

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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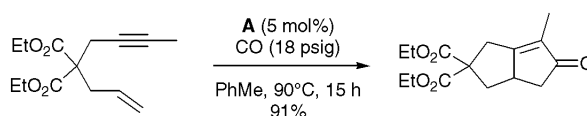
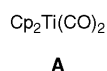
The journals regularly covered by the abstractors are:

Angewandte Chemie International Edition
 Bulletin of the Chemical Society of Japan
 Chemical Communications
 Chemistry A European Journal
 Chemistry Letters
 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

Dicyclopentadienyldicarbonyltitanium(II)

Catalyst

A catalyses the Pauson-Khand type conversion of 1,6-, 1,7- and 1,8-enynes to bicyclic cyclopentenones.



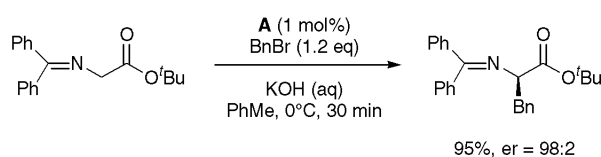
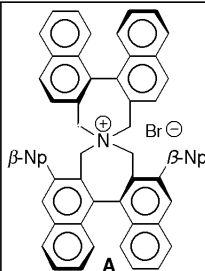
34 examples (yields 57-95%).

F. A. Hicks, N. M. Kablaoui, S. L. Buchwald *J. Am. Chem. Soc.* **1999**, *121*, 5881.

C₂-Symmetrical phase-transfer catalyst

Catalyst

A mediates the enantioselective phase transfer alkylation of a prochiral protected glycine derivative.



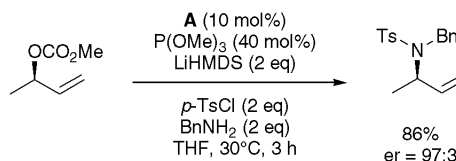
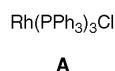
9 examples (yields 41-95%, %ee = 90-96%).

T. Ooi, M. Kameda, K. Maruoka *J. Am. Chem. Soc.* **1999**, *121*, 6519.

Tris(triphenylphosphine)rhodium(I) chloride

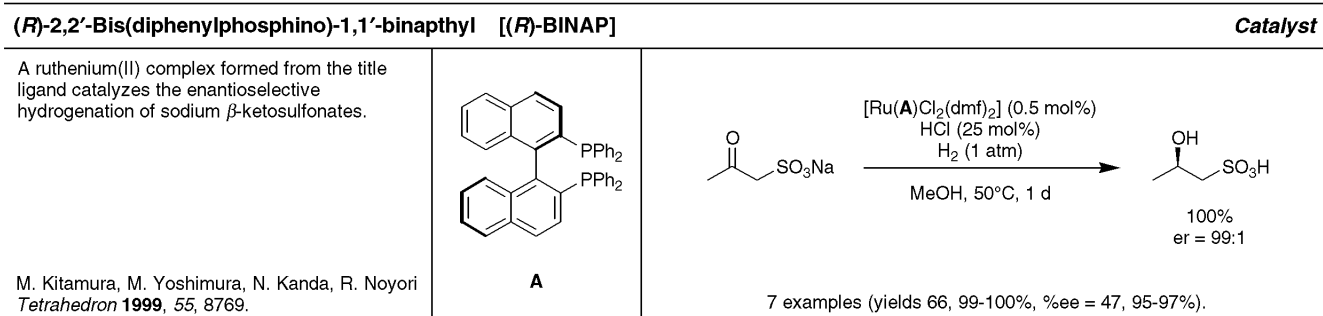
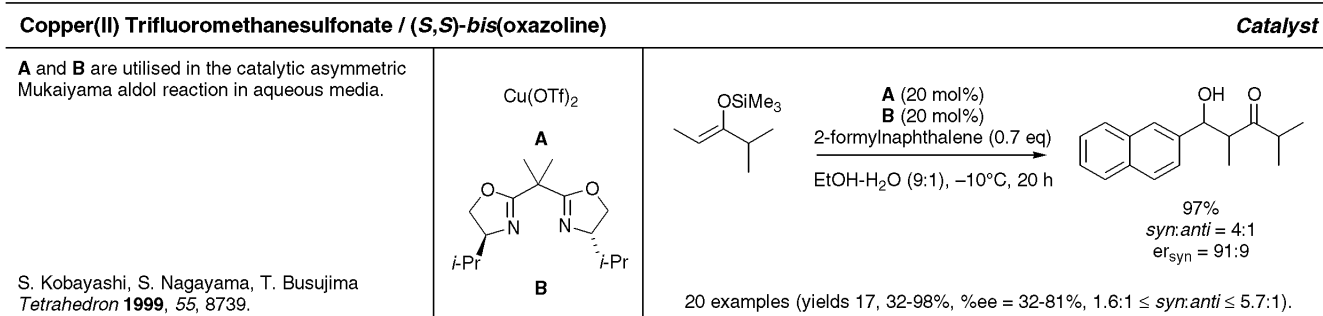
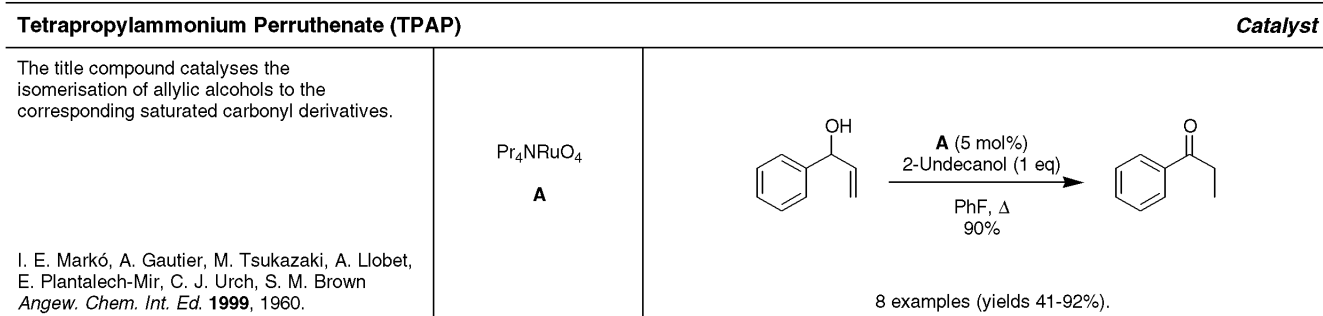
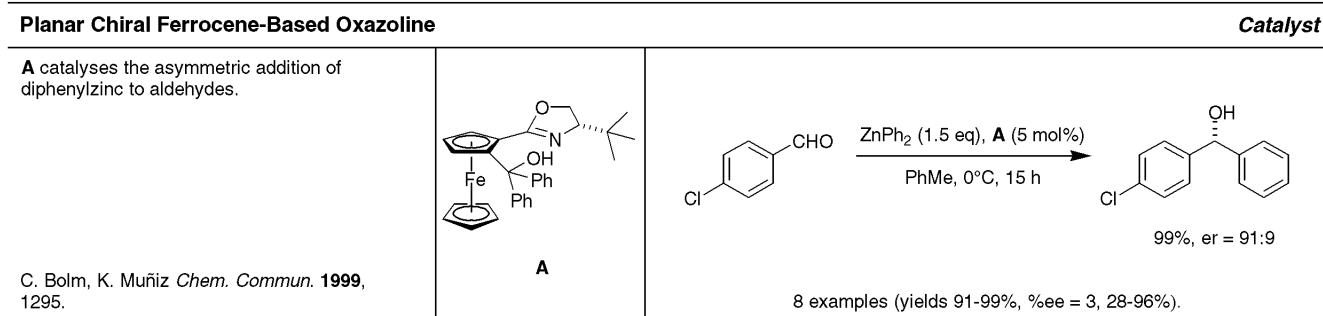
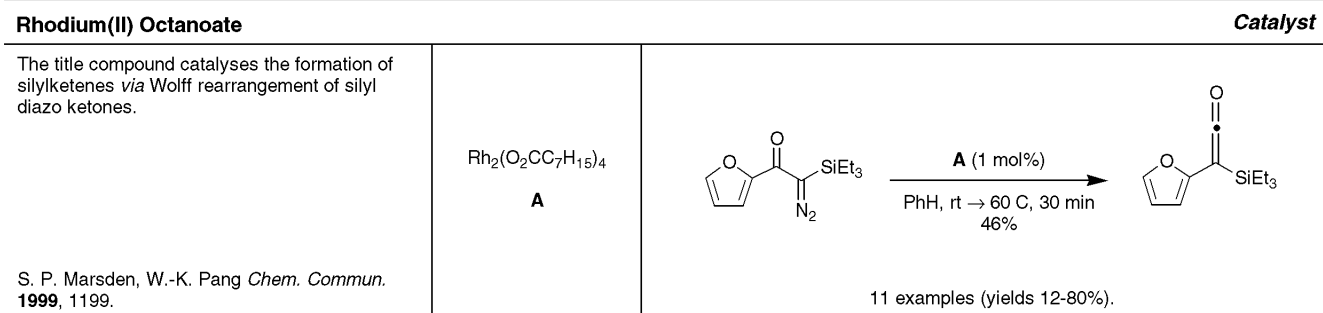
Catalyst

The enantiospecific amination of monosubstituted allylic carbonates is reported.



9 examples (yields 84-91%, %ee = 84-94%).

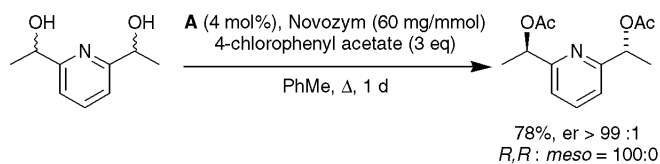
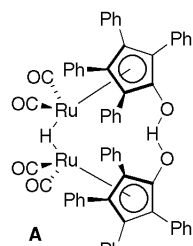
P. A. Evans, J. E. Robinson, J. D. Nelson *J. Am. Chem. Soc.* **1999**, *121*, 6761.



Ruthenium-based Isomerisation Catalyst

Catalyst

Enzymatic acylation of secondary symmetrical diols in combination with Ru-catalyzed diol isomerization leads to efficient dynamic kinetic resolution. The title catalyst is readily prepared from $\text{Ru}_3(\text{CO})_{12}$ and tetraphenylcyclopentadienone.



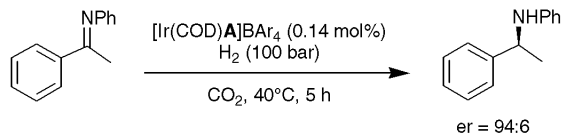
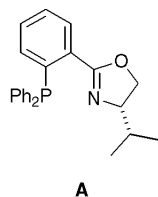
B. A. Persson, F. F. Huerta, J.-E. Bäckvall *J. Org. Chem.* **1999**, *64*, 5237.

10 examples (yields 43-90%, %ee > 96%, 38:62 \leq *R,R*: *meso* \leq 100:0).

(4*S*)-4-Isopropyl-3-[(2-diphenylphosphino)phenyl]oxazoline

Ligand

An Iridium(I) catalyst prepared from the title ligand mediates the enantioselective hydrogenation of imines in supercritical carbon dioxide.



S. Kainz, A. Brinkmann, W. Leitner, A. Pfaltz *J. Am. Chem. Soc.* **1999**, *121*, 6421.

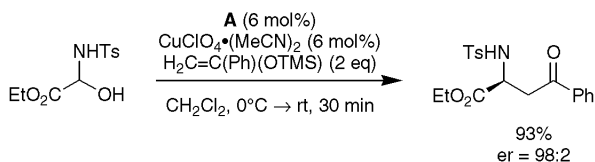
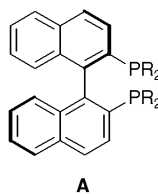
Ar = 3,5-Bis(trifluoromethyl)phenyl

2 examples (%ee = 72, 87%) using a variety of catalytic systems are described.

(R)-2,2'-Bis(ditolylphosphino)-1,1'-binaphthyl ((*R*)-ToI BINAP)

Ligand

The title ligand is utilised in the Cu(I) catalysed asymmetric alkylation of *N,O*- and *N,N*-acetals and hemiacetals.



D. Ferraris, B. Young, T. Dudding, W. J. Drury III, T. Lectka *Tetrahedron* **1999**, *55*, 8869.

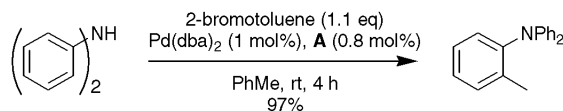
R = 4-MeC₆H₄

17 examples (yields 73-93%, %ee = 42-95%).

Tri-*tert*-butylphosphine

Ligand

Palladium(0) catalyzed amination of aryl bromides and chlorides using **A** is reported.



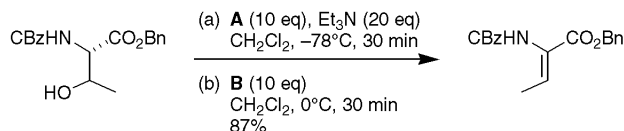
J. F. Hartwig, M. Kawatsura, S. I. Hauck, K. H. Shaughnessy, L. M. Alcazar-Roman *J. Org. Chem.* **1999**, *64*, 5575.

27 examples (yields 59-99%).

Thionylchloride / 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)

Reagent

The stereoselective preparation of α,β -dehydrated amino acids from β -hydroxyamino acids by elimination of an *in-situ* formed sulfamidite ester is reported.



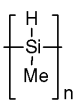
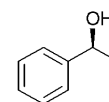
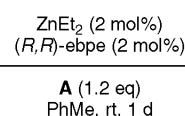
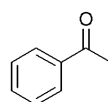
M. M. Stohlmeyer, H. Tanaka, T. J. Wandless *J. Am. Chem. Soc.* **1999**, *121*, 6100.

16 examples (yields 55-95%) are described.

Polymethylhydrosiloxane

Reagent

A in combination with C_2 -symmetrical *N,N*-ethylenebis(1-phenylethylamine) (ebpe) reduces stereoselectively a variety of acetophenones.

**A**

94%, er = 88:12

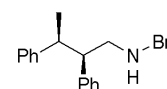
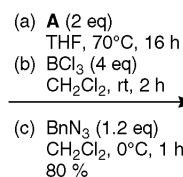
H. Mimoun, J. Y. de Saint Laumer, L. Giannini, R. Scopelliti, C. Floriani *J. Am. Chem. Soc.* **1999**, *121*, 6158.

10 examples (yields 94-100%, %ee = 18-80%).

Borane-Tetrahydrofuran Complex

Reagent

A highly stereoselective rearrangement of acyclic tertiary organoboranes obtained by hydroboration of tetrasubstituted olefins is reported.

**A**

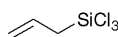
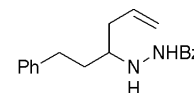
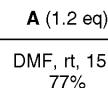
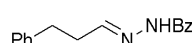
H. Laaziri, L. O. Bromm, F. Lhermitte, R. M. Gschwind, P. Knochel *J. Am. Chem. Soc.* **1999**, *121*, 6940.

10 examples (yields 51-92%).

Allyltrichlorosilane

Reagent

Homoallylic hydrazines are formed by the addition of **A** to benzoylhydrazones. In a similar fashion, *syn*- and *anti*-adducts are stereoselectively obtained from (*E*)- and (*Z*)-crotyltrichlorosilanes respectively.

**A**

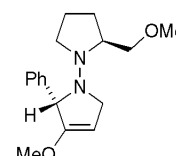
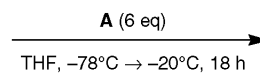
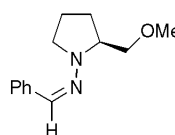
S. Kobayashi, R. Hirabayashi *J. Am. Chem. Soc.* **1999**, *121*, 6942.

19 examples using **A**, (*E*)- and (*Z*)-crotyltrichlorosilanes (yields 48-96%).

1-Methoxy-1-allenyllithium

Reagent

The title reagent is used in reactions with SAMP-hydrazones to afford α -allenyl hydrazines and/or methoxy-3-pyrrolines, depending on the nature of the solvent.

**A**

88%

dr = 100:1

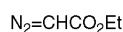
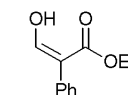
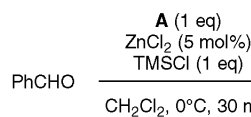
V. Breuil-Desvergnès, P. Compain, J.-M. Vatele, J. Goré *Tetrahedron Lett.* **1999**, *40*, 5009.

12 examples (yields 0, 8-88%, %de = 93-99%) are reported.

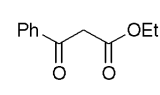
Ethyl Diazoacetate

Reagent

The title reagent reacts with aldehydes in the presence of a Lewis acid catalyst to afford the corresponding β -keto or α -formyl esters, depending upon the nature of the catalyst employed.

**A**

67%



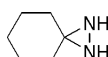
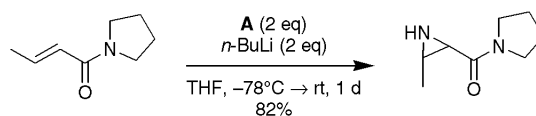
23%

S. Kanemasa, T. Kanai, T. Araki, E. Wada *Tetrahedron Lett.* **1999**, *40*, 5055.

18 examples (yields 0, 14-90%) are reported.

3,3-Pentamethylenediaziridine**Reagent**

The title reagent effects *cis*-selective aziridination of *cis*- or *trans*- α,β -unsaturated amides.

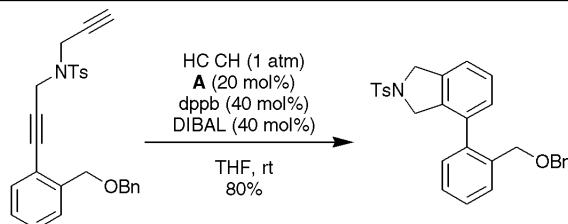
**A**

5 examples (yields 39-82%) are reported.

K. Hori, H. Sugihara, Y. N. Ito, T. Katsuki *Tetrahedron Lett.* **1999**, *40*, 5207.

Bis(acetoacetonato)nickel(II)**Reagent**

The title reagent is used in the synthesis of biaryls using a nickel-catalysed [2+2+2] cycocyclisation.

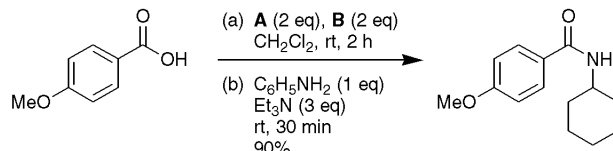
Ni(acac)₂**A**

6 examples (yields 53-94%) are reported.

Y. Sato, K. Ohashi, M. Mori *Tetrahedron Lett.* **1999**, *40*, 5231.

Trichloroacetonitrile / Triphenylphosphine**Reagent**

The title reagent pair converts carboxylic acids into acid chlorides. The acid chlorides were subsequently reacted with various amines to afford the corresponding amides.

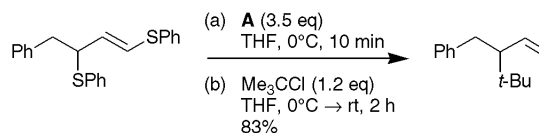
Cl₃CCN**A**PPh₃**B**

16 examples (yields 70-99%) are reported.

D. O. Jang, D. J. Park, J. Kim *Tetrahedron Lett.* **1999**, *40*, 5323.

Titanocene Complex**Reagent**

The title reagent is used in the titanocene(II)-promoted desulfurative tertiary alkylation of 1,3-bis(phenylthio)alk-1-enes and β,γ -unsaturated thioacetals.

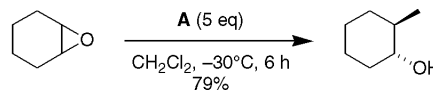
Cp₂Ti[P(OEt)₃]₂**A**

16 examples (yields 57-85%) are reported.

T. Takeda, N. Nozaki, N. Saeki, T. Fujiwara *Tetrahedron Lett.* **1999**, *40*, 5353.

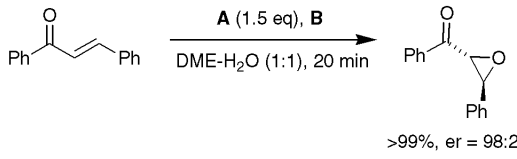
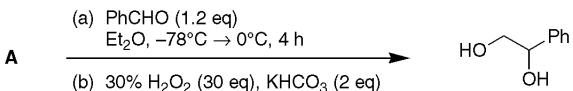
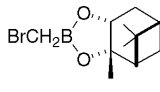
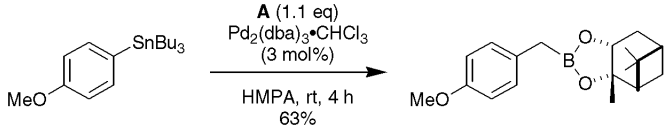
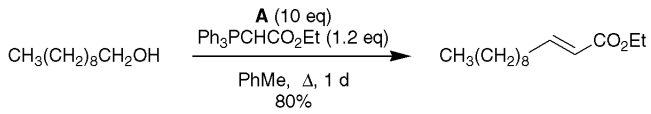

Bis(dimethyl)aluminoxane**Reagent**

A (generated *in situ* from Me₂Al and H₂O) is used for the alkylation of epoxides *via* double activation of the substrate.

(Me₂Al)₂O**A**

5 examples (yields 71-94%) are reported.

N. Abe, H. Hanawa, K. Maruoka, M. Sasaki, M. Miyashita *Tetrahedron Lett.* **1999**, *40*, 5369.

Sodium percarbonate / Poly-L-leucine (PLL)		Reagent
The title reagent pair is used for the catalytic asymmetric epoxidation of enones.	$\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$ A PLL B	 <p>3 examples (yields 94->99%, %ee = 87-96%) are reported.</p>
J. V. Allen, K.-H. Drauz, R. W. Flood, S. M. Roberts, J. Skidmore <i>Tetrahedron Lett.</i> 1999 , <i>40</i> , 5417.		
(2-Pyridyldimethylsilyl)methylithium		Reagent
The title reagent reacts with an electrophile followed by oxidation to give the corresponding alcohol.	$2\text{-PyMe}_2\text{SiCH}_2\text{Li}$ A	A <p>(a) PhCHO (1.2 eq) Et_2O, $-78^\circ\text{C} \rightarrow 0^\circ\text{C}$, 4 h (b) 30% H_2O_2 (30 eq), KHCO_3 (2 eq) KF (2 eq) MeOH-THF (1:1), 50°C 82%</p>  <p>10 examples (yields 55-99%) are reported.</p>
K. Itami, K. Mitsudo, J. Yoshida <i>Tetrahedron Lett.</i> 1999 , <i>40</i> , 5537.		
Pinanediol bromomethylboronate		Reagent
Pd-catalysed cross-coupling of A with aryl- and alkenylstannanes yields the corresponding homologated benzylic or allylic boronates.	 A	 <p>12 examples (yields 0, 60-86%) are reported.</p>
J. R. Falck, M. Bondlela, J. Ye, S.-D. Cho <i>Tetrahedron Lett.</i> 1999 , <i>40</i> , 5647.		
Manganese Dioxide		Reagent
<i>In-situ</i> alcohol oxidation-Wittig reaction using A is applied to semi-activated and unactivated alcohols to furnish α,β -unsaturated esters.	MnO_2 A	 <p>12 examples (yields 0, 51-86%).</p>
L. Blackburn, X. Wei, R. J. K. Taylor <i>Chem. Commun.</i> 1999 , 1337.		
Tris(dimethylamino)sulfonium Difluorotrimethylsilicate (TASF)		Reagent
A mediates the deprotection of <i>N</i> -[2-(trimethylsilyl)ethanesulfonyl]aziridines (<i>N</i> -(Ses)-aziridines) under mild conditions.	$(\text{Me}_2\text{N})_3\text{S}(\text{Me}_3\text{SiF}_2)$ A	 <p>5 examples (yields 60-95%).</p>
P. Dauban, R. H. Dodd <i>J. Org. Chem.</i> 1999 , <i>64</i> , 5304.		