

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:

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The journals regularly covered by the abstractors are:

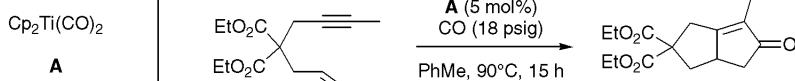
Angewandte Chemie International Edition
Bulletin of the Chemical Society of Japan
Chemical Communications
Chemistry A European Journal
Chemistry Letters
Collection Czechoslovak Chemical Communications
European Journal of Organic Chemistry
Helvetica Chimica Acta
Heterocycles
Journal of the American Chemical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

Article Identifier:
1437-210X,E;1999,0,11,1993,1998,ftx,en;X01199SS.pdf

Dicyclopentadienyldicarbonyltitanium(II)

Catalyst

A catalyses the Pauson-Khand type conversion of 1,6-, 1,7- and 1,8-enynes to bicyclic cyclopentenones.



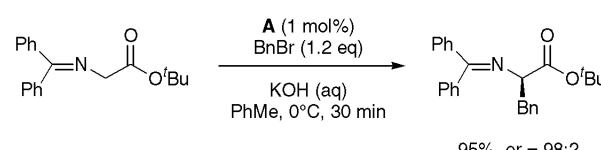
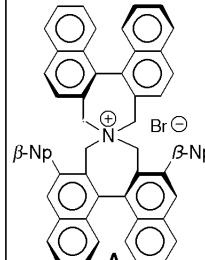
34 examples (yields 57-95%).

F. A. Hicks, N. M. Kablaoui, S. L. Buchwald *J. Am. Chem. Soc.* **1999**, *121*, 5881.

C₂-Symmetrical phase-transfer catalyst

Catalyst

A mediates the enantioselective phase transfer alkylation of a prochiral protected glycine derivative.



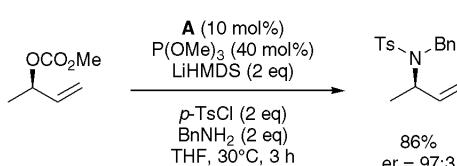
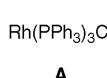
T. Ooi, M. Kameda, K. Maruoka *J. Am. Chem. Soc.* **1999**, *121*, 6519.

9 examples (yields 41-95%, %ee = 90-96%).

Tris(triphenylphosphine)rhodium(I) chloride

Catalyst

The enantiospecific amination of monosubstituted allylic carbonates is reported.

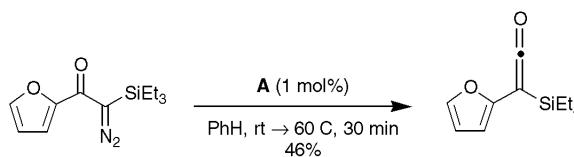
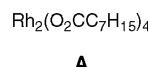


P. A. Evans, J. E. Robinson, J. D. Nelson *J. Am. Chem. Soc.* **1999**, *121*, 6761.

9 examples (yields 84-91%, %ee = 84-94%).

Rhodium(II) Octanoate**Catalyst**

The title compound catalyses the formation of silylketenes via Wolff rearrangement of silyl diazo ketones.

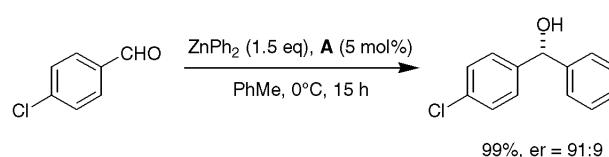
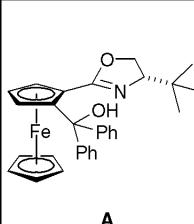


S. P. Marsden, W.-K. Pang *Chem. Commun.* 1999, 1199.

11 examples (yields 12-80%).

Planar Chiral Ferrocene-Based Oxazoline**Catalyst**

A catalyses the asymmetric addition of diphenylzinc to aldehydes.

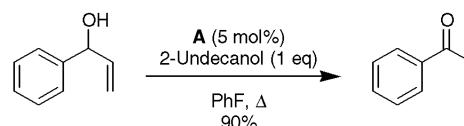


C. Bolm, K. Muñiz *Chem. Commun.* 1999, 1295.

8 examples (yields 91-99%, %ee = 3, 28-96%).

Tetrapropylammonium Perruthenate (TPAP)**Catalyst**

The title compound catalyses the isomerisation of allylic alcohols to the corresponding saturated carbonyl derivatives.

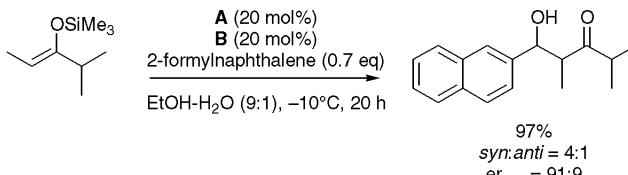
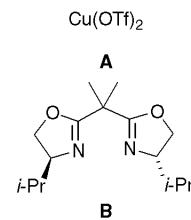


I. E. Markó, A. Gautier, M. Tsukazaki, A. Llobet, E. Plantalech-Mir, C. J. Urch, S. M. Brown *Angew. Chem. Int. Ed.* 1999, 1960.

8 examples (yields 41-92%).

Copper(II) Trifluoromethanesulfonate / (S,S)-bis(oxazoline)**Catalyst**

A and **B** are utilised in the catalytic asymmetric Mukaiyama aldol reaction in aqueous media.

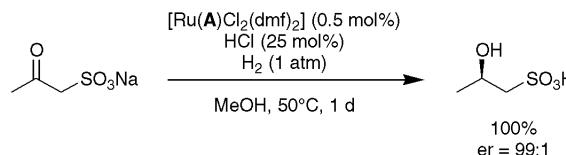
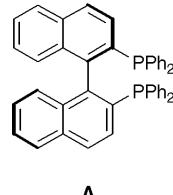


S. Kobayashi, S. Nagayama, T. Busujima *Tetrahedron* 1999, 55, 8739.

20 examples (yields 17, 32-98%, %ee = 32-81%, 1.6:1 ≤ syn:anti ≤ 5.7:1).

(R)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl [(R)-BINAP]**Catalyst**

A ruthenium(II) complex formed from the title ligand catalyzes the enantioselective hydrogenation of sodium β -ketosulfonates.

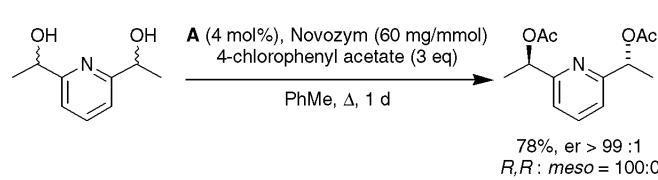
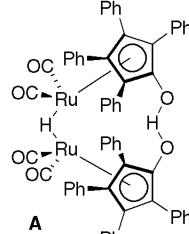


M. Kitamura, M. Yoshimura, N. Kanda, R. Noyori *Tetrahedron* 1999, 55, 8769.

7 examples (yields 66, 99-100%, %ee = 47, 95-97%).

Catalyst**Ruthenium-based Isomerisation Catalyst**

Enzymatic acylation of secondary symmetrical diols in combination with Ru-catalyzed diol isomerization leads to efficient dynamic kinetic resolution. The title catalyst is readily prepared from $\text{Ru}_3(\text{CO})_{12}$ and tetraphenylcyclopentadienone.

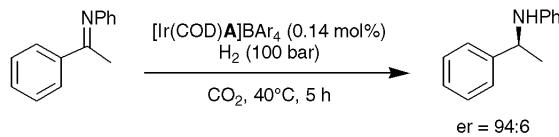
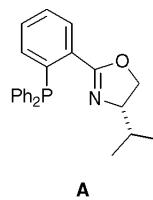


B. A. Persson, F. F. Huerta, J.-E. Bäckvall *J. Org. Chem.* **1999**, *64*, 5237.

10 examples (yields 43–90%, %ee > 96%, 38:62 ≤ R,R : meso ≤ 100:0).

Ligand**(4*S*)-4-Isopropyl-3-[(2-diphenylphosphino)phenyl]oxazoline**

An Iridium(I) catalyst prepared from the title ligand mediates the enantioselective hydrogenation of imines in supercritical carbon dioxide.

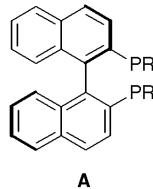


S. Kainz, A. Brinkmann, W. Leitner, A. Pfaltz *J. Am. Chem. Soc.* **1999**, *121*, 6421.

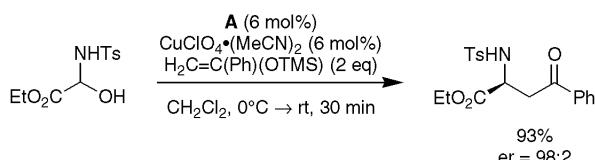
2 examples (%ee = 72, 87%) using a variety of catalytic systems are described.

Ligand**(*R*)-2,2'-Bis(ditolylphosphino)-1,1'-binaphthyl ((*R*)-Tol BINAP)**

The title ligand is utilised in the Cu(I) catalysed asymmetric alkylation of *N*,*O*- and *N,N*-acetals and hemiacetals.



A
R = 4-MeC6H4

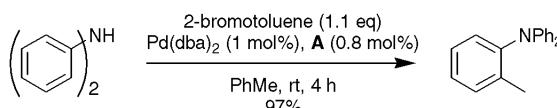


D. Ferraris, B. Young, T. Dudding, W. J. Drury III, T. Lectka *Tetrahedron* **1999**, *55*, 8869.

17 examples (yields 73–93%, %ee = 42–95%).

Ligand**Tri-*tert*-butylphosphine**

Palladium(0) catalyzed amination of aryl bromides and chlorides using A is reported.

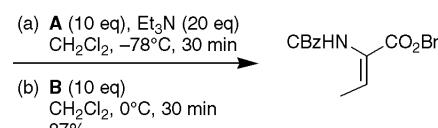
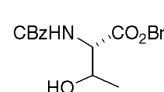
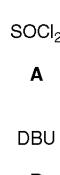


J. F. Hartwig, M. Kawatsura, S. I. Hauck, K. H. Shaughnessy, L. M. Alcazar-Roman *J. Org. Chem.* **1999**, *64*, 5575.

27 examples (yields 59–99%).

Reagent**Thionylchloride / 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)**

The stereoselective preparation of α,β -dehydrated amino acids from β -hydroxyamino acids by elimination of an *in-situ* formed sulfamidite ester is reported.

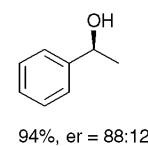
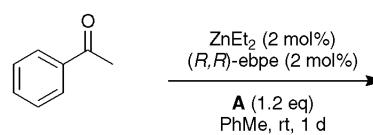
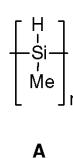


M. M. Stohlmeyer, H. Tanaka, T. J. Wandless *J. Am. Chem. Soc.* **1999**, *121*, 6100.

16 examples (yields 55–95%) are described.

Polymethylhydrosiloxane**Reagent**

A in combination with C₂-symmetrical *N,N'*-ethylenebis(1-phenylethylamine) (ebpe) reduces stereoselectively a variety of acetophenones.

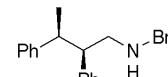
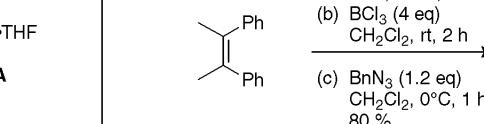


H. Mimoun, J. Y. de Saint Laumer, L. Giannini, R. Scopelliti, C. Floriani *J. Am. Chem. Soc.* **1999**, *121*, 6158.

10 examples (yields 94-100%, %ee = 18-80%).

Borane-Tetrahydrofuran Complex**Reagent**

A highly stereoselective rearrangement of acyclic tertiary organoboranes obtained by hydroboration of tetrasubstituted olefins is reported.

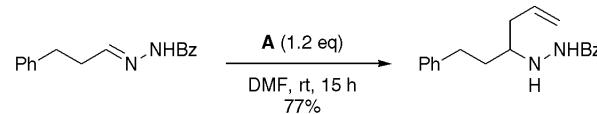
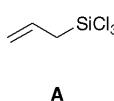


H. Laaziri, L. O. Bromm, F. Lhermitte, R. M. Gschwind, P. Knochel *J. Am. Chem. Soc.* **1999**, *121*, 6940.

10 examples (yields 51-92%).

Allyltrichlorosilane**Reagent**

Homoallylic hydrazines are formed by the addition of **A** to benzoylhydrazones. In a similar fashion, *syn*- and *anti*-adducts are stereoselectively obtained from (*E*)- and (*Z*)-crotyltrichlorosilanes respectively.

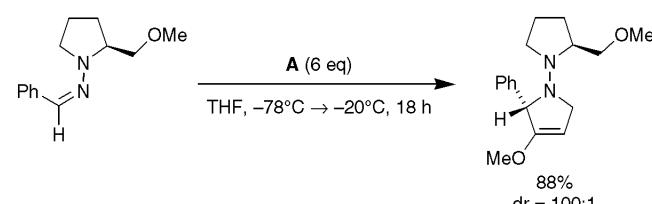
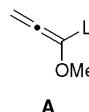


S. Kobayashi, R. Hirabayashi *J. Am. Chem. Soc.* **1999**, *121*, 6942.

19 examples using **A**, (*E*)- and (*Z*)-crotyltrichlorosilanes (yields 48-96%).

1-Methoxy-1-allenyllithium**Reagent**

The title reagent is used in reactions with SAMP-hydrazones to afford α -allenyl hydrazines and/or methoxy-3-pyrrolines, depending on the nature of the solvent.

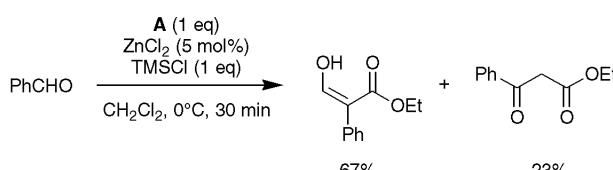
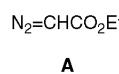


V. Breuil-Desvergne, P. Compain, J.-M. Vatèle, J. Goré *Tetrahedron Lett.* **1999**, *40*, 5009.

12 examples (yields 0, 8-88%, %de = 93-99%) are reported.

Ethyl Diazoacetate**Reagent**

The title reagent reacts with aldehydes in the presence of a Lewis acid catalyst to afford the corresponding β -keto or α -formyl esters, depending upon the nature of the catalyst employed.



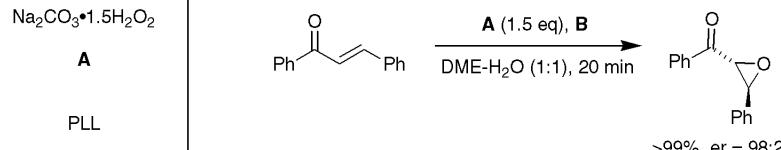
S. Kanemasa, T. Kanai, T. Araki, E. Wada *Tetrahedron Lett.* **1999**, *40*, 5055.

18 examples (yields 0, 14-90%) are reported.

3,3-Pentamethylenediaziridine	Reagent
The title reagent effects <i>cis</i> -selective aziridination of <i>cis</i> - or <i>trans</i> - α,β -unsaturated amides.	<p style="text-align: center;">A</p>
K. Hori, H. Sugihara, Y. N. Ito, T. Katsuki <i>Tetrahedron Lett.</i> 1999 , <i>40</i> , 5207.	5 examples (yields 39-82%) are reported.
Bis(acetoacetonato)nickel(II)	Reagent
The title reagent is used in the synthesis of biaryls using a nickel-catalysed [2+2] cocompilation.	<p style="text-align: center;">A</p>
Y. Sato, K. Ohashi, M. Mori <i>Tetrahedron Lett.</i> 1999 , <i>40</i> , 5231.	6 examples (yields 53-94%) are reported.
Trichloroacetonitrile / Triphenylphosphine	Reagent
The title reagent pair converts carboxylic acids into acid chlorides. The acid chlorides were subsequently reacted with various amines to afford the corresponding amides.	<p style="text-align: center;">A</p> <p style="text-align: center;">B</p>
D. O. Jang, D. J. Park, J. Kim <i>Tetrahedron Lett.</i> 1999 , <i>40</i> , 5323.	16 examples (yields 70-99%) are reported.
Titanocene Complex	Reagent
The title reagent is used in the titanocene(II)-promoted desulfurative tertiary alkylation of 1,3-bis(phenylthio)alk-1-enes and β,γ -unsaturated thioacetals.	<p style="text-align: center;">A</p>
T. Takeda, N. Nozaki, N. Saeki, T. Fujiwara <i>Tetrahedron Lett.</i> 1999 , <i>40</i> , 5353.	16 examples (yields 57-85%) are reported.
Bis(dimethyl)alumininoxane	Reagent
A (generated <i>in situ</i> from Me_3Al and H_2O) is used for the alkylation of epoxides <i>via</i> double activation of the substrate.	<p style="text-align: center;">A</p>
N. Abe, H. Hanawa, K. Maruoka, M. Sasaki, M. Miyashita <i>Tetrahedron Lett.</i> 1999 , <i>40</i> , 5369.	5 examples (yields 71-94%) are reported.

Sodium percarbonate / Poly-L-leucine (PLL)**Reagent**

The title reagent pair is used for the catalytic asymmetric epoxidation of enones.

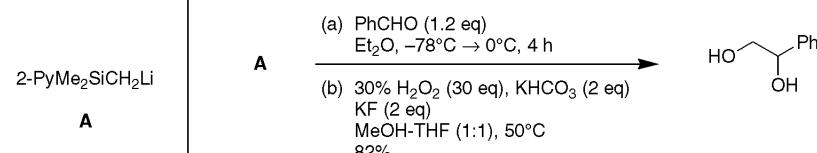


J. V. Allen, K.-H. Drauz, R. W. Flood, S. M. Roberts, J. Skidmore *Tetrahedron Lett.* **1999**, *40*, 5417.

3 examples (yields 94->99%, %ee = 87-96%) are reported.

(2-Pyridyldimethylsilyl)methylolithium**Reagent**

The title reagent reacts with an electrophile followed by oxidation to give the corresponding alcohol.

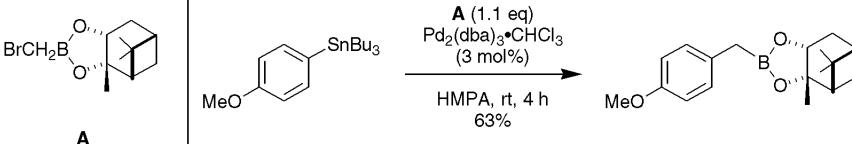


K. Itami, K. Mitsudo, J. Yoshida *Tetrahedron Lett.* **1999**, *40*, 5537.

10 examples (yields 55-99%) are reported.

Pinanediol bromomethylboronate**Reagent**

Pd-catalysed cross-coupling of **A** with aryl- and alkynylstannanes yields the corresponding homologated benzylic or allylic boronates.

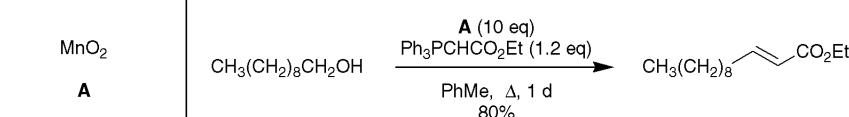


J. R. Falck, M. Bondela, J. Ye, S.-D. Cho *Tetrahedron Lett.* **1999**, *40*, 5647.

12 examples (yields 0, 60-86%) are reported.

Manganese Dioxide**Reagent**

In-situ alcohol oxidation-Wittig reaction using **A** is applied to semi-activated and unactivated alcohols to furnish α,β -unsaturated esters.

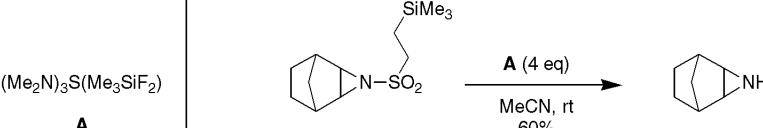


L. Blackburn, X. Wei, R. J. K. Taylor *Chem. Commun.* **1999**, 1337.

12 examples (yields 0, 51-86%).

Tris(dimethylamino)sulfonium Difluorotrimethylsilicate (TASF)**Reagent**

A mediates the deprotection of *N*-[2-(trimethylsilyl)ethanesulfonyl]aziridines (*N*-Ses-aziridines) under mild conditions.



P. Dauban, R. H. Dodd *J. Org. Chem.* **1999**, *64*, 5304.

5 examples (yields 60-95%).