

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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Article Identifier:
1437-210X,E;2000,0,01,2151,2158,ftx,en;X00100SS.pdf

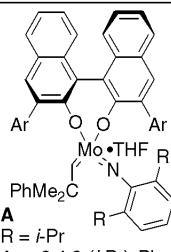
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Chemical Communications
Chemistry A European Journal
Chemistry Letters
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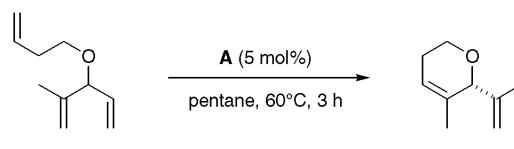
Chiral Mo-Binol RCM Catalyst

Catalyst

A and a methyl substituted analogue mediate asymmetric ring closing metathesis (ARCM).



S. S. Zhu, D. R. Cefalo, D. S. La, J. Y. Jamieson, W. M. Davies, A. H. Hoveyda, R. R. Schrock *J. Am. Chem. Soc.* **1999**, *121*, 8251.

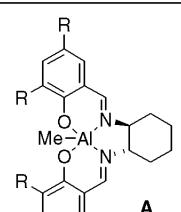


3 examples (yields 77-98%, %ee = 89-99%).

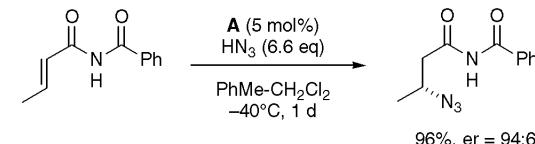
(S,S)-Methylaluminium-salen Complex

Catalyst

A catalyses the enantioselective Michael-addition of hydrazoic acid to a variety of α,β -unsaturated *N*-benzoylimides.



J. K. Myers, E. N. Jacobson *J. Am. Chem. Soc.* **1999**, *121*, 8956.



8 examples (yields 60-99%, %ee = 58-97%).

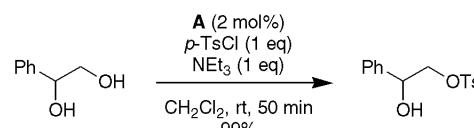
Dibutyltin Oxide

Catalyst

The title reagent catalyses the selective sulfonylation of α -heterosubstituted primary alcohols.



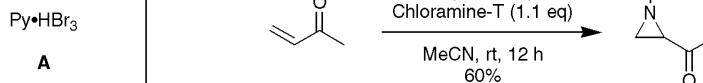
M. J. Martinelli, N. K. Nayyar, E. D. Moher, U. P. Dhokte, J. M. Pawlak, R. Vaidyanathan *Org. Lett.* **1999**, *1*, 447.



6 examples (yields 86-99%) are reported.

Catalyst**Pyridinium Hydrobromide Perbromide**

A catalyses the aziridination of olefins using Chloramine-T (*N*-chloro-*N*-sodio-*p*-toluenesulfonamide) as a nitrogen source to afford the corresponding aziridines in moderate to good yields.

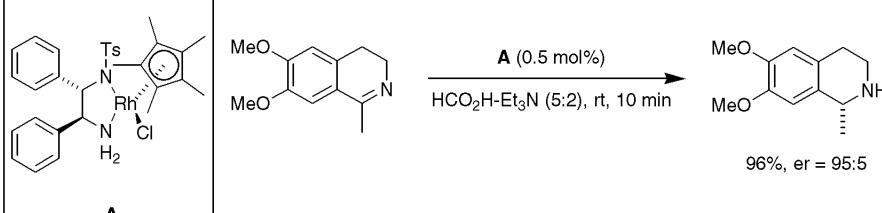


S. I. Ali, M. D. Nikalje, A. Sudalai *Org. Lett.* **1999**, 1, 705.

20 examples (yields 20–70%) are reported.

Asymmetric Hydrogenation Catalyst**Catalyst**

The title reagent catalyses the asymmetric transfer hydrogenation of imines, using a $\text{Et}_3\text{N}-\text{HCO}_2\text{H}$ azeotrope as the hydrogen source.

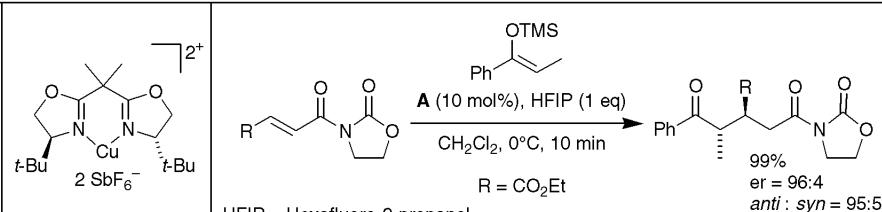


J. Mao, D. C. Baker *Org. Lett.* **1999**, 1, 841.

9 examples (yields 85–96%, %ee = 3, 68–99%) are reported.

[Cu(*S,S*-*t*-Bu-bisoxazoline)](SbF₆)₂**Catalyst**

The title reagent catalyses the enantioselective Michael addition of enolsilanes to unsaturated ester derivatives.

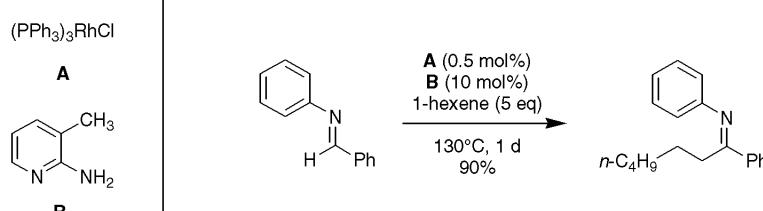


D. E. Evans, M. C. Willis, J. N. Johnston *Org. Lett.* **1999**, 1, 865.

13 examples (yields 56–99%, %ee = 75–99%) are reported.

Chlorotris(triphenylphosphine)rhodium(I) / 2-Amino-3-picoline**Catalyst**

The title reagent pair catalyse the transformation of aldimines to ketimines.

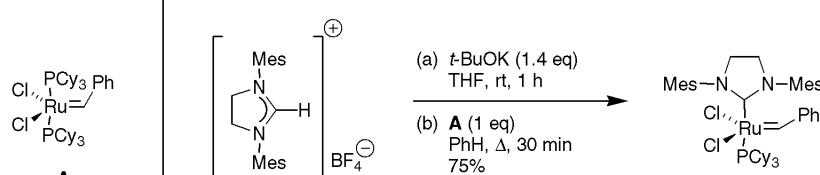


C.-H. Jun, J.-B. Hong *Org. Lett.* **1999**, 1, 887.

7 examples (yields 0, 41–90%) are reported.

Bis(tricyclohexylphosphine)benzylidene Ruthenium Dichloride**Catalyst**

The title reagent is used to prepare a new family of 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene-substituted ruthenium-based complexes. The complexes exhibit increased ring-closing metathesis activity compared to that of the parent complex **A**.

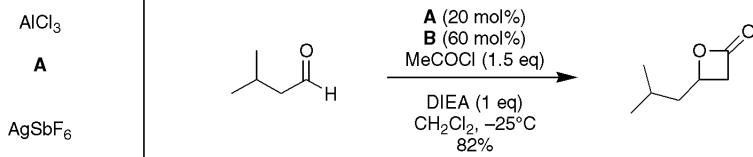


M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs *Org. Lett.* **1999**, 1, 953.

3 examples of complex formation and 14 examples of ring-closing metathesis (yields 31–100%) are reported.

Aluminium(III) Chloride / Silver Hexafluoroantimonate**Catalyst**

The title reagent pair catalyses the cyclocondensation of various acyl halides and aldehydes to afford β -lactones in good yields.

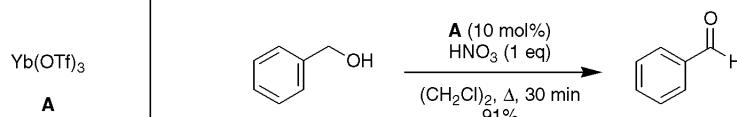


S. G. Nelson, Z. Wan, T. J. Peelen, K. L. Spencer
Tetrahedron Lett. **1999**, *40*, 6535.

9 examples (yields 65-93%) are reported.

Ytterbium(III) Trifluoromethanesulfonate**Catalyst**

The title reagent catalyses the selective oxidation of benzyl alcohols to benzaldehydes using nitric acid as the oxidant.

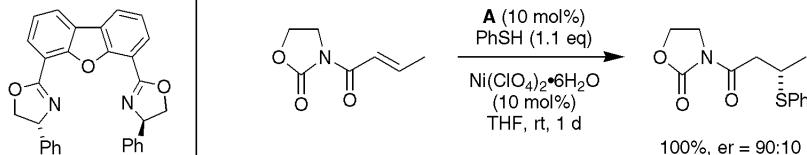


A. G. M. Barrett, D. C. Braddock, R. M. McKinnell, F. J. Waller *Synlett* **1999**, 1489.

13 examples (yields 0, 33-95%) are reported.

(R,R)-4,6-Dibenzofurandiyl-2,2'-bis(4-phenyloxazoline)**Ligand**

A Ni(II) catalyst formed from the title ligand catalyses the asymmetric conjugate addition of thiols to an oxazolidinone.

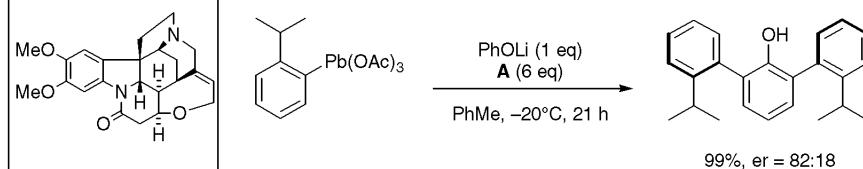


S. Kanemasa, Y. Oderaotsuhi, E. Wada *J. Am. Chem. Soc.* **1999**, *121*, 8675.

12 examples (yields 26-100%, %ee = 78-97%).

Brucine**Ligand**

A mediates the asymmetric coupling of phenols with aryllead species.

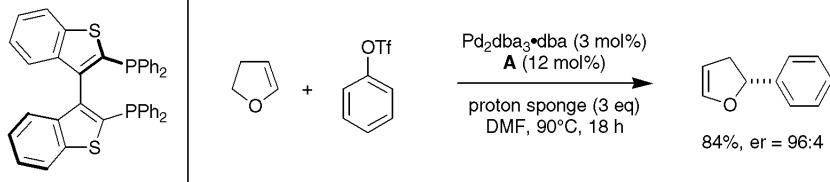


S. Saito, T. Kano, H. Muto, M. Nakadai, H. Yamamoto *J. Am. Chem. Soc.* **1999**, *121*, 8943.

18 examples (yields 49-99%, %ee = 46-93%).

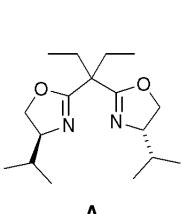
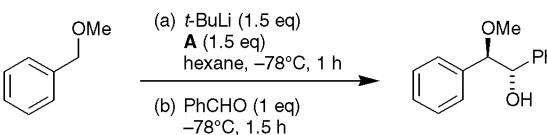
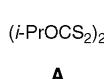
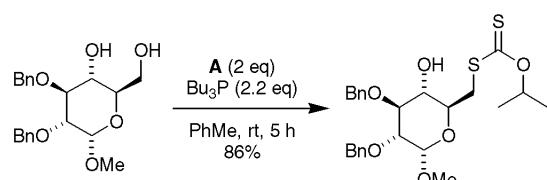
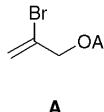
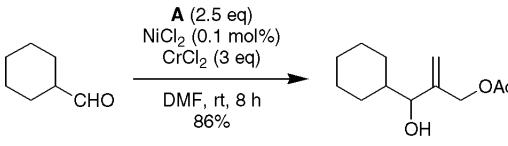
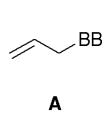
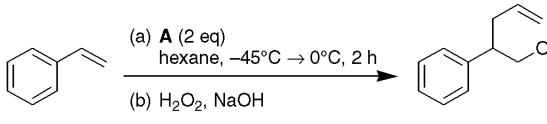
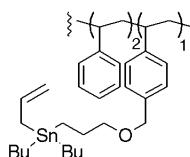
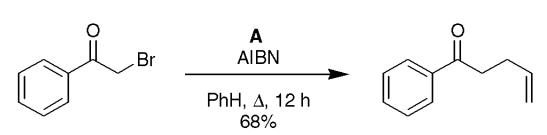
(R)-(+)-2,2'-Bis(diphenylphosphino)-3,3'-bi(benzo[b]thiophene) [(R)-BITIANP]**Ligand**

Regio- and enantioselective Heck reactions of dihydrofuran with aryl and alkenyl triflates in the presence of ligand A are reported.



L. F. Tietze, K. Thede, F. Sannicola *Chem. Commun.* **1999**, 1811.

6 examples (yields 76-93%, %ee = 86-96%).

Chiral Bis(oxazoline)		Ligand
The reaction of a chiral α -methoxybenzylolithium species (generated using <i>t</i> -BuLi and A) with aldehydes is reported. The 1,2-diol monomethyl ether products are generated with high enantio- and diastereoselectivity.		 Reaction conditions: (a) <i>t</i> -BuLi (1.5 eq), A (1.5 eq), hexane, -78°C, 1 h; (b) PhCHO (1 eq), -78°C, 1.5 h. Yield: 6 examples (yields 17, 68->95%, 58:42 \leq anti:syn \leq 91:9, ee _{anti} = 37->98%).
K. Tomooka, L.-F. Wang, N. Komine, T. Nakai <i>Tetrahedron Lett.</i> 1999 , <i>40</i> , 6813.		
O,O-Diisopropylthiocarbonate Disulfide		Reagent
The title reagent is used in a novel one-pot synthesis of thiosugar-derived S-xanthates.		 Reaction conditions: A (2 eq), Bu ₃ P (2.2 eq), PhMe, rt, 5 h, 86% yield. Yield: 10 examples (yields 27, 77-87%) are reported.
D. Gueyraud, A. Tatibouët, Y. Gareau, P. Rollin <i>Org. Lett.</i> 1999 , <i>1</i> , 521.		
2-Bromoallyl Acetate		Reagent
The title reagent is used in Ni(II) / Cr(II)-mediated coupling reactions with a variety of aliphatic and aryl aldehydes.		 Reaction conditions: A (2.5 eq), NiCl ₂ (0.1 mol%), CrCl ₂ (3 eq), DMF, rt, 8 h, 86% yield. Yield: 5 examples (yields 40-93%) are reported.
R. E. Taylor, J. P. Ciavarri <i>Org. Lett.</i> 1999 , <i>1</i> , 467.		
Allyldibromoborane		Reagent
The title reagent is used for the allylboration of alkenes.		 Reaction conditions: (a) A (2 eq), hexane, -45°C \rightarrow 0°C, 2 h; (b) H ₂ O ₂ , NaOH. Yield: 7 examples (yields 33-93%) are reported.
D. E. Frantz, D. A. Singleton <i>Org. Lett.</i> 1999 , <i>1</i> , 485.		
Allylstannane Reagent on Non-Cross-linked Polystyrene Support		Reagent
Free radical allylation reactions using A as a cleaner reagent than allyltributyltin are reported.		 Reaction conditions: A , AIBN, PhH, Δ , 12 h, 68% yield. Yield: 6 examples (yields 50-73%) are reported.
E. J. Enholm, M. E. Gallagher, K. M. Moran, J. S. Lombardi, J. P. Schulte II <i>Org. Lett.</i> 1999 , <i>1</i> , 689.		

Dimethyl Sulfoxide	Reagent
The title reagent is used in the selective rhodium-catalysed oxidation of secondary alcohols for a convenient one-pot synthesis of ketals.	<p style="text-align: center;">A (1.2 eq) Re(O)Cl₃(PPh₃)₂ (5 mol%) (CH₂OH)₂ (4 eq) 2,4,6-collidine (5 mol%) PhMe, Δ, 7 h 81%</p>
J. B. Arterburn, M. C. Perry <i>Org. Lett.</i> 1999 , <i>1</i> , 769.	9 examples (yields 67-100%) are reported.
N-Chloro- <i>tert</i> -butylsulfonamide, Sodium Salt	Reagent
The title reagent is used as a nitrogen source for the catalytic aminohydroxylation and aziridination of olefins.	<p style="text-align: center;">A (1.2 eq) $K_2OsO_2(OH)_4$ (0.5 mol%) $t\text{-}BuOH\text{-}H_2O$ (1:1), rt, 12 h 84%</p>
A. V. Gontcharov, H. Liu, K. B. Sharpless <i>Org. Lett.</i> 1999 , <i>1</i> , 783.	10 examples of aminohydroxylations (yields 71-94%) and 9 examples of aziridinations (yields 24, 65-95%) are reported.
Menthyl (<i>S</i>)-2-Bromophenylsulfinate	Reagent
The title reagent is used in the enantioselective preparation of 4-substituted cyclohexenes by radical fragmentation of <i>o</i> -bromophenyl sulfoxides.	<p style="text-align: center;">A cis : trans = 1:3 MADP = Methylaluminium diphenoxide Ph 300 W sun lamp PhH, 10°C, 12 h 57%, er = 93:7</p>
C. Imboden, F. Villar, P. Renaud <i>Org. Lett.</i> 1999 , <i>1</i> , 873.	7 examples (yields 65-75%, %ee = 0, 70-86%) are reported.
Diethylaminotrimethylsilane	Reagent
The title reagent mediates the intermolecular self-aldo condensation of various naked aldehydes.	<p style="text-align: center;">A (0.5 eq) 50°C, 16 h 51%</p>
H. Hagiwara, H. Ono, N. Komatsubara, T. Hoshi, T. Suzuki, M. Ando <i>Tetrahedron Lett.</i> 1999 , <i>40</i> , 6627.	6 examples (yields 27-54%) are reported.
Hexabutylditin	Reagent
The title reagent is used in a one-pot method for the generation of tributylstannylmanganate. The subsequent delivery of the Bu3Sn moiety to a variety of organic substrates and unique stereoselective <i>trans</i> -addition behaviour to propargylic alcohols is demonstrated.	<p style="text-align: center;">(a) $i\text{-}PrMgCl$ (b) A (1.5 eq) Me_4MnLi_2 (1.5 eq) THF, 0°C, 30 min (c) $CH_2=CHCH_2Br$ (5 eq) 43%</p>
S. Usugi, J. Tang, H. Shinokubo, K. Oshima <i>Synlett</i> 1999 , 1417.	7 examples (yields 42-91%) are reported.

Methyl Cyanoformate	Reagent
The title reagent is used with a secondary alkylamine to efficiently transform ketones into <i>O</i> -methoxycarbonyl cyanohydrins. This functional group shows potential as a protecting group for ketones.	<p>D. Poirier, D. Berthiaume, R. P. Boivin <i>Synlett</i> 1999, 1423.</p>
	7 examples (yields 15-98%) are reported.
Dimethylamine-Borane Complex	Reagent
A Pd(0)-catalysed reduction of aryl perfluorosulfonates using A is reported.	<p>B. H. Lipshutz, D. J. Buzard, R. W. Vivian <i>Tetrahedron Lett.</i> 1999, 40, 6871.</p>
	12 examples (yields 71-96%) are reported.
Diphenylsilane	Reagent
The rhodium-catalysed reduction of esters to alcohols utilising the title reagent is reported.	<p>T. Ohta, M. Kamiya, K. Kusui, T. Michibata, M. Nobutomo, I. Furukawa <i>Tetrahedron Lett.</i> 1999, 40, 6963.</p>
	8 examples (yields 63-98%) are described.
N-Acetylcysteine	Reagent
A is used in the synthesis of amidines from nitriles. The reported procedure is mild and compatible with a large number of functional groups.	<p>U. E. W. Lange, B. Schäfer, D. Baucke, E. Buschmann, H. Mack <i>Tetrahedron Lett.</i> 1999, 40, 7067.</p>
	10 examples (yields 66-94%).
Bis(2,2,2-trifluoroethyl)-(2-oxopropyl)phosphonate	Reagent
The title reagent is used in a highly selective synthesis of (<i>Z</i>)- α,β -unsaturated ketones.	<p>W. Yu, M. Su, Z. Jin <i>Tetrahedron Lett.</i> 1999, 40, 6725.</p>
	7 examples (yields 81-98%, 3:1 $\leq Z:E \leq$ 100:0).