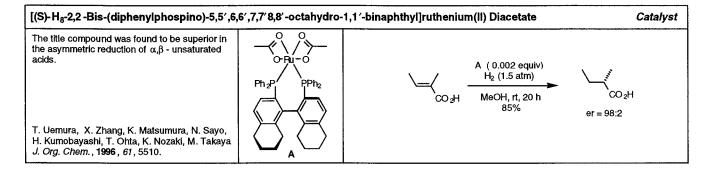
## SYNTHESIS ALERTS

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.

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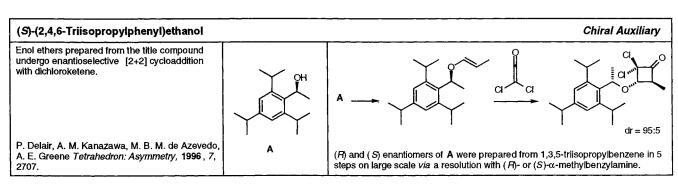


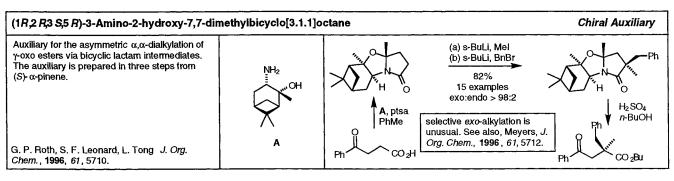
Aluminium Tris(4-bromo-2,6-diphenylpl	nenoxide)		Catalyst
The title compound is a powerful promoter of the Claisen rearangement of allyl vinyl ethers.  S. Saito, K. Shimada, H. Yamamoto <i>Synlett</i> , 1996, 720.	Ph O Al Ph 3	A, CH <sub>2</sub> Cl <sub>2</sub> -78°C, 13 h 62%	► O EZ = 200:1

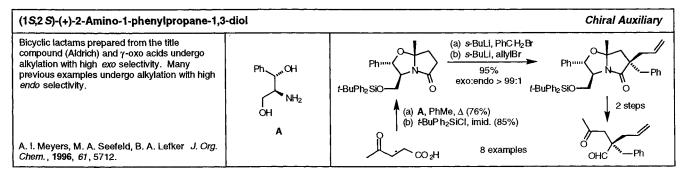
Methyltrioxorhenium		Catalyst
Catalyses the oxidation of secondary amines to nitrones with $\rm H_2O_2$ or urea- $\rm H_2O_2$ complex (UHP).	O II O PHO CH <sub>3</sub>	A (2 mol %) UHP (3 eq)  MeOH, rt, 24 h 65%  8 examples (yields 60-95%).
A. Goti, L. Nannelli <i>Tetrahedron Lett.</i> , <b>1996</b> , 37, 6025.		

### Cobalt(II) Bromide Catalyst Catalyses the direct acylation and allylation of diorganozine compounds. A (10 mol %) THE / NMP -10°C, 0.5 h CoBr<sub>2</sub> 84% (80% if FeCl<sub>3</sub> used) Α 6 Examples of acylation (yields 74-A (10 mol %) Pent<sub>2</sub>Zn, THF -10°C, 1 h 84%). 8 Examples of allylation (yields 84-90%) all S<sub>N</sub>2. Illustrated C. K. Reddy, P. Knochel Angew. Chem. Int. Ed. R = n-Pentyl reaction gives exclusively S<sub>N2</sub>' Engl., 1996, 35, 1700. 90%. > 98% E product with CuCN•2LiCl catalyst.

Bis{[(1 <i>R,</i> 2 <i>R,</i> 5 <i>R</i> )-2-methyl-5-methylethylcyclohexyl]methyl}boron Bromide			Catalyst
Chiral mediator for the asymmetric addition of thioester enolates to a silylimine. Used in the synthesis of taxol side-chain.  C. Gennari, A. Vulpetti, M. Donghi, N. Mongelli, E. Vanotti <i>Angew. Chem. Int. Ed. Engl.</i> , 1996, 35, 1723.	Br Br A	TBSO  (a) <b>A</b> , Et <sub>3</sub> N, CH <sub>2</sub> Cl <sub>2</sub> , Et <sub>2</sub> O, 0°C $\rightarrow$ rt, 5 h  (b) PhCH=NSiMe <sub>3</sub> $-78 \rightarrow -5$ °C  Followed by workup, nitrogen desilylation and acylation.  (a) <b>A</b> , Et <sub>3</sub> N, CH <sub>2</sub> Cl <sub>2</sub> , Ph NH O 71% overall anti : syn = 5 er (anti) > 5	SPh yield 97:3







### (1R,2R)-2-[(N-Dimethylphosphonyl-N-methyl)amino]-1-phenylpropane-1-thiol

Ligand

Enantioselective alkylation of benzaldehyde with diethylzinc using the title compound as ligand.

Peper, R. M. Kellogg Tetrahedron: Asymmetry, 1996, 7, 2755.

### Polymer-Bound Dihydroquinidine Ligand for Asymmetric Dihydroxylation

Ligand

Soluble polymer-bound ligand accelerated catalysis; application to asymmetric dihydroxylation.

OMe

Ligand A (0.25 eq) NMO (1.5 eq) OsO<sub>4</sub> (0.01 eq) MeCN-H<sub>2</sub>O (10:1) 89% (er = 94:6)

The ligand A is highly efficient owing to its solubility in this solvent system and it can be easily recovered after the reaction.

### (2S,3S)-1-Benzyl-3-(1-hydroxyethyl-1-methyl)-2-methyl)aziridine

Ligand

Aziridines derived from L-serine, L-threonine and L-allo-threonine may be used to control the stereoselectivity of dialkylzinc reagents to imines.

H. Han, K. D. Janda J. Am. Chem. Soc., 1996,

118,7632.

P. G. Andersson, D. Gujijarro, D. Tanner Synlett, 5 different ligands examined with the imine shown. 1996, 727.

## Homochiral Bis(phosphines) Derived from Carbohydrates

Ligand

Ligand

The conformationally locked ligands may be used in asymmetric Pd-catalysed nucleophilic allylic substitution. Note that a change in the substitution of the aromatic ring of the phosphinite affects the stereochemistry of the

reaction.

N. Nomura, Y. C. Mermet-Bouvier, T. V. RajanBabu Synlett, 1996, 745.

R = Cymene

$$\begin{array}{c} \text{Ph} & \begin{array}{c} \text{A ( 1 mol.\%)} \\ \text{NaCH(CO}_2\text{Et})_2 \end{array} & \begin{array}{c} \text{Ph} \\ \text{CH(CO}_2\text{Et})_2 \end{array} \end{array} \\ \hline \text{CH(CO}_2\text{Et})_2 \\ \text{THF, rt} \\ 100\% \end{array} & \begin{array}{c} \text{re} = 77:23 \end{array}$$

Using B as a ligand resulted in a complete reversal of stereochemistry.

### N,N '-Bis(diphenylphosphinyl)-N,N '-dimethyl-1,2-diaminoethane

Nickel(0) complexes derived from ligand A catalyse the alkylation of allylic acetates with dimethyl malonate.

7 examples; yields typically quantative. BTSA = N,O-bis(trimethylsilyl)acetamide

H. Bricout, J. Carpentier, A. Mortreux Tetrahedron Lett., 1996, 37, 6105.

Ligand

Ligand

Ligand

Reagent

Reagent

### (1S,2S)-2-Dimethylamino-1-phenylpropan-1-ol

The title compound, a derivative of (+)-pseudoephedrine, effects asymmetric epoxidation of  $\alpha,\beta$ -unsaturated ketones by oxygen in the presence of diethylzinc.

ation of  $\alpha$ , $\beta$ -unsaturated ketones by en in the presence of diethylzinc.

### **Dipeptide Imine Ligands**

Ed. Engl., 1996, 35, 1725.

Catalyst for the enantioselective Ti(IV)-catalysed addition of TMSCN to *meso*-epoxides. The peptide sequence and arene were optimised for particular substrates via a combinatorial approach.

D. Enders, J. Zhu, G. Raabe Angew. Chem. Int.

B. M. Cole, K. D. Shimizu, C. A. Krueger, J. P. A. Harrity, M. L. Snapper, A. H. Hoveyda *Angew. Chem. Int. Ed. Engl.*, **1996**, *35*, 1668.

Total of 6 examples (yields 48-65%, ee 46-86%). Catalytic activity highly substrate dependent. For other epoxides (3 examples) peptide sequence and arene portion **must** be reoptimised for high induction and yield.

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### (1,3-Dioxolan-2-yl)methylmagnesium Bromide

Grignard reagent A adds to otherwise unreactive carbohydrate ketones.

M. Schmeichel, H. Redlich Synthesis 1996, 1002.

### 1-Hydroxy-6,8-diphenyl-1,2,3,4-tetrahydro-2-oxa-1-boranaphthalene

Stereoselective reduction of  $\beta$ -hydroxy ketones to 1,3-diols with the aid of a terphenylboronic acid.

High yielding stereoselective preparation of 1,3-diols

H. Yamashita, K. Narasaka Bull. Chem. Soc.

Jpn., **1996** , *69*, 539.

# [M(p-Toluenesulfonyl)imino]phenyliodinane The title compound reacts with enol silanes to give α-tosylamino ketones. Ph—I = N—Ts A A has also been used for aziridination: D. A. Evans, M. M. Faul, M. T. Bilodeau J. Am. Chem. Soc. 1994, 116, 2742.

2-[(Trimethylsilyl)oxy]ethoxymethylene-1			Reagent	
The title compound undergoes asymmetric aldol reaction catalysed by an oxazaborolidinone derived from L-valine to give dithiolane-protected $\beta$ -hydroxy- $\alpha$ -oxo ester derivatives.	OEt	+ A	O TsN, B, O (1.1 eq) H CH <sub>2</sub> Cl <sub>2</sub> , -78°C, 3 h	OH O OEt 88% (er = 99:1)
S. Kiyooka, M. A. Hena <i>Tetrahedron: Asymmetry</i> ,		The soft nucleophile A give:	s good enantioselectivity	even at 10°C (7 examples).

(Trimethylsilyl)diazomethyllithium	***************************************	R	eagent
Ynolates derived from the reaction of the title compound with carbon monoxide serves as metallated (trimethylsilyl)ketene equivalents.	Me ₃Si Li A	$ \begin{bmatrix} A \\ CO (1 atm) \end{bmatrix} $ $ \begin{bmatrix} Me_3Si \longrightarrow OLi \end{bmatrix} $ $ (a) AlMe_3 (1.1 eq), -78 \rightarrow 0^{\circ}C $ $ (b) \bigcirc O -78 \rightarrow 0^{\circ}C $ $ 93\% $	iMe₃ ≕ O
H. Kai, K. Iwamoto, N. Chatani, S. Murai <i>J. Am. Chem. Soc.</i> , <b>1996</b> , <i>118</i> , 7634.		Aziridine opening and 1,4-Michael addition have also been studied	

Magnesium Bis(hexamethydisilazide)		Reagent
The title compound generates enolates from unsymmetrical ketones with about the same regioselectivity as LDA.	SMT, N Mg SMT 2	(a) A (2 eq), HMPA (3.5 eq) -75°C, 3 h  (b) TMSCI 75%  97:3
Bonafoux, D.; Bordeau, M.; Biran, C.; Cazaeu, P. <i>J. Org. Chem.</i> , <b>1996</b> , <i>61</i> , 5532.	A	The selectivity is independent of temperature, but is dependent upon the nature of the co-solvent.

# N-Aryl(trifluoroacetimidoyl)trimethylsilanes Reagent The title compounds may be used to incorporate the trifluoromethyl molety in molecules. The tetrabutylammonium cation affords greater thermodynamic stability of the carbanions. SiMe 3 F<sub>3</sub> CNAr A: Ar = 2,6-DiMe-C<sub>6</sub>H<sub>3</sub> B: Ar = 4-MeOC<sub>6</sub>H<sub>4</sub> C: Ar = 4-ClC <sub>6</sub>H<sub>4</sub> A new procedure for generation of the trimethylsilyl derivatives B and C is given.

Phenyliodine(III) Bis(trifluoroacetate) Reagen			Reagent	
The title reagent effects phenolic oxidative coupling.  Y. Kita, T. Takeshi, M. Gyoten, H. Tohma, M. Zenk, J. Eichborn <i>J. Org. Chem.</i> , 1996, <i>61</i> , 5857.	Phi(OCOCF <sub>3</sub> ) <sub>2</sub>	OH OMe OMe	<b>A</b> (1.1 eq) CF <sub>3</sub> CH <sub>2</sub> OH -40°C, 10 min. 70% F <sub>3</sub> CO	OMe

Dilauroyl Peroxide			Reagent
Xanthates can be reductively cleaved by heating in propan-2-ol in the presence of a stolchiometric amount of dilauroyl peroxide.  A. Liard, B. Quiclet-Sire, S. Z. Zard <i>Tetrahedron Lett.</i> , <b>1996</b> , <i>37</i> , 5877.	C <sub>11</sub> H <sub>23</sub> O O C <sub>11</sub> C <sub>11</sub> H <sub>23</sub>	CCOPh  A (1.3 eq)  Δ, 2-PrOH:CICH <sub>2</sub> CH <sub>2</sub> CI (1:1)  74%  Ets  11 examples; yields 50-95%. The S-undecyl xar byproduct is nonpolar and easily removed.	OCOPh O

Cyclopentenone-Derived Planar Chiral $\eta^2$	-Manganese Comple	x	Reagent
The title compound was used to control facial selectivity in the asymmetric aldol and alkylation reactions of the kinetic enolate of cyclopent-2-en-1-one.  D. Schinzer, H. Bärmann Angew. Chem. Int. Ed. Engl., 1996, 35, 1678.	oc-Mn	(a) CH <sub>2</sub> =CHC (b) Δ, MeCN, (c) Δ, MeCN, (a) (CH <sub>3</sub> ) <sub>2</sub> CHC (b) Δ, MeCN, (a) (CH <sub>3</sub> ) <sub>2</sub> CHC (b) Δ, MeCN, (b) Δ, MeCN, (c) Δ, MeCN, (d) Δ, MeCN, (e) Δ, MeCN, (f) Δ,	27% overall, er = 93 : 7

Cyanomethyl Pent-4-enoate		Reagent
Reagent for the resolution of amines via enzymatic acylation.  S. Takayama, W. J. Moree, C. Wong <i>Tetrahedron Lett.</i> , <b>1996</b> , <i>37</i> , 6287.	NC A	

