

Synthesis Alerts is a 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:

Stephen Brand, John Christopher, Emma Guthrie, Philip Kocienski, Louise Lea, Russell McDonald, Graeme McAllister and Robert Narquizian of Glasgow University.

Georg Thieme Verlag does not accept responsibility for the accuracy, content, or selection of the data.

Article Identifier:

1437-210X,E,1999,0,09,1703,1706,ftx,en:X00999SS.pdf

The journals regularly covered by the abstractors are:

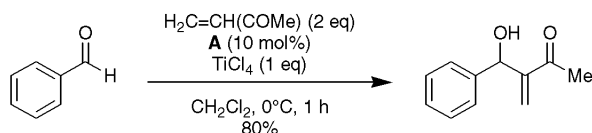
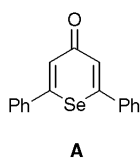
Angewandte Chemie International Edition
 Bulletin of the Chemical Society of Japan
 Chemical Communications
 Chemistry A European Journal
 Chemistry Letters
 European Journal of Organic Chemistry
 Helvetica Chimica Acta
 Heterocycles
 Journal of the American Chemical Society
 Journal of Organic Chemistry
 Organometallics
 Perkin Transactions 1
 Synlett
 Synthesis
 Tetrahedron
 Tetrahedron Asymmetry and Tetrahedron Letters

(S,S)-Ethylenebistetrahydroindenyldimethylzirconium		Catalyst
Enantioselective hydrogenation of tetrasubstituted double bonds using A is reported.		<p>89% <i>cis</i> : <i>trans</i> = 98:2 <i>er</i> = 98:2</p>
M. V. Troutman, D. H. Apella, S. L. Buchwald <i>J. Am. Chem. Soc.</i> 1999 , <i>121</i> , 4916.	A	8 examples (yields 34-94%, 90:10 ≤ <i>cis</i> : <i>trans</i> ≤ 99:1, % <i>ee</i> = 52-92%).
Trimethylsilyl chloride		Catalyst
The title catalyst promotes the TiCl ₄ /Bu ₃ N-mediated cross aldol additions of sterically crowded ketones and α-hetero substituted ketones, and also the Claisen condensation between methyl esters.		<p>80%</p>
Y. Yoshida, N. Matsumoto, R. Hamasaki, Y. Tanabe <i>Tetrahedron Lett.</i> 1999 , <i>40</i> , 4227.	A	18 examples of aldol additions (yields 42-98%) and 5 examples of Claisen condensation (yields 54-95%) are reported.
Cinchonidine-derived Chiral Quaternary Ammonium Salt		Catalyst
The title reagent catalyses the enantioselective synthesis of β-hydroxy-α-amino acid esters by aldol coupling of aldehydes and a glycinate.		<p>6 examples (yields 48-81%, 1:1 ≤ <i>syn</i> : <i>anti</i> ≤ 13:1, %<i>ee</i>_{syn} = 72-95%) are reported.</p> <p>70%; <i>syn</i>:<i>anti</i> = 6:1 <i>er</i>_{syn} = 98:2</p>
M. Horikawa, J. Busch-Petersen, E. J. Corey <i>Tetrahedron Lett.</i> 1999 , <i>40</i> , 3843.	A	

2,6-Diphenyl-4H-selenopyran-4-one

Catalyst

A is reported as an effective catalyst for the Baylis-Hillman reaction.



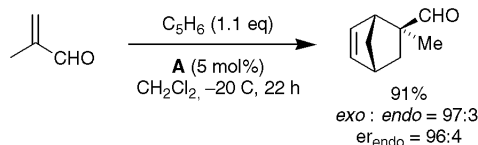
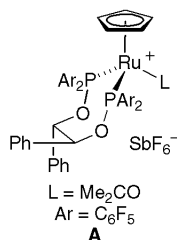
T. Iwama, H. Kinoshita, T. Kataoka *Tetrahedron Lett.* **1999**, *40*, 3741.

21 examples (yields 43-100%) using **A** are reported. Use of a thiopyranthione analogue of **A** produces similar results.

Chiral Ru Lewis Acid

Catalyst

The readily prepared title compound mediates the asymmetric Diels-Alder reaction between enals and dienes. The high stability of **A** makes recycling possible.



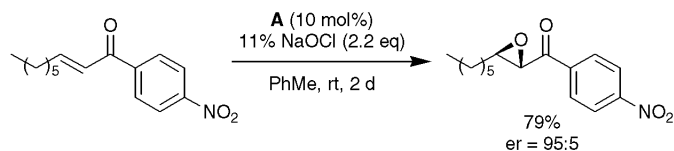
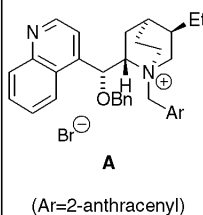
E. P. Kündig, C. M. Saudan, G. Bernardinelli *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 1220.

4 examples (yields 29-93%, 10:90 ≤ exo : endo ≤ 93:7, %ee = 91-96%) are reported.

Cinchona Alkaloid-derived Phase-Transfer Catalyst

Catalyst

A is used in the phase-transfer catalysed asymmetric epoxidation of α,β -unsaturated ketones.



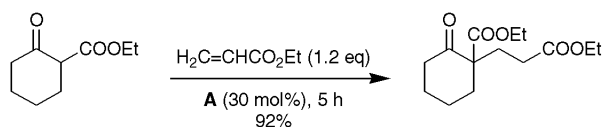
B. Lygo, P. G. Wainwright *Tetrahedron* **1999**, *55*, 6289.

19 examples (yields 40, 77-99%, %ee = 71-90%).

Trifluoromethanesulfonic Acid

Catalyst

The title compound catalyses the Michael addition reaction of β -ketoesters under solvent-free conditions.



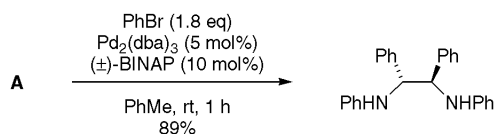
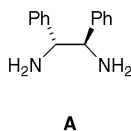
H. Kotsuki, K. Arimura, T. Ohishi, R. Maruzasa *J. Org. Chem.* **1999**, *64*, 3770.

14 examples (yields 0, 51-99%).

(S,S)-1,2-Diphenyl-1,2-diaminoethane

Chiral Auxiliary

The title reagent is used to prepare *N,N*-diaryl-1,2-diphenyl-1,2-diaminoethanes via palladium catalysed aromatic amino coupling.

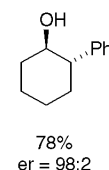
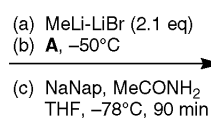
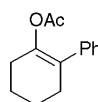
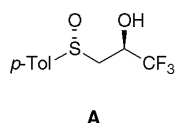


I. Cabanal-Duvillard, P. Mangeney *Tetrahedron Lett.* **1999**, *40*, 3877.

7 examples (yields 0, 33-97%) are reported.

(R)-1-[(R)-p-Toluenesulfinyl]-3,3,3-trifluoropropan-2-ol**Chiral Auxiliary**

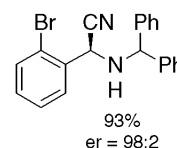
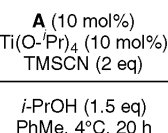
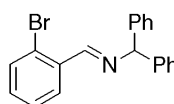
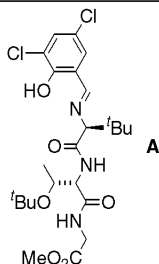
An efficient synthesis of *trans*-2-phenylcyclohexanol utilising in a key step the enantioselective protonation of an enolate is reported.



G. Asensio, A. Cuenca, M. Medio-Simón, P. Gaviña *Tetrahedron Lett.* **1999**, *40*, 3939.

Tripeptide Schiff Base**Ligand**

The titanium-catalysed enantioselective addition of cyanide to imines is reported. The resulting amino nitrile products can be readily converted to the corresponding amino acids.

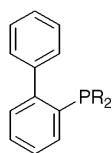


C. A. Krueger, K. W. Kuntz, C. D. Dzierba, W. G. Wirschun, J. D. Gleason, M. L. Snapper, A. H. Hoveyda *J. Am. Chem. Soc.* **1999**, *121*, 4284.

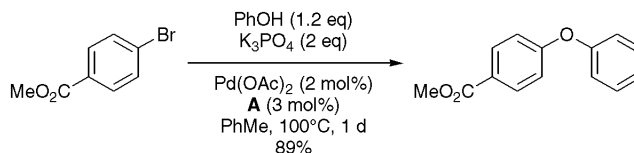
7 examples using **A** or closely related analogues (yields 82-99%, %ee = 90-97%) are reported.

2-[Di-(1-adamantyl)phosphino]biphenyl**Ligand**

The Pd-catalysed formation of diaryl ethers using the bulky, electron-rich phosphine ligand **A** or the related di-*tert*-butyl ligand is reported.



R = 1-adamantyl

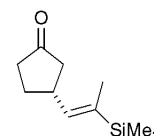
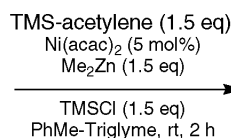
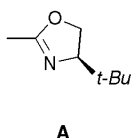


25 examples (yields 61-95%).

A. Aranyos, D. W. Old, A. Kiyomori, J. P. Wolfe, J. P. Sadighi, S. L. Buchwald *J. Am. Chem. Soc.* **1999**, *121*, 4369.

(S)-4-tert-Butyl-2-methyloxazoline**Ligand**

Ligand **A** is used in the nickel-catalysed asymmetric coupling of enones and metallated alkynes in the presence of TMSCl.

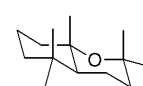
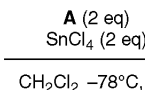
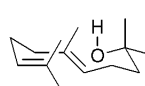
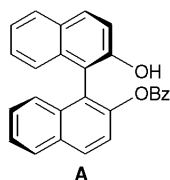


4 examples (yields 5-75%, %ee = 38-81%).

S.-i. Ikeda, D.-M. Cui, Y. Sato *J. Am. Chem. Soc.* **1999**, *121*, 4712.

(R)-2,2'-Binaphtholmonobenzoate**Ligand**

SnCl₄ and **A** promote the enantioselective cyclization of polypropenoids.

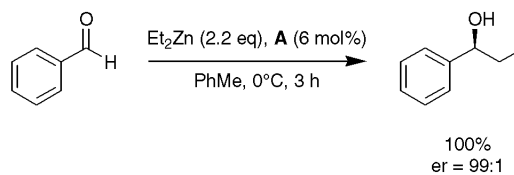
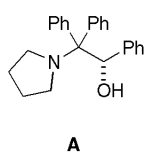


K. Ishihara, S. Nakamura, H. Yamamoto *J. Am. Chem. Soc.* **1999**, *121*, 4906.

12 examples (yields 54-98%, %de = 12-90%, %ee = 36-54%).

(S)-1,2,2-Triphenyl-2-(1-pyrrolidinyl)ethanol**Ligand**

A mediates the highly enantioselective addition of diethylzinc to aldehydes.

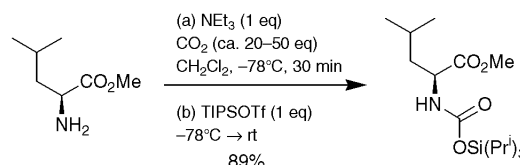
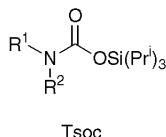


K. S. Reddy, L. Solà, A. Moyano, M. A. Pericàs, A. Riera *J. Org. Chem.* **1999**, *64*, 3969.

22 examples (yields 85-100%, %ee = 90-98%).

Triisopropylsilyloxycarbonyl (Tsoc)**Protecting Group**

The Tsoc group is stable towards conditions used to deprotect Boc, Cbz and Fmoc groups. It is easily cleaved by TBAF in THF at 0°C in 10 min. It can be removed selectively in the presence of secondary TBS ethers.

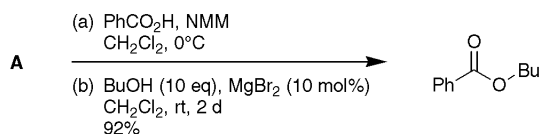
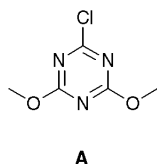


B. H. Lipshutz, P. Papa and J. M. Keith *J. Org. Chem.* **1999**, *64*, 3792.

10 examples; yields 56-94%. *tert*-Butyldiphenylsilyloxycarbamates can be prepared in a similar fashion (1 example).

2-Chloro-4,6-dimethoxy-1,3,5-triazine (CDMT)**Reagent**

Triazines obtained from **A** and a carboxylic acid are employed as acylating reagents for ester synthesis from primary, secondary and tertiary alcohols.

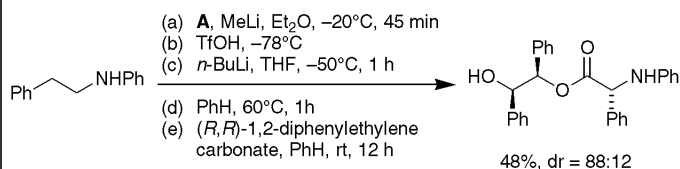


J. E. Kaminski, Z. J. Kaminski, J. Góra *Synthesis* **1999**, 593.

14 examples (yields 24-92%).

Dicyclopentadienylzirconium Dichloride**Reagent**

The asymmetric synthesis of α -amino acid esters is reported *via* the dynamic kinetic resolution of racemic zirconaziridines utilising a cyclic carbonate with C₂-symmetry as an optically active CO₂ synthon.

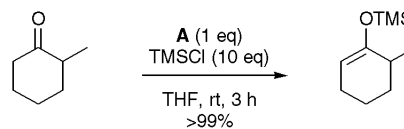
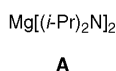


J. A. Tunge, D. A. Gateley, J. N. Norton *J. Am. Chem. Soc.* **1999**, *121*, 4520

4 examples (yields 48-77%, %de \geq 72%).

Magnesium bis(diisopropylamide)**Reagent**

A (prepared *in situ* from diisopropylamine and dibutylmagnesium) is reported as a reagent for the synthesis of less highly substituted silyl enol ethers at ambient temperature. In addition, high *E*-enolisation selectivity is observed for benzylic ketones, the reverse of the selectivity observed with LDA.



G. Lessène, R. Tripoli, P. Cazeau, C. Biran, M. Bordeau *Tetrahedron Lett.* **1999**, *40*, 4037.

6 examples (yields 80-99%, selectivity for the kinetic product \geq 95:5) and 2 examples using benzylic ketones (yields > 99%, 80:20 \leq *E*:*Z* \leq 91:9).