

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

The journals regularly covered by the abstractors are:

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Article Identifier:

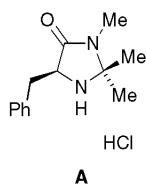
1437-210X,E;2000,0,10,1341,1346,ftx,en;X01000SS.pdf

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

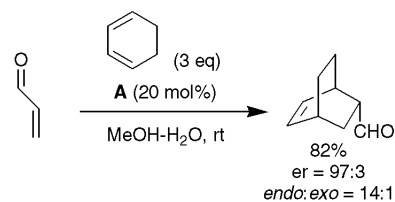
### (S)-4-Benzyl-1,2,2-trimethylimidazolin-5-one

Catalyst

Amine **A** catalyses enantioselective Diels-Alder reactions.



K. A. Ahrendt, C. J. Borths, D. W. C. MacMillan  
*J. Am. Chem. Soc.* **2000**, *122*, 4243.



12 examples (yields 72-99%, %ee = 83-96%) are reported.

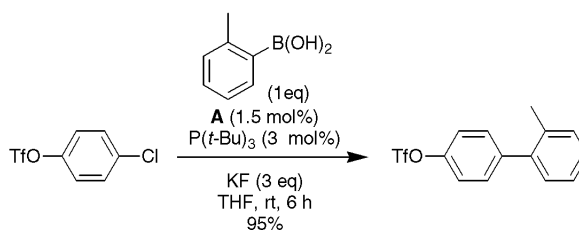
### Tris(dibenzylideneacetone)dipalladium(0)

Catalyst

The title reagent is used in combination with  $P(t\text{-Bu})_3$  or  $\text{PCy}_3$  to prepare versatile catalysts for Suzuki cross-coupling of arylboronic acids with aryl and vinyl halides and triflates. Chemoselectivity is achieved by the use of either **A**/ $P(t\text{-Bu})_3$  for halides or **A**/ $\text{PCy}_3$  for triflates.



A. F. Littke, C. Dai, G. C. Fu *J. Am. Chem. Soc.*  
**2000**, *122*, 4020.

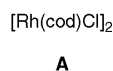


51 examples (yields 75-99%) are reported.

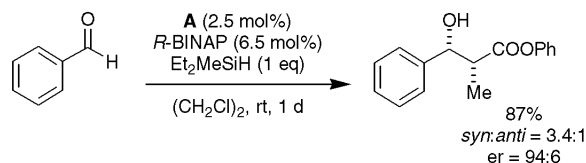
### Bis[chloro(cyclooctadienyl)rhodium]

Catalyst

The title reagent catalyses enantioselective reductive aldol reactions.



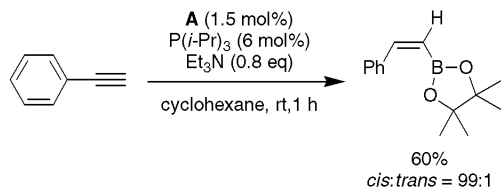
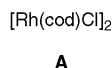
S. J. Taylor, M. O. Duffey, J. P. Morken *J. Am. Chem. Soc.* **2000**, *122*, 4528.



6 examples (yields 0, 54-82%, %ee<sub>syn</sub> = 45-88%, %ee<sub>anti</sub> = 7-99%, syn:anti = 1.8:1-5.1:1) are reported.

## Catalyst

The title reagent catalyses the *trans*-hydroboration of terminal alkynes to afford (*Z*)-1-alkenylboron compounds.



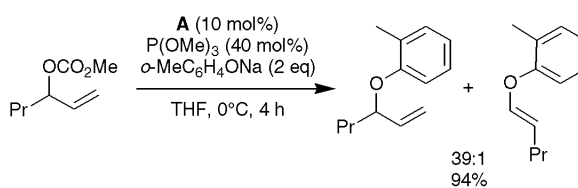
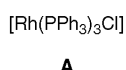
T. Ohmura, Y. Yamamoto, N. Miyaura *J. Am. Chem. Soc.* **2000**, *122*, 4990.

13 examples (yields 59-86%, *cis:trans* = 89:11-99:1).

## Chlorotris(triphenylphosphine)rhodium(I)

## Catalyst

The title reagent catalyses allylic alkylation of *ortho*-substituted sodium phenolates.



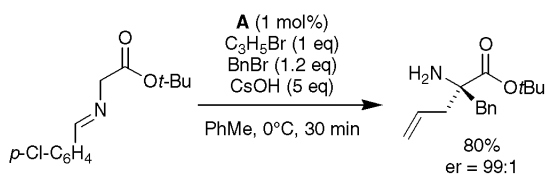
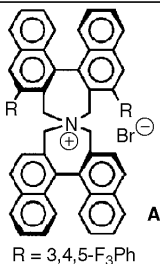
P. A. Evans, D. K. Leahy *J. Am. Chem. Soc.* **2000**, *122*, 5012.

12 examples (yield 80-95%) are reported.

## Chiral Phase-Transfer Catalyst

## Catalyst

**A** acts as a chiral phase-transfer catalyst.



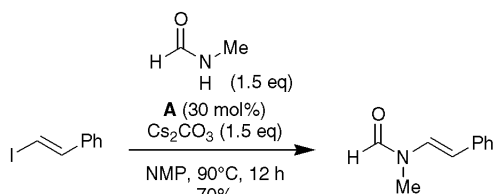
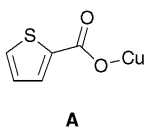
T. Ooi, M. Takeuchi, M. Kameda, K. Maruoka *J. Am. Chem. Soc.* **2000**, *122*, 5228.

12 examples (yields 58-85%, %ee = 92-99%).

## Copper(I) Thiophenecarboxylate (CuTC)

## Catalyst

The title reagent catalyses the substitution of vinyl iodides and amides for the preparation of enamides.



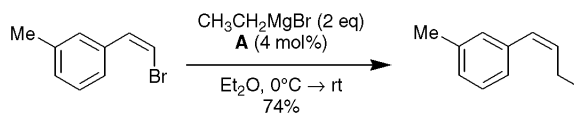
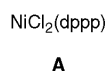
R. Shen, J. A. Porco, Jr *Org. Lett.* **2000**, *2*, 1333.

9 examples (yields 36-75%) are reported.

## [1,3-Bis(diphenylphosphino)propane]dichloronickel(II)

## Catalyst

The title reagent is used in the nickel-catalysed cross-coupling reaction of (1*Z*)-1-bromoalkenes with alkyl Grignard reagents.

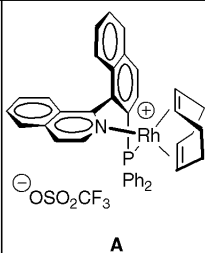


J. Uenishi, R. Kawahama, Y. Izaki, O. Yonemitsu *Tetrahedron* **2000**, *56*, 3493.

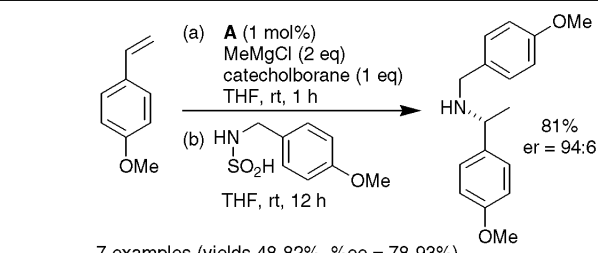
13 examples (yields 58-85%) are reported.

**(S)-[1-(2-Diphenylphosphino-1-naphthyl)isoquinonline](cyclooctadiene)rhodium(I) Trifluoromethanesulfonate** **Catalyst**

The title reagent is employed in a two-step procedure comprising the catalytic asymmetric hydroboration/amination of alkenes.



E. Fernandez, K. Maeda, M. W. Hooper, J. M. Brown *Chem. Eur. J.* **2000**, 1840.

**Palladium(II) Acetate / Triisopropylphosphite** **Catalyst**

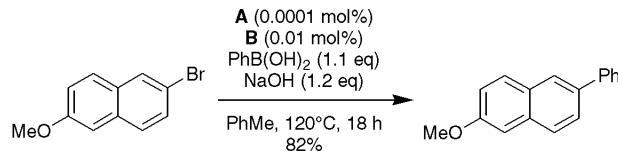
The title reagent pair catalyse the Suzuki reaction of various aryl chlorides and bromides.

Pd(OAc)<sub>2</sub>

**A**

P(Oi-Pr)<sub>3</sub>

**B**

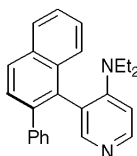


A. Zapf, M. Beller *Chem. Eur. J.* **2000**, 1830.

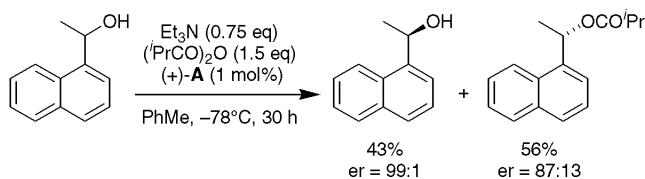
11 examples (yields 45-94%) are reported.

**(±)-Diethyl[3-(2-phenylnaphthyl)(4-pyridyl)]amine** **Catalyst**

The title reagent catalyses nonenzymatic enantioselective acylations.



A. C. Spivey, T. Fekner, S. E. Spey *J. Org. Chem.* **2000**, 65, 3154.



9 examples (%ee<sub>alcohol</sub> = 18-97%, %ee<sub>ester</sub> = 72-84%).

**Palladium(II) Acetate / Triphenylphosphine** **Catalyst**

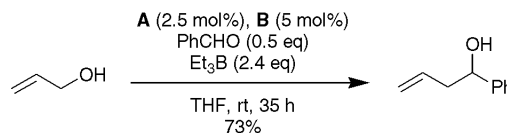
The title reagent pair, in the presence of triethylborane, promotes the allylation of benzaldehyde with a variety of allyl alcohols in good yield.

Pd(OAc)<sub>2</sub>

**A**

PPh<sub>3</sub>

**B**

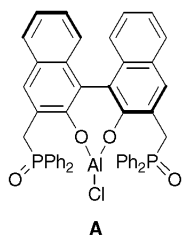


M. Kimura, T. Tomizawa, Y. Horino, S. Tanaka, Y. Tamaru *Tetrahedron Lett.* **2000**, 41, 3627.

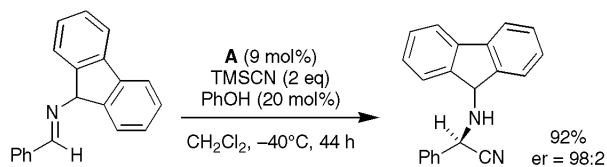
6 optimized examples (yields 57-81%) are reported.

**Chiral Lewis Acid** **Catalyst**

The title reagent catalyses the asymmetric Strecker-type reaction.



M. Takamura, Y. Hamashima, H. Usuda, M. Kanai, M. Shibasaki *Angew. Chem. Int. Ed.* **2000**, 39, 1650.

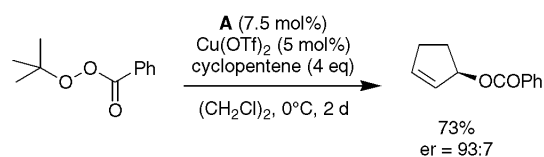
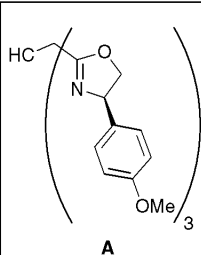


13 examples (yields 66-97%, %ee = 70-96%) are reported.

## Ligand

## Tridentate Tris(oxazoline) Ligand

The title ligand is an efficient ligand for copper-mediated asymmetric oxidation (Kharasch-Sosnovsky reaction) of cycloalkenes.



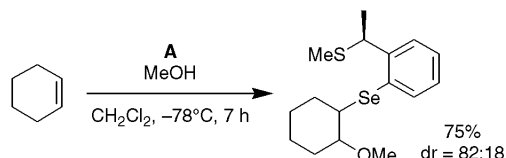
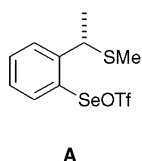
Y. Kohmura, T. Katsuki *Tetrahedron Lett.* **2000**, *41*, 3941.

4 examples (yields 25-80%, %ee = 82-88%) are reported.

## Reagent

## [(S)-1-(Methylthio)ethyl]phenylselenenyl Trifluoromethanesulfonate

The title reagent is used for the asymmetric selenomethoxylation and selenohydroxylation of alkenes.



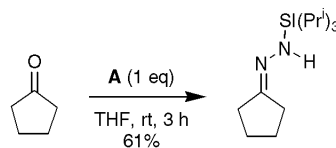
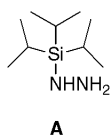
M. Tiecco, L. Testaferri, L. Bagnoli, F. Marini, A. Temperini, C. Tomassini, C. Santi *Tetrahedron Lett.* **2000**, *41*, 3241.

11 examples (yields 72-87%, 82:18 ≤ dr ≤ 96:4) are reported.

## Reagent

## Triisopropylsilylhydrazine

The title reagent converts aldehydes and ketones to their triisopropylsilyl (TIPS) hydrazones.



J. C. Justo de Pomar, J. A. Soderquist *Tetrahedron Lett.* **2000**, *41*, 3285.

6 examples (yields 61-86%, 75:25 ≤ E:Z ≤ 89:11) are reported.

## Reagent

## Ferric Chloride / Acetic Anhydride

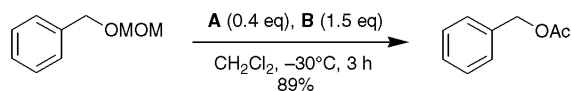
The title reagents are involved in the facile transformation of MOM-protected alcohols into the corresponding acetates.

FeCl<sub>3</sub>

**A**

Ac<sub>2</sub>O

**B**



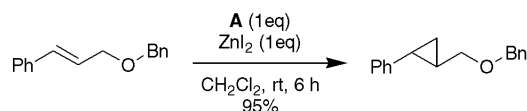
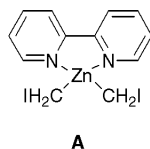
M. P. Bosch, I. Petschen, A. Guerrero *Synthesis* **2000**, 300.

12 examples (yields 20-95%).

## Reagent

## Bisiodomethyl-1,1'-dipyridyl Zinc

**A** is an isolable and storable haloalkylzinc reagent used for cyclopropanation reactions.



A. B. Charette, J.-F. Marcoux, C. Molinaro, A. Beauchemin, C. Brochu, E. Isabel *J. Am. Chem. Soc.* **2000**, *122*, 4508.

3 examples (yield 88-95%) are reported.

Gallium(III) Chloride		Reagent
<p><b>A</b> serves as a <math>\pi</math>-bond coordinating Lewis-acid, which provides a useful level of chelation control to heteroatoms.</p>	<p>GaCl<sub>3</sub> <b>A</b></p>	<p>6 examples (yields 49–89%) are reported.</p>
<p>N. Asao, T. Asano, T. Ohishi, Y. Yamamoto <i>J. Am. Chem. Soc.</i> <b>2000</b>, <i>122</i>, 4817.</p>		

Diethylzirconocene		Reagent
<p>The title reagent is used in the coupling reaction of azazirconacyclopentadienes with alkynes to form substituted pyridines.</p>	<p>Cp<sub>2</sub>ZrEt<sub>2</sub> <b>A</b></p>	<p>10 examples (yields 42–66%) are reported.</p>
<p>T. Takahashi, F.-Yu Tsai, M. Kotora <i>J. Am. Chem. Soc.</i> <b>2000</b>, <i>122</i>, 4994.</p>		

Trimethylaluminium		Reagent
<p>The title reagent is used in a one-step procedure tethering usually nonreactive dienes and dienophiles in intramolecular Diels-Alder reactions.</p>	<p>AlMe<sub>3</sub> <b>A</b></p>	<p>8 examples (yields 0, 21–77%) are reported.</p>
<p>F. Bertozzi, R. Olsson, T. Frejd <i>Org. Lett.</i> <b>2000</b>, <i>2</i>, 1283.</p>		

Zirconium(IV) Chloride / Sodium Borohydride		Reagent
<p>The title reagent pair reduces nitro compounds to primary amines.</p>	<p>ZrCl<sub>4</sub> <b>A</b>  NaBH<sub>4</sub> <b>B</b></p>	<p>10 examples (yields 78–92%) are reported.</p>
<p>K. P. Chary, S. R. Ram, D. S. Iyengar <i>Synlett</i> <b>2000</b>, 683.</p>		

Cationic Ruthenium Allenylidene Complex		Reagent
<p>The title reagent acts as a precatalyst for various ring-closing metathesis (RCM) reactions. The counterion affects selectivity and reactivity.</p>	<p><b>A</b></p>	<p>13 examples (yields 40–93%) are reported.</p>
<p>A. Fürstner, M. Liebl, C. W. Lehmann, M. Picquet, R. Kunz, C. Bruneau, D. Touchard, P. H. Dixneuf <i>Chem. Eur. J.</i> <b>2000</b>, 1847.</p>		

Cerium(III) Chloride Heptahydrate / Sodium Iodide		Reagent
The title reagent pair mediates a simple and efficient conversion of alcohols into alkyl iodides.	<p><math>\text{CeCl}_3 \cdot 7\text{H}_2\text{O}</math></p> <p><b>A</b></p> <p>NaI</p> <p><b>B</b></p>	<p>14 examples (yields 69-93%) are reported.</p>
<p>M. D. Deo, E. Marcantoni, E. Torregiani, G. Bartoli, M. C. Bellucci, M. Bosco, L. Sambri <i>J. Org. Chem.</i> <b>2000</b>, <i>65</i>, 2830.</p>		
Diiodosilane		Reagent
The title reagent mediates mild and efficient conversion of carbamates to ureas via isocyanates.	<p><math>\text{SiI}_2\text{H}_2</math></p> <p><b>A</b></p>	<p>10 examples (yields 0, 57-94%) are reported.</p>
<p>S. Gastaldi, S. M. Weinreb, D. Stien <i>J. Org. Chem.</i> <b>2000</b>, <i>65</i>, 3239.</p>		
Potassium Trimethylsilylanolate		Reagent
The title reagent mediates the hydrolysis of nitriles to primary amides.	<p><math>\text{K}^+ [\text{Me}_3\text{SiO}]^-</math></p> <p><b>A</b></p>	<p>9 examples (yields 32, 67-83%) are reported.</p>
<p>K. J. Merchant <i>Tetrahedron Lett.</i> <b>2000</b>, <i>41</i>, 3747.</p>		
Sodium (-)-(S)-1-(2,4,6-Triisopropylphenyl)ethoxide		Reagent
Michael addition of the title reagent to an $\alpha,\beta$ -unsaturated ketone, followed by Wittig methylenation gives enantiomerically pure (>99% ee) diene.	<p><b>A</b></p>	<p>1 example (%ee &gt;99%) is reported.</p>
<p>V. Narkevitch, K. Schenk, P. Vogel <i>Angew. Chem. Int. Ed.</i> <b>2000</b>, <i>39</i>, 1806.</p>		
Trichloroacetic Acid / Sodium Trichloroacetate		Reagent
The title reagent pair is used in a one-pot, three step conversion of aldehydes to vinyl dichlorides.	<p><math>\text{Cl}_3\text{CCO}_2\text{H}</math></p> <p><b>A</b></p> <p><math>\text{Cl}_3\text{CCO}_2\text{Na}</math></p> <p><b>B</b></p>	<p>9 examples (yields 85-95%) are reported.</p>
<p>Z. Wang, S. Campagna, G. Xu, M. E. Pierce, J. M. Fortunak, P. N. Confalone <i>Tetrahedron Lett.</i> <b>2000</b>, <i>41</i>, 4007.</p>		