

Synthesis Alerts is a monthly feature to help readers of *Synthesis* keep abreast of new reagents, catalysts, ligands, chiral auxiliaries, and protecting groups which have appeared in the recent literature. Emphasis is placed on new developments but established reagents, catalysts etc are also covered if they are used in novel and useful reactions. In each abstract, a specific example of a transformation is given in a concise format designed to aid visual retrieval of information.

Synthesis Alerts is a personal selection by:

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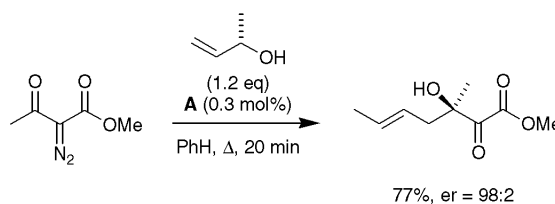
The journals regularly covered by the abstractors are:

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

Dirhodium Tetraacetate

Catalyst

A is involved in a Rhodium carbenoid-initiated Claisen rearrangement resulting in an enantioselective synthesis of α -hydroxy compounds.



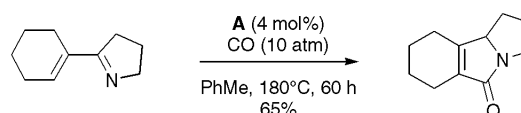
28 examples (yields 45-80%, %ee = 45-98%).

J. L. Wood, G. A. Monitz, D. A. Pflum, B. M. Stoltz, A. A. Holubec, H.-J. Dietrich *J. Am. Chem. Soc.* **1999**, *121*, 1748.

Triruthenium Dodecacarbonyl

Catalyst

A catalyses the carbonylative [4+1] cycloaddition of α,β -unsaturated imines to yield unsaturated γ -lactams.



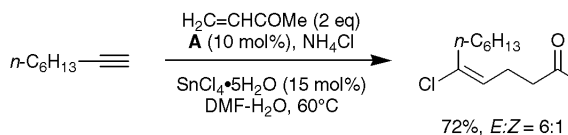
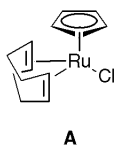
9 examples (yields 51-96%)

T. Morimoto, N. Chatani, S. Murai *J. Am. Chem. Soc.* **1999**, *121*, 1758.

η^4 -Cycloocta-1,4-dienyl- η^5 -cyclopentadienylruthenium Chloride

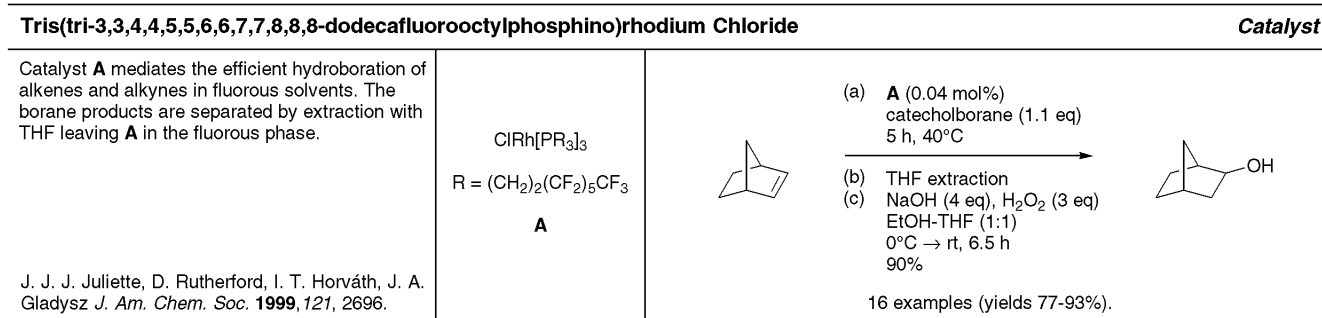
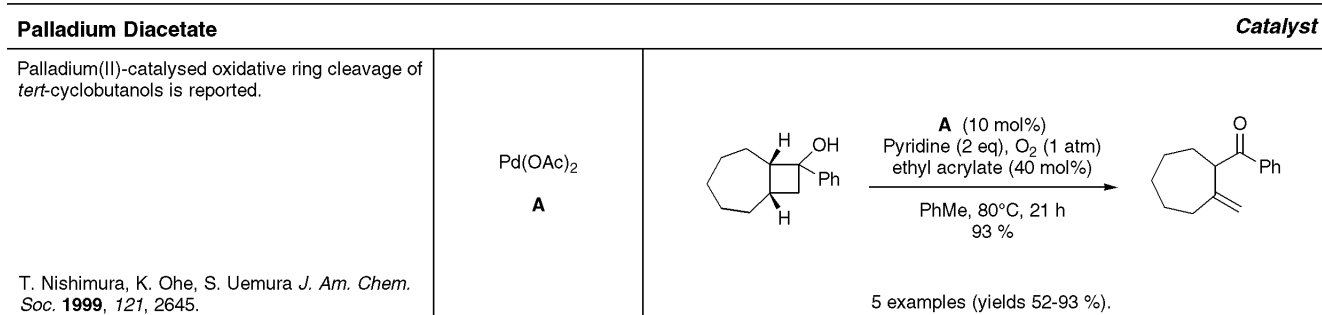
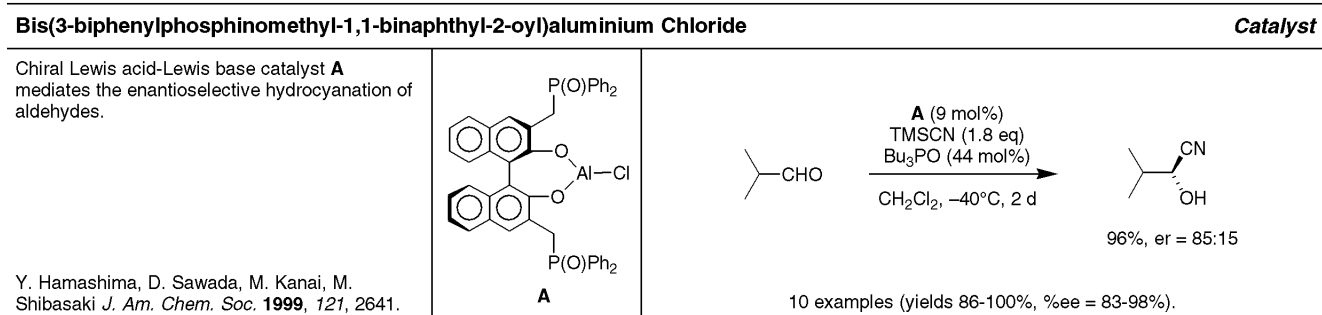
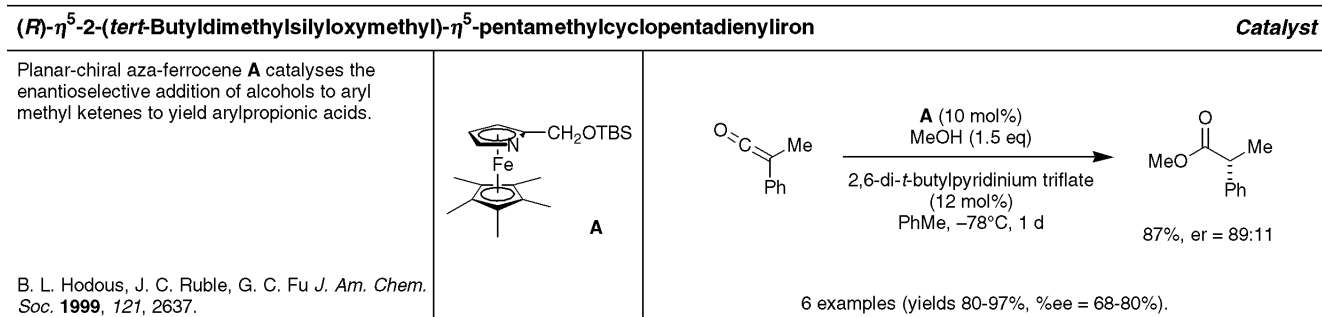
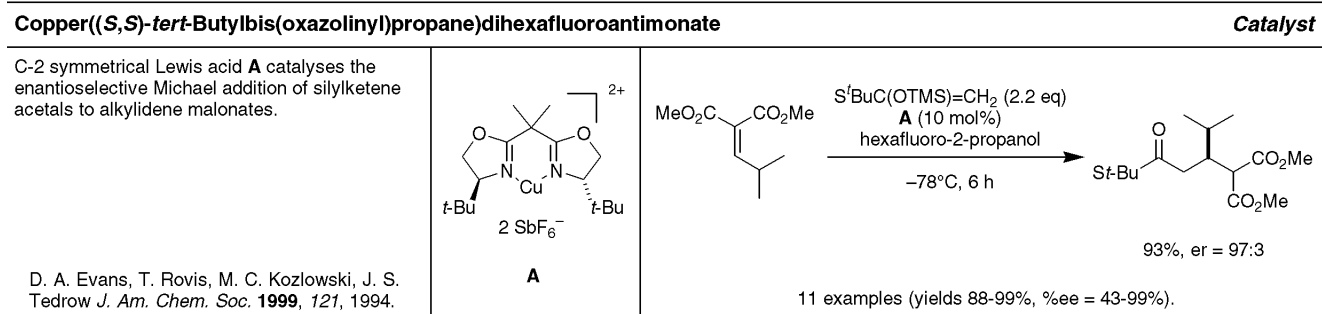
Catalyst

E-vinyl chlorides are stereoselectively formed from terminal alkynes, vinyl ketones and a chloride source in the presence of catalyst **A**.



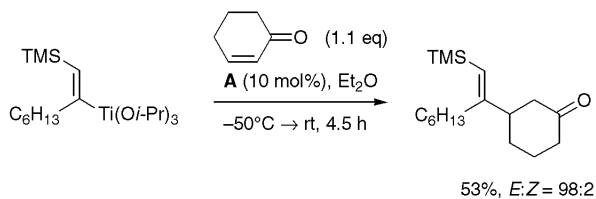
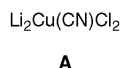
16 examples (yields 60-83%, 4:1 \leq E:Z \leq 15:1).

B. Trost, A. B. Pinkerton *J. Am. Chem. Soc.* **1999**, *121*, 1988.



Dilithiumdichlorocyanocuprate**Catalyst**

(β -Silylalkenyl)titanium reagents, obtained by treatment of silylated alkynes with $\text{Ti}(\text{O}-i\text{-Pr})_4$ and $i\text{-PrMgCl}$ followed by addition of a proton source, react in the presence of **A** with a range of electrophiles.

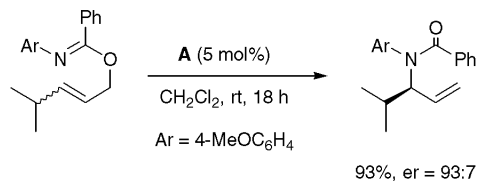
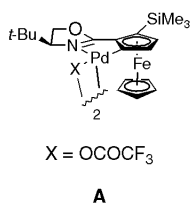


H. Urabe, T. Hamada, F. Sato *J. Am. Chem. Soc.* **1999**, *121*, 2931.

3 examples (yields 53-84%, *E:Z* \geq 98:2).

Bis-(2'-trimethylsilylferrocen-1-yl-5(R)-tert-butylloxazoline Palladium Trifluoroacetate**Catalyst**

A catalyses the enantioselective rearrangement of allylic imidates to allylic amides.

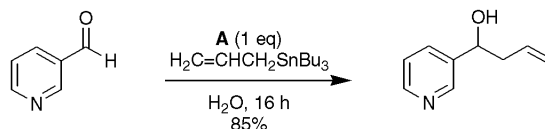


Y. Donde, L. E. Overman *J. Am. Chem. Soc.* **1999**, *121*, 2933.

12 examples (yields 11-97%, %ee = 63-96%).

Trifluoromethanesulfonic Acid**Catalyst**

The title reagent catalyses the addition of allyltributylstannane to carbonyl compounds in water to give the corresponding homoallylic alcohols.

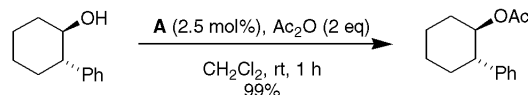


T.-P. Loh, J. Xu *Tetrahedron Lett.* **1999**, *40*, 2431.

7 examples (yields 59-92%) are reported.

Copper Trifluoromethanesulfonate**Catalyst**

The title reagent catalyses the acylation of alcohols, phenols, amines and thiols.

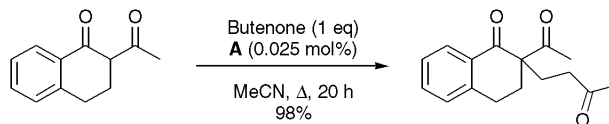
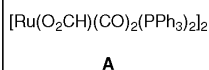


P. Saravanan, V. K. Singh *Tetrahedron Lett.* **1999**, *40*, 2611.

39 examples (yields 79-99%).

[Ru(O₂CH)(CO)₂(PPh₃)₂]₂**Catalyst**

The title complex catalyses the Michael addition of soft carbonucleophiles to butenone.

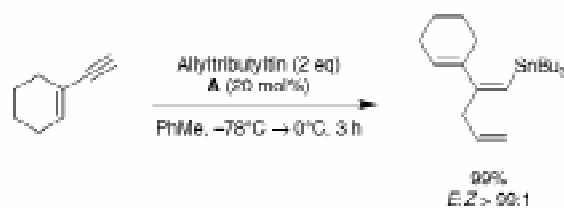


M. Picquet, C. Bruneau, P. H. Dixneuf *Tetrahedron* **1999**, *55*, 3937.

16 examples (yields 20-98%) are reported.

Zirconium(IV) Chloride*Catalyst*

The title Lewis acid catalyses the allylstannylation of unactivated alkynes to give stannyl 1,4-dienes with predominantly *E*-geometry.

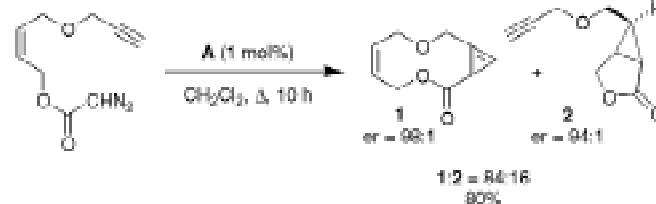
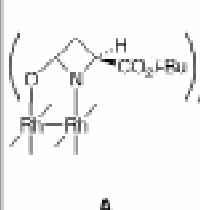


Y. Matsukawa, N. Asao, H. Kitahara, Y. Yamamoto *Tetrahedron* **1999**, *55*, 3779.

20 examples (yields 0, 32–99%, 0:100 ≤ *E:Z* ≤ 100:0).

Chiral Dirhodium Catalyst*Catalyst*

Enantioselective cyclopropanation is achieved by intramolecular addition of metal carbene A to alkynes.

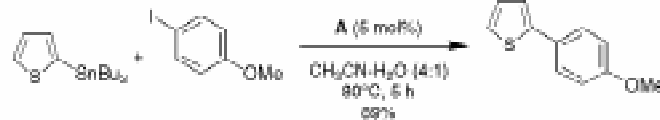
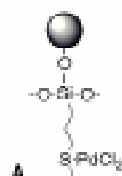


M. P. Doyle, D. G. Ens, C. S. Peterson, V. Lynch *Angew. Chem. Int. Ed.* **1999**, *38*, 700.

2 examples (yields 65, 80%).

Silica-supported Poly[3-(2-cyanoethylsulfanyl)propylsiloxane Palladium] Complex*Catalyst*

The title catalyst is used in the cross-coupling of organostannanes with organic iodides in an aqueous medium.

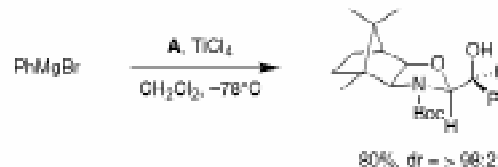
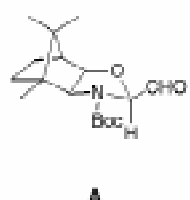


S.-K. Kang, T.-G. Baik, S.-Y. Song *Synlett* **1999**, 327.

12 examples (yields 71–90%).

Camphor-derived 2-Formyloxazolidine*Chiral Auxiliary*

The title chiral auxiliary is used for the synthesis of highly enantioselectively enriched *O*-protected α -hydroxy aldehydes by the addition of Grignard reagents or allyltributylstannane.

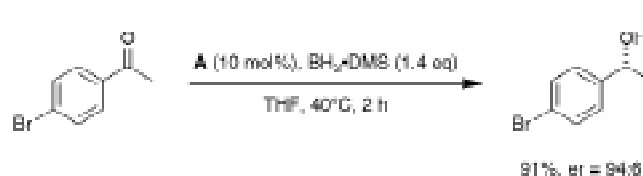
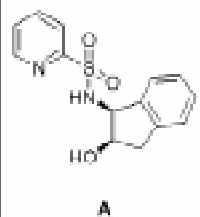


L. Colombo, M. Di Giacomo *Tetrahedron Lett.* **1999**, *40*, 1077.

Synthesis of A and 6 examples (yields 54–90%, %de = 0, 20–96%) are reported.

(1*S*,2*R*)-1-(Pyridine-2-sulfonamido)indan-2-ol*Ligand*

The title ligand is used in the enantioselective reduction of a variety of ketones.

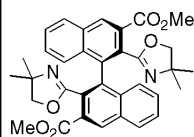
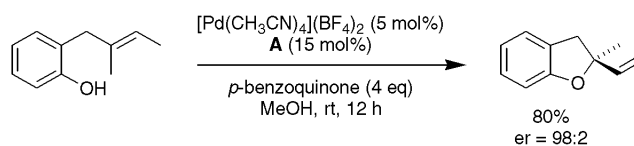


M. P. Gibl, G. R. Cook, P. Liu *Tetrahedron Lett.* **1999**, *40*, 2477.

6 examples (yields 60–92%, %ee = 71–89%).

(S)-2,2'-Bis(4,4-dimethyloxazol-2-yl)-3,3'-bis(methoxycarbonyl)-1,1'-binaphthyl**Ligand**

A is reported as a novel ligand for the catalytic asymmetric Wacker-type cyclisation.

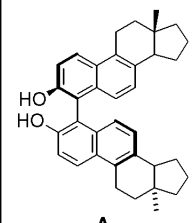
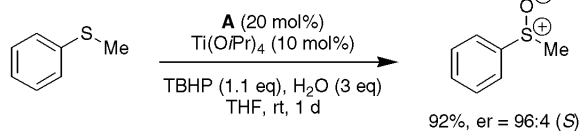
**A**

2 examples (yields 30, 80%, %ee = 4, 96%).

Y. Uozumi, H. Kyota, K. Kato, M. Ogasawara, T. Hayashi *J. Org. Chem.* **1999**, *64*, 1620.

(S,S)-4,4'-Bis(3-hydroxy-estra-1,3,5(10),6,8-pentaene**Ligand**

A is an effective ligand for the catalytic asymmetric oxidation of sulfides to sulfoxides.

**A**

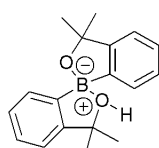
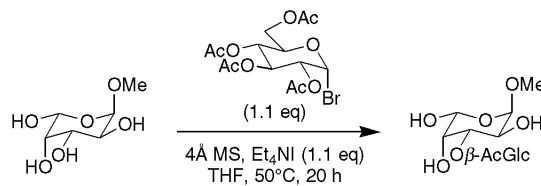
5 examples (yields 43-78%, %ee = 85-92%).

TBHP = *tert*-butyl hydroperoxide

C. Bolm, O. A. G. Dabard *Synlett* **1999**, 360.

Glycosidation Mediator**Reagent**

The title reagent allows the regiospecific glycosidation of unprotected carbohydrate acetals.

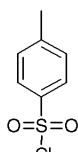
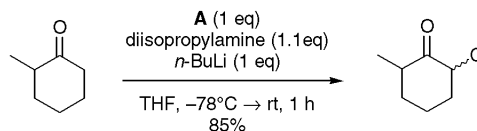
**A**

12 examples (yields 15-93%).

K. Oshima, Y. Aoyama *J. Am. Chem. Soc.* **1999**, *121*, 2315.

p-Toluenesulfonyl Chloride**Reagent**

The title reagent is used for the chlorination of ketones at the α -position.

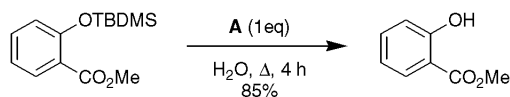
**A**

8 examples (yields 49-85%) are reported.

K. M. Brummond, K. D. Gesenberg *Tetrahedron Lett.* **1999**, *40*, 2231.

Zinc Tetrafluoroborate**Reagent**

The title reagent is used for the selective deprotection of *tert*-butyldimethylsilyl ethers under mild conditions.

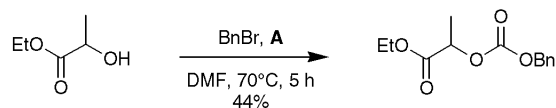
**A**

26 examples (yields 0, 80-96%) are reported.

B. C. Ranu, U. Jana, A. Majee *Tetrahedron Lett.* **1999**, *40*, 1985.

Cesium Carbonate**Reagent**

The title reagent (with tetrabutylammonium iodide (TBAI) in some cases) facilitates the *O*-alkylation of alcohols with alkyl halides, giving rise to the exclusive formation of mixed alkyl carbonates. The preceding paper details a similar ether synthesis utilising CsOH.

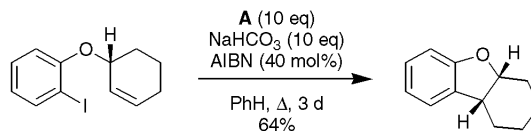


F. Chu, E. E. Dueno, K. W. Jung
Tetrahedron Lett. **1999**, *40*, 1847.

9 examples (yields 44-97%) are reported.

Hypophosphorous Acid**Reagent**

The title reagent and its corresponding 1-ethylpiperidine salt are used to mediate carbon-carbon bond forming radical reactions in both aqueous and organic media. The methods used avoid many of the problems associated with tributyltin hydride methodology.

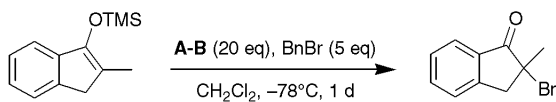


S. R. Graham, J. A. Murphy, D. Coates
Tetrahedron Lett. **1999**, *40*, 2415.

10 examples (yields 63-94%) are reported.

Cesium Fluoride / Cesium Hydroxide**Reagent**

Fusion of a 1:1 mixture of the title reagent pair results in a glassy solid which is used as an effective heterogeneous desilylating agent to form a variety of carbon anions from trimethylsilylated precursors.

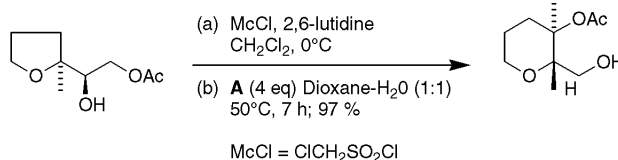


J. Busch-Petersen, Y. Bo, E. J. Corey
Tetrahedron Lett. **1999**, *40*, 2065.

10 examples (yields 0, 65-91%). Examples using CsCl as an alternative to **B** are also reported.

Zinc Acetate**Reagent**

Treatment of cyclic ethers having a chloromethanesulfonate leaving group on the side chain with **A** results in a stereoselective rearrangement reaction to afford ring-expanded products.

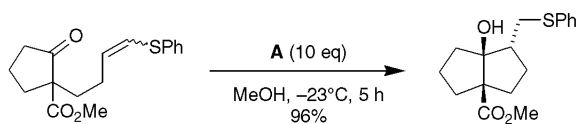


N. Hori, K. Nagasawa, T. Shimizu, T. Nakata
Tetrahedron Lett. **1999**, *40*, 2145.

3 examples (yields 89-97%).

Magnesium**Reagent**

The title reagent is used in the intramolecular ketyl radical cyclisation of ketones tethered to carbon-carbon multiple bonds. The reagent provides an alternative to the use of samarium iodide.

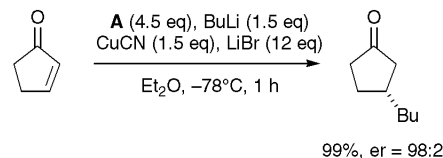
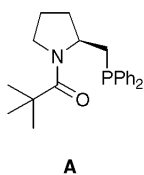


G. H. Lee, S. J. Ha, I. K. Yoon, C. S. Pak
Tetrahedron Lett. **1999**, *40*, 2581.

10 examples (yields 0, 10-96%).

(S)-(-)-N-(2,2'-Dimethylpropionyl)-2-[(diphenylphosphino)methyl]pyrrolidine**Reagent**

Asymmetric conjugate addition of lithium organocopper reagents in the presence of the title phosphine is reported with moderate to excellent stereoselectivity.

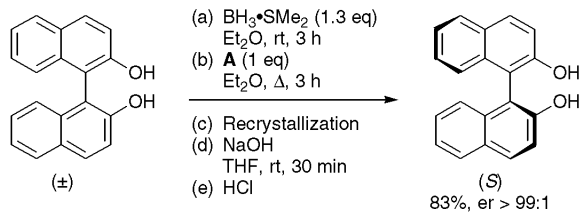
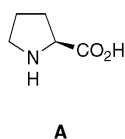


M. Kanai, Y. Nakagawa, K. Tomioka *Tetrahedron* **1999**, *55*, 3831.

66 examples using **A** (yields 26-99%, %ee 44-95%).

(S)-Proline**Reagent**

Resolution of 1,1'-Bi-2-naphthol (BINOL) has been achieved using the title amino acid and borane-dimethylsulfide. The resolution proceeds via a cyclic boronate ester.

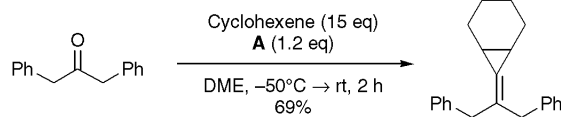
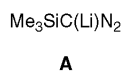


Z. Shan, Y. Xiong, D. Zhao *Tetrahedron* **1999**, *55*, 3893.

The (*R*)-isomer was isolated in 79% yield as a single enantiomer.

Lithium Trimethylsilyldiazomethane**Reagent**

The title reagent is utilised in the methylene cyclopropanation of a range of ketones.

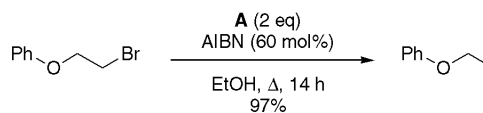
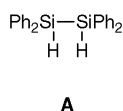


A. Sakai, T. Aoyama, T. Shioiri *Tetrahedron* **1999**, *55*, 3687.

16 examples (yields 26-69%).

1,1,2,2-Tetraphenyldisilane**Reagent**

A is utilised as a radical reagent in the reduction of alkyl bromides, addition to olefins and alkylation of heteroaromatic bases with alkyl bromides.

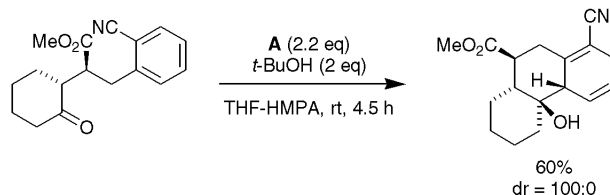


O. Yamazaki, H. Togo, S. Matsubayashi, M. Yokoyama *Tetrahedron* **1999**, *55*, 3735.

3 examples of reduction (yields 49-97%), 7 examples of radical addition to olefins (yields 20, 43-88%) and 12 examples of the alkylation of heteroaromatic bases (yields 0, 47-93%) are described.

Samarium Diiodide**Reagent**

Intramolecular attack of ketyl radical anions on aryl substituents induced by reagent **A** is reported. 1,4-Cyclohexadiene derivatives with two new asymmetric centres are isolated with complete diastereoselectivity.



C. U. Dinesh, H.-U. Reissig *Angew. Chem. Int. Ed.* **1999**, *38*, 789.

5 examples (yields 24-91%, %de = 100%).

Hexamethylphosphorous Triamide (HMPT)		Reagent
<p>Secondary and tertiary amides have been synthesized from tribromoethyl esters in one step using the title compound. Similarly esters of primary and secondary alcohols have been prepared using PBu_3, in the presence of DMAP.</p>	<p>HMPT A</p>	<p>6 examples of amide formation (yields 57-88%).</p>
<p>J. J. Hans, R. W. Driver, S. D. Burke <i>J. Org. Chem.</i> 1999, <i>64</i>, 1430.</p>		
Chlorosulfonyl Isocyanate (CSI)		Reagent
<p>The title compound mediates the [3 + 2] annulation of allylsilanes to yield 2-pyrrolidinones.</p>	<p>ClSO_2NCO A</p>	<p>5 examples (yields 54-75%, %de 84-96%).</p>
<p>C. W. Roberson, K. A. Woerpel <i>J. Org. Chem.</i> 1999, <i>64</i>, 1434.</p>		
1-{1-[(Trimethylsilyl)methyl]prop-2-enyl}-1H-benzotriazole		Reagent
<p>The title reagent mediates the regioselective synthesis of 2-alkyl-substituted 1,3-butadienes.</p>	<p>A</p>	<p>13 examples (yields 60-90%).</p>
<p>A. R. Katritzky, L. Serdyuk, D. Toader, X. Wang <i>J. Org. Chem.</i> 1999, <i>64</i>, 1888.</p>		
Triethylsilane / Sodium Triacetoxymethylborohydride		Reagent
<p>The title reagent pair in the presence of palladium on carbon mediate a one-pot reductive alkylation of amines by <i>S</i>-ethyl thioesters.</p>	<p>Et_3SiH A $\text{NaBH}(\text{OAc})_3$ B</p>	<p>7 examples (yields 67-96%).</p>
<p>Y. Han, M. Chorev <i>J. Org. Chem.</i> 1999, <i>64</i>, 1972.</p>		
Trimethylsilyl Cyanide		Reagent
<p>A in the presence of AgClO_4 effects the conversion of alkenes into tertiary isocyanides.</p>	<p>Me_3SiCN A</p>	<p>9 examples (yields 60-94%).</p>
<p>Y. Kitano, K. Chiba, M. Tada <i>Synlett</i> 1999, 288.</p>		