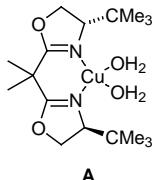
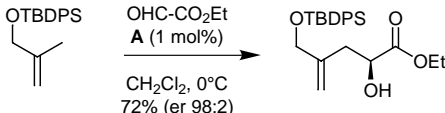
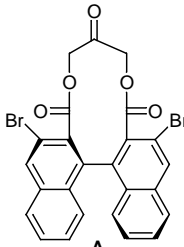
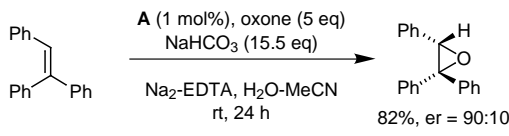
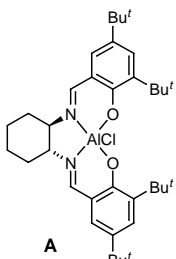
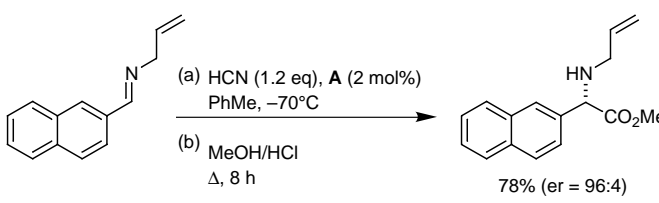


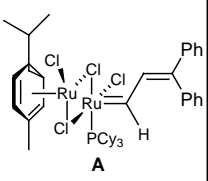
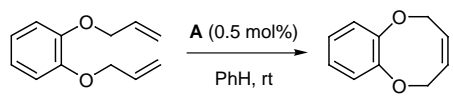
SYNTHESIS ALERTS

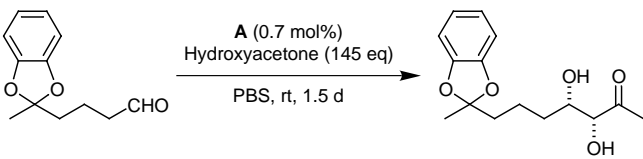
Synthesis Alerts is a new monthly feature to help readers of *Synthesis* keep abreast of new reagents, catalysts, ligands, chiral auxiliaries, and protecting groups which have appeared in the recent literature. Emphasis is placed on new developments but established reagents, catalysts etc are also covered if they are used in novel and useful reactions. In each abstract, a specific example of a transformation is given in a concise format designed to aid visual retrieval of information.

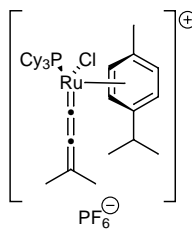
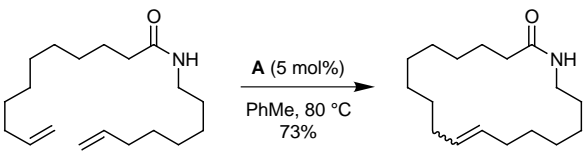
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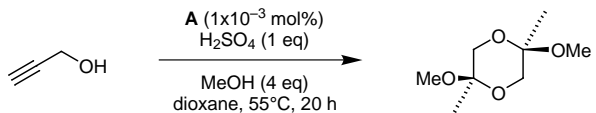
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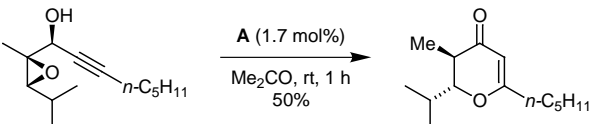
[Cu(S,S)-<i>t</i>-Bu-bis-oxazoliny](H₂O)₂](SbF₆)₂		Catalyst
<p>The title catalyst is one of three related Cu(II)-based Lewis acids which efficiently catalyse the enantioselective addition of a variety of olefins to glyoxylate esters to provide α-hydroxy esters. These catalysts also catalyse enantioselective Diels-Alder and aldol reactions.</p> <p>D. A. Evans, C. S. Burgey, N. A. Paras, T. Vojkovsky, S. W. Tregay, <i>J. Am. Chem. Soc.</i>, 1998, 120, 5824.</p>	 <p style="text-align: center;">A</p>	 <p>9 examples; yields typically >80%, ee 93%. The blue solid aquo complex A is only slightly less reactive than the corresponding anhydro complex. Replacement of the <i>t</i>-Bu by Ph and the hexafluoroantimonate by triflate gives a complex which results in opposite (<i>R</i>) stereochemistry.</p>
(<i>R</i>)-2,10-Dibromo-5<i>H</i>-dinaphtho[2,1-<i>g</i>:1',2'-<i>i</i>][1,5]dioxacycloundecin-3,6,9(7<i>H</i>)-trione		Catalyst
<p>The title compound is one of a set of three related C₂-symmetric ketones which form dioxirane intermediates with oxone which can epoxidise alkenes enantioselectively.</p> <p>D. Yang, M.-K. Wong, Y.-C. Yip, X.-C. Wang, M.-W. Tang, J.-H. Zheng, K.-K. Cheung <i>J. Am. Chem. Soc.</i>, 1998, 120, 5943.</p>	 <p style="text-align: center;">A</p>	 <p>14 different ketone analogs were examined of which 3 gave good results but the reaction appears to be restricted to phenyl substituted alkenes.</p>
Chiral (Salen)Al(III) complex		Catalyst
<p>The chiral (Salen)Al(III) complex A catalyzes the enantioselective addition of HCN to <i>N</i>-allyl imines. Catalyst A is easily prepared on a large scale and has an indefinite shelf life.</p> <p>M. S. Sigman, E. N. Jacobsen <i>J. Am. Chem. Soc.</i>, 1998, 120, 5315.</p>	 <p style="text-align: center;">A</p>	 <p>7 examples of arylimines (91-99% yield, ee 79-95%) Addition to cyclohexylimine (1 example) or <i>tert</i>-butyl imines 4 examples) gives lower yields and lower ee.</p>

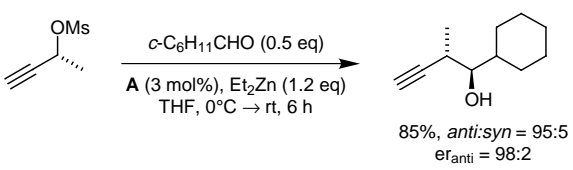
[(<i>p</i> -Cymene)(Cl)Ru(<i>m</i> -Cl) ₂ Ru(Cl)(PCy ₃)-(CHCHCPh ₂)]		Catalyst
<p>The Grubbs metathesis catalyst reacts with [(<i>p</i>-cymene)RuCl₂]₂ to form bimetallic bridged-chloride ruthenium carbenes which are more active than the Grubbs catalyst in ring opening polymerisation reactions and ring closing metathesis reactions.</p> <p>E. L. Dias, R. H. Grubbs <i>Organometallics</i>, 1998, 17, 2758.</p>	 <p style="text-align: center;">A</p>	 <p style="text-align: center;">A (0.5 mol%) PhH, rt</p>

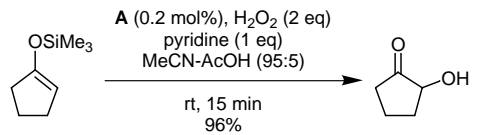
Aldolase Antibody 38C2		Catalyst
<p>The title antibody catalyses an asymmetric aldol reaction between hydroxyacetone and a functionalised aldehyde. The process represents the first time a catalytic antibody has been used to decrease the total number of synthetic steps and to increase the enantioselectivity of natural product syntheses.</p> <p>B. List, D. Shabat, C. F. Barbas III, R. A. Lerner <i>Chem. Eur. J.</i> 1998, 4, 881.</p>	<p>Antibody 38C2</p> <p style="text-align: center;">A</p>	 <p style="text-align: center;">A (0.7 mol%) Hydroxyacetone (145 eq) PBS, rt, 1.5 d</p> <p>Use of the antibody is illustrated by the short synthesis of various brevicomin derivatives.</p> <p>PBS = phosphate buffered saline, pH 7.4.</p> <p style="text-align: right;">55% er = 99:1</p>

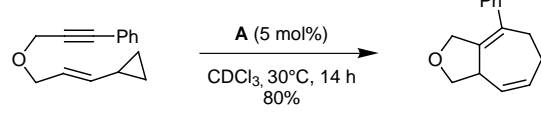
Cationic allenylidene ruthenium complex		Catalyst
<p>A is utilised as a catalyst for ring closing olefin metathesis.</p> <p>A. Fürstner, M. Picquet, C. Bruneau, P. H. Dixneuf <i>Chem. Commun.</i> 1998, 1315.</p>	 <p style="text-align: center;">A</p>	 <p style="text-align: center;">A (5 mol%) PhMe, 80 °C 73%</p> <p>6 examples (yields 40-90%). The catalyst is easily prepared in three steps from ruthenium(III) chloride.</p>

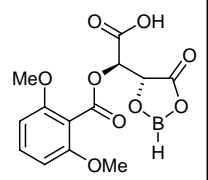
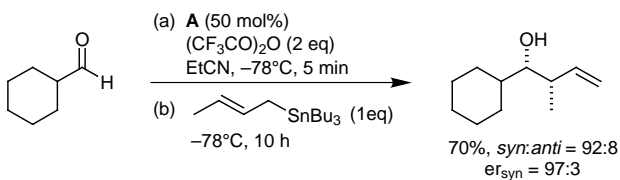
Methyl(triphenylphosphane)gold(I)		Catalyst
<p>A is an excellent catalyst for the efficient addition of alcohols to alkynes in the presence of a Lewis or Brønsted acid co-catalyst.</p> <p>J. H. Teles, S. Brode and M. Chabanas <i>Angew. Chem. Int. Ed.</i> 1998, 37, 1415.</p>	<p>[Ph₃PAuCH₃]</p> <p style="text-align: center;">A</p>	 <p style="text-align: center;">A (1x10⁻³ mol%) H₂SO₄ (1 eq) MeOH (4 eq) dioxane, 55 °C, 20 h</p> <p>7 examples (no yields given).</p>

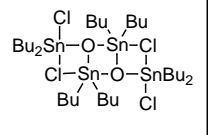
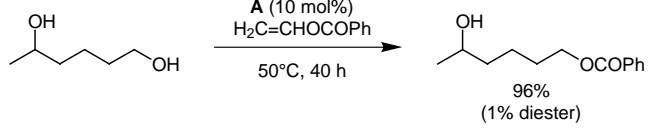
Mercury(II) sulfate		Catalyst
<p>The title compound catalyses the rearrangement of 1-alkynyl-2,3-epoxy alcohols affording a stereocontrolled route to 2,3-dihydro-4<i>H</i>-pyran-4-ones.</p> <p>C. M. Marson, S. Harper, C. A. Oare, T. Walsgrove <i>J. Org. Chem.</i> 1998, 63, 3798.</p>	<p>HgSO₄</p> <p style="text-align: center;">A</p>	 <p style="text-align: center;">A (1.7 mol%) Me₂CO, rt, 1 h 50%</p> <p>7 examples (yields 50-80%).</p>

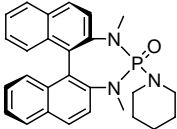
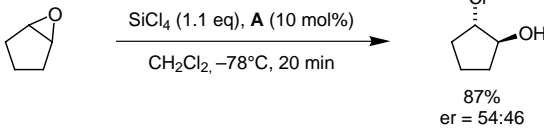
Tetrakis(triphenylphosphine)palladium(0)		Catalyst
<p>The title compound catalyses the synthesis of enantioenriched homopropargylic alcohols from propargylic mesylates <i>via</i> chiral allenylzinc intermediates.</p> <p>J. A. Marshall, N. D. Adams <i>J. Org. Chem.</i> 1998, <i>63</i>, 3812.</p>	$\text{Pd(PPh}_3)_4$ A	 <p>85%, <i>anti:syn</i> = 95:5 <i>er</i>_{anti} = 98:2</p> <p>11 examples (yields 47-85%, 68:32 ≤ <i>anti:syn</i> ≤ 95:5, %<i>ee</i>_{anti} 86-96%).</p>

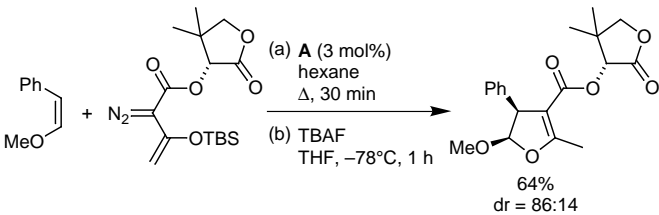
Methyltrioxorhenium (MTO)		Catalyst
<p>The title compound catalyses the facile oxidation of silyl enol ethers with hydrogen peroxide</p> <p>S. Stankovic, J. H. Espenson <i>J. Org. Chem.</i> 1998, <i>63</i>, 4129.</p>	MeReO_3 A	 <p>96%</p> <p>8 examples (yields 60-100%).</p>

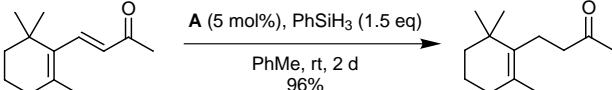
Tetracarbonyldi-μ-chlorodirhodium(I)		Catalyst
<p>The title compound is a selective catalyst for the [5 + 2] cycloaddition of vinylcyclopropanes and alkynes.</p> <p>P. A. Wender, D. Sperandio <i>J. Org. Chem.</i> 1998, <i>63</i>, 4164.</p>	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$ A	 <p>80%</p> <p>9 examples (yields 0, 78-89%).</p>

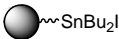
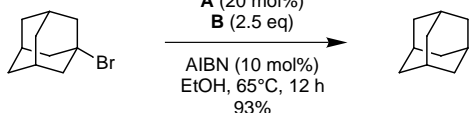
Chiral (acyloxy)borane (CAB)		Catalyst
<p>The modified CAB Lewis acid A gives better <i>syn/anti</i> selectivity than the Keck BINOL/Ti catalyst in additions of crotyltributyltin to aldehydes. However, allylations are more enantioselective with the Keck catalyst. A is formed <i>in situ</i> from the corresponding tartrate ester and $\text{BH}_3 \cdot \text{THF}$.</p> <p>J. A. Marshall, M. R. Palovich <i>J. Org. Chem.</i> 1998, <i>63</i>, 4381.</p>	 <p>A</p>	 <p>70%, <i>syn:anti</i> = 92:8 <i>er</i>_{syn} = 97:3</p> <p>9 examples (yields 42-74%, 78:22 ≤ <i>syn:anti</i> ≤ 98:2, %<i>ee</i>_{syn} = 55-93%).</p>

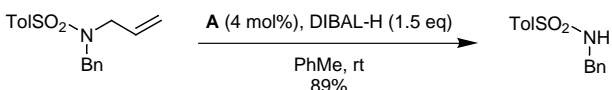
1,3-Dichlorotetrabutyl-distannoxane		Catalyst
<p>The title reagent catalyses the highly selective acylation of alcohols.</p> <p>A. Orita, A. Mitsutome, J. Otera <i>J. Org. Chem.</i> 1998, <i>63</i>, 2420.</p>	 <p>A</p>	 <p>96% (1% diester)</p> <p>17 examples of the acylation of alcohols (yields, 0, 92-99%) and 6 examples of the selective acylation of primary hydroxyls in the presence of secondary hydroxyls (yields 84-99%) are reported.</p>

Chiral Binaphthylphosphoramidate		Catalyst
<p>The title Lewis base catalyses the enantioselective ring opening of epoxides with silicon tetrachloride.</p> <p>S. E. Denmark, P. A. Barsanti, K.-T. Wong, R. A. Stavenger <i>J. Org. Chem.</i> 1998, 63, 2428.</p>	 <p style="text-align: center;">A</p>	 <p style="text-align: center;">87% er = 54:46</p> <p>5 examples (yields 87-95%, %ee 2-87%).</p>

Rhodium(II) octanoate		Catalyst
<p>Rhodium catalysed decomposition of 2-diazo-3-siloxybutenoates containing a chiral auxiliary in the presence of vinyl ethers results in the diastereoselective synthesis of cyclopropanes with high asymmetric induction. Desilylation and ring expansion produces 2,3-dihydrofurans with retention of stereochemistry.</p> <p>H. M. L. Davies, G. Ahmed, R. L. Calvo, M. R. Churchill, D. G. Churchill <i>J. Org. Chem.</i> 1998, 63, 2641.</p>	<p style="text-align: center;">$\text{Rh}_2(\text{OOOct})_4$</p> <p style="text-align: center;">A</p>	 <p style="text-align: center;">64% dr = 86:14</p> <p>5 examples (yields 43-77%, %de 67-86%) are reported.</p>

Hexakis(triphenylphosphine)copper(I) hydride		Catalyst
<p>The title catalyst (Stryker's reagent) mediates the conjugate reduction of enones and enals with phenylsilane or tributyltin hydride.</p> <p>B. H. Lipshutz, J. Keith, P. Papa, R. Vivian <i>Tetrahedron Lett.</i> 1998, 39, 4627.</p>	<p style="text-align: center;">$[(\text{Ph}_3\text{P})\text{CuH}]_6$</p> <p style="text-align: center;">A</p>	 <p style="text-align: center;">96%</p> <p>11 examples (yields 70-100%) are described.</p>

Polymer-supported dibutyltin iodide / sodium borohydride		Catalyst
<p>A polymer-supported organotin hydride generated <i>in situ</i> from the title reagent pair reduces 1-bromoadamantane.</p> <p>G. Dumartin, M. Pourcel, B. Delmond, O. Donard, M. Pereyre <i>Tetrahedron Lett.</i> 1998, 39, 4663.</p>	 <p style="text-align: center;">A</p> <p style="text-align: center;">NaBH₄</p> <p style="text-align: center;">B</p>	 <p style="text-align: center;">93%</p> <p>1 example is reported. When reductions are run at a catalytic level contaminating tin residues are minimal.</p>

Dichlorobis(diphenylphosphino)propane Nickel(II)		Catalyst
<p>The title catalyst mediates <i>N</i>-deallylation using trimethylaluminium or diisobutylaluminium hydride.</p> <p>T. Taniguchi, K. Ogasawara <i>Tetrahedron Lett.</i> 1998, 39, 4679.</p>	<p style="text-align: center;">$(\text{Ph}_3\text{P})_2\text{Cl}_2\text{Ni}$</p> <p style="text-align: center;">A</p>	 <p style="text-align: center;">89%</p> <p>31 examples of the <i>N</i>-deallylation of amines, amides, sulfonamides and <i>N</i>-heterocycles (yields 38-95%) are reported.</p>

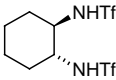
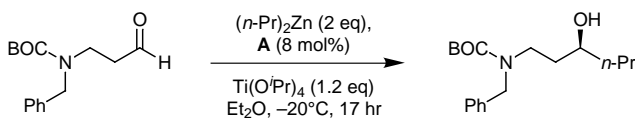
Hafnium(IV) trifluoromethanesulfonate / trifluoromethanesulfonic acid		Catalyst
<p>The title catalyst system mediates the Friedel-Crafts acylation of benzene, chlorobenzene and fluorobenzene.</p> <p>S. Kobayashi, S. Iwamoto <i>Tetrahedron Lett.</i> 1998, 39, 4697.</p>	<p>Hf(OTf)₄</p> <p>A</p> <p>TfOH</p> <p>B</p>	<p>9 examples (yields 60-83%) are described</p>

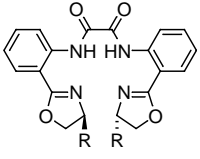
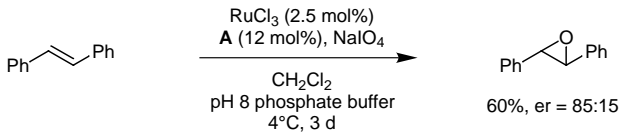
(4S)-4-(2-Naphthyl)oxazolidin-2-one		Chiral Auxiliary
<p>The title chiral auxiliary and its enantiomer, new Evans auxiliary analogs, are synthesised from 2-vinylnaphthalene in two steps in high yield and excellent enantiomeric excess. The synthesis involves a unique solution-to-solid Sharpless AA asymmetric aminohydroxylation process.</p> <p>G. Li, R. Lenington, S. Willis, S. H. Kim <i>J. Chem. Soc., Perkin Trans. 1</i> 1998, 1753.</p>	<p>A</p>	<p>The (4R) enantiomer was synthesised in a similar manner (yield 54%, %ee 93-99%).</p>

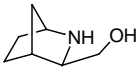
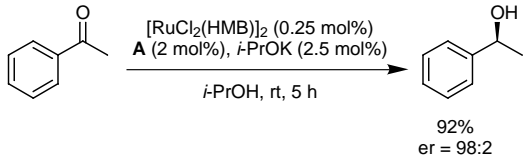
(R)-(-)-2-(1-Methylhydrazino)butan-1-ol		Chiral Auxiliary
<p>The enantioselective synthesis of α-phenylalkanimines via intermediate addition of Grignard reagents to chiral hydrazones derived from the title reagent is described.</p> <p>P. Bataille, M. Paterne, E. Brown <i>Tetrahedron: Asymmetry</i> 1998, 9, 2181.</p>	<p>A</p>	<p>7 examples (yields 32-54%, %ee 90-92%).</p>

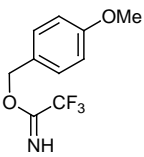
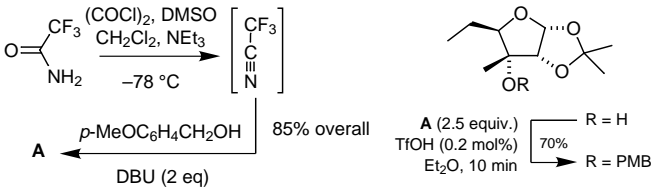
2,2'-Bis(diphenylphosphinoamino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (H ₈ -BDPAB)		Ligand
<p>The title ligand promotes the Rh-catalysed asymmetric hydrogenation of enamides leading to chiral arylamine derivatives with excellent ee.</p> <p>F.-Y. Zhang, C.-C. Pai, A. S. C. Chan <i>J. Am. Chem. Soc.</i>, 1998, 120, 5808.</p>	<p>(R)-A</p>	<p>7 examples; yields typically 100% and ee ≥ 95%. Other aromatic enamides include C₆H₅, p-CF₃C₆H₄, p-CH₃C₆H₄, p-ClC₆H₄, p-FC₆H₄, m-CH₃C₆H₄. The reaction is insensitive to the electronic features of the arene substituents but ortho-substituted arenes do not react for steric reasons.</p>

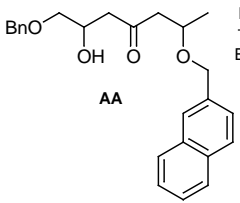
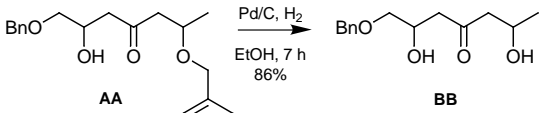
N-Methyl-bis[(R)-1-naphthyl]ethylamine		Ligand
<p>Highly diastereo- and enantio-selective 1,3-dipolar cycloadditions of nitrones are catalysed by a complex derived from the title compound, (S)-BINOL, and Yb(OTf)₃.</p> <p>S. Kobayashi, M. Kawamura <i>J. Am. Chem. Soc.</i>, 1998, 120, 5840.</p>	<p>A</p>	<p>8 examples; yields typically >88%, ee 79, 85, 89-96%</p>

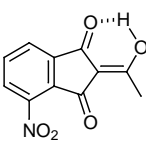
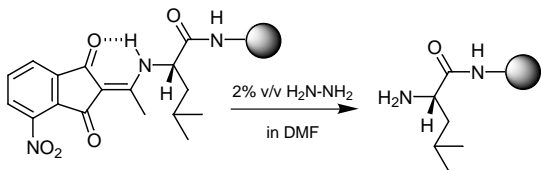

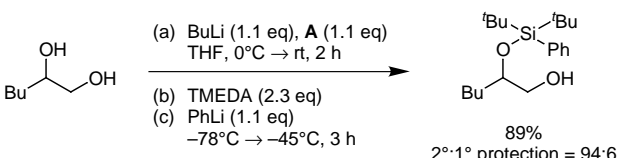
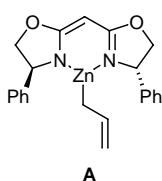
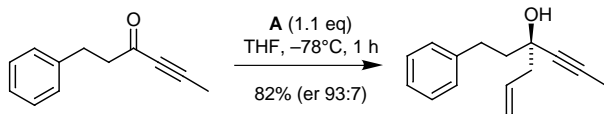
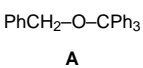
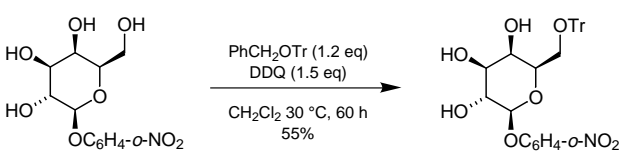
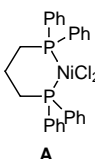
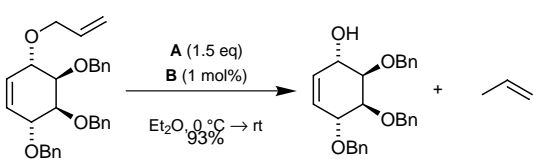
(1 <i>R</i> ,2 <i>R</i>)-Bis(trifluoromethanesulfonamido)cyclohexane		Ligand
<p>The title reagent catalyses the stereoselective addition of functionalised dialkylzincs to 1,2-, 1,3- and 1,4-aminoaldehydes.</p>	 <p style="text-align: center;">A</p>	 <p style="text-align: right;">90%, er > 99:1</p>
		<p>9 examples (yields 42, 74-90%, %ee 24->98%). In addition, 5 examples of 1,2 addition to α,β-unsaturated aminoaldehydes (yields 66-86%, %ee 79-95%) are reported.</p>

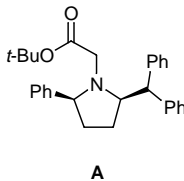
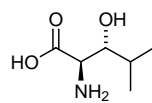
<i>N,N'</i> -Bis[2-(4,5-dihydrooxazol-2-yl)phenyl]oxalamides		Ligand
<p>Synthesis of the title ligands and their use in asymmetric catalysis is reported.</p>	 <p style="text-align: center;">R = <i>i</i>-Pr A R = <i>t</i>-Bu B</p>	 <p style="text-align: right;">60%, er = 85:15</p>
		<p>One example of enantioselective epoxidation and 3 examples of enantioselective cobalt-catalyzed Michael addition of malonates to chalcone utilising ligand B are reported (yields 12-17%, %ee = 75-89%).</p>

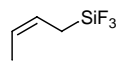
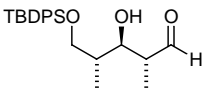
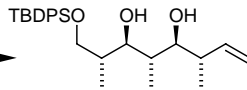
(1 <i>S</i> ,3 <i>R</i> ,4 <i>R</i>)-2-Azanorbornylmethanol		Ligand
<p>A is an efficient ligand for ruthenium-catalysed asymmetric transfer hydrogenation of ketones.</p>	 <p style="text-align: center;">A</p>	 <p style="text-align: right;">92% er = 98:2</p>
		<p>7 examples (yields 53-98%, %ee 83-97%) are reported. HMB = hexamethylbenzene.</p>

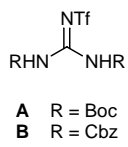
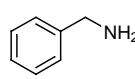
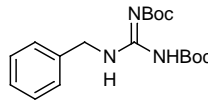
<i>p</i> -Methoxybenzyl trifluoroacetimidate		Protecting Group
<p>The title reagent is much more stable than the popular trichloroacetimidate used for the protection of alcohols as their <i>p</i>-methoxybenzyl ethers. Reagent A (bp 120-125°C/0.3 mmHg) can be stored at rt for up to one month at rt.</p>	 <p style="text-align: center;">A</p>	 <p style="text-align: right;">85% overall</p> <p style="text-align: right;"> A (2.5 equiv.) TfOH (0.2 mol%) Et2O, 10 min R = H R = PMB </p>
		<p>Acetimidates with ClCF₂C, F(CF₂)₂, F(CF₂)₃, H(CF₂)₄ and H(CF₂)₆ are also reported. The analogous 3,4-dimethoxybenzyl trifluoroacetimidate is also a stable crystalline solid, mp 73-74°C.</p>

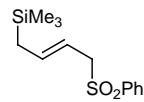
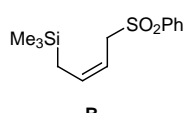
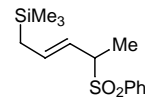
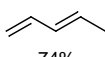
2-Naphthylmethyl ethers		Protecting Group
<p>2-Naphthylmethyl ethers undergo hydrogenolysis selectively in the presence of benzyl ethers under standard conditions (Pd/C, EtOH). Hydrogenolysis of benzyl ethers is inhibited by 2-methylnaphthalene.</p>	 <p style="text-align: center;">AA</p>	 <p style="text-align: right;">86%</p> <p style="text-align: right;">BB</p>
		<p>8 examples; yields 86-97%. Selectivity postulated to arise from the high affinity of the electron-rich naphthalene ring for the palladium surface.</p>

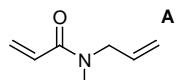
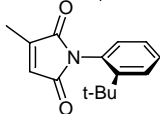
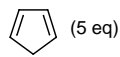
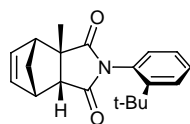
2-Acetyl-4-nitroindan-1,3-dione		Protecting Group
<p>The title compound reacts with primary amines to form <i>N</i>-1-(4-nitro-1,3-dioxindan-2-ylidene)ethyl (Nde) derivatives as stable yellow amorphous solids in good yields. The Nde protecting group is stable towards the reagents commonly employed in solid phase peptide synthesis and its deprotection with 2% hydrazine in DMF can be easily monitored visually.</p> <p>B. Kellam, B. W. Bycroft, W. C. Chan, S. R. Chhabra <i>Tetrahedron</i>, 1998, 54, 6817.</p>	 <p style="text-align: center;">A</p>	
Di- <i>tert</i> -butylchlorosilane		Protecting Group
<p>A novel one-pot selective silylation of the internal hydroxyl group of 1,2-diols is reported.</p> <p>K. Tanino, T. Shimizu, M. Kuwahara, I. Kuwajima <i>J. Org. Chem</i> 1998, 63, 2422.</p>	 <p style="text-align: center;">A</p>	 <p>10 examples (yields 76-96%). Selectivity for the secondary hydroxyl 93:7).</p>
BOX-Zn-CH ₂ CH=CH ₂		Reagent
<p>The title compound adds the allyl ligand with high enantioface selectivity to alkynyl ketones.</p> <p>M. Nakamura, A. Hirai, M. Sogi, E. Nakamura <i>J. Am. Chem. Soc.</i>, 1998, 120, 5846.</p>	 <p style="text-align: center;">A</p>	 <p>11 examples; yields 54-93%, ee typically 86%. Highest ees are observed with hindered ketones. (e.g. adamantyl ethynyl ketone). Addition to heptanal gave low ee.</p>
Benzyl triphenylmethyl ether		Reagent
<p>The title reagent reacts with DDQ to give an O-trityl benzaldehyde carbocation which can be used to deliver an O-trityl protecting group.</p> <p>M. Oikawa, H. Yoshizaki, S. Kusumoto <i>Synlett</i>, 1998, 757.</p>	 <p style="text-align: center;">A</p>	 <p>13 examples; yields 38-99%. Structurally simple primary alcohols work best. Secondary alcohols can participate but the yields are lower.</p>
[Bis-1,3-diphenylphosphinopropane]nickel(II) chloride/diisobutylaluminum hydride		Reagent
<p>The title reagent pair effects the clean and efficient deprotection of allyl ethers. The reaction can also be applied to the deprotection of <i>N</i>-allylamines.</p> <p>T. Taniguchi, K. Ogasawara <i>Angew. Chem. Int. Ed. Engl.</i>, 1998, 37, 1136; <i>Tetrahedron Lett.</i>, 1998, 39, 4679.</p>	 <p style="text-align: center;">A</p> <p style="text-align: center;">(i-Bu)₂AlH B</p>	 <p>22 examples; yields generally ≥ 80%. TBS, THP, benzyl, MOM, acetyl, pivaloyl, benzoyl and 4-MeOC₆H₄ are not affected. 1° allyl ethers cleave in preference to 2° allyl ethers. Sodium borohydride in aqueous ethanol can also be used for the cleavage.</p>

<i>N</i>-tert-Butoxycarbonylmethyl-2-diphenylmethyl-4-phenyloxazolidine		Reagent
<p>The lithium enolate of the title glycine equivalent undergoes a highly stereoselective aldol reaction with a variety of aldehydes. Removal of the chiral auxiliary produces chiral β-hydroxy-α-amino acids of <i>erythro</i> stereochemistry.</p> <p>E. J. Iwanowicz, P. Blomgren, P. T. W. Cheng, K. Smith, W. F. Lau, Y. Y. Pan, H. H. Gu, M. F. Malley and J. Z. Gougoutas <i>Synlett</i> 1998, 664.</p>	 <p>A</p>	<p>(a) LDA, THF, -78°C, 1 h (b) <i>i</i>-PrCHO, -78°C, 1 h</p> <p>A $\xrightarrow{\text{(a) LDA, THF, } -78^{\circ}\text{C, 1 h}}$ $\xrightarrow{\text{(b) } i\text{-PrCHO, } -78^{\circ}\text{C, 1 h}}$ $\xrightarrow{\text{4 steps}}$ $\xrightarrow{\text{85\%}}$ </p> <p>94%, dr = 99:1</p> <p>5 examples (aldol yields 73–94%, %de 84–98%).</p>

(<i>Z</i>)-Crotyltrifluorosilane		Reagent
<p>The crotylation of β-hydroxy α-methyl aldehydes with the title reagent offers an excellent way to install the <i>anti</i>, <i>anti</i>-dipropionate stereotriad.</p> <p>S. R. Chemler, W. R. Roush <i>J. Org. Chem.</i> 1998, 63, 3800.</p>	 <p>A</p>	<p>TBDPSO  $\xrightarrow{\text{A (3.2 eq), DIEA (5 eq), 4\AA MS, CH}_2\text{Cl}_2, 0^{\circ}\text{C, 36 h}}$ </p> <p>75%, dr = 93:7</p> <p>7 examples (yields 44–76%, 50:50 \leq <i>anti</i>, <i>anti</i> : other diastereomers \leq 96:4).</p>

<i>N,N</i>-di-Boc-<i>N'</i>-triflylguanidine and <i>N,N</i>-di-Cbz-<i>N'</i>-triflylguanidine		Reagent
<p>The title diprotected triflylguanidines are a new class of guanidinylation reagents.</p> <p>K. Feichtinger, C. Zapf, H. L. Sings, M. Goodman <i>J. Org. Chem.</i> 1998, 63, 3804.</p>	 <p>A R = Boc B R = Cbz</p>	<p> $\xrightarrow{\text{A (0.9 eq), NEt}_3 (1.0 \text{ eq}), \text{CH}_2\text{Cl}_2, \text{rt, 30 min}}$ </p> <p>100%</p> <p>11 examples of the guanidinylation of amines, amino acids and peptides (yields 75–100%) are reported.</p>

(<i>E</i>)- and (<i>Z</i>)-1-(Phenylsulfonyl)-4-(trimethylsilyl)-2-butenes		Reagent
<p>A and B are synthetic equivalents for the 1-(1,3-butadienyl) anion and the 1,1-(1,3-butadienyl) dianion. Deprotonation and reaction with an electrophile gives the corresponding product with stereochemical retention. Elimination of the products from A or B gives selectively the (<i>E</i>)-butadiene.</p> <p>T. P. Meagher, L. Yet, C.-N. Hsiao, H. Shechter <i>J. Org. Chem.</i> 1998, 63, 4181.</p>	 <p>A</p>  <p>B</p>	<p>(a) BuLi (1.1 eq), THF, -78°C, 20 min (b) MeI (1.3 eq), THF, rt, 1 h</p> <p>A $\xrightarrow{\text{(a) BuLi (1.1 eq), THF, } -78^{\circ}\text{C, 20 min}}$ $\xrightarrow{\text{(b) MeI (1.3 eq), THF, rt, 1 h}}$  $\xrightarrow{\text{TBAF (2 eq), THF, } 0^{\circ}\text{C, 30 min}}$ </p> <p>74% <i>E:Z</i> > 98:2</p> <p>14 examples of the synthesis of (<i>E</i>)-1-substituted-1,3-butadienes (yields 51–88%, <i>E:Z</i> > 98:2) and 3 examples of A or B acting as a dianion equivalent (yields 71–98%) are reported.</p>

<i>N</i>-Acryl-<i>N</i>-allyl-<i>o</i>-tert-butylanilide (A) and <i>N</i>-(<i>o</i>-tert-Butylphenyl)-2-methylmaleimide (B)		Reagent
<p>Iodine- or Lewis acid-mediated asymmetric Diels-Alder reaction of the axially chiral title compounds with various dienes proceeds with high <i>endo</i> and diastereofacial selectivity.</p> <p>O. Kitagawa, H. Izawa, K. Sato, A. Dobashi, T. Taguchi <i>J. Org. Chem.</i> 1998, 63, 2634.</p>	 <p>A</p>  <p>B</p>	<p> (5 eq) $\xrightarrow{\text{Et}_2\text{AlCl (1 eq), CH}_2\text{Cl}_2, \text{rt, 20 min}}$ </p> <p>100%, <i>endo:exo</i> = 97:3 <i>er</i> = 98:2</p> <p>Synthesis of A and B and 4 examples of Diels-Alder reactions (yields 84–100%, <i>endo:exo</i> \geq 20:1, diastereofacial selectivity \geq 14:1) are reported.</p>