# Catalytic Asymmetric Synthesis of *β*-Hydroxy-α-amino Acids: Highly Enantioselective Hydrogenation of *β*-Oxy-α-acetamidoacrylates

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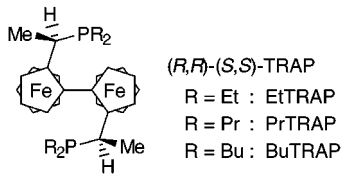
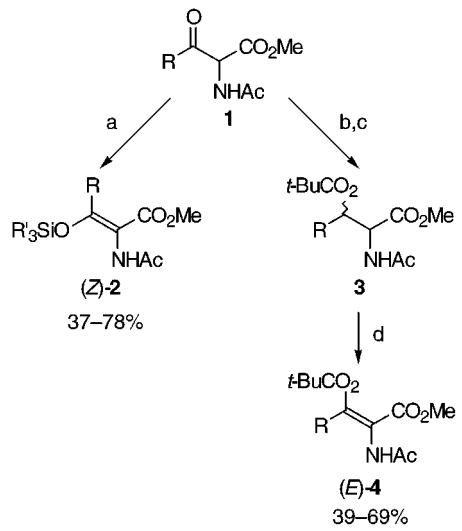
Optically active *β*-hydroxy-α-amino acids are not only important constituents of biologically active peptides and related compounds[1] but also useful chiral precursors in organic synthesis.[2] Various stereocontrolled syntheses of optically active *β*-hydroxy-α-amino acids have been reported.[3] *threo*-*β*-Hydroxy-α-amino acids are conveniently prepared by highly enantioselective hydrogenation of the corresponding ketone precursors or aldol reaction of α-isocyanocarboxylates.[4,5] However, *erythro*-*β*-hydroxy-α-amino acids with high enantiomeric excess have not been accessible by catalytic asymmetric synthesis.[6,7]

In the preceding paper,[8] we reported that transchelating chiral diphosphine TRAPs[9] with linear alkyl P substituents (Et- and BuTRAP) are effective for asymmetric hydrogenation of *β*,*β*-dialkyl-substituted-α-acetamidoacrylates catalyzed by rhodium complexes.[10] The asymmetric hydrogenation provides an efficient synthetic route to various optically active *β*-branched-α-amino acids. Herein, we describe a new efficient enantioselective synthesis of optically active *erythro*- and *threo*-*β*-hydroxy-α-amino acids by TRAP−rhodium-catalyzed asymmetric hydrogenation of the respective (*Z*)- and (*E*)-*β*-oxy-α-acetamidoacrylates, which are both prepared stereoselectively from the corresponding *β*-keto-α-(*N*-acetylamino)carboxylate precursors.




**Scheme 1**[a]




[a] (a) NaH, THF, −78 to 0 °C, 1 h then $R'_3SiCl$, −78 °C to rt; (b) $NaBH_4$, EtOH, rt; (c) *t*-BuCOCl, $Et_3N$, cat. DMAP, THF, rt; (d) *t*-BuOCl, benzene, rt, then DABCO, rt.

According to Scheme 1, (*Z*)-*β*-siloxy-α-acetamidoacrylates (*Z*)-**2a**−**i** were synthesized with high stereoselectivity in good yields by reaction of the sodium enolate of **1** with trialkylchlorosilane.[11] The pure (*Z*)-**2**, which was easily obtained through purification by flash column chromatography on *silica gel*, was employed as the starting olefinic substrate. On the other hand, (*E*)-*β*-pivaloyloxy-α-acetamidoacrylates (*E*)-**4** were prepared in good yields as follows: The carbonyl group of **1** was chemoselectively reduced with $NaBH_4$ to give the corresponding alcohol, which was esterified with pivaloyl chloride, giving **3** as a mixture of diastereoisomers. N-Chlorination of **3** with *tert*-butyl hypochlorite, followed by dehydrochlorination with DABCO, resulted in the formation of pure (*E*)-**4** with migration of the C−N double bond initially formed.

Asymmetric hydrogenations of (*Z*)-*β*-siloxy-α-acetamidoacrylates (*Z*)-**2a** ($R'_3Si$ = dimethylthexylsilyl (TDS)) were carried out at atmospheric pressure of hydrogen in the presence of 1 mol % of rhodium catalyst generated in situ by mixing $[Rh(COD)_2]ClO_4$ and (*R*,*R*)-(*S*,*S*)-TRAP (1:1.1) bearing linear alkyl P substituents.[12] The results

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(2) Coppola, G. M.; Schuster, H. F. *Asymmetric Synthesis: Construction of Chiral Molecules Using Amino Acids*; John Wiley & Sons: Toronto, 1987.

(3) Williams, R. M. *Synthesis of Optically Active* α-Amino Acids; Pergamon: Oxford, 1989.

(4) For synthesis of *threo*-*β*-hydroxy-α-amino acids by catalytic asymmetric hydrogenation of 2-(*N*-acetylamino)-3-ketoalkanoates, see: (a) Noyori, R.; Ikeda, T.; Ohkuma, T.; Widhalm, M.; Kitamura, M.; Takaya, H.; Akutagawa, S.; Sayo, N.; Saito, T.; Taketomi, T.; Kumobayashi, H. *J. Am. Chem. Soc.* **1989**, *111*, 9134. (b) Genet, J. P.; Pinel, C.; Mallart, S.; Juge, S.; Thorimbert, S.; Laffitte, J. A. *Tetrahedron: Asymmetry* **1991**, *2*, 555.

(5) For synthesis of *threo*-*β*-hydroxy-α-amino acids by catalytic asymmetric aldol reaction of α-isocyanoacetates, see: (a) Ito, Y.; Sawamura, M.; Hayashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 6405. (b) Sawamura, M.; Ito, Y. *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; Chapter 7.2, p 367.

(6) For synthetic transformations to optically active *erythro*-*β*-hydroxy-α-amino acids, see: (a) Hale, K. J.; Manaviazar, S.; Delisser, V. M. *Tetrahedron* **1994**, *50*, 9181. (b) Beaulieu, P. L. *Tetrahedron Lett.* **1991**, *32*, 1031.

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(8) Sawamura, M.; Kuwano, R.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 9602.

(9) General name for these diphosphines: (*S*,*S*)-2,2″-bis[(*R*)-1-(dialkylphosphino)ethyl]-1,1′-biferrocene: (a) Sawamura, M.; Hamashima, H.; Ito, Y. *Tetrahedron: Asymmetry* **1991**, *2*, 593. (b) Sawamura, M.; Hamashima, H.; Sugawara, M.; Kuwano, R.; Ito, Y. *Organometallics* **1995**, *14*, 4549. (c) Kuwano, R.; Sawamura, M.; Okuda, S.; Asai, T.; Ito, Y.; Redon, M.; Krief, A. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2807.

(10) (a) Burk, M. J.; Feng, S.; Gross, M. F.; Tumas, W. *J. Am. Chem. Soc.* **1995**, *117*, 8277. (b) Burk, M. J.; Gross, M. F.; Martinez, J. P. *J. Am. Chem. Soc.* **1995**, *117*, 9375.

(11) (*E*)-**2** was not found in $^1H$ NMR spectrum of the crude product, although a trace amount of (*E*)-**2** was detected by TLC analysis.

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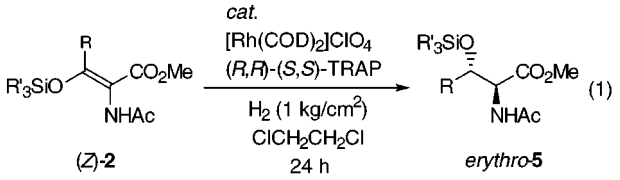
**Table 1. Enantioselective Hydrogenation of (*Z*)-2 Catalyzed by (*R,R*)-(*S,S*)-TRAP−Rhodium Complex[a]**



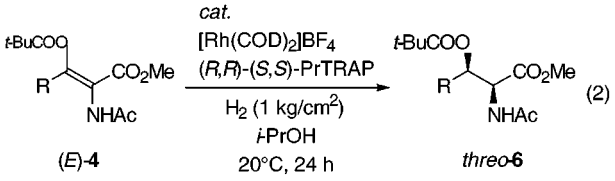

**2a:** R = Me, R'$_3$Si = TDS
**2b:** R = Me, R'$_3$Si = TBDMS
**2c:** R = Me, R'$_3$Si = TBDPS
**2d:** R = Et, R'$_3$Si = TDS
**2e:** R = Et, R'$_3$Si = TBDMS
**2f:** R = Pr, R'$_3$Si = TBDMS
**2g:** R = MeOCH$_2$, R'$_3$Si = TBDMS
**2h:** R = EtO$_2$C(CH$_2$)$_3$, R'$_3$Si = TBDMS
**2i:** R = *i*-Pr, R'$_3$Si = TBDMS

| | | | | | *erythro*-**5** | |
|---|---|---|---|---|---|---|
| entry | **2** | TRAP | temp, °C | convn, %[b] | yield, %[c] | ee, %[d] (confign) |
| 1 | **2a** | EtTRAP | 30 | 100 | 75 | 88 (2*S*,3*S*) |
| 2 | **2a** | PrTRAP | 30 | 100 | 95 | 93 (2*S*,3*S*) |
| 3 | **2a** | BuTRAP | 30 | 100 | 96 | 88 (2*S*,3*S*) |
| 4 | **2a** | PrTRAP | 20 | 100 | 98 | 95 (2*S*,3*S*) |
| 5 | **2b** | PrTRAP | 20 | 100[e] | 48 | 94 (2*S*,3*S*) |
| 6 | **2c** | PrTRAP | 20 | 16 | 7 | 92 (2*S*,3*S*) |
| 7 | **2d** | PrTRAP | 20 | 0 | | |
| 8 | **2e** | PrTRAP | 20 | 100 | 93 | 95 (2*S*,3*S*) |
| 9 | **2f** | PrTRAP | 20 | 100 | 93 | 94 (2*S*,3*S*) |
| 10[f] | **2g** | PrTRAP | 20 | 100 | 89 | 97 (2*S*,3*R*) |
| 11 | **2h**[g] | PrTRAP | 20 | 100 | 99 | 94 (2*S*,3*S*) |
| 12 | **2i** | PrTRAP | 20 | 0 | | |

[a] All reactions were carried out at 1 kg/cm$^2$ of hydrogen pressure in 1,2-dichloroethane for 24 h unless otherwise noted. **2** (0.5 M):[Rh(COD)$_2$]ClO$_4$:TRAP = 100:1:1.1. [b] Determined by $^1$H NMR analysis of crude product. [c] Isolated yield by flash column chromatography. [d] Determined by HPLC analysis with SUMICHIRAL OA-3000. [e] $^1$H NMR analysis of the workup mixture indicated that the hydrogenation product, *erythro*-**5**, was accompanied by the hydrolysis product (38%). [f] 2 mol % of catalyst was used. [g] Diethyl ester was used.

are summarized in Table 1. The hydrogenations proceeded stereospecifically to yield *erythro*-(2*S*,3*S*)-**5a**, which was isolated by flash column chromatography. PrTRAP gave higher enantioselectivity than Et- and BuTRAP (entries 1−3). The enantioselectivity increased up to 95% ee by carrying out the hydrogenation at 20 °C with PrTRAP ligand on the rhodium complex (entry 4). Hydrogenation of TBDMS enol ether (*Z*)-**2b** provided *erythro*-**5b** (94% ee) in 48% yield, which was accompanied by the hydrolysis product, methyl 2-(*N*-acetylamino)-3-oxobutanoate (**1a**, R = Me) (entry 5). The hydrogenation reaction of *tert*-butyldiphenylsilyl (TBDPS) enol ether (*Z*)-**2c** proceeded sluggishly (entry 6), probably because a larger silyl substituent such as the TBDPS group interfered with the coordination of (*Z*)-**2c** to the rhodium complex. The crucial role of the silyl group is also observed in the asymmetric hydrogenation of (*Z*)-3-siloxy-2-(*N*-acetylamino)-2-pentenoate (**2d** and **2e**, R = Et). The hydrogenation of TDS ether (*Z*)-**2d** did not work at all (entry 7). However, the TBDMS ether (*Z*)-**2e**, whose silyl group may be slightly less bulky than that of **2d**, was subjected to the hydrogenation at 20 °C for 24 h to furnish *erythro*-(2*S*,3*S*)-**5e** with 95% ee in 93% chemical

**Table 2. Asymmetric Hydrogenation of (*E*)-4 Catalyzed by (*R,R*)-(*S,S*)-PrTRAP−Rhodium Complex[a]**




| entry | R (**4**) | product | convn, %[b] | yield, %[c] | ee, %[d](confign) |
|---|---|---|---|---|---|
| 1 | Me (**4a**) | **6a** | 100 | 99 | 97 (2*S*,3*R*) |
| 2 | Et (**4b**) | **6b** | 100 | 97 | 91 (2*S*,3*R*) |
| 3[e] | Bu (**4c**) | **6c** | 100 | 95 | 89 (2*S*,3*R*) |
| 4 | Ph (**4d**) | **6d** | 16 | 12[e] | 73 (2*S*,3*R*) |

[a] All reactions were carried out at 20 °C and 1 kg/cm$^2$ of hydrogen pressure in 2-propanol for 24 h unless otherwise noted. **4** (0.25 M):[Rh(COD)$_2$]BF$_4$:TRAP = 100:1:1.1. [b] Determined by $^1$H NMR analysis of crude product. [c] Isolated yield by flash column chromatography. [d] Determined by HPLC analysis with SUMICHIRAL OA-3000. [e] The reaction was carried out in 0.5 M solution of **4**.

yield (entry 8). Various *erythro*-*β*-hydroxyl-α-amino acid derivatives **5f**−**h** bearing a primary alkyl group at the *β*-position were prepared with high enantioselectivity from (*Z*)-**2f**−**h** by the asymmetric hydrogenation catalyzed by the PrTRAP−rhodium complex (entries 9−11). However, the hydrogenation of (*Z*)-**2i** with a secondary alkyl *β*-substituent gave no hydrogenation product (entry 12). The hydrogenation product *erythro*-**5a** was easily hydrolyzed to L-(2*S*,3*S*)-*allo*-threonine with 1 N hydrochloric acid in 77% yield.

(*E*)-*β*-Pivaloyloxy-α-acetamidoacrylates (*E*)-**4** also were hydrogenated with high enantioselectivity in the presence of cationic PrTRAP−rhodium catalyst, giving *threo*-(2*S*,3*R*)-**6** (Table 2). The sense of enantioselection at the α-carbon in the hydrogenation of (*E*)-**4** is the same as that of (*Z*)-**2**. Hydrogenation of (*E*)-**4a** led to 97% ee of *N*-acetyl-*O*-pivaloyl-L-threonine methyl ester (**6a**) in 99% yield (entry 1). Et- and BuTRAP were less selective (87% ee and 90% ee, respectively). Although *β*-alkyl substituents of (*Z*)-**2** did not affect enantioselectivity in the asymmetric hydrogenations, the enantioselectivity of the hydrogenation of (*E*)-**4** slightly decreased with longer *β*-alkyl substituents (entries 2 and 3). Disappointingly, PrTRAP−rhodium catalyst showed low catalytic activity for the hydrogenation of (*E*)-**4d** bearing a *β*-aromatic substituent, giving *threo*-(2*S*,3*R*)-**6d** with moderate enantiomeric excess (entry 4).

In conclusion, we succeeded in the highly enantioselective synthesis of *erythro*- and *threo*-*β*-hydroxy-α-amino acids (up to 97% ee) by PrTRAP−rhodium catalyzed asymmetric hydrogenation of (*Z*)- and (*E*)-*β*-oxy-α-acetamidoacrylates, both of which were stereoselectively prepared from the corresponding *β*-keto-α-(*N*-acetylamino)alkanoate precursors.

## Experimental Section

**Materials.** Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. 1,2-Dichloroethane and 2-propanol were distilled from $CaH_2$ under nitrogen. Tetrahydrofuran (THF) and benzene were distilled from sodium−benzophenone ketyl. MeOH was distilled from Mg(OMe)$_2$. [Rh(COD)$_2$]ClO$_4$,[13] [Rh(COD)$_2$]BF$_4$,[13] PrTRAP[9c], and 2-(*N*-acetylamino)-3-ketocarboxylates **1**[4b] were prepared

(12) Use of [Rh(COD)$_2$]BF$_4$ and [Rh(COD)$_2$]OTf as catalyst precursor accelerated hydrolysis reaction to give **1**.

(13) Schenck, T. G.; Downes, J. M.; Milne, C. R. C.; Mackenzie, P. B.; Boucher, H.; Whelan, J.; Boshnich, B. *Inorg. Chem.* **1985**, *24*, 2334.

according to the literature procedures. Flash column chromatography was performed with silica gel 60 (230−400 mesh, E. Merck) except for purifications of **2a**−**i**, which were performed with silica gel 60 N (spherical, neutral) (40−100 $\mu$m, Kanto Chemical).

**Methyl (*Z*)-2-(*N*-Acetylamino)-3-(dimethylthexylsiloxy)-2-butenoate (2a).** A solution of methyl 2-(*N*-acetylamino)-3-ketobutanoate (346 mg, 2.0 mmol) in THF (3.0 mL) was added to a suspension of NaH (52.8 mg, 2.2 mmol) in THF (4.0 mL) at −78 °C. After 1 h of stirring at 0 °C, dimethylthexylsilyl chloride (395 mg, 2.2 mmol) was added to the mixture at −78 °C. After 1 h of stirring at room temperature, the mixture was filtered through Celite pad and evaporated under reduced pressure. The residue was purified by flash column chromatography (*n*-hexane/AcOEt = 1/1), giving 461 mg (73%) of **2a**: white solid; mp 64−65 °C; $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 0.26 and 0.27 (a pair of s, 6 H), 0.90 (d, $J$ = 6.9 Hz, 6 H), 0.91 (s, 6 H), 1.69 (septet, $J$ = 6.9 Hz, 1 H), 2.04 and 1.85 (a pair of s, 3 H), 2.29 and 2.40 (a pair of s, 3 H), 3.73 (s, 3 H), 6.42 and 6.03 (a pair of br s, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ −1.7, 18.4, 19.7 and 19.8 (a pair of s), 20.1 and 20.9 (a pair of s), 23.0, 25.1, 33.8, 51.7, 111.0, 158.5, 166.2, 168.5; IR (KBr) 3240, 1724, 1660 cm$^{-1}$, Anal. Calcd for $C_{15}H_{29}NO_4Si$: C, 57.11; H, 9.27; N, 4.44. Found: C, 56.89; H, 9.38; N, 4.29.

**Methyl (*Z*)-2-(*N*-Acetylamino)-3-(*tert*-butyldimethylsiloxy)-2-butenoate (2b).** In 63% yield: white solid; $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 0.22 and 0.23 (a pair of s, 6 H), 0.95 (s, 9 H), 2.04 and 1.85 (a pair of s, 3 H), 2.30 and 2.41 (a pair of s, 3 H), 3.73 (s, 3 H), 6.42 and 6.05 (a pair of br s, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ −3.8, 18.0, 20.1, 23.0, 25.4 and 25.3 (a pair of s), 51.7, 110.8, 158.8, 166.2, 168.5.

**Methyl (*Z*)-2-(*N*-Acetylamino)-3-(*tert*-butyldiphenylsiloxy)-2-butenoate (2c).** In 78% yield: white solid; $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 1.04 (s, 9 H), 1.88 (s, 3 H), 2.09 and 2.14 (a pair of s, 3 H), 3.69 (s, 3 H), 6.35 and 6.16 (br s, 1 H), 7.39−7.53 (m, 6 H), 7.65−7.74 (m, 4 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 19.3, 20.5, 22.8, 26.2, 51.6, 110.2, 128.2, 130.5, 132.3, 135.1, 159.8, 166.2, 168.7.

**Methyl (*Z*)-2-(*N*-Acetylamino)-3-(dimethylthexylsiloxy)-2-pentenoate (2d).** In 76% yield: white solid; $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 0.24 and 0.25 (a pair of s, 6 H), 0.87−0.94 (m, 12 H), 1.13 and 1.18 (a pair of t, $J$ = 7.4 and 7.4 Hz, 3 H), 1.73 (septet, $J$ = 6.9 Hz, 1 H), 2.04 and 1.85 (a pair of s, 3 H), 2.63 and 2.78 (a pair of q, $J$ = 7.4 and 7.4 Hz, 2 H), 3.73 (s, 3 H), 6.45 and 6.04 (a pair of br s, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ −2.0, 12.3 and 12.0 (a pair of s), 18.4, 19.8 and 19.7 (a pair of s), 23.0, 25.2, 26.2 and 27.2 (a pair of s), 33.7, 51.7, 111.1, 162.5, 165.9, 168.5.

**Methyl (*Z*)-2-(*N*-Acetylamino)-3-(*tert*-butyldimethylsiloxy)-2-pentenoate (2e).** In 78% yield: white solid; mp 65−66 °C; $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 0.21 and 0.22 (a pair of s, 6 H), 0.96 and 0.95 (a pair of s, 9 H), 1.13 and 1.18 (a pair of t, $J$ = 7.5 and 7.5 Hz, 3 H), 2.04 and 1.86 (a pair of s, 3 H), 2.64 and 2.78 (a pair of q, $J$ = 7.5 and 7.5 Hz, 2 H), 3.73 (s, 3 H), 6.43 and 6.05 (a pair of br s, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ −4.0, 12.2 and 11.9 (a pair of s), 18.2, 23.0, 25.5 and 25.3 (a pair of s), 26.3 and 27.1 (a pair of s), 51.7, 110.9, 162.9, 165.9, 168.5; IR (KBr) 3260, 1734, 1660 cm$^{-1}$; HRMS(FAB) calcd for $C_{14}H_{28}NO_4Si$ $(M + H)^+$ 302.1787, found 302.1791.

**Methyl (*Z*)-2-(*N*-Acetylamino)-3-(*tert*-butyldimethylsiloxy)-2-hexenoate (2f).** In 58% yield: white solid; mp 52−54 °C; $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 0.20 and 0.21 (a pair of s, 6 H), 0.93 and 0.99 (a pair of t, $J$ = 7.5 and 7.2 Hz, 3 H), 0.96 and 0.95 (a pair of s, 9 H), 1.50−1.70 (m, 2 H), 2.04 and 1.86 (a pair of s, 3 H), 2.61 and 2.75 (a pair of t, $J$ = 7.7 and 7.8 Hz, 2 H), 3.73 (s, 3H), 6.47 and 6.04 (a pair of br s, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$, TMS) $\delta$ −4.0, 13.6 and 13.8 (a pair of s), 18.2, 21.0, 23.0, 25.5, 34.7 and 35.5 (a pair of s), 51.7, 111.7, 161.1, 165.9, 168.4; IR (KBr) 3252, 1734, 1654 cm$^{-1}$. Anal. Calcd for $C_{15}H_{29}NO_4Si$: C, 57.11; H, 9.27; N, 4.44. Found: C, 56.81; H, 9.12; N, 4.37.

**Methyl (*Z*)-2-(*N*-Acetylamino)-3-(*tert*-butyldimethylsiloxy)-4-methoxy-2-butenoate (2g).** In 58% yield: pale yellow solid; mp 63−67 °C; $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 0.22 (s, 6 H), 0.95 (s, 9 H), 2.07 (s, 3 H), 3.32 (s, 3 H), 3.76 (s, 3 H), 4.35 (s, 2 H), 6.61 (br s, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ −4.3, 18.4, 22.9, 25.6, 51.9, 57.6, 68.5, 113.3, 153.6, 165.5, 168.3; IR (KBr) 3184, 1728, 1654 cm$^{-1}$; HRMS(FAB) calcd for $C_{14}H_{28}NO_5Si$ $(M + H)^+$ 318.1737, found 318.1734.

**Diethyl (*Z*)-2-(*N*-Acetylamino)-3-(*tert*-butyldimethylsiloxy)-2-heptenedioate (2h).** In 55% yield: colorless oil; $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 0.21 and 0.22 (a pair of s, 6 H), 0.96 (s, 9 H), 1.25 (t, $J$ = 7.2 Hz, 3 H), 1.27 (t, $J$ = 7.2 Hz, 3 H), 1.82−1.98 (m, 2 H), 2.03 and 1.87 (a pair of s, 3 H), 2.34 and 2.38 (a pair of t, $J$ = 7.5 and 7.5 Hz, 2 H), 2.69 and 2.81 (a pair of t, $J$ = 7.8 and 7.7 Hz, 2 H), 4.12 (q, $J$ = 7.2 Hz, 2 H), 4.20 (q, $J$ = 7.2 Hz, 2 H), 6.48 and 6.05 (a pair of br s, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ −4.1, 14.1, 18.2 and 19.9 (a pair of s), 22.8, 22.9, 25.4, 25.5, 32.0 and 32.9 (a pair of s), 33.4 and 33.6 (a pair of s), 60.2, 60.6, 112.6, 159.5, 165.3, 168.3, 173.2; IR (neat) 3268, 1740, 1668 cm$^{-1}$. Anal. Calcd for $C_{19}H_{35}NO_6Si$: C, 56.83; H, 8.78; N, 3.49. Found: C, 56.88; H, 8.92; N, 3.46.

**Methyl (*Z*)-2-(*N*-Acetylamino)-3-(*tert*-butyldimethylsiloxy)-4-methyl-2-pentenoate (2i).** In 37% yield: white solid; $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 0.21 and 0.23 (a pair of s, 6 H), 1.00 and 0.99 (a pair of s, 9 H), 1.11 and 1.13 (a pair of d, $J$ = 6.8 and 6.3 Hz, 6 H), 2.05 and 1.85 (a pair of s, 3 H), 2.40 (septet, $J$ = 6.8 Hz, 1 H), 3.73 (s, 3 H), 6.34 and 5.89 (a pair of br s, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ −3.8 and −3.7 (a pair of s), 18.9 and 19.0 (a pair of s), 19.3 and 19.9 (a pair of s), 19.6, 23.2, 25.9, 30.5 and 30.7 (a pair of s), 51.8, 110.2 and 109.3 (a pair of s), 165.1, 166.7, 169.1.

**Methyl 2-(*N*-Acetylamino)-3-pivaloyloxybutanoate (3a).** $NaBH_4$ (96 mg, 2.5 mmol) was added to a solution of methyl 2-(*N*-acetylamino)-3-ketobutanoate (877 mg, 5.1 mmol) in MeOH (10 mL) at 0 °C. The solution was stirred at room temperature for 1 h. After $NH_4Cl$ solid was added, the mixture was evaporated under reduced pressure. The residue was passed through a short silica gel column (AcOEt), giving 730 mg (82%) of crude methyl 2-(*N*-acetylamino)-3-hydroxybutanoate. A mixture of the crude product and DMAP (26 mg, 0.22 mmol) was diluted with THF (8 mL) and $Et_3N$ (548 mg, 5.4 mmol). Pivaloyl chloride (655 mg, 5.4 mmol) was added to the solution at 0 °C. The mixture was stirred at room temperature for 2 h. After saturated aqueous $NaHCO_3$ was added, the mixture was extracted three times with AcOEt. The organic layer was washed with brine, dried over $Na_2SO_4$, and evaporated under reduced pressure. The residue was purified by flash column chromatography (*n*-hexane/AcOEt = 1/1), giving 790 mg (60% from **1a**) of **3a** as a mixture of diastereoisomers (*erythro*/*threo* = 82/18). The mixture was used without further purification: white solid. *erythro*-**3a**: $^1$H NMR (200 MHz, $CDCl_3$, TMS) $\delta$ 1.18 (s, 9 H), 1.34 (d, $J$ = 6.6 Hz, 3 H), 2.04 (s, 3 H), 3.78 (s, 3 H), 4.81 (dd, $J$ = 8.4, 3.5 Hz, 1 H), 5.10 (dq, $J$ = 3.5, 6.6 Hz, 1 H), 6.35 (br d, 1 H). *threo*-**3a**: $^1$H NMR (200 MHz, $CDCl_3$, TMS) $\delta$ 1.17 (s, 9 H), 1.26 (d, $J$ = 6.3 Hz, 3 H), 2.11 (s, 3 H), 3.72 (s, 3 H), 4.83 (dd, $J$ = 9.3, 3.0 Hz, 1 H), 5.37 (dq, $J$ = 3.0, 6.3 Hz, 1 H), 6.05 (br d, 1 H).

**Methyl 2-(*N*-Acetylamino)-3-pivaloyloxypentanoate (3b).** In 67% yield (*erythro*/*threo* = 80/20): white solid. *erythro*-**3b**: $^1$H NMR (200 MHz, $CDCl_3$, TMS) $\delta$ 0.95 (t, $J$ = 7.5 Hz, 3 H), 1.19 (s, 9 H), 1.60−1.90 (m, 2 H), 2.03 (s, 3 H), 3.76 (s, 3 H), 4.78−4.96 (m, 2 H), 6.44 (br d, 1 H).

**Methyl 2-(*N*-Acetylamino)-3-pivaloyloxyheptanoate (3c).** In 57% yield (*erythro*/*threo* = 79/21): white solid. *erythro*-**3c**: $^1$H NMR (200 MHz, $CDCl_3$, TMS) $\delta$ 0.84−0.95 (m, 3 H), 1.19 (s, 9 H), 1.23−1.42 (m, 4 H), 1.47−1.85 (m, 2 H), 2.03 (s, 3 H), 3.76 (s, 3 H), 4.82 (dd, $J$ = 8.3, 2.9 Hz, 1 H), 4.98 (ddd, $J$ = 9.1, 5.0, 2.9 Hz, 1 H), 6.44 (br d, 1 H).

**Methyl 2-(*N*-Acetylamino)-3-phenyl-3-pivaloyloxypropanoate (3d).** In 76% yield (*erythro*/*threo* = 90/10): white solid. *erythro*-**3c**: $^1$H NMR (200 MHz, $CDCl_3$, TMS) $\delta$ 1.24 (s, 9 H), 2.00 (s, 3 H), 3.72 (s, 3 H), 5.22 (dd, $J$ = 8.9, 4.3 Hz, 1 H), 5.94 (br d, 2 H), 6.13 (d, $J$ = 4.3 Hz, 1 H), 7.25−7.42 (m, 5 H).

**Methyl (*E*)-2-(*N*-Acetylamino)-3-pivaloyloxy-2-butenoate (4a).** *tert*-Butyl hypochlorite (229 mg, 2.1 mmol) was added to a solution of **3a** (493 mg, 1.9 mmol) in benzene (4 mL). After the solution was stirred at room temperature for 120 h, DABCO (256 mg, 2.3 mmol) was added at 0 °C. After being stirred at room temperature for 3 h, the mixture was filtered through Celite pad and evaporated under reduced pressure. The residue was purified by flash column chromatography (*n*-hexane/AcOEt = 1/1), giving 351 mg (72%) of **4a**: white solid; mp 110−113 °C; $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 1.29 (s, 9 H), 1.99 (s, 3 H),

2.13 (s, 3 H), 3.72 (s, 3 H), 6.69 and 6.33 (a pair of br s, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 18.5, 22.9, 26.8, 39.0, 52.1, 117.3, 155.5, 163.5, 169.2, 175.9; IR (KBr) 3312, 1746, 1670 cm$^{-1}$. Anal. Calcd for $C_{12}H_{19}NO_5$: C, 56.02; H, 7.44; N, 5.44. Found: C, 55.72; H, 7.49; N, 5.40.

**Methyl (*E*)-2-(*N*-Acetylamino)-3-pivaloyloxy-2-pentenoate (4b).** In 69% yield: white solid; mp 87−89 °C; $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 1.06 and 1.08 (a pair of t, $J$ = 7.6 and 7.5 Hz, 3 H), 1.31 and 1.34 (a pair of s, 9 H), 2.12 and 2.00 (a pair of s, 3 H), 2.40 and 2.51 (a pair of q, $J$ = 7.6 and 7.5 Hz, 2 H), 3.71 and 3.74 (a pair of s, 3 H), 6.80 and 6.39 (a pair of br s, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 9.61, 22.8, 24.8, 27.0, 39.1, 52.0, 116.7, 159.0, 163.6, 169.8, 175.8; IR (KBr) 3292, 1756, 1734, 1668 cm$^{-1}$. Anal. Calcd for $C_{13}H_{21}NO_5$: C, 57.55; H, 7.80; N, 5.16. Found: C, 57.50; H, 8.05; N, 5.01.

**Methyl (*E*)-2-(*N*-Acetylamino)-3-pivaloyloxy-2-heptenoate (4c).** In 68% yield: white solid; mp 91−94 °C; $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 0.89 (t, $J$ = 7.3 Hz, 3 H), 1.18−1.53 (m, 4 H), 1.30 (s, 9 H), 2.11 and 2.00 (a pair of s, 3 H), 2.36 and 2.47 (a pair of t, $J$ = 7.6 and 7.3 Hz, 2 H), 3.71 and 3.73 (a pair of s, 3 H), 6.83 and 6.41 (a pair of br s, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 13.7, 22.4, 23.0, 27.0, 27.5, 31.3, 39.1, 52.1, 117.1, 158.7, 163.6, 169.6, 175.7; IR (KBr) 3296, 1762, 1734, 1668 cm$^{-1}$; HRMS(FAB) calcd for $C_{15}H_{26}NO_5$ (M + H)$^+$ 300.1811, found 300.1815.

**Methyl (*E*)-2-(*N*-Acetylamino)-3-phenyl-3-pivaloyloxy-2-propenoate (4d).** In 91% yield: white solid; $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 1.27 (s, 9 H), 1.99 (s, 3 H), 3.79 (s, 3 H), 6.93 and 6.46 (a pair of br s, 1 H), 7.34−7.47 (m, 5 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 22.7, 26.8, 38.9, 52.4, 118.7, 127.8, 128.7, 130.0, 133.3, 148.6, 164.0, 169.2, 175.6.

**General Procedure of Asymmetric Hydrogenation of 2.** A solution of $[Rh(COD)_2]ClO_4$ (4.2 mg, 10 $\mu$mol) and (*R*,*R*)-(*S*,*S*)-PrTRAP (7.2 mg, 11 $\mu$mol) in 1,2-dichloroethane (2.0 mL) was stirred at room temperature for 10 min, and **2** (1.0 mmol) was added. Immediately, the flask was cooled at −78 °C, successively evacuated, and filled with hydrogen in the flask. After 24 h of stirring at 20 °C, the mixture was directly purified by flash column chromatography, giving optically active *erythro*-**5**.

**Methyl (2*S*,3*S*)-2-(*N*-Acetylamino)-3-(dimethylthexylsiloxy)butanoate (5a).** Colorless oil; $[\alpha]^{20}_D$ = +54.3 (*c* 1.01, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 0.07 (s, 3 H), 0.08 (s, 3 H), 0.82 (s, 3 H), 0.83 (s, 3 H), 0.86 (d, $J$ = 6.9 Hz, 3 H), 0.87 (d, $J$ = 6.9 Hz, 3 H), 1.27 (d, $J$ = 6.5 Hz, 3 H), 1.59 (septet, $J$ = 6.9 Hz, 1 H), 2.02 (s, 3 H), 3.75 (s, 3 H), 4.09 (dq, $J$ = 6.5, 3.3 Hz, 1 H), 4.52 (dd, $J$ = 8.0, 3.3 Hz, 1 H), 6.22 (br d, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ −3.2, −2.7, 18.4, 18.5, 20.0, 20.2, 20.6, 23.1, 24.7, 34.1, 52.0, 58.3, 69.9, 169.4, 170.5; IR (neat) 3304, 1756, 1660 cm$^{-1}$. Anal. Calcd for $C_{15}H_{31}NO_4Si$: C, 56.74; H, 9.84; N, 4.41. Found: C, 56.50; H, 10.00; N, 4.28.

**Methyl (2*S*,3*S*)-2-(*N*-Acetylamino)-3-(*tert*-butyldimethylsiloxy)butanoate (5b).** Colorless oil; $[\alpha]^{20}_D$ = +47.1 (*c* 0.32, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 0.04 (s, 3 H), 0.05 (s, 3 H), 0.87 (s, 9 H), 1.27 (d, $J$ = 6.6 Hz, 3 H), 2.03 (s, 3 H), 3.76 (s, 3 H), 4.09 (dq, $J$ = 3.3, 6.6 Hz, 1 H), 4.53 (dd, $J$ = 8.3, 3.3 Hz, 1 H), 6.26 (br d, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ −5.2, −4.7, 17.8, 20.6, 23.2, 25.5, 52.1, 58.3, 69.9, 169.5, 170.6; IR (neat) 3292, 1750, 1660 cm$^{-1}$.

**Methyl (2*S*,3*S*)-2-(*N*-Acetylamino)-3-(*tert*-butyldimethylsiloxy)pentanoate (5e).** Colorless oil; $[\alpha]^{20}_D$ = +47.2 (*c* 1.02, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 0.05 (s, 3 H), 0.06 (s, 3 H), 0.88 (s, 9 H), 0.98 (t, $J$ = 7.5 Hz, 3 H), 1.50−1.73 (m, 2 H), 2.03 (s, 3 H), 3.75 (s, 3 H), 3.85 (dt, $J$ = 3.2, 6.7 Hz, 1 H), 4.67 (dd, $J$ = 7.8, 3.2 Hz, 1 H), 6.20 (br d, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ −4.8, −4.5, 9.9, 17.9, 23.2, 25.6, 27.2, 52.0, 56.2, 75.4, 169.4, 170.6; IR (neat) 3296, 1750, 1660 cm$^{-1}$. Anal. Calcd for $C_{14}H_{29}NO_4Si$: C, 55.41; H, 9.63; N, 4.62. Found: C, 55.14; H, 9.80; N, 4.57.

**Methyl (2*S*,3*S*)-2-(*N*-Acetylamino)-3-(*tert*-butyldimethylsiloxy)hexanoate (5f).** Colorless oil; $[\alpha]^{20}_D$ = +49.6 (*c* 1.00, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 0.05 (s, 3 H), 0.06 (s, 3 H), 0.87 (s, 9 H), 0.94 (t, $J$ = 7.2 Hz, 3 H), 1.25−1.66 (m, 4 H), 2.03 (s, 3 H), 3.75 (s, 3 H), 3.93 (dt, $J$ = 3.0, 6.5 Hz, 1 H), 4.65 (dd, $J$ = 7.8, 3.0 Hz, 1 H), 6.22 (br d, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ −4.8, −4.6, 14.0, 17.9, 18.7, 23.2, 25.6, 36.5, 52.1, 56.7, 73.8, 169.4, 170.5; IR (neat) 3304, 1750, 1660 cm$^{-1}$. Anal. Calcd for $C_{15}H_{31}NO_4Si$: C, 56.74; H, 9.84; N, 4.41. Found: C, 57.03; H, 9.83; N, 4.23.

**Methyl (2*S*,3*R*)-2-(*N*-Acetylamino)-3-(*tert*-butyldimethylsiloxy)-4-methoxybuanoate (5g).** Yellow oil; $[\alpha]^{20}_D$ = +43.6 (*c* 1.00, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 0.065 (s, 3 H), 0.069 (s, 3 H), 0.87 (s, 9 H), 2.03 (s, 3 H), 3.36 (s, 3 H), 3.39 (dd, $J$ = 10.1, 5.9 Hz, 1 H), 3.53 (dd, $J$ = 10.1, 5.3 Hz, 1 H), 3.75 (s, 3 H), 4.13 (dt, $J$ = 3.5, 5.6 Hz, 1 H), 4.76 (dd, $J$ = 8.3, 3.5 Hz, 1 H), 6.38 (br d, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ −5.3, −4.7, 18.0, 23.1, 25.6, 52.2, 55.7, 59.0, 72.1, 74.6, 169.6, 170.4; IR (neat) 3304, 1754, 1662 cm$^{-1}$. Anal. Calcd for $C_{14}H_{29}NO_5Si$: C, 52.63; H, 9.14; N, 4.38. Found: C, 52.45; H, 9.41; N, 4.27.

**Diethyl (2*S*,3*S*)-2-(*N*-Acetylamino)-3-(*tert*-butyldimethylsiloxy)pimelate (5h).** Colorless oil; $[\alpha]^{20}_D$ = +42.3 (*c* 1.03, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 0.05 (s, 3 H), 0.06 (s, 3 H), 0.87 (s, 9 H), 1.26 (t, $J$ = 7.2 Hz, 3 H), 1.29 (t, $J$ = 7.1 Hz, 3 H), 1.59−1.83 (m, 4 H), 2.03 (s, 3 H), 2.34 (t, $J$ = 7.2 Hz, 2 H), 3.94 (dt, $J$ = 2.7, 6.6 Hz, 1 H), 4.13 (q, $J$ = 7.1 Hz, 2 H), 4.19 (dq, $J$ = 10.8, 7.2 Hz, 1 H), 4.25 (dq, $J$ = 10.8, 7.2 Hz, 1 H), 4.61 (dd, $J$ = 2.7, 7.7 Hz, 1 H), 6.26 (br d, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ −4.8, −4.6, 14.1, 17.9, 21.1, 23.2, 25.6, 33.8, 34.1, 56.5, 60.2, 61.4, 73.7, 169.4, 169.8, 173.4; IR (neat) 3320, 1740, 1666 cm$^{-1}$. Anal. Calcd for $C_{19}H_{37}NO_6Si$: C, 56.54; H, 9.24; N, 3.47. Found: C, 56.64; H, 9.52; N, 3.42.

**General Procedure of Asymmetric Hydrogenation of 4.** A solution of $[Rh(COD)_2]BF_4$ (1.0 mg, 2.5 $\mu$mol) and (*R*,*R*)-(*S*,*S*)-PrTRAP (1.8 mg, 2.7 $\mu$mol) in 2-propanol (1.0 mL) was stirred at room temperature for 10 min, and **4** (0.25 mmol) was added. Immediately, the flask was cooled at −78 °C, successively evacuated, and filled with hydrogen in the flask. After 24 h of stirring at 20 °C, the solution was evaporated under reduced pressure. The residue was purified by flash column chromatography, giving optically active *threo*-**6**.

**Methyl (2*S*,3*R*)-2-(*N*-Acetylamino)-3-pivaloyloxybutanoate (6a).** Colorless oil; $[\alpha]^{20}_D$ = +60.7 (*c* 1.03, $CHCl_3$). The optical rotation of authentic (2*S*,3*R*)-**6a** was $[\alpha]^{20}_D$ = +61.5 (*c* 1.01, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 1.17 (s, 9 H), 1.26 (d, $J$ = 6.3 Hz, 3 H), 2.11 (s, 3 H), 3.72 (s, 3 H), 4.83 (dd, $J$ = 9.3, 3.0 Hz, 1 H), 5.37 (dq, $J$ = 3.0, 6.3 Hz, 1 H), 6.05 (br d, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 16.7, 23.1, 27.0, 38.7, 52.6, 55.4, 70.2, 170.4, 170.5, 177.3; IR (neat) 3320, 1756, 1740, 1660. Anal. Calcd for $C_{12}H_{21}NO_5$: C, 55.58; H, 8.16; N, 5.40. Found: C, 55.36; H, 8.14; N, 5.36.

**Methyl (2*S*,3*R*)-2-(*N*-Acetylamino)-3-pivaloyloxypentanoate (6b).** White solid; mp 49−53 °C; $[\alpha]^{20}_D$ = +73.0 (*c* 0.996, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 0.93 (t, $J$ = 7.5 Hz, 3 H), 1.19 (s, 9 H), 1.57−1.69 (m, 2 H), 2.09 (s, 3 H), 3.72 (s, 3 H), 4.88 (dd, $J$ = 9.3, 2.7 Hz, 1 H), 5.23 (ddd, $J$ = 7.5, 6.6, 2.7 Hz, 1 H), 6.00 (br d, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 9.6, 23.1, 24.3, 27.1, 38.9, 52.6, 53.9, 74.6, 170.3, 170.8, 177.5; IR (KBr) 3308, 1762, 1738, 1658 cm$^{-1}$. Anal. Calcd for $C_{13}H_{23}NO_5$: C, 57.12; H, 8.48; N, 5.12. Found: C, 56.95; H, 8.63; N, 4.84.

**Methyl (2*S*,3*R*)-2-(*N*-Acetylamino)-3-pivaloyloxyheptanoate (6c).** Pale yellow oil; $[\alpha]^{20}_D$ = +69.8 (*c* 1.02, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 0.89 (t, $J$ = 6.9 Hz, 3 H), 1.19 (s, 9 H), 1.24−1.36 (m, 4 H), 1.51−1.64 (m, 2 H), 2.09 (s, 3 H), 3.71 (s, 3 H), 4.85 (dd, $J$ = 9.5, 2.7 Hz, 1 H), 5.29 (ddd, $J$ = 7.7, 6.3, 2.7 Hz, 1 H), 5.97 (br d, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 13.8, 22.2, 23.1, 27.1, 27.2, 30.7, 38.8, 52.5, 54.2, 73.2, 170.2, 170.8, 177.4; IR (neat) 3320, 1740, 1660 cm$^{-1}$. Anal. Calcd for $C_{15}H_{27}NO_5$: C, 59.78; H, 9.03; N, 4.65. Found: C, 59.67; H, 8.96; N, 4.51.

**Methyl (2*S*,3*R*)-2-(*N*-Acetylamino)-3-pivaloyloxy-3-phenylpropanoate (6d).** White solid; $^1$H NMR (200 MHz, $CDCl_3$, TMS) 1.24 (s, 9 H), 1.94 (s, 3 H), 3.69 (s, 3H), 5.10 (dd, $J$ = 9.4, 4.3 Hz, 1 H), 6.00 (br d, 1 H), 6.23 (d, $J$ = 4.3 Hz, 1 H), 7.21−7.49 (m, 5 H).

**Hydrolysis of *erythro*-(2*S*,3*S*)-5a (L-(2*S*,3*S*)-*allo*-Threonine).** A mixture of *erythro*-(2*S*,3*S*)-**5a** (79 mg, 0.25 mmol, 95% ee) and 1 N hydrochloric acid (1.0 mL) was heated at 100 °C for 3 h. After evaporation under reduced pressure, the residue was purified by ion exchange column (Amberlite IR-120B, $H^+$ form), giving 33 mg (77%) of L-*allo*-threonine: $[\alpha]^{26}_D$ = +8.5 (*c* 0.45, $H_2O$), lit.[14] $[\alpha]^{24}_D$ = +9.3 (*c* 3.8, $H_2O$); $^1$H NMR (300 MHz, $D_2O$,

1,4-dioxane as external std at $\delta$ 3.55) $\delta$ 0.61 (d, $J$ = 6.6 Hz, 3 H), 2.95 (br s, 1 H), 3.62 (br q, 1 H).

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**Supporting Information Available:** Assignments of stereochemistry of **2**, **4**, **5**, and **6** and $^{1}$H and $^{13}$C NMR spectra of **2e**, **2g**, and **4c** (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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