

Asymmetric Synthesis of Chrysanthemic Acid Catalyzed by Chiral Copper(II) Complexes

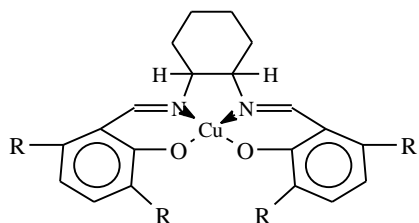
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Pyrethroids are useful as insecticides. However, among the several isomers of Pyrethroids, such as Allethrin, only one exhibits the highest insecticide activity, the other is not as effective, or even ineffective at all. Asymmetric synthesis of chrysanthemic acid, an important intermediate of Pyrethroids, is a method of great advantage in producing such compounds because a small quantity of catalyst can provide a large amount of single enantiomer product.

In this paper, five chiral copper(II) complexes derived from (R,R)- and (S,S)-1,2-diamino cyclohexane (**Scheme 1**), (R)-1-(p-nitrophenyl)-2-amino-propylene-1,3-glycol (**Scheme 2**) were synthesized. C-III and C-V were studied further because they exhibit higher stereoselectivity in cyclopropanation of 2,5-dimethyl-2,4-hexadiene(DMHDE) with methyl diazoacetate in preliminary experiments. The results of cyclopropanation of DMHDE with different diazotate catalyzed by C-III, C-V are listed in **Table 1**.

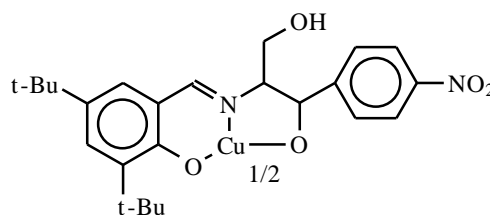


C-I: R=H, (R,R),
(S,S)

C-II: R=H,

C-III: R=t-Bu, (R,R), C-IV: R=t-Bu, (S,S)

Scheme 1



Scheme 2 C-V

Table 1. Enantioselective cyclopropanation catalyzed by C-III, C-V.

Cat.	R*	Yield(%)	Cis(%)	L-Trans(%)	D-Trans(%)	Trans(% e.e)	Cis/Trans
C-III	Me	68.9	38.3	25.5	36.2	17.3	38.3/61.7
C-III	Et	67.4	33.8	24.4	41.8	26.3	33.8/66.2
C-III	<i>n</i> -Pr	62.0	30.9	25.6	43.5	25.9	30.9/69.1
C-III	<i>n</i> -Bu	63.1	27.2	18.6	54.2	48.9	27.2/72.8
C-III	L-Men	49.2	13.9	6.7	78.0	84.2	14.1/85.9
C-V	Me	73.1	29.1	25.8	43.6	25.6	29.5/70.5
C-V	Et	76.2	31.2	25.0	43.8	27.4	31.2/68.8
C-V	L-Men	51.0	20.5	5.7	73.8	85.5	20.5/79.5

*Me=Methyl, Et=Ethyl, *n*-Pr= *n*-Propyl *n*-Bu= *n*-Butyl L-Men=L-Menthyl

The enantioselectivity can be tuned by steric and electronic factors. As shown in table, when the R of ligand is *t*-butyl and R of N₂CHCOOR is the bulky menthyl, the e.e value of R-trans isomer reaches 84.2% and 85.5%, the ratio of trans/cis is 85.9/14.1 and 79.5/20.5 using C-III and C-V respectively. The ligands can be easily synthesized and their raw material are cheap, so it is hopeful to be industrialized.