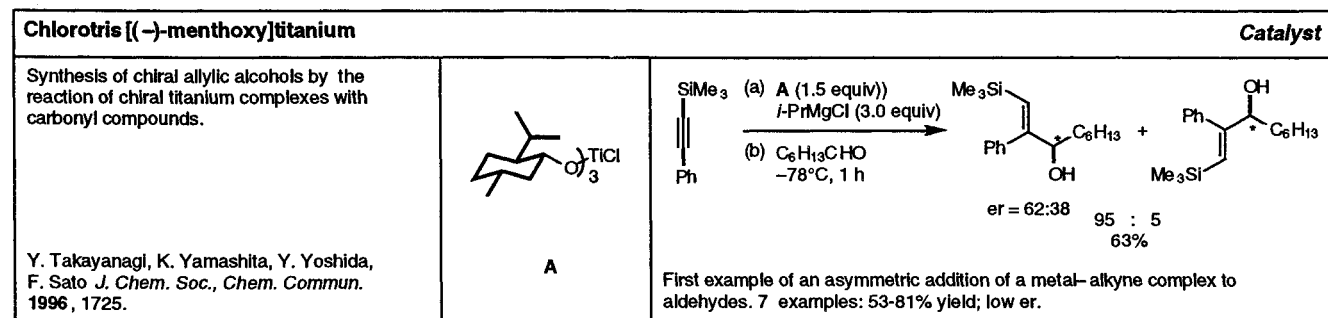
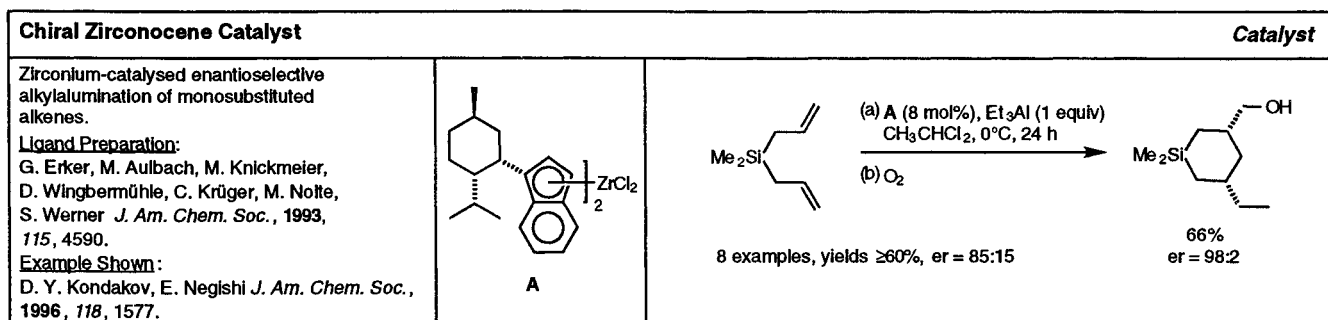
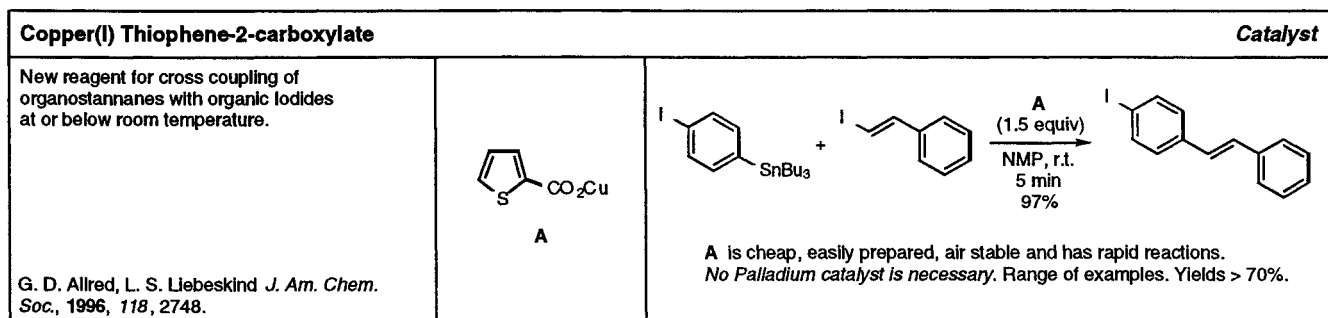


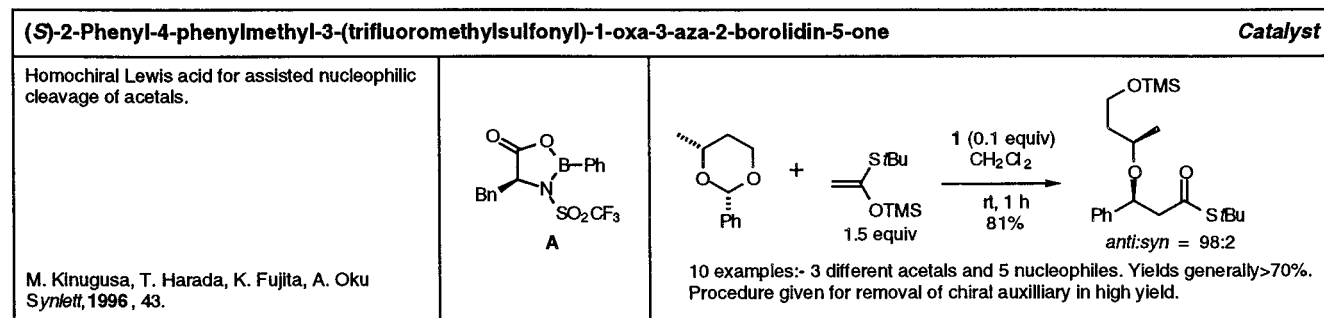
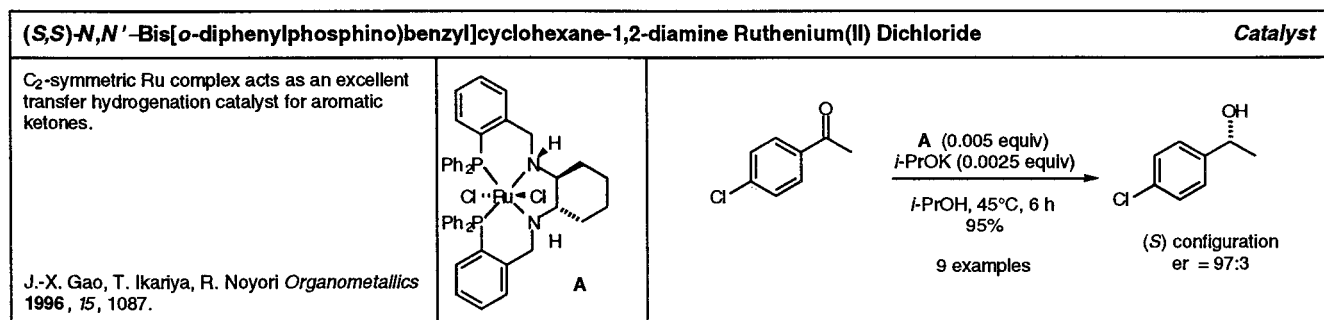
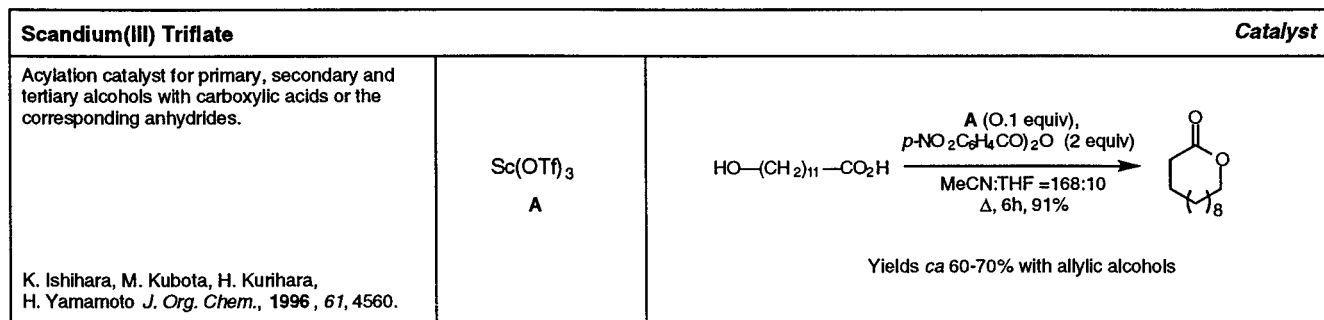
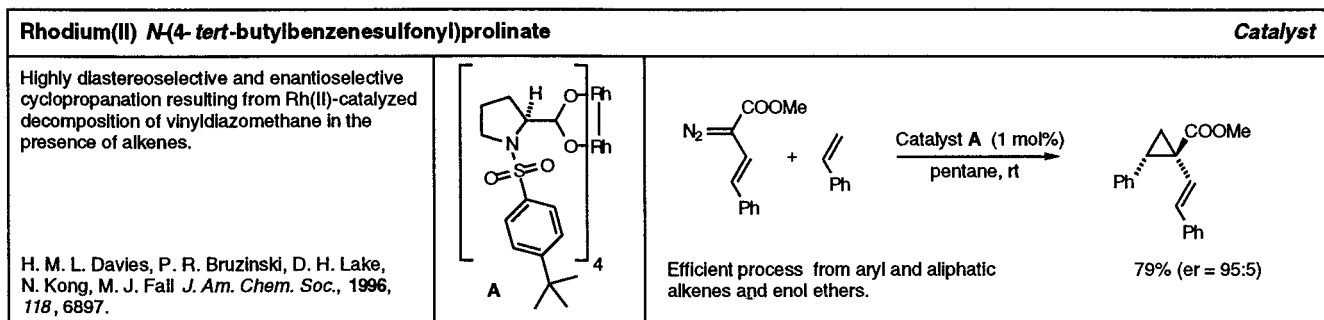
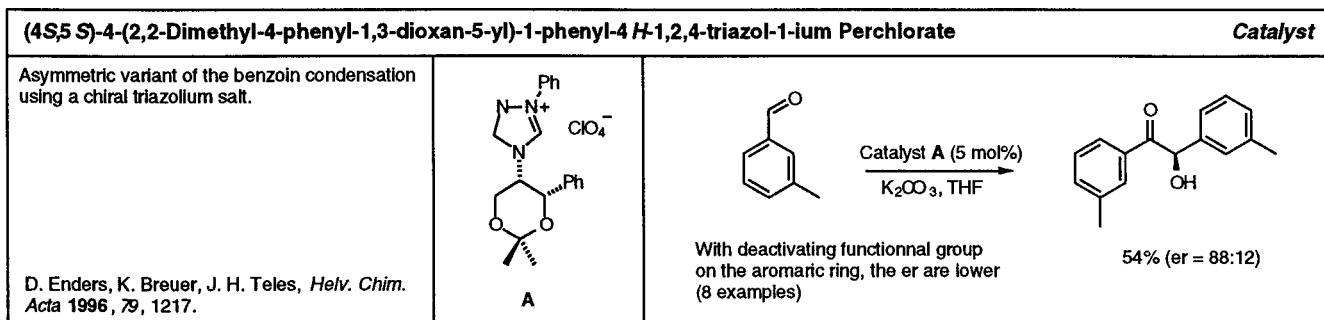
# SYNTHESIS ALERTS

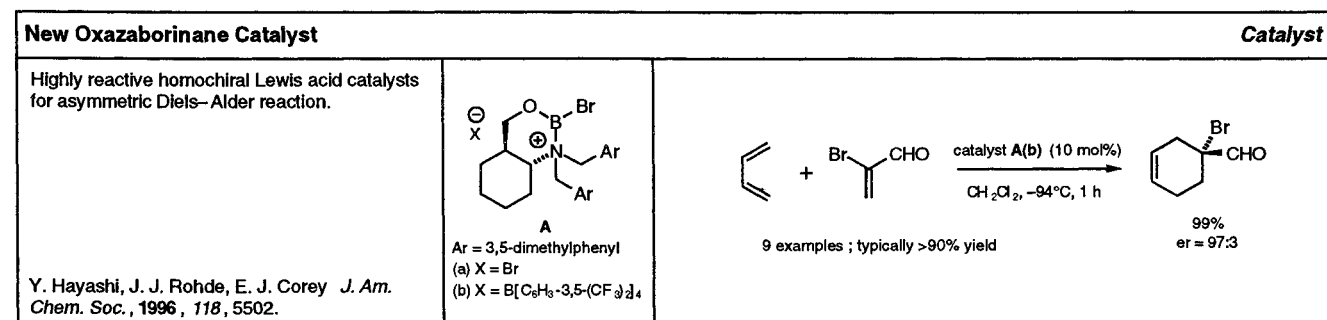
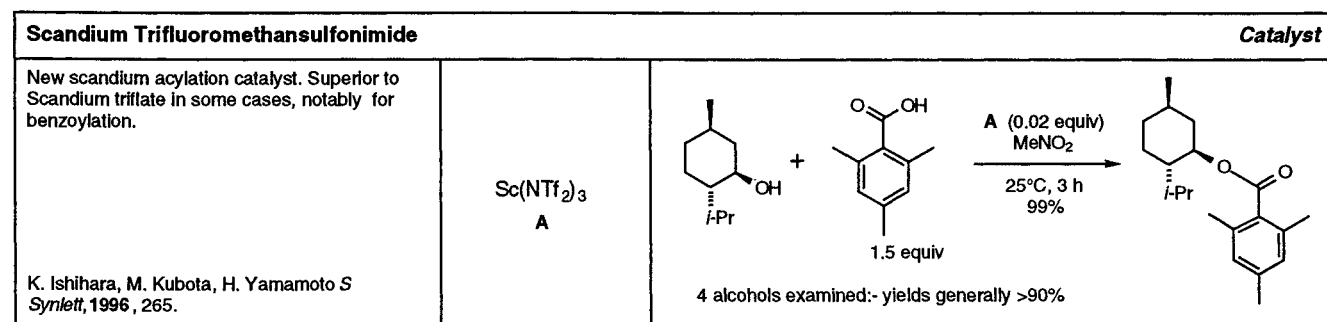
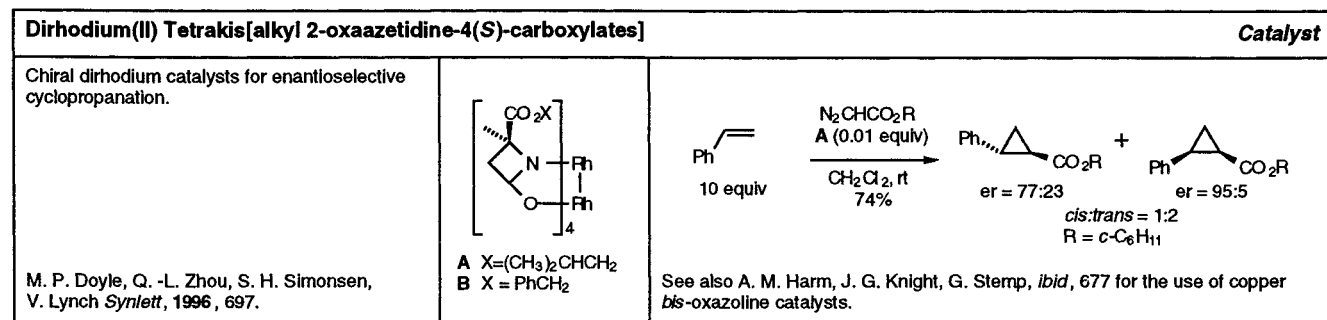
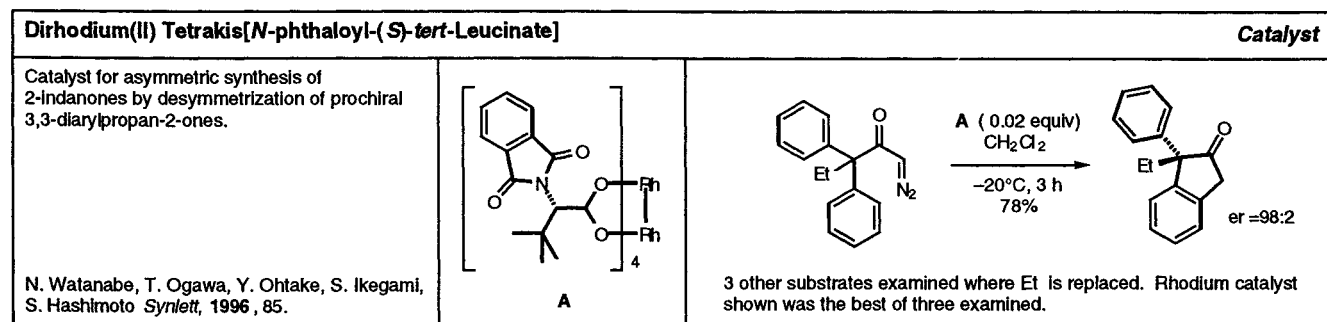
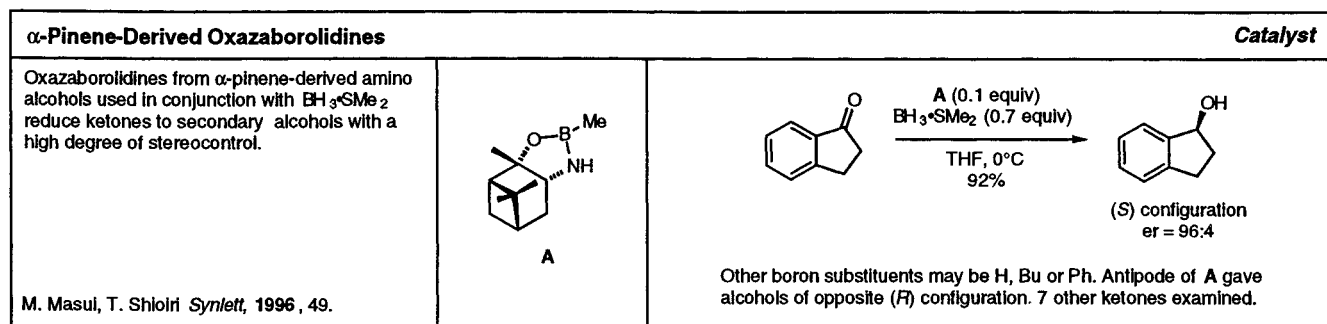
*Synthesis Alerts* is a new monthly feature to help readers of *Synthesis* keep abreast of new reagents, catalysts, ligands, chiral auxiliaries, and protecting groups which have appeared in the recent literature. Emphasis is placed on new developments but established reagents, catalysts etc are also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

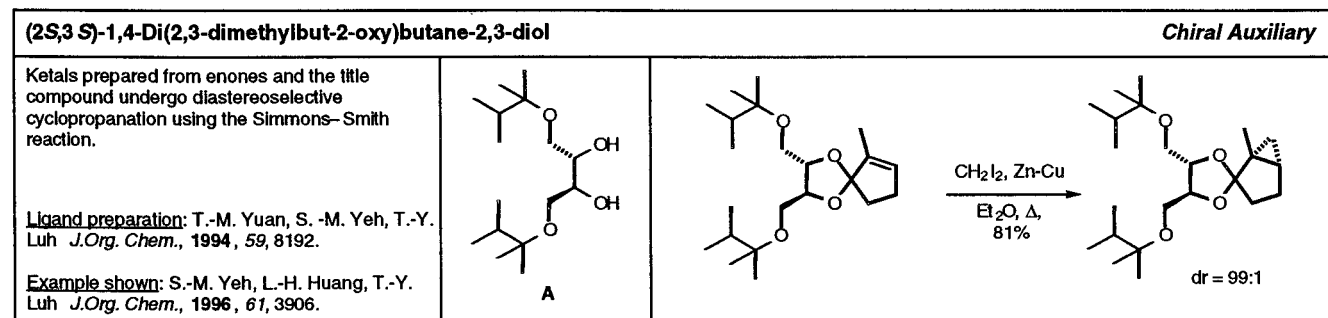
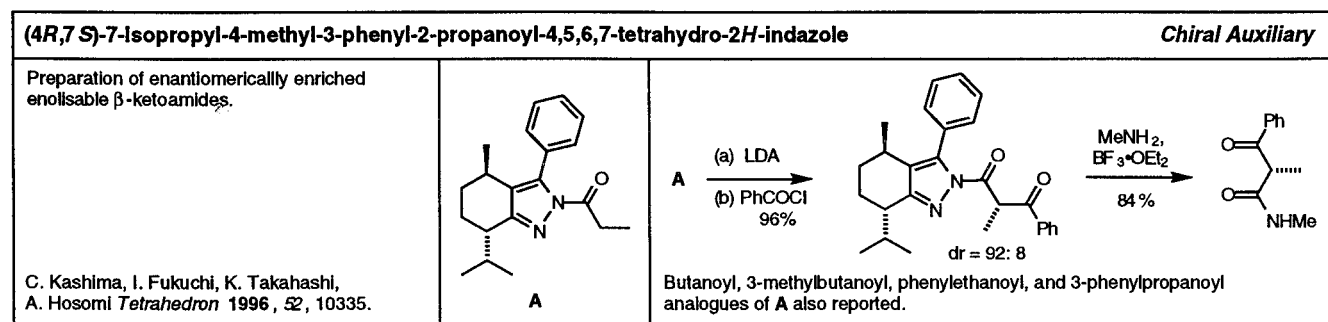
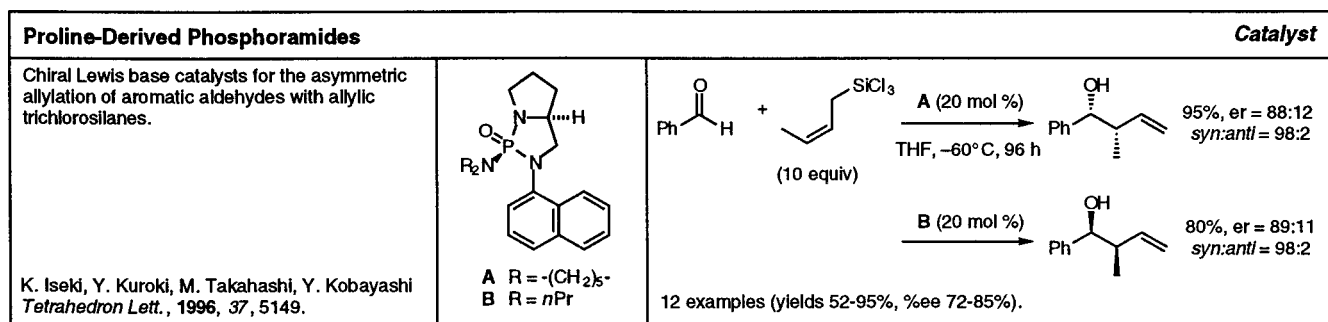
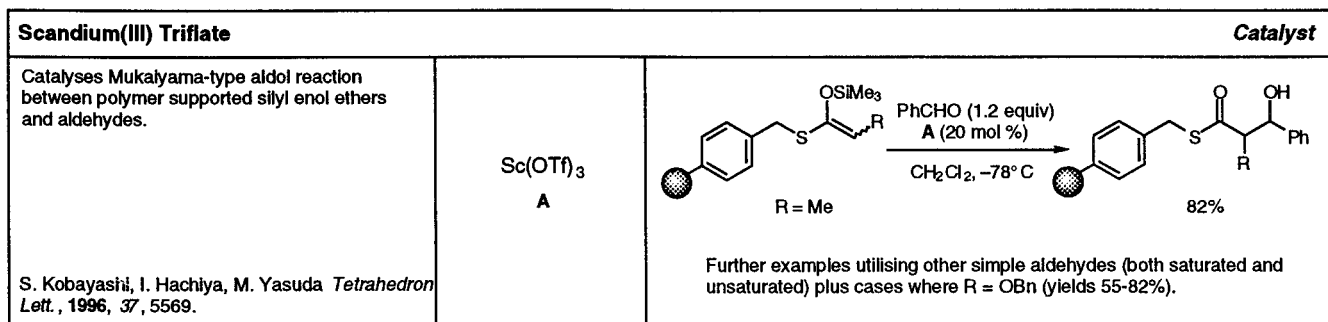
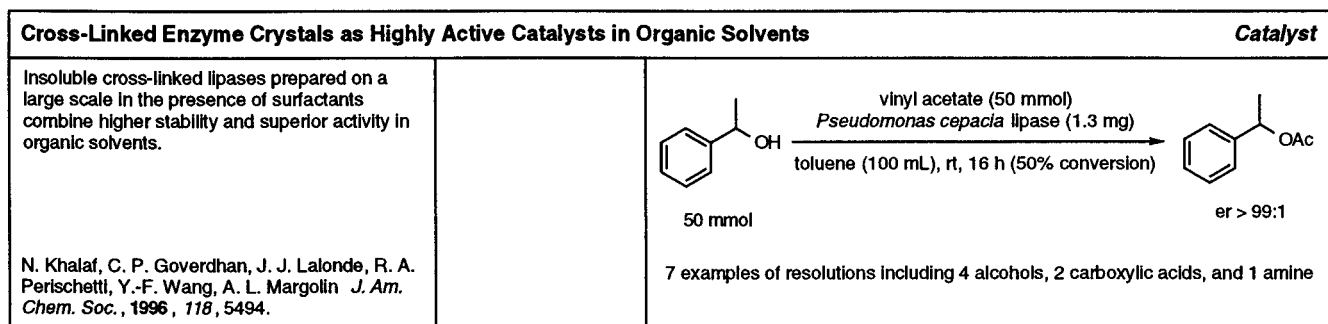
Georg Thieme Verlag does not accept responsibility for the accuracy, content, or selection of the data.

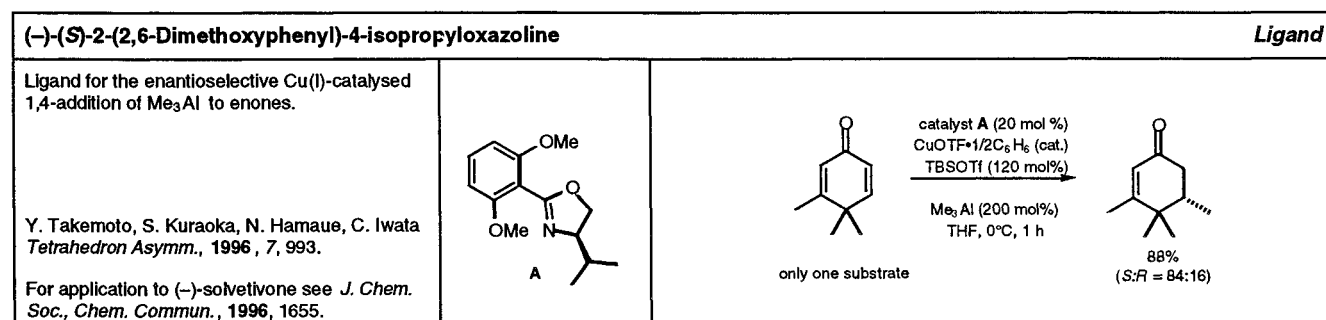
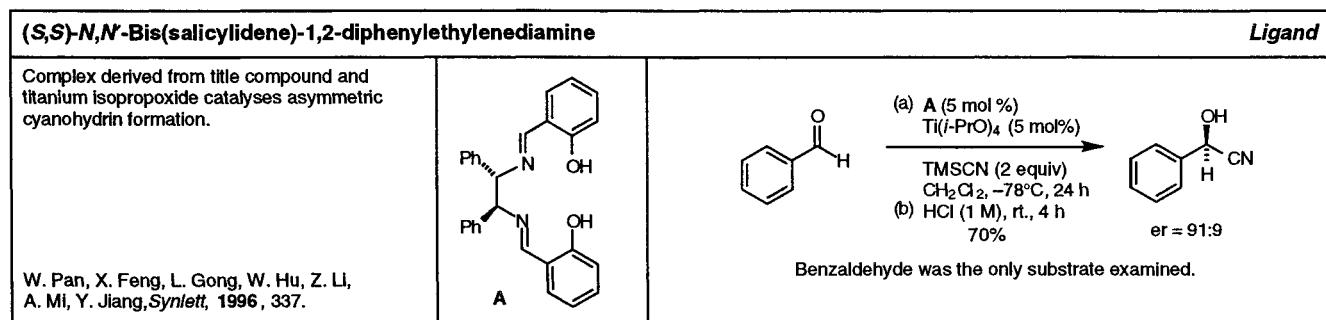
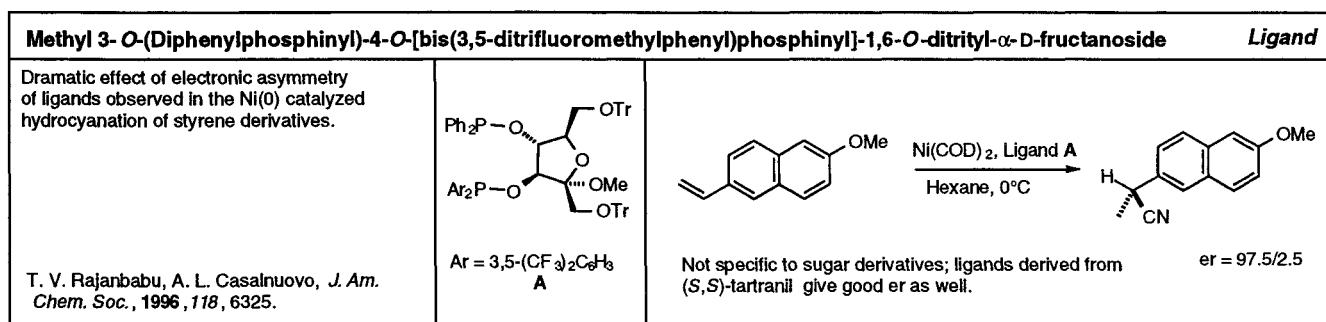
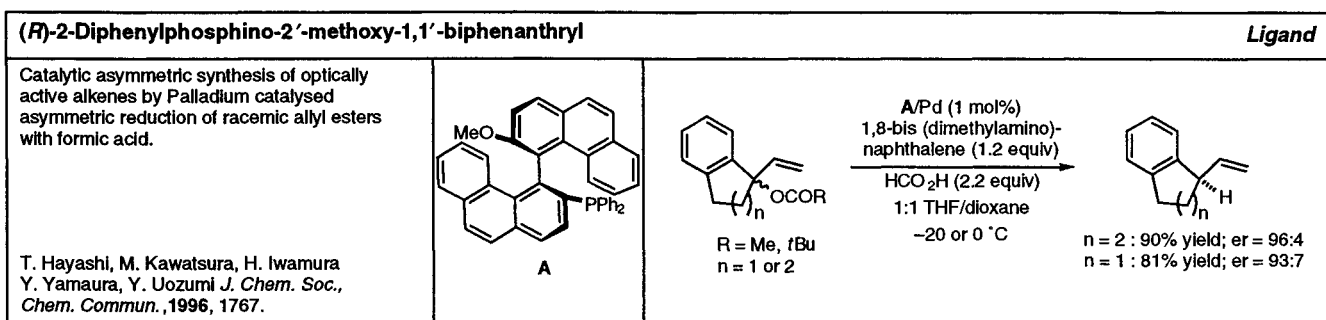
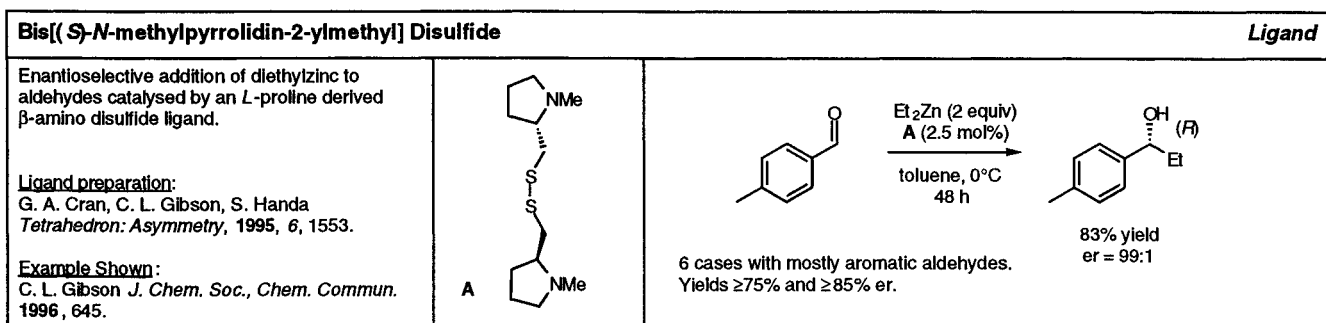


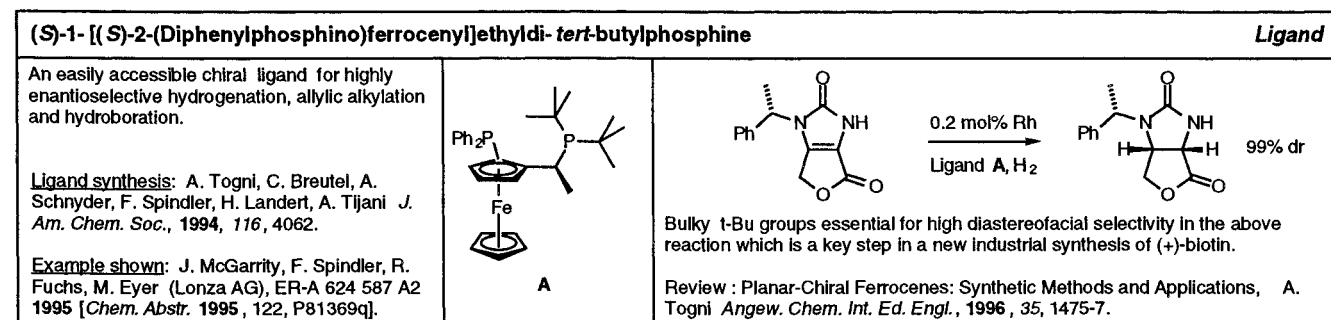
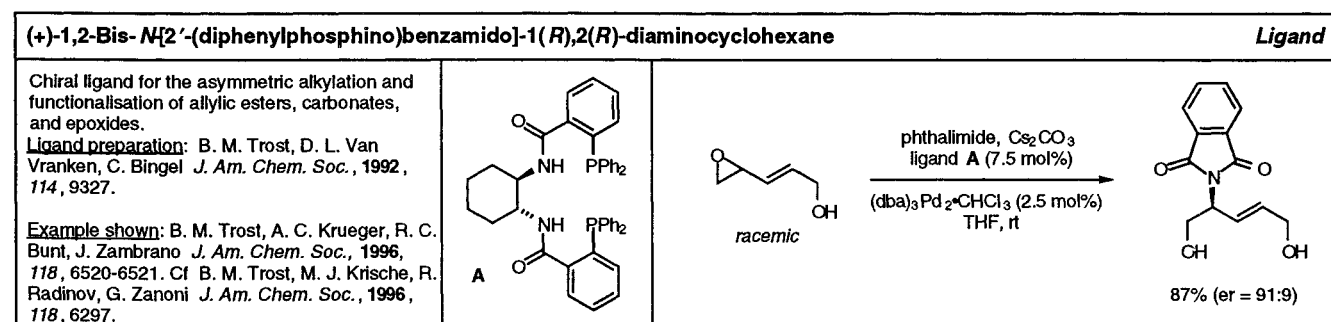
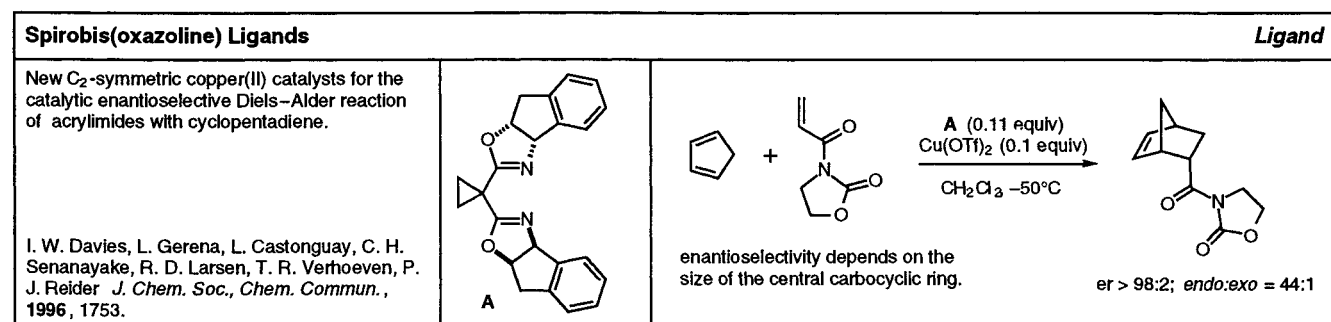
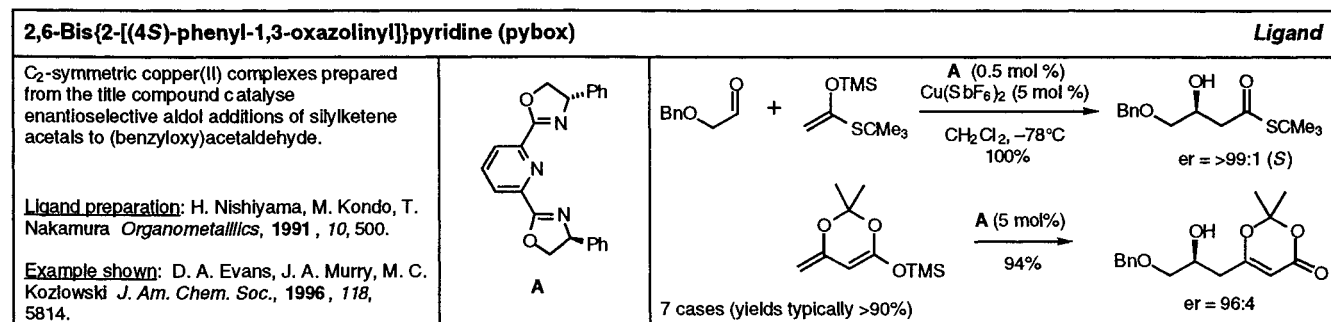
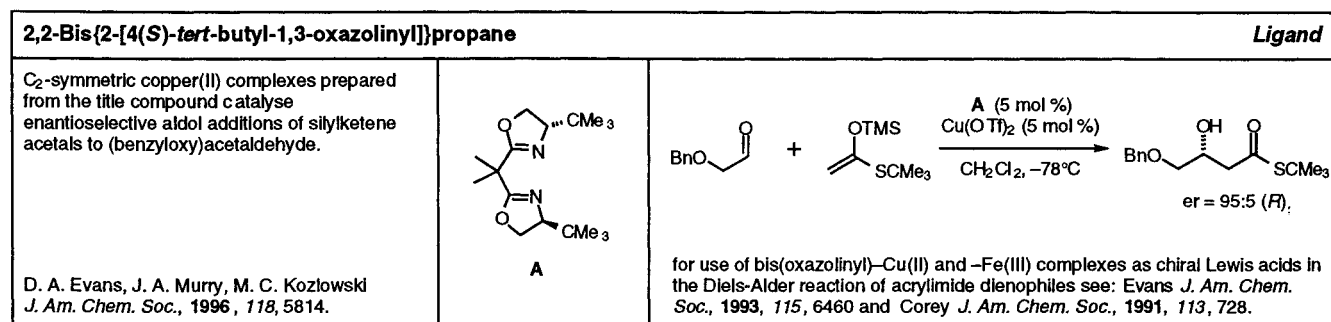


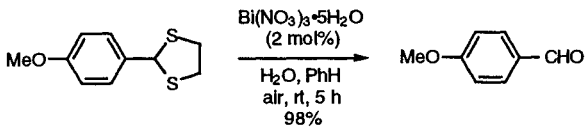
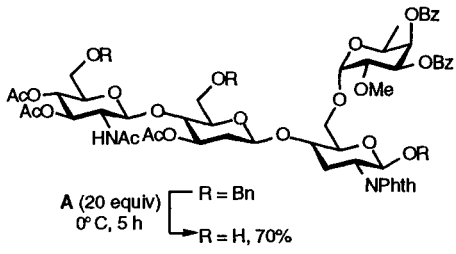
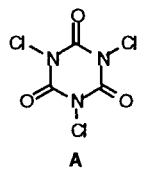
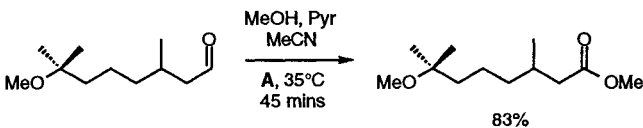
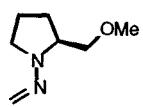
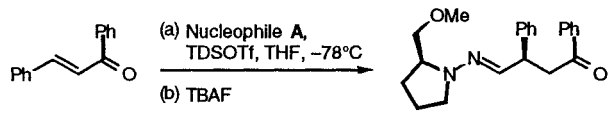
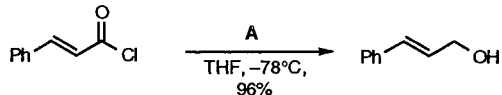


3,4,5-Trifluorobenzeneboronic Acid		Catalyst
Extremely active amidation catalyst.		<p>11 examples (yields typically &gt;90%)</p>
K. Ishihara, S. Ohara, H. Yamamoto <i>J. Org. Chem.</i> , 1996, 61, 4196.	A	
Indium(III) Chloride		Catalyst
Indium(III) Chloride (20 mol%) catalyses the Mukayama directed aldol reaction of the enol silane derived from acetophenone with aldehydes in water.	$\text{InCl}_3$	<p>6 cases using the same enol silane derivative above (yields 85-96%) All aldehyde substrates lack <math>\alpha</math>-hydrogens</p>
T.-P. Loh, J. Pei, G.-Q. Cao <i>J. Chem. Soc., Chem. Commun.</i> , 1996, 1819.		
Tris(dibenzylideneacetone)dipalladium(0)-Chloroform Adduct		Catalyst
A highly active "ligandless" catalyst system for the cycloisomerization of enynes.	$(\text{dba})_3\text{Pd}_2\cdot\text{CHCl}_3$ A	<p>Formic acid reduces Pd(2+) to Pd(0). Use of 1,2-dichloroethane as solvent gave a fast rate at rt.</p>
B. M. Trost, Y. Li <i>J. Am. Chem. Soc.</i> , 1996, 118, 6625.		
(S,S)-Ethylenebis( $\eta^5$ -tetrahydroindenyl)titanium Difluoride		Catalyst
Catalytic asymmetric hydrosilylation of imines can be accomplished with a catalyst prepared by treatment of the title compound with PhSiH <sub>3</sub> and pyrrolidine in MeOH-THF at 60°C.		<p>9 cases (yields typically 80-97%, er &gt; 95:5)</p>
X. Verdaguer, U. E. W. Lange, M. T. Reding, S. L. Buchwald <i>J. Am. Chem. Soc.</i> , 1996, 118, 6784.	A	
Chiral Catalytic Membranes		Catalyst
Noyori's BINAP complex and Jacobsen's chiral salen complex occluded in an elastomeric type polydimethylsiloxane (PMDS) matrix give a regenerable catalytically active membrane.		<p>Catalyst occluded in PMDS catalysed asymmetric hydrogenation of methyl acetoacetate in up to dr 85:15</p>
I. F. J. Vankelecom, D. Tas, R. F. Parton, V. Van de Vyver, P. A. Jacobs <i>Angew. Chem. Int. Ed. Engl.</i> , 1996, 35, 1346.		<p>Catalyst occluded in PMDS catalysed epoxidation of styrene in up to dr 78:22</p>

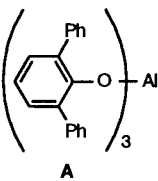
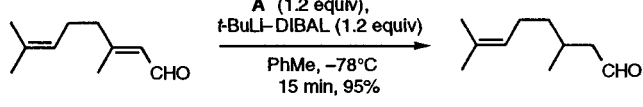
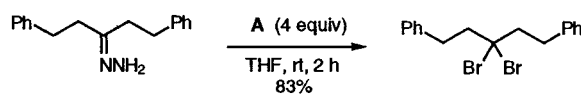
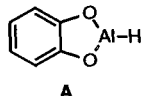
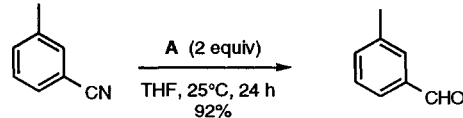
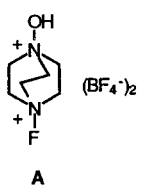
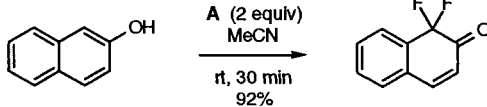
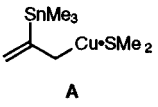
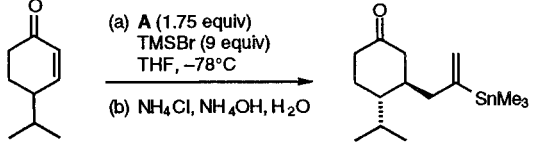


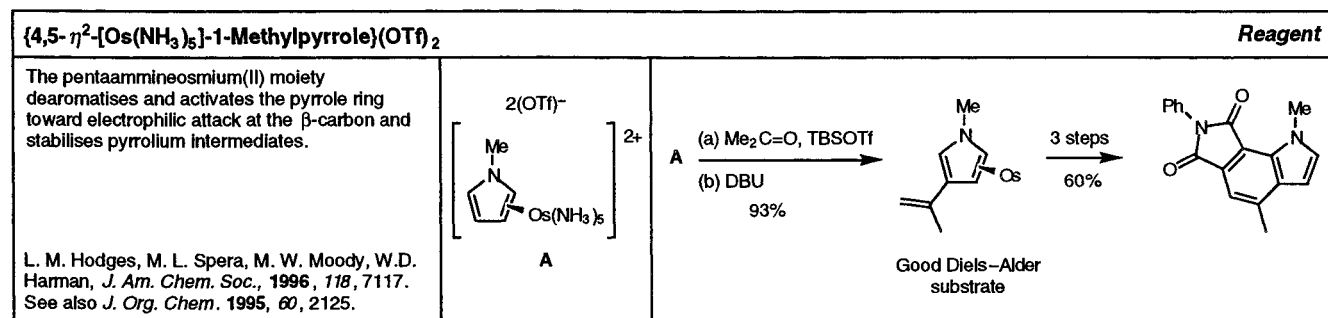
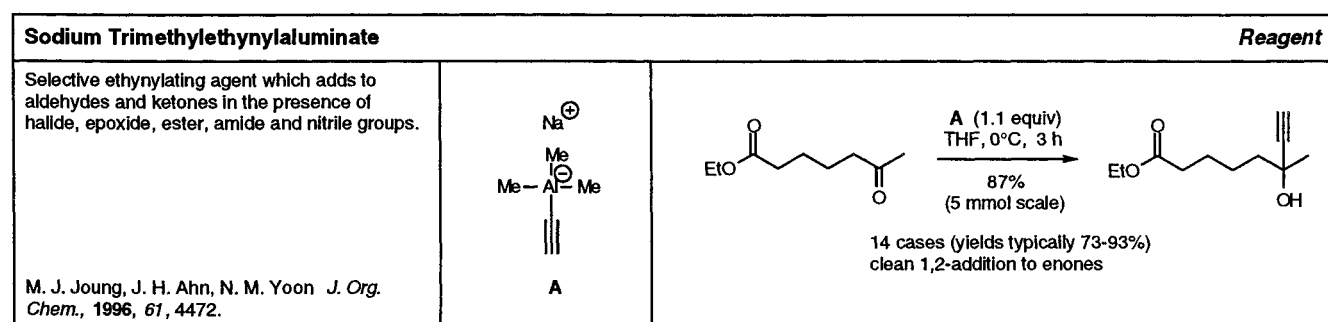
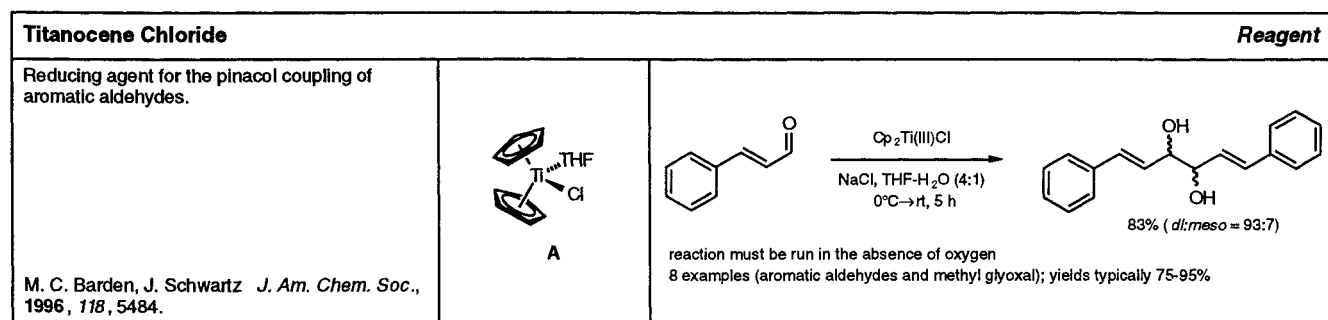
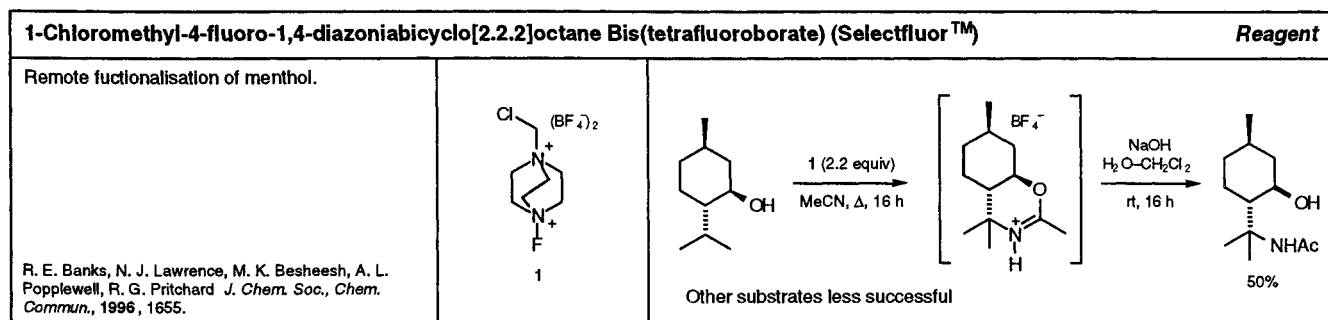
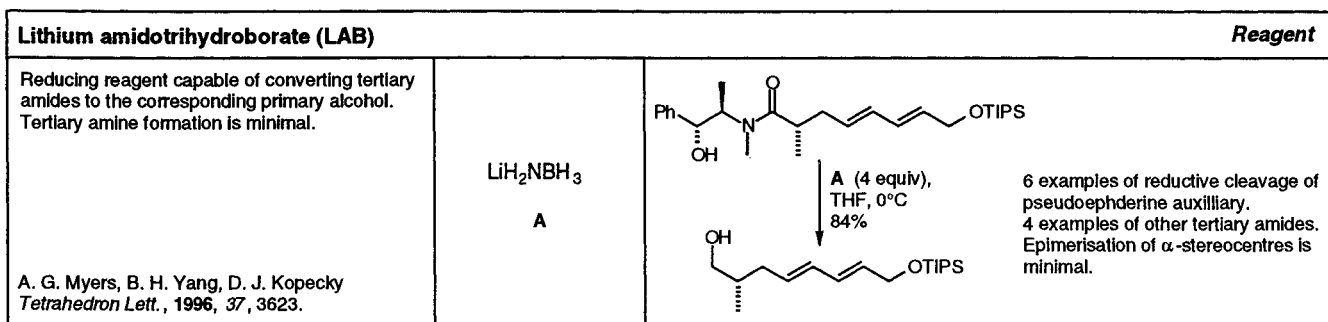


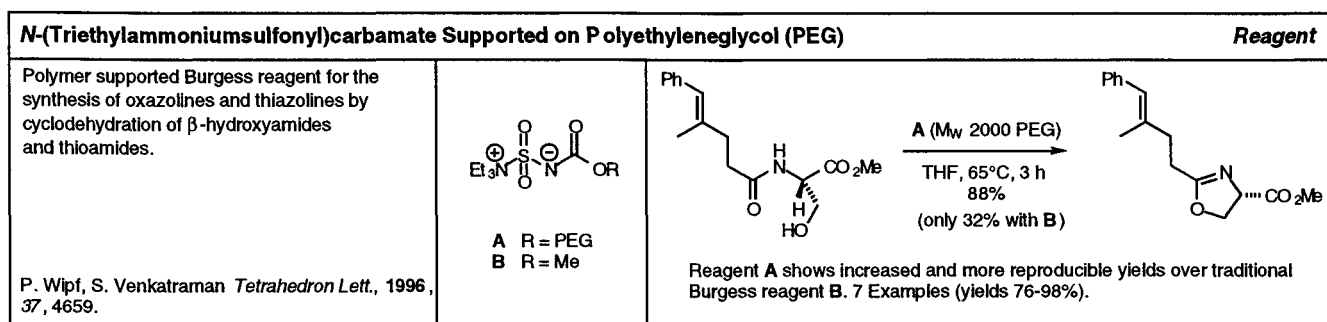
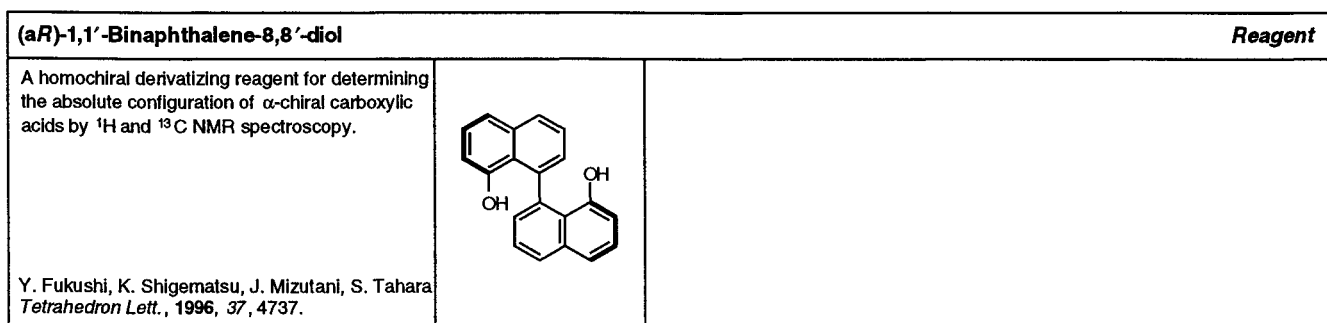
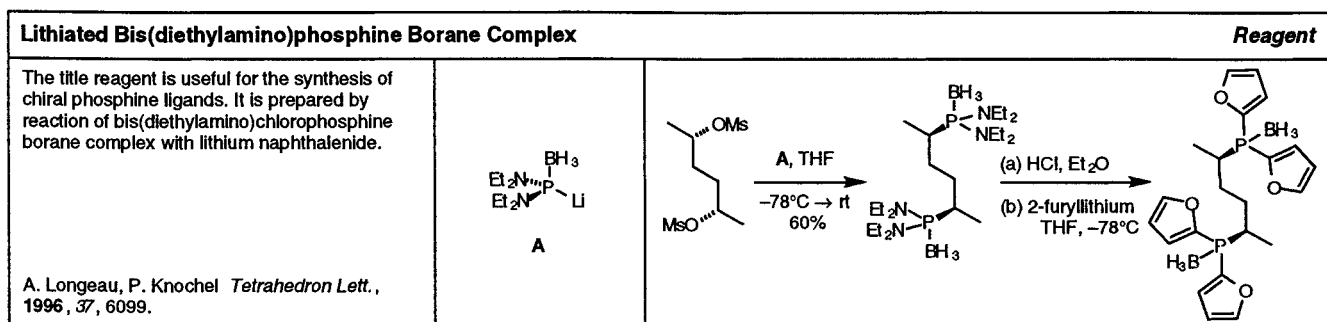
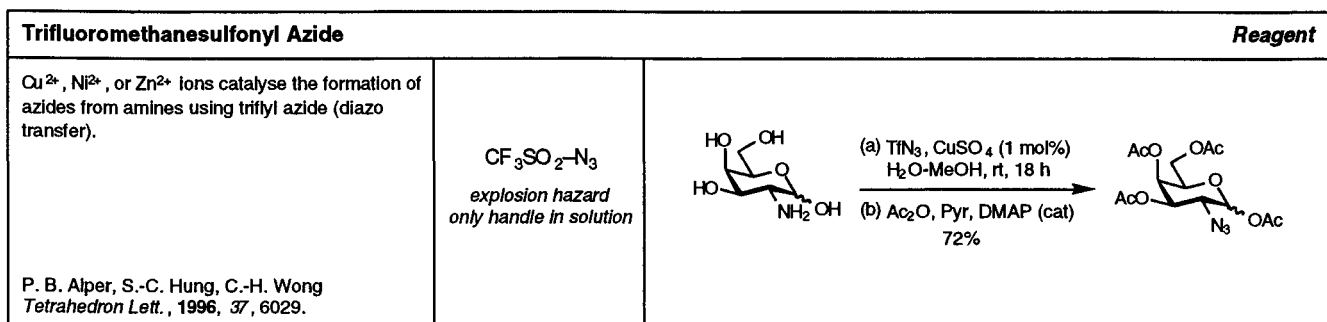
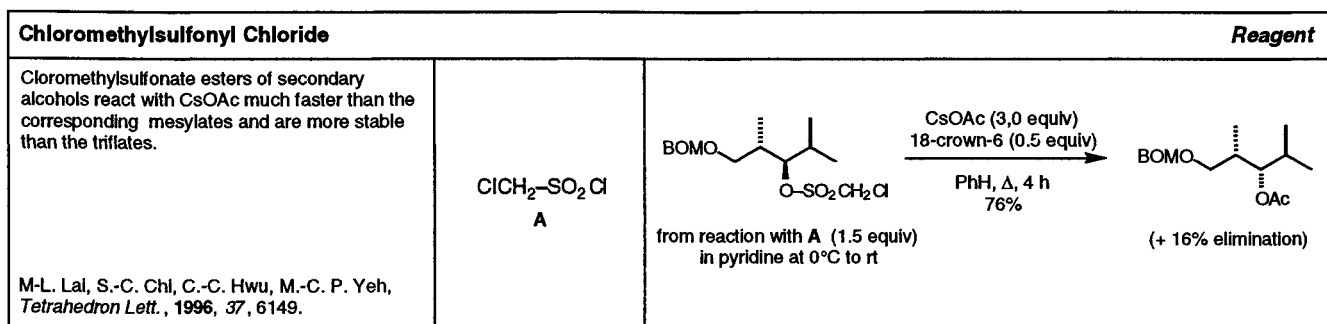


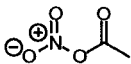
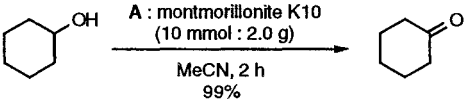
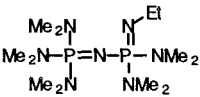
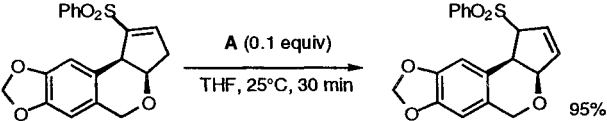
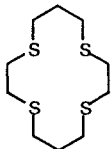
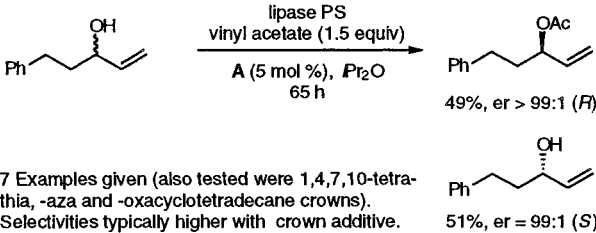
Bismuth(III) Nitrate		Protecting Group
Deprotection of <i>S,S</i> -acetals using air and a catalytic amount of bismuth nitrate (2-20 mol%).	$\text{Bi}(\text{NO}_3)_3$	 <p>16 examples; mostly aryl-substituted dithiolanes</p>
N. Komatsu, A. Taniguchi, M. Uda, H. Suzuki <i>J. Chem. Soc., Chem. Commun.</i> , 1996, 1847.		
Iron(III) Chloride		Protecting Group
Debenzylates complex oligosaccharides in good to excellent yields. Alkenes, acetates, benzoates, phthalimides, acyl amides and sensitive glycosidic linkages unaffected by reaction conditions.	$\text{FeCl}_3$ A	 <p>4 other examples including a monosaccharide containing an olefinic sidechain (yields 38-85%).</p>
R. Rodebaugh, J. S. Debenham, B. Fraser-Reid <i>Tetrahedron Lett.</i> , 1996, 37, 5477.		
Trichloroisocyanuric Acid		Reagent
Oxidises aldehydes to methyl esters.	 A	 <p>Simple 1 step procedure. Yields <math>\geq 70\%</math>.</p>
G. A. Hiegel, C. D. Bayne, Y. Donde, G. S. Tamashiro, L. A. Hilberath <i>Synth. Commun.</i> , 1996, 2633.		
Formaldehyde SAMP-hydrazone		Reagent
Enantioselective nucleophilic formylation and cyanation of conjugated enones via Michael addition of formaldehyde SAMP-hydrazone	 A	 <p>7 examples using cyclic or linear enones</p> <p>76% (dr = 99:1)</p>
J. -M. Lassaletta, R. Fernández, E. Martín-Zamora, E. Díez <i>J. Am. Chem. Soc.</i> , 1996, 118, 7002-7003		
Diisopropoxytitanium(III) Tetrahydroborate		Reagent
Chemoselective reducing reagent generated <i>in situ</i> from diisopropoxytitanium dichloride and benzyltriethylammonium borohydride.	$(i\text{-PrO})_2\text{TIBH}_4$ A	 <p>Aldehydes (10 examples), ketones (8), carboxylic acids (12) are all reduced to the alcohol in high yield. Compatible with amides, azides, esters, ethers, halogens, nitriles and oximes. For stereoselective reduction of epoxyketones see: <i>Tetrahedron</i>, 1996, 52, 9137.</p>
K. S. Ravikumar, S. Chandrasekaran, <i>J. Org. Chem.</i> , 1996, 61, 826.		



Aluminium Tris(2,6-diphenylphenoxide)		Reagent
Used in conjunction with "ate" complexes derived from <i>n</i> -BuLi/DIBAL to effect 1,4-reduction of enals and enones.		 <p>11 enones (yields &gt;94%) and 5 enals (yields &gt;80%) examined</p>
S. Salto, H. Yamamoto, <i>J. Org. Chem.</i> , 1996, 61, 2928.		
Copper(II) Bromide-Lithium <i>tert</i> -Butoxide		Reagent
Reagent for transformation of hydrazones to $\alpha$ , $\alpha$ -dibromides.	$t\text{-BuOCuBr}$ A	 <p>7 ketones and 2 aldehydes examined: yields usually &gt;70%</p>
T. Takeda, R. Sasaki, A. Kamura, S. Yamauchi, T. Fujiwara <i>Synlett</i> , 1996, 273.		
1,3,2-Benzodioxaluminole (Catecholalane)		Reagent
Reagent for selective reduction of nitriles to aldehydes.		 <p>11 nitriles (aliphatic and aromatic) reduced to aldehydes in high yield.</p>
J. S. Cha, S. W. Chang, O. O. Kwon, J. M. Kim <i>Synlett</i> , 1996, 165.		
1-Fluoro-4-hydroxy-1,4-diazoniabicyclo[2.2.2]octane Bis(tetrafluoroborate) (Accufluor™-NFTh)		Reagent
The commercially available title compound generates $\alpha$ , $\alpha$ -difluoroketones from phenols.		 <p>4 other phenols examined. Phenyl-substituted alkynes gave <math>\alpha</math>,<math>\alpha</math>-difluorophenones.</p>
S. Stavber, M. Zupan <i>Synlett</i> , 1996, 693.		
2-(Trimethylstannyl)allylcopper(I)-Dimethyl Sulfide		Reagent
Novel functionalised copper(I) reagent. Its preparation and conjugate addition to enones is described.		 <p>7 enones: Yields 40-60% if 4° centre created, otherwise &gt;80%. Corresponding germanium equally effective.</p>
E. Piers, A. M. Kaller <i>Synlett</i> , 1996, 549.		





Acetyl Nitrate		Reagent
<p>Acetyl nitrate when supported on montmorillonite or chrysotile oxidises 1° or 2° alcohols to corresponding carbonyl derivatives in good to excellent yields.</p> <p>A. P. de Oliveira Filho, B. G. Moreira, P. J. S. Moran, J. A. R. Rodrigues <i>Tetrahedron Lett.</i>, 1996, 37, 5029.</p>	 <p>A</p>	 <p>7 Examples listed. 1° Alcohols oxidise slower than 2° with no formation of carboxylic acids. Hydroquinones are oxidised efficiently under mild conditions to quinones.</p>
<p>Phosphazene Base P<sub>2</sub>-Et</p> <p>Allows for the isomerisation of vinyl- to allyl-sulfones, being superior to DBU or t-BuOK in this respect.</p> <p>Z. Jin, S. H. Kim, P. L. Fuchs <i>Tetrahedron Lett.</i>, 1996, 37, 5247.</p>		 <p>A</p>  <p>In above case DBU effected only 75% conversion over 48 h and t-BuOK gave none of the desired product. 7 Other examples (yields 92-99%) with degree of allyl/vinyl sulfone ratio being substrate dependent.</p>
<p>1,4,8,11-Tetrathiacyclotetradecane</p> <p>Thiacrown ethers enhance enantioselectivity and rate of lipase catalysed transesterification of allylic alcohols.</p> <p>Y. Takagu, J. Teramoto, H. Kihara, T. Itoh <i>Tetrahedron Lett.</i>, 1996, 37, 4991.</p>		 <p>A</p>  <p>7 Examples given (also tested were 1,4,7,10-tetra-thia, -aza and -oxacyclotetradecane crowns). Selectivities typically higher with crown additive.</p>