

**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, Derek Johnston, Philip Kocienski, Alexander Kuhl, Catherine McCusker, Robert Narquizian, and Sukhjinder Uppal of Glasgow University.


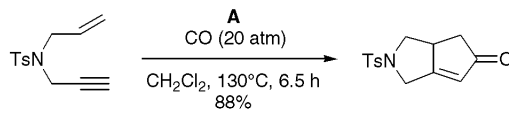
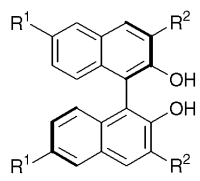
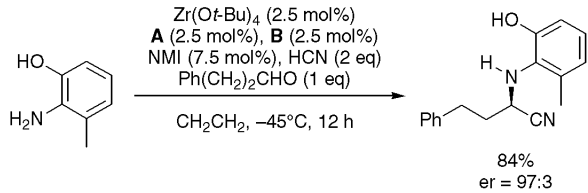

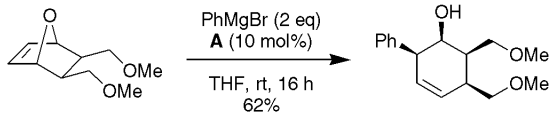
The journals regularly covered by the abstractors are:

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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  
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 Organometallics  
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 Tetrahedron  
 Tetrahedron Asymmetry and Tetrahedron Letters

Article Identifier:

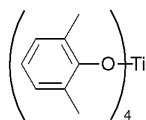
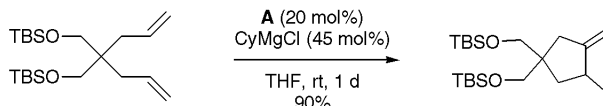
1437-210X,E;2000,0,06,0904,0909,ftx,en;X00600SS.pdf

Cobalt on Silica		Catalyst
The title reagent catalyses the Pauson-Khand reaction.	 <p><b>A</b></p>	 <p>88%</p> <p>6 examples (yields 11-96%) are reported.</p>
S.-W. Kim, S. U. Son, S. I. Lee, T. Hyeon, Y. K. Chung <i>J. Am. Chem. Soc.</i> <b>2000</b> , <i>122</i> , 1550.		
<i>(R)</i> -6,6'-Dibromo-1,1'-bi-naphthol [ <i>(R)</i> -6-Br-BINOL] / <i>(R)</i> -3,3'-Dibromo-1,1'-bi-naphthol [ <i>(R)</i> -3-Br-BINOL]		Catalyst
The title reagent pair is used to prepare a chiral zirconium binuclear catalyst for the catalytic asymmetric Strecker-type reaction of aldimines.	 <p><b>A</b> R<sup>1</sup> = Br, R<sup>2</sup> = H  <b>B</b> R<sup>1</sup> = H, R<sup>2</sup> = Br</p>	 <p>84% er = 97:3</p> <p>18 examples (yields 55-100%, %ee = 74-94%) are reported.</p>
H. Ishitani, S. Komiyama, Y. Hasegawa, S. Kobayashi <i>J. Am. Chem. Soc.</i> <b>2000</b> , <i>122</i> , 762.		
Iron(III) Chloride		Catalyst
The title reagent catalyses the carbometallation of olefins.	 <p><b>A</b></p>	 <p>62%</p> <p>21 examples (yields 4-96%) are reported.</p>
M. Nakamura, A. Hirai, E. Nakamura <i>J. Am. Chem. Soc.</i> <b>2000</b> , <i>122</i> , 978.		

## Titanium(IV) 2,6-Dimethylphenoxide

## Catalyst

**A** in combination with a reducing agent mediates the cycloisomerisation of 1,6- and 1,7-dienes.

**A**

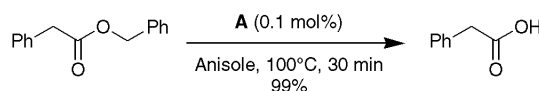
8 examples (yields 44-92%).

S. Okamoto, T. Livinghouse *J. Am. Chem. Soc.* **2000**, *122*, 1223.

## Scandium(III) Tris(trifluoromethanesulfonyl)methide

## Catalyst

The title reagent is a highly active homogeneous catalyst for the debenzylation of benzyl esters, benzyl ethers and *N*-benzylamides.

**A**

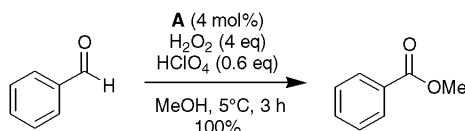
4 examples (yields 89-99%) are reported.

K. Ishihara, Y. Hiraiwa, H. Yamamoto *Synlett* **2000**, 80.

## Vanadium Pentoxide

## Catalyst

The title reagent catalyses the oxidative transformation of aldehydes to the corresponding esters.

**A**

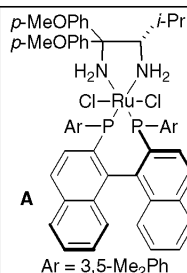
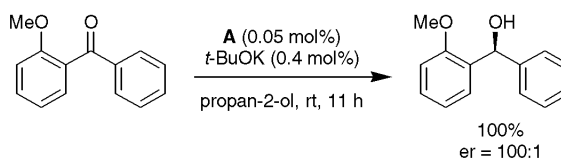
14 examples (yields 83-100%) are reported.

R. Gopinath, B. K. Patel *Org. Lett.* **2000**, *2*, 577.

## Chiral Ruthenium Catalyst

## Catalyst

The title reagent catalyses the asymmetric hydrogenation of *ortho*-substituted benzophenones and benzoylferrocene to chiral diarylmethanols.

**A**Ar = 3,5-Me<sub>2</sub>Ph

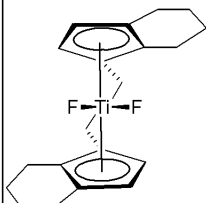
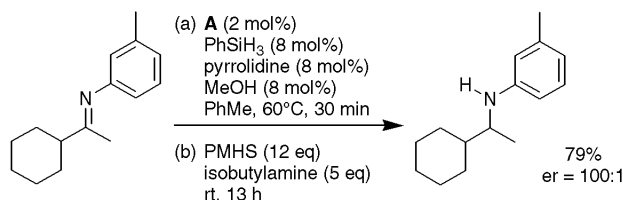
11 examples (yields 95-100%, %ee = 8, 47-99%) are reported.

T. Ohkuma, M. Koizumi, H. Ikehira, T. Yokozawa, R. Noyori *Org. Lett.* **2000**, *2*, 659.

Ethylene bis(η<sup>5</sup>-tetrahydroindenyl)titanium Difluoride ((EBTHI)TiF<sub>2</sub>)

## Catalyst

The title reagent catalyses the asymmetric reduction of *N*-aryl imines with polymethylhydrosiloxane (PMHS) to yield chiral amines.

**A**

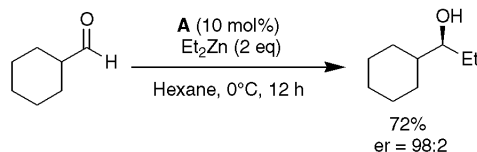
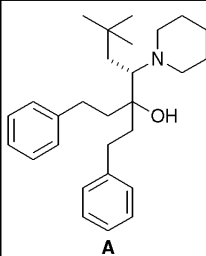
13 examples (yields 0, 63-100%, %ee = 6-99%) are reported.

M. C. Hansen, S. L. Buchwald *Org. Lett.* **2000**, *2*, 713.

## Catalyst

**M-[(S)-2-Hydroxy-1-neopentyl-4-phenyl-2-(2-phenylethyl)-butyl]-piperidine**

The title ligand catalyses the enantioselective addition of diethylzinc to aliphatic and aromatic aldehydes.



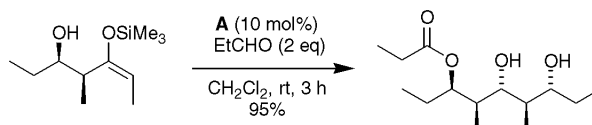
Y. Kawanami, T. Mitsue, M. Miki, T. Sakamoto, K. Nishitani *Tetrahedron* **2000**, *56*, 175.

8 examples (yields 64-91%, %ee = 85-97%) are reported.

## Catalyst

**Titanium(IV) Isopropoxide**

The title reagent catalyses a tandem aldol-Tischchenko reaction affording stereocontrolled polypropionate products.



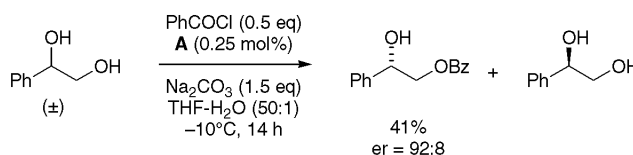
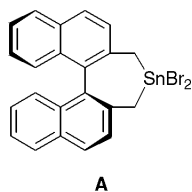
C. Delas, C. Moïse *Synthesis* **2000**, 251.

2 examples (yields 95%) are reported.

## Catalyst

**(S)-4,4-Dibromo-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]stannepin**

The title homochiral stannane catalyses the selective monobenzoylation of one enantiomer of racemic 1,2-diols.



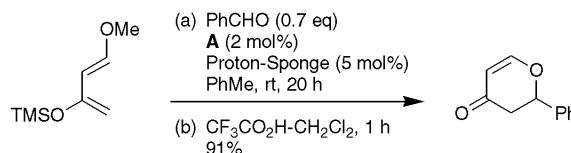
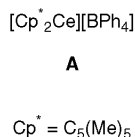
F. Iwasaki, T. Maki, O. Onomura, W. Nakashima, Y. Matsumura *J. Org. Chem.* **2000**, *65*, 996.

5 examples (yields 25-41%, %ee = 44-84%).

## Catalyst

**Bis(pentamethylcyclopentadienyl)cerium(III) Tetraphenylborate**

The title metallocenium complex catalyses hetero Diels-Alder reactions.



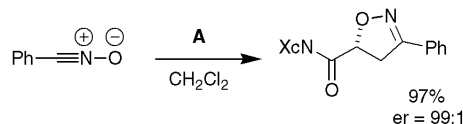
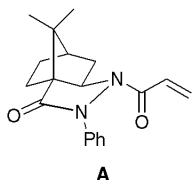
G. A. Molander, R. M. Rzasa *J. Org. Chem.* **2000**, *65*, 1215.

6 examples (yields 62-91%).

**Camphor-derived N-Acryloylhydrazide**

## Chiral Auxiliary

The title auxiliary reacts with various nitrile oxides to afford the cycloadducts with high diastereoselectivity. The auxiliary is removed using L-Selectride.

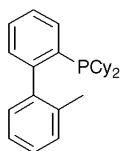
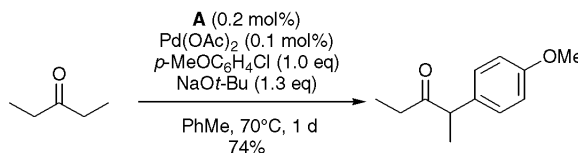


K.-S. Yang, J.-C. Lain, C.-H. Lin, K. Chen *Tetrahedron Lett.* **2000**, *41*, 1453.

14 examples (yields 75-97%, %ee = 96-98%) are reported.

**2-Methyl-2'-dicyclohexylphosphinobiphenyl****Ligand**

The title ligand is used in combination with Pd(OAc)<sub>2</sub> to catalyse the  $\alpha$ -arylation of ketones.

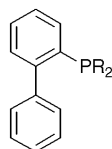
**A**

14 examples (yields 61-93%) are reported.

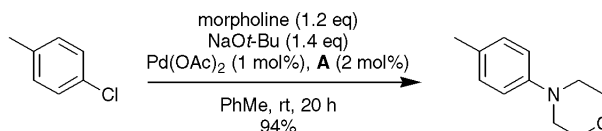
J. M. Fox, X. Huang, A. Chieffi, S. L. Buchwald  
*J. Am. Chem. Soc.* **2000**, *122*, 1360.

 **$\alpha$ -(Di-*tert*-butylphosphino)biphenyl and  $\alpha$ -(Di-cyclohexylphosphino)biphenyl****Ligand**

Palladium complexes supported by the title ligands are efficient catalysts for the catalytic amination of aryl halides, bromides and triflates.



**A** R = *t*-Bu  
**B** R = Cy

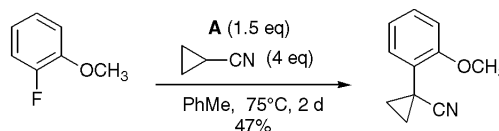
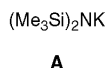


110 examples using **A** or **B** (yields 56-100%).

J. P. Wolfe, H. Tomori, J. P. Sadighi, J. Yin, S. L. Buchwald  
*J. Org. Chem.* **2000**, *65*, 1158.

**Potassium Bis(trimethylsilyl)amide (KHMSD)****Reagent**

The title reagent is used for the preparation of tertiary benzylic nitriles *via* the addition of secondary nitriles to fluoroarenes.

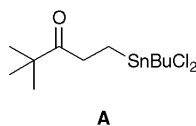
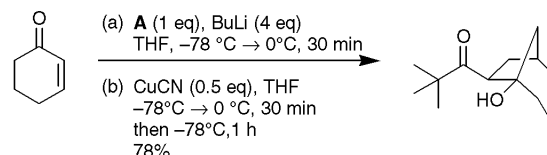


15 examples (yields 28-95%) are reported.

S. Caron, E. Vazquez, J. M. Wojcik  
*J. Am. Chem. Soc.* **2000**, *122*, 712.

**(4,4-Dimethyl-3-oxopentyl)(butyl)dichlorostannane****Reagent**

**A** undergoes transmetalation to the corresponding *Z*-dianion, which can be used in a tandem Michael- and 1,2-addition sequence.

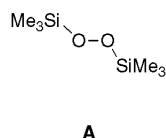
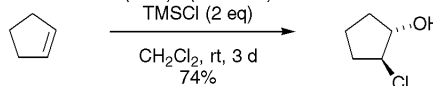
**A**

10 examples (yields 30-78%).

I. Ryu, H. Nakahira, M. Ikebe, N. Sonoda, S.-y. Yamato, M. Komatsu  
*J. Am. Chem. Soc.* **2000**, *122*, 1219.

**Bis(trimethylsilyl) Peroxide (BTSP)****Reagent**

Hydroxyhalogenation of C-C double bonds by **A** in combination with a trimethylsilyl halide is reported. Use of TMSOAc leads to *trans*- $\beta$ -acetoxo diols.

**A**

8 examples (yields 66-92%).

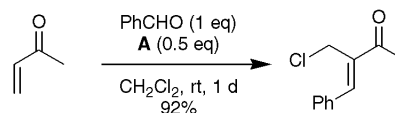
I. Sakurada, S. Yamasaki, R. Göttlich, T. Iida, M. Kanai, M. Shibasaki  
*J. Am. Chem. Soc.* **2000**, *122*, 1245.

## Reagent

## Titanium(IV) Tetrachloride

The title reagent mediates the vicinal difunctionalisation of  $\alpha,\beta$ -unsaturated acyclic ketones to synthesise multifunctional trisubstituted alkenes.

TiCl<sub>4</sub>  
A



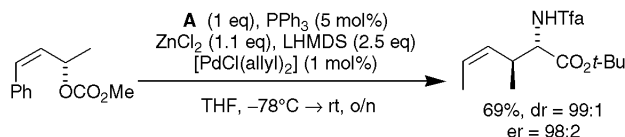
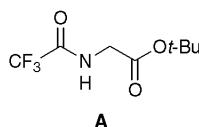
G. Li, J. Gao, H.-X. Wei, M. Enright *Org. Lett.* **2000**, *2*, 617.

8 examples (yields 62-92%) are reported.

## Reagent

N-Trifluoroacetyl Glycine *tert*-Butyl Ester

The highly reactive chelated amino acid ester enolate of **A** is used as a nucleophile in palladium-catalysed allylic alkylations in which the  $\pi$ - $\sigma$ - $\pi$ -isomerisation of  $\pi$ -alkyl intermediates can be suppressed almost completely.



U. Kazmaier, F. L. Zumpe *Angew. Chem. Int. Ed.* **2000**, *39*, 802.

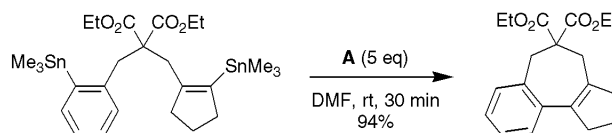
4 examples (yields 69-87%, %de = 85-98%, %ee = 96-97%).

## Reagent

## Copper(I) Chloride

The title reagent induces the intramolecular coupling of aryl- and alkenyltrimethylstannanes to form five-, six-, and seven-membered rings.

CuCl  
A



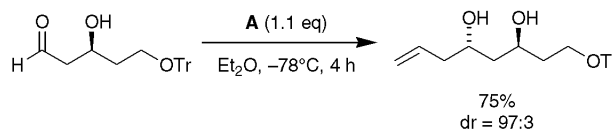
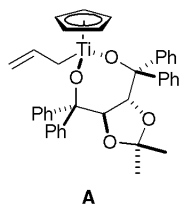
E. Piers, J. G. K. Yee, P. L. Gladstone *Org. Lett.* **2000**, *2*, 481.

9 examples (yields 62-97%) are reported.

## Reagent

## Chiral Allyltitanium TADDOLate

The title reagent is used for the enantioselective allyltitanation of chiral  $\beta$ -hydroxy aldehydes to afford syn- or anti-1,3-diols.



S. BouzBouz, J. Cossy *Org. Lett.* **2000**, *2*, 501.

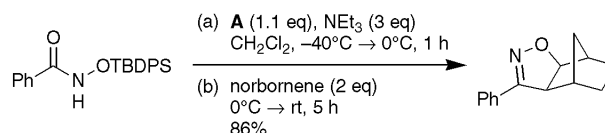
5 examples (yields 75-85%, %de = 93-96%) are reported.

## Reagent

## Trifluoromethanesulfonic Anhydride

The title reagent is used to generate nitrile oxides from *O*-silylated hydroxamic acids. Under mild conditions in the presence of olefins, *O*-silylated hydroxamic acids afford isoxazoline cycloadducts.

Tf<sub>2</sub>O  
A

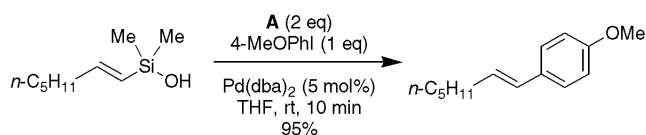


D. Muri, J. W. Bode, E. M. Carreira *Org. Lett.* **2000**, *2*, 539.

6 examples (yields 54-88%) are reported.

**Tetrabutylammonium Fluoride (TBAF)****Reagent**

The title reagent mediates palladium(0)-catalysed cross coupling between alkenylsilanols and aryl or vinyl iodides. Up to 5% of the geometrical isomer is observed from isomerically pure starting materials.

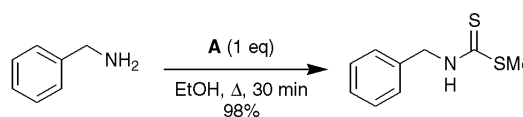
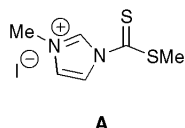


S. E. Denmark, D. Wehrli *Org. Lett.* **2000**, *2*, 565.

26 examples (yields 64-95%) are reported.

**3-Methyl-1-(methylthiocarbonyl)-imidazolium iodide****Reagent**

The title compound acts as an efficient methylthiocarbonyl and thiocarbonyl transfer reagent in the synthesis of dithiocarbamates and thioureas. The conditions provide a mild, less hazardous alternative to thiophosgene.

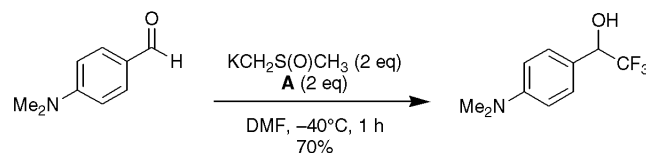


P. K. Mohanta, S. Dhar, S. K. Samal, H. Ila, H. Junjappa *Tetrahedron* **2000**, *56*, 629.

33 examples (yields 60-97%) are reported.

**Fluoroform****Reagent**

**A** is used in the preparation of trifluoromethylcarbinols from aldehydes.

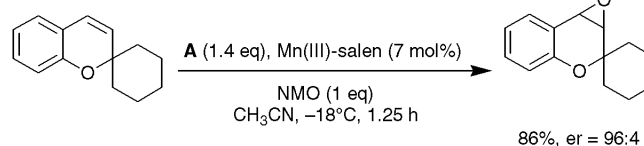
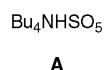


B. Folléas, I. Marek, J.-F. Normant, L. Saint-Jalmes *Tetrahedron*, **2000**, *56*, 275.

9 examples (yields 42-72%) are reported.

**Tetrabutylammonium Monopersulfate****Reagent**

The title reagent acts as an oxidant in a series of Mn(III)-salen catalysed enantioselective epoxidation reactions. The reagent shows advantages over the commonly used oxone in that it is readily soluble in various solvents and can be used to oxidise sensitive compounds.

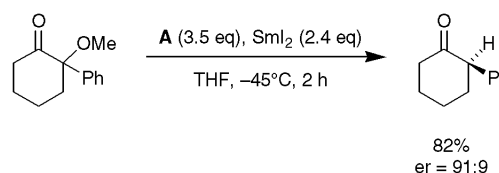
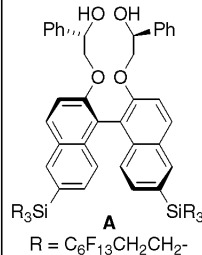


P. Pietikäinen *Tetrahedron* **2000**, *56*, 417.

5 examples (yields 72-97%, %ee = 72-93%).

**Chiral Fluorous BINOL Derivative [(R,S)-FDHPEB]****Reagent**

**A** is used as a fluorous chiral proton source in the enantioselective protonation of a samarium enolate.



Y. Nakamura, S. Takeuchi, Y. Ohgo, D. P. Curran *Tetrahedron* **2000**, *56*, 351.

1 example is reported. **A** can be readily recovered and recycled.