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:

Robert Chow, John Christopher, Derek Johnston, Philip Kocienski, Alexander Kuhl, Catherine McCusker, Robert Narquizian, and Sukhjinder Uppal of Glasgow University.

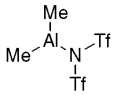
Article Identifier:
1437-210X,E;2000,0,05,0754,0758,ftx,en;X00500SS.pdf

The journals regularly covered by the abstractors are:

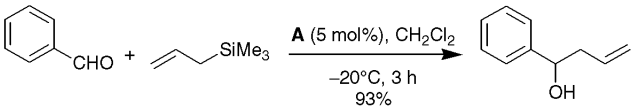
Angewandte Chemie International Edition
Bulletin of the Chemical Society of Japan
Chemical Communications
Chemistry A European Journal
Chemistry Letters
Collection Czechoslovak Chemical Communications
European Journal of Organic Chemistry
Helvetica Chimica Acta
Heterocycles
Journal of the American Chemical Society
Journal of Organic Chemistry
Organic Letters
Organometallics
Perkin Transactions 1
Synlett
Synthesis
Tetrahedron
Tetrahedron Asymmetry and Tetrahedron Letters

Dimethylaluminium Bis(trifluoromethylsulfonyl)amide ***Catalyst***

A and a similar catalyst promote a variety of important C-C bond forming reactions including Michael additions and aldol reactions.



A



16 examples including the use of catalyst **A** in 4 Mukaiyama aldol reactions, 2 cross-aldol reactions and 2 Michael additions (yields 81-99%). 6 chemoselective aldol reactions using a similar catalyst are also reported (yields 67-84%).

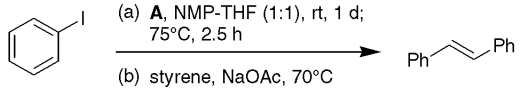
A. Marx, H. Yamamoto *Angew. Chem. Int. Ed.* **2000**, *39*, 178.

Pd colloids ***Catalyst***

Transmission electron microscopic investigations show that the title colloids, generated *in situ* from simple palladium salts such as $Pd(OAc)_2$ or $PdCl_2$, are involved in the catalysis of phosphane-free Heck and Suzuki reactions.

n-$Oct_4N^+(HCO_2^-)$ stabilised Pd colloid

A



1 example to demonstrate the direct involvement of palladium nanoparticles in a Heck reaction is described.

M. T. Reetz, E. Westermann *Angew. Chem. Int. Ed.* **2000**, *39*, 165.

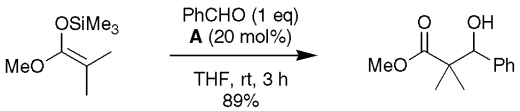
Tris(2,4,6-trimethoxyphenyl)phosphine (TTMPP) ***Catalyst***

A catalyses aldol reactions between ketene silyl acetals and aldehydes.

PAr_3

A

Ar = 2,4,6-$(MeO)_3Ph$



11 examples (yields 48-93%) are reported.

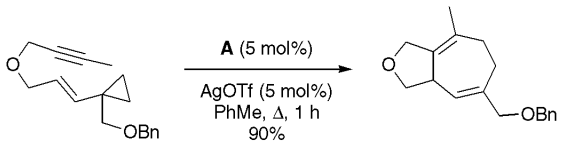
S. Matsukawa, N. Okano, T. Imamato *Tetrahedron Lett.* **2000**, *41*, 103.

Tris(triphenylphosphino)ruthenium(I) Chloride — *Catalyst*

In combination with AgOTf, **A** catalyses the [5+2]-cycloaddition of substituted cyclopropanes.

$RhCl(PPh_3)_3$

A

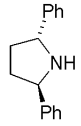


7 examples (yields 73-90%).

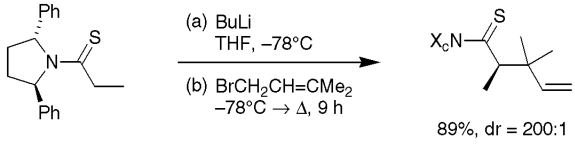
P. A. Wender, A. J. Dyckman, C. O. Husfeld, D. Kadereit, J. A. Love, H. Rieck *J. Am. Chem. Soc.* **1999**, *121*, 10442.

(+)-*trans*-2,5-Diphenylpyrrolidine — *Chiral Auxiliary*

A is used as a chiral auxiliary in asymmetric Thio-Claisen rearrangements.



A

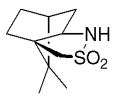


10 examples (yields 81-100%, %de = 77-99%).

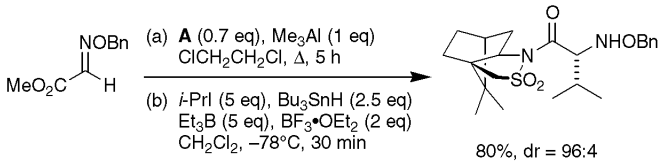
S. He, S. A. Kozmin, V. H. Rawal *J. Am. Chem. Soc.* **2000**, *122*, 190.

(1*R*)-(+)-2,10-Camphorsultam — *Chiral Auxiliary*

The title reagent is used in the asymmetric synthesis of α-amino acids based on diastereoselective carbon radical addition to glyoxylic imine derivatives.



A



8 examples (yields 15-86%, %de = 90-96%) are reported. The α-amino acids are afforded after mild hydrolysis with LiOH.

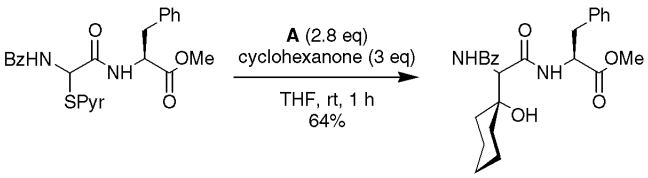
H. Miyabe, C. Ushiro, M. Ueda, K. Yamakawa, T. Naito *J. Org. Chem.* **2000**, *65*, 176.

Samarium Diiodide — *Ligand*

The title reagent mediates the selective alkylation of peptides *via* reductive samariation.

SmI_2

A

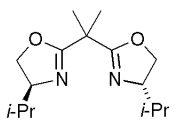


8 examples (yields 30-64%).

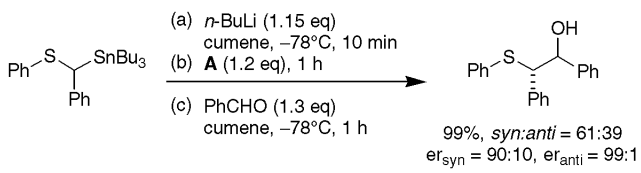
M. Ricci, L. Madariaga, T. Skrydstrup *Angew. Chem. Int. Ed.* **2000**, *39*, 242.

2,2-Bis{2-[(4*S*)-isopropyl-1,3-oxazolinyl]}propane — *Ligand*

The title ligand induces highly stereoselective asymmetric addition reactions of primary α-sulfinyl carbanions.



A



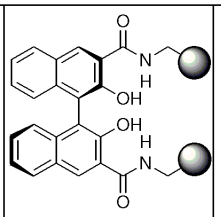
8 examples (yields 44-100%, 38:62 ≤ *syn*:*anti* ≤ 80:20, %ee = 59->99%).

S. Nakamura, R. Nakagawa, Y. Watanabe, T. Toru *Angew. Chem. Int. Ed.* **2000**, *39*, 353.

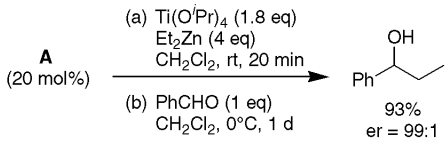
Polymer-supported BINOL ligand — *Ligand*

The title ligand mediates the titanium-catalysed addition of diethylzinc to aldehydes with higher enantioselectivity than the analogous system based on unsupported [Ti(BINOL)(^{i}PrO)$_2$].

X.-W. Yang, J.-H. Sheng, C.-S. Da, H.-S. Wang, W. Su, R. Wang, A. S. C. Chan *J. Org. Chem* **2000**, *65*, 295.



A

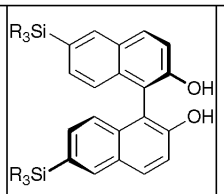


19 examples (yields 52-97%, %ee 57-99%).

(*R*)-6,6′-Bis[tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecaflouorooctyl)silyl]-1,1′-binaphth-2,2′-diol [(R)-FBINOL] — *Ligand*

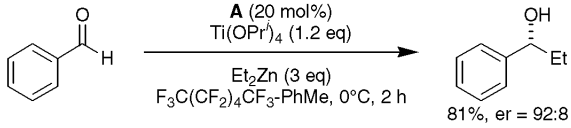
A is used in the Ti-catalysed asymmetric alkylation of aromatic aldehydes with diethylzinc.

Y. Nakamura, S. Takeuchi, Y. Ohgo, D. P. Curran *Tetrahedron Lett.* **2000**, *41*, 57.



A

R = $C_2H_4C_6F_{13}$



1 example (yield 81%) is reported. The recovered catalyst can be reused without compromising yield or enantioselectivity.

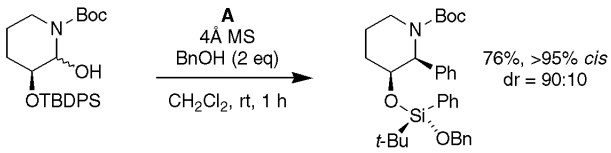
Montmorillonite K10 clay — *Reagent*

A is utilised in a novel aryl migration from silicon to carbon, which forms an efficient approach to the asymmetric synthesis of α-aryl β-hydroxy cyclic amines and silanols.

K. Tomooka, A. Nakazaki, T. Nakai *J. Am. Chem. Soc.* **2000**, *122*, 408.

K10

A



5 examples (yields 36-92%, >95% *cis*, %de at Si = 81->95 %).

Ethylmagnesium Bromide / Bis(cyclopentadienyl)zirconium Dichloride — *Reagent*

The title reagents generate a zirconocene (ethylene) complex which mediates the [1,2]-addition-deoxygenative cyclopropanation of α,β-unsaturated ketones.

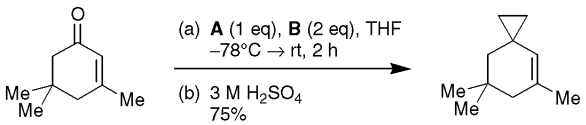
P. Bertus, V. Gandon, J. Szymoniak *Chem. Commun.* **2000**, 171.

EtMgBr

A

Cp_2ZrCl_2

B



8 examples (yields 31-91%).

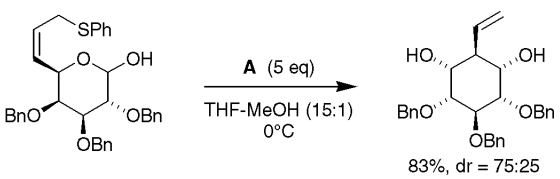
Samarium Diiodide — *Reagent*

The title reagent mediates the stereoselective construction of 5- and 6- member carbocycles from the corresponding carbohydrates.

T. Kan, S. Nara, T. Ozawa, H. Shirahana, F. Matsuda *Angew. Chem. Int. Ed.* **2000**, *39*, 355.

SmI_2

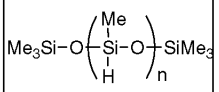
A



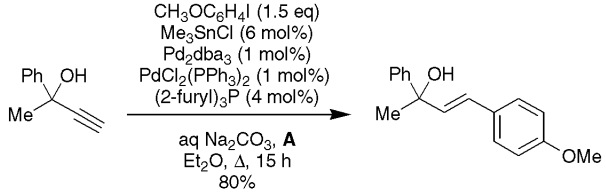
4 examples (yields 71-91%) are reported.

Polymethylhydrosiloxane (PMHS) — *Reagent*

The title reagent is used to regenerate trimethyltin hydride in tin-catalysed Stille cross-couplings.



A



7 examples (yields 75-91%) are reported.

R. E. Maleczka, Jr., W. P. Gallagher, I. Terstiege *J. Am. Chem. Soc.* **2000**, *122*, 384.

Potassium *tert*-Butoxide / *n*-Butyllithium — *Reagent*

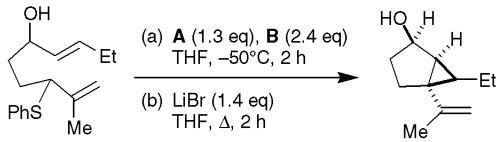
The title reagent pair mediates tandem lithium-ene cyclisation and thiophenoxide expulsion to yield fused vinylcyclopropanes. An allylic lithium oxyanionic group is used to enhance reactivity and control stereochemistry in an anionic cyclisation.

t-BuOK

A

n-BuLi

B



72%, dr = 100:0

12 examples (yields 0, 72-99%) are reported.

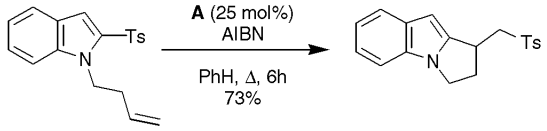
D. Cheng, K. R. Knox, T. Cohen *J. Am. Chem. Soc.* **2000**, *122*, 412.

Phenylseleno-*p*-toluenesulfonate — *Reagent*

The title reagent acts as a radical chain initiator in a cyclisation reaction that produces a new class of fused indoles. It can be used as a less toxic alternative to tri-*n*-butyltin hydride.

TsSePh

A

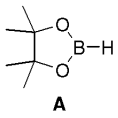


3 examples (yields 64-88%) are reported.

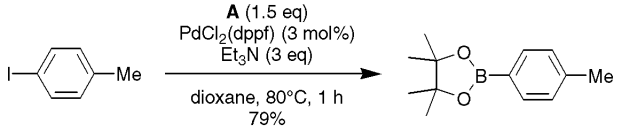
S. Caddick, C. L. Shering, S. N. Wadman *Tetrahedron* **2000**, *56*, 465

Pinacolborane — *Reagent*

The title reagent is used in a palladium-catalysed coupling reaction with aryl halides or triflates to yield arylboronates.



A

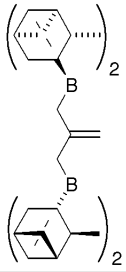


27 examples (yields 43-93%) are reported.

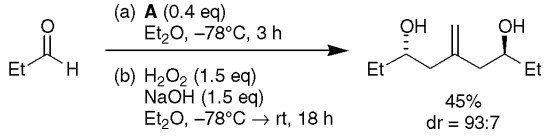
M. Murata, T. Oyama, S. Watanabe, Y. Masuda *J. Org. Chem.* **2000**, *65*, 164.

(*S*,*S*)-1,3-Bis(diisopinocampheylboryl)-2-methylenepropane — *Reagent*

The title reagent is used for the double allylboration of aldehydes under Brown's salt-free conditions to allow the enantioselective preparation of C_2-symmetric 3-methylenepentane-1,5-diols.



A



45%
dr = 93:7
er > 98:2

11 examples (yields 38-58%, %de = 51-90%, %ee > 95%).

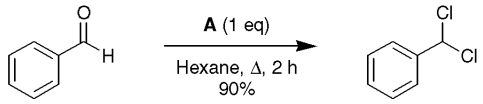
A. G. M. Barrett, D. C. Braddock, P. D. de Koning, A. J. P. White, D. J. Williams *J. Org. Chem.* **2000**, *65*, 375.

Boron Trichloride — *Reagent*

The title reagent is used for chlorination of aromatic aldehydes to give geminal dichlorides.

BCl_3

A



G. W. Kabalka, Z. Wu *Tetrahedron Lett.* **2000**, *41*, 579.

9 examples (yields 76-99%) are reported.

Samarium Diiodide / Samarium(III) Trifluoromethanesulfonate — *Reagent*

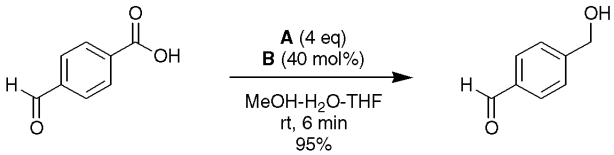
The facile reduction of carboxylic acids in the presence of an aldehyde group to give the corresponding alcohols using the title reagent pair is reported.

SmI_2

A

$Sm(OTf)_3$

B

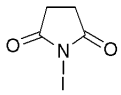


Y. Kamochi, T. Kudo *Tetrahedron Lett.* **2000**, 41, 341.

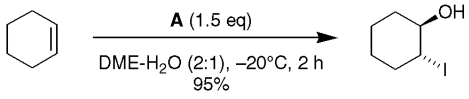
19 examples (yields 49-99%) are reported.

N-Iodosuccinimide (NIS) — *Reagent*

The title reagent is used for the conversion of alkenes into iodohydrins.



A



M. Smietana, V. Gouverneur, C. Mioskowski *Tetrahedron Lett.* **2000**, *41*, 193.

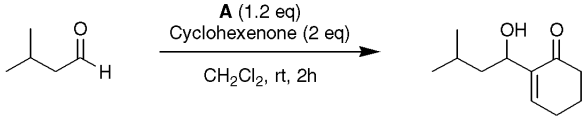
12 examples (yields 0, 80-100%) are reported.

Titanium Tetrachloride — *Reagent*

The title reagent mediates Baylis-Hillman and aldol reactions without the direct use of a Lewis base.

$TiCl_4$

A

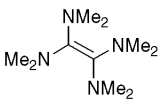


G. Li, H.-X. Wei, J. J. Gao, T. D. Caputo *Tetrahedron Lett.* **2000**, *41*, 1.

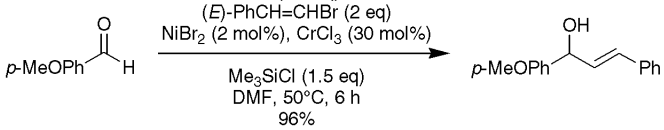
8 examples (yields 47-68%) of Baylis-Hillman reactions and 4 examples (yields 45-82%) of aldol reactions are reported.

Tetrakis(dimethylamino)ethylene (TDAE) — *Reagent*

The title reagent promotes the alkenylation of aldehydes in the presence of catalytic amounts of $NiBr_2$ and $CrCl_3$.



A



M. Kuroboshi, M. Tanaka, S. Kishimoto, K. Goto, M. Mochizuki, H. Tanaka *Tetrahedron Lett.* **2000**, *41*, 81.

5 examples (yields 0-96%) are reported.