Phosphoramidites in synthesis

Robert Straker

Literature Review – July 2014

Phosphoramidites in synthesis

Content

Introduction

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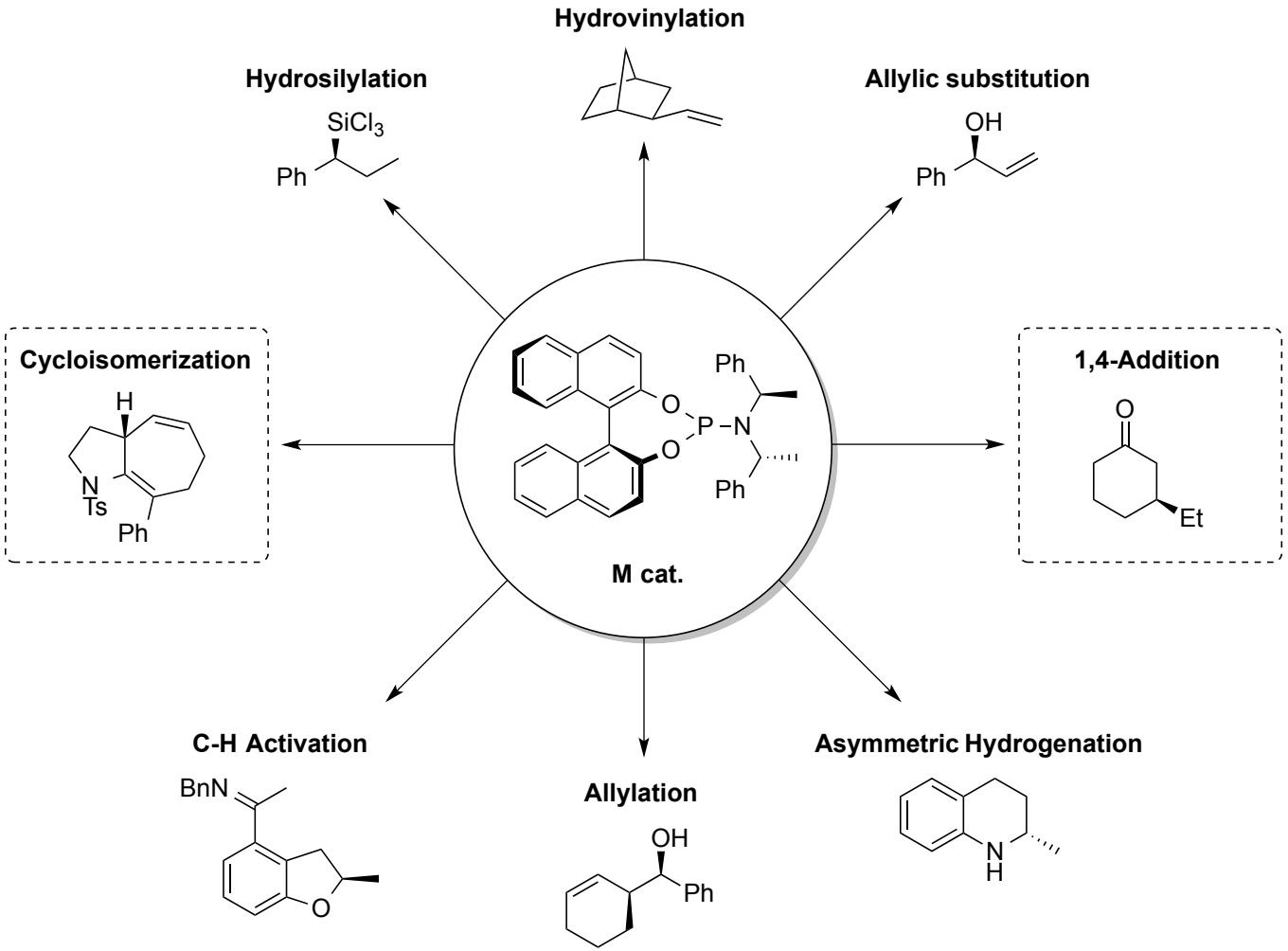
Phosphoramidites in synthesis

Introduction – History: Privileged Ligands[1]



1. Teichert, J. F.; Feringa, B. L., *Angew. Chem. Int. Ed.* 2010, *49*, 2486-2528

Phosphoramidites in synthesis

Introduction – History

Ben L. Feringa

• Obtained his PhD in 1978 at the University of Groningen under the guidance of Prof. Hans Wynberg

• Appointed full professor in 1988 at the University of Groningen.

• Knighted in 2008 by Her Majesty the Queen of the Netherlands.

• First introduced phosphoramidites in 1994, describing them as "interesting chiral ligands".[2]

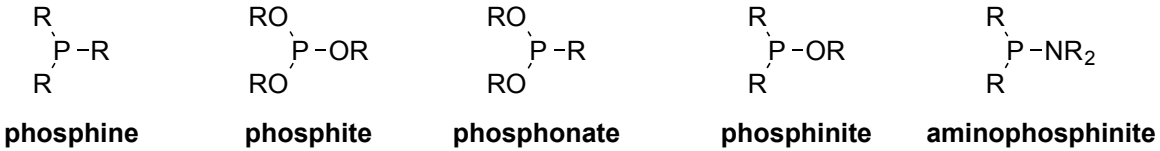
2. Hulst, R.; de Vries, N. K.; Feringa, B. L., *Tetrahedron: Asymmetry* 1994, *5*, 699-708

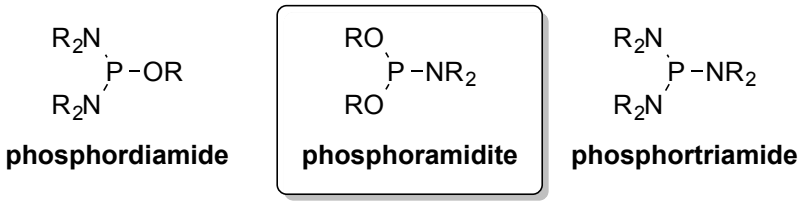
Phosphoramidites in synthesis

Introduction – Structure

Trivalent Phosphorous

- Phosphoramidites are one of a family of amides of trivalent phosphorous acid H_3PO_3.
- Distinct from other trivalent phosphorous ligands as they contain one P-N bond and two P-O bonds.
- Both phosphorous and nitrogen possess unshared lone pairs, which can act as metal binding sites





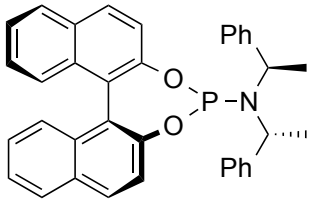
1. Teichert, J. F.; Feringa, B. L., *Angew. Chem. Int. Ed.* 2010, *49*, 2486-2528

Phosphoramidites in synthesis

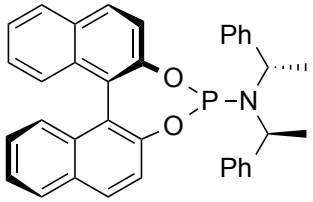
Introduction – Structure

Modular Framework

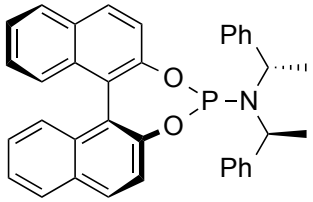
- Stereodescrimination can originate from either the diol or amine component – matched/ mismatched.
- Possible to tune the steric and electronic properties with a variety of readily available building blocks.
- Phosphrous has a pseudotetrahedral geometry, whilst nitrogen is usually trigonal planar.[3]



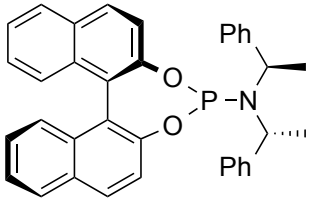
(*S*,*R*,*R*)-**L2**



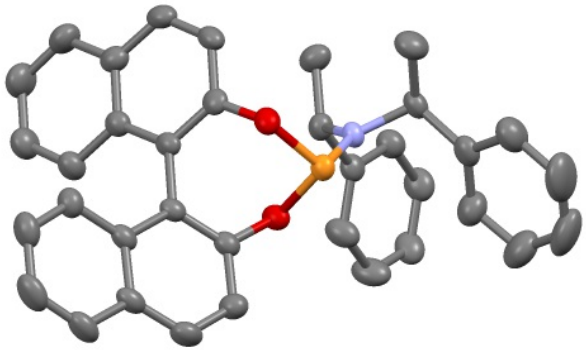
(*R*,*S*,*S*)-*ent*-**L2**



(*S*,*S*,*S*)-**L2b**



(*R*,*R*,*R*)-*ent*-**L2b**



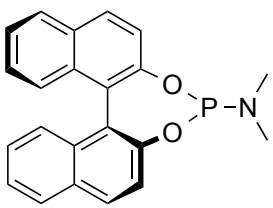
X-Ray crystal structure of (*S*,*R*,*R*)-**L2**

3. Holscher, M.; Francio, G.; Leitner, W., *Organometallics*, 2004, *23*, 5606-5617

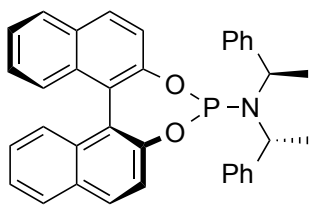
Phosphoramidites in synthesis

Introduction – Structure

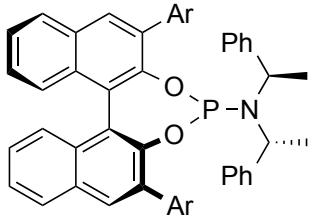
Commonly used classes of phosphoramidite ligand[1]



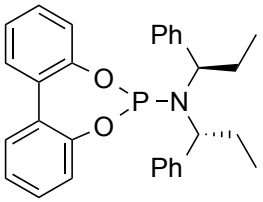
chiral BINOL, achiral amine
(*S*)-**L1** (MonoPhos)



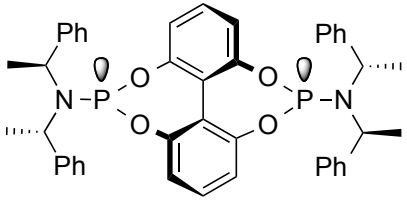
chiral BINOL, chiral amine
(*S*,*R*,*R*)-**L2**



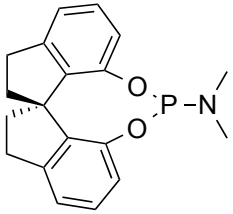
3,5-disubstituted BINOL
(*S*,*S*,*S*)-**L3**



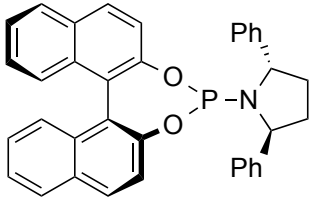
flexible biphenol
(*R*,*R*)-**L4**



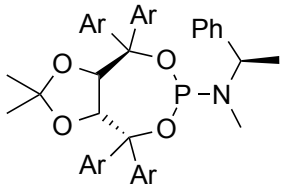
dibridged biphenyl
cis-(*S*,*S*,*aR*,*S*,*S*)-**L5**



spirobiindanediol
(*R*)-**L6**



chiral pyrrolidine
(*S*,*S*,*S*)-**L7**



TADDOL backbone
(*S*,*S*,*R*)-**L8**

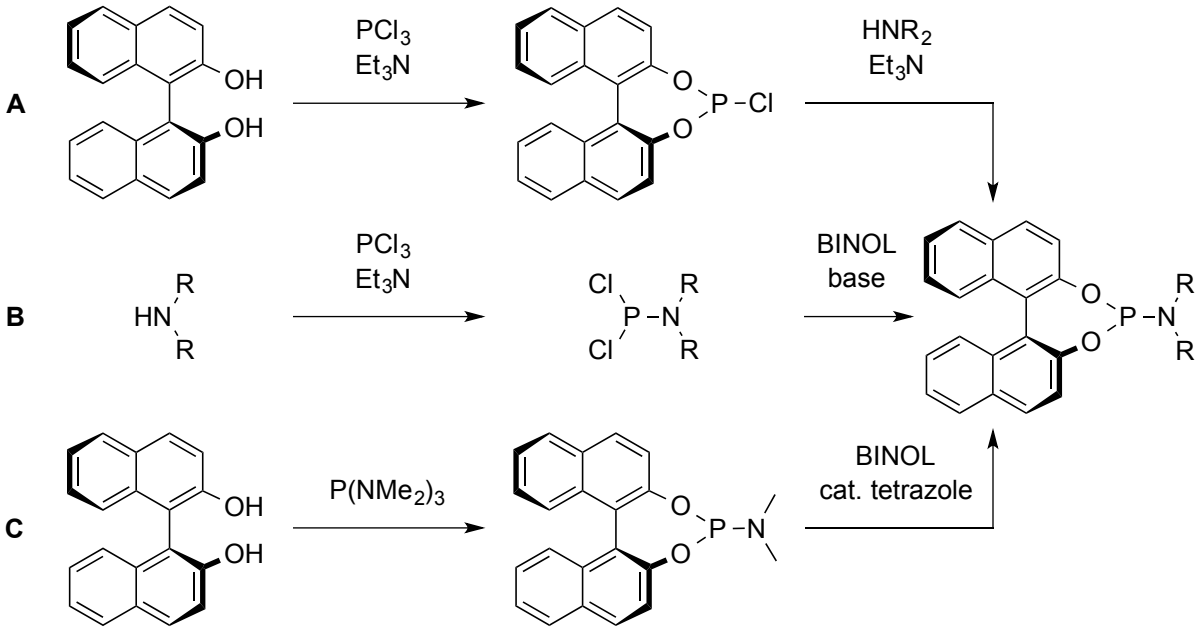
1. Teichert, J. F.; Feringa, B. L., *Angew. Chem. Int. Ed.* 2010, *49*, 2486-2528

Phosphoramidites in synthesis

Introduction – Synthesis

Three main routes to phosphoramidite ligands have been established:

- A is the most commonly adopted.[4]
- B is preferred for more sterically encumbered amines.[5]
- C represents an efficient synthesis of MonoPhos, which can undergo subsequent amine exchange.[2]



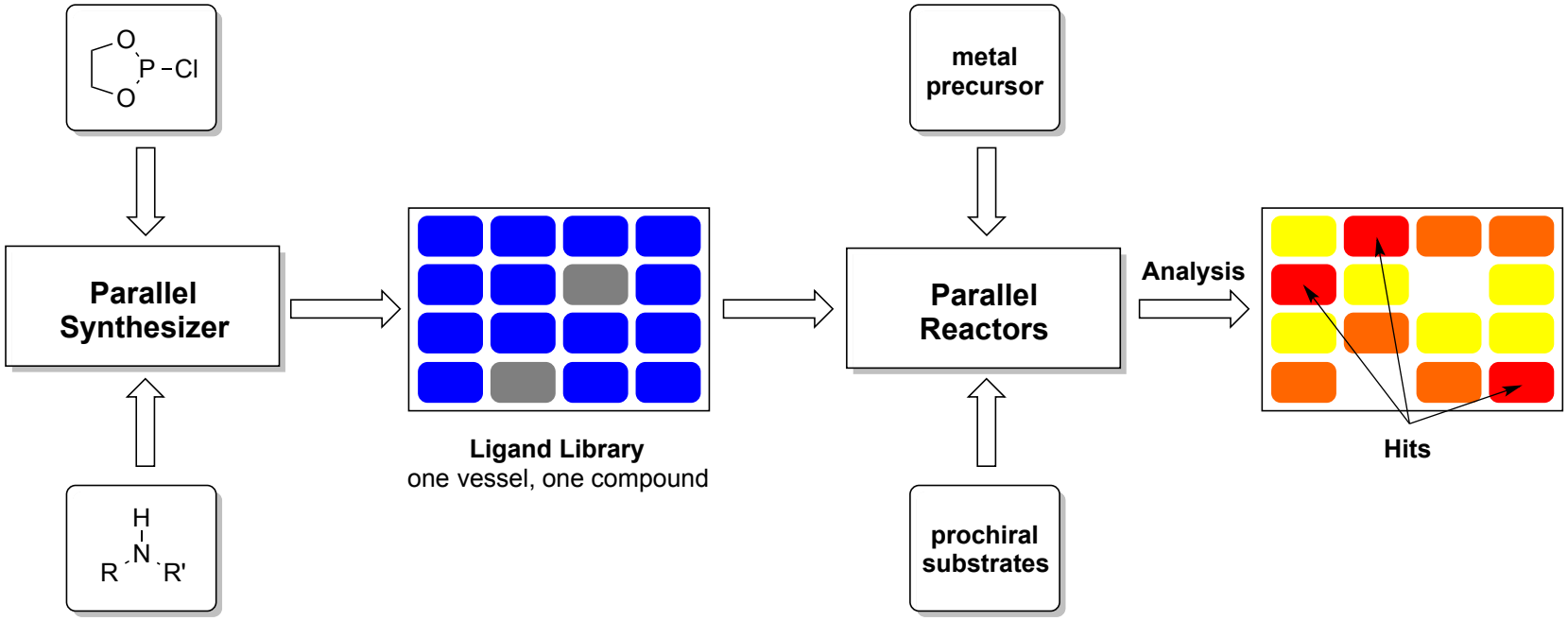
4. de Vries, A. H.; Meetsma, A.; Feringa, B. L., *Angew. Chem. Int. Ed.* 1996, *35*, 2374-2376
5. Alexakis, A.; Polet, D.; Rosset, S.; March, S., *J. Org. Chem.* 2004, *69*, 5660-5667
2. Hulst, R.; de Vries, N. K.; Feringa, B. L., *Tetrahedron: Asymmetry* 1994, *5*, 699-708

Phosphoramidites in synthesis

Introduction – Synthesis

Fully automated parallel synthesis and *in situ* screening of ligand libraries[6]

- Modular nature of phosphoramidites makes them ideally suited to parallel synthesis approach.
- Particularly useful for highly substrate dependant reactions as ligand libraries can be stored and reused.



6. Lefort, L.; Boogers, J. A. F.; de Vries, A. H. M.; de Vries, J. G., *Org. Lett.* 2004, *6*, 1733-1735

1,4-Addition of organometallic nucleophiles

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Literature Review – July 2014

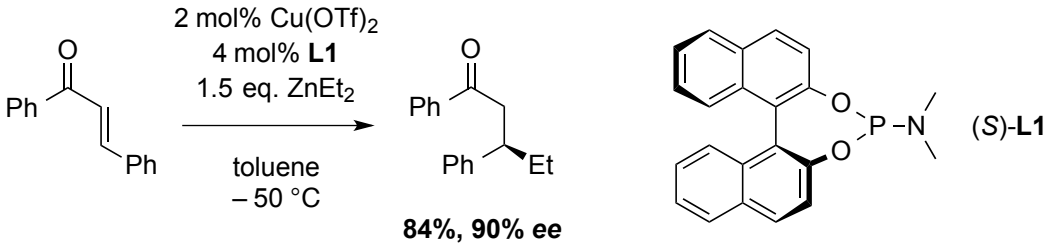
UNIVERSITY OF OXFORD

Phosphoramidites in synthesis

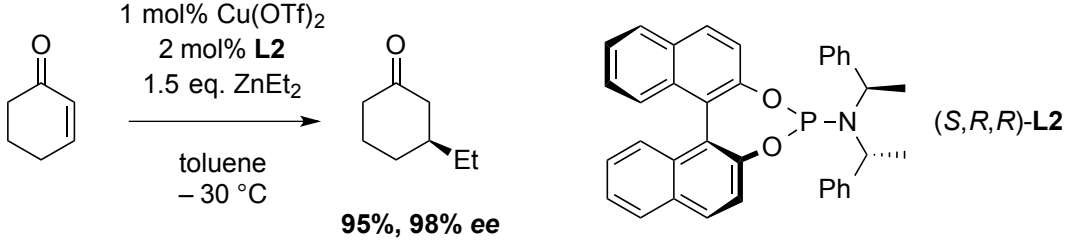
Application – 1,4-Addition of organometallic nucleophiles

Copper-catalyzed asymmetric conjugate addition with dialkyl zinc reagents[4]

- Demonstrated by Feringa *et al.,* high chemo- and enantioselectivity with cyclic and acyclic enones.



- Further explored ligand substituents and discovered additional chiral centres were beneficial.[7]



4. de Vries, A. H.; Meetsma, A.; Feringa, B. L., *Angew. Chem. Int. Ed.* 1996, *35*, 2374-2376
7. Feringa, B. L.; Pineschi, M.; Arnold, L. A.; Imbos, R.; de Vries, A. H. M., *Angew. Chem. Int. Ed.* 1997, *36*, 2620-2623

Phosphoramidites in synthesis

Application – 1,4-Addition of organometallic nucleophiles

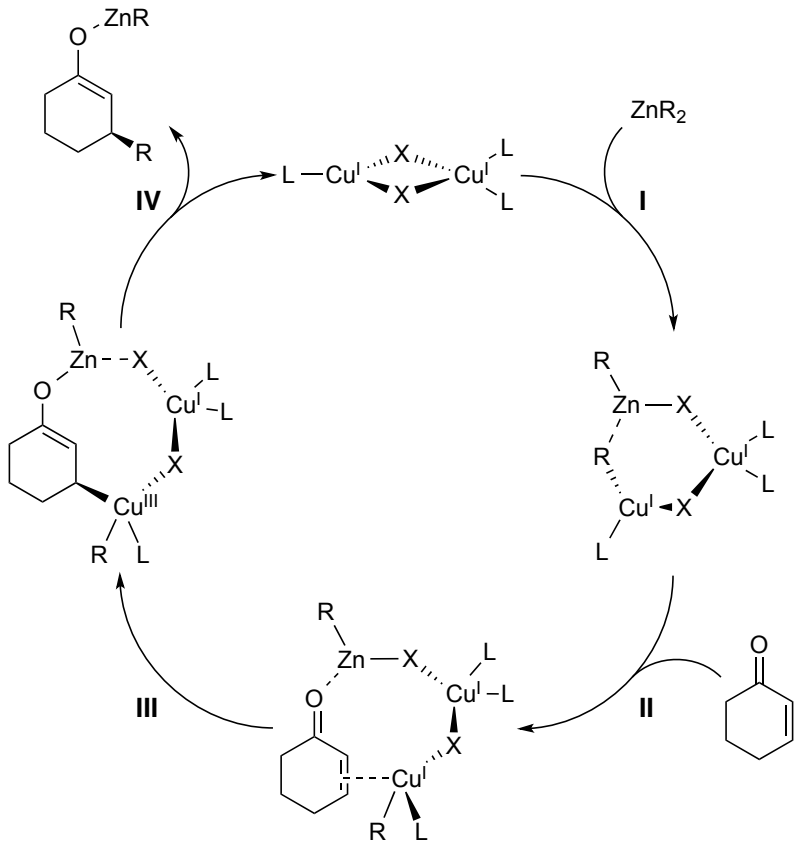
Catalytic Cycle – Gschwind *et al.*[8,9]

I – Alkyl transfer of dialkyl zinc reagent to dimeric copper(I) precatalyst.

II – π coordination of Cu^{I} centre to alkene moiety of Michael acceptor. Zinc(II) acts as a Lewis acid, binding to the carbonyl group.

III – Oxidative 1,4-addition of Cu^{I} to activated enone.

IV – Reductive elimination, releasing zinc enoate and copper(I) complex, rate determining step.



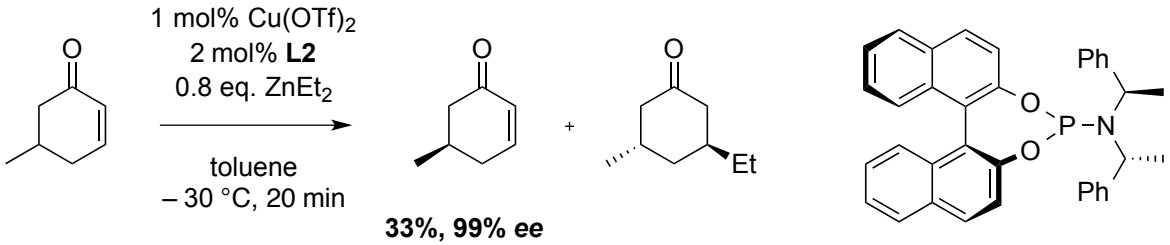
8. Zhang, H.; Gschwind, R. M., *Chem. Eur. J.* 2007, *13*, 6691-6700
9. Schober, K.; Zhang, H.; Gschwind, R. M., *J. Am. Chem. Soc.* 2008, *130*, 12310-12317

Phosphoramidites in synthesis

Application – 1,4-Addition of organometallic nucleophiles

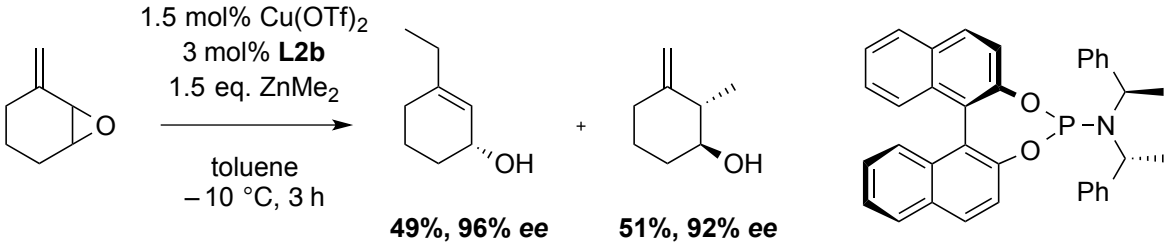
Kinetic Resolution Reactions

• Selective conversion of one enantiomer of starting material to conjugate addition product.[10]



(*S*,*R*,*R*)-**L2**

• Ligand delivers nucleophile in S_N2' fashion to one enantiomer and S_N2 to the other.[11]



(*R*,*R*,*R*)-*ent*-**L2b**

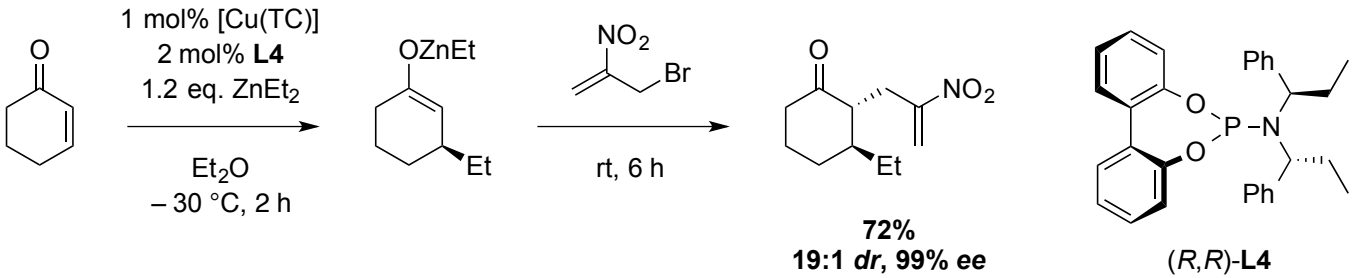
10. Naasz, R.; Arnold, L. A.; Minaard, A. J.; Feringa, B. L., *Angew. Chem. Int. Ed.* 2001, *40*, 927-930
11. Bertozzi, F.; Crotti, P.; Macchia, F.; Pineschi, M.; Feringa, B. L., *Angew. Chem. Int. Ed.* 2001, *40*, 930-932

Phosphoramidites in synthesis

Application – 1,4-Addition of organometallic nucleophiles

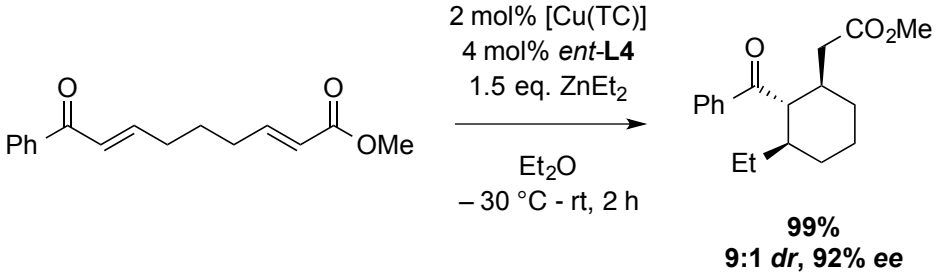
Intermolecular trapping of zinc enolates with electrophiles

• Alexakis demonstrated highly diastereoselective trapping of zinc enolate intermediates.[12]



Intramolecular Michael reaction

• Chemoselective conjugate addition, followed by trapping with tethered electrophile.[13]



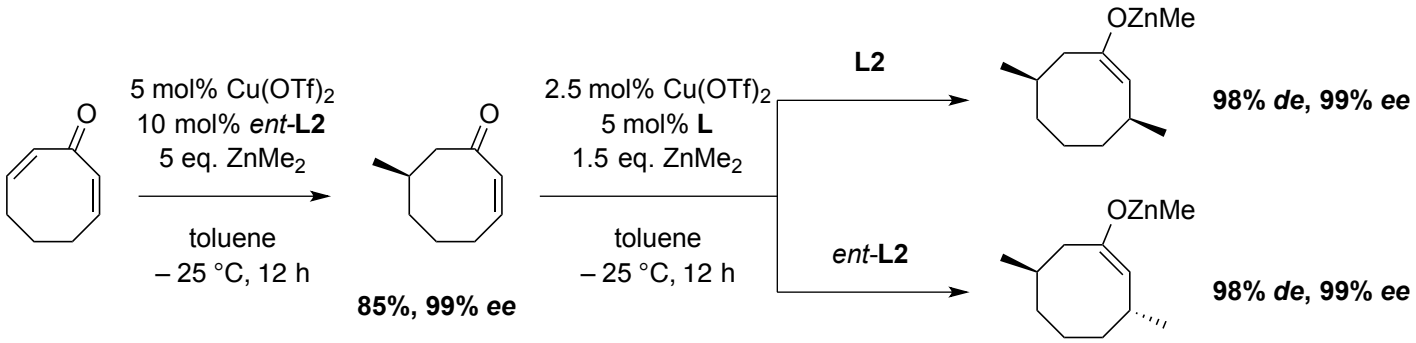
12. Rathgeb, X.; March, S.; Alexakis, A., *J. Org. Chem.* 2006, *71*, 5737-5742
13. Li, K.; Alexakis, A., *Tetrahedron Lett.* 2005, *46*, 8019-8022

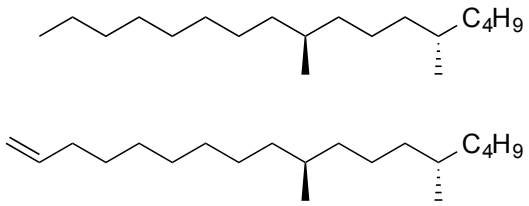
Phosphoramidites in synthesis

Application – 1,4-Addition of organometallic nucleophiles

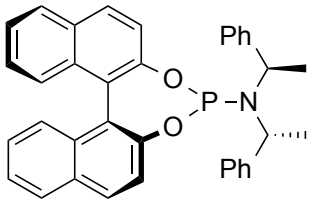
Construction of 1,5-dimethyl arrays – Application to Natural Products[14]

- Judicious choice of catalyst allows construction of all four diastereomers of isoprenoid building blocks.
- Selective oxidative ring opening of the corresponding silyl enol ether prevents racemization.





Insect pheramones
(Lyonetia prunifoliella)



(*S*,*R*,*R*)-**L2**

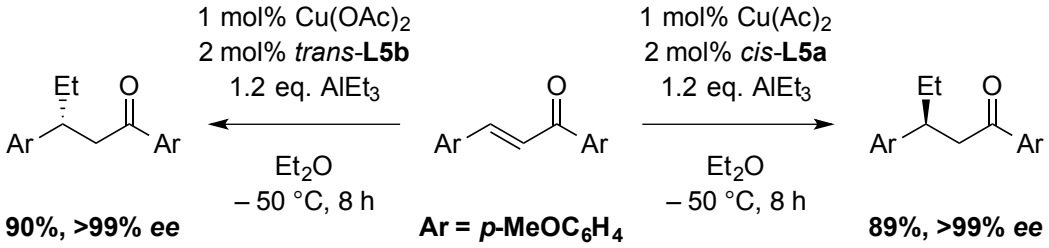
14. van Summeren, R. P.; Reijmer, S. J. W.; Feringa, B. L.; Minaard, A. J., *Chem. Comm.* 2005, 1387-1389

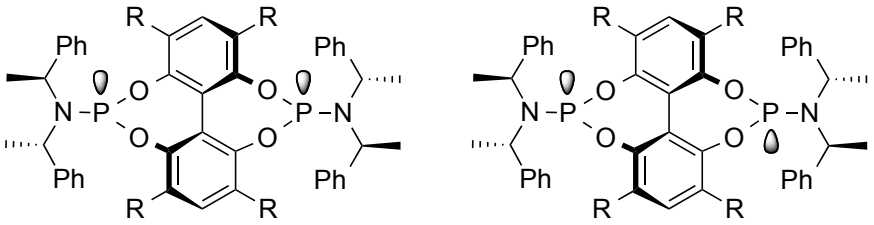
Phosphoramidites in synthesis

Application – 1,4-Addition of organometallic nucleophiles

Reversal of stereoselectivity: Substituent Effect – Zhang *et al.*[15,16]

- Backbone substituents in D_2-symmetric ligands can switch enantioselectivity absolutely.
- Matched and mismatched cases with *cis*- and *trans*-dibridged phosphoramidites.





cis-(*S,S,aR,S,S*)-**L5x**
x = a, R = H; x = b, R = Me

trans-(*S,S,aR,S,S*)-**L5x**
x = a, R = H; x = b, R = Me

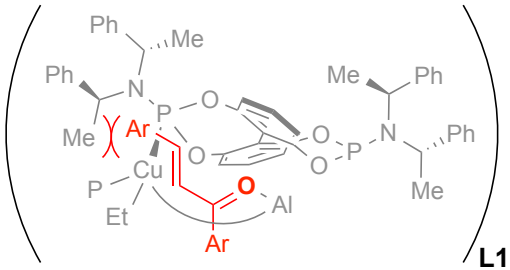
15. Zhang, H.; Fang, F.; Xie, F.; Yang, G.; Zhang, W., *Tetrahedron Lett.* 2010, *51*, 3119-3122
16. Yu, H.; Xie, F.; Ma, Z.; Liu, Y.; Zhang, W., *Adv. Synth. Catal.* 2012, *354*, 1941-1947

Phosphoramidites in synthesis

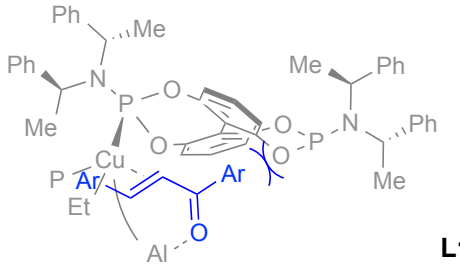
Application – 1,4-Addition of organometallic nucleophiles

Reversal of stereoselectivity: Substituent Effect – Zhang *et al.*[15,16]

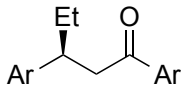
- Unfavourable steric interaction of the amine substituent with the substrate in L5a-TS2.
- Overriding steric interaction of backbone substituent with substrate in L5b-TS1.



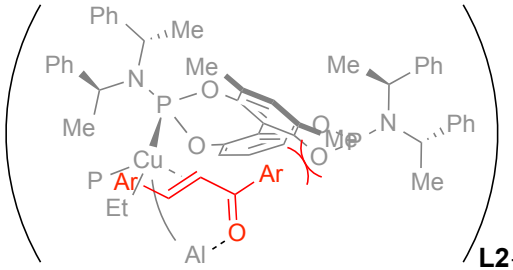
L1-TS2



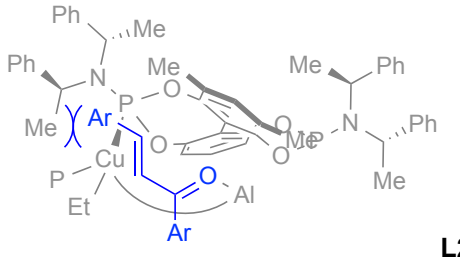
L1-TS1



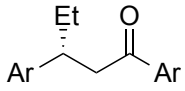
***S* product**



L2-TS1



L2-TS2



***R* product**

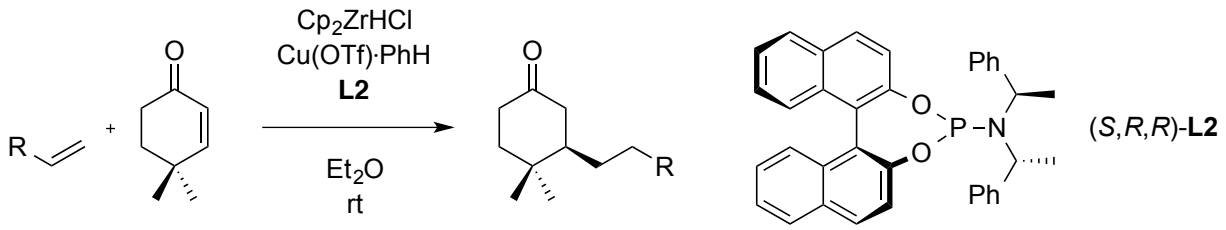
15. Zhang, H.; Fang, F.; Xie, F.; Yang, G.; Zhang, W., *Tetrahedron Lett.* 2010, *51*, 3119-3122
16. Yu, H.; Xie, F.; Ma, Z.; Liu, Y.; Zhang, W., *Adv. Synth. Catal.* 2012, *354*, 1941-1947

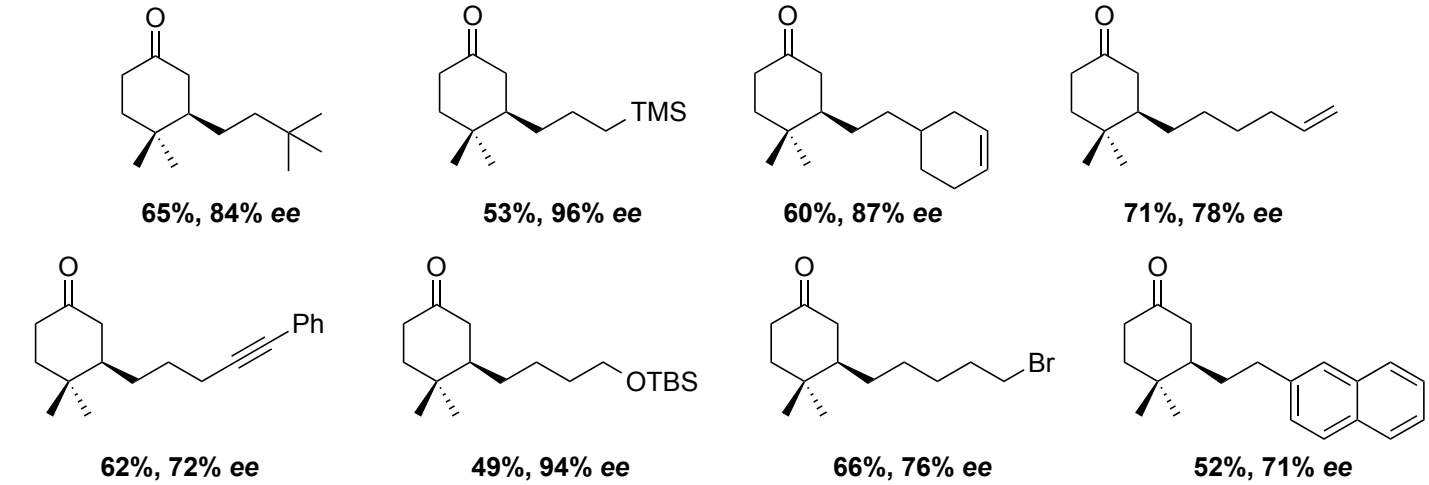
Phosphoramidites in synthesis

Application – 1,4-Addition of organometallic nucleophiles

In situ generation of organometallic nucleophiles – Fletcher *et al.*[17]

- Hydro-zirconation of alkene allows preparation of a variety of previously inaccessible nucleophiles.





65%, 84% *ee* | **53%, 96% *ee*** | **60%, 87% *ee*** | **71%, 78% *ee***

62%, 72% *ee* | **49%, 94% *ee*** | **66%, 76% *ee*** | **52%, 71% *ee***

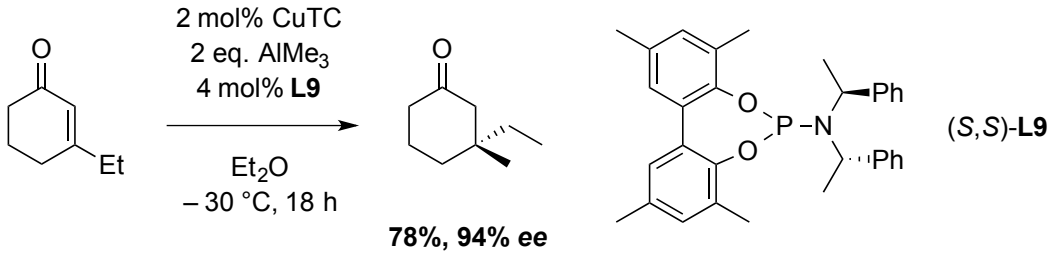
17. Maksymowicz, R. M.; Roth, P. M. C.; Fletcher, S. P., *Nat. Chem.* 2012, *4*, 649-654

Phosphoramidites in synthesis

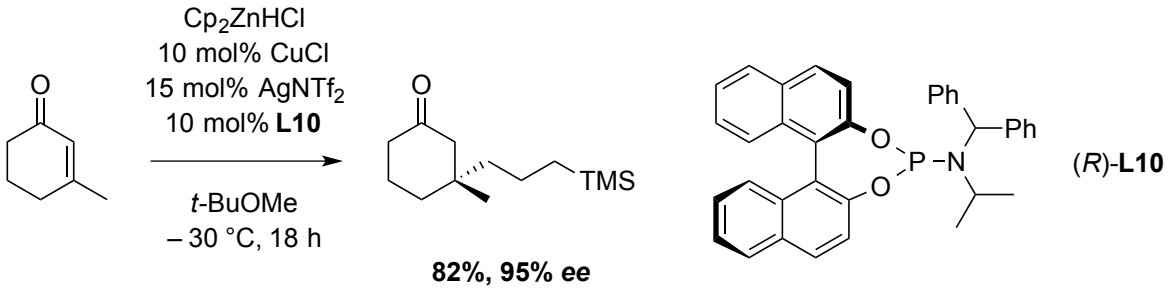
Application – 1,4-Addition of organometallic nucleophiles

Generation of chiral all-carbon-quarternary centres

• Alexakis *et al*. addressed the issue of sterically encumbered Michael acceptors with stronger lewis acids.[18]



• The Fletcher group applied their hydro-metallation approach to broaden the scope of available substituents.[19]



18. d' Augustin, M.; Palais, L.; Alexakis, A., *Angew. Chem. Int. Ed.* 2005, *44*, 1376-1378
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Cycloaddition reactions

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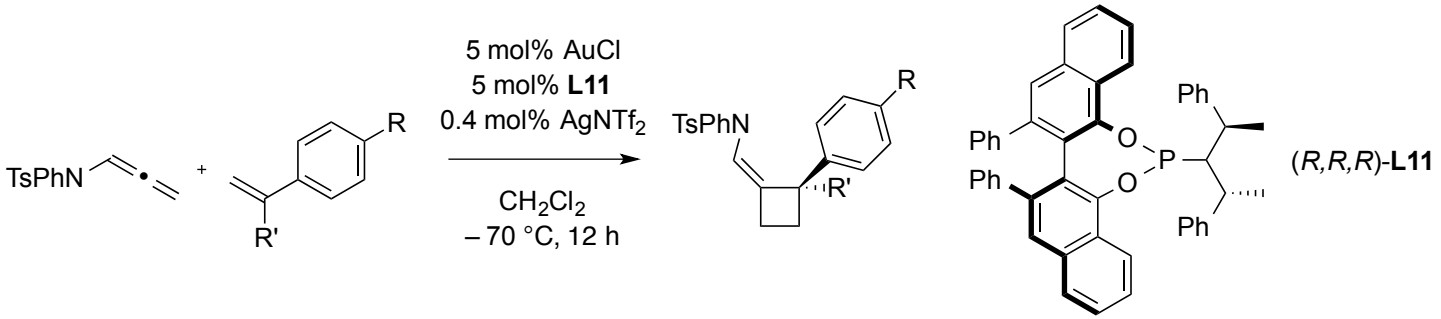
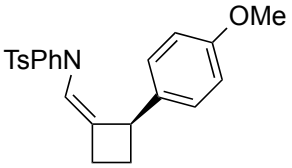
Literature Review – July 2014

Phosphoramidites in synthesis

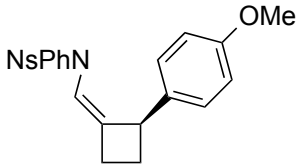
Application – Cycloaddition reactions

Gold-catalyzed intermolecular [2+2] cycloaddition[20]

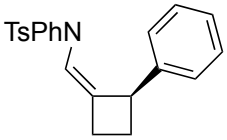




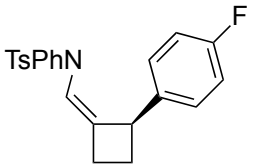
99%, 84% *ee*



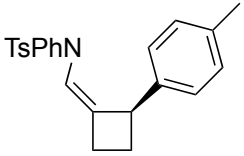
77%, 95% *ee*



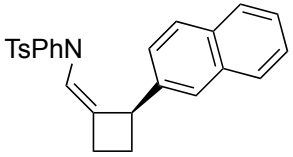
69%, 86% *ee*



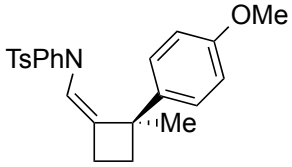
79%, 87% *ee*



95%, 72% *ee*



52%, 90% *ee*



78%, 90% *ee*

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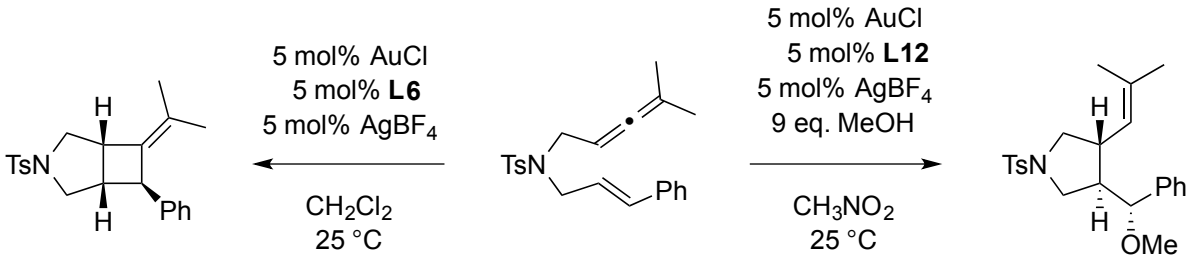
Phosphoramidites in synthesis

Application – Cycloaddition reactions

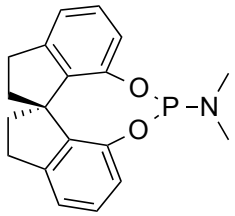
Gold-catalyzed intramolecular [2+2] cycloaddition[21]

- Formation of 3,4-substituted pyrollidines from allenenes – synthesis of Natural Product.
- Choice of ligand and nucleophile favours formation of either *cis*- or *trans*-substituted products.

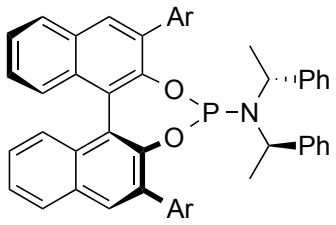


86%, 94% *ee*

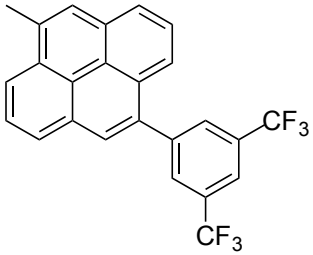
86%, 92% *ee*



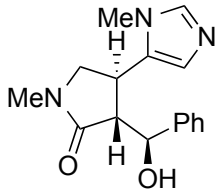
(*R*)-**L6**



(*S,S,S*)-**L12**



Ar



(-)-isocynometrine

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Phosphoramidites in synthesis

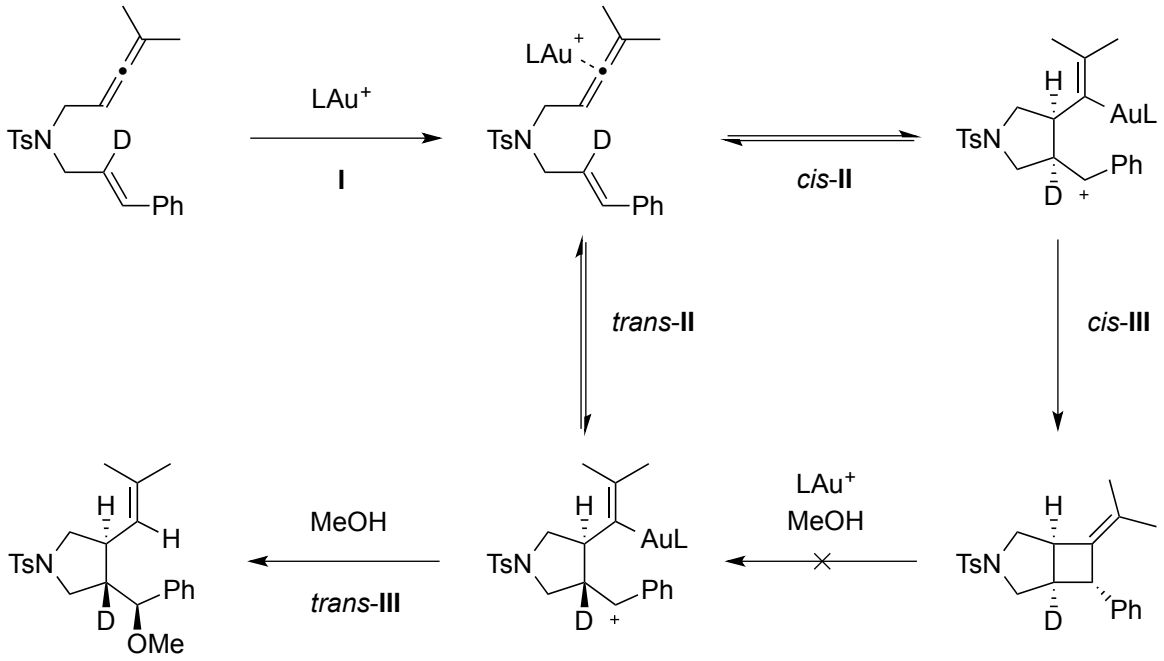
Application – Cycloaddition reactions

Gold-catalyzed intramolecular [2+2] cycloaddition[21]

I – Coordination of chiral Gold complex to allene moiety.

II – Reversible *cis*- or *trans*-insertion of alkene into activated allene – SD.

III – Nucleophilic trapping of carbocation with intramolecular migration or exogenous nucleophile – SD.



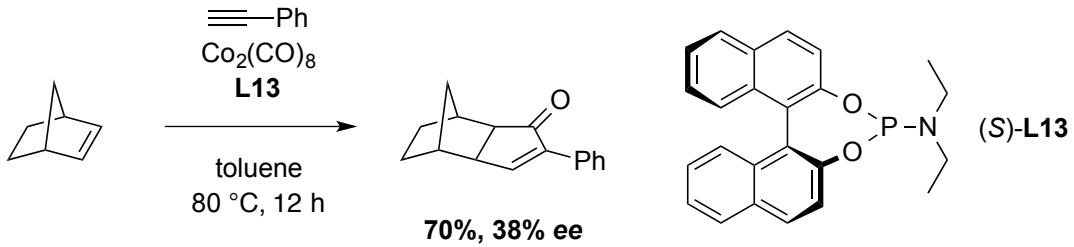
21. Gonzalez, A. Z.; Benitez, D.; Tkatchouk, E.; Goddard, W. A.; Toste, F. D., *J. Am. Chem. Soc.* 2011, *133*, 5500-5507

Phosphoramidites in synthesis

Application – Cycloaddition reactions

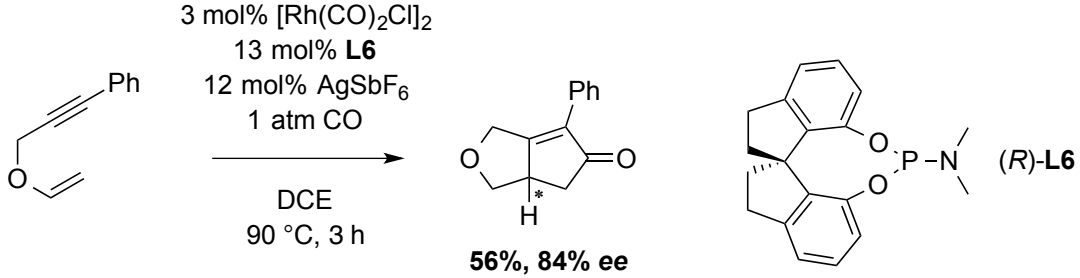
Cobalt-mediated intermolecular [2+2+1] Pauson-Khand cycloaddition[22]

- First use of phosphoramidite ligands in intermolecular cycloaddition, reaction of alkyne and norbornene.



Rhodium-catalyzed intramolecular [2+2+1] Pauson-Khand cycloaddition[23]

- Formation of bicyclic products from 1,6-enynes under carbon monoxide atmosphere.



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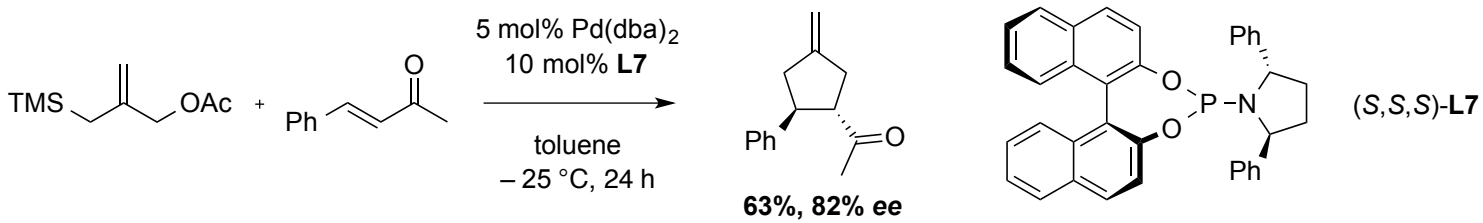
Phosphoramidites in synthesis

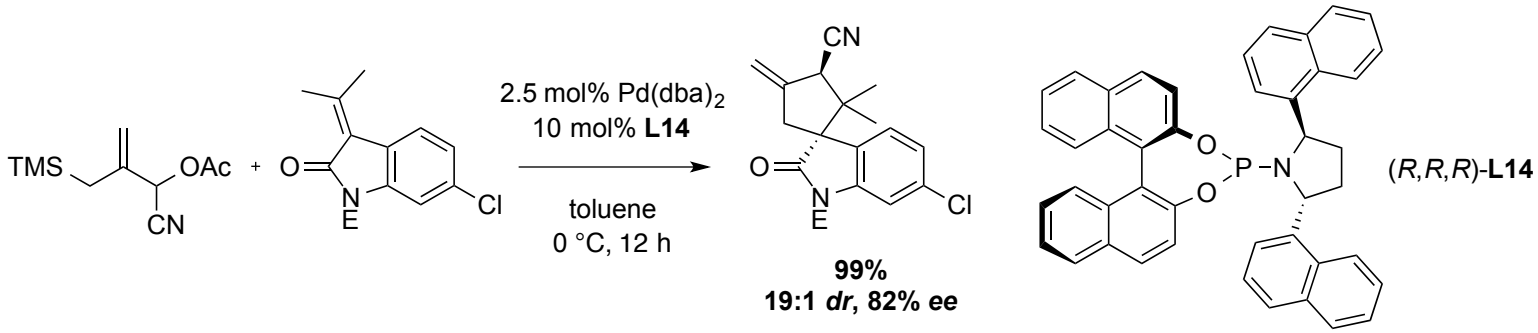
Application – Cycloaddition reactions

Palladium-catalyzed intermolecular [3+2] cycloaddition – Trost *et al.*[24]

• Cycloaddition of trimethylene unit, a useful transformation to provide 5-membered carbocycles.[25]



• Modification of ligand substituent allows application to oxindoles in the generation of spirocycles.[26]



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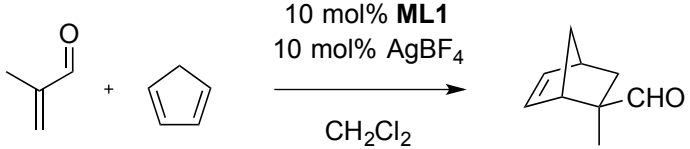
Phosphoramidites in synthesis

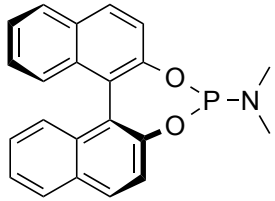
Application – Cycloaddition reactions

Ruthenium-catalyzed intermolecular [4+2] Diels-Alder cycloaddition[27]

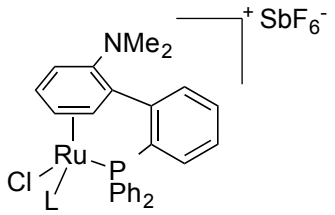
- Preformed chiral Ru complex acts as a Lewis acid, high regioselectivity and moderate enantioselectivity.



93:7 *dr*, 70% *ee*



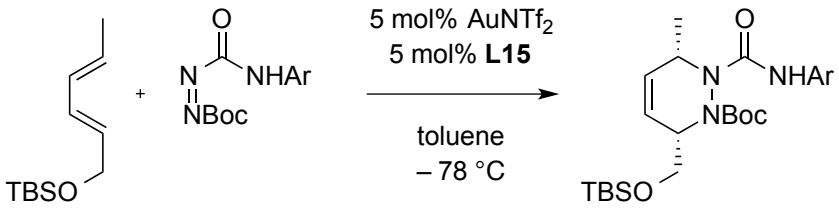
(*S*)-**L1**



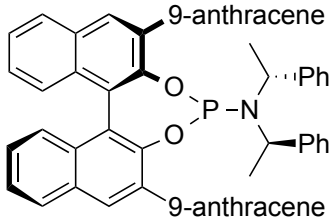
ML1

Gold-catalyzed intermolecular [4+2] azo hetero-Diels-Alder[28]

- Diazene dienophiles provide multifunctional heterocycles – Natural Products.



99%
>20:1 *dr*, 97% *ee*



(*R*,*S*,*S*)-**L15**

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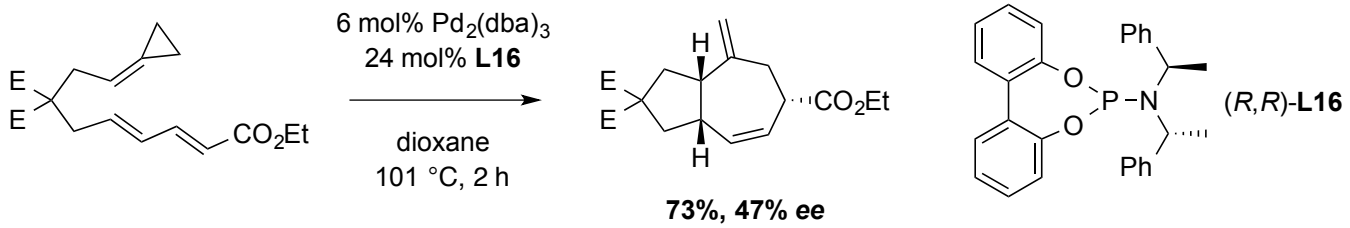
Phosphoramidites in synthesis

Application – Cycloaddition reactions

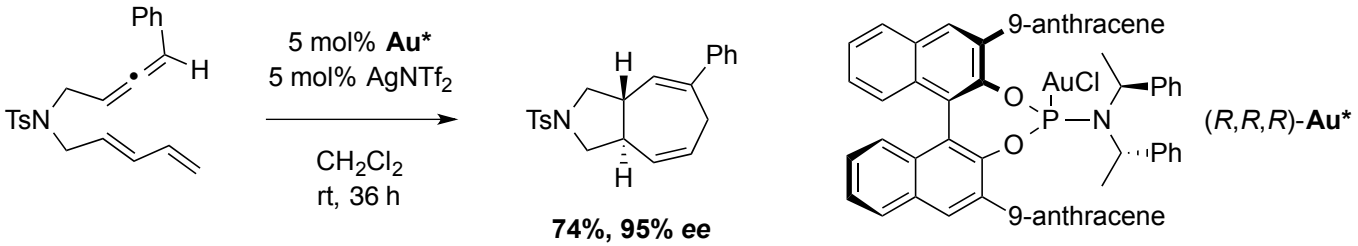
Palladium-catalyzed intramolecular [4+3] cycloaddition[29]

• First example of metal-catalyzed intramolecular [4+3], diene-tethered alkylidenecyclopropanes.



Gold-catalyzed intramolecular [4+3] cycloaddition[30]

• Highly diastereo- and enantioselective cycloaddition of allenedienes.



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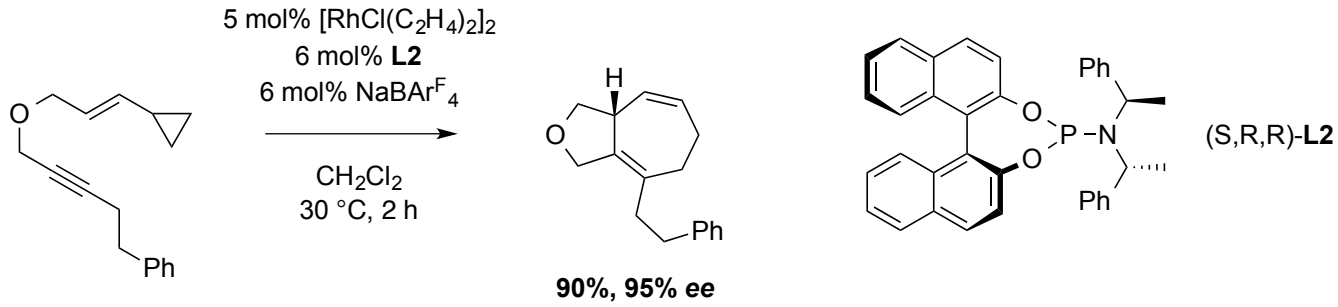
Phosphoramidites in synthesis

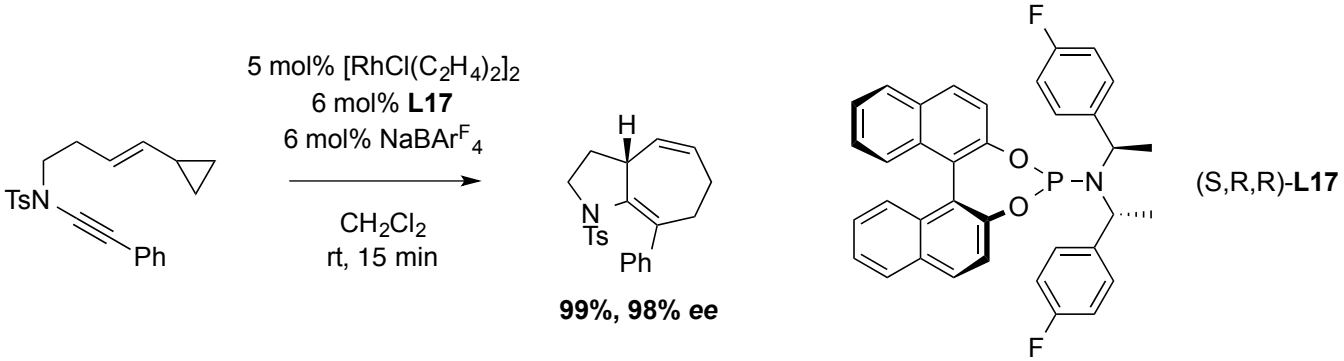
Application – Cycloaddition reactions

Rhodium-catalyzed intramolecular [5+2] cycloaddition

- Reaction of alkyne-tethered vinylcyclopropanes gave bicyclic products with high enantioselectivity.[31]



- Reaction of ynamide-vinylcyclopropanes, improved rate of reaction with Fluoride-substituted ligand.[32]



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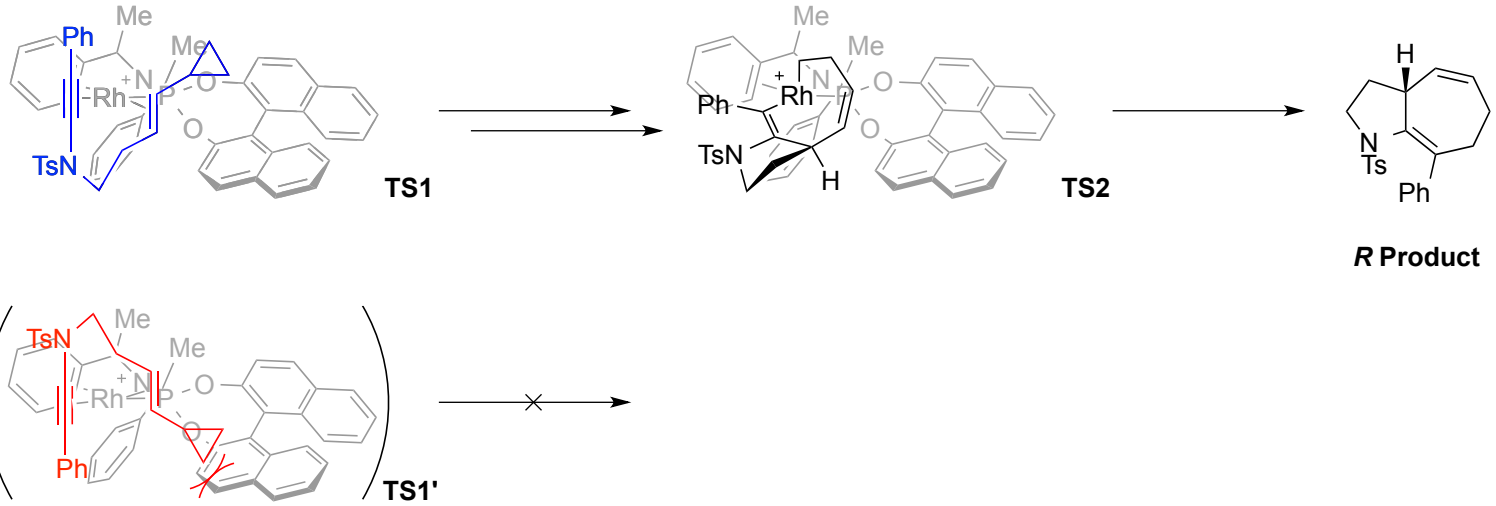
Phosphoramidites in synthesis

Application – Cycloaddition reactions

Rhodium-catalyzed intramolecular [5+2] cycloaddition[31]

- Unfavourable interaction of substrate cyclopropane moiety with ligand BINOL backbone in TS1'.
- Coordination of Rh to substrate in TS1 is followed by oxidative cyclopropane cleavage and insertion of alkyne to give the metallocycle in TS2.
- Reductive elimination gives the *R* product.



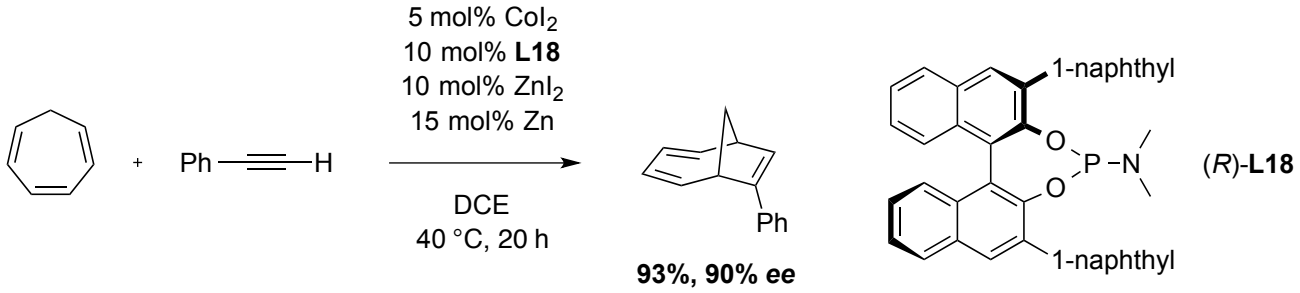
31. Shintani, R.; Nakatsu, H.; Takatsu, K.; Hayashi, T., *Chem. Eur. J.* 2009, *15*, 8692-8694

Phosphoramidites in synthesis

Application – Cycloaddition reactions

Cobalt-catalyzed intermolecular [6+2] cycloaddition[33]

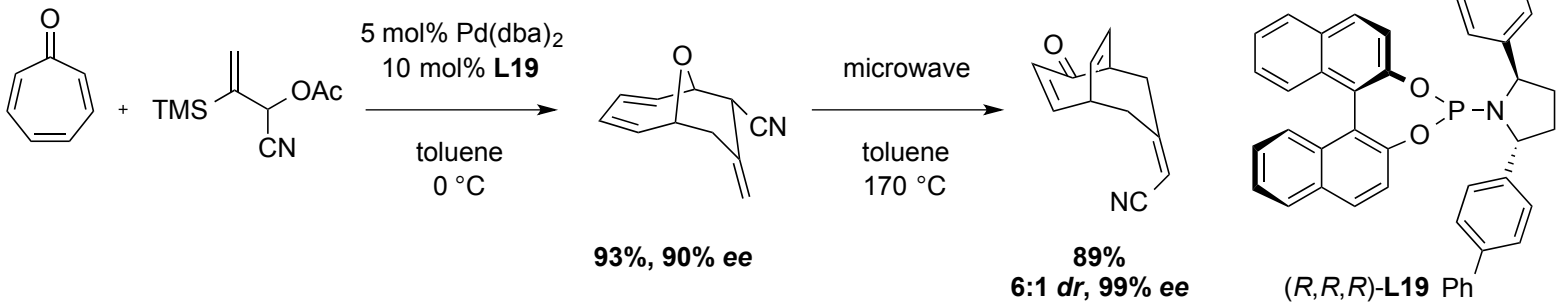
- Formation of bicyclo[4.2.1]nonatrienes, confirmed by vibrational circular dichroism (VCD) experiments.



93%, 90% *ee*

Palladium-catalyzed intermolecular [6+3] cycloaddition[34]

- Reaction of trimethylenemethane with tropones to give bicyclo[4.3.1] and [3.3.2]decadienes.



93%, 90% *ee*

89%
6:1 *dr*, 99% *ee*

33. Toselli, N.; Martin, D.; Achard, M.; Tenaglia, T. B.; Buono, G., *Adv. Synth. Catal.* 2008, *350*, 280-286
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Miscellaneous Reactions

Robert Straker

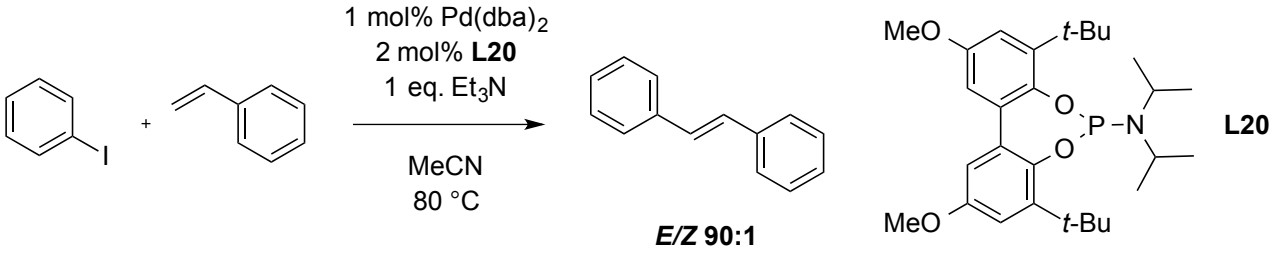
Literature Review – July 2014

Phosphoramidites in synthesis

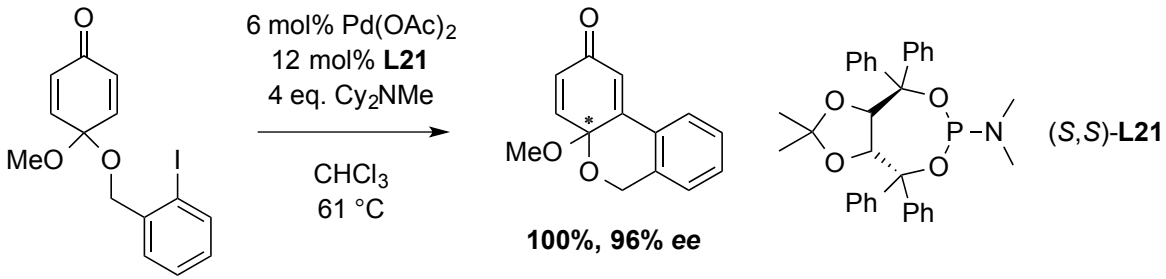
Miscellaneous Reactions

Palladium-catalyzed Heck reactions

• Highly *E* selective arylation of styrene, with only trace amounts of diphenylethylene observed.[35]



• Asymmetric intramolecular cross-coupling reaction using TADDOL-derivative phosphoramidites.[36]



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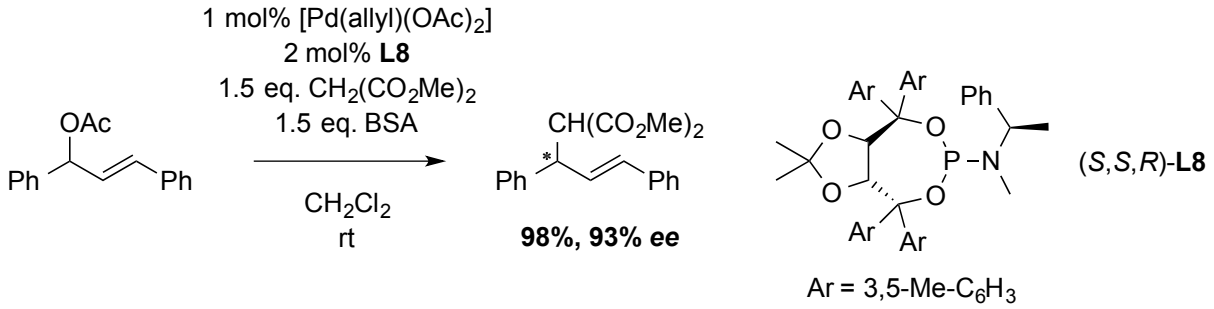
Phosphoramidites in synthesis

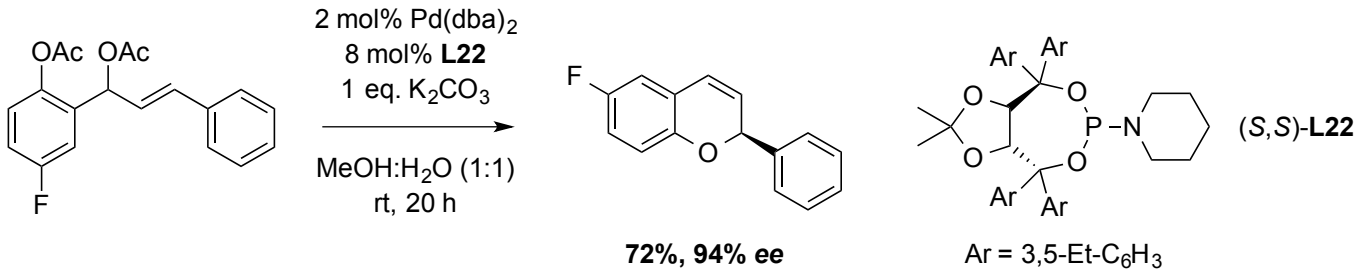
Miscellaneous Reactions

Palladium–catalyzed allylic substitution reactions

• Asymmetric allylic alkylation (AAA) reaction using TADDOL-phosphoramidites.[37]



• Synthesis of biologically active chromenes *via* 6-*endo*-trig cyclization reaction.[38]



37. Boele, M. D. K.; Kamer, P. C. J.; Lutz, M.; de Vries, J. G.; van Leeuwen, P. W. N. M.; van Strijdonck, G. P. F., *Chem. Eur. J.* 2004, *10*, 6232-6246

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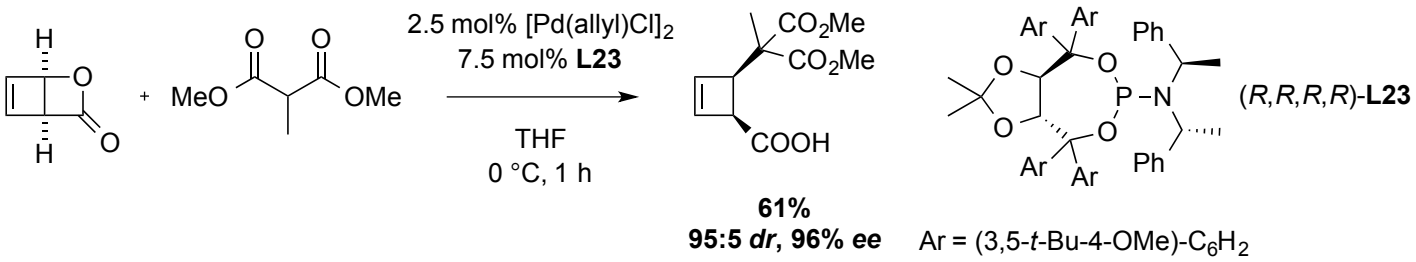
Phosphoramidites in synthesis

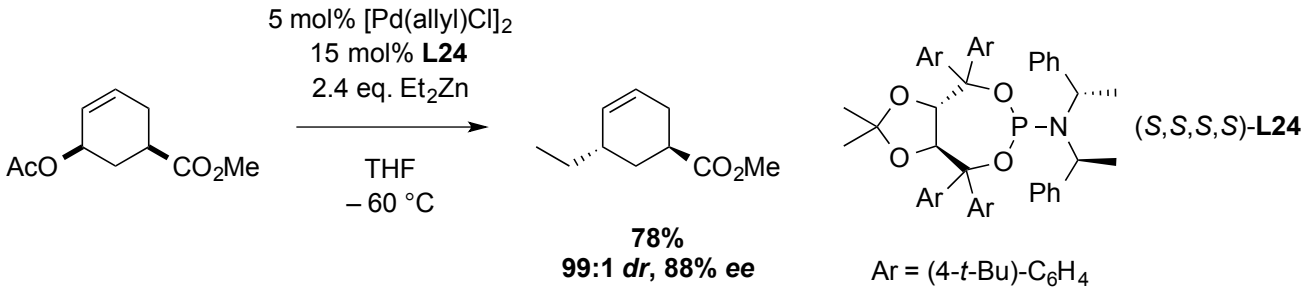
Miscellaneous Reactions

Palladium-catalyzed deracemization reactions

• Asymmetric allylic alkylation (AAA) reaction of strained lactones.[39]



• Overriding natural “umpolung” chemistry with unsual ligand effect.[40]



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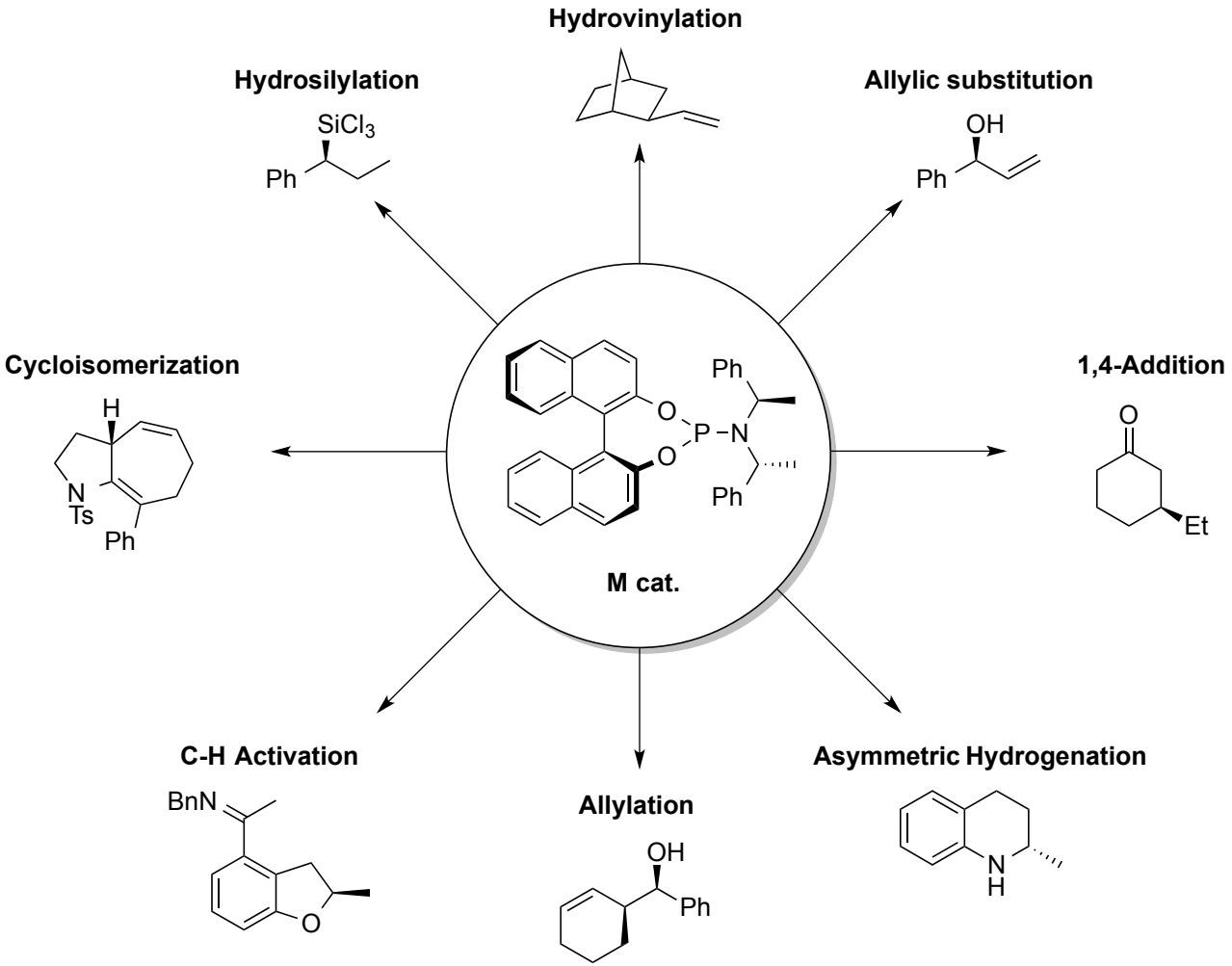
Phosphoramidites in synthesis

Summary



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Questions?

Robert Straker

Literature Review – July 2014

Phosphoramidites in synthesis

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