

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:

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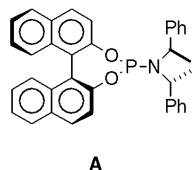
The journals regularly covered by the abstractors are:

Angewandte Chemie International Edition
 Bulletin of the Chemical Society of Japan
 Chemical Communications
 Chemistry A European Journal
 Chemistry Letters
 European Journal of Organic Chemistry
 Helvetica Chimica Acta
 Heterocycles
 Journal of the American Chemical Society
 Journal of Organic Chemistry
 Organometallics
 Perkin Transactions 1
 Synlett
 Synthesis
 Tetrahedron
 Tetrahedron Asymmetry and Tetrahedron Letters

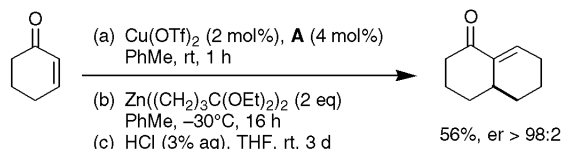
(S)-2,2'-Binaphthoyl-(R,R)-di(1-phenylethyl)aminoylphosphine

Catalyst

A mediates enantioselective 1,4-addition of ω -functionalised zinc reagents to a variety of cyclohexenones. Subsequent aldol condensation of the liberated aldehydes led to bicyclo[4.4.0]decalones with high stereoselectivity.



A



5 examples (combined yields 27-88%, %ee = 84-98%).

R. Naasz, L. A. Arnold, M. Pineschi, E. Keller, B. L. Feringa *J. Am. Chem. Soc.* **1999**, *121*, 1104.

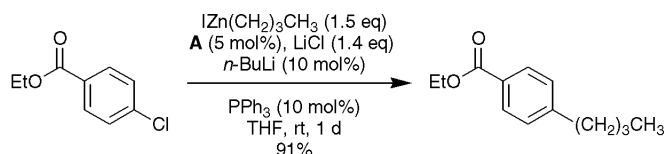
Nickel(II) chloride

Catalyst

The title reagent catalyses the substitution reaction of aryl chlorides with functionalised organozinc iodides.

NiCl_2

A



10 examples (yields 73-96%) are reported.

B. H. Lipshutz, P. A. Blomgren, S.-K. Kim *Tetrahedron Lett.* **1999**, *40*, 197.

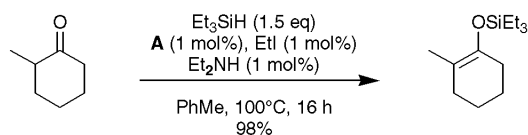
Palladium on carbon

Catalyst

Dehydrogenative silylation of ketones with hydrosilanes in the presence of **A** with diethylamine and ethyl iodide as cocatalysts is described.

Pd/C

A



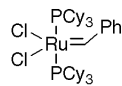
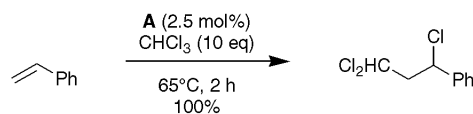
13 examples (19, 68-98%) are reported.

M. Igarashi, Y. Sugihara, T. Fuchikami *Tetrahedron Lett.* **1999**, *40*, 711.

Tributylphosphine		Catalyst
The title catalyst is used in the reaction of electron deficient olefins or imines with substituted 2-alkynoates or 2,3-allenoates giving [3+2] cycloaddition products.	<p style="text-align: center;">A</p>	<p>8 examples (yields 33-81%), reactions performed with triphenylphosphine resulted in lower yields.</p>
Z. Xu, X. Lu <i>Tetrahedron Lett.</i> 1999 , 40, 549.		
Palladium/Carbon Ethylenediamine Complex		Catalyst
Partial hydrogenation of aromatic aldehydes and ketones to benzylic alcohols has been achieved using the title catalyst.	<p style="text-align: center;">A</p>	<p>10 examples (yields 86-99%).</p>
H. Sajiki, K. Hattori, K. Hirota <i>J. Chem. Soc., Perkin Trans. 1</i> 1998 , 4043.		
Chiral Phase Transfer Catalyst		Catalyst
Phase-transfer catalysed asymmetric Darzens reactions of cyclic α -chloroketones are reported.	<p style="text-align: center;">A</p> <p>Ar = quinolinyl Ar' = 4-F₃CC₆H₄</p>	<p>7 examples (65-99%, %ee = 50-86%).</p>
S. Arai, Y. Shirai, T. Ishida, T. Shioiri <i>Chem. Commun.</i> 1999 , 49.		
Dichloro(<i>p</i>-isopropyltolyl)ruthenium(II)		Catalyst
A convenient protocol for ring closing metathesis reactions is described. A solution of commercially available catalyst A and PCy ₃ is heated together with the diene substrate under neon light.	<p style="text-align: center;">A</p>	<p>9 examples (yields 65-90%) are described.</p>
A. Fürstner, L. Ackermann <i>Chem. Commun.</i> 1999 , 95.		
[Ir(cod)(PPh₂Me)₂]PF₆		Catalyst
Iridium-catalysed isomerization of the double bond of 3-(silyloxy)-1-propenylboronates is reported. The methodology is utilised in the synthesis of (γ -(silyloxy)allyl)boronic esters.	<p style="text-align: center;">A</p>	<p>5 examples (yields 47-94%, E/Z \geq 98/2).</p>
Y. Yamamoto, T. Miyairi, T. Ohmura, N. Miyaoura <i>J. Org. Chem.</i> 1999 , 64, 296.		

[Bis(tricyclohexylphosphine)benzylidene]ruthenium Dichloride**Catalyst**

The title compound catalyses the chemo- and regioselective addition of chloroform across mono- and 1,1-disubstituted olefins.

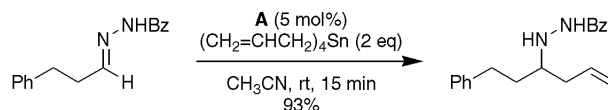
**A**

7 examples (yields <10-100%).

J. A. Tallarico, L. M. Malnick, M. L. Snapper *J. Org. Chem.* **1999**, *64*, 344.

Scandium(III) Trifluoromethanesulfonate**Catalyst**

A catalyses the formation of homoallylic hydrazines from benzoylhydrazones and tetraallyltin. The products are readily cleaved allowing access to homoallylic amines.

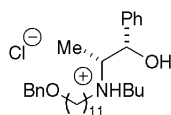
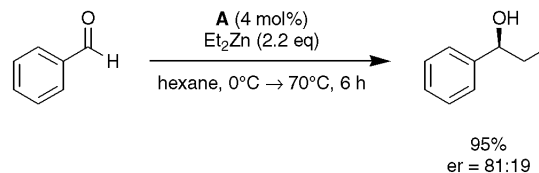
Sc(OTf)₃**A**

7 examples (yields 81-100%) are described.

S. Kobayashi, K. Sugita, H. Oyamada, *Synlett*, **1999**, *1*, 138.

(1*S*,2*R*)-2-[*N,N*-(11-Benzyloxyundecyl)-*N*-butylammonium]-1-phenylpropan-1-ol**Catalyst**

The title reagent catalyses the enantioselective addition of diethylzinc to aromatic aldehydes.

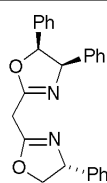
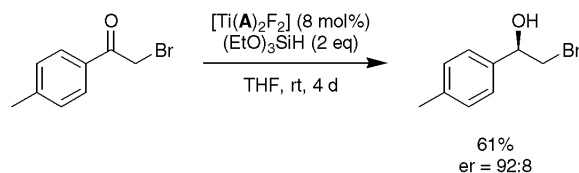
**A**

9 examples (yields 13-95%, %ee = 44-82%).

H. C. Hailes, J. Madden *Synlett* **1999**, 105.

Bis[4*R*,5*S*]-4,5-diphenyl-1,3-oxazolin-2-yl]methane**Ligand**

Chiral titanium complexes prepared from the title ligand catalyse the enantioselective reduction of ketones in the presence of triethoxysilane.

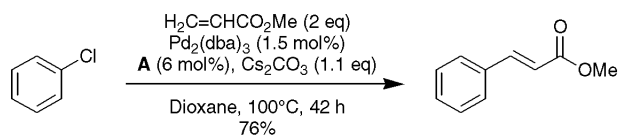
**A**

8 examples (yields 50-64%, %ee = 65-85%).

M. Bandini, P. G. Cozzi, L. Negro, A. Umani-Ronchi *Chem. Commun.* **1999**, 39.

Tri-*tert*-butylphosphine**Ligand**

A new catalyst system for the Heck coupling of aryl chlorides utilising **A** is reported.

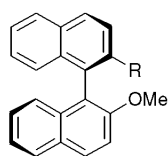
P(*t*Bu)₃**A**

6 examples (yields 70-84%).

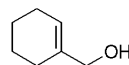
A. F. Littke, G. C. Fu *J. Org. Chem.* **1999**, *64*, 10.

N*-Benzyl-*N*-hydroxy-(2'-methoxy-1,1'-binaphth-2-yl)carboxamide*Ligand**

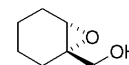
A vanadium catalyst derived from the title ligand is utilised in the asymmetric epoxidation of allylic alcohols.



R = CON(OH)Bn

AVO(O^tPr)₃ (5 mol%)**A** (7.5 mol%)Ph₃COOH (1.5 eq)

PhMe, -20°C, 2 d

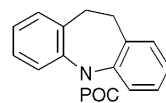
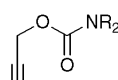
61%
er = 94:6

10 examples (yields 14-96%, %ee = 38-94%).

N. Murase, Y. Hoshino, M. Oishi, H. Yamamoto *J. Org. Chem.* **1999**, *64*, 338.

Prop-2-ynyloxy carbonyl (POC) Group**Protecting Group**

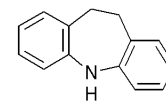
The prop-2-ynyloxy carbonyl (POC) function, developed as a new protecting group for amines, can be cleaved under mild and neutral conditions. The protecting group is stable to both acidic and basic conditions.

(PhCH₂NEt₃)₂MoS₄ (1 eq)

Ultrasound

CH₃CN, rt, 45 min

88%

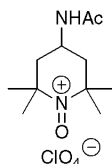
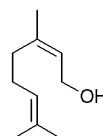


5 examples (yields 80-88%) are reported.

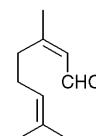
S. Sinha, P. Ilankumaran, S. Chandrasekaran *Tetrahedron Lett.* **1999**, *40*, 771.

4-Acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium Perchlorate**Reagent**

The readily prepared, stable, nonhygroscopic title compound is used in the oxidation of alcohols to ketones or aldehydes. The reaction is colorimetric, does not require anhydrous conditions, and the oxidant can be easily regenerated.

**A****A** (1.05 eq)CH₂Cl₂

99%

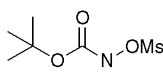
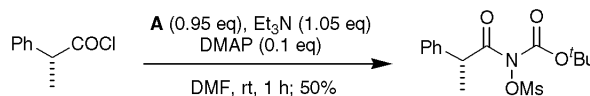


20 examples (yields 96-100%).

J. M. Bobbitt *J. Org. Chem.* **1998**, *63*, 9367.

N*-tert-Butyloxycarbonyl-*O*-methanesulfonylhydroxylamine*Reagent**

The title compound mediates a modified Lossen rearrangement in which no Lewis acid is required. The reaction proceeds with retention of configuration of the migrating group.

**A**

2,6-DTBP (1 eq), BnOH (1.1 eq)

CH₃CN, Δ, 16 h

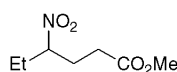
69%

4 examples using **A** (yields 43-82%) and 8 examples using different alcohols or amines (yields 53-81%) are reported.

J. A. Stafford, S. S. Gonzales, D. G. Barrett, E. M. Suh, P. L. Feldman *J. Org. Chem.* **1998**, *63*, 10040.

Dimethyldioxirane**Reagent**

The oxidation of nitronate anions generated from the corresponding nitroalkanes using the title reagent is described, providing a mild and efficient alternative to the traditional Nef reaction.

**A**(a) *t*-BuOK (1.1 eq)

THF, rt, 5 min

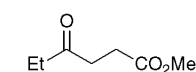
(b) H₂O (1 eq)

rt, 2 min

(c) **A** (1.2 eq)

rt, 5 min

90%

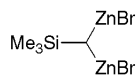
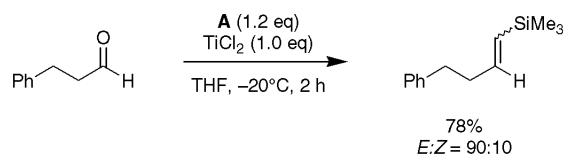


9 examples (yields 64-99%).

W. Adam, M. Makosza, C. R. Saha-Möllner, C.-G. Zhao *Synlett* **1998**, 1335.

Bis(bromozinc)methyltrimethylsilane**Reagent**

The olefination of aldehydes and ketones using the title reagent in combination with titanium(II) chloride is described.

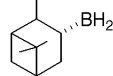
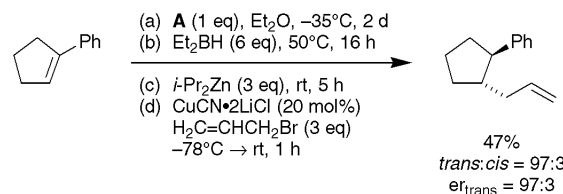
**A**

6 examples (yields 42-92%, 53:47 ≤ E:Z ≤ 90:10).

S. Matsubara, T. Mizuno, T. Otake, M. Kobata, K. Utimoto, K. Takai *Synlett* **1998**, 1369.

Monoisopinocampheylborane**Reagent**

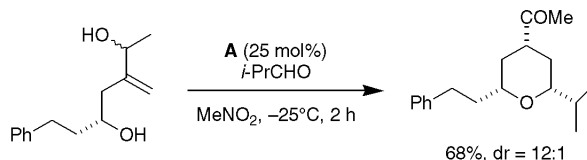
Hydroboration of trisubstituted olefins with **A** followed by treatment with Et₂BH and *i*-Pr₂Zn affords diastereomerically pure organozinc reagents which are trapped by various electrophiles with retention of configuration.

**A**18 examples (yields 35-77%, *trans:cis* > 97:3, %ee = 20-96%) are described.

A. Boudier, F. Flachsmann, P. Knochel *Synlett* **1998**, 1438.

Trifluoromethanesulfonic Acid**Reagent**

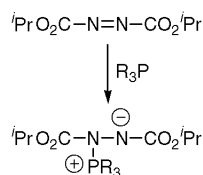
The stereoselective synthesis of 2,4,6-trisubstituted tetrahydropyrans employing a Prins cyclisation and subsequent pinacol rearrangement is described.

**A**7 examples (yields 50-81%, 2,4,6-*cis*:2,6-*cis*,4-*anti* >6:1).

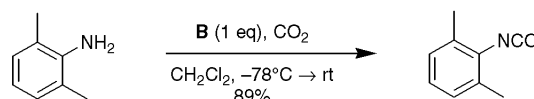
M. J. Cloninger, L. E. Overman
J. Am. Chem. Soc. **1999**, 121, 1092.

Diisopropylazodicarboxylate (DIAD)**Reagent**

Adducts **A** and **B** derived from the title reagent are utilised in the preparation of alkyl and hindered aryl isocyanates from primary amines and carbon dioxide using Mitsunobu technology.



R = Ph **A**
R = Bu **B**

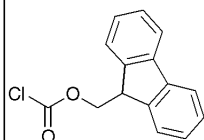
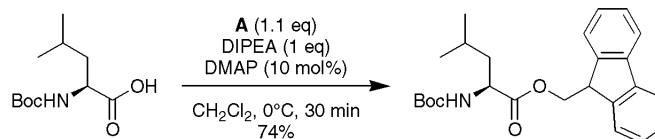


19 examples (yields 0, 11-92%) are reported.

M. J. Horvath, D. Saylik, W. R. Jackson, P. S. Elmes, C. G. Lovel, K. Moody *Tetrahedron Lett.* **1999**, 40, 363.

9-Fluorenylmethylchloroformate**Reagent**

The title reagent is used in the synthesis of 9-fluorenylmethyl esters of *N*-protected amino acids.

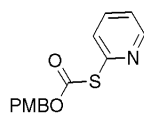
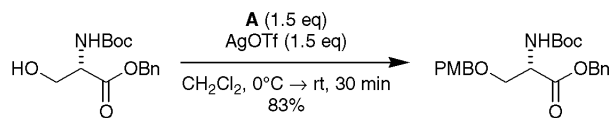
**A**

9 examples (yields 25-84%) are reported.

S. A. M. Mérette, A. P. Burd, J. J. Deadman
Tetrahedron Lett. **1999**, 40, 753.

4-Methoxybenzyl-2-pyridylthiocarbonate (PMB-TOPCAT)**Reagent**

A is utilised in the conversion of primary, secondary and tertiary alcohols to *p*-methoxybenzyl ethers under neutral conditions. The method can be adapted to solid-phase on the Wang resin.

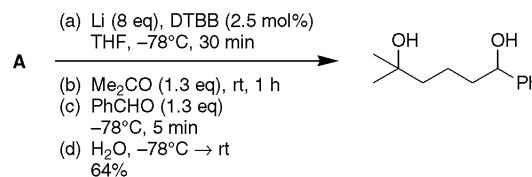
**A**

The preparation of **A** and 10 examples of etherification (yields 70-92%) are reported.

S. Hanessian, H. K. Huynh *Tetrahedron Lett.* **1999**, *40*, 671.

3-Phenoxy-1-chloropropane**Reagent**

The title reagent is used as a 1,3-dilithio propane source in the formation of 1,5-diols from carbonyl compounds.

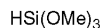
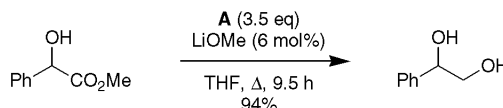
**A**

9 examples (yields 45-70%) are reported.

F. Foubelo, M. Yus *Tetrahedron Lett.* **1999**, *40*, 743.

Trimethoxysilane**Reagent**

The title reagent reduces hydroxyesters to diols in the presence of lithium methoxide. Lactones without a hydroxyl group and tosylimines are also reduced.

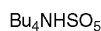
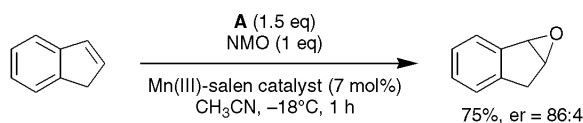
**A**

20 examples (yields 13-100%) are described.

M. Hojo, C. Murakami, A. Fujii, A. Hosomi *Tetrahedron Lett.* **1999**, *40*, 911.

Tetrabutylammonium Monopersulfate**Reagent**

Asymmetric Mn(III)-salen catalysed epoxidation under mild conditions using **A** as the oxidant are reported.

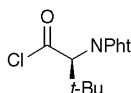
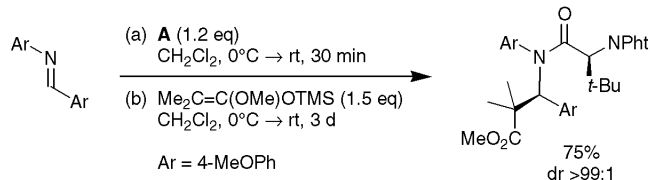
**A**

5 examples (yields 72-97%, %ee = 72-93%).

P. Pietikäinen *Tetrahedron Lett.* **1999**, *40*, 1001.

N,N*-Phthaloyl-*tert*-leucine Chloride*Reagent**

The steric course of the Mannich reaction is efficiently directed by the use of *N*-phthaloylamino acids. Chiral β -amino acid esters are obtained with excellent stereoselectivity.

**A**

16 examples (yields 17-91%, %de = 82->98%).

R. Müller, H. Goesmann, H. Waldmann *Angew. Chem. Int. Ed.* **1999**, *38*, 184.