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### SYNTHESIS ALERTS

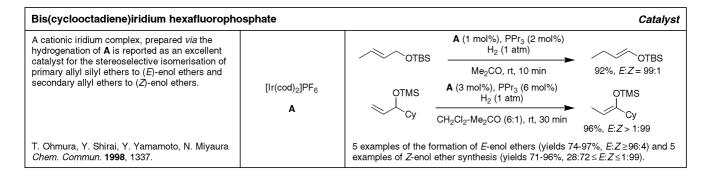
Synthesis Alerts is a new monthly feature to help readers of Synthesis keep abreast of new reagents, catalysts, ligands, chiral auxiliaries, and protecting groups which have appeared in the recent literature. Emphasis is placed on new developments but established reagents, catalysts etc are also covered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

Synthesis Alerts is a personal selection by Stephen Brand, John Christopher, Emma Guthrie, Philip Kocienski, Louise Lea, Alastair McDonald, Graeme McAllister 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, Chemical Communications, Chemistry A European Journal, Chemistry Letters, European Journal of Organic Chemistry, Helvetica Chimica Acta, Heterocycles, Journal of the American Chemical Society, Journal of Organic Chemistry, Organometallics, Perkin Transactions 1, Synlett, Synthesis, Tetrahedron, Tetrahedron Asymmetry and Tetrahedron Letters.

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| 2-(1-Dimethylaminoethyl)ferrocenecarbaldehyde   |              | Catalyst                                 |  |
|---|--------------|--|--|
| A is an effective catalyst for the asymmetric alkylation of aldehydes with diethylzinc. | CHO  Fe NMe2 | Ph H                                     |  |
| S. Fukuzawa, H. Kato <i>Synlett</i> <b>1998</b> , 727                                   |              | 12 examples (yields 55-97%, %ee 80-93%). |  |

| Bis[bis(1 <i>H</i> ,1 <i>H</i> ,2 <i>H</i> ,2 <i>H</i> -perfluorooctyl)phenylphosphino]palladium dichloride  |  | Catalyst                                |     |
|--|--|---|-----|
| Novel fluorinated phosphine palladium complexes are prepared and employed as catalysts in carbon-carbon bond forming reactions in supercritical carbon dioxide (scCO <sub>2</sub> ). | PdL <sub>2</sub> Cl <sub>2</sub> <b>A</b> CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> F <sub>13</sub> Ph—P. | Ph— | -Ph |
| M. A. Carroll, A. B. Holmes <i>Chem. Commun.</i> <b>1998</b> , 1395.   | CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> F <sub>13</sub><br>L  | 6 examples (yields 18-91%).             |     |



# Tungsten alkylidene complex A is reported as a catalyst for the efficient ring closing metathesis of diyne substrates to give cycloalkynes. [W( CCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>3</sub>] A [W( CCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>3</sub>] A A Fürstner, G. Seidel Angew. Chem. Int. Ed. 1998, 37, 1734.

| Dimethyltin(IV) Dichloride  |   | Catalyst   |
|---|---|--|
| The title catalyst mediates the selective monobenzoylation of a variety of cyclic and acyclic diols, in the presence of benzoyl chloride. | Me <sub>2</sub> SnCl <sub>2</sub><br><b>A</b> | HO OH A (10 mol%), BzCl (1.2 eq) HO OBz  THF, rt, 12 h 46% (+ 6% dibenzoate)   |
| T. Maki, F. Iwasaki, Y. Matsumura <i>Tetrahedron Lett.</i> <b>1998</b> , <i>39</i> , 5601.  |   | 10 examples (yields 46-100%) are described. The procedure exhibits high diol selectivity; for example <i>anti</i> cyclohexane 1,2-diol was selectively monobenzoylated in the presence of 1-butanol. |

| O-(9)-Allyl-N-9-anthracenylmethylcinchonidium bromide  |         |  | Catalyst                                      |
|--|---------|--|---|
| The title phase transfer catalyst mediates the asymmetric alkylation of glycine derived imines with alkyl halides and Michael acceptors. | Br Anth | Ph Of Bu CsOH•H₂O (10 eq)  | Ph Ot-Bu $(\bar{C}H_2)_4CI$ 88% B $er = 99:1$ |
| E.J. Corey, M.C. Noe, F. Xu <i>Tetrahedron Lett.</i> <b>1998</b> , <i>39</i> , 5347.   | Α       | 4 examples (yields 85-94%, %ee =91-99%) are describree steps to (S)-tert-butyl pipecolate. | ibed. <b>B</b> is converted in                |

| Scandium Trisdodecylsulphate (STDS)   |  | Catalyst   |
|---|--|--|
| The title catalyst mediates the aldol reaction of silylenol ethers with aldehydes in aqueous media. | Sc(OSO <sub>3</sub> C <sub>12</sub> H <sub>25</sub> ) <sub>3</sub><br><b>A</b> | OTMS OH O  Me Ph (1.5 eq) Ph  Me 91% sym.anti = 40:60  |
| S. Kobayashi, T. Wakabayashi <i>Tetrahedron Lett.</i> <b>1998</b> , <i>39</i> , 5389.               |  | 16 examples (yields 80-98%, 24:76≤ <i>syn:anti</i> ≤ 79:21) are described, including the use of water-sensitive silylketene acetals. |

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### Catalyst Palladium acetate/BINAP Benzophenone hydrazone reacts with **A** (1 mol%) **B** (1 mol %) Pd(OAc)<sub>2</sub> bromoarenes in the presence of the title reagent pair to give N-aryl hydrazones which then react with a ketone in the presence of TsOH•H<sub>2</sub>O to NaOBu<sup>t</sup> (1.4 eq) PhMe, 100°C 85% give indoles. The overall route represents a novel 1 eq 1 ea approach to the Fischer indole synthesis. PPh<sub>2</sub> TsOH•H<sub>2</sub>O (2 eq) .PPh<sub>2</sub> 2-hexanone, EtOH, 74% Н S. Wegaw, B. H. Yang, S. L. Buchwald, J. Am. 8 examples; yields 1st step 83-97%; yields 2nd step 74-95% (1case <5%) Chem. Soc., 1998, 120, 6621. В

| Tin(II) triflate   |                      | Catalyst   |
|--|----------------------|--|
| a-Crotylation of aldehydes occurs on reaction with 2,3-dimethyl-4-penten-2-ol in the presence of catalytic amounts of <b>A</b> .  J. Nokami, K. Yoshizane, H. Matsuura, S. | Sn(OTf)₂<br><b>A</b> | OH  1.5 eq  A (10 mol%) $CH_2Cl_2$ , 4Å MS $-25^{\circ}C$ , 6 h $95\%$ 6 examples; 70-97% yield. Different Lewis acids and tertiary homoallylic alcohols |
| Sumida, <i>J. Am. Chem. Soc.</i> , <b>1998</b> , <i>120</i> , 6609.  |                      | were also examined.  |

| Tetrakis(triphenylphosphine)palladium(0)   |  | Catalyst  |
|--|--|---|
| Alkylidenemalononitriles undergo alkoxyallylation with allylic carbonates in the presence of 5 mol% of the title catalyst to give the corresponding alkoxylallylation products in high yields. | Pd(PPh <sub>3</sub> ) <sub>4</sub><br><b>A</b> | NC CN OCO <sub>2</sub> MOM NC CN LiBF <sub>4</sub> NC CN A, THF, rt 89% OMOM MeCN-H <sub>2</sub> O 83%                  |
| H. Nakamura, M.Sekido, M. Ito, Y. Yamamoto, <i>J. Am. Chem. Soc.</i> , <b>1998</b> , <i>120</i> , 6838.  |  | 11 examples, 66-99% yield. Crotylcarbonates gave a mixture of $\alpha$ - and $\gamma$ -adducts with little selectivity. |

| Phenyltrimethylammonium bromide  |   |   | Catalyst                              |
|--|---|---|---------------------------------------|
| A simple bromine-catalysed process for the direct formation of N-sulfonyl aziridines from alkenes and chloramine-T is described. Allylic alcohols are especially good substrates for the reaction. |   | Ts-(Cl)N <sup>-</sup> Na <sup>+</sup> (1.1 eq)  A (0.1 eq), MeCN, rt, 12 h  | Ts N                                  |
|  | PhCH <sub>2</sub> NMe <sub>3</sub> <sup>+</sup> Br <sup>-</sup> | 76%   | ОН                                    |
| J. U. Jeong, B. Tao, I. Sagasser, H. Henniges, K. B. Sharpless, <i>J. Am. Chem. Soc.</i> , <b>1998</b> , <i>120</i> , 6844.  | Α   | 9 examples including terminal, 1,1-disubstituted, 1,2-disubstituted, and trisubstituted alkenes (yields 51-95%). 9 examples of allylic alcohols (yields 30%, 70-97%). | N—Ts<br>87% ( <i>syn:anti</i> = 2,5:1 |

# (R)-3,3'-Di(2-hydroxyphenyl)-2,2'-dihydroxy-1,1'-binaphthyl Boronic ester A prepared from the title reagent is a Brønsted acid which catalyses the enantioselective Diels-Alder reaction of various α,β-enals with isoprene and cyclopentadiene. K. Ishihara, H. Kurihara, M. Matsumoto, H. Yamamoto, J. Am. Chem. Soc., 1998, 120, 6920. Catalyst A (10 mol%) CH<sub>2</sub>Cl<sub>2</sub>, -78°C Br 99% (er 97:3)

### (S,S)-Chiraphos(NiCl<sub>2</sub>)

Catalyst

The title catalyst effects asymmetric addition of Grignard reagents to unsaturated cyclic acetals.

E. Gomez-Bengoa, N. M. Heron, M. T. Didiuk, C. A. Luchaco, A. H. Hoveyda *J. Am. Chem. Soc.*, **1998**, *120*, 7649.

EtMgBr (90%, er = 92:8); i-BuMgCl (63%, er = 85:15); PhMgBr (67%, er = 91:9); PhCH $_2$ CH $_2$ MgCl (81%, er 92:8). Added phosphine important.

### Benzylidene-bis(tricyclohexylphosphine)dichlororuthenium

Catalyst

Five-, six-, and seven-membered carbocyclic and heterocyclic alkenylboronates are synthesised in high yield via metathesis of alkenylboronates using the Grubbs catalyst.

J. Renaud, S. G. Ouellet, *J. Am. Chem. Soc.*, **1998**, *120*, 7995.

10 examples (yields 66-96%). The reactions must be run under high dilution conditions (0.004-0.05 M) to minimise dimerisation. The reaction rates varied widely from <6 h to 260 h but the reasons are not clear.

### Triethylphosphite

Ligand

**A** is used as a ligand in the palladium catalysed Heck reaction. Turnover numbers for the reaction are among the highest ever recorded.

P(OEt)<sub>3</sub>

M. Beller, A. Zapf Synlett 1998, 792

5 examples (yields 15-79%, turnover numbers 660-15,000).  $\mathsf{DMA} = N, N\text{-} dimethyl \ acetamide.$ 

### (1S,3R,4R)-2-Azabicyclo[2.2.1]heptane-3-bis(phenyl)methanol

Ligand

The oxazaborolidine prepared *in situ* from the title amino alcohol and trimethylborate catalyses the asymmetric reduction of ketones by borane in excellent yield.

NH CPh₂OH

P. Pinho, D. Guijarro, P. G. Andersson *Tetrahedron* **1998**, *54*, 7897.

8 examples (yields >95%, %ee 47-89%).

### Tris [3,5-bis (trifluoromethyl) phenyl] phosphine

Ligand

**A** is reported as a novel ligand in the Heck and Stille reactions in supercritical carbon dioxide (scCO<sub>2</sub>).

CO<sub>2</sub>Me (5 eq) (OAc)<sub>2</sub> (3 mol%), Et<sub>3</sub>N (3 eq) A (6 mol%), scCO<sub>2</sub>, 90°C 345 bar, 1 d

D. K. Morita, D. R. Pesiri, S. A. David, W. H. Glaze, W. Tumas *Chem. Commun.* **1998**, 1397.

Λ

3 examples (conversion 94->99%) are reported.

94% conversion

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### (S,S)-2,2'-Bis(4-isopropyloxazolyl)-1,1'-binaphthyl ((S,S)-ip-boxax)

Ligand

Catalytic asymmetric Wacker-type cyclisation is efficiently catalysed by an in situ generated cationic palladium complex derived from the title ligand.

 $Pd(CH_3CN)_4(BF_4)_2$  (2 mol%) A (4 mol%) Benzoquinone (4 eq) MeOH, Δ, 5 h 85% er = 98:2

Y. Uozumi, K. Kato, T. Hayashi J. Org. Chem. **1998**, *63*, 5071.

3 examples (yields 85-93%, %ee 92-97%).

### 1,1'-Bis(diphenylphosphino)ferrocene (DPPF)

Ligand

Ligand

The title ligand is utilised in the highly regioselective ligand-controlled Heck-arylation reactions of allyltrimethylsilane, delivering branched  $\beta$ -products.

Allyltrimethylsilane (2.5 eq)  $Pd(OAc)_2$  (3 mol%), **A** (7 mol%)  $Et_3N$  (2 eq) SiMe<sub>3</sub> OTf MeCN, Microwave (50 W), 5 min 64% regioselectivity = 97:3

K. Olofsson, M. Larhed, A. Hallberg J. Org. Chem. 1998, 63, 5076.

8 examples (yields 28-85%, regioselectivity ≥ 78:22)

R,R-MeDuPHOS

A Rhodium complex derived from the title ligand mediates the enantioselective hydrogenation of enol acetates.

N.W. Boaz Tetrahedron Lett. 1998, 39, 5505.

9 examples (yields > 95%, %ee 64-99%) are described. Enol acetates are reduced faster than alkenes and alkynes, although after time alkynes are reduced to the corresponding alkenes.

### (S,S)-3,3-Bis(4-isopropyl-1,3-oxazolyl)pentane

Ligand

The title ligand mediates the enantioselective [2,3]-Wittig rearrangement of allyl ethers.

K. Tomooka, N. Komine, T. Nakai Tetrahedron Lett. 1998, 39, 5513.

5 examples (yields >90%, %ee 2-89%) are described. Labelling studies suggest enantioselectivity arises from the lithiation step.

### (R)-2-Hydroxy-2'-methoxy-1,1'-binaphthyl (BINOL-Me)

Ligand

A Barium(II) complex derived from the title ligand mediates the asymmetric aldol reaction of acetophenone with a variety of aldehydes

Y. M. A. Yamada, M. Shibasaki Tetrahedron Lett. **1998**, *39*, 5561.

6 examples (yields 77-99%, %ee = 54-70%) are described. Aldehydes with acidic  $\alpha$ -hydrogens do not undergo self-condensation.

### ${\it Bis} \hbox{${\rm [2-(diphenylphospino)phenyl]}$ ether (DPEphos)}$

Ligand

The title ligand in combination with Palladium(II) mediates the catalytic arylation of anilines.

J. P. Sadighi, M. C. Harris, S. L. Buchwald *Tetrahedron Lett.* **1998**, *39*, 5327.

Chiral biosoxazoline Ligand

O-Benzylhydroxylamine undergoes enantioselective conjugate addition to N-crotonoyl pyrazoles in the presence of the title ligand (10 mol%) and MgBr<sub>2</sub>. Use of Y(OTf)<sub>3</sub> or Yb(OTf)<sub>3</sub> gives the opposite enantiomer.

M. P. Sibi, J. J. Shay, M. Liu, C. P. Jasperse, *J. Am. Chem. Soc.*, **1998**, *120*, 6615.

6 examples; 24-80% yield; ee 83-95% (using 30% MgBr<sub>2</sub>)

Oxalic Acid Reagent

The title reagent cleaves ketone SAMP-hydrazones to give the corresponding ketones. The chiral auxilary SAMP is recovered in good yield.

D. Enders, T. Hundertmark, R. Lazny *Synlett* **1998**, 721.

8 examples (yields 84-98%, %ee 90-99%).

### Scandium(III) Trifluoromethanesulfonate

Reagent

Reagent

Treatment of aziridine carboxylates with indole derivatives in the presence of  ${\bf A}$  produces the tryptophan derivatives in good yield

tryptophan derivatives in good yield

Y. L. Bennani, G.-D. Zhu, J. C. Freeman *Synlett* **1998**, 754.

Sc(OTf)<sub>3</sub>

11 examples (yields 0, 22-85%) are reported.

### Nitronium Tetrafluoroborate

The title reagent is utilised for the efficient nitration of electron-rich aromatic compounds, with good to excellent regioselectivity. Dinitration can also be achieved in moderate to high yield.

[NO<sub>2</sub>]<sup>+</sup> [BF<sub>4</sub>]

C. L. Dwyer, C. W. Holzapfel *Tetrahedron* **1998**, *54*, 7843.

9 examples of mononitration (yields 32-81%) and 3 examples of dinitration using 2 eq of  $\bf A$  (yields 22-78%) are reported.

C-D Chen, J-W Huang, M-k Leung, H-h Li

Tetrahedron 1998, 54, 9067.

### S,S-Dimethyl Deithiocarbonate (DMDTC) Reagent A wide range of symmetrical alkyl and aryl ketones are prepared by reaction of the title carbonyl dication synthon with a variety of (a) Cul (0.5 eq) cuprate reagents. Et<sub>2</sub>O, -25°C, 2 h MgBr (b) **A** (0.3 eq), -25°C → rt, 4 h 11 examples (yields 46-96%).

Allyldiisopropylphenylsilane Reagent  $ZrCl_4$  promoted [3+2] cycloaddition of **A** to  $\alpha,\beta$ -unsaturated ketones affords silyl-substituted cyclopentanes with high stereoselectivitiy. A (1.3 eq) ZrCl<sub>4</sub> (1.3 eq) Si(*i*-Pr)<sub>2</sub>Ph PhMe, -78°C→ -20°C Si(Ph)(i-Pr)<sub>2</sub> 5 h 89% single stereoisomer Α T. Akiyama, E. Hoshi, S. Fujiyoshi *J. Chem. Soc., Perkin Trans.* 1 1998, 2121. 5 examples (yields 60-89%).

### 2,2-Bis( $\eta^5$ -cyclopentadienyl)-1-(2-methylphenyl)-3-phenyl-1-aza-2-zircona-4-cyclopentene Reagent The title reagent is employed as a homoenolate (a) t-BuCOMe (1.1 eq) equivalent in stereoselective synthesis. PhMe, $\Delta$ C<sub>5</sub>H<sub>5</sub>NO (1.2 eq) t-Bu, THF-H<sub>2</sub>O (20:1), rt, 8 h (c) THF-0.1M HCI (1:1) rt, 6 h 64% dr > 99:1D. Enders, M. Kroll, G. Raabe, J. Runsink Angew. 8 examples (yields 51-78%, %de 84-98%) of the formation of $\gamma$ -butyrolactols. Chem. Int. Ed. 1998, 37, 1673.

Phosphazene base Reagent A two step synthesis of *trans*-2-arylcyclopropane carboxylates with high enantioselectivity is reported using base **A**. The phosphazene base A (1 ea) provides a very reactive "naked" anion and thus Me<sub>2</sub>N  $NMe_2$ reaction times are greatly reduced from the =P−NMe<sub>2</sub> EtN=F CO<sub>2</sub>Et standard 24 -72 h with NaH. Enantioselectivity is ŃMe₂ Me₂N also improved. er = 99:1Α 5 examples (c. 90% conversion (no yields given), %ee = 95-99%). A. Solladié-Cavallo, A. Diep-Vohuule, T. Isarno *Angew. Chem. Int. Ed.* **1998**, *37*, 1689.

| tert-Butyl Hypofluorite   |                    | Reagent  |
|---|--------------------|--|
| A is an electrophilic <i>tert</i> -butoxylation agent. Reaction with several benzylic double bonds, enols, and benzylic enol derivatives is reported. | t-BuOF<br><b>A</b> | A (5 eq)  CHCl <sub>3</sub> , 0°C, 15 min 70%  MeO |
| I. Ben-David, E. Mishani, S. Rozen <i>J. Org. Chem.</i> <b>1998</b> , <i>63</i> , 4632.   |                    | 13 examples (yields 20-70%)                        |

### 1-Benzoyl-2(S)-isopropyl-4-methoxy-6(S)-carbomethoxy-(1,2)(5,6)-tetrahydro-1,3-pyrimidine Reagent

Α

C<sub>12</sub>H<sub>25</sub>CHO

The title compound mediates enantioselective synthesis of  $\alpha$ -substituted aspartic acids

$$N = \bigvee_{\substack{N \\ \text{Bz}}} OCH_3$$

E. Juaristi, H. López-Ruiz, D. Madrigal, Y. Ramírez-Quirós, J. Escalante J. Org. Chem.

1998, 63, 4706.

4 examples of synthesis of  $\alpha$ -alkyl aspartic acids (yields 44-61%, %de  $\geq$  97%).

### 2-[(Trimethylsilyl)oxy]furan (TMSOF)

Reagent A is utilised in an enantioselective aldol reaction. The procedure is applied to a synthesis of (+)-Muricatacin.

(a) Ti(O-*i*-Pr)<sub>4</sub> (20 mol%) (*R*)-Binol (40 mol%) CH<sub>2</sub>Cl<sub>2</sub>, -20°C, 1.5 h (b) H<sub>2</sub>, Pd/C, PhMe, rt, 12 h

48%

er = 90:10

Reagent

Reagent

M. Szlosek, X. Franck, B. Figadère, A. Cavé J. Org. Chem. 1998, 63, 5169.

5 examples of aldol reactions of achiral aldehydes (yields 20-95%, 53:47 ≤ syn/anti ≤ 70:30, %ee 54-90%) are reported

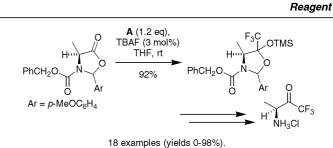
### (Trifluoromethyl)trimethylsilane

The title compound reacts with a variety of amino acid derived *N*-substituted oxazolidin-5-ones. The adducts can be transformed into trifluoromethyl ketones via mild acid hydrolysis.

M. W. Walter, R. M. Adlington, J. E. Baldwin, C. J. Schofield *J. Org. Chem.* **1998**, *63*, 5179.

F<sub>3</sub>C-SiMe<sub>3</sub>

Α



Samarium(II) lodide Reagent

The title reagent regioselectively cleaves diallyl acetals to generate  $\alpha$ -allyloxy carbanions, which subsequently undergo [2,3] -Wittig rearrangement.

Sml<sub>2</sub> Α

5 examples (yields 0, 22-81%) are described. A cross-coupling experiment indicates the intermediacy of an allyloxy carbanion (i.e. non Barbier-type coupling)

K. Hioki, K. Kono, S. Tani, M. Kunishima Tetrahedron Lett. 1998, 39, 5229.

### **Chromium Trioxide / Sodium Periodate**

The title reagent pair mediates the direct oxidation of primary alcohols to the corresponding carboxylic acid.

CrO<sub>3</sub> Α H<sub>5</sub>IO<sub>4</sub>

M. Zhao, J. Li, Z. Song, R. Desmond, D.M. Tschaen, E. J. J. Grabowski, P.J. Reider Tetrahedron Lett. 1998, 39, 5323,

В

9 examples of oxidation to a carboxylic acid (yields 73-98%) and 2 examples of oxidation to a ketone (yields 98%, 100%) are described. An alpha-amino alcohol is oxidised without racemisation to the corresponding amino acid.

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### 9-Borabicyclo[3.3.1]nonane The title reagent initiates the low-temperature radical reduction of a wide range of typical precursors. A (4 mol%), N<sub>2</sub> PhMe, 0°C, 88% V. T. Perchyonok, C.H. Schiesser Tetrahedron 7 examples are described for the use of Bu<sub>3</sub>SnH and Ph<sub>3</sub>SnH as reductants

V. T. Perchyonok, C.H. Schiesser *Tetrahedron Lett.* **1998**, *39*, 5437.

at 0°C and -78°C (yields 52-100%).

### $Titanium (IV)\ Isopropoxide\ /\ Isopropylmagnesium\ chloride\ /\ Tri-\textit{$n$-butyltin}\ chloride$ Reagent The above reagent trio effects the conversion of Ti(Oi-Pr)4 propargyllic carbonates to propargyl stannanes A (1.5 eq), B (3 eq) Α CI C (1.2 eq) i-PrMgCl Et<sub>2</sub>O, -50°C → 0°C, 3h ĊCO₂Et 82% . SnBu₃ В n-Bu<sub>3</sub>SnCl 11 examples (yields 66-87%) are described. Phenyl substituted alkynes D. K. An, S. Okamoto, F. Sato Tetrahedron Lett. С **1998**, *39*, 4861. cause partial product isomerisation to the corresponding allenes.

Methyldichlorocerium(III) Reagent The title reagent is used to prepare methylketones from the corresponding tertiary amides as an alternative to the Weinreb amide MeLi CeCl<sub>3</sub> (1\_eq) technology. **A** (1 eq) THF THF, -78°C, 15 min -78°C 85% MeCeCl<sub>2</sub> Α 10 examples (yields 0, 20-95%) are described. The reaction has been optimised M. Kurosu, Y. Kishi Tetrahedron Lett. 1998, 39, for the amine such that an excess of **A** can be used without polyalkylation.

# A new chiral derivatising agent derived from the title compound is described which allows the enantiomeric purities of chiral alcohols to be determined by <sup>31</sup>P NMR spectroscopy. C. Anaya de Parrodi, G. E. Moreno, L. Quintero, E. Juaristi *Tetrahedron: Asymmetry* 1998, 9, 2093. Reagent A diethylaniline (5 eq) PCl<sub>3</sub> (1 eq) 2-butanol (0.8 eq) CDCl<sub>3</sub>-CH<sub>2</sub>Cl<sub>2</sub> (10:1) rt, 30 min 6 examples of the derivatization of alcohols. Very large differences in the 3<sup>1</sup>P chemical shifts for the diastereomeric phosphonamides are observed.

| Triisopropylsilanethiol   |                                   | Reagent   |
|---|-----------------------------------|---|
| The title reagent has been employed for the synthesis of 2-(triisopropylsilyloxy)alkylthiols from epoxides.  J. C. Justo de Pomar, J. A. Soderquist Tetrahedron Lett. 1998, 39, 4409. | ( <i>i</i> -Pr)₃Si—SH<br><b>A</b> | A (1 eq), DBU (1 eq)  THF, Δ, 12 h 65%  9 examples (yields 59-92%) are described. |

## Methyl chlorodifluoroacetate The title reagent mediates the trifluoromethylation of an alkyl iodide. CF<sub>3</sub> CIF<sub>2</sub>C OMe A SO<sub>2</sub>Me 1 example is reported. In addition, a one-pot trifluoromethylation of alcohols using chlorodifluoroacetic anhydride is described. 2 examples (yields 61, 74%).

| Ethyl (triphenylphosphoranylidine)acetate   | / Zinc                                    |  | Reagent       |
|---|---|--|---------------|
| The title reagent pair mediates the alkylation of acid chlorides and chloroformates.                          | OEt<br>PPh <sub>3</sub><br><b>A</b><br>Zn | CI O CI PhMe, rt, 3 h 80%                  | PPh₃<br>CO₂Et |
| H. M. Meshram, G. S. Reddy, M. M. Reddy, J. S. Yadav <i>Tetrahedron Lett.</i> <b>1998</b> , <i>39</i> , 4107. | В   | 13 examples (yields 80-85%) are described. |               |

| Lithium Azidohydridodiisobutylaluminate   |  | Reagent  |
|---|--|--|
| The title reagent, prepared as a solution in THF from DIBAL and lithium azide, mediates the opening of epoxides with azide. | ⊝<br>Bu <sup>i</sup><br>H−Al−N <sub>3</sub><br>Bu <sup>i</sup> □ | OH N <sub>3</sub> OH N <sub>3</sub> OH N <sub>3</sub> THF, rt, 2 h 76% |
| Y. S. Youn, I. S. Cho, B. Y. Chung <i>Tetrahedron Lett.</i> <b>1998</b> , <i>39</i> , 4337.                                 | A  | 5 examples (yields 70-78%) are described.                              |

| Dibenzyl peroxydicarbonate  |                  |                 | Reagent  |
|---|------------------|-----------------|--|
| The title reagent mediates the stereoselective α-oxidation of chiral dienolates.  M. Sugiura, Y. Yagi, S-Y. Wei, T. Nakai Tetrahedron Lett. <b>1998</b> , <i>39</i> , 4351. | O OBn<br>BnO O A | (a) LHMDS (1 ec | X <sub>c</sub> 61%<br>dr = 99:1<br>OCO <sub>2</sub> Bn 89% Z |

| Triethyl orthoacrylate  |                   | Reagent   |
|---|-------------------|---|
| Reaction of the title reagent with zirconocene-butene complex generates a γ,γ-diethoxylallyl zirconium reagent which adds to aldehydes and ketones (1,2) or enones (1,4) to give 1,1-diethoxycyclopropanes in good yield.  H. Ito, H. Kuroi, H. Ding, T. Taguchi, <i>J. Am. Chem. Soc.</i> , <b>1998</b> , <i>120</i> , 6623. | OEt<br>OEt<br>OEt | A "Cp <sub>2</sub> Zr" OEt OEt OEt C-C <sub>6</sub> H <sub>11</sub> CHO (1.2 eq) OH OEt |