



Note

Palladium-catalyzed asymmetric allylic substitutions in the presence of chiral phosphine-imine type ligands

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ABSTRACT

Chiral bidentate phosphine-imine type ligand **L9** is fairly effective in the asymmetric allylic substitution of 1,3-diphenylpropenyl acetate with dimethyl malonate to give the corresponding adduct in moderate yield and good ee.

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1. Introduction

Homogeneous enantioselective catalysis with chiral transition metal complexes is an attractive synthetic methodology, where a small amount of chiral materials can produce a large amount of chiral products [1–3]. Chiral C₂-symmetric ligand 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (**BINAP**) **LA** [4–7] and C₁-symmetric ligand 2-(diphenylphosphino)-1,1'-binaphthyl (**MOP**) **LB** (X = OMe) [8–10] possessing the axially chiral 1,1'-binaphthalene framework have been widely utilized in asymmetric catalysis (Fig. 1). Significant efforts have been devoted to the design and synthesis of novel binaphthalene-templated ligands. Representative examples are the binaphthyl P,X-heterodonor ligands **LB** where X is a variety of heteroatoms (X = NMe₂, SMe, AsPh₂, P(O)Ph₂, P(S)Ph₂, PAr₂) [11–18], phosphane–phosphite ligand **BINAPHOS LC** [19–21], and phosphine–pyridine ligand **LD** [22], derived from 2-amino-2'-hydroxy-1,1'-binaphthyl (**NOBIN**). Most of these axially chiral ligands are effective in the palladium-catalyzed asymmetric allylic substitution of 1,3-diphenylpropenyl acetate with dimethyl malonate in the presence of a base, which has become a famous and fundamental asymmetric C–C bonding formation reaction [23]. On the other hand, recently, phosphine-imine type (salen-type) chiral

ligands have attracted much attention because they can coordinate with a variety of transition metal ions to afford the corresponding stable chiral metal complexes in good yields and these chiral metal complexes are in general quite efficient in many asymmetric reactions including asymmetric allylic alkylation [24].

These results have promoted us to explore new chiral phosphine-imine type ligands for asymmetric reactions since we envisioned that these chiral ligands can also coordinate with a variety of metal ions under mild conditions. In this paper we wish to report that the chiral phosphine-imine type ligand **L9** prepared from (R)-(–)-2-(diphenylphosphino)-1,1'-binaphthyl-2'-amine is fairly effective in the asymmetric allylic substitution of 1,3-diphenylpropenyl acetate with dimethyl malonate to give the corresponding adduct in moderate yield and good ee. In the mean time, its bidentate coordination pattern to the Pd metal center with both P and N atoms has been unambiguously established by X-ray diffraction.

2. Results and discussion

2.1. Synthesis of ligands **L1–L13**

Chiral phosphine-imine type ligands **L1–L13** were synthesized from the reaction of salicylaldehydes as well as its analogs with (R)-(–)-2-(diphenylphosphino)-1,1'-binaphthyl-2'-amine in absolute ethanol under reflux for 12 h, respectively (Scheme 1). After usual workup, these ligands can be obtained in good yields.

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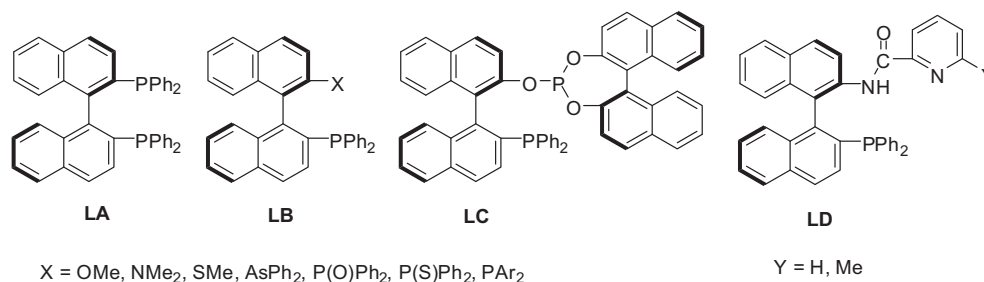
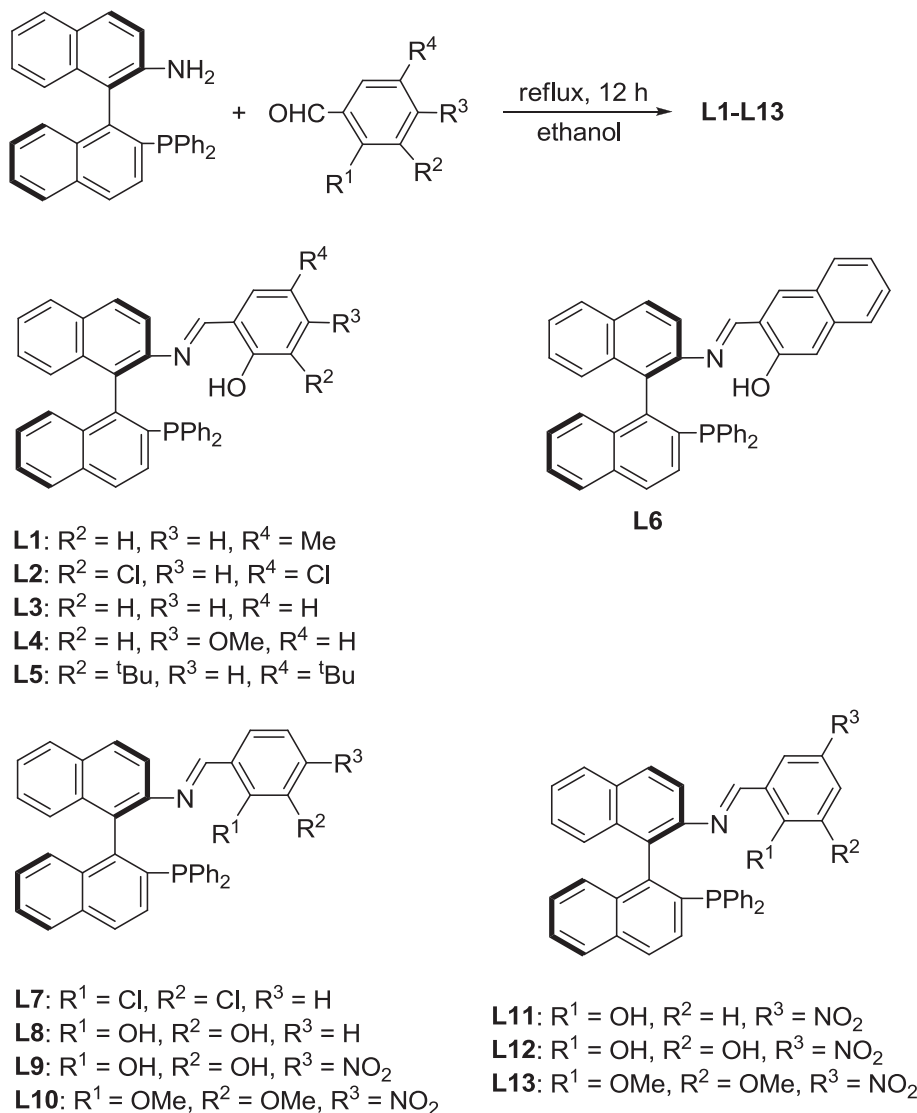


Fig. 1. The structure of C₂-symmetric BINAP and C₁-symmetric binaphthyl P,X-heterodonor ligands.

2.2. Catalytic asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate in the presence of chiral phosphine-imine type ligands

Initial examinations using 1,3-diphenylpropenyl acetate and dimethyl malonate as the substrates in the presence of chiral phosphine-imine type ligand **L1** and Pd(II) salt were aimed at determining the optimal conditions and the results of these experiments are summarized in Table 1. We found that using

bis(trimethylsilyl)acetamide (BSA) as an organic base, the corresponding product was obtained in moderate to good yields in a variety of solvents in the presence of **L1** (15 mol %) and palladium salt (5 mol %) at room temperature and up to 35% ee was achieved using tetrahydrofuran (THF) as a solvent (Table 1, entries 1–3). By screening chiral phosphine-imine type ligands **L1–L13** in THF and some salt additives, we found that **L9** was the best chiral phosphine-imine type ligand for this asymmetric allylic alkylation,



Scheme 1. Preparation of phosphine-imine type ligands **L1–L13**.

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