

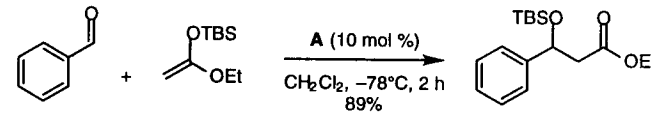
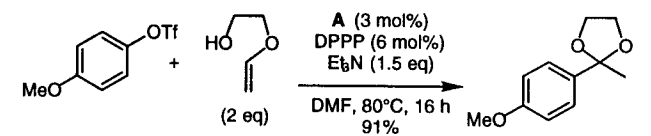
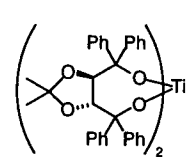
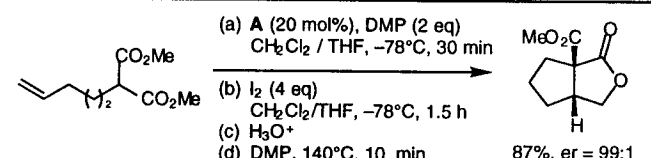
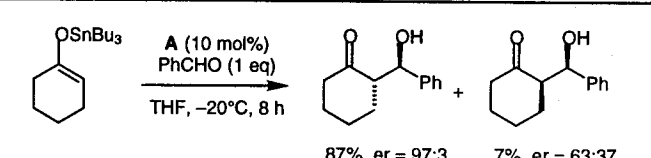
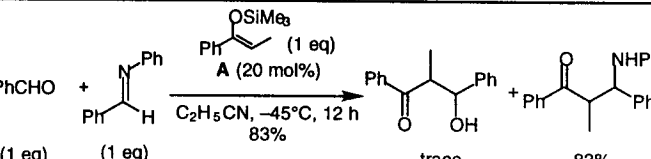
# SYNTHESIS ALERTS

**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.

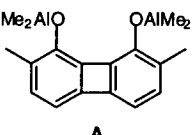
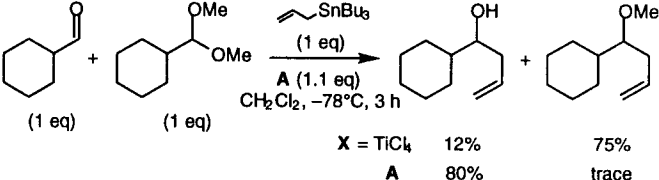
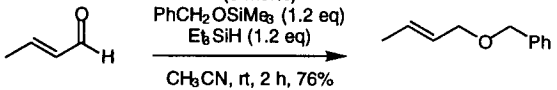
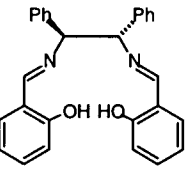
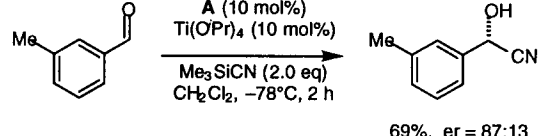
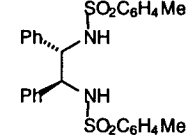
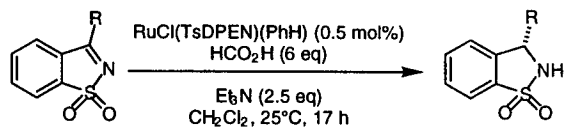
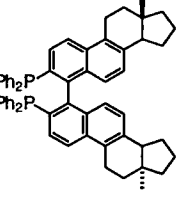
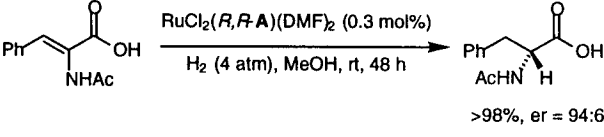
**Synthesis Alerts** is a personal selection by Paul Blakemore, John Christopher, Louise Lea, Philip Kocienski, J.-Y. Le Brazidec, Robert Narquizian and Christopher Smith of the University of Glasgow. The journals regularly covered by the abstractors are: *Angewandte Chemie International Edition*, *Bulletin 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*.

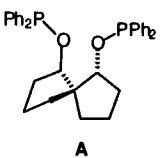
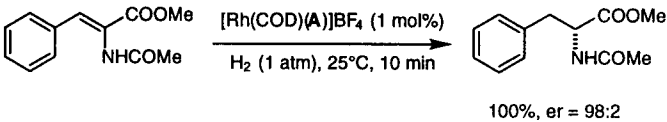
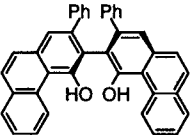
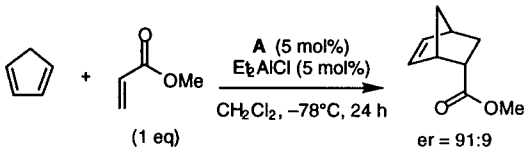
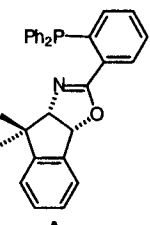
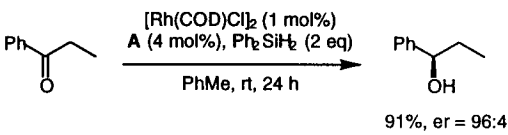
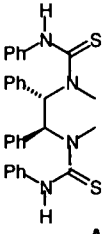
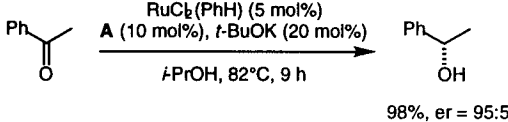
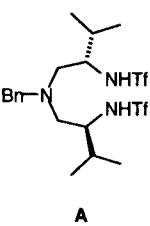
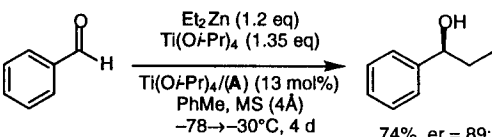
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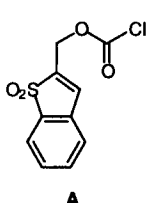
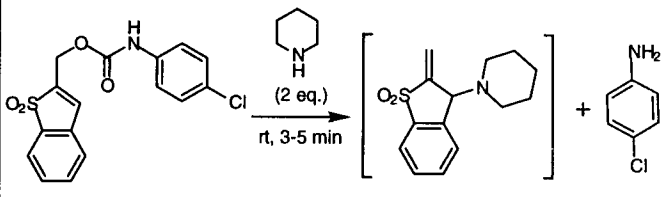
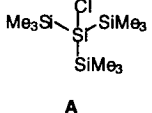
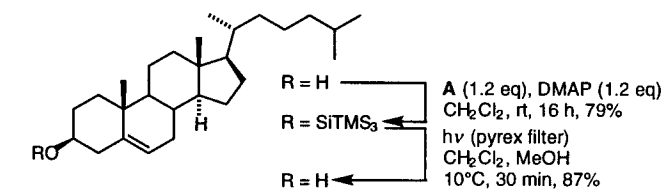
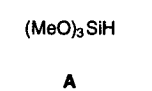
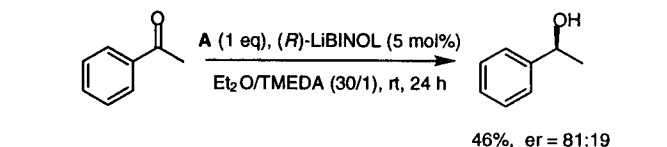
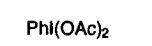
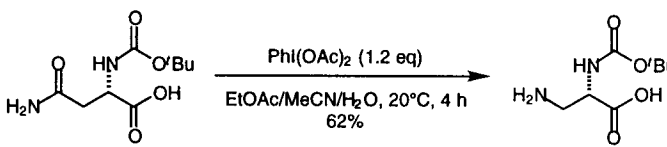
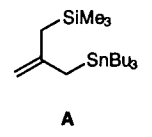
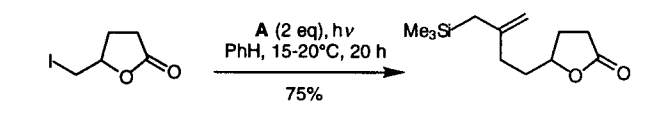
<p><b>(acac)<sub>2</sub>Rh(CO)<sub>2</sub></b> <span style="float: right;"><b>Catalyst</b></span></p>	
<p>The title reagent together with 1,4-bis(diphenylphosphino)butane catalyses the addition of aryl- and alkenylboronic acids to enones.</p>	<p>(acac)<sub>2</sub>Rh(CO)<sub>2</sub></p> <p>7 enones and 6 arylboronic acids were used. Yields usually &gt;80%</p>
<p>M. Sakai, H. Hayashi, N. Niyaura, <i>Organometallics</i>, <b>1997</b>, <i>16</i>, 4229.</p>	
<p><b>Trimethylsilyl Bis(trifluoromethanesulfonyl)amide</b> <span style="float: right;"><b>Catalyst</b></span></p>	
<p>The title compound is an effective mild catalyst for the Friedel-Crafts alkylation of anisole.</p>	<p>TMSNTf<sub>2</sub></p> <p>2 other examples and the bis allylation of aldehydes are also described.</p>
<p>A. Ishii, O. Kotera, T. Saeki, K. Mikami <i>Synlett</i> <b>1997</b>, 1145.</p>	
<p><b>Dirhodium(II) Tetrakis[3(S)-phthalimido-2-piperidinoate]</b> <span style="float: right;"><b>Catalyst</b></span></p>	
<p>The title reagent catalyses the enantioselective cyclopropanation of alkenes by <math>\alpha</math>-diazoesters. The diastereoselectivity achieved is moderate.</p>	<p>A</p> <p>R = phthalimide</p> <p>7 examples (yields <i>trans</i> 26-77%, %ee 89-98%; yields <i>cis</i> 15-37%, %ee 82-98%).</p> <p>43%, er = 97:3 37%, er = 98:2</p>
<p>S. Kitagaki, H. Matsuda, N. Watanabe, S. Hashimoto <i>Synlett</i> <b>1997</b>, 1171.</p>	

<b>Tributyltin Perchlorate</b>		<b>Catalyst</b>
Organotin perchlorates are a new class of mild Lewis acids which activate aldehydes towards the Mukaiyama aldol reaction.	$\text{Ph}_3\text{CCl}_4\text{O}_4 + \text{Bu}_3\text{SnH}$ $\downarrow$ $\text{Bu}_3\text{SnClO}_4$ <b>A</b>	 <p>The ketene silyl acetal reacts faster with aldehydes than with acetals in the presence of the organotin perchlorates.</p>
J. Chen, J. Otera <i>Tetrahedron</i> <b>1997</b> , 14275.		
<b>Palladium(II) Acetate</b>		<b>Catalyst</b>
Cyclic ketals of acetophenones are synthesised from vinyl ethers and aryl triflates, aryl bromides or iodobenzene in the presence of a catalytic amount of <b>A</b> and the bidentate ligand DPPP.	$\text{Pd}(\text{OAc})_2$ <b>A</b>	 <p>8 examples (yields 33-91%).</p> <p>DPPP = 1,3-bis(diphenylphosphino)propane</p>
M. Larhed, A. Hallberg, <i>J. Org. Chem.</i> <b>1997</b> , 62, 7858.		
<b>Titanium Ditaddolate</b>		<b>Catalyst</b>
Iodocarbocyclisation reactions of 4-alkenylmalonate derivatives proceed with excellent enantioselectivity in the presence of catalyst <b>A</b> .	 <b>A</b>	 <p>87%, er = 99:1</p> <p>8 examples (yields 60-97%, %ee = 95-99%).</p> <p>DMP = 2,6-dimethoxyppyridine</p>
T. Inoue, O. Kitagawa, A. Saito, T. Taguchi <i>J. Org. Chem.</i> <b>1997</b> , 62, 7384		
<b>(R)-BINAP•Silver(I) Triflate Complex</b>		<b>Catalyst</b>
The title reagent catalyses the enantioselective aldol reaction between tin enolates and aldehydes.	$(R)\text{-BINAP}\cdot\text{AgOTf}$ <b>A</b>	 <p>87%, er = 97:3      7%, er = 63:37</p> <p>16 examples (yields 33-98%, %ee (major diastereoisomer) 41-96%). Acyclic Z tin enolates yield <i>syn</i> aldol adducts with very high diastereoselectivity (dr &gt; 99:1).</p>
A. Yanagisawa, Y. Matsumoto, H. Nakashima, K. Asakawa, H. Yamamoto <i>J. Am. Chem. Soc.</i> <b>1997</b> , 119, 9319.		
<b>Ytterbium(III) Triflate</b>		<b>Catalyst</b>
The title Lewis acid catalyses the selective attack of various silylated and stannylated nucleophiles upon aldimines in the presence of aldehydes.	$\text{Yb}(\text{OTf})_3$ <b>A</b>	 <p>83%</p> <p>12 examples of enolate addition (yields 81-93%); 8 examples of allylation (yields 31-94%); 6 examples of cyanation (yields 65-100%). In each of these competitive experiments only the adduct resulting from addition to aldimine was observed.</p>
S. Kobayashi, S. Nagayama <i>J. Am. Chem. Soc.</i> <b>1997</b> , 119, 10049.		

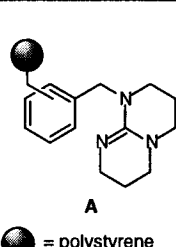
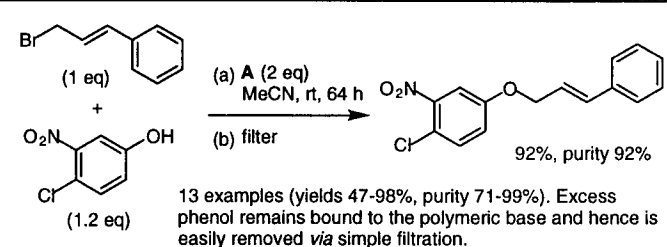
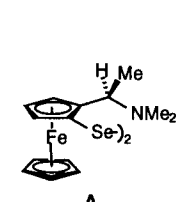
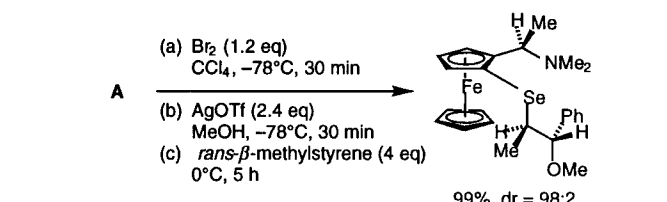
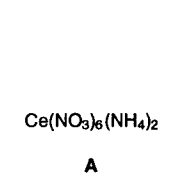
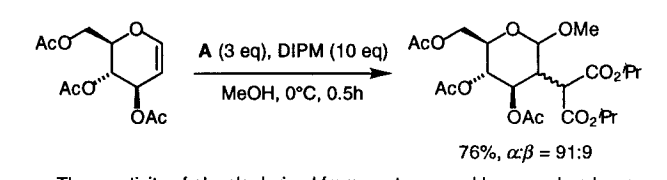
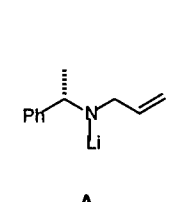
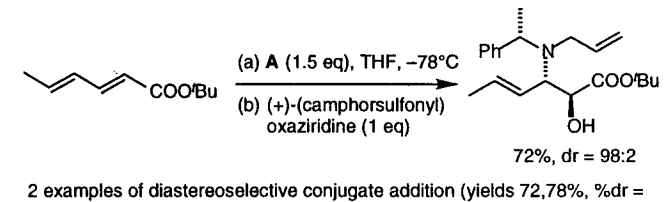

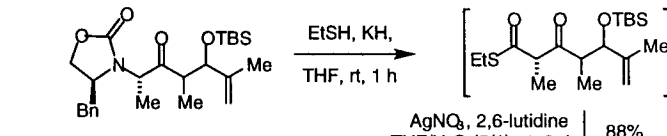
Copper(II) Triflate•Benzene Complex		Catalyst
Catalyses the synthesis of aryl ethers from phenols and aryl bromides and iodides.	$\text{Cu}(\text{OTf})_2 \cdot \text{PhH}$ A	<p>A (2.5 mol%) AcOEt (5 mol%) Cs<sub>2</sub>CO<sub>3</sub> (2 eq) PhMe, Δ, 12 h 80%</p> <p>20 examples (yields 20-93%). In certain instances the addition of 1-naphthoic acid was necessary to obtain acceptable yields.</p>
J.-F. Marcoux, S. Doye, S. L. Buchwald <i>J. Am. Chem. Soc.</i> <b>1997</b> , <i>119</i> , 10539.		
Bis(acetonitrile)(1,5-cyclooctadiene)rhodium Tetrafluoroborate		Catalyst
Aryltrimethylstannanes react with aldehydes in the presence of a catalytic amount of a cationic rhodium complex A, affording the corresponding arylated secondary alcohols in good yields.	$[\text{Rh}(\text{cod})(\text{MeCN})_2]\text{BF}_4$ A	<p>A (2 mol%) THF, 60°C, 24 h 87%</p> <p>16 examples (yields 29-96%).</p>
S. Oi, M. Moro, Y. Inoue <i>Chem. Commun.</i> <b>1997</b> , 1621.		
Bis(tricyclohexylphosphine)benzylidene Ruthenium(IV) Dichloride		Catalyst
The title reagent was used to catalyse the crossed and ring closing olefin metathesis of peptidic substrates. The latter process was achieved with contaminant cleavage from a solid support.	$\text{Cl}_2(\text{PCy}_6)_2\text{Ru}=\text{CHPh}$ A	<p>(a) A (4 mol%) CH<sub>2</sub>Cl<sub>2</sub>, Δ, 12 h (b) TFA, (c) ●-Cl solid-phase peptide synthesis</p> <p>● = tritylpolystyrene</p> <p>A (15 mol%) 70%</p>
J. Pernstorfer, M. Schuster, S. Blechert <i>Chem. Commun.</i> <b>1997</b> , 1949.		
Bis(tricyclohexylphosphine)benzylidene Ruthenium(IV) Dichloride		Catalyst
Triynes are isomerised to benzene derivatives by the catalytic action of the title reagent.	$[\text{PhCH}=\text{Ru}(\text{PCy}_6)_2\text{Cl}_2]$ A	<p>A (5 mol%) CH<sub>2</sub>Cl<sub>2</sub>, rt, 2 h 68%</p> <p>5 examples (yields 15-88%) including 2 examples of the formation of nitrogen heterocycles.</p>
J.-U. Peters, S. Blechert <i>Chem. Commun.</i> <b>1997</b> , 1983.		
Trityl Tetrakis(pentafluorophenyl)borate		Catalyst
Catalyses the stereoselective glycosylation of alcoholic nucleophiles by 3,4,6-tri-O-benzyl-2-deoxyglucopyranose.	$\text{TrB}(\text{C}_6\text{F}_5)_4$ A	<p>A (5 mol%) Drierite PhH:PhMe 0°C, 1 h</p> <p>(1 eq) (1.3 eq)</p> <p>7 examples (yields 82-93%, α:β &gt; 83:17).</p> <p>91%, α:β = 90:10</p>
K. Takeuchi, S. Higuchi, T. Mukaiyama <i>Chem. Lett.</i> <b>1997</b> , 969.		

(2,7-Dimethyl-1,8-biphenylenedioxy)bis(dimethylaluminium)		Catalyst
<p>The title Lewis acid selectively activates carbonyls toward nucleophilic attack in the presence of dimethyl acetals.</p> <p>T. Ooi, E. Tayama, M. Takahashi, K. Maruoka <i>Tetrahedron Lett.</i> <b>1997</b>, <i>38</i>, 7403.</p>	 <p style="text-align: center;"><b>A</b></p>	 <p style="text-align: center;"><b>X = TiCl<sub>4</sub></b>    12%    75% <b>A</b>    80%    trace</p> <p>15 competitive reactions between various carbonyl compounds and their dimethyl acetals employing allyl tin and silyl ketene acetal nucleophiles (yields 80-97%, carbonyl adduct : acetal adduct &gt; 87:13).</p>
Bismuth(III) Bromide		Catalyst
<p>The reductive homocoupling of carbonyl compounds and heterocoupling of a carbonyl compound with an alkoxy silane is effected with triethylsilane and a catalytic quantity of the title reagent.</p> <p>N. Komatsu, J. Ishida, H. Suzuki <i>Tetrahedron Lett.</i> <b>1997</b>, <i>38</i>, 7219.</p>	<p style="text-align: center;"><b>BiBr<sub>3</sub></b></p> <p style="text-align: center;"><b>A</b></p>	 <p style="text-align: center;"><b>A (6 mol%)</b> <b>PhCH<sub>2</sub>OSiMe<sub>3</sub> (1.2 eq)</b> <b>Et<sub>3</sub>SiH (1.2 eq)</b> <b>CH<sub>3</sub>CN, rt, 2 h, 76%</b></p> <p>11 examples of homocoupling (yields 0, 61-93%), 13 examples of heterocoupling (yields 0, 58-96%).</p>
(1S,2S)-N,N-Bis(salicylidene)-1,2-diphenylethane-1,2-diamine		Ligand
<p>The titanium(IV) isopropoxide complex of the title ligand catalyses the enantioselective addition of trimethylsilylcyanide to aldehydes.</p> <p>Y. Jiang, L. Gong, X. Feng, W. Hu, W. Pan, Z. Li, A. Mi <i>Tetrahedron</i> <b>1997</b>, 14327.</p>	 <p style="text-align: center;"><b>A</b></p>	 <p style="text-align: center;"><b>A (10 mol%)</b> <b>Ti(OPr)<sub>4</sub> (10 mol%)</b> <b>Me<sub>3</sub>SiCN (2.0 eq)</b> <b>CH<sub>2</sub>Cl<sub>2</sub>, -78°C, 2 h</b></p> <p style="text-align: center;">69%, er = 87:13</p> <p>13 examples (yields 60-80%, %ee 40-87%).</p>
(1S,2S)-N-(p-Toluenesulfonyl)-1,2-diphenylethylenediamine (TsDPEN)		Ligand
<p>A ruthenium catalyst prepared from the title ligand is used for the asymmetric reduction of N-sulfonylimines to the corresponding sulfams.</p> <p>K. H. Ahn, C. Ham, S-K. Kim, C-W. Cho <i>J. Org. Chem.</i> <b>1997</b>, <i>62</i>, 7047.</p>	 <p style="text-align: center;"><b>A</b></p>	 <p style="text-align: center;"><b>RuCl(TsDPEN)(PhH) (0.5 mol%)</b> <b>HCO<sub>2</sub>H (6 eq)</b> <b>Et<sub>3</sub>N (2.5 eq)</b> <b>CH<sub>2</sub>Cl<sub>2</sub>, 25°C, 17 h</b></p> <p style="text-align: center;"><b>R = t-Bu</b>    75%, er = 96:4 <b>R = Bn</b>    59%, er = 98:2</p>
4,4'-Bis(3-diphenylphosphino-estra-1,3,5(10),6,8-pentaene)		Ligand
<p>Enantioselective hydrogenation is performed with a ruthenium catalyst derived from ligand A.</p> <p>V. Enev, C. L. J. Ewers, M. Harre, K. Nickisch, J. T. Mohr <i>J. Org. Chem.</i> <b>1997</b>, <i>62</i>, 7092.</p>	 <p style="text-align: center;"><b>A</b></p>	 <p style="text-align: center;"><b>RuCl<sub>2</sub>(R,R-A)(DMF)<sub>2</sub> (0.3 mol%)</b> <b>H<sub>2</sub> (4 atm), MeOH, rt, 48 h</b></p> <p style="text-align: center;">&gt;98%, er = 94:6</p> <p>3 examples (yields &gt;98%, %ee 86-97%).</p>

<b>(1<i>R</i>,5<i>R</i>,6<i>R</i>)-1,6-Bis(diphenylphosphino)spiro[4,4]nonane</b> <span style="float: right;"><i>Ligand</i></span>		
<p>Rhodium complexes of the novel title ligand catalyse the enantioselective hydrogenation of enamides.</p> <p>A. S. C. Chan, W. Hu, C.-C. Pai, C.-P. Lau <i>J. Am. Chem. Soc.</i> <b>1997</b>, <i>119</i>, 9570.</p>	 <p><b>A</b></p>	 <p>100%, er = 98:2</p> <p>13 examples of closely related acetamidoacrylic acids and esters (all yields quantitative, %ee 95-98%).</p>
<b>(<i>S</i>)-VAPOL</b> <span style="float: right;"><i>Ligand</i></span>		
<p>The aluminium complex derived from the title ligand catalyses the asymmetric Diels-Alder reaction between methyl acrylate and cyclopentadiene. The catalytic species exhibits an autoinduction whereby cooperative interaction of product and initial catalyst forms a more selective catalyst species.</p> <p>D. P. Heller, D. R. Goldberg, W. D. Wulff <i>J. Am. Chem. Soc.</i> <b>1997</b>, <i>119</i>, 10551.</p>	 <p><b>A</b></p>	 <p>er = 91:9</p> <p>Various carbonyl ligands were tested as additives to mimic the positive cooperativity between product and catalyst (eg addition of adamantyl aldehyde to the above reaction manifold resulted in %ee of 98.5).</p>
<b>(3<i>aR</i>,8<i>bS</i>)-2-[2-(Diphenylphosphino)phenyl]-3<i>a</i>,8<i>b</i>-dihydro-4,4-dimethyl-4<i>H</i>-indenol[1,2-<i>d</i>]oxazole</b> <span style="float: right;"><i>Ligand</i></span>		
<p>A rhodium complex derived from the title ligand catalyses the enantioselective hydrosilylation of ketones.</p> <p>The ligand <b>A</b> is also effective for palladium catalysed enantioselective amination: A. Sudo, K. Saigo <i>J. Org. Chem.</i> <b>1997</b>, <i>62</i>, 5508.</p> <p>A. Sudo, H. Yoshida, K. Saigo <i>Tetrahedron: Asymmetry</i> <b>1997</b>, <i>8</i>, 3205.</p>	 <p><b>A</b></p>	 <p>91%, er = 96:4</p> <p>8 examples (yields 83-97%, %ee 52-94).</p>
<b>(<i>R,R</i>)-(-)-<i>N,N'</i>-Dimethyl-1,2-diphenyl-1,2-ethylenyldiphenylthiourea</b> <span style="float: right;"><i>Ligand</i></span>		
<p>The ruthenium complex derived from the title ligand catalyses the enantioselective hydride transfer reduction of ketones.</p> <p>F. Touchard, F. Fache, M. Lemaire <i>Tetrahedron: Asymmetry</i> <b>1997</b>, <i>8</i>, 3319.</p>	 <p><b>A</b></p>	 <p>98%, er = 95:5</p> <p>6 examples (yields 93-98%, %ee 62-94%). Various other thiourea ligands and pre-catalyst metal complexes (Rh, Ir) were also investigated.</p>
<b>(2<i>S</i>,6<i>S</i>)-4-Benzyl-1,7-di(trifluoromethanesulfonyl)-2,6-diisopropyl-1,4,7-triazaheptane</b> <span style="float: right;"><i>Ligand</i></span>		
<p>The titanium catalyst derived from Ti(O<i>i</i>-Pr)<sub>4</sub> and the title ligand catalyses the enantioselective addition of diethylzinc to benzaldehyde. Ligands of this class are easily obtained by the nucleophilic opening of amino acid derived aziridines.</p> <p>M. Cernerud, A. Skinning, I. Bérgère, C. Moberg <i>Tetrahedron: Asymmetry</i> <b>1997</b>, <i>8</i>, 3437.</p>	 <p><b>A</b></p>	 <p>74%, er = 89:11</p> <p>9 examples of the above reaction employing various triamine ligands and conditions (yields 11-74%, %ee 0-78%).</p>

<b>1,1-Dioxobenzo[ b]thiophene-2-ylmethoxycarbonyl Chloride</b>		<b>Protecting Group</b>
<p>The title reagent is a source of the 1,1-dioxobenzo[<i>b</i>]thiophene-2-ylmethoxycarbonyl (Bsmoc) group for the protection of amino groups during SPPS. It is more labile than Fmoc towards base. An advantage over the Fmoc group is that the deprotection and scavenging event are identical.</p> <p>L. A. Carpino, M. Philbin, M. Ismail, G. A. Truran, E. M. E. Mansour, S. Iguchi, D. Ionescu, A. El-Faham, C. Reimer, R. Warrass, and M. S. Weiss, <i>J. Am. Chem. Soc.</i>, <b>1997</b>, <i>119</i>, 9915.</p>	 <p style="text-align: center;"><b>A</b></p>	 <p style="text-align: center;"><b>A</b> (2 eq.) rt, 3-5 min</p>
<b>Tris(trimethylsilyl)silyl (Sisyl)</b>		<b>Protecting Group</b>
<p>The sisyl group provides primary and unhindered secondary alcohols with a photo labile protecting group. Sisyl ethers are resistant to acid hydrolysis and selected fluoride reagents.</p> <p>M. A. Brook, C. Gottardo, S. Balduzzi, M. Mohamed <i>Tetrahedron Lett.</i> <b>1997</b>, <i>38</i>, 6997.</p>	 <p style="text-align: center;"><b>A</b></p>	 <p style="text-align: center;"><b>A</b> (1.2 eq), DMAP (1.2 eq) CH<sub>2</sub>Cl<sub>2</sub>, rt, 16 h, 79% hv (pyrex filter) CH<sub>2</sub>Cl<sub>2</sub>, MeOH 10°C, 30 min, 87%</p> <p>10 examples of protection/deprotection sequences (protection yields 74-97%, deprotection yields 62-95%).</p>
<b>Trimethoxysilane</b>		<b>Reagent</b>
<p>Transient hypervalent silicon hydrides generated by the title reagent and a chiral alkoxide, effect the asymmetric reduction of ketones.</p> <p>R. Schiffrers, H. B. Kagan <i>Synlett</i> <b>1997</b>, 1175.</p>	 <p style="text-align: center;"><b>A</b></p>	 <p style="text-align: center;"><b>A</b> (1 eq), (<i>R</i>)-LiBINOL (5 mol%) Et<sub>2</sub>O/TMEDA (30/1), rt, 24 h</p> <p style="text-align: center;">46%, er = 81:19</p> <p>11 examples (yields 39-91%, %ee 0-93%). Greater enantioselectivity was observed when employing more sterically encumbered ketones.</p>
<b>Iodosobenzene Diacetate (PIDA)</b>		<b>Reagent</b>
<p>The Hofmann rearrangement of protected asparagines to β-amino-L-alanines is performed with the title reagent.</p> <p>L. Zhang, G. S. Kauffman, J. A. Pesti, J. Yin <i>J. Org. Chem.</i> <b>1997</b>, <i>62</i>, 6918.</p>	 <p style="text-align: center;"><b>A</b></p>	 <p style="text-align: center;"><b>A</b> (1.2 eq) EtOAc/MeCN/H<sub>2</sub>O, 20°C, 4 h 62%</p> <p>6 examples (yields 59-93%).</p>
<b>Trimethyl[2-[(tributylstannyl)methyl]-2-propenyl]silane</b>		<b>Reagent</b>
<p>Radical allylations are performed with the title reagent.</p> <p>D. L. J. Clive, C. C. Paul, Z. Wang <i>J. Org. Chem.</i> <b>1997</b>, <i>62</i>, 7028.</p>	 <p style="text-align: center;"><b>A</b></p>	 <p style="text-align: center;"><b>A</b> (2 eq), hv PhH, 15-20°C, 20 h 75%</p> <p>9 examples (yields 45-86%). 7 examples of allylation using the corresponding triphenylstannyl reagent are also reported (yields 42-90%).</p>

Tin(II) Catecholate		Reagent
Optically active homoallyl alcohols are produced in high yields and enantioselectivities from chiral allylating reagents generated from the title compound.		<p>98%, er = 96:4</p> <p>13 examples (yields 83-99%, %ee 55-94%).</p> <p>DTBT = di-<i>tert</i>-butyl tartrate</p>
K. Yamada, T. Tozawa, M. Nishida, T. Mukaiyama <i>Bull. Chem. Soc. Jpn.</i> <b>1997</b> , <i>70</i> , 2301.		
N-Fluorobenzenesulfonimide		Reagent
Electrophilic fluorination of a sodium enolate with the title compound occurred with excellent diastereoselectivity.		<p>68%, dr &gt; 99:1</p> <p>The utility of the fluorination was demonstrated by the synthesis of 4-deoxy-4-fluoro-D-arabinopyranose.</p>
F. A. Davis, P. V. N. Kasu, G. Sundarababu, H. Qi <i>J. Org. Chem.</i> <b>1997</b> , <i>62</i> , 7546.		
(-)-Sparteine		Reagent
2-Substituted indolines and 2,7-disubstituted indolines are synthesised with excellent enantioselectivity <i>via</i> asymmetric lithiation with <i>-</i> BuLi / A of the parent indoline and subsequent substitution.		<p>77%, er = 96:4</p> <p>7 examples of the substitution of <i>N</i>-Boc indoline (yields 11-70%, %ee 30-&gt;98) and 5 examples of the substitution of <i>N</i>-Boc-7-chloroindoline (yields 32-90%, %ee = 10-78) are reported.</p>
K. M. B. Gross, Y. M. Jun, P. Beak <i>J. Org. Chem.</i> <b>1997</b> , <i>62</i> , 7679.		
Bis(trimethylsilyl)methylzinc		Reagent
Mixed diorganozinc reagents prepared from the title compound are used for enantioselective addition to aldehydes. The method avoids the use of a large excess of diorganozinc reagents.	$(\text{Me}_3\text{SiCH}_2)_2\text{Zn}$	<p>98%, er = 96:4</p> <p>12 examples using a variety of aldehydes and mixed diorganozinc reagents are reported (yields 74-98%, %ee = 74-&gt;95).</p> <p>TMSM = (trimethylsilyl)methyl</p>
C. Lutz, P. Knochel <i>J. Org. Chem.</i> <b>1997</b> , <i>62</i> , 7895.		
Zirconocene Dichloride		Reagent
The title reagent in the presence of a catalytic amount of silver(I) perchlorate converts 3-methyl-3,4-epoxy esters to 2,7,8-trioxabicyclo[3.2.1]octane (ABO) ortho ester derivative which are less prone to acid hydrolysis than Corey's 2,6,7-trioxabicyclo[2.2.2]octane (OBO) ortho ester derivatives.	$\text{Cp}_2\text{ZrCl}_2$	<p>99%</p>
P. Wipf, W. Xu, H. Kim, H. Takahashi <i>Tetrahedron</i> , <b>1997</b> , <i>53</i> , 16575		

Polymer Supported 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (PTBD)		Reagent
Acts as a base and reagent scavenger for the synthesis of aryl ethers from phenols and alkyl or aryl halides.	 <p><b>A</b> ● = polystyrene</p>	 <p>(a) <b>A</b> (2 eq) MeCN, rt, 64 h (b) filter</p> <p>92%, purity 92%</p> <p>13 examples (yields 47-98%, purity 71-99%). Excess phenol remains bound to the polymeric base and hence is easily removed <i>via</i> simple filtration.</p>
W. Xu, R. Mohan, M. M. Morrissey <i>Tetrahedron Lett.</i> <b>1997</b> , <i>38</i> , 7337.		
Chiral Ferrocenylselenium Reagent		Reagent
Asymmetric methoxyselenylation of alkenes is achieved with good diastereoselectivity using a chiral ferrocenylselenium triflate.	 <p><b>A</b></p>	 <p>(a) Br<sub>2</sub> (1.2 eq) CCl<sub>4</sub>, -78°C, 30 min (b) AgOTf (2.4 eq) MeOH, -78°C, 30 min (c) <i>trans</i>-β-methylstyrene (4 eq) 0°C, 5 h</p> <p>99%, dr = 98:2</p> <p>12 examples (yields 96-99%, %de 15-96%). Of several chiral selenium compounds investigated, <b>A</b> gave the highest diastereoselectivities.</p>
S. Fukuzawa, K. Takahashi, H. Kato, H. Yamazaki <i>J. Org. Chem.</i> <b>1997</b> , <i>62</i> , 7711.		
Ammonium Cerium(IV) Nitrate (CAN)		Reagent
Malonate radicals generated by the action of the title reagent, add regioselectively to glycols to afford 2-C-branched carbohydrates.	 <p><b>A</b> Ce(NO<sub>3</sub>)<sub>6</sub>(NH<sub>4</sub>)<sub>2</sub></p>	 <p><b>A</b> (3 eq), DIMP (10 eq) MeOH, 0°C, 0.5 h</p> <p>76%, α:β = 91:9</p> <p>The reactivity of glycols derived from pentoses and hexoses has been examined under the above conditions (8 examples).</p> <p>DIMP = diisoprylmalonate</p>
T. Linker, T. Sommermann, F. Kahlenberg <i>J. Am. Chem. Soc.</i> <b>1997</b> , <i>119</i> , 9377.		
Lithium (S)-(α-Methylbenzyl)allylamide		Reagent
The chiral lithium amide <b>A</b> adds stereoselectively to α,β,γ,δ-unsaturated dienocates in a 1,4-fashion. The resultant β-amino ester products can be elaborated to various unsaturated β-amino acid derivatives.	 <p><b>A</b></p>	 <p>(a) <b>A</b> (1.5 eq), THF, -78°C (b) (+)-(camphorsulfonyl)oxaziridine (1 eq)</p> <p>72%, dr = 98:2</p> <p>2 examples of diastereoselective conjugate addition (yields 72,78%, %dr = 98:2). Various conditions are given for the synthesis of useful <i>N</i>-Boc adducts from the (α-methylbenzyl)allylamine products.</p>
S. G. Davies, D. R. Fenwick, O. Ichihara <i>Tetrahedron: Asymmetry</i> <b>1997</b> , <i>8</i> , 3387.		
Ethanethiol		Reagent
Oxazolidinone chiral auxiliaries can be removed from substrates prone to epimerisation and/or elimination <i>via</i> a novel mild decarboxylation process.	 <p><b>A</b> EtSH</p>	 <p>EtSH, KH THF, rt, 1 h</p> <p>AgNO<sub>3</sub>, 2,6-lutidine THF/H<sub>2</sub>O (5/1), rt, 2 d</p> <p>88%</p> <p>5 examples of one-pot decarboxylation of β-ketoimide adducts (yields 74-98%). The methodology is highlighted with aldol and Diels-Alder reactions.</p>
D. A. Evans, D. H. Brown Ripin, J. S. Johnson, E. A. Shaughnessy <i>Angew. Chem. Int. Ed. Engl.</i> <b>1997</b> , <i>36</i> , 2119.		



N-(Benzyloxyiminoacetyl)-camphor-10,2-sultam		Reagent
Highly diastereoselective radical addition to the camphor sultam derivative <b>A</b> was achieved providing a convenient method for the synthesis of a variety of enantiomerically pure $\alpha$ -amino acids.		<p>16 examples (yields 25-86%, %de 72-&gt;96%). Several reaction conditions are investigated, with variation in the reaction temperature, solvent and Lewis acid.</p>
H. Miyabe, C. Ushiro, T. Naito <i>Chem. Commun.</i> <b>1997</b> , 1789.		
Magnesium Sulfate		Reagent
<i>t</i> -Butyl esters are prepared directly from <i>t</i> -BuOH and carboxylic acids in the presence of the title reagent and a catalytic quantity of sulfuric acid. <i>t</i> -Butyl ethers are also accessible via an analogous procedure.	MgSO <sub>4</sub> <b>A</b>	<p>14 examples of ester formation (yields 60-93%) and 13 examples of ether formation (yields 0, 67-95%).</p>
S. W. Wright, D. L. Hageman, A. S. Wright, L. D. McClure <i>Tetrahedron Lett.</i> <b>1997</b> , 38, 7345.		
<i>iso</i> -Propyl Magnesium Chloride / Diiodomethane		Reagent
The title pair of reagents effect the directed cyclopropanation of allylic alcohols.	MgCl <b>A</b>  CH <sub>2</sub> I <sub>2</sub> <b>B</b>	<p>5 examples of 2° allylic alcohols (yields 50-82%, <i>syn:anti</i> = 83:17 to 100:0).</p>
C. Bolm, D. Pupowicz <i>Tetrahedron Lett.</i> <b>1997</b> , 38, 7349.		
<i>N,N</i> -Dibenzylformamide Dimethyl Acetal		Reagent
Reaction of primary amines with <i>N,N</i> -dibenzyl formamide dimethyl acetal ( <b>A</b> , prepared <i>in situ</i> from dibenzylamine and DMF dimethyl acetal) affords <i>N,N</i> -dibenzyl formamidines. The resultant protected amine can be liberated by hydrogenolysis over Pearlman's catalyst.		<p>20% Pd(OH)<sub>2</sub>/C (0.5 eq wt.) H<sub>2</sub> (70 psi), <i>t</i>-BuOH, H<sub>2</sub>O rt, 5 h, 95%</p> <p>9 examples of protection/deprotection sequences (protection yields 49-99%, deprotection yields 52-99%).</p>
S. Vincent, S. Mons, L. Lebeau, C. Mioskowski <i>Tetrahedron Lett.</i> <b>1997</b> , 38, 7527.		
Iodobenzene Diacetate on Alumina		Reagent
The title reagent rapidly oxidises alcohols to carbonyl compounds in a solvent-less system under microwave irradiation.	PhI(OAc) <sub>2</sub> <b>A</b>	<p>9 examples (yields 43-96%).</p>
R. S. Varma, R. Dahiya, R. K. Saini <i>Tetrahedron Lett.</i> <b>1997</b> , 38, 7029.		

Methyl (Trifluoromethyl)dioxirane		Reagent
<p>The title reagent (generated <i>in situ</i> from oxone® and 1,1,1-trifluoroacetone) oxidatively cleaves aryl oxazolines to nitroesters. Saponification of the latter yields carboxylic acids.</p>	<p>(a) oxone® (30 eq) CF<sub>3</sub>COCH<sub>3</sub>, NaHCO<sub>3</sub> (93 eq) Na<sub>2</sub>•EDTA (0.4 mM), CH<sub>3</sub>CN, rt</p> <p>(b) 5% NaOH, MeOH 100°C, 12 h, 88%</p>	<p>6 examples (yields 80-95%).</p>
<p>D. Yang, Y.-C. Yip, X.-C. Wang <i>Tetrahedron Lett.</i> <b>1997</b>, <i>38</i>, 7083.</p>		
Dimethylethoxyvinylsilane		Reagent
<p>Zincated hydrazones add regioselectively to vinyl silanes.</p>	<p>(a) <i>t</i>-BuLi (1 eq), Et<sub>2</sub>O -70°C → 0°C, 4 h</p> <p>(b) ZnBr<sub>2</sub> (1 eq) -70°C → 0°C 30 min</p> <p>(c) BuLi (1 eq) -70°C → 0°C 30 min</p> <p>(d) A (2 eq) rt, 2 d</p> <p>64%, dr = 72:28</p>	<p>11 examples (yields 45-97%).</p>
<p>E. Nakamura, K. Kubota <i>Tetrahedron Lett.</i> <b>1997</b>, <i>38</i>, 7099.</p>		
2,4,4,6-Tetrabromocyclohexa-2,5-dienone / Triphenylphosphine		Reagent
<p>The phosphonium salt C (generated <i>in situ</i> from the title reagents) converts sterically unhindered silyl ethers directly into the corresponding bromides.</p>	<p>9 examples (yields 0, 47-99%). TMS, TES and TBDMS ethers all successfully transformed (1° and 2°); 1° TIPS ether cleaved very slowly and 1° TBDPS stable to the reaction conditions.</p>	
<p>A. Tanaka, T. Oritani <i>Tetrahedron Lett.</i> <b>1997</b>, <i>38</i>, 7223.</p>		
2,2,2-Trifluorodiazoethane		Reagent
<p>Carbohydrate sulfates react with the title reagent to form trifluoroethyl sulfate esters. These are resistant to a variety of conditions commonly used to remove standard carbohydrate protecting groups.</p>	<p>SO<sub>3</sub>•pyr, CH<sub>3</sub>CN 80°C, 1 h</p> <p>A (10 eq), CH<sub>3</sub>CN rt, 5 min, 93%</p> <p>KOtBu (5 eq) <i>t</i>-BuOH, Δ, 1 h 88%</p>	<p>6 examples of sulfation/protection (yields 46-93%) and 3 examples of deprotection (yields 82-96%).</p>
<p>A. D. Proud, J. C. Prodger, S. L. Flitsch <i>Tetrahedron Lett.</i> <b>1997</b>, <i>38</i>, 7243.</p>		
Zirconium Tetrachloride		Reagent
<p>Ketone homologation to produce α-methoxy ketones (via hydroxy sulfone rearrangement) is effected with good yield and total regioselectivity by the use of the title reagent.</p>	<p>ZrCl<sub>4</sub> (6 eq) CH<sub>2</sub>Cl<sub>2</sub>, rt, 15 min 87%</p> <p>PhSO<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub> (1 eq) BuLi (1 eq), THF, -78°C 91%</p>	<p>8 examples with aryl alkyl ketones, dialkyl ketones and cycloalkanones (yields for second step 24, 50-90%).</p>
<p>N. Phillipson, M. S. Anson, J. G. Montana, R. J. K. Taylor <i>J. Chem. Soc., Perkin Trans. 1</i> <b>1997</b>, 2821.</p>		