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, Emma Guthrie, Derek Johnston, Philip Kocienski, Alexander Kuhl, Robert Narquizian, and Sukhjinder Uppal of Glasgow University.

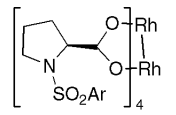
The journals regularly covered by the abstractors are:

Angewandte Chemie International Edition
Bulletin of the Chemical Society of Japan
Chemical Communications
Chemistry A European Journal
Chemistry Letters
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

Article Identifier:
1437-210X,E;2000,0,09,1341,1346,ftx,en;X00900SS.pdf

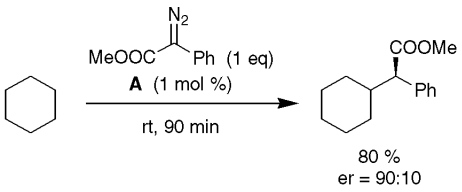
Dirhodium Tetrakis[*S*-(*N*-dodecylbenzenesulfonyl)prolinate] — *Catalyst*

The title reagent catalyses the asymmetric C-H activation of a range of alkanes and tetrahydrofurans by a C-H insertion mechanism.



Ar = *p*-($C_{11}H_{23}$)C_6H_4

A

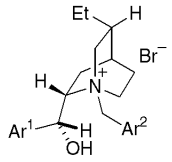


22 examples (yields 20-81%, %ee = 20, 75-97%).

H. M. L. Davies, T. Hansen, M. R. Churchill *J. Am. Chem. Soc.* **2000**, *122*, 3063.

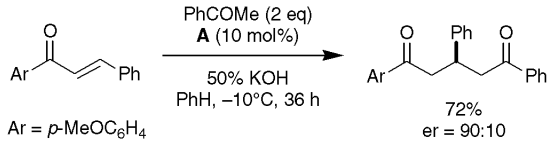
N-(9-Anthracenylmethyl)cinchonidinium Bromide — *Catalyst*

Highly enantioselective Michael reactions are catalysed by chiral ammonium salt **A.** A similar catalyst used in the synthesis of (*S*)-ornithine is reported.



A

Ar^1 = 4-Quinoline
Ar^2 = 9-Anthracene



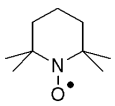
Ar = *p*-$MeOC_6H_4$

1 example (yield 72%, %ee = 80%) is reported.

F.-Y. Zhang, E. J. Corey *Org. Lett.* **2000**, *2*, 1097.

2,2,6,6-Tetramethylpiperidinyl-1-oxy (TEMPO) / Oxone® — *Catalyst*

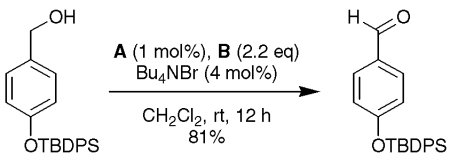
The title reagent pair mediate the mild oxidation of primary and secondary alcohols to aldehydes and ketones in the presence of ammonium quaternary salts.



A

$2KHSO_5.KHSO_4.K_2SO_4$

B



9 examples (yields 37-96%) are reported.

C. Bolm, A. S. Magnus, J. P. Hildebrand *Org. Lett.* **2000**, *2*, 1173.

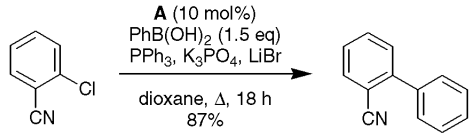
Nickel on Charcoal

Catalyst

The title reagent is used as an alternative to palladium in Suzuki cross-couplings to afford biaryl adducts. Most yields compare favourably with equivalent nickel catalysis under homogenous conditions.

Ni/C

A



B. H. Lipshutz, J. A. Sclafani, P. A. Blomgren *Tetrahedron* **2000**, *56*, 2139.

11 examples (yields 67-92%) are reported.

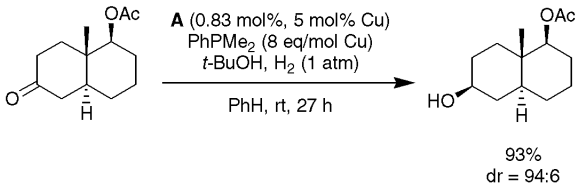
Triphenylphosphine-Stabilised Copper(I) Hydride Complex

Catalyst

The title reagent catalyses the hydrogenation of decalin and steroidal ketones and enones.

$[Ph_3P)CuH]_6$

A



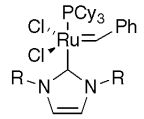
J.-X. Chen, J. F. Daeuble, J. M. Stryker *Tetrahedron* **2000**, *56*, 2789.

6 examples (yields 82-100%, %de = 28-88%).

Ruthenium Carbene Complex with *N,N'*-Bis(mesityl)imidazol-2-ylidene Ligand

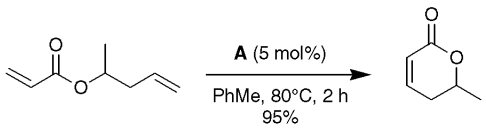
Catalyst

The title reagent constitutes an excellent precatalyst for ring-closing metathesis reactions allowing the formation of tri- and tetrasubstituted cycloalkenes, α,β-unsaturated lactones and lactams.



A

R = Mesityl



A. Fürstner, O. R. Thiel, L. Ackermann, H.-J. Schanz, S. P. Nolan *J. Org. Chem.* **2000**, *65*, 2204.

25 examples (yields 42-98%) are reported.

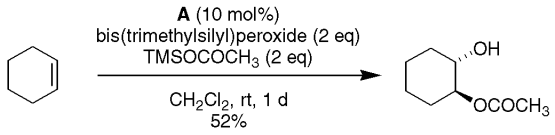
Dichlorotin Oxide

Catalyst

The title reagent catalyses the direct synthesis of *trans* β-azidohydrins and 1,2-diol derivatives from olefins.

$(Cl_2SnO)_n$

A



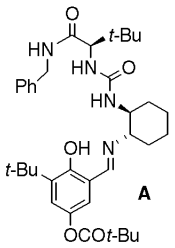
I. Sakurada, S. Yamasaki, M. Kanai, M. Shibasaki *Tetrahedron Lett.* **2000**, *41*, 2415.

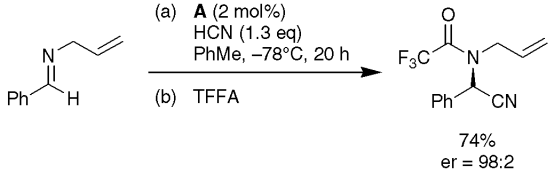
13 examples (yields 34-65%) are reported.

Chiral Salicylaldehyde Imine

Catalyst

The title reagent is used as a catalyst for the asymmetric Strecker reaction.





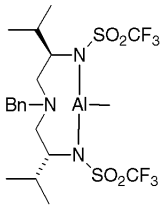
M. Sigman, P. Vachal, E. N. Jacobsen *Angew. Chem. Int. Ed.* **2000**, *39*, 1279.

21 examples (yields 69-99%, %ee = 77-97%) are reported.

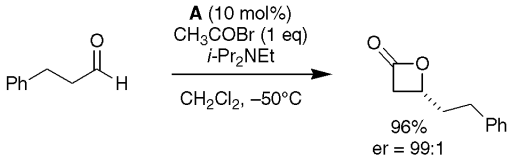
Aluminium(III) Triamine Complex

Catalyst

The title reagent catalyses enantioselective β-lactone synthesis based on asymmetric acyl halide-aldehyde cyclocondensation reactions.



A



7 examples (yields 48, 80-96%, %ee = 91-99%) are reported.

S. G. Nelson, K. L. Spencer *Angew. Chem. Int. Ed.* **2000**, *39*, 1323.

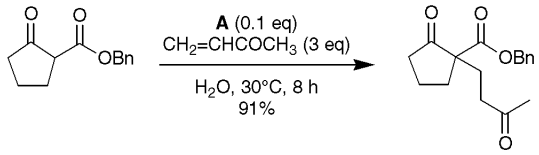
Scandium Tris(dodecyl sulfate) (STDS)

Catalyst

The title reagent catalyses reactions of various β-ketoesters with enones in water to afford the corresponding Michael adducts in high yields.

$Sc(O_3SOC_{12}H_{25})_3$

A



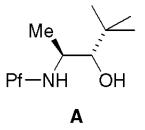
8 examples (yields 68-100%) are reported.

Y. Mori, K. Kakumoto, K. Manabe, S. Kobayashi *Tetrahedron Lett.* **2000**, *41*, 3107.

(3*S*,4*S*)-2,2-Dimethyl-4-[*N*-(9′-phenylfluoren-9′-yl)amino]pentan-3-ol

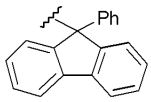
Ligand

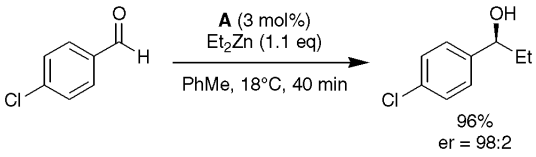
The title ligand mediates the catalytic enantioselective addition of diethylzinc to aldehydes.



A

Pf =





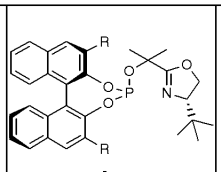
13 examples (yields 82-98%, %ee = 54-98%).

M. R. Paleo, I. Cabeza, F. J. Sardina *J. Org. Chem.* **2000**, *65*, 2108.

(–)-{2-[4′*S*)-(4′-*tert*-Butyloxazolin-2′-yl)]-2-methylethyl}-{(*R*)-[3,3′-bis(4-biphenylyl)](binaphthyl-2,2′-diyl}phosphite

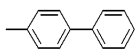
Ligand

The title compound acts as an efficient ligand for the enantioselective copper-catalysed 1,4-addition of organozinc reagents to enones.



A

R =



4 examples (yields 41-95%, %ee = 34-95%) are reported.

I. H. Escher, A. Pfaltz *Tetrahedron* **2000**, *56*, 2879.

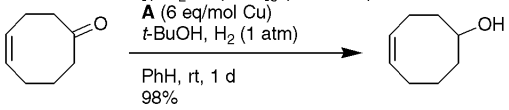
Dimethylphenylphosphine

Ligand

The title reagent stabilises copper(I) hydride complexes to catalyse chemoselective hydrogenation of unsaturated ketones and aldehydes to unsaturated alcohols.

Me_2PPh

A



14 examples (yields 30-99%) are reported.

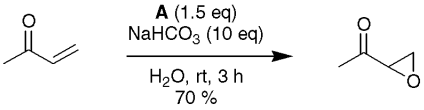
J.-X Chen, J. F. Daeuble, D. M. Brestensky, J. M. Stryker *Tetrahedron* **2000**, *56*, 2153.

Hydrogen Peroxide — *Reagent*

The title reagent is used in bicarbonate-catalysed epoxidation of alkenes.

H_2O_2

A



H. Yao, D. E. Richardson *J. Am. Chem. Soc.* **2000**, *122*, 3220.

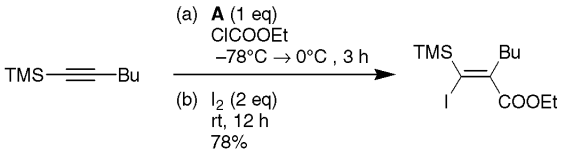
13 examples (yields 20-99%) are reported.

Dicyclopentadienyldiethylzirconium — *Reagent*

The title reagent is used along with chloroformate for the metallo-esterification of alkynes in the preparation of highly substituted propenoates.

Cp_2ZrEt_2

A

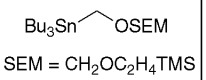


T. Takahashi, C. Xi, Y. Ura, K. Nakajima *J. Am. Chem. Soc.* **2000**, *122*, 3228.

13 examples (yields 44-94%) are reported.

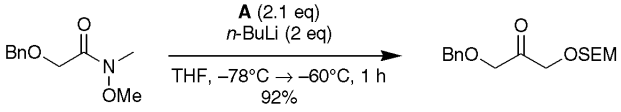
Tri-*n*-butyl[2-(trimethylsilyl)-ethoxymethoxymethyl]stannane — *Reagent*

The title reagent is a protected precursor of a hydroxymethyl anion which reacts with various carbonyl and carboxyl electrophiles.



SEM = $CH_2OC_2H_4TMS$

A



E. Fernandez-Megia, S. V. Ley *Synlett* **2000**, 455.

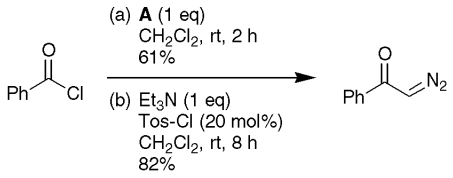
11 examples (yields 25, 66-99%) are reported.

N-Isocyanotriphenyliminophosphorane — *Reagent*

The title reagent is used for the conversion of acyl chlorides into the corresponding α-diazoketones.

$CN\text{-}N{=}PPh_3$

A

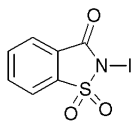


E. Aller, P. Molina, A. Lorenzo *Synlett* **2000**, 526.

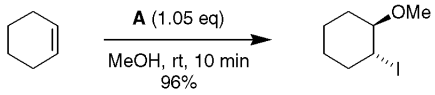
8 examples (yields 23-74% over 2 steps) are reported.

N-Iodosaccharin — *Reagent*

The title reagent is used for the iodination of alkenes and ativated aromatics.



A



D. Dolenc *Synlett* **2000**, 544.

16 examples (yields 30-97%) are reported.

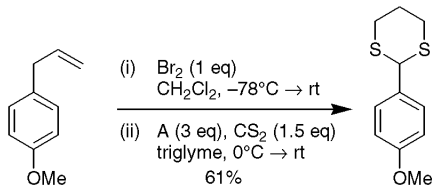
Sodium Borohydride — *Reagent*

The title reagent is used along with carbon disulfide in a one-pot direct transformation of 1,*n*-alkyl dihalides into 1,3-dithianes and -dithiepines.

Y. Wan, A. N. Kurchan, L. A. Barnhurst, A. G. Kutateladze *Org. Lett.* **2000**, *2*, 1133.

$NaBH_4$

A

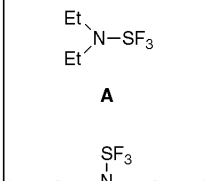


6 examples (yields 36-83%) are reported.

Diethylaminosulfur Trifluoride (DAST) / Bis(2-Methoxyethyl)aminosulfur Trifluoride (Deoxo-Fluor) — *Reagent*

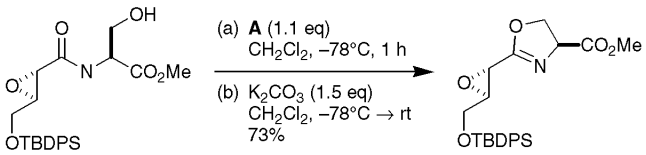
The title reagents mediate the cyclisation of highly functionalised β-hydroxy amides to oxazolines. The one-pot synthesis of oxazoles from β-hydroxy amides is also described.

A. J. Phillips, Y. Uto, P. Wipf, M. J. Reno, D. R. Williams *Org. Lett.* **2000**, *2*, 1165.



A

B



22 examples with **A** (yields 27-92%) and 16 examples with **B** (yields 49-91%) are reported.

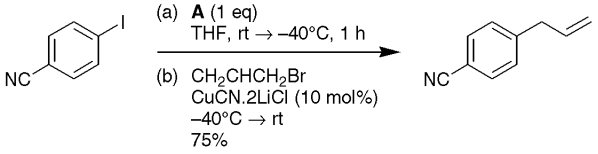
iso-Propylmagnesium Bromide — *Reagent*

The title reagent is used to form polyfunctional magnesium reagents which undergo various copper-catalysed reactions such as 1,4-additions. Magnesium reagents formed on solid phase are also reported.

M. Rottländer, L. Boymond, L. Bérillon, A. Leprêtre, G. Varchi, S. Avolio, H. Laaziri, G. Quéguiner, A. Ricci, G. Cahiez, P. Knochel *Chem. Eur. J.* **2000**, *6*, 767.

i-PrMgBr

A

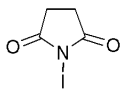


9 examples (yields 72-95%) are reported.

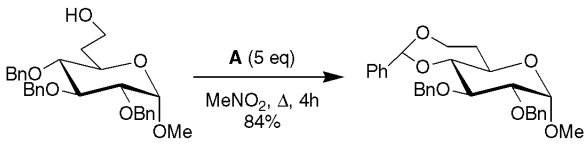
N-Iodosuccinimide — *Reagent*

The title reagent is used for the deprotection of benzyl ethers or the selective protection of alcohols next to benzyl ethers to form their benzylidene equivalents.

J. Madsen, C. Viuf, M. Bols *Chem. Eur. J.* **2000**, *6*, 1140.



A



5 examples (yields 27-84%) are reported.

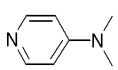
Tributylphosphine / 4-(Dimethylamino)pyridine (DMAP) — *Reagent*

The title reagent pair mediates the transesterification of 2,2,2-trihaloethyl esters.

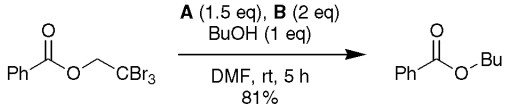
J. J. Hans, R. W. Driver, S. D. Burke *J. Org. Chem.* **2000**, *65*, 2114.

PBu_3

A



B



13 examples (yields 11, 44-81%) are reported.

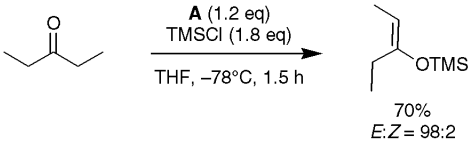
Lithium *tert*-Butyltritylamide (LTBTA)

Reagent

The title reagent acts as a superhindered base.

$(t\text{-Bu})(Ph_3C)NLi$

A



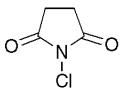
J. Busch-Peterson, E. J. Corey *Tetrahedron Lett.* **2000**, *41*, 2515.

10 examples (yields 56-85%, 2:98 ≤ *E*:*Z* ≤ 98 :2).

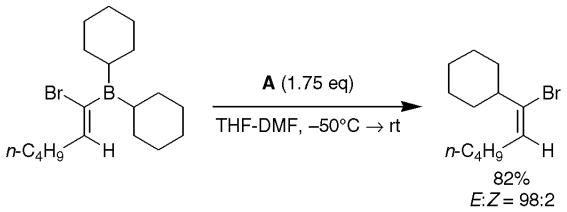
N-Chlorosuccinimide

Reagent

The title reagent is used to convert [(*Z*)-1-bromo-1-alkenyl]dialkylboranes to provide1,2-disubstituted (*E*)-vinyl bromides stereoselectively.



A



M. Hoshi, K. Shirakawa *Tetrahedron Lett.* **2000**, *41*, 2595.

8 examples (yields 41-82%, *E*:*Z* = 98:2).

Bis(triphenylphosphino)dichloropalladium / Copper Iodide

Reagent

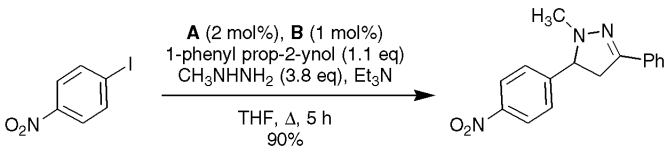
The title reagent pair is used for the coupling-isomerisation sequence of a haloarene, a propargyl alcohol and a hydrazine to form 3,5-disubstituted 2-pyrazolines.

$(Ph_3P)_2PdCl_2$

A

CuI

B



T. J. J. Muller, M. Ansorge, D. Aktah *Angew. Chem. Int. Ed.* **2000**, *39*, 1253.

4 examples (63-90%) are reported.

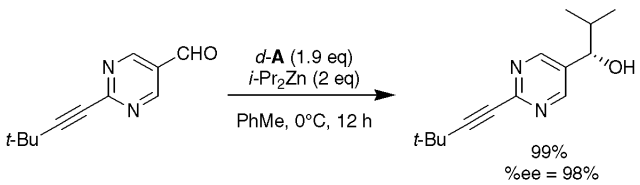
Sodium Chlorate

Reagent

d- or *l*- crystals of the title reagent are used for the asymmetric synthesis of pyrimidylalkanols.

$NaClO_3$

A



I. Sato, K. Kadowaki, K. Soai *Angew. Chem. Int. Ed.* **2000**, *39*, 1510.

2 examples (yields 98 and 99%, %ee = 98%) are reported.

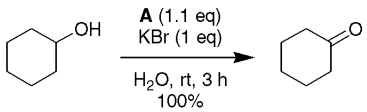
Iodosobenzene

Reagent

The title reagent is used for the oxidation of alcohols. In certain cases, KBr is necessary for activation.

PhI=O

A



H. Tohma, S. Takizawa, T. Maegawa, Y. Kita *Angew. Chem. Int. Ed.* **2000**, *39*, 1306.

14 examples (yields 76-100%) are reported.