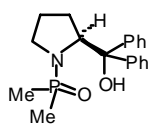
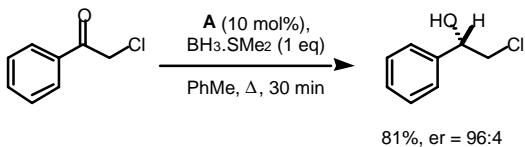

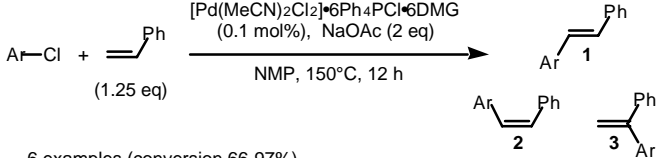
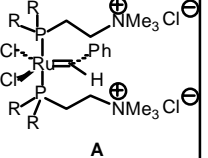
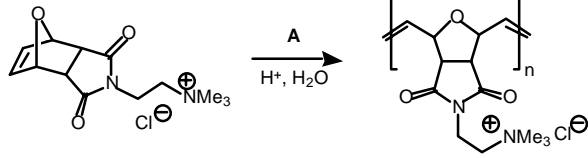


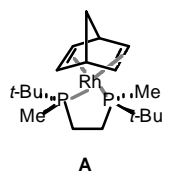
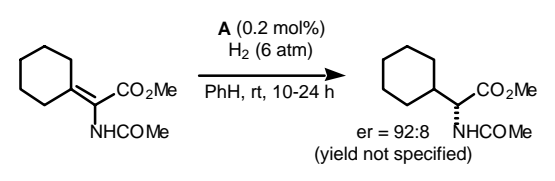
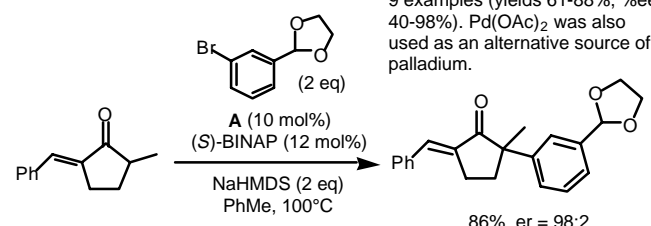
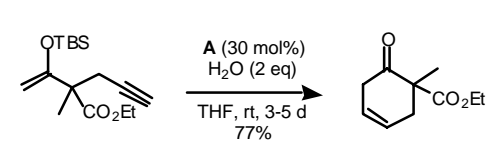
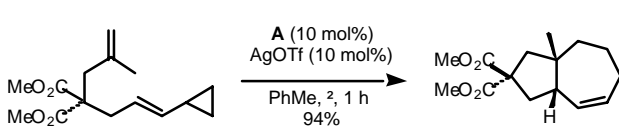
SYNTHESIS ALERTS

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.

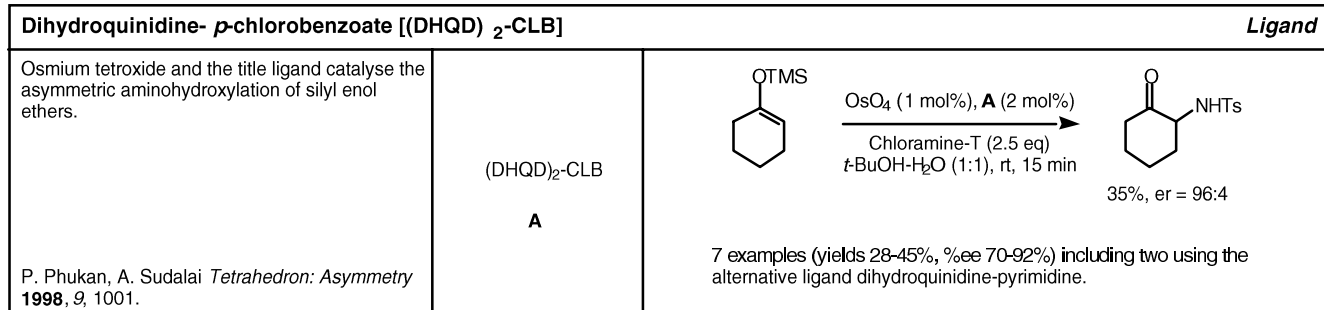
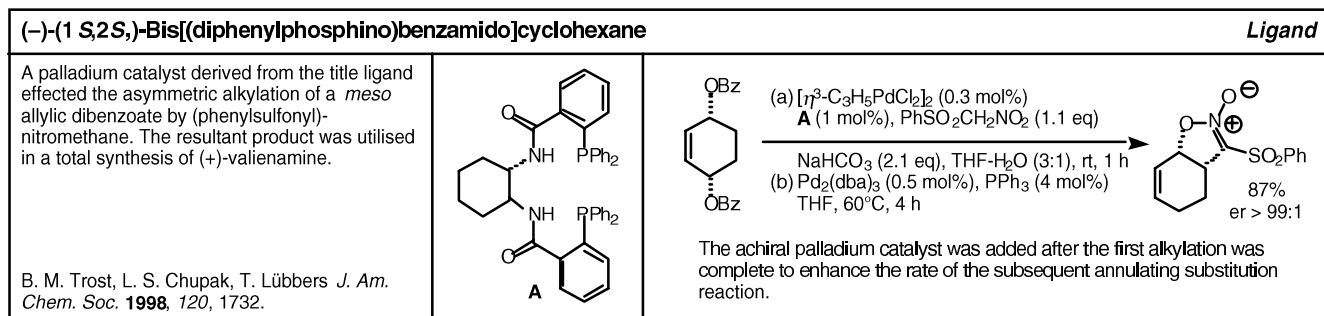
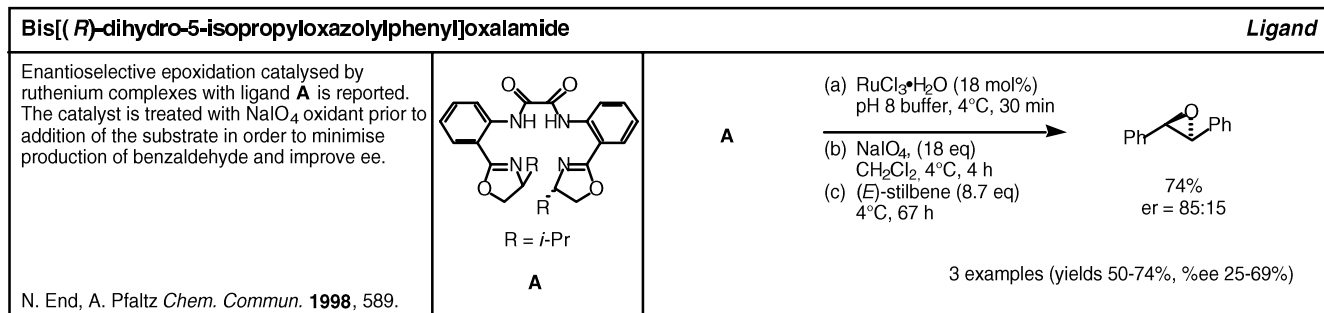
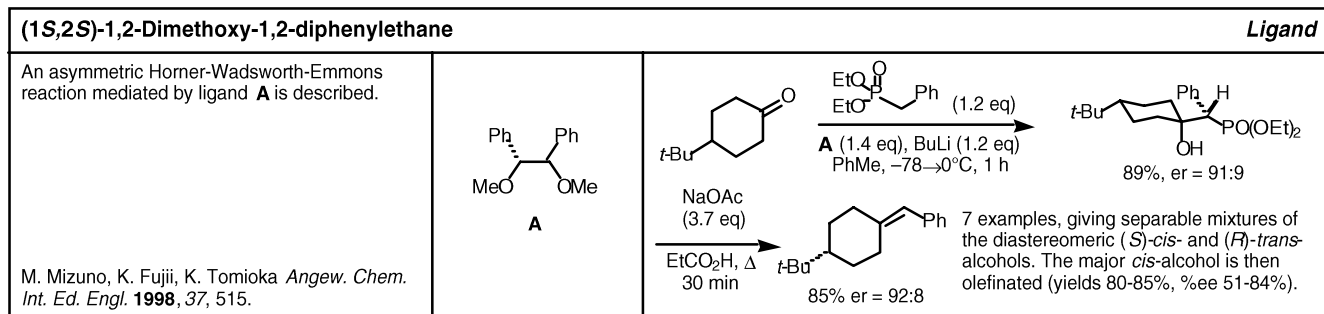
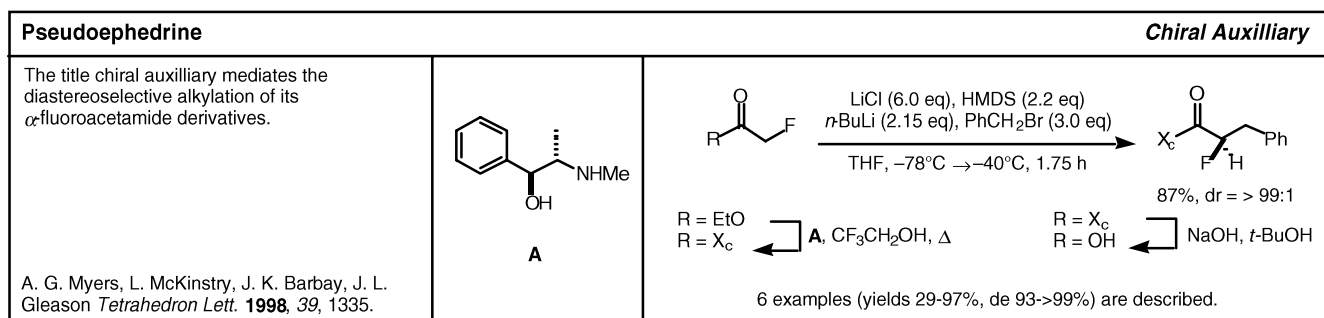
Synthesis Alerts is a personal selection by Paul Blakemore, Stephen Brand, John Christopher, Emma Guthrie, Philip Kocienski, Louise Lea, Graham McAllister, Russell McDonald and Robert Narquizian of Glasgow University. The journals regularly covered by the abstractors are: *Angewandte Chemie International Edition*, *Bulletin of the Chemical Society of Japan*, *Chemistry A European Journal*, *Chemistry Letters*, *European Journal of Organic Chemistry*, *Helvetica Chimica Acta*, *Heterocycles*, *Journal of Organic Chemistry*, *Journal of the American Chemical Society*, *Organometallics*, *Synlett*, *Synthesis*, *Tetrahedron*, *Tetrahedron Asymmetry* and *Tetrahedron Letters*.

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<p>(S)-N-(Dimethylphosphoryl)-α,α-diphenylpyrrolidine-2-methanol Catalyst</p>	
<p>The title phosphinamide catalyses the asymmetric reduction of ketones by borane.</p>	 <p style="text-align: center;">A</p>
<p>B. Burns, N. P. King, H. Tye, J. R. Studley, M. Gamble, M. Wills <i>J. Chem. Soc., Perkin Trans 1</i> 1998, 1027.</p>	 <p style="text-align: center;">81%, er = 96:4</p> <p style="text-align: center;">2 examples (yields 81 and 90%, %ee 92 and 62%).</p>
<p>Tetraphenylphosphonium Chloride Catalyst</p>	
<p>The combination of a Pd(II) catalyst and A in the presence of small amounts of <i>N,N</i>-dimethylglycine (DMG) currently represents the most active and selective catalyst system for Heck reactions of normally unreactive halides.</p>	 <p style="text-align: center;">A</p>
<p>M. T. Reetz, G. Lohmer, R. Schwickardi <i>Angew. Chem. Int. Ed. Engl.</i> 1998, 37, 481.</p>	 <p style="text-align: center;">6 examples (conversion 66-97%).</p> <p style="text-align: center;">NMP = <i>N</i>-methylpyrrolidinone Ar = <i>p</i>-benzaldehyde</p> <p style="text-align: center;">98% conversion (1:2:3 = 98:<1:2), only 1% of undesired scrambling products</p>
<p>Water-Soluble Ruthenium Metathesis Catalyst Catalyst</p>	
<p>The title reagent, in the presence of a Brønsted acid, catalyses living ring opening metathesis polymerisation (ROMP) in aqueous media.</p>	 <p style="text-align: center;">A</p> <p style="text-align: center;">R = cyclohexyl</p>
<p>D. M. Lynn, B. Mohr, R. H. Grubbs <i>J. Am. Chem. Soc.</i> 1998, 120, 1627.</p>	 <p style="text-align: center;">The presence of acid not only serves to remove small concentrations of hydroxide ions (which cause significant catalyst decomposition), but also accelerates polymerisation and yields a true living system.</p>

1,2-Bis(<i>tert</i> -butylmethylphosphino)ethane Rhodium(I) Norbornadiene Complex		Catalyst
<p>The synthesis of a new class of P-chiral phosphine ligands and their application to the rhodium(I) catalysed asymmetric hydrogenation of α-(acylamino)-arylates is described.</p> <p>T. Imamoto, J. Watanabe, Y. Wada, H. Masuda, H. Yamada, H. Tsuruta, S. Matsukawa, K. Yamaguchi <i>J. Am. Chem. Soc.</i> 1998, <i>120</i>, 1635.</p>	 <p style="text-align: center;">A</p>	 <p style="text-align: center;">er = 92:8 (yield not specified)</p> <p>10 examples employing A (%ee 55-99.9%); 11 other examples employing analogous catalysts.</p>
(Dibenzylideneacetone)palladium(0)		Catalyst
<p>The title reagent in the presence of (<i>S</i>)-BINAP catalyses the enantioselective arylation of ketone enolates to afford quaternary stereogenic centres.</p> <p>J. Åhman, J. P. Wolfe, M. V. Troutman, M. Palucki, S. L. Buchwald <i>J. Am. Chem. Soc.</i> 1998, <i>120</i>, 1918.</p>	<p>$\text{Pd}_2(\text{dba})_3$</p> <p style="text-align: center;">A</p>	 <p style="text-align: center;">86%, er = 98:2</p> <p>9 examples (yields 61-88%, %ee 40-98%). $\text{Pd}(\text{OAc})_2$ was also used as an alternative source of palladium.</p>
Tungsten Pentacarbonyl Tetrahydrofuran Complex		Catalyst
<p>The title reagent catalyses the <i>endo-dig</i> cyclisation of ω-acetylenic silyl enol ethers.</p> <p>K. Maeyama, N. Iwasawa <i>J. Am. Chem. Soc.</i> 1998, <i>120</i>, 1928.</p>	<p>$\text{W}(\text{CO})_5 \cdot \text{THF}$</p> <p style="text-align: center;">A</p>	 <p style="text-align: center;">77%</p> <p>6 examples (yields 73-93%). The process is only successful for terminal acetylenes.</p>
Tris(triphenylphosphine)rhodium(I) Chloride		Catalyst
<p>The title reagent catalyses the intramolecular [5+2] cycloaddition of alkenes to tethered vinyl cyclopropanes.</p> <p>P. A. Wender, C. O. Husfeld, E. Langkopf, J. A. Love <i>J. Am. Chem. Soc.</i> 1998, <i>120</i>, 1940.</p>	<p>$\text{RhCl}(\text{PPh}_3)_3$</p> <p style="text-align: center;">A</p>	 <p style="text-align: center;">94%</p> <p>6 examples (yields 77-94%). All substrates possessing a 3-carbon tether between olefins yielded <i>cis</i> 5,7-ring systems, those with a 4-carbon tether yielded <i>trans</i> 6,7-ring systems.</p>

(R)-3,3'-Bis(2'',5''-dihexyloxyphenyl)-1,1'-binaphthol		Catalyst
A catalyses the enantioselective addition of diethylzinc to aldehydes.		<p>23 examples of aromatic, aliphatic and aryl or alkyl substituted α,β-unsaturated aldehydes (yields 62-97%, %ee 90->99%).</p>
W.-S. Huang, Q.-S. Hu, L. Pu <i>J. Org. Chem.</i> 1998 , <i>63</i> , 1364.	R = n-C ₆ H ₁₃	
(4R,5R)-2,2-Dimethyl-$\alpha,\alpha,\alpha',\alpha'$-tetraphenyl-1,3-dioxolane-4,5-dimethanol [(R,R)-TADDOL]		Catalyst
A catalyses the C-alkylation of aldimine Schiff's bases of alanine esters under phase-transfer conditions.		<p>5 examples (crude yields 45-95%, %ee 20-75%).</p>
Y. N. Belokon, K. A. Kochetkov, T. D. Churkina, N. S. Ikonnikov, A. A. Chesnokov, O. V. Larionov, V. S. Parmar, R. Kumar, H. B. Kagan <i>Tetrahedron: Asymmetry</i> 1998 , <i>9</i> , 851.	A	
N-Anthracenylmethyl Cinchodinium Hydroxide		Catalyst
The title catalyst mediates the enantioselective epoxidation of α,β -unsaturated ketones under phase transfer conditions.		<p>8 examples (yields 42-93%, %ee 69-87%). The <i>pseudo</i> enantiomer of A gives comparable but opposite enantioselectivity in these epoxidations.</p>
B. Lygo, P. G. Wainright <i>Tetrahedron Lett.</i> 1998 , <i>39</i> , 1599.	A	
Homochiral Oxazaborolidine		Catalyst
The title catalyst mediates the enantioselective reduction of an α -bromo ketone with BH ₃ .		<p>Yield unspecified. 11 other related catalysts were used in the above reduction (%ee 12-96%).</p>
R. Hett, C. H. Senanayake, S. A. Wald <i>Tetrahedron Lett.</i> 1998 , <i>39</i> , 1705.	A	
(3S)-N,N'-Bis(p-methoxybenzyl)-3-isopropylpiperazine-2,5-dione		Chiral Auxiliary
Chiral auxiliary A employs a chiral relay network for the synthesis of enantiomerically pure α -amino acids. Non-stereogenic N-benzyl protecting groups enhance diastereocontrol during enolate alkylation.		<p>6 examples of the alkylation of A (yields 63-90%, %de 89-98%).</p>
S. D. Bull, S. G. Davies, S. W. Epstein, J. V. A. Ouzman <i>Chem. Commun.</i> 1998 , 659.	A	



(S)-(+)-2-[2-(Diphenylphosphino)phenyl]-4-(benzyl)oxazoline [(S)-bn-phox] Ligand		
The asymmetric aza-Claisen rearrangement of allyl imidates catalysed by homochiral palladium(II) complexes is reported.		<p>Ar = 4-CF₃C₆H₄</p> <p>30%, er = 91:9</p> <p>4 examples (yields 30-88%, %ee 28-81%).</p>
10-N-[(Naphthylmethyl)sulfonyl]borneol Ligand		
The title compound mediates the enantioselective alkylation of ketones with diethyl- and dimethyl- zinc.		<p>89%, er = 95:5</p> <p>14 examples (yields 3-95%, %ee 0, 34-86%) are described</p> <p>R = 1-naphthylmethyl</p>
2,4-Dinitrobenzenesulfonamide Protecting Group		
The 2,4-dinitrobenzenesulfonamide protecting group for amines can be removed with thioacids to give the corresponding amide.		<p>87%</p> <p>SO₂</p> <p>R¹ = <i>p</i>-methoxybenzyl R² = CH₂CH=CH₂</p> <p>8 examples (yields 81-96%) are described.</p>
Titanium Isopropoxide Reagent		
A new titanium reagent A prepared from the reaction of titanium isopropoxide with lithium in the presence of TMSCl, is utilised in the synthesis of heterocycles with dry air or pure nitrogen as the nitrogen source.		<p>72%</p> <p>5 examples (yields 37-72% in dry air, 51-90% in pure nitrogen). The methodology is applied to a formal total synthesis of (±)-lycoperidine. Preparation of A is described.</p>
2-Trimethylsilyl-1,3-dioxolane Reagent		
A new method is described for the generation of hydroxymethyl anion equivalents by photo-induced electron transfer catalysis (PET catalysis) starting from α-silyl ethers.		<p>15%, dr = 86:14 (50%, dr = 1.9:1)</p> <p>10 examples of photoinduced radical additions of α-silyl ethers to electron poor alkenes (yields 15-64%, %de 28-72%).</p> <p>ADC = 9,10-Anthracenedicarbonitrile</p>

Reagent		
<i>o</i>-Diphenylphosphanylbenzoic Acid		
<i>ortho</i> -Diphenylphosphanylbenzoyl esters direct diastereoselective addition of Gilman cuprates to α,β -unsaturated enoates.		
B. Breit <i>Angew. Chem. Int. Ed. Engl.</i> 1998 , 37, 525.		7 examples (yields 60-93%, %de 60-90%).
Reagent		
Cerium(IV) Ammonium Nitrate		
A novel tandem [3 + 2]-type cycloaddition using a CAN-mediated ring-opening reaction of cyclopropylamines is reported. The previously unreported accelerative effect of the <i>N</i> -benzyl group for oxidative ring opening is also described.		
Y. Takemoto, S. Yamagata, S. Furuse, H. Hayase, T. Echigo, C. Iwata <i>Chem. Commun.</i> 1998 , 651.		6 examples (yields 42-77%).
Reagent		
Dimethylphenylsilyllithium		
A reacts with tertiary amides to give enediamines, which can be isolated in good yield when the α -carbon is branched. The enediamines can be hydrolysed to α -amino ketones.		
I. Fleming, U. Ghosh, S. R. Mack, B. P. Clark <i>Chem. Commun.</i> 1998 , 711.		12 examples of the synthesis of α -amino ketones (yields 6-92%). Various reactions of enediamines are also reported.
Reagent		
Dichloro(2,2,2-trifluoroethoxy)oxovanadium(V)		
The title reagent promotes the one-electron oxidative cyclisation of silyl enol ethers onto allyl silanes. The unsymmetrical coupling of silyl enol ethers can also be achieved employing the title reagent.		
K. Ryter, T. Livinghouse <i>J. Am. Chem. Soc.</i> 1998 , 120, 2658.		5 examples of oxidative cyclisation (yields 71-83%).
Reagent		
1,1-Bis(tributylstannyl)-3-[(methoxymethyl)oxy]propane		
A novel method of three-carbon elongation using the title reagent is reported.		
N. Isono, M. Mori <i>J. Org. Chem.</i> 1998 , 63, 1773		13 examples of the reaction of A with aldehyde, ketone, ester or alkyl halide electrophiles (yields 48-85%).

