

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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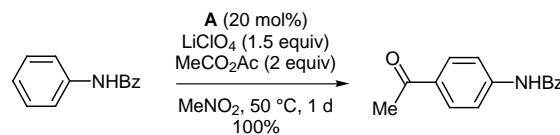
The journals regularly covered by the abstractors are:

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 I
 Synlett
 Synthesis
 Tetrahedron
 Tetrahedron Asymmetry and Tetrahedron Letters

Gallium(III) Trifluoromethanesulfonate

Catalyst

The title reagent promotes the Friedel-Crafts acylation of aniline derivatives.



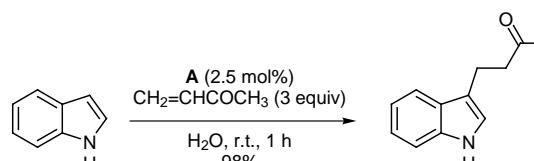
Kobayashi, S.; Komoto, I.; Matsuo, J.
Adv. Synth. Catal. **2001**, *343*, 71.

22 examples (yields 0–100%).

Scandium Tris(dodecylsulfate)

Catalyst

The title reagent promotes the conjugate addition of indoles to electron-deficient olefins in water.



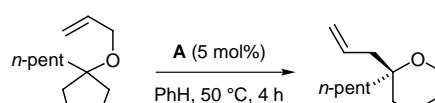
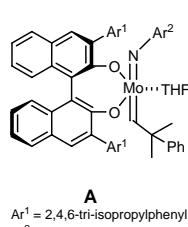
Manabe, K.; Aoyama, N.; Kobayashi, S.
Adv. Synth. Catal. **2001**, *343*, 175.

9 examples (yields 47–98%).

Molybdenum-based Chiral Complex

Catalyst

Reagent A catalyses olefin metathesis for the enantioselective synthesis of unsaturated cyclic tertiary ethers.

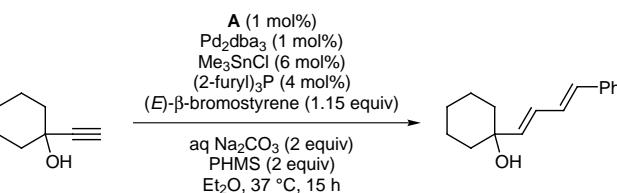
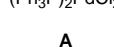


Cefalo, D. R.; Kiely, A. F.; Wuchrer, M.; Jamieson, J. Y.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2001**, *123*, 3139.

5 examples (yields 73–95%, %ee 74–96%).

Bis(triphenylphosphine)palladium Dichloride**Catalyst**

The title catalyst is used for the one-pot tandem Pd-catalysed hydro-stannylation/Stille coupling protocol for the stereoselective generation of vinyltins and their subsequent union.

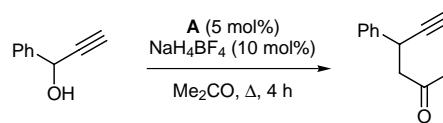
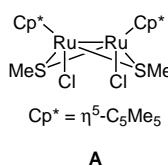


Gallagher, W. P.; Terstiege, I.; Maleczka, R. E. Jr. *J. Am. Chem. Soc.* **2001**, 123, 3194.

18 examples (yields 0–91%).

Thiolate-bridged Diruthenium Complex**Catalyst**

Reagent A promotes the alkylation of propargylic alcohols with ketones to afford γ -keto acetylenes.

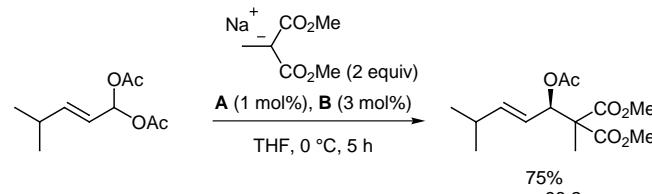
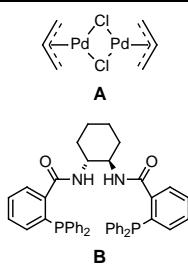


Nishibayashi, Y.; Wakiji, I.; Ishii, Y.; Uemura, S.; Hidai, M. *J. Am. Chem. Soc.* **2001**, 123, 3393.

18 examples (yields 50–88%).

 π -Allylpalladium Chloride Dimer/Chiral Phosphine Ligand**Catalyst**

The title reagent pair promotes the asymmetric addition of malonate nucleophiles to geminal dicarboxylates.

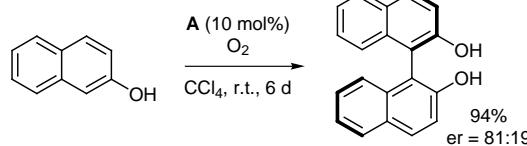
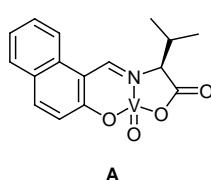


Trost, B. M.; Lee, C. B. *J. Am. Chem. Soc.* **2001**, 123, 3671.

18 examples (yields 62–97%).

Chiral Tridentate Oxovanadium(IV) Complex**Catalyst**

The title reagent catalyses the asymmetric oxidative coupling of various 3-, 6-, and 7-substituted 2-naphthols under oxygen to afford BINOLs.

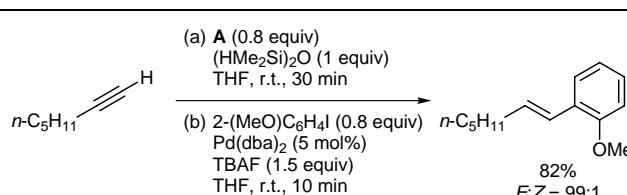
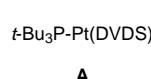


Hon, S.-W.; Li, C.-H.; Kuo, J.-H.; Barhate, N. B.; Liu, Y.-H.; Wang, Y.; Chen, C.-T. *Org. Lett.* **2001**, 3, 869.

7 examples (yields 75–100%, %ee 35–68%).

Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane [Pt(DVDS)] -Tris(tert-butyl)phosphine Complex**Catalyst**

The title reagent catalyses the hydrosilylation of terminal alkynes to give disiloxanes, which then undergo palladium-catalysed cross-coupling with aryl and alkenyl iodides to afford the corresponding alkenes.

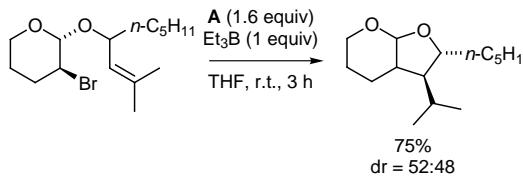
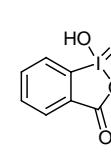
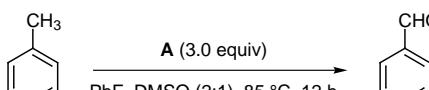
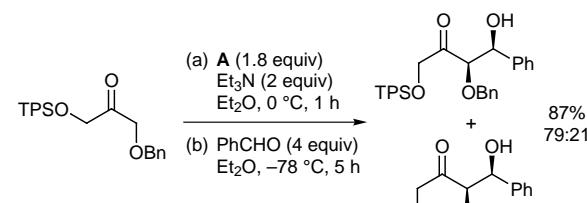
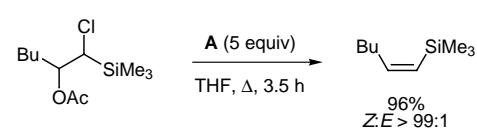
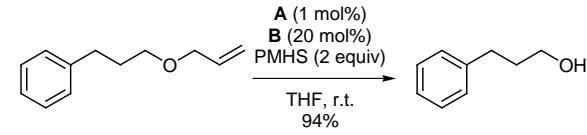


Denmark, S. E.; Wang, Z. *Org. Lett.* **2001**, 3, 1073.

19 examples (yields 67–94%).

N,N'-Dicyclohexyl-1,4-diazabutadiene/Palladium Diacetate			Catalyst
The title reagent pair catalyses the Suzuki–Miyaura cross-coupling of aryl halides with arylboronic acids.	<p>A: Cy-N=C=N-Cy (N,N'-dicyclohexyl-1,4-diazabutadiene)</p> <p>B: Pd(OAc)₂ (Palladium Diacetate)</p>	<p>A (3 mol%), B (3 mol%) Cs₂CO₃ (2 equiv) PhB(OH)₂ (1.5 equiv) dioxane, 80 °C, 3 h 99%</p>	
Grasa, G. A.; Hillier, A. C.; Nolan, S. P. <i>Org. Lett.</i> 2001 , 3, 1077.	18 examples (yields 20–99%) are reported.		
Nickel Bis(diphenylphosphanyl)ethane Dibromide			Catalyst
The title reagent catalyses the regio- and stereoselective cyclisation of oxanorbornenes with alkyl propiolates.	<p>A: [NiBr₂(dppe)]</p>	<p>A (5 mol%) Zn (2.75 equiv) Me-C≡C-CO₂Me (1.2 equiv) MeCN, 80 °C, 12 h 87%</p>	
Rayabarapu, D. K.; Sambaiah, T.; Cheng, C.-H. <i>Angew. Chem. Int. Ed.</i> 2001 , 40, 1286.	15 examples (yields 56–89%) are reported.		
Tetrakis(triphenylphosphine)palladium			Catalyst
The title reagent catalyses the [3+2] cycloaddition of alkylidene-cyclopropanes with aldehydes.	<p>A: Pd(PPh₃)₄</p>	<p>Pd(PPh₃)₄ (2 mol%) P(OBu)₃ (4 mol%) 120 °C, 5 h 75%</p>	
Nakamura, I.; Oh, B. H.; Saito, S.; Yamamoto, Y. <i>Angew. Chem. Int. Ed.</i> 2001 , 40, 1298.	10 examples (yields 38–86%).		
Vanadyl Acetylacetone			Catalyst
The title reagent catalyses the selective oxidation of olefins to vicinal syn-diols by aqueous hydrogen peroxide, osmium tetroxide and <i>N</i> -methylmorpholine (NMM).	<p>A: VO(acac)₂</p>	<p>A (2 mol%) OsO₄ (2 mol%), NMM (23 mol%) Et₄NOAc (2 equiv), H₂O₂ (1.5 equiv) Me₂CO–H₂O (3:1), r.t., 16 h</p>	
Ell, A. H.; Jonsson, S. Y.; Börje, A.; Adolfsson, H.; Bäckvall, J.-E. <i>Tetrahedron Lett.</i> 2001 , 42, 2569.	6 examples (yields 66–89%).		
(R)-(+)-(4,4'-Bi-1,3-benzodioxol)-5,5'-diylbis(diphenylphosphine) (SEGPHEOS)			Ligand
The title ligand is used in the asymmetric ruthenium-catalysed hydrogenation of various carbonyl compounds.	<p>A: (R)-(+)-(4,4'-Bi-1,3-benzodioxol)-5,5'-diylbis(diphenylphosphine)</p>	<p>A (0.01 mol%) H₂ (30 kg/cm²) MeOH, 65 °C, 7 h 100% er = 100:1</p>	
Saito, T.; Yokozawa, T.; Ishizaki, T.; Moroi, T.; Sayo, N.; Miura, T.; Kumabayashi, H. <i>Adv. Synth. Catal.</i> 2001 , 343, 264.	7 examples (yields 99–100%, %ee 93–99%).		

2,6-Bis{[(S)-2-(diphenylhydroxymethyl)pyrrolidinyl]-1-methyl}-4-methylphenol		Ligand
Ligand A is used in combination with diethylzinc to promote the asymmetric aldol reaction.		<p>A (2.5 mol%) Et₂Zn (5 mol%) HOCH₂COPh (1.5 equiv) 4 Å MS THF, -35 °C, 1 d</p> <p>83% dr = 31:1 er = 96:4</p> <p>10 examples (yields 62–97%, %de 50–100%, %ee 81–98%).</p>
Trost, B. M.; Ito, H.; Silcoff, E. R. <i>J. Am. Chem. Soc.</i> 2001 , <i>123</i> , 3367.		
(1<i>R</i>,2<i>R</i>)-1,2-Bis(dicyclohexylphosphanyl)cyclohexane		Ligand
The title ligand is used for the rhodium-catalysed enantioselective hydroboration of styrene derivatives.		<p>A (1.2 mol%) [Rh(cod)₂]BF₄ (1 mol%) catecholborane (1.2 equiv) DME, -35 °C, 3 h</p> <p>85% er = 96:4</p> <p>10 examples (yields 50–85%, %ee 58–93%).</p>
Demay, S.; Volant, F.; Knochel, P. <i>Angew. Chem. Int. Ed.</i> 2001 , <i>40</i> , 1235.		
Bisoxazoline Ligand		Ligand
The title ligand is used for conjugate radical addition to dehydroalanines followed by enantioselective H-atom transfer.		<p>A (1.3 equiv) Mg(ClO₄)₂ (1.3 equiv) EtLi (5 equiv) Bu₃SnH (2 equiv) Et₃B (6.7 equiv), O₂ CH₂Cl₂, -78 °C, 3 h</p> <p>72% er = 93:7</p> <p>7 examples (yields 54–76%, %ee 27–83%).</p>
Sibi, M. P.; Asano, Y.; Sausker, J. B. <i>Angew. Chem. Int. Ed.</i> 2001 , <i>40</i> , 1293.		
Arduengo-type Stabilised Carbene		Ligand
The title reagent accelerates the copper-catalysed conjugate addition of diethylzinc to enones.		<p>A (5 mol%) Cu(OTf)₂ (4.5 mol%) THF-PhMe (1:1), -20 °C, 30 min 100%</p> <p>100%</p> <p>8 examples (yields 3, 48–100%).</p>
Fraser, P. K.; Woodward, S. <i>Tetrahedron Lett.</i> 2001 , <i>42</i> , 2747.		
Menthyl Binaphthylphosphite		Ligand
The title reagent is used in the rhodium-catalysed enantioselective hydrogenation of prochiral olefins.		<p>A (0.1 mol%) [Rh(COD)₂]BF₄ (0.05 mol%) H₂ (10 bar) CH₂Cl₂, r.t., 12 h</p> <p>100% er = 98:2</p> <p>2 examples (yields 100%, %ee 75–96%).</p>
Chen, W.; Xiao, J. <i>Tetrahedron Lett.</i> 2001 , <i>42</i> , 2897.		

Bis(cyclopentadienyl)zirconium Chloride Hydride (Schwartz Reagent)			Reagent
The title reagent is used for the triethylborane-induced radical reaction of halogeno acetals bearing an allyl moiety.	$\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ A		
Fujita, K.; Nakamura, T.; Yorimitsu, H. Oshima K. <i>J. Am. Chem. Soc.</i> 2001 , 123, 3137.			13 examples (yields 46–94%, %de 2–64%).
O-Iodoxybenzoic Acid (IBX)			Reagent
The title reagent promotes the selective oxidation at carbon adjacent to aromatic systems.			
Nicolaou, K. C.; Baran, P. S.; Zhong, Y.-L. <i>J. Am. Chem. Soc.</i> 2001 , 123, 3183.			28 examples (yields 50–95%).
Chlorodicyclohexylborane			Reagent
The title reagent, in the presence of a tertiary amine, is used in the asymmetric boron aldol additions of <i>O</i> -protected α,α' -dioxygenated ketones.	$(\text{Cyclohexyl})_2\text{BH}$ A		
Murga, J.; Falomir, E.; Carda, M.; González, F.; Marco, J. A. <i>Org. Lett.</i> 2001 , 3, 901.			11 examples (yields 30–92%).
Samarium Diiodide			Reagent
The title reagent induces β -elimination of <i>O</i> -acetyl 1-chloro-1-trimethylsilylalkan-2-ols to afford (<i>Z</i>)-vinylsilanes.	SmI_2 A		
Concellón, J. M.; Bernad, P. L.; Bardales, E. <i>Org. Lett.</i> 2001 , 3, 937.			10 examples (yields 92–96%, 2:98 > <i>E</i> : <i>Z</i> < 85:15%).
Tetrakis(triphenylphosphine)palladium(0)/Zinc Chloride			Reagent
The title reagent pair is used in combination with polymethyl-hydrosiloxane (PMHS) for the selective cleavage of allyl ethers, amines and esters.	$\text{Pd}(\text{PPh}_3)_4$ A ZnCl_2 B		
Chandrasekhar, S.; Raji, Reddy C.; Jagadeeshwar, Rao R. <i>Tetrahedron</i> 2001 , 57, 3435.			26 examples (yields 85–94%).