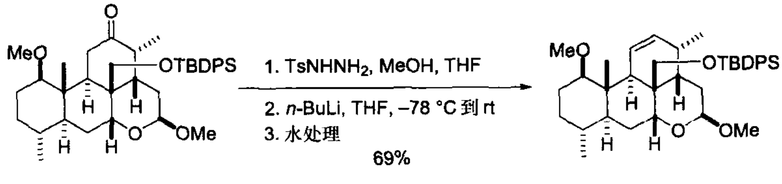
Example 1[2]



Example 2[3]

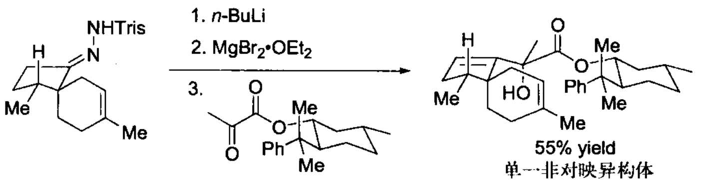


Example 3[7]



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

Example 4[8]



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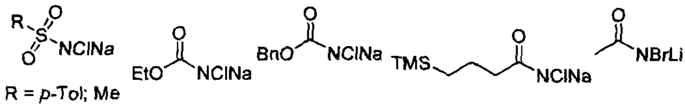
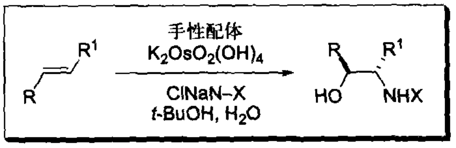
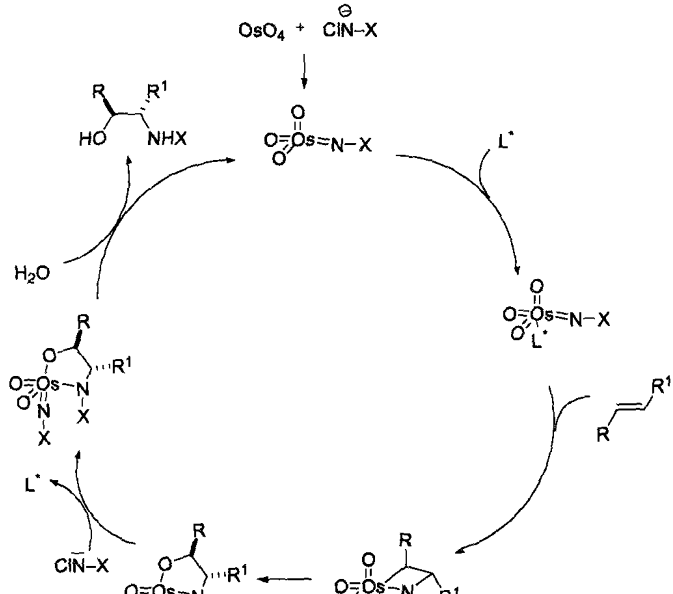
Sharpless 不对称羟胺化反应

Os促进的氮和氧对烯烃*cis*-加成反应。位置选择性由配体控制，氮的来源（X-NClNa）包括：

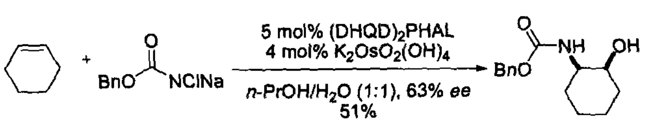




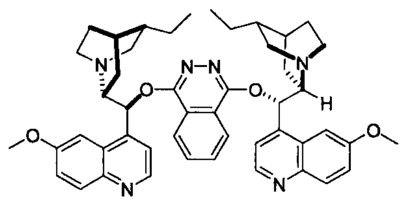
催化循环：



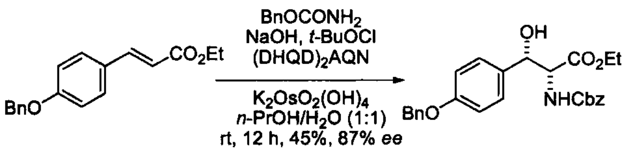
Example 1[1b]



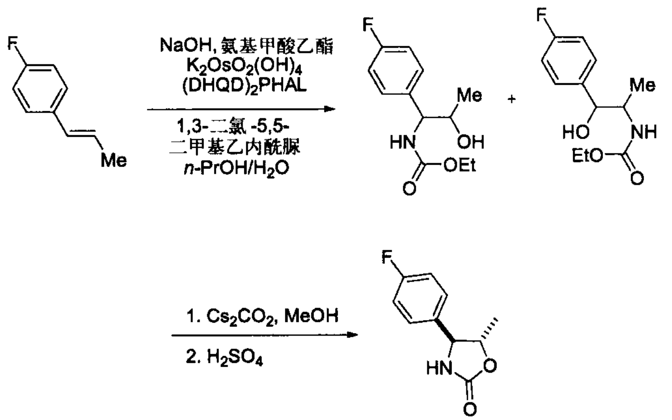
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_232,



Example 2[2]



Example 3[6]



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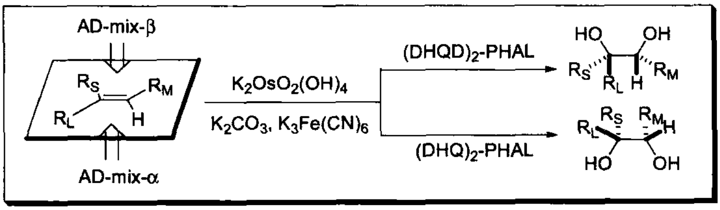
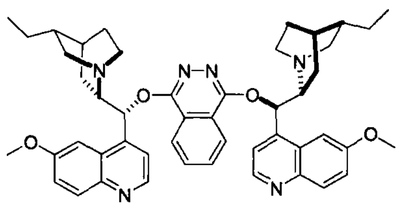
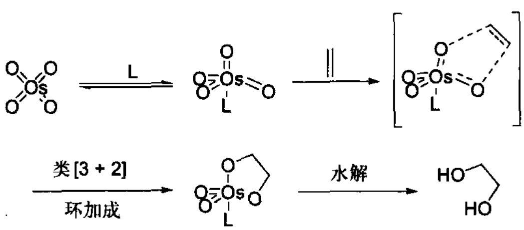
Sharpless 不对称双羟化反应

用Os催化剂在金鸡纳碱存在下对映选择性地对烯烃进行 *cis*-双羟化反应。

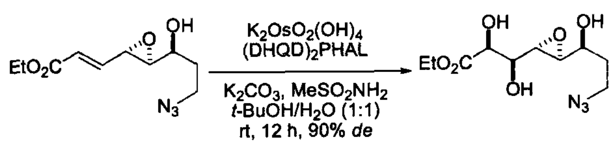




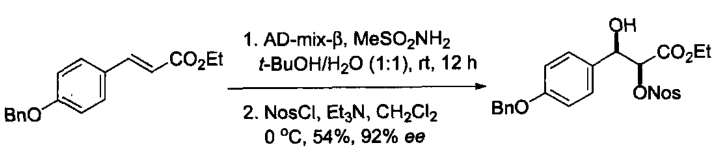
协同[3 + 2] 环加成机理：[5]



Example 1[2]

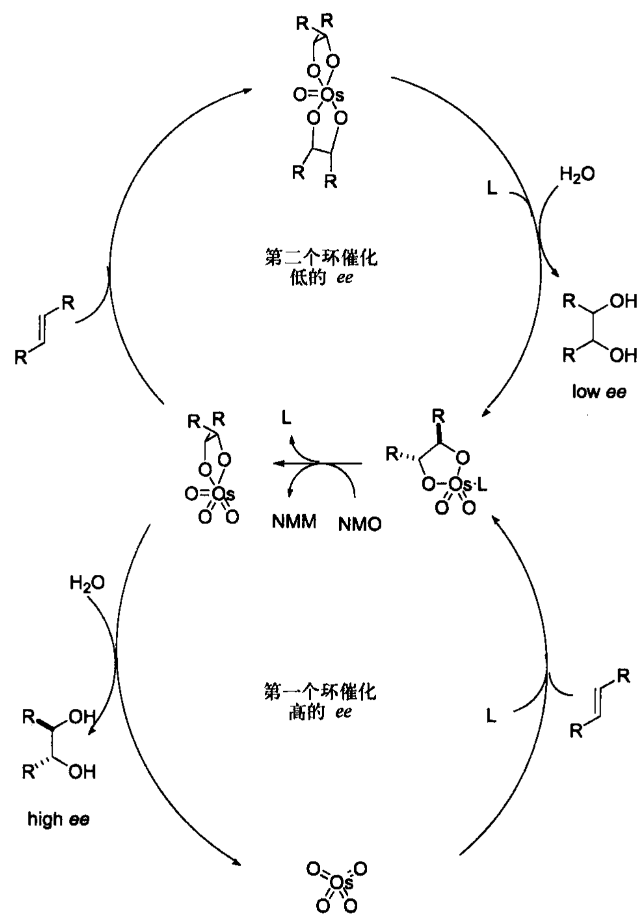


Example 2[4]

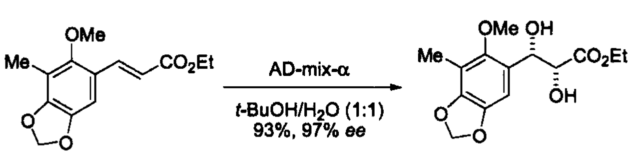


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_233,

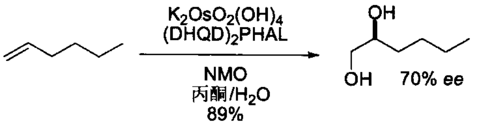
催化循环(第二个循环在低浓度烯烃时无作用)：



Example 3[9]



Example 4[10]



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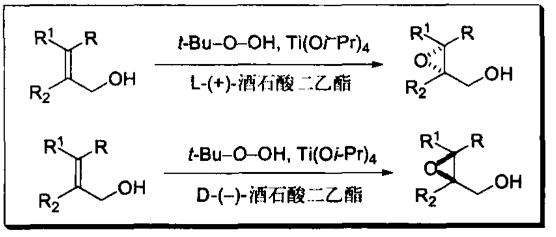
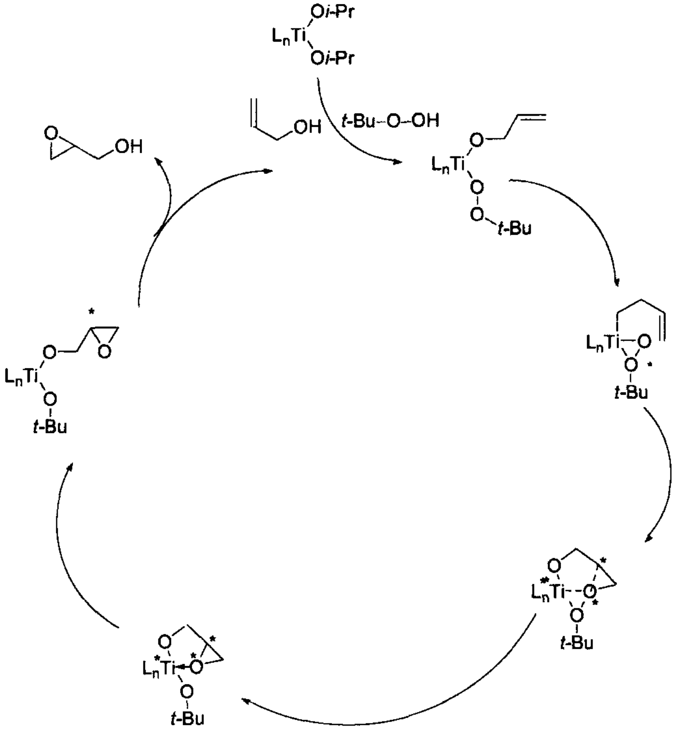
Sharpless 不对称环氧化反应

用^{t}BuOK、Ti(O^{i}Pr)$_4$和光学纯的酒石酸二酯对映选择性地对烯丙醇进行的环氧化反应。

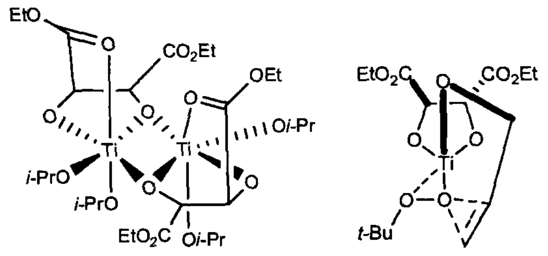


催化循环：

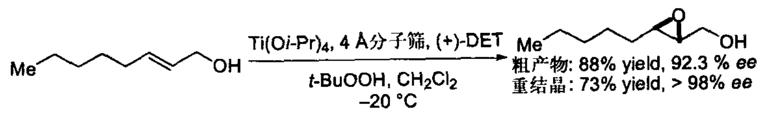


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_234,

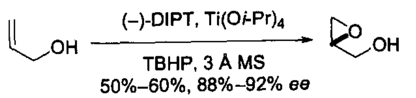
公认的活化催化剂和过渡态：



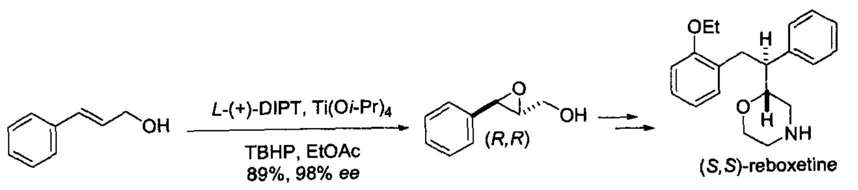
Example 1[3]



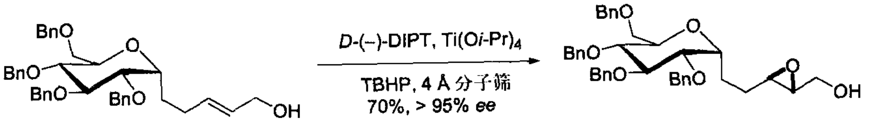
Example 2[3]



Example 3[11]



Example 4[12]



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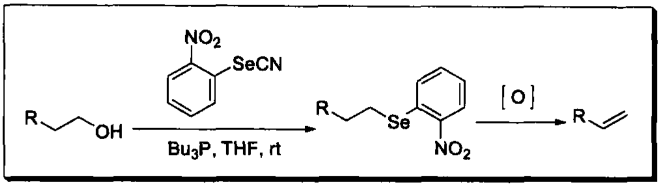
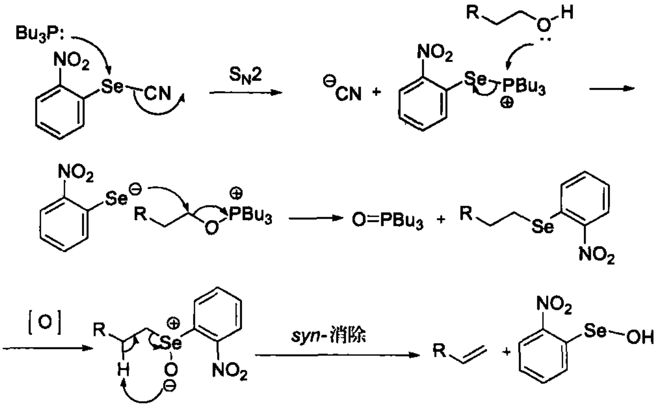
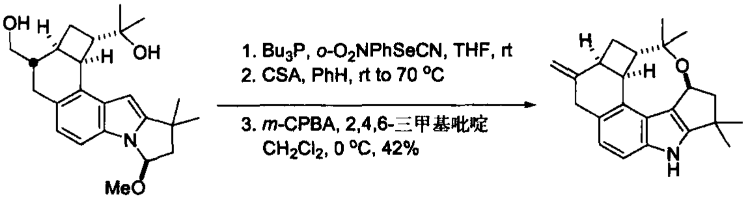
Sharpless 烯烃合成反应

从邻硝基硒基腈和PBu_3出发或由其它途径制得的邻硝基硒基化物发生*syn*-氧化消除反应来合成烯烃。

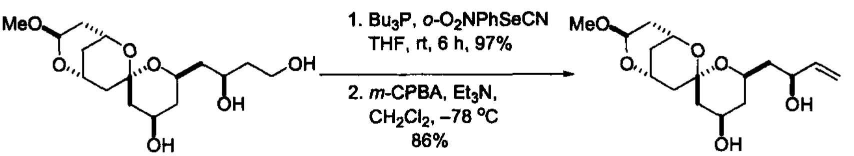




Example 1[3]

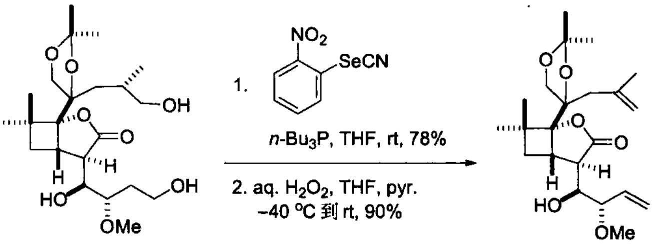


Example 2[6]

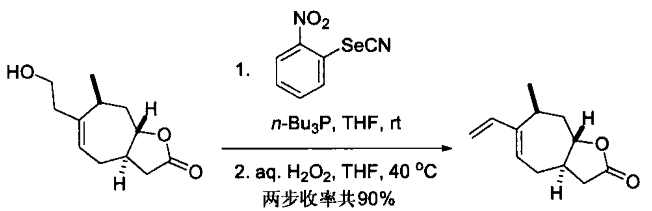


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_235,

Example 3[9]



Example 4[10]



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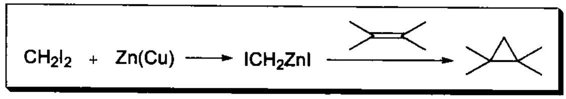
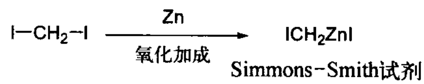
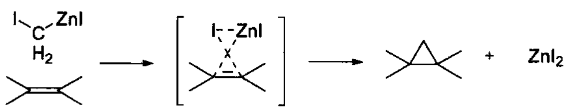
Simmons-Smith 反应

烯烃用CH_2I_2-Zn(Cu) 进行的环丙烷化反应。

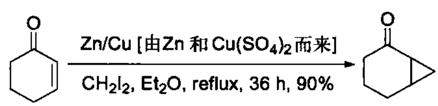




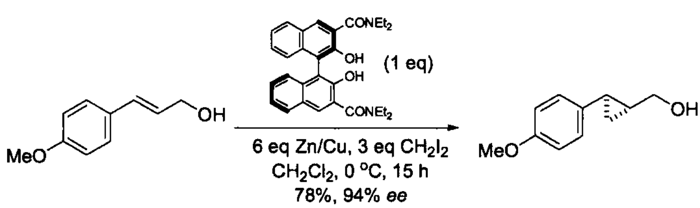
$$2\ ICH_2ZnI \rightleftharpoons (ICH_2)_2Zn + ZnI_2$$



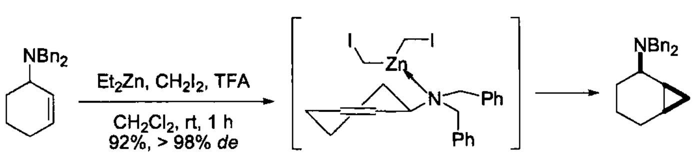
Example 1[2]



Example 2, 一个不对称模式[3]

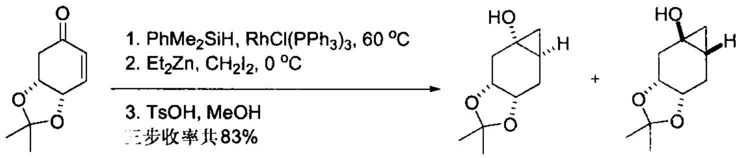


Example 3, 烯丙基胺和氨基甲酸酯的非对映选择性的Simmons–Smith环丙烷化反应[9]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_236,

Example 4[10]



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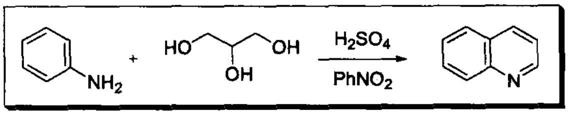
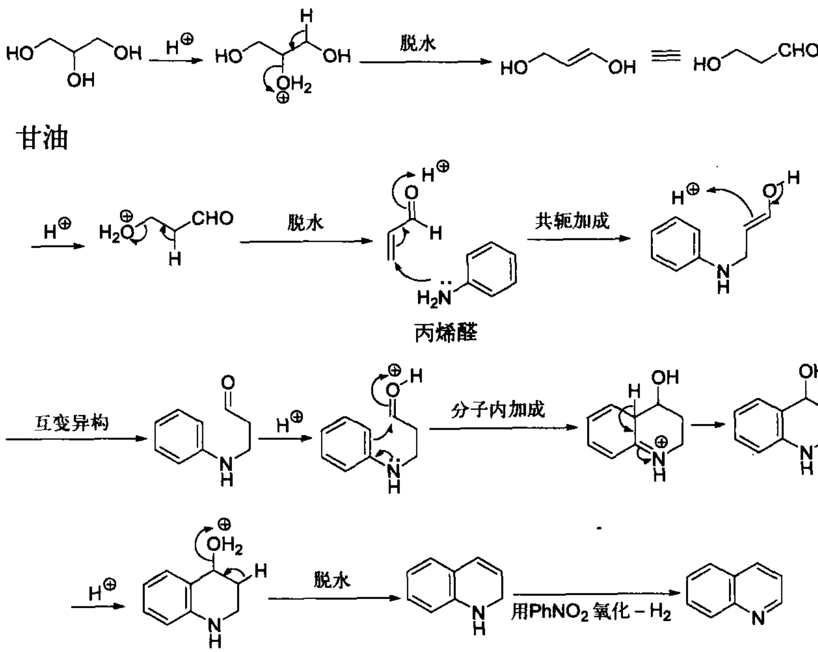
Skraup 喹啉合成反应

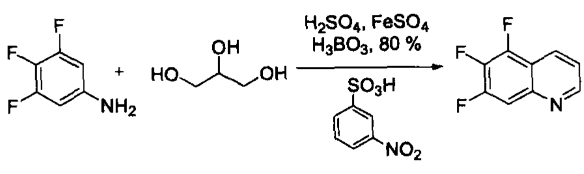
苯胺、甘油、硫酸和氧化剂(如$PhNO_2$)反应得到喹啉的合成反应。





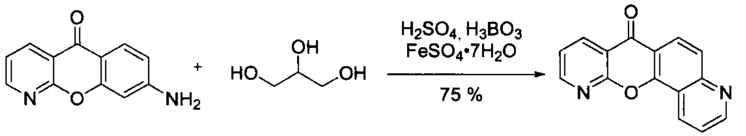
另一个机理请见第196页上的Doebner–von Miller 反应。

Example 1[5]

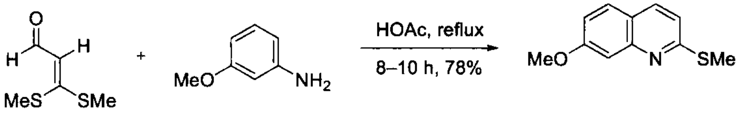


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_237,

Example 2[6]



Example 3, 一个修正的 Skraup 喹啉合成[8]



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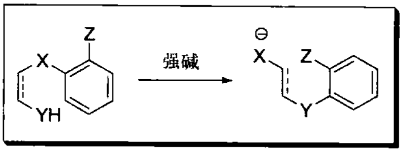
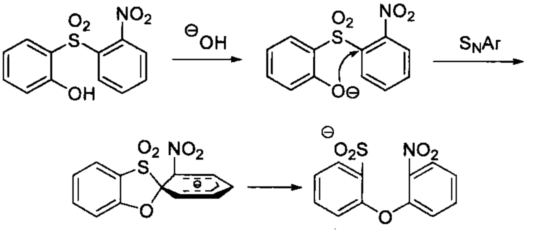
Smiles 重排反应

分子内的亲核芳香重排反应。通式为：



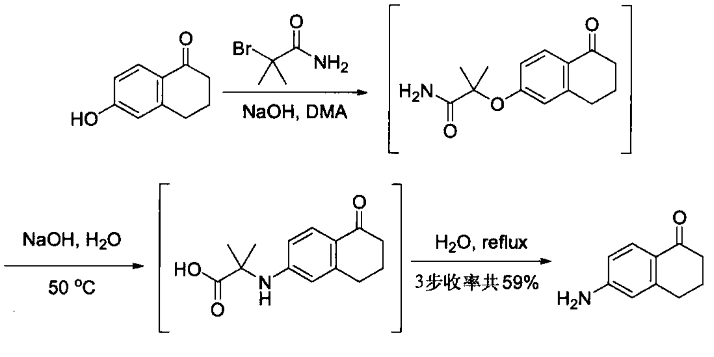
X=S, SO, SO_2, O, CO_2
YH=OH, NHR, SH, CH_2R, CONHR
Z=NO_2, SO_2R

e.g.:

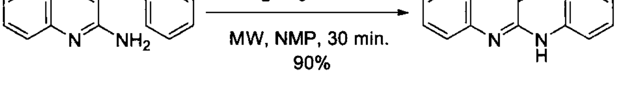


螺环负离子中间体 (Meisenheimer 配合物)

Example 1[7]



Example 2, 微波促进的Smiles 重排[9]



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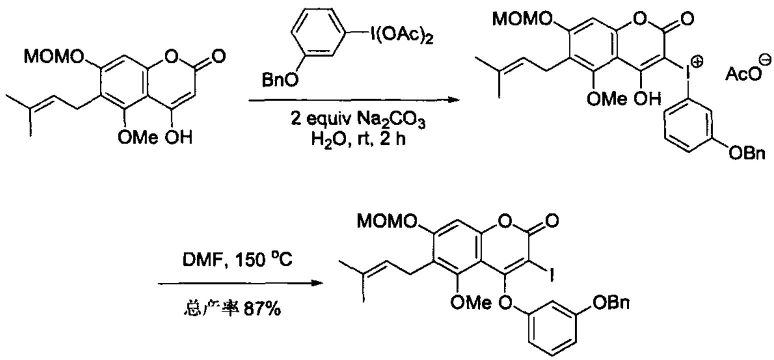
Example 3[10]



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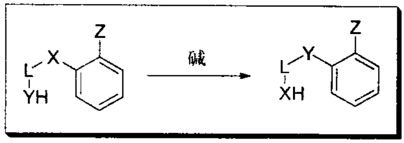
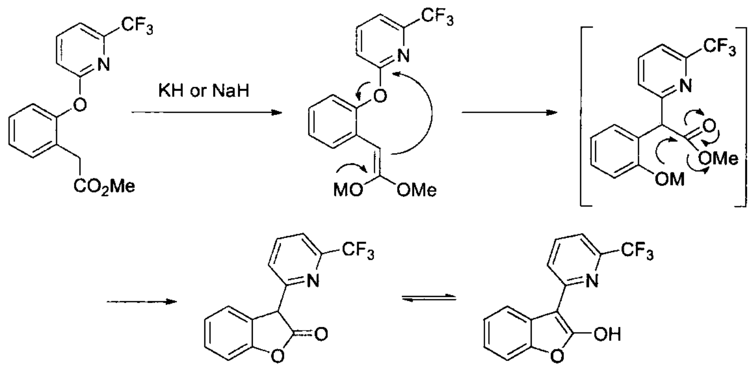
Truce-Smile 重排反应

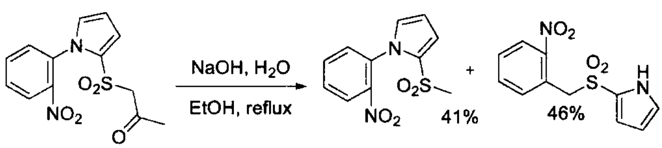
Smiles重排反应的变异（Y是碳）。



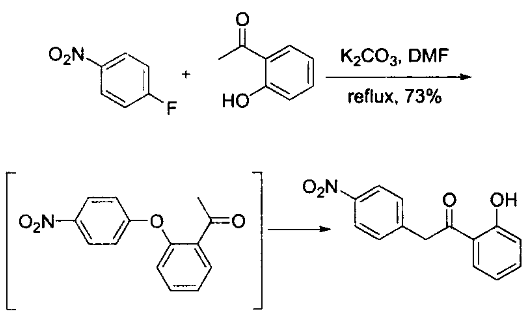
Example 1[6]



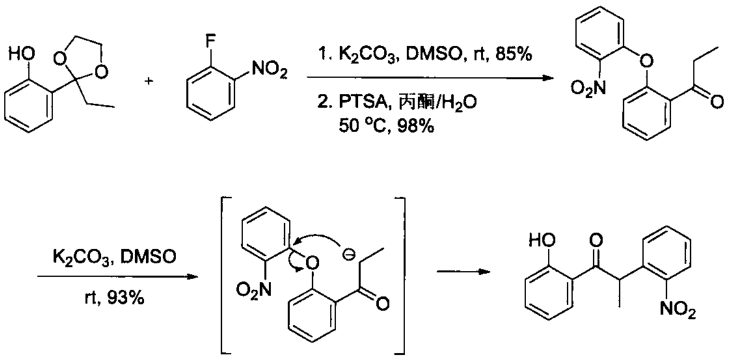
Example 2[7]



Example 3[8]



Example 4[10]



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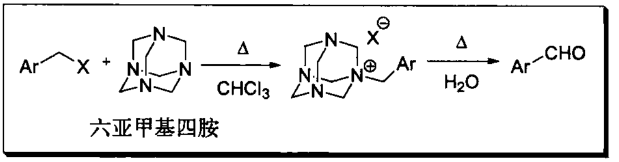
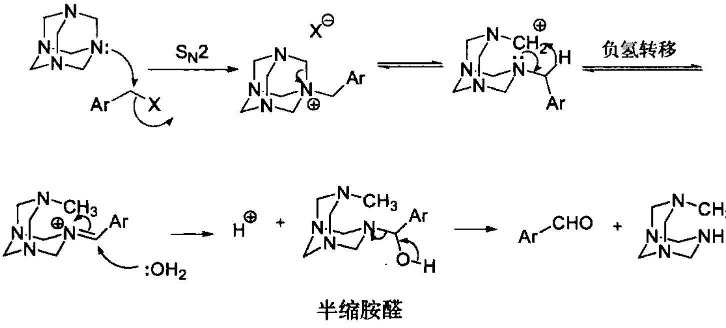
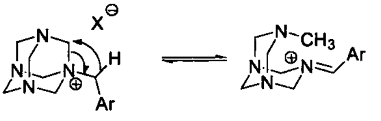
Sommelet 反应

苄卤用六亚甲基四胺转化为相应的苯甲醛。参见第171页上的Delepine氨基化反应。

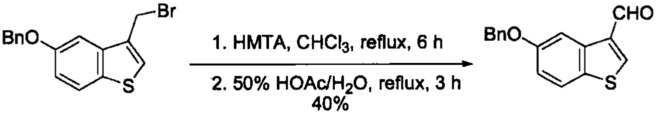




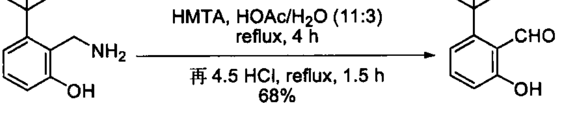
负氢的转移和六亚甲基四胺的开环可以同步进行。



Example 1[3]



Example 2[4]



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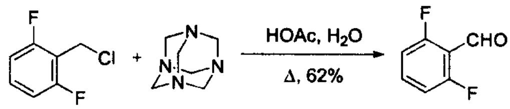
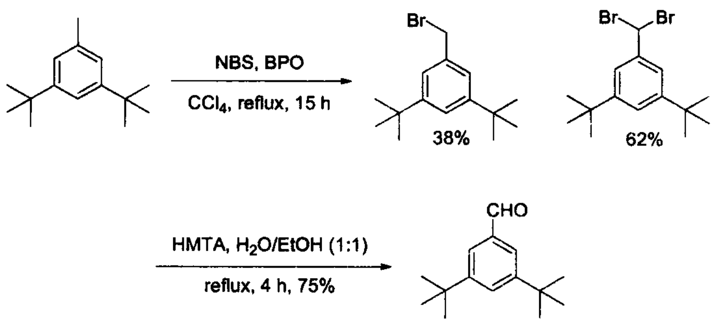
Example 3[7]



Example 4[8]



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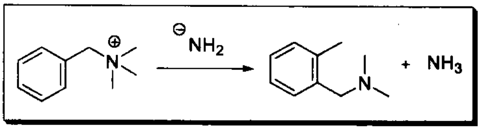
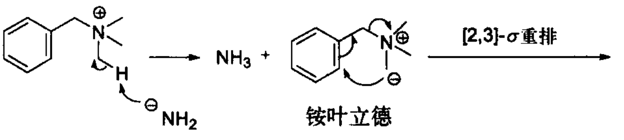
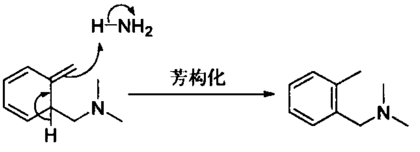
Sommelet-Hauser 重排反应

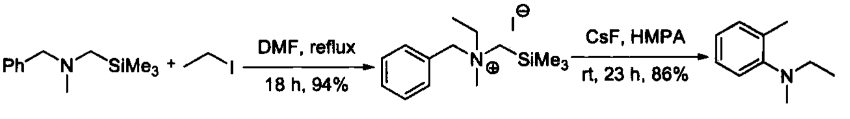
苄基季铵盐用氨基碱金属处理经叶立德中间体发生[2,3]-Wittig重排反应。



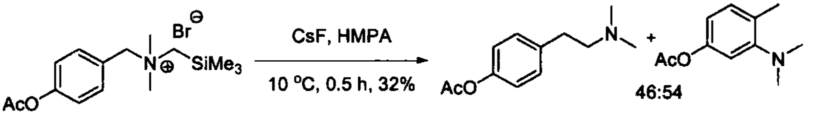




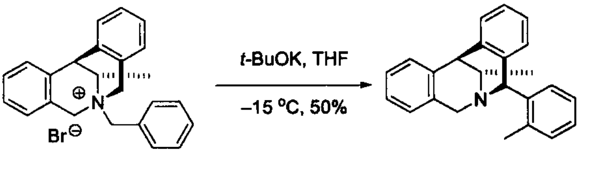
Example 1[3]



Example 2[4]



Example 3[8]



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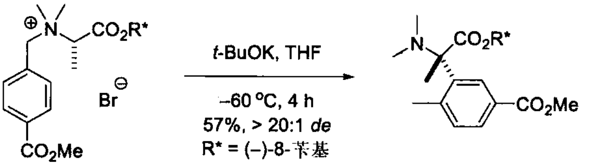
Example 4[10]



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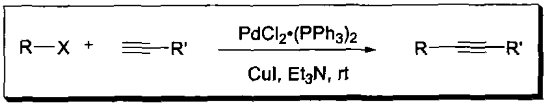
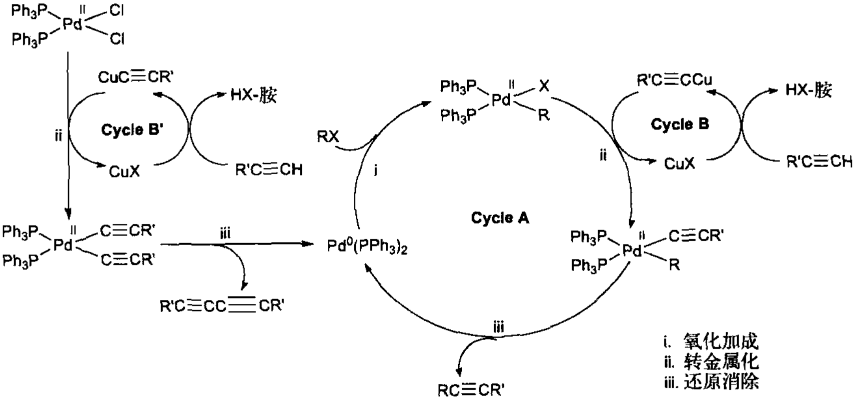
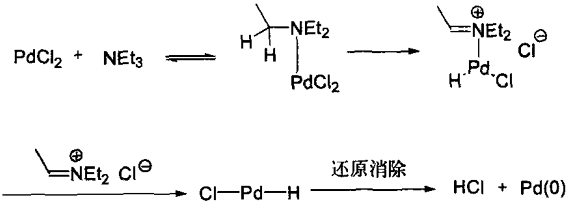
Sonogashira 反应

Pd-Cu催化下的卤代烃和端基炔烃之间的交叉偶联反应。参见第90页上的Cadiot-Chodkiewicz交叉偶联反应和第98页上的Castro-Stephens交叉偶联反应。Castro-Stephens交叉偶联反应要用到化学计量的铜，而其变异反应，Sonogashira交叉偶联反应只需催化量的Pd-Cu。

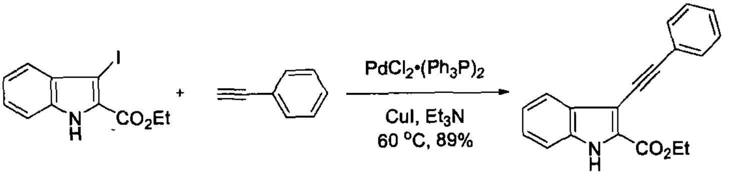




Et_3N可还原Pd(Ⅱ)为Pd(0)，自身则同时被氧化成亚胺离子。

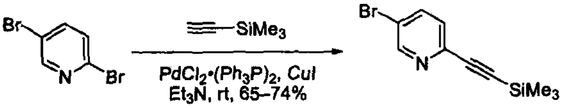


Example 1[2]

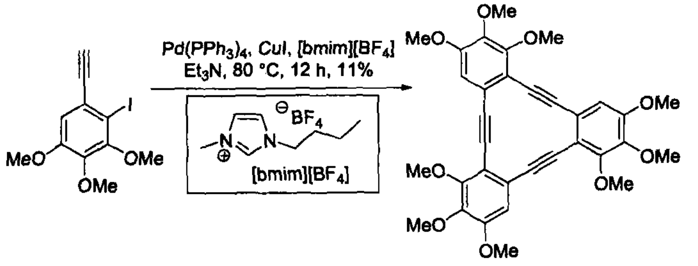


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_241,

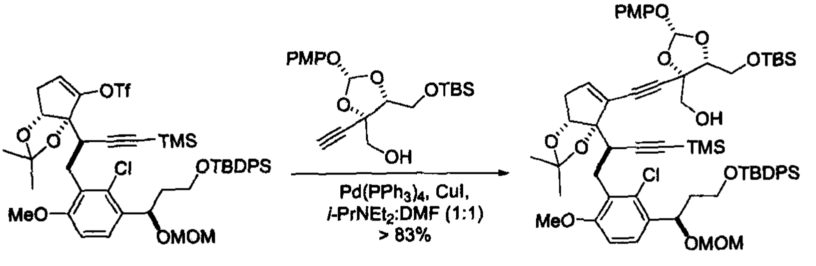
Example 2[3]



Example 3[8]



Example 4[9]



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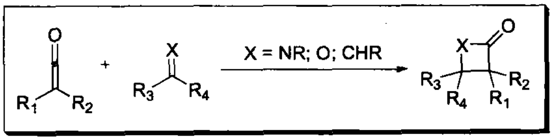
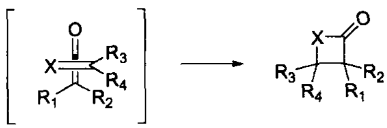
Staudinger 烯酮环加成反应

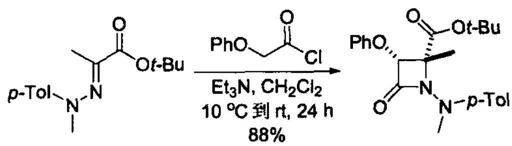
烯酮和亚胺发生[2+2]环加成反应生成 β-内酰胺的合成反应。其他可与烯酮反应的组分包括：烯烃反应后生成环丁烷，羰基则反应后生成 β-内酯。



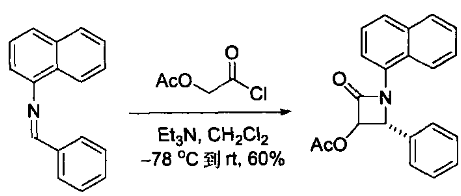


折迭的过渡态

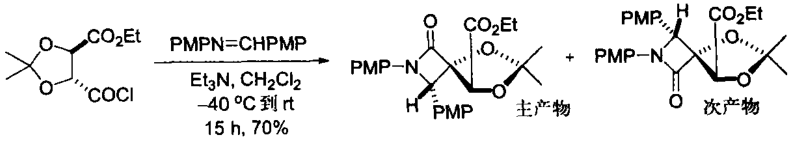
Example 1[6]



Example 2[7]

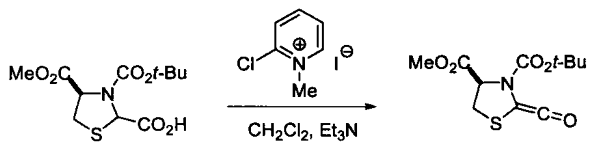


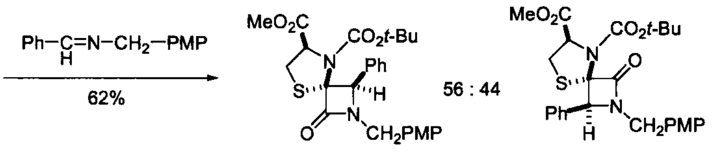
Example 3[9]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_242,

Example 4[10]





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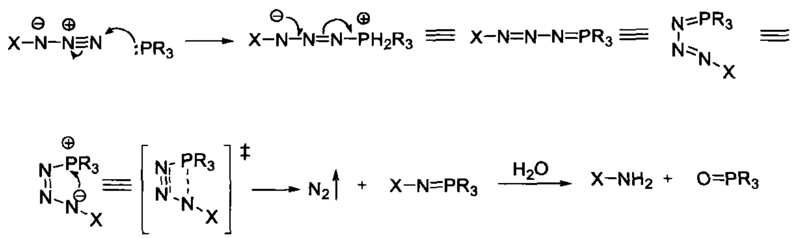
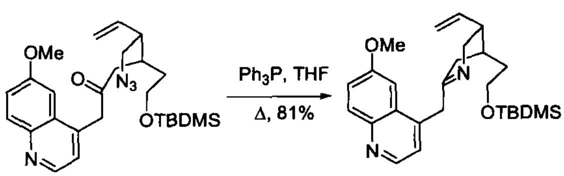
Staudinger 还原反应

叔膦（如Ph_3P）和有机叠氮化物反应生成偶磷氮基化合物（即亚氨基正膦）。

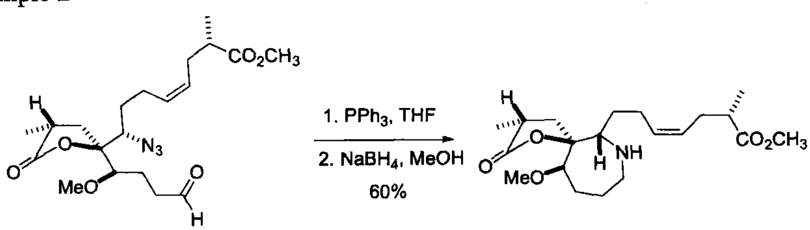
$$X{-}N_3 \xrightarrow{PR_3} \underset{\text{叠氮膦}}{X{-}N{=}N{-}N{=}PR_3} \xrightarrow{-\,N_2} X{-}N{=}PR_3$$



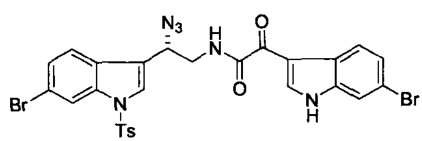
Example 1[2]



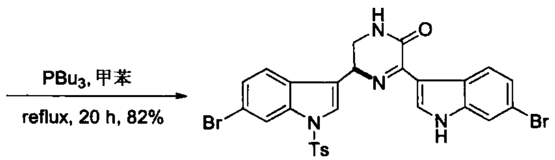
Example 2[3]



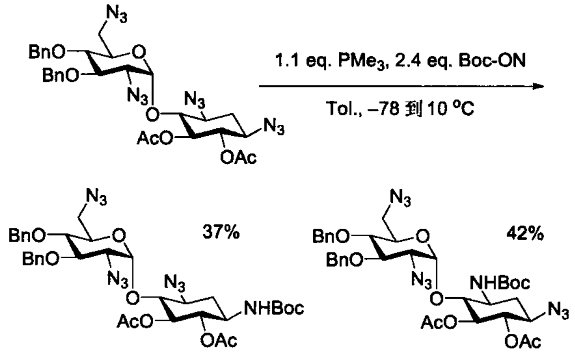
Example 3[4]



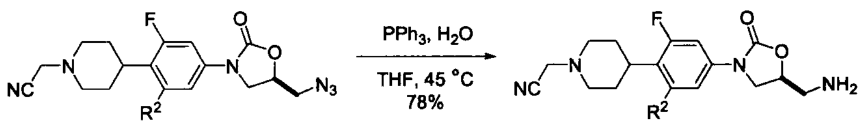
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_243,



Example 4[8]



Example 5[9]



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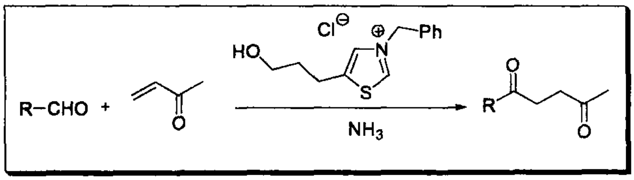
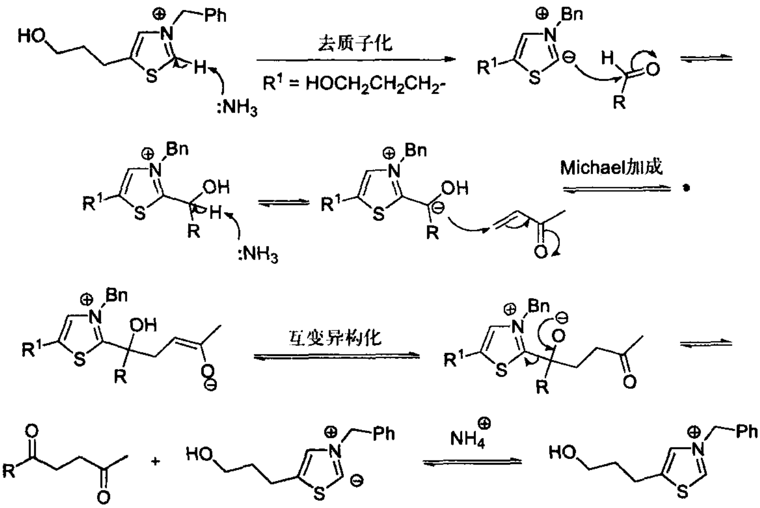
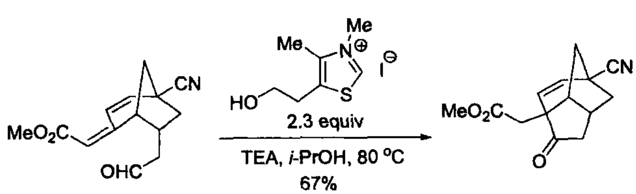
Stetter 反应

从醛、α,β-不饱和酮和酯生成1,4-二羰基衍生物的反应。噻唑催化剂相当于是一个安全的CN^-。亦称Michael-Stetter反应。参见第38页上的Benzoin（苯偶姻）缩合反应。

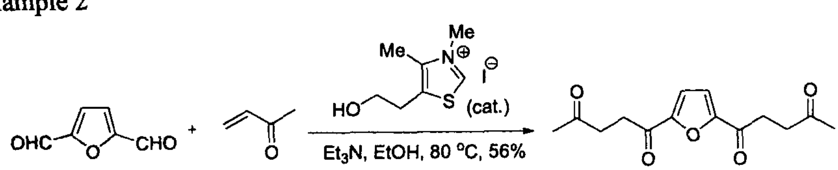




Example 1, 分子内Stetter 反应[2]

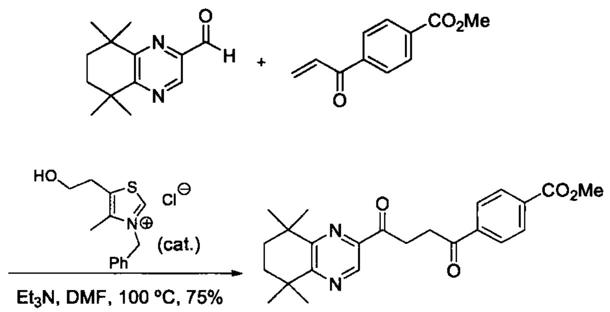


Example 2[3]

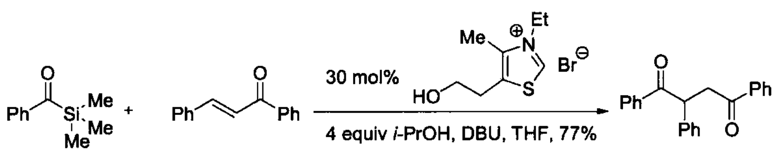


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_244,

Example 3[5]



Example 4, 含硅的-Stetter 反应[9]



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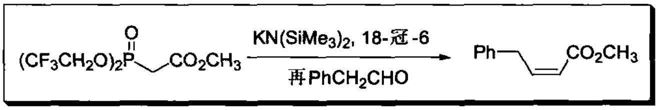
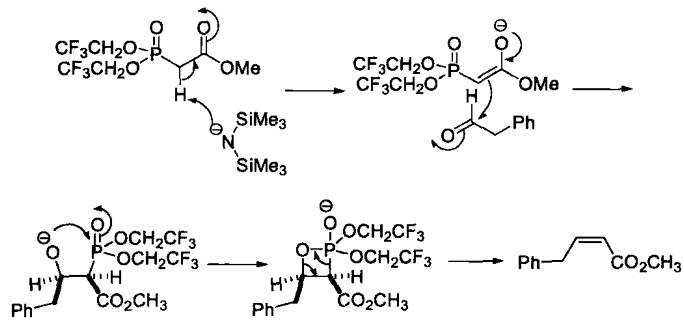
Still-Gennari 磷酸酯反应

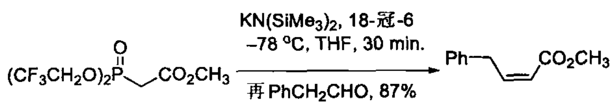
Horner-Emmons反应的变异，用双-三氟乙基磷酸酯反应后生成Z-烯烃。



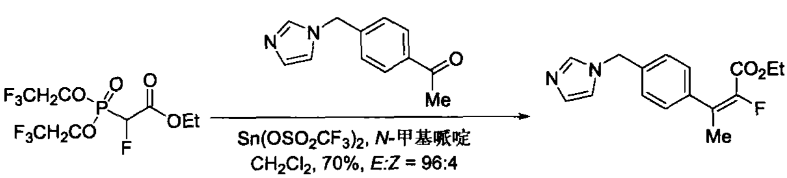


赤式异构体，动力学加成物

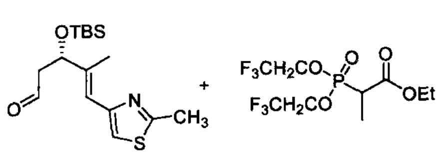
Example 1[2]



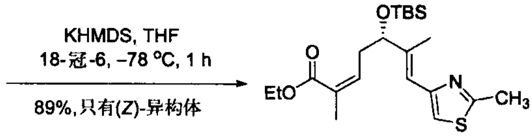
Example 2[3]



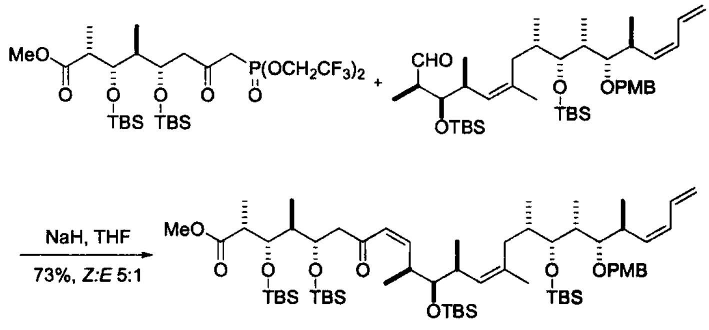
Example 3[4]



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



Example 4[9]



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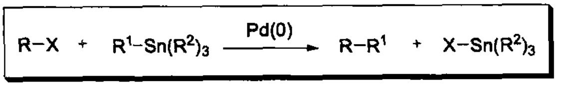
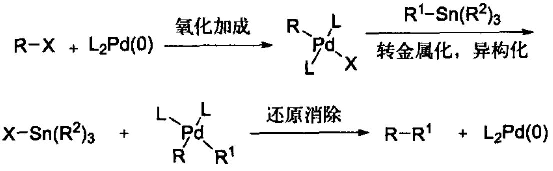
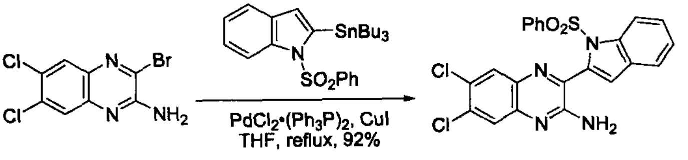
Stille 偶联反应

Pd催化的有机锡化物和卤代烃、三氟磺酸酯等的交叉偶联反应。催化循环请参见第325页上的Kumada交叉偶联反应。

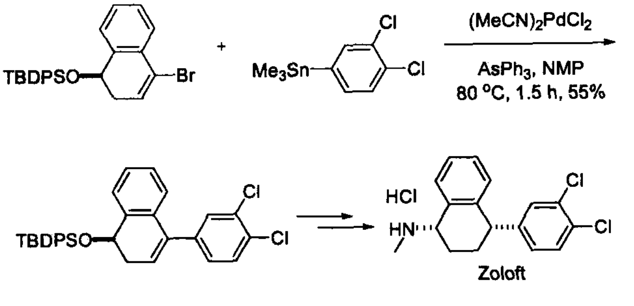




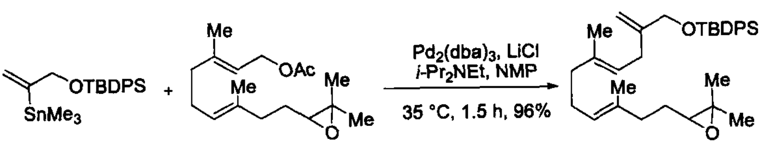
Example 1[4]



Example 2[5]

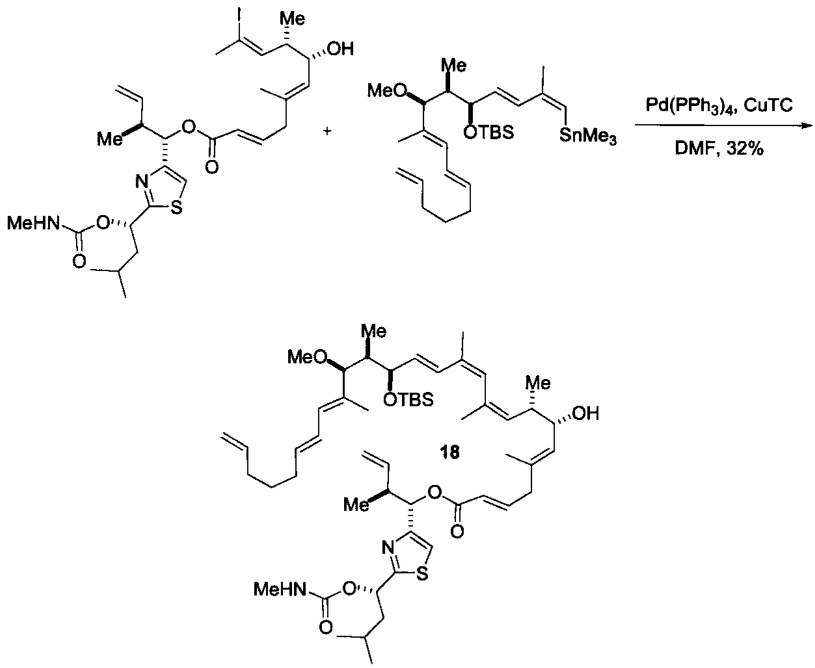


Example 3, π-烯丙基 Stille 偶联[8]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_246,

Example 4[9]



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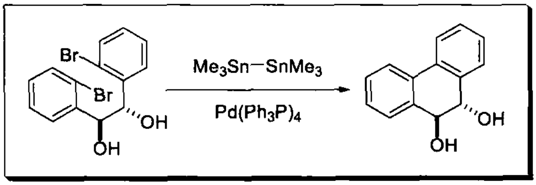
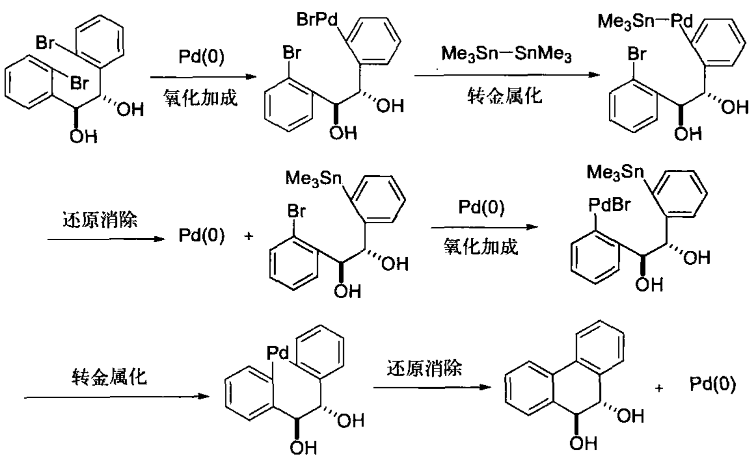
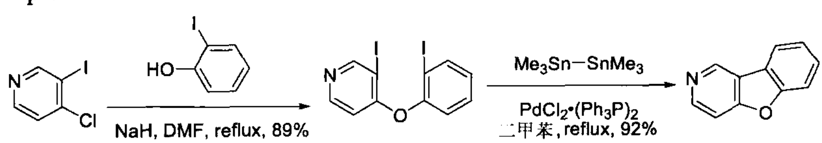
Stille-Kelly 反应

Pd催化下二芳基卤用二锡试剂进行分子内偶联反应。





Example 1[6]



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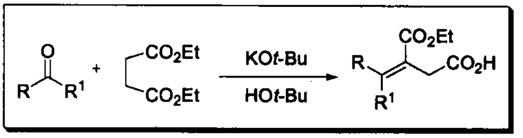
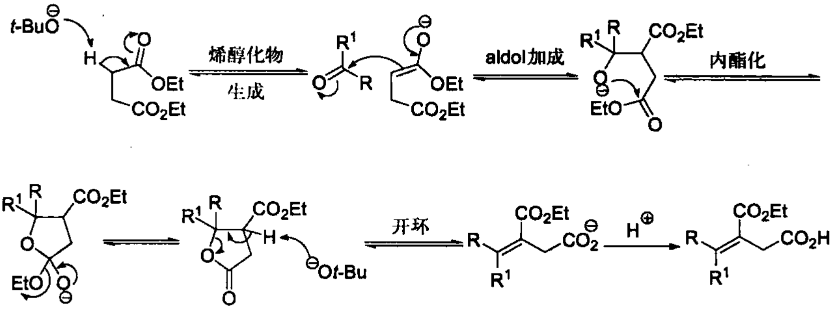
J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_247,

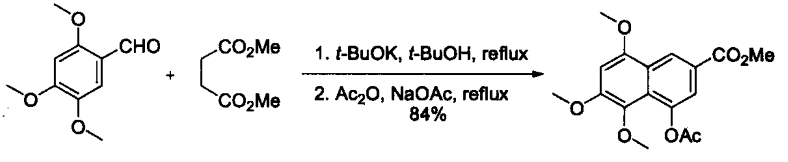
Stobbe 缩合反应

丁二酸二酯及其衍生物和羰基化合物在碱存在下的缩合反应。

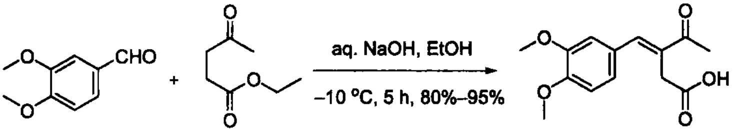




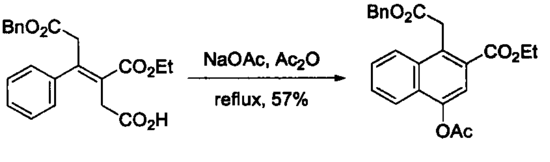
Example 1, Stobbe 缩合和环化[5]



Example 2, Stobbe 缩合[6]

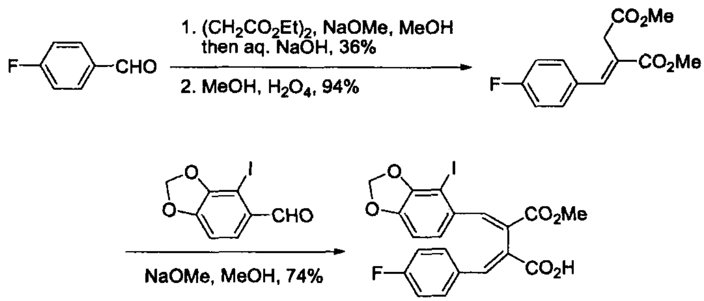


Example 3, Stobbe 产物的环合[7]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_248,

Example 4, 先后两步的Stobbe缩合[9]



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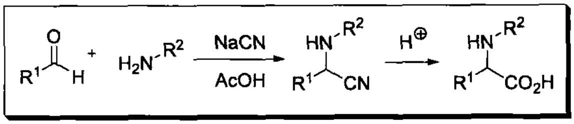
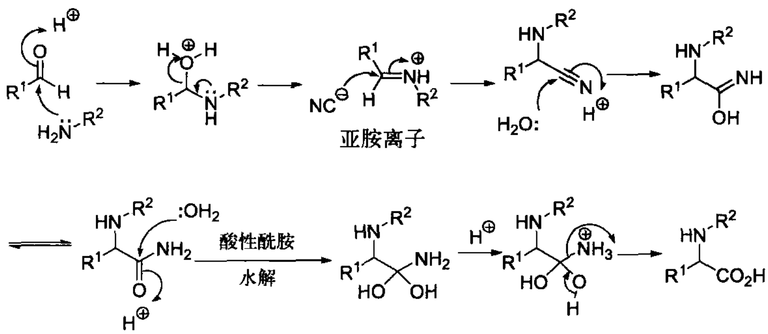
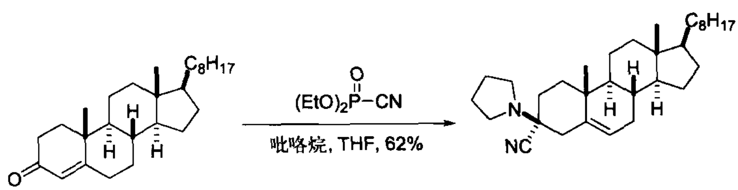
Strecker 氨基酸合成反应

NaCN促进的醛（酮）和氨缩合给出 α-氨基腈再水解生成 α-氨基酸。

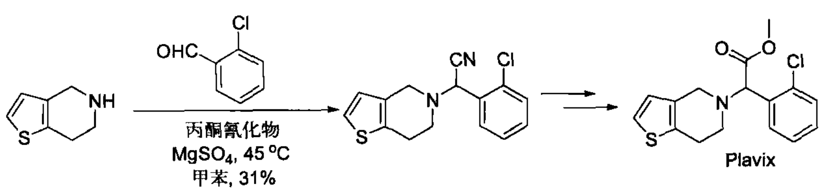




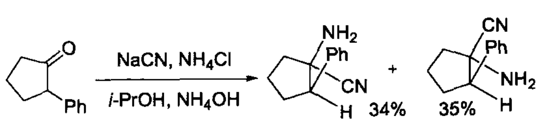
Example 1, 可溶性氰根离子源[2]



Example 2[3]

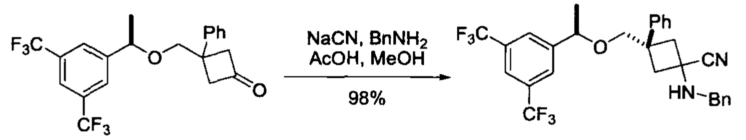


Example 3[8]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_249,

Example 4[9]



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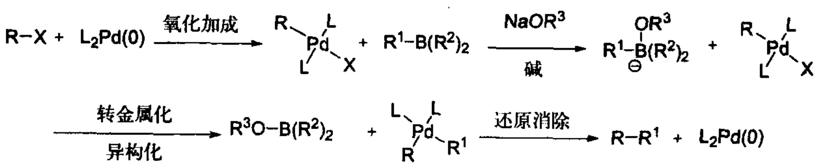
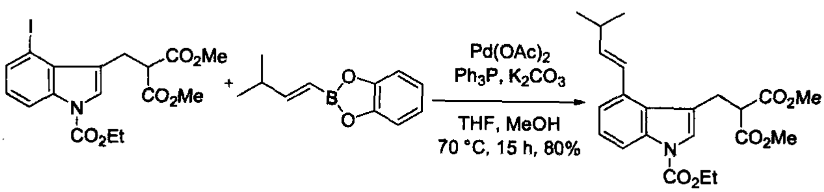
Suzuki-Miyaura 偶联反应

Pd催化下有机硼化物和卤代烃、三氟磺酸酯等在碱存在下（若无碱作为活化剂，转金属化将难以发生）进行的交叉偶联反应。催化循环请参见第325页上的Kumada交叉偶联反应。

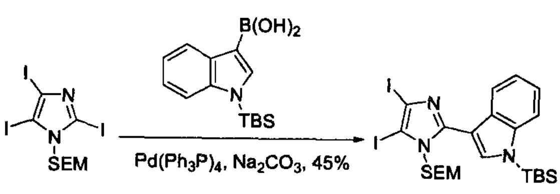
$$R{-}X \; + \; R^1{-}B(R^2)_2 \xrightarrow[NaOR^3]{L_2Pd(0)} R{-}R^1$$



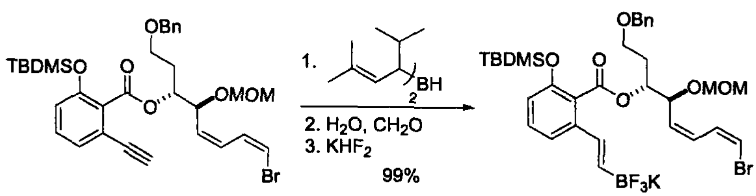
Example 1[2]



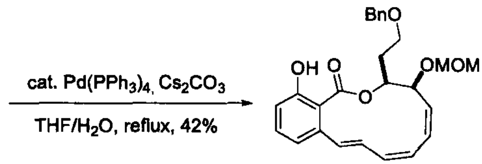
Example 2[4]



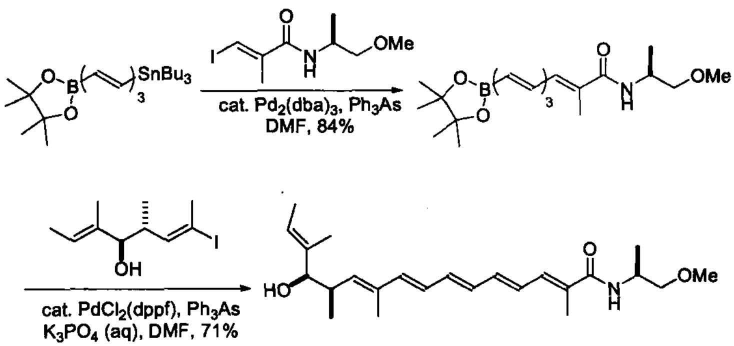
Example 3, 分子内 Suzuki–Miyaura 偶联[8]



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



Example 4[9]



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译者注：A.Suzuki（铃木章）于2010年和E.Negishi、R.F.Heck共享诺贝尔化学奖。

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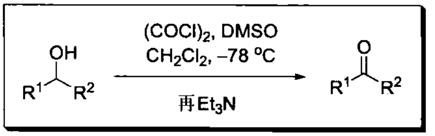
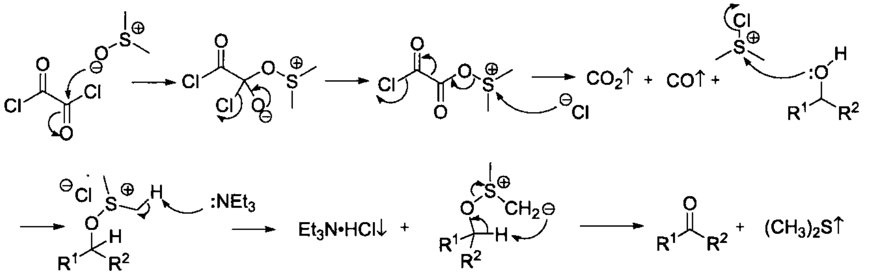
Swern 氧化反应

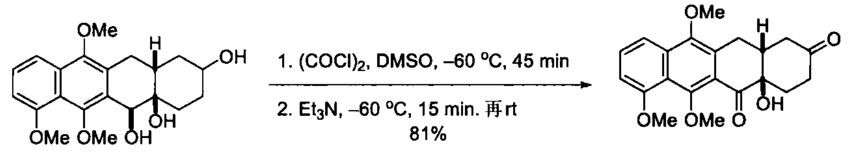
醇用$(COCl)_2$、DMSO氧化并用Et_3N淬灭后生成相应的羰基化合物。



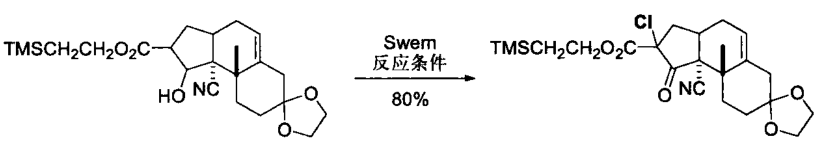


硫叶立德

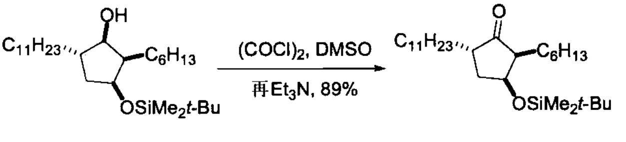
Example 1[2]



Example 2[3]

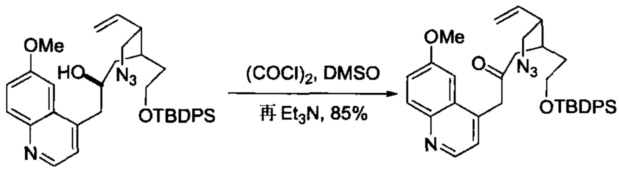


Example 3[5]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_251,

Example 4[7]



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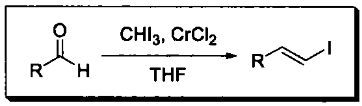
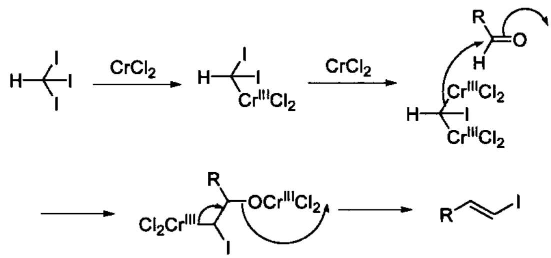
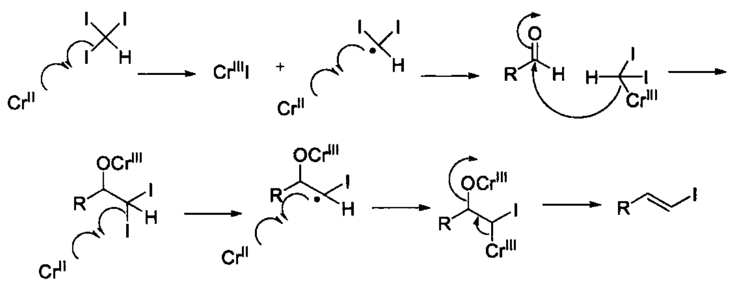
Takai 反应

用CHI_3和$CrCl_2$立体选择性地将醛转化为*E*-烯基碘代物。

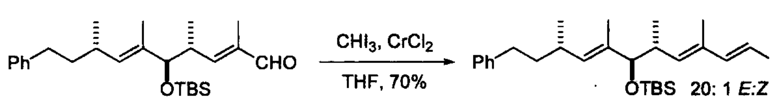




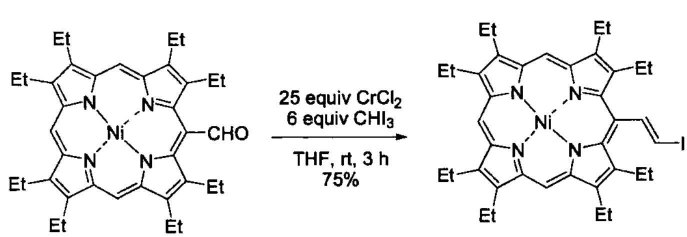
最近推出的一个自由基机理:[10]



Example 1[2]

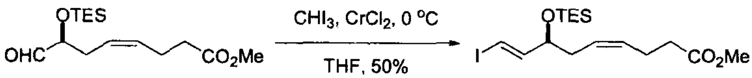


Example 2[3]

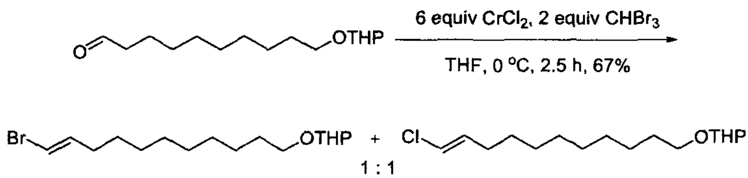


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_252,

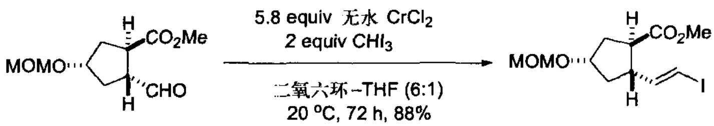
Example 3[4]



Example 4, 一个 Br/Cl 变异反应[9]



Example 5[10]



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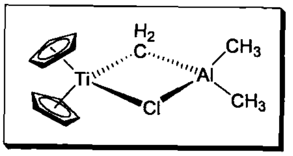
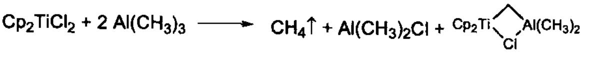
Tebbe 试剂

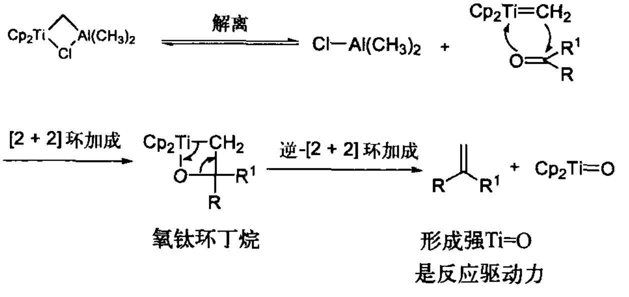
Tebbe 试剂，即*μ*-氯双环戊二烯基二甲基铝-*μ*-亚甲基钛，可将羰基化合物转化为*exo*-烯烃。



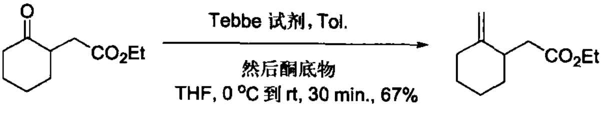
制备:[2,6]



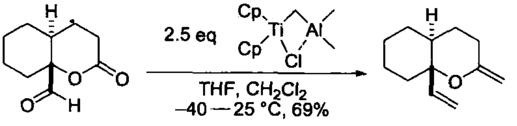
机理:[3]



Example 1, 酮[2]



Example 2, 二重Tebbe 反应[4]



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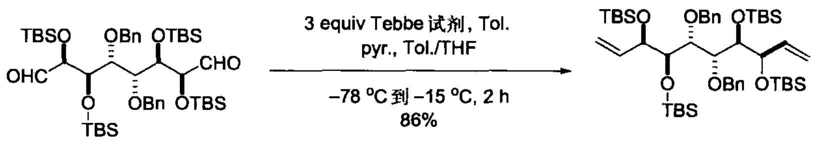
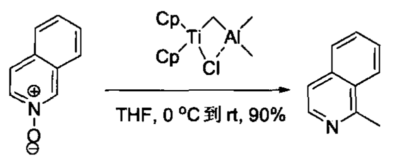
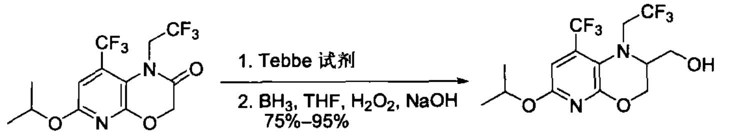
Example 3, 二重Tebbe反应[5]



Example 4, *N*-氧化物[6]



Example 5, 酰胺[11]



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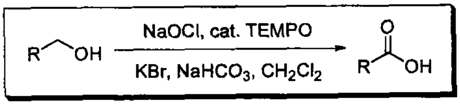
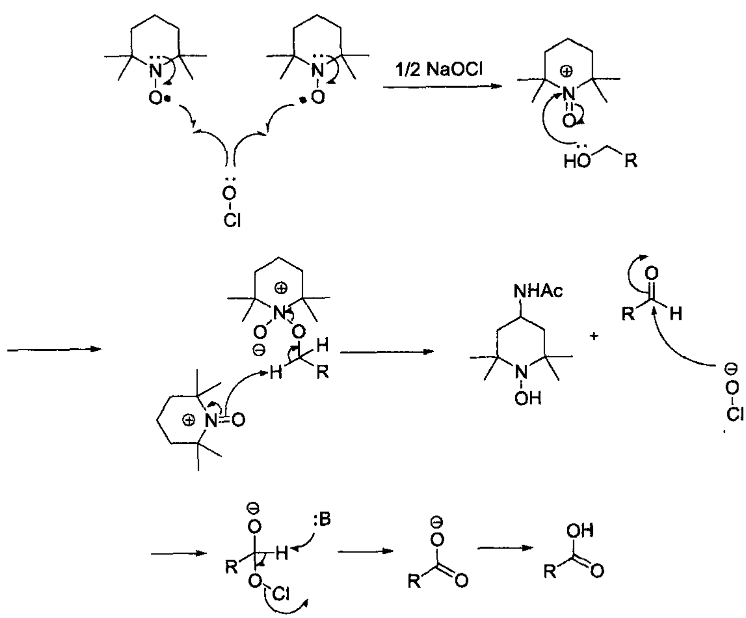
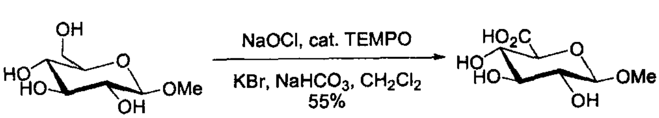
TEMPO 氧化反应

TEMPO，即2,2,6,6-四甲基哌啶N-氧化物，是一个稳定的硝酰自由基，可作为催化剂用于氧化反应。





Example 1[4]



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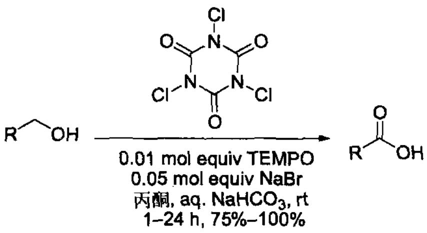
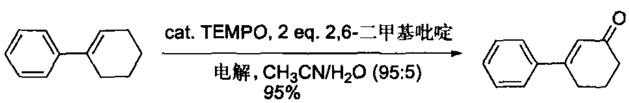
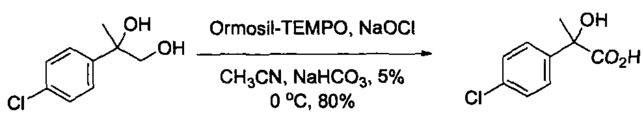
Example 2, 三氯异氰脲/TEMPO 氧化[5]



Example 3[8]



Example 4[10]



"Ormosil-TEMPO"是一种有纳米结构的涂抹在TEMPO上的疏水性硅胶溶胶。

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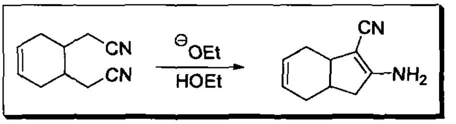
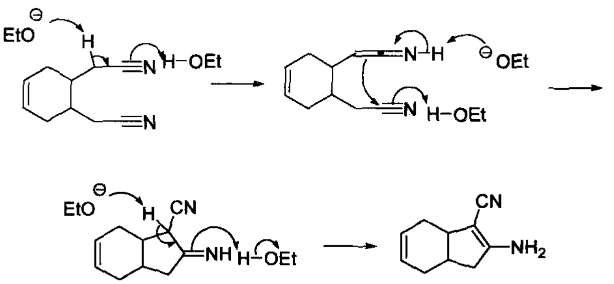
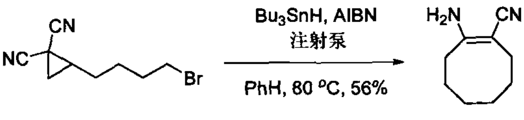
Thorpe-Ziegler 反应

分子内的Thorpe反应模式，碱催化下将二腈缩合成亚胺后异构为烯胺。

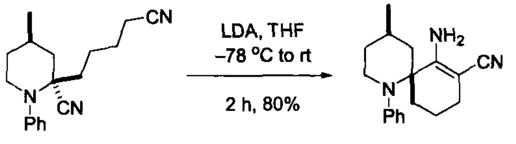




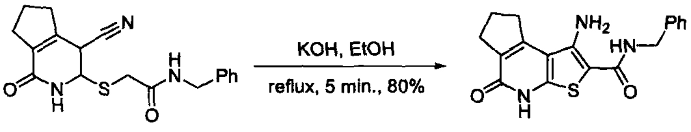
Example 1, 一个自由基Thorpe–Ziegler 反应[2]



Example 2[5]



Example 3[8]



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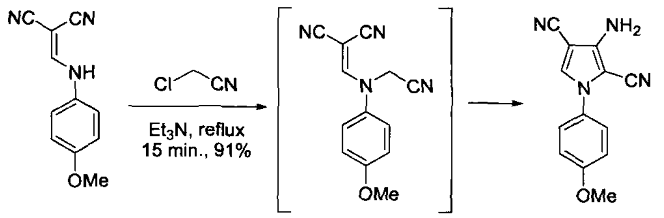
Example 4[9]



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   (b) Ziegler, K. *et al. Ann.* **1933**, *504*, 94–130. 齐格勒（Karl Ziegler, 1898-1973）出生于德国的Helsa, 1920年在University of Marburg的von Auwers指导下获得Ph.D学位。1943年任马普研究所（Max-Planck-Institut fur Kohlenforsschung at Mulheim/Ruhr）所长。他和纳塔（Giulio Natta, 1903-1979）于1963年因聚合物化学的工作共享诺贝尔化学奖。Ziegler-Natta催化剂被广泛用于聚合反应。
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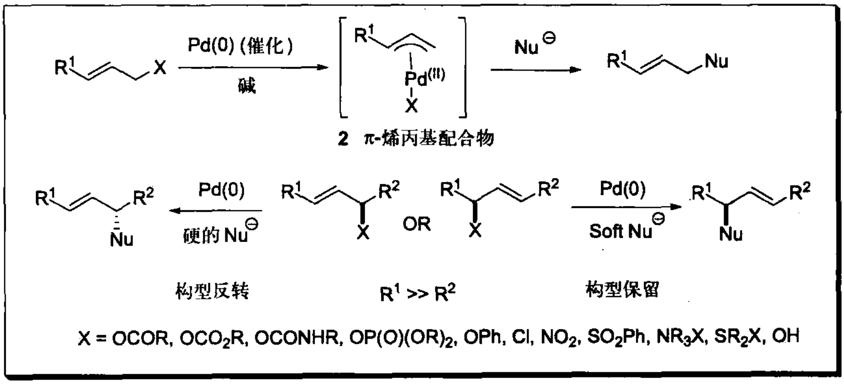
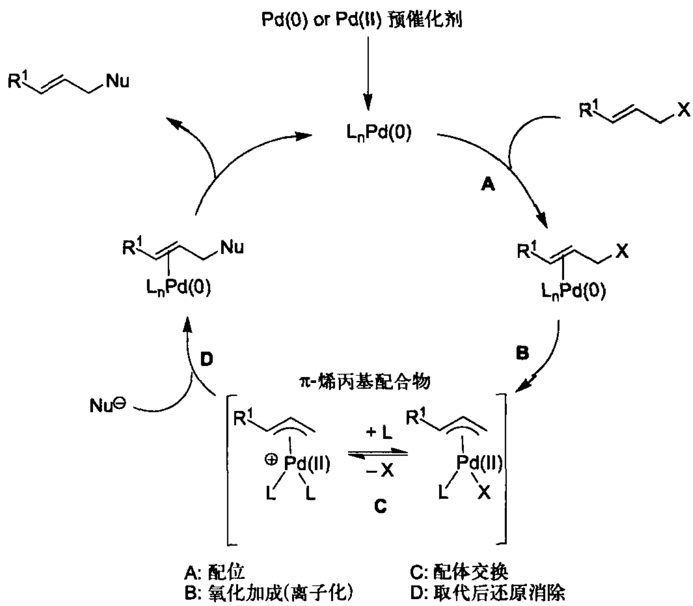
Tsuji-Trost 反应

Tsuji-Trost反应是Pd催化下碳亲核物种在烯丙基位上的取代反应。这些反应经过 π-烯丙基钯中间体过程。



催化循环：



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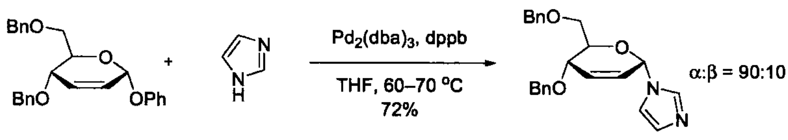
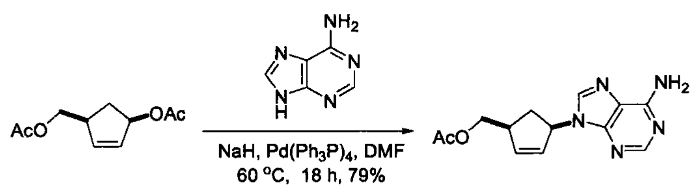
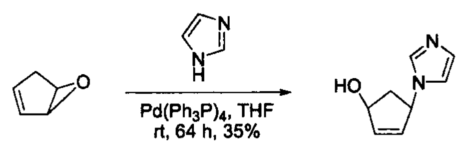
Example 1, 烯丙基醚[3]



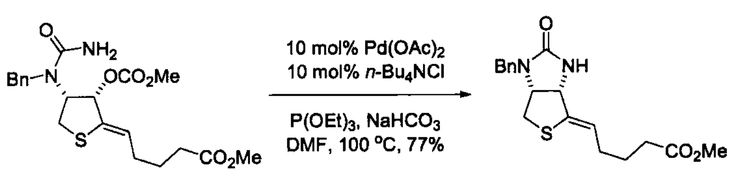
Example 2, 乙酸烯丙酯[3]



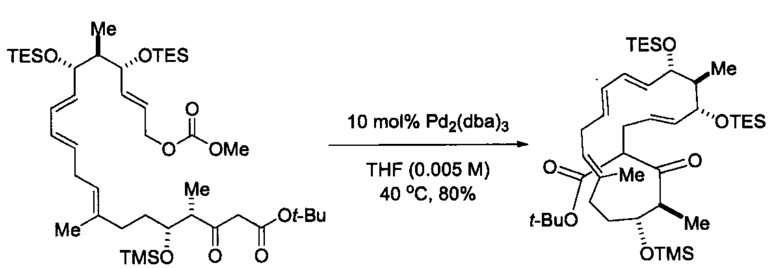
Example 3, 烯丙基环氧化物[5]



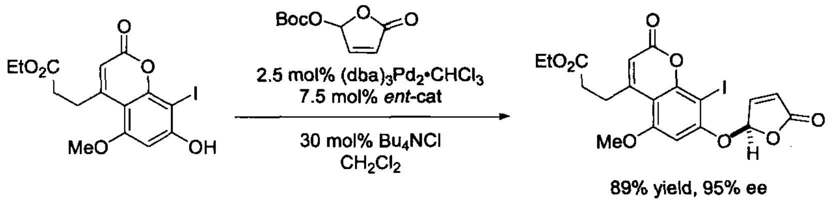
Example 4, 分子内 Tsuji–Trost 反应[6]

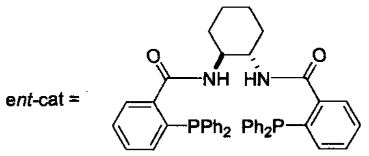


Example 5, 分子内 Tsuji–Trost 反应[7]



Example 6, 不对称 Tsuji–Trost 反应[8]





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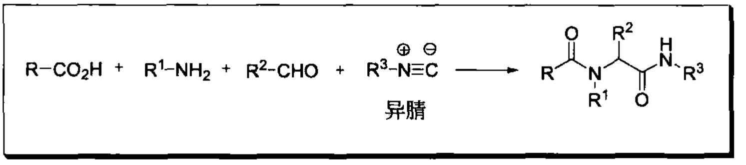
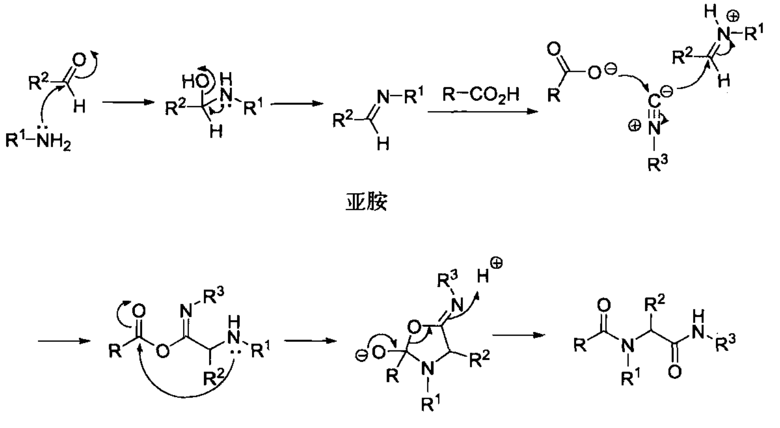
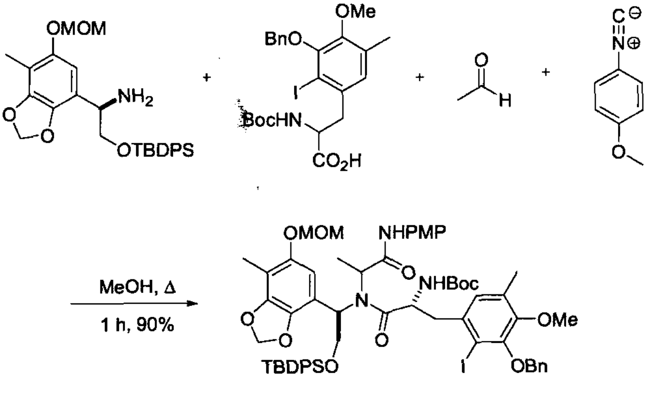
Ugi 反应

羧酸、C-异氰酸酯、苯胺和羰基化合物的四组分缩合（4CC）给出二酰胺的反应。参见第415页上的Passerini反应。





Example 1[2]



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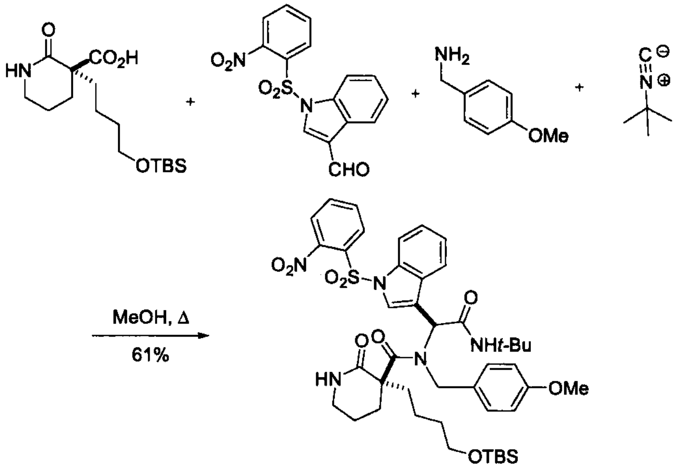
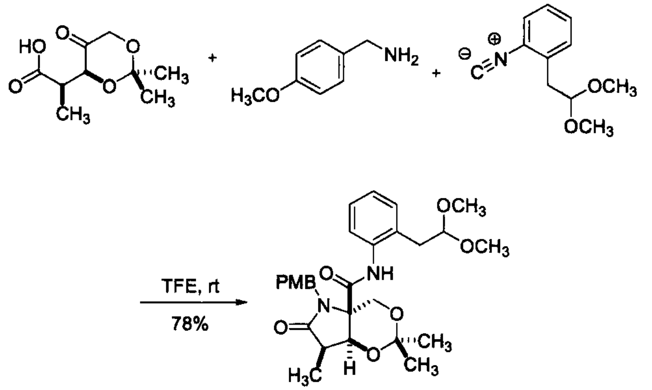
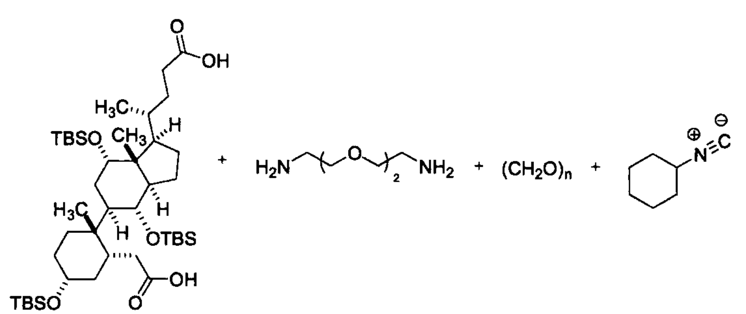
Example 2[5]

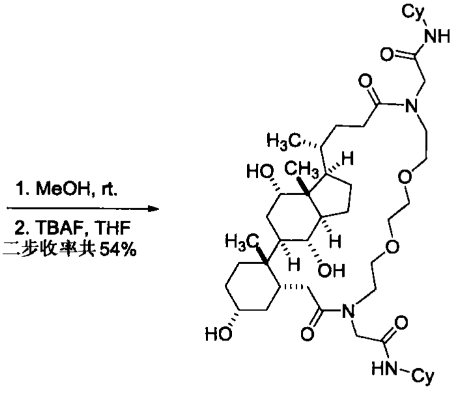


Example 3[7]



Example 4[8]





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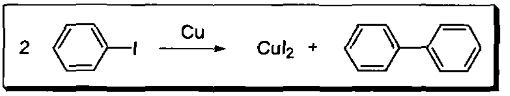
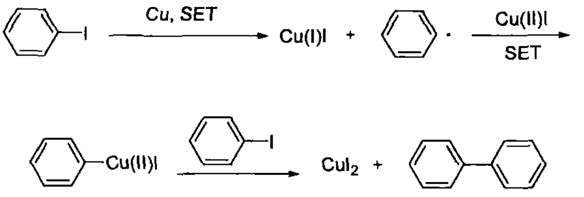
Ullmann 偶联反应

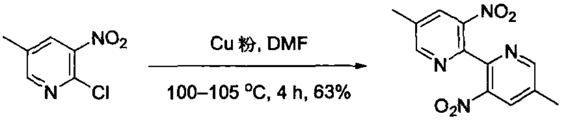
芳基卤在Cu、Ni或Pd存在下偶联为联芳基化合物。



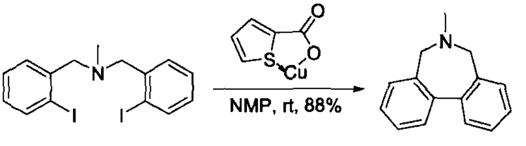


从PhI到PhCuI的转化是一步氧化加成过程。

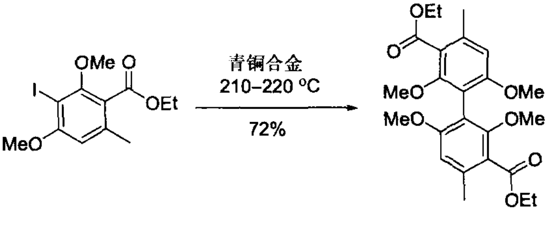
Example 1[3]



Example 2, CuTC 催化的 Ullmann 偶联[4]

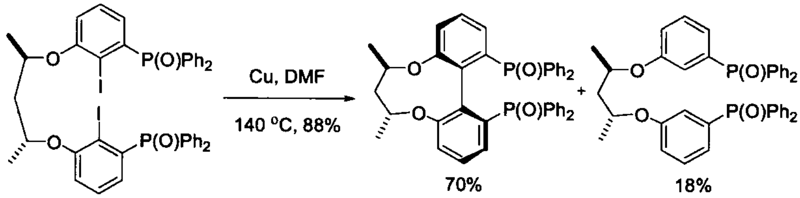


Example 3[5]

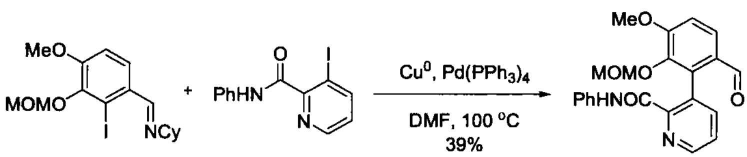


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_258,

Example 4[8]



Example 5[9]



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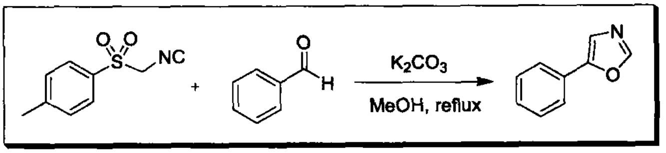
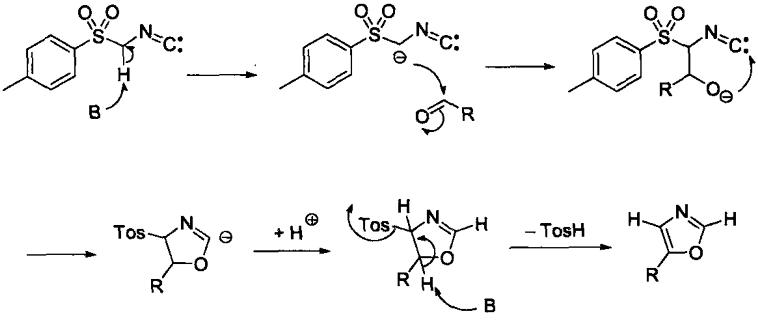
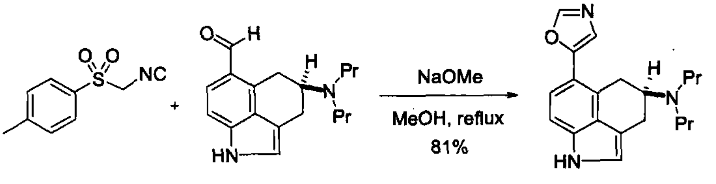
van Leusen 噁唑合成反应

异氰酸对甲苯磺酸甲基酯（TosMIC，亦称 van Leusen 试剂）和醛在质子性溶剂和回流温度下反应得到5-取代噁唑。





Example 1[3]



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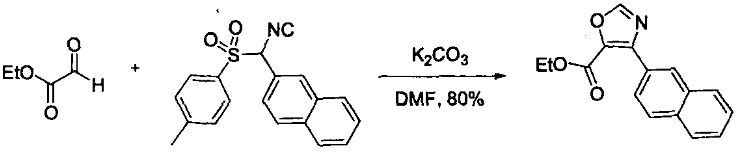
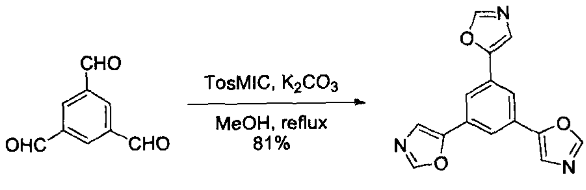
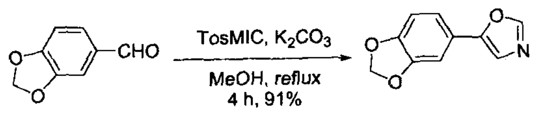


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_259,

Example 3[9]



Example 4[10]



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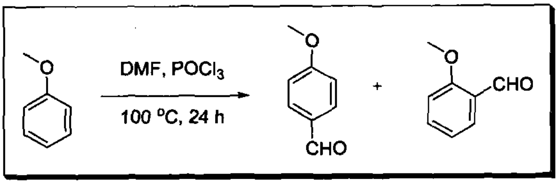
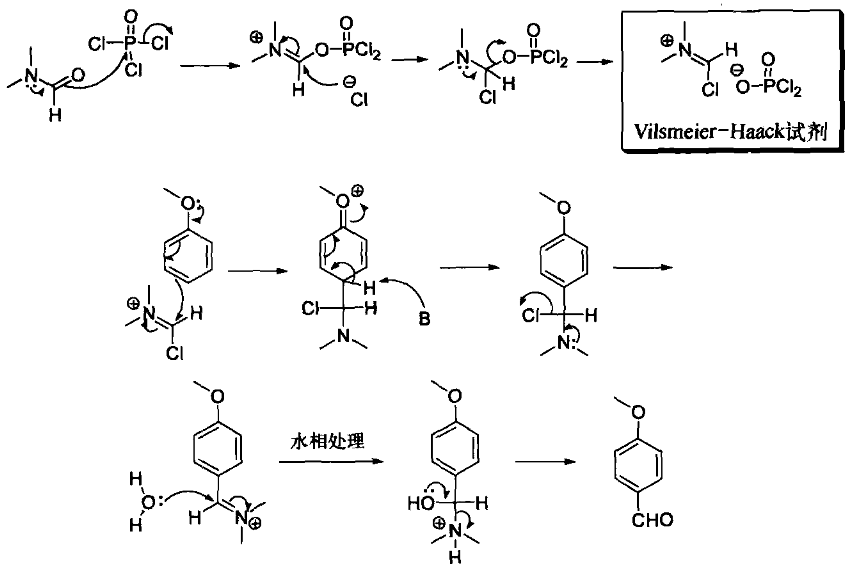
Vilsmeier-Haack 反应

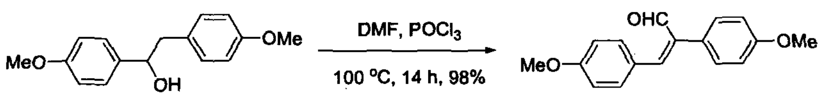
Vilsmeier试剂，即氯代亚胺盐，是一个弱亲电物种，最好与富电子的碳环和杂环化合物反应。



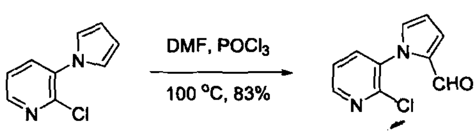
34% 4%



Example 1[2]

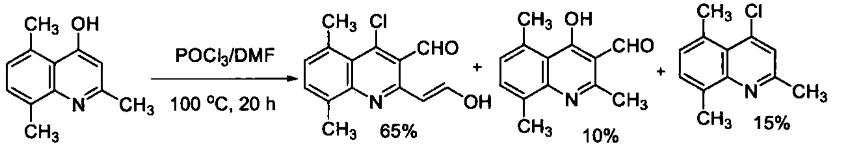


Example 2[3]



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

Example 3[9]



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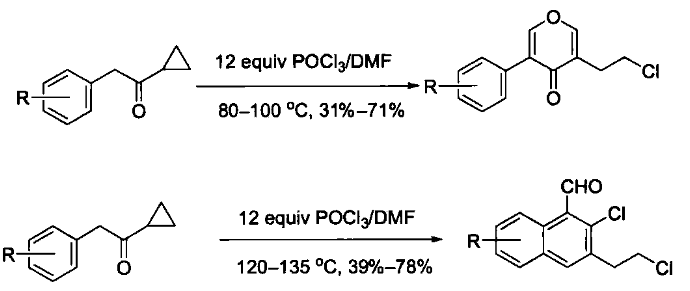

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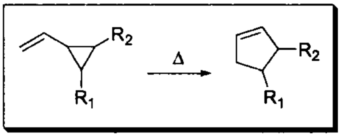
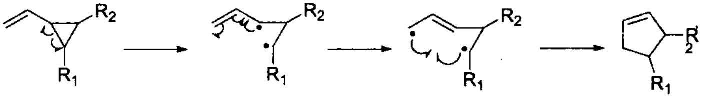
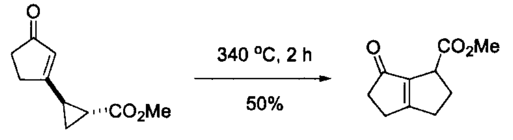
Vinylcyclopropane-cyclopentene（烯基环丙烷-环戊烯）重排反应

烯基环丙烷经双自由基历程转化为环戊烯的重排反应。





Example 1[1]



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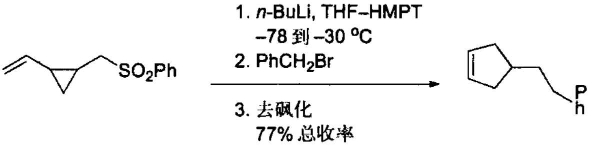

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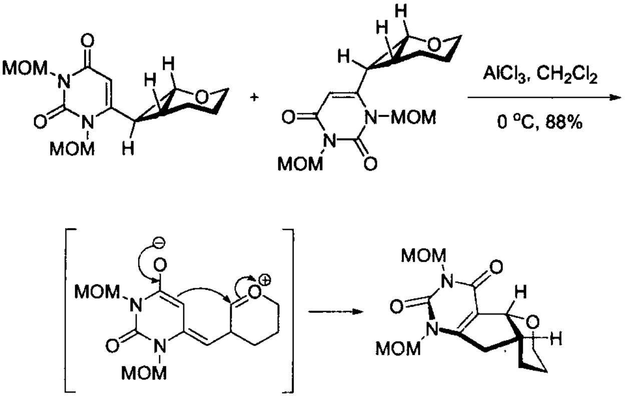
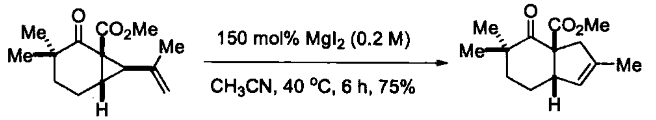


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_261,

Example 4[10]



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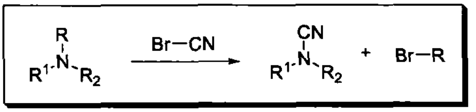
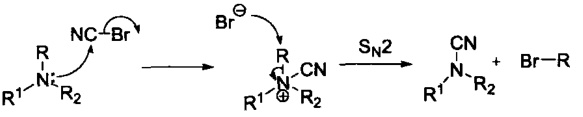
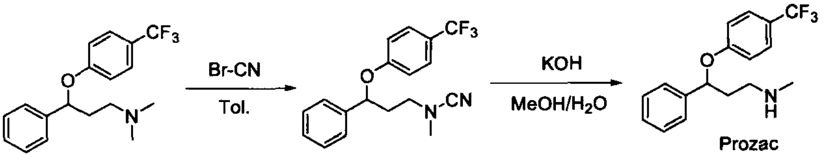
von Braun 反应

与von Braun降解反应（酰胺到腈）不同，von Braun反应是叔胺和BrCN反应生成氰基酰胺的反应。

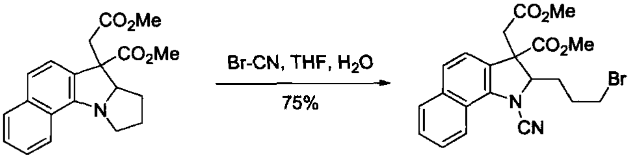




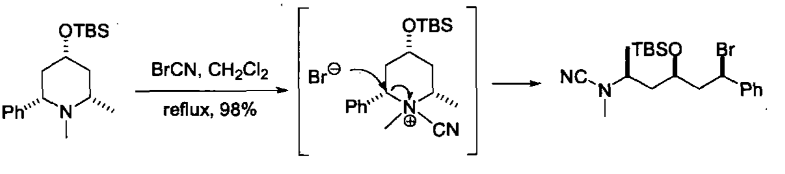
Example 1[4]



Example 2[5]



Example 3[9]



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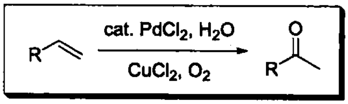
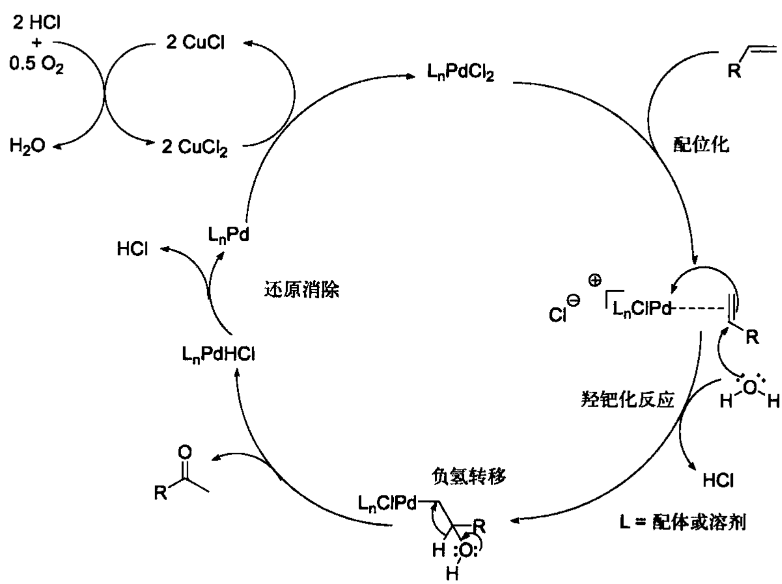
Wacker 氧化反应

Pd催化下烯烃氧化为酮，根据条件也可氧化为醛。





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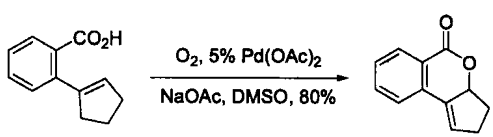

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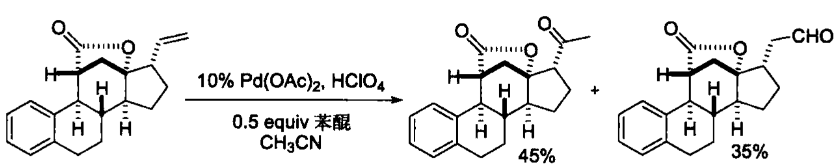
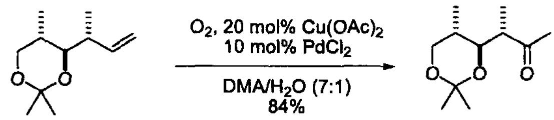
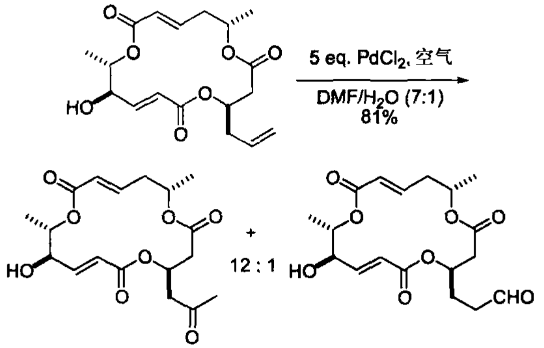


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_263,

Example 3[9]



Example 4[10]



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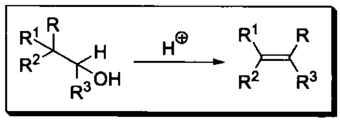
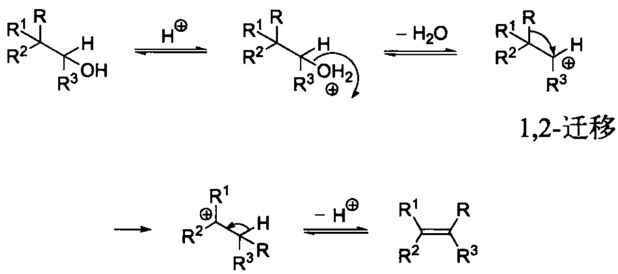
Wagner-Meerwein 重排反应

酸催化下醇中的烷基迁移给出多取代烯烃的反应。





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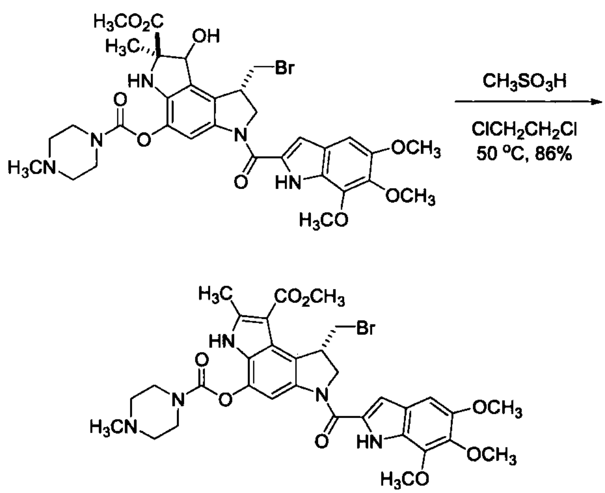
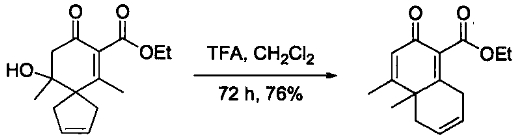
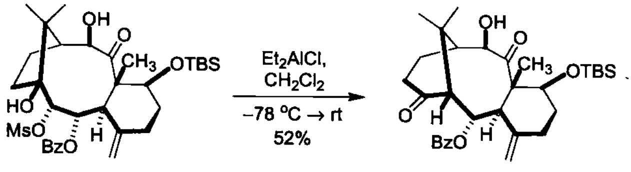


Example 2, 二重 Wagner–Meerwein 重排[6]

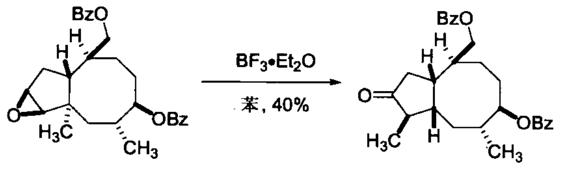


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_264,

Example 3[7]



Example 4[9]



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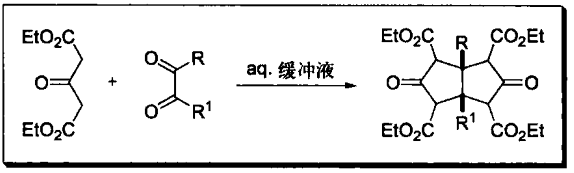
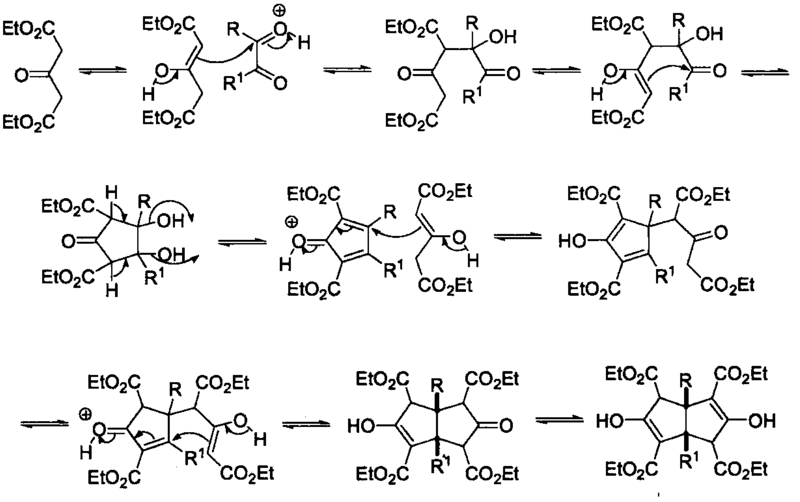
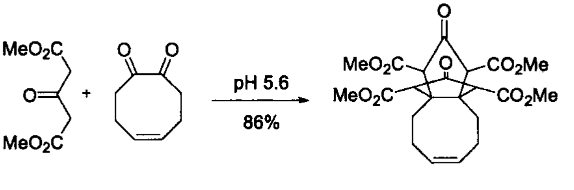
Weiss-Cook 反应

cis-双环[3.3.0]辛-3,7-二酮的合成反应。产物常常发生脱羧反应。





Example 1[2]



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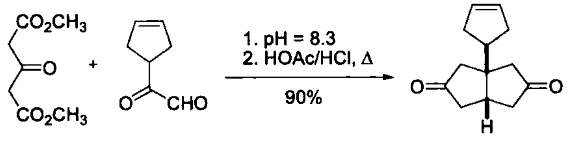
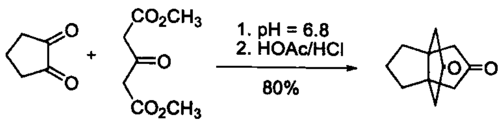
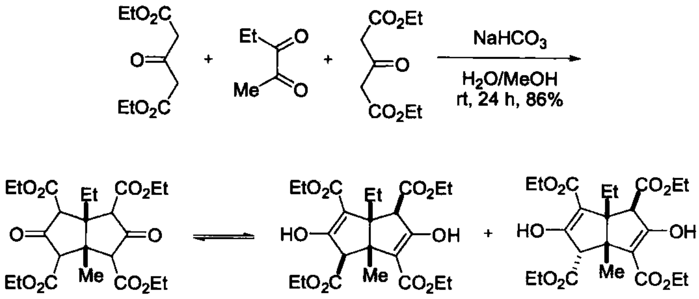


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_265,

Example 3[4]



Example 4[9]



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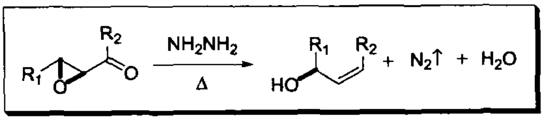
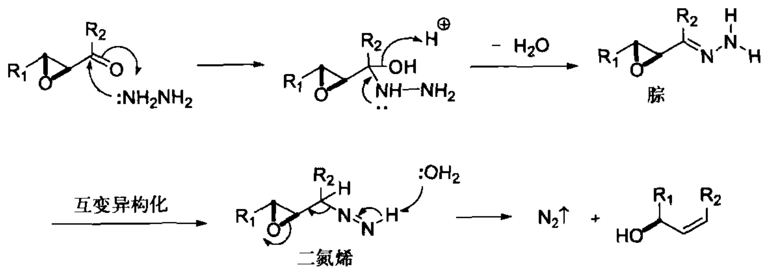
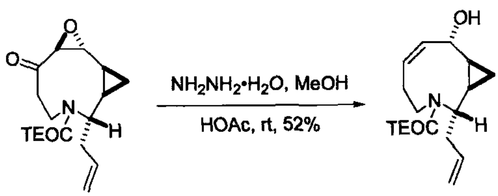
Wharton 碎裂化反应

α,β-环氧酮用肼还原为烯丙基醇。

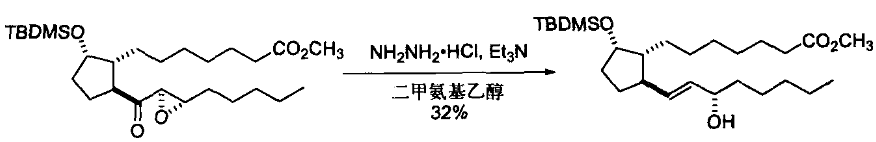




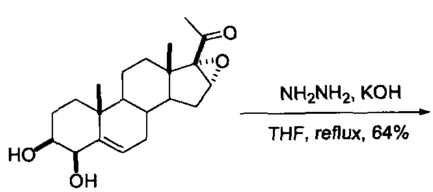
Example 1[5]



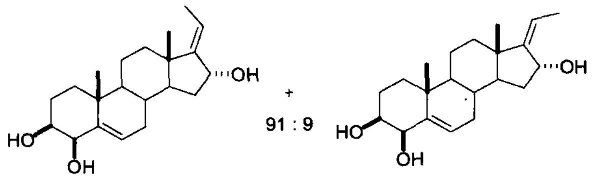
Example 2[6]



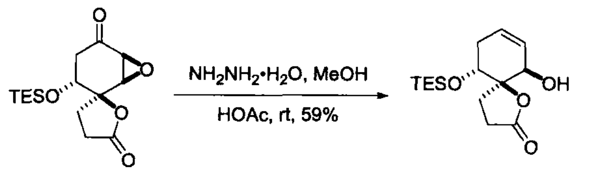
Example 3[7]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_266,



Example 4[8]



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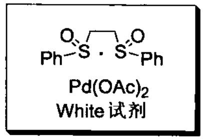
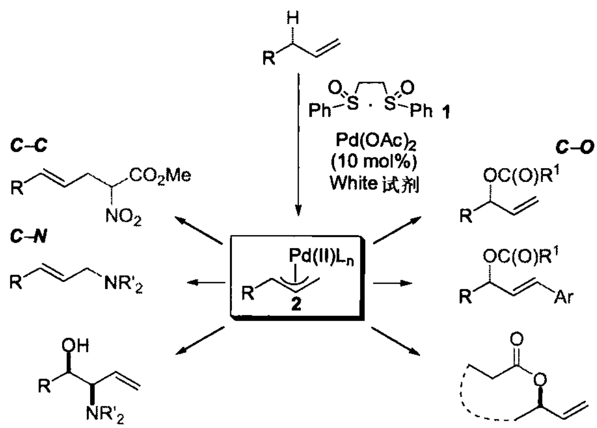
White 试剂



White试剂1是一个多用途的可购得的用于烯丙基C—H键氧化的试剂，可以从相对惰性的烯丙基C—H键出发构筑有用的C—O、C—N和C—C键（**Figure 1**）。[1-11] White试剂可实现新的可预见的断键，从而能流畅地用来合成配位物分子。[2,4,7,8]广泛存在的α-烯烃能发生分子内和分子间的C—H键氧化且带有高度的化学选择性、位置选择性和立体选择性。机理研究表明，White试剂促进烯丙基C—H键断裂给出π-烯丙基钯中间体**2**，**2**再与*O*-、*N*-、*C*-亲核物种反应进行官能团化。[3]（**Figure 1**）

Figure 1



一般的有机官能团，如Lewis碱的酚**3**，[3]酸敏感的缩酮**4**，[8]高度活泼的三氟磺酸酯**6**，[11]和肽**5**[5]都可容忍该温和的反应条件。（**Figure 2**）所有这些实例中都可经柱层析后得到单一的位置异构体和烯基异构体产物。

本方法的艺术性也体现在构筑C—N键的反应中，C—N键的生成一般需要经官能团转化或使用预先氧化的材料生成C—C键的方法来实现的。用White试剂实现的烯丙基氨化反应可以减少从氧代中间体所需的官能团操作而流畅地合成含氮分子，如合成L-acosamine 衍生物**9**[7]所需的中间体（–）-**8**。（**Figure 3A**）用C—H键氨化到（–）-**8**的步骤位于合成中部，并未有官能团化

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的操作，收率要高于另一条从C—O键转化为C—N键的路线。分子间C—H键氨化法也已用于构筑(+)-去氧负霉素的同系物12，全过程只需五步较少的步骤，总收率要优于另一条需取代C—O键的路线(**Figure 3B**)。[8]

Figure 2

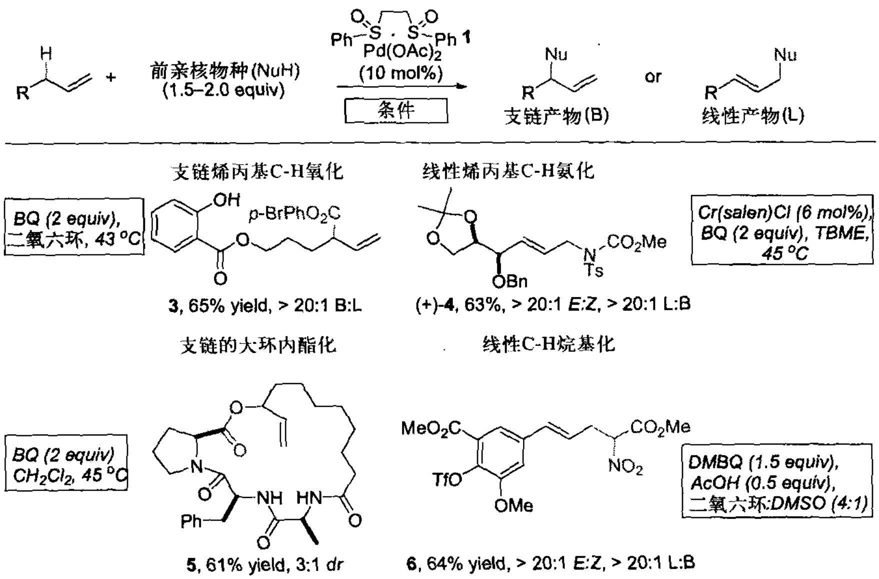
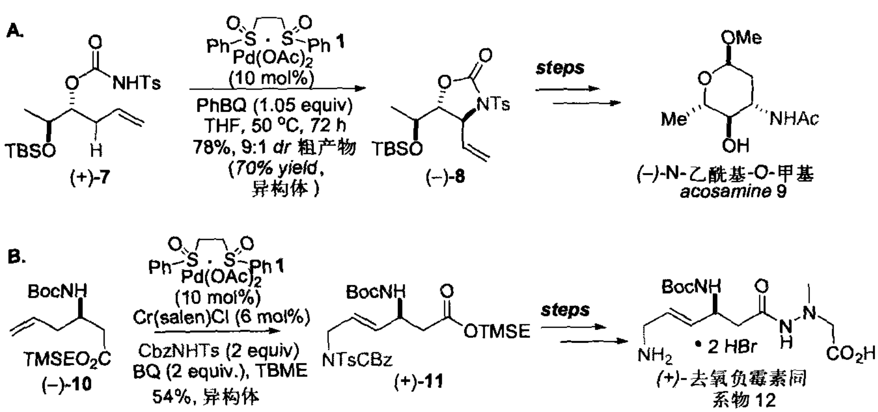


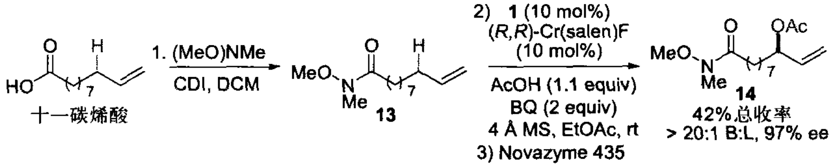
Figure 3



烯丙基C—H键的氧化也同样可以减少从双氧代中间体所需的操作而流畅地合成含氧分子。如，通过手性的烯丙基C—H键氧化-酶促拆分程序能从

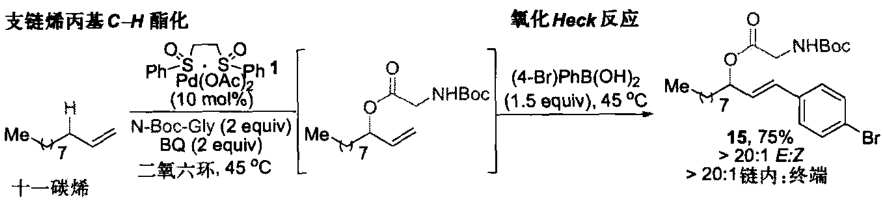
可购得的单氧代前体11-十一碳烯酸出发以97% *ee*值和42%总收率经3步反应完成双氧代化合物**14**的合成[10]（**Figure 4**）。另一条需通过保护-去保护和动力学拆分程序合成相似分子的路线给出的最佳收率为50%。

Figure 4



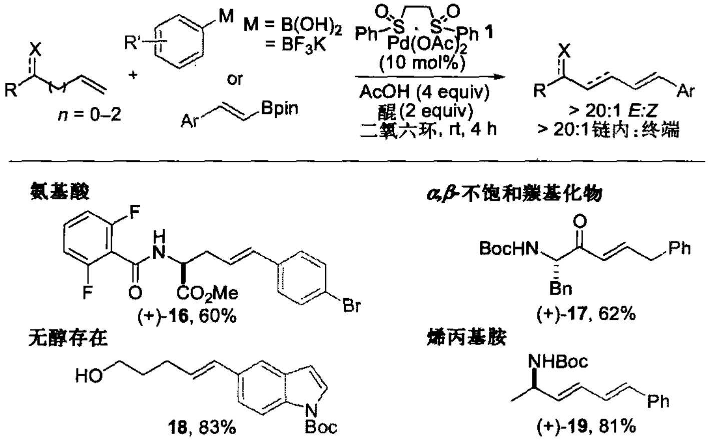
除了烯丙基C—H键氧化外，White试剂还可催化分子间的Heck芳基化反应。值得注意的是，本芳基化反应可使用完全电中性的α-烯烃和芳基硼酸在酸性的氧化条件下进行。一锅煮的烯丙基C—H键氧化-烯基C—H键芳基化反应可高度位置选择性和立体选择性地完成*E*-芳基化烯丙基酯的合成（**Figure 5**）。这个三组分的偶联反应能从廉价的烃类原料出发快速地合成多官能团产物。*N*-Boc-甘氨酸烯丙基酯**7**通过可购得的烯烃、氨基酸和硼酸试剂之间的一步反应来合成。**15**这类化合物可转化为与药物相关的二肽基肽酶Ⅳ抑制剂。[6]

Figure 5



除了上面介绍的一锅煮方法外，White试剂还可催化螯合物控制的在各种α-烯烃和有机硼烷化合物之间以高产率、高区域选择性和立体选择性地进行氧化Heck反应（**Figure 6**）。[9]与其他的Heck芳基化反应不同，在本反应所用的温和条件下无Pd—H键的异构化发生。芳基硼酸、苯乙烯基频呐醇硼酸酯和芳基三氟硼酸钾（硼酸活化）都能容忍一般的反应条件。

Figure 6



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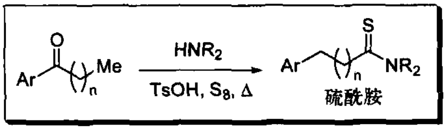
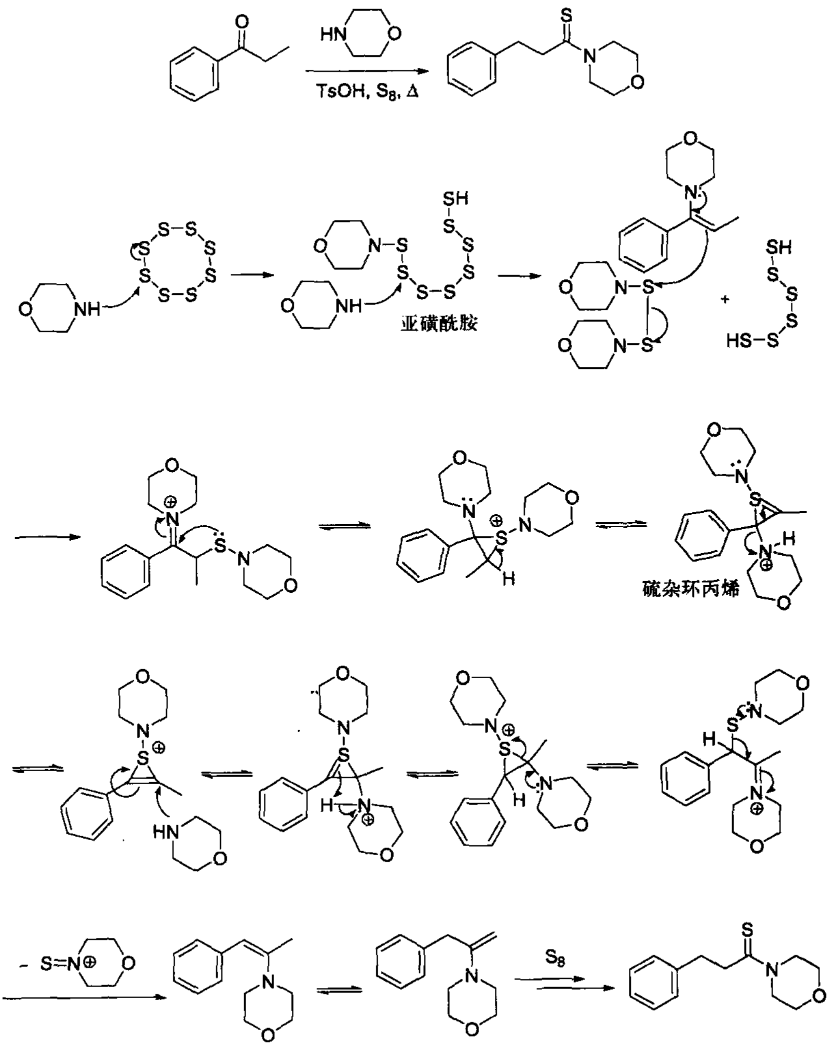
Willgerodt-Kindler 反应

酮经官能团迁移转化为硫酰胺的反应。

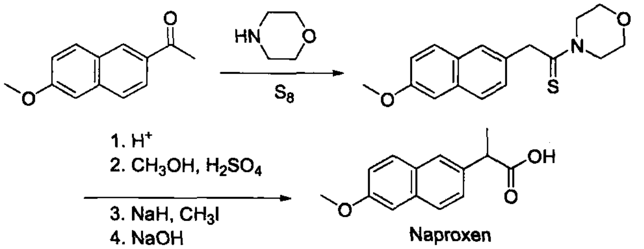


按照Carmack提出的机理,[2]最不寻常的一个从亚甲基到亚甲基的羰基迁移是经由高度活泼的含硫杂环中间体通过一个复杂的途径而实现的。亚磺酰胺是异构化的催化剂:

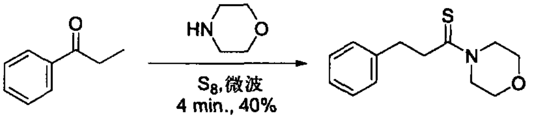


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_268,

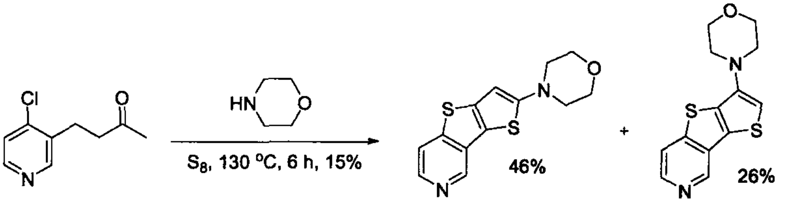
Example 1, Willgerodt-Kindler反应是最早合成消旋Neproxen程序中的关键一步。[3]



Example 2[5]



Example 3, Willgerodt–Kindler 反应条件下的一个串联增环反应:[10]



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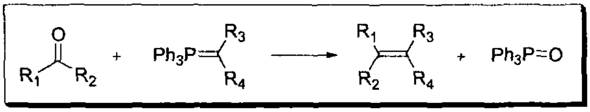
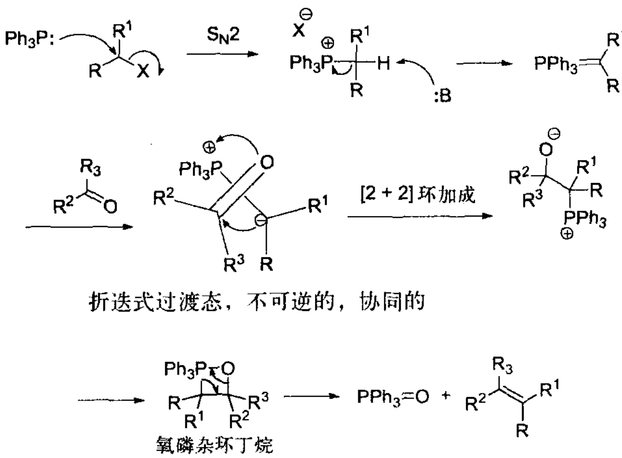
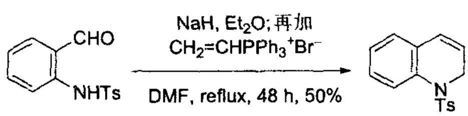
Wittig 反应

用磷叶立德使羰基进行烯基化的反应。通常得到Z-烯烃为主的产物。

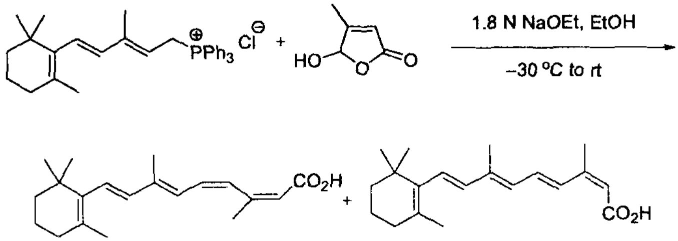




Example 1[3]



Example 2[4]



2-*cis*-4-*cis*-维 A 酸　　　　Accutane

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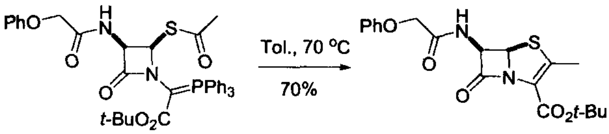
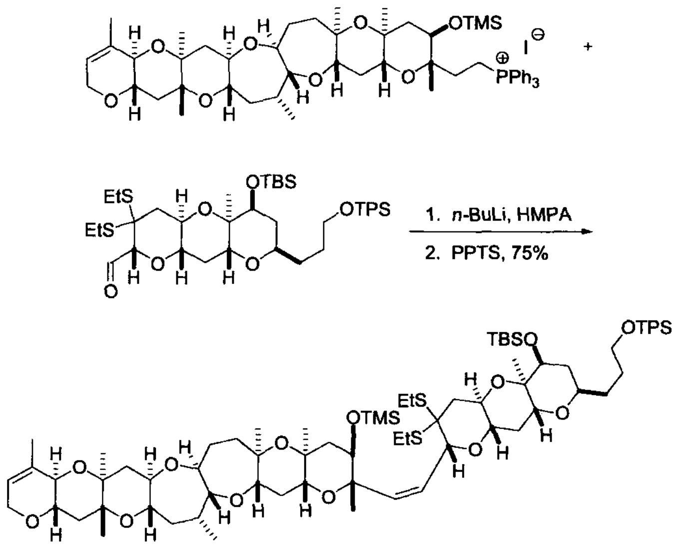
Example 3[5]



Example 4[9]



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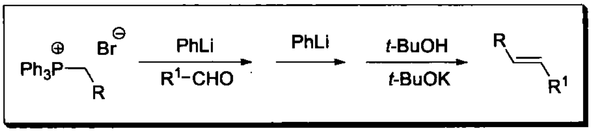
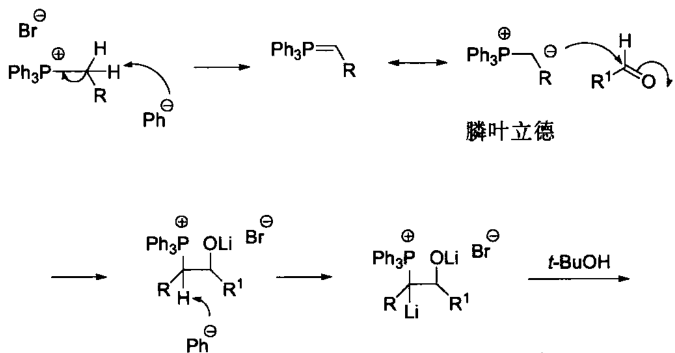
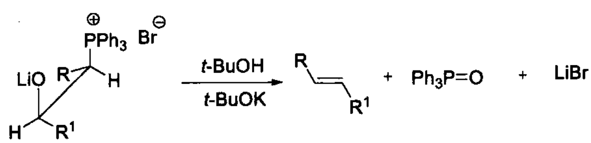
Wittig反应的Schlosser修正程序

不稳定的磷叶立德和醛进行的正常Wittig反应给出*Z*-烯烃为主的产物。用Wittig反应的Schlosser修正程序进行的反应则给出*E*-烯烃为主的产物。



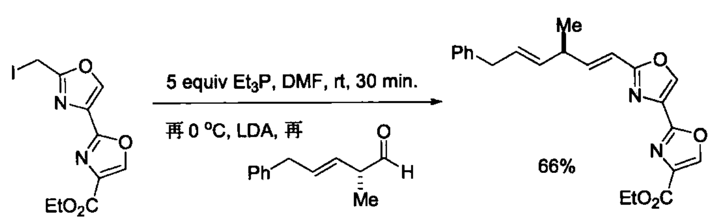


这些条件使赤式配合物转向苏式配合物：

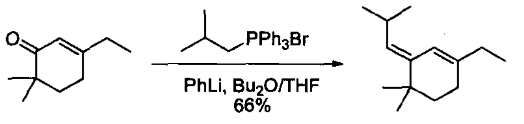


苏式的LiBr配合物

Example 1[6]



Example 2[10]



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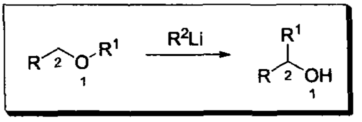
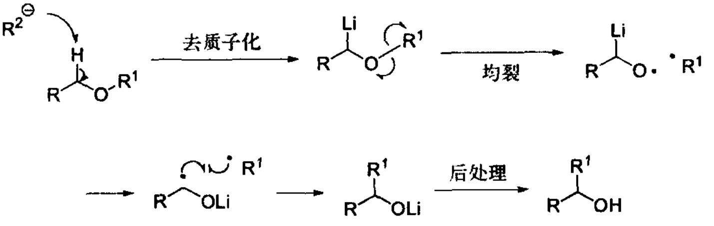
[1,2]- Wittig重排反应

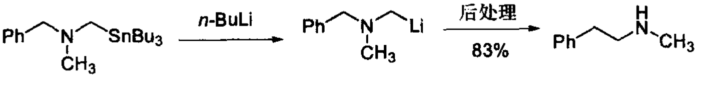
醚用烷基锂一类碱处理转化为醇的反应。



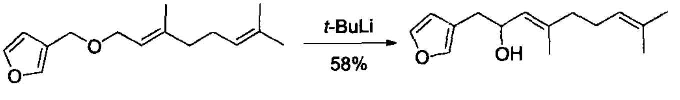
[1,2]-Wittig 重排应该是经过一个自由基机理：



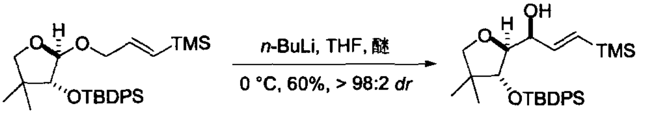
Example 1, 含氮的[1,2]-Wittig 重排[2]



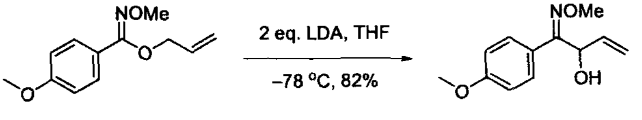
Example 2[3]



Example 3[4]



Example 4[6]



Example 5[8]

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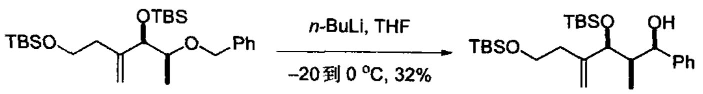
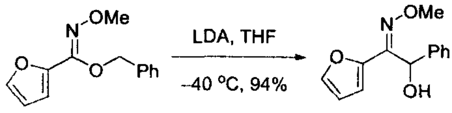


Example 6[9]



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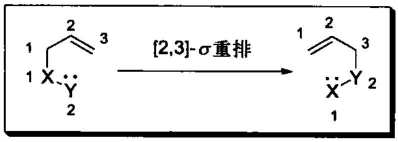
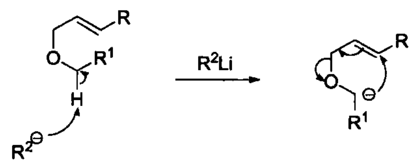
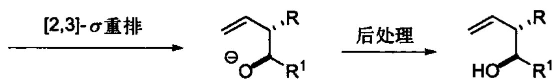
[2,3]-Wittig重排反应

烯丙基醚用碱处理转化为高烯丙基醇的反应。亦称Still-Wittig重排反应。参见第517页上的Sommelet-Hauser重排反应。

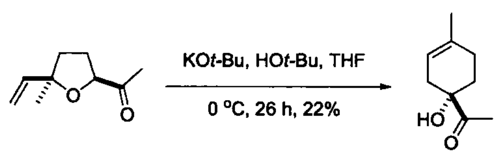




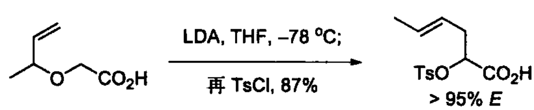
R^1 = 炔基、烯基、Ph、COR、CN.



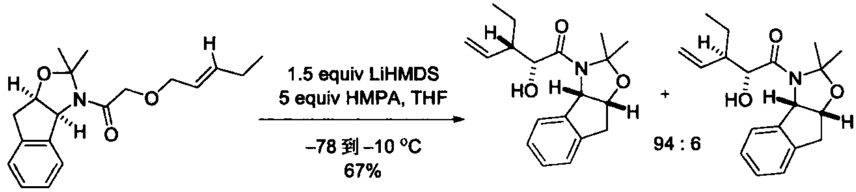
Example 1[2]



Example 2[3]



Example 3[5]



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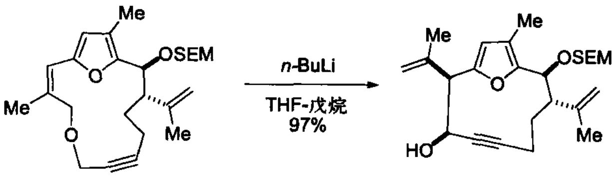
Example 4[6]



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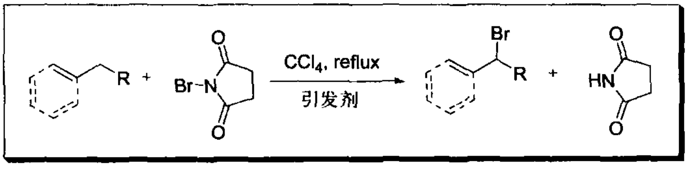
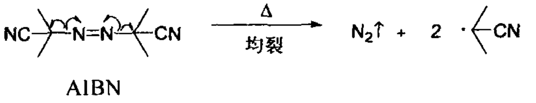
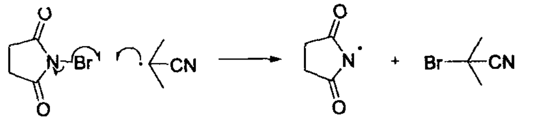
Wohl-Ziegler 反应

Wohl-Ziegler反应是烯丙基或苄基底物用NBS在自由基引发条件下处理得到烯丙基或苄基溴化物的反应。促进自由基引发的条件有通用的自由基引发剂、光和/或热，一般应用的溶剂是CCl_4。

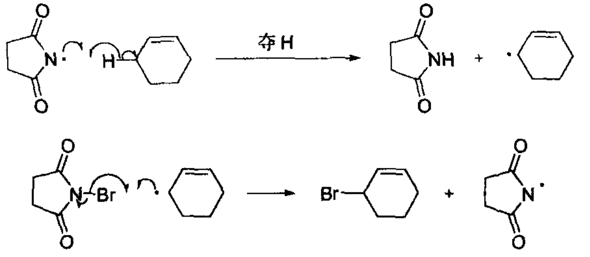


引发：



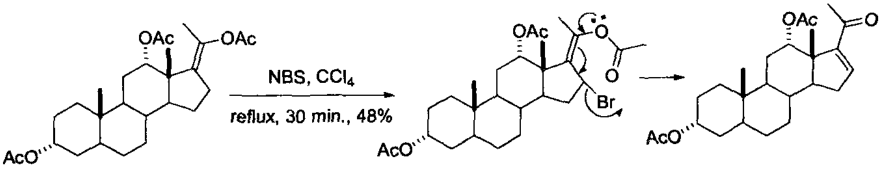


增长：



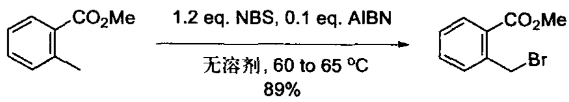
从下一个自由基链反应中可产生丁二酰亚胺自由基。

Example 1[3]

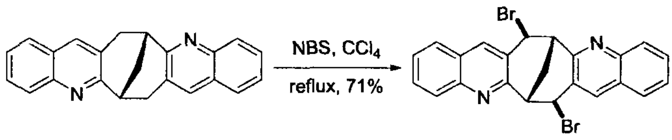


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_272,

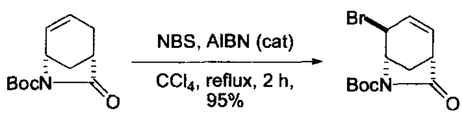
Example 2[7]



Example 3[8]



Example 4[9]



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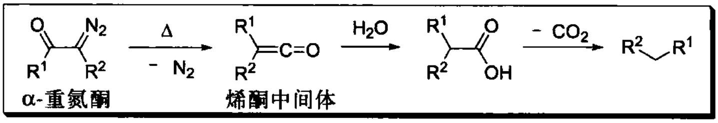
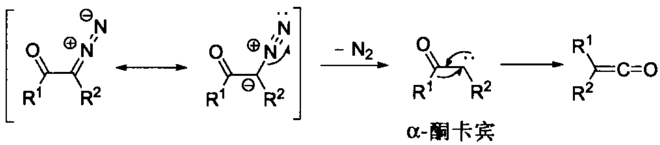
Wolff 重排反应

α-重氮酮转化为烯酮的反应。

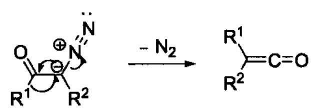


分步机理:

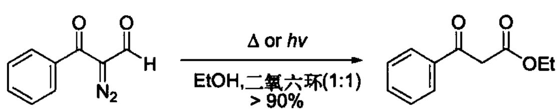


烯酮用水处理给出同碳羧酸。

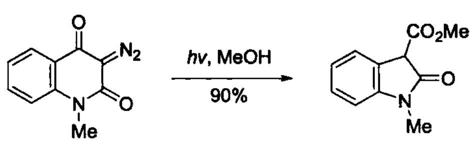
协同机理:



Example 1[2]

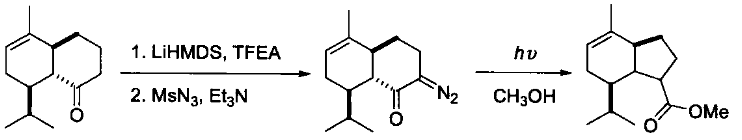


Example 2[3]

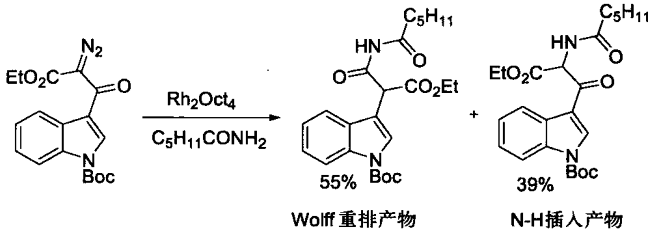


J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_273,

Example 3[4]



Example 4[9]



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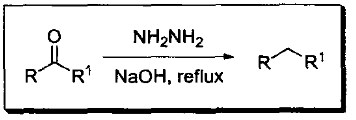
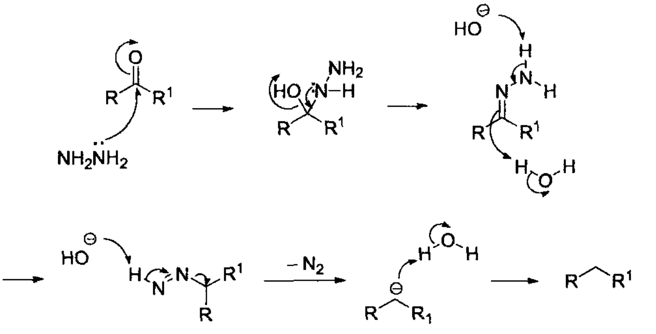
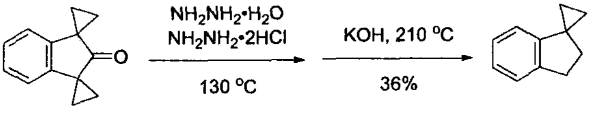
Wolff-Kishner 还原反应

羰基用碱性肼还原为亚甲基的反应。

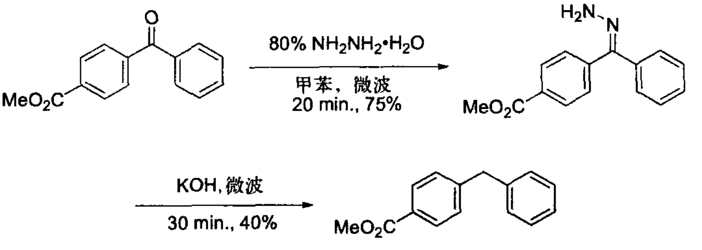




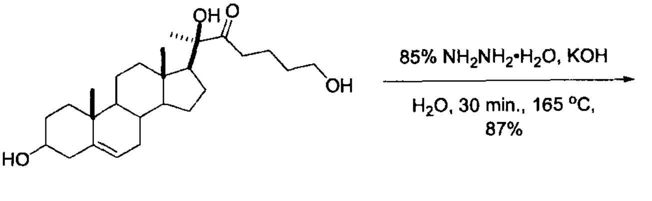
Example 1，黄鸣龙修正程序，此处失去了一分子乙烯。



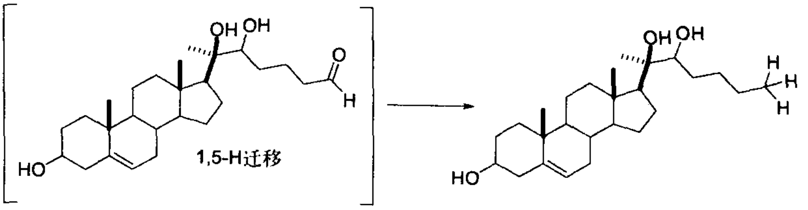
Example 2[7]



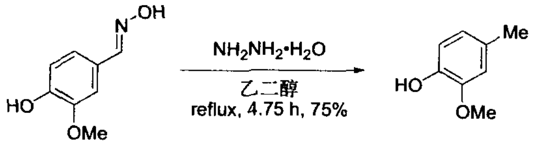
Example 3[8]



J.J. Li, *Name Reactions*, 4th ed., DOI 10.1007/978-3-642-01053-8_274,



Example 4, 黄鸣龙修正法[10]



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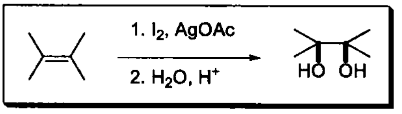
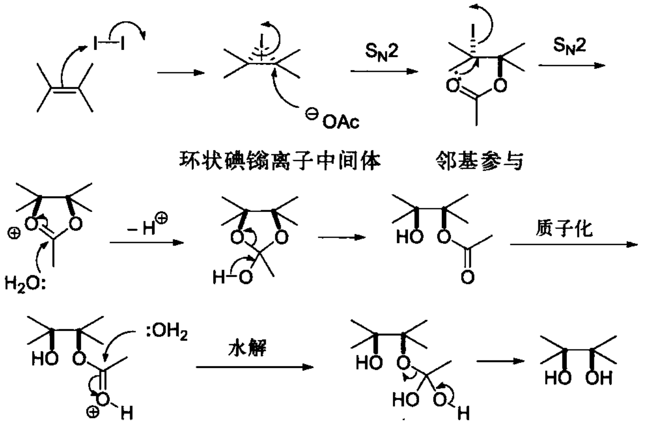
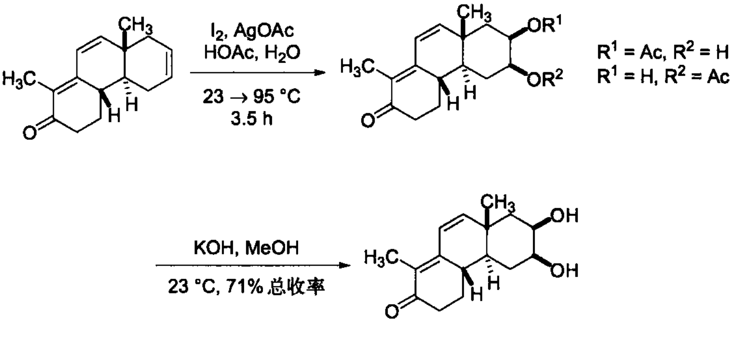
Woodward *cis*-双羟化反应

参见第447页上的Prevost *trans*-双羟化反应。

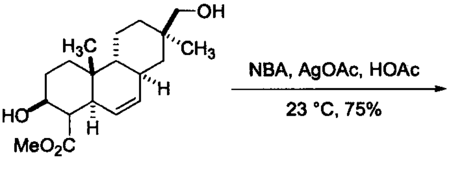




Example 1[1]



Example 2[6]



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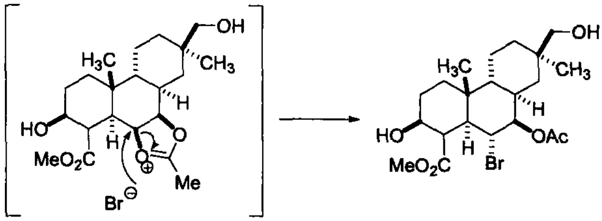

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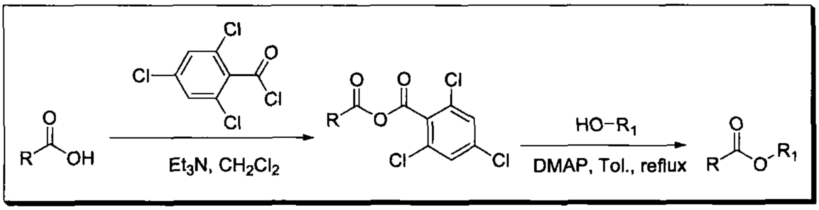
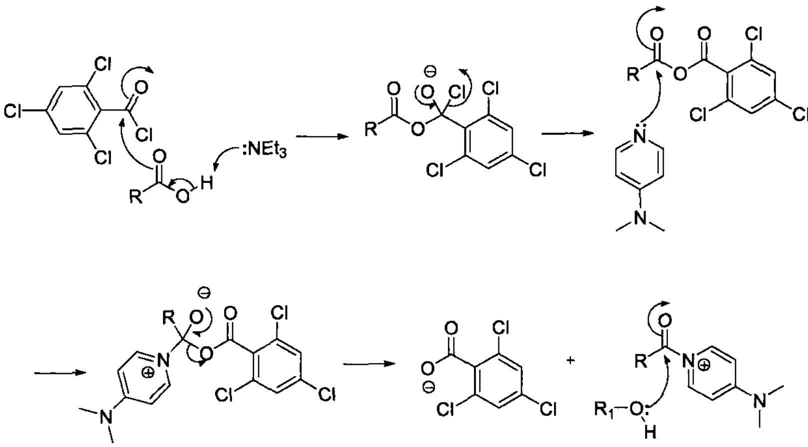
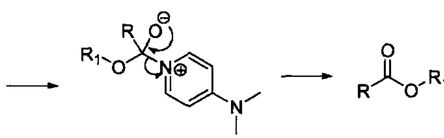
Yamaguchi 酯化反应

用2,4,6-三氯苯甲酰氯（Yamaguchi试剂）进行的酯化反应。

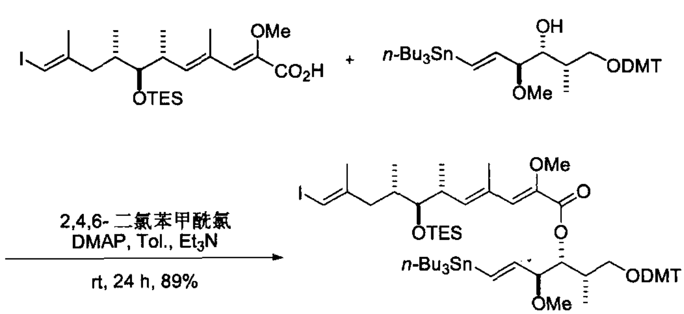




氯取代的大体积砌块阻碍了混合酸酐中间体中其他羰基的进攻。



Example 1, 分子间偶联



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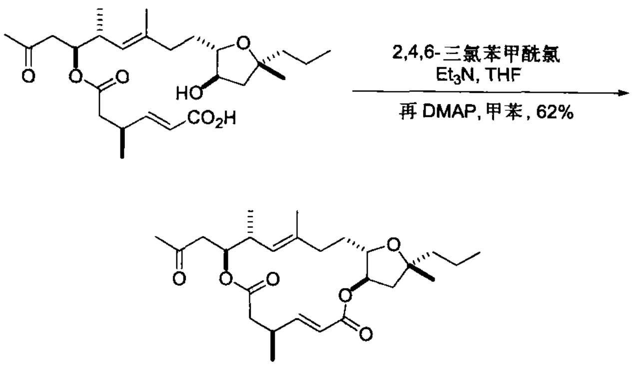
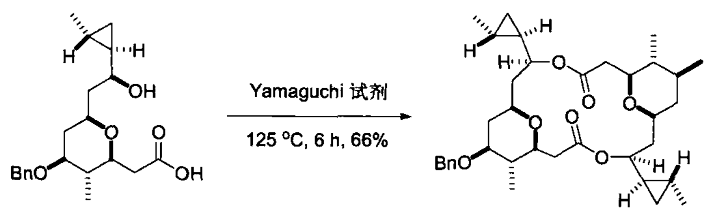
Example 2, 分子内偶联[7]



Example 3, 二聚反应[8]



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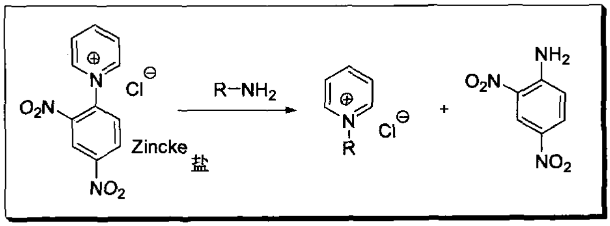
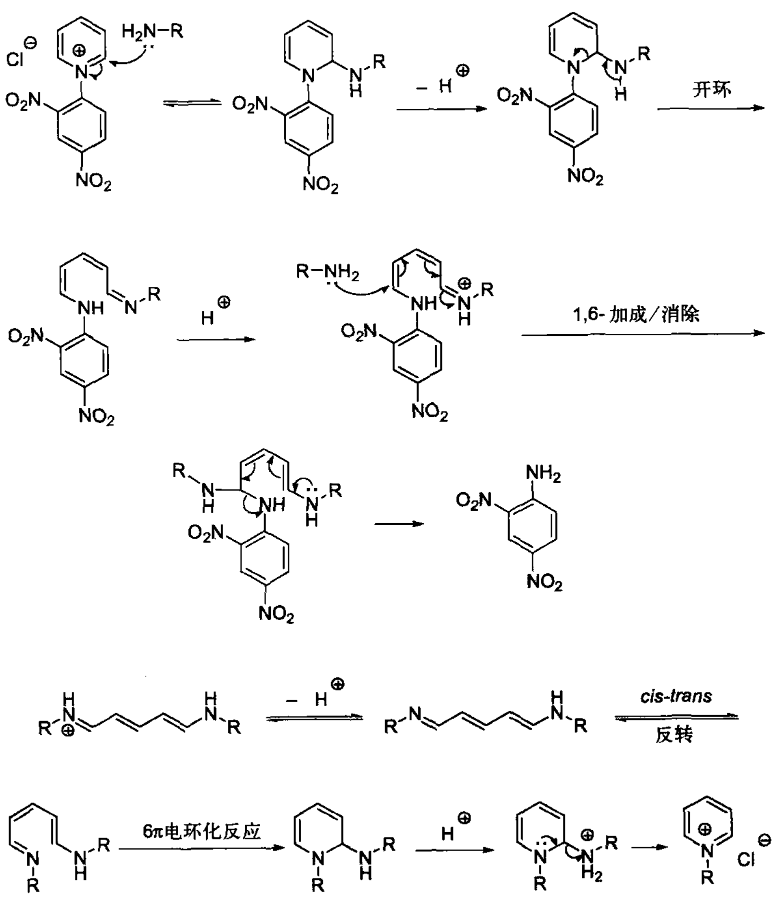
Zincke 取代吡啶盐的合成

Zincke反应是一个总的将*N*-（2,4-二硝基苯基）吡啶盐（Zincke盐）用适当的苯胺或烷基胺处理后转化为*N*-芳基化、*N*-烷基化吡啶鎓的胺交换过程。





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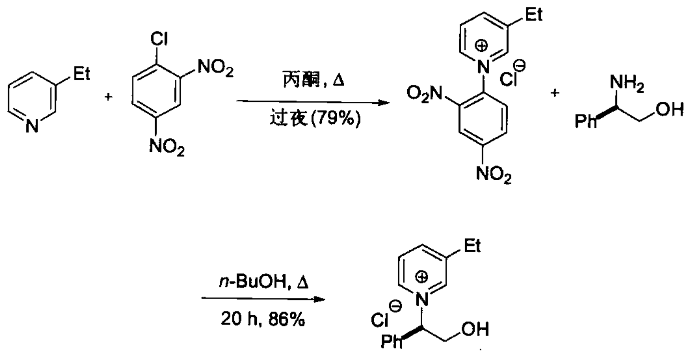
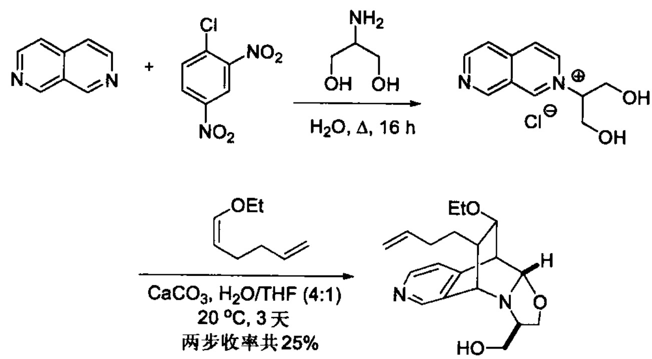
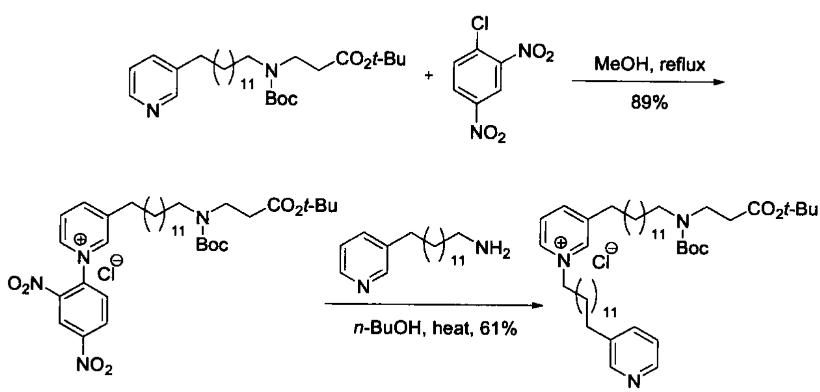
Example 1[5]



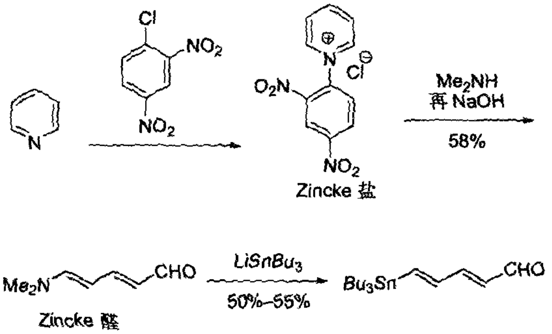
Example 2[6]



Example 3[9]



Example 4[10]



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内容提要＝国内外涉及有机人名反应的著作也有一些，但本书是颇有特色的一种。它并不追求齐全，但富有时代感，着眼于反应是否创新及有应用价值。全书精选了３００多个有机人名反应，每个反应均给出一步一步详尽的电子转移机理过程。新版本进一步增加了相关人名反应在合成中的应用，并增补了最新的参考文献，其中有相当部分是综述类论文，以帮助读者更好地理解和认识有机反应，同时为深入应用有机反应提供了方便。因此，本书在２００２年初版发行后深受市场欢迎，故近年来不断修订补充。本书中文版将根据其２００９年７月出版的第４版翻译而成。