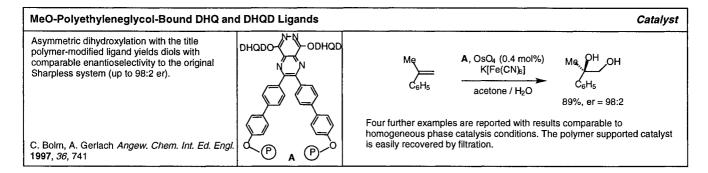
SYNTHESIS ALERTS

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 Glasgow. 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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Ruthenium Hydride and Dihydride Phosphine Complexes		Catalyst
The title complexes act as very active catalysts for transfer hydrogenation of ketones and imines by propan-2-ol. E. Mizushima, M. Yamaguchi, T. Yamagishi Chem. Lett. 1997, 237.	RuHCi(PPh ₃) ₃ A RuH ₂ (PPh ₃) ₄ B	A (0.1 mol%) KOH (20 mol%) 2-naphth Me propan-2-ol, 1 h, 85°C 83% B (0.5 mol%) KOH (20 mol%) NHBn Me propan-2-ol, 18 h, 85°C Ph Me B (0.5 mol%) KOH (20 mol%) NHBn We propan-2-ol, 18 h, 85°C Ph Me Me Me Me Me NHBn Me Me Me Me Me Me Me Me Me M

$(1S,5R,8S)$ -8-Hydroxy-8- $(\beta$ -naphthylmethyl)-2- $(4$ -pyridyl)-2-azabicyclo[3.3.0]octane		Catalyst			
Nonenzymatic kinetic resolution of racemic alcohols through an induced fit process. T. Kawabata, M. Nagato, K. Takasu, K. Fuji J. Am. Chem. Soc. 1997, 119, 3169.	HH		r (i-BuCO) ₂ O (1.4 eq) A (5 mol%) 2,4,6-collidine (1 eq) PhMe, rt, 5h of ring size (4 examples) a ples) has been studied.	OCO/Pr + OCO/Bu 69% and the nature of the	OCO'Pr OH 27%, er = 88:12 e ester functional

Palladium catalyzed intermolecular carbon oxygen bond formation: a new synthesis of aryl ethers. Pd₂(dba)₃ A A (1.5 mol%) Tol-BINAP (3.6 mol%) NaH (2.0 eq) PhMe, 50°C 65% A comparison between catalysed and uncatalysed etherification reactions was carried out (12 examples).

Methylrhenium Trioxide (MTO)		Catalyst
Aqueous catalysis: methyl rhenium trioxide as a homogeneous catalyst for the Diels-Alder reaction.	Me FIRO A	A (1 mol%) H ₂ O, rt, 18 h 90% isomer ratio > 99:1
Z. Zu, J. H. Espenson J. Am. Chem. Soc. 1997, 119, 3507.		The eta -substituted dienophiles are less reactive under these conditions (32 examples).

Bis(triphenylphosphine)palladium Dichloride		Catalyst
Catalyses the cross-coupling reaction of unsaturated vinyl chlorides with Grignard reagents. P. Ramiandrasoa, B. Bréhon, A. Thivet, M. Alami, G. Cahiez <i>Tetrahedron Lett.</i> 1997 , <i>38</i> , 2447.	PdCl₂(PPh₃)₂ A	C ₅ 11 C ₁ C ₁ A (5 mol%) Eta N (8 eq) THF, rt, 20 min 55% 16 examples (yields 42-95%). All products were isomerically pure.

Magnesium Triflimide		Catalyst
A useful alternative to magnesium perchlorate for the catalysis of nucleophilic substitution reactions of allylic and benzylic acetates.	Mg(NTE) ₂	OMe (2 eq) OTBS A (10 mol%) CH ₂ Cb, rt, 1 h 99% 10 examples (yields 48, 76-99%). In the majority of cases catalyst A is
P. A. Grieco, S. T. Handy <i>Tetrahedron Lett.</i> 1997 , <i>38</i> , 2645.		superior to Mg(CIO ₄) ₂ .

Catalyst

Tetra-n-propylammonium Perruthenate (TPAP)

Treatment of alkyl boranes with a catalytic quantity of TPAP (A) in the presence of *N*-methylmorpholine *N*-oxide (NMO) results in their oxidation to carbonyl compounds. A hydroboration / oxidation sequence provides a one-pot synthesis of carbonyl compounds from olefins.

(a) BH₃*SMe₂ (0.33 eq) Et₂O, rt, 3 h (b) 4Å MS, NMO (3 eq) A (5 mol%), CH₂Cl₂ rt. 1 h.70%

9 examples (yields 50-98%). A slightly modified procedure allows for the oxidation of an olefin in the presence of a ketone.

M. H. Yates Tetrahedron Lett. 1997, 38, 2813.

Chiral Diiron Acyl Complex Chiral Auxiliary Synthesis of and asymmetric cycloaddition with chiral diiron acyl complexes. Boc Boc! Acryloyl (a) CH₂C½, rt chloride THF (b) Ce(IV) HNEts+ 42%, er = 20:1 6 examples S. R. Gilbertson, O. D. Lopez J. Am. Chem. Soc. 1997, 119, 3399. A

(2S)-(N-Benzoylpyrrolidin-2-yl)diphenylcarbinol Ligand The title compound is a ligand for the asymmetric Nozaki-Hiyama coupling of organochromium (a) n-BuLi, THF, 0°C reagents with aldehydes. (b) CrCb (4 eq), -30°C, 1 h (8 eq) (c) C₃H₅Br (2 eq) p-CIC₆H₄CHO (1 eq) ОН 5 examples employing ligand **A** (yields 43-84%, %ee 49-98%). K. Sugimoto, S. Aoyagi, C. Kibayashi J. Org. THF, -30°C, 12 h Chem. 1997, 62, 2322. 47%, er = 99:1

2,2'-Bis[(4S)-4-isopropyl-1,3-oxazolin-2-yl]biphenyl Ligand The title ligand forms one diastereoisomer when complexed with Cu(I). The resultant complex (1.3eq)catalyses the asymmetric cyclopropanation of .CO₂Et styrene. Cu(I)OTf(PhH)_{0.5} ĊO₂Eŧ A (1.1 mol%) CH2Cl2, rt, 24 h 19%, er = 80:20 53%, er = 75:25 4 examples of the cyclopropanation of styrene, including the use of Y. Imai, W. Zhang, T. Kida, Y. Nakatsuji, I. Ikeda menthyl diazoacetate (yields 60-72%, trans:cis ≥ 68:32, %ee 49-92%). Tetrahedron Lett. 1997, 38, 2681.

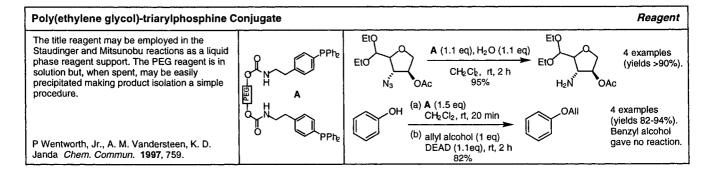
(1,1')-Bi(dibenzofuranyl)-2,2 '-diol (BIFOL) Ligand Resolution of the C2-symmetric title compound via recrystallisation of a 1:1 mixture of diastereomeric cyclic phosphoramidates gave POCI₃ H₂Ń both enantiomers in good yield and with >98% enantiopurity. 89% fractional recrystallisation (+)-(R)-A, 65% overall from EtOH A. E. Sollewijn Gelpke, J. Fraanje, K. Goubitz, H. LiAlH₄ (-)-(S)-A, 56% overall Schenk, H. Hiemstra Terahedron 1997, 53, 5899 (±)- A

N-Substituted-2,5-bis[(tri isopropylsilyl)oxy]pyrrole (BISOP) **Protecting Group** (a) Os Primary amines are diprotected as their BISOP 0ء "Hex derivatives A. (1.1 eq) (a) t-BuLi, Et₂O OTIPS PhH, Δ, 2 h -40°C (b) AcCl, A, 1h (c) TIPSOTf (2.2 eq) Et₃N (3.2 eq) CH₂Cl₂, rt, 2 h 83% 7 examples of protection (yields 68-87%). (b) n-HexCHO 87% NBISOP (a) dil. HCl_(aq) (2 eq) THF, rt (b) NH₂NH₂•H₂O EtOH, Δ, 72% OTIPS R = BISOP S. F. Martin, C. Limberakis Tetrahedron Lett. Α 1997, 38, 2617.

Eth-1-ynyl-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane		Reagent
The title reagent is a novel and easy to handle propiolate anion equivalent; a concise preparation is presented.		$= \underbrace{\begin{array}{c} \text{(a) BuLi, THF} \\ -10^{\circ}\text{C, 1 h} \\ \text{(b)} \\ \text{36\%} \end{array}}_{\text{H}_{3}\text{C}} \underbrace{\begin{array}{c} \text{OH} \\ \text{H}_{3}\text{C} \\ \text{OH} \\ \text{OH}$
P. Ducray, H. Lamotte, B. Rosseau <i>Synthesis</i> 1997, 404.	A	7 examples of the addition of metallated A to various electrophiles (yields 61-95%). The bridged ortho ester is easily cleaved to yield the corresponding acid.

Triallylmanganylmagnesium Chloride		Reagent
The title reagent was used for the allylation and diallylation of acetylenic compounds in moderate to good yields. J.Tang, K. Okada, H. Shinokubo, K. Oshima Tetrahedron 1997, 53, 5061.	(CH₂=CHCH₂)₃MnMgCl A	HQ n -C ₆ H ₁₃ a) A, THF-HMPA $+$ $+$ $+$ $+$ $+$ $+$ $+$ $+$ $+$ $+$

Poly-(L)-Leucine		Reagent
Urea-hydrogen peroxide complex in an organic solvent in the presence of DBU and the title polymer causes rapid asymmetric epoxidation of enones.	Poly-(Ł)-Leucine	Ph Ph Urea-H ₂ O ₂ (1.2 eq) Ph
P. A. Bentley, S. Bergeron, M. W. Cappi, D. E. Hibbs, M. B. Hursthouse, T. C. Nugent, R. Pulido, S. M. Roberts, L. E. Wu <i>Chem. Commun.</i> 1997, 739.		4 examples (yields 0, 67-87%, er > 20:1). The product epoxides may be alkylated (at C=O) with RLi + Cel ₃ .



Chem. Commun. 1997, 763.

Diethyl isopropylthioborane Reagent With this borane, efficient catalytic asymmetric prop-2-ynylation of achiral aldehydes with **A** (1.2 eq) (S)-BINOL-Ti(O'Pr)₄, (10 mol%) allenyltributylstannane promoted by a BINOL-Ti(IV) complex is achieved with high er. Et₂BS/Pr CH₂=C=CHSnBu₃ (1.2 eq) CH2Cl2, --20°C, 9 h 75%, er = 96:4 7 examples (yields 52-86%, %ee 88-95%). The reaction may also be performed with (S)-BINOL-Zr(OPr)₄. C.-M. Yu, S.-K. Yoon, H.-S. Choi, K. Baek

Novel stereoselective synthesis of 2-amino saccharides

Novel stereoselective synthesis of 2-amino saccharides

(a) A (1 eq), (CF₃CO)₂O OH OPMB

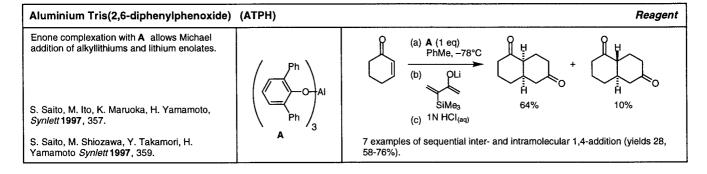
(b) silica gel or H₀O+ OPMB

75%,
$$\alpha\beta = 1:7$$

The formation of labile aziridine intermediate occured either on the α or β face depending on the substitution pattern of glycals (9 examples).

Phthalimidesulfenyl Chloride	1,090	Reagent
Sulfenimide derivatives generated by reaction of the title compound with phenols react with pyridine to generate o-thioquinones which undergo cycloaddition with electron-rich alkenes and alkynes to give 1,4-benzooxathiins.	NSCI	MeQ OH A (excess) MeQ OH pyridine (2 eq) CHCl ₃ , rt SNPhth CHCl ₆ , 60°C, 50 h (2 eq) 58%
G. Capozzi, C. Falciani, S. Menichetti, C. Nativi <i>J. Org. Chem.</i> 1997 , <i>62</i> , 2611.		12 examples (yields 44-89%).

Quinolinium fluorochromate (QFC)		Reagent
The title compound selectively desilylates 1° TBS ethers with concomitant oxidation of the liberated alcohol to aldehydes in the presence of secondaryTBS ethers.	[FCrO₃] [⊙]	OTBDMS C_4H_9 OTBDMS $OTBDMS$
S. Chandrasekhar, P. K. Mohanty, M. Takhi, J. Org. Chem. 1997, 62, 2628.		



Reagent

B-Chlorodi iso pinocampheylborane (DIP-Chloride™)

An $in \ situ$ preparation of DIP-ChlorideTM (A) is described.

NaBH₄ (0.25 eq)

BCb₆ (0.26 eq), DME
-10°C \rightarrow 40°C, 2.5 h

A

M. Zhao, A. O. King, R. D. Larsen, T. R. Verhoeven, P. J. Reider *Tetrahedron Lett.* **1997**, *38*, 2641.

Reduction of an oxo ester with this material gave the corresponding hydroxy ester quantitatively with %ee 94-97%.

DME = 1,2-Dimethoxyethane

Dimethylaluminium Chloride / N-Methoxy- N-methylamine Hydrochloride

Reagent

Bu OH

ŌMOM

ОМе

N-Methoxy-N-methyl amides (Weinreb amides) can be efficiently prepared from lactones and esters by treatment with the title reagent pair.

Me₂AlCl

A

MeONHMe•HCl

R

MOMO Bu A (5 eq), B (5 eq)

TBDPSO CH₂Cl₂, rt, 1.5 h

TBDPSO TBDPSO

T. Shimizu, K. Osako, T. Nakata *Tetrahedron* Lett. **1997**, *38*, 2685.

11 examples (yields 21, 84-99%). In each case the analogous reaction employing Me $_3$ Al in the place of **A**, requires extended reaction time and is lower yielding.

Lithium t-Butyl- N-tosyloxycarbamate (LiBTOC)

Reagent

The title reagent provides a competent (+)NHBoc synthon. Chiral *cis*-aminoindanol derived amide cyanocuprates are electrophilically aminated by **A** in a highly diastereoselective manner.

A NOTE

Bn (a) BuLi (1.1 eq) THF, -78°C (b) CuCN (1.1 eq) NHR (1.1 eq) (C) -78°C, 30 min (77%, dr > 99:1

 7 examples of amination (yields 51-77%, %de 96, >99%).

N. Zheng, J. D. Armstrong III, J. C. McWilliams, R. P. Volante *Tetrahedron Lett.* **1997**, *38*, 2817.

(2R)-N-[(R)-p-Tolylsulfinyl]bornane-10,2-sultam

Reagent

The use of camphor sultam **A** as a chiral sulfinyl transfer reagent is described.

95%, er = 98:2

(a) LiHMDS THF, -78° C (b) H_2O (1 eq) p-Td $\stackrel{\bigcirc}{S}$ $\stackrel{\bigcirc}{N}$ (c) i-PrCHO (1.1 eq) -20° C \rightarrow 5°C 65%, er > 199:1

W. Oppolzer, O. Froelich, C. Wiaux-Zamar, G.
Bernardinelli *Tetrahedron Lett.* 1997, *38*, 2825.

A 13 examples of preparation of sulfoxides (yields 79-97%, %ee 96->99%) and 6 examples of the preparation of sulfinimines (yields 65-84%, %ee 98, >99.5%). In all cases Oppolzer's bornane-10,2-sultam was recoverable in high yield (>85%) and with excellent optical purity.

η ²-Propenetitaniumdi *iso*propoxide

Reagent

Treatment of cyclic allylic bromides and carbonates with **A** yields the corresponding allylic titanium complexes. These undergo diastereoselective addition to aldehydes and imines.

Ti(O/Pr)₄ /PrMgCl (2 eq)

S. Hikichi, Y. Gao, F. Sato *Tetrahedron Lett.* 1997, 38, 2867.

10 examples, including one example of addition to an imine (yields 3, 26-98%, syn:anti > 80:20). Low yields and stereoselectivities are observed for 6 and 7 membered rings.