

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.

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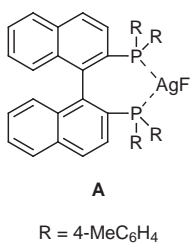
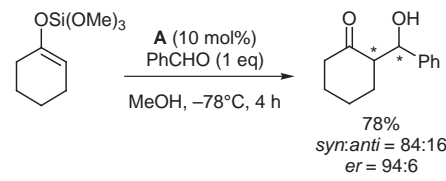
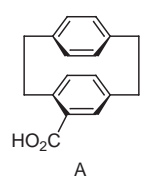
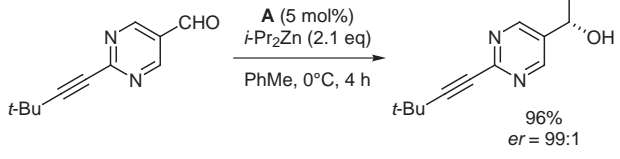
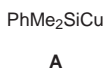
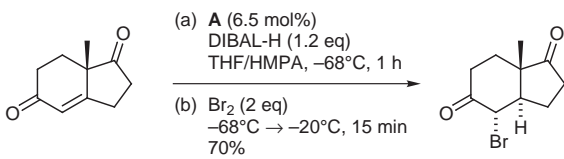
Fabrize Anizon, Robert Chow, Derek Johnston, Philip Kocienski, and Sukhjinder Uppal of Glasgow University.

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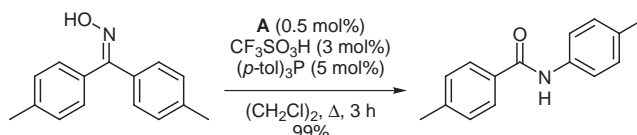
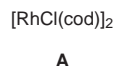
(R)-p-Tol-BINAP · AgFCOMplex		Catalyst
<p>The title reagent catalyses the enantioselective aldol reaction of trimethoxysilyl enol ethers with aldehydes.</p> <p>Yanagisawa, A.; Nakatsuka, Y.; Asakawa, K.; Kageyama, H.; Yamamoto, H. <i>Synlett</i> 2001, 69.</p>	 <p>A R = 4-MeC₆H₄</p>	 <p>11 examples (yields 56-87%, 74:26 > <i>syn:anti</i> > 99:1, %ee 85-97%).</p>
(R)-4-Carboxy[2.2]paracyclophane		Catalyst
<p>Reagent A acts as a chiral initiator in the enantioselective addition of diisopropylzinc to 2-alkynylpyrimidine-5-carbaldehyde to afford the corresponding 2-alkynylpyrimidyl alkanol.</p> <p>Tanji, S.; Ohno, A.; Sato, I.; Soai, K. <i>Org. Lett.</i> 2001, 3, 287.</p>	 <p>A</p>	 <p>1 example (yield 96%, %ee 97%) and 2 other initiators are reported.</p>
Dimethylphenylsilylcopper(I)		Catalyst
<p>The title reagent catalyses the reductive bromination of the Hajos dione.</p> <p>Daniewski, A. R.; Liu, W. <i>J. Org. Chem.</i> 2001, 66, 626.</p>	 <p>A</p>	 <p>1 example (70% yield) is reported.</p>

[Rh(dppe)]ClO₄		Catalyst
<p>The title reagent catalyses an intramolecular hydroacylation reaction for the synthesis of eight-membered rings. Examples with [Rh(dppe)]OTf are also reported.</p> <p>Aloise, A. D.; Layton, M. E.; Shair, M. D. <i>J. Am. Chem. Soc.</i> 2000, <i>122</i>, 12610.</p>	<p>[Rh(dppe)]ClO₄</p> <p>A</p>	<p>A (20 mol%) ethylene (CH₂Cl)₂, 65°C, 2 h 65%</p> <p>5 examples (yields 54-65%) are reported.</p>
Ruthenium Carbonyl		Catalyst
<p>The title reagent catalyses the intramolecular cyclo-coupling of ketones, alkenes or alkynes, and carbon monoxide for the synthesis of functionalised γ-butyrolactones.</p> <p>Tobisu, M.; Chatani, N.; Asaumi, T.; Amako, K.; Ie, Y.; Fukumoto, Y.; Murai, S. <i>J. Am. Chem. Soc.</i> 2000, <i>122</i>, 12663.</p>	<p>Ru₃(CO)₁₂</p> <p>A</p>	<p>A (2.5 mol%) P(4-CF₃C₆H₅)₃ (7.5 mol%) ethylene (3 atm) CO (5 atm) PhMe, 160°C, 20 h 94%</p> <p>56 examples (yields 13-99%) are reported.</p>
[RhCl(CO)₂]₂		Catalyst
<p>The title reagent catalyses the carbonylation of sp³ C-H bonds adjacent to the nitrogen of cyclic alkylamines.</p> <p>Chatani, N.; Asaumi, T.; Ikeda, T.; Yorimitsu, S.; Ishii, Y.; Kakiuchi, F.; Murai, S. <i>J. Am. Chem. Soc.</i> 2000, <i>122</i>, 12882.</p>	<p>[Rh(CO)₂]₂</p> <p>A</p>	<p>A (4 mol%) CO (10 atm) ethylene (5 atm) 2-propanol, 160°C, 1.5 d 68%</p> <p>8 examples (yields 12-84%) are reported.</p>
Tetrabutylammonium Chloride		Catalyst
<p>The title reagent catalyses the azidolysis of epoxides to give the corresponding azido alcohol in solvent free conditions.</p> <p>Schneider, C. <i>Synlett</i> 2000, 1840.</p>	<p><i>n</i>-Bu₄NF</p> <p>A</p>	<p>(a) A (10 mol%) Me₃SiN₃ (1 eq) rt, 1 d (b) <i>p</i>-TsOH, MeOH rt, 30 min 89%</p> <p>7 examples (yields 5-89%) are reported.</p>
Molybdenum Metathesis Catalyst		Catalyst
<p>Reagent A, when activated in situ by dichloromethane, catalyses the cross metathesis reaction of functionalised alkynes.</p> <p>Fürstner, A.; Mathes, C. <i>Org. Lett.</i> 2001, <i>3</i>, 221.</p>	<p>Mo[N(<i>t</i>-Bu)(Ar)₃]</p> <p>A</p> <p>Ar = 3,5-dimethylphenyl</p>	<p>A (10 mol%) Ph-C≡C-Me CH₂Cl₂/PhMe, 80°C 71%</p> <p>15 examples (yields 47-82%) are reported.</p>

Chloro(1,5-cyclooctadiene)rhodium(I) Dimer

Catalyst

The title reagent catalyses the Beckmann rearrangement of oximes to give the corresponding amides.



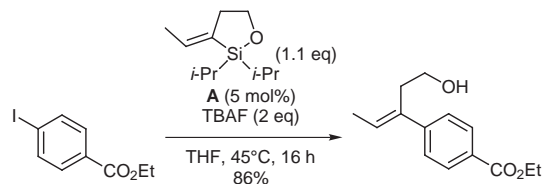
Arisawa, M.; Yamaguchi, M. *Org. Lett.* **2001**, *3*, 311.

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

Bis(dibenzylideneacetone)palladium

Catalyst

The title reagent catalyses the cross-coupling of alkydenesilacyclopentanes with aryl or alkenyl halides to give trisubstituted homoallylic alcohols.



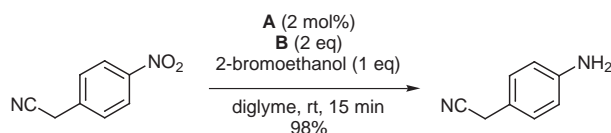
Denmark, S. E.; Pan, W. *Org. Lett.* **2001**, *3*, 61.

13 examples (yields 45-88%) are reported.

Phthalocyanatoiron [PcFe(II)] / Sodium Borohydride

Catalyst

The title reagent pair, in the presence of 2-bromoethanol, catalyses the reduction of nitroarenes.



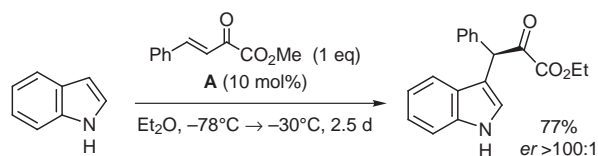
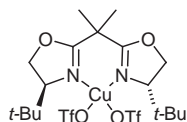
Wilkinson, H. S.; Tanuory, G. J.; Wald, S. A.; Senanayake, C. H. *Tetrahedron Lett.* **2001**, *42*, 167.

7 examples (yields 67-95%) are reported.

[[(S)-t-Bu-BOX]Cu(OTf)₂] Complex

Catalyst

The title reagent catalyses the asymmetric Friedel-Crafts alkylation of β,γ-unsaturated α-ketoesters.



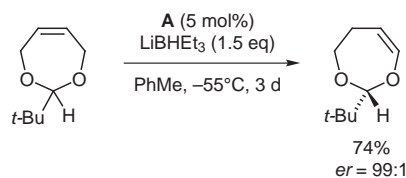
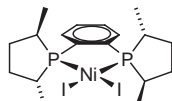
Jensen, K. B.; Thorhauge, J.; Hazell, R. G.; Jorgensen, K. A. *Angew. Chem. Int. Ed.* **2001**, *40*, 160.

13 examples (yields 69-99%, %ee 79-99.5%).

1,2-Bis(phospholanyl)benzene-Modified Diiodonickel Complex

Catalyst

The title reagent, when activated with LiBHET₃, catalyses the highly enantioselective isomerization of 4,7-dihydro-1,3-dioxepins.

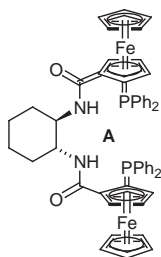


Frauenrath, H.; Brethauer, D.; Reim, S.; Maurer, M.; Raabe, G. *Angew. Chem. Int. Ed.* **2001**, *40*, 177.

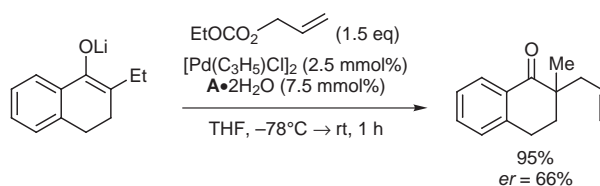
3 examples (yields 74-75%, %ee 90-98%) are reported.

(*R,R,Sp,Sp*)-Bis-*N*-[2-(diphenylphosphino)ferrocenylcarbonyl]-diaminocyclohexane Derivative**Ligand**

The title ligand is used in palladium-catalysed asymmetric alkylation of ketone enolates.



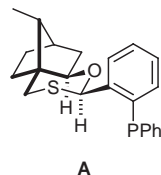
You, S.-L.; Hou, X.-L.; Dai, L.-X.; Zhu, X.-Z. *Org. Lett.* **2001**, 3, 149.



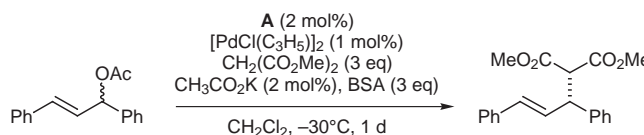
3 examples (yields 77-95%, %ee 66-87%) are reported.

(1*R,3R,5R,8S*)-11,11-Dimethyl-4-oxa-5-(2-diphenylphosphino)phenyl-6-thiatricyclo[6.2.1.0]undecane**Ligand**

The title ligand is used in palladium-catalysed asymmetric allylic substitution reactions.



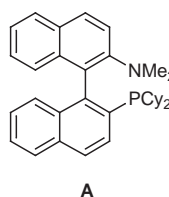
Nakano, H.; Okuyama, Y.; Yanagida, M.; Hongo, H. *J. Org. Chem.* **2001**, 66, 620.



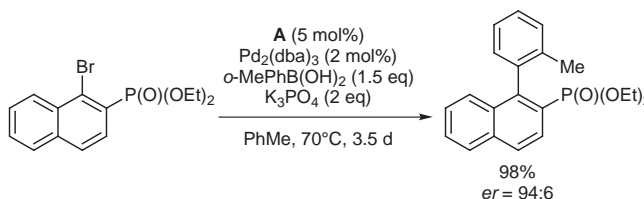
4 examples (yields 74-98%, %ee 76-94%) are reported.

(*S*)-(+)-2-Cyclohexylphosphino-2'-dimethylamino-1,1'-binaphthyl**Ligand**

The title ligand is used in the Pd-catalysed asymmetric Suzuki coupling for the preparation of biaryl compounds.



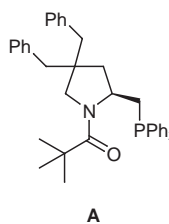
Yin, J.; Buchwald, S. L. *J. Am. Chem. Soc.* **2000**, 122, 12051.



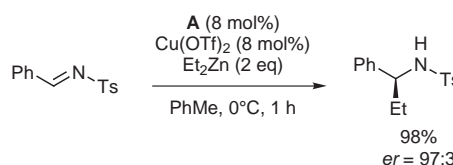
17 examples (yields 74-98%, %ee 57-92%) are reported.

Chiral Amidophosphine**Ligand**

Ligand **A** is used in the Cu-catalysed asymmetric addition of diethylzinc to *N*-sulfonylimines.



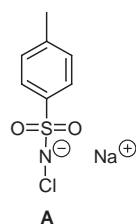
Fujihara, H.; Nagai, K.; Tomioka, K. *J. Am. Chem. Soc.* **2000**, 122, 12055.



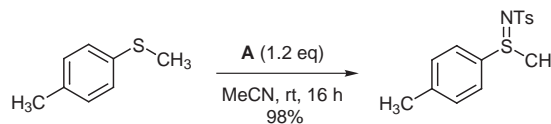
16 examples (yields 22-99%, %ee 5-94%) are reported.

Chloramine-T**Reagent**

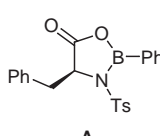
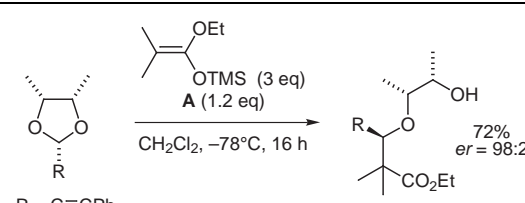
The title reagent is used for the preparation of *N*-sulfonylsulfilimines from sulfides.

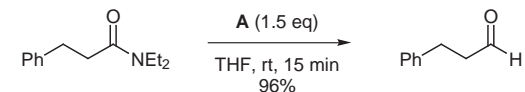


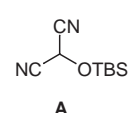
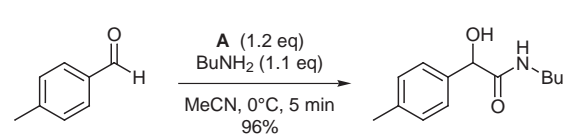
Marzinzik, A. L.; Sharpless, K. B. *J. Org. Chem.* **2001**, 66, 594.

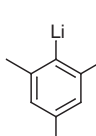
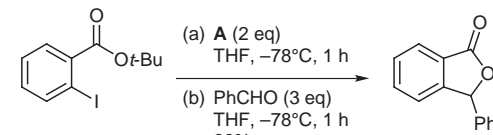


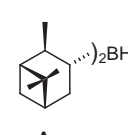
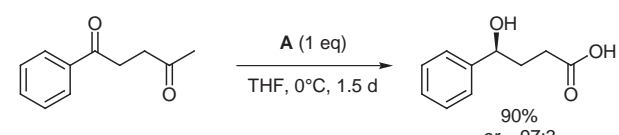
15 examples (yields 70-99%) are reported.

Chiral Oxazaborolidinone		Reagent
The title reagent mediates the enantioselective ring-cleavage of diastereomeric 1,3-dioxolane acetals.		
Harada, T.; Yamanaka, H.; Oku, A. <i>Synlett</i> 2001 , 61.	A	R = C≡CPh 6 examples (yields 46-92%, %ee 83-98%) are reported.

Cp ₂ Zr(H)Cl (Schwartz reagent)		Reagent
The title reagent reduces tertiary amides to aldehydes.	Cp ₂ Zr(H)Cl A	
White, J. M.; Rao Tunoori, A.; Georg, G. I. <i>J. Am Chem. Soc.</i> 2000 , <i>122</i> , 11995.		16 examples (yields 74-99%) are reported.

tert-Butyldimethylsilyloxymalononitrile		Reagent
The title reagent is used in a one-pot synthesis of α-silyloxyamides from aldehydes and ketones.		
Nemoto, H.; Ma, R.; Suzuki, I.; Shibuya, M. <i>Org. Lett.</i> 2000 , <i>2</i> , 4245.	A	26 examples (yields 35-97%) are reported.

Mesityllithium		Reagent
The title reagent is used as a selective lithiating agent for the preparation of aryllithium compounds having alkoxy carbonyl groups.		
Kondo, Y.; Asai, M.; Miura, T.; Uchiyama, M.; Sakamoto, T. <i>Org. Lett.</i> 2001 , <i>3</i> , 13.	A	8 examples (yields 57-97%) are reported.

Diisopinocampheylborane		Reagent
The title reagent is used for the reduction of α-, β-, and γ-keto acids to give corresponding hydroxy acids with high enantioselectivity.		
Ramachandran, P. V.; Brown, H. C.; Pitre, S. <i>Org. Lett.</i> 2001 , <i>3</i> , 17.	A	6 examples (yields 75-90%, %ee 77-90%) are reported.

Copper(I) Thiophene-2-carboxylate (CuTC)		Reagent
<p>The title reagent mediates the Pd-catalysed cross-coupling of thioalkyne derivatives with boronic acids to give functionalized alkynes.</p>	<p>CuTC A</p>	<p>11 examples (yields 39-91%) are reported.</p>
<p>Savarin, C.; Srogl, J.; Liebeskind, L. S. <i>Org. Lett.</i> 2001, <i>3</i>, 91.</p>		
Tetrabromomethane/Methanol		Reagent
<p>The title reagent pair is used for the highly chemoselective esterification of <i>sp</i>³-C tethered carboxylic acids in the presence of <i>sp</i>²-C and <i>sp</i>-C tethered carboxylic acids.</p>	<p>CBr₄ A MeOH B</p>	<p>11 examples (yields 39-91%) are reported.</p>
<p>Lee, A. S.-Y.; Yang, H.-C.; Su, F.-Y. <i>Tetrahedron Lett.</i> 2001, <i>42</i>, 301.</p>		
Cyanomethylenetriethylphosphorane (CMMP)		Reagent
<p>The title reagent mediates Mitsunobu-type alkylation of prenyl and geranyl phenyl sulfone with primary and secondary alcohols.</p>	<p>NC=PMe₃ A</p>	<p>12 examples (yields 54-100%) are reported.</p>
<p>Uemoto, K.; Kawahito, A.; Matsushita, N.; Sakamoto, I.; Kaku, H.; Tsunoda, T. <i>Tetrahedron Lett.</i> 2001, <i>42</i>, 905.</p>		
Iodomethylzinc 2,4,6-Trichlorophenoxide		Reagent
<p>The title reagent is used for the cyclopropanation of alkyl-substituted alkenes.</p>	<p>A</p>	<p>6 examples (yields 90-98%) are reported.</p>
<p>Charette, A. B.; Francoeur, S.; Martel, J.; Wilb, N. <i>Angew. Chem. Int. Ed.</i> 2000, <i>39</i>, 4539.</p>		
Phenylaziridine		Reagent
<p>The title reagent undergoes [3+2] dipolar cycloaddition with geminal alkenes, in the presence of a Lewis acid, to give single products.</p>	<p>A</p>	<p>4 examples (yields 72-78%) are reported.</p>
<p>Ungureanu, I.; Klotz, P.; Mann, A. <i>Angew. Chem. Int. Ed.</i> 2000, <i>39</i>, 4615.</p>		