

**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:

Stephen Brand, John Christopher, Emma Guthrie, Philip Kocienski, Louise Lea, Russell McDonald, Graeme McAllister and Robert Narquizian of Glasgow University.

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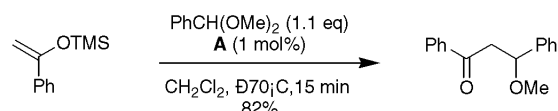
The journals regularly covered by the abstractors are:

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

### Biismuth tris-trifluoromethanesulfonate

### Catalyst

The title reagent acts as a water-stable equivalent of trimethylsilyl triflate, efficiently catalysing Mukaiyama aldol reactions. The activity of **A** is higher than corresponding rare earth catalysts and it can be recovered after reaction.



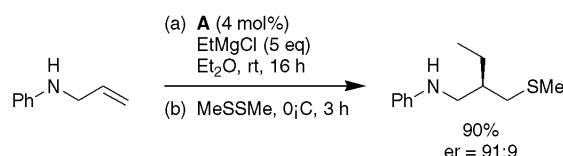
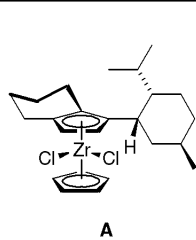
C. Le Roux, L. Ciliberti, H. Laurent-Robert, A. Laporterie, J. Dubac *Synlett* **1998**, 1249.

17 examples (yields 55-95%).

### ( $\eta^5$ -Cyclopentadienyl)( $\eta^5$ -{1-(1*S*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl}-4,5,6,7-tetrahydroindenyl)zirconium dichloride

### Catalyst

Complex **A** catalyses the asymmetric alkylation of terminal alkenes in high yield and good to moderate selectivity. Preparation of Cp<sub>2</sub>ZrCl<sub>2</sub>·2THF, an intermediate in the formation of **A**, is also discussed.



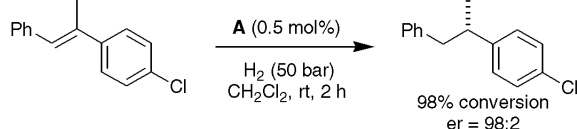
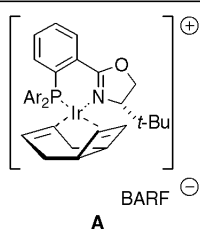
L. Bell, D. C. Brookings, G. J. Dawson, R. J. Whitby, R. V. H. Jones, M. C. H. Standen *Tetrahedron* **1998**, 54, 14617.

34 examples using a variety of solvents, organomagnesium reagents and electrophiles (yields 27-92%, %ee 20-81%).

### Chiral cationic iridium complex

### Catalyst

The enantioselective hydrogenation of unfunctionalised aryl substituted olefins and allyl alcohols is reported. The air-stable chiral cationic iridium catalyst **A** gives high enantioselectivity.



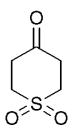
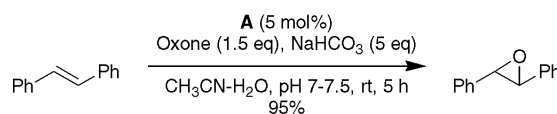
BARF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate

A. Lightfoot, P. Schnider, A. Pfaltz *Angew. Chem. Int. Ed.* **1998**, 37, 2897.

6 examples (conversion 42, 81-97%, %ee 95->99%). 4 examples of hydrogenation with a related catalyst (conversions 95->99%, %ee = 81-96%) are also reported.

**4-Oxothiane-S,S-dioxide****Catalyst**

The title compound catalyses the epoxidation of olefins.

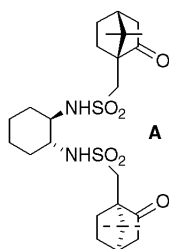
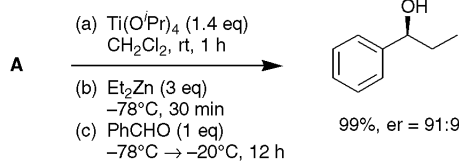
**A**

15 examples (yields 80-95%).

D. Yang, Y.-C. Yip, G.-S. Jiao, M.-K. Wong *J. Org. Chem.* **1998**, *63*, 8952.

**(1*R*,2*R*)-*N,N'*-Bis[(1*S*,4*R*)-7,7-dimethyl-2-oxo-bicyclo[2.2.1]heptylmethanesulfonyl]-1,2-cyclohexyldiamine****Catalyst**

A Ti(IV) catalyst derived from the title ligand mediates the enantioselective addition of diethylzinc to aldehydes.

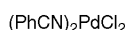
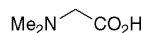
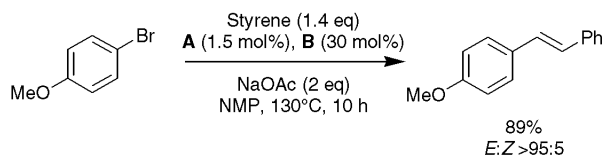
**A**

7 examples (yields 91-99%, %ee 59-90%).

C.-D. Hwang, B.-J. Uang *Tetrahedron: Asymmetry* **1998**, *9*, 3979.

**Bis(benzonitrile) Palladium(II) Dichloride / *N,N*-Dimethylglycine****Catalyst**

The title reagent pair mediates the phosphine-free Heck reaction of aryl bromides and olefins.

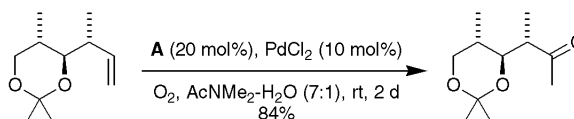
**A****B**

9 examples (conversions 60-100%, *E:Z* > 95:5) are described.

M. T. Reetz, E. Westermann, R. Lohmer, G. Lohmer *Tetrahedron Lett.* **1998**, *39*, 8449.

**Copper(II) Acetate****Catalyst**

The title reagent catalyses the Wacker oxidation of terminal olefins to methyl ketones.

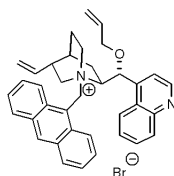
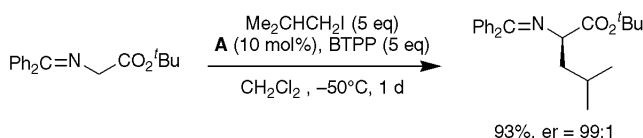
**A**

8 examples (yields 62-91%) are described.

A. B. Smith, Y. S. Cho, G. K. Friestad *Tetrahedron Lett.* **1998**, *39*, 8765.

***O*-Allyl-*N*-anthracenylmethyl cinchonidinium bromide****Catalyst**

The title catalyst mediates the enantioselective alkylation of glycine-derived imines in the presence of a phosphazene base, under homogeneous conditions.

**A**

16 examples (yields 83-96%, %ee 84-97%) are described. The pseudoenantiomer of **A**, gives comparable and opposite enantioselectivity.

BTPP = *tert*-Butylimino-tri(pyrrolidino)phosphorane.

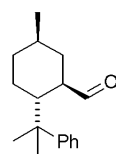
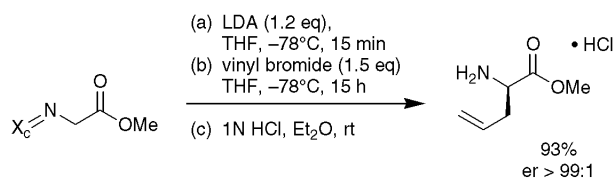
M. J. O'Donnell, F. Delgado, C. Hostettler, R. Schwesinger *Tetrahedron Lett.* **1998**, *39*, 8775.

|   |  |  |
|---|--|--|
| <b>(1<i>S</i>,2<i>R</i>)-1,2-Diphenylethylenediamine / Magnesium(II) iodide</b>   |  | <b>Catalyst</b>  |
| The title catalyst mediates the enantioselective magnesium-catalysed aza-Diels-Alder reaction with Danishefsky's diene.   | <p><b>A</b></p> <p>MgI<sub>2</sub></p> <p><b>B</b></p> | <p><b>A</b> (11 mol%) <b>B</b> (10 mol%)<br/>2,6-lutidine (11 mol%)<br/>CH<sub>3</sub>CN, rt, 18 h</p> <p>64%, er = 99:1</p> <p>1 example is described. Conditions were optimised using high throughput screening methods.</p>   |
| S. Bromidge, P. C. Wilson, A. Whiting <i>Tetrahedron Lett.</i> <b>1998</b> , 39, 8905.  |  |  |
| <b>Ru<sub>3</sub>(CO)<sub>12</sub></b>  |  | <b>Catalyst</b>  |
| The title compound catalyses the direct carbonylation at a C–H bond β to a directing nitrogen atom in aza-heterocycles. The higher the p <i>K</i> <sub>a</sub> of the conjugate acid of the heterocycle, the better the directing effect of the nitrogen.                     | <p><b>A</b></p>  | <p><b>A</b> (4 mol%)<br/>o-MeC<sub>6</sub>H<sub>4</sub>-CH=CH<sub>2</sub> (4 eq.)<br/>CO (5 atm), PhMe, 160°C<br/>78%</p> <p>The reaction also worked with 2-methylbenzothiazole, 2,2,3-trimethyl-3<i>H</i>-indole, 1-methylbenzotriazole, and 2-methylimidazo[1,2-<i>a</i>]pyridine but 2-methylbenzoxazole failed. Yields generally 25-80%</p> |
| T. Fukuyama, N. Chatani, J. Tatsumi, F. Kakiuchi, S. Murai <i>J. Am. Chem. Soc.</i> <b>1998</b> , 120, 11522.   |  |  |
| <b>Planar Chiral 4-(Pyrrolidino)pyridine</b>  |  | <b>Catalyst</b>  |
| The title compound catalyses the enantioselective construction of quaternary centres via rearrangement of <i>O</i> -acyl azlactones.  | <p><b>A</b></p>  | <p><b>A</b> (2 mol%)<br/>t-amyl alcohol<br/>0°C, 2-6 h</p> <p>93% (er = 96:4)</p> <p>16 examples. Yields 93-95% (ee 88-92%)</p>  |
| J. C. Ruble, G. Fu <i>J. Am. Chem. Soc.</i> <b>1998</b> , 120, 11532.   |  |  |
| <b>Titanocene</b>   |  | <b>Catalyst</b>  |
| Styrenes undergo a double vicinal alkylation reaction with two of the same 1° or 2° bromoalkanes in the presence of the title compound. Two different bromoalkanes can be used if one is 1° or 2° and the other 3°. The reaction involves a regioselective carbomagnesiation. | <p><b>A</b></p>  | <p>Cl-(CH<sub>2</sub>)<sub>5</sub>-Br (1.1 eq)<br/>t-BuBr (1.1 eq)<br/><b>A</b> (5 mol%), BuMgCl (2.2 eq)<br/>THF, 0°C, 1 h</p> <p>12 examples; yields 46-94%. The reaction can be used to form rings: e.g., styrene reacts with 1,4-dibromobutane to give phenylcyclohexane in 46% yield.</p>   |
| J. Terao, K. Saito, S. Nii, N. Kambe, N. Sonoda <i>J. Am. Chem. Soc.</i> <b>1998</b> , 120, 11822.  |  |  |
| <b>[Pt(C<sub>2</sub>H<sub>4</sub>)Cl<sub>2</sub>]<sub>2</sub> (Zeise's Dimer)</b>   |  | <b>Catalyst</b>  |
| 1,2-Cyclopropanated monosaccharides undergo ring opening in the presence of alcohols to give C-branched glycosides.   | <p><b>A</b></p>  | <p><b>A</b> (3.7 mol%)<br/>H<sub>2</sub>C=CH-CH<sub>2</sub>OH (2 equiv)<br/>CH<sub>2</sub>Cl<sub>2</sub>, rt, 15 h<br/>92% (α only)</p> <p>9a only</p> <p>16 examples (1 furanoid), yields 51-97% (α/β usually ≥ 7:1)</p>  |
| J. Beyer, R. Madsen <i>J. Am. Chem. Soc.</i> <b>1998</b> , 120, 12137.  |  |  |

|  |   |  |
|--|---|--|
| <b>Scandium Triflate</b>   |   | <b>Catalyst</b>  |
| <p>Treatment of primary and secondary trialkylsilyl ethers with a catalytic amount (usually 0.5 mol%) of scandium triflate and 5 equivalents of water in acetonitrile provides an efficient and practical method for deprotection.</p> <p>T. Oriyama, Y. Kobayashi, K. Noda <i>Synlett</i>, <b>1998</b>, 1047.</p> | <p>Sc(OTf)<sub>3</sub><br/><b>A</b></p>                   | <p>Alkyl silyl ethers can be cleaved selectively in the presence of phenolic silyl ethers. TMS, TES, and TBS ethers are all cleaved within an hour whereas TIPS and TBDPS require up to 24 h but the yields are 93-98% in all 17 cases examined</p>  |
| <b>RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub></b>   |   | <b>Catalyst</b>  |
| <p>The first example of Rh(I)-catalysed regio- and stereoselective addition of chloroformates to terminal alkynes is reported.</p> <p>R. Hua, S. Shimada, M. Tanaka <i>J. Am. Chem. Soc.</i> <b>1998</b>, 120, 12364.</p>  | <p>RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub><br/><b>A</b></p> | <p>11 examples including alkyl and aryl alkynes; yields generally 62-91%. Regioselectivity 94:6 to 100:0.</p>  |
| <b>Copper(I) iodide</b>  |   | <b>Catalyst</b>  |
| <p>CuI catalyses coupling of enantiopure <math>\alpha</math>-amino acids with aryl halides gives <i>N</i>-aryl-<math>\alpha</math>-amino acids with retention of configuration</p> <p>D. MA, Y. Zhang, J. Yao, S. Wu, F. Tao <i>J. Am. Chem. Soc.</i> <b>1998</b>, 120, 12459.</p>                                 | <p>CuI<br/><b>A</b></p>                                   | <p>26 examples with yields from 0% (serine, glutamic acid and glycine) to 92% (phenylalanine). Aryl bromides and iodides work well but aryl chlorides do not. The reaction tolerates <i>N</i>-methyl groups in the amino acid and MeO, Cl, HO and CO<sub>2</sub>H groups in the arene.</p> |
| <b>(S)-4-Phenyl-2-oxazolidinone</b>  |   | <b>Chiral Auxiliary</b>  |
| <p>The title auxiliary is utilised in the asymmetric synthesis of <math>\beta</math>-amino alcohols. Cleavage of the auxiliary is achieved using Na / NH<sub>3</sub>.</p> <p>T. Tomoyasu, K. Tomooka <i>Synlett</i> <b>1998</b>, 1147.</p>   |   | <p>7 examples (yields 58-85 %, %de = 8-42%).</p>   |
| <b>(S)-4-Phenyl-2-oxazolidinone</b>  |   | <b>Chiral Auxiliary</b>  |
| <p>The title auxiliary mediates the diastereoselective conjugate addition of organocuprates to its <i>N</i>-enoyl derivatives.</p> <p>D. R. Williams, W. S. Kissel, J. J. Li <i>Tetrahedron Lett.</i> <b>1998</b>, 39, 8593.</p>   |   | <p>9 examples (yields 65-99%, %de 67-99%) are described. The title auxiliary gives better yields and diastereoselectivity than the corresponding benzyloxazolidinone.</p>  |

**8-Phenylmenthyl****Chiral Auxiliary**

Auxiliary **A** and its (2*S*)- epimer are utilised in the synthesis of mono- or dialkylated  $\alpha$ -amino acids.

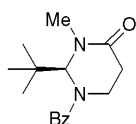
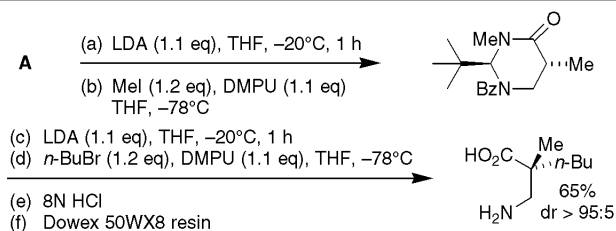
**A**

7 examples (yields 57-89%, %ee  $\geq$  98%).

L. Meyer, J.-M. Poirier, P. Duhamel, L. Duhamel *J. Org. Chem.* **1998**, *63*, 8094.

**1-Benzoyl-2(S)-tert-butyl-3-methylperhydropyrimidin-4-one****Chiral Auxiliary**

**A** represents a masked chiral derivative of  $\beta$ -alanine. Double alkylation of **A** followed by acid hydrolysis affords enantiopure  $\alpha,\alpha$ -dialkylated  $\beta$ -amino acids in good yields.

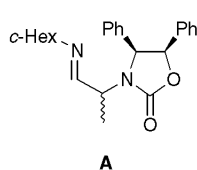
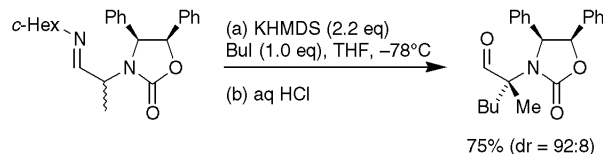
**A**

4 examples (yields 65-84%, %de >95%).

E. Juaristi, M. Balderas, Y. Ramírez-Quirós *Tetrahedron: Asymmetry* **1998**, *9*, 3881.

**(4*R*,5*S*)-Diphenyl-2-oxazolidinone****Chiral Auxiliary**

The cyclohexylimine of propanal bearing the title auxiliary in the  $\alpha$ -position (**A**), undergoes asymmetric alkylation to give  $\alpha,\alpha$ -disubstituted amino aldehydes.

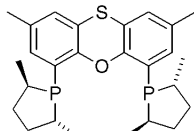
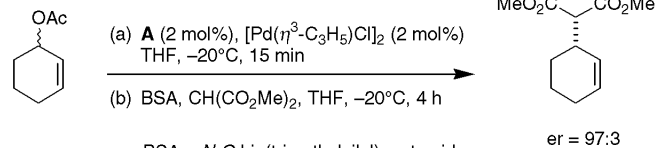
**A**

6 examples (48-75% yields; dr  $\geq$  (0:10))

S. Wenglowky, L. S. Hegedus *J. Am. Chem. Soc.* **1998**, *120*, 12468

**(*R,R*)-Duthixantphospholane****Ligand**

The synthesis and application of **A** in palladium catalysed asymmetric allylic alkylations is reported.

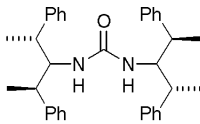
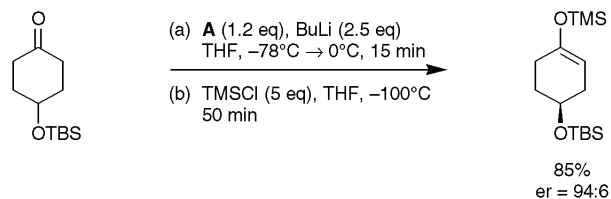
**A**

BSA = *N,O*-bis(trimethylsilyl)acetamide  
11 examples (%ee = 24-97%) and 4 examples with a related ligand (%ee = 66-82%) are reported.

P. Dierkes, S. Ramdeehul, L. Barloy, A. De Cian, J. Fischer, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. A. Osborn *Angew. Chem. Int. Ed.* **1998**, *37*, 3116.

***N,N'*-Di[(*S,S*)-2,4-diphenyl-3-pentyl]urea****Ligand**

The synthesis and application of the novel nitrogen ligand **A** is described.

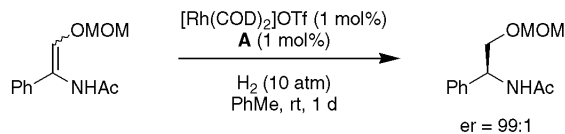
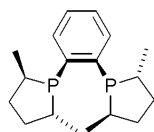
**A**

6 examples (yields 84-91%, %ee = 83-88%) and 1 example of enantioselective alkylation (yield 83%, 81%ee) are reported.

C.-D. Graf, C. Malan, P. Knochel *Angew. Chem. Int. Ed.* **1998**, *37*, 3014.

**(*R,R*)-1,2-Bis-(2,5-dimethylphospholane)benzene [(*R,R*)-Me-DuPhos]****Ligand**

A cationic Rh complex derived from the title ligand mediates the asymmetric hydrogenation of enamides.

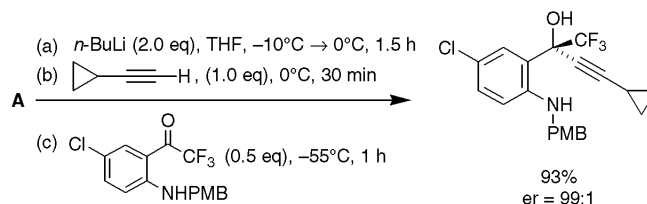
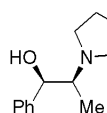


G. Zhu, A. L. Casalnuovo, X. Zhang *J. Org. Chem.* **1998**, *63*, 8100.

9 examples (%ee 95-98%).

**(1*R*,2*S*)-*N*-Pyrrolidinylnorephedrine****Ligand**

**A** mediates a highly enantioselective addition of Li-cyclopropyl acetylide to a *p*-methoxybenzyl-protected ketoaniline.

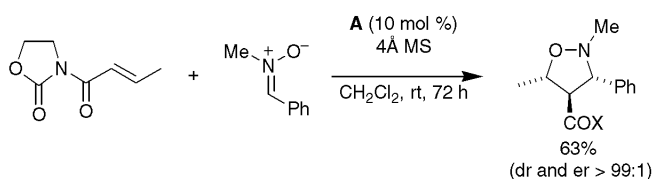
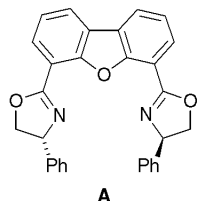


M. E. Pierce, R. L. Parsons, L. A. Radesca, Y. S. Lo, S. Silverman, J. R. Moore, Q. Islam, A. Choudhury, J. M. D. Fortunak, D. Nguyen, C. Luo, S. J. Morgan, W. P. Davis, P. N. Confalone, C. Chen, R. D. Tillyer, L. Frey, L. Tan, F. Xu, D. Zhao, A. S. Thompson, E. G. Corley, E. J. J. Grabowski, R. Reamer, P. J. Reider *J. Org. Chem.* **1998**, *63*, 8536.

1 example. **A** can be recycled without significant loss of optical purity.

**(*R,R*)-4,6-Dibenzofurandiyl-2,2'-bis(4-phenoxazoline) (*R,R*-DBFOX/Ph)****Ligand**

Complexes derived from the title ligand and nickel(II) perchlorate catalyze enantioselective nitron 1,3-dipolar cycloadditions to 3-(2-alkenyl)-2-oxazolidinones. 4Å molecular sieves are essential for high stereoselectivity.

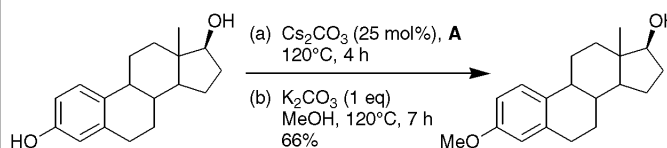
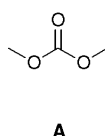


S. Kanemasa, Y. Oderaotshi, J. Tanaka, E. Wada *J. Am. Chem. Soc.* **1998**, *120*, 12355.

14 examples with excellent dr and er in all but one of the cases.

**Dimethyl Carbonate****Reagent**

The title reagent is used in the presence of catalytic cesium carbonate to *O*-methylate phenols. Selective methylation of phenols in the presence of alcohols can be achieved.

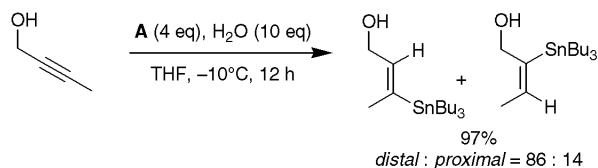
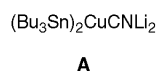


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3 examples (yields 66-100%).

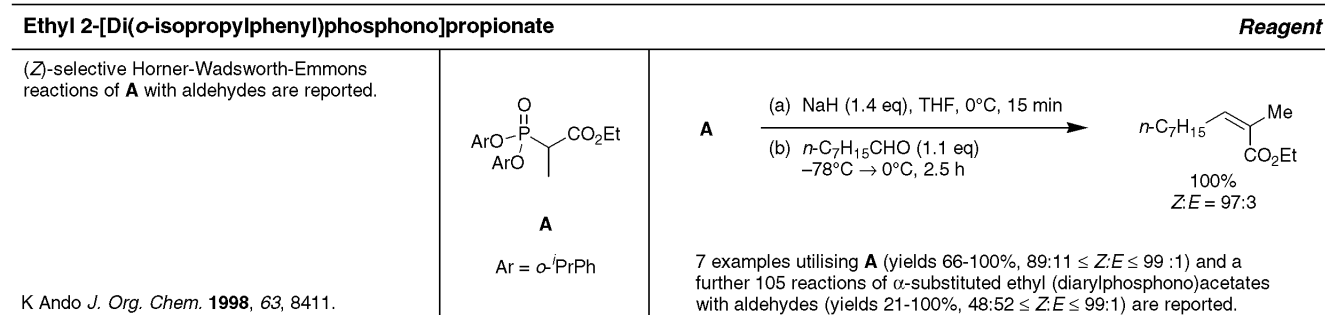
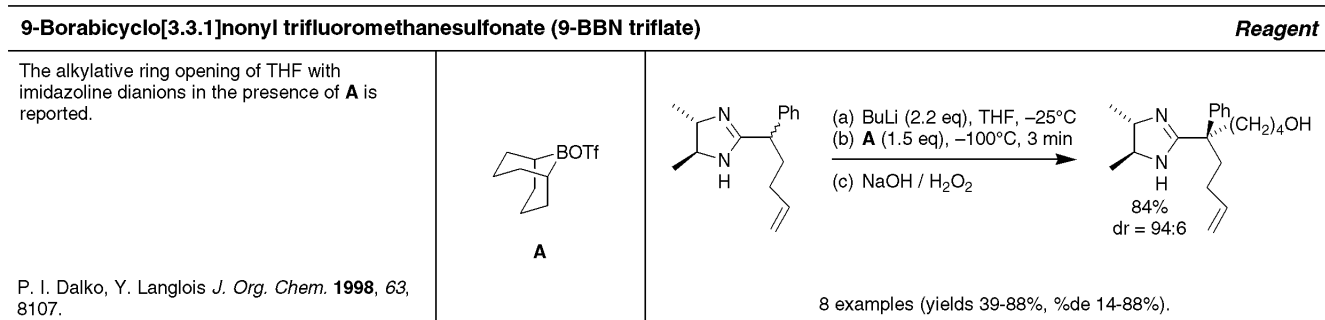
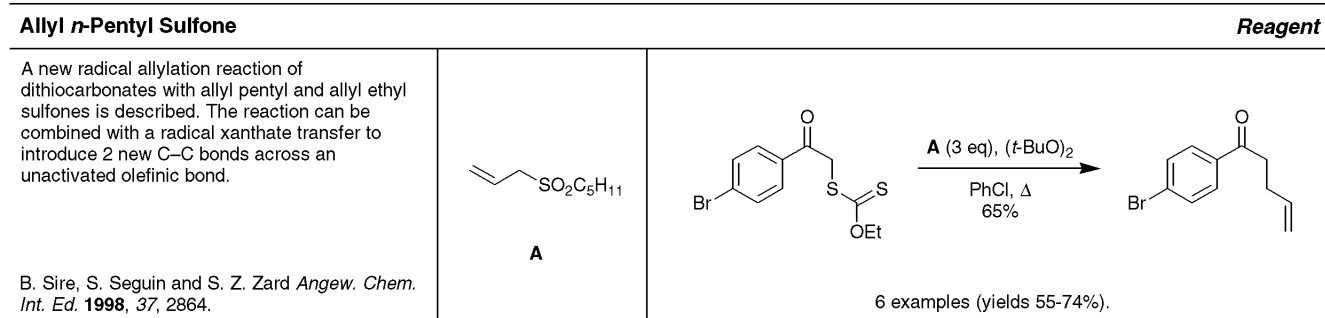
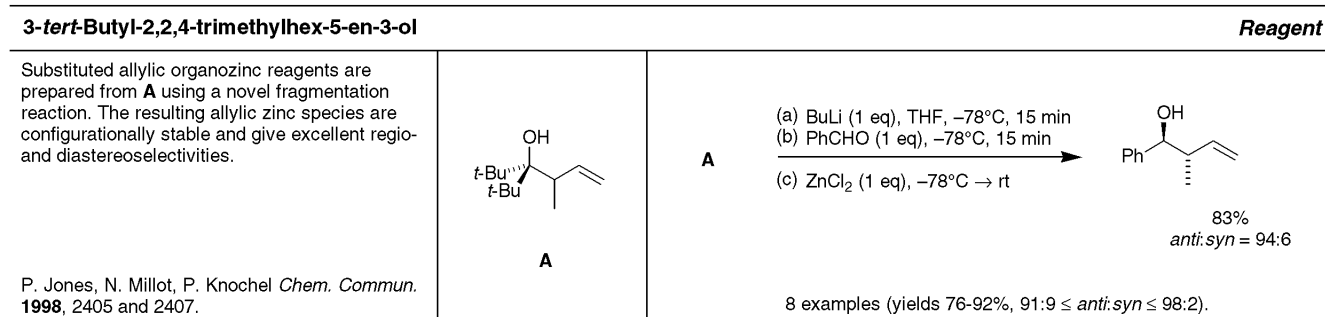
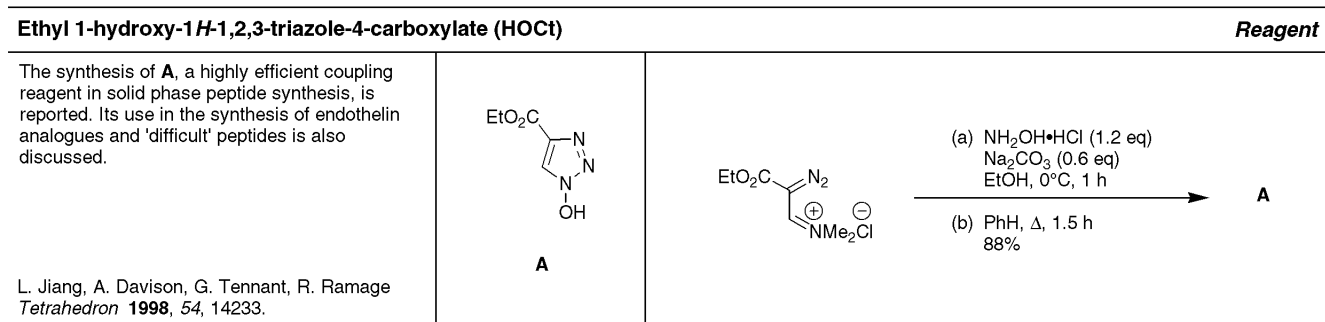
**(*Bu*<sub>3</sub>Sn)<sub>2</sub>CuCNLi<sub>2</sub>****Reagent**

**A** is used in the stannyl cupration of an alkyne. In the presence of a proton source the products are found to be a mixture of *distal* and *proximal* isomers resulting from *cis* addition.



J.-F. Betzer, A. Pancrazi *Synlett* **1998**, 1129.

1 example of addition to an alkyne and 2 examples of addition to enynes (yields 78, 80%) are reported.



|   |   |   |
|---|---|---|
| <b>Allyl acetoacetate</b> <span style="float: right;"><i>Reagent</i></span>   |   |   |
| Pd catalysed regioselective $\beta$ -acetonation- $\alpha$ -allylation of activated olefins utilising <b>A</b> is reported.   |   | <p><b>A</b> (1.2 eq)<br/>Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol%)<br/>THF, rt, 2 h<br/>89%</p> <p>10 examples (yields 19-91%).</p>  |
| J.-G. Shim, H. Nakamura, Y. Yamamoto <i>J. Org. Chem.</i> <b>1998</b> , <i>63</i> , 8470.   |   |   |
| <b>Copper(I) chloride</b> <span style="float: right;"><i>Reagent</i></span>   |   |   |
| <b>A</b> mediates the intramolecular conjugate addition of alkenyltrimethylstannane functions to $\alpha,\beta$ -alkynic esters to give functionalised cyclobutane derivatives. | CuCl<br><b>A</b>                                      | <p><b>A</b> (2.5 eq), AcOH (5.0 eq)<br/>DMF, 0°C, 15 min<br/>85%</p> <p>7 examples (yields 73-95%).</p>   |
| E. Piers, E. M. Boehringer, J. G. K. Yee <i>J. Org. Chem.</i> <b>1998</b> , <i>63</i> , 8642.   |   |   |
| <b>Diisopinocampheyl (Z)-(<math>\gamma</math>-chloroallyl)borane</b> <span style="float: right;"><i>Reagent</i></span>  |   |   |
| Diastereoselective chloroallylboration of $\alpha$ -chiral aldehydes using <b>A</b> or its enantiomer is reported.  |   | <p><b>A</b> (1.5 eq)<br/>THF, -95°C, 4 h<br/>60%, dr = 99:1</p> <p>5 examples using <b>A</b> (yields 56-65%, %de = 22-98%) and 5 examples with the enantiomer of <b>A</b> (yields 55-65%, %de = 70-99%) are reported.</p>   |
| S. Hu, S. Jayaraman, A. C. Oehlschlager <i>J. Org. Chem.</i> <b>1998</b> , <i>63</i> , 8843.  |   |   |
| <b>Chlorotitanium triisopropoxide</b> <span style="float: right;"><i>Reagent</i></span>   |   |   |
| <b>A</b> mediates the coupling of esters or amides with vinyltributylstannane or vinyltrimethylsilane to yield trisubstituted cyclopropylstannanes.                             | CITi(O- <i>i</i> -Pr) <sub>3</sub><br><b>A</b>        | <p>Bu<sub>3</sub>Sn-CH=CH<sub>2</sub> (1 eq)<br/><b>A</b> (1.1 eq)<br/><math>\alpha</math>-C<sub>5</sub>H<sub>9</sub>MgCl (4 eq)<br/>THF, rt, 1 h<br/>51%</p> <p>11 examples (yields 7-71%).</p>  |
| K. Lee, S.-I. Kim, J. K. Cha <i>J. Org. Chem.</i> <b>1998</b> , <i>63</i> , 9135.   |   |   |
| <b>Lithium tri-<i>n</i>-butyl borohydride</b> <span style="float: right;"><i>Reagent</i></span>   |   |   |
| The title reagent mediates the chelation-controlled reduction of $\alpha$ - and $\beta$ -oxygenated ketones.  | Li <sup><i>n</i></sup> Bu <sub>3</sub> BH<br><b>A</b> | <p><b>A</b> (3 eq)<br/>Et<sub>2</sub>O-pentane-CH<sub>2</sub>Cl<sub>2</sub><br/>-78°C, 30 min<br/>syn:anti = 6.5:1</p> <p>8 examples (yields &gt; 70%, %de = 62-&gt;99%) are described. In all cases selectivity for the chelation controlled product is higher than in THF, and compared to use of Zn(BH<sub>4</sub>)<sub>2</sub>.</p> |
| A.-M. Faucher, C. Brochu, S. R. Landry, I. Duchesne, S. Hantos, A. Roy, A. Myles, C. Legault <i>Tetrahedron Lett.</i> <b>1998</b> , <i>39</i> , 8425.                           |   |   |



| Scandium(III) Trifluoromethanesulfonate / Triphenylphosphine  |  | Reagent  |
|---|--|--|
| The title reagent pair mediates the Reformatsky reaction of $\alpha$ -bromo carboxylic acid derivatives with aldehydes. | <p>Sc(OTf)<sub>3</sub></p> <p><b>A</b></p> <p>PPh<sub>3</sub></p> <p><b>B</b></p>                            | <p>62%<br/>syn:anti = 11:89</p> <p>5 examples (yields 0, 9–93, 98:2 <math>\leq</math> syn:anti <math>\leq</math> 11:89) are described.</p>   |
| H. Kagoshima, Y. Hashimoto, K. Saigo<br><i>Tetrahedron Lett.</i> <b>1998</b> , 39, 8465.                                |  |  |
| Triisopropylsilylethynyl Triflate   |  | Reagent  |
| The title reagent undergoes alkylation with a variety of alkyl iodides under photochemical activation.                  | <p>TIPS—C<math>\equiv</math>C—S(=O)(=O)—CF<sub>3</sub></p> <p><b>A</b></p>                                   | <p>72%</p> <p>14 examples (yields 35–84%) are described. Reactions are run at low concentration to minimise polymerisation of <b>A</b>.</p>  |
| J. Xiang, P. L. Fuchs <i>Tetrahedron Lett.</i> <b>1998</b> , 39, 8597.  |  |  |
| Copper(II) Fluoride   |  | Reagent  |
| The title reagent mediates the palladium catalysed cross-coupling of aryl bromides with silylketene acetals.            | <p>CuF<sub>2</sub></p> <p><b>A</b></p>   | <p>81%</p> <p>5 examples (yields 75–95%) are described.</p>  |
| F. Agnelli, G. A. Sulikowski <i>Tetrahedron Lett.</i> <b>1998</b> , 39, 8807.   |  |  |
| N-Boc-3-trichloromethyloxaziridine  |  | Reagent  |
| Synthesis of the title reagent and its use as an electrophilic amination reagent is reported.                           | <p>Cl<sub>3</sub>C—O—N—Boc</p> <p><b>A</b></p>   | <p>56%</p> <p>3 examples (yields 56–100%) of reaction with amine nucleophiles are described. By-products arising from reaction with released chloral are lower than for the corresponding <i>p</i>-cyanobenzyl derivative of <b>A</b>.</p> |
| J. Vidal, J.-C. Hannachi, G. Hourdin, J.-C. Mulatier, A. Collet <i>Tetrahedron Lett.</i> <b>1998</b> , 39, 8845.        |  |  |
| Phenylboronic acid / N-methylmorpholine N-oxide (NMO) / Osmium tetroxide  |  | Reagent  |
| The title compounds mediate the dihydroxylation of polyenes using Narasaka's modification of the Upjohn procedure.      | <p>PhB(OH)<sub>2</sub></p> <p><b>A</b></p> <p>NMO</p> <p><b>B</b></p> <p>OsO<sub>4</sub></p> <p><b>C</b></p> | <p>72%</p> <p>6 examples (yields over 2 steps 29–73%).</p>   |
| A. Gypser, D. Michel, D. S. Nirschl, K. B. Sharpless <i>J. Org. Chem.</i> <b>1998</b> , 63, 7322.                       |  |  |

| <b>Copper(I) iodide</b>   |  | <b>Reagent</b>   |
|---|--|--|
| <p>The title reagent mediates the nucleophilic displacement of (<i>E</i>)-allylic carbamates by Grignard reagents to give (<i>Z</i>)-alkenes.</p>   |  | <p>J. H. Smitrovich and K. A. Woerpel <i>J. Am. Chem. Soc.</i> <b>1998</b>, <i>120</i>, 12998.</p>                                       |
| <p>2 Allylic carbamates and 4 Grignard reagents were used to establish the scope of the reaction. Yields 68-90%. The stereoselectivity is reversed if organolithium reagents are used instead of Grignard reagents.</p>                                   |  |  |
| <b>Titanium Tetrachloride</b>   |  | <b>Reagent</b>   |
| <p><b>A</b> is utilised in the oxygen-directed carbocyclisation of 2,3-epoxy alcohols to achieve a stereoselective construction of polyfunctionalised seven-membered rings by 7-<i>endo-tet</i> ring closure.</p>   |  | <p>C. M. Marson, J. McGregor, A. Khan, T. J. Grinter <i>J. Org. Chem.</i> <b>1998</b>, <i>63</i>, 7833.</p>                              |
| <p>4 examples (yields 0, 42-98%).</p>   |  |  |
| <b>(<i>o</i>-<i>o'</i>-Biphenylenedioxy)methylaluminium</b>   |  | <b>Reagent</b>   |
| <p>Reaction of the title compound with propargylic alcohols gives a propargyloxyaluminium reagent which transfers the alkynyl group to an aldehyde. Owing to the reversible nature of the reaction, transfer requires an electron deficient aldehyde.</p> |  | <p>T. Ooi, T. Miura and K. Maruoka <i>J. Am. Chem. Soc.</i> <b>1998</b>, <i>120</i>, 10790.</p>  |
| <p>From reaction of <b>A</b> with Ph-C≡C-CMe2OH in CH<sub>2</sub>Cl<sub>2</sub> for 30 min at rt</p> <p>6 examples; 42-99% yields. In a few cases catalytic amounts <b>A</b> could be used.</p>   |  |  |
| <b>(<i>R,R</i>)-2-Butyl-4,5-bis(dimethylaminocarbonyl)-1,3-dioxaborolane</b>  |  | <b>Reagent</b>   |
| <p>The title compound, which is prepared from commercial (<i>R,R</i>)-(+)-<i>N,N,N',N'</i>-tetramethyltartaric acid diamide, mediates the enantioselective Simmons-Smith cyclopropanation of allylic alcohols and homoallylic alcohols.</p>               |  | <p>A. B. Charette, H. Juteau, H. Lebel, C. Molinaro <i>J. Am. Chem. Soc.</i> <b>1998</b>, <i>120</i>, 11943.</p>                         |
| <p>17 allylic alcohols, 3 homoallylic alcohols, and 4 dienols were used. Yields generally &gt;80% with &gt;90% ee.</p>  |  |  |
| <b>Tungsten (-)-Menthyl(oxy)(aryl)carbene complex</b>   |  | <b>Reagent</b>   |
| <p>The title complexes undergo asymmetric benzopentaannulation on reaction with alkynyllithiums and methyl triflate.</p>  |  | <p>J. Barluenga, A. A. Trabanco, J. Flórez, J. García-Granda, M.-A. Llorca, <i>J. Am. Chem. Soc.</i> <b>1998</b>, <i>120</i>, 12129.</p> |
| <p>2 examples</p>   |  |  |