

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.

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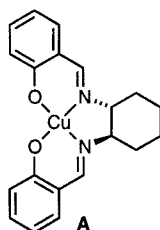
The journals regularly covered by the abstractors are:

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 1
Synlett
Synthesis
Tetrahedron
Tetrahedron Asymmetry and Tetrahedron Letters

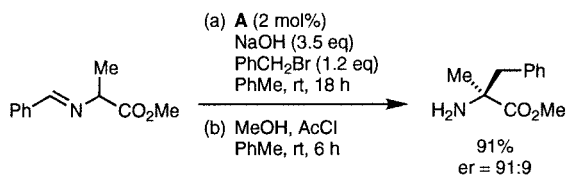
Copper(II) (Salen) Complex

Catalyst

The title complex is used as a phase transfer catalyst for the asymmetric synthesis of α -methyl α -amino acids.



Y. N. Belokon, R. G. Davies, M. North
Tetrahedron Lett. **2000**, 41, 7245.

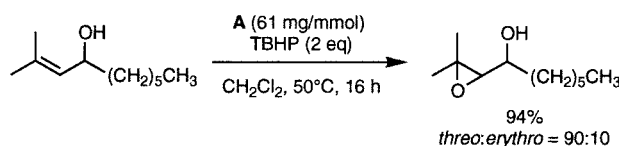
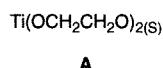


12 examples (yields 0, 42-95%, %ee = 43-86%) are reported.

Polymeric Titanium(IV) Glycolate

Catalyst

Reagent **A** catalyses the epoxidation of allylic alcohols by *t*-butyl hydroperoxide (TBHP) under heterogeneous conditions. One other Ti(IV) catalyst is shown.



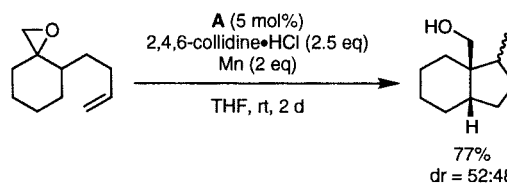
A. Massa, A. Scettri *Synlett* **2000**, 1348.

4 examples (yields 50-95%) are reported.

Titanocene Dichloride

Catalyst

The title reagent catalyses 5-*exo* cyclisations of epoxides to afford substituted cyclopentanes and tetrahydrofurans.

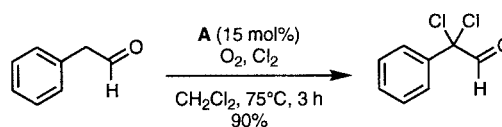
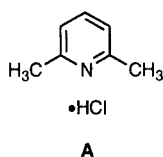


A. Gansauer, M. Pierobon *Synlett* **2000**, 1357.

11 examples (yields 54-90%) are reported.

2,6-Lutidine Hydrochloride**Catalyst**

The title reagent catalyses the chlorination of aldehydes with chlorine for the preparation of 2,2-dichloroaldehydes.

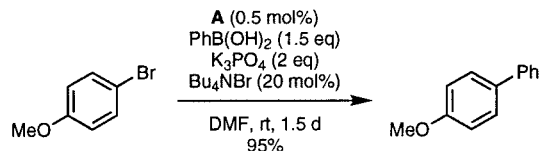
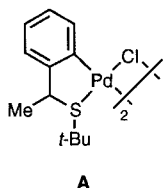


F. Bellesia, L. De Buyck, F. Ghelfi, E. Libertini, U. M. Pagnoni, F. Roncaglia *Tetrahedron* **2000**, *56*, 7507.

6 examples (yields 90-98%) are reported.

Sulfur-Containing Palladacycle**Catalyst**

Palladacycle **A** is a catalyst precursor for the Suzuki cross-coupling reaction of aryl halides with phenylboronic acid under mild conditions.

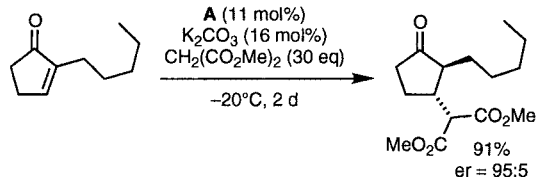
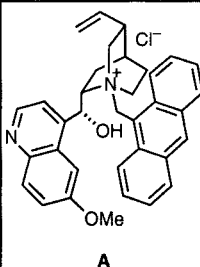


D. Zim, A. S. Gruber, G. Ebeling, J. Dupont, A. L. Monteiro *Org. Lett.* **2000**, *2*, 2881.

19 examples (yields 13-99%) are reported.

N-Methylantracenyloquininium Chloride**Catalyst**

The title reagent promotes the Michael addition of dimethyl malonate to enones by asymmetric solid-liquid phase-transfer catalysis in solvent-free conditions.

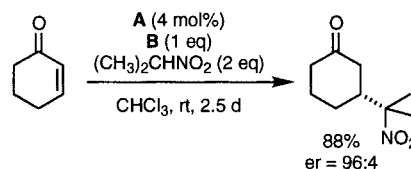
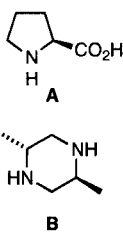


T. Perrard, J.-C. Plaquevent, J.-R. Desmurs, D. Hebraut *Org. Lett.* **2000**, *2*, 2959.

1 example (yield 91%, %ee = 90%) is reported.

L-Proline / trans-2,5-Dimethylpiperazine**Catalyst**

The title reagent pair catalyse the asymmetric conjugate addition of nitroalkanes to cycloalkenones.

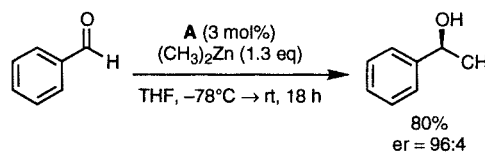
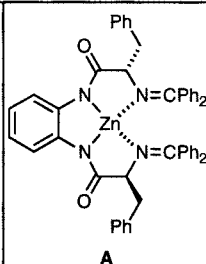


S. Hanessian, V. Pham *Org. Lett.* **2000**, *2*, 2975.

15 examples (yields 30-88%, %ee = 62-93%) are reported.

C₂-Symmetric Zinc(II)-L-Phe-L-Phe Complex**Catalyst**

Reagent **A** catalyses the enantioselective addition of dialkylzincs to aliphatic and aromatic aldehydes.



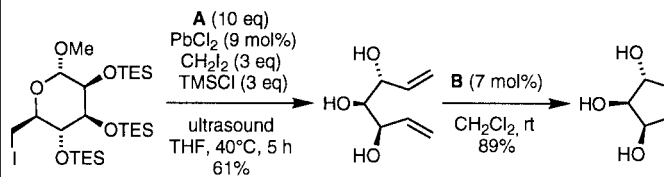
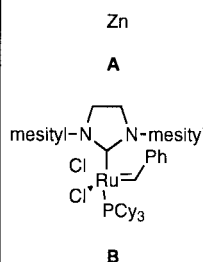
B. D. Dangel, R. Polt *Org. Lett.* **2000**, *2*, 3003.

4 examples (yields 27-80%, %ee = 86-96%) are reported.

Zinc / Ruthenium Carbene Catalyst

Catalyst

The carbocyclisation of carbohydrates is accomplished by a novel **A**-mediated domino reaction to give functionalised dienes followed by **B**-catalysed ring-closing olefin metathesis.



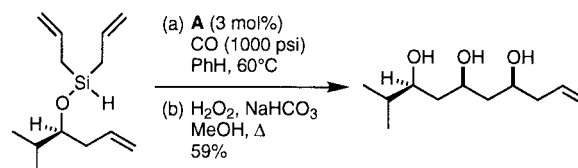
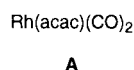
L. Hyltoft, R. Madsen *J. Am. Chem. Soc.* **2000**, *122*, 8444.

16 examples of diene formation (yields 54-100%) and 8 examples of RCM (yields 56-95%) are reported.

(Acetylacetonato)dicarbonylrhodium(I)

Catalyst

The title reagent catalyses tandem intramolecular silylformylation-allylsilylation of diallylsilanes in an approach to polyol synthesis.



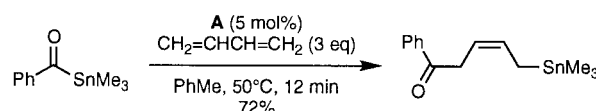
M. J. Zacuto, J. L. Leighton *J. Am. Chem. Soc.* **2000**, *122*, 8587.

5 examples (yields 45-65%) are reported.

Bis(1,5-cyclooctadiene)nickel(0)

Catalyst

The title reagent catalyses the stereoselective acylstannylation of 1,3-dienes. Transformation of the resulting ϵ -oxoallylstannanes to unconjugated enones are also reported.



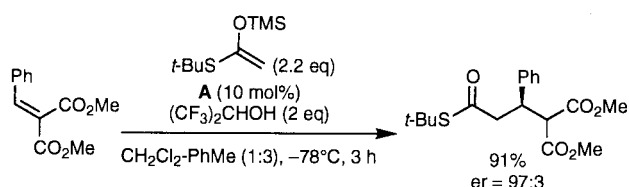
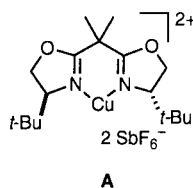
E. Shirakawa, Y. Nakao, H. Yoshida, T. Hiyama *J. Am. Chem. Soc.* **2000**, *122*, 9030.

11 examples (yields 36-86%) are reported.

C₂-Symmetric Bis(oxazoline)-Copper(II) Complex

Catalyst

The title reagent catalyses the enantioselective Mukaiyama Michael reaction of alkylidene malonates and enolsilanes.



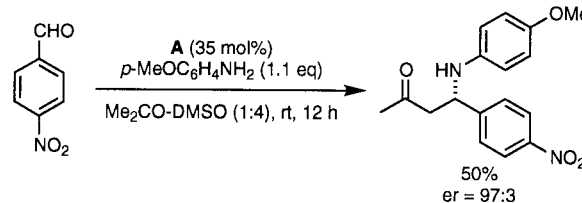
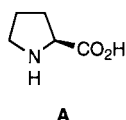
D. A. Evans, T. Rovis, M. C. Kozlowski, C. W. Downey, J. S. Tedrow *J. Am. Chem. Soc.* **2000**, *122*, 9134.

19 examples (yields 10-99%, %ee = 0-99%) are reported.

L-Proline

Catalyst

The title reagent catalyses the enantioselective three-component Mannich reaction.

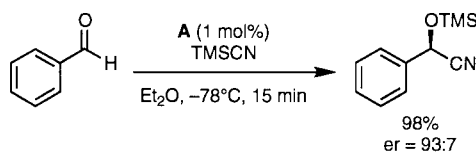
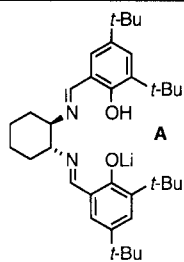


B. List *J. Am. Chem. Soc.* **2000**, *122*, 9336.

7 examples (yields 35-90%, %ee = 70-96%) are reported.

Mono Lithium Salt of (*R,R*)-(-)-*N,N'*-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine [(*R,R*)-(-)-SALEN] **Catalyst**

The title reagent catalyses the asymmetric addition of trimethylsilylcyanide to aldehydes to afford TMS ethers of cyanohydrins.

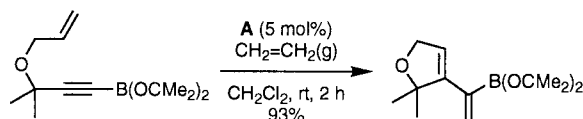
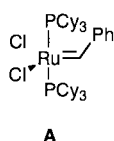


I. P. Holmes, H. B. Kagan *Tetrahedron Lett.* **2000**, *41*, 7457.

13 examples (yields 64-99%, %ee = 0-97%) are reported.

Grubbs' Catalyst**Catalyst**

The title reagent catalyses enyne metathesis of acetylenic boronates for the construction of cyclic 1,3-dialkenylboronic esters.

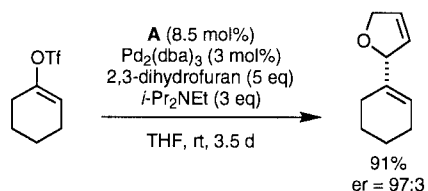
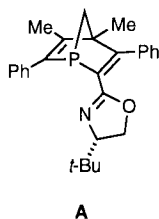


J. Renaud, C.-D. Graf, L. Oberer *Angew. Chem. Int. Ed.* **2000**, *39*, 3101.

9 examples (yields 65-95%) are reported.

Bidentate N,P Ligand**Ligand**

Ligand **A** is applied in the palladium-catalysed asymmetric allylation and Heck reaction. **A** is from a new class of phosphine-oxazoline ligands, bearing a chiral phosphanorborniadienyl (P-donor) and an oxazoline (N-donor).

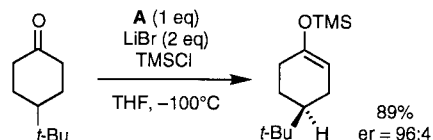
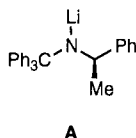


S. R. Gilbertson, D. G. Genov, A. L. Rheingold *Org. Lett.* **2000**, *2*, 2885.

The synthesis of **A** and 2 examples of application (yields 91-100%, %ee = 93-94%) are reported.

Lithium *N*-Trityl-*N*-(*R*)-1-Phenethylamide**Reagent**

The title reagent is a readily available and useful base for the enantioselective formation of chiral enolates from achiral ketones.

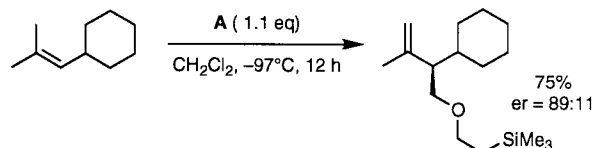
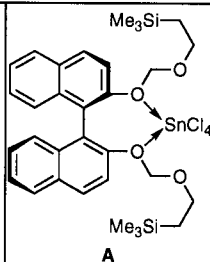


J. Busch-Petersen, E. J. Corey *Tetrahedron Lett.* **2000**, *41*, 6941.

4 examples (yields 50-89%, %ee = 89-92%) are reported.

(*R*)-2,2'-Bis[2-(trimethylsilyl)ethoxymethoxy]-1,1'-binaphthyl-Tin Tetrachloride Complex [(*R*)-BINOL-(SEM)₂•SnCl₄] **Reagent**

The title reagent is used for the enantioselective Prins reaction (acetal-ene reaction) of trisubstituted alkenes to afford optically active homoallylic ethers.



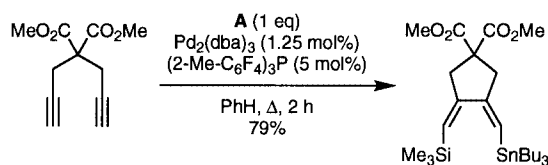
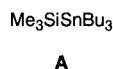
K. Ishihara, H. Nakamura, H. Yamamoto *Synlett* **2000**, 1245.

4 examples (yields 75-92%, %ee = 73-84%) are reported.

Sodium Bromate / Sodium Hydrosulfite		Reagent
<p>The title reagent pair is used for the chemoselective cleavage of benzyl ether protecting groups in the presence of benzyloxycarbonyl functions.</p>	<p>NaBrO₃ A Na₂S₂O₄ B</p>	<p>7 examples (yields 68-95%) are reported.</p>
<p>M. Adinolfi, L. Guariniello, A. Iadonisi, L. Mangoni <i>Synlett</i> 2000, 1277.</p>		
Tetrabutylammonium Fluoride / Acetic Acid		Reagent
<p>The title reagent pair selectively deprotects <i>t</i>-butyldiphenylsilyl ethers in the presence of <i>t</i>-butyldimethylsilyl ethers.</p>	<p>Bu₄NF A AcOH B</p>	<p>4 examples (yields 68-100%) are reported.</p>
<p>S. Higashibayashi, K. Shinko, T. Ishizu, K. Hashimoto, H. Shirahama, M. Nakata <i>Synlett</i> 2000, 1306.</p>		
(3 <i>aR</i> ,7 <i>aR</i>)-2-Allyloctahydro-1 <i>H</i> -1,3-dimethyl-1,3,2-benzadiazaphosphole 2-Oxide		Reagent
<p>The anion derived from A is used in asymmetric 1,4-addition reactions to α,β-unsaturated carbonyl compounds.</p>	<p>A</p>	<p>12 examples (yields 48-93%) are reported.</p>
<p>S. Hanessian, A. Gomtsyan, N. Malek <i>J. Org. Chem.</i> 2000, <i>65</i>, 5623.</p>		
(R,R)-5,6-Diphenyl-1,4-dioxan-2-one		Reagent
<p>The boron enolate of A undergoes asymmetric aldol reactions with aldehydes to give protected <i>anti</i>-1,2-diols.</p>	<p>A</p>	<p>8 examples (yields 70-92%, %de = 60-90%) are reported.</p>
<p>M. B. Andrus, B. B. V. S. Sekhar, E. L. Meredith, N. K. Dalley <i>Org. Lett.</i> 2000, <i>2</i>, 3035.</p>		
1,3-Dichloro-5,5-dimethylhydantoin		Reagent
<p>The title reagent is used in a one-pot preparation of chiral 4,5-disubstituted oxazolidin-2-ones utilising a modified Sharpless asymmetric aminohydroxylation of β-substituted styrene derivatives followed by base-mediated ring closure.</p>	<p>A</p>	<p>8 examples (yields 28-81%, %ee = 81-98%) are reported.</p>
<p>N. S. Barta, D. R. Sidler, K. B. Somerville, S. A. Weissman, R. D. Larsen, P. J. Reider <i>Org. Lett.</i> 2000, <i>2</i>, 2821.</p>		

(Trimethylsilyl)tributylstannane**Reagent**

The title reagent mediates the cyclisation of 1,6-diyne to afford chiral (Z,Z)-1,3-dienes. The helical chirality in 1,4-disubstituted (Z,Z)-1,3-dienes is demonstrated.

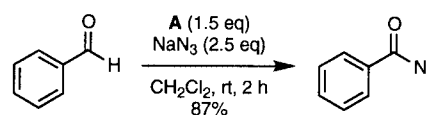
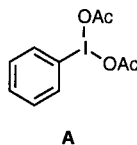


S. Gréau, B. Radetich, T. V. RajanBabu *J. Am. Chem. Soc.* **2000**, *122*, 8579.

5 examples (yields 66-79%) are reported.

(Diacetoxyiodo)benzene (DIB)**Reagent**

Aroyl azides are readily prepared from the corresponding aryl aldehydes with the aid of the title reagent and sodium azide.

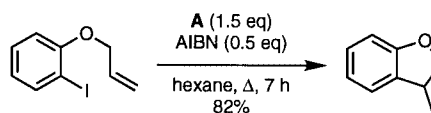
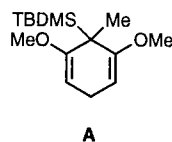


D.-J. Chen, Z.-C. Chen *Tetrahedron Lett.* **2000**, *41*, 7361.

8 examples (yields 43-92%) are reported.

t*-Butyl-(2,6-dimethoxy-1-methylcyclohexa-2,5-dienyl)-dimethylsilane*Reagent**

The title reagent is used as an alternative to toxic tin hydrides in free radical chemistry.

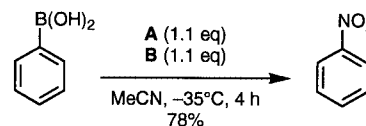
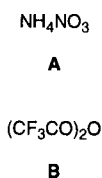


A. Studer, S. Amrein *Angew. Chem. Int. Ed.* **2000**, *39*, 3080.

12 examples (yields 42-99%) are reported.

Ammonium Nitrate / Trifluoroacetic Anhydride**Reagent**

The title reagent pair is used for the regioselective *ipso*-nitration of arylboronic acids to afford nitroarenes. Dinitro products are obtained under different conditions.

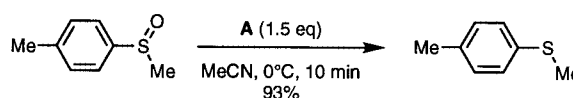


S. Salzbrunn, J. Simon, G. K. S. Prakash, N. A. Petasis, G. A. Olah *Synlett* **2000**, 1485.

8 examples (yields 52-79%) are reported.

Titanium Tetraiodide**Reagent**

The title reagent is used for the chemoselective deoxygenation of sulfoxides.



M. Shimizu, K. Shibuya, R. Hayakawa *Synlett* **2000**, 1437.

19 examples (yields 80-97%) are reported.