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

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The journals regularly covered by the abstractors are:

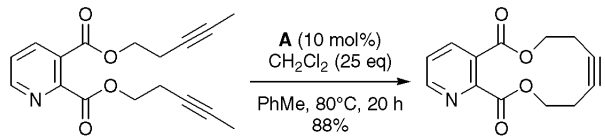
Angewandte Chemie International Edition
Bulletin of the Chemical Society of Japan
Chemical Communications
Chemistry A European Journal
Chemistry Letters
Collection Czechoslovak Chemical Communications
European Journal of Organic Chemistry
Helvetica Chimica Acta
Heterocycles
Journal of the American Chemical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

Chlorotris(3,5-dimethylphenyl)*tert*-butylamidomolybdenum(IV) — ***Catalyst***

A mediates the efficient ring-closing metathesis of functionalized diynes.

[MoCl(N*t*-Bu(*m*-Xyl)$_3$]

A



9 examples (yields 60-91%)

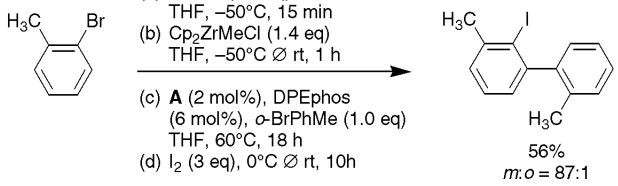
A. Fürstner, C. Mathes, C. W. Lehmann *J. Am. Chem. Soc.* **1999**, *121*, 9453.

Tris(dibenzylideneacetone)dipalladium(0) — ***Catalyst***

A catalyses cross-coupling of bromoarenes with zirconocene stabalized aryne complexes, obtained by halogen metal exchange and transmetallation. Iodination of the *in-situ* formed zirconocene arene complexes gives rise to the final products.

$Pd_2(dba)_3$

A



17 examples (yields 40-90%, 27:1 • *meta* : *ortho* •100:0).

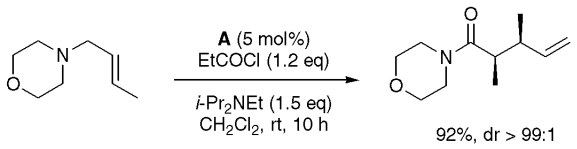
M. Frid, D. Pérez, A. J. Peat, S. L. Buchwald *J. Am. Chem. Soc.* **1999**, *121*, 9469.

Tetrachlorobis(tetrahydrofuranyl)titanium(IV) — ***Catalyst***

A mediates the acyl Claisen rearrangement of *N*-crotyl morpholine derivatives and ketenes formed *in-situ* from acid chlorides.

[$TiCl_4(THF)_2$]

A



10 examples (yields 70-95%, %de = 80-98%)

T. P. Yoon, V. M. Dong, D. W. C. MacMillan *J. Am. Chem. Soc.* **1999**, *121*, 9726.

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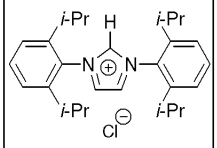
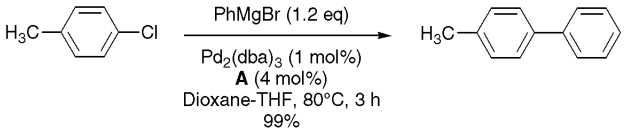
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene Hydrochloride — *Catalyst*

A and a Pd(0)-source mediate the cross-coupling of aryl chlorides with aryl Grignard reagents.



A



16 examples (yields 0, 69-99%).

J. Huang, S. P. Nolan *J. Am. Chem. Soc.* **1999**, *121*, 9889.

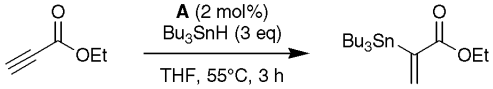
Molybdenum Isocyanide Complex — *Catalyst*

A catalyses the regioselective hydrostannation of several types of alkynes, giving preferentially α-stannylated products.

$Mo(CO)_3(R)_3(MoBI_3)$

R = CN*t*-Bu

A



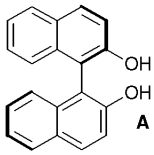
98%
$\alpha:\beta$ = 92:8

11 examples (yields 38-98%, 63:37 ≤ $\alpha:\beta$ ≤ 95:5) are reported.

U. Kazmaier, D. Schauss, M. Pohlman *Org. Lett.* **1999**, *1*, 1017.

1,1′-Binaphthalene-2,2′-diol / Dichloro-di-isopropoxytitanium(IV) — *Catalyst*

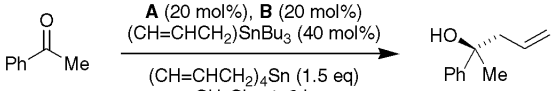
The title reagent pair catalyse the asymmetric allylation of ketones.



A

$Cl_2Ti(O\textit{i}\text{-}Pr)_2$

B



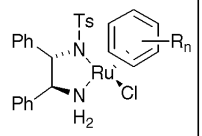
77%
er = 83:17

8 examples (yields 75-91%, %ee = 29-65%) are reported.

S. Casolari, D. D'Addario, E. Tagliavini *Org. Lett.* **1999**, *1*, 1061.

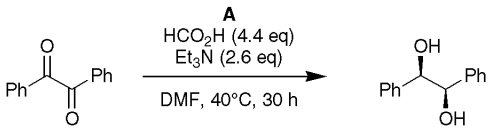
N-p-(Toluenesulfonyl)-1,2-diphenylethylenediamine(η^6-arene)ruthenium(II) Chloride — *Catalyst*

The title reagent catalyses the asymmetric transfer hydrogenation of benzils to prepare chiral hydrobenzoins.



R_n = 1-CH_3-4-$CH(CH_3)_2$

A



100%
dl:meso = 98.6:1.4
er >100:1

5 examples (yields 67-100%, %ee > 99%) are reported.

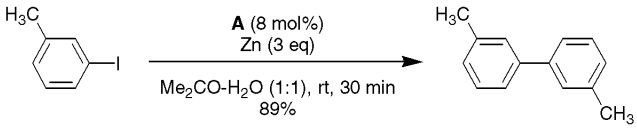
K. Murata, K. Okano, M. Miyagi, H. Iwane, R. Noyori, T. Ikariya *Org. Lett.* **1999**, *1*, 1119.

Palladium(II) Acetate — *Catalyst*

A catalyses the Ullmann-type reductive coupling of aryl halides under an air atmosphere in aqueous acetone.

$Pd(OAc)_2$

A



13 examples (yields 0, 64-96%) are reported.

S. Venkatraman, C.-J. Li *Org. Lett.* **1999**, *1*, 1133.

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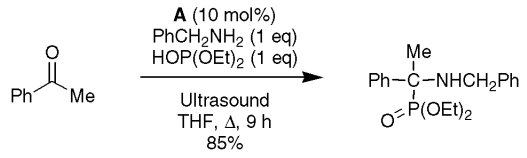
Indium(III) Chloride — *Catalyst*

The title reagent catalyses the one-pot preparation of α-amino phosphonates from aldehydes or ketones and amines.

$InCl_3$

A

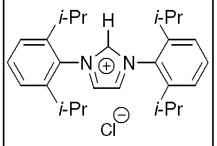


24 examples (yields 76-95%) are reported.

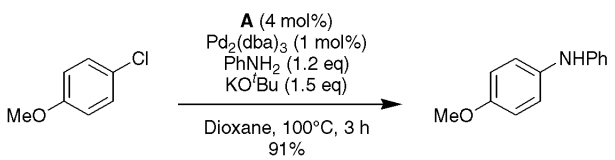
B. C. Ranu, A. Hajra, U. Jana *Org. Lett.* **1999**, *1*, 1141.

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene Hydrochloride — *Catalyst*

The title reagent catalyses the amination of aryl halides.



A

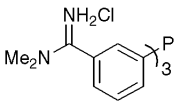


16 examples (yields 59-99%) are reported.

J. Huang, G. Grasa, S. P. Nolan *Org. Lett.* **1999**, *1*, 1307.

Guanidinium Phosphine Ligand / Palladium(II) Acetate — *Catalyst*

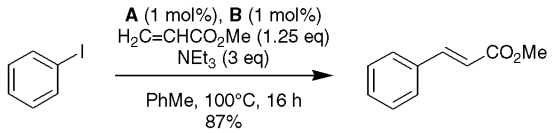
The title reagent pair, supported on glass beads, is utilised in Heck reactions and Sonogashira couplings. The catalyst is recyclable and features low leaching of palladium into the system.



A

$Pd(OAc)_2$

B

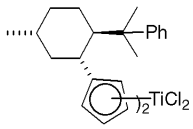


7 examples of Heck reactions (yields 55-87%) and 4 examples of Sonogashira couplings (yields 58-87%) are reported.

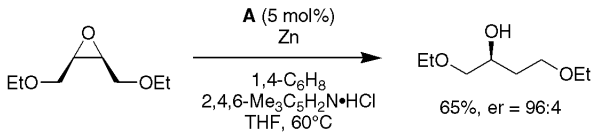
M. P. Leese. J. M. J. Williams *Synlett* **1999**, 1645.

Chiral Titanocene Dichloride Complex — *Catalyst*

A catalyses the enantioselective opening of *meso*-epoxides *via* a β-titanoxy radical intermediate.



A



6 examples (yields 60-68%, %ee = 74-93%) are reported.

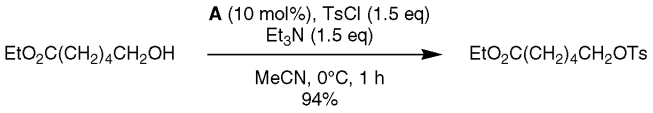
A. Gansäuer, T. Lauterbach, H. Bluhm, M. Noltemeyer *Angew. Chem. Int. Ed.* **1999**, *38*, 2909.

1,6-Bis(dimethylamino)hexane — *Catalyst*

A is used in the tosylations of various alcohols. The reported method has advantages over the more traditional use of pyridine / TsCl in that the reaction rate is higher, and undesirable chlorination reactions are avoided. **A** can also be used in mesylation reactions.

$Me_2N(CH_2)_6NMe_2$

A



6 examples (yields 92-95%) are reported.

Y. Yoshida, K. Shimonishi, Y. Sakakura, S. Okada, N.Aso, Y. Tanabe *Synthesis* **1999**, 1633.

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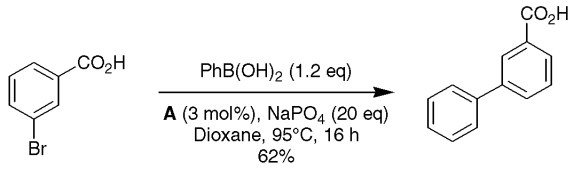
Bis(triethylamino)nickel(II) Dichloride — *Catalyst*

The title reagent can be used as an alternative to $Pd(PPh_3)_4$ in the catalysis of Suzuki reactions. **A** is effective in the presence of water and the lack of phosphine ligands prevents unwanted side reactions occurring.

N. E. Leadbeater, S. M. Resouly *Tetrahedron* **1999**, *55*, 11889

$NiCl_2(NEt_3)_2$

A

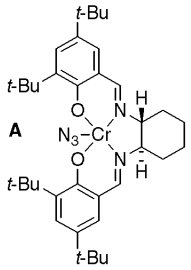


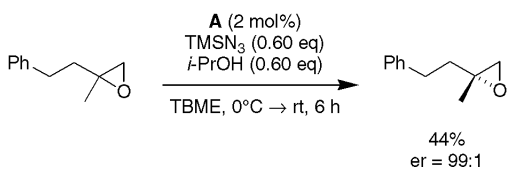
8 examples (yields 0, 48-80%).

Chiral Chromium Salen Catalyst — *Catalyst*

A is reported as an efficient catalyst for the kinetic resolution of 2,2-disubstituted epoxides.

H. Lebel, E. N. Jacobsen *Tetrahedron Lett.* **1999**, *40*, 7303.



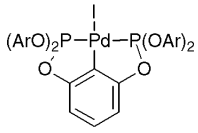


7 examples (yields 42-48%, %ee = 80-99%).

Palladium Catalyst — *Catalyst*

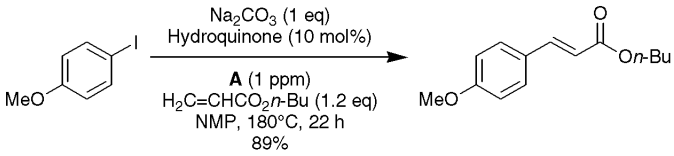
A is reported to be a highly active catalyst for the Heck reaction.

F. Miyazaki, K. Yamaguchi, M. Shibasaki *Tetrahedron Lett.* **1999**, *40*, 7379.



Ar = *p*-OMe

A



3 examples (yields 95-100%) are described.

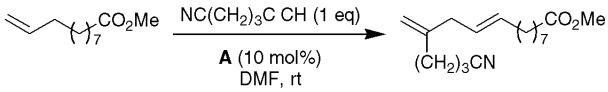
Ruthenium Catalyst — *Catalyst*

A is reported as an effective catalyst for alkene-alkyne coupling.

B. M. Trost, F. D. Toste *Tetrahedron Lett.* **1999**, *40*, 7739.

$[CpRu(MeCN_3)]^+PF_6^-$

A

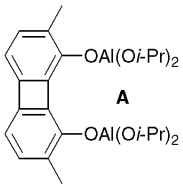


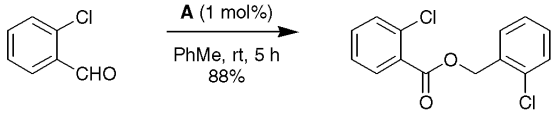
15 examples (yields 62-91%, 1.2:1 ≤ regioselectivity ≤ 100:0) are described.

(2,7-Dimethyl-1,8-biphenylenedioxy)bis(diisopropoxyaluminium) — *Catalyst*

The high-speed Tishchenko reaction of aldehydes using **A** is reported. Highly stereoselective intramolecular Tishchenko reduction of β-hydroxy ketones is also described.

T. Ooi, T. Miura, K. Takaya, K. Maruoka *Tetrahedron Lett.* **1999**, *40*, 7695.





6 examples of the Tishchenko reaction (yields 67-99%) and 2 examples of reduction (yields 92, 99%, 96:4 ≤ *anti*:*syn* ≤ 99:1) are described.

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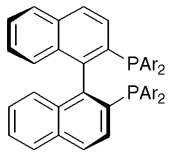
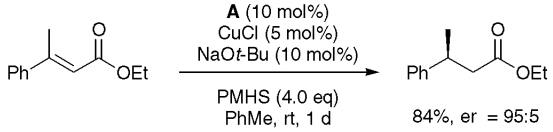
2,2′-Bis(di-*p*-tolylphosphino)-1,1′-binapthyl — *Ligand*

A Cu(I)-catalyst formed from the title ligand is used in the asymmetric conjugate reduction of α,β-unsaturated esters.



Ar = *p*-tolyl

A



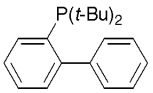
9 examples (yields 84-98%, %ee 80-91%).

PMHS = polmethylhydrosiloxane

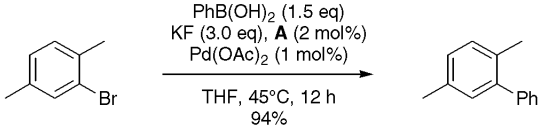
D. H. Appella, Y. Moritani, R. Shintani, E. M. Ferreira, S. L. Buchwald *J. Am. Chem. Soc.* **1999**, *121*, 9473.

o-(Di-*tert*-butylphosphino)biphenyl — *Ligand*

A in combination with $Pd(OAc)_2$ catalyses the efficient Suzuki-coupling of aryl bromides and chlorides.



A

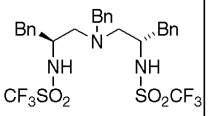


21 examples (yields 81-98%).

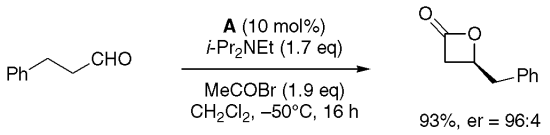
J. P. Wolfe, R. A. Singer, B. H. Yang, S. L. Buchwald *J. Am. Chem. Soc.* **1999**, *121*, 9550.

Chiral Bis(trifluoromethanesulfonamide) Ligand — *Ligand*

Asymmetric acyl halide-aldehyde cyclocondensations are mediated by ligand **A** and Me_3Al or Et_2AlCl.



A

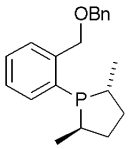


10 examples (yields 56-91%, %ee = 54-93%).

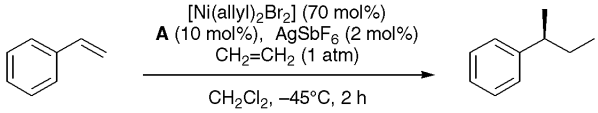
S. G. Nelson, T. J. Peelen, Z. Wan *J. Am. Chem. Soc.* **1999**, *121*, 9742.

(*R,R*)-(2′-Benzyloxymethylphenyl)-2,5-dimethylphospholane — *Ligand*

A is reported as an efficient ligand in the Ni-mediated hydrovinylation of styrene.



A



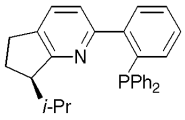
94%, er = 74:26

5 examples (yields 2-94%, %ee = 29-50%).

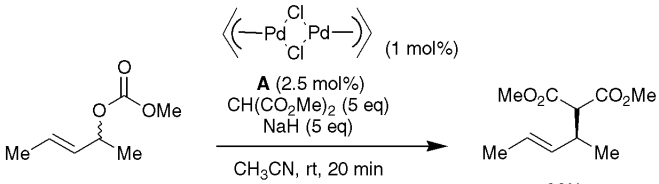
M. Nandi, J. Jin, T. V. RajanBabu *J. Am. Chem. Soc.* **1999**, *121*, 9899.

Chiral 2-(phosphinoaryl)pyridine Ligand — *Ligand*

Asymmetric allylic alkylations using a palladium catalyst derived from ligand **A** are reported.



A



82%
er = 89:11

4 examples (yields 77-85%, %ee = 71-93%) are reported.

K. Ito, R. Kashiwagi, K. Iwasaki, T. Katsuki *Synlett* **1999**, 1563.

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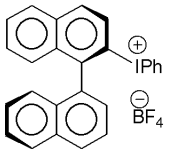
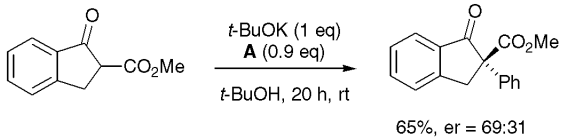
1,1′-Binaphthyl-2-yl(phenyl)iodonium Tetrafluoroborate — *Reagent*

Chiral diaryliodonium salt **A** and analogues are utilised in the asymmetric α-phenylation of cyclic β-keto esters.



A

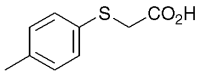


9 examples (yields 15-71%, %ee = 37-53%).

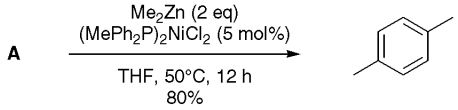
M. Ochiai, Y. Kitagawa, N. Takayama, Y. Takaoka, M. Shiro *J. Am. Chem. Soc.* **1999**, *121*, 9233.

p-Tolylthioglycolic Acid — *Reagent*

A and similar thioglycolic acids, undergo Ni-mediated cross-couplings with organozinc reagents.



A

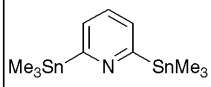


18 examples (yields 40-100%).

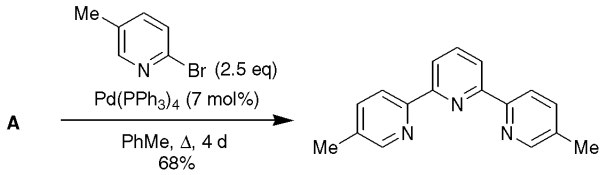
J. Srogl, W. Liu, D. Marshall, L. S. Liebeskind *J. Am. Chem. Soc.* **1999**, *121*, 9449.

2,6-Bis(trimethyltin)pyridine — *Reagent*

The title reagent is used in Stille-type coupling procedures to prepare new pyridine-based ligands for supramolecular chemistry.



A

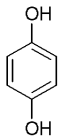


Preparation of **A** (69%) and 3 examples of ligand synthesis (yields 42-68%) are reported.

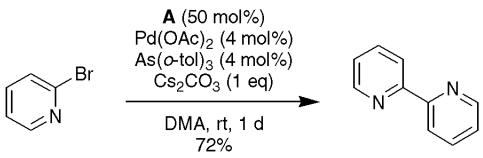
U. S. Schubert, C. Eschbaumer *Org. Lett.* **1999**, *1*, 1027.

Hydroquinone — *Reagent*

The title reagent is used as a homogeneous reductant in the palladium-catalysed Ullmann-type homocoupling of aryl halides.



A

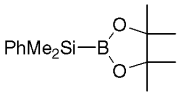


17 examples (yields 54-95%) are reported.

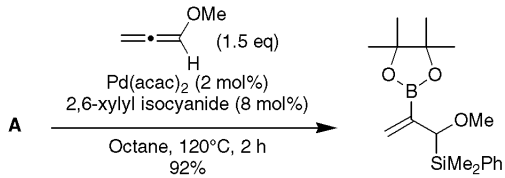
D. D. Hennings, T. Iwama, V. H. Rawal *Org. Lett.* **1999**, *1*, 1205.

(Dimethylphenylsilyl)pinacolborane — *Reagent*

The title reagent is used in the palladium catalysed regioselective silaboration of 3-substituted 1,2-dienes. The utility of the 2-boryl allylsilane derivatives is demonstrated by Pd-catalysed coupling reactions with aryl halides.



A



7 examples (yields 79-99%, regioselectivity > 86:14) are reported.

M. Suginome, Y. Ohmori, Y. Ito *Synlett* **1999**, 1567.

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Iodoethane / Ethylmagnesium Bromide — *Reagent*

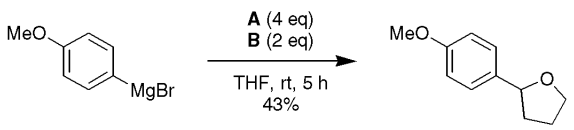
The title reagent pair are used in the coupling reaction of arylmagnesium compounds and THF to prepare 2-aryltetrahydrofurans.

EtI

A

EtMgBr

B

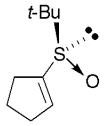


8 examples (yields 12-78%) are reported.

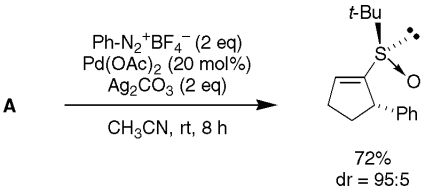
A. Inoue, H. Shinokubo, K. Oshima *Synlett* **1999**, 1582.

(*R*)-1-*tert*-Butylsulfinyl-1-cyclopentene — *Reagent*

The title reagent is used in an asymmetric Heck reaction with a variety of *para*- and *meta*-substituted arenediazonium tetrafluoroborates.



A



8 examples (yields 0, 54-79%, %de = 82-92%) are reported.

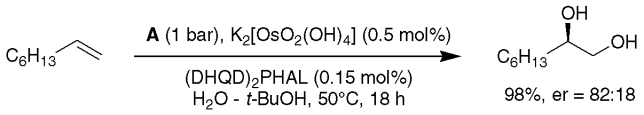
J. Priego, J. C. Carretero *Synlett* **1999**, 1603.

Molecular Oxygen — *Reagent*

Oxygen is used in atom-efficient osmium-catalyzed dihydroxylations in which both oxygen atoms are incorporated into the product.

O_2

A



10 examples (yields 51-98%, %ee = 54-96%).

C. Döbler, G. Mehltretter, M. Beller *Angew. Chem. Int. Ed.* **1999**, *38*, 3026.

N,N,N′,N′-Tetramethylazodicarboxamide (TMAD) / Tributylphosphine — *Reagent*

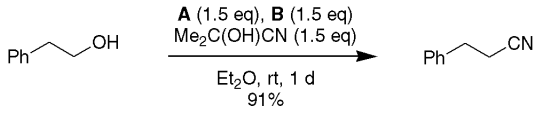
The title reagent pair are utilised in the direct transformation of primary and secondary alcohols to the corresponding nitriles in the presence of acetone cyanohydrin.

$Me_2NCON{=}NCONMe_2$

A

PBu_3

B



7 examples (yields 6, 75-96%) are described.

T. Tsunoda, K. Uemoto, C. Nagino, M. Kawamura, H. Kaku, S. Itô *Tetrahedron Lett.* **1999**, *40*, 7355.

Trimethylsilylsulfonyl Chloride / Iodosobenzene — *Reagent*

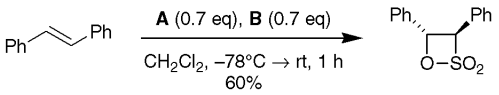
A method for the preparation of sulfur trioxide *in situ* from the title reagent pair in the absence of Lewis bases is described. The procedure is utilised in the preparation of sultones from alkenes.

Me_3SiSO_3Cl

A

PhIO

B



6 examples (yields 50-69%) are reported.

A. R. Bassindale, I. Katampe, M. G. Maesano, P. Patel, P. G. Taylor *Tetrahedron Lett.* **1999**, *40*, 7417.

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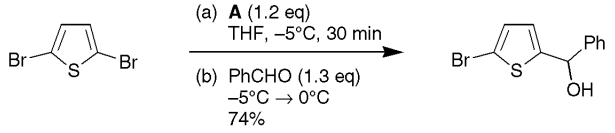
iso-Propylmagnesium Bromide — *Reagent*

A (or *i*-Pr_2Mg) is utilised in the preparation of polyfunctional aryl or heteroaryl magnesium reagents from brominated precursors. Excellent chemoselectivity is observed in the Br-Mg exchange of di- or tribromoheterocycles.

i-PrMgBr

A



M. Abarbri, F. Dehmel, P. Knochel *Tetrahedron Lett.* **1999**, *40*, 7449.

18 examples using **A** or *i*-Pr_2Mg (yields 55-88%) are described.

Diethylaminotrimethylsilane / Methyl Iodide — *Reagent*

The title reagents mediate the ring-opening iodosilation of cyclic ethers.

Et_2NSiMe_3

A

MeI

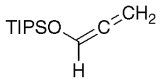
B

J. Ohshita, A. Iwata, F. Kanetani, A. Kunai, Y. Yamamoto, C. Matui *J. Org. Chem.* **1999**, *64*, 8024.

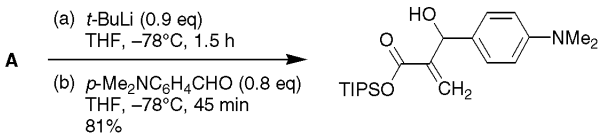
24 examples, including the use of different halide sources (yields 33-90%) are described.

1-Triisopropylsilyloxy-1,2-propadiene — *Reagent*

The title reagent reacts with aldehydes or ketones to give α,β-unsaturated acyl silanes.



A

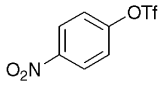


I. A. Stergiades, M. A. Tius *J. Org. Chem.* **1999**, *64*, 7457.

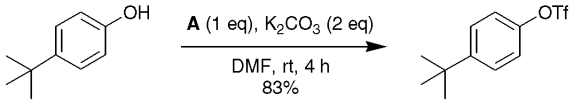
21 examples (yields 27-92%) are described.

4-Nitrophenyltrifluoromethanesulfonate — *Reagent*

The title reagent is reported as a new trifluoromethanesulfonyl transfer agent.



A

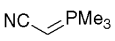


L. Neuville, A. Bigot, M. E. T. H. Dau, J. Zhu *J. Org. Chem.* **1999**, *64*, 7638.

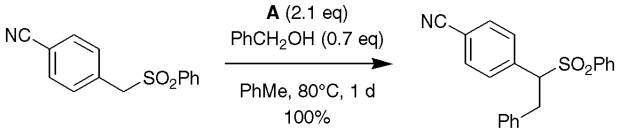
9 examples (yields 60-92%) are reported.

Cyanomethylenetrimethylphosphorane (CMMP) — *Reagent*

The title compound mediates the alkylation of arylmethyl phenyl sulfones with primary and secondary alcohols. Arylmethyl phenyl sulfones of pKa up to 23.5 can be utilized in the CMMP mediated Mitsunobu reaction.



A



T. Tsunoda, K. Uemoto, T. Ohtani, H. Kaku, S. Itô *Tetrahedron Lett.* **1999**, *40*, 7359.

12 examples (yields 83-100%).

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