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.1,2 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-C2-symmetric.3 Applications and uses of 1a and 1b are described.

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.4

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.3,5

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The Pd-catalysed desymmetrisation of meso diesters is a proven and highly versatile method for providing monosubstituted products of high ee.\textsuperscript{2,6}

\[
\begin{align*}
\text{R} & \quad \text{OR} \quad \text{OR} \\
n & \quad a \quad \text{a} \\
\text{H} & \quad \text{SO}_2\text{Ph} \\
\text{H} & \quad \text{O} \quad \text{O} \\
\end{align*}
\]

\[\text{R} = \text{PhCO-} \quad \text{Nu = } \text{E}_2\text{CH-} \quad \text{E = CO}_2\text{Me}\]

\[\text{93 \% ee} \quad \text{80 \% Yield}\]

\[
\begin{align*}
\text{Carbovir} & \\
\text{Aristeromycin} & \\
\end{align*}
\]

\[\text{a. Pd} \text{dba}_2\text{Cl}_2 \cdot \text{CHCl}_3, \text{1a, E}_2\text{CH}^\text{\textsuperscript{\textup{\textregistered}}}\text{Na, THF, rt}\]

\[\text{b. Pd} \text{dba}_2\text{Cl}_2 \cdot \text{CHCl}_3, \text{1a, lithium[(phenyl-sulfonyl)methylene]nitronate, THF, rt}\]

\[\text{95 \% ee} \quad \text{94 \% Yield}\]

References


