## 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, Stephen Brand, John Christopher, Emma Guthrie, Philip Kocienski, Louise Lea, Graham McAllister, Russell McDonald 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, Chemistry A European Journal, Chemistry Letters, European Journal of Organic Chemistry, Helvetica Chimica Acta, Heterocycles, Journal of Organic Chemistry, Journal of the American Chemical Society, Organometallics, Synlett, Synthesis, Tetrahedron, Tetrahedron Asymmetry and Tetrahedron Letters.

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| Scandium(III) Trifluoromethanesulfonate |  |  |
| :--- | :--- | :--- |
| A catalyses the Friedel-Crafts alkylation of a <br> range of aromatic componds with <br> methanesulfonates derived from secondary <br> alcohols. |  |  |
|  |  |  |
| H. Kotsuki, T. Oshisi, M. Inoue Synlett 1998, 255. |  |  |


| Chiral (Salen) Mn(III) Complex / Ammonium Acetate |  |
| :--- | :--- | :--- | :--- |
| The title reagent pair catalyse the asymmetric |  |
| epoxidation of various unfunctionalised olefins by |  |
| hydrogen peroxide. |  |
| P. Pietikäinen Tetrahedron $1998,54,4319$. | 3 examples given (yields $71-90 \%$, \%ee 84-96\%). |


| Microencapsulated Scandium(III) Trifluoromethanesulfonate Catalyst |  |  |
| :---: | :---: | :---: |
| Polystyrene microcapsules (MC) of scandium(III) triflate were found to catalyse a wide variety of reactions (eg. imino aldol, aldol, Mannich, Michael, Friedel-Crafts acylation). The microencapsulated form of the Lewis acid was found to be more active than monomeric material and could be recovered via simple filtration. <br> S. Kobayashi, S. Nagayama J. Am. Chem. Soc. 1998, 120, 2985. | $\mathrm{MC} \mathrm{Sc}(\mathrm{OTf})_{3}$ <br> A | Various reactions are illustrated (yields $>76 \%$ ). In each case no decrease in activity was noted when the catalyst was re-used in subsequent transformations. The simple preparation of the catalyst is described. |


| 1,10-Phenanthroline-Palladium(I) Complex |  | Catalyst |
| :---: | :---: | :---: |
| The title reagent catalyses the tandem cyclisation/hydrosilylation of functionalised 1,6-dienes to afford the corresponding trans cyclopentanes. <br> R. A. Widenhoefer, M. A. DeCarli J. Am. Chem. Soc. 1998, 120, 3805 |  <br> Ar $=3,5$-bis(trifluoromethyl)phenyl |  |


| Tris(dibenzylideneacetone)dipalladium(0)-Chloroform Adduct Catalyst |  |  |
| :---: | :---: | :---: |
| The title reagent catalyses the regio- and stereoselective hydrocarboxylation of arylallenes. <br> M. Al-Masum, Y. Yamamoto J. Am. Chem. Soc. 1998, 120, 3809. | $\mathrm{Pd}_{2} \mathrm{dba}_{3}{ }^{\circ} \mathrm{CHCl}_{3}$ <br> A |  |


| Nickel(II) Acetylacetonate |  | Catalyst |
| :---: | :---: | :---: |
| The title reagent catalyses the homoallylation of benzaldehyde with 1,3-dienes. <br> M. Kimura, A. Ezoe, K. Shibata, Y. Tamaru J. Am. Chem. Soc. 1998, 120, 4033. | $\mathrm{Ni}(\mathrm{acac})_{2}$ <br> A | 10 examples (yields 55-95\%). High 1,2-, 1,3- and 1,2,3-diastereoselectivities are typically obtained ( 1,3 -anti:syn > 15:1, 1:15 < 1,2-anti:syn < 5.2:1). |


| Molybdenum Metathesis Catalyst |  | Catalyst |
| :---: | :---: | :---: |
| The title reagent catalyses the asymmetric ring-closing metathesis (ARCM) of racemic 1,6-dienes. <br> J. B. Alexander, D. S. La, D. R. Cefalo, A. H. Hoveyda, R. R. Schrock J. Am. Chem. Soc. 1998, 120, 4041. |  <br> A <br> $\mathrm{Ar}=2,5$-di isqpropylphenyl | 8 examples (product yields $<5,40-55 \%$, $\%$ ee $<5,45-93 \%$; recovered diene 17-50\%, \%ee <5, 57, 91-99\%). |


| Sodium Lanthanum Tris(binaphthoxide) |  | Catalyst |
| :---: | :---: | :---: |
| The title reagent catalyses the enantioselective Michael addition of thiols to cycloalkenones. Analogous complex B catalyses enantioselective protonation in the Michael addition of thiols to acyclic thioenoates. <br> E. Emori, T. Arai, H. Sasai, M. Shibasaki J. Am. Chem. Soc. 1998, 120, 4043. |  | 6 examples of enantioselective conjugate addition employing A (yields $56-94 \%$, \%ee $56-90 \%$ ). 5 examples of asymmetric protonation in Michael reactions employing B (yields 50-98\%, \%ee 75-93\%). |


| Butylstannonic Acid |  | Catalyst |
| :---: | :---: | :---: |
| The title catalyst mediates the transesterification of esters under mild conditions. <br> R. L. E. Furlán, E. G. Mata, O. A. Mascaretti Tetrahedron Lett. 1998, 39, 2257. |  <br> A | 12 examples (yields $0,46-100 \%$ ) are described. The use of $\mathbf{A}$ in the acetylation / deacetylation of alcohols is also described. |


| N-(1,2,3,4,6,7,8,9-Octahydroa | onyl)ephedrine |  | Chiral Auxiliary |  |
| :---: | :---: | :---: | :---: | :---: |
| The title auxilliary mediates the stereoselective aldol reaction of propionate derivatives. <br> J.-F. Liu, A. Abiko, Z. Pei, D. C. Buske, S. Masamune Tetrahedron Lett. 1998, 39, 1873. |  <br> A |  |   | For: $\mathrm{R}=n-\mathrm{Bu}$ $i-\mathrm{Pr}_{2} \mathrm{NEt}, 95 \%$ syn:anti = 93:7 dr = 97:3 <br> For: $\mathrm{R}=c$-hex $\mathrm{NEt}_{3}, 95 \%$ anti:syn $=98: 2$ $\mathrm{dr}=86: 14$ |


| 17-Diphenylphosphino-2,5,8,11,14-pentaoxabicyclo[13.4.0]nonadeca-15,17,19-triene [igand |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| A Palladium(0) complex derived from the title ligand catalyses the cyanation of aryl halides with sodium cyanide. <br> T. Okano, M. Iwahara, J. Kiji Synlett 1998, 243. |  <br> A |  | $\mathrm{NaCN}(3 \mathrm{eq})$ <br> $\mathrm{PhPdBr}\left[\mathrm{PPh}_{2}(\mathrm{bc}-5)\right]_{2}(0.3 \mathrm{~mol} \%)$A $(0.7 \mathrm{~mol} \%)$ <br> dioxane, ${ }^{2}, 20 \mathrm{~h}$ <br> $91 \%$6 examples (yields $85-93 \%$. |  |


| N-[2-(Diphenylphosphino)benzylidene]-2-phenylethylamine |  | Ligand |
| :---: | :---: | :---: |
| A palladium(0) complex derived from the title ligand effects the syn selective carbostannylation of acetylenes by alkynyl stannanes. <br> E. Shirakawa, H. Yoshida, T. Kurahashi, Y. Nakao, T. Hiyama J. Am. Chem. Soc. 1998, 120, 2975. |  <br> A | 10 examples (yields $52-82 \%$ ). Addition is always exclusively synalthough regioselectivity is highly substrate dependent. |


| (R,R)-4,6-Dibenzofurandiyl-2,2 '-bis(4-phenyloxazoline) (DBFOX/Ph) |  |  | Ligand |
| :---: | :---: | :---: | :---: |
| Various cationic aqua complexes derived from the title ligand and transition metal(II) perchlorates catalyse highly enantioselective Diels-Alder reactions. The catalytic species are reasonably robust and can exhibit extreme chiral amplification. <br> S. Kanemasa, Y. Oderaotoshi, S. Sakaguchi, H. Yamamoto, J. Tanaka, E. Wada, D. P. Curran J. Am. Chem. Soc. 1998, 120, 3074. |  <br> A | The above reaction is extensively investigated in all regards ( $\mathrm{Mg}, \mathrm{Mn}, \mathrm{Fe}, \mathrm{Cu}, \mathrm{Zn}, \mathrm{Co}, \mathrm{Cr}$, Ga metal complexes are all studied). All yields and enantioselectivities are excellent in optimised cases (comparable to the illustrated example). |  $\begin{aligned} & 96 \%, \text { er }>99: 1 \\ & \text { endo: exo }=97: 3 \end{aligned}$ |


| Bis(dihydroquininyl)anthraquinone |  |  | Ligand |
| :---: | :---: | :---: | :---: |
| The title ligands mediate the regioselective aminohydroxylation of cinnamates to phenyl serines with high enantioselectivity. <br> B. Tao, G. Schlingloff, K. B. Sharpless Tetrahedron Lett. 1998, 39, 2507. |  <br> A Alk ${ }^{*}=$ dihydroquininyl B Alk* $=$ quinidinyl |  |  $\begin{gathered} \mathbf{X}=\mathbf{A}: \\ \\ \\ \mathrm{er}=98 \% \\ =98: 2 \end{gathered}$ |



| Phenyldimethylsilyllithium |  | Reagent |
| :---: | :---: | :---: |
| Toluene- $p$-sulfonamides of secondary amines and indoles are cleaved by the title reagent in good yield. <br> I. Fleming, J. Frackenpohl, H. Ila J. Chem. Soc., Perkin Trans 1 1998, 1229. | $\mathrm{PhMe}_{2} \mathrm{SiLi}$ <br> A | 7 examples (yields $72-91 \%$ ). Aziridine toluene- $p$-sulfonamides are opened by $\mathbf{A}$ to give $\beta$-silylethyl sulfonamides. <br> Ts = p-toluenesulfonyl |


| (Trifluoromethyl)trimethylsilane |  |  |  | Reagent |
| :---: | :---: | :---: | :---: | :---: |
| A novel nucleophilic trifluoromethylation of esters with $\mathbf{A}$ is reported. The ester functionality is converted into the trifluoromethylcarbonyl group without formation of double addition products and the reaction is applicable to both enolisable and non-enolisable esters. | Me3SiCF3 <br> A |  | $\xrightarrow[\substack{\text { TBAF }(2.5 \mathrm{~mol} \%) \\ \text { Pentane, }-78^{\circ} \mathrm{C} \rightarrow \mathrm{rt}, 24 \mathrm{~h} \\ 85 \%}]{\mathbf{A}(1.25 \mathrm{eq})}$ |  |
| J. Wiedemann, T. Heiner, G. Mloston, G. K. S. Prakash, G. A. Olah Angew. Chem. Int. Ed. 1998, 37, 820. |  |  | 8 examples (yields 0, 68-95\%). |  |


| Titanocene Dichloride Reagent |  |  |
| :---: | :---: | :---: |
| A 3-step synthesis of indoles is described. Pivotal aryl alkyl dibromide intermediates are realised via regioselective insertion of an olefin into a titanocene benzyne complex. <br> K. Aoki, A. J. Peat, S. L. Buchwald J. Am. Chem. Soc. 1998, 120, 3068. | $\mathrm{Cp}_{2} \mathrm{TiCl}_{2}$ <br> A | Subsequent annulation with $\mathrm{BnNH}_{2}$ under $\mathrm{Pd}(0)$ catalysis, followed by deprotection/ oxidation affords indole products. 10 examples (yields ( $3-4$ steps) 18-54\%). |


| 2,2'-Azobis isobutyronitrile (AIBN) / Tributyltin Hydride |
| :--- | :--- | :--- |
| Tin(IV) radical enolates formed by the action of <br> $\mathrm{Bu}_{3} \mathrm{Sn}^{\circ}$ on $\alpha$-allyloxy enones undergo facile <br> [3,3]-sigmatropic rearrangement. <br> E. . Enholm, K. M. Moran, P. E. Whitley, M. A. |
| Battiste J. Am. Chem. Soc. 1998, 120,3807. |



| (+)- - -Fluoro-2,10-(3,3-dichlorocamphorsultam) |  |  |
| :--- | :--- | :--- |
| The title compound mediates the electrophilic |  |  |
| asymmetric fluorination of enolates. |  |  |
| F. A. Davis, P. Zhou, C. K. Murphy, G. <br> Sundarababu, H. Qi, W. Han, R. M. Przeslawski, <br> B.-C. Chen, P. J. Carroll J. Org. Chem. 1998, 63, <br> 2273. | A | (b) $\mathbf{A}(1.5 \mathrm{eq})$ |


| Samarium(II) lodide / Tetrakis(triphenylphosphine) Palladium |  |  |
| :---: | :---: | :---: |
| The title reagent pair mediates the ring contraction of methyl 5 -vinylpyranosides to 2 -vinyl cyclopentanols with moderate trans selectivity. <br> J. M. Aurrecoechea, B. López Tetrahedron Lett. 1998, 39, 2857. | Sml2 <br> A <br> $\mathrm{Pd}(\mathrm{PPh} 3) 4$ <br> B |  |



| Manganese / Copper(II) Chloride |  | Reagent |
| :---: | :---: | :---: |
| The title reagent pair mediates the homo- and cross-coupling of alkyl halides in aqueous media. <br> J. Ma, T.-K. Chan Tetrahedron Lett. 1998, 39, 2499. | $\begin{gathered} \mathrm{Mn} \\ \mathbf{A} \\ \mathrm{CuCb}_{2} \\ \mathbf{B} \end{gathered}$ | 8 examples of homo-coupling (yields $52-100 \%$ ) and 2 examples of cross-Coupling with an allyl bromide (yields 62, 79\%) are described. |


| Tributyltin Hydride |  |  |
| :--- | :--- | :--- |
| The title reagent mediates the reductive <br> decomplexation of acetylene <br> biscobalthexacarbonyl complexes to form the <br> corresponding cis alkenes. |  |  |
| S. Hosokawa, M . Isobe Tetrahedron Lett. 1998, <br> 39, 2609. |  |  |


| Carbomethoxypropionyl Cyanide Reagent |  |  |
| :---: | :---: | :---: |
| The title reagent reacts regioselectively with ketone enolates to form 1,3-dicarbonyl compounds. <br> Q. Tang, S. E. Sen Tetrahedron Lett. 1998, 39, 2249. |  <br> A |  |


| 1,1,2,2-Tetraphenyldisilane Reagent |  |  |
| :---: | :---: | :---: |
| The title reagent participates in the reduction of alkyl bromides, addition to alkenes and alkylation of heterocyclic bases. <br> O. Yamazaki, H. Togo, S. Matsubayashi, M. Yokoyama Tetrahedron Lett. 1998, 39, 1921. | $\mathrm{Ph}_{2} \mathrm{HSi}-\mathrm{SiHPh}_{2}$ <br> A |  |


| Dichloroindium Hydride |  | Reagent |
| :---: | :---: | :---: |
| Dichloroindium hydride mediates the reduction of aldehydes, ketones and alkyl halides. <br> T. Miyai, K. Inoue, M. Yasuda, I. Shibata, A. Baba Tetrahedron Lett. 1998, 39, 1929. | A | 16 examples (yields $23-99 \%$ ) are described. Nitro, cyano and ester groups are unreactive. |

