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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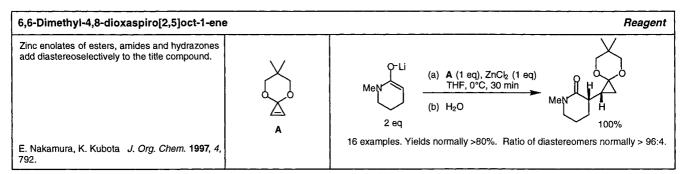
(Diethoxymethyl)diphenylphosphine Oxid	le	Re	eagent
Ketene acetals formed from Horner-Wittig reaction of the title compound with aldehydes undergo Sharpless asymmetric dihydroxylation to give homochiral α-hydroxy esters.	EtO Ph	7 other examples with aryl and alkyl substituted aldehydes are reported with moderate to good overall	98 : 2 -
A. Kirschning, G. Dräger, A. Jung Angew. Chem. Int. Ed. Engl. 1997, 36, 253.		yields (23 –94%) and good to excellent enantiomeric excess (er = 85 : 15 to > 99 : 1).	`CO₂Et

Diisopropylzinc			Reagent
Boron-zinc exchange using the title compound generates diastereomerically pure cycloalkylzinc compounds which react with carbon electrophiles in the presence of CuCN•2 LiCl.	<i>i</i> -Pr₂Zn	(a) CuCN•2 LiCl (2 eq) (2 eq) (b) Allyl bromide (2 eq), THF (2 eq) (2 eq), THF (46% overall expenses to the content of the co	Ph
L. Micouin, M. Oestreich, P. Knochel Angew. Chem. Int. Ed. Engl. 1997, 36, 245.		5 other examples with moderate overall yields (36–57%) and good diastereoselectivity (<i>trans</i> : <i>cis</i> = 90 : 10 to 98 : 2).	

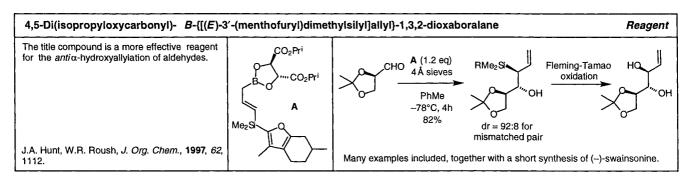
Magnesium tert-Butyl Peroxide		Reagent
Asymmetric epoxidation of chalcone derivatives with tert-butyl hydroperoxide in the presence of (+)-diethyl tartrate and Bu ₂ Mg proceeds with moderate yields and good stereoselectivity.	<i>t-</i> BuOOH, Bu₂Mg (+)-DEŤ	Ph t-BuOOH (1.5 eq) Bu ₂ Mg (0.1 eq) (+)-DET (0.11 eq) toluene/ THF, 1 day 46%, er = 96: 4
C. L. Elston, R. F. W. Jackson, S. J. F. MacDonald, P. J. Murray <i>Angew. Chem. Int. Ed.</i> <i>Engl.</i> 1997 , <i>36</i> , 410.		4 other examples, yields = 36–61%, er = 90.5 : 9.5 to 97 : 3.

Trifluoromethylzinc Bromide		Reagent
Pyranosyl fluorides are prepared by treatment of peracetylated pyranoses and pyranosyl bromides with the title reagent. R. Miethchen, C. Hager, M. Hein Synthesis 1997, 159.	CF ₃ ZnBr∙2LiCl A	AcO OH CF_3ZnBr/TiF_4 AcO Ac

Aminoiminomethanesulfinic Acid		Reagent
Deoxygenation of α,β-epoxy ketones may be achieved with the title reducing agent under phase transfer conditions. R. B. des Santos, T. J. Brockson, U. Brochson <i>Tetrahedron Lett.</i> 1997 , <i>38</i> , 745.	H ₂ N OH	A (1.3 eq) Bu ₄ NBr (cat), 6% NaOH (aq), THF, 1.5 h 6 examples; yields generally >85%



Tetrapropylammonium Perruthenate		Reagent
Transmutation of secondary nitro groups to ketones with the title reagent is facile under mild conditions. Y. Tokunaga, M. Ihara, K. Fukumoto, <i>J. Chem. Soc., Perkin Trans.</i> 1 1997, <i>3</i> , 185.	Pr ₄ NRuO ₄ A	A (0.1 eq), NMO (1.2 eq), K ₂ CO ₈ (5 eq), Ph 4Å sieves, CH ₂ Cb, rt 89% Only three substrates were examined but the reaction conditions were optimised for general use.



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Reagent

(Trifluoroacetyl)benzotriazole

Trifluoroacetylation of alcohols and amines is achieved simply by stirring the title reagent with substrate of choice in THF at room temperature. Heating may be necessary in some cases.

A. R. Katritzky, B. Yang, D. Semenzin *J. Org. Chem.* **1997**, 726.

M. Sudharshan, P. G. Hultin Synlett 1997, 171.

18 examples:- yields usually >80%.

Samarium		Reagent
Samarium metal and a catalytic amount of iodine in methanol reduce alkyl and aryl azides to amines. Under the same conditions aroyl and sulfonyl azides are transformed to the corresponding amides.	Sm	N ₃ $\frac{\text{Sm (1 eq), l}_2 (20 \text{ mol \%})}{\text{MeOH, rt} \rightarrow \Delta, 8 \text{ h}}$ NH ₂
Y. Huang, Y. Zhang, Y. Wang <i>Tetrahedron Lett.</i> 1997, 38, 1065.		15 examples (yields 70-93%). No over reduction of product amides was observed. Halide and carbonyl moieties are not reduced.

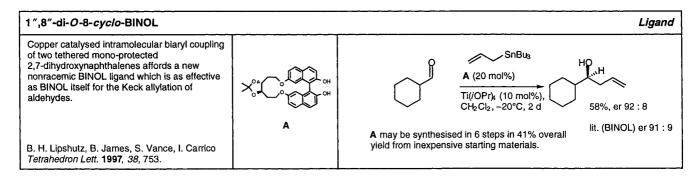
4-Nitrophenyltriflate			Reagent
The easily accessible arene A is an excellent reagent for the preparation of anyl triflates from the corresponding phenols. A is a crystalline, non-hygroscopic and highly stable solid.	O ₂ N OTf	OMe OH OH A (1 eq) K ₂ CO ₃ (2 eq) DMF, rt, 2 h CHO OMe OTf OTf OHO	
J. Zhu, A. Bigot, M. Elise, T. H. Dau <i>Tetrahedron Lett.</i> 1997, <i>38</i> , 1181.		5 useful examples (yields 75-92%).	

Triazidochlorosilane		Reagent
Treatment of primary amides with the title compound (abbreviated TACS) prepared in situ yields the corresponding 5-substituted 1 H-tetrazoles. A. S. El-Ahl, S. S. Elmorsy, A. H. Elbeheery, F. A. Amer Tetrahedron Lett. 1997, 38, 1257.	SiCl ₄ + NaN ₃ (3 eq)	SiCl ₄ (1 eq) NH ₂ NaN ₃ (3 eq) CH ₃ CN, Δ 2.5 h O ₂ N 76% 8 examples (yields 76-94%).

[Bis(η⁵-cyclopentadienyl)-bis(triethylphosphitidyl)]titanium(II) Reagent Reaction of the title compound with a thioacetal gives a low valent titanium reagent which reacts with carbonyls to give alkenes. Cp₂Ti[P(OEt)₃]₂ A Cp₂Ti[P(OEt)₃]₂ A From esters, these conditions lead to corresponding enol ethers (18 examples).

Samarium(II) Iodide				Reagent
Facile synthesis of chiral γ-butyrolactones by reaction of <i>N</i> -methylephedrinyl α,β-unsaturated esters with ketones mediated by samarium iodide. S. Fukuzawa, K. Seki, M. Tatsuzawa, K. Mutoh <i>J. Am. Chem. Soc.</i> 1997 , <i>119</i> , 1482.	Sml ₂	Ph NMe ₂ + Ph (20 examples)	A (2 eq), t-BuOH THF, −78 → 23°C 86%	Ph. 0 0 0 er = 95:5

N, N, N', N'-Tetraethyl-2,2 '-dihydroxy-1,	'-binaphthyl-3,3 '-die	carboxamide Ligano
The title compound is an efficient chiral ligand for the asymmetric Simmons-Smith cyclopropanation of allylic alcohols and for asymmetric addition of diethylzinc to aldehydes. H. Kitajima, K. Ito, Y. Aoki, T. Karsuki Bull. Chem Soc. Jpn. 1997, 70, 207.	OH OH CONE	TBDPSO OH $(a) \ E_{\mathbb{k}} Zn \ (6 \ eq),$ $Zn_{\mathbb{k}} \longrightarrow$ TBDPSO OH $(b) \ CH_2 Cl_2 \ (3 \ eq),$ $CH_2 Cl_2 \ 0^{\circ} C \rightarrow rt$ 59%, er 93.5:6.5 8 examples of cyclopropanation; yields 44-89%; er 82:18 to 97:3.



Ligand

Asymmetric cyclopropanation of allylic alcohols in the Simmons-Smith reaction using the title compound as a ligand.

$$\begin{array}{c} Zn(CH_2I)_2 \ (1 \ eq), \\ A \ (0.1 \ eq), \\ ZnI_2 \ (1 \ eq), \\ CH_2Cl_2 \ O^{\circ}C, \ 30 \ min. \\ 91\% \end{array} \begin{array}{c} Ph._{I_1} \\ Ph._{I_2} \\ Ph._{I_3} \\ Ph._{I_4} \\ Ph._{I_4} \\ Ph._{I_5} \\$$

S. Denmark, S.P. O'Connor J. Org. Chem. 1997, 3, 584.

(2R,2'R)-Bis(diphenylphosphino)-(1 R,1'R)-dicyclopentane

Highly enantioselective Rh-catalyzed hydrogenation with the title ligand.

[Rh(COD)₂]BF₄ (0.01 eq) СООН A (0.011 eq), NEts (0.5 eq) THF, rt, 24 h

Ligand A has been prepared in three steps from 1,1'-dicyclopentene (7 examples).

er = 96.3/3.7

Chiral auxiliary

Catalyst

Catalyst

G. Zhu, P. Cao, Q. Jiang, X. Zhang J. Am. Chem. Soc. 1997, 119, 1799.

(1R,3R)-1,3-Diphenylpropane-1,3-diol

The bisethers prepared from the title compound and 1-bromo-2-naphthol (Mitsunobu reaction) undergo highly diastereoselective homocoupling of the corresponding organolithium derivatives.

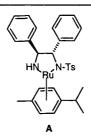
T. Sugimura, H. Yamada, S. Inoue, A. Tai Tetrahedron: Asymmetry 1997, 8, 649.

(1S,2S)-N-p-Toluenesulfonyl-1,2-diphenylethylenediamino Ruthenium

The title Ru(II) hydrogen transfer catalyst is

employed for the kinetic resolution of racemic secondary alcohols.

S. Hashiguchi, A. Fujii, K.-J. Haack, K. Matsumura, T. Ikariya, R. Noyori Angew. Chem Int. Ed. Engl. 1997, 36, 288.



A (0.2 mol%) acetone Me₂N 28°C, 30 h

p-Cymene Complex

В Recovery of B = 44% C er = 98.5 : 1.5

Resolution of 11 α-unsaturated alcohols is reported with similar yields and er. Preparation of the catalyst: Angew. Chem. Int. Ed. Engl. 1997, 36, 285.

(1R,2R,4S,6S)-2-(2-Anisyl)bicyclo[2.2.2]octane-2,5-diol (BODOL)

Ti complexes of the title diol catalyse the enantioselective reduction of ketones with catecholborane with good to excellent

enantioselectivity (er up to 98.5: 1.5).

Α

A (10 mol%)

er (6 examples).

4Å molecular sieves t-BuOMe-10% hexane

catecholborane (2 eq)

> 97%

er = 98.5 : 1.5 -50°C, 4.5 h

6 other examples reported with yields between 48 and >98%, er = 70:30 to 99: 1. The 2-phenyl analogue of A is also employed with similar yields and

Ytterbium (II) Aromatic Imine Dianion Co	mplex	Catalyst
The title compound catalyses the isomerisation of terminal alkynes to internal ones. Y. Makioka, A. Saiki, K. Takaki, Y. Taniguchi, T. Kitamura, Y. Fujiwara Chem. Lett. 1997, 27.	Ph Yb(hmpa) _n Ph Ph	8 examples; yields 39-89% These Yb-imine complexes do not afford 1,2 and/or 2,4-diene byproducts typical of base catalysed isomerizations (e.g. with sodium alkoxides).

Tetracyanoethylene		Catalyst
The title compound is the first π-acid catalyst for the esterification of a variety of acids. Y. Masaki, N. Tanaka, T. Miura <i>Chem. Lett.</i> , 1997, 55.	NC CN	C ₁₁ H ₂₃ OH A (20 mol%) Me ₃ S OH C ₁₁ H ₂₃ SiMe ₃ r.t., 24 h 93% This study includes 12 alcohols and 13 carboxylic acids. Transesterification using A may also be accomplished but 60°C is required.

Scandium Triflate Catal					
The title triflate was found to be the most efficient catalyst, from a series of group 3 and 4 metal triflates, for the Fries rearrangement of phenyl or 1-naphthyl acylates and for direct acylation of phenois and 1-naphthols with acid chlorides. cf A. G. M. Barrett and D. C. Braddock, Chem. Commun. 1997, 351, for the esterification of alcohols using the title reagent as catalyst. S. Kobayashi, M. Moriwaki, I. Hachiya Bull. Chem. Soc. Jpn. 1997, 70, 267.	Sc(OTf) ₃	c-C ₆	A (5 mol%) LiClO₄-Mel PhMe, 50°0 mol%) 1₁1COCl (1.1 eq) O₄-MeNO₂, e, 50°C, 6 h	NO ₂ ,	78% Yields from the acylation protocol are superior to the Fries rearrangement.

Nickel (II) Acetoacetonate		Catalyst
A catalyses the smooth tellurium-zinc exchange of diaryltellurides (or diarylditellurides) to the corresponding arylzinc derivatives. T. Stüdemann, V. Gupta, L. Engman, P. Knochel Tetrahedron Lett.1997, 38, 1005.	Ni(acac) ₂ A	(a) CuCN•2LiCl (b) CH ₂ =CHCH ₂ Br (a) CuCN•2LiCl (b) CH ₂ =CHCH ₂ Br (a) CuCN•2LiCl (b) CH ₂ =CHCH ₂ Br (c) CuCN•2LiCl (d) CuCN•2LiCl (e) CuCN•2LiCl (f) CH ₂ =CHCH ₂ Br (f) CuCN•2LiCl (h) CH ₂ =CHCH ₂ Br (h) CuCN•2LiCl (h) CH ₂ =CHCH ₂ Br (h) CuCN•2LiCl (h) CuCN•2LiCl

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