

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 Narquian and Christopher Smith of the University of Glasgow. The journals regularly covered by the abstractors are: Angewandte Chemie International Edition, Bulletin de la Societe Chimie de France, Bulletin of the Chemical Society of Japan, Chemische Berichte, Chemistry Letters, Helvetica Chimica Acta, Journal of Organic Chemistry, Journal of Organometallic Chemistry, Journal of the American Chemical Society, Liebigs Annalen, Tetrahedron Letters.

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(2<i>R</i>,3<i>S</i>,5<i>R</i>,6<i>R</i>)-3-Acetoxymethyl-2,3,5,6-bis(isopropylidenedioxy)cyclohexanone			Catalyst
The title reagent catalyses the asymmetric epoxidation of olefins by Oxone®.			Oxone® (1.4 eq) A (10 mol%) K ₂ CO ₃ (5.8 eq) DME-buffer (1.5:1) -10°C, 4 h 90%, er = 83:17
Z-X. Wang, Y. Shi <i>J. Org. Chem.</i> 1997, 62, 8622.			12 examples of epoxidation of <i>trans</i> -, <i>cis</i> -, terminal and trisubstituted olefins (yields 34-95%, %ee 52-94%).
2,2'-Bis(diphenylphosphanyl)-1,1 '-binaphthyl)palladium(II) Dichloride			Catalyst
A conceptually new approach to the asymmetric catalytic protonation of enol silyl ethers is described, which employs water as the proton source and a chiral palladium complex as the catalyst.			(a) A (5 mol%), AgOTf (5 mol%) 4Å MS, DMF-H ₂ O, rt, 30 min (b) <i>i</i> -P ₂ NH (0.5 mol%), 50°C, 18 h 68%, er = 80:20
M. Sugiura and T. Nakai <i>Angew. Chem., Int. Ed. Engl.</i> 1997, 36, 2366.			6 examples (yields 67-86%, %ee 32-76%).
(1,10-Phenanthroline)copper(I) Chloride			Catalyst
The title reagent catalyses the anaerobic oxidation of alcohols to the corresponding carbonyl compounds.			A (5 mol%), K ₂ CO ₃ (10 mol%) DBAD (1 eq), 70°C, 3h 87%
I.E. Markó, M. Tsukazaki, P.R. Giles, S.M. Brown and C.J. Urch <i>Angew. Chem., Int. Ed. Engl.</i> 1997, 36, 2208.			10 examples (yields 79-93%). The presence of the azodicarboxylate is essential for the turnover of the catalytic cycle. DBAD = Di- <i>tert</i> -butyl azodicarboxylate

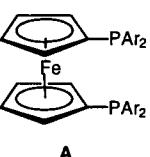
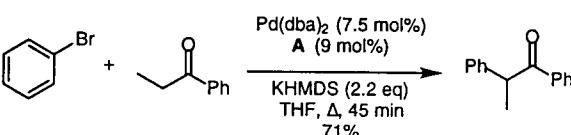
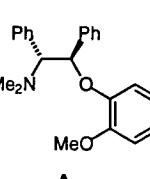
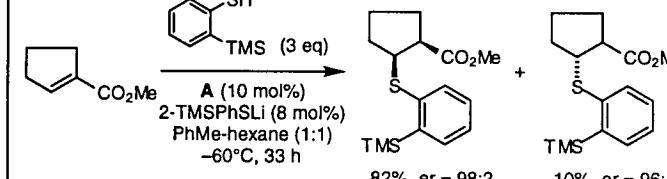
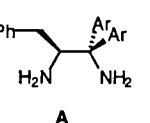
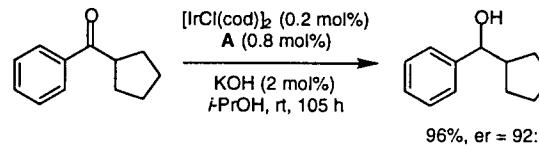
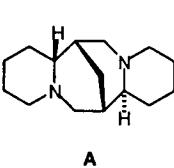
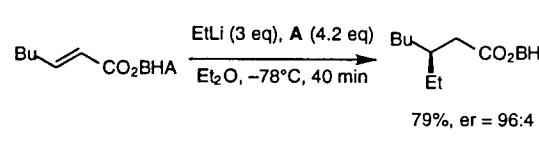
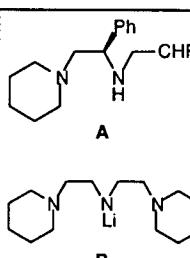
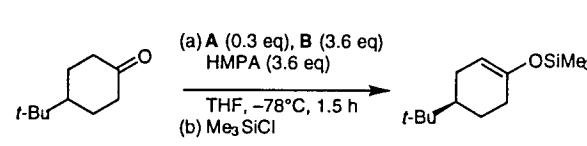
Triphenylphosphine		Catalyst
A one-pot synthesis of conjugated amides and esters via triphenylphosphine catalysed isomerisation of pentafluorophenyl esters is described.	PPh_3 A	<p>5 examples (yields 63-81%). Intermediate pentafluorophenyl esters are coupled directly with amines/alcohols.</p>
U. Kazmaier <i>Chem. Commun.</i> 1997, 2305.		
Potassium Osmate Dihydrate		Catalyst
A highly efficient catalytic aminohydroxylation process is described, providing racemic, <i>N</i> -protected β -amino alcohols. The excellent yields, rapid turnover rates, low loads of catalyst, high concentration of substrate and the necessity for only one equivalent of chloramine salt greatly simplifies product isolation and makes this process ideal for large scale application.	$\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$ A	<p>15 examples of aminohydroxylation (yields 51-99%). Also 6 examples of aziridines, prepared directly from regioisomeric mixtures of hydroxy-sulfonamides (yields 81-97%).</p>
A.E. Rubin, K.B. Sharpless <i>Angew. Chem., Int. Ed. Engl.</i> 1997, 36, 2637.		
2,6-Bis-[(diidopropylphosphanyl)methyl]-3,5-dimethylbenzylpalladium(II) Trifluoroacetate		Catalyst
The air stable title complex is a highly active catalyst for the Heck reaction.		<p>9 examples employing catalyst A (yields 79-100%). 2 other 'PCP' Pd(II) complexes are also investigated.</p>
M. Ohff, A. Ohff, M. E. van der Boom, D. Milstein <i>J. Am. Chem. Soc.</i> 1997, 119, 11687.	TFA = OCOCF_3	NMP = <i>N</i> -methylpyrrolidinone
Tetrakis(triphenylphosphine)platinum(0)		Catalyst
The title reagent catalyses the regioselective hydrothiocarboxylation of acetylenes with carbon monoxide and thiols.	$\text{Pt}(\text{PPh}_3)_4$ A	<p>12 examples (yields 61-99%). Use of RhH(CO)(PPh3)3 in place of A yields regiometric products with carbon monoxide and phenylthio groups introduced into the terminal and internal positions respectively.</p>
A. Ogawa, J.-I. Kawakami, M. Mihara, T. Ikeda, N. Sonoda, T. Hirao <i>J. Am. Chem. Soc.</i> 1997, 119, 12380.		
Sodium Tungstate Dihydrate		Catalyst
The title reagent catalyses the hydrogen peroxide oxidation of primary and secondary alcohols to carboxylic acids and ketones respectively. Reactions take place in the absence of organic solvents.	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ A	<p>6 examples of oxidation of 2° alcohols (yields 83-96%); 4 examples of oxidation of 1° alcohols (yields acids 52-87%). 2° alcohols are oxidised 4-5 times faster than 1° alcohols and hydroxyl groups can be oxidised selectively in the presence of olefins.</p>
K. Sato, M. Aoki, J. Takagi, R. Noyori <i>J. Am. Chem. Soc.</i> 1997, 119, 12386.	PTC = methyltrioctylammonium hydrogensulfate	

[Bis(tricyclohexylphosphine)benzylidene]ruthenium Dichloride			Catalyst
The title reagent catalyses the intermolecular metathesis reaction between acetylenes and ethylene gas to yield 1,3-dienes directly.			
A. Kinoshita, N. Sakakibara, M. Mori <i>J. Am. Chem. Soc.</i> 1997, 119, 12388.			7 examples (yields 48-81%).
O-(9-Allyl-N-(9-anthracyl methyl)cinchonidinium Bromide			Catalyst
The title reagent catalyses the enantioselective phase transfer alkylation of <i>tert</i> -butylglycinate benzophenone Schiff base.			
E. J. Corey, F. Xu, M. C. Noe <i>J. Am. Chem. Soc.</i> 1997, 119, 12414. B. Lygo, P. G. Wainwright <i>Tetrahedron Lett.</i> 1997, 38, 8595.			11 examples (yields 67-91%, %ee 94-99.5%). 81%, er = 98:2
Rhodium(I) Acetylacetonatedicarbonyl			Catalyst
The title reagent catalyses the intramolecular silylformylation of homoallylic silyl ethers.			
J. L. Leighton, E. Chapman <i>J. Am. Chem. Soc.</i> 1997, 119, 12416.			7 examples (yields 10, 54-79%, cis:trans > 4:1).
Tetra-<i>n</i>-propylammonium Perruthenate (TPAP)			Catalyst
The title reagent catalyses the aerobic oxidation of alcohols to the corresponding carbonyl compounds.			
I. E. Markó, P. R. Giles, M. Tsukazaki, I. Chellé-Regnaut, C. J. Urch, S. M. Brown <i>J. Am. Chem. Soc.</i> 1997, 119, 12661.			10 examples (yields 56-89%).
Bismuth(III) Chloride / (+)-Diethyl Tartrate			Catalyst
A complex prepared <i>in situ</i> from the title reagents catalyses the asymmetric trimethylsilylcyanation of aldehydes with moderate enantioselectivity.			
M. Wada, T. Takahashi, T. Domae, T. Fukuma, N. Miyoshi, K. Smith <i>Tetrahedron: Asymmetry</i> 1997, 8, 3939.			7 examples (yields 0, 87-100%, %ee 20-72%). 87%, er = 79:21

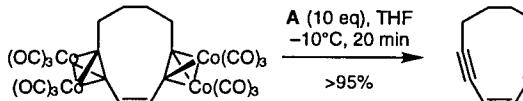
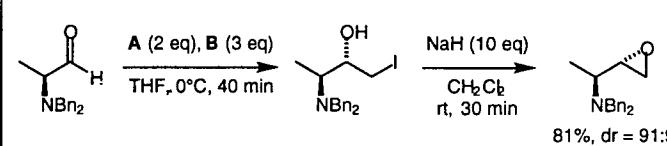
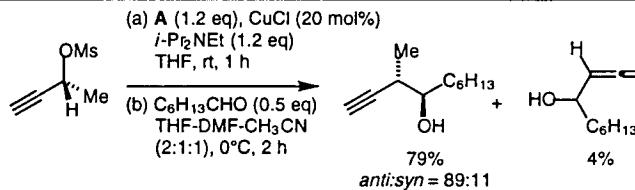
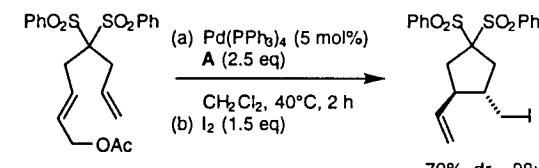
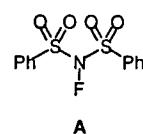
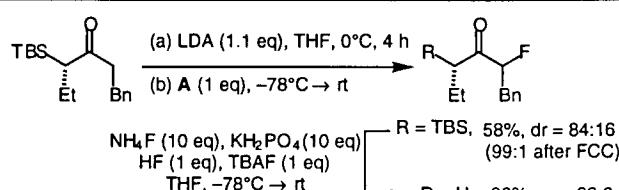
Copper(II) Triflate		Catalyst
The title reagent catalyses aldol reactions of silyl enol ethers with aldehydes and allylation reactions of tetraallyltin with carbonyl compounds in aqueous media.	$\text{Cu}(\text{OTf})_2$ A	<p>9 examples of aldol reactions (yields 57-95%, <i>syn:anti</i> > 70:30); 10 examples of allylation (yields 67-100%).</p>
S. Kobayashi, S. Nagayama, T. Busujima <i>Chemistry Letters</i> 1997, 959.		
Tris(acetylacetonato)iron(III)		Catalyst
An efficient synthesis of enantiomerically pure ketones from thioesters and Grignard reagents.	$\text{Fe}(\text{acac})_3$ A	<p>23 examples given with primary (Et, hexyl), secondary (<i>i</i>-Pr) and aromatic Grignard reagents (yields 65-99%, %ee 58-99%).</p>
W. Oppolzer, C. Darcel, P. Rochet, S. Rosset, J. De Brabander <i>Helv. Chim. Acta</i> 1997, 80, 1319.		
$\alpha,\alpha,\alpha',\alpha'$-Tetraphenyl-2,2-dimethyl-1,3-dioxolan-4,5-dimethanolato-titanium Ditosylate		Catalyst
The title reagent catalyses the regio-, diastereo- and enantioselective 1,3-dipolar cycloaddition between nitrones and oxazolidinone enolates.	 A	<p>5 examples given (yields 65-82%) with complete regioselectivity and high <i>endo</i> selectivity (%ee 48-70%).</p>
K.B. Jensen, K.V. Gothelf, K.A. Jørgensen <i>Helv. Chim. Acta</i> 1997, 80, 2039.		
[Bis(tricyclohexylphosphine)benzylidene]ruthenium Dichloride		Catalyst
The synthesis of polyoxygenated macrocyclics by ring-closing metathesis utilising A is described.	 A	<p>6 examples for the preparation of macrocyclic polyethers are given (yields 72 - 92%), with ring sizes ranging from 15 to 21. Lower yields are observed with <i>trans</i>-disubstituted tetrahydropyrans.</p>
M. Delgado, J. D. Martin <i>Tetrahedron Lett.</i> 1997, 38, 8387.		
(1<i>R</i>, 2<i>R</i>)-1-(<i>cis</i>-2,6-Dimethylpiperidino)-1-phenyl-3-trityloxypropanol-2-ol		Catalyst
Amino alcohol A catalyses the enantioselective addition of diethylzinc to a variety of aromatic and aliphatic aldehydes. Modelling studies have identified the structural parameters key to high enantioselectivity.	 A	<p>8 examples (yields > 99%, %ee 90 - 98%).</p>
A. Vidal-Ferran, A. Moyano, M. A. Pericas, A. Riera <i>Tetrahedron Lett.</i> 1997, 38, 8773.		

Di-μ-trifluoroacetyl bis[(R)-N,N-dimethylferrocenylethylamine] Dipalladium(II)			Catalyst
The title catalyst mediates the enantioselective rearrangement of 2-alkenyl imides to allylic amides.			
T. K. Hollis, L. E. Overman <i>Tetrahedron Lett.</i> 1997, 38, 8837.	9 examples (yields 39-97%, %ee 8-61%). Comparison of the rearrangement of the above imide using 8 similar catalysts has been made.		
Tetrakis(triphenylphosphite)nickel(0)			Catalyst
The title catalyst mediates the Heck reaction of aryl and vinyl halides with olefins and alkynes.			
S. Iyer, C. Ramesh, A. Ramani <i>Tetrahedron Lett.</i> 1997, 38, 8533.	12 examples (yields 16 - 95%). NMP = 1-methylpyrrolidinone		
N-Propenoyl Camphor-10,2-sultam			Chiral Auxiliary
A modification of the Baylis-Hillman reaction using camphor-based acrylates gives products with high optical purity. A two step procedure to convert these products to aldol adducts is also described.			
L. J. Brzezinski, S. Rafel, J. W. Leahy <i>Tetrahedron</i> 1997, 53, 16423.	7 examples (yields 33-98%, %ee > 99%).		
(1<i>R</i>,2<i>R</i>,3<i>S</i>,4<i>S</i>)-3-Methyl-5-norbornene-2-carboxaldehyde			Chiral Auxiliary
A conceptually novel reaction cycle to allow the highly enantioselective asymmetrication of both cyclic and acyclic <i>meso</i> -1,2-diols is described.			
H. Fujioka, Y. Nagatomi, H. Kitagawa, Y. Kita <i>J. Am. Chem. Soc.</i> 1997, 119, 12016.	8 examples (overall yields (3 steps) 47-73%). 90%, er = 99:1		
(<i>R</i>)-3,3'-Bis(<i>N,N</i>-diethylaminomethyl)-2,2'-dihydroxy-1,1'-binaphthyl			Ligand
The complex derived from the title ligand and scandium(III) triflate catalyses the enantioselective 1,4-addition of 2-(trimethylsilyloxy)furan to oxazolidinone enoates.			
H. Kitajima, K. Ito, T. Katsuki <i>Tetrahedron</i> 1997, 53, 17015.	Optimisation of the above reaction is presented (yields 44-94%, %ee 0-73%), various solvents additives and Lewis acids were investigated.		

Homochiral Phosphine Ligand		Ligand
The copper catalysed conjugate addition of <i>n</i> -butyl Grignard to enones in the presence of chiral ferrocenyl phosphine oxazoline ligands has been shown to provide useful levels of asymmetric induction.		 6 examples (yields 39-87%, %ee 12-83%).
E. L. Stangeland, T. Sammakia <i>Tetrahedron</i> 1997, 53, 16503.	A	
(R,R)-2,2,5,5-Tetramethyl-3,4-hexanediol		Ligand
A is used as a chiral ligand in the titanium(IV) catalysed enantioselective oxidation of sulfides.		 8 examples of the oxidation of aryl alkyl sulfides (yields 30-92%, %ee = 33-95%). The catalyst system was ineffective for dialkyl sulfides. CHP = cumene hydroperoxide
Y. Yamanoi, T. Immamoto <i>J. Org. Chem.</i> 1997, 62, 8560.	A	
(S,S,S)-2,2'-Bi-<i>o</i>-tolyl-1,1'-diphenylbis(oxazoline)		Ligand
An efficient synthetic route to ligand A and its application in the catalytic asymmetric allylic oxidation of cyclohexene is reported.		
M. B. Andrus, D. Asgari, J. A. Sclafani <i>J. Org. Chem.</i> 1997, 62, 9365.	A	
Homochiral Phosphoramidate		Ligand
The Cu(II) complex formed from Cu(OTf)2 and the title ligand catalyses the asymmetric 1,4-addition of organometallic reagents to enones with complete stereocontrol. Highly enantioselective tandem conjugate addition-aldol reactions are also possible.		 13 examples (yields 53-95%, %ee 10, 53, 93->98%). Subsequent regio- and enantioselective trapping of the zinc enolate formed from the conjugate addition is also reported: 10 examples (yields 64-92%, %ee 91->99%).
B.L. Feringa, M. Pineschi, L.A. Arnold, R. Imbos and A.H.M. de Vries <i>Angew. Chem., Int. Ed. Engl.</i> 1997, 36, 2620.	A	
Tris(4-perfluorohexylphenyl)phosphine		Ligand
The title compound is a competent Pd(0) ligand which is soluble in the fluorous phase. Palladium catalysed cross-coupling reactions between arylzinc bromides and aryl iodides are carried out in a two-phase toluene / perfluoroctyl bromide system employing ligand A . All palladium residues remain in the fluorous phase after the reaction and can be easily separated and recycled.		 9 examples (yields 87-99%).
B. Betzemeier, P. Knochel <i>Angew. Chem., Int. Ed. Engl.</i> 1997, 36, 2623.	A	

1,1'-Bis(di-<i>o</i>-tolylphosphino)ferrocene (dtpf)		Ligand
The title ligand forms complexes with Pd(0) that catalyse the direct α -arylation of ketone enolates by aryl halides.	 <p>A Ar = <i>o</i>-tolyl</p>	 <p>Phenyl bromide + Phenyl propanone $\xrightarrow[\text{KHMDS (2.2 eq)}]{\text{Pd(dba)}_2 \text{ (7.5 mol\%)}, \text{A (9 mol\%)}} \text{ THF, } \Delta, 45 \text{ min}$ 71%</p>
B. C. Hamann, J. F. Hartwig <i>J. Am. Chem. Soc.</i> 1997, 119, 12382.		12 examples (yields 47-94%). As illustrated β -hydrogen elimination does not cause appreciable problems and mono-arylation occurs selectively.
[(1<i>R</i>,2<i>S</i>)-2-(2-Methoxyphenoxy)-1,2-diphenylethyl]dimethylamine		Ligand
The title ligand mediates the enantioselective 1,4-addition of lithium thiophenolates to methyl enoates.	 <p>A</p>	 <p>Methyl cinnamate $\xrightarrow[\text{-60}^\circ\text{C, 33 h}]{\text{A (10 mol\%)}, \text{2-TMSPhSLi (8 mol\%)}, \text{PhMe-hexane (1:1)}}$ 82%, er = 98:2 10%, er = 96:4</p>
K. Nishimura, M. Ono, Y. Nagaoka, K. Tomioka <i>J. Am. Chem. Soc.</i> 1997, 119, 12974.		11 examples (yields 66-99%, %ee 81-97%).
(<i>R</i>)-1-Benzyl-2,2-di(4-methoxyphenyl)ethane-1,2-diamine		Ligand
The title ligand forms a complex with $[\text{IrCl}(\text{cod})_2]$ which catalyses the asymmetric transfer hydrogenation of aryl alkyl ketones.	 <p>A Ar = <i>p</i>-MeOPh</p>	 <p>[$\text{IrCl}(\text{cod})_2$ (0.2 mol%), A (0.8 mol%) $\xrightarrow[\text{i-PrOH, rt, 105 h}]{\text{KOH (2 mol\%)}}$ 96%, er = 92:8</p>
S.-I. Inoue, K. Nomura, S. Hashiguchi, R. Noyori, Y. Izawa <i>Chemistry Letters</i> 1997, 657.		12 examples (yields 5, 79-97%, %ee 21, 76-93%).
(<i>-</i>)-Sparteine		Ligand
The title diamine mediates the enantioselective conjugate addition of organolithiums to (2,6-di- <i>tert</i> -butyl-4-methoxyphenyl) (BHA) alkenoates.	 <p>A</p>	 <p>$\xrightarrow[\text{Et}_2\text{O, } -78^\circ\text{C, 40 min}]{\text{EtLi (3 eq), A (4.2 eq)}}$ 79%, er = 96:4</p>
Y. Asano, A. Iida, K. Tomioka <i>Tetrahedron Lett.</i> 1997, 38, 8973.		8 examples (yields 77-98%, %ee 42-99%). The use of a different ligand is optimum for vinyl and phenyl lithiums. A was recoverable in good yield.
(<i>S</i>)-(2-Piperidino-1-phenylethyl) (2,2,2-trifluoroethyl)amine		Reagent
Catalytic asymmetric deprotonation of prochiral 4-substituted cyclohexanones has been achieved with good enantiomeric excess. The position of equilibrium between a chiral bidentate amine and an achiral tridentate lithium amide has been exploited to achieve this result.	 <p>A B</p>	 <p>$\xrightarrow[\text{(b) } \text{Me}_3\text{SiCl}]{\text{(a) A (0.3 eq), B (3.6 eq), HMPA (3.6 eq)} \text{ in THF, } -78^\circ\text{C, 1.5 h}}$ 70%, er = 85:15</p>
T. Yamashita, D. Sato, T. Kiyoto, A. Kumar, K. Koga <i>Tetrahedron</i> 1997, 16987.		36 examples employing 6 tridentate ligands (yields 43-83%, %ee 31-88%).

1,4-Di-O-benzyl-2-tert-butylidemethylsilyl- D-threitol			Reagent
Enantioselective desymmetrization of 2,2',6,6'-tetrahydroxybiphenyl has been achieved using 1,4-di-O-benzyl-D-threitol. This was applied to the preparation of axially chiral (S)-6,6'-disubstituted-2,2'-biphenyldiols.			(a) A, DEAD, PPh ₃ , THF, 45°C, 45 h (b) TBAF, THF (c) DEAD, PPh ₃ , THF, 60°C, 3 h
T. Harada, T. M. T. Tuyet, K. Hashimoto, M. Hatsuda, A. Oku <i>Synlett</i> 1997, 1426.			
			86%, er > 98:2
trans-1,1-Di-tert-butyl-2,3-dimethylsilirane			Reagent
The title reagent inserts diastereoselectively into formamides to produce stereodefined N,O-acetals. Conversion of the latter to useful chiral 1,3-diols is described.			
J. T. Shaw, K. A. Woerpel <i>Tetrahedron</i> 1997, 53, 16597.			
Bis(chloromethyl) Ether			Reagent
Cycloadditions between the carbonyl ylide generated from A and a variety of dipolarophiles are reported.			
M. Hojo, H. Aihara, Y. Sugino, K. Sakata, S. Nakamura, C. Murakami, A. Hosomi <i>J. Org. Chem.</i> 1997, 62, 8610.			
Manganese			Reagent
Allylation and pinacol-coupling reactions of aromatic aldehydes are promoted by manganese in aqueous media. In both cases complete chemoselectivity towards aromatic aldehydes is observed.			
C.-J. Li, Y. Meng, X.-H. Yi <i>J. Org. Chem.</i> 1997, 62, 8632.			
[3-(Dimethylamino)propyl- C ₂ N]dimethylgallium			Reagent
Palladium-catalysed methylation of aryl and vinyl halides by A is reported. A is particularly useful for the selective methylation of aromatic bromides and iodides containing vulnerable functions that do not withstand other common organometallic alkylating agents.			
J. Blum, D. Gelman, W. Baidossi, E. Shakh, A. Rosenfeld, Z. Aizenshtat, B. C. Wassermann, M. Frick, B. Heymer, S. Schutte, S. Wemik, H. Schumann <i>J. Org. Chem.</i> 1997, 62, 8681.			

Tetrabutylammonium Fluoride (TBAF)			Reagent
Decomplexation of cobalt carbonyl-complexed acetylenes is reported.	Bu ₄ NF A		
G. B. Jones, J. M. Wright, T. M. Rush, G. W. Plourde, T. F. Kelton, J. E. Mathews, R. S. Huber, J. P. Davidson <i>J. Org. Chem.</i> 1997, 62 , 9379.			4 examples (yields 81->99%).
Samarium / Diiodomethane			Reagent
α-Amino aldehydes are transformed into a variety of optically pure derivatives via iodomethylation using the title reagents.	Sm A CH ₂ I ₂ B		
J. M. Concellón, P. L. Bernad, J. A. Pérez-Andrés <i>J. Org. Chem.</i> 1997, 62 , 8902.			3 examples of amino epoxides (yields 74-81%, %de = 80-82%). Examples of the preparation of protected iodohydrins, azetidinium salts, allylamines and β-amino alcohols are also reported, with generally high yields and diastereoselectivities.
Trichlorosilane			Reagent
Homopropargyl and allenylcarbinols are prepared from nonracemic propargyl mesylates via the allenyl and propargyl trichlorosilanes. The ratio of homopropargyl to allenic product is highly dependent upon the substitution of the starting alkyne.	HSiCl ₃ A		
J. A. Marshall, N. D. Adams <i>J. Org. Chem.</i> 1997, 62 , 8976.			4 examples (yields 72-92%, product ratios of at least 86:14 in favour of the homopropargyl product). 4 examples of the corresponding trimethylsilyl alkyne gave predominantly the allenylcarbinol product (yields 55-92%).
Ethylzinc Trifluoromethanesulfonate			Reagent
Palladium-catalysed Zn-ene reactions with the title reagent occur with excellent <i>trans</i> -selectivity in the ring closure. This complements the known reaction using diethylzinc which shows a high <i>cis</i> -selectivity.	EtZnOTf A		
W. Oppolzer, F. Schröder, S. Kahl <i>Helv. Chim. Acta</i> 1997, 80 , 2047.			8 examples (yields 51-80%, %de 92->99%).
N-Fluorobenzenesulfonimide			Reagent
Regio- and enantioselective synthesis of α-fluoroketones by electrophilic fluorination of α-silylketone enolates with <i>N</i> -fluorobenzenesulfonimide.			
D. Enders, M. Potthoff, G. Raabe, J. Runsink <i>Angew. Chem., Int. Ed. Engl.</i> 1997, 36 , 2362.			5 examples (yields 95-99%, %ee ≥ 96%).

1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane Bis(tetrafluoroborate) (Selectfluor™)			Reagent
Treatment of glycals with the title reagent in the presence of a nucleophile provides 2-deoxy-2-fluorosugars in high yield.			
M. D. Burkart, Z. Zhang, S.-C. Hung, C.-H. Wong <i>J. Am. Chem. Soc.</i> 1997, 119, 11743.			9 examples (yields 40-97%). Stereochemistry of the fluorine addition is directed by steric constraints of the glycal. Also 1 example of transformation of 1-hydroxy sugar to glycosyl fluoride (70% yield) and the use of A as an activator for thioglycosides.
Tetrahydrothiophene			Reagent
Aryl-, alkenyl- and benzyl sulfonium salt derivatives of A are superb participants in a variety of metal catalysed coupling reactions (eg. Stille, Suzuki).			8 examples of benzylic Stille couplings (yields 42-82%); 15 examples of aryl / benzyl / alkenyl Suzuki couplings (yields 58-95%); 2 examples of Ni catalysed coupling with aryl / alkenyl zincs (yields 75, 95%). TFP = trifurylphosphine
J. Srogl, G. D. Allred, L. S. Liebeskind <i>J. Am. Chem. Soc.</i> 1997, 119, 12376.			
Trimethyl Orthoformate / Tin(IV) Chloride			Reagent
The pinacol rearrangement of a variety of 1,2-diols, under mild anhydrous conditions, using the title reagent pair is described.			5 examples (yields 66-97%, 5 min → 4 d).
Y. Kita, Y. Yoshida, S. Mihara, D.-F. Fang, K. Higuchi, A. Furukawa, H. Fujioka <i>Tetrahedron Lett.</i> 1997, 38, 8315.			
η^2-Allyltitanium(II) Di Isopropoxide			Reagent
The title catalyst mediates the diastereoselective cyclisation of bis-unsaturated amino acid derivatives to optically active piperidines and pyrrolidines.			7 examples of the preparation of piperidines (yields 55-93%) and 2 examples of the preparation of pyrrolidines (yields 76%, 77%).
Y. Takayama, S. Okamoto, F. Sato <i>Tetrahedron Lett.</i> 1997, 38, 8351.			
Copper(I) Chloride / PhenylDimethylSilane			Reagent
Conjugate reduction of α,β -unsaturated compounds has been achieved, under mild conditions, using the title reagent pair.			2 examples of enoates (yields 95, 96%) and 6 examples of enones (yields 13%, 81 - 100%). DMI = 1,3-dimethylimidazolidinone
H. Ito, T. Ishizuka, K. Arimoto, K. Miura, A. Hosomi <i>Tetrahedron Lett.</i> 1997, 38, 8887.			