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# Synthesis and characterization of new chiral octadentate nitrogen ligands and related copper(II) complexes as catalysts for stereoselective oxidation of catechols

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**Abstract**

Three new octadentate ligands, namely (*R*)-*N*,*N*′-dimethyl-*N*,*N*′-bis{3-[bis(1-methyl-2-imidazolylmethyl )]aminopropyl}-1,1′-binaphthyl-2,2′-diamine, (*R*)-DABN-3Im$_4$, (*R*)-*N*,*N*′-dimethyl-*N*,*N*′-bis{4-[bis(1-methyl-2-benzimidazolylmethyl)]aminobutyl}-1,1′-binaphthyl-2,2′-dia-mine, (*R*)-DABN-4Bz$_4$, and (*S*)-*N*2,*N*6-dimethyl-*N*2,*N*6-bis{2′-[bis(1-methyl-2-benzimidazolylmethyl)]aminomethyl}benzyl-2,6-dia-mino-1-exanol acetate, L-Lys-4Bz$_4$, were employed for the synthesis of dinuclear and trinuclear copper(II) complexes. The ligands contain two side arms of different nature and length which carry tridentate aminobis(benzimidazole) or aminobis(imidazole) residues as metal binding sites (A sites) connected to a central (*R*)-1,1′-binaphthyl-2,2′-diamine or L-lysine residue which can bind a third metal ion (B site). The chiroptical properties of the ligands and the complexes have been described. The complexes were tested as catalysts in the oxidation of 3,5-di-*tert*-butylcatechol, L-, D-Dopa and L-, D-Dopa methyl esters by dioxygen to give the corresponding quinones. The catalytic efficiency is moderate, but the complexes exhibit significant enantio-differentiating ability towards L-, D-Dopa methyl esters, albeit their enantio-differentiating ability towards L-, D-Dopa is lower. The (*R*)-1,1′-binaphthyl-2,2′-diamine spacer in the (*R*)-DABN complexes has much stronger recognition power than the aliphatic L-lysine spacer in the L-Lys complexes. In addition, the highest stereoselectivity in the catalytic oxidation is obtained with the (*R*)-DABN-3Im$_4$ complexes, containing carbon chains of three atoms between the (*R*)-1,1′-binaphthyl-2,2′-diamine groups and the tridentate donor units at the A metal binding sites. In all cases, the preferred enantiomeric substrate has the L configuration, which is dictated by the chirality of the spacer residue.


*Keywords:* Copper complexes; Chiral complexes; Trinuclear complexes; Catechol oxidase; Stereoselective oxidations

## 1. Introduction

In biological systems, the oxidation of organic substrates with molecular oxygen is often carried out by multicopper enzymes, which serve as highly efficient oxidation catalysts [1–6]. These enzymes generally contain dinuclear or trinuclear copper clusters. In the first case, two three-coordinated copper centres with histidine ligands are present, as it was initially shown for hemocyanin, the dioxygen carrier protein in arthropods and molluscs [7]; the best known members of this family are tyrosinase, which catalyzes the hydroxylation of phenols (phenolase activity) and the oxidation of catechols to quinones (catecholase activity) [8,9], and catechol oxidase, which only catalyzes the oxidation of catechols to quinines [10–12]. These proteins are classified as Type 3 copper proteins because their dinuclear clusters are strongly antiferromagnetically coupled and therefore EPR silent in

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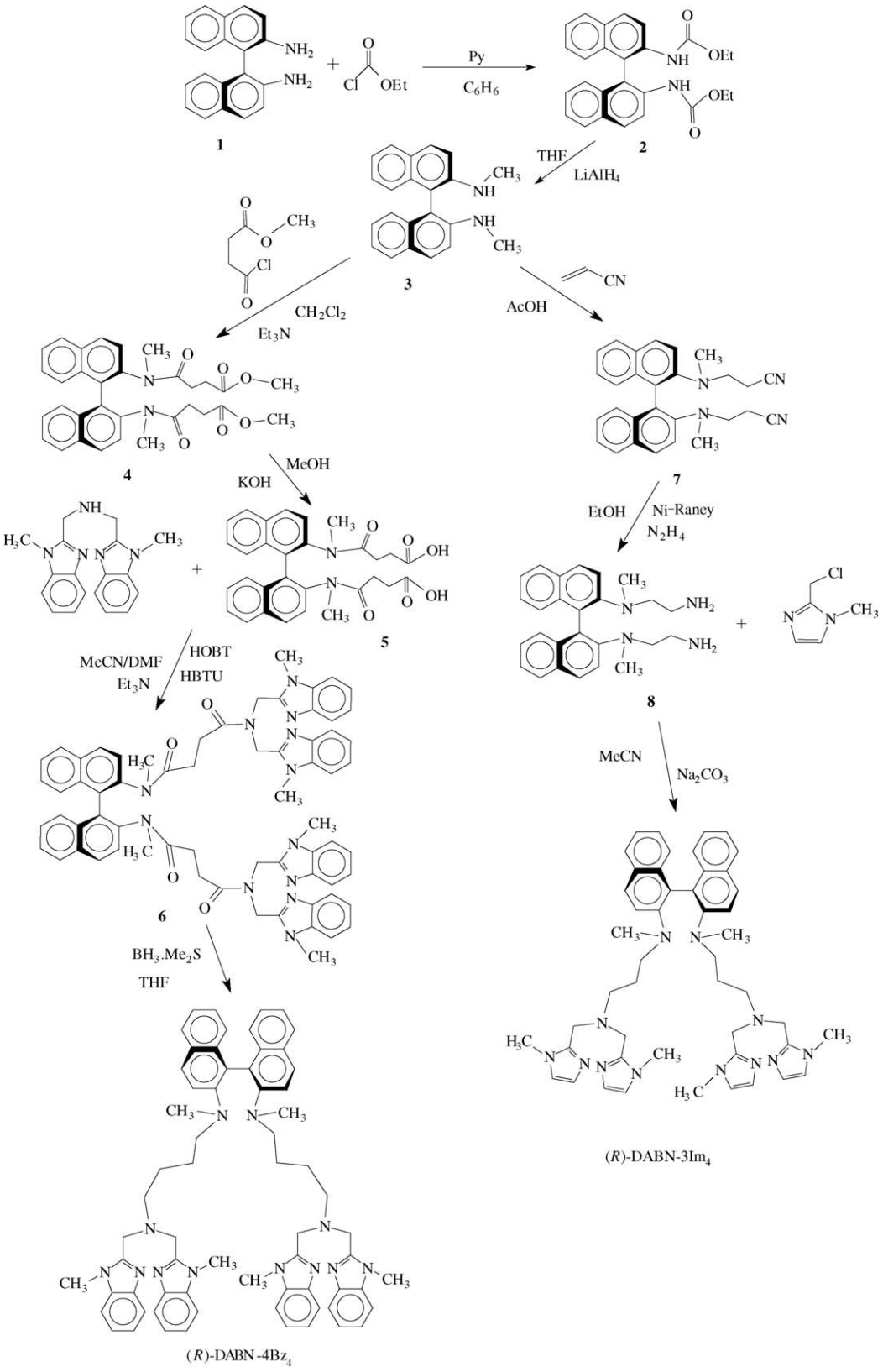


Fig. 1. Synthetic routes for the preparation of the ligands (*R*)-DABN-3Im$_4$ and (*R*)-DABN-4Bz$_4$.