# *SYNTHESIS ALERTS*

***Synthesis Alerts*** is a new monthly feature to help readers of Synthesis keep abreast of new reagents, catalysts, ligands, chiral auxiliaries, and protecting groups which have appeared in the recent literature. Emphasis is placed on new developments but established reagents, catalysts etc are also covered if they are used in novel and useful reactions. In each abstract, a specific example of a transformation is given in a concise format designed to aid visual retrieval of information.

***Synthesis Alerts*** is a personal selection by Paul Blakemore, Brian Dymock, Philip Hall, Philip Kocienski, J.-Y. Le Brazidec and Alessandro Pontiroli of the University of Southampton. The journals regularly covered by the abstractors are: Angewandte Chemie International Edition, Bulletin de la Societe Chimie de France, Bulletin of the Chemical Society of Japan, Chemische Berichte, Chemistry Letters, Helvetica Chimica Acta, Journal of Organic Chemistry, Journal of Organometallic Chemistry, Journal of the American Chemical Society, Liebigs Annalen, Tetrahedron Letters.



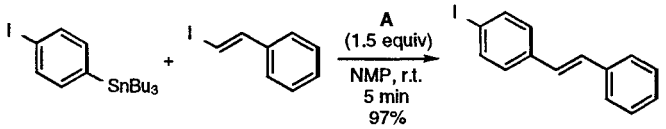
**Copper(I) Thiophene-2-carboxylate** — ***Catalyst***

New reagent for cross coupling of organostannanes with organic Iodides at or below room temperature.

G. D. Allred, L. S. Liebeskind *J. Am. Chem. Soc.*, **1996**, *118*, 2748.



A



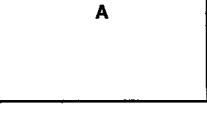

A is cheap, easily prepared, air stable and has rapid reactions. *No Palladium catalyst is necessary.* Range of examples. Yields > 70%.

**Chiral Zirconocene Catalyst** — ***Catalyst***

Zirconium-catalysed enantioselective alkylalumination of monosubstituted alkenes.

Ligand Preparation:
G. Erker, M. Aulbach, M. Knickmeier, D. Wingbermühle, C. Krüger, M. Nolte, S. Werner *J. Am. Chem. Soc.*, **1993**, *115*, 4590.

Example Shown:
D. Y. Kondakov, E. Negishi *J. Am. Chem. Soc.*, **1996**, *118*, 1577.



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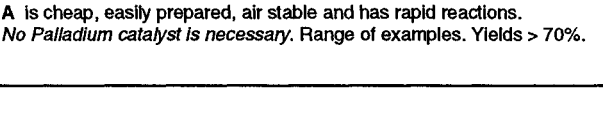


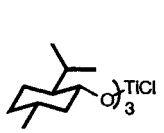

8 examples, yields ≥60%, er = 85:15

66%
er = 98:2

**Chlorotris[(–)-menthoxy]titanium** — ***Catalyst***

Synthesis of chiral allylic alcohols by the reaction of chiral titanium complexes with carbonyl compounds.

Y. Takayanagi, K. Yamashita, Y. Yoshida, F. Sato *J. Chem. Soc., Chem. Commun.* **1996**, 1725.



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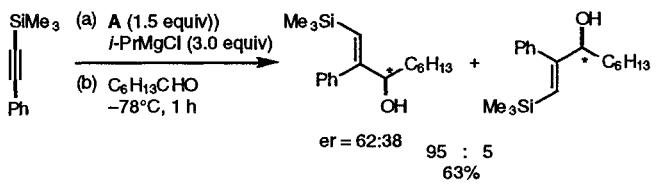


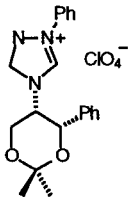

er = 62:38

95 : 5
63%

First example of an asymmetric addition of a metal–alkyne complex to aldehydes. 7 examples: 53-81% yield; low er.

## (4*S*,5 *S*)-4-(2,2-Dimethyl-4-phenyl-1,3-dioxan-5-yl)-1-phenyl-4 *H*-1,2,4-triazol-1-ium Perchlorate — *Catalyst*

Asymmetric variant of the benzoin condensation using a chiral triazolium salt.



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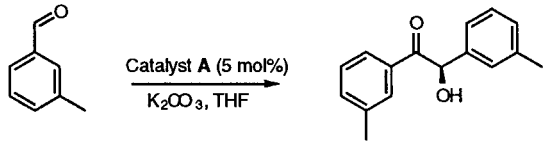


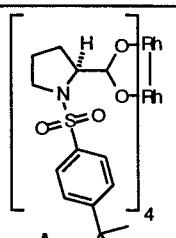

With deactivating functionnal group on the aromaric ring, the er are lower (8 examples)

54% (er = 88:12)

D. Enders, K. Breuer, J. H. Teles, *Helv. Chim. Acta* **1996**, *79*, 1217.

## Rhodium(II) *N*-(4-*tert*-butylbenzenesulfonyl)prolinate — *Catalyst*

Highly diastereoselective and enantioselective cyclopropanation resulting from Rh(II)-catalyzed decomposition of vinyldiazomethane in the presence of alkenes.



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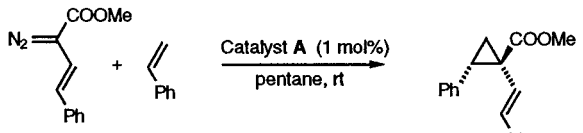



Efficient process from aryl and aliphatic alkenes and enol ethers.

79% (er = 95:5)

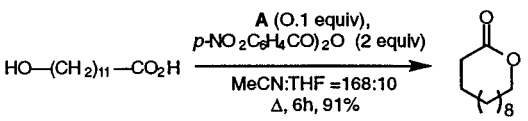
H. M. L. Davies, P. R. Bruzinski, D. H. Lake, N. Kong, M. J. Fall *J. Am. Chem. Soc.*, **1996**, *118*, 6897.

## Scandium(III) Triflate — *Catalyst*

Acylation catalyst for primary, secondary and tertiary alcohols with carboxylic acids or the corresponding anhydrides.

$Sc(OTf)_3$

A

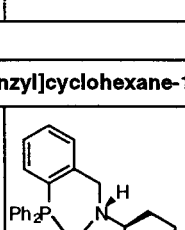



Yields *ca* 60-70% with allylic alcohols

K. Ishihara, M. Kubota, H. Kurihara, H. Yamamoto *J. Org. Chem.*, **1996**, *61*, 4560.

## (*S*,*S*)-*N*,*N*′-Bis[*o*-diphenylphosphino)benzyl]cyclohexane-1,2-diamine Ruthenium(II) Dichloride — *Catalyst*

$C_2$-symmetric Ru complex acts as an excellent transfer hydrogenation catalyst for aromatic ketones.



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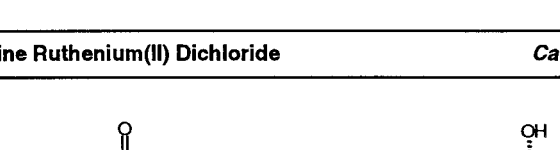
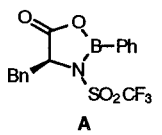



(*S*) configuration
er = 97:3

J.-X. Gao, T. Ikariya, R. Noyori *Organometallics* **1996**, *15*, 1087.

## (*S*)-2-Phenyl-4-phenylmethyl-3-(trifluoromethylsulfonyl)-1-oxa-3-aza-2-borolidin-5-one — *Catalyst*

Homochiral Lewis acid for assisted nucleophilic cleavage of acetals.



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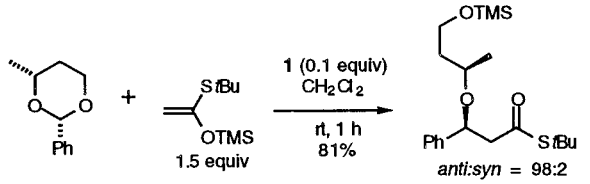



10 examples:- 3 different acetals and 5 nucleophiles. Yields generally>70%. Procedure given for removal of chiral auxilliary in high yield.

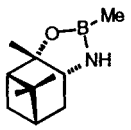
M. Kinugusa, T. Harada, K. Fujita, A. Oku *Synlett*, **1996**, 43.

## α-Pinene-Derived Oxazaborolidines

*Catalyst*

Oxazaborolidines from α-pinene-derived amino alcohols used in conjunction with $BH_3{\cdot}SMe_2$ reduce ketones to secondary alcohols with a high degree of stereocontrol.

M. Masui, T. Shioiri *Synlett*, **1996**, 49.



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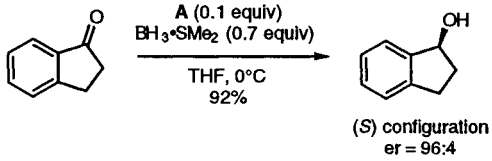


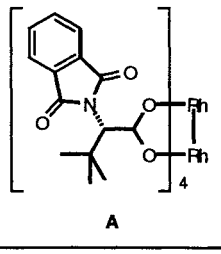

Other boron substituents may be H, Bu or Ph. Antipode of **A** gave alcohols of opposite (*R*) configuration. 7 other ketones examined.

## Dirhodium(II) Tetrakis[*N*-phthaloyl-(*S*)-*tert*-Leucinate]

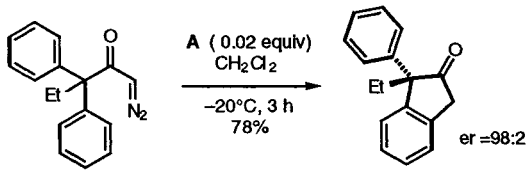
*Catalyst*

Catalyst for asymmetric synthesis of 2-indanones by desymmetrization of prochiral 3,3-diarylpropan-2-ones.

N. Watanabe, T. Ogawa, Y. Ohtake, S. Ikegami, S. Hashimoto *Synlett*, **1996**, 85.



A



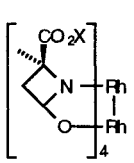

3 other substrates examined where Et is replaced. Rhodium catalyst shown was the best of three examined.

## Dirhodium(II) Tetrakis[alkyl 2-oxaazetidine-4(*S*)-carboxylates]

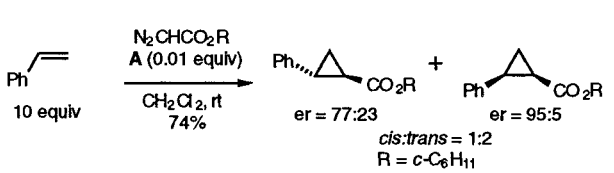
*Catalyst*

Chiral dirhodium catalysts for enantioselective cyclopropanation.

M. P. Doyle, Q. -L. Zhou, S. H. Simonsen, V. Lynch *Synlett*, **1996**, 697.



**A** X=$(CH_3)_2CHCH_2$
**B** X = $PhCH_2$




See also A. M. Harm, J. G. Knight, G. Stemp, *ibid*, 677 for the use of copper *bis*-oxazoline catalysts.

## Scandium Trifluoromethansulfonimide

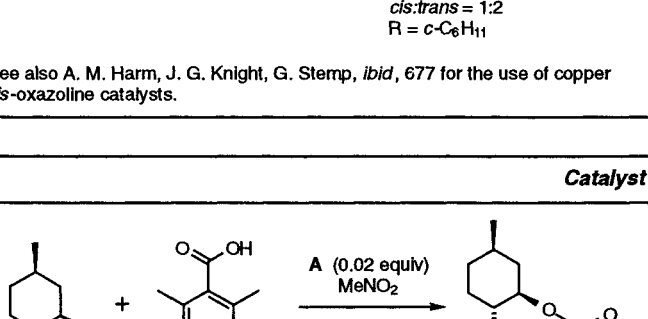
*Catalyst*

New scandium acylation catalyst. Superior to Scandium triflate in some cases, notably for benzoylation.

K. Ishihara, M. Kubota, H. Yamamoto *S Synlett*, **1996**, 265.

$Sc(NTf_2)_3$

**A**



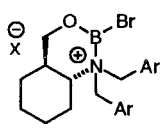

4 alcohols examined:- yields generally >90%

## New Oxazaborinane Catalyst

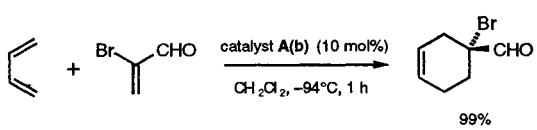
*Catalyst*

Highly reactive homochiral Lewis acid catalysts for asymmetric Diels–Alder reaction.

Y. Hayashi, J. J. Rohde, E. J. Corey *J. Am. Chem. Soc.*, **1996**, *118*, 5502.



**A**
Ar = 3,5-dimethylphenyl
(a) X = Br
(b) X = $B[C_6H_3\text{-}3,5\text{-}(CF_3)_2]_4$

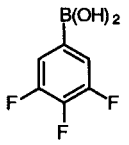



9 examples ; typically >90% yield

## 3,4,5-Trifluorobenzeneboronic Acid

*Catalyst*

Extremely active amidation catalyst.



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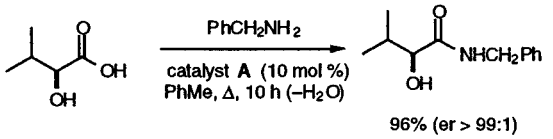



96% (er > 99:1)

11 examples (yields typically >90%)

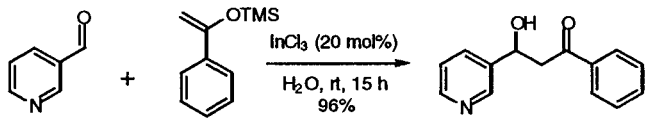
K. Ishihara, S. Ohara, H. Yamamoto *J. Org. Chem.*, **1996**, *61*, 4196.

## Indium(III) Chloride

*Catalyst*

Indium(III) Chloride (20 mol%) catalyses the Mukaiyama directed aldol reaction of the enol silane derived from acetophenone with aldehydes in water.

$InCl_3$




6 cases using the same enol silane derivative above (yields 85-96%)
All aldehyde substrates lack α-hydrogens

T.-P. Loh, J. Pei, G.-Q. Cao *J. Chem. Soc., Chem. Commun.*, **1996**, 1819.

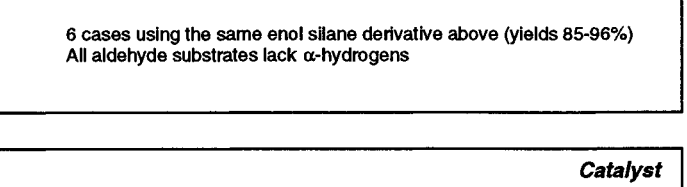
## Tris(dibenzylideneacetone)dipalladium(0)–Chloroform Adduct

*Catalyst*

A highly active "ligandless" catalyst system for the cycloisomerization of enynes.

$(dba)_3Pd_2{\cdot}CHCl_3$

A



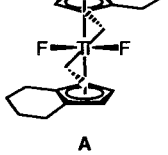

Formic acid reduces Pd(2+) to Pd(0). Use of 1,2-dichloroethane as solvent gave a fast rate at rt.

B. M. Trost, Y. Li *J. Am. Chem. Soc.*, **1996**, *118*, 6625.

## (*S,S*)-Ethylenebis($\eta^5$-tetrahydroindenyl)titanium Difluoride

*Catalyst*

Catalytic asymmetric hydrosilylation of imines can be accomplished with a catalyst prepared by treatment of the title compound with $PhSiH_3$ and pyrollidine in MeOH–THF at 60°C.



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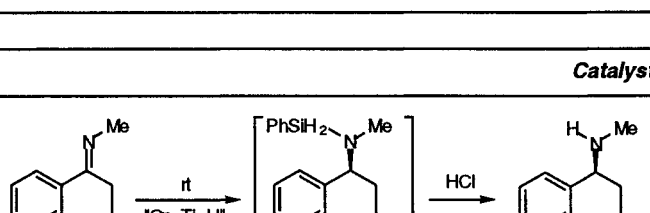



80% (er = 98:2)

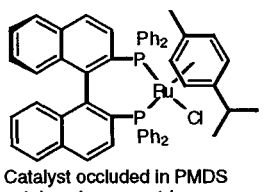
9 cases (yields typically 80-97%, er > 95:5)

X. Verdaguer, U. E. W. Lange, M. T. Reding, S. L. Buchwald *J. Am. Chem. Soc.*, **1996**, *118*, 6784.

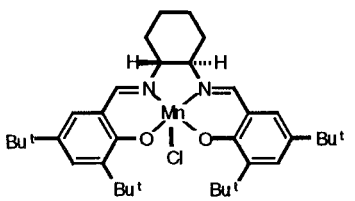
## Chiral Catalytic Membranes

*Catalyst*

Noyori's BINAP complex and Jacobsen's chiral salen complex occluded in an elastomeric type polydimethylsiloxane (PMDS) matrix give a regenerable catalytically active membrane.




Catalyst occluded in PMDS catalysed asymmetric hydrogenation of methyl acetoacetate in up to dr 85:15




Catalyst occluded in PMDS catalysed epoxidaton of styrene in up to dr 78:22

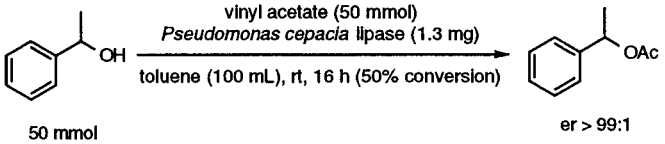
I. F. J. Vankelecom, D. Tas, R. F. Parton, V. Van de Vyver, P. A. Jacobs *Angew. Chem. Int. Ed. Engl.*, **1996**, *35*, 1346.

## Cross-Linked Enzyme Crystals as Highly Active Catalysts in Organic Solvents

*Catalyst*

Insoluble cross-linked lipases prepared on a large scale in the presence of surfactants combine higher stability and superior activity in organic solvents.

N. Khalaf, C. P. Goverdhan, J. J. Lalonde, R. A. Perischetti, Y.-F. Wang, A. L. Margolin *J. Am. Chem. Soc.*, **1996**, *118*, 5494.




7 examples of resolutions including 4 alcohols, 2 carboxylic acids, and 1 amine

## Scandium(III) Triflate

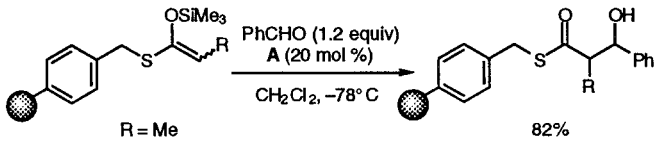
*Catalyst*

Catalyses Mukaiyama-type aldol reaction between polymer supported silyl enol ethers and aldehydes.

S. Kobayashi, I. Hachiya, M. Yasuda *Tetrahedron Lett.*, **1996**, *37*, 5569.

$Sc(OTf)_3$

**A**



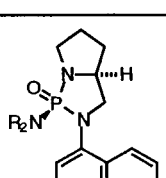

Further examples utilising other simple aldehydes (both saturated and unsaturated) plus cases where R = OBn (yields 55-82%).

## Proline-Derived Phosphoramides

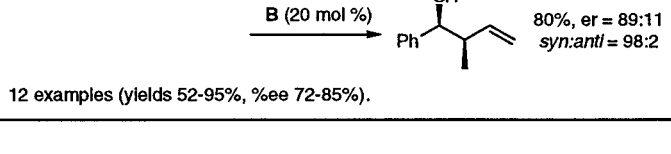
*Catalyst*

Chiral Lewis base catalysts for the asymmetric allylation of aromatic aldehydes with allylic trichlorosilanes.

K. Iseki, Y. Kuroki, M. Takahashi, Y. Kobayashi *Tetrahedron Lett.*, **1996**, *37*, 5149.



**A** R = -$(CH_2)_5$-
**B** R = *n*Pr



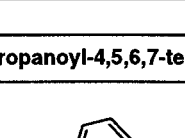

12 examples (yields 52-95%, %ee 72-85%).

## (4*R*,7 *S*)-7-Isopropyl-4-methyl-3-phenyl-2-propanoyl-4,5,6,7-tetrahydro-2*H*-indazole

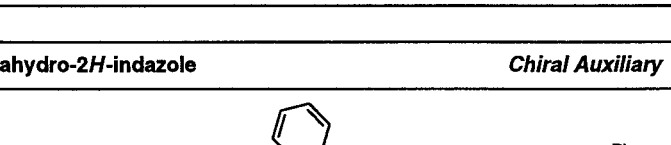
*Chiral Auxiliary*

Preparation of enantiomerically enriched enolisable β-ketoamides.

C. Kashima, I. Fukuchi, K. Takahashi, A. Hosomi *Tetrahedron* **1996**, *52*, 10335.



**A**




Butanoyl, 3-methylbutanoyl, phenylethanoyl, and 3-phenylpropanoyl analogues of **A** also reported.

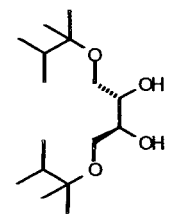
## (2*S*,3 *S*)-1,4-Di(2,3-dimethylbut-2-oxy)butane-2,3-diol

*Chiral Auxiliary*

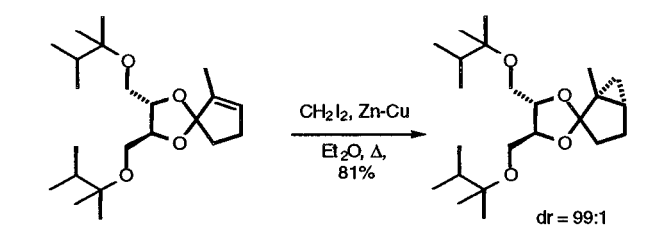
Ketals prepared from enones and the title compound undergo diastereoselective cyclopropanation using the Simmons–Smith reaction.

Ligand preparation: T.-M. Yuan, S. -M. Yeh, T.-Y. Luh *J.Org. Chem.*, **1994**, *59*, 8192.

Example shown: S.-M. Yeh, L.-H. Huang, T.-Y. Luh *J.Org. Chem.*, **1996**, *61*, 3906.



**A**

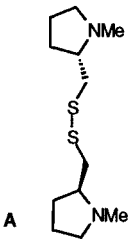


## Bis[(*S*)-*N*-methylpyrrolidin-2-ylmethyl] Disulfide — *Ligand*

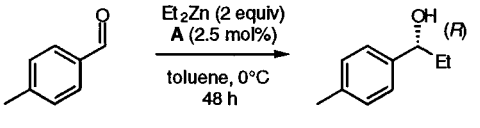
Enantioselective addition of diethylzinc to aldehydes catalysed by an *L*-proline derived β-amino disulfide ligand.

Ligand preparation:
G. A. Cran, C. L. Gibson, S. Handa *Tetrahedron: Asymmetry*, **1995**, *6*, 1553.

Example Shown:
C. L. Gibson *J. Chem. Soc., Chem. Commun.* **1996**, 645.




A



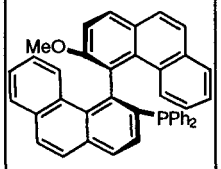

83% yield
er = 99:1

6 cases with mostly aromatic aldehydes.
Yields ≥75% and ≥85% er.

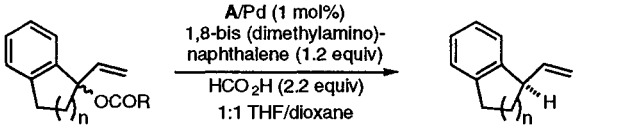
## (*R*)-2-Diphenylphosphino-2′-methoxy-1,1′-biphenanthryl — *Ligand*

Catalytic asymmetric synthesis of optically active alkenes by Palladium catalysed asymmetric reduction of racemic allyl esters with formic acid.

T. Hayashi, M. Kawatsura, H. Iwamura
Y. Yamaura, Y. Uozumi *J. Chem. Soc., Chem. Commun.*, **1996**, 1767.




A



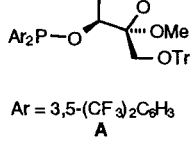

R = Me, *t*Bu
n = 1 or 2

n = 2 : 90% yield; er = 96:4
n = 1 : 81% yield; er = 93:7

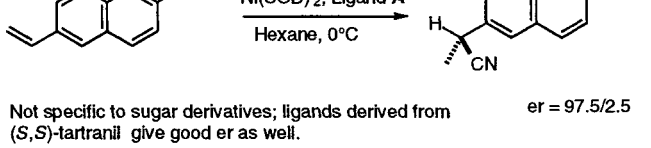
## Methyl 3-*O*-(Diphenylphosphinyl)-4-*O*-[bis(3,5-ditrifluoromethylphenyl)phosphinyl]-1,6-*O*-dityrityl-α-D-fructanoside — *Ligand*

Dramatic effect of electronic asymmetry of ligands observed in the Ni(0) catalyzed hydrocyanation of styrene derivatives.

T. V. Rajanbabu, A. L. Casalnuovo, *J. Am. Chem. Soc.*, **1996**, *118*, 6325.




Ar = 3,5-$(CF_3)_2C_6H_3$
A



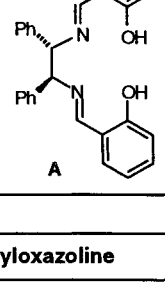

Not specific to sugar derivatives; ligands derived from (*S*,*S*)-tartranil give good er as well.

er = 97.5/2.5

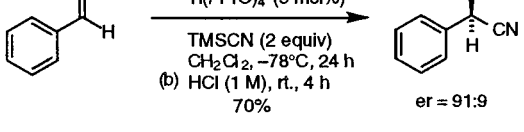
## (*S*,*S*)-*N*,*N*′-Bis(salicylidene)-1,2-diphenylethylenediamine — *Ligand*

Complex derived from title compound and titanium isopropoxide catalyses asymmetric cyanohydrin formation.

W. Pan, X. Feng, L. Gong, W. Hu, Z. Li, A. Mi, Y. Jiang, *Synlett*, **1996**, 337.




A




er = 91:9

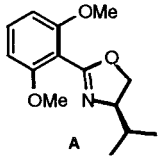
Benzaldehyde was the only substrate examined.

## (–)-(*S*)-2-(2,6-Dimethoxyphenyl)-4-isopropyloxazoline — *Ligand*

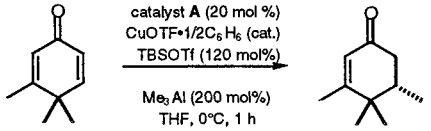
Ligand for the enantioselective Cu(I)-catalysed 1,4-addition of $Me_3Al$ to enones.

Y. Takemoto, S. Kuraoka, N. Hamaue, C. Iwata *Tetrahedron Asymm.*, **1996**, *7*, 993.

For application to (–)-solvetivone see *J. Chem. Soc., Chem. Commun.*, **1996**, 1655.




A



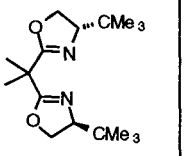

only one substrate

88%
(*S*:*R* = 84:16)

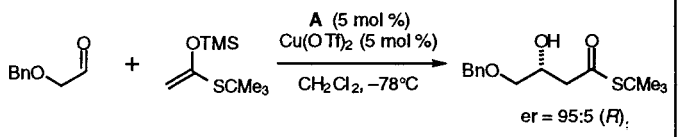
## 2,2-Bis{2-[4(*S*)-*tert*-butyl-1,3-oxazolinyl]}propane — *Ligand*

$C_2$-symmetric copper(II) complexes prepared from the title compound catalyse enantioselective aldol additions of silylketene acetals to (benzyloxy)acetaldehyde.

D. A. Evans, J. A. Murry, M. C. Kozlowski *J. Am. Chem. Soc.*, **1996**, *118*, 5814.



A



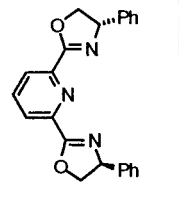

for use of bis(oxazolinyl)–Cu(II) and –Fe(III) complexes as chiral Lewis acids in the Diels-Alder reaction of acrylimide dienophiles see: Evans *J. Am. Chem. Soc.*, **1993**, *115*, 6460 and Corey *J. Am. Chem. Soc.*, **1991**, *113*, 728.

## 2,6-Bis{2-[(4*S*)-phenyl-1,3-oxazolinyl]}pyridine (pybox) — *Ligand*

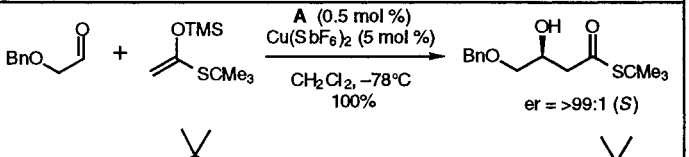
$C_2$-symmetric copper(II) complexes prepared from the title compound catalyse enantioselective aldol additions of silylketene acetals to (benzyloxy)acetaldehyde.

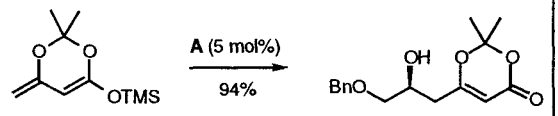
Ligand preparation: H. Nishiyama, M. Kondo, T. Nakamura *Organometallics*, **1991**, *10*, 500.

Example shown: D. A. Evans, J. A. Murry, M. C. Kozlowski *J. Am. Chem. Soc.*, **1996**, *118*, 5814.



A



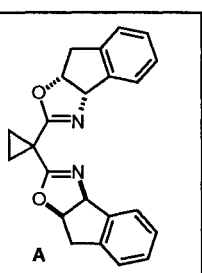




7 cases (yields typically >90%)

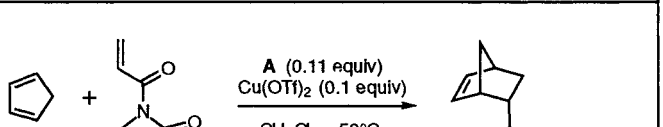
## Spirobis(oxazoline) Ligands — *Ligand*

New $C_2$-symmetric copper(II) catalysts for the catalytic enantioselective Diels–Alder reaction of acrylimides with cyclopentadiene.

I. W. Davies, L. Gerena, L. Castonguay, C. H. Senanayake, R. D. Larsen, T. R. Verhoeven, P. J. Reider *J. Chem. Soc., Chem. Commun.*, **1996**, 1753.



A



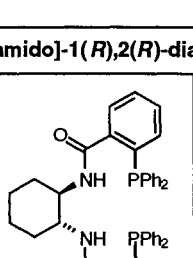

enantioselectivity depends on the size of the central carbocyclic ring.

## (+)-1,2-Bis-*N*-[2′-(diphenylphosphino)benzamido]-1(*R*),2(*R*)-diaminocyclohexane — *Ligand*

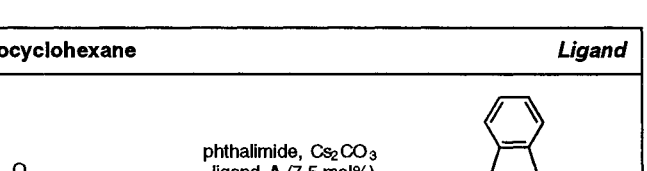
Chiral ligand for the asymmetric alkylation and functionalisation of allylic esters, carbonates, and epoxides.

Ligand preparation: B. M. Trost, D. L. Van Vranken, C. Bingel *J. Am. Chem. Soc.*, **1992**, *114*, 9327.

Example shown: B. M. Trost, A. C. Krueger, R. C. Bunt, J. Zambrano *J. Am. Chem. Soc.*, **1996**, *118*, 6520-6521. Cf B. M. Trost, M. J. Krische, R. Radinov, G. Zanoni *J. Am. Chem. Soc.*, **1996**, *118*, 6297.




A

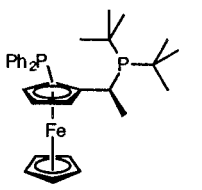



## (*S*)-1-[(*S*)-2-(Diphenylphosphino)ferrocenyl]ethyldi-*tert*-butylphosphine — *Ligand*

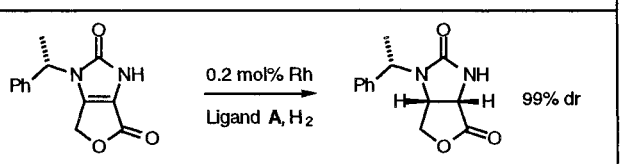
An easily accessible chiral ligand for highly enantioselective hydrogenation, allylic alkylation and hydroboration.

Ligand synthesis: A. Togni, C. Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijani *J. Am. Chem. Soc.*, **1994**, *116*, 4062.

Example shown: J. McGarrity, F. Spindler, R. Fuchs, M. Eyer (Lonza AG), ER-A 624 587 A2 **1995** [*Chem. Abstr.* **1995**, 122, P81369q].




A




Bulky t-Bu groups essential for high diastereofacial selectivity in the above reaction which is a key step in a new industrial synthesis of (+)-biotin.

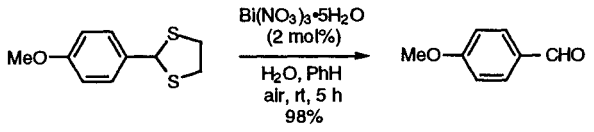
Review : Planar-Chiral Ferrocenes: Synthetic Methods and Applications, A. Togni *Angew. Chem. Int. Ed. Engl.*, **1996**, *35*, 1475-7.

## Bismuth(III) Nitrate

*Protecting Group*

Deprotection of *S,S*-acetals using air and a catalytic amount of bismuth nitrate (2-20 mol%).

$Bi(NO_3)_3$




16 examples; mostly aryl-substituted dithiolanes

N. Komatsu, A. Taniguchi, M. Uda, H. Suzuki *J. Chem. Soc.,Chem. Commun.*,**1996**, 1847.

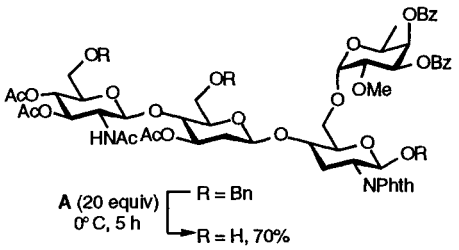
## Iron(III) Chloride

*Protecting Group*

Debenzylates complex oligosaccharides in good to excellent yields. Alkenes, acetates, benzoates, phthalimides, acyl amides and sensitive glycosidic linkages unaffected by reaction conditions.

$FeCl_3$

**A**



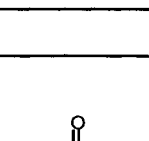

4 other examples including a monosaccharide containing an olefinic sidechain (yields 38-85%).

R. Rodebaugh, J. S. Debenham, B. Fraser-Reid *Tetrahedron Lett.*, **1996**, *37*, 5477.

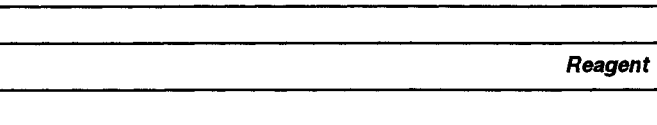
## Trichloroisocyanuric Acid

*Reagent*

Oxidises aldehdes to methyl esters.




**A**



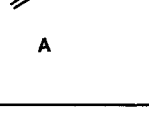

Simple 1 step procedure. Yields ≥70%.

G. A. Hiegel, C. D. Bayne, Y. Donde, G. S. Tamashiro, L. A. Hilberath *Synth. Commun.*, **1996**, 2633.

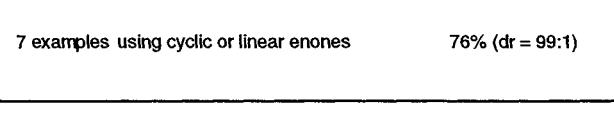
## Formaldehyde SAMP-hydrazone

*Reagent*

Enantioselective nucleophilic formylation and cyanation of conjugated enones *via* Michael addition of formaldehyde SAMP-hydrazone




**A**




7 examples using cyclic or linear enones

76% (dr = 99:1)

J. -M. Lassaletta, R. Fernández, E. Martín-Zamora, E. Díez *J. Am. Chem. Soc.*, **1996**, *118*, 7002-7003

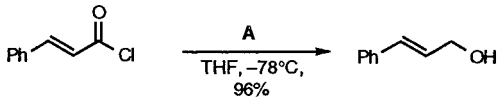
## Diisopropoxytitanium(III) Tetrahydroborate

*Reagent*

Chemoselective reducing reagent generated *in situ* from diisopropoxytitanium dichloride and benzyltriethylammonium borohydride.

$(i\text{-PrO})_2TiBH_4$

**A**

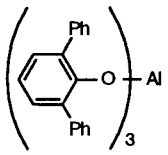



Aldehydes (10 examples), ketones (8), carboxylic acids(12) are all reduced to the alcohol in high yield. Compatible with amides, azides, esters, ethers, halogens, nitriles and oximes. For stereoselective reduction of epoxyketones see: *Tetrahedron*, **1996**, *52*, 9137.

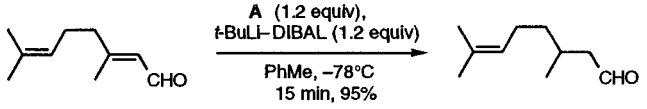
K. S. Ravikumar, S. Chandrasekaran, *J. Org. Chem.*,**1996**, *61*, 826.

## Aluminium Tris(2,6-diphenylphenoxide) — Reagent

Used in conjunction with "ate" complexes derived from *n*-BuLi/ DIBAL to effect 1,4-reduction of enals and enones.




A




11 enones ( yields >94%) and 5 enals ( yields >80%) examined

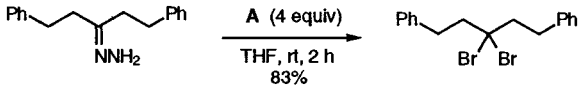
S. Saito, H. Yamamoto, *J. Org. Chem.*, **1996**, *61*, 2928.

## Copper(II) Bromide–Lithium *tert*-Butoxide — Reagent

Reagent for transformation of hydrazones to *gem*-dibromides.

*t*-BuOCuBr

A

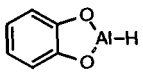



7 ketones and 2 aldehydes examined: yields usually >70%

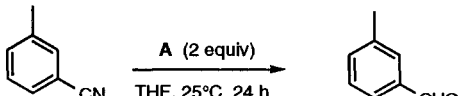
T. Takeda, R. Sasaki, A. Kamura, S. Yamauchi, T. Fujiwara *Synlett*, **1996**, 273.

## 1,3,2-Benzodioxaluminole (Catecholalane) — Reagent

Reagent for selective reduction of nitriles to aldehydes.




A

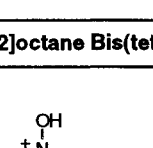



11 nitriles (aliphatic and aromatic) reduced to aldehydes in high yield.

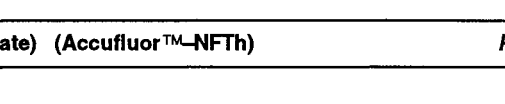
J. S. Cha, S. W. Chang, O. O. Kwon, J. M. Kim *Synlett*, **1996**, 165.

## 1-Fluoro-4-hydroxy-1,4-diazoniabicyclo[2.2.2]octane Bis(tetrafluoroborate) (Accufluor™–NFTh) — Reagent

The commercially available title compound generates α, α-difluoroketones from phenols.




A

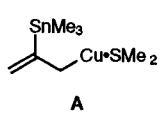



4 other phenols examined. Phenyl-substituted alkynes gave α,α-difluorophenones.

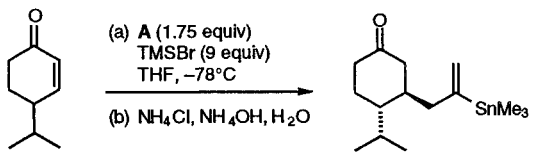
S. Stavber, M. Zupan *Synlett*, **1996**, 693.

## 2-(Trimethylstannyl)allylcopper(I)–Dimethyl Sulfide — Reagent

Novel functionalised copper(I) reagent. Its preparation and conjugate addition to enones is described.




A




7 enones: Yields 40-60% if 4° centre created, otherwise >80%. Corresponding germanium equally effective.

E. Piers, A. M. Kaller *Synlett*, **1996**, 549.

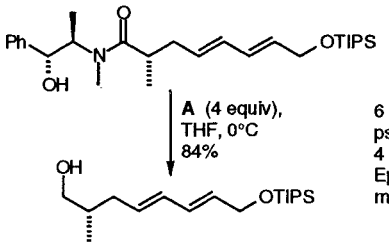
## Lithium amidotrihydroborate (LAB) — *Reagent*

Reducing reagent capable of converting tertiary amides to the corresponding primary alcohol. Tertiary amine formation is minimal.

A. G. Myers, B. H. Yang, D. J. Kopecky *Tetrahedron Lett.*, **1996**, *37*, 3623.

$LiH_2NBH_3$

**A**

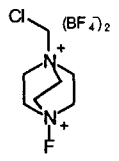



6 examples of reductive cleavage of pseudoephderine auxilliary.
4 examples of other tertiary amides.
Epimerisation of α-stereocentres is minimal.

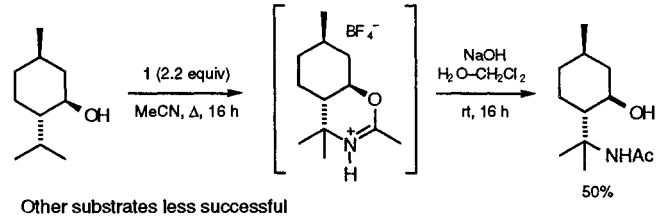
## 1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane Bis(tetrafluoroborate) (Selectfluor™) — *Reagent*

Remote fuctionalisation of menthol.

R. E. Banks, N. J. Lawrence, M. K. Besheesh, A. L. Popplewell, R. G. Pritchard *J. Chem. Soc., Chem. Commun.*, **1996**, 1655.




**1**

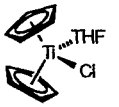



Other substrates less successful

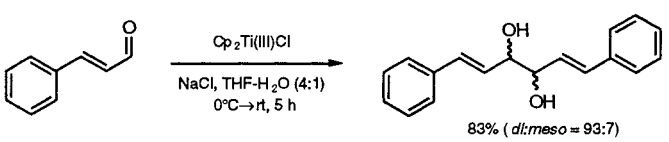
## Titanocene Chloride — *Reagent*

Reducing agent for the pinacol coupling of aromatic aldehydes.

M. C. Barden, J. Schwartz *J. Am. Chem. Soc.*, **1996**, *118*, 5484.




**A**




83% (*dl*:*meso* = 93:7)

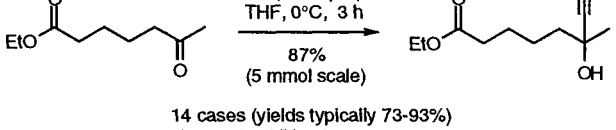
reaction must be run in the absence of oxygen
8 examples (aromatic aldehydes and methyl glyoxal); yields typically 75-95%

## Sodium Trimethylethynylaluminate — *Reagent*

Selective ethynylating agent which adds to aldehydes and ketones in the presence of halide, epoxide, ester, amide and nitrile groups.

M. J. Joung, J. H. Ahn, N. M. Yoon *J. Org. Chem.*, **1996**, *61*, 4472.


**A**

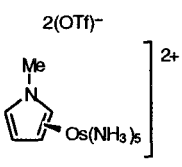



14 cases (yields typically 73-93%)
clean 1,2-addition to enones

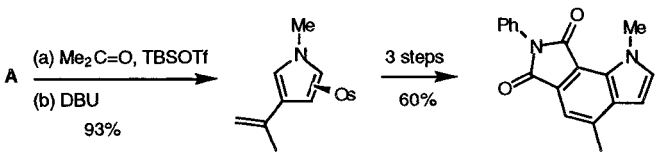
## {4,5-$\eta^2$-[Os(NH$_3$)$_5$]-1-Methylpyrrole}(OTf)$_2$ — *Reagent*

The pentaammineosmium(II) moiety dearomatises and activates the pyrrole ring toward electrophilic attack at the β-carbon and stabilises pyrrolium intermediates.

L. M. Hodges, M. L. Spera, M. W. Moody, W.D. Harman, *J. Am. Chem. Soc.*, **1996**, *118*, 7117. See also *J. Org. Chem.* **1995**, *60*, 2125.



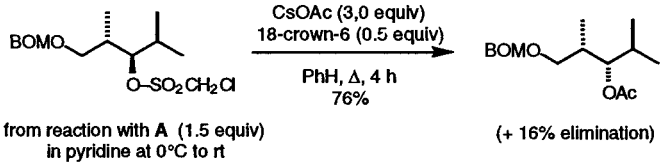

**A**




Good Diels–Alder substrate

## Chloromethylsulfonyl Chloride — *Reagent*

Cloromethylsulfonate esters of secondary alcohols react with CsOAc much faster than the corresponding mesylates and are more stable than the triflates.




$ClCH_2–SO_2Cl$

**A**

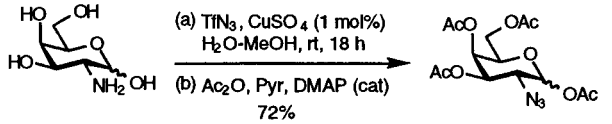
from reaction with **A** (1.5 equiv) in pyridine at 0°C to rt

(+ 16% elimination)

M-L. Lai, S.-C. Chi, C.-C. Hwu, M.-C. P. Yeh, *Tetrahedron Lett.*, **1996**, *37*, 6149.

## Trifluoromethanesulfonyl Azide — *Reagent*

$Cu^{2+}$, $Ni^{2+}$, or $Zn^{2+}$ ions catalyse the formation of azides from amines using triflyl azide (diazo transfer).



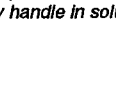

$CF_3SO_2–N_3$

*explosion hazard only handle in solution*

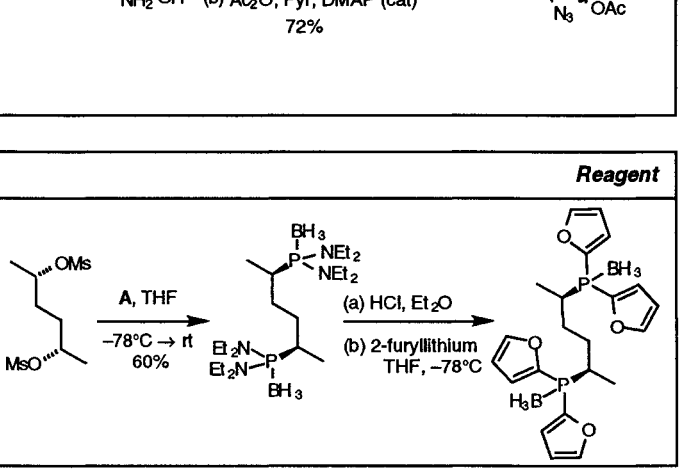
P. B. Alper, S.-C. Hung, C.-H. Wong *Tetrahedron Lett.*, **1996**, *37*, 6029.

## Lithiated Bis(diethylamino)phosphine Borane Complex — *Reagent*

The title reagent is useful for the synthesis of chiral phosphine ligands. It is prepared by reaction of bis(diethylamino)chlorophosphine borane complex with lithium naphthalenide.



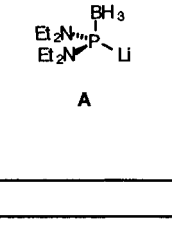

**A**




A. Longeau, P. Knochel *Tetrahedron Lett.*, **1996**, *37*, 6099.

## (a*R*)-1,1′-Binaphthalene-8,8′-diol — *Reagent*

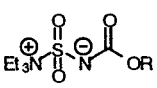
A homochiral derivatizing reagent for determining the absolute configuration of α-chiral carboxylic acids by $^1H$ and $^{13}C$ NMR spectroscopy.



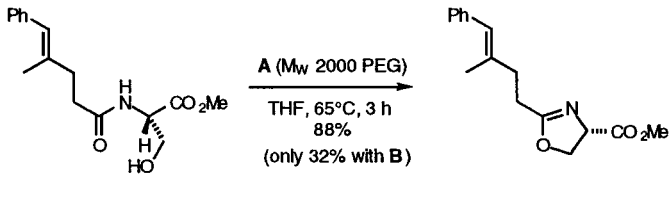

Y. Fukushi, K. Shigematsu, J. Mizutani, S. Tahara *Tetrahedron Lett.*, **1996**, *37*, 4737.

## *N*-(Triethylammoniumsulfonyl)carbamate Supported on Polyethyleneglycol (PEG) — *Reagent*

Polymer supported Burgess reagent for the synthesis of oxazolines and thiazolines by cyclodehydration of β-hydroxyamides and thioamides.




**A** R = PEG
**B** R = Me

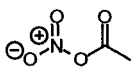



Reagent **A** shows increased and more reproducible yields over traditional Burgess reagent **B**. 7 Examples (yields 76-98%).

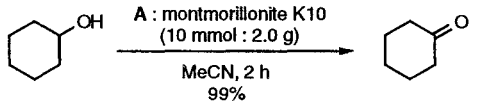
P. Wipf, S. Venkatraman *Tetrahedron Lett.*, **1996**, *37*, 4659.

## Acetyl Nitrate — *Reagent*

Acetyl nitrate when supported on montmorillonite or chrysatile oxidises 1° or 2° alcohols to corresponding carbonyl derivatives in good to excellent yields.



A

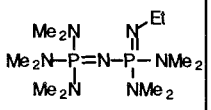



7 Examples listed. 1° Alcohols oxidise slower than 2° with no formation of carboxylic acids. Hydroquinones are oxidised efficiently under mild conditions to quinones.

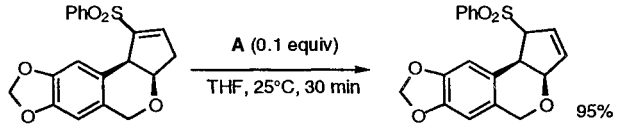
A. P. de Oliveira Filho, B. G. Moreira, P. J. S. Moran, J. A. R. Rodrigues *Tetrahedron Lett.*, **1996**, *37*, 5029.

## Phosphazene Base $P_2$-Et — *Reagent*

Allows for the isomerisation of vinyl- to allyl-sulfones, being superior to DBU or *t*-BuOK in this respect.



A

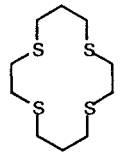



In above case DBU effected only 75% conversion over 48 h and *t*-BuOK gave none of the desired product. 7 Other examples (yields 92-99%) with degree of allyl/vinyl sulfone ratio being substrate dependent.

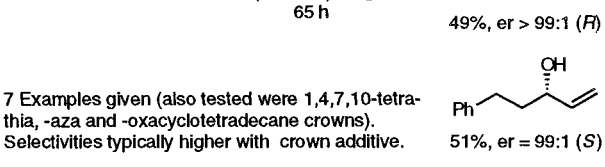
Z. Jin, S. H. Kim, P. L. Fuchs *Tetrahedron Lett.*, **1996**, *37*, 5247.

## 1,4,8,11-Tetrathiacyclotetradecane — *Reagent*

Thiacrown ethers enhance enantioselectivity and rate of lipase catalysed transesterification of allylic alcohols.



A




7 Examples given (also tested were 1,4,7,10-tetrathia, -aza and -oxacyclotetradecane crowns). Selectivities typically higher with crown additive.

Y. Takagu, J. Teramoto, H. Kihara, T. Itoh *Tetrahedron Lett.*, **1996**, *37*, 4991.