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.

The journals regularly covered by the abstractors are:

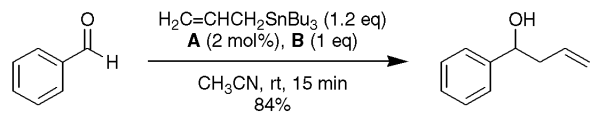
Angewandte Chemie International Edition
Bulletin of the Chemical Society of Japan
Chemical Communications
Chemistry A European Journal
Chemistry Letters
European Journal of Organic Chemistry
Helvetica Chimica Acta
Heterocycles
Journal of the American Chemical Society
Journal of Organic Chemistry
Organometallics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

Ytterbium Trifluoromethanesulfonate / Benzoic acid — ***Catalyst***

The title reagent pair catalyse the allylation of aldehydes with allyltributyltin in acetonitrile.

$Yb(OTf)_3$ **A**

$PhCO_2H$ **B**



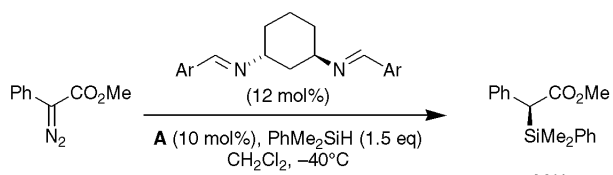
9 examples (yields 68-96%) are reported.

H. C. Aspinall, N. Greeves, E. G. McIver *Tetrahedron Lett.* **1998**, *39*, 9283.

Copper(I) Triflate — ***Catalyst***

In the presence of a chiral Schiff base, the title reagent catalyses the asymmetric carbenoid insertion of methyl aryl acetates into the silicon-hydrogen bonds of silanes.

CuOTf **A**

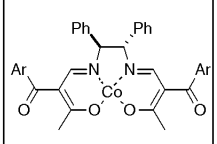


5 examples (yields 45-82%, %ee = 40-84%).

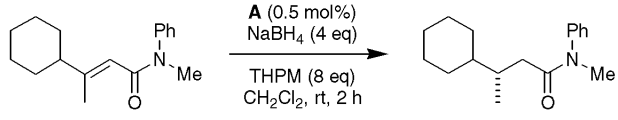
L. A. Dakin, S. E. Schaus, E. N. Jacobsen, J. S. Panek *Tetrahedron Lett.* **1998**, *39*, 8947.

Chiral Cobalt(II) Complex — ***Catalyst***

Enantioselective 1,4-reduction of α,β-unsaturated carboxamides catalysed by the title compound is achieved in high yield and excellent selectivity.



Ar = mesityl **A**



99%, er = 96:4

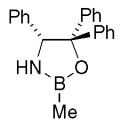
12 examples (yields 69-99%, %ee = 49-91%).

THPM=Tetrahydropyran-2-methanol

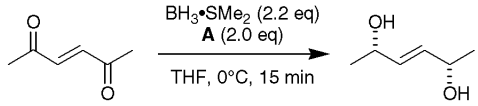
T. Yamada, Y. Ohtsuka, T. Ikeno *Chem. Lett.* **1998**, 1129.

(*R*)-*B*-Methyl-4,5,5-triphenyl-1,3,2-oxazaborolidine — *Catalyst*

The title compound catalyses the borane-mediated reduction of symmetric diketones in high yield and with excellent selectivity.



A



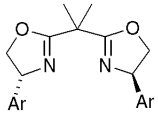
98%, *dl*:*meso* = 86:14
er = 99:1

J. Bach, R. Berenguer, J. Garcia, M. López, J. Manzanal, J. Vilarrasa *Tetrahedron* **1998**, *54*, 14947.

10 examples with both unsaturated and saturated diketones (yields 75-98%, 93:7 ≤ *dl*:*meso* ≤ 58:42, %ee = 40-99%) are described.

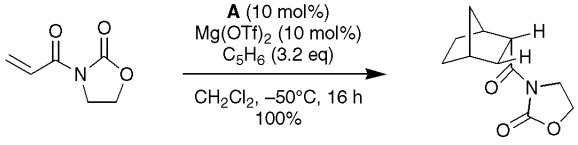
2,2-*Bis*{2-[(4*R*)-(2′-naphthyl)-1,3-oxazolinyl]}propane — *Catalyst*

The title compound catalyses the asymmetric Diels-Alder reaction between *N*-alkenoyl oxazolidin-2-one derivatives and cyclopentadiene with high enantioselectivity.



A

Ar = 2-Napth



100%
endo:*exo* 90:10
er_{endo} = 97:3

S. Crosignani, G. Desimoni, G. Faita, P. Righetti *Tetrahedron* **1998**, *54*, 15721.

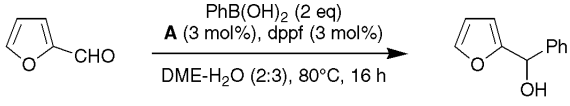
2 examples (yields 100%, *endo*:*exo* = 90:10 and 88:12, $\%ee_{endo}$ = 94, 92%).

(Acetylacetonato)dicarbonylrhodium(I) — *Catalyst*

The rhodium catalysed addition of organoboronic acids to aldehydes is reported.

[Rh(acac)(CO)$_2$]

A



M. Sakai, M. Ueda, N. Miyaura *Angew. Chem. Int. Ed.* **1998**, *37*, 3279.

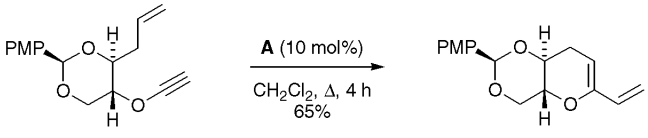
18 examples (yields 0, 43-99%).

Benzylidene-bis(tricyclohexylphosphine)dichlororuthenium — *Catalyst*

Ring-closing enyne metathesis is used to prepare alkenyl substituted six- and seven membered cyclic enol ethers in moderate to good yield.

$Cl_2Ru(PCy_3)_2CHPh$

A



J. S. Clark, G. P. Trevitt, D. Boyall, B. Stammen *Chem. Commun.* **1998**, 2629.

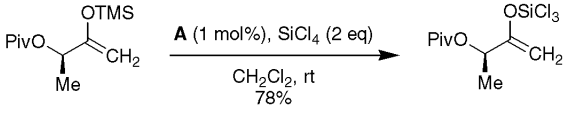
5 examples (yields 20-77%).

Mercury(II) Acetate — *Catalyst*

The title compound catalyses transsilylation from trimethylsilyl to trichlorosilyl enol ethers.

$Hg(OAc)_2$

A

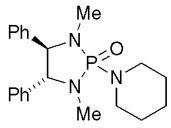


S. E. Denmark, R. A. Stavenger, S. B. D. Winter, K.-T. Wong, P. A. Barsanti *J. Org. Chem.* **1998**, *63*, 9517.

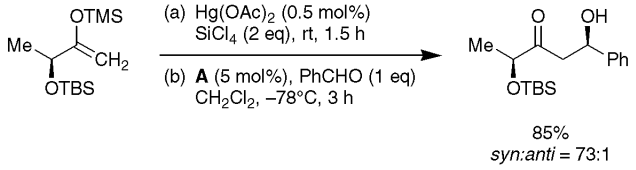
14 examples (yields 60-83%).

Homochiral Phosphoramide Lewis Base ***Catalyst***

A catalyses the highly 1,4-*syn* selective aldol addition of trichlorosilyl enolates to aldehydes.



A



4 examples (yields 77-85%, 6:1 ≤ *syn:anti* ≤ 73:1).

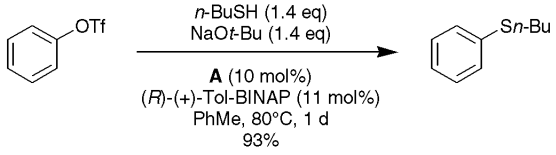
S. E. Denmark, R. A. Stavenger *J. Org. Chem.* **1998**, *63*, 9524.

Palladium(II) Acetate ***Catalyst***

The title compound catalyses the synthesis of aryl sulfides from aryl triflates.

$Pd(OAc)_2$

A

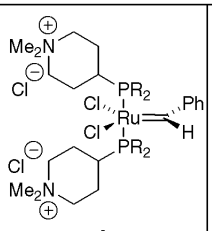


9 examples (yields 54-93%).

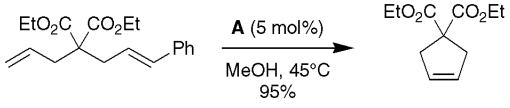
N. Zheng, J. C. McWilliams, F. J. Fleitz, J. D. Armstrong III, R. P. Volante *J. Org. Chem.* **1998**, *63*, 9606.

Benzylidene-bis[*N,N*-dimethyl-4-piperidinium-dicyclohexylphosphine]dichlororuthenium ***Catalyst***

The title compound catalyses ring-closing metathesis in methanol or water.



A
R = *c*-C_6H_9



8 examples (yields 5, 55->95%).

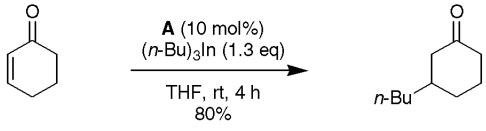
T. A. Kirkland, D. M. Lynn, R. H. Grubbs *J. Org. Chem.* **1998**, *63*, 9904.

Bis(1,5-cyclooctadiene)nickel(0) ***Catalyst***

The title compound catalyses the conjugate addition of triorganoindium compounds to α,β-unsaturated systems.

$Ni(COD)_2$

A

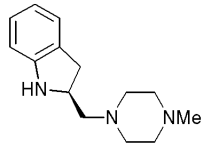


10 examples (yields 50-88%).

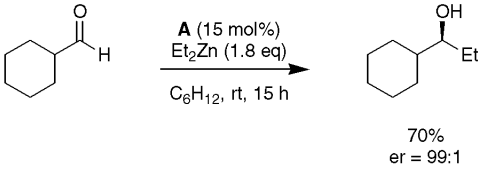
I. Pérez, J. Pérez Sestelo, M. A. Maestro, A. Mouriño, L. A. Sarandeses *J. Org. Chem.* **1998**, *63*, 10074.

(*S*)-2-(4-Methylpiperazin-1-ylmethyl)indoline ***Catalyst***

The title compound catalyses the enantioselective addition of dialkylzincs to aldehydes.



A



8 examples (yields 67-91%, %ee 59-97%)

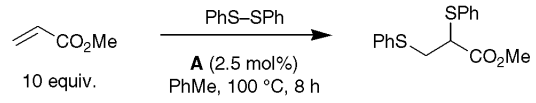
M. Asami, H. Watanabe, K. Honda, S. Inoue *Tetrahedron: Asymmetry* **1998**, *9*, 4165.

Cp*RuCl(cod) — *Catalyst*

The first addition of organic disulfides to alkenes catalysed by the title compound enables the rapid synthesis of *vicinal*-dithioethers.

Cp*RuCl(cod)

A



T. Kondo, S. Uenoyama and T. Mitsudo *J. Am. Chem. Soc.* **1999**, *121*, 482.

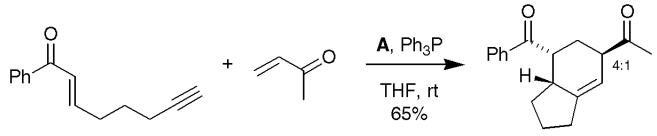
Ethylene, 6 terminal alkenes and norbornene were substrates giving adducts in 55-95% yield. RS–SR where R = Ph, Bu, Me.

$Ni(COD)_2$ — *Catalyst*

The title compoound catalyses the [2+2+2] cycloaddition between an alkynyl enone and an electron-deficient alkene.

$Ni(COD)_2$

A



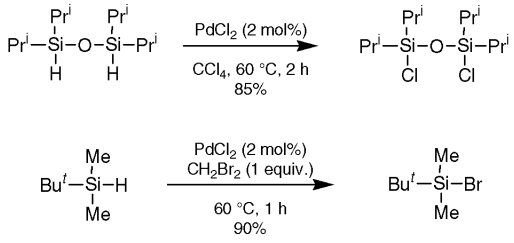
J. Seo, H. M. P. Chui, M. J. Heeg and J. Montgomery *J. Am. Chem. Soc.* **1999**, *121*, 476.

5 examples (yields 17-75%). Substitution on either of the enone moieties depresses the yield.

Palladium(II) Chloride — *Catalyst*

The title compound catalyses the conversion of silanes to halosilanes in halocarbon solvents. Two examples reported.

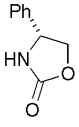
$PdCl_2$



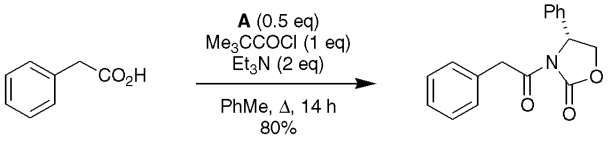
C. Ferreri, C. Constantino. R. Romeo, C. Chatgilialoglu *J. Am. Chem. Soc.,* **1999**, 40, 1197.

(*R*)-4-Phenyl-2-oxazolidinone — *Chiral Auxiliary*

A novel method for the *N*-acylation of 2-oxazolidinone chiral auxiliaries with acids in the presence of pivaloyl chloride and triethylamine is described.



A

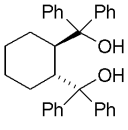


M. Prashad, H.-Y. Kim, D. Har, O. Repic, T. J. Blacklock *Tetrahedron Lett.* **1998**, *39*, 9369.

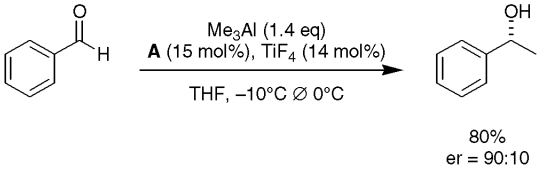
27 examples (yields 14, 44-93%) utilising **A** and 2 other auxiliaries are described.

(1*R*,2*R*)-Cyclohexane-1,2-diphenylmethanol — *Ligand*

The title ligand is utilised in the Ti(IV)-catalysed asymmetric addition of trimethylaluminium to aldehydes.



A



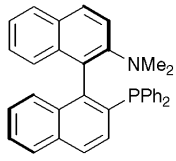
B. L. Pagenkopf, E. M. Carreira *Tetrahedron Lett.* **1998**, *39*, 9593.

12 examples (yields 41-93%, %ee = 54-85%) are reported.

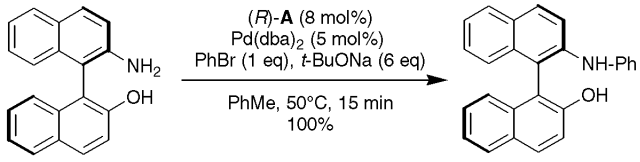
2-Amino-2′-diphenylphosphino-1,1′-binaphthyl (MAP)

Ligand

The title compound exhibits a dramatic accelerating effect on the Pd(0)-catalysed Hartwig-Buchwald *N*-phenylation of an amino alcohol and a diamine.



A



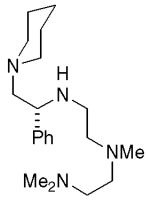
Synthesis of **A** and 2 examples of *N*-phenylation (yields 100%) are described.

S. Vyskocil, M. Smrcina, P. Kocovsky *Tetrahedron Lett.* **1998**, *39*, 9289.

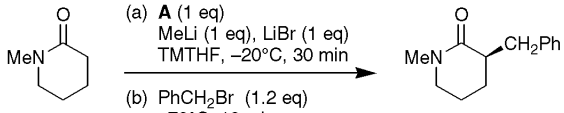
N-[(2*S*)-6,9-Dimethyl-2-phenyl-3,6,9-triazadecyl]piperidine

Ligand

A in the presence of lithium bromide is utilised in the enantioselective alkylation of lactams and lactones with active alkylating agents in non-chelating solvents.



A



64%, er = 99:1

11 examples (yields 7-76%, %ee = 68-98%).

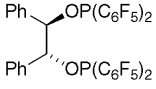
TMTHF = 2,2,5,5-tetramethyltetrahydrofuran

J. Matsuo, S. Kobayashi, K. Koga *Tetrahedron Lett.* **1998**, *39*, 9723.

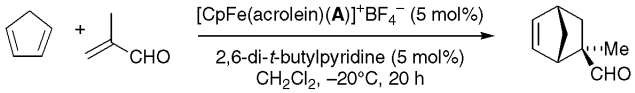
(*R,R*)-1,2-Diphenyl-1,2-[di-(pentafluorophenyl)-phosphanoxy]ethane

Ligand

Ligand **A** (BIPHOP-F) derived from (*R,R*) or (*S,S*)-hydrobenzoin is reported. The ligand is effective in the Fe(II) catalysed Diels Alder reaction of α,β-enals with dienes.



A



69%
er = 99:1
endo:*exo* = 98:2

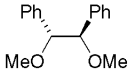
5 examples (yields 44-86%, %ee = 85-99%).

M. E. Bruin, E. P. Kündig *Chem. Commun.* **1998**, 2635.

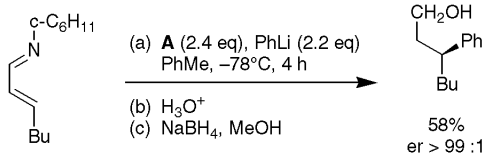
(1*R*,2*R*)-1,2-Dimethoxy-1,2-diphenylethane

Ligand

A mediates the enantioselective conjugate addition of organolithiums to naphthaldehyde imine and cyclic and acyclic α,β-unsaturated aldimines.



A



58%
er > 99 :1

9 examples using **A** (yields 19-82%, %ee = 59->99%) and 6 examples using (2*S*,3*S*)-2,3-dimethoxybutane (yields 42-80%, %ee = 80-94%) are reported.

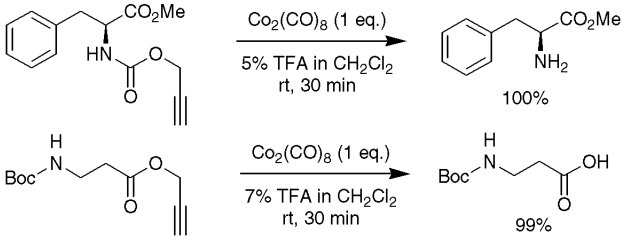
M. Shindo, K. Koga, K. Tomioka *J. Org. Chem.* **1998**, *63*, 9351.

Dicobalt Octacarbonyl

Protecting Group

Propargyloxycarbonyl (Proc) groups and propargyl esters are inert to TFA and Lewis acids but are cleaved by treatment with 5% TFA in dichloromethane in the presence of 1 eq. of the title compound.

$Co_2(CO)_8$



Y. Fukase, K. Fukase, S. Kusumoto *Tetrahedron Lett.* **1999**. *40*, 1169.

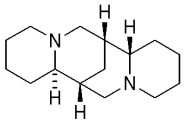
sec-Butyllithium / (–)-sparteine — *Reagent*

The title reagent pair induces the enantioselective carbanion cyclization of (*E*)-6-phenyl-5-hexenyl carbamates to afford *trans*-1,2-disubstituted cyclopentane derivatives.

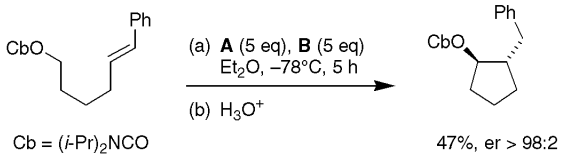
K. Tomooka, N. Komine, T. Sasaki, H. Shimizu, T. Nakai *Tetrahedron Lett.* **1998**, *39*, 9715.

s-BuLi

A



B



2 examples (yields 40, 47%, %ee > 95%) are described.

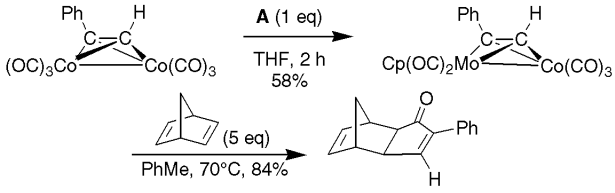
Sodium Cyclopentadienyl)tricarbonylmolybdate — *Reagent*

A is used to form mixed Co/Mo alkyne complexes which are used to facilitate cyclopentenone formation, in an asymmetric variant of the Pauson-Khand reaction.

D. T. Rutherford, S. D. R. Christie *Tetrahedron Lett.* **1998**, *39*, 9805.

$Na[CpMo(CO_3)]$

A

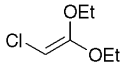


8 examples of Pauson-Khand reactions with both Norbornene and Norbornadiene (yields 32-97%) are reported.

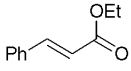
1,1,-Diethoxy-2-chloroethene — *Reagent*

Di-*tert*-butylbiphenyl (DBB) catalysed lithiation of **A** and condensation with a variety of carbonyl compounds is reported. Formation and reaction of 2-methyl-4-ethoxy butadienyl lithium is also described.

M. Si-Fodil, H. Ferreira, J. Gralak, L. Duhamel *Tetrahedron Lett.* **1998**, *39*, 8975.



A

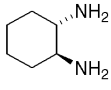


20 examples (yields 0, 50-100 %).

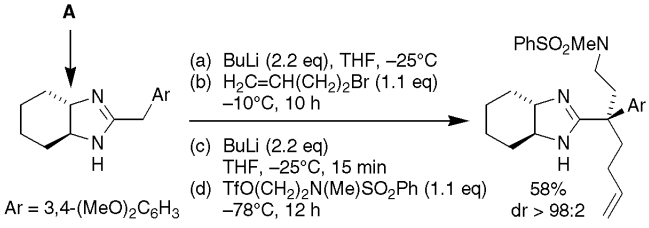
(*S*,*S*)-1,2-Diaminocyclohexane — *Reagent*

Stereoselective alkylation of a C_2 symmetric imidazoline derived from **A** is reported, allowing efficient formation of a quaternary benzylic centre.

P. I. Dalko, V. Brun, Y. Langlois *Tetrahedron Lett.* **1998**, *39*, 8979.



A

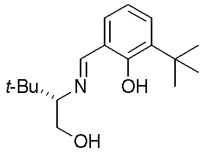


2 examples (yields 58, 70%, %de = 75, >95%).

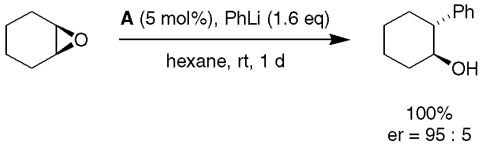
Chiral Schiff Base — *Reagent*

Aldimine **A** catalyses the enantioselective ring opening of cyclohexene oxides with phenyl lithium.

N. Oguni, Y. Miyagi, K. Itoh *Tetrahedron Lett.* **1998**, *39*, 9023.



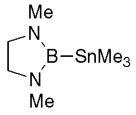
A



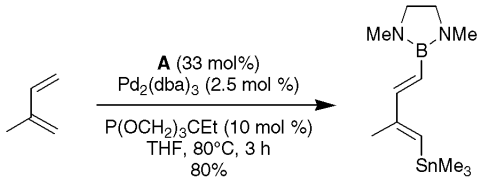
3 examples (yields 53-92%, %ee = 76-86 %).

1,3-Dimethyl-2-trimethylstannyl-2-bora-1,3-diazacyclopentane — *Reagent*

Regio- and stereoselective 1,4-addition of **A** to 1,3-dienes under palladium catalysis is reported. Reaction of the products with aldehydes provides a facile method for the preparation of homoallyl alcohols.



A



3 examples yields 80-87 %.

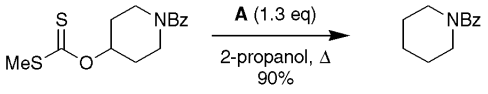
S. Onozawa, Y. Hatanaka, M. Tanaka *Tetrahedron Lett.* **1998**, *39*, 9043.

Lauroyl Peroxide — *Reagent*

The title reagent is utilised in a modified Barton-McCombie reaction.

$[CH_3(CH_2)_{10}CO]_2O_2$

A



6 examples yields 45-90%. When benzene is used as the solvent an oxygen-sulfur rearrangement of the xanthate occurs.

B. Quiclet-Sire, S. Z. Zard *Tetrahedron Lett.* **1998**, *39*, 9435.

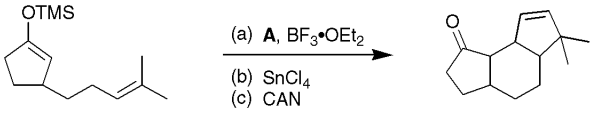
Hexacarbonyl (propiolaldehyde diethyl acetal) dicobalt — *Reagent*

A one-pot synthesis of tricyclic ring systems *via* an intermolecular Nicholas reaction followed by a tandem intramolecular Nicholas reaction is reported.

$Co_2(CO)_6[R]$

A

R = HC CCH(OEt)$_2$

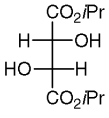


4 examples (yields 35-45%).

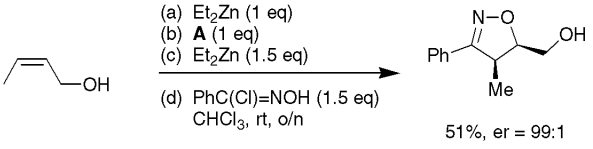
E. Tyrrell, C. Tillett *Tetrahedron Lett.* **1998**, *39*, 9535.

(*R*,*R*)-Diisopropyltartrate (DIPT) — *Reagent*

Asymmetric 1,3-dipolar cycloaddition of nitrile oxides to γ-substituted allylic alcohols in the presence of **A** is reported, yielding 3,4,5-trisubstituted-2-oxazolines with high regio-and enantioselectivity.



A



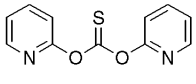
51%, er = 99:1

14 examples (yields 20-82%, %ee = 89-98%).

Y. Yoshida, Y. Ukaji, S. Fujinami, K. Inomata *Chem. Lett.* **1998**, 1023.

O,*O′*-Di(2-pyridyl) thiocarbonate (DPTC) — *Reagent*

A variety of carboxylic esters have been prepared from the corresponding acids and hindered alcohols using the title compound and a catalytic amount of DMAP.



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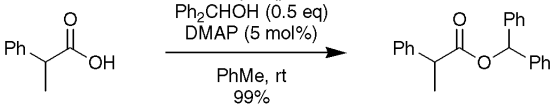
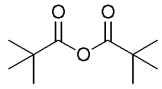


15 examples (yields 79-99%).

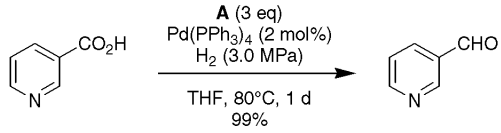
K. Saitoh, I. Shiina, T. Mukaiyama *Chem. Lett.* **1998**, 679.

Pivalic Anhydride — *Reagent*

Hydrogenation of carboxylic acids to the corresponding aldehydes catalysed by palladium in the presence of **A** is reported.



A



19 examples (yields 13, 63-99%) are described.

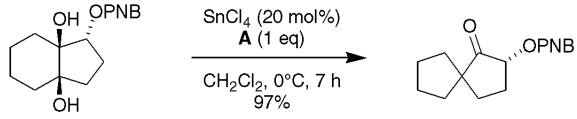
K. Nagayama, I. Shimizu, A. Yamamoto *Chem. Lett.* **1998**, 1143.

Trimethyl Orthoformate — *Reagent*

The non-dehydrative Pinacol coupling of a variety of diols in the presence of **A** and a Lewis acid is reported.

$HC(OMe)_3$

A



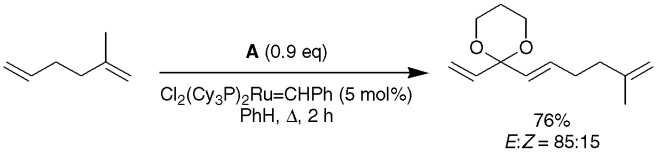
15 examples using a variety of Lewis acids (yields 0, 15-97%) are reported.

Y. Kita, Y. Yoshida, S. Mihara, A. Furukawa, K. Higuchi, D.-F. Fang, H. Fujioka *Tetrahedron* **1998**, *54*, 14689.

Cyclopropenone Propane-1,3-Diyl Ketal — *Reagent*

Ring opening cross metathesis of **A** and terminal olefins is described. The reaction is carried out in the presence of Grubbs ruthenium catalyst to afford 1,4-divinyl ketone ketals.

A

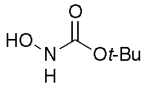


11 examples (yields 28-86%, 80:20 ≤ *E*:*Z* ≤ 96:4).

M. Michaut, J.-L. Parrain, M. Santelli *Chem. Commun.* **1998**, 2567.

tert-Butyl-*N*-Hydroxycarbamate — *Reagent*

The nitrogen nucleophile **A** reacts with non-racemic chiral tricarbonylchromium(0) complexes of benzylic ethers with retention of configuration to provide a novel approach to non-racemic *N*-hydroxycarbamates and amines.



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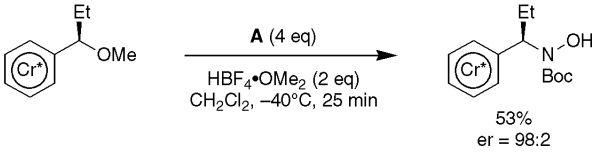
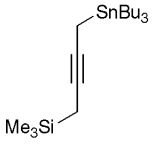


5 examples (yields 43-85%, %ee = 80-99%).

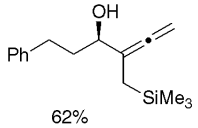
D. Albanese, S. E. Gibson, E. Rahimian *Chem. Commun.* **1998**, 2571.

(4-Trimethylsilylbut-2-ynyl)stannane — *Reagent*

Catalytic enantioselective addition of **A** to aldehydes provides trimethylsilylmethylallenyl alcohols with high enantioselectivity. The adducts can be converted to dienyl alcohols with retention of configuration, by reaction with an electrophile.



A



8 examples (yields 39-83%, %ee = 83-97%).

C.-M. Yu, S.-K. Yoon, S.-J. Lee, J.-Y. Lee, S. S. Kim *Chem. Commun.* **1998**, 2749.