

PII: S0957-4166(97)00452-7

# An efficient asymmetric synthesis of nitroolefinic lactones with chiral nitroenamines possessing bulky chiral leaving groups

Xiaowu Yang and Rui Wang \*

Department of Biology, State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P. R. China

Abstract: An efficient asymmetric nitroolefination of enolates 4a-c, 5 afforded multifunctional group nitroolefinic lactones 7a-e and 8a,b containing stereogenic quaternary carbon centers using bulky chiral nitroenamines 1a,b-3a,b as chiral auxiliaries. Studies on the effect of the bulkiness of leaving group showed that bulky nitroenamines 1a,b gave higher ees and yields than those of the less bulky 2a,b-3a,b. A possible cyclic transition model is proposed to elucidate the S selectivity. © 1997 Elsevier Science Ltd

## Introduction

The efficient synthesis of enantiomerically pure multifunctional molecules containing stereogenic quaternary carbon centers has long fascinated organic chemists due to their considerable utilities as chiral blocks for many biologically active natural products such as terpenes, steroids, and alkaloids.<sup>1</sup> A number of reactions,<sup>2</sup> for example, asymmetric Heck reactions, asymmetric Michael reactions, asymmetric alkylations, and Diels-Alder cyclozations, have been employed for the asymmetric synthesis of quaternary carbon centers since the pioneering work of Yamada and his coworkers.<sup>3</sup> Among the methods reported so far.<sup>4</sup> the synthesis of nitroolefinic lactones containing stereogenic quaternary carbon centers in enantiomerically pure form through an asymmetric nitroolefination reaction was attractive because these compounds are multifunctional molecules, readily transformed into other functional groups, and versatile intermediates as chiral building blocks for the synthesis of natural products.<sup>5</sup> Using them as chiral starting materials, the asymmetric synthesis of 5-methyl-8hydroxybicyclo[3,3,0]-2-octanone, a key intermediate of marine sesquiterpene-(-)- $\Delta^{9(12)}$ -capnellene, Aspidosperma and Hunteria types indole alkaloids, (-)-physostigmine, and diterpenoids have been accomplished.<sup>6</sup> In this asymmetric nitroolefination reaction, (S)-2-methoxymethyl- pyrrolidine (SMP) was used as the chiral auxiliary and leaving group. However, a drawback of this asymmetric reaction was that enantioselectivities as well as the yields with some substrates such as  $\alpha$ -substituted ketones and y-lactones were low.<sup>5a,b</sup> Recently, the Node group improved the asymmetric nitroolefination with modified nitroenamines.<sup>7</sup> Here, we wish to report some new progress for this reaction. On the basis of the strategy that increasing the bulkiness of the auxiliary can increase enantioselectivities,<sup>8</sup> and in order to study the effects of the  $R_1$  group in the chiral auxiliary on the reaction, we synthesized bulky chiral nitroenamines 1a,<sup>9</sup> 1b-3a,b. Under their induction, the asymmetric nitroolefination of zinc enolates 4a-c, 5 of  $\alpha$ -substituted-y-lactones,  $\alpha$ -methyl- $\delta$ -lactone gave a series of multifunctional nitroolefinic lactones 7a-e, 8a,b possessing a stereogenic quaternary carbon in high enantioselectivity as well as the yield through an addition-elimination process (Scheme 1).<sup>10</sup> The effects of the bulkiness of the  $R_1$  group,  $\alpha$ -substituent on the enolates, the equivalent number of enolates, and the solvent on the asymmetric nitroolefination reactions were studied.

<sup>\*</sup> Corresponding author. Email: wangrui@lzu.edu.cn



Scheme 1.

#### **Results and discussion**

2-(Methoxydisubstituted)methylpyrrolidines **9a-c** were prepared in a five-step sequence, esterification of carbonyl group, N-protection, Grignard reaction, methylation of hydroxy group, and deprotection, starting from L-proline.<sup>11</sup> Amine exchange reaction of **9a-c** with morpholino enamines **10a**,b<sup>6a</sup> in an anhydrous methanol solution afforded the desired chiral nitroenamines **1a**,b-**3a**,b (Scheme 2). All the new nitroenamines were crystalline, therefore, they were obtained in enantiomerically pure form by recrystallization. The *E* configuration of the double bond was determined mainly by NMR data including the chemical shift and the coupling constant.<sup>12</sup>





At first DL-morpholino enamines 10a,b were used to explore the reaction conditions. The reaction of 10a,b with zinc enolates 4a-c, 5 gave racemic nitroolefinic lactones 7a-e and 8a,b. On the basis of the conditions, chiral nitroenamines 1a,b-3a,b reacted quickly with 4 equivalents of zinc enolates in tetrahydrofuran (THF) or dimethoxyethane (DME) at  $-78^{\circ}$ C to give chiral 7a-e and 8a,b in high enantioselectivity and yield.

The results of the asymmetric nitroolefination are compiled in Table 1. Enantisoelectivities with nitroenamines **1a,b-3a,b** having bulky group ( $R_1$ =Ph, Et, Me) were remarkably improved, compared with the previous results using SMP ( $R_1$ =H) as a chiral auxiliary.<sup>5a</sup> Both the ees and the yields increased when the bulkiness of the  $R_1$  group was increased (run 1-8-10; 3-9-11; 13-16-18; 15-17-19). The enantioselectivity depended on the bulkiness of  $R_1$  in the chiral nitroenamines, namely, the order was Ph>Et>Me>H, which indicated that increase in the bulkiness of the chiral auxiliary increased the enantioselectivity of the reaction. The bulkiness of  $\alpha$ -substituent ( $R_3$ ) in the enolate too had a little effect on the reaction (run 1-5-7; 3-6): the ee value decreased 20% and the yields decreased ~12% when the bulkiness of  $R_3$  was increased. After many experiments, we found that three equivalents

run	enolate		nitroenamine		solv.	time	prod.	yield <sup>b</sup>	ee <sup>C</sup>	[α] <sub>D</sub> 18
	n	R₃	Rı	R2		(min)		(%)	(%)	(CHCI3)d
1	1	Me	Ph	н	THF	10	7a	98	95	- 35.6
2 <sup>e</sup>	1	Me	Ph	н	THF	20	7a	89	86	- 34.3
3	1	Me	Ph	Ме	THF	10	7b	96	>99	- 55.6
4 <sup>e</sup>	1	Me	Ph	Me	THF	30	7b	89	88	- 54.7
5	1	Et	Ph	н	THF	10	-7c	93	78	- 31.8
6	1	Et	Ph	Me	THF	10	7d	88	86	- 29.9
7	1	allyl	Ph	н	THF	10	7e	86	75	- 34.8
8	1	Me	Et	н	THF	5	7a	94	92	- 35.0
9	1	Me	Et	Me	THF	5	7b	94	97	- 56.1
10	1	Me	Me	н	THF	5	7a	90	89	- 35.2
11	1	Ме	Me	Me	THF	5	7b	87	94	- 55.5
12	2	Me	Ph	н	DME	15	8a	86	96	- 11.6
13	2	Me	Ph	н	THF	30	8a	95	93	- 10.9
14	2	Ме	Ph	Ме	DME	15	8b	82	94	- 49.0
15	2	Ме	Ph	Me	THF	15	8b	93	>99	- 47.4
16	2	Ме	Et	н	THF	10	8a	89	87	- 9.7
17	2	Ме	Et	Ме	THF	10	8b	91	92	- 48.8
18	2	Me	Me	н	THF	5	8a	84	81	- 8.3
19	2	Me	Me	Me	THF	5	8b	86	87	- 48.2
20	3	Me	no reaction under the above conditions							

Table 1. Asymmetric nitroolefination of  $\alpha$ -substituted lactone enolates<sup>a</sup>

a) 4 equivalents of zinc enclate were used; b) isolated yield; c) determined by 400M Hz <sup>1</sup>HNMR with Eu(hfc)3 as chiral shift reagent; d) absolute configuration was S; e) 3 equivalents of zinc enclate were used.

of zinc enolate were essential for completing the reaction and four equivalents of zinc enolate were necessary to obtain high enantioselectivity as well as high yield. Both the ee and the yield rose and the reaction time shortened when the equivalent number of zinc enolates was increased (run 1–4). Studies on the effect of solvent on the reaction showed that the reaction yields using THF as a solvent were higher than those using DME as a solvent (run 12–15). The reaction of  $\alpha$ -methyl- $\epsilon$ -lactone enolate **6** with **1a,b–3a,b** didn't give the desired products under different conditions (run 20). It was presumed that the zinc enolate **6** was unstable at  $-78^{\circ}$ C.

The S configuration of stereogenic quaternary carbon of 7a–e, 8a,b was determined by circular dichroism (CD) spectra.<sup>7</sup> The stereochemistry of the double bond was determined by chemical shift and the coupling constant: the chemical shift of olefinic hydrogen in the nitroolefinic lactones was deshielded 1.67 ppm when the double bond was the *E* configuration, and deshielded 0.46 ppm when the double bond was the *Z* configuration, compared with those of the normal olefinic hydrogen. On the basis of the value ( $\delta 5.25$  ppm) of the normal olefinic hydrogen, the chemical shift of the *E* double bond of nitroolefinic lactones should be 6.92 ppm and that of the *Z* double bond should be 5.71 ppm.<sup>13</sup> The chemical shift of the above products 7b, 7d, and 8b (R<sub>2</sub>=Me) was  $\delta_{7.0 \text{ ppm}}$ , proving the *E* 

configuration of the double bond. The coupling constant of **7a**, **7c**, **7e**, and **8a** ( $R_2$ =H) was 13.5–13.8 Hz, which proved that the stereochemistry of the double bond was the *E* type also.

From the above results, we concluded: (1) the enantioselectivities of the asymmetric nitroolefination reaction with nitroenamines 1a,b-3a,b were much higher than those with the previous nitroenamines.<sup>5a</sup> and increased when the bulkiness of the chiral auxiliary was increased. The best results were obtained using chiral nitroenamines 1a,b having a bulkier Ph group, and the steric effect of chiral induced reagents was very important; (2) three equivalents of zinc enolate were essential for completing the asymmetric nitroolefination reaction. A possible cyclic transition model is shown in Scheme 3. Two equivalents of zinc enolate were consumed to form complex A by the coordination with nitroenamine. Zinc enolate can attack A from the topside or the underside. When it attacks A from the topside, two equivalents of zinc enolate seem to be enough to complete the reaction. However, the steric effect of the  $R_1$  group inhibits the approach from the topside.<sup>14</sup> When it attacks A from the underside, another zinc enolate has to be consumed. Although it is necessary to consume three equivalents of enolate. the approach of the enolate to A was easy.<sup>15</sup> In addition, it is clear that transition state C was more stable than transition state **B**, because the zinc chelation involving 5,6-ring system is too strained to form a new carbon-carbon bond.<sup>7</sup> So, zinc enolate attacked mainly from the underside, leading to the S isomer, which explains the very high enantio-selectivities of the reaction and why it is necessary to consume three equivalents of zinc enolate.



Scheme 3.

#### **Experimental**

All reactions were carried out under an argon atmosphere with dry, freshly distilled solvent under anhydrous condition unless otherwise stated. THF, DME, and ether were distilled from sodiumbenzophenone and diisopropylamine was distilled from calcium hydride under argon atmosphere before use. n-Butyllithium (1.55 M in n-hexane) and ZnCl<sub>2</sub> solution (0.85 M in Et<sub>2</sub>O) were prepared in the normal way.<sup>6a</sup> Melting points were uncorrected, and recorded on X-4 melting point apparatus; <sup>1</sup>H NMR spectra were recorded on Bruker AM80, AM400 MHz instruments in CDCl<sub>3</sub> with TMS as an internal standard; IR spectra were recorded on a Nicolet 170SX spectrometer; mass spectra were recorded on VG-ZAB mass spectrometer; optical rotations were taken on a WZZ automatic polarimeter.

## General procedure for nitroenamines 1a,b-3a,b

To a solution of morpholino nitroenamine 10 (14 mmol) in 40 ml methanol was added dropwise a 7 ml methanol solution of pyrrolidine 9 (7 mmol). The mixture was stirred at room temperature for 5 h. After filtration the residue was washed with methanol ( $10 \text{ ml} \times 5$ ). The filtrate was combined and evaporated to give a red solid, which was purified by flash column chromatography (ethyl acetate:petroleum ether) to give a yellow solid. The resulting solid was recrystallized to give the optically pure nitroenamines.

## (E)-1-[(S)-2-(Methoxydiphenyl)methylpyrrolidino]-2-nitroethene 1a

Pale yellow crystals, yield 71.3%; m.p. 185°C (EtOH);  $[\alpha]_D^{25}$  -473 (c 0.19, CHCl<sub>3</sub>): <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.41-1.72 (m, 2H, CH<sub>2</sub>), 1.81-2.50 (m, 3H, CH<sub>2</sub>, CHN), 2.82 (m, 1H, CHN), 2.97 (s, 3H, CH<sub>3</sub>), 4.86 (m, 1H, CHN), 6.59, 8.67 (ABq, 2H, J=10.8 Hz), 7.36-7.42 (m, 10H, Ar); IR (KBr)  $\gamma$ : 1610 (C=N<sup>+</sup>), 1470, 1312, 1255, 766, 703 cm<sup>-1</sup>; MS m/z: 338 (M<sup>+</sup>).

#### (E)-1-[(S)-2-(Methoxydiphenyl)methylpyrrolidino]-2-nitropropene 1b

Pale yellow crystals, yield 80.2%; m.p. 181°C (EtOH);  $[\alpha]_D^{25}$  -75 (c 0.18, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.41-2.10 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>), 2.81 (s, 3H, CH<sub>3</sub>), 2.40 (m, 1H, CH<sub>2</sub>N), 2.92 (s, 3H, CH<sub>3</sub>), 3.21 (m, 1H, CH<sub>2</sub>N), 4.76 (m, 1H, CHN), 7.38-7.42 (m, 10H, Ar), 8.63 (s, 1H); IR (KBr)  $\gamma$ : 1620 (C=N<sup>+</sup>), 1440, 1261, 768, 703 cm<sup>-1</sup>; MS m/z: 352 (M<sup>+</sup>).

## (E)-1-[(S)-2-(Methoxydiethyl)methylpyrrolidino]-2-nitroethene 2a

Colourless crystals, yield 78%; m.p. 73°C (Et<sub>2</sub>O);  $[\alpha]_D^{25}$  -68.7 (c 0.36, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 0.7–1.1 (m, 6H, CH<sub>3</sub>×2), 1.2–2.1 (m, 8H, CH<sub>2</sub>×2, CH<sub>2</sub>CH<sub>2</sub>), 3.0–3.2 (m, 5H, CH<sub>3</sub>O, CH<sub>2</sub>N), 3.86 (m, 1H, CHN), 6.61, 8.71 (ABq, 2H, J=10.8 Hz); IR (KBr)  $\gamma$ : 2999, 1608 (C=N<sup>+</sup>), 1305, 1240 cm<sup>-1</sup>; MS m/z: 242 (M<sup>+</sup>).

#### (E)-1-[(S)-2-(Methoxydiethyl)methylpyrrolidino]-2-nitropropene 2b

Pale yellow crystals, yield 81%; m.p. 118°C (n-hexane);  $[\alpha]_D^{18}$  +354 (c 0.34, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 0.78–0.97 (m, 6H, CH<sub>3</sub>×2), 1.41–2.01 (m, 8H, CH<sub>2</sub>×2, CH<sub>2</sub>CH<sub>2</sub>), 2.27 (s, 3H, CH<sub>3</sub>), 3.21 (s, 3H, CH<sub>3</sub>O), 3.47–3.80 (m, 3H, CH<sub>2</sub>N, CHN), 8.58 (s, 1H); IR (KBr)  $\gamma$ : 2949, 1618 (C=N<sup>+</sup>), 1388, 1234 cm<sup>-1</sup>; MS m/z 256 (M<sup>+</sup>).

#### (E)-1-[(S)-2-(Methoxydimethyl)methylpyrrolidino]-2-nitroethene 3a

Pale yellow crystals, yield 83.2%; m.p. 81°C (n-hexane);  $[\alpha]_D^{17}$  -47.6 (c 0.56, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.06, 1.16 (ds, 6H, CH<sub>3</sub>×2), 1.76–2.2 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>), 3.14–3.3 (m, 5H, CH<sub>3</sub>O, CH<sub>2</sub>N), 3.5–3.7 (m, 1H, CHN), 6.68, 8.66 (ABq, 2H, J=10.8 Hz); IR (KBr)  $\gamma$ : 2929, 1607 (C=N<sup>+</sup>), 1468, 1304, 1236 cm<sup>-1</sup>; MS m/z 214 (M<sup>+</sup>).

## (E)-1-[(S)-2-(Methoxydimethyl)methylpyrrolidino]-2-nitropropene 3b

Yellow crystals, yield 87.1%; m.p. 86–87°C (n-hexane);  $[\alpha]_D^{17}$  +539.8 (c 0.25, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.04, 1.11 (ds, 6H, CH<sub>3</sub>×2), 1.6–2.1 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>), 2.26 (s, 3H, CH<sub>3</sub>), 3.19 (m, 3H, CH<sub>3</sub>O), 3.48–3.7 (m, 3H, CHN, CH<sub>2</sub>N), 8.5 (s, 1H); IR (KBr)  $\gamma$ : 2947, 1614 (C=N<sup>+</sup>), 1385, 1246 cm<sup>-1</sup>; MS m/z: 228 (M<sup>+</sup>).

#### General procedure for asymmetric nitroolefination

Lithium diisopropylamine (LDA) was prepared by adding 1.3 ml n-BuLi in hexane (1.55 M, 2 mmol) to a solution of diisopropylamine (0.29 ml, 2.1 mmol) in dry THF or DME (2.5 ml) at  $-78^{\circ}$ C followed by stirring for 10 min at 0°C. A solution of  $\alpha$ -substituted lactone (2 mmol) in THF or DME (4 ml) was added dropwise to the resulting LDA solution at  $-78^{\circ}$ C by syringe. After being stirred for 1 h at  $-78^{\circ}$ C, an equimolar amount of ZnCl<sub>2</sub> (0.85 M in Et<sub>2</sub>O) was added to the above lithium enolate. To the resulting zinc enolate was added a solution of chiral nitroenamine (0.5 mmol) in 0.4 ml THF (DME) at  $-78^{\circ}$ C. The reaction mixture was performed under the conditions shown in Table 1. After no change was detected by TLC, the reaction mixture was transferred into a solution of 0.5 N HCl-ice by a tube, extracted with Et<sub>2</sub>O (15 ml×4), washed with saturated brine, and dried over MgSO<sub>4</sub>. The resulting residue was purified by column chromatography (silica gel, AcOEt-petroleum ether) to give the desired nitroolefins, which were identified by <sup>1</sup>H NMR, MS, and IR.

#### 2-Methyl-2-[(E)-2-nitroethenyl]-4-butanolide 7a

Pale yellow oil, <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.52 (s, 3H, CH<sub>3</sub>), 2.35 (m, 1H, CH<sub>2</sub>), 2.52 (m, 1H, CH<sub>2</sub>), 4.45 (m, 2H, CH<sub>2</sub>O), 7.16, 7.32 (ABq, 2H, J=13.9 Hz); IR (CHCl<sub>3</sub>)  $\gamma$ : 771, 531, 352, 1177 cm<sup>-1</sup>; MS m/z: 172 (M<sup>+</sup>+1).

#### 2-Methyl-2-[(E)-2-nitroprop-1-enyl]-4-butanolide 7b

Pale yellow crystals, m.p. 41°C (n-hexane); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.53 (s, 3H, CH<sub>3</sub>), 2.26 (s, 3H, CH<sub>3</sub>), 2.47 (m, 2H, CH<sub>2</sub>), 4.40 (m, 2H, CH<sub>2</sub>O), 7.36 (s, 1H); IR (CHCl<sub>3</sub>)  $\gamma$ : 1769, 1521, 1331, 1191 cm<sup>-1</sup>; MS m/z: 186 (M<sup>+</sup>+1).

### 2-Ethyl-2-[(E)-2-nitroethenyl]-4-butanolide 7c

Pale yellow oil, <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.0 (t, 3H, CH<sub>3</sub>, J=7.6 Hz), 1.70–1.84 (m, 2H, CH<sub>2</sub>), 2.3–2.4 (m, 2H, CH<sub>2</sub>), 4.26 (dd, 2H, CH<sub>2</sub>O, J=7.6 Hz), 7.15, 7.32 (ABq, 2H, J=13.8 Hz); IR (CHCl<sub>3</sub>)  $\gamma$ : 1770, 1529, 1352, 1181 cm<sup>-1</sup>; MS m/z: 186 (M<sup>+</sup>+1).

### 2-Ethyl-2-[(E)-2-nitroprop-1-enyl]-4-butanolide 7d

Pale yellow oil, <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.04 (t, 3H, CH<sub>3</sub>, J=7.6 Hz), 1.70–1.84 (m, 2H, CH<sub>2</sub>), 2.26 (s, 3H, CH<sub>3</sub>), 2.33–2.51 (m, 2H, CH<sub>2</sub>), 4.26 (dd, 2H, CH<sub>2</sub>O, J=7.6 Hz), 7.33 (s, 1H); IR (CHCl<sub>3</sub>)  $\gamma$ : 1771, 1528, 1333, 1192 cm<sup>-1</sup>; MS m/z: 200 (M<sup>+</sup>+1).

### 2-Allyl-2-[(E)-2-nitroethenyl]-4-butanolide 7e

Pale yellow oil, <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.37 (m, 1H, CH<sub>2</sub>), 2.51 (m, 1H, CH<sub>2</sub>), 2.56 (d, 2H, CH<sub>2</sub>, J=7.4 Hz), 4.40 (m, 2H, CH<sub>2</sub>O), 5.30 (dd, 2H, CH=CH<sub>2</sub>, J=10.3, 10.9 Hz), 5.76 (m, 1H, CH=CH<sub>2</sub>), 7.12, 7.27 (ABq, 2H, J=13.5 Hz); IR (CHCl<sub>3</sub>)  $\gamma$ : 1771, 1532, 1352, 1177 cm<sup>-1</sup>; MS m/z: 198 (M<sup>+</sup>+1).

#### 2-Methyl-2-[(E)-2-nitroethenyl]-5-pentanolide 8a

Pale yellow oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.54 (s, 3H, CH<sub>3</sub>), 1.92–2.12 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>), 4.39–4.45 (m, 2H, CH<sub>2</sub>O), 7.08, 7.34 (ABq, 2H, J=13.5 Hz); IR (CHCl<sub>3</sub>)  $\gamma$ : 1723, 1525, 1346, 1265 cm<sup>-1</sup>; MS m/z: 186=(M<sup>+</sup>+1).

## 2-Methyl-2-[(E)-2-nitroprop-1-enyl]-5-pentanolide 8b

Colorless needles, m.p. 60°C (n-hexane); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.56 (s, 3H, CH<sub>3</sub>), 1.9–2.15 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>), 2.24 (s, 3H, CH<sub>3</sub>), 4.42 (m, 2H, CH<sub>2</sub>O), 7.19 (s, 1H); IR (CHCl<sub>3</sub>)  $\gamma$ : 1730, 1524, 1330, 1153 cm<sup>-1</sup>; MS m/z: 200 (M<sup>+</sup>+1).

#### Acknowledgements

We thank the National Natural Science Foundation of China, Fok Ying Tung (Hong Kong) Education Foundation, and the State Education Commission of China for financial supports. R. Wang wishes to express his thanks to Prof. K. Fuji and Prof. M. Node, who introduced him to the studies of asymmetric reactions.

### References

- (a) Martin, S. F. Tetrahedron 1980, 36, 419. (b) Pfan, M.; Revial, G.; Guingant, A. and d'Angelo, J. J. Am. Chem. Soc. 1985, 107, 2734. (c) Isaka, M.; Nakamura, E. J. Am. Chem. Soc. 1990, 112, 7428. (d) Ramachandran, P. V.; Chen, G. M.; Brown, H. C. J. Org. Chem. 1996, 61, 88. (e) Tetrahedron: Asymmetry 1993, 4, 1006.
- (a) Meyer, A. I.; Fleming, S. A. J. Am. Chem. Soc. 1986,108, 306; (b) Tomioka, K.; Yasuds.; Koga, K. Tetrahedtron Lett. 1986, 27, 715; (c) Kagechika, K.; Ohshima, T.; Shibasaki, M. Tetrahedron 1993, 43, 1773. (d) Desmaele, D.; d'Angelo, J. Tetrahedron: Asymmetry 1994, 5, 1645; (e) Hiroi, K.; Anzai, T.; Ogata, T.; Sailo, M. Tetrahedron Lett. 1996, 37, 239.
- (a) Yamada, S.; Hiroi, K.; Achiwa, K. Tetrahedron Lett. 1969, 10, 4223. (b) Yamada, S.; Otani, G. *ibid*, 4237. (c) Sone, T.; Terashima, S.; Yamada, S. Chem. Pharm. Bull. 1976, 24, 1293.
- 4. (a) Wang, R.; Yang, X. W. Chemistry (Chin. Chem. Soc., Taipei) 1996, 54, 169. (b) Fuji, K. Chem. Rev. 1993, 93, 2037. (c) Tomioka, K.; Koga, K. J. Syn. Org. Chem. Jpn. 1986, 44, 545, and references cited therein.
- (a) Fuji, K.; Node, M.; Nagasawa, H.; Naniwa, Y.; Taga, T.; Machida, K.; Snatzke, G. J. Am. Chem. Soc. 1989, 111, 7921. (b) Fuji, K.; Node, M. Synlett, 1991, 603 (c) Corey, E. J.; Estreicher, H. J. Am. Chem. Soc. 1978, 100,6294. (d) Seebach, D.; Beck, A. K.; Golinski, Hay, T. N.; Laube, T. Helv. Chim. Acta. 1985, 68, 162. (e) Kraus, G. A.; Thurston, J.; Thomas, P. J.; Jacobson, R. A.; Su. Y. Tetrahedron Lett. 1988, 29, 1879.
- (a) Wang, R.; Fuji, K.; Node, M. Science in China (Series B), 1992, 22, 021. (b) Node, M.; Nagasawa, H.; Fuji, K. J. Org. Chem. 1990, 55, 517. (c) Node, M.; Hao, X. J.; Fuji, K. Chem. Lett. 1991, 57. (d) Hao, X. J.; Node, M.; Fuji, K. J. Chem. Soc., Perkin I 1992, 1505.
- 7. (a) Node, M.; Kurosaki, R.; Hosomi, K.; Inoue, T.; Nishide, K. Tetrahedron Lett. 1995, 36, 99:
  (b) Nishide, K.; Kurosaki, R.; Hosomi, K.; Imazato, H.; Inoue, T.; Node, M.; Ohmori, T.; Fuji, K. Tetrahedron 1995, 51,10857.
- (a) Boche, G.; Schrott, W. Tetrahedron Lett. 1982, 23, 5403; (b) Duhamel, P.; Eddine, J. J.; Valnot, J. Y. Tetrahedron Lett. 1984, 25, 2355; ibid, 1987, 28, 3801.
- 9. Fuji, K.; Kawabata, T.; Ohmori, T.; Node, M. Synlett 1995, 367.
- (a) Wang, R.; Yang, X. W.; Jia, Q.; Ni, J. M. Progress in Natural Science, 1997 in press; (b) Yang, X. W.; Wang, R.; Liu, D. X. Book of Abstract for Fifth Eurasia Conference on Chemical Science, Guangzhou: Zhoushan Univ Press, 1996, 504.
- (a) Yang, X. W.; Wang, R. Chem. J. of Chin. Univ. 1997, 18, 911. (b) Enders, D.; Kipphardt, H.; Gerdes, P.; Brenavalle, L. J. Bull. Soc. Chim. Belg. 1988, 97, 691; (c) Wang, R.; Yang, X. W. The First Conference for Worldwide Young Chinese Chemists, Beijing, 1995, 276.
- (a) Mannschreck, A.; Koelle, U. Tetrahedron Lett. 1967, 8, 863; (b) Rajappa, S.; Nagarajan, K. J. Chem. Soc. perkin II 1978, 912; (c) Fetell, I.; Feuer, H. J. Org. Chem. 1978, 43, 1238.
- 13. Seebach, D.; Leitz, H. F.; Ehrig, V. Chem. Ber. 1975, 108, 1924.
- (a) Cram, D. J.; Elhafez, F. A. A. J. Am. Chem. Soc. 1952, 74, 5828; (b) Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. J. Org. Chem. 1980, 45, 1066.
- (a) Mitteilung, V.; Fr'ater, V. G. Helv. Chim. Acta. 1979, 62,2825; (b) Enders, D.; Zamponi, A.; Ranbe, G.; Runsink, J. synthesis, 1993, 725.

(Received in Japan 31 July 1997; accepted 10 September 1997)