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:

Robert Chow, John Christopher, Emma Guthrie, Philip Kocienski, Alexander Kuhl, Catherine McCusker, Robert Narquizian, and Sukhjinder Uppal of Glasgow University.

Article Identifier:
1437-210X,E;2000,0,04,0603,0608,ftx,en;X00400SS.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
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

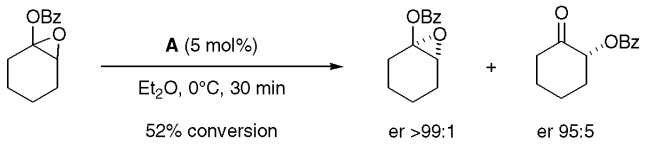
Di-(*R*)-binaphthol/Tetraisopropoxytitanium(IV) ***Catalyst***

Kinetic resolution of racemic enol ester epoxides into chiral α-acyloxy ketones is achieved by a mixture of 2 equivalents of BINOL and titanium isopropoxide.

X. Feng, L. Shu, Y. Shi *J. Am. Chem. Soc.* **1999**, *121*, 11002.

$[(R)\text{-BINOL}]_2Ti(O^iPr)_4$

A

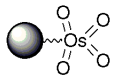


16 examples (conversions 49-69%, %ee = 22-99%).

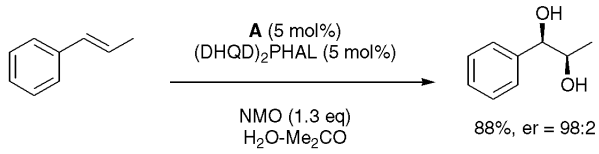
Polymer-Supported Osmium Catalyst ***Catalyst***

The asymmetric dihydroxylation of olefins by OsO_4 encapsulated in an acrylonitrile-butadiene-polystyrene polymer is reported.

S. Kobayashi, M. Endo, S. Nagayama *J. Am. Chem. Soc.* **1999**, *121*, 11229.



A



13 examples (yields 36-98%, %ee = 60-98%).

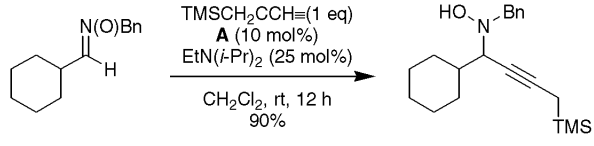
Zinc Trifluoromethanesulfonate ***Catalyst***

A mediates the addition of terminal alkynes to nitrones, aldehydes, ketones and *N*-tosyl aldimines.

D. E. Frantz, R. Fässler, E. M. Carreira *J. Am. Chem. Soc.* **1999**, *121*, 11245.

$Zn(OTf)_2$

A



16 examples (yields 43-99%).

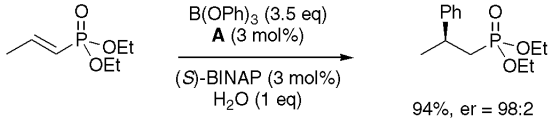
Diethylene(acetoacetonato)rhodium(I) — *Catalyst*

A, in combination with chiral ligands, catalyses the asymmetric 1,4-addition of phenylboronic acids to 1-alkenylphosphonates.

T. Hayashi, T. Senda, Y. Takaya, M. Ogasawara *J. Am. Chem. Soc.* **1999**, *121*, 11591.

$[Rh(acac)(\eta^2\text{-}C_2H_4)_2]$

A

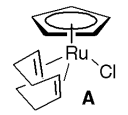


18 examples (yields 5-98%, %ee = 84-99%).

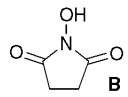
Cyclopentadienyl(1,4-cyclooctadiene)ruthenium(I) Chloride / *N*-Hydroxysuccinimide — *Catalyst*

The title reagent pair catalyse the cycloisomerisation-oxidation of homopropargyl alcohols.

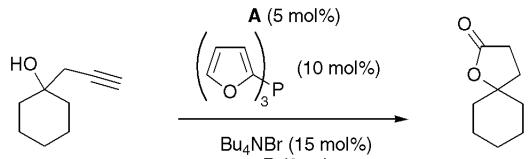
B. M. Trost, Y. H. Rhee *J. Am. Chem. Soc.* **1999**, *121*, 11680.



A



B

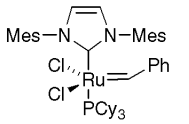


11 examples (yields 48-76%).

1,3-Dimesityl-4,5-dihydroimidazol-2-ylidene ruthenium benzylidene — *Catalyst*

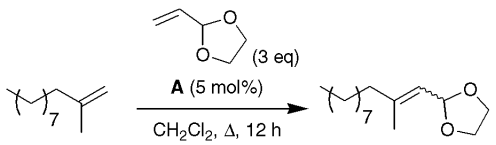
The title reagent is used in the preparation of trisubstituted alkenes *via* intermolecular olefin cross-metathesis.

A. K. Chatterjee, R. H. Grubbs *Org. Lett.* **1999**, *1*, 1751.



Mes = C_6H_2-2,4,6-Me_3

A



6 examples (yields 53-87%, 2.3:1 ≤ *E*:*Z* ≤ 4:1) are reported.

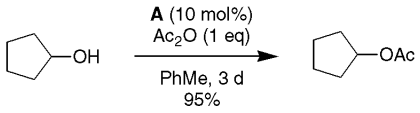
Sodium Tetracarbonylcobaltate — *Catalyst*

The title reagent catalyses the acylation of alcohols with acetic anhydride. The first example of a catalysed Staudinger reaction using a similar reagent is also reported.

H. Wack, W. J. Drury III, A. E. Taggi, D. Ferraris, T. Lectka *Org. Lett.* **1999**, *1*, 1985.

$NaCo(CO)_4$

A



4 examples (yields 95-100%) are reported.

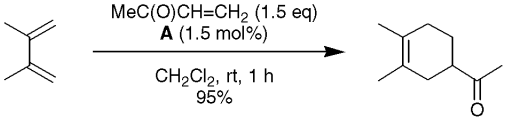
Scandium Tris(perfluorobutanesulfonyl)methide Complex — *Catalyst*

The title reagent is shown to be an efficient Lewis acid catalyst for Friedel-Crafts acylation and Diels-Alder reactions.

J. Nishikido, F. Yamamoto, H. Nakajima, Y. Mikami, Y. Matsumoto, K. Mikami *Synlett* **1999**, 1990.

$Sc[C(SO_2C_4F_9)_3]_3$

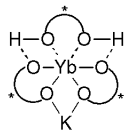
A



1 example of a Friedel–Crafts acylation (yield 93%) and 1 example of a Diels–Alder reaction (yield 95%) are reported.

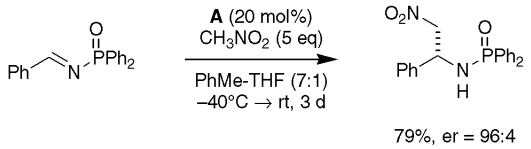
(*R*)-Binaphthol / Yb(O*i*-Pr)$_3$ / KO*t*-Bu — *Catalyst*

A, generated from the title reagents catalyses an asymmetric nitro-Mannich-type reaction to give nitroamine products.



* 1,1-binaphthyl skeleton

A



79%, er = 96:4

5 examples (yields 41-93%, %ee = 69-91%).

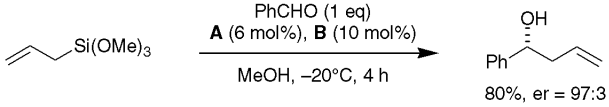
K.-i. Yamada, S. J. Harwood, H. Gröger, M. Shibasaki *Angew. Chem. Int. Ed.* **1999**, *38*, 3504.

p-2,2′-Bis(di-*p*-tolylphosphanyl)-1,1′-binaphthyl - Silver(I) Fluoride Complex — *Catalyst*

The title compound catalyses the asymmetric addition of allylic trimethoxysilanes to aldehydes generating the corresponding homoallylic alcohols.

(*R*)-*p*-Tol-BINAP•AgF

A



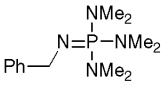
80%, er = 97:3

6 examples (yields 67-93%, %ee = 78-94%) and 3 similar examples using γ-substituted allyltrimethoxysilanes (yields 77-99, %ee = 60-62%, 92:8 ≤ *anti*:*syn* ≤ 94:6).

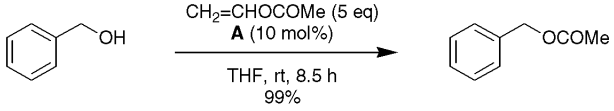
A. Yanagisawa, H. Kageyama, Y. Nakatsuka, K. Asakawa, Y. Matsumoto, H. Yamamoto *Angew. Chem. Int. Ed.* **1999**, *38*, 3701.

Benzylimino[tris(dimethylamino)]phosphorane — *Catalyst*

The title reagent catalyses the acylation of primary alcohols with enol esters in excellent yield and high selectivity.



A

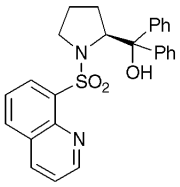


13 examples, including the selective protection of primary hydroxyls in the presence of secondary hydroxyls (yields 74-99%).

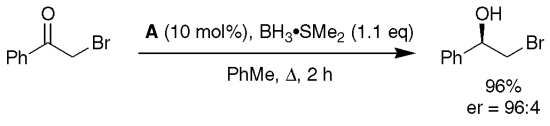
P. Ilankumaran, J. G. Verkade *J. Org. Chem.* **1999**, *64*, 9063.

Diphenyl-(S)-[*N*-8-quinolinesulfonyl]-2-pyrrolidin-2-yl)methanol — *Catalyst*

The title compound catalyses the enantioselective borane reduction of aromatic ketones.



A



96%
er = 96:4

6 examples (yields 89-99%, %ee = 65-91%).

G.-S. Yang, J.-B. Hu, G. Zhao, Y. Ding, M.-H. Tang *Tetrahedron: Asymmetry* **1999**, *10*, 4307.

Palladium Diacetate / Tri-*tert*-butylphosphine — *Catalyst*

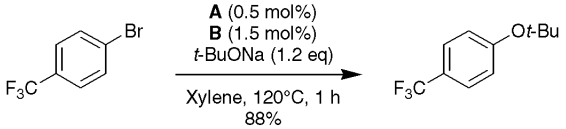
The title reagent pair catalyses the reaction of aryl halides with sodium *t*-butoxide to give aryl *t*-butyl ethers.

$Pd(OAc)_2$

A

$P(t\text{-}Bu)_3$

B

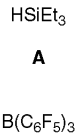


12 examples (yields 20-94%).

M. Watanabe, M. Nishiyama, Y. Koie *Tetrahedron Lett.* **1999**, *40*, 8837.

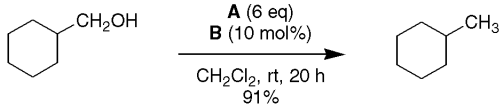
Triethylsilane / Tri(pentafluorophenyl)borane — *Catalyst*

A novel reduction of alcohols and alkyl ethers using the title reagent pair is reported.



A

B

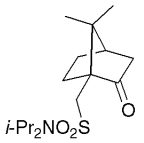


V. Gevorgyan, J.-X. Liu, M. Rubin, S. Benson, Y. Yamamoto *Tetrahedron Lett.* **1999**, *40*, 8919.

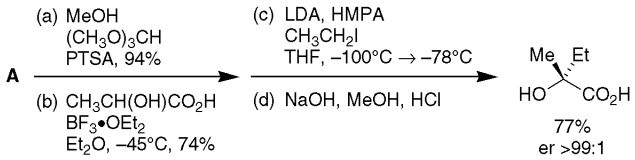
10 examples of the reduction of alcohols (yields 86-99%) and 11 examples of alkyl ethers (yields 0, 87-99%).

(1*S*)-(+)-*N*,*N*-Di*iso*propyl-10-camphorsulfonamide — *Chiral Auxiliary*

The title reagent is employed in the enantioselective synthesis of α-hydroxy acids.



A

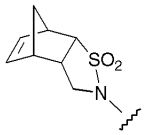


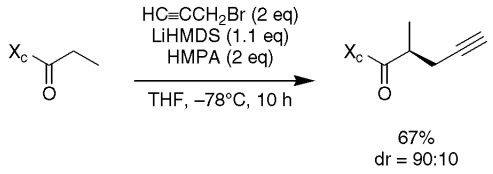
J.-W. Chang, D.-P. Jang, B.-J. Uang, F.-L. Liao, S.-L. Wang *Org. Lett.* **1999**, *1*, 2061.

5 examples of alkylations (yields 67-82%, %de > 98%) and 3 examples of the subsequent hydrolysis to acids (yields 94-98%) are reported.

Tricyclic Chiral Sultam Auxiliary — *Chiral Auxiliary*

The use of the illustrated chiral auxiliary in asymmetric alkylations is described.



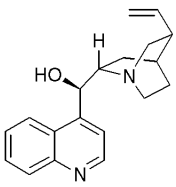


J. Lin, W. H. Chan, A. W. M. Lee, W. Y. Wong *Tetrahedron* **1999**, *55*, 13983.

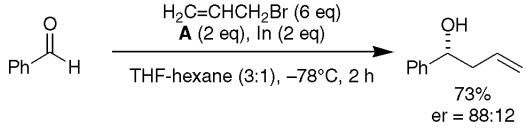
13 examples (yields 35-86%, %de = 0, 20-94%).

(–)-Cinchonidine — *Ligand*

The title reagent is used in the enantioselective indium-mediated allylation of aldehydes.



A

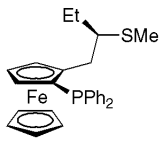


T.-P. Loh, J.-R. Zhou, Z. Yin *Org. Lett.* **1999**, *1*, 1855.

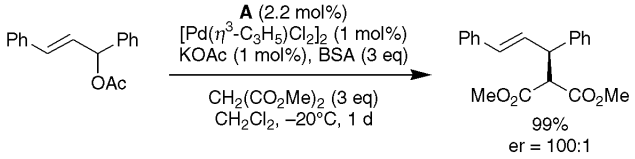
14 examples (yields 73-99%, %ee = 41-90%) are reported.

2-{[(*R*)-2-Methylthiobutyl]-1-ferrocenyl}diphenylphosphane — *Ligand*

A, which has planar and central chirality, is utilised in Pd-catalysed allylic substitutions.



A

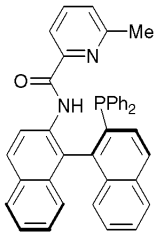


D. Enders, R. Peters, J. Runsink, J. W. Bats *Org. Lett.* **1999**, *1*, 1863.

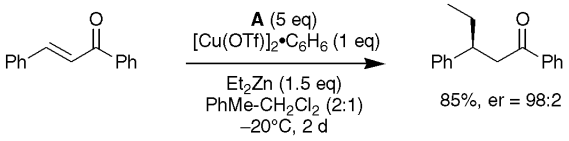
2 examples (yields 50, 99%, %ee = 94, 98%) are reported.

(*S*)-(+)-2-(6-Methyl-2-pyridinylcarboxamido)-2′-(diphenylphosphanyl)-1,1′-binaphthyl — *Ligand*

A promotes the Cu-catalysed enantioselective 1,4-addition of diethylzinc to acyclic enones.



A



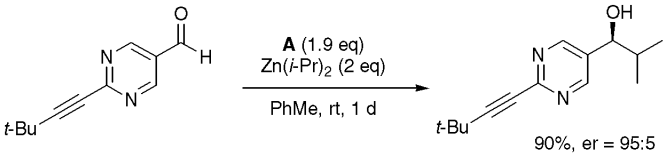
7 examples (yields 53-97%, %ee = 86-98%).

X. Hu, H. Chen, X. Zhang *Angew. Chem. Int. Ed.* **1999**, *38*, 3518.

d-Quartz — *Reagent*

A or its *l*-enantiomorph promotes the enantioselective addition of di*iso*propyl zinc to a pyrimidinyl carbaldehyde.

SiO_2

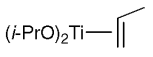


17 examples (yields 90-97%, %ee = 80-97%).

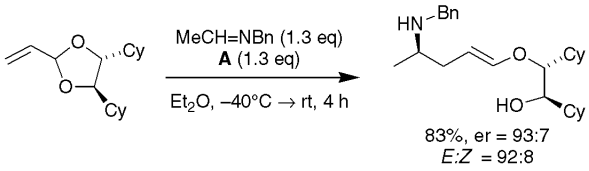
K. Soai, S. Osanai, K. Kadowaki, S. Yonekubo, T. Shibata, I. Sato *J. Am. Chem. Soc.* **1999**, *121*, 11235.

Diisopropyloxy-η^2-propenetitanium(II) — *Reagent*

A, in combination with chiral acetals, serves as a chiral propionaldehyde homoenolate equivalent which reacts with imines.



A



6 examples (yields 71-85%, %ee = 83-88%, *E*:*Z* ≥ 92:8).

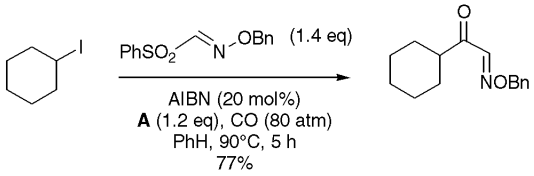
X. Teng, Y. Takayama, S. Okamoto, F. Sato *J. Am. Chem. Soc.* **1999**, *121*, 11916.

Allyltributyltin — *Reagent*

A mediates the carbonylative radical coupling of alkyl iodides with phenylsulfonyl oxime ethers.

$Bu_3SnCH_2CH{=}CH_2$

A



13 examples (yields 19-85%).

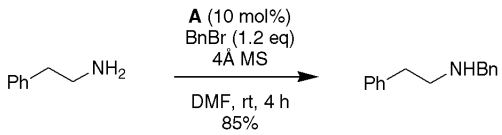
I. Ryu, H. Kuriyama, S. Minakata, M. Komatsu, J.-Y. Yoon, S. Kim *J. Am. Chem. Soc.* **1999**, *121*, 12190.

Cesium Hydroxide Monohydrate — *Reagent*

The title reagent promotes the selective *N*-alkylation of primary amines.

$CsOH{\bullet}H_2O$

A



23 examples (yields 45-93%) are reported.

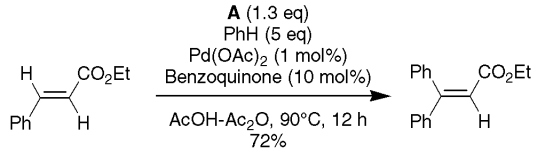
R. N. Salvatore, A. S. Nagle, S. E. Schmidt, K. W. Jung *Org. Lett.* **1999**, *1*, 1893.

tert-Butyl Hydroperoxide — *Reagent*

The title reagent is used in the oxidative palladium-catalysed coupling of arenes with olefins.

^{t}BuOOH

A



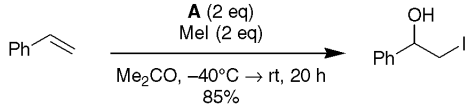
C. Jia, W. Lu, T. Kitamura, Y. Fujiwara *Org. Lett.* **1999**, *1*, 2097.

23 examples (yields 10-74%) are reported.

Dimethyldioxirane — *Reagent*

The title reagent is used to generate stable neutral solutions of hypoiodous acid, which is trapped *in situ* by addition to olefins to afford the corresponding iodohydrins.

A



G. Asensio, C. Andreu, C. Boix-Bernardini, R. Mello, M. E. González-Nuñez *Org. Lett.* **1999**, *1*, 2125.

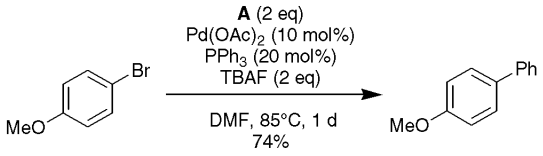
14 examples (yields 0, 44-85%) are reported.

Phenyltrimethoxysilane — *Reagent*

The title reagent is used in palladium-catalysed cross coupling reactions with aryl halides.

$PhSi(OCH)_3$

A

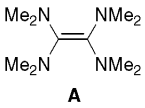


M. E. Mowery, P. DeShong *Org. Lett.* **1999**, *1*, 2137.

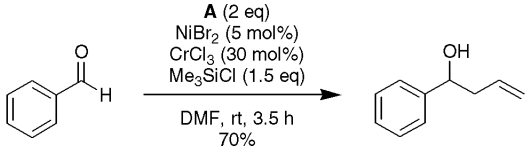
8 examples (yields 29, 62-86%) are reported.

Tetrakis(dimethylamino)ethylene (TDAE) — *Reagent*

The title reagent is a potent electron source in the chromium-mediated allylation of aldehydes and ketones.



A



M. Kuroboshi, K. Goto, M. Mochizuki, H. Tanaka *Synlett* **1999**, 1930.

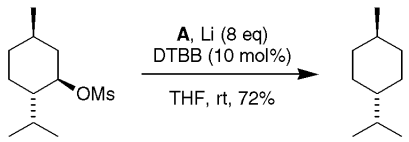
10 examples (yields 0, 36-94%) are reported.

Nickel(II) Chloride Dihydrate — *Reagent*

A in conjunction with lithium and catalytic di-*tert*butylbiphenyl (DTBB) reduces alkyl and aryl mesylates, dimesylates and triflates to the corresponding hydrocarbons. The reaction conditions also provide a reasonable alternative to the Birch reduction.

$NiCl_2 \cdot 2H_2O$

A



G. Radivoy, F. Alonso, M. Yus *Tetrahedron* **1999**, *55*, 14479.

19 examples (yields 21-85%).