

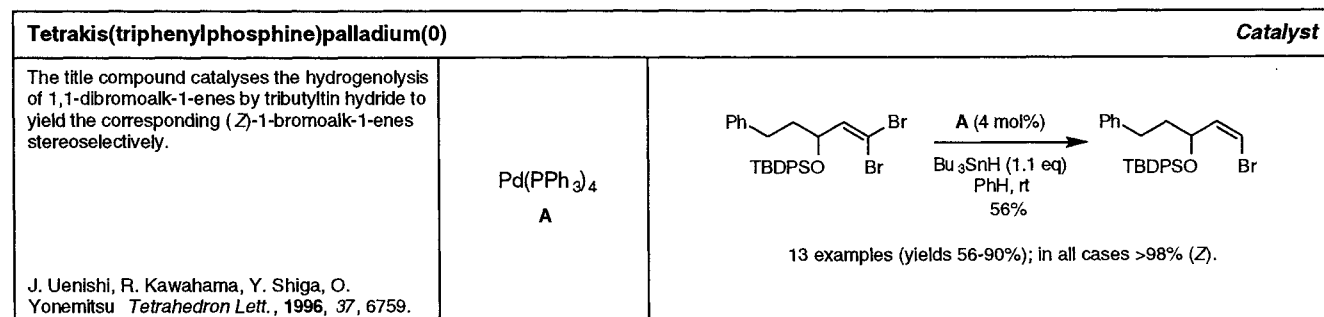
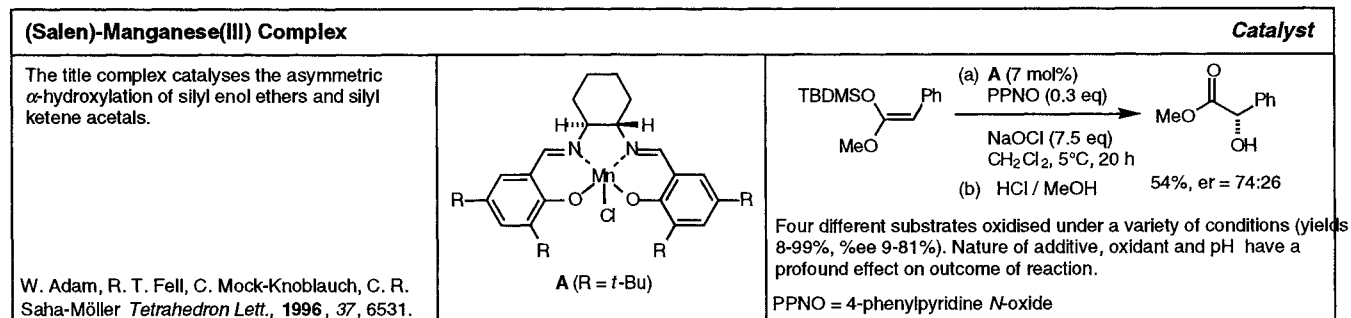
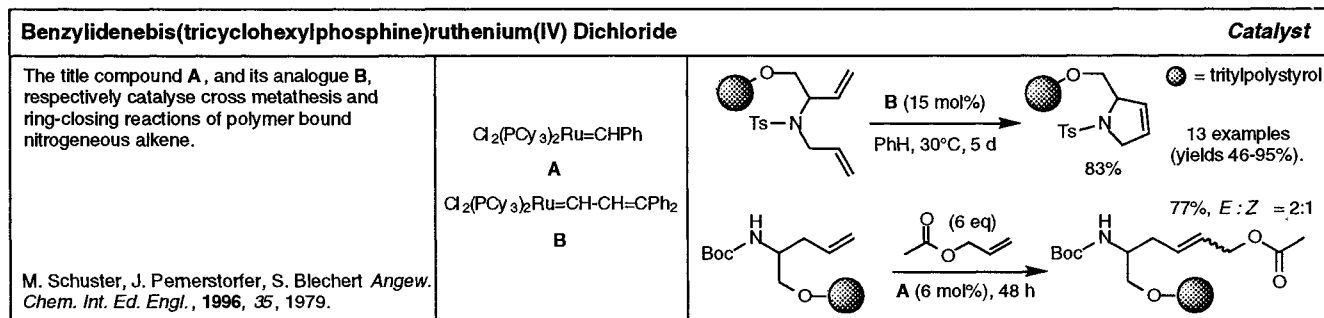
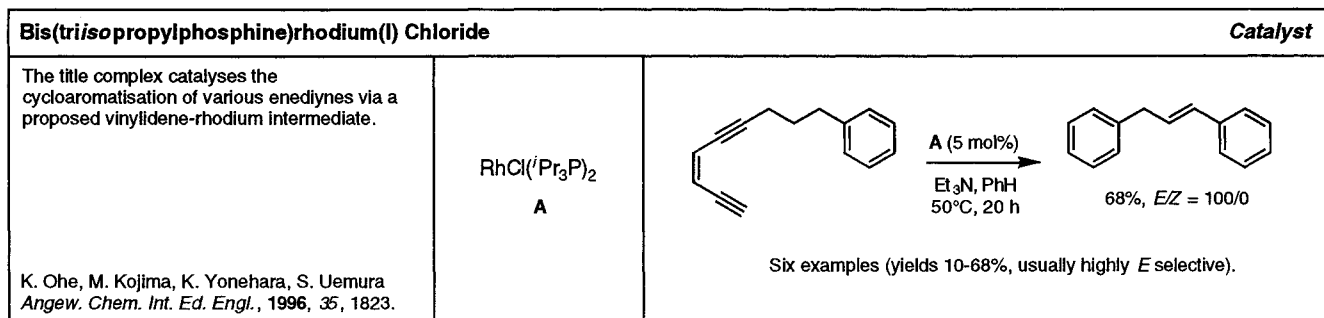
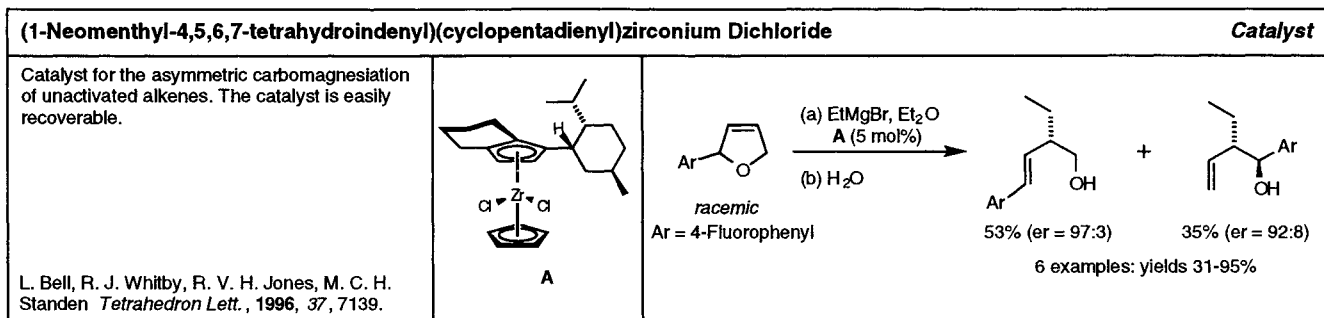
# SYNTHESIS ALERTS

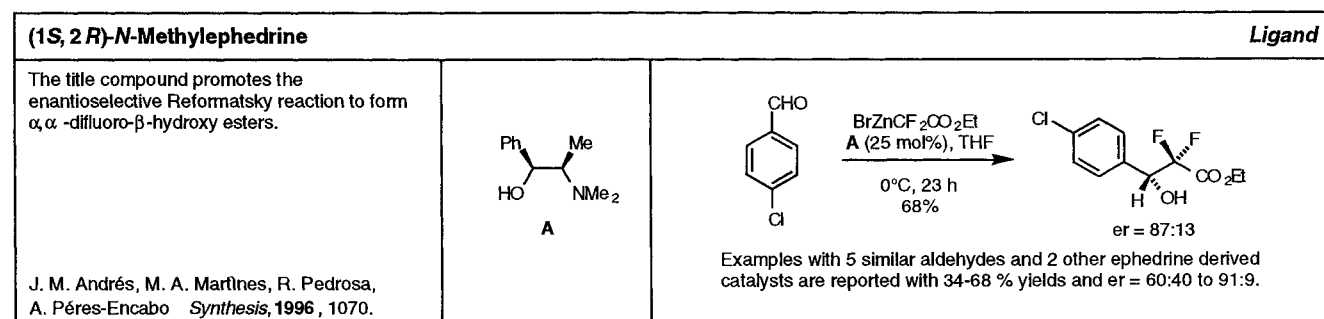
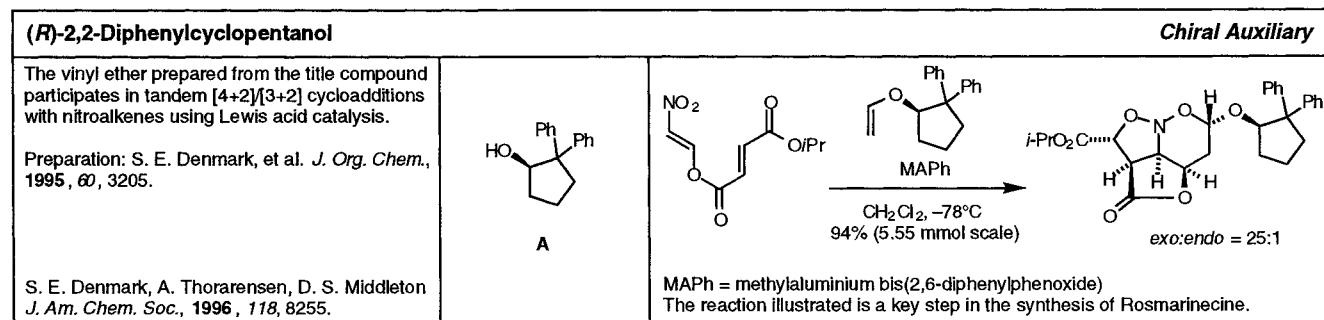
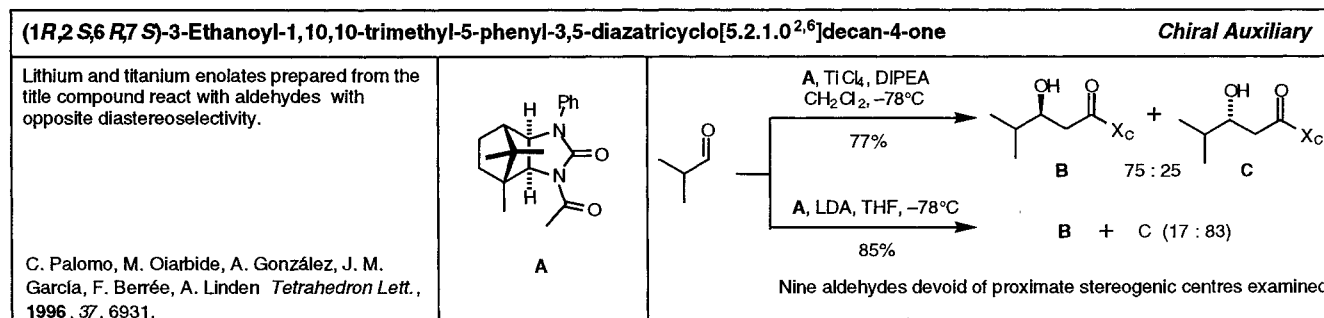
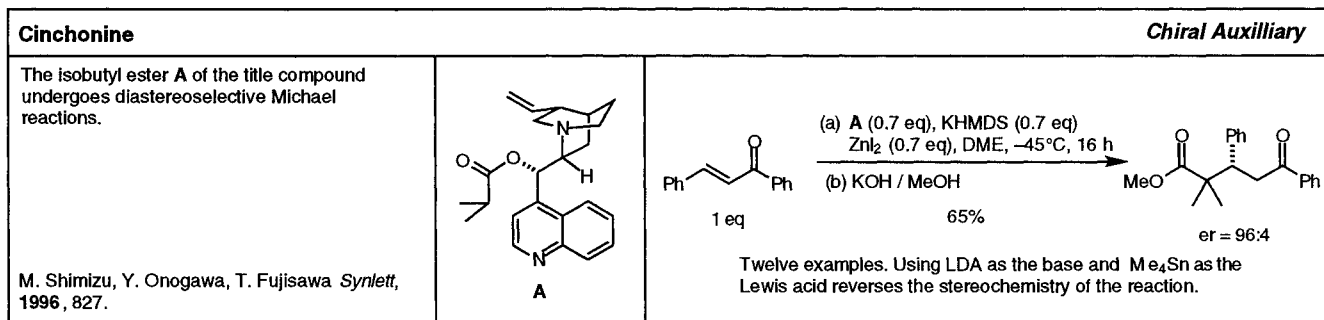
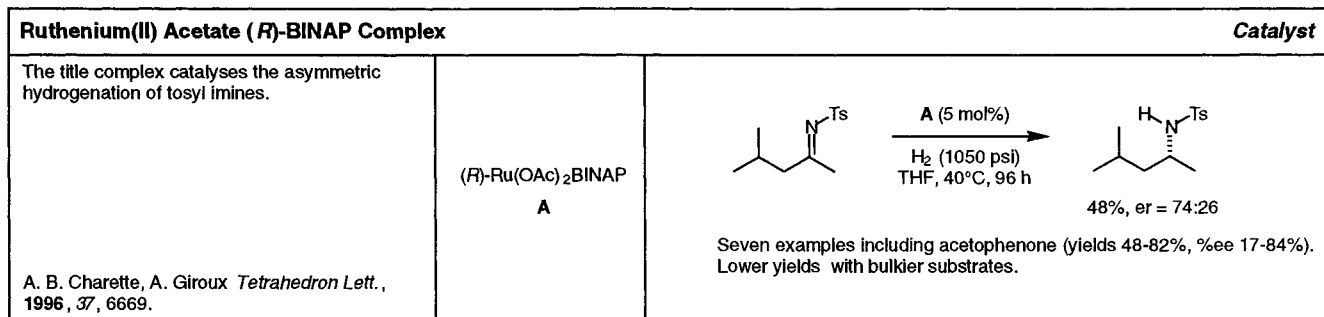
*Synthesis Alerts* is a new monthly feature to help readers of *Synthesis* keep abreast of new reagents, catalysts, ligands, chiral auxiliaries, and protecting groups which have appeared in the recent literature. Emphasis is placed on new developments but established reagents, catalysts etc are also 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.

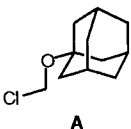
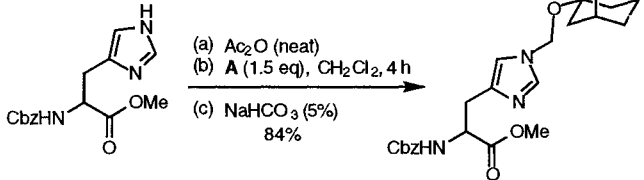
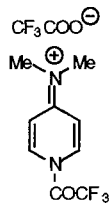
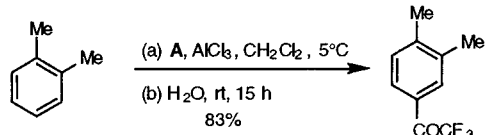
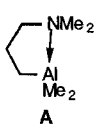
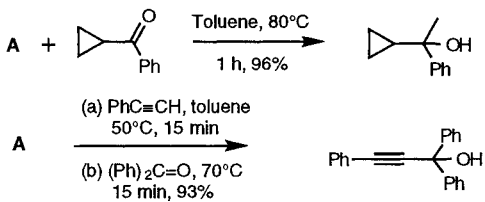
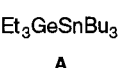
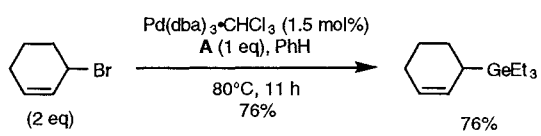
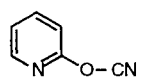
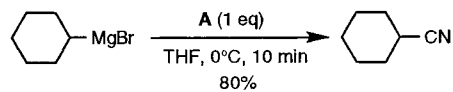
*Synthesis Alerts* is a personal selection by Paul Blakemore, Brian Dymock, Philip Hall, Philip Kocienski, J.-Y. Le Brazidec and Alessandro Pontiroli of the University of Southampton. The journals regularly covered by the abstractors are: *Angewandte Chemie International Edition*, *Bulletin de la Societe Chimie de France*, *Bulletin of the Chemical Society of Japan*, *Chemische Berichte*, *Chemistry Letters*, *Helvetica Chimica Acta*, *Journal of Organic Chemistry*, *Journal of Organometallic Chemistry*, *Journal of the American Chemical Society*, *Liebigs Annalen*, *Tetrahedron Letters*.

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Lithium Tetrakis([bis(trifluoromethyl)phenyl]methoxy)aluminate		Catalyst
<p>The title compound catalyses the 1,4- addition of silyl ketene acetals to enones.</p> <p>T. J. Barbarich, S. T. Handy, S. M. Miller, O. P. Anderson, P. A. Grieco, S. H. Strauss <i>Organometallics</i>, 1996, 15, 3776.</p>	<p style="text-align: center;">A</p>	<p style="text-align: center;">5 examples:- yields &gt; 81%</p> <p style="text-align: center;">A also catalyses the S<sub>N</sub>2 displacement of allylic acetates.</p>
18-Crown-6		Catalyst
<p>The title compound was used to synthesise vinyl ethers under phase transfer conditions.</p> <p>G. Bellucci, C. Chiappe, G. L. Moro <i>Synlett</i>, 1996, 880.</p>	<p style="text-align: center;">A</p>	<p style="text-align: center;">10 examples; yields typically &gt;75%</p>
Scandium Trifluoromethanesulfonate		Catalyst
<p>The title compound is a highly active acetalisation catalyst. For its use as a Friedel-Crafts catalyst see <i>Synlett</i>, 1996, 871.</p> <p>K. Ishihara, Y. Karumi, M. Kubota, H. Yamamoto <i>Synlett</i>, 1996, 839.</p>	<p style="text-align: center;">A</p>	<p style="text-align: center;">4 examples:- yields &gt;87%</p> <p style="text-align: center;">The title compound was also useful for the preparation of 1,3-dioxolanones and -dioxanones with α- and β-hydroxy acids.</p>

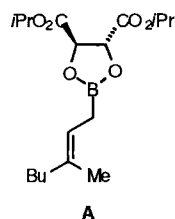




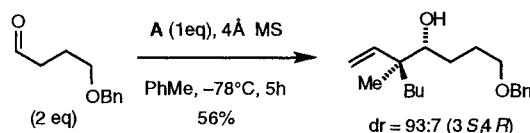
<b>[(1-Adamantyl)oxy]methyl Chloride</b>		<b>Protecting Group</b>
The title compound is a histidine protecting group. The 1-adamantylloxymethyl group is cleaved with trifluoroacetic acid.	 A	 (a) Ac <sub>2</sub> O (neat) (b) A (1.5 eq), CH <sub>2</sub> Cl <sub>2</sub> , 4 h (c) NaHCO <sub>3</sub> (5%) 84%
Y. Okada, J. Wang, T. Yamamoto, Y. Mu, T. Yokoi <i>J. Chem. Soc., Perkin Trans. 1</i> , 1996, 2139.		
<b>4-Dimethylamino-1-trifluoroacetylpyridinium Trifluoroacetate</b>		<b>Reagent</b>
Aryltrifluoromethyl ketones are obtained upon treatment of aromatic compounds with the title iminium salt in presence of aluminium chloride.	 A	 (a) A, AlCl <sub>3</sub> , CH <sub>2</sub> Cl <sub>2</sub> , 5°C (b) H <sub>2</sub> O, rt, 15 h 83%
G. Simchen, A. Schmidt <i>Synthesis</i> , 1996, 1093.		A is stable and easy to handle.
<b>[(3-Dimethylamino)propyl]dimethylaluminium</b>		<b>Reagent</b>
The title complex effects methylation and ethynylation of carbonyl compounds in high yields.	 A	 (a) PhC=CH, toluene, 50°C, 15 min (b) (Ph) <sub>2</sub> C=O, 70°C, 15 min, 93%
W. Baidossi, A. Rosenfeld, B. C. Wassermann, S. Schutte, H. Schumann, J. Blum <i>Synthesis</i> , 1996, 1127.		α, β-Unsaturated carbonyl compounds undergo 1,4 addition of methyl or ethynyl groups.
<b>(Triethylgermyl)tributylstannane</b>		<b>Reagent</b>
The title compound gives allylic germanes on reaction with allylic bromides in the presence of Pd(0).	 A	 Pd(dba) <sub>3</sub> ·CHCl <sub>3</sub> (1.5 mol%) A (1 eq), PhH 80°C, 11 h 76%
T. Nakano, K. Ono, T. Migita <i>Chem. Lett.</i> 1996, 697.		Eight examples; yields 20-92%
<b>2-Pyridyl Cyanate</b>		<b>Reagent</b>
The title compound reacts with Grignard reagents to give nitriles.	 A	 A (1 eq) THF, 0°C, 10 min 80%
J. S. Koo, J. I. Lee <i>Synth. Commun.</i> 1996, 26, 3709.		Ten examples; yields 72-97%.

**(S,S)-4,5-Di(isopropoxycarbonyl)-2-[(E)-3-methylhept-2-enyl]-2-bora-1,3-dioxolane** **Reagent**

The title compound undergoes enantioselective addition to aldehydes with the generation of a quaternary centre.



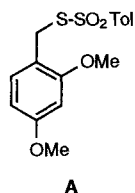
Y. Yamamoto, S. Hara, A. Suzuki *Synlett*, 1996, 883.



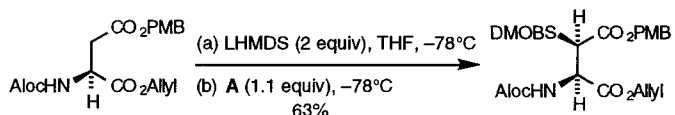
Yields are generally >75% when the aldehyde contains unfunctionalised side chains.

**2,4-Dimethoxybenzylthio Methylphenylsulfonate** **Reagent**

The title compound is an electrophilic sulfonylating agent for the preparation of thiols bearing the acid-labile 2,4-dimethoxybenzyl protecting group.



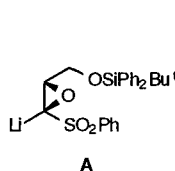
N. Shibata, J. E. Baldwin, A. Jacobs, M. E. Wood *Tetrahedron*, 1996, 52, 12839.



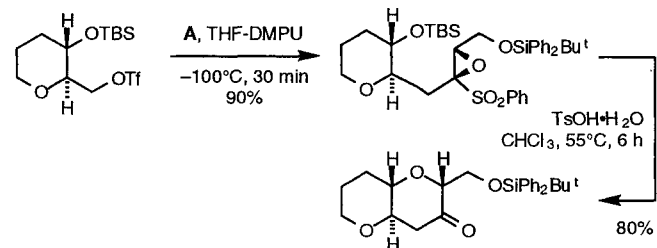
The 2,4-dimethoxybenzyl (DMOB) protecting group can be removed using mercury(II) trifluoroacetate, the free thiol being liberated by treatment of the resulting mercury(II) salt with hydrogen sulfide

**(1R,2S)-1-Lithio-1-phenylsulfonyl-2-(((tert-butylidiphenyl)silyl)oxy)methyl)oxirane** **Reagent**

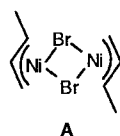
The presence of the sulfone moiety in the title compound ensures a 6-endo cyclisation which has been applied to the synthesis of polycyclic trans-fused tetrahydropyrans.



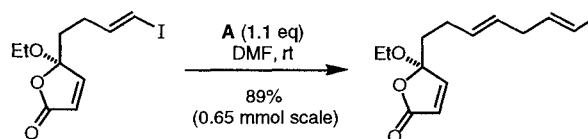
Y. Mori, K. Yaegashi, H. Furukawa *J. Am. Chem. Soc.*, 1996, 118, 8158.

**Bis(π-crotyl)nickel Bromide** **Reagent**

The title compound undergoes coupling with alkenyl iodides to give 1,4-dienes. Unlike most crotyl metal reagents, it reacts preferentially at the less hindered terminus.



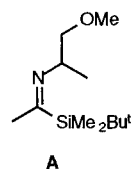
T. E. Kedar, M. W. Miller, L. S. Hegedus *J. Org. Chem.*, 1996, 61, 6121.



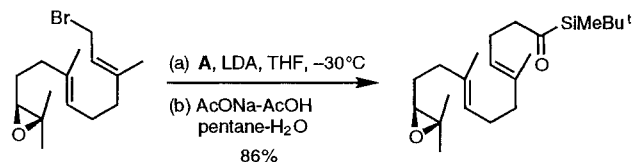
Single example taken from a synthesis of (+)-Cerulenin

**1-((tert-Butyldimethyl)silyl)-1-[N-(2-methoxy-1-methylethyl)imino]ethane** **Reagent**

The azaenolate derived from treating the title compound with LDA undergoes alkylation to give products which hydrolyse to acyl tert-butyldimethylsilanes.



E. J. Corey, S. Lin *J. Am. Chem. Soc.*, 1996, 118, 8765.



The example illustrated is a key step in the synthesis of Dammarenediol II

Bromotri(perfluorohexylethyl)stannane		Reagent
<p>Arylstannanes prepared from the title compound undergo Stille coupling reactions. The tin byproducts are separated by simple extraction into a perfluoroalkane phase which is immiscible with water and organic solvents.</p> <p>D. P. Curran, M. Hoshino <i>J. Org. Chem.</i>, <b>1996</b>, <i>61</i>, 6480.</p>	<p>(C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>SnBr A</p> <p>80°C, 22 h 98%</p> <p>Extract into a liquid perfluoroalkane</p>	
<p>↑ 74% 4-MeOC<sub>6</sub>H<sub>4</sub>M where M = MgX or Li</p>		
Iodobenzene Diacetate		Reagent
<p>The title compound together with trimethylsilyl halides haloacetoxyates 1,4-dimethoxynaphthalenes.</p> <p>P. A. Evans, T. A. Brandt <i>Tetrahedron Lett.</i>, <b>1996</b>, <i>37</i>, 6443.</p>	<p>A</p> <p>(a) A (1.1 eq) TMSBr (2.2 eq) CH<sub>2</sub>Cl<sub>2</sub>, 0°C (b) A (2 eq), 50 min</p> <p>80%</p>	
<p>By control of stoichiometry and subtle changes in reaction conditions mono- and dibromo derivatives can also be procured. Nine examples (yields 71-75%).</p>		
2,3-Dichloro-5,6-dicyano-1,4-benzoquinone		Reagent
<p>The title compound selectively deprotects primary allyl ethers.</p> <p>J. S. Yadav, S. Chandrasekhar, G. Sumithra, R. Kache <i>Tetrahedron Lett.</i>, <b>1996</b>, <i>37</i>, 6603.</p>	<p>A (1.2 eq)</p> <p>CH<sub>2</sub>Cl<sub>2</sub>:H<sub>2</sub>O (9:1), rt</p> <p>70%</p>	
<p>Total of 11 well-chosen examples (yields 70-92%).</p>		
(S)-4-tert-Butyl-3-pivaloyl-1,3-thiazolidine-2-thione		Reagent
<p>Kinetic resolution of <i>sec</i>-alcohols is achieved via pivaloylation with the thiazolidinethione A.</p> <p>S. Yamada, T. Ohe <i>Tetrahedron Lett.</i>, <b>1996</b>, <i>37</i>, 6777.</p>	<p>A (0.2 eq)</p> <p>Et<sub>3</sub>N (1 eq) hexane, rt, 14 h</p> <p>87%, er = 92:8</p>	
<p>Twenty examples of kinetic resolution of benzylic <i>sec</i>-alcohols. Includes the use of some slightly different thiazolidines and oxazolidines (yields 49-99%, %ee 19-84%).</p>		
Silver Tetrafluoroborate		Reagent
<p>Silver induced ring expansion of cyclopropyl <i>N</i>-chloroaminal derivatives gives β-lactams.</p> <p>N. De Kimpe, K. A. Tehrani, G. Fonck <i>J. Org. Chem.</i>, <b>1996</b>, <i>61</i>, 6500.</p>	<p>AgBF<sub>4</sub> A</p> <p>(a) t-BuOCl (1.05 eq), CH<sub>2</sub>Cl<sub>2</sub>, 0°C, 30 min (b) A (1.05 eq), CH<sub>2</sub>Cl<sub>2</sub>, rt, 3 h (c) H<sub>2</sub>O</p> <p>95%</p>	
<p>Six examples (yields 41-95%)</p>		