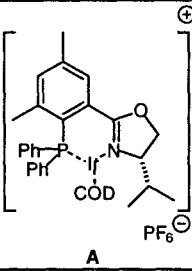
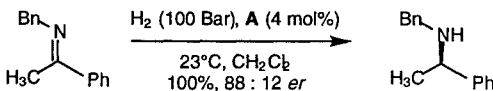
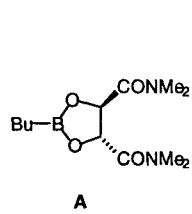
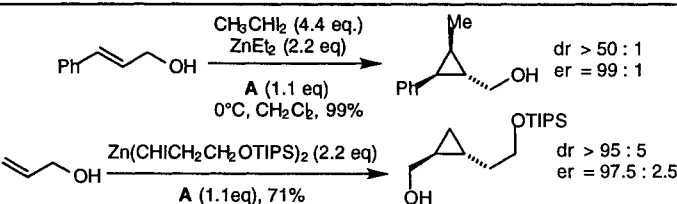
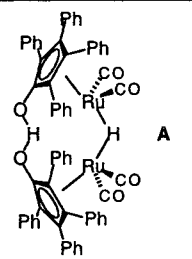
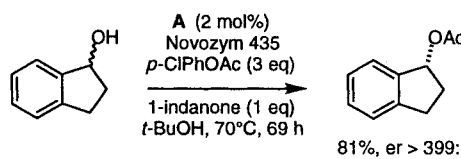


SYNTHESIS ALERTS

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, 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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(Phosponodihydrooxazole)Ir(I) Complexes		Catalyst
<p>Hydrogenation of imines with the title iridium complexes gives chiral amines in excellent yields and fair to good <i>er</i> (up to 89.5 : 10.5 <i>er</i>).</p> <p>P. Schnider, G. Koch, R. Prétôt, G. Wang, F. M. Bohnen, C. Krüger, A. Pfaltz <i>Chem. Eur. J.</i> 1997, <i>3</i>, 887.</p>	 <p style="text-align: center;">A</p>	 <p>Reactions with 12 similar substrates and 4 other catalysts are reported with yields = 64 - 100% and <i>er</i> = 58.5 : 42.5 to 89.5 - 10.5.</p>
<p>(<i>R, R</i>)-(+)-<i>N, N, N', N'</i>-Tetramethyltartaric Acid Diamide</p> <p>Enantiomerically enriched (up to 99 : 1 <i>er</i>) 1,2,3-substituted cyclopropanes are obtained from reaction of allylic alcohols with alkylzinc reagents in presence of the catalyst A. The first cyclopropanation using a functionalised alkylzinc reagent is also presented.</p> <p>A. B. Charette, J. Lemay <i>Angew. Chem. Int. Ed. Engl.</i> 1997, <i>36</i>, 1090.</p>	 <p style="text-align: center;">A</p>	 <p>5 other examples reported for the top reaction, yields = 80 - 87%, <i>er</i> = 95 : 5 - 97 : 3, <i>dr</i> = 10 : 1 - 50 : 1).</p>
<p>Ruthenium Catalyst</p> <p>Enzymatic resolution under substrate-racemising conditions using the title ruthenium catalyst leads to benzylic acetates in excellent yield and enantioselectivity.</p> <p>A. L. E. Larsson, B.A. Persson, J.-E. Bäckvall <i>Angew. Chem. Int. Ed. Engl.</i> 1997, <i>36</i>, 1211.</p>	 <p style="text-align: center;">A</p>	 <p>Resolution of α-methylbenzyl alcohol is also presented (yield 92%, <i>er</i> > 99.7 : 0.3).</p>

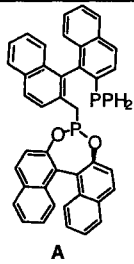
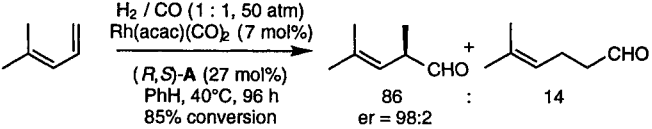
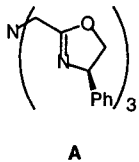
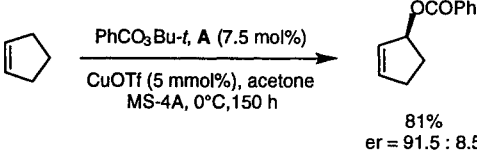
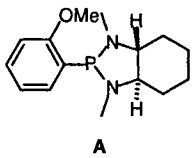
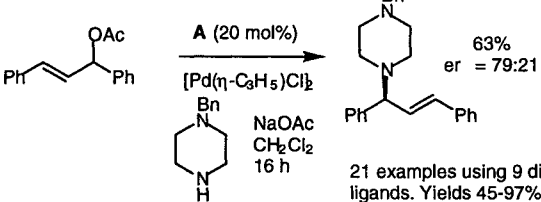
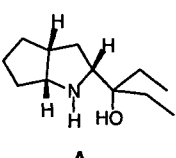
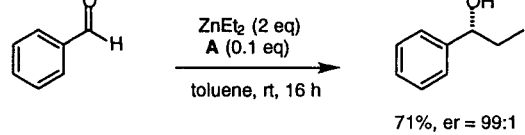
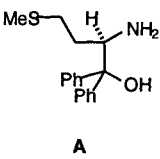
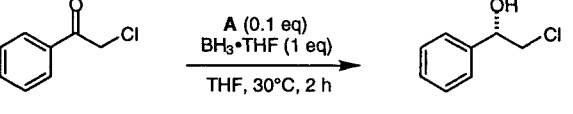
Nickel-Stabilised Zirconium		Catalyst
Ni-stabilised zirconium is a reusable, solid catalyst which efficiently catalyses the chemoselective reduction of nitroarenes, aldehydes and ketones.	$Zr_{0.8}Ni_{0.2}O_2$ A	<p>19 examples; yields 72-96%.</p>
T. T. Upadhy, S. P. Katdare, D. P. Sabde, V. Ramaswamy, A. Sudalai <i>Chem. Commun.</i> 1997 , 1119.		

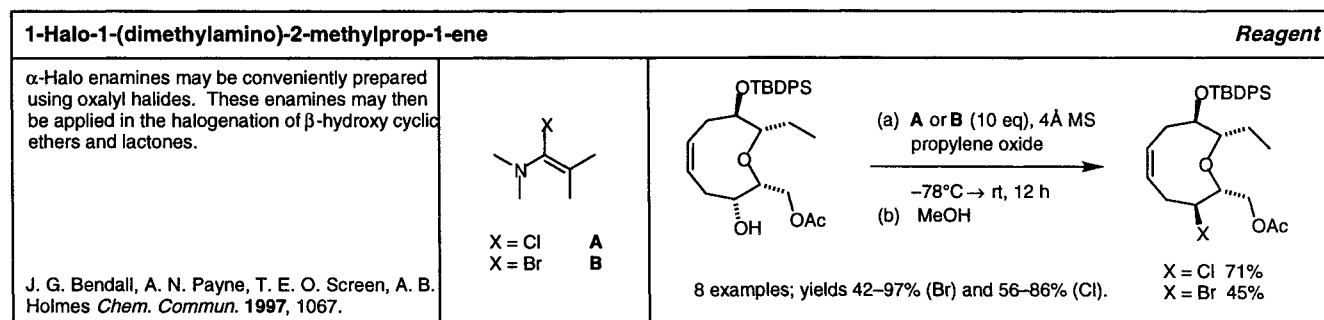
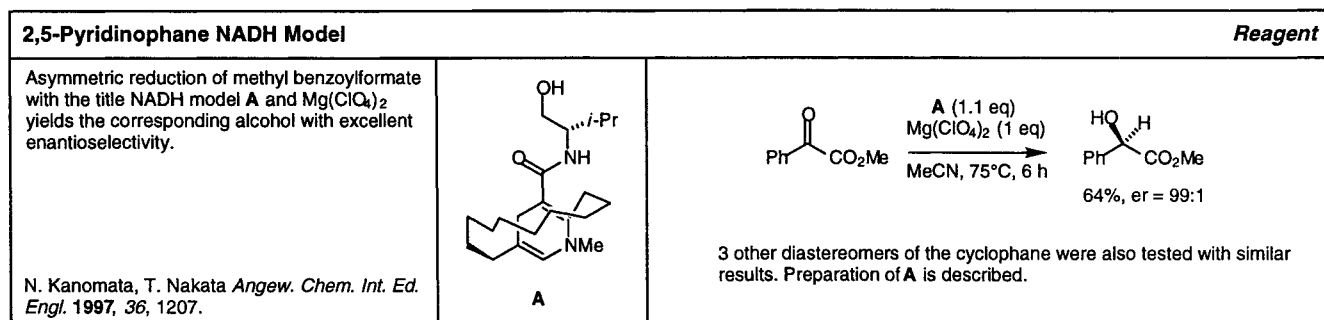
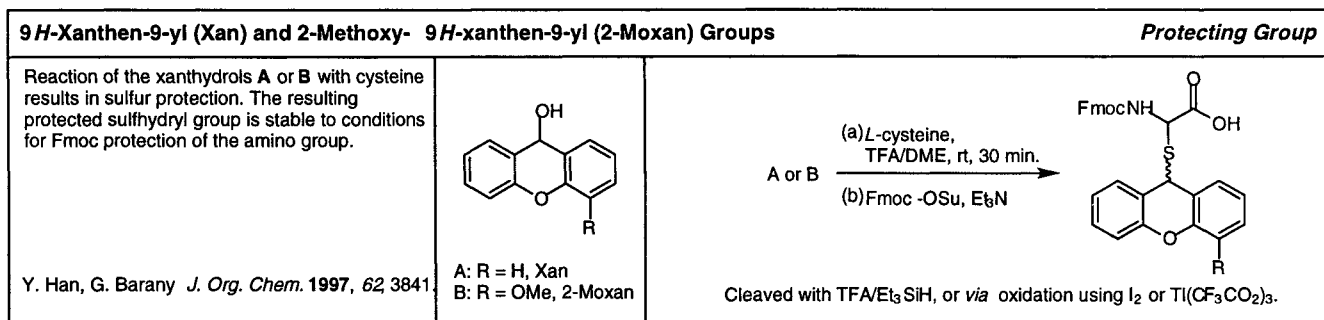
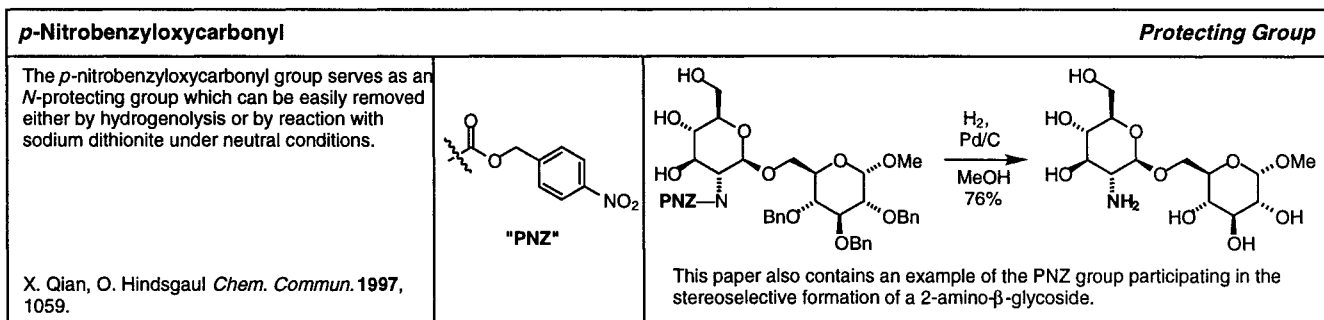
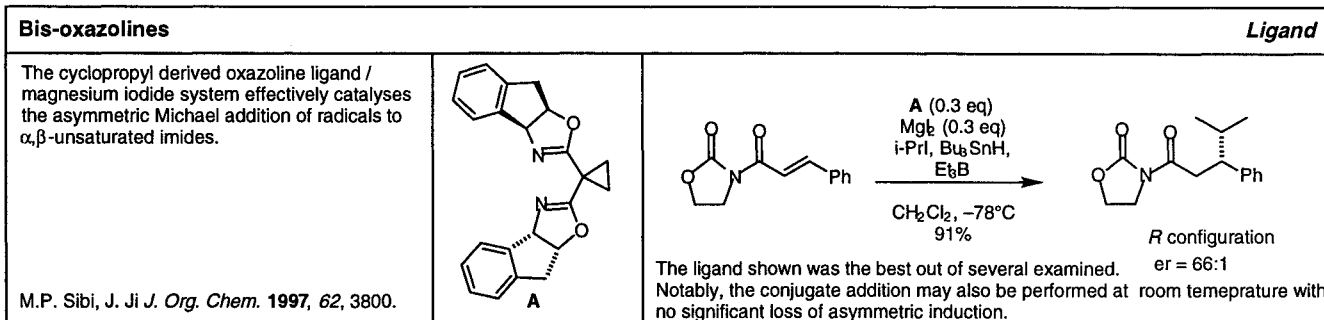
Cobalt(II) Complex Catalysts		Catalyst
Enantioselective borohydride reductions of <i>N</i> -diphenylphosphinyl imines using optically active cobalt(II) complex catalysts progress in high yield and ee.		<p>10 examples using 3 different catalysts. Yields >80%. <i>er</i> >9:1. The products may be hydrolysed to amines in 85% yield with HCl/MeOH.</p>
K. D. Sugi, T. Nagata, T. Yamada, T. Mukaiyama <i>Chem. Lett.</i> 1997 , 493.		

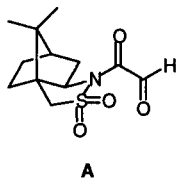
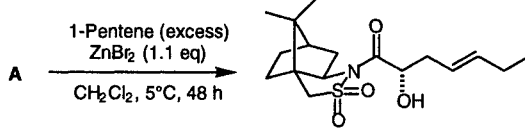
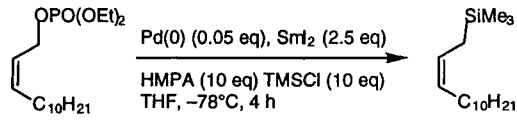
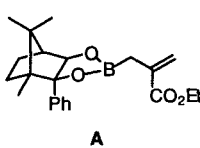
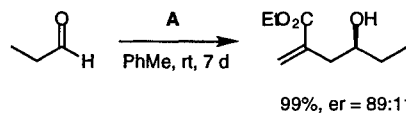
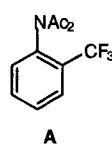
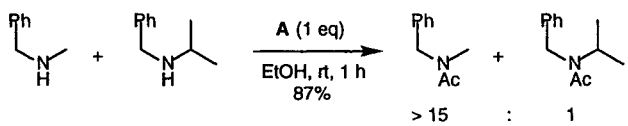
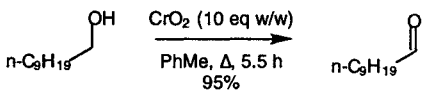
Polymer-Enlarged Oxazaborolidine		Catalyst
A polymer-enlarged homogeneously soluble oxazaborolidine catalyst for the asymmetric reduction of ketones by borane.		<p>(4 examples)</p>
M. Felder, G. Giffels, C. Wandrey <i>Tetrahedron: Asymmetry</i> 1997 , 8, 1975.		

Copper(I) Iodide		Catalyst
Using cuprous iodide in NMP, vinyl stannanes may be coupled with iodides. No palladium catalyst is necessary	CuI A	<p>15 different examples. Manganese bromide may be used instead of copper iodide, but in most cases the yields are slightly depressed.</p>
S.-K. Kang, J.-S. Kim, S.-C. Choi, <i>J. Org. Chem.</i> 1997 , 62, 4208.		

Copper(I) Chloride		Catalyst
Reaction of alkynylsilanes with the title reagent A in 1,3-dimethyl-2-imidazolidinone (DMI) results in the first direct alkynyl group transfer from silicon to copper. The resultant alkynylcopper(I) species are quenched <i>in situ</i> with acyl halides to form alkynyl ketones in good yield.	CuCl A	<p>11 examples (yields 10, 69-98%).</p>
H. Ito, K. Arimoto, H. Sensui, A. Hosomi <i>Tetrahedron Lett.</i> 1997 , 38, 3977.		

(R)-2-(Diphenylphosphino)-1,1'-binaphthalen-2'-yl (S)-1,1'-binaphthalene-2,2'-diyl Phosphite (BINAPHOS) Ligand		
<p>Asymmetric hydroformylation of conjugated dienes using BINAPHOS-Rh(I) complex as a catalyst yields β,γ-unsaturated aldehydes with high regio- and enantioselectivity.</p> <p>T. Horiuchi, T. Ohta, E. Shirakawa, K. Nozaki, H. Takaya <i>Tetrahedron</i> 1997, <i>53</i>, 7795.</p>	 <p>A</p>	<p> H_2 / CO (1 : 1, 50 atm) $\text{Rh}(\text{acac})(\text{CO})_2$ (7 mol%) (R,S)-A (27 mol%) PhH, 40°C, 96 h 85% conversion </p> <p>  86 : 14 er = 98:2 </p> <p>4 examples (yields 60-96%, %ee 88-97%).</p>
Cu(II)-tris(oxazoline) Complexes Catalyst		
<p>The optically active title complexes catalyse allylic oxidation of cycloalkenes with poor to very good enantioselectivity.</p> <p>K. Kawasaki, T. Katsuki <i>Tetrahedron</i> 1997, <i>53</i>, 6337.</p>	 <p>A</p>	<p> $\text{PhCO}_3\text{Bu-t}$, A (7.5 mol%) CuOTf (5 mmol%), acetone MS-4A, 0°C, 150 h </p> <p>  81% er = 91.5 : 8.5 </p> <p>Reactions under a variety of conditions led to lower yields (8 - 70%) and er between 41 : 59 and 96.5 : 3.5.</p>
Diazaphospholidines Ligand		
<p>Allylic substitutions using diazaphospholidine ligands may be achieved in up to 89% ee.</p> <p>H. Tye, D. Smyth, C. Eldred, M. Wills <i>Chem. Commun.</i> 1997, 1053.</p>	 <p>A</p>	<p> A (20 mol%) $[\text{Pd}(\eta\text{-C}_3\text{H}_5)\text{Cl}]_2$ NaOAc CH_2Cl_2 16 h </p> <p>  63% er = 79:21 </p> <p>21 examples using 9 different ligands. Yields 45-97%; er = 94.5:5.5 to 63:37.</p>
(2R,3aR,6aR)-1,1-Diethyl-(octahydro-cyclopenta[b]pyrrole-2'-yl)methanol Ligand		
<p>Synthesis and application of new β-amino alcohols based on the octahydro-cyclopenta[b]pyrrole system in the catalytic enantioselective addition of diethylzinc to benzaldehyde.</p> <p>J. Wilken, M. Kossenjans, H. Gröger, J. Martens <i>Tetrahedron: Asymmetry</i> 1997, <i>8</i>, 2007.</p>	 <p>A</p>	<p> ZnEt_2 (2 eq) A (0.1 eq) toluene, rt, 16 h </p> <p>  71%, er = 99:1 </p> <p>The reactivity of several β-amino alcohols has been examined (13 examples).</p>
(S)-2-Amino-1,1-diphenyl-4-(methylthio)butan-1-ol Ligand		
<p>Sulfur-containing β-amino alcohols as ligand in enantioselective synthesis.</p> <p>W. Trentmann, T. Mehler, J. Martens <i>Tetrahedron: Asymmetry</i> 1997, <i>8</i>, 2033.</p>	 <p>A</p>	<p> A (0.1 eq) $\text{BH}_3\cdot\text{THF}$ (1 eq) THF, 30°C, 2 h </p> <p>  85%, er = 97.5:2.5 </p> <p>The reactivity of cyclic and acyclic sulfur-containing β-amino alcohols has been examined (40 examples).</p>



<i>N</i>-Glyoxyloyl-(2<i>R</i>)-bornane-10,2-sultam		Reagent
<p>The asymmetric ene reaction of <i>N</i>-glyoxyloyl-(2<i>R</i>)-bornane-10,2-sultam with alk-1-ene promoted by different Lewis acids has been examined.</p> <p>A. Jezewski, K. Chajewska, Z. Wielogórski, J. Jurczak <i>Tetrahedron: Asymmetry</i> 1997, <i>8</i>, 1741.</p>	 <p style="text-align: center;">A</p>	 <p style="text-align: center;">50.5%, dr = 90:10</p> <p>The reactivity of A and its methoxy hemiacetal has been checked with pent-1-ene and hex-1-ene using different Lewis acid (20 examples).</p>
Samarium Diiodide		
<p>Highly regio- and stereoselective synthesis of allylsilanes via palladium(0)-catalyzed reductive metallation of allylic phosphates with SmI₂-HMPA system.</p> <p>T. Hanamoto, A. Sugino, T. Kikukawa, J. Inanaga <i>Bull. Soc. Chim. Fr.</i> 1997, <i>134</i>, 391.</p>	<p style="text-align: center;">SmI₂</p>	 <p style="text-align: center;">(17 examples) 69%, <i>E:Z</i> = 3:97</p>
Chiral Allyl Bornonate		
<p>The bornane derived functionalised boronate A effects the asymmetric allylation of aldehydes. The resultant γ-hydroxy esters are precursors to chiral α-methylene-γ-lactones.</p> <p>I. Chataigner, J. Lebreton, F. Zammattio, J. Villiéras <i>Tetrahedron Lett.</i> 1997, <i>38</i>, 3719.</p>	 <p style="text-align: center;">A</p>	 <p style="text-align: center;">99%, er = 89:11</p> <p>5 examples (yields 67-99%, %ee 30, 78-96%). Use of chiral aldehydes results in double stereodifferentiation.</p>
2-Trifluoromethyl- <i>N,N</i>-diacetylaniline		
<p>An efficient, easily prepared, reagent for the acetylation of amines. Less hindered amines are acetylated in the presence of more hindered amines with excellent selectivity.</p> <p>Y. Murakami, K. Kondo, K. Miki, Y. Akiyama, T. Watanabe, Y. Yokoyama <i>Tetrahedron Lett.</i> 1997, <i>38</i>, 3751.</p>	 <p style="text-align: center;">A</p>	 <p style="text-align: center;">87% > 15 : 1</p> <p>13 examples (yields 70-99%). Variation in reaction conditions can influence steric differentiation.</p>
Chromium Dioxide (Magtrieve™)		
<p>A mild selective oxidant for a variety of alcohols being superior to activated MnO₂ in most cases. The reagent is magnetically retrievable and may be regenerated simply by heating in air.</p> <p>R. A. Lee, D. S. Donald <i>Tetrahedron Lett.</i> 1997, <i>38</i>, 3857.</p>	<p style="text-align: center;">CrO₂</p>	 <p style="text-align: center;">95%</p> <p>5 examples (yields 61-95%). In each case identical transformations are attempted with MnO₂ (for the illustrated example yield <10% with MnO₂).</p>

