

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.

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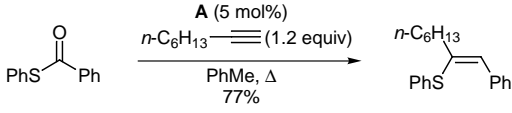
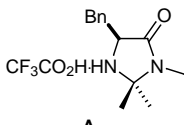
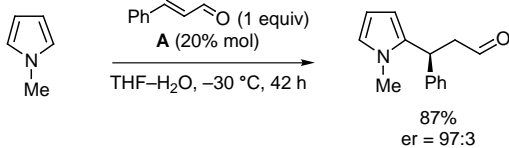
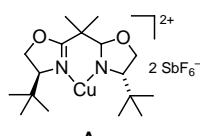
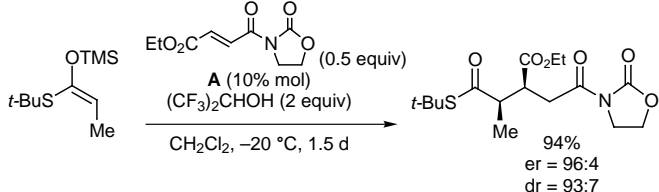
Elyse Bourque, Robert Chow, Jennifer Delaney, Marcel de Puit and Sukhjinder Uppal of Department of Chemistry, Leeds University, Leeds LS2 9JT, UK.

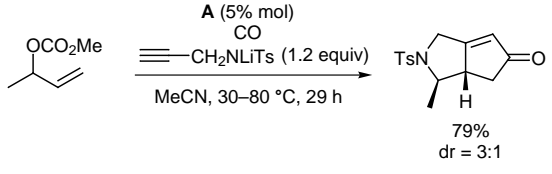
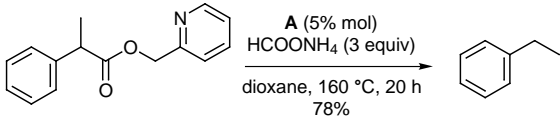
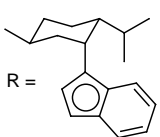
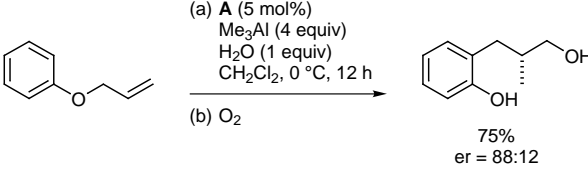
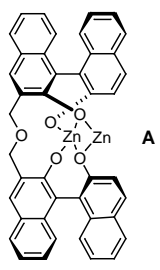
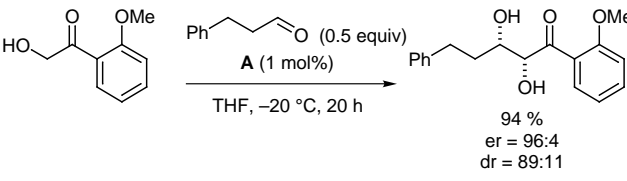
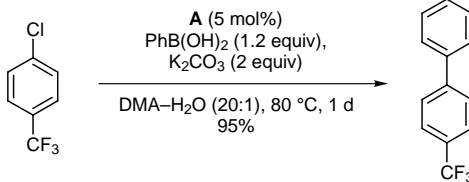
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ISSN 0039-7881

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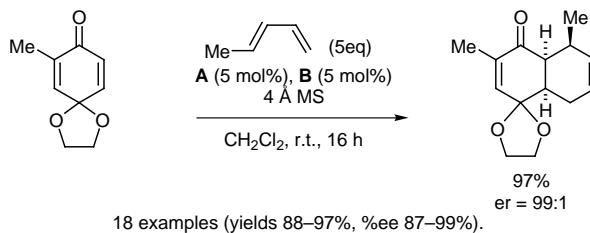
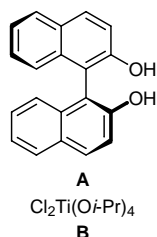
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Helvetica Chimica Acta
Heterocycles
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Journal of Organic Chemistry
Organic Letters
Organometallics
Perkin Transactions I
Synlett
Synthesis
Tetrahedron
Tetrahedron Asymmetry and Tetrahedron Letters

Tetrakis(triphenylphosphine)platinum(0)		Catalyst
The title reagent catalyses the carbolithiation of alkynes.	Pt(PPh ₃) ₄ A	 <p>16 examples (yields 0,33–85%).</p>
Sugoh, K.; Kuniyasu, H.; Sugae, T.; Ohtaka, A.; Takai, Y.; Tanaka, A.; Machino, C.; Kambe, N.; Kurosawa, H. <i>J. Am. Chem. Soc.</i> 2001 , 123, 5108.		
Imidazolidinone		Catalyst
The title reagent promotes the asymmetric Friedel–Crafts alkylation of pyrroles with α,β -unsaturated aldehydes.	 A	 <p>7 examples (yields 72–90%, %ee 87–93%).</p>
Paras, N. A.; MacMillan, D. W. C. <i>J. Am. Chem. Soc.</i> 2001 , 123, 4370.		
Bis(oxazoline) Copper(II) Complex		Catalyst
The title reagent promotes enantioselective and diastereoselective Michael additions of enolsilanes to unsaturated imide derivatives.	 A	 <p>33 examples (yields 40–99%, %ee 40–99%, %de 46–98%).</p>
Evans, D. A.; Scheidt, K. A.; Johnston, J. N.; Willis, M. C. <i>J. Am. Chem. Soc.</i> 2001 , 123, 4480.		

Rhodium(I) Complex		Catalyst
<p>The title reagent promotes regio- and diastereoselective tandem allylic alkylation/Pauson–Khand annulation reactions.</p> <p>Evans, P. A.; Robinson, J. E. <i>J. Am. Chem. Soc.</i> 2001, <i>123</i>, 4609.</p>	<p>[RhCl(CO)dppp]₂</p> <p>A</p>	 <p>A (5 mol%) CO ≡CH₂NLiTs (1.2 equiv) MeCN, 30–80 °C, 29 h</p> <p>79% dr = 3:1</p> <p>9 examples (yields 63–84%, %de 50–90%).</p>
Triruthenium Dodecacarbonyl		Catalyst
<p>The title reagent promotes reductive decarboxylation of esters involving the cleavage of acyl-oxygen bonds of esters.</p> <p>Chatani, N.; Tatamidani, H.; Ie, Y.; Kakiuchi, F.; Murai, S. <i>J. Am. Chem. Soc.</i> 2001, <i>123</i>, 4849.</p>	<p>Ru₃(CO)₁₂</p> <p>A</p>	 <p>A (5 mol%) HCOONH₄ (3 equiv) dioxane, 160 °C, 20 h</p> <p>78%</p> <p>18 examples (yields 0–100%).</p>
Chiral Zirconocene		Catalyst
<p>The title reagent, in the presence of water, promotes the asymmetric carboalumination of terminal alkenes, following the trimethylaluminum-mediated aromatic Claisen reaction in a tandem process.</p> <p>Wipf, P.; Ribe, S. <i>Org. Lett.</i> 2001, <i>3</i>, 1503.</p>	<p>ZrCl₂R₂</p> <p>A</p> <p>R = </p>	 <p>(a) A (5 mol%) Me₃Al (4 equiv) H₂O (1 equiv) CH₂Cl₂, 0 °C, 12 h (b) O₂</p> <p>75% er = 88:12</p> <p>9 examples (yields 39–78%, %ee 60–80%).</p>
Zn-Zn-Linked BINOL Complex		Catalyst
<p>The title reagent promotes asymmetric aldol reactions to afford α,β-dihydroxy ketones.</p> <p>Kumagai, N.; Matsunaga, S.; Yoshikawa, N.; Ohshima, T.; Shibasaki, M. <i>Org. Lett.</i> 2001, <i>3</i>, 1539.</p>	 <p>A</p>	 <p>Ph-CHO (0.5 equiv) A (1 mol%) THF, -20 °C, 20 h</p> <p>94% er = 96:4 dr = 89:11</p> <p>13 examples (yields 73–95%, %ee 77–99%, %de 20–94%).</p>
Palladium/Carbon		Catalyst
<p>The title reagent catalyses the Suzuki cross-coupling reaction of phenylboronic acid with aryl chlorides.</p> <p>LeBlond, C. R.; Andrews, A. T.; Sun, Y.; Sowa, J. R. Jr. <i>Org. Lett.</i> 2001, <i>3</i>, 1555.</p>	<p>Pd/C</p> <p>A</p>	 <p>A (5 mol%) PhB(OH)₂ (1.2 equiv), K₂CO₃ (2 equiv) DMA–H₂O (20:1), 80 °C, 1 d</p> <p>95%</p> <p>7 examples (yields 32–95%).</p>

(S)-BINOL/Titanium Dichlorodiisopropoxide**Catalyst**

The title reagent pair catalyses the enantioselective Diels–Alder reaction of achiral 1,4-quinone monoketals with various dienes.

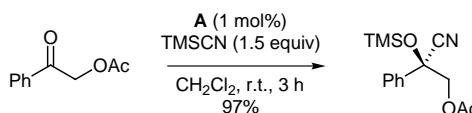


Breuning, M.; Corey, E. J. *Org. Lett.* **2001**, 3, 1559.

18 examples (yields 88–97%, %ee 87–99%).

Indium Tribromide**Catalyst**

The title reagent catalyses the addition of trimethylsilyl cyanide to α -hetero-substituted ketones.

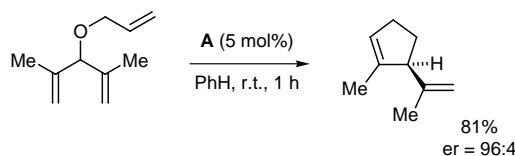
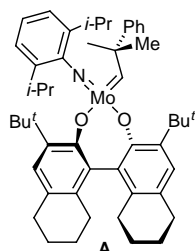


Bandini, M.; Cozzi, P. G.; Melchiorre, P.; Umani-Ronchi, A. *Tetrahedron Lett.* **2001**, 42, 3041.

10 examples (yields 27–99%).

Molybdenum-based Chiral Catalyst**Catalyst**

The title reagent catalyses enantioselective olefin metathesis.

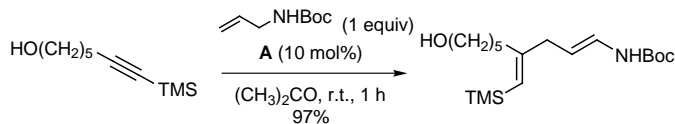
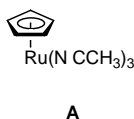


Aeilts, S. L.; Cefalo, D. R.; Bonitatebus, P. J.; Houser, J. H.; Hoveyda, A. H.; Schrock, R. R. *Angew. Chem. Int. Ed.* **2001**, 40, 1452.

7 examples (yields 54–86%, %ee 92–98%).

Ruthenium Complex**Catalyst**

The title reagent catalyses the 3-carbon chain extension of alkynes to give enamides.

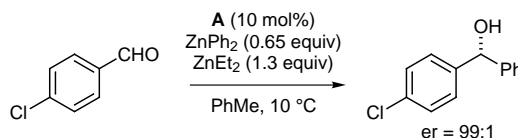
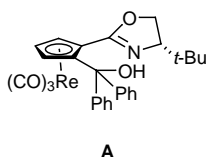


Trost, B. M.; Surivet, J.-P. *Angew. Chem. Int. Ed.* **2001**, 40, 1468.

20 examples (yields 50–97%).


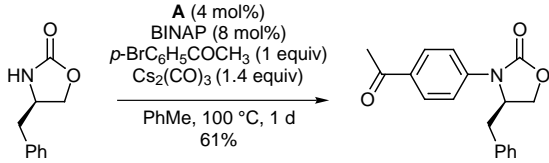
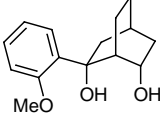
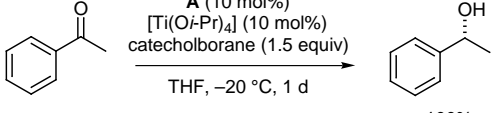
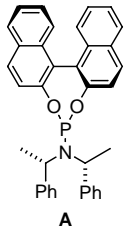
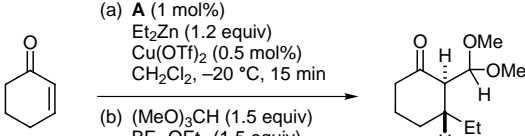
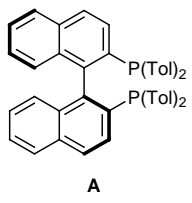
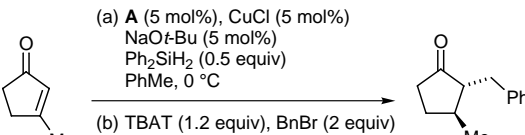
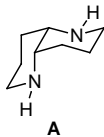
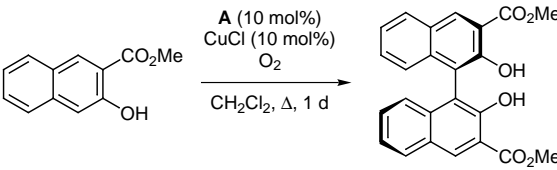
Planar Chiral η^5 -Cyclopentadienylrhenium(I)tricarbonyl Complex**Catalyst**

The title reagent catalyses enantioselective phenyl transfer to aldehydes.

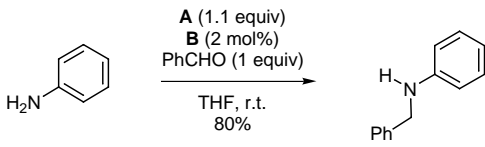
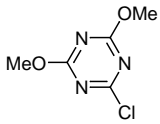
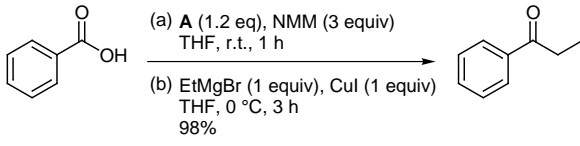
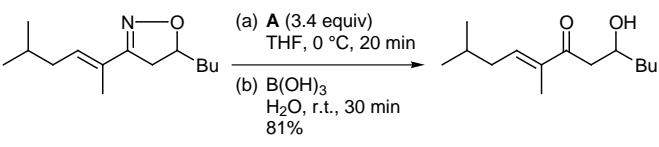
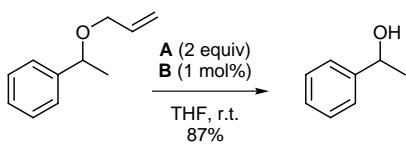
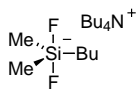
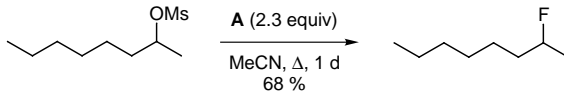


Bolm, C.; Kesselgruber, M.; Hermanns, N.; Hildebrand, J. P.; Raabe, G. *Angew. Chem. Int. Ed.* **2001**, 40, 1488.

9 examples (%ee 78–99%).

Tris(dibenzylideneacetone)dipalladium(0)		Catalyst
<p>The title reagent catalyses the intermolecular coupling of aryl bromides and oxazolidinones.</p> <p>Madar, D. J.; Kopecka, H.; Pireh, D.; Pease, J.; Pliushchev, M.; Sciotti, R. J.; Wiedeman, P. E.; Djuric, S. W. <i>Tetrahedron Lett.</i> 2001, 42, 3681.</p>	 <p>A</p>	 <p>A (4 mol%) BINAP (8 mol%) <i>p</i>-BrC₆H₄COCH₃ (1 equiv) Cs₂(CO)₃ (1.4 equiv) PhMe, 100 °C, 1 d 61%</p> <p>9 examples (yields 15–77%).</p>
2-(2-Anisyl)-bicyclo[2.2.2]octane-2,6-diol (BODOL)		Ligand
<p>The title ligand is employed in the titanium-catalysed asymmetric reduction of ketones with catecholborane.</p> <p>Sarvary, I.; Almqvist, F.; Frejd, T. <i>Chem.–Eur. J.</i> 2001, 7, 2158.</p>	 <p>A</p>	 <p>A (10 mol%) [Ti(O-<i>i</i>-Pr)₄] (10 mol%) catecholborane (1.5 equiv) THF, –20 °C, 1 d 100% er = 98:2</p> <p>15 examples (yields 50–100%, %ee 48–98%).</p>
Phosphoramidate		Ligand
<p>The title reagent promotes the formation of homochiral zinc enolates in a tandem enantioselective conjugate addition.</p> <p>Alexakis, A.; Trevitt, G. P.; Bernardinelli, G. <i>J. Am. Chem. Soc.</i> 2001, 123, 4358.</p>	 <p>A</p>	 <p>(a) A (1 mol%) Et₂Zn (1.2 equiv) Cu(OTf)₂ (0.5 mol%) CH₂Cl₂, –20 °C, 15 min (b) (MeO)₃CH (1.5 equiv) BF₃·OEt₂ (1.5 equiv) CH₂Cl₂, –20 to 0 °C, 2 h 66%</p> <p>6 examples (yields 54–66%).</p>
2,2'-Bis(di- <i>p</i> -tolylphosphino)-1,1'-binaphthyl [(<i>S</i>)- <i>p</i> -tol-BINAP]		Ligand
<p>The title ligand is employed in the copper-catalysed asymmetric conjugate reduction of β-substituted enones for the synthesis of enantiomerically enriched 2,3-disubstituted cyclopentenones.</p> <p>Yun, J.; Buchwald, S. L. <i>Org. Lett.</i> 2001, 3, 1129.</p>	 <p>A</p>	 <p>(a) A (5 mol%), CuCl (5 mol%) NaO-<i>t</i>-Bu (5 mol%) Ph₂SiH₂ (0.5 equiv) PhMe, 0 °C (b) TBAT (1.2 equiv), BnBr (2 equiv) CH₂Cl₂–PhMe (1:1), r.t., 1 d 62% dr = 92:8</p> <p>8 examples (yields 42–67%, %de 80–94%).</p>
1,5-Diazadecalin		Ligand
<p>The title ligand is employed in the copper-catalysed enantioselective oxidative biaryl coupling of substituted 2-naphthol derivatives.</p> <p>Li, X.; Yang, J.; Kozlowski, M. C. <i>Org. Lett.</i> 2001, 3, 1137.</p>	 <p>A</p>	 <p>A (10 mol%) CuCl (10 mol%) O₂ CH₂Cl₂, Δ, 1 d</p> <p>6 examples (yields 32–89%, %ee 13–90%).</p>

Modular Pyridinyl Peptide Ligand		Ligand
<p>The title ligand is applied in the copper-catalysed asymmetric allylic substitution of di- and trisubstituted alkenes.</p> <p>Luchaco-Cullis, C. A.; Mizutani, H.; Murphy, K. E.; Hoveyda, A. H. <i>Angew. Chem. Int. Ed.</i> 2001, <i>40</i>, 1456.</p>	<p style="text-align: center;">A</p>	<p style="text-align: center;">6 examples (yields 34–96%, %ee 66–82%).</p>
1,3-Dimethyl-5-[(dimethylamino)methylene]-2,4,6-(1 <i>H</i> ,3 <i>H</i> ,5 <i>H</i>)-trioxypyrimidine		Reagent
<p>The title reagent is used to protect aminosugars and other primary amides.</p> <p>Dekany, G.; Bornaghi, L.; Papageorgiou, J.; Taylor, S. <i>Tetrahedron Lett.</i> 2001, <i>42</i>, 3129.</p>	<p style="text-align: center;">A</p>	<p style="text-align: center;">2 examples (yields 86–90%).</p>
4-Isopropyl-3-(methylthiomethyl)-5,5-diphenyloxazolidin-2-one		Reagent
<p>The lithiated derivative of A is used as a chiral formyl anion equivalent for the preparations of 1,2-diols, 2-amino alcohols, 2-hydroxy esters, and 4-hydroxy-2-alkenoates.</p> <p>Gaul, C.; Schärer, K.; Seebach, D. <i>J. Org. Chem.</i> 2001, <i>66</i>, 3059.</p>	<p style="text-align: center;">A</p>	<p style="text-align: center;">30 examples (yields 25–92%, %de 24–94%).</p>
β -Borylallylsilane		Reagent
<p>The title reagent is used for the synthesis of cyclic alkenylboranes through an acetalisation-cyclisation sequence with aldehydes.</p> <p>Suginome, M.; Ohmori, Y.; Ito, Y. <i>J. Am. Chem. Soc.</i> 2001, <i>123</i>, 4601.</p>	<p style="text-align: center;">A</p>	<p style="text-align: center;">9 examples (yields 34–94%).</p>
Triethylboron		Reagent
<p>The title reagent plays a dual role as radical initiator and in situ derivitisation reagent in hydrogen transfer reactions involving acyclic 1,2- and 1,3-diols.</p> <p>Bouvier, J.-P.; Jung, G.; Liu, Z.; Gurérin, B.; Guindon, Y. <i>Org. Lett.</i> 2001, <i>3</i>, 1391.</p>	<p style="text-align: center;">A</p>	<p style="text-align: center;">4 examples (yields 78–90%, %de 20–91%).</p>

Phenylsilane/Dibutyltin Chloride		Reagent
<p>The title reagent pair promotes the direct reductive amination of aldehydes and ketones.</p> <p>Apodaca, R.; Xiao, W. <i>Org. Lett.</i> 2001, 3, 1745.</p>	<p>PhSiH₃ A</p> <p>Bu₂SnCl₂ B</p>	 <p>20 examples (yields 13–91%).</p>
2-Chloro-4,6-dimethoxy[1,3,5]triazine		Reagent
<p>The title reagent converts carboxylic acids into activated esters under mild conditions, which are subsequently reacted with a Grignard/Cul reagent to give the corresponding ketones.</p> <p>De Luca, L.; Giacomelli, G.; Porcheddu, A. <i>Org. Lett.</i> 2001, 3, 1519.</p>	 <p>A</p>	 <p>10 examples (yields 48, 90–98%) are reported.</p>
Samarium Iodide		Reagent
<p>The title reagent is used as a reducing agent in the selective reduction of conjugated Δ²-isoxazolines, which after hydrolysis with B(OH)₃, gives the corresponding unsaturated β-hydroxy ketones.</p> <p>Bode, J. W.; Carreira, E. M. <i>Org. Lett.</i> 2001, 3, 1587.</p>	<p>Sml₂ A</p>  <p>10 examples (yields 56–90%).</p>	
Polymethylhydrosiloxane (PMHS)-Zinc Chloride/Tetrakis(triphenylphosphine)palladium(0)		Reagent
<p>The title reagent pair is used for the selective cleavage of allyl ethers, amines and esters.</p> <p>Chandrasekhar, S.; Raji, Reddy C.; Jagadeeshwar Rao, Rao R. <i>Tetrahedron</i> 2001, 57, 3435.</p>	<p>PMHS-ZnCl₂ A</p> <p>Pd(PPh₃)₄ B</p>	 <p>26 examples (yields 85–94%).</p>
Tetrabutylammonium Butyldifluorodimethylsilicate		Reagent
<p>The title reagent is used as a nucleophilic fluorinating agent.</p> <p>Kvícala, J.; Mysík, P.; Paleta, O. <i>Synlett</i> 2001, 545.</p>	 <p>A</p>	 <p>11 examples (yields 10–81%).</p>