

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

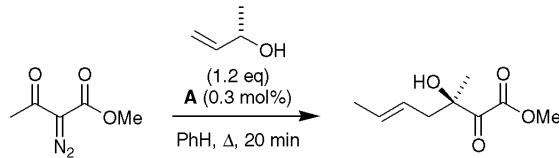
Tetrahedron Asymmetry and Tetrahedron Letters

Dirhodium Tetraacetate

Catalyst

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

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.

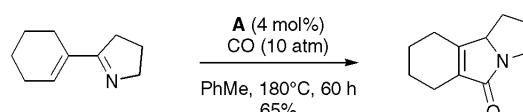


28 examples (yields 45-80%, %ee = 45-98%).

Triruthenium Dodecacarbonyl

Catalyst

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



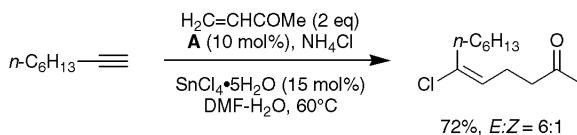
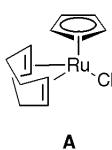
9 examples (yields 51-96%).

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**.

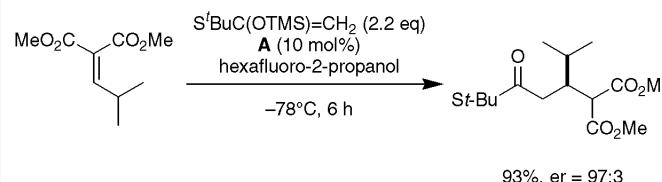
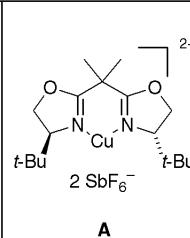


16 examples (yields 60-83%, 4:1 \leq *E:Z* \leq 15:1).

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

Copper((*S,S*)-*tert*-Butylbis(oxazolinyl)propane)dihexafluoroantimonate**Catalyst**

C-2 symmetrical Lewis acid **A** catalyses the enantioselective Michael addition of silylketene acetals to alkylidene malonates.

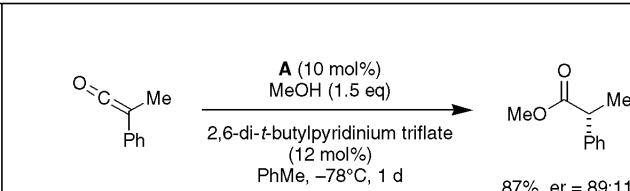
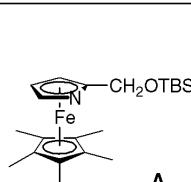


D. A. Evans, T. Rovis, M. C. Kozlowski, J. S. Tedrow *J. Am. Chem. Soc.* **1999**, *121*, 1994.

11 examples (yields 88-99%, %ee = 43-99%).

(R)-η⁵-2-(*tert*-Butyldimethylsilyloxy)methyl)-η⁵-pentamethylcyclopentadienyliron**Catalyst**

Planar-chiral aza-ferrocene **A** catalyses the enantioselective addition of alcohols to aryl methyl ketenes to yield arylpropionic acids.

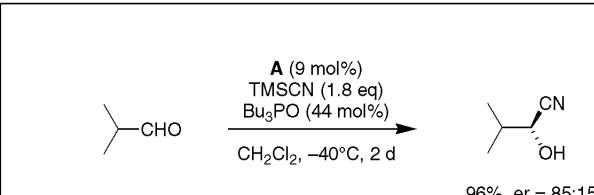
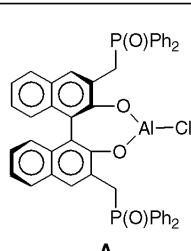


B. L. Hodous, J. C. Ruble, G. C. Fu *J. Am. Chem. Soc.* **1999**, *121*, 2637.

6 examples (yields 80-97%, %ee = 68-80%).

Bis(3-biphenylphosphinomethyl-1,1-binaphthyl-2-oyl)aluminium Chloride**Catalyst**

Chiral Lewis acid-Lewis base catalyst **A** mediates the enantioselective hydrocyanation of aldehydes.

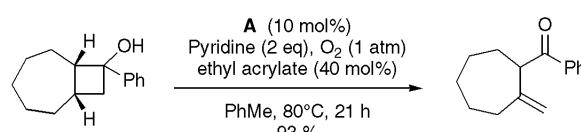
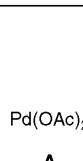


Y. Hamashima, D. Sawada, M. Kanai, M. Shibasaki *J. Am. Chem. Soc.* **1999**, *121*, 2641.

10 examples (yields 86-100%, %ee = 83-98%).

Palladium Diacetate**Catalyst**

Palladium(II)-catalysed oxidative ring cleavage of *tert*-cyclobutanols is reported.

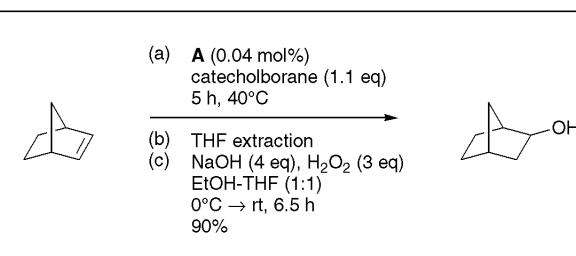
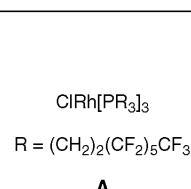


T. Nishimura, K. Ohe, S. Uemura *J. Am. Chem. Soc.* **1999**, *121*, 2645.

5 examples (yields 52-93%).

Tris(tri-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorooctylphosphino)rhodium Chloride**Catalyst**

Catalyst **A** mediates the efficient hydroboration of alkenes and alkynes in fluoruous solvents. The borane products are separated by extraction with THF leaving **A** in the fluoruous phase.

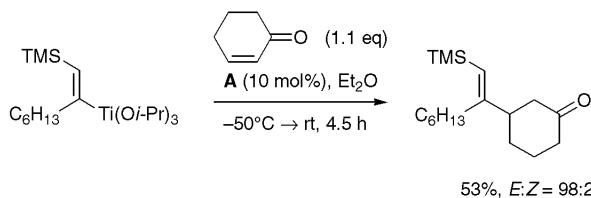
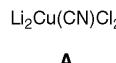


J. J. J. Juliette, D. Rutherford, I. T. Horváth, J. A. Gladysz *J. Am. Chem. Soc.* **1999**, *121*, 2696.

16 examples (yields 77-93%).

Dilithiumdichlorocyanocuprate**Catalyst**

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

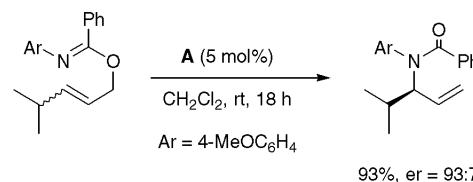
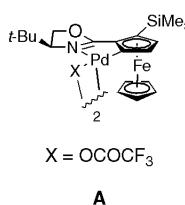


H. Urabe, T. Hamada, F. Sato *J. Am. Chem. Soc.* 1999, 121, 2931.

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

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

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

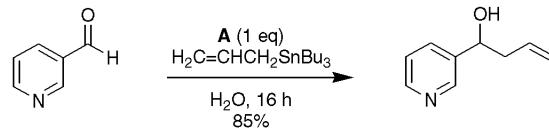


Y. Donde, L. E. Overman *J. Am. Chem. Soc.* 1999, 121, 2933.

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.

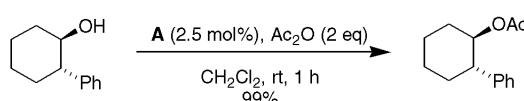


T.-P. Loh, J. Xu *Tetrahedron Lett.* 1999, 40, 2431.

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

Copper Trifluoromethanesulfonate**Catalyst**

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

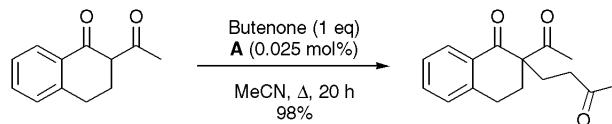
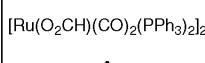


P. Saravanan, V. K. Singh *Tetrahedron Lett.* 1999, 40, 2611.

39 examples (yields 79-99%) are reported.

[Ru(O₂CH)(CO)₂(PPh₃)₂]₂**Catalyst**

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

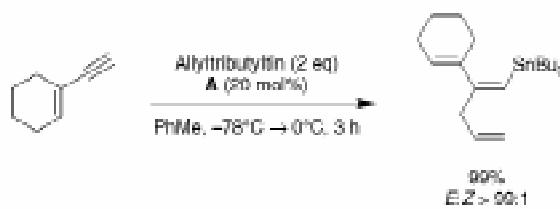


M. Picquet, C. Bruneau, P. H. Dixneuf *Tetrahedron* 1999, 55, 3937.

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

Zirconium(IV) Chloride**Catalyst**

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

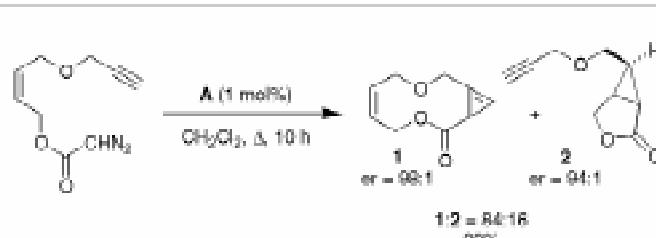
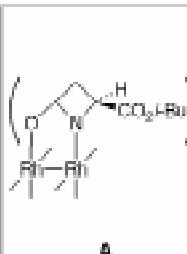


Y. Matsukawa, N. Asao, H. Kitahara, Y. Yamamoto *Tetrahedron* 1999, 55, 3779.

20 examples (yields 0, 32-99%, 0:100 to *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. Eno, C. S. Peterson, V. Lynch *Angew. Chem. Int. Ed.* 1999, 38, 709.

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.

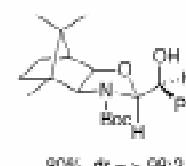
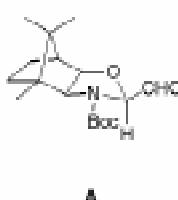


S.-K. Kang, T.-G. Baik, S.-Y. Song *Synlett* 1999, 927.

12 examples (yields 71-89%).

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.

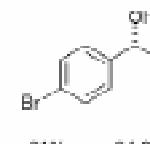
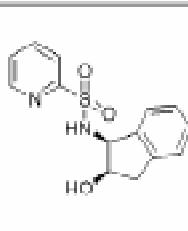


L. Colombo, M. Di Giacomo *Tetrahedron Lett.* 1999, 40, 1977.

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.

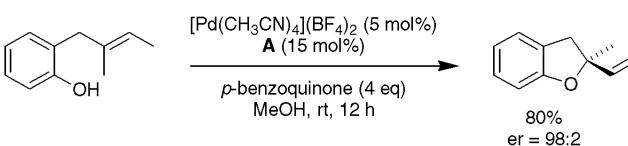
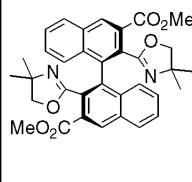


M. P. Gibi, G. R. Cook, P. Liu *Tetrahedron Lett.* 1999, 40, 2477.

6 examples (yields 60-82%, %ee = 71-89%).

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

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

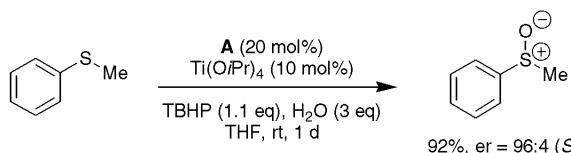
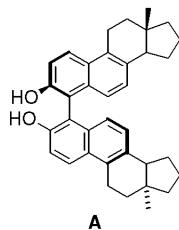


Y. Uozumi, H. Kyota, K. Kato, M. Ogasawara, T. Hayashi *J. Org. Chem.* **1999**, *64*, 1620.

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

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

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



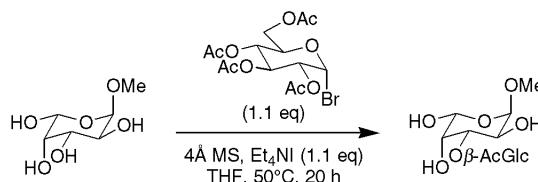
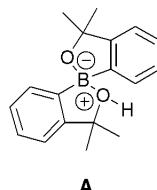
C. Bolm, O. A. G. Dabard *Synlett* **1999**, 360.

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

TBHP = *tert*-butyl hydroperoxide

Glycosidation Mediator**Reagent**

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

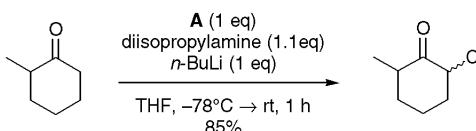
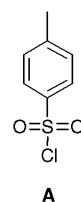


K. Oshima, Y. Aoyama *J. Am. Chem. Soc.* **1999**, *121*, 2315.

12 examples (yields 15-93%).

p-Toluenesulfonyl Chloride**Reagent**

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

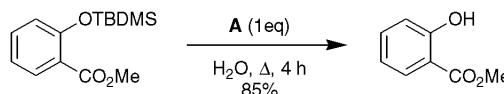


K. M. Brummond, K. D. Gesenberg *Tetrahedron Lett.* **1999**, *40*, 2231.

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

Zinc Tetrafluoroborate**Reagent**

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

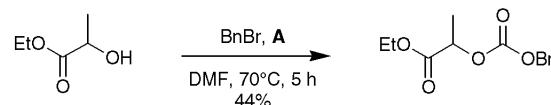


B. C. Ranu, U. Jana, A. Majee *Tetrahedron Lett.* **1999**, *40*, 1985.

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

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.

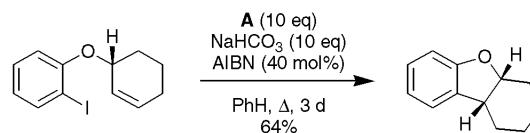


F. Chu, E. E. Dueno, K. W. Jung
Tetrahedron Lett. **1999**, *40*, 1847.

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.

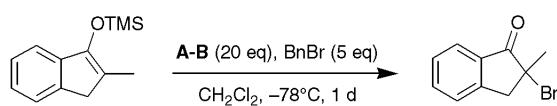
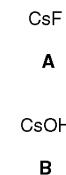


S. R. Graham, J. A. Murphy, D. Coates
Tetrahedron Lett. **1999**, *40*, 2415.

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.

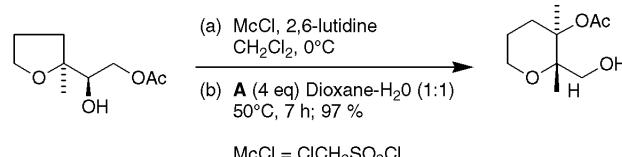


J. Busch-Petersen, Y. Bo, E. J. Corey
Tetrahedron Lett. **1999**, *40*, 2065.

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.

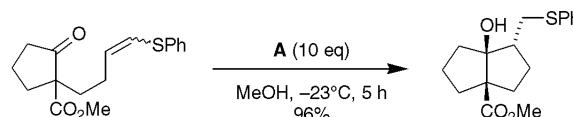


N. Hori, K. Nagasawa, T. Shimizu, T. Nakata
Tetrahedron Lett. **1999**, *40*, 2145.

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.

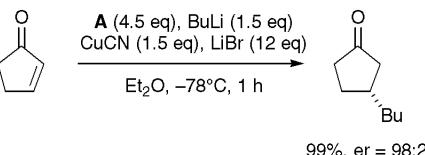
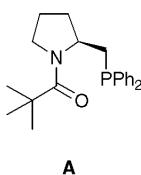


G. H. Lee, S. J. Ha, I. K. Yoon, C. S. Pak
Tetrahedron Lett. **1999**, *40*, 2581.

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

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

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

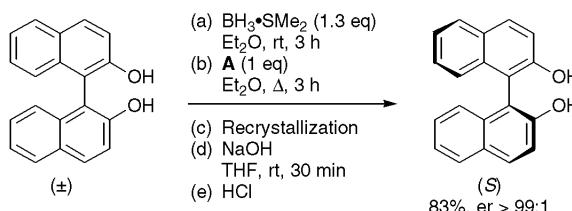
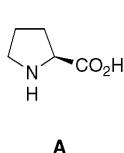


M. Kanai, Y. Nakagawa, K. Tomioka *Tetrahedron* 1999, 55, 3831.

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.

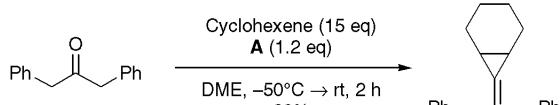
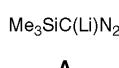


Z. Shan, Y. Xiong, D. Zhao *Tetrahedron* 1999, 55, 3893.

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.

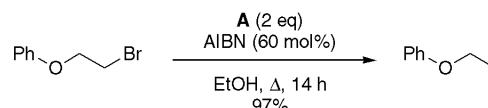
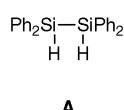


A. Sakai, T. Aoyama, T. Shioiri *Tetrahedron* 1999, 55, 3687.

16 examples (yields 26-69%).

1,1,2,2-Tetr phenyldisilane**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.

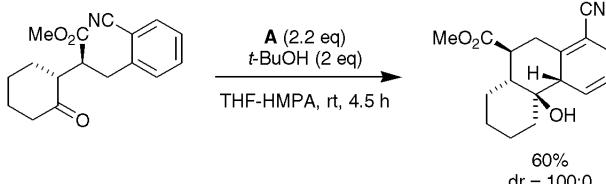


O. Yamazaki, H. Togo, S. Matsubayashi, M. Yokoyama *Tetrahedron* 1999, 55, 3735.

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.

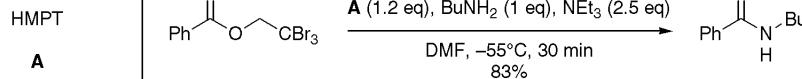


C. U. Dinesh, H.-U. Reissig *Angew. Chem. Int. Ed.* 1999, 38, 789.

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

Hexamethylphosphorous Triamide (HMPT)**Reagent**

Secondary and tertiary amides have been synthesised 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.

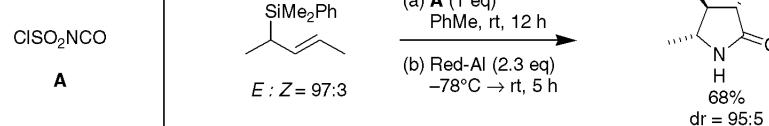


J. J. Hans, R. W. Driver, S. D. Burke *J. Org. Chem.* **1999**, *64*, 1430.

6 examples of amide formation (yields 57-88%).

Chlorosulfonyl Isocyanate (CSI)**Reagent**

The title compound mediates the [3 + 2] annulation of allylsilanes to yield 2-pyrrolidinones.

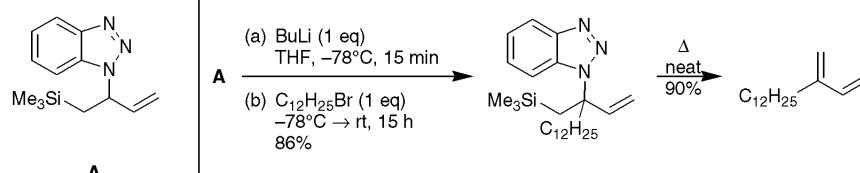


C. W. Roberson, K. A. Woerpel *J. Org. Chem.* **1999**, *64*, 1434.

5 examples (yields 54-75%, %de 84-96%).

1-[1-[(Trimethylsilyl)methyl]prop-2-enyl]-1*H*-benzotriazole**Reagent**

The title reagent mediates the regioselective synthesis of 2-alkyl-substituted 1,3-butadienes.

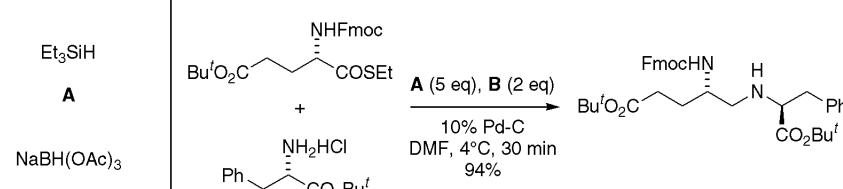


A. R. Katritzky, L. Serdyuk, D. Toader, X. Wang *J. Org. Chem.* **1999**, *64*, 1888.

13 examples (yields 60-90%).

Triethylsilane / Sodium Triacetoxyborohydride**Reagent**

The title reagent pair in the presence of palladium on carbon mediate a one-pot reductive alkylation of amines by *S*-ethyl thioesters.

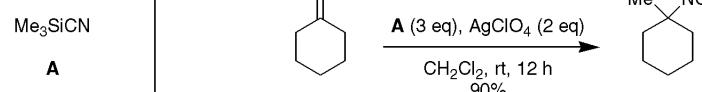


Y. Han, M. Choev *J. Org. Chem.* **1999**, *64*, 1972.

7 examples (yields 67-96%).

Trimethylsilyl Cyanide**Reagent**

A in the presence of AgClO_4 effects the conversion of alkenes into tertiary isocyanides.



Y. Kitano, K. Chiba, M. Tada *Synlett* **1999**, 288.

9 examples (yields 60-94%).