

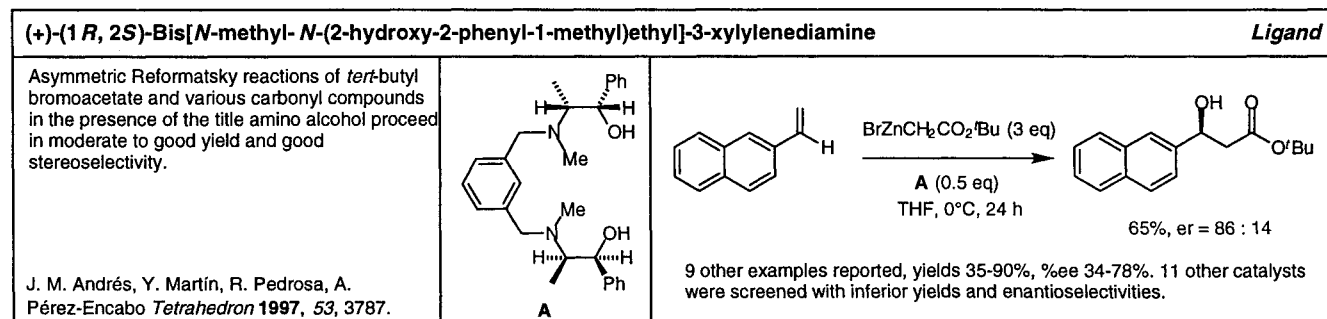
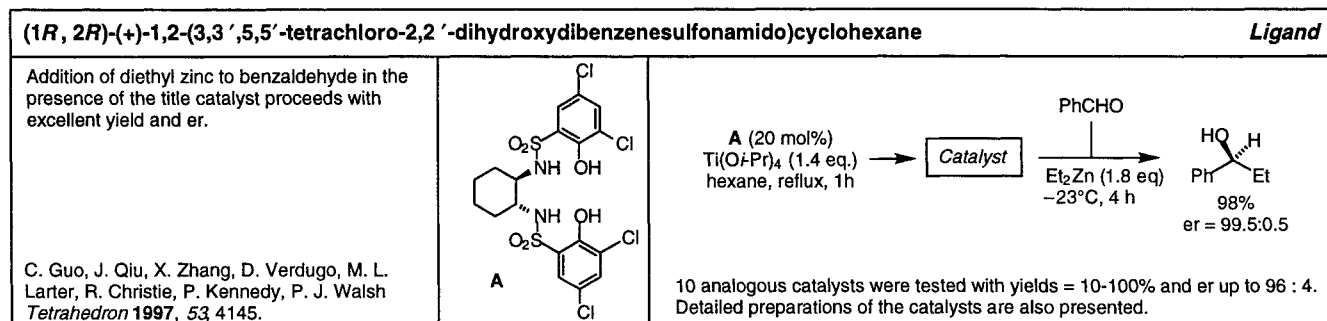
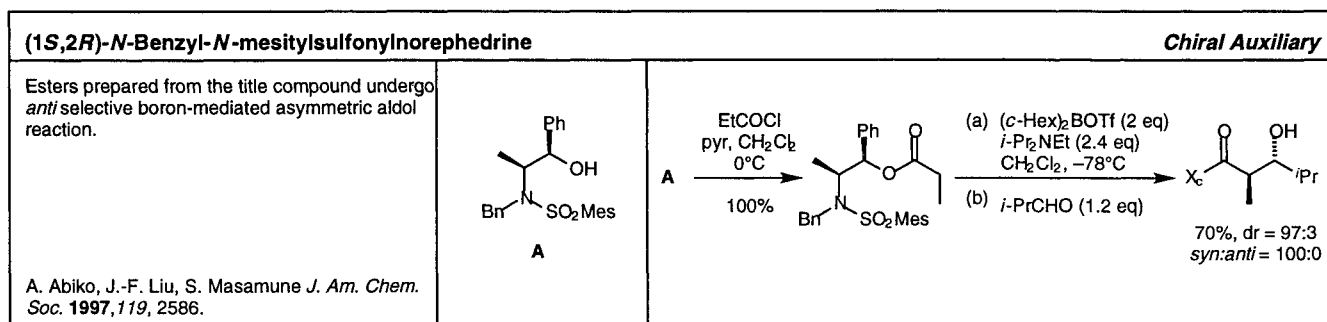
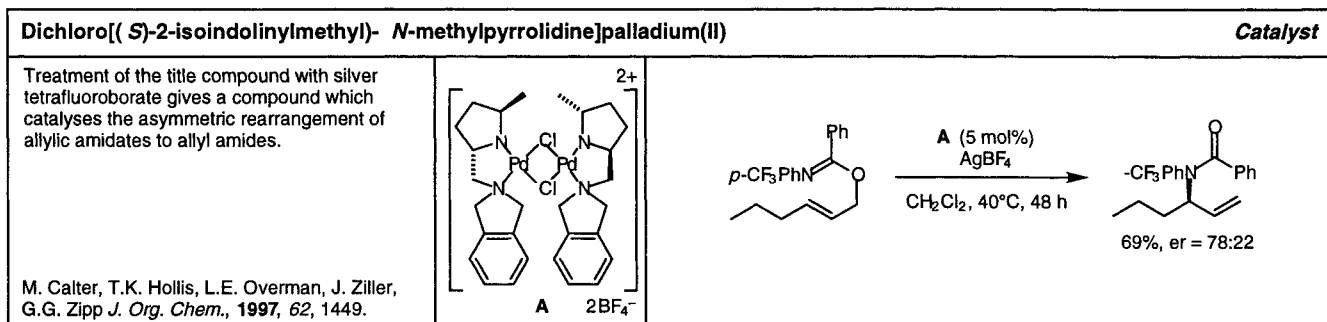
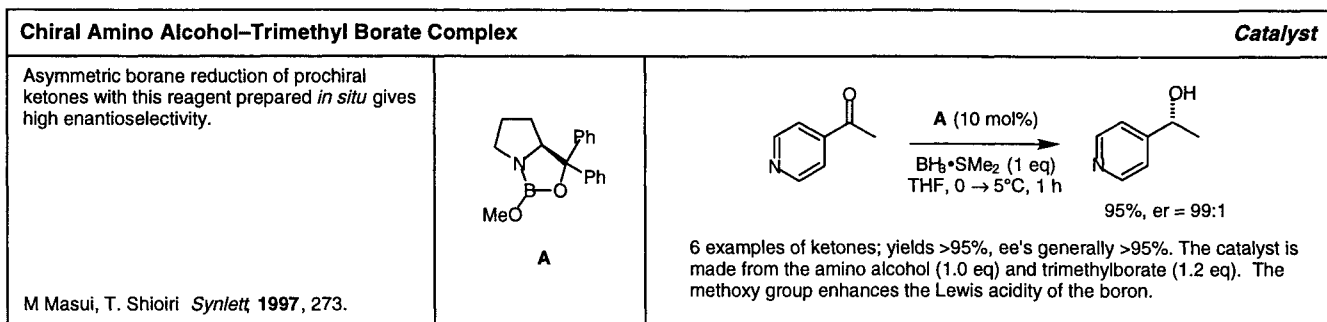
# SYNTHESIS ALERTS

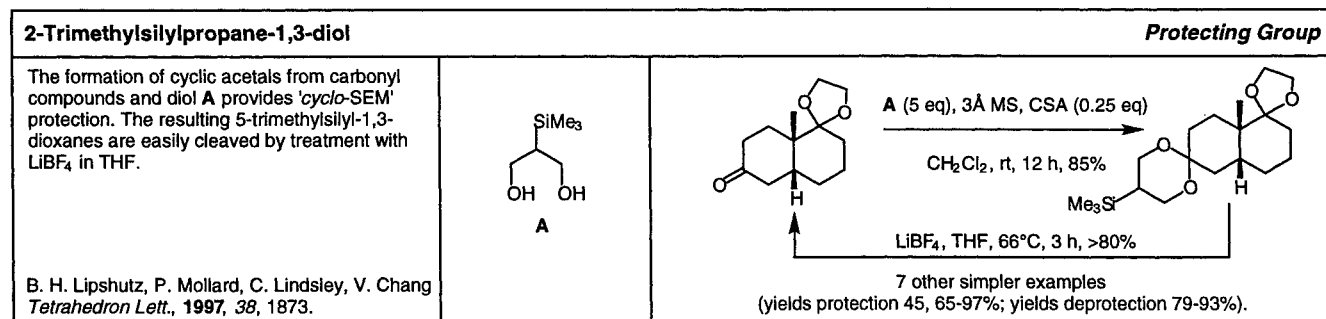
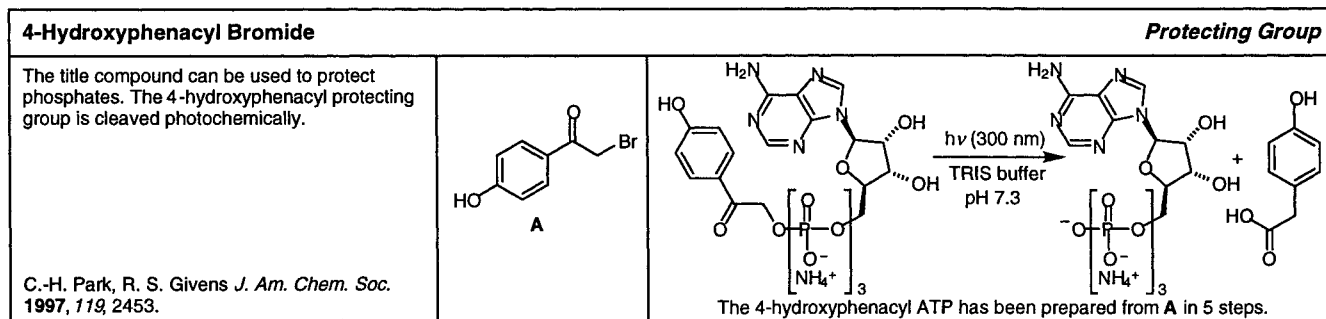
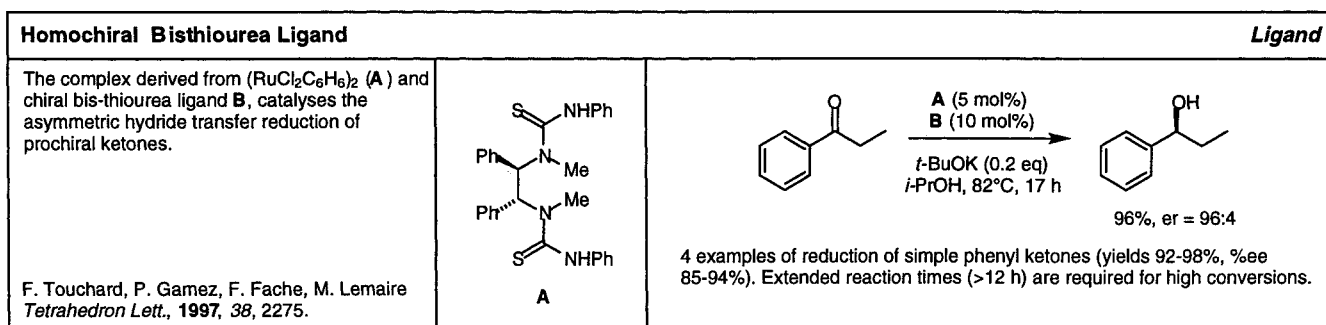
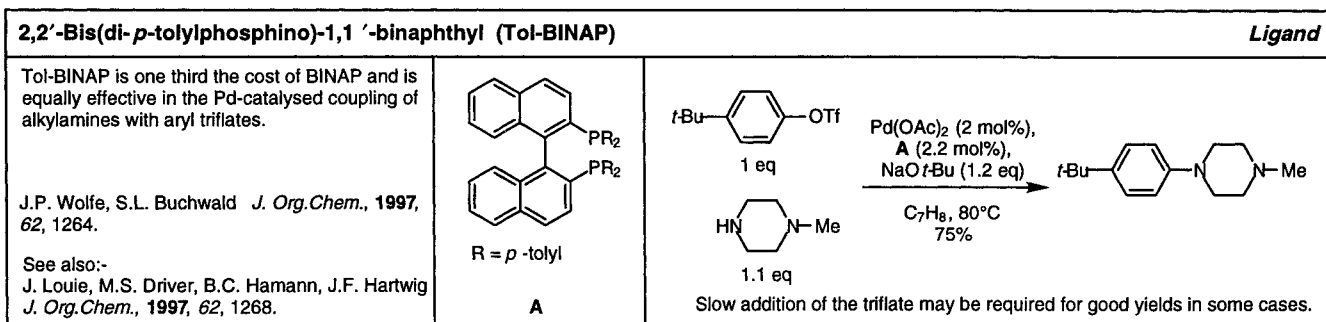
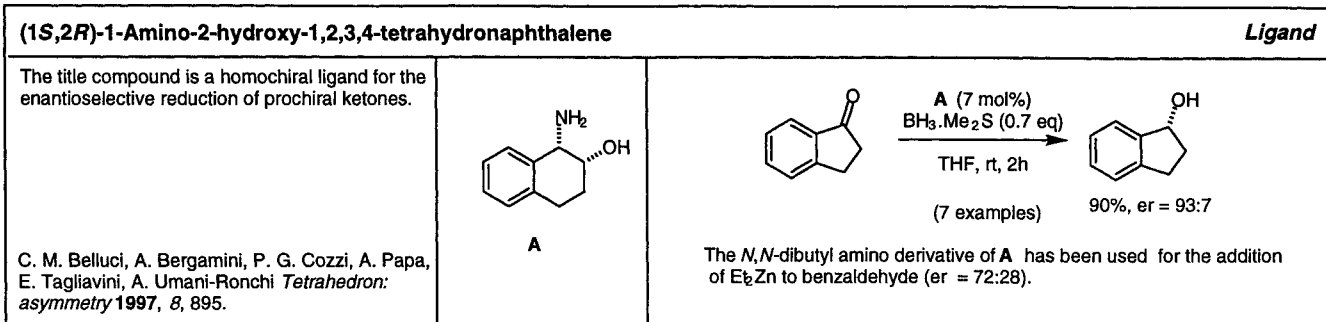
**Synthesis Alerts** is a new monthly feature to help readers of Synthesis keep abreast of new reagents, catalysts, ligands, chiral auxiliaries, and protecting groups which have appeared in the recent literature. Emphasis is placed on new developments but established reagents, catalysts etc are also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

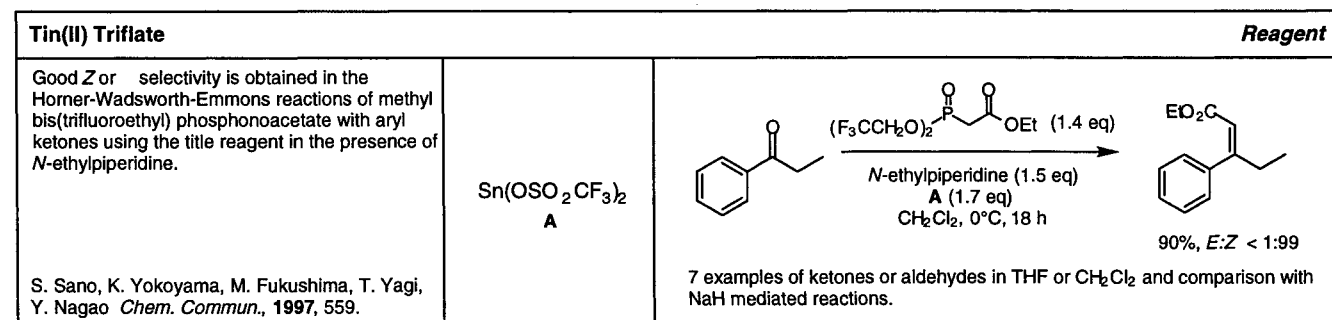
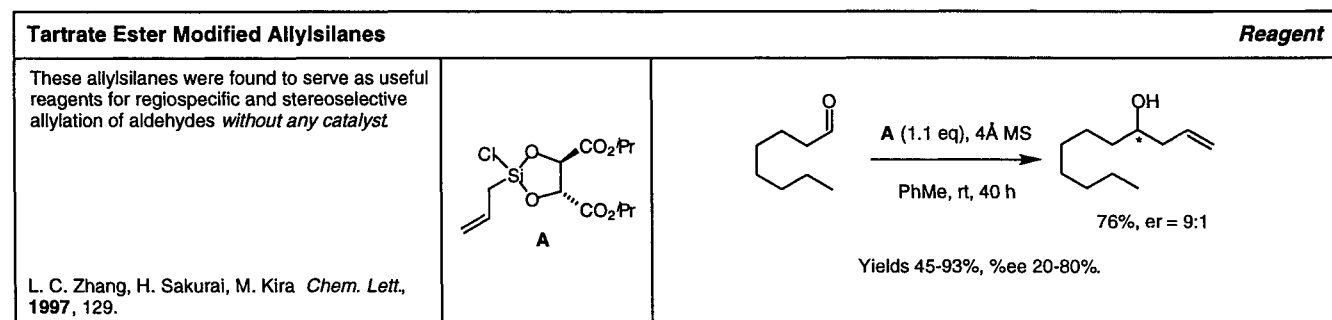
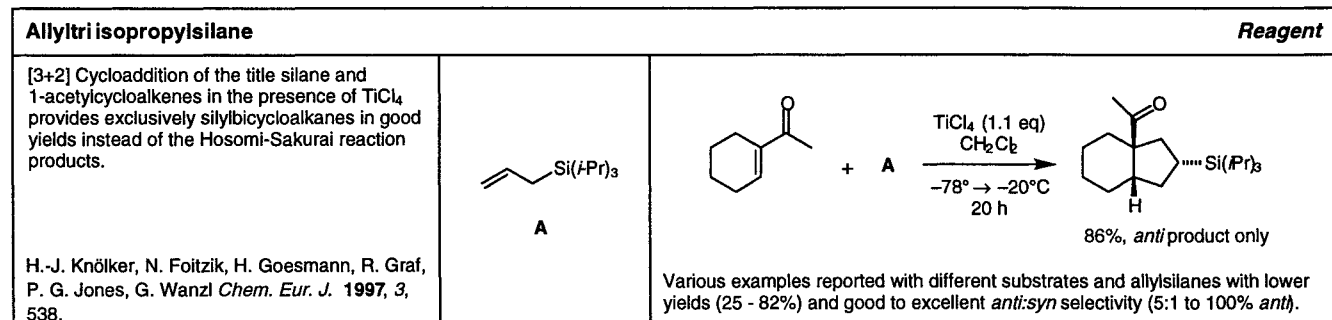
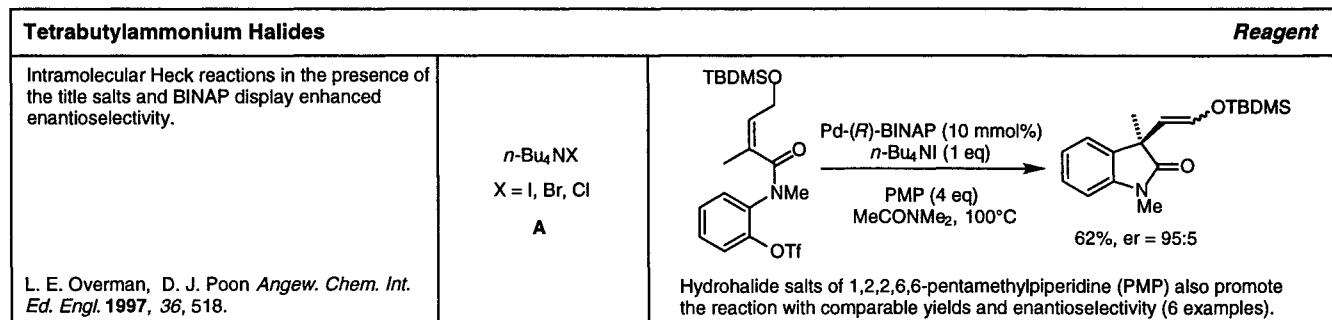
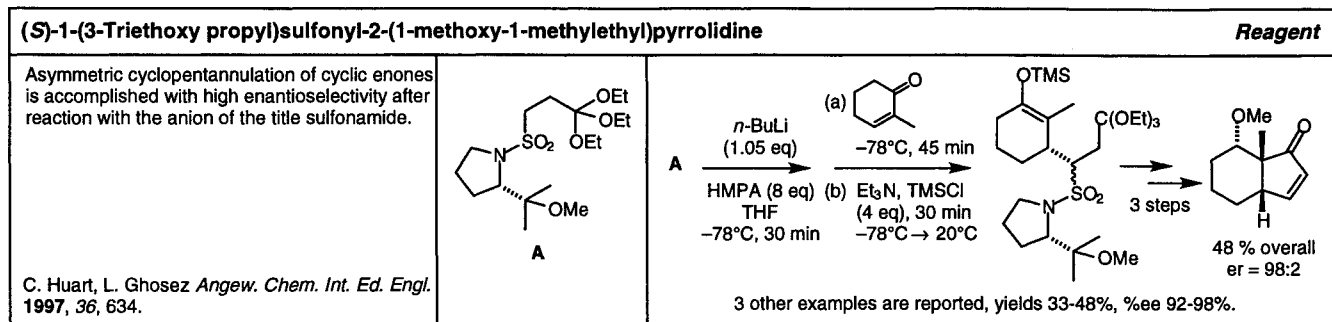
**Synthesis Alerts** is a personal selection by Paul Blakemore, Brian Dymock, Philip Hall, Philip Kocienski, J.-Y. Le Brazidec and Alessandro Pontiroli of the University of Glasgow. The journals regularly covered by the abstractors are: *Angewandte Chemie International Edition*, *Bulletin de la Societe 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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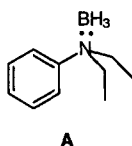
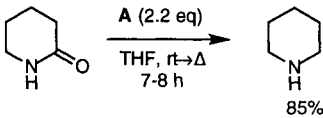
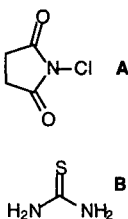
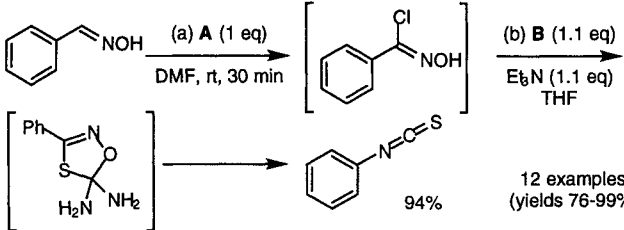
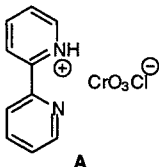
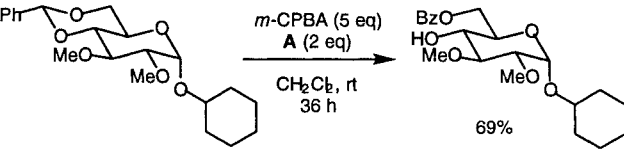
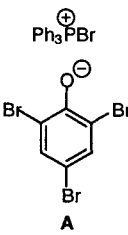
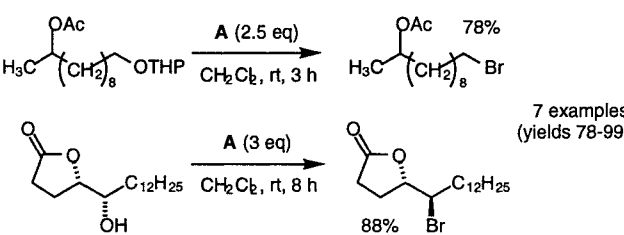
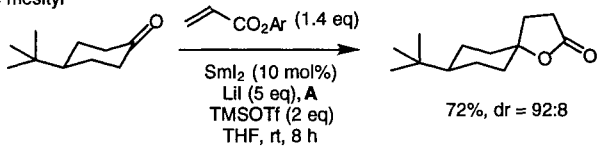
Tetrakis(triphenylphosphine)palladium		Catalyst
<p>A cross-coupling reaction of alkyltrifluorosilanes with aryl halides was achieved using the title catalyst with excess tetrabutylammonium fluoride.</p> <p>H. Matsuhashi, S. Asai, K. Hirabayashi, Y. Hatanaka, A. Mori, T. Hiyama <i>Bull. Chem. Soc. Jpn.</i>, <b>1997</b>, <i>70</i>, 437.</p>	<p><math>\text{Pd}(\text{PPh}_3)_4</math></p> <p>A</p>	<p>30 examples with 6 different trifluorosilanes and 14 aryl bromides and iodides. Yields generally 60-80%.</p>
Trityl Tetrakis(pentafluorophenyl)borate		Catalyst
<p>Catalytic stereoselective synthesis of several glycosides from thioglycosides is achieved by this catalyst with sodium periodate.</p> <p>H. Uchiro, T. Mukaiyama <i>Chem. Lett.</i>, <b>1997</b>, 121.</p>	<p><math>\text{TrB}(\text{C}_6\text{F}_5)_4</math></p> <p>A</p>	<p>10 examples; yields all &gt;90%. <math>\alpha:\beta = 8:92</math></p>
Lanthanide(III) Triflates		Catalyst
<p>These triflates (1-10 mol%) catalyse the nitration of simple arenes using <i>stoichiometric</i> quantities of 69% nitric acid.</p> <p>F. J. Waller, A. G. M. Barrett, D. C. Braddock, D. Ramprasad <i>Chem. Commun.</i>, <b>1997</b>, 613.</p>	<p><math>\text{Ln}(\text{OSO}_2\text{CF}_3)_3</math></p> <p>A</p>	<p>5 different catalysts with <i>m</i>-xylene (Ln = La, Eu, Pr, Sc, Yb). The only byproduct is water and the catalyst may be recycled by evaporation.</p>







Sodium on Solid Support		Reagent
5-20 wt% of sodium on NaCl, glass powder, poly(ethylene) or poly(propylene) gave good yields for the acylation reaction of carboxylic acids.	Na/support A	<p>8 examples with mostly NaCl as the solid support. Yields 60-70%. The reagent may be prepared <i>via</i> low temperature (-33°C) deposition of sodium from its solution in liquid ammonia.</p>
M. Makosza, K. Grela <i>Synlett</i> <b>1997</b> , 267.		
Methylalumoxane		Reagent
This extremely strong Lewis acid is a useful reagent for organic reactions such as the Diels-Alder reaction and amidation of esters.	<p>A</p>	<p>7 examples of the Diels-Alder reaction; yields generally &gt;85%.</p>
M. Akakura, H. Yamamoto <i>Synlett</i> <b>1997</b> , 277.		
Diisopropylzinc-Magnesium Bromide Complex		Reagent
<i>i</i> -Pr <sub>2</sub> Zn, generated <i>in situ</i> from <i>i</i> -Pr <sub>2</sub> MgBr (2 eq) and ZnBr <sub>2</sub> (1 eq), leads to a smooth iodine-zinc exchange in secondary alkyl iodides.	<i>i</i> -Pr <sub>2</sub> Zn•MgBr <sub>2</sub> A	<p>8 examples, yields 60-80%. Racemisation occurs with chiral alkyl iodides.</p>
L. Micouin, P. Knochel <i>Synlett</i> <b>1997</b> , 327.		
Tetrachlorosilane		Reagent
Trichlorosilyl ethers prepared from trimethylsilyl ethers and the title compound undergo highly selective asymmetric aldol reactions.	SiCl <sub>4</sub> A	<p>The <i>anti</i> aldol product is favored in the presence of the Lewis base promoter (B) (11 examples). In the absence of B the <i>syn</i> product is favored (15 examples).</p> <p>A (3 eq) 0°C, 78% M = SnBu<sub>3</sub> M = SiCl<sub>3</sub></p> <p>(a) A (1.5 eq), Et<sub>2</sub>O (0.3 M solution) rt, 1 h (b) CuCN•LiCl (2 eq) (c) allyl bromide (3 eq), -78 → 0°C</p> <p>95%, er = 97:3 syn:anti = 1:61</p>
S. E. Denmark, K.-T. Wong, R. A. Stavenger <i>J. Am. Chem. Soc.</i> <b>1997</b> , 119, 2333.		
Lithium Tri- <i>tert</i> -butylzincate		Reagent
The title compound metallates alkyl and aryl iodides to the corresponding mixed zincates which react with electrophiles <i>without transfer of the tert-butyl group</i> .	( <i>t</i> -Bu) <sub>3</sub> ZnLi A	<p>(a) A (1 eq) -78°C, 4 h (b) benzoyl chloride -78°C → rt, 12 h</p> <p>56%</p>
Y. Kondo, M. Fujinami, M. Uchiyama, T. Sakamoto <i>J. Chem. Soc., Perkin Trans. I</i> <b>1997</b> , 799.		

<b><i>N,N</i>-Diethylaniline•Borane (DEANB) Complex</b>		<b>Reagent</b>
<p>The commercially available complex <b>A</b> effectively reduces a variety of functional groups, including: aldehydes, ketones, carboxylic acids, amides and lactams.</p> <p>See following paper for use of DEANB (<b>A</b>) as borane source in CBS reduction reactions.</p> <p>A. M. Salunkhe, E. R. Burkhardt <i>Tetrahedron Lett.</i>, <b>1997</b>, <i>38</i>, 1519.</p>	 <p style="text-align: center;"><b>A</b></p>	 <p>11 varied examples (yields 51, 85-94%). <b>A</b> is also an effective hydroboration reagent, showing good regioselectivity.</p>
<b><i>N</i>-Chlorosuccinimide / Thiourea</b>		<b>Reagent</b>
<p>Successive treatment of aldoximes with NCS (<b>A</b>), followed by thiourea (<b>B</b>) and triethylamine, produces the corresponding isothiocyanates in excellent yield.</p> <p>J. N. Kim, K. S. Jung, H. J. Lee, J. S. Son <i>Tetrahedron Lett.</i>, <b>1997</b>, <i>38</i>, 1597.</p>	 <p style="text-align: center;"><b>A</b></p> <p style="text-align: center;"><b>B</b></p>	 <p>12 examples (yields 76-99%).</p>
<b>2,2'-Bipyridinium Chlorochromate / 3-Chloroperoxybenzoic Acid</b>		<b>Reagent</b>
<p>Oxidative cleavage of benzylidene acetals to hydroxy esters is effected by the title reagent pair. Possible oxidation of the released hydroxyl function is negligible.</p> <p>F. A. Luzzio, R. A. Bobb <i>Tetrahedron Lett.</i>, <b>1997</b>, <i>38</i>, 1733.</p>	 <p style="text-align: center;"><b>A</b></p>	 <p>10 examples (yields 48, 69-79%).</p>
<b>Bromotriphenylphosphonium 2,4,6-Tribromophenoxide</b>		<b>Reagent</b>
<p>Primary and secondary alcohols are smoothly converted to the corresponding bromides under mild conditions by treatment with <b>A</b>. THP ethers can also be directly transformed to bromides with <b>A</b>.</p> <p>A. Tanaka, T. Oritani <i>Tetrahedron Lett.</i>, <b>1997</b>, <i>38</i>, 1955.</p>	 <p style="text-align: center;"><b>A</b></p>	 <p>7 examples (yields 78-99%).</p>
<b>Zinc Amalgam</b>		<b>Reagent</b>
<p>A complex system of <b>A</b>, LiI and TMSOTf allows for the <i>in situ</i> regeneration of SmI<sub>2</sub> from Sm(III) species. Thus SmI<sub>2</sub> mediated reactions can be made catalytic in samarium.</p> <p>E. J. Corey, G. Z. Zheng <i>Tetrahedron Lett.</i>, <b>1997</b>, <i>38</i>, 2045.</p>	<p style="text-align: center;">Zn•Hg <b>A</b></p>	<p>Ar = mesityl</p>  <p>5 examples of spiroannulation of ketones with mesityl acrylate (yields 70-84%). Also demonstrated: deoxygenation of styrene oxide (67% yield), and cyclisation of 6-iodo-1-phenylhex-1-yne (82% yield).</p>