

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

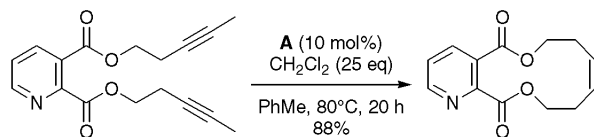
Chlorotrakis(3,5-dimethylphenyl)tert-butylamidomolybdenum(IV)

Catalyst

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



A



9 examples (yields 60-91%)

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

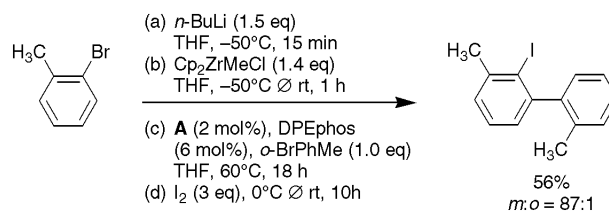
Tris(dibenzylideneacetone)dipalladium(0)

Catalyst

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



A



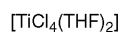
17 examples (yields 40-90%, 27:1 • meta : ortho • 100:0).

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

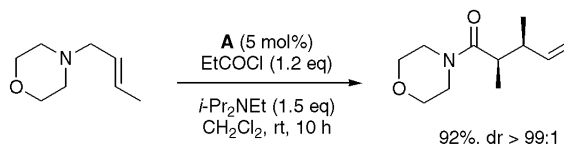
Tetrachlorobis(tetrahydrofuranyl)titanium(IV)

Catalyst

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



A

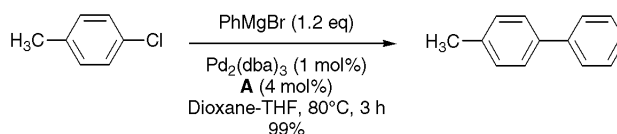
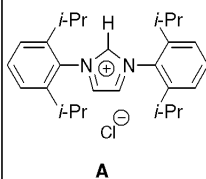


10 examples (yields 70-95%, %de = 80-98%)

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

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

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

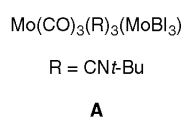


J. Huang, S. P. Nolan *J. Am. Chem. Soc.* **1999**, *121*, 9889.

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

Molybdenum Isocyanide Complex

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

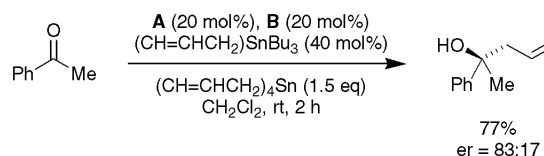
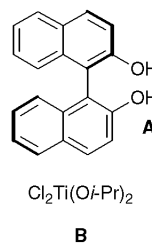


U. Kazmaier, D. Schauss, M. Pohlman *Org. Lett.* **1999**, *1*, 1017.

11 examples (yields 38-98%, 63:37 \leq α : β \leq 95:5) are reported.

1,1'-Binaphthalene-2,2'-diol / Dichloro-di-isopropoxytitanium(IV)

The title reagent pair catalyse the asymmetric allylation of ketones.

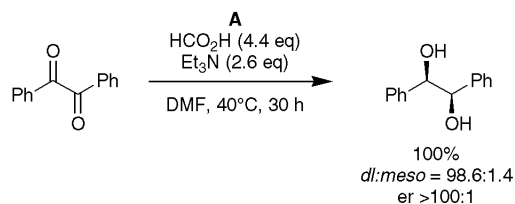
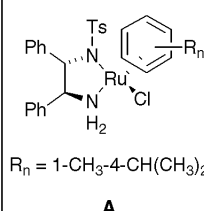


S. Casolari, D. D'Addario, E. Tagliavini *Org. Lett.* **1999**, *1*, 1061.

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

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

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

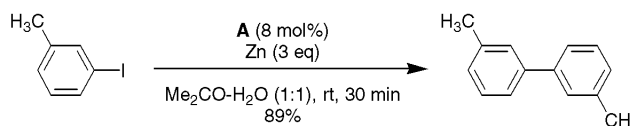


K. Murata, K. Okano, M. Miyagi, H. Iwane, R. Noyori, T. Ikariya *Org. Lett.* **1999**, *1*, 1119.

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

Palladium(II) Acetate

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



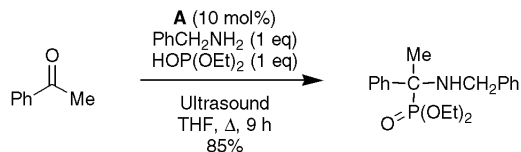
S. Venkatraman, C.-J. Li *Org. Lett.* **1999**, *1*, 1133.

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

Catalyst

Indium(III) Chloride

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



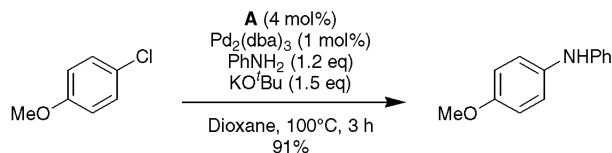
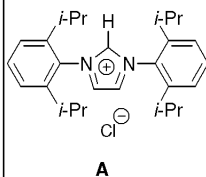
B. C. Ranu, A. Hajra, U. Jana *Org. Lett.* **1999**, *1*, 1141.

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

Catalyst

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

The title reagent catalyses the amination of aryl halides.



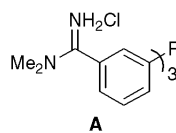
J. Huang, G. Grasa, S. P. Nolan *Org. Lett.* **1999**, *1*, 1307.

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

Catalyst

Guanidinium Phosphine Ligand / Palladium(II) Acetate

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.



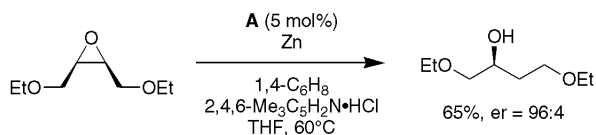
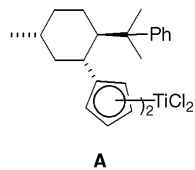
M. P. Leese, J. M. J. Williams *Synlett* **1999**, 1645.

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

Catalyst

Chiral Titanocene Dichloride Complex

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



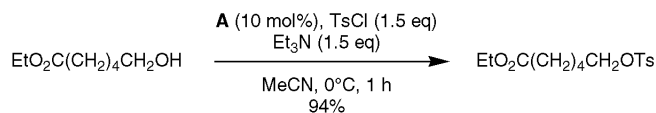
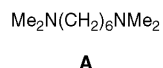
A. Gansäuer, T. Lauterbach, H. Bluhm, M. Noltemeyer *Angew. Chem. Int. Ed.* **1999**, *38*, 2909.

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

Catalyst

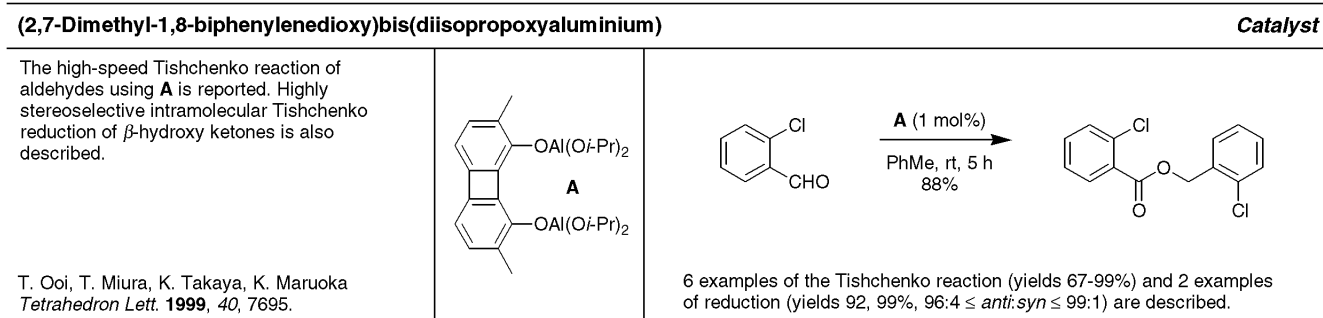
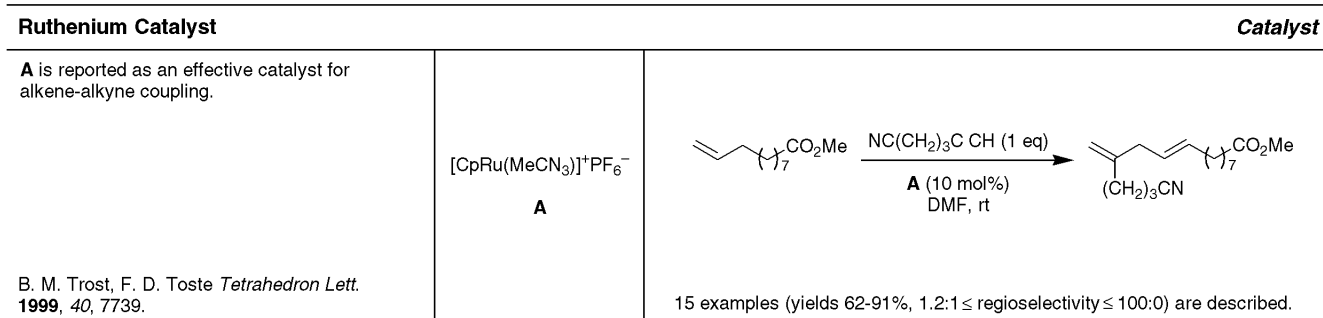
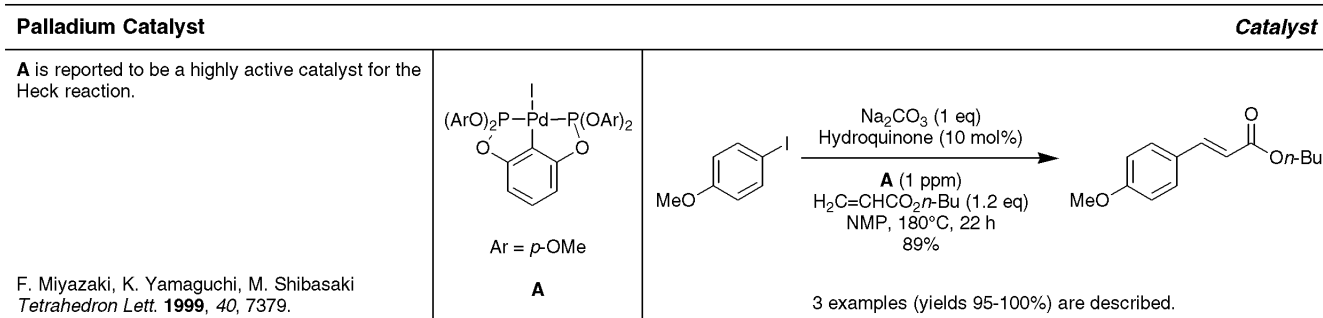
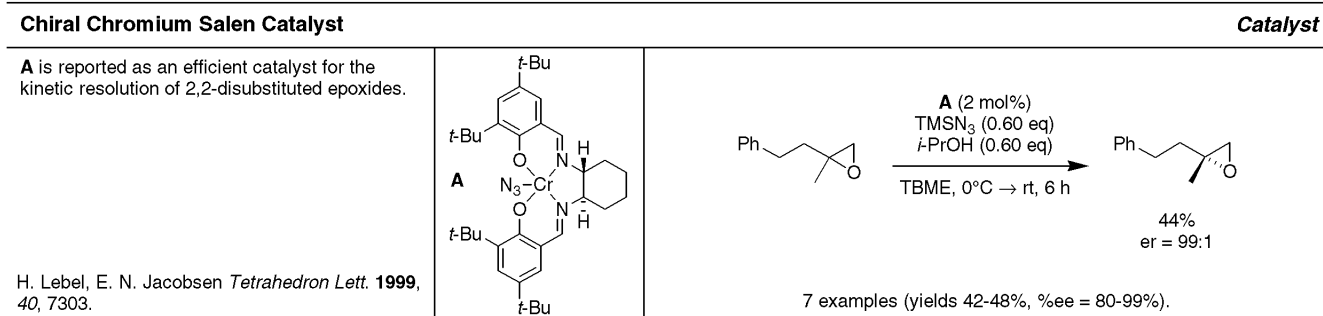
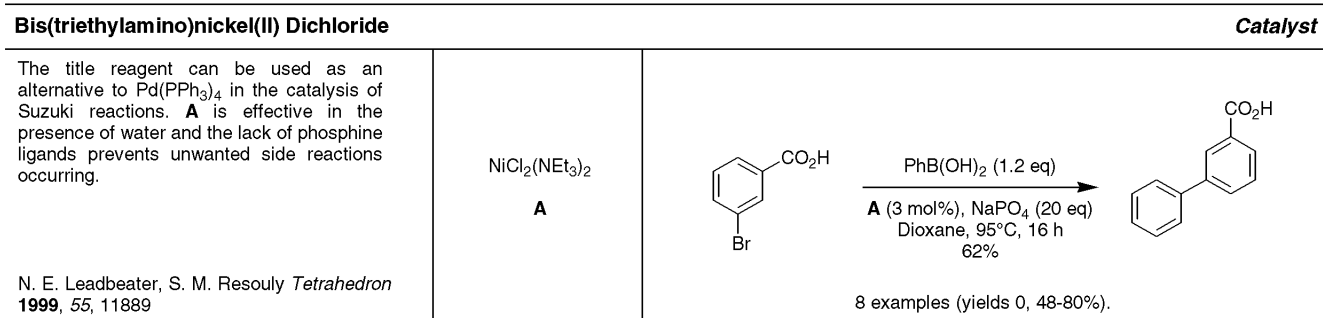
1,6-Bis(dimethylamino)hexane

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.



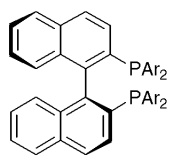
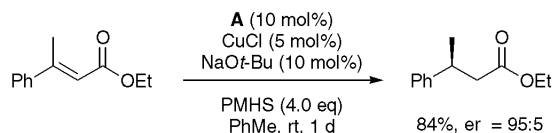
Y. Yoshida, K. Shimonishi, Y. Sakakura, S. Okada, N. Aso, Y. Tanabe *Synthesis* **1999**, 1633.

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



2,2'-Bis(di-*p*-tolylphosphino)-1,1'-binaphthyl**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**

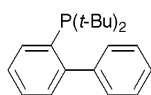
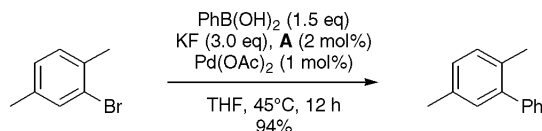
9 examples (yields 84-98%, %ee 80-91%).

PMHS = polymethylhydrosiloxane

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.

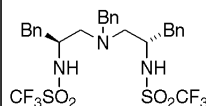
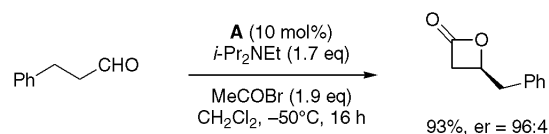
**A**

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 Me₃Al or Et₂AlCl.

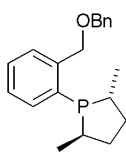
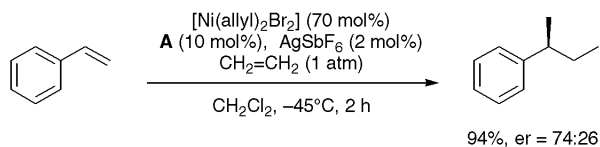
**A**

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.

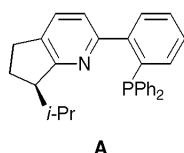
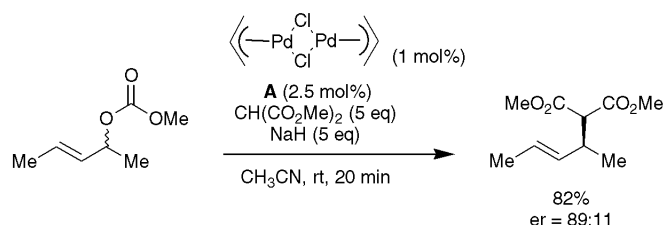
**A**

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

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

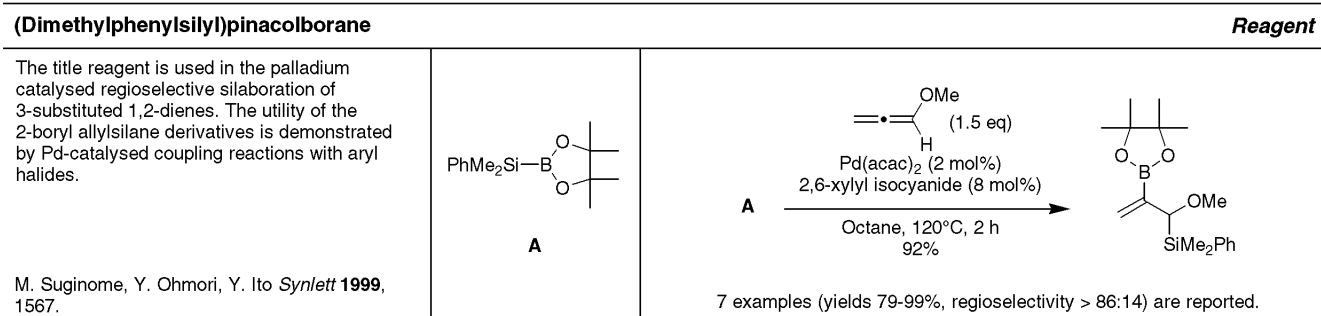
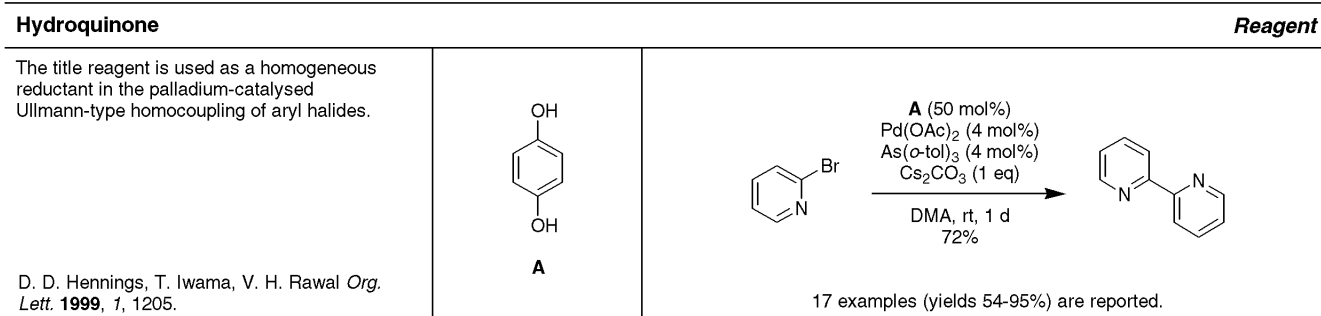
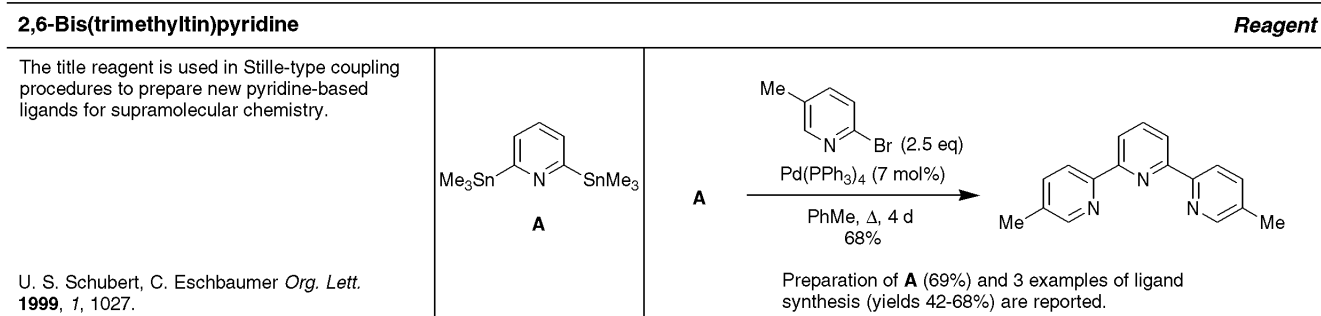
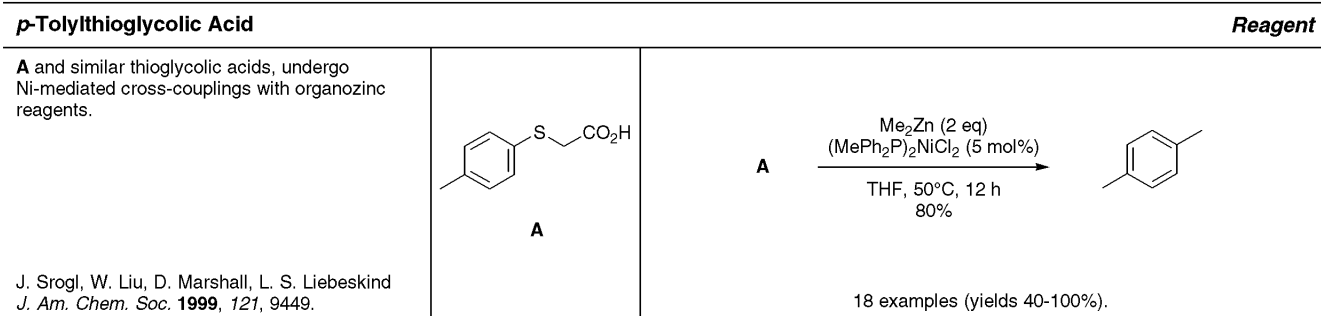
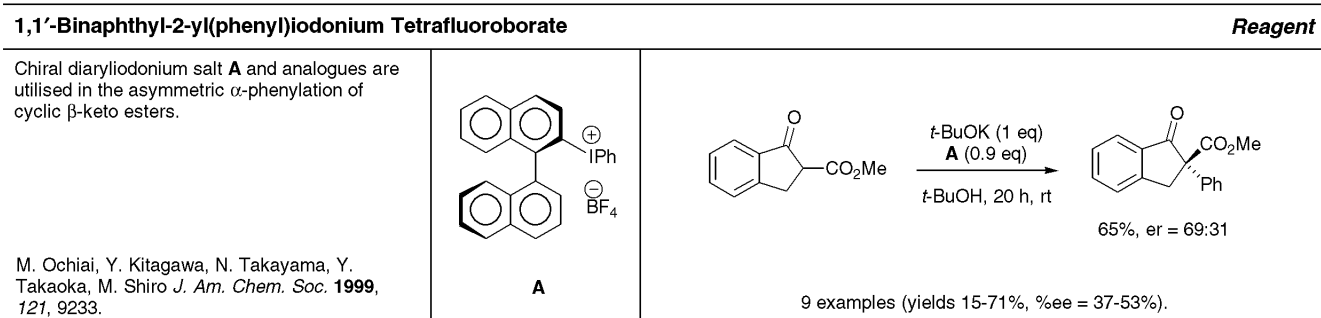
Chiral 2-(phosphinoaryl)pyridine Ligand**Ligand**

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

**A**

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

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



Iodoethane / Ethylmagnesium Bromide		Reagent
<p>The title reagent pair are used in the coupling reaction of arylmagnesium compounds and THF to prepare 2-aryltetrahydrofurans.</p> <p>A. Inoue, H. Shinokubo, K. Oshima <i>Synlett</i> 1999, 1582.</p>	<p>Etl</p> <p>A</p> <p>EtMgBr</p> <p>B</p>	<p>8 examples (yields 12-78%) are reported.</p>
(R)-1-tert-Butylsulfinyl-1-cyclopentene		Reagent
<p>The title reagent is used in an asymmetric Heck reaction with a variety of <i>para</i>- and <i>meta</i>-substituted arenediazonium tetrafluoroborates.</p> <p>J. Priego, J. C. Carretero <i>Synlett</i> 1999, 1603.</p>	<p>A</p>	<p>8 examples (yields 0, 54-79%, %de = 82-92%) are reported.</p>
Molecular Oxygen		Reagent
<p>Oxygen is used in atom-efficient osmium-catalyzed dihydroxylations in which both oxygen atoms are incorporated into the product.</p> <p>C. Döbler, G. Mehlretter, M. Beller <i>Angew. Chem. Int. Ed.</i> 1999, <i>38</i>, 3026.</p>	<p>O₂</p> <p>A</p>	<p>10 examples (yields 51-98%, %ee = 54-96%).</p>
N,N,N',N'-Tetramethylazodicarboxamide (TMAD) / Tributylphosphine		Reagent
<p>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.</p> <p>T. Tsunoda, K. Uemoto, C. Nagino, M. Kawamura, H. Kaku, S. Itô <i>Tetrahedron Lett.</i> 1999, <i>40</i>, 7355.</p>	<p>Me₂NCON=NCONMe₂</p> <p>A</p> <p>PBu₃</p> <p>B</p>	<p>7 examples (yields 6, 75-96%) are described.</p>
Trimethylsilylsulfonyl Chloride / Iodosobenzene		Reagent
<p>A method for the preparation of sulfur trioxide <i>in situ</i> from the title reagent pair in the absence of Lewis bases is described. The procedure is utilised in the preparation of sultones from alkenes.</p> <p>A. R. Bassindale, I. Katampe, M. G. Maesano, P. Patel, P. G. Taylor <i>Tetrahedron Lett.</i> 1999, <i>40</i>, 7417.</p>	<p>Me₃SiSO₃Cl</p> <p>A</p> <p>PhIO</p> <p>B</p>	<p>6 examples (yields 50-69%) are reported.</p>

<i>iso</i>-Propylmagnesium Bromide		Reagent
<p>A (or <i>i</i>-Pr₂Mg) 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.</p> <p>M. Abarbri, F. Dehmel, P. Knochel <i>Tetrahedron Lett.</i> 1999, <i>40</i>, 7449.</p>	<p>(a) A (1.2 eq) THF, -5°C, 30 min (b) PhCHO (1.3 eq) -5°C → 0°C 74%</p>	<p>18 examples using A or <i>i</i>-Pr₂Mg (yields 55-88%) are described.</p>
Diethylaminotrimethylsilane / Methyl Iodide		Reagent
<p>The title reagents mediate the ring-opening iododisilation of cyclic ethers.</p> <p>J. Ohshita, A. Iwata, F. Kanetani, A. Kunai, Y. Yamamoto, C. Matui <i>J. Org. Chem.</i> 1999, <i>64</i>, 8024.</p>	<p>A (1.0 eq), B (2.0 eq) PhMe, 50°C, 12 h 60%</p>	<p>24 examples, including the use of different halide sources (yields 33-90%) are described.</p>
1-Trisopropylsilyloxy-1,2-propadiene		Reagent
<p>The title reagent reacts with aldehydes or ketones to give α,β-unsaturated acyl silanes.</p> <p>I. A. Stergiades, M. A. Tius <i>J. Org. Chem.</i> 1999, <i>64</i>, 7457.</p>	<p>A (a) <i>t</i>-BuLi (0.9 eq) THF, -78°C, 1.5 h (b) <i>p</i>-Me₂NC₆H₄CHO (0.8 eq) THF, -78°C, 45 min 81%</p>	<p>21 examples (yields 27-92%) are described.</p>
4-Nitrophenyltrifluoromethanesulfonate		Reagent
<p>The title reagent is reported as a new trifluoromethanesulfonyl transfer agent.</p> <p>L. Neville, A. Bigot, M. E. T. H. Dau, J. Zhu <i>J. Org. Chem.</i> 1999, <i>64</i>, 7638.</p>	<p>A (1 eq), K₂CO₃ (2 eq) DMF, rt, 4 h 83%</p>	<p>9 examples (yields 60-92%) are reported.</p>
Cyanomethylenetriethylphosphorane (CMMP)		Reagent
<p>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.</p> <p>T. Tsunoda, K. Uemoto, T. Ohtani, H. Kaku, S. Itô <i>Tetrahedron Lett.</i> 1999, <i>40</i>, 7359.</p>	<p>A (2.1 eq) PhCH₂OH (0.7 eq) PhMe, 80°C, 1 d 100%</p>	<p>12 examples (yields 83-100%).</p>