

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:

Elyse Bourque, Jennifer Delaney, Marcel de Puit and Sukhjinder Uppal, Department of Chemistry, Leeds University, Leeds, LS2 9JT, UK.

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Journal of the American Chemical Society
Journal of Organic Chemistry
Organic Letters
Organometallics
Perkin Transactions I
Synlett
Synthesis
Tetrahedron
Tetrahedron Asymmetry and Tetrahedron Letters

Tetrakis[<i>N</i> -(4-dodecylphenyl)-sulfonyl]-prolinate] Dirhodium		Catalyst
<p>The title reagent promotes the catalytic asymmetric synthesis of highly functionalised cyclopentenes by a [3+2] cycloaddition. Davies, H. M. L.; Xiang, B.; Kong, N.; Stafford, D. G. <i>J. Am. Chem. Soc.</i> 2001, <i>123</i>, 7461.</p>	<p style="text-align: center;">A</p>	<p style="text-align: center;">6 examples (yields 49–79%, %ee 70–99%).</p>
Oxygen/Palladium(II) Acetate		Catalyst
<p>The title reagent pair promotes enantioselective oxidations of alcohols. Jensen, D. R.; Pugsley, J. S.; Sigman, M. S. <i>J. Am. Chem. Soc.</i> 2001, <i>123</i>, 7475.</p>	<p>Pd(OAc)₂ A</p> <p>O₂ B</p>	<p style="text-align: center;">12 examples (%conv 44–72%, %ee 66–99%).</p>
Iodosylbenzene/ <i>p</i> -Toluenesulfonamide/Tetrakis(acetonitrile)copper(I) Hexafluorophosphate		Catalyst
<p>The title reagents promote the formation of aziridines via a copper-catalysed nitrogen transfer. Dauban, P.; Sanière, L.; Tarrade, A.; Dodd, R. H. <i>J. Am. Chem. Soc.</i> 2001, <i>123</i>, 7707.</p>	<p>TsNH₂ A</p> <p>PhI=O B</p> <p>Cu(CH₃CN)₄PF₆ C</p>	<p style="text-align: center;">8 examples (yields 44–76%).</p>

Oxygen/Palladium(II) Norbornadiene dichloride

Catalyst

The title reagents promote enantioselective oxidations of alcohols.

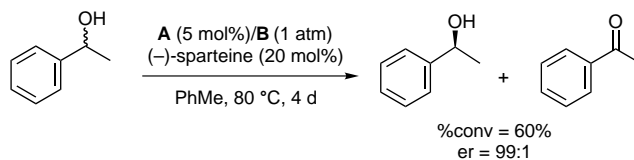
Ferreira, E. M.; Stoltz, B. M. *J. Am. Chem. Soc.* **2001**, *123*, 7725.

Pd(nbd)Cl₂

A

O₂

B



11 examples (%conv 48–70%, %ee 69–100%).

Copper(I) Iodide/(±)-Trans-1,2-cyclohexanediamine

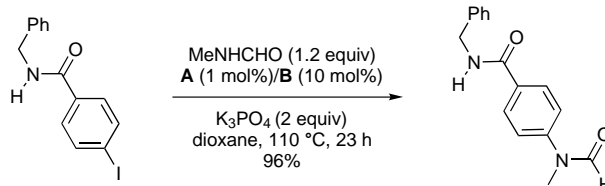
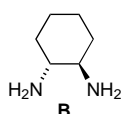
Catalyst

The title reagent pair promotes the amidation of aryl halides and the N-arylation of nitrogen heterocycles.

Klapars, A.; Antilla, J. C.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2001**, *123*, 7727.

CuI

A



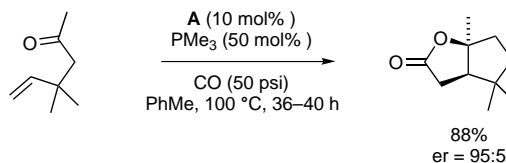
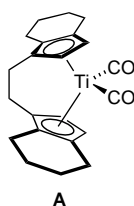
48 examples (yields 62–100%).

Ansa-Titanocene Dicarboxylate Complex

Catalyst

The title reagent promotes the formation of γ -butyrolactones via a catalytic asymmetric cyclocarbonylation.

Mandal, S. K.; Amin, S. R.; Crowe, W. E. *J. Am. Chem. Soc.* **2001**, *123*, 6457.



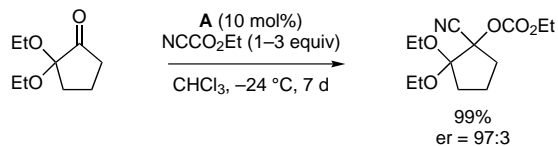
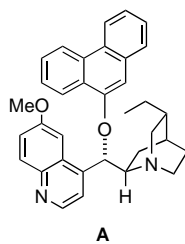
8 examples (yields 80–96%, %ee 0–90%).

9-Dihydroquinidylloxyphenanthrene

Catalyst

The title reagent promotes the cyanation of ketones to afford optically pure cyanohydrin carbonates.

Tian, S. K.; Deng, L. *J. Am. Chem. Soc.* **2001**, *123*, 6195.



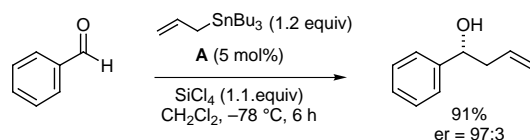
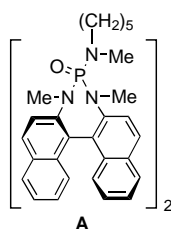
4 examples (yields 65–99%, %ee 90–96%).

Binaphthyl Bis-phosphoramidate^{a)}

Catalyst

The title reagent promotes catalytic enantioselective allylation and propargylation of aldehydes.

Denmark, S. E.; Wynn, T. *J. Am. Chem. Soc.* **2001**, *123*, 6199.



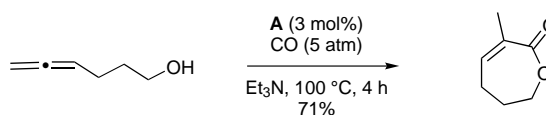
8 examples (yields 65–94%, %ee 11–94%).

^{a)}(*R,R*)-*N,N*-Bis[4,5-dihydro-3,5-dimethyl-4-(3*H*-dinapto[2,1-*d'*:1',2'-*f'*]-[1,3,2]-2-oxo-diazaphosphepino)]-*N,N*-dimethyl-1,5-pentanediamine

Catalyst

Triruthenium Dodecacarbonyl

The title reagent catalyses the cyclocarbonylation of allenyl alcohols to give 7- and 8-membered lactones. Yoneda, E.; Zhang, S.-W.; Onitsuka, K.; Takahashi, S. *Tetrahedron Lett.* **2001**, 42, 5459.

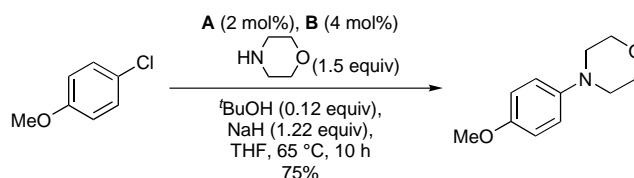
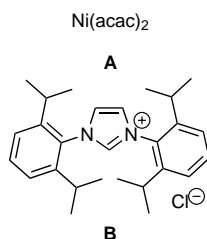


7 examples (yields 66–85%).

Nickel(II) Acetylacetonate/1,3-Bis-(2,6-diisopropylphenyl)-3H-imidazol-1-ium

Catalyst

The title reagent pair catalyses the amination of aryl chlorides. Gradel, B.; Brenner, E.; Schneider, R.; Fort, Y. *Tetrahedron Lett.* **2001**, 42, 5689.

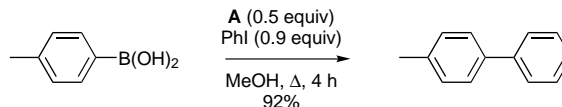


13 examples (yields 47–99%).

Palladium Black

Catalyst

The title reagent catalyses the Suzuki coupling of arylboronic acids with aryl iodides. Kabalka, G. W.; Namboodiri, V.; Wang, L. *Chem. Commun.* **2001**, 775.

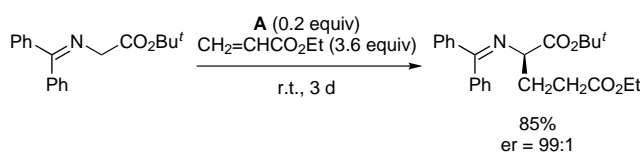
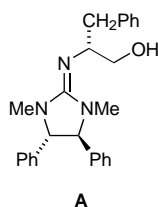


18 examples (yields 74–98%).

Modified Guanidine

Catalyst

The title reagent efficiently catalyses the asymmetric solvent-free Michael reaction of a prochiral glycine derivative with acrylate or its related compounds. Ishikawa, T.; Araki, Y.; Kumamoto, T.; Seki, H.; Fukuda, K.; Isobe, T. *Chem. Commun.* **2001**, 245.

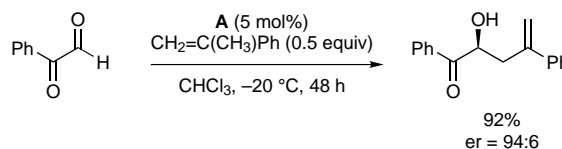
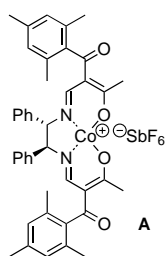


4 examples (yields 79–98%, %ee 55–97%).

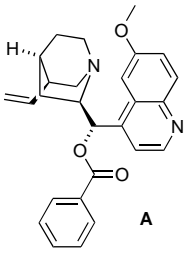
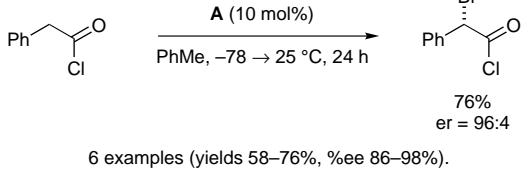
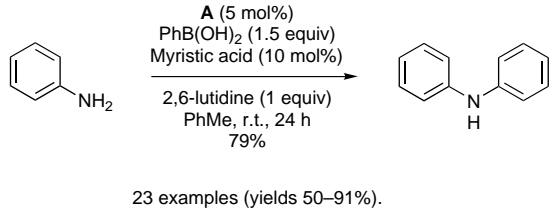
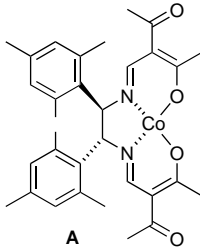
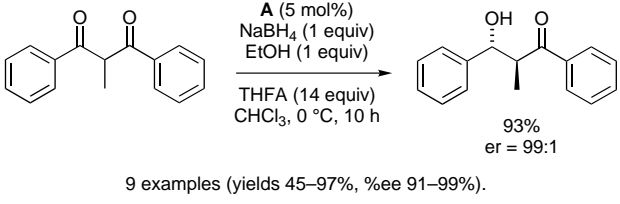
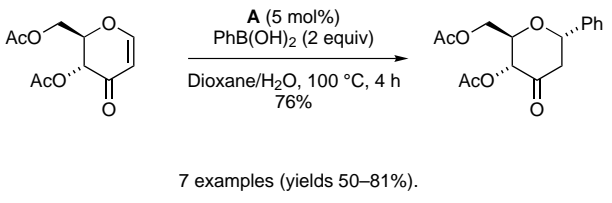
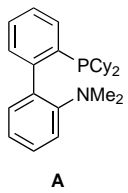
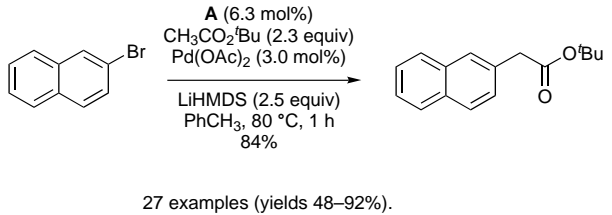
 β -Ketoiminato Cationic Cobalt(III) Complex

Catalyst

The title reagent catalyses the enantioselective carbonyl-ene reaction. Kezuka, S.; Ikeno, T.; Yamada, T. *Org. Lett.* **2001**, 3, 1937.

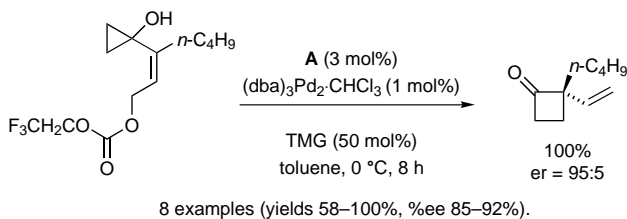
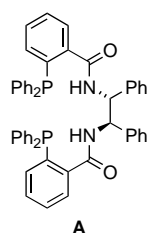


8 examples (yields 56–92%, %ee 76–94%).

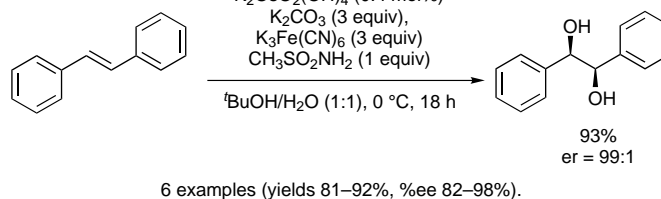
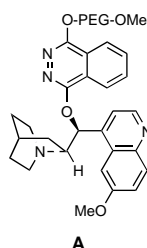
Benzoylquinine		Catalyst
<p>The title reagent catalyses the enantioselective α-bromination of acid chlorides.</p> <p>Hafez, A. M.; Taggi, A. E.; Wack, H.; Esterbrook, J.; Lectka, T. <i>Org. Lett.</i> 2001, 3, 2049.</p>		
Copper(II) Acetate		Catalyst
<p>The title reagent catalyses the coupling of arylboronic acids and amines.</p> <p>Antilla, J. C.; Buchwald, S. L. <i>Org. Lett.</i> 2001, 3, 2077.</p>	<p>Cu(OAc)₂</p> <p>A</p>	
β -Ketoiminato Cobalt Complex		Catalyst
<p>The title reagent catalyses the reductive desymmetrization of 2-alkyl-1,3-diketones.</p> <p>Ohtsuka, Y.; Koyasu, K.; Ikeno, T.; Yamada, T. <i>Org. Lett.</i> 2001, 3, 2543.</p>		
Cationic Rhodium Complex		Catalyst
<p>The title reagent catalyses the 1,4-addition of arylboronic acids to acetylated enones derived from glycals.</p> <p>Ramnauth, J.; Poulin, O.; Bratovanov, S. S.; Rakhit, S.; Maddaford, S. P. <i>Org. Lett.</i> 2001, 3, 2571.</p>	<p>Rh(I)(cod)₂BF₄</p> <p>A</p>	
(2'-Dicyclohexylphosphanyl)biphenyl-2-yl)-dimethylamine		Ligand
<p>The title reagent promotes α-arylation of esters in the presence of palladium(II) acetate.</p> <p>Moradi, W. A.; Buchwald, S. L. <i>J. Am. Chem. Soc.</i> 2001, 123, 7996.</p>		

(+)-1,2-Bis-*N*-[2'-(diphenyl-phosphino)benzoyl]-1(*R*),2(*R*)-diamino-1,2-diphenylethane**Ligand**

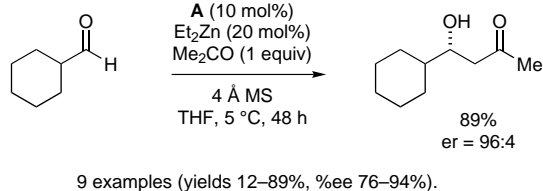
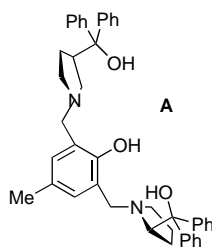
The title ligand promotes a catalytic asymmetric Wagner–Meerwein shift when complexed with palladium.
Trost, B. M.; Yasukata, T. *J. Am. Chem. Soc.* **2001**, *123*, 7162.

**(DHQD)₂PHAL-PEG-OMe****Ligand**

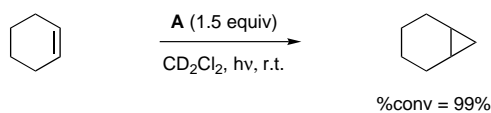
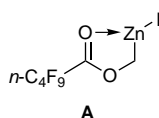
The title reagent is a soluble polymer-bound ligand, which when complexed to osmium, catalyses the asymmetric dihydroxylation of alkenes.
Kuang, Y. Q.; Zhang, S. Y. Y.; Wei, L. *Tetrahedron Lett.* **2001**, *42*, 5925.

**Phenol Ligand****Ligand**

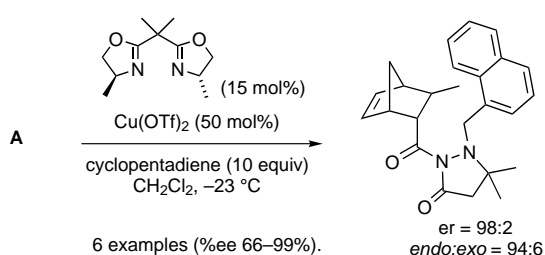
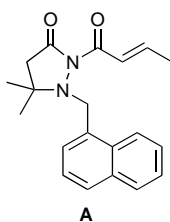
The title ligand promotes the zinc-catalysed direct asymmetric aldol reaction of acetone.
Trost, B. M.; Silcoff, E. R.; Ito, H. *Org. Lett.* **2001**, *3*, 2497.

**Ethylzincmethyl Perfluoropentanoate****Reagent**

The title reagent promotes the formation of cyclopropanes from various alkenes.
Charette, A. B.; Beauchemin, A.; Francoeur, S. *J. Am. Chem. Soc.* **2001**, *123*, 8139.

**1-(1-Naphthylmethyl)-2-[(*E*)-2-butenoyl]-5,5-dimethylpyrazolidin-3-one****Reagent**

The title reagent promotes enantioselective Diels–Alder reactions by a novel strategy involving a chiral relay.
Sibi, M. P.; Venkatraman, L.; Liu, M.; Jasperse, C. P. *J. Am. Chem. Soc.* **2001**, *123*, 8444.

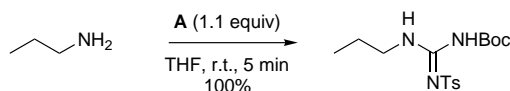
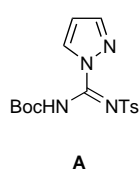


Potassium Trimethylsilanolate		Reagent
<p>The title reagent promotes the palladium-catalysed cross-coupling reaction of organosilicon compounds with organic iodides. Denmark, S. E.; Sweis, R. F. <i>J. Am. Chem. Soc.</i> 2001, 123, 6439.</p>	<p>KOSiMe₃ A</p>	<p>$n\text{-C}_5\text{H}_{11}\text{SiMe}_2\text{OH}$ (1.1 equiv) A (2 equiv) Pd(dba)₂ (5 mol%) DMF, r.t., 7.5 h 86% 14 examples (yields 76–95%).</p>
Dicyclohexylmethylamine		Reagent
<p>The title reagent promotes the Heck reaction of aryl chlorides and bromides with olefins, in the presence of Pd/P(<i>t</i>-Bu)₃ catalyst. Littke, A. F.; Fu, G. C. <i>J. Am. Chem. Soc.</i> 2001, 123, 6989.</p>	<p>Cy₂NMe A</p>	<p>CO_2Me (1.1 equiv) A (1.1 equiv) P(<i>t</i>-Bu)₃ (3 mol%) Pd₂(dba)₃ (1.5 mol%) dioxane, r.t., 36 h 79% 30 examples (yields 52–97%).</p>
Dimethyldioxirane		Reagent
<p>The title reagent promotes epoxidations of 1-amidoallenes as a general entry to chiral nitrogen-substituted oxyallyl cation equivalents for stereoselective [4+3] cycloaddition. Xiong, H.; Hsung, R. P.; Berry, C. R.; Rameshkumar, C. <i>J. Am. Chem. Soc.</i> 2001, 123, 7174.</p>	<p> A</p>	<p>A (2–3 equiv) ZnCl₂ (2.0 equiv) furan (10 equiv) THF, –40 °C, 8 h 40% dr = 95:5 8 examples (yields 40–83%, %de 5–90%).</p>
Tin(II) Triflate		Reagent
<p>The title reagent promotes the formation of optically pure 2,5-disubstituted-3-pyrrolidinones via an asymmetric [3+2] cycloaddition reaction involving chiral alkenyl Fischer carbene complexes and imines. Kagoshima, H.; Okamura, T.; Akiyama, T. <i>J. Am. Chem. Soc.</i> 2001, 123, 7182.</p>	<p>Sn(OTf)₂ A</p>	<p>(a) NPh (1.2 equiv) A (0.2 equiv) ClCH₂CH₂Cl, Δ, 3 h 51% (b) 6M HCl THF, r.t., 3 h 96% er = 99:1 9 examples (yields 85–98%, %ee 96–99%).</p>
Chiral Sulfide		Reagent
<p>The title reagent mediates the aziridination of imines with alkyl bromides via the imino Corey–Chaykovsky reaction. Saito, T.; Sakairi, M.; Akiba, D. <i>Tetrahedron Lett.</i> 2001, 42, 5451.</p>	<p> A</p>	<p>A (1 equiv), BnBr (3 equiv), K₂CO₃ (3 equiv) MeCN, r.t. 99% dr = 75:25 er = 97:3 10 examples (yields 79–99%, %de 8–58%, %ee 42–95%).</p>

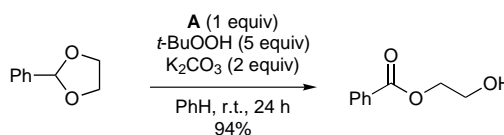
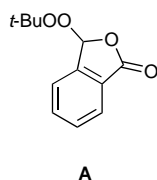
Titanium Tetraisopropoxide/Isopropylmagnesium Bromide		Reagent
<p>The title reagent pair, when reacted with 2-alkynyl tetramethylethylene acetals and then aldehydes, provides a one-pot route to 2-substituted and 2,3-disubstituted furans.</p> <p>Teng, X.; Takeshi, W.; Okamoto, S.; Sato, F. <i>Tetrahedron Lett.</i> 2001, <i>42</i>, 5501.</p>	<p>Ti(OⁱPr)₄ A</p> <p>ⁱPrMgBr B</p>	<p>11 examples (yields 55–99%).</p>
Cesium Carbonate		Reagent
<p>The title reagent reacts with primary amines, alkyl halides and carbon dioxide in a 3-component coupling reaction. The resultant carbamate is then N-alkylated with a different alkyl halide to give aliphatic N-alkyl carbamates.</p> <p>Salvatore, R. N.; Ledger, J. A.; Jung, K. W. <i>Tetrahedron Lett.</i> 2001, <i>42</i>, 6023.</p>	<p>Cs₂(CO)₃ A</p>	<p>11 examples (yields 52–92%).</p>
Copper(I) Thiophene-2-carboxylate (CuTC)		Reagent
<p>The title reagent mediates the non-basic, room-temperature, palladium-catalysed coupling of aryl and alkenyl iodides with boronic acids.</p> <p>Savarin, C.; Liebeskind, L. S. <i>Org. Lett.</i> 2001, <i>3</i>, 2149.</p>	<p>A</p>	<p>11 examples (yields 72–90%).</p>
Nickel(II) Acetylacetonate/Diethylzinc		Reagent
<p>The title reagent pair promotes a reductive homoallylic cyclization of ω-dienyl aldehydes.</p> <p>Shibata, K.; Kimura, M.; Shimizu, M.; Tamaru, Y. <i>Org. Lett.</i> 2001, <i>3</i>, 2181.</p>	<p>Ni(acac)₂ A</p> <p>Et₂Zn B</p>	<p>6 examples (yields 57–74%).</p>
N-(tert-Butoxycarbonyl)-N-[4-(dimethylazaniumylidene)-1,4-dihydropyridin-1-ylsulfonyl]janzanide		Reagent
<p>The title reagent can be used for the sulfamoylation of amines.</p> <p>Winum, J.-Y.; Toupet, L.; Barragan, V.; Dewynter, G.; Montero, J.-L. <i>Org. Lett.</i> 2001, <i>3</i>, 2241.</p>	<p>A</p>	<p>10 examples (yields 35–100%).</p>

tert*-Butyl[pyrazol-1-yl(toluene-4-sulfonylimino)methyl] Carbamate*Reagent**

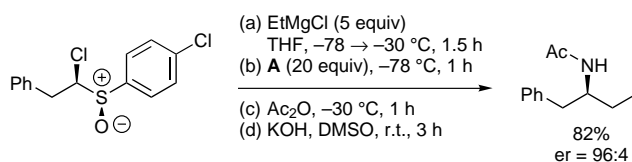
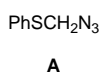
The title reagent can be used for the preparation of guanidine-containing peptides.
Zhang, Y.; Kennan, A. J. *Org. Lett.* **2001**, 3, 2341.

**1-*tert*-Butylperoxy-1,2-benziodoxol-3(1*H*)-one****Reagent**

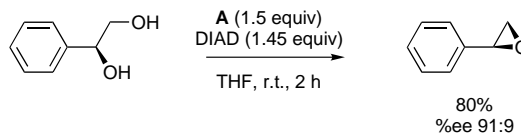
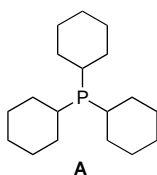
The title reagent can be used for the oxidative cleavage of five-membered cyclic acetals to the corresponding hydroxy esters under mild conditions.
Sueda, T.; Fukuda, S.; Ochiai, M. *Org. Lett.* **2001**, 3, 2387.

**Azidomethyl Phenyl Sulfide****Reagent**

The title reagent can be used for the amination of Grignard reagents.
Hoffmann, R. W.; Holzer, B.; Knopff, O. *Org. Lett.* **2001**, 3, 1945.

**Tricyclohexylphosphine****Reagent**

The title reagent promotes the Mitsunobu cyclodehydration of chiral phenethane-1,2-diols when used with diisopropylazodicarboxylate (DIAD).
Weissman, S. A.; Rossen, K.; Reider, P. J. *Org. Lett.* **2001**, 3, 2513.

**Lithium Bis(trimethylsilyl)amide****Reagent**

The title reagent can be used for the palladium-catalysed synthesis of arylamines from aryl halides.
Lee, S.; Jorgenson, M.; Hartwig, J. F. *Org. Lett.* **2001**, 3, 2729.

