

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:

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

The journals regularly covered by the abstractors are:

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 Chemical Communications
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 Organic Letters
 Organometallics
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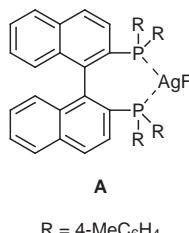
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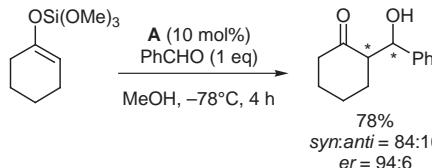
(R)-p-Tol-BINAP·AgFComplex

Catalyst

The title reagent catalyses the enantioselective aldol reaction of trimethoxysilyl enol ethers with aldehydes.



Yanagisawa, A.; Nakatsuka, Y.; Asakawa, K.; Kageyama, H.; Yamamoto, H. *Synlett* **2001**, 69.

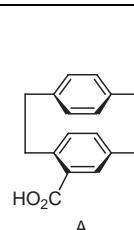


11 examples (yields 56–87%, 74:26 > syn:anti > 99:1, %ee 85–97%).

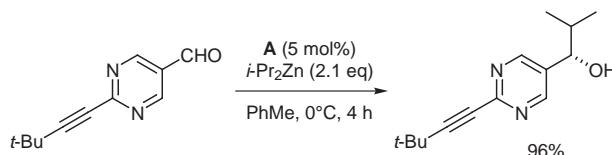
(R)-4-Carboxy[2.2]paracyclophane

Catalyst

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.



Tanji, S.; Ohno, A.; Sato, I.; Soai, K. *Org. Lett.* **2001**, 3, 287.

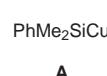


1 example (yield 96%, %ee 97%) and 2 other initiators are reported.

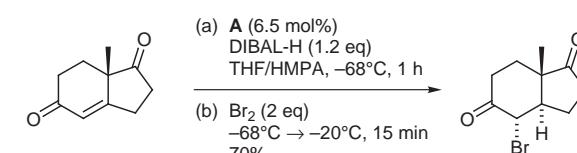
Dimethylphenylsilylcopper(I)

Catalyst

The title reagent catalyses the reductive bromination of the Hajos dione.



Daniewski, A. R.; Liu, W. *J. Org. Chem.* **2001**, 66, 626.



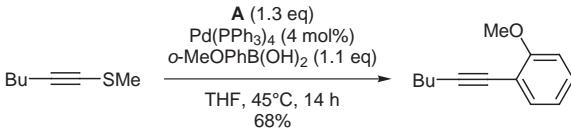
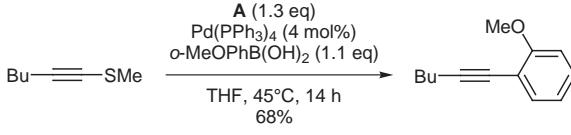
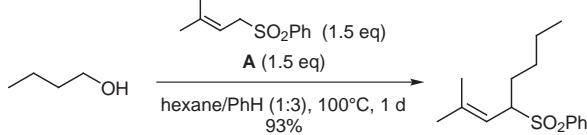
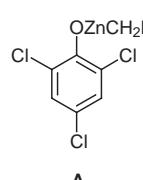
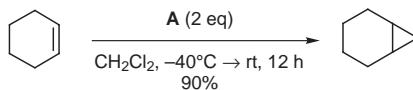
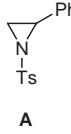
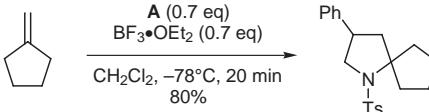
1 example (70% yield) is reported.

[Rh(dppe)]ClO ₄	Catalyst
The title reagent catalyses an intramolecular hydroacylation reaction for the synthesis of eight-membered rings. Examples with [Rh(dppe)]OTf are also reported. Aloise, A. D.; Layton, M. E.; Shair, M. D. <i>J. Am. Chem. Soc.</i> 2000 , 122, 12610.	<p style="text-align: center;">5 examples (yields 54-65%) are reported.</p>
Ruthenium Carbonyl	Catalyst
The title reagent catalyses the intramolecular cyclo-coupling of ketones, alkenes or alkynes, and carbon monoxide for the synthesis of functionalised γ -butyrolactones. Tobisu, M.; Chatani, N.; Asaumi, T.; Amako, K.; Ie, Y.; Fukumoto, Y.; Murai, S. <i>J. Am. Chem. Soc.</i> 2000 , 122, 12663.	<p style="text-align: center;">56 examples (yields 13-99%) are reported.</p>
[RhCl(CO) ₂] ₂	Catalyst
The title reagent catalyses the carbonylation of sp^3 C-H bonds adjacent to the nitrogen of cyclic alkylamines. Chatani, N.; Asaumi, T.; Ikeda, T.; Yorimitsu, S.; Ishii, Y.; Kakiuchi, F.; Murai, S. <i>J. Am. Chem. Soc.</i> 2000 , 122, 12882.	<p style="text-align: center;">8 examples (yields 12-84%) are reported.</p>
Tetrabutylammonium Chloride	Catalyst
The title reagent catalyses the azidolysis of epoxides to give the corresponding azido alcohol in solvent free conditions. Schneider, C. <i>Synlett</i> 2000 , 1840.	<p style="text-align: center;">7 examples (yields 5-89%) are reported.</p>
Molybdenum Metathesis Catalyst	Catalyst
Reagent A, when activated in situ by dichloromethane, catalyses the cross metathesis reaction of functionalised alkynes. Fürstner, A.; Mathes, C. <i>Org. Lett.</i> 2001 , 3, 221.	<p style="text-align: center;">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.	[RhCl(cod)] ₂ A	<p>A (0.5 mol%) CF₃SO₃H (3 mol%) (p-tol)₃P (5 mol%) (CH₂Cl)₂, Δ, 3 h 99%</p>
Arisawa, M.; Yamaguchi, M. <i>Org. Lett.</i> 2001 , 3, 311.		16 examples (yields 30-99%) are reported.
Bis(dibenzylideneacetone)palladium		Catalyst
The title reagent catalyses the cross-coupling of alkylidenesilacyclopentanes with aryl or alkenyl halides to give trisubstituted homoallylic alcohols.	Pd(dba) ₂ A	<p>i-Pr i-Pr A (5 mol%) TBAF (2 eq) THF, 45°C, 16 h 86%</p>
Denmark, S. E.; Pan, W. <i>Org. Lett.</i> 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.	PcFe(II) A NaBH ₄ B	<p>A (2 mol%) B (2 eq) 2-bromoethanol (1 eq) diglyme, rt, 15 min 98%</p>
Wilkinson, H. S.; Tanuory, G. J.; Wald, S. A.; Senanayake, C. H. <i>Tetrahedron Lett.</i> 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.	 A	<p>Ph-CH=CH-CO₂Me (1 eq) A (10 mol%) Et₂O, -78°C → -30°C, 2.5 d 77% er >100:1</p>
Jensen, K. B.; Thorhauge, J.; Hazell, R. G.; Jorgensen, K. A. <i>Angew. Chem. Int. Ed.</i> 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 LiBHET ₃ , catalyses the highly enantioselective isomerization of 4,7-dihydro-1,3-dioxepins.	 A	<p>A (5 mol%) LiBHET₃ (1.5 eq) PhMe, -55°C, 3 d 74% er = 99:1</p>
Frauenrath, H.; Brethauer, D.; Reim, S.; Maurer, M.; Raabe, G. <i>Angew. Chem. Int. Ed.</i> 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.	<p>A</p>	<p>EtOCO₂CH=CH₂ (1.5 eq) [Pd(C₃H₅)Cl]₂ (2.5 mmol%) A•2H₂O (7.5 mmol%) THF, -78°C → rt, 1 h 95% er = 66%</p>	3 examples (yields 77-95%, %ee 66-87%) are reported.
You, S.-L.; Hou, X.-L.; Dai, L.-X.; Zhu, X.-Z. <i>Org. Lett.</i> 2001 , 3, 149.			
(1<i>R</i>,3<i>R</i>,5<i>R</i>,8<i>S</i>)-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.	<p>A</p>	<p>A (2 mol%) [PdCl(C₃H₅)₂] (1 mol%) CH₂(CO₂Me)₂ (3 eq) CH₃CO₂K (2 mol%), BSA (3 eq) CH₂Cl₂, -30°C, 1 d</p>	4 examples (yields 74-98%, %ee 76-94%) are reported.
Nakano, H.; Okuyama, Y.; Yanagida, M.; Hongo, H. <i>J. Org. Chem.</i> 2001 , 66, 620.			
(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.	<p>A</p>	<p>A (5 mol%) Pd₂(dba)₃ (2 mol%) o-MePhB(OH)₂ (1.5 eq) K₃PO₄ (2 eq) PhMe, 70°C, 3.5 d 98% er = 94:6</p>	17 examples (yields 74-98%, %ee 57-92%) are reported.
Yin, J.; Buchwald, S. L. <i>J. Am. Chem. Soc.</i> 2000 , 122, 12051.			
Chiral Amidophosphine			Ligand
Ligand A is used in the Cu-catalysed asymmetric addition of diethylzinc to <i>N</i> -sulfonylimines.	<p>A</p>	<p>A (8 mol%) Cu(OTf)₂ (8 mol%) Et₂Zn (2 eq) PhMe, 0°C, 1 h 98% er = 97:3</p>	16 examples (yields 22-99%, %ee 5-94%) are reported.
Fujihara, H.; Nagai, K.; Tomioka, K. <i>J. Am. Chem. Soc.</i> 2000 , 122, 12055.			
Chloramine-T			Reagent
The title reagent is used for the preparation of <i>N</i> -sulfonylsulfilimines from sulfides.	<p>A</p>	<p>A (1.2 eq) MeCN, rt, 16 h 98%</p>	15 examples (yields 70-99%) are reported.
Marzinzik, A. L.; Sharpless, K. B. <i>J. Org. Chem.</i> 2001 , 66, 594.			

Chiral Oxazaborolidinone		Reagent
The title reagent mediates the enantioselective ring-cleavage of diastereomeric 1,3-dioxolane acetals.	<p>A</p>	<p>R = C≡CPh</p> <p>6 examples (yields 46–92%, %ee 83–98%) are reported.</p>
Harada, T.; Yamanaka, H.; Oku, A. <i>Synlett</i> 2001 , 61.		
Cp₂Zr(H)Cl (Schwartz reagent)		Reagent
The title reagent reduces tertiary amides to aldehydes.	<p>Cp₂Zr(H)Cl</p> <p>A</p>	<p>Ph-CH₂-CH₂-C(=O)-NEt₂ → Ph-CH₂-CH₂-C(=O)H</p> <p>THF, rt, 15 min 96%</p> <p>16 examples (yields 74–99%) are reported.</p>
White, J. M.; Rao Tunoori, A.; Georg, G. I. <i>J. Am Chem. Soc.</i> 2000 , 122, 11995.		
tert-Butyldimethylsilyloxymalononitrile		Reagent
The title reagent is used in a one-pot synthesis of α -silyloxyamides from aldehydes and ketones.	<p>CN OTBS</p> <p>A</p>	<p>Benzaldehyde + A (1.2 eq), BuNH₂ (1.1 eq) in MeCN, 0°C, 5 min 96%</p> <p>26 examples (yields 35–97%) are reported.</p>
Nemoto, H.; Ma, R.; Suzuki, I.; Shibuya, M. <i>Org. Lett.</i> 2000 , 2, 4245.		
Mesyllithium		Reagent
The title reagent is used as a selective lithiating agent for the preparation of aryllithium compounds having alkoxycarbonyl groups.	<p>A</p>	<p>(a) A (2 eq) THF, -78°C, 1 h</p> <p>(b) PhCHO (3 eq) THF, -78°C, 1 h 69%</p> <p>8 examples (yields 57–97%) are reported.</p>
Kondo, Y.; Asai, M.; Miura, T.; Uchiyama, M.; Sakamoto, T. <i>Org. Lett.</i> 2001 , 3, 13.		
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.	<p>A</p>	<p>3-phenylpropanoic acid → (R)-3-hydroxy-2-phenylpropanoic acid THF, 0°C, 1.5 d 90% er = 97:3</p> <p>6 examples (yields 75–90%, %ee 77–90%) are reported.</p>
Ramachandran, P. V.; Brown, H. C.; Pitre, S. <i>Org. Lett.</i> 2001 , 3, 17.		

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