

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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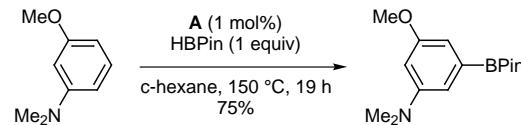
The journals regularly covered by the abstractors are:

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 I
 Synlett
 Synthesis
 Tetrahedron
 Tetrahedron Asymmetry and Tetrahedron Letters

Hartwig's Pre-catalyst

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

Cp^{*}Rh(η⁴-C₆Me₆)
A



Catalyst

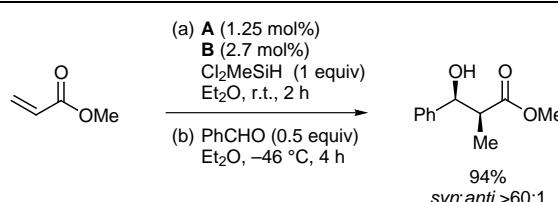
Tse, M. K.; Cho, J.-Y.; Smith, M. R. III
Org. Lett. **2001**, 3, 2831.

9 examples (yields 53–88%).

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

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

[codRhCl]₂
A
 DuPhos
B



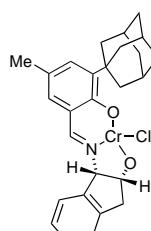
Catalyst

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

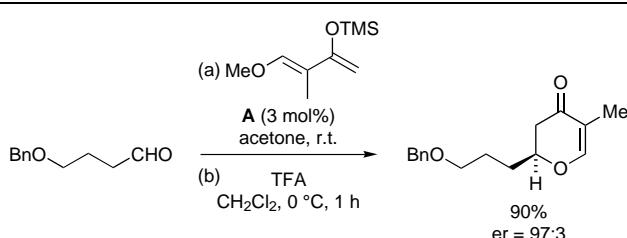
9 examples (yields 71–98%).

Tridentate Chromium(III) 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.



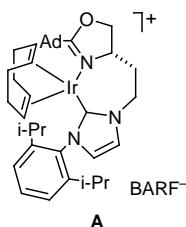
Cox, J. M.; Rainier, J. D. *Org. Lett.*
2001, 3, 2919.



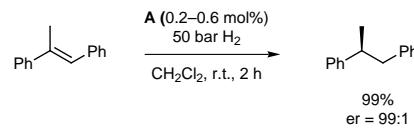
Catalyst

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.



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

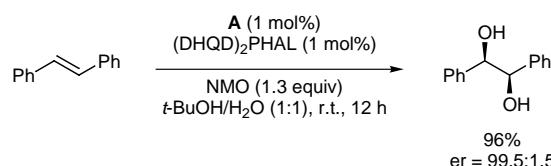
^a(*i*⁴-1,5-Cyclooctadiene){1-[{(4*S*)-2-(1-adamantyl-4-5-dihydrooxazolyl)-ethylidene]3-(2,6-diisopropylphenyl)imidazolin-2-ylidene}iridinium(I) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate

Osmium Tetroxide**Catalyst**

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



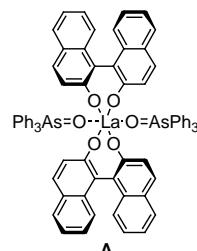
Choudary, B. M.; Chowdari, N. S.; Kantam, M. L.; Raghavan, K. V. *J. Am. Chem. Soc.* **2001**, 123, 9220.



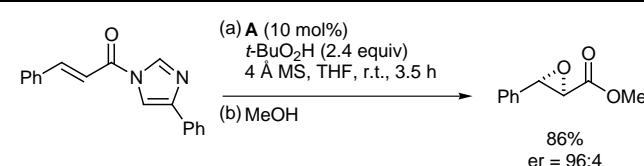
9 examples (yields 89–97%, %ee 77–99%).

Lanthanum-(S)-1,1'-bi-2-naphthol-triphenylarsine Oxide**Catalyst**

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



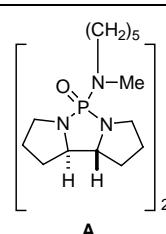
Nemoto, T.; Ohshima, T.; Shibasaki, M. *J. Am. Chem. Soc.* **2001**, 123, 9474.



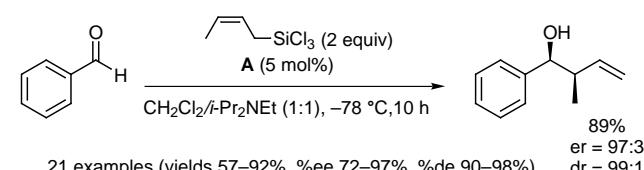
10 examples (yields 79–93%, %ee 72–97%).

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.



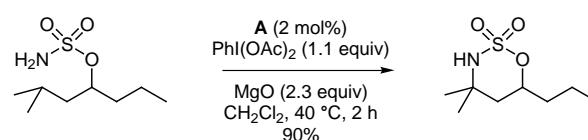
^a*N,N*'-Dimethyl-*N,N*-bis-{(3'a*R*,4'a*R*)-7'-oxooctahydro-6'a,7'a-diaza-7'-phosphacyclopenta[a]pentale-7'-yl}-pentane-1,5-diamine

Rhodium(II) Acetate Dimer**Catalyst**

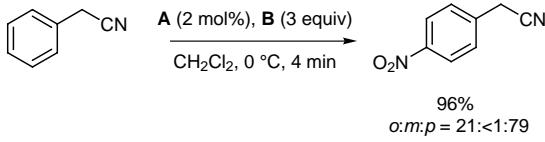
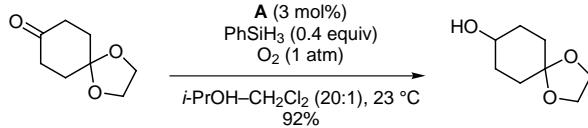
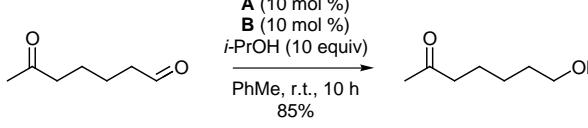
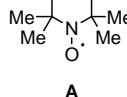
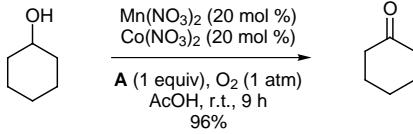
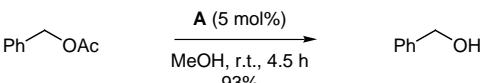
The title reagent promotes the formation of 1,3-difunctionalized amine derivatives through selective C-H bond oxidation.



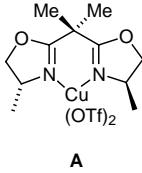
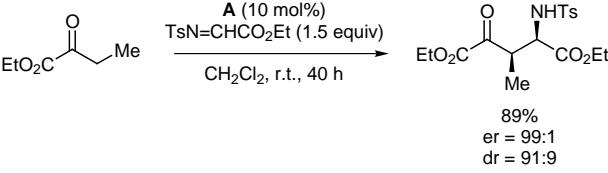
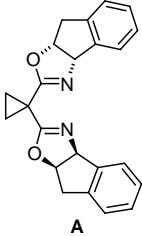
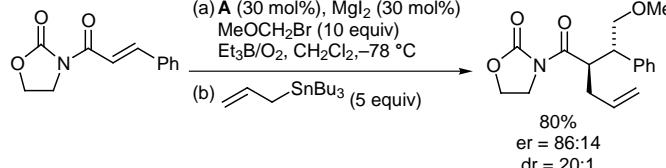
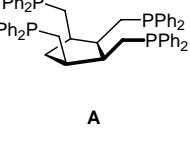
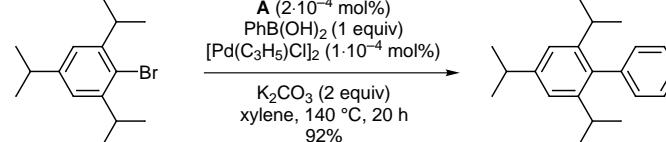
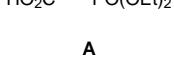
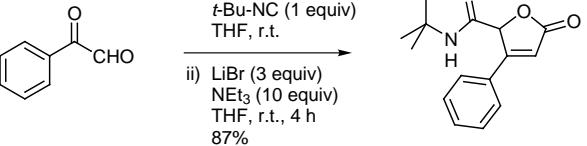
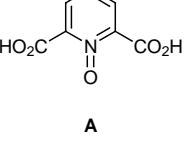
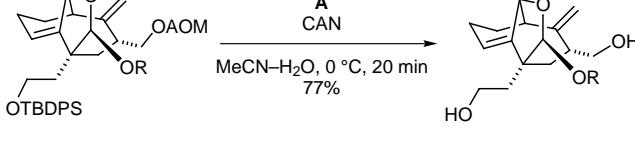
Espino, C. G.; Wehn, P. M.; Chow, J.; Du Bois, J. *J. Am. Chem. Soc.* **2001**, 123, 6935.



9 examples (yields 60–91%).

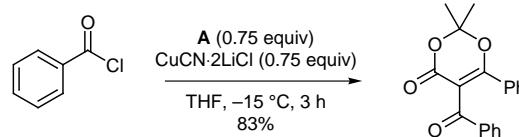
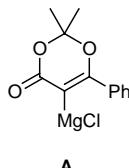
Iron(III) Acetylacetone/Dinitrogen Pentoxide			Catalyst
The title reagent pair provides mild conditions for the nitration of aromatics in high yields.	Fe(acac) ₃ A N ₂ O ₅ B		
Bak, R. R.; Smallridge, A. J. <i>Tetrahedron Lett.</i> 2001 , <i>42</i> , 6767.			7 examples (yields 91–99%).
Tris(dipivaloylmethanato)manganese (III)			Catalyst
The title reagent catalyses the reduction of saturated aldehydes and ketones by phenylsilane in the presence of dioxygen.	Mn(dpm) ₃ A		
Magnus, P.; Fielding, M. R. <i>Tetrahedron Lett.</i> 2001 , <i>42</i> , 6633.			23 examples (yields <1–99%).
(±)-BINOL/Zr(O<i>i</i>Pr)₄-<i>i</i>-PrOH			Catalyst
The title reagent pair catalyses the selective reduction of aldehydes in the presence of ketones.	(±)-BINOL A Zr(O <i>i</i> Pr) ₄ <i>i</i> -PrOH B		
Lorca, M.; Kuhn, D.; Kurosu, M. <i>Tetrahedron Lett.</i> 2001 , <i>42</i> , 6243.			13 examples (yields 50–100 %).
Manganese(II) Nitrate/Cobalt(II) Nitrate/2,2',6,6'-Tetramethylpiperidine-<i>N</i>-oxyl			Catalyst
The title reagents catalyse the selective oxidation of aldehydes and ketones to primary and secondary alcohols.			
Caccheto, A.; Fontana, F.; Minisci, F.; Recupero, F. <i>Tetrahedron Lett.</i> 2001 , <i>42</i> , 6651.			11 examples (yields 96–100%).
Neutral Organotin Catalyst			Catalyst
The title reagent catalyses the deprotection of acetyl esters.	[<i>t</i> -Bu ₂ SnOH(Cl)] ₂ A		
Orita, A.; Hamada, Y.; Nakano, T.; Toyoshima, S.; Otera, J. <i>Chem.-Eur. J.</i> 2001 , <i>7</i> , 3321.			18 examples (yields 21–100%).

Nitrosyl(salen)ruthenium(II) Complex			Catalyst
The title reagent catalyses the asymmetric epoxidation of conjugated olefins under irradiation.	RuCl(C ₆₀ H ₄₄ N ₂ O ₂)(NO) A	<p style="text-align: center;">A (2 mol%) 2,6-Cl₂C₆H₃NO (1 equiv) Et₂O, r.t., 32 h</p> <p style="text-align: right;">64% er = 88:12</p>	
Nakata, K.; Takeda, T.; Mihara, J.; Hamada, T.; Irie, R.; Katsuki, T. <i>Chem.-Eur. J.</i> 2001 , <i>7</i> , 3776.			11 examples (yields 32–83%, %ee 71–98%).
Wilkinson's Catalyst			Catalyst
The title reagent catalyses the methylenation of aldehydes.	RhCl(PPh ₃) ₃ A	<p style="text-align: center;">A (2.5 mol%) TMSCHN₂ (1.4 equiv) i-PrOH (1.1 equiv) PPh₃ (1.1 equiv) THF, r.t., 0.5 h</p> <p style="text-align: right;">88%</p>	
Lebel, H.; Paquet, V.; Proulx, C. <i>Angew. Chem. Int. Ed.</i> 2001 , <i>40</i> , 2887.			12 examples (yields 60–98%).
Rhodium Complex			Catalyst
The title reagent catalyses the tandem silylformylation–allylsilylation of alkynes.	Rh(acac)(CO) ₂ A	<p style="text-align: center;">(a) A (0.1 mol%) CO (1000 psi) PhH, 60 °C, 3 h (b) <i>n</i>-Bu₄NF (3 equiv) THF, Δ, 2 h (c) Ac₂O, py</p> <p style="text-align: right;">8 examples (yields 63–83%).</p>	
O'Malley, S. J.; Leighton, J. L. <i>Angew. Chem. Int. Ed.</i> 2001 , <i>40</i> , 2915.			
Indium(III) Triflate			Catalyst
The title reagent catalyses the conversion of homoallylic alcohols into the thermodynamically preferred regioisomers.	In(OTf) ₃ A	<p style="text-align: center;">A (10 mol%) CH₂Cl₂, r.t.</p> <p style="text-align: right;">81% E:Z = 100:0</p>	
Loh, T.-P.; Tan, K.-T.; Hu, Q.-Y. <i>Angew. Chem. Int. Ed.</i> 2001 , <i>40</i> , 2921.			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.	<p style="text-align: center;">A</p>	<p style="text-align: center;">A (20 mol%) C₃H₇NO₂ (1.5 equiv) Et₃N (20 mol%) CH₂Cl₂, r.t., 5 d</p> <p style="text-align: right;">81% er = 97:3 dr = 95:5</p>	
Nishiaki, N.; Knudsen, K. R.; Goethelf, K. V.; Jørgensen, K. A. <i>Angew. Chem. Int. Ed.</i> 2001 , <i>40</i> , 2992.			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.		 <p>A (10 mol%) TsN=CHCO₂E_t (1.5 equiv) CH₂Cl₂, r.t., 40 h</p> <p>89% er = 99:1 dr = 91:9</p> <p>4 examples (yields 70–98%, %ee 78–98%, %de 50–82%).</p>
Juhl, K.; Gathergood, N.; Jørgensen, K. A. <i>Angew. Chem. Int. Ed.</i> 2001 , <i>40</i> , 2995.		
{3aS-[2(3'aR,8'aS),3aa,8aa]-2-2'-(cyclopropylidene)-bis{3a,8a-dihydro-8H-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.		 <p>(a) A (30 mol%), MgI₂ (30 mol%) MeOCH₂Br (10 equiv) Et₃B/O₂, CH₂Cl₂, -78 °C</p> <p>(b) $\text{PhCH}=\text{CHCH}_2\text{SnBu}_3$ (5 equiv)</p> <p>80% er = 86:14 dr = 20:1</p> <p>16 examples (yields 66–95%, %ee 53–97%, %de 41–98%).</p>
Sibi, M. P.; Chen, J. <i>J. Am. Chem. Soc.</i> 2001 , <i>123</i> , 9472.		
cis,cis,cis-1,2,3,4-Tetrakis(diphenylphosphinomethyl)cyclopentane		Ligand
The title reagent, when complexed with [PdCl(C ₅ H ₅) ₂], catalyses the Suzuki cross-coupling of sterically hindered substrates.		 <p>A ($2 \cdot 10^{-4}$ mol%) PhB(OH)₂ (1 equiv) [Pd(C₅H₅)Cl]₂ ($1 \cdot 10^{-4}$ mol%) K₂CO₃ (2 equiv) xylene, 140 °C, 20 h 92%</p> <p>25 examples (yields 0–100%).</p>
Feuerstein, M.; Doucet, H.; Santelli, M. <i>Tetrahedron Lett.</i> 2001 , <i>42</i> , 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.		 <p>i) A (1 equiv) <i>t</i>-Bu-NC (1 equiv) THF, r.t. ii) LiBr (3 equiv) NEt₃ (10 equiv) THF, r.t., 4 h 87%</p> <p>5 examples (yields 52–87%).</p>
Beck, B.; Magnin-Lachaux, M.; Herdtweck, E.; Domling, A. <i>Org. Lett.</i> 2001 , <i>3</i> , 2875.		
2,6-Pyridinecarboxylic Acid N-Oxide		Reagent
The title reagent is used for the cleavage of a <i>p</i> -anisoloxymethyl-protected alcohol.		 <p>A CAN MeCN-H₂O, 0 °C, 20 min 77%</p> <p>1 example (yield 77%).</p>
Clive, D. L. J.; Sun, S. <i>Tetrahedron Lett.</i> 2001 , <i>42</i> , 6267.		

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

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

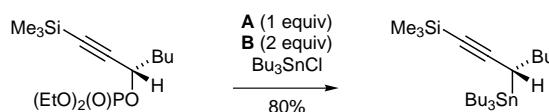
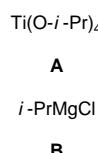


10 examples (yields 57–83%).

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.

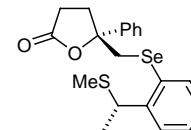
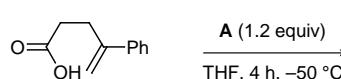
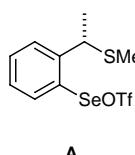


4 examples (yields 77–80%)

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.



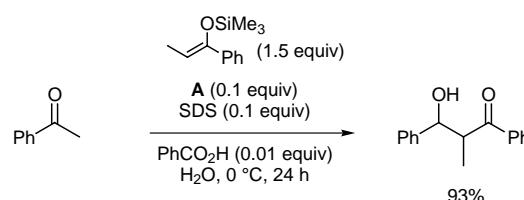
95%
dr = 89:11

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.



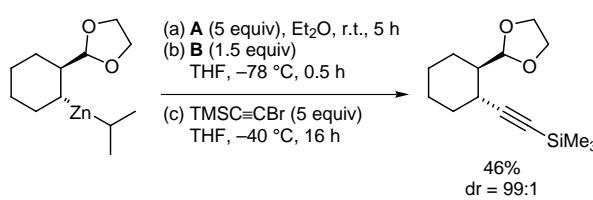
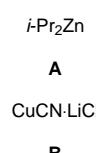
93%
syn:anti = 94:6

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.



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

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