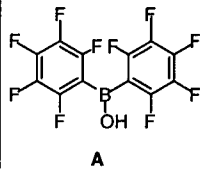
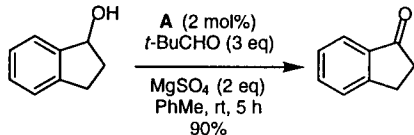

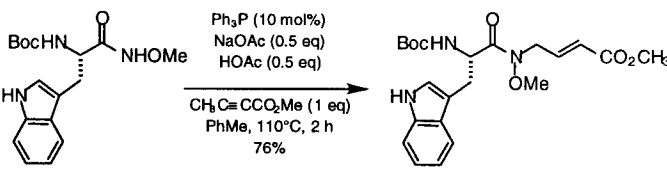

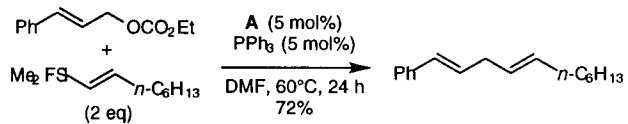


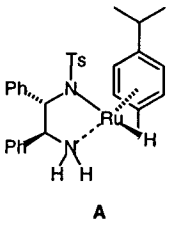
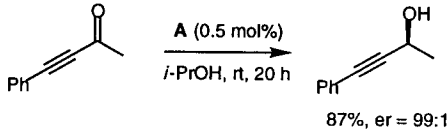
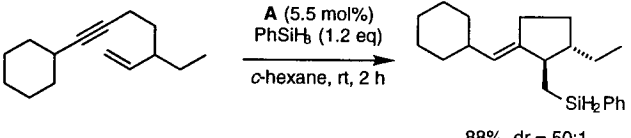
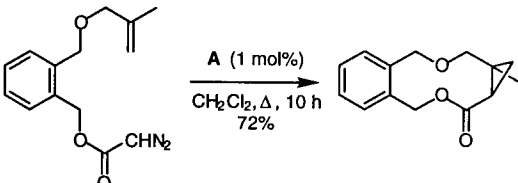
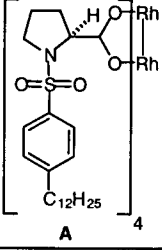
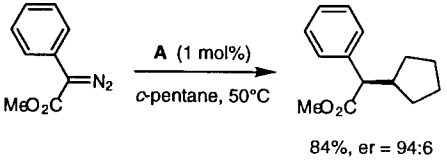
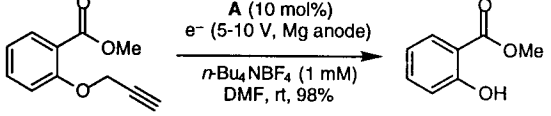
SYNTHESIS ALERTS

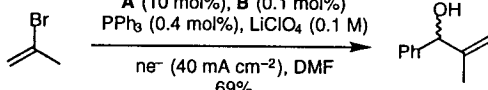
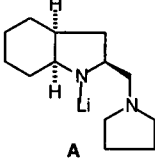
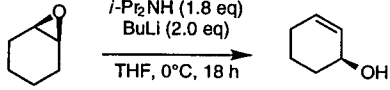
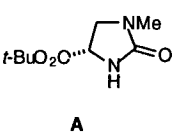
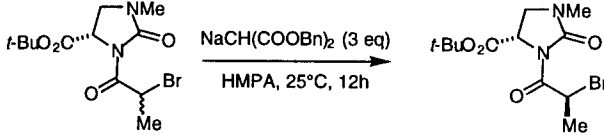
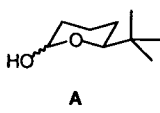
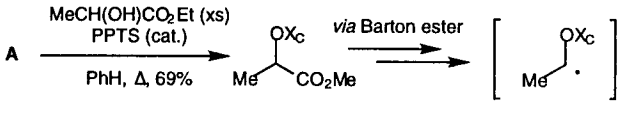
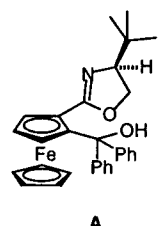
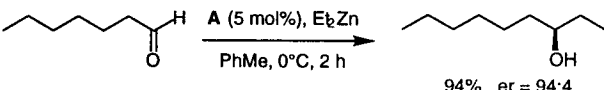
Synthesis Alerts is a monthly feature to help readers of Synthesis keep abreast of new reagents, catalysts, ligands, chiral auxiliaries, and protecting groups which have appeared in the recent literature. Emphasis is placed on new developments but established reagents, catalysts etc are also covered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

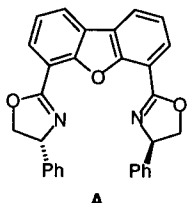
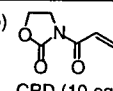
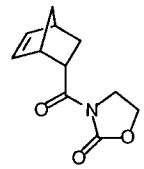
Synthesis Alerts is a personal selection by Paul Blakemore, John Christopher, Louise Lea, Philip Kocienski, J.-Y. Le Brazidec, Robert Narquizian and Christopher Smith of the University of Glasgow. The journals regularly covered by the abstractors are: *Angewandte Chemie International Edition*, *Bulletin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

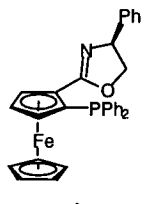
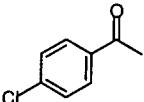
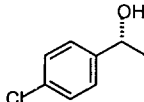
Georg Thieme Verlag does not accept responsibility for the accuracy, content, or selection of the data.

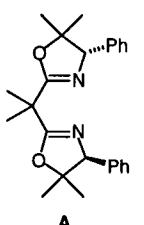
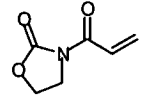
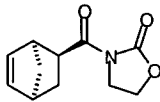
Bis(pentafluorophenyl)borinic Acid		Catalyst
<p>The title compound is a highly effective Oppenauer oxidation catalyst for allylic and benzylic alcohols.</p> <p>K. Ishihara, H. Kurihara, H. Yamamoto <i>J. Org. Chem.</i> 1997, <i>62</i>, 5664.</p>	 <p style="text-align: center;">A</p>	 <p style="text-align: center;">10 examples (yields 20-99%).</p>
Triphenylphosphine		Catalyst
<p>γ-Addition of nitrogen-based nucleophiles to alkynoates is mediated by catalyst A in a sodium acetate / acetic acid buffered system. Competitive Michael addition was not problematic.</p> <p>B. M. Trost, G. R. Dake <i>J. Org. Chem.</i> 1997, <i>62</i>, 5670.</p>	 <p style="text-align: center;">A</p>	 <p style="text-align: center;">4 examples (yields 67-76%).</p>
Palladium(II) Acetate		Catalyst
<p>The cross-coupling of allylic carbonates with vinylsilanes without fluoride ion activation is catalysed by palladium(II) acetate.</p> <p>H. Matsuhashi, S. Asai, K. Hirabayashi, Y. Hatanaka, A. Mori, T. Hiyama <i>Bull. Chem. Soc. Jpn</i> 1997, <i>70</i>, 1943.</p>	 <p style="text-align: center;">A</p>	 <p style="text-align: center;">12 examples of cross-coupling of vinylsilanes with allylic carbonates (yields 0, 40-99%). The cross-coupling of arylsilanes and allylic carbonates using Pd₂(dba)₃·CHCl₃ as the catalyst is also described (10 examples, yields 33-97%).</p>

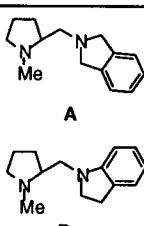
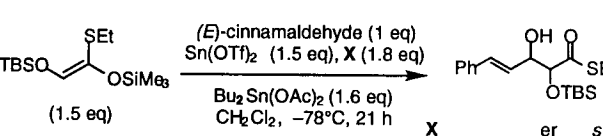
[[1 <i>S</i> ,2 <i>S</i>]- <i>N</i> -(<i>p</i> -Toluenesulfonyl)-1,2-diphenylethylenediamine][η^6 - <i>p</i> -cymene]hydridoruthenium(II) Catalyst		
Asymmetric transfer hydrogenation of α,β -acetylenic ketones. K. Matsumura, S. Hashiguchi, T. Ikariya, R. Noyori <i>J. Am. Chem. Soc.</i> 1997 , <i>119</i> , 8738.	 A	 14 examples (yields 70-99%, %ee 90->99%). The method is not suitable for unsubstituted ethynyl ketones but is applicable to silylated derivatives.
Bis(η^5 -pentamethylcyclopentadienyl)methyl Yttrium(III) Tetrahydrofuran Complex Catalyst		
The title reagent is an effective pre-catalyst for the sequential cyclisation/silylation of 1,6- and 1,7-enynes. G. A. Molander, W. H. Retsch <i>J. Am. Chem. Soc.</i> 1997 , <i>119</i> , 8817.	$\text{Cp}^*_2\text{YCH}_3\cdot\text{THF}$ A $\text{Cp}^* = \text{C}_5\text{Me}_5$	 15 examples (yields 49-93%, %de 34-96%). The influence of allylic substitution on the diastereomeric ratio and the formation of 6-membered rings have also been examined.
Tetra(perfluorobutyrate)dirhodium(II) Catalyst		
Macrocycle formation by catalytic intramolecular cyclopropanation. A new general methodology for the synthesis of macrolides. M. P. Doyle, C. S. Peterson, M. N. Protopopova, A. B. Marnett, D. L. Parker, Jr., D. G. Ene, V. Lynch <i>J. Am. Chem. Soc.</i> 1997 , <i>119</i> , 8826.	$\text{Rh}_2(\text{pfb})_4$ A	 11 examples of cyclisation via intramolecular cyclopropanation (yields 24-89%). The reactivity of several ligands has also been investigated.
Tetra[(<i>S</i>)- <i>N</i> -(<i>p</i> -dodecylphenyl)sulfonylproline]dirhodium(II) Catalyst		
The title reagent catalyses asymmetric intermolecular carbenoid C-H insertion reactions. H. M. L. Davies, T. Hansen <i>J. Am. Chem. Soc.</i> 1997 , <i>119</i> , 9075.	 A	 19 examples (yields 34-96%, %ee 3, 60-93%). Tetrahydrofuran, <i>n</i> -hexane and <i>n</i> -heptane are also reactive.
Tris(2,2'-bipyridyl)nickel(II) Tetrafluoroborate Catalyst		
Catalyses the electrochemical reductive cleavage of propargyl ethers and esters. S. Olivero, E. Duñach <i>Tetrahedron Lett.</i> 1997 , <i>38</i> , 6193.	$\text{Ni}(\text{bipy})_3(\text{BF}_4)_2$ A	 11 examples (yields of acids/alcohols 18, 77-99%). Halogenated substrates may be over-reduced and longer chain propargyl derivatives can undergo a variety of isomerisations. bipy = 2,2'-bipyridine

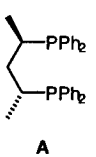
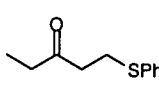
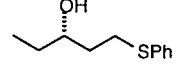
Palladium(II) Acetate		Catalyst
<p>A combination of Cr(II) and Pd(0) species catalyse the electrochemically driven reaction of vinyl and aryl halides with aldehydes (<i>cf</i> the Nozaki-Hiyama-Kishi reaction).</p> <p>R. Grigg, B. Putnikovic, C. J. Urch <i>Tetrahedron Lett.</i> 1997, <i>38</i>, 6307.</p>	<p>CrCl₂ A</p> <p>Pd(OAc)₂ B</p>	<p>PhCHO (1.2 eq) A (10 mol%), B (0.1 mol%) PPh₃ (0.4 mol%), LiClO₄ (0.1 M) ne⁻ (40 mA cm⁻²), DMF 69%</p>  <p>7 examples (yields 51-69%).</p>
Homochiral Lithium Amide Base		Catalyst
<p>The lithium amide A effects the enantioselective deprotonation of <i>meso</i> epoxides to yield chiral allylic alcohols. The chiral base can be regenerated <i>in situ</i> by LDA.</p> <p>M. Asami, T. Suga, K. Honda, S. Inoue <i>Tetrahedron Lett.</i> 1997, <i>38</i>, 6425.</p>	 <p>A</p>	<p>A (20 mol%) <i>i</i>-Pr₂NH (1.8 eq) BuLi (2.0 eq) THF, 0°C, 18 h</p>  <p>89%, <i>er</i> = 97:3</p> <p>Optimisation of the above example is described together with two other examples (cyclooctene oxide, (Z)-4-octene oxide: yields 73, 84%; %ee 53, 86% respectively).</p>
<i>tert</i> -Butyl (4 <i>S</i>)-1-Methyl-2-oxoimidazolidine-4-carboxylate		Chiral Auxiliary
<p>Stereoselective carbon-carbon bond formation by dynamic kinetic resolution using A as a chiral auxiliary is described.</p> <p>A. Kubo, H. Kubota, M. Takahashi, K. Numani. <i>J. Org. Chem.</i> 1997, <i>62</i>, 5830.</p>	 <p>A</p>	<p><i>t</i>-BuO₂C...NMe NaCH(COOBn)₂ (3 eq) HMPA, 25°C, 12 h</p>  <p>82%, <i>dr</i> = 94:6</p> <p>11 examples (yields 45-97%, %de = 36-92%).</p>
(2 <i>RS</i> ,6 <i>S</i>)-6- <i>tert</i> -Butyl-2-hydroxytetrahydropyran		Chiral Auxiliary
<p>A rationally designed chiral auxiliary for the diastereoselective addition of hydroxyalkyl radicals to acrylates and nitroalkenes.</p> <p>P. Garner, J. T. Anderson <i>Tetrahedron Lett.</i> 1997, <i>38</i>, 6647.</p>	 <p>A</p>	<p>MeCH(OH)CO₂Et (xs) PPTS (cat.) PhH, Δ, 69%</p> <p>via Barton ester</p>  <p>48%, <i>dr</i> = 90:10</p> <p>2 other inferior auxiliaries were also examined together with the radical addition to 2-nitropropene (yield 43%, <i>dr</i> = 97:3 at -78°C)</p>
Ferrocene Oxazoline Ligand		Ligand
<p>An efficient ligand for the asymmetric addition of diethylzinc to aliphatic and aromatic aldehydes.</p> <p>C. Bolm, K. M. Fernández, A. Seger, G. Raabe <i>Synlett</i> 1997, 1051.</p>	 <p>A</p>	<p>A (5 mol%), Et₂Zn PhMe, 0°C, 2 h</p>  <p>94%, <i>er</i> = 94:4</p> <p>8 examples (yields 83-94%, %ee 78-95%).</p>

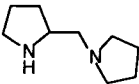
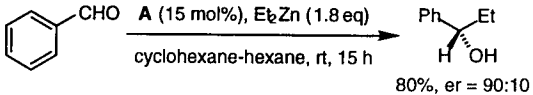
(<i>R,R</i>)-4,6-Dibenzofurandiyl-2,2'-bis(4-phenyloxazoline) (DBFOX/Ph)		Ligand
<p>The cationic aqua complexes of the C₂-symmetric ligand A are highly effective Lewis acid catalysts in the Diels-Alder reactions of α,β-unsaturated carbonyl dienophiles and cyclopentadiene (CPD).</p> <p>S. Kanemasa, Y. Oderaotoshi, H. Yamamoto, J. Tanaka, E. Wada, D. P. Curran <i>J. Org. Chem.</i> 1997, <i>62</i>, 6454.</p>	 <p>A</p>	<p> $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (10 mol%) (a) A (10 mol%), CH_2Cl_2, rt, 2 h (b)  (1 eq), CPD (10 eq), CH_2Cl_2, -40°C, 14 h 96%, er > 99:1 <i>endo:exo</i> = 97:3 3 examples (yields 90-100%, %ee = 89-94, <i>endo:exo</i> = 92:8 - 93:7). </p> 

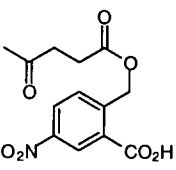
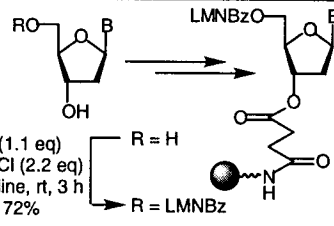
Chiral (Phosphinoferrocenyl)oxazolines		Ligand
<p>The enantioselective transfer hydrogenation of aryl alkyl ketones is performed with ruthenium complexes of the title ligand.</p> <p>T. Sammakia, E. L. Stangeland, <i>J. Org. Chem.</i>, 1997, <i>62</i>, 6104.</p>	 <p>A</p>	<p> $\text{RuCl}_2(\text{PPh}_3)_2$ (0.20 mol%), A (0.26 mol%), <i>i</i>-PrOK (2.5 mol%), <i>i</i>-PrOH, 28°C, 6 h   83%, er = 97:3 9 examples (yields 75-92%, %ee 84-96%). </p>

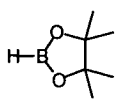
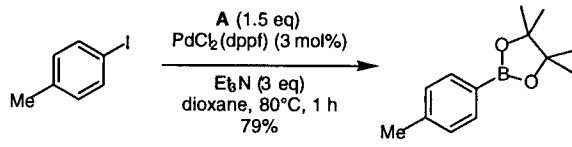
(4<i>S</i>)-2,2'-(1-Methylethylidene)bis(4-phenyl-4,5-dihydrooxazole)		Ligand
<p>Enantioselective Diels-Alder reactions using novel bis(oxazoline) ligand-metal triflate catalysts.</p> <p>J. M. Takacs, D. A. Quincy, E. C. Lawson, M. J. Reno, M. A. Yougman <i>Tetrahedron: Asymmetry</i> 1997, <i>8</i>, 3073. J. M. Takacs, D. A. Quincy, W. Shay, B. E. Jones, C. R. Ross <i>Tetrahedron: Asymmetry</i> 1997, <i>8</i>, 3079.</p>	 <p>A</p>	<p> A (22 mol%), $\text{Mg}(\text{OTf})_2$ (20 mol%), cyclopentadiene (12 eq), CH_2Cl_2, rt, 1 d   95%, er = 94:6 <i>endo:exo</i> = 2.5:1 19 examples (yields 15-99%, %ee (<i>endo</i>) 6-88%). The cycloaddition has been studied using zinc, copper and magnesium triflates; various bis(oxazoline) ligands were also tested. </p>


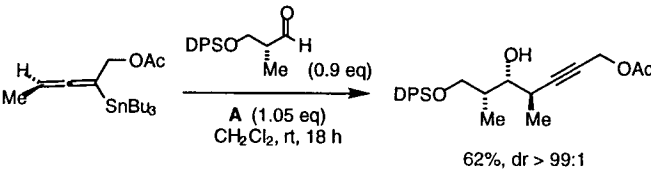
(S)-1-Methyl-2-[(isoindoliny)methyl]pyrrolidine / (S)-1-Methyl-2-[(indoliny)methyl]pyrrolidine		Ligand												
<p>Both enantiomers of 2,3-dihydroxy thioester derivatives were prepared with excellent stereochemical control by chiral Lewis acid controlled synthesis. The differentially substituted (S)-proline-derived indoliny diamines A and B provide complementary stereocontrol when ligated to a tin Lewis acid.</p> <p>S. Kobayashi, M. Horibe <i>Chem Eur. J.</i> 1997, <i>3</i>, 1472.</p>	 <p>A B</p>	<div style="text-align: center;">  </div> <p>16 examples (yields 61-94%, %ee 96->99%) and 4 examples of chiral diamines.</p> <table border="1"> <thead> <tr> <th></th> <th>X</th> <th>er</th> <th><i>syn:anti</i></th> </tr> </thead> <tbody> <tr> <td>A</td> <td>84%</td> <td>> 99:1</td> <td>> 99:1</td> </tr> <tr> <td>B</td> <td>80%</td> <td>1:99</td> <td>99:1</td> </tr> </tbody> </table>		X	er	<i>syn:anti</i>	A	84%	> 99:1	> 99:1	B	80%	1:99	99:1
	X	er	<i>syn:anti</i>											
A	84%	> 99:1	> 99:1											
B	80%	1:99	99:1											

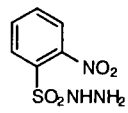
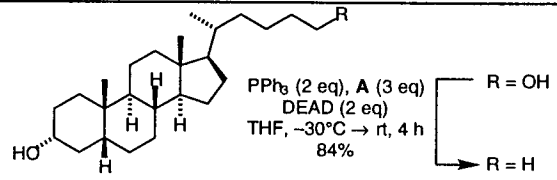
2,4-Bis(diphenylphosphino)pentane (Skewphos)		Ligand
<p>The commercially available Skewphos ligand (A, either enantiomer) forms complexes with Ru(II) that catalyse the asymmetric hydrogenation of functionalised ketones.</p> <p>D. Blanc, J.-C. Henry, V. Ratovelomanana-Vidal, J. P. Genêt <i>Tetrahedron Lett.</i> 1997, <i>38</i>, 6603.</p>	 <p>A</p>	<p> (S,S)-SkewphosRuBr₂ (2 mol%), H₂ (30 bar), MeOH, rt, 30 min   100%, er = 98:2 14 examples, including ketophosphonates and ketoesters (yields 96-100%, %ee 88-95%). </p>


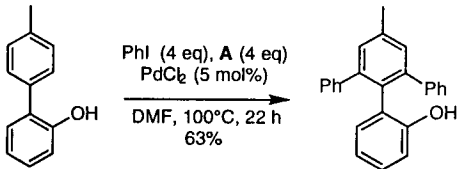
(S)-2-(1-Pyrrolidinylmethyl)pyrrolidine		Ligand
Enantioselective addition of diethylzinc to aldehydes is catalysed by the title compound.		 <p>6 examples (yields 22-86%, %ee 5-87%). Yields and enantioselectivities are highest for aromatic aldehydes.</p>
M. Asami, S. Inoue <i>Bull. Chem. Soc. Jpn.</i> 1997 , <i>70</i> , 1687.		

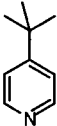
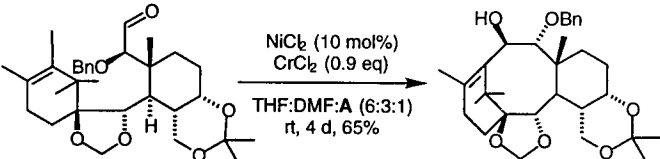
2-(Levulinoyloxymethyl)-5-nitrobenzoic Acid (LMNBzOH)		Protecting Group
A novel base labile protecting group for the 5'-hydroxyl groups of nucleosidic 3'-phosphoramidates. Protection and deprotection steps are typically higher yielding and solid-phase synthesis cleaner when employing LMNBz protection as opposed to DMTr or levulinyl groups.		 <p>(a) solid-phase oligonucleotide synthesis (b) c.NH₄OH, rt, 3 h (c) HCl(aq) (pH 2), rt, 1 d</p> <p>6 examples.</p> <p>B = Thymidine, TPSCI = 2,4,6-triisopropylbenzenesulfonyl chloride</p>
K. Kamaike, H. Takahashi, T. Kakinuma, K. Morohoshi, Y. Ishido <i>Tetrahedron Lett.</i> 1997 , <i>38</i> , 6857.		

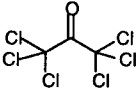
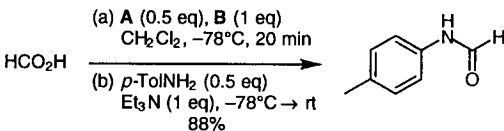
Pinacolborane		Reagent
Palladium-catalysed coupling of aryl halides and the title reagent provides a convenient synthesis of arylboronates.		 <p>13 examples (yields 49-84%).</p>
M. Murata, S. Watanabe, Y. Masuda <i>J. Org. Chem.</i> 1997 , <i>62</i> , 6458.		

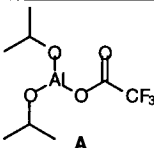
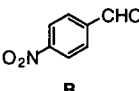
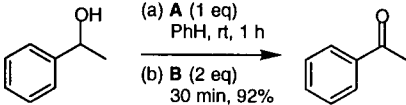
Butyltin Trichloride		Reagent
A combination of an allenylstannane and the title reagent resulted in high enantio- and diastereoselectivity in addition to aldehydes.		 <p>4 examples (yields 58-66%, only one adduct obtained in each case).</p>
J. A. Marshall, M. R. Palovich <i>J. Org. Chem.</i> 1997 , <i>62</i> , 6001.		

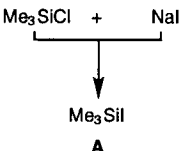

o-Nitrobenzenesulfonylhydrazine		Reagent
Single-step process for the reductive deoxygenation of unhindered alcohols.		 <p>10 examples (yields 66-87%). Acyclic 2° alcohols can be deoxygenated when modified conditions are employed. For certain functionalised substrates diazene decomposition is followed by radical cyclisation/transposition before hydrogen atom quench.</p>
A. G. Myers, M. Movassaghi, B. Zheng <i>J. Am. Chem. Soc.</i> 1997 , <i>119</i> , 8572.		

Cesium Carbonate		Reagent
<p>Cesium carbonate is used as a base in the palladium catalysed regioselective mono- and diarylation reactions of 2-phenylphenols and naphthols with aryl halides.</p>	 <p>A</p>	 <p>8 examples (yields 56-73%).</p>
<p>T. Satoh, Y. Kawamura, M. Miura, N. Nomara <i>Angew. Chem. Int. Ed. Engl.</i> 1997, <i>36</i>, 1740</p>		

4- <i>tert</i> -Butylpyridine		Reagent
<p>The title reagent is a beneficial additive in the Ni(II) / Cr(II) mediated coupling reaction of organohalides and triflates with aldehydes (the Nozaki-Hiyama-Kishi reaction). The additive allows for homogeneous reactions, improves reproducibility and inhibits homocoupling.</p>	 <p>A</p>	 <p>The illustrated example failed in the absence of A. 4 examples extolling the virtues of the additive (yields 65-85%). A new improved work-up procedure employing serinate salts is also described.</p>
<p>D. P. Stamos, X. C. Sheng, S. S. Chen, Y. Kishi <i>Tetrahedron Lett.</i> 1997, <i>38</i>, 6355.</p>		

Triphenylphosphine / Hexachloroacetone		Reagent
<p>The title pair of reagents rapidly convert carboxylic acids to acyl chlorides at low temperature. The highly reactive formyl chloride can be conveniently prepared with this methodology.</p>	 <p>A</p> <p>B PPh_3</p>	 <p>3 examples (yields 73-99%).</p>
<p>G. B. Villeneuve, T. H. Chan <i>Tetrahedron Lett.</i> 1997, <i>38</i>, 6489.</p>		

Diisopropoxyaluminium Trifluoroacetate (DIPAT) / 4-Nitrobenzaldehyde		Reagent
<p>The title reagent pair effect the accelerated Oppenauer oxidation of 2° alcohols.</p>	 <p>A</p>  <p>B</p>	 <p>14 examples of 2° alcohols (yields 70-99%). 1° alcohols are not oxidised under the described conditions.</p>
<p>K. G. Akamanchi, B. A. Chaudhari <i>Tetrahedron Lett.</i> 1997, <i>38</i>, 6925.</p>		

Iodotrimethylsilane		Reagent
<p>The title reagent (generated <i>in situ</i>) effects the rapid reduction of azides to amines.</p>	 <p>A</p>	 <p>14 examples (yields 90-98%).</p>
<p>A. Kamal, N. V. Rao, E. Laxman <i>Tetrahedron Lett.</i> 1997, <i>38</i>, 6945.</p>		