

**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:

Stephen Brand, John Christopher, Emma Guthrie, Philip Kocienski, Louise Lea, Russell McDonald, Graeme McAllister and Robert Narquizian of Glasgow University.

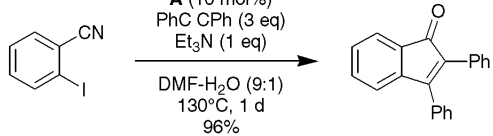
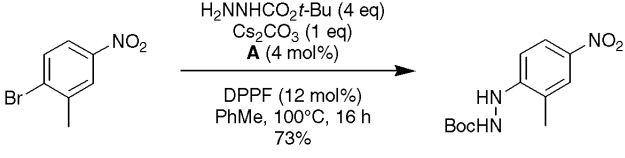
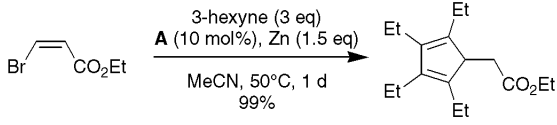
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Article Identifier:

1437-210X,E,1999,0,06,1386,1395,ftx,en:X00899SS.pdf

The journals regularly covered by the abstractors are:

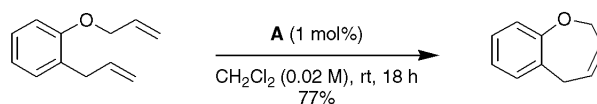
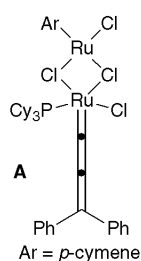
Angewandte Chemie International Edition  
 Bulletin of the Chemical Society of Japan  
 Chemical Communications  
 Chemistry A European Journal  
 Chemistry Letters  
 European Journal of Organic Chemistry  
 Helvetica Chimica Acta  
 Heterocycles  
 Journal of the American Chemical Society  
 Journal of Organic Chemistry  
 Organometallics  
 Perkin Transactions 1  
 Synlett  
 Synthesis  
 Tetrahedron  
 Tetrahedron Asymmetry and Tetrahedron Letters

<b>Palladium Bis(dibenzylideneacetone)</b>		<b>Catalyst</b>
<p><b>A</b> is utilised in carbocycle synthesis via the carbopalladation of nitriles.</p>	<p>Pd(dba)<sub>2</sub> <b>A</b></p>	 <p>5 examples (yields 65-96%).</p>
<p>R. C. Larock, Q. Tian, A. A. Pletnev <i>J. Am. Chem. Soc.</i> <b>1999</b>, <i>121</i>, 3238.</p>		
<b>Palladium(II) Tris(dibenzylideneacetone)</b>		<b>Catalyst</b>
<p>The title reagent is used to catalyse the coupling of aryl bromides with <i>tert</i>-butylcarbazate to afford regioselectively, the corresponding aryl hydrazides.</p>	<p>Pd<sub>2</sub>(dba)<sub>3</sub> <b>A</b></p>	 <p>16 examples (yields 18-84%) are reported.</p>
<p>Z. Wang, R. T. Skerlj, G. J. Bridger <i>Tetrahedron Lett.</i> <b>1999</b>, <i>40</i>, 3543.</p>		
<b>Nickel(II) Bromide</b>		<b>Catalyst</b>
<p>The title compound catalyses the coupling of alkynes with (<i>Z</i>)-3-halopropenoates. The product of the reaction is dependent on the halogen employed.</p>	<p>NiBr<sub>2</sub> <b>A</b></p>	 <p>5 examples of cyclopentadiene synthesis (yields 35, 55-99%). The use of (<i>Z</i>)-3-iodopropenoates yields pyrones (4 examples, yields 59-71%).</p>
<p>M. Kotora, M. Ishikawa, F.-Y. Tsai, T. Takahashi <i>Tetrahedron</i> <b>1999</b>, <i>55</i>, 4969.</p>		

## Ruthenium Allenylidene Metathesis Catalyst

## Catalyst

Catalyst **A** is reported to be highly effective for the ring closing metathesis of  $\alpha,\omega$ -dienes to give variously functionalised 4,6,7,8,15,16 and 18 membered mono- and bicyclic ring systems.



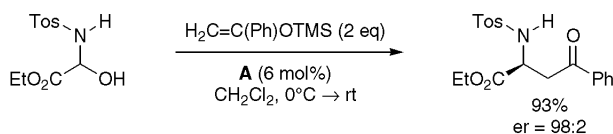
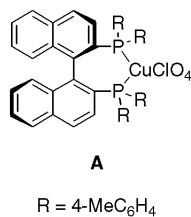
A. Fürstner, A. F. Hill, M. Liebl, J. D. E. T. Wilton-Ely *Chem. Commun.* **1999**, 601.

12 examples (yields 60-94%).

*(R)*-Tol-BINAP•CuClO<sub>4</sub>

## Catalyst

The title compound catalyses the enantioselective alkylation of *N,O*-acetal.



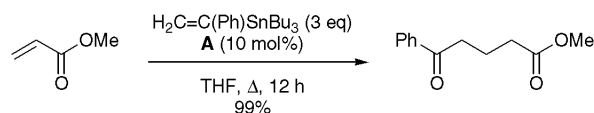
D. Ferraris, T. Dudding, B. Young, W. J. Drury III, T. Lectka *J. Org. Chem.* **1999**, *64*, 2168.

13 examples (yields 73-93%, %ee = 42-96%).

## Tetrabutylammonium Bromide

## Catalyst

**A** catalyses the Michael addition of tin ketone enolates to  $\alpha,\beta$ -unsaturated esters.



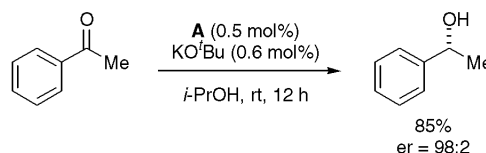
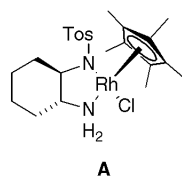
M. Yasuda, N. Ohigashi, I. Shibata, A. Baba *J. Org. Chem.* **1999**, *64*, 2180.

8 examples (yields 16-100%).

Cp\**Rh*Cl[(1*R*, 2*R*)-*N*-(*p*-toluenesulfonyl)-1,2-cyclohexanediamine]

## Catalyst

**A** catalyses the asymmetric transfer hydrogenation of aromatic ketones.



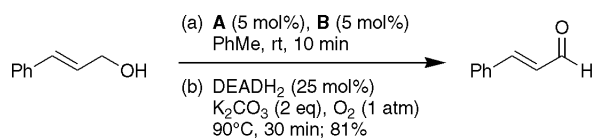
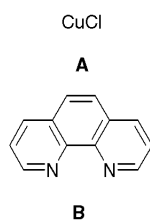
K. Murata, T. Ikariya, R. Noyori *J. Org. Chem.* **1999**, *64*, 2186.

9 examples (yields 22->99%, %ee = 87->99%).

## Copper(I) Chloride / 1,10-Phenanthroline

## Catalyst

The title reagent pair are utilised in an efficient aerobic oxidation of alcohols to aldehydes or ketones.



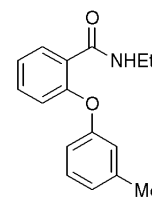
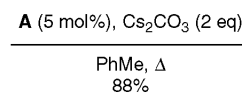
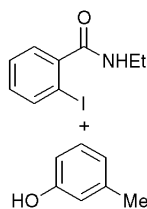
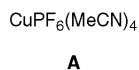
I. E. Markó, P. R. Giles, M. Tsukazaki, I. Chellé-Regnaut, A. Gautier, S. M. Brown, C. J. Urch *J. Org. Chem.* **1999**, *64*, 2433.

DEADH<sub>2</sub> = diethylhydrazinodicarboxylate

17 examples (yields 40-100%) are reported.

**Tetrakis(acetonitrile)copper(I) Hexafluorophosphate****Catalyst**

**A**, a convenient, air insensitive copper source, is utilised in the Buchwald catalytic Ullman diaryl ether synthesis.

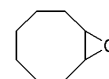
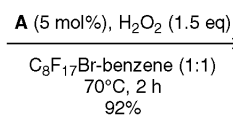
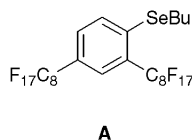


17 examples (yields 47-97%).

A. V. Kalinin, J. F. Bower, P. Riebel, V. Snieckus  
*J. Org. Chem.* **1999**, *64*, 2986.

**2,4-Bis(perfluorooctyl)phenyl Butylselenide****Catalyst**

The title reagent catalyses the epoxidation of olefins using hydrogen peroxide in a fluoruous biphasic system.

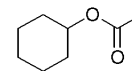
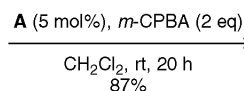
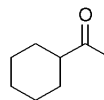


10 examples (yields 63-97%).

B. Betzemeier, F. Lhermitte, P. Knochel *Synlett*  
**1999**, 489.

**Scandium Triflate****Catalyst**

The title compound is used in the Baeyer-Villiger oxidation of a series of carbonyl compounds. The reaction rate can be accelerated by the use of TfOH as an alternative acid catalyst.

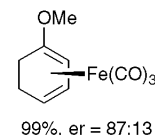
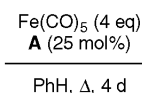
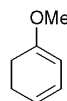
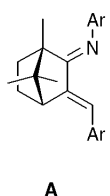


12 examples (yields 0, 65-100%).

H. Kotsuki, K. Arimura, T. Araki, T. Shinohara,  
*Synlett* **1999**, 462.

**(1S,4S)-2-(4-Methoxyphenylimino)-2-(4-methoxyphenylmethylidene)-1,7,7-trimethylbicyclo[2.2.1]heptane****Catalyst**

Catalyst **A** is used in the preparation of planar-chiral tricarbonyliron-diene complexes.

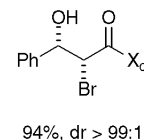
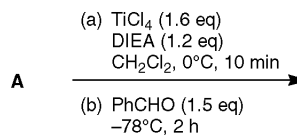
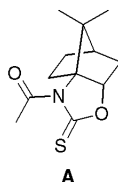


6 examples (yields 12-99%, %ee = 24-73%).

H. J. Knölker, H. Goesmann, H. Hermann, D. Herzberg, G. Rohde *Synlett* **1999**, 421.

**Scalemic Oxazolidinethione****Chiral Auxiliary**

Asymmetric bromination-aldolization of **A** is used to synthesise enantiopure  $\alpha$ -bromo- $\beta$ -hydroxy acids.

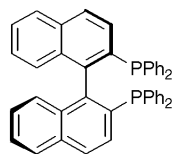
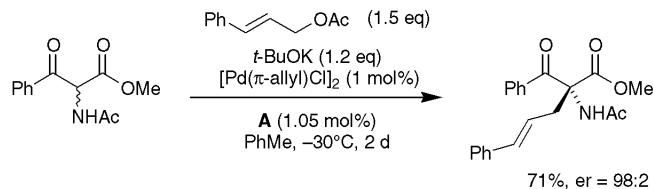


4 examples of bromination-aldolization (yields 90-94%) are reported.

Y.-C. Wang, D.-W. Su, C.-M. Lin, H.-L. Tseng,  
C.-L. Li, T.-H. Yan *Tetrahedron Lett.* **1999**, *40*,  
3577.

**(R)-2,2'-Bis(diphenylphosphanyl)binaphthyl****Ligand**

Ligand **A**, in combination with  $[\text{Pd}(\pi\text{-allyl})\text{Cl}]_2$ , allows the enantioselective allylation of  $\alpha$ -acetamido- $\beta$ -ketoesters.

**A**

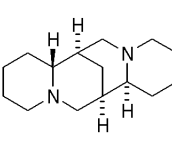
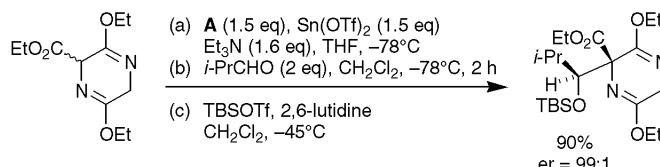
71%, er = 98:2

9 examples (yields 40-96%, %ee = 76-95%).

R. Kuwano, Y. Ito *J. Am. Chem. Soc.* **1999**, *121*, 3236.

**(-)-Sparteine****Ligand**

**A** is used in a tin-mediated enantioselective aldol-type reaction, allowing the preparation of  $\alpha$ -substituted serines.

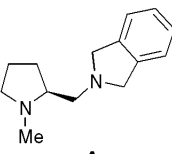
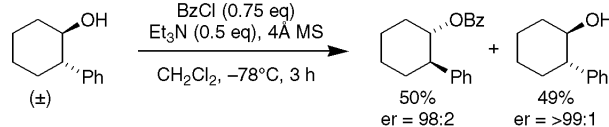
**A**90%  
er = 99:1

4 examples (yields 72-90%, %ee = 84-98%).

S. Sano, T. Ishii, T. Miwa, Y. Nagao *Tetrahedron Lett.* **1999**, *40*, 3013.

**(S)-1-Methyl-2-[(dihydroisoindol-2-yl)methyl]pyrrolidine****Ligand**

The title diamine is employed in the catalytic asymmetric acylation of racemic secondary alcohols. The method allows a quick and efficient separation of enantiomers.

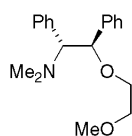
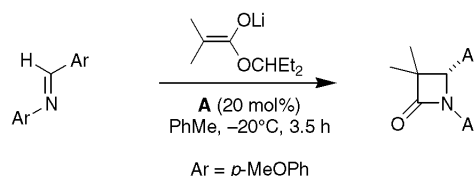
**A**50%  
er = 98:249%  
er = >99:1

10 examples (yields 39-50%, %ee = 46-97%).

T. Sano, K. Imai, K. Ohashi, T. Oriyama *Chem. Lett.* **1999**, 265.

**(3R,4R)-2-Methyl-3,4-diphenyl-2-aza-5,8-dioxanonane****Ligand**

Chiral tridentate ligand **A** promotes the condensation of a lithium ester enolate with imines to give the enantiomerically enriched  $\beta$ -lactams.

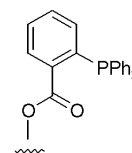
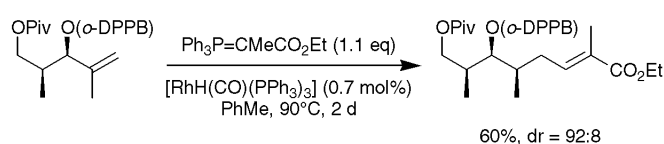
**A**Ar = *p*-MeOPh

6 examples (yields 90-99%, %ee = 65-90%).

K. Tomioka, H. Fujieda, S. Hayashi, M. A. Hussein, T. Kambara, Y. Nomura, M. Kanai, K. Koga *Chem. Commun.* **1999**, 715.

**ortho-Diphenylphosphanylbenzoic Acid****Ligand**

Ligand **A** directs the stereoselective hydroformylation of methallyl and homomethallyl alcohols in a novel domino hydroformylation-Wittig reaction protocol.

**A**

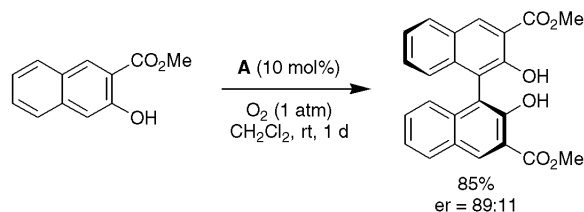
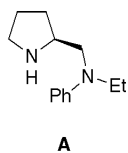
60%, dr = 92:8

9 examples (yields 36, 60-82%, %de = 80-&gt;99%).

B. Breit, S. K. Zahn *Angew. Chem. Int. Ed.* **1999**, *38*, 969.

**(S)-N-Ethyl-N-phenyl-2-pyrrolidinemethanamine****Ligand**

A copper(I) complex derived from the title ligand catalyses the enantioselective oxidative coupling of 2-naphthols.

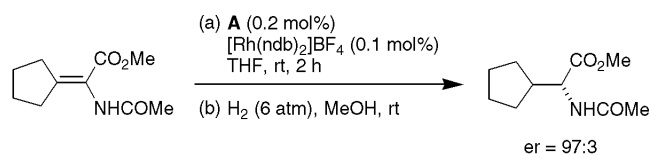
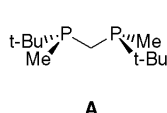


M. Nakajima, I. Miyoshi, K. Kanayama, S.-i. Hashimoto, M. Noji, K. Koga *J. Org. Chem.* **1999**, *64*, 2264.

10 examples (yields 58-95%, %ee = 5-78%).

**Bis[(R)-tert-butylmethylphosphanyl]methane****Ligand**

A is a simple but efficient ligand which exhibits high levels of enantioselectivity in representative catalytic asymmetric reactions.

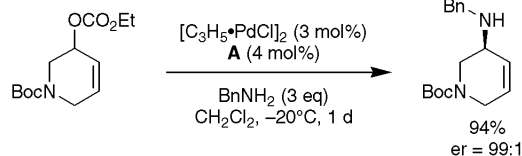
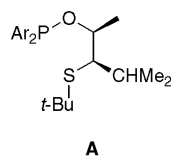


Y. Yamano, T. Imamoto *J. Org. Chem.* **1999**, *64*, 2988.

9 examples of hydrogenation of dehydroamino acids (%ee ≥ 87%), 8 examples of hydrosilylation of ketones (yields 81-99%, %ee 80-97%) and 4 examples of the Michael addition of diethylzinc to  $\alpha,\beta$ -unsaturated ketones (yields 73-96%, %ee = 70-97%) are reported.

**[(2S,3R)-3-(tert-Butylthio)-4-methylpent-2-oxyl]bis( $\alpha$ -naphthyl)phosphine****Ligand**

The title mixed phosphorus / sulfur ligand is utilised in asymmetric palladium-catalysed allylic alkylations and aminations.

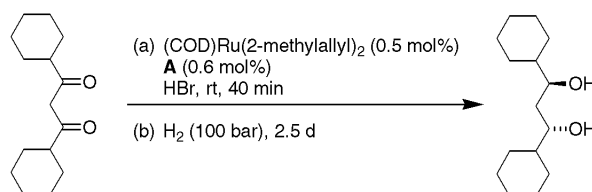
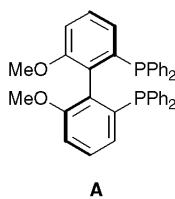


D. A. Evans, K. R. Campos, J. S. Tedrow, F. E. Michael, M. R. Gagné *J. Org. Chem.* **1999**, *64*, 2994.

10 examples (yields 28-97%, %ee = 90-99%).

**(R)-(+)-6,6'-Dimethoxy-2,2'-bis(diphenylphosphanyl)-1,1'-biphenyl****Ligand**

The ruthenium catalysed hydrogenation of a series of symmetrical 1,3-diketones using a variety of ligands is discussed. A offers the best results allowing access to enantiopure anti-1,3-diols.

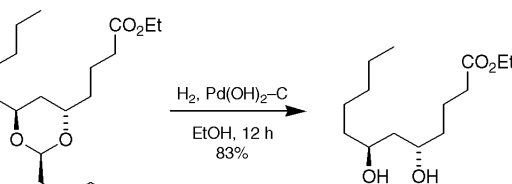
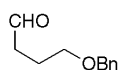


D. Blanc, V. Ratovelomanana-Vidal, A. Marinetti, J. P. Genêt *Synlett* **1999**, 480.

19 examples (%de = 89 to 99%, %ee = 69 to 99%).

**4-Benzyloxybutanal****Protecting Group**

4-Benzyloxybutanal acetals (BOB) can be used for the relay deprotection of 1,3-diols under very mild conditions. Hydrogenolysis of the benzyloxy group produces a primary alcohol which, under the reaction conditions, undergoes intramolecular transketalisation to release the diol.



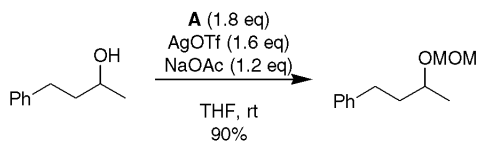
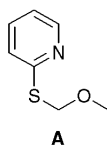
N. A. Powell and S. D. Rychnovsky *J. Org. Chem.*, **1999**, *64*, 2026.

two examples

## 2-(Methoxymethylthio)pyridine

## Protecting Group

The title reagent together with AgOTf and NaOAc introduces a MOM group onto acid-sensitive alcohols in THF at rt. Primary, secondary and tertiary alcohols react at roughly comparable rates though phenols are slower.



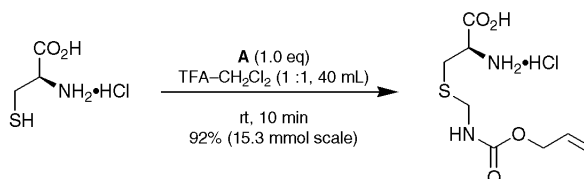
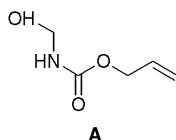
B. F. Marcune, S. Karady, U.-H. Dolling, and T. J. Novak, *J. Org. Chem.*, 1999, **64**, 2446.

13 examples; yields 14% (4-nitrophenol) to 98%. Triphenylmethanol was protected in 47% yield.

## Allyloxycarbonylaminoethyl (Allocam) Group

## Protecting Group

Brief treatment of thiols with *N*-hydroxymethyl carbamic acid allyl ester (**A**, mp 57 °C) under acid catalysis gives *S*-Allocam derivatives which are stable towards mild base (piperidine in DMF) but labile towards acid conditions typically used to cleave *t*-Bu esters and Boc derivatives. The Allocam group is cleaved with Pd(0) and Bu<sub>3</sub>SnH.

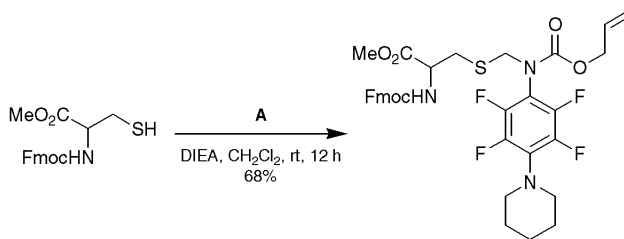
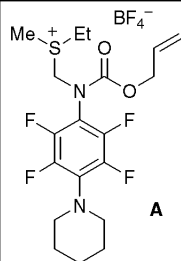


A. M. Kimbonguila, A. Merzouk, F. Guibé, and A. Loffet, *Tetrahedron*, 1999, **55**, 6931.

*N*-[2,3,5,6-Tetrafluoro-4-(*N*-piperidino)-phenyl]-*N*-allyloxycarbonylaminoethyl (Fnam) Group

## Protecting Group

Reaction of reagent **A** (4 steps from pentafluoroaniline) with a thiol in the presence of (*i*-Pr)<sub>2</sub>NEt introduces the *S*-Fnam group which is stable towards piperidine and TFA. It is cleaved with Pd(0) in the presence of Bu<sub>3</sub>SnH, PhSiH<sub>3</sub> or *N,N*-dimethylbarbituric acid.

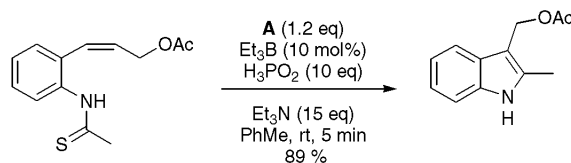


P. Gomez-Martinez, A. M. Kimbonguila, and F. Guibé, *Tetrahedron*, 1999, **55**, 6945.

Tri-*n*-butyltin Hydride

## Reagent

A wide range of *cis*-alkenyl substituted *ortho*-thioanilides undergo cyclisation mediated by **A** to afford indoles.



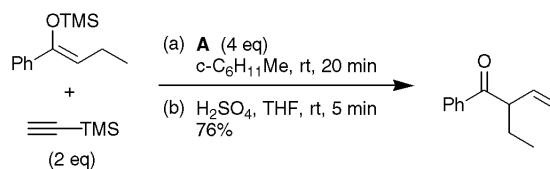
H. Tokuyama, T. Yamashita, M. T. Reding, Y. Kaburagi, T. Fukuyama *J. Am. Chem. Soc.* 1999, **121**, 3791.

18 examples (yields 36, 68-94%).

## Gallium Trichloride

## Reagent

The title reagent mediates the ethenylation of silyl enol ethers.



M. Yamaguchi, T. Tsukagoshi, M. Arisawa *J. Am. Chem. Soc.* 1999, **121**, 4074.

12 examples (yields 57-76%).

1-Fluoro-4-hydroxy-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (NFTh)		Reagent
The title reagent is an electrophilic fluorinating agent used to fluorinate aromatic rings, olefins, dienol acetates and enol ethers.		
A. J. Poss, G. A. Shia <i>Tetrahedron Lett.</i> <b>1999</b> , <i>40</i> , 2673.	<b>A</b>	12 examples (yields 43-92%) are reported.

Picolinic Acid		Reagent
<b>A</b> and 6-methyl picolinic acid are used as partners in the Mitsunobu reaction, and offer the added advantage that the resulting esters can be cleaved under essentially neutral conditions using $\text{Cu}(\text{OAc})_2$ and methanol.		
T. Sammakia, J. S. Jacobs <i>Tetrahedron Lett.</i> <b>1999</b> , <i>40</i> , 2685.	<b>A</b>	8 examples of the Mitsunobu reaction (yields 79-95%) and 10 examples of copper promoted methanolysis (yields 72-95%) are reported.

Benzotriazol-1-yloxy- <i>N,N</i> -dimethylmethaniminium Hexachloroantimonate (BOMI)		Reagent
The novel coupling reagent <b>A</b> is used in the synthesis of oligopeptides.		
P. Li, J. C. Xu <i>Tetrahedron Lett.</i> <b>1999</b> , <i>40</i> , 3605.	<b>A</b>	Preparation of <b>A</b> and 5 examples of oligopeptide synthesis (yields 84-91%) are reported.

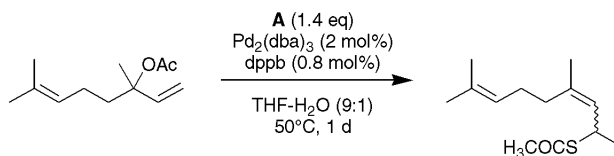
2-Amino-4,6-dimethyl-1,3,5-triazine		Reagent
The osmium-catalyzed asymmetric aminohydroxylation of olefins utilizing <b>A</b> as the nitrogen source is reported.		
L. J. Goossen, H. Liu, K. R. Dress, K. B. Sharpless <i>Angew. Chem. Int. Ed.</i> <b>1999</b> , <i>38</i> , 1080.	<b>A</b>	11 examples using <b>A</b> and four similar heterocycles are reported (yields 45-97%, %ee = 37-98%).

Tris(triphenylphosphanyl)copper(I) Fluoride Bis(ethanol) Complex		Reagent
Conjugate reduction of $\alpha,\beta$ -unsaturated ketones with dimethylphenylsilane using the title reagent is reported.		
A. Mori, A. Fujita, H. Kajiro, Y. Nishihara, T. Hiyama <i>Tetrahedron</i> <b>1999</b> , <i>55</i> , 4573.	<b>A</b>	8 examples (yields 52->99%). DMA = <i>N,N</i> -dimethylacetamide

## Reagent

## Potassium Thioacetate

Palladium(0)-catalysed synthesis of allylic thioacetates using **A** is reported.



11 examples (yields 22, 51-91%).

dppb = 1,4-bis(diphenylphosphanyl)butane

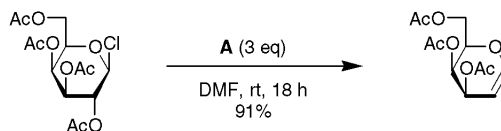
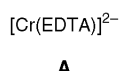
91%  
E:Z = 56:44

S. Divekar, M. Safi, M. Soufiaoui, D. Sinou  
*Tetrahedron* **1999**, *55*, 4369.

## Reagent

## Chromium(II) EDTA Complex

The title complex is used in the preparation of acylated pyranoid glycals in good to high yield.



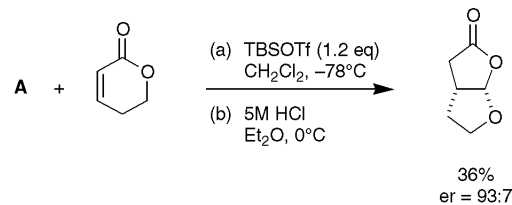
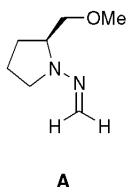
12 examples (yields 0, 61-91%) are reported.

G. Kovács, K. Tóth, Z. Dinya, L. Somsák, K. Micskei  
*Tetrahedron* **1999**, *55*, 5253.

## Reagent

## Formaldehyde SAMP-hydrazone

Asymmetric synthesis of 2,8-dioxabicyclo [3.3.0]octan-3-one derivatives is reported by a stepwise Michael addition- $\alpha$ -alkylation and subsequent hydrolytic domino reaction protocol, employing **A** as a neutral formyl anion equivalent and 5,6-dihydro-2H-pyran-2-one as a Michael acceptor.



36%  
er = 93:7

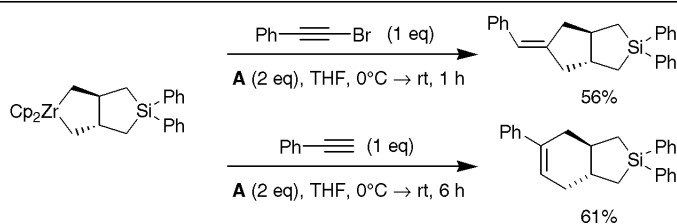
5 examples (yields 66-98%, %de  $\geq$  98%, %ee = 80->98%).

D. Enders, J. Vázquez, G. Raabe  
*Chem. Commun.* **1999**, 701.

## Reagent

## Copper(I) Chloride

5- and 6-membered carbocycles are obtained from zirconacyclopentanes by a novel carbometallation of alkynes in the presence of **A**.



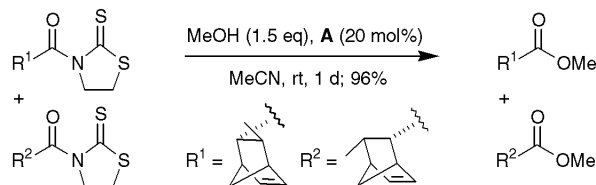
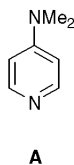
6 examples with activated alkynes (yields 55-78%) and 5 examples with non-activated alkynes (yields 50-78%).

Y. Liu, B. Shen, M. Kotora, T. Takahashi  
*Angew. Chem. Int. Ed.* **1999**, 949.

## Reagent

## 4-(Dimethylamino)pyridine (DMAP)

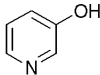
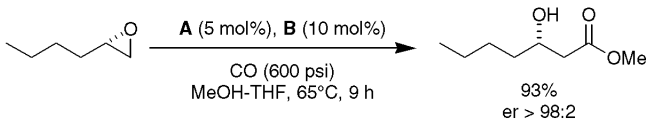
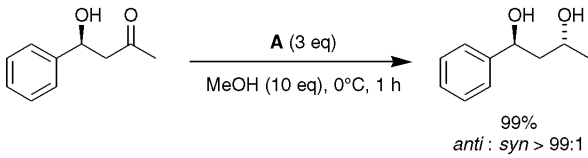
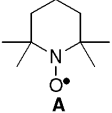
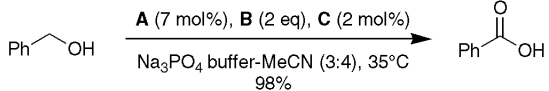
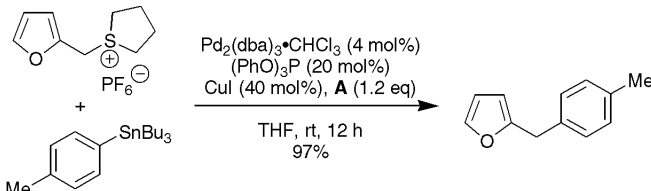
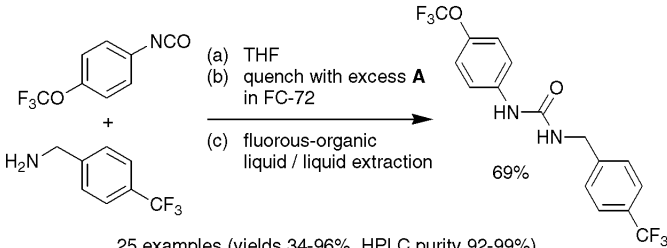
**A** promotes the deacylation of carboxthioimide adducts without racemisation.

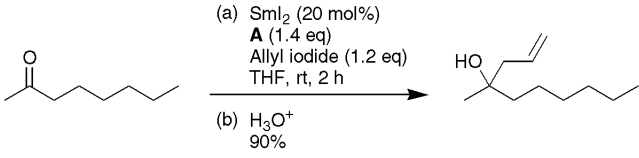
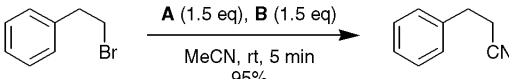
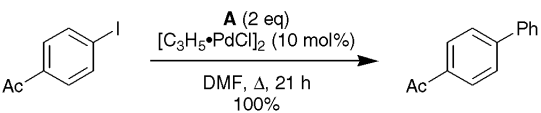
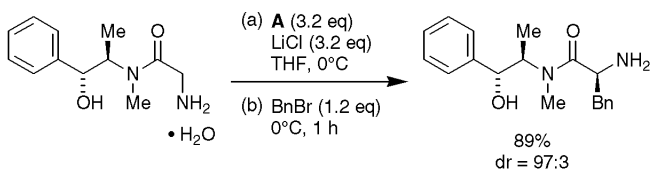
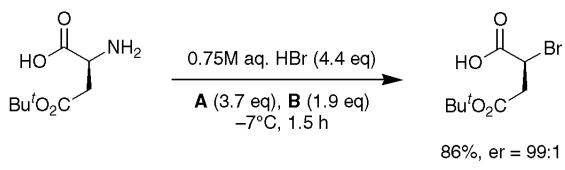


8 examples (yields 89-97%) and 4 examples of using camphor based *N*-acyloxazolidinethiones (yields 87-96%) are reported.

D.-W. Su, Y.-C. Wang, T.-H. Yan  
*Chem. Commun.* **1999**, 545.



Dicobalt octacarbonyl / 3-Hydroxypyridine		Reagent
<p>The title reagent pair mediates the regioselective carbomethoxylation of chiral epoxides yielding enantiomerically pure <math>\beta</math>-hydroxy esters.</p>	<p><math>\text{Co}_2(\text{CO})_8</math></p> <p><b>A</b></p>  <p><b>B</b></p>	 <p>8 examples (yields 86-95%, %ee &gt; 99%).</p>
<p>K. Hinterding, E. N. Jacobsen <i>J. Org. Chem.</i> <b>1999</b>, <i>64</i>, 2164.</p>		
Samarium Diiodide		Reagent
<p>The title reagent reduces <math>\beta</math>-hydroxy ketones to anti 1,3-diols.</p>	<p><math>\text{SmI}_2</math></p> <p><b>A</b></p>	 <p>8 examples (yields 67-99%, 50:50 <math>\leq</math> anti : syn 97:3).</p>
<p>G. E. Keck, C. A. Wager, T. Sell, T. T. Wager <i>J. Org. Chem.</i> <b>1999</b>, <i>64</i>, 2172.</p>		
2,2,6,6-Tetramethylpiperidinyl-1-oxy / Sodium Chlorite / Sodium Hypochlorite		Reagent
<p>The title reagents oxidise primary alcohols to carboxylic acids in good yields.</p>	 <p><b>A</b></p> <p><math>\text{NaClO}_2</math></p> <p><b>B</b></p> <p><math>\text{NaOCl}</math></p> <p><b>C</b></p>	 <p>12 examples (yields 85-100%).</p>
<p>M. Zhao, J. Li, E. Mano, Z. Song, D. M. Tschaen, E. J. J. Grabowski, P. J. Reider <i>J. Org. Chem.</i> <b>1999</b>, <i>64</i>, 2564.</p>		
Benzyltrimethylammonium Diphenylphosphinate		Reagent
<p><b>A</b> is a highly effective tri-<i>n</i>-butylstannyl scavenger. <i>n</i>-<math>\text{Bu}_3\text{SnOP}(\text{O})\text{Ph}_2</math> precipitates from concentrated solutions, facilitating the copper-catalysed Stille coupling reaction.</p>	<p><math>\text{Ph}_2\text{P}(\text{O})\text{O}^-\text{BnMe}_3\text{N}^+</math></p> <p><b>A</b></p>	 <p>10 examples (yields 49-97%).</p>
<p>S. Zhang, D. Marshall, L. S. Liebeskind <i>J. Org. Chem.</i> <b>1999</b>, <i>64</i>, 2796.</p>		
<i>N,N</i> -Bis[3-[tris(2-perfluorohexylethyl)silyl]propyl]amine		Reagent
<p>The use of <b>A</b> as a fluoros amine scavenger for purification in solution phase parallel synthesis of ureas is reported.</p>	<p><math>\text{Si}(\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2)_3</math></p> <p><b>A</b></p>	 <p>25 examples (yields 34-96%, HPLC purity 92-99%).</p>
<p>B. Linclau, A. K. Sing, D. P. Curran <i>J. Org. Chem.</i> <b>1999</b>, <i>64</i>, 2835.</p>		

		<i>Reagent</i>
<p><b>Mischmetall</b></p> <p>Mischmetall is an alloy of the light Lanthanides (La 33%, Ce 50%, Nd 12%, Pr 4%, Others 1%). Available at low cost, <b>A</b> is an efficient coreductant for catalytic reactions of samarium diiodide.</p> <p>F. Hélon, J.-L. Namy <i>J. Org. Chem.</i> <b>1999</b>, <i>64</i>, 2944.</p>	<p>Mischmetall</p> <p><b>A</b></p>	 <p>(a) SmI<sub>2</sub> (20 mol%)  <b>A</b> (1.4 eq)            Allyl iodide (1.2 eq)            THF, rt, 2 h            (b) H<sub>3</sub>O<sup>+</sup>            90%</p> <p>10 examples (yields 52-91%).</p>
<p><b>Trimethylsilyl Cyanide / Tetrabutylammonium Fluoride (TBAF)</b></p> <p>Hypervalent azido- and cyanosilicate derivatives, prepared <i>in situ</i> by the reaction of trimethylsilyl azide or trimethylsilyl cyanide, respectively, with TBAF, are effective sources of nucleophilic azide or cyanide. Primary or secondary halides undergo efficient azide or cyanide displacement with the silicate derivatives.</p> <p>E. D. Soli, A. S. Manoso, M. C. Patterson, P. DeShong, D. A. Favor, R. Hirschmann, A. B. Smith III <i>J. Org. Chem.</i> <b>1999</b>, <i>64</i>, 3171.</p>	<p>TMSCN</p> <p><b>A</b></p> <p>TBAF</p> <p><b>B</b></p>	 <p><b>A</b> (1.5 eq), <b>B</b> (1.5 eq)            MeCN, rt, 5 min            95%</p> <p>24 examples (yields 0-95%) are reported.</p>
<p><b>Tetrabutylammonium Triphenyldifluorosilicate (TBAT)</b></p> <p><b>A</b>, a hypervalent silicon reagent, mediates the synthesis of unsymmetrical biaryls by palladium-catalysed cross coupling reactions of arenes.</p> <p>M. E. Mowery, P. DeShong <i>J. Org. Chem.</i> <b>1999</b>, <i>64</i>, 3266.</p>	<p>[Bu<sub>4</sub>N]<sup>+</sup> [Ph<sub>3</sub>SiF<sub>2</sub>]<sup>-</sup></p> <p><b>A</b></p>	 <p><b>A</b> (2 eq)            [C<sub>3</sub>H<sub>5</sub>•PdCl]<sub>2</sub> (10 mol%)            DMF, Δ, 21 h            100%</p> <p>13 examples (yields 0-100%).</p>
<p><b>Lithium hexamethyldisilazide</b></p> <p><b>A</b> is utilized in the synthesis of highly enantioenriched α-amino acids.</p> <p>A. G. Myers, P. Schnider, S. Kwon, D. W. Kung <i>J. Org. Chem.</i> <b>1999</b>, <i>64</i>, 3322.</p>	<p>LHMDS</p> <p><b>A</b></p>	 <p>(a) <b>A</b> (3.2 eq)            LiCl (3.2 eq)            THF, 0°C            (b) BnBr (1.2 eq)            0°C, 1 h            • H<sub>2</sub>O</p> <p>89%            dr = 97:3</p> <p>12 examples (yields 56-91%, %de = 89-97%).</p>
<p><b>Potassium Bromide / Sodium Nitrite</b></p> <p>Enantiopure α-bromoacids are prepared from the corresponding amino acids using the title reagent pair.</p> <p>A. J. Souers, S. Schürer, H. Kwack, A. A. Virgilio, J. A. Ellman <i>Synthesis</i> <b>1999</b>, 583.</p>	<p>KBr</p> <p><b>A</b></p> <p>NaNO<sub>2</sub></p> <p><b>B</b></p>	 <p>0.75M aq. HBr (4.4 eq)  <b>A</b> (3.7 eq), <b>B</b> (1.9 eq)            -7°C, 1.5 h</p> <p>86%, er = 99:1</p> <p>5 examples (yields 54-86%, %ee = 95-98%)</p>