SYNTHESIS ALERTS 1631

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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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 1

Synlett

Synthesis

Tetrahedron

Tetrahedron Asymmetry and Tetrahedron Letters

Y. N. Belokon, M. North, T. Parsons *Org. Lett.* **2000**, *2*, 1617.

Ytterbium Tridecaflide Catalyst

The title reagent is used in a fluorous biphase catalytic Friedel–Crafts acylation of arenes with acid anhydrides. The catalyst is recovered by extraction of the spent acylation reaction mixture with perfluoromethyldecalin.

A. G. M. Barrett, D. C. Braddock, D. Catterick, D.

Chadwick, J. P. Henschke, R. M. McKinnell

Synlett 2000, 847.

Yb[C(SO₂C₆F₁₃)₃]₃

A

OMe
A (10 mol%)
Ac₂O (2 eq)
benzotrifluoride, 40°C, 4 h
74%

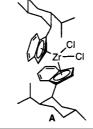
1 example (yield 74%) and 2 other ytterbium tris(perfluoroalkanesulfonyl)methide catalysts are reported

8 examples (%ee = 68-95%) are reported.

er = 97:3

Chiral Zirconocene Catalyst Catalyst

Reagent A catalyses the enantioselective methylalumination of terminal alkenes. The reaction is accelerated by the addition of either water or methylaluminoxane.



P. Wipf, S. Ribe Org. Lett. 2000, 2, 1713.

10 examples (yields 35-94%, %ee = 55-90%) are reported.

Pd(PhCN)₂Cl₂ / Tri-tert-butylphosphine

The title reagent pair serves as an efficient and versatile catalyst for Sonagashira reactions of aryl bromides at room temperature. Pd(PhCN)2Cl2 A (3 mol%), B (6 mol%) Cul (2 mol%), HN(i-Pr)₂ (1.2 eq) Α -Ph (1.2 eq) dioxane, rt, 30 min $P(t-Bu)_3$ В T. Hundertmark, A. F. Littke, S. L. Buchwald, G. C. Fu Org. Lett. 2000, 2, 1729. 12 examples (yields 63-95%) are reported

trans-RuCl₂[(R)-xylbinap][(R)-daipen]

Catalyst

The title reagent acts as an efficient catalyst for asymmetric hydrogenation of hetero-aromatic ketones

$$\begin{array}{c} p\text{-MeOC}_{6}\text{H}_{4} \\ p\text{-MeOC}_{6}\text{H}_{4} \\ \end{array} \\ \begin{array}{c} \text{H}_{2}\text{N} \\ \text{H}_{2}\text{N} \\ \text{Cl-Ru-Cl} \\ \text{Ar}_{2}\text{P}' \\ \end{array} \\ \text{Ar} = 3.5\text{-}(\text{CH}_{3})_{2}\text{C}_{6}\text{H}_{3} \\ \\ \text{A} \end{array}$$

A (0.02 mol%) t-BuOK (0.15 mol%) H₂ (8 atm) 2-propanol, rt, 12 h 98% er > 100:1

T. Ohkuma, M. Koizumi, M. Yoshida, R. Noyori Org. Lett. 2000, 2, 1749.

14 examples (yields 51, 91-98%, %ee = 91-100%) are reported.

Palladium-Thiourea-1,3-bis(diphenylphosphino)propane complex

Catalyst

The title complex catalyses the carbonylative annulation of iodophenol acetates with arylacetylenes to construct the corresponding

Pd(Ph₃P)₂Cl₂ Α H₂NCSNH₂ В dppp С

A (5 mol%), B (5 mol%) C (0.005 mol%) DBU (5 eq) HNEt2, 40°C, 2 d 92% 8 examples (yields 68-92%) are reported.

Palladium/Carbon-Ethylenediamine

H. Miao, Z. Yang Org. Lett. 2000, 2, 1765.

Catalyst

The title reagent pair catalyse the chemoselective hydrogenation of olefin, nitro and azide functions in the presence of epoxides.

Pd/C Α H₂NCH₂CH₂NH₂ В

A/B (5 mol%) THF, rt, 3 h 98%

14 examples (yields 85-100%) are reported.

Chiral Zirconium Catalyst Catalyst

The title reagent catalyses the anti-selective aldol reaction of silyl enol ethers with aldehydes

H. Sajiki, K. Hattori, K. Hirota Chem. Eur. J. 2000,

 $_{\prime}$ O t Bı `O^tBı Α

(E) OSiMe₃ OPh (1.05 eq) ОН A (10 mol%) C2H5OH (80 mol%) PhMe, 0°C, 18 h 98% anti:syn = 95:5 er = 100:1

H. Ishitani, Y. Yamashita, H. Shimizu, S. Kobayashi J. Am. Chem. Soc. 2000, 122, 5403.

12 examples (yields 38-98%, %ee = 81-99%) are reported.

SYNTHESIS ALERTS 1633

Catalyst **Palladium Acetate**

The title reagent in combination with tri-n-butylphosphine catalyses the intramolecular cyclisation of alkynes and imines to synthesise

A (5 mol%) n-Bu₃P (20 mol%) Pd(OAc)₂ 1.4-dioxane, 100°C, 1 d 58%

A. Takeda, S. Kamijo, Y. Yamamoto J. Am.

Chem. Soc. 2000, 122, 5662.

RuCp(MeCN)₃PF₆ Catalyst

The title reagent catalyses the hydrative cyclisation and [4+2] cycloadddition of yne-enones to afford pyrans and cyclic diketones

A (5 %) CSA (10 mol%) H₂O (1.3 eq) MeO₂ RuCp(MeCN)₃PF₆ acetone, rt, 4 h MeO₂C MeO₂C 70%

B. M. Trost, R. E. Brown, F. D. Toste J. Am. Chem. Soc. 2000, 122, 5877.

14 examples (yields 45-89%) are reported.

9 examples (yields 55-71%) are reported.

Perflouroalkyl-Substituted 2,2'-Bipyridine

The title reagent is used as a catalyst ligand for the oxidation of various alcohols to aldehydes and ketones under fluorous biphasic conditions.

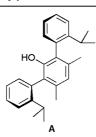
A (2 mol%) CuBr□Me₂S (2 mol%) ОН TEMPO (3.5 mol%) C₈F₁₈/PhCl, 90°C, O₂, 4 h

B. Betzemeier, M. Cavazzini, S. Quici, P. Knochel Tetrahedron Lett. 2000, 41, 4343.

13 examples (yields 31, 69-96%) are reported.

(R,R)-2,6-Bis(2-isopropylphenyl)-3,5-dimethylphenol

The title reagent is an effective chiral auxiliary in asymmetric Mannich-type reactions of certain aldimines



BuLi (1 eq) (a) THF, -78°C, 30 min OMe (b) Et₂Zn (1 eq) NΗ (1 eq) 82% THF, -78°C, 27 h dr = 96:4

13 examples (yields 29-82%, %ee = 84-98%) are reported

S. Saito, K. Hatanaka, H. Yamamoto Org. Lett.

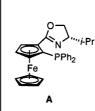
2(S)-(Diphenylphosphino)-1-[4(S)-isopropyl-2-oxazolin-2-yl]ferrocene [(S)-i-Pr-DIPOF]

Ligand

Catalyst

Chiral Auxiliary

The title ligand is used in the enantioselective ring opening of oxabicyclic alkenes.



A (5 mol%) Pd(CH₃CN)₂Cl₂ (5 mol%) OTBDPS Me_2Zn (2 eq) OTBDPS **OTBDPS** OTBDPS $(CH_2CI)_2$, Δ 87% er = 96:4

M. Lautens, S. Hiebert, J.-L. Renaud Org. Lett. 2000. 2. 1971

8 examples (yields 19-92%, %ee = 87-95%) are reported.

Ligand

Reagent

Reagent

Reagent

Diphosphine Ferrocene Ligand

The title ligand mediates the rhodium-catalysed asymmetric ring-opening reaction of oxabenzonorbornadienes using alcohol and amine nucleophiles.

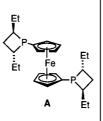
PPh₂

M. Lautens, K. Fagnou, T. Rovis *J. Am. Chem. Soc.* **2000**, *1*22, 5650.

16 examples (yields 53-96%, %ee = 45-99%) are reported.

Diphosphetanylferrocene (FerroTANE)

The title ligand is used in the enantioselective rhodium-catalysed hydrogenation of itaconate derivatives.



 $\begin{array}{c} \text{HO}_2\text{C} \overset{(E)}{\longrightarrow} \text{Ph} \\ \text{O} \\ \text{N} \\ \text{N} \\ \text{N} \\ \text{N} \\ \text{MeOH, 20°C, 3 h} \\ \\ \text{er = 99:1} \\ \end{array}$

U. Berens, M. J. Burk, A. Gerlach, W. Hems Angew. Chem. Int. Ed. 2000, 39, 1981.

13 examples (%ee = 88-99%) are reported

1-(2-Methyoxyethoxy)-1-vinylcyclopropane

The title reagent is used as a five-carbon component in metal-catalysed [5+2] cycloadditions to prepare substituted cycloheptenones.



H———CO₂Me (1.2 eq) [Rh(CO)₂Cl)₂ (0.5 mol%) (CH₂Cl)₂, 80°C, 10 min 84%

P. A. Wender, A. J. Dyckman, C. O. Husfeld, M. J. C. Scanio *Org. Lett.* **2000**, *2*, 1609.

11 examples (yields 75-97%) are reported.

Bis(2,4-dichlorophenyl)chlorophosphate

The title reagent is used in a one-pot preparation of alkyl azides from alkanols.

(Cl₂PhO)₂POCI

C. Yu, B. Liu, L. Hu Org. Lett. 2000, 2, 1959.

8 examples (yields 76-92%) are reported.

Bis(2,2,2-trifluoroethyl)bromophosphonoacetate

The title reagent is used in the presence of t-BuOK and 18-C-6 to prepare (E)- α -bromoacrylates by Horner-Wadsworth-Emmons (HWE) reaction with various aldehydes.

$$(CF_3CH_2O)_2$$
 P
 Br
 CO_2Me

K. Tago, H. Kogen Org. Lett. 2000, 2, 1975.

12 examples (yields 47-100%, 9:1 $\leq E:Z \leq$ 100:0) are reported.