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:

Elyse Bourque, Robert Chow, Jennifer Delaney, Marcel de Puit and Sukhjinder Uppal, Department of Chemistry, Leeds University, Leeds, LS2 9JT, UK.

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 I
Synlett
Synthesis
Tetrahedron
Tetrahedron Asymmetry and Tetrahedron Letters

Synthesis 2001, No. 16, 30 10 2001. Article Identifier:
1437-210X,E;2001,0,16,2521,2526,ftx,en;X01601SS.pdf.

ISSN 0039-7881

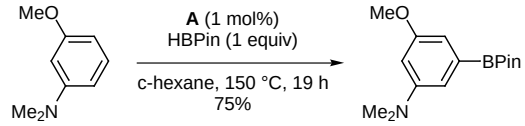
Hartwig's Pre-catalyst ***Catalyst***

The title reagent promotes regioselective aromatic borylations in cyclohexane to afford aryl boronate esters.

Tse, M. K.; Cho, J.-Y.; Smith, M. R. III *Org. Lett.* **2001**, *3*, 2831.

$Cp^*Rh(\eta^4\text{-}C_6Me_6)$

A



9 examples (yields 53–88%).

Chloro(1,5-cyclooctadiene)rhodium(I) Dimer/Me-DuPhos ***Catalyst***

The title reagent pair promotes the two-step reductive aldol reaction.

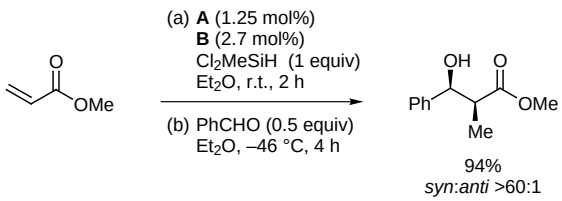
Zhao, C.-X.; Bass, J.; Morken, J. P. *Org. Lett.* **2001**, *3*, 2839.

$[codRhCl]_2$

A

DuPhos

B



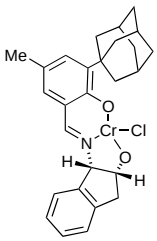
94%
syn:*anti* >60:1

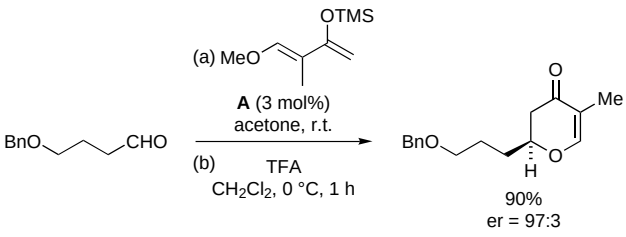
9 examples (yields 71–98%).

Tridentate Chromium(III) Catalyst ***Catalyst***

Reagent A promotes the asymmetric reaction between an aldehyde and a substituted diene in an entry into the A-D ring system of Gambierol.

Cox, J. M.; Rainier, J. D. *Org. Lett.* **2001**, *3*, 2919.



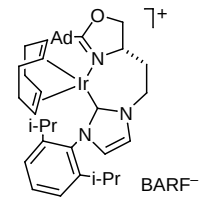


90%
er = 97:3

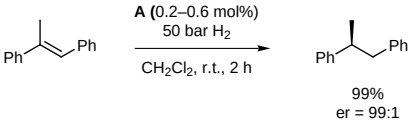
1-Adamantyl Oxazoline Iridinium Complex[a] ***Catalyst***

The title reagent promotes asymmetric hydrogenation of aryl alkenes

Powell, M. T.; Hou, D.-R.; Perry, M. C.; Cui, X.; Burgess, K. *J. Am. Chem. Soc.* **2001**, *123*, 8878.



A



99%
er = 99:1

8 examples (yields 90–99%, %ee 31–98%).

[a](h^4-1,5-Cyclooctadiene){1-[(4S)-2-(1-adamantyl-4-5-dihydrooxazolyl)-ethyl]-3-(2,6-diiso-propylphenyl)imidazolin-2-ylidene}iridinium(I) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate

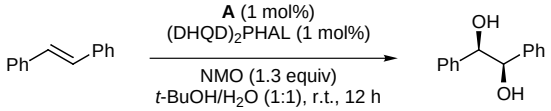
Osmium Tetroxide ***Catalyst***

The title reagent, when immobilized on layered double hydroxides (LDH), promotes asymmetric dihydroxylation of olefins.

Choudary, B. M.; Chowdari, N. S.; Kantam, M. L.; Raghavan, K. V. *J. Am. Chem. Soc.* **2001**, *123*, 9220.

LDH-OsO_4

A



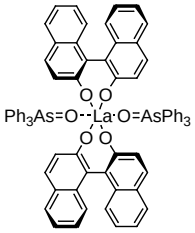
96%
er = 99.5:1.5

9 examples (yields 89–97%, %ee 77–99%).

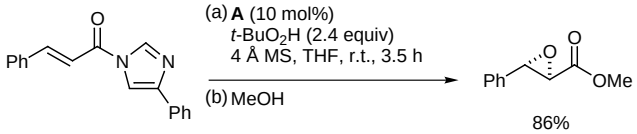
Lanthanium-(*S*)-1,1′-bi-2-naphthol-triphenylarsine Oxide ***Catalyst***

The title reagent catalyse the asymmetric synthesis of α,β-epoxy esters.

Nemoto, T.; Ohshima, T.; Shibasaki, M. *J. Am. Chem. Soc.* **2001**, *123*, 9474.



A



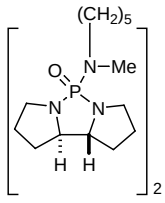
86%
er = 96:4

10 examples (yields 79–93%, %ee 72–97%).

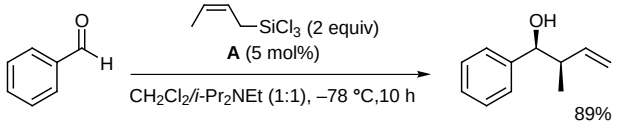
Aminio Phosphoryl Derivative[a] ***Catalyst***

The title reagent promotes catalytic, enantioselective addition of allylic trichlorosilanes to aldehydes.

Denmark, S. E.; Fu, J. *J. Am. Chem. Soc.* **2001**, *123*, 9488.



A



89%
er = 97:3
dr = 99:1

21 examples (yields 57–92%, %ee 72–97%, %de 90–98%).

[a]*N*,*N*′-Dimethyl-*N*,*N*′-bis-{(3′a*R*,4′a*R*)-7′-oxooctahydro-6′a,7′a-diaza-7′-phosphacyclopenta[a]pentalene-7′-yl}-pentane-1,5-diamine

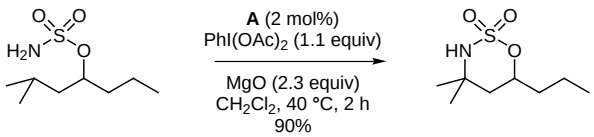
Rhodium(II) Acetate Dimer ***Catalyst***

The title reagent promotes the formation of 1,3-difunctionalized amine derivatives through selective C-H bond oxidation.

Espino, C. G.; Wehn, P. M.; Chow, J.; Du Bois, J. *J. Am. Chem. Soc.* **2001**, *123*, 6935.

$Rh_2(OAc)_4$

A



9 examples (yields 60–91%).

Iron(III) Acetylacetonate/Dinitrogen Pentoxide ***Catalyst***

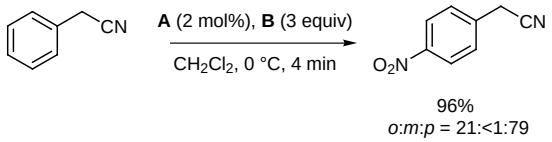
The title reagent pair provides mild conditions for the nitration of aromatics in high yields.

$Fe(acac)_3$

A

N_2O_5

B



96%
o:*m*:*p* = 21:<1:79

7 examples (yields 91–99%).

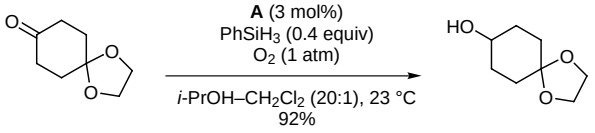
Bak, R. R.; Smallridge, A. J. *Tetrahedron Lett.* **2001**, *42*, 6767.

Tris(dipivaloylmethanato)manganese (III) ***Catalyst***

The title reagent catalyses the reduction of saturated aldehydes and ketones by phenylsilane in the presence of dioxygen.

$Mn(dpm)_3$

A



23 examples (yields <1–99%).

Magnus, P.; Fielding, M. R. *Tetrahedron Lett.* **2001**, *42*, 6633.

(±)-BINOL/Zr(O*i*Pr)4·*i*-PrOH ***Catalyst***

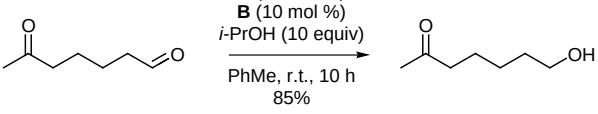
The title reagent pair catalyses the selective reduction of aldehydes in the presence of ketones.

(±)-BINOL

A

$Zr(O\text{-}i\text{-}Pr)_4$ *i*-PrOH

B

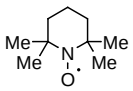


13 examples (yields 50–100 %).

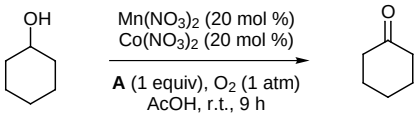
Lorca, M.; Kuhn, D.; Kurosu, M. *Tetrahedron Lett.* **2001**, *42*, 6243.

Manganese(II) Nitrate/Cobalt(II) Nitrate/2,2′,6,6′-Tetramethylpiperidine-*N*-oxyl ***Catalyst***

The title reagents catalyse the selective oxidation of aldehydes and ketones to primary and secondary alcohols.



A



11 examples (yields 96–100%).

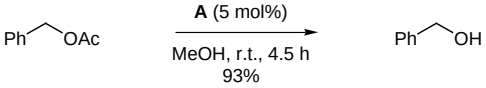
Caccheto, A.; Fontana, F.; Minisci, F.; Recupero, F. *Tetrahedron Lett.* **2001**, *42*, 6651.

Neutral Organotin Catalyst ***Catalyst***

The title reagent catalyses the deprotection of acetyl esters.

$[t\text{-}Bu_2SnOH(Cl)]_2$

A



18 examples (yields 21–100%).

Orita, A.; Hamada, Y.; Nakano, T.; Toyoshima, S.; Otera, J. *Chem.–Eur. J.* **2001**, *7*, 3321.

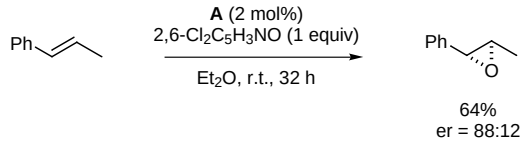
Nitrosyl(salen)ruthenium(II) Complex ***Catalyst***

The title reagent catalyses the asymmetric epoxidation of conjugated olefins under irradiation.

Nakata, K.; Takeda, T.; Mihara, J.; Hamada, T.; Irie, R.; Katsuki, T. *Chem.–Eur. J.* **2001**, *7*, 3776.

$RuCl(C_{60}H_{44}N_2O_2)(NO)$

A



11 examples (yields 32–83%, %ee 71–98%).

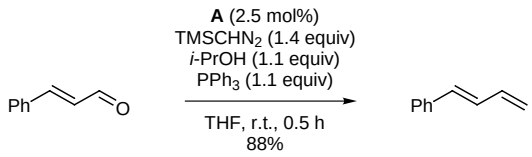
Wilkinson's Catalyst ***Catalyst***

The title reagent catalyses the methylenation of aldehydes.

Lebel, H.; Paquet, V.; Proulx, C. *Angew. Chem. Int. Ed.* **2001**, *40*, 2887.

$RhCl(PPh_3)_3$

A



12 examples (yields 60–98%).

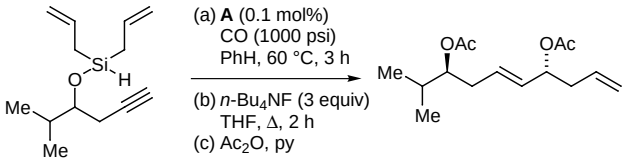
Rhodium Complex ***Catalyst***

The title reagent catalyses the tandem silylformylation–allylsilylation of alkynes.

O'Malley, S. J.; Leighton, J. L. *Angew. Chem. Int. Ed.* **2001**, *40*, 2915.

$Rh(acac)(CO)_2$

A



8 examples (yields 63–83%).

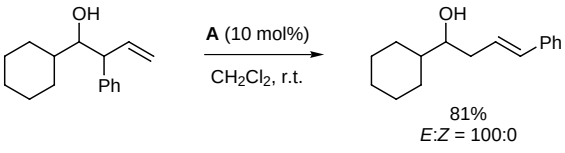
Indium(III) Triflate ***Catalyst***

The title reagent catalyses the conversion of homoallylic alcohols into the thermodynamically preferred regioisomers.

Loh, T.-P.; Tan, K.-T.; Hu, Q.-Y. *Angew. Chem. Int. Ed.* **2001**, *40*, 2921.

$In(OTf)_3$

A

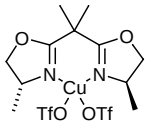


11 examples (yields 19–81%, 55:45 < *E*:*Z* > 100:0).

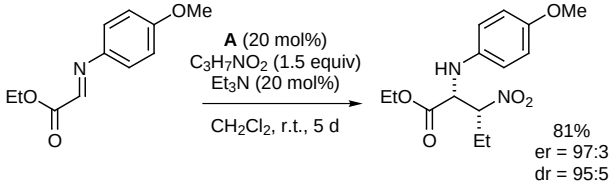
Bisoxazoline-Copper Complex ***Catalyst***

The title reagent catalyses the enantioselective addition of nitro compounds to imines.

Nishiwaki, N.; Knudsen, K. R.; Gothelf, K. V.; Jørgensen, K. A. *Angew. Chem. Int. Ed.* **2001**, *40*, 2992.



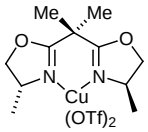
A



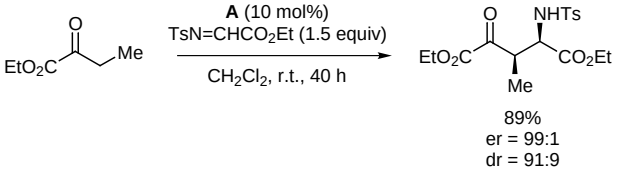
6 examples (yields 38–81%, %ee 74–99%, %de 10–90%).

Bisoxazoline-Copper(II) Complex ***Catalyst***

The title reagent catalyses the asymmetric direct Mannich reactions of carbonyl with α-imino esters.



A

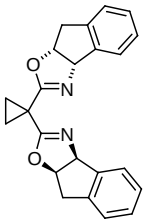


4 examples (yields 70–98%, %ee 78–98%, %de 50–82%).

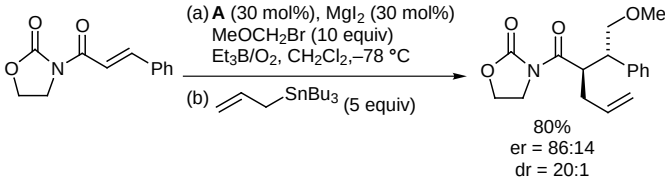
Juhl, K.; Gathergood, N.; Jørgensen, K. A. *Angew. Chem. Int. Ed.* **2001**, *40*, 2995.

{3a*S*-[2(3′a*R*,8′a*S*),3aa,8aa]}-2-2′-(cyclopropylidene)-bis{3a,8a-dihydro-8*H*-indeno[1,2-d]-oxazole} ***Ligand***

The title reagent, when complexed to a Cu or Mg Lewis acid, promotes enantioselective tandem addition-trapping reactions to enoate derivatives.



A

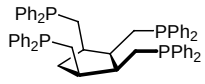


16 examples (yields 66–95%, %ee 53–97%, %de 41–98%).

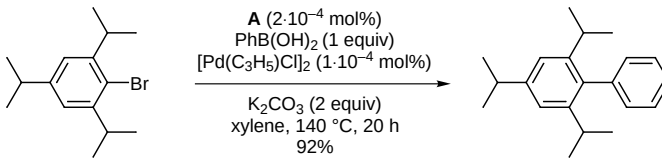
Sibi, M. P.; Chen, J. *J. Am. Chem. Soc.* **2001**, *123*, 9472.

cis*,*cis*,*cis*-1,2,3,4-Tetrakis(diphenylphospinomethyl)cyclopentane** ***Ligand

The title reagent, when complexed with $[PdCl(C_3H_5)]_2$, catalyses the Suzuki cross-coupling of sterically hindered substrates.



A

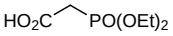


25 examples (yields 0–100%).

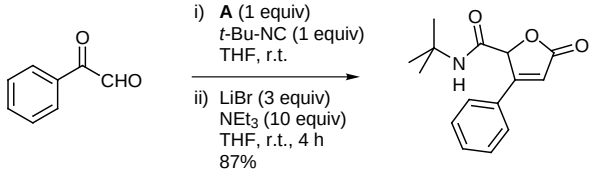
Feuerstein, M.; Doucet, H.; Santelli, M. *Tetrahedron Lett.* **2001**, *42*, 6667.

Diethylphosphonoacetic Acid ***Reagent***

The title reagent is applied in a one-pot multicomponent reaction of isocyanides, glyoxals and acetophosphonic acid diethylesters, followed by an intramolecular Wittig-type reaction for the synthesis of butenolides.



A

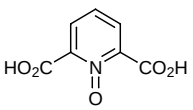


5 examples (yields 52–87%).

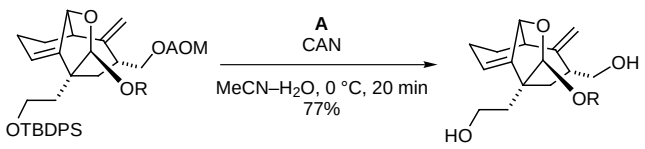
Beck, B.; Magnin-Lachaux, M.; Herdtweck, E.; Domling, A. *Org. Lett.* **2001**, *3*, 2875.

2,6-Pyridinecarboxylic Acid *N*-Oxide ***Reagent***

The title reagent is used for the cleavage of a *p*-anisoloxymethyl-protected alcohol.



A

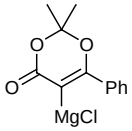


1 example (yield 77%).

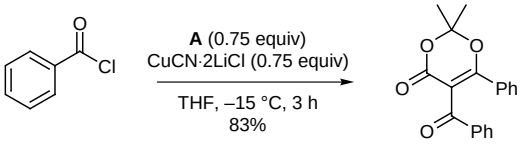
Clive, D. L. J.; Sun, S. *Tetrahedron Lett.* **2001**, *42*, 6267.

5-Magnesiated-1,3-dioxin-4-one ***Reagent***

The title reagent can be reacted with a wide variety of electrophiles.



A



10 examples (yields 57–83%).

Vu, V. A.; Berillon, L.; Knochel, P. *Tetrahedron Lett.* **2001**, *42*, 6847.

Titanium Isopropoxide/Isopropylmagnesium Chloride ***Reagent***

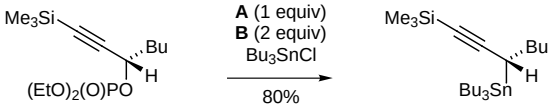
The title reagent pair is used for the preparation of optically active propargyl stannanes from the corresponding propargyl phosphates.

$Ti(O\text{-}i\text{-}Pr)_4$

A

i -PrMgCl

B

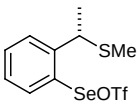


4 examples (yields 77–80%)

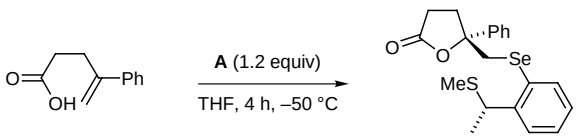
Okamoto, S.; Matsuda, S.-I.; An, D. K.; Sato, F. *Tetrahedron Lett.* **2001**, *42*, 6323.

2-(1*S*)-1-(Methylthio)ethylphenyl Selenyl Triflate ***Reagent***

The title reagent promotes asymmetric selenocyclization reactions.



A



95%
dr = 89:11

17 examples (yields 40–95%, %de 50–88%).

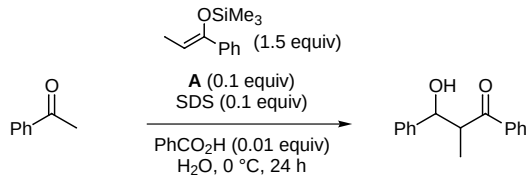
Tiecco, M.; Testaferri, L.; Silvia, S.; Sternativo, S.; Bagnoli, L.; Santi, C.; Temperini, A. *Tetrahedron Asymmetry.* **2001**, *12*, 1493.

Diphenylborinic Acid ***Reagent***

The title reagent can be used as a boron source for Mukaiyama aldol reactions in water.

Ph_2BOH

A



93%
syn:*anti* = 94:6

13 examples (yields 51–93%, %de 6–94%).

Mori, Y.; Manabe, K.; Kobayashi, S. *Angew. Chem. Int. Ed.* **2001**, *40*, 2816.

Diisopropylzinc/Copper Cyanide·Lithium Chloride ***Reagent***

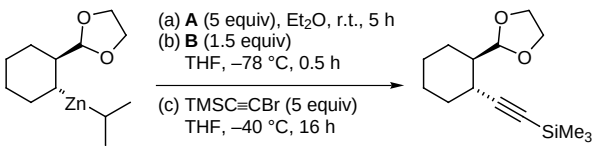
The title reagent pair is used for sequential boron-zinc exchange and copper-mediated allylation of the hydroboration products of unsaturated acetals.

$i\text{-}Pr_2Zn$

A

CuCN·LiCl

B



46%
dr = 99:1

16 examples (yields 46–69%, %de 6–98%).

Hupe, E.; Knochel, P. *Angew. Chem. Int. Ed.* **2001**, *40*, 3023.