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SYNTHESIS OF CHIRAL DEPSIPEPTIDE BUILDING BLOCK VIA ASYMMETRIC HYDROSILYLATION

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SYNTHESIS OF CHIRAL DEPSIPEPTIDE BUILDING BLOCK VIA ASYMMETRIC HYDROSILYLATION

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ABSTRACT

Asymmetric hydrosilylation of N-(α -ketoacyl)- α -amino esters was performed, catalyzed by rhodium(I) complex of chiral 2-(2-pyridyl)-4-carbomethoxy-1,3-thiazolidine or Rh(PPh₃)₃Cl. The N-(α -hydroxyacyl)- α -amino esters were synthesized in high stereoselectivity.

Recently, asymmetric hydrosilylation of ketones, olefins and imines has received very much attention.¹ We have also reported some results in this field.² But, application of asymmetric hydrosilylation of functional ketones on enantioselective synthesis has received very little attention.

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We now report preliminary results of the asymmetric hydrosilylation of one kind of functional ketones, N-(α -ketoacyl)- α -amino esters, which affords the chiral depsipeptides building block, N-(α -hydroxyacyl)- α amino esters.

The *N*-(α -ketoacyl)- α -amino esters (1) were readily prepared in high yields by the reaction of α -ketoacyl chloride with hydrogen chloride salts of α -amino acid methyl esters in the presence of *N*-methylmorphorine³ (Equation 1).

$$R_{1}COCOCI + CIH H_{2}NCH(R_{2})COOMe \longrightarrow R_{1}COCONHCH(R_{2})COOMe$$
(1)

The asymmetric hyrosilylation of N-(α -ketoacyl)- α -amino esters (1) followed by methanolysis were carried out by using diphenylsilane as reducing agent and rhodium(I) complexes as catalysts (Equation 2). The ligands

$$1 + Ph_2SiH_2 \xrightarrow{ICatl^*} HOC^*H(R_1)CONHC^*H(R_2)COOMe$$
(2)

using in the reaction were achiral ligand, PPh₃, or chiral ligand 2-(2-pyridyl)-4-carbomethoxy-1,3-thiazolidine (A).⁴ The procedure was as follows:



Reaction was run with 5 mmol of 1.6 mmol of Ph_2SiH_2 , 0.025 mmol of Rh(I) catalyst at room temperature for 48 h. Methanolysis was carried out by using 10 ml of methanol containing 0.1 g of *p*-toluenesulphonic acid (TsOH) at 40°C for 1 h. After the solvent was removed, the residue was submitted to short column chromatography on silica gel to give product 2. Thus, the conversion was calculated. Since determination of the optical purities of the products 2 by ¹HNMR using shift reagent resulted in unsatisfactory separation of key signals, all products 2 were transformed

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CHIRAL DEPSIPEPTIDE BUILDING BLOCK

to the corresponding trifluoroacetates 3 by reacting with trifluoroacetic anhydride in the presence of *N*-methyl morpholine (Equation 3). The trifluoroacetates 3 were submitted to ¹⁹F NMR analysis using Eu(fod)₃ as shift reagent, and the optical purities were successfully determined. Results are shown in table.

As shown in table, asymmetric induction by the Rh(I)-chiral ligand A predominates over that by the chiral center involved in the substrate 1. Achiral catalyst $Rh(PPh_3)_3Cl$ has also relatively large asymmetric induction caused by the chiral center in the substrate 1. The predominate configura-

$$2 + (CF_3CO)_2O \longrightarrow CF_3COOC^*H(R_1)CONHC^*H(R_2)COOMe$$

$$3$$
(3)

2	Catalyst	Conversion (%)	(R,S)/(S,S)	% D.E. ^c
HOCH(Me)CO-	Rh(I)-A ^a	84	87/13	74
Phe-OMe	Rh(PPh ₃) ₃ Cl	65	35/65	30
HOCH(Me)CO-	Rh(I)-A ^a	81	89/11	78
Ala-OMe	Rh(PPh ₃) ₃ Cl	52	48/52	4
HOCH(Me)CO-	Rh(I)-A ^a	79	90/10	80
Val-OMe	Rh(PPh ₃) ₃ Cl	73	29/71	42
HOCH(Me)CO-	Rh(I)-A ^a	79	89/11	78
Leu-OMe	Rh(PPh ₃) ₃ Cl	64	34/66	32
HOCH(Me)CO-	Rh(I)-A ^a	80	88/12	76
Gly-OMe ^b	Rh(PPh ₃) ₃ Cl	66	50/50	0
HOCH(Ph)CO-	Rh(I)-A ^a	86	90/10	80
Phe-OMe	Rh(PPh ₃) ₃ Cl	63	23/77	54
HOCH(Ph)CO-	Rh(I)-A ^a	84	92/8	84
Ala-OMe	Rh(PPh ₃) ₃ Cl	60	44/56	12
HOCH(Ph)CO-	Rh(I)-A ^a	81	93/7	86
Val-OMe	Rh(PPh ₃) ₃ Cl	73	28/72	44
HOCH(Ph)CO-	Rh(I)-A ^a	80	91/9	82
Leu-OMe	Rh(PPh ₃) ₃ Cl	67	28/72	44
HOCH(Ph)CO-	Rh(I)-A ^a	80	89/11	78
Gly-OMe ^b	Rh(PPh ₃) ₃ Cl	65	50/50	0

Table. Asymmetric Hydrosilylation Results of 1

^aRh(I)-A was prepared with 0.0125 mmol of [Rh(COD)Cl₂]₂ and 0.125 mmol of chiral ligand A in situ. ^bThe isomer ratio was R/S, since the Glyine is an achiral amino acid. ^cDiastereomeric excess.

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tions of the product 2 were (R,S) when using Rh(I)-ligand A as catalyst, while they are (S,S) when using achiral catalyst $Rh(PPh_3)_3Cl$.

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