

# SYNLETT Spotlight 43

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

## 1,2-Bis-*N*-[2'-(diphenylphosphino)-benzo/naphtho]-1,2-diamino-cyclohexane – Trost Modular Ligands

Compiled by Ian J. S. Fairlamb

Ian Fairlamb was born in 1975 and received his B.Sc. at the Manchester Metropolitan University (UK) in 1996. After completing a PhD in Organic Chemistry in 1999 with Dr Julia M. Dickinson at the same institution, he continued his studies as a Postdoctoral Researcher with Dr Guy C. Lloyd-Jones at the University of Bristol (UK) on a project broadly titled *Mechanisms in Palladium Catalysis*. Since November 2001 he is leading his own research group at the University of York working on the application of transition metal catalysts to the synthesis of important targets.

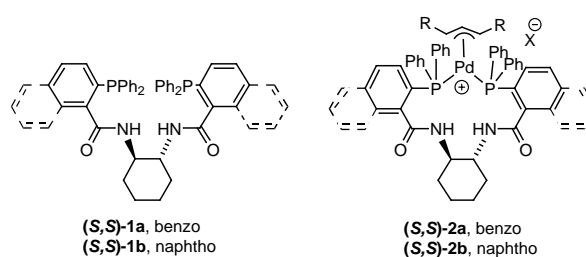
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### Introduction

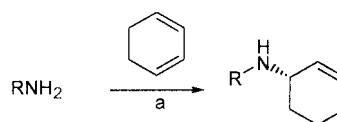
Over the past ten years Trost et al. have developed a modular approach to ligand design for the Pd-catalysed asymmetric allylic alkylation (AAA) reaction. Much attention has focused on ligands such as **1a** and its variant **1b** which, under appropriate conditions, provide outstanding selectivity in a broad range of Pd-catalysed reactions.<sup>1,2</sup> It should be noted that the mode of ligand bonding is not exclusively P,P-chelating, as in complexes **2a** and **2b**, and that ligand coordination is non-C<sub>2</sub>-symmetric.<sup>3</sup> Applications and uses of **1a** and **1b** are described.



Figure

### Abstracts

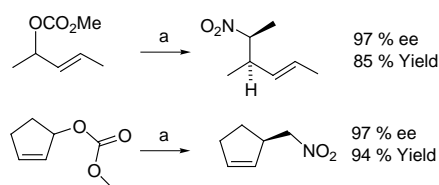
The regioselective 1:1 hydroamination of dienes affords allylic amines in excellent yields. The reaction is broad for a wide range of anilines and proceeds with high enantioselectivity when the naphtho modular ligand **1b** is employed.<sup>4</sup>



a. [Pd(π-allyl)Cl]<sub>2</sub> (5 mol%),  
Ligand **1a** or **1b** (11 mol%), THF, rt

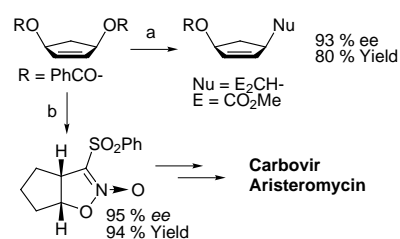
Lig.	R	Yield	ee
<b>1a</b>	Ph	65	11
<b>1b</b>	Ph	87	89
<b>1b</b>	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	78	86
<b>1b</b>	<i>p</i> -EtO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub>	83	95
<b>1b</b>	<i>p</i> -F <sub>3</sub> CC <sub>6</sub> H <sub>4</sub>	73	95

The Pd-catalysed AAA reaction of a range of nitroalkanes with acyclic and cyclic allyl esters, employing ligand **1a**, proceeds in high yields and enantioselectivities providing that catalyst loadings are low.<sup>3,5</sup>



a. Pd<sub>2</sub>dba<sub>3</sub>·CHCl<sub>3</sub>, **1a**, (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NCl, BSA, RNO<sub>2</sub> (R = Me, Et), CH<sub>2</sub>Cl<sub>2</sub>, rt

The Pd-catalysed desymmetrisation of meso diesters is a proven and highly versatile method for providing monosubstituted products of high ee.<sup>2,6</sup>



a.  $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ , **1a**,  $\text{E}_2\text{CH}^- \text{Na}^+$ , THF, rt  
 b.  $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ , **1a**, lithium[(phenyl-sulfonyl)methylene]nitronate, THF, rt

## References

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- (4) Löber, O.; Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 4366.
- (5) (a) Trost, B. M.; Surivet, J.-P. *J. Am. Chem. Soc.* **2000**, *122*, 6291. (b) Trost, B. M.; Surivet, J.-P. *Angew. Chem. Int. Ed.* **2000**, *39*, 3122.
- (6) Trost, B. M.; Li, L.; Guile, S. D. *J. Am. Chem. Soc.* **1992**, *114*, 8745.