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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(S,S)-Ethylenebistetrahydroindenylidimethylzirconium

Enantioselective hydrogenation of tetrasubstituted double bonds using A is reported.

\[
\text{Me}^+\text{Zn}^-\text{Me}
\]

A


The title catalyst promotes the TiCl₄·Bu₃N-mediated cross aldol additions of sterically crowded ketones and α-hetero substituted ketones, and also the Claisen condensation between methyl esters.

\[
\text{Me}_3\text{SiCl}
\]

A


Trimethylsilyl chloride

Catalyst

\[
\text{MeO}_2\text{COH} \xrightarrow{\text{TiCl}_4 (1.2 \text{ eq}), \text{Bu}_3\text{N} (1.2 \text{ eq})} \text{MeO}_2\text{COH} + \text{PhCHO}
\]

\[
\text{CH}_2\text{Cl}_2, -78^\circ\text{C}, 3 \text{ h}
\]

80%

18 examples of aldol additions (yields 42-98%) and 5 examples of Claisen condensation (yields 54-95%) are reported.

Cinchonidine-derived Chiral Quaternary Ammonium Salt

Catalyst

The title reagent catalyses the enantioselective synthesis of β-hydroxy-α-amino acid esters by aldol coupling of aldehydes and a glycinate.

\[
\text{H}^+\text{N}^-\text{OBn}^-\text{HF}^-
\]

A


6 examples (yields 48-81%, 1:1 ≤ syn : anti ≤ 13:1, %ee_{syn} = 72-95%) are reported.

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
Helvatica 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
2,6-Diphenyl-4H-selenopyran-4-one

A is reported as an effective catalyst for the Baylis-Hillman reaction.

![Chemical structure of A](image)


21 examples (yields 43-100%) using A are reported. Use of a thiopyranone analogue of A produces similar results.

Chiral Ru Lewis Acid

The readily prepared title compound mediates the asymmetric Diels-Alder reaction between enals and dienes. The high stability of A makes recycling possible.

![Chemical structure of A](image)


4 examples (yields 29-93%, 10:90 ≤ exo : endo ≤ 98:3, %ee = 91-96%) are reported.

Cinchona Alkaloid-derived Phase-Transfer Catalyst

A is used in the phase-transfer catalysed asymmetric epoxidation of α,β-unsaturated ketones.

![Chemical structure of A](image)


19 examples (yields 40, 77-99%, %ee = 71-90%).

Trifluoromethanesulfonic Acid

The title compound catalyses the Michael addition reaction of β-ketoesters under solvent-free conditions.

![Chemical structure of A](image)


14 examples (yields 0, 51-99%).

(S,S)-1,2-Diphenyl-1,2-diaminoethane

The title reagent is used to prepare N,N'-diaryl-1,2-diphenyl-1,2-diaminoethanes via palladium catalysed aromatic amino coupling.

![Chemical structure of A](image)


7 examples (yields 0, 33-97%) are reported.
### (R)-1-[(R)-p-Toluenesulfonyl]-3,3,3-trifluoropropan-2-ol

An efficient synthesis of trans-2-phenylcyclohexanol utilizing in a key step the enantioselective protonation of an enolate is reported.


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### Tripeptide Schiff Base

The titanium-catalysed enantioselective addition of cyanide to imines is reported. The resulting amino nitrile products can be readily converted to the corresponding amino acids.


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7 examples using A or closely related analogues (yields 82-99%, %ee = 90-97%) are reported.

### 2-[(E)-1-adamantyl]phosphino]biphenyl

The Pd-catalysed formation of diaryl ethers using the bulky, electron-rich phosphine ligand A or the related di-tent-butyl ligand is reported.


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R = 1-adamantyl

25 examples (yields 61-95%).

### (S)-4-tert-Butyl-2-methylloxazoline

Ligand A is used in the nickel-catalysed asymmetric coupling of enones and metallated alkynes in the presence of TMSCl.


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4 examples (yields 5-75%, %ee = 38-81%).

### (R)-2,2′-Binaphthylmonobenzoate

SnCl₂ and A promote the enantioselective cyclization of polyisoprenoids.


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12 examples (yields 54-98%, %de = 12-90%, %ee = 36-54%).
(S)-1,2,2-Triphenyl-2-(1-pyrrolidinyl)ethanol

A mediates the highly enantioselective addition of diethylzinc to aldehydes.


22 examples (yields 85-100%, enantiomeric excess = 90-98%).

Triisopropylsilyloxy carbonyl (Tsoc)

The Tsoc group is stable towards conditions used to deprotect Boc, Cbz and Fmoc groups. It is easily cleaved by TBAP in THF at 0°C in 10 min. It can be removed selectively in the presence of secondary TBS ethers.


10 examples; yields 56-94%, tert-Butyldiphenylsilyloxy carbamates can be prepared in a similar fashion (1 example).

2-Chloro-4,6-dimethoxy-1,3,5-triazine (CDMT)

Triazines obtained from A and a carboxylic acid are employed as acylating reagents for ester synthesis from primary, secondary and tertiary alcohols.


14 examples (yields 24-92%).

Dicyclopentadienylzirconium Dichloride

The asymmetric synthesis of α-amino acid esters is reported via the dynamic kinetic resolution of racemic zirconaziridines utilising a cyclic carbonate with C₂-symmetry as an optically active CO₂ synthon.


4 examples (yields 48-77%, ee ≥ 72%).

Magnesium bis(dilisopropylamide)

A (prepared in situ from dilisopropylamine and dibutylmagnesium) is reported as a reagent for the synthesis of less highly substituted styryl ethers at ambient temperature. In addition, high E-enolisation selectivity is observed for benzyl ketones, the reverse of the selectivity observed with LDA.


6 examples (yields 80-99%, selectivity for the kinetic product ≥ 95.5) and 2 examples using benzyl ketones (yields > 99%, 80.20 ≤ E : Z ≤ 91.9).