**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
- 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

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**Catalytic enantioselective addition of terminal alkynes to aldehydes.**


![Reaction diagram](image)

Reaction works best when the aldehyde has an \(\alpha\)-branch. Lower yields but useful ee’s obtained even with unbranched aldehydes. The reaction can be performed without solvent in which case no aqueous workup is necessary. 10 Aldehydes and 15 different alkynes used: yields typically >80%, ee’s >90%.

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**Enantioselective hydrometallation–alkylation: equivalent to umpolung of a Michael addition.**


![Reaction diagram](image)

alkylation with propargyl bromide and 1-bromoalkynes also reported

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**Chiral guanidine base in asymmetric Michael addition reactions of glycine imine.**


![Reaction diagram](image)

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A remarkably stable rhodium Lewis acid catalyst for hydrosilation, Mukaiyama aldol and cyclopropanation reactions. 

**Novel Lewis Acid**

A is a remarkably stable, cationic, three-coordinate 14e complex that can be generated in situ. It forms η1-complexes with carbonyls in dichloromethane solution.

**Asymmetric Addition**

Catalytic asymmetric allyl transfer reactions promoted by a BINOL-Ti complex.


**Asymmetric Addition**

Salen-derived catalysts containing secondary basic groups in the addition of diethylzinc to aldehydes.


**Asymmetric Addition**

Appendage of a quaternary centre to an indole via aryllead(IV) reagents.


**Heteroannulation**

Metalloiminium ion cyclisation terminated by a 2-(methylthio)-3-(trimethylsilyl)-1-propenyl moiety.

Intramolecular [2+2] photocycloaddition/thermal fragmentation approach toward 5–8–5 ring systems. 

Electrophilic cyclisations of vinylcyclopropanols to tethered aldehydes. 

Highly diastereoselective aldol additions of a chiral ethyl ketone enolate under Lewis base catalysis. 

Group-selective hydroalumination of bis-alkynyl carbins: application to malyngolide. 

Oxidative ring contraction of a glycal derivative: application to the synthesis of (+)-pyrenolide D. 


RuO$_2$-catalysed oxidative cyclisation of 1,5-dienes to cis-2,5-bis(hydroxymethyl)tetrahydrofuranyldiols. Piccialli, V.; Cavallo, N. Tetrahedron Lett. 2001, 42, 4695.


Enantioselective crotylation of aldehydes via an allyl transfer reaction from a chiral crotyl donor.
Nokami, J.; Ohga, M.; Nakamoto, H.; Matsubara, T.; Hussain, I.; Kataoka, K.

\[ \text{R-CHO (0.5 equiv.)} \rightarrow \text{TsOH-H}_2\text{O (10 mol%)} \rightarrow \text{CH}_2\text{Cl}_2, 20 \degree \text{C}, 20 \text{~h} \rightarrow \text{H}_2\text{O} \rightarrow \text{OH} \rightarrow \text{R} \rightarrow \text{H} \rightarrow >99\% \text{ ee} \]

9 examples; 2 failed: citronellal and 2-octenal. The corresponding asymmetric allylation reaction gave lower ee.

Thiazolium-catalysed cross-coupling of aldehydes with acylimines.
Murry, J. A.; Frantz, D. E.; Sohelia, A.; Tillyer, R.; Grabowski, E. J.; Reider, P. J.

\[ \text{Hydrometallation} \]

Hydrozirconation of stannylalkynes. Synthesis of 1,1-dibromo- and 1,1-diiodo alkynes.

Annulation of aromatic imines via directed C–H activation with Wilkinson’s catalyst.

N–C sp³ Coupling

Iridium-catalysed allylic amination of allylic esters.

Terminal (E)- and (Z)-allylic carbonates and acetates only. 1° and 2° amines used include pyrrolidine, morpholine, cyclopentylamine, n-butylamine, tert-butylamine and benzylamine.

$\text{[2+2+2] Cycloaddition}$

\[
\text{CpCo(C}_2\text{H}_4\text{)}_2 \rightarrow \text{acetylene} \rightarrow 46\%
\]

(a) $\text{KOH}$

(b) $\text{Fe(NO)}_3$

Pd(0)-, Ni(0)- or radical-mediated cyclisation reactions

\[\text{[2+2+2] Cycloaddition}\]

$\text{[2,3]-Sigmatropic Rearrangement}$

\[\text{Diastereoselective [2,3]-sigmatropic rearrangement of metallated O-allylic-(N-benzyl)hydroxylamines.}\]


$\text{Enantioselective 1,2-Addition}$

\[\text{Catalytic enantioselective cyanosilylation of ketones.}\]

Yabu, K.; Masumoto, S.; Yamasaki, S.; Hamashima, Y.; Kanai, M.; Du, W.; Curran, D. P.; Shibasaki, M.

$\text{Asymmetric 1,2-Addition}$

\[\text{Polymer-bound tert-butanesulfinamide.}\]


$\text{Alkyl–alkyl Suzuki cross-coupling of bromoalkanes.}\$


$\text{sp}^3-\text{sp}^3 \text{ Coupling}$

\[\text{10 examples; yields 66-93%. Tricyclohexylphosphane is uniquely effective. With other phosphanes, β-elimination competes or predominates.}\]

\[\text{Polymer-bound tert-butanesulfinamide.}\]