

ENANTIOSELECTIVE SYNTHESIS OF (S)-3-(4-THIAZOLYL)-2-*tert*-BUTOXYCARBONYLAMINOPROPIONIC ACID: A CHIRAL BUILDING BLOCK FOR RENIN INHIBITOR

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Abstract – (S)-3-(4-Thiazolyl)-2-*tert*-butoxycarbonylaminopropionic acid (**6**), an important structural constituent of the renin inhibitor, has been synthesized from (Z)-3-(4-thiazolyl)-2-benzoylaminoprop-2-enoic acid (**4b**) by enantioselective hydrogenation using the Ru-(S)-*p*-tolyl-BINAP complex as the key step, and then followed by acid hydrolysis and *tert*-butoxycarbonylation.

INTRODUCTION

Based on the concept of isosterism in medicinal chemistry, 3-(4-thiazolyl)-L-alanine can be considered as an annular equivalent of L-histidine. Furthermore, (S)-3-(4-thiazolyl)-2-*tert*-butoxycarbonylaminopropionic acid (**6**) has become an interesting component in the preparation of a potential renin inhibitory active peptide by its corporation.¹ Several preparations of **6** are known:

a) The synthesis from (S)-benzyloxycarbonyl-5-oxo-4-oxazolidinoneacetic acid, which was derived from the commercially available *N*-benzyloxycarbonyl-L-aspartic acid.²

b) The enzymatic resolution of the ethyl ester of *N*-acetyl-3-(4-thiazolyl)-DL-alanine by chymotrypsin² or acetylase.³

c) The synthesis from the methyl ester of *N-tert*-butoxycarbonyl-L-aspartic acid.⁴

On the other hand, the enantioselective hydrogenation with the Ru-BINAP complex catalyst is one of the most powerful tools for the synthesis of optically active compounds.⁵ In particular, the enantioselective

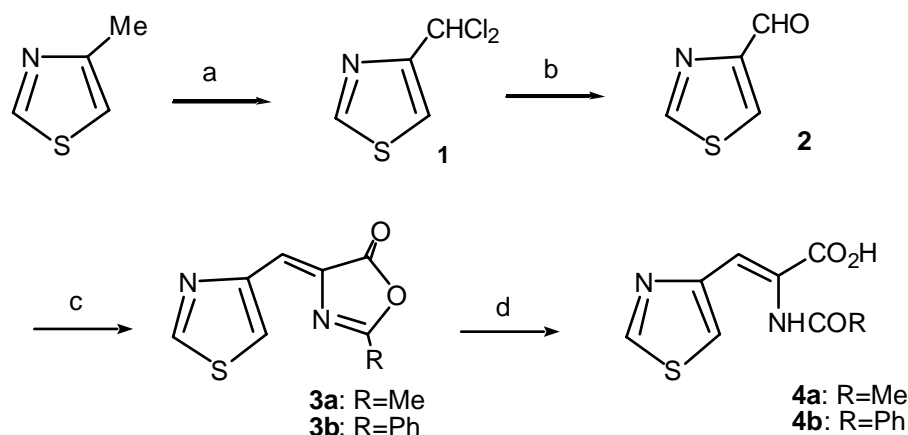
hydrogenation of 3-substituted 2-propenoic acids and 3-phenyl-2-aminoprop-2-enoic acid are well known.⁶⁻⁹ The enantioselective hydrogenation of a five-membered heterocycle substituted 2-acylaminoprop-2-enoic acid using chiral diphosphinerhodium catalysts has also been reported.¹⁰ However, that of the 3-(4-thiazolyl)-2-acylaminoprop-2-enoic acids (**4a**) and (**4b**) is unknown.

We have studied the enantioselective hydrogenation of **4a** and **4b** in order to develop the synthesis of **6**. We now report the efficient synthesis of **6** from 3-(4-thiazolyl)-2-benzoylaminopropanoic acid (**5b**) via the enantioselective hydrogenation of **4b** using Ru-*p*-tolyl-BINAP complex catalyst.¹¹

RESULTS AND DISCUSSION

The preparation of (*Z*)-3-(4-thiazolyl)-2-acylaminoprop-2-enoic acids (**4a**) and (**4b**) as substrates for the enantioselective hydrogenation is illustrated in scheme 1. The chlorination of 4-methylthiazole with Cl₂ gas in conc. H₂SO₄ and SO₃ in the presence of a catalytic amount of AIBN at 100°C for 20 h afforded a mixture of 4-dichloromethylthiazole (**1**) and 4-chloromethylthiazole in 45% and 21% yields, respectively.¹²

Scheme 1



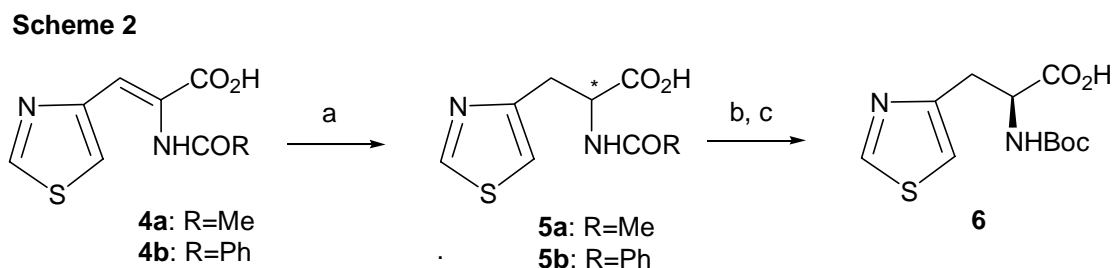
Reagents and conditions: a) Cl₂/SO₃/PCl₃/H₂SO₄, 100°C, 20 h. b) 10% H₂SO₄, 100°C, 2 h c) RCONHCH₂CO₂H, AcONa, rt, 20 min. d) **3a**: 25% aqueous acetone, reflux, 2 h **3b**: NaOH, 100°C, 45 min.

The dichloride (**1**) was then treated with 10% H₂SO₄ at 100°C for 2 h to give 4-thiazolecarbaldehyde (**2**) in 85% yield. Subsequently, **2** was condensed with acetylglycine and hippuric acid to give 4-thiazolylazlactone (**3a**) and (**3b**) in 52% and 84% yields, respectively. The treatment of **3a** with aqueous acetone solution gave **4a** in 68% yield. Alternatively, **3b** in aqueous NaOH solution was refluxed to give **4b** in 85% yield.

We examined the hydrogenation of **4a** and **4b** in the presence of the Ru-(*S*)- or (*R*)-*p*-tolyl-BINAP

complex as a catalyst under several different conditions. The results are summarized in Table 1.

The reaction was carried out in a polar solvent such as MeOH or MeOH/H₂O. It was found that the reaction temperature affected the enantioselectivity of the product. Upon the hydrogenation of **4a** and **4b** at 20°C, the reaction proceeded at a significantly slower rate, therefore a longer reaction time was required to complete the reaction, but the optical yield was in a moderate range (56-77% ee) (Entries 1~4). When the temperature was raised from 20°C to 60°C, the reaction rate accelerated, but the enantioselectivity was lower than the others (Entry 5). The reaction at 35°C gave a result similar to that at 60°C in yield and enantioselectivity (Entry 6). In addition, it is known that the hydrogenation using the Ru-*p*-tolyl-BINAP complex as a catalyst can be carried out in the presence of triethylamine;⁶ however, the enantioselective hydrogenation of **4b** could not be effected in the presence of a triethylamine (Entry 7).



Reagents and conditions : a) H₂, 5MPa, Ru₂Cl₄[(*S*)- or (*R*)-*p*-tolyl-BINAP] ₂Et₃N, MeOH, b) HCl, reflux, 20 h. c) (*t*-Boc₂O, THF rt, 40 h.

Table 1. Asymmetric hydrogenation of 4a and 4b

Entry	Substrate	Catalyst ^A	Solvent	Temp. (°C)	Time (h)	Yield (%)	E.e. (%) ^C	Config.
1	4a	(+)-A	MeOH	20	120	100	75	(<i>R</i>)- 5a
2	4a	(-)-A	MeOH	20	120	100	77	(<i>S</i>)- 5a
3	4b	(+)-A	MeOH	20	140	100	60	(<i>R</i>)- 5b
4	4b	(-)-A	MeOH	20	140	98	56	(<i>S</i>)- 5b
5	4b	(-)-A	MeOH	60	42	100	51	(<i>S</i>)- 5b
6	4b	(-)-A	MeOH/H ₂ O (10/1)	35	120	100	55	(<i>S</i>)- 5b
7	4b	(-)-A	MeOH/H ₂ O (10/1) ^B	35	120	11	—	(<i>S</i>)- 5b

Reaction conditions: H₂ press. 5 MPa. catalyst; 1 mole%,

^A(+)-A; an empirical formula Ru₂Cl₄[(*R*)-(+)-*p*-tolyl-BINAP] ₂Et₃N, (-)-A; Ru₂Cl₄[(*S*)-(-)-*p*-tolyl-BINAP] ₂Et₃N.

^BEntry 7 was carried out in the presence of 1.1 eq. mole triethylamine.

^CThe ee value of **5a** was determined by HPLC after being converted to **6**. The ee value of **5b** was determined by HPLC after being converted to the corresponding methyl ester.

The absolute configurations of **5a** and **5b** were determined by comparison with the optical rotations in the literature² after conversion to **6**. The enantiomeric excess of 3-(4-thiazolyl)-2-benzoylaminopropanoic acid (**5b**) was determined by HPLC after converting it to the corresponding methyl ester using diazomethane (Entries 3~7). However, that of 3-(4-thiazolyl)-2-acetylaminopropanoic acid (**5a**) could not

be determined using similar HPLC conditions. The enantiomeric excess of **5a** was determined by HPLC after converting it to **6** (Entries 1 and 2).

Furthermore, the recrystallization of **5b** (Entry 3, 60% ee) using EtOAc/MeOH gave the pure compound **5b** in 40% yield with 100% ee. Attempts to obtain the pure compound (**5a**) under similar recrystallizations were unsuccessful. The target compound (**6**) was derived from **5b** in 57% with 99% ee by the usual method; acid hydrolysis and *tert*-butoxycarbonylation (Scheme 2 and see EXPERIMENTAL).

CONCLUSION

We have described the efficient synthesis of the chiral building block for the renin inhibitor. (*S*)-3-(4-Thiazolyl)-2-*tert*-butoxycarbonylamino propionic acid (**6**) was synthesized from 3-(4-thiazolyl)-2-benzoylamino propanoic acid (**5b**) *via* the enantioselective hydrogenation of (*Z*)-3-(4-thiazolyl)-2-benzoylamino prop-2-enoic acid **4b** using an optically active Ru-(*S*)-*p*-tolyl-BINAP complex catalyst.

EXPERIMENTAL

All reagents and solvents were obtained from commercial sources and used without further purification. Melting points were determined using a Yanagimoto micro melting apparatus and are uncorrected. The IR spectra were run on a JASCO IR-810. The ¹H-NMR spectra were recorded in CDCl₃ or CD₃OD with TMS as the internal standard using a Bruker AM-400 (400MHz) spectrometer. MS spectra were run on a Hitachi M-80A spectrometer at 70eV. Optical rotations were recorded using a JASCO DIP-4 digital polarimeter. The HPLC was done using a Hitachi L-6000 [column, with a L-4000 UV as the detector, Optical purity; CHIRALCEL OC, 4.6 mm ID x 250 mm; eluent: 2-propanol/*n*-hexane = 35:65, flow rate, 1 mL/min; detector, UV (254 nm)]; chemical purity; [column: Inertsil ODS-2 (250 mm x 4.6 mm); eluent: MeCN/H₂O, 7:3 (pH 2.3; adjusted by using H₃PO₄); flow rate: 0.5 mL/min; detection: UV (254 nm)].

4-Thiazolecarbaldehyde (**2**)

4-Methylthiazole (50 g, 0.5 mol, Aldrich) was dissolved in a mixture of 98% H₂SO₄ (46 g) and concentrated H₂SO₄ containing 25% SO₃ (47.5 g). PCl₃ (1 mL) was added and AIBN (1.5 g) in 98% H₂SO₄ (36 g) was then added to the mixture over a period of 10 h with stirring at 85-90°C. During this time a stream of Cl₂ gas was continually introduced into the reaction mixture. The mixture was then degassed *in vacuo* at 60°C, cooled and quenched by pouring over 300 g of crushed ice. The quenched mixture was then extracted with 3 x 200 mL of benzene. The benzene extracts were combined, washed

with NaHCO₃ solution, dried over anhydrous MgSO₄, and the benzene evaporated *in vacuo*. The residue was distilled at 53-54°C/0.5 torr to give 4-dichloromethylthiazole (37.5 g, 45%). The benzene extract water layer was treated with conc. NH₄OH until the pH reached 6.0, and the resulting oil extracted into benzene. The benzene extract was dried over anhydrous MgSO₄, and the benzene evaporated *in vacuo*. The residue was distilled at 48-49°C/0.7 torr to give 4-chloromethylthiazole (14.0 g, 21%). 4-Dichlorothiazole (24 g, 0.143 mol) in 10% H₂SO₄ (300 mL) was refluxed under N₂ at 125-130°C for 2 h. The mixture was then cooled to rt and a 10% NaOH solution was added until the solution reached pH 6. The mixture was then extracted with 3 x 200 mL of CHCl₃. The organic layer was washed with water, dried over anhydrous MgSO₄ and concentrated *in vacuo* to give **2** (13.7 g, 85%). mp 65-66°C. lit.,¹² 65-67°C, lit.,¹³ 59-61°C. ¹H NMR (CDCl₃): δ 8.32 (d, *J* = 1.9, 1H), 8.99 (d, *J* = 1.9, 1H), 10.12 (s, 1H); IR ν_{max} (CHCl₃) 1700, 1585, 1425 cm⁻¹. MS: m/z 113 (62%, M⁺), 85 (100), 58 (72), 57 (56), 45 (40), 29 (24).

4-Thiazolylazlactone (3a)

A mixture of **2** (3.2 g, 28 mmol), acetylglycine (3.25 g, 28 mmol), sodium acetate (12.35 g, 0.15 mol) and acetic anhydride (30 mL) were heated for 20 min at 100°C. The reaction products were cooled, filtrated and washed with water. The crude product was recrystallized from acetone to give **3a** (2.8 g, 52%). mp 115-118°C. Anal. Calcd for C₈H₆N₂O₂S: C, 49.47; H, 3.11; N, 14.42. Found: C, 49.61; H, 3.09; N, 14.44. ¹H NMR (CDCl₃): δ 7.53-7.59 (m, 3H), 7.62-7.66 (m, 1H), 8.18-8.21 (m, 2H), 8.83 (d, *J* = 2.1, 1H), 8.90 (d, *J* = 2.1, 1H); IR ν_{max} (CHCl₃) 3440, 1710, 1650, 1520 cm⁻¹; MS: m/z 194 (95%, M⁺), 166 (19), 148 (3), 124 (100), 97 (38), 60 (14), 43 (87).

4-Thiazolylazlactone (3b)

A mixture of **2** (10.2 g, 90 mmol), hippuric acid (7.4 g, 90 mmol), sodium acetate (36.3 g, 0.43 mol) and acetic anhydride (50 mL) was heated for 20 min at 100°C. The reaction products were cooled, filtrated and washed with water. The crude product was recrystallized from CHCl₃ to give **3b** (19.4 g, 84%). mp 174-176°C. Anal. Calcd for C₁₃H₈N₂O₂S: C, 60.92; H, 3.15; N, 10.93. Found: C, 61.08; H, 3.09; N, 10.85. ¹H NMR (CDCl₃): δ 7.53-7.59 (m, 3H), 7.62-7.66 (m, 1H), 8.18-8.21 (m, 2H), 8.83 (d, *J* = 2.1, 1H), 8.90 (d, *J* = 2.1, 1H); IR ν_{max} (CHCl₃) 3620, 1800, 1660, 1520 cm⁻¹. MS: m/z 256 (13%, M⁺), 105 (100), 77 (56), 69 (10), 51 (6).

(Z)-3-(4-Thiazolyl)-2-acetylamino prop-2-enoic acid (4a)

The mixture of **3a** (2.5 g, 12.9 mmol) and 25% aqueous acetone (80 mL) was refluxed for 2 h. The reaction mixture was then concentrated *in vacuo*. The residue was extracted with CHCl₃ and washed with water. The solvent was removed and the solid residue was recrystallized from MeOH to give **4a** (1.86 g, 68%) as a solid. mp 185-187°C. Anal. Calcd for C₈H₈N₂O₃S: C, 45.27; H, 3.80; N, 13.20. Found: C, 45.31; H, 3.78; N, 13.05. ¹H NMR (CD₃OD): δ 7.09 (s, 1H), 7.53-7.64 (m, 3H), 7.82 (d, *J* = 1.9, 1H),

7.99-8.02 (m, 2H), 9.11 (d, $J = 1.5$, 1H); IR ν_{\max} (CHCl₃) 3440, 1710, 1650, 1520 cm⁻¹; MS: m/z 212 (43%, M⁺), 194 (3), 184 (7), 170 (68), 168 (67), 126 (100), 99 (80), 93 (95), 82 (5), 72 (13).

(Z)-3-(4-Thiazolyl)-2-benzoylaminoprop-2-enoic acid (4b)

The mixture of **3b** (19 g, 74 mmol) and 0.3% NaOH (780 mL) was stirred at 100°C for 45 min. The reaction mixture was then cooled and filtered. The filtrate was carefully acidified with 10% HCl to give a solid. The solid was washed with acetone and ether. The crude product was recrystallized from a mixture of EtOAc and MeOH to give **4b** (21.7 g, 85%). mp 206-208°C. Anal. Calcd for C₁₃H₁₀N₂O₃S: C, 56.92; H, 3.67; N, 10.21. Found: C, 59.88; H, 3.61; N, 10.16. ¹H NMR (CD₃OD): δ 7.09 (s, 1H), 7.53-7.64 (m, 3H), 7.82 (d, $J = 1.9$, 1H), 7.99-8.02 (m, 2H), 9.11(d, $J = 1.5$, 1H); IR ν_{\max} (CHCl₃): 3440, 1710, 1650, 1520 cm⁻¹; MS: m/z 275 (80%, M⁺+1), 257 (27), 231 (23), 230 (27), 153 (14), 122 (6), 105 (100), 77 (17).

(S)-3-(4-Thiazolyl)-2-acetylamino propanoic acid (5a)

Into a 100 mL autoclave were charged **4a** (0.5 g, 2.35 mmol) in MeOH (20 mL) and Ru₂Cl₄[(S)-(-)-*p*-tolyl-BINAP]₂Et₃N (20 mg, 0.022 mmol) under an atmosphere of N₂. The atmosphere was then replaced with H₂ at a pressure of 5 MPa. The reaction mixture was stirred for the appropriate time and at the temperature (see Table 1). The reaction solution was concentrated *in vacuo* and the solid residue was recrystallized from CHCl₃ to give **5a** (0.45 g, 90%) as a solid. For the measurement of the enantiomeric purity by HPLC, **5a** was converted into **6**. mp 166-170°C, The enantiomeric purity was 77% ee. [α]_D²³ -8.0° (*c* 1.0, MeOH). ¹H NMR (CD₃OD) δ 3.40 (dd, $J = 8.5, 14.5$, 1H), 3.52 (dd, $J = 4.5, 14.5$, 1H), 7.35 (s, 1H), 7.41-7.46 (m, 2H), 7.50-7.55 (m, 1H), 7.76-7.78 (m, 1H), 8.95(d, $J = 1.8$, 1H); IR ν_{\max} (CHCl₃): 3410, 3310, 1705, 1630, 1520 cm⁻¹; MS: m/z 214 (11%, M⁺), 169 (16), 155 (15), 127 (100), 111 (60), 99 (95), 74 (23), 43 (78). HRMS calcd for C₈H₁₀N₂O₃S: 214.2386, Found: 214.2394.

(S)-3-(4-Thiazolyl)-2-benzoylaminopropanoic acid (5b)

Into a 100 mL autoclave were charged **4b** (1.0 g, 3.6 mmol) in MeOH (20 mL) and Ru₂Cl₄[(S)-(-)-*p*-tolyl-BINAP]₂Et₃N (20 mg, 0.022 mmol) under an atmosphere of N₂. The atmosphere was then replaced with H₂ at a pressure of 5 MPa. The reaction mixture was stirred for the appropriate time and at the temperature (see Table 1). The reaction solution was concentrated *in vacuo* and the solid residue was recrystallized from a mixture of EtOAc and MeOH to give **5b** (0.41 g, 40%). For the measurement of the enantiomeric purity by HPLC, **5b** were converted into the methyl ester of **5b** using diazomethane. The enantiomeric purity was 100% ee. [(S)-tr 21.7 min, (R)-tr 27.4 min]. mp 198-200°C, [α]_D²³ -22.0° (*c* 1.0, MeOH). ¹H NMR (CD₃OD): δ 3.40 (dd, $J = 8.5, 14.5$, 1H), 3.52 (dd, $J = 4.5, 14.5$, 1H), 7.35 (s, 1H), 7.41-7.46 (m, 2H) 7.50-7.55 (m, 1H), 7.76-7.78 (m, 1H), 8.95 (d, $J = 1.8$, 1H); IR ν_{\max} (CHCl₃): 3410, 3310, 1705, 1630, 1520 cm⁻¹. MS: m/z 276 (6%, M⁺), 232 (6), 171 (5), 155 (6), 127 (36), 111 (24), 105 (100), 99 (36), 77 (30). HRMS calcd for C₁₃H₁₂N₂O₃S: 276.3094, Found: 276.3098.

(S)-3-(4-Thiazolyl)-2-tert-butoxycarbonylaminopropanoic acid (6)

5b (0.30 g, 1.4 mmol) and 6 N HCl (25 mL) were refluxed for 20 h and then cooled to rt. The reaction mixture was concentrated *in vacuo*. The residue was washed with toluene to remove the benzoic acid. The crude product (0.24 g) was dissolved in THF (25 mL) and adjusted to pH 9 with 3N NaOH solution. Di-*tert*-butyl dicarbonate (0.23 g, 1.05 mmol) in THF (5 mL) was added to the mixture and stirred for 40 h at rt. The solvent was removed *in vacuo* and the residue was adjusted to pH 2 with 3 N HCl, and then extracted with EtOAc (50 mL), washed with brine and dried using anhydrous MgSO₄. The solvent was concentrated *in vacuo* and the solid residue was recrystallized from acetone to give **6** (0.18 g, 57%) as a solid. The enantiomeric purity was 99% ee. [(*S*)- tr 7.8 min., (*R*)- tr 9.6 min]. mp 122-123°C, lit.,² mp 122-123°C, $[\alpha]_{\text{D}}^{24} +11.0^{\circ}$ (*c* 1.0, MeOH). $[\alpha]_{\text{D}}^{24} +125.9^{\circ}$ (*c* 1.0, CHCl₃) lit.,² $[\alpha]_{\text{D}} +124.9$ (*c* 1.04, CHCl₃), ¹H NMR (CDCl₃): δ 1.46 (s, 9H), 3.31-3.39 (m, 1H), 3.49-3.55 (m, 1H), 4.5 (m, 1H), 5.61-5.65 (m, 1H), 7.18 (s, 1H), 8.89-8.91 (m, 1H); IR ν_{max} (CHCl₃): 3430, 1710, 1505 cm⁻¹; MS: *m/z* 273 (9%, M⁺+1), 259 (4), 257 (4), 217 (90), 199 (100), 173 (28), 153 (6), 127 (50), 111 (3), 99 (23), 71 (18).

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