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Article

(2*S*,3*R*)-3-하이드록시호모세린락톤의 입체선택적 합성 : 바이닐글라이신 OBO Ester 유도체의 입체선택적인 이중알콜화 반응

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Stereoselective Synthesis of (2*S*,3*R*)-3-Hydroxyhomoserine Lactone via *anti* Selective Dihydroxylation of an OBO Group-Protected Vinyl Glycine Analog

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초 록

(2*S*,3*R*)-3-hydroxyhomoserine lactone (HSL)은 생리학적 활성을 가지는 다양한 종류의 화합물을 합성하기 위한 중간체로 활용되어 왔다. 본 논문에서는 OBO ester로 보호된 바이닐글라이신 유도체에 이중알콜화 반응을 수행하여 효율적인 HSL 합성 결과를 보고하고자 한다. 바이닐글라이신의 비고리 conformation은 크기가 큰 OBO ester에 의해 조절되었으며 *N*-inside conformation을 통해 이중알콜화 반응이 진행됨으로써 높은 *anti* 선택성(> 10 : 1)을 얻을 수 있었다. 이러한 결과를 바탕으로 *N*-Cbz-L-serine을 출발물질로 사용하여 총 7단계 34%의 수율로 HSL을 합성할 수 있었다. 본 연구의 결과는 amino diol 구조를 가지는 다양한 생리활성 천연물들의 입체선택적인 합성에 유용하게 활용될 수 있을 것으로 기대된다.

Abstract

(2*S*,3*R*)-3-hydroxyhomoserine lactone (HSL) has been used as a key intermediate for the synthesis of various biologically active compounds. In this study, we demonstrated an efficient synthesis of HSL via *anti* selective dihydroxylation of a protected vinyl glycine analog with an oxabicyclo[2.2.2]octyl orthoester (OBO) ester group. Because the acyclic conformation of the substrate was efficiently controlled by the bulky OBO ester group, a diastereoselectivity of > 10 : 1 was obtained in the dihydroxylation reaction without the use of a chiral reagent. By using this result, the target compound **1** can be obtained from commercially available *N*-Cbz-L-serine **2** in seven steps with an overall yeid of 34%. This result could be applied to the stereoselective synthesis of biologically active molecules containing a vicinal amino diol moiety.

Keywords: *(2S,3R)-3-Hydroxyhomoserine lactone, Dihydroxylation, Vinyl glycine analog, Stereoselective synthesis, OBO ester*

1. Introduction

Osmium tetroxide (OsO_4)-catalyzed dihydroxylation of a chiral allylic amine is one of the simplest and most convenient methods to synthesize an amino diol moiety, which is found in a variety of natural products and synthetic compounds[1-3]. Due to the flexible conformation of acyclic allylic amines, many substrates often show low or inconsistent selectivity in the dihydroxylation reaction[4]. We have previously demonstrated that the acyclic conformation of chiral allylic amines can efficiently be controlled by *N*-protection groups and these strategies provided diastereoselective amino diols. For example, *N*-diarylmethylene[5-9] or *N*,*N*-diBoc[10] group-derived allylic amines provided enhanced stereochemical results compared to those with typically used *N*-carbamate or *N*-acyl groups. These methods afforded high diastereoselectivities without the use of chiral reagents or catalysts and moreover some of our results were better than those obtained using

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well-established Sharpless asymmetric dihydroxylation reactions.

Interestingly, the acyclic conformation of allylic amines was also determined by the side group of the substrate. We have also reported that the dihydroxylation of *N*-Boc or *N*-diarylmethylene group derivatives of monosubstituted allylic amines showed higher *anti* selectivities as the side alkyl group of the substrates became larger[5]. In particular, an allylic amine derived from *tert*-butyl glycine provided excellent *anti* selectivity (20 : 1)[11]. These observations suggested that a bulky OBO ester group in the monosubstituted allylic amine would induce good selectivity without any chiral agents. The resulting amino diol would be a useful synthetic intermediate because the OBO ester can easily be converted to other polar functional groups. In this study, we demonstrate the highly *anti* selective dihydroxylation of a protected vinyl glycine substrate with an OBO ester group and the facile synthesis of (2*S*,3*R*)-3-hydroxyhomoserine lactone (HSL 1) as an application of this synthetic method.

2. Experiments

2.1. General methods

Materials were obtained from commercial suppliers and were used without further purification. Methylene chloride was distilled from calcium hydride immediately prior to use. Similarly, THF was distilled from sodium benzophenone ketyl. MeOH was dried with molecular sieves (4 Å). Air- or moisture-sensitive reactions were conducted under nitrogen or argon atmosphere using oven-dried glassware and the standard syringe/septa technique. The reactions were monitored with a SiO_2 TLC plate under UV light (254 nm) followed by visualization with a ninhydrin solution. Column chromatography was performed on silica gel 60 (70~230 mesh). Optical rotations were determined at ambient temperature with a digital polarimeter and the average values of more than five measurements were considered. ^{1}H NMR spectra were acquired at 300 MHz in $CDCl_3$ unless stated otherwise and data were reported as follows in ppm (δ) against an internal standard (TMS, 0.0 ppm): chemical shift (multiplicity, integration, and coupling constant in Hz).

2.2. *O*-(*tert*-butyldimethylsilyl)-*N*-(benzyloxycarbonyl)-L-serine (3)

To an ice-cold solution of **2** (10.513 g, 43.946 mmol) in dimethylformamide (DMF, 30 mL), *tert*-butyldimethylsilyl chloride (TBDMSCl, 8.280 g, 54.933 mmol) and imidazole (8.973 g, 131.840 mmol) were added under stirring in a nitrogen atmosphere for 1 h at 0 ℃. After the mixture was warmed to room temperature and stirred for another 10 h. The reaction mixture was quenched by the addition of an aq. 50% NH_4Cl solution (30 mL). Then, the resulting mixture was extracted with Et_2O (30 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc = 4 : 1 to 1 : 1) to give **3** (14.770 g, 41.780 mmol, 95%) as a white solid. MP: 84 ℃; +31.4 (c 0.81, $CHCl_3$); ^{1}H NMR 0.05 (s, 6H), 0.86 (s, 9H), 3.84 (dd, 1H, *J* = 10.0, 4.0), 4.13 (dd, 1H, *J* = 10.0, 2.7), 4.43~4.47 (m, 1H), 5.12 (d, 1H, *J* = 12.2), 5.16 (d, 1H, *J* = 12.2), 5.58 (d, 1H, *J* = 8.1), 7.32~7.37 (m, 5H); ^{13}C NMR 5.6, 18.1, 25.7, 55.5, 63.3, 67.2, 128.2, 128.3, 128.6, 136.1, 156.1, 175.2; HRMS (EI) calcd for $C_{17}H_{27}NO_5Si$ $[M + H]^+$ 353.1658, found 353.1658.

2.3. *O*-(*tert*-butyldimethylsilyl)-*N*-(benzyloxycarbonyl)-L-serine-3-methyl-3-(hydroxymethyl)oxetane ester (4)

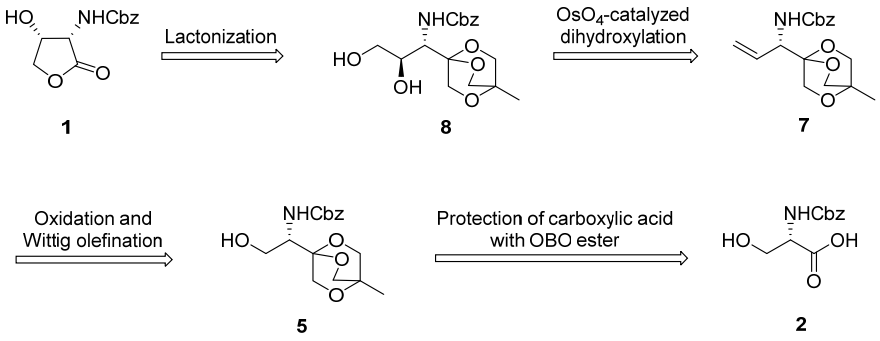
Carboxylic acid **3** (3.656 g, 10.343 mmol) was dissolved in dichloromethane (DCM, 50 mL) and then 3-methyl-3-oxetanemethanol (1.11 mL, 11.377 mmol), *N*,*N*'-dicyclohexylcarbodiimide (DCC, 2.347 g, 11.377 mmol) and 4-dimethylaminopyridine (DMAP) (0.063 g, 0.517 mmol) was added at 0 ℃. After 1 h, DCM was evaporated under reduced pressure and the residual mixture was filtered through a celite pad followed by rinsing with Et_2O (20 × 2 mL). Then, the solvent was evaporated under reduced pressure. The resulting residue was purified by SiO_2 column chromatography (hexane/EtOAc = 4 : 1) to give **4** (3.992 g, 9.122 mmol, 88%) as a colorless oil; +1.3 (c 0.85, $CHCl_3$); ^{1}H NMR 0.01 (s, 3H), 0.02 (s, 3H), 0.86 (s, 9H), 1.33 (s, 3H), 3.87 (dd, 1H, *J* = 10.1, 2.7), 4.46 (dt, 1H, *J* = 8.7, 2.7), 4.43~4.47 (m, 1H), 5.12 (d, 1H, *J* =12.2), 5.16 (d, 1H, *J* = 12.2), 5.58 (d, 1H, *J* = 8.7), 7.32~7.37 (m, 5H); ^{13}C NMR -5.6, -5.5, 18.2, 21.0, 25.7, 39.1, 55.5, 63.3, 67.2, 69.6, 79.4, 128.2, 128.3, 128.6, 136.1, 156.1, 170.5. HRMS (EI) calcd for $C_{22}H_{35}NO_6Si$ $[M]^+$ 437.2234, found 437.2233.

2.4. *O*-(*tert*-butyldimethylsilyl)-1-[*N*-(benzyloxycarbonyl)-(1*S*)-1-amino-2-ethanol]-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane (5)

Oxetanylmethyl ester **4** (6.867 g, 15.692 mmol) was dissolved in dry DCM (50 mL) and the resulting mixture was cooled to 0 ℃ under an argon atmosphere. $BF_3 \cdot OEt_2$ (1.0 mL, 7.846 mmol) diluted in DCM (5 mL) was added to the reaction mixture. After 30 min, the reaction mixture was warmed to room temperature. After 8 h, triethylamine (TEA, 10.9 mL, 78.46 mmol) was added to the reaction mixture and the reaction was proceeded for an additional 30 min. Then, a saturated aq. $NaHCO_3$ solution (30 mL) was added to the reaction mixture and the resulting mixture was extracted with DCM (30 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by SiO_2 column chromatography (hexane/EtOAc = 1 : 1) to give the OBO ester **5** (3.795 g, 11.737 mmol, 75%) as a white solid. MP: 104 ℃; -20.8 (c 0.75, $CHCl_3$); ^{1}H NMR 0.82 (s, 3H), 2.58 (br s, 1H), 3.67~3.71 (dd, 1H, *J* = 10.0, 4.0), 3.92 (s, 6H), 3.84~3.96 (m, 2H), 5.09 (d, 1H, *J* = 11.9), 5.15 (d, 1H, *J* = 11.9), 5.33 (d, 1H, *J* = 8.9), 7.31~7.37 (m, 5H); ^{13}C NMR 14.2, 30.5, 55.3, 61.8, 66.9, 72.7, 108.2, 128.0, 128.1, 128.4, 136.4, 156.4; HRMS (EI) calcd for $C_{16}H_{21}NO_6$ $[M]^+$ 323.1369, found 323.1369.

2.5. (1*S*)-Benzyl-(1-(4-methyl-2,5,7-trioxabicyclo[2.2.2]octan-1-yl) allyl)carbamate (7)

OBO ester **5** (0.624 g, 1.930 mmol) was dissolved in dry DCM (10 mL) under a nitrogen atmosphere. Dess-Martin periodinane (15 wt% solution in DCM (6.5 mL, 3.281 mmol) was added to the reaction mixture at 0 ℃. The mixture was stirred for 1.5 h at room temperature. After the reaction was complete, a saturated aq. Na_2SO_3 solution (20 mL) was added to quench the reaction. The aqueous layer was washed



Scheme 1. Retrosynthetic analysis of HSL 1.

with Et_2O (30 mL × 2). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated to give the crude aldehyde **6** as a white solid. The crude product was used without further purification. To a solution of methyltriphenylphosphonium bromide (1.379 g, 3.860 mmol) in dry THF (30 mL) at -78 ℃, KHMDS (0.5 M in toluene, 11.6 mL, 5.790 mmol) was added and stirred at room temperature. After 1 h, the abovementioned crude aldehyde in dry THF (10 mL) was added dropwise at -78 ℃. The resulting mixture was stirred for 1.5 h at room temperature and then it was extracted with Et_2O (30 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by SiO_2 column chromatography (hexane/EtOAc = 1 : 1) to give **7** (0.433 g, 1.356 mmol, 70%) as a colorless oil. ^{1}H NMR 0.82 (s, 3H), 3.91 (s, 6H), 4.41 (br s, 1H), 5.08~5.13 (m, 3H), 5.22 (d, 1H, *J* = 10.4), 5.28 (d, 1H, *J* = 17.2), 5.92 (m, 1H), 7.32~7.37 (m, 5H); ^{13}C NMR 14.3, 30.7, 57.1, 66.9, 72.9, 107.9, 116.7, 128.1, 128.3, 128.5, 133.2, 136.5, 155.9; HRMS (EI) calcd for $C_{17}H_{27}NO_5Si$ $[M]^+$ 319.1420, found 319.1419.

2.6. Benzyl ((1*S*,2*R*)-2,3-dihydroxy-1-(4-methyl-2,5,7-trioxabicyclo [2.2.2]octan-1-yl)propyl)carbamate (8)

To a solution of olefin **7** (302 mg, 0.946 mmol) in THF (10 mL), NMO (0.244 g, 2.081 mmol) and OsO_4 (0.024 g. 0.095 mmol) were added at room temperature. The resulting mixture was stirred for 24 h at room temperature. After the reaction was complete, a saturated aqueous Na_2SO_3 solution (10 mL) was added. The aqueous layer was extracted with Et_2O (20 mL × 2). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product. The crude mixture was purified by silica gel column chromatography (hexane: EtOAc = 1 : 4) to give a diastereomeric mixture of the diol **8** in quantitative yield as a waxy oil. -3.2 (c 0.34, $CHCl_3$); ^{1}H NMR 0.82 (s, 3H) 2.83 (br s, 1H), 3.62~3.74 (br s, 3H) 3.82 (br s, 1H), 3.91 (s, 6H), 5.12 (q, 2H, *J* = 12.1), 5.24 (d, 1H, *J* = 9.0), 7.32~7.37 (m, 5H); ^{13}C NMR 14.3, 30.7, 55.8, 63.6, 67.5, 71.7, 72.9, 108.8, 128.3, 128.4, 128.7, 136.3, 157.2; For acetylation, the crude diol was dissolved in DCM (20 mL) and then Ac_2O (0.4 mL, 4.729 mmol), TEA (0.66 mL, 4.729 mmol), and DMAP (11.6 mg, 0.095 mmol) were added. After 3 h at room temperature, the reaction was quenched by adding an aqueous $NaHCO_3$ solution (20 mL). The resulting mixture was then extracted with Et_2O (20 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (hexane/EtOAc = 2 : 1) to give **9** (0.352 g, 0.806 mmol, 85%) as a waxy solid (> 10 : 1 diastereomeric mixture).

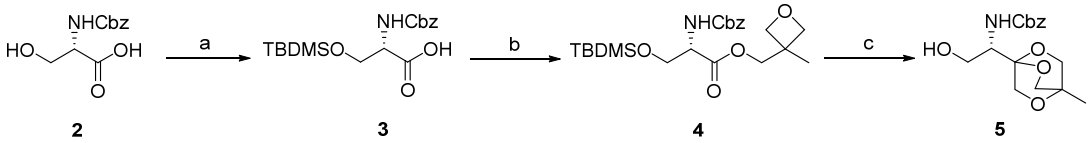
2.7. Benzyl ((2*S*,3*R*)-3-hydroxy-1-oxo-tetrahydrofuran-2-yl)carbamate (1)

To a solution of amino diol **8** (62 mg, 0.175 mmol), HCl in 1,4-dioxane (15 mL) was added. The reaction mixture was stirred at room temperature under a nitrogen atmosphere. After 3 h, a saturated aq. $NaHCO_3$ solution (20 mL) was added at 0 ℃. The resulting solution was extracted with Et_2O (20 mL × 2) and then the organic layer was rinsed with distilled water (20 mL × 2) to remove residual acid. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product. The crude mixture was purified by silica gel column chromatography (hexane/EtOAc = 1 : 2) to give a single isomer of the lactone **1** (34.2 mg, 0.136 mmol, 78%) as a white solid.; MP 148 ℃; +0.1 (c 0.32, EtOAc); ^{1}H NMR (DMSO-d_6) 4.11 (d, 1H, *J* = 9.7), 4.32 (m, 1H), 4.43 (dd, 1H, *J* = 3.0, 10.0), 4.70 (q, 1H, *J* = 4.5), 5.08 (s, 2H), 5.74 (s, 1H), 7.32~7.39 (m, 5H), 7.54 (d, 1H, *J* = 9.2); ^{13}C NMR (DMSO-d_6) δ 54.3, 65.7, 67.3, 73.2, 127.8, 128.2, 128.3, 136.6, 156.3, 174.4.

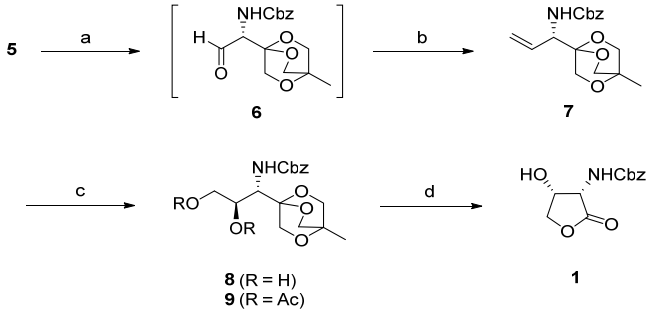
3. Results and Discussion

The retrosynthetic analysis for the synthesis of HSL **1** is outlined in Scheme 1. The suitably protected serine **5** could be prepared from the *N*-Cbz protected L-serine **2** in 3 steps. The key step of this strategy is the stereoselective dihydroxylation of the monosubstituted olefin **7**. Due to the large size of the OBO ester group, the dihydroxylation reaction of **7** may provide high *anti* selectivity. Finally, the final product **1** would be obtained by acid-mediated cyclization reaction of the amino diol **8**.

Synthetic steps for obtaining the OBO-protected serine derivative **5** are shown in Scheme 2. First, the side alcohol group of **2** was protected with *tert*-butyldimethylsilyl (TBDMS) and then esterification of carboxylic acid using 1.1 equivalent of 3-methyl-3-oxetanemethanol



Scheme 2. Synthesis of protected serine 5. Reagent and conditions: a) TBDMSCl, imidazole, DMF, 0 ℃ to rt, 95%; b) 3-methyl-3-oxetanemethanol, DCC, DMAP, DCM, 0 ℃ to rt, 88%; c) $BF_3 \cdot OEt_2$ under Ar, DCM, 0 ℃, 75%



Scheme 3. Synthesis of HSL 1 via OsO_4-catalyzed dihydroxylation. Reagent and conditions: a) Dess-Martin periodinane, DCM, rt; b) Ph_3PCH_3Br, KHMDS, THF, -78 ℃ to rt, 70% (from 5 over 2 steps); (c) OsO_4, NMO, THF, rt, quantitative (for 8) and then Ac_2O, TEA, DMAP, DCM, 85% (for 9); (d) 4 M HCl in dioxane, rt, 3 h, 78%

gave the ester **4** in 84% yield in 2 steps. To prepare the similar oxetanylmethyl esters, the previously reported procedures utilized the use of an excess of alcohols[12] or a tosylated 3-methyl-3-oxetanemethanol [13,14]. Using a modified procedure in this study, the desired oxetanylmethyl ester could be obtained in higher yield and shorter reaction time and therefore the present method can be a more convenient route than the previously reported ones. Next, treatment of the ester **4** with $BF_3 \cdot OEt_2$ at 0 ℃ afforded the OBO ester **5** with concomitant removal of the TBDMS group.

An oxidation of the primary alcohol group in **5** by using Dess-Martin periodinane followed by Wittig olefination provided the corresponding monosubstituted olefin **7** in 70% over 2 steps (scheme 3). The OsO_4-catalyzed dihydroxylation of the chiral allylic amine **7** was proceeded in non-aqueous condition at room temperature. This reaction was highly efficient and thus the resulting amino diol **8** was isolated in quantitative yield. Due to some broad peaks in the ^{1}H-NMR spectrum, the diastereomeric ratio of **8** could not be measured exactly. After *in situ* acetylation of the crude diol product, the *anti* to *syn* ratio of the diacetate **9** was determined to be more than 10 : 1.

The diastereoselectivity observed in the dihydroxylation reaction of **7** can be explained by the following transition state model (Figure 1). According to the Houk model, a deactivating substituent such as the *N*-Cbz group may take up the "*N*-inside" conformer to minimize its orbital overlap with the C-C double bond, when there is no severe $A^{1,3}$ allylic strain[11,15]. On the other hand, the "*N*-outside conformer" is strongly disfavored due to the large repulsive interaction between the OBO ester and vinylic proton. Therefore, the reaction would take place in the "*N*-inside" conformer of **7** and then addition of OsO_4 from the less hindered side (bottom) would induce a highly *anti* selective result.

As an application of the present method, (2*S*,3*R*)-3-hydroxyhomoserine lactone (HSL **1**) could be synthesized via a simple procedure. For conversion of the amino diol to the target compound, **8** was treated with HCl in MeOH (acetyl chloride in MeOH) at 0 ℃ and then heated under reflux. The lactone **1** was obtained in 75% yield; however, unknown impurities mixed with the product could not be separated completely. As an alternative route, we utilized HCl in dioxane, which is an aprotic solvent, for the final cyclization step (Scheme 3). Under this condition, the lactonization of **8** proceeded at room temperature and the desired product was obtained with a much lower amount of impurity. After SiO_2 column purification of the crude compound, HSL was obtained as a single isomer in 78% yield.[16]

HSL has been utilized as a useful building block for stereoselective synthesis of various biologically active compounds such as rhizobitoxine[17], quorum sensing autoinducer[18], and a key intermediate of potent drug candidates (Scheme 4)[19,20]. For the synthesis of HSL, several previous studies adopted a two-steps strategy; 1) dihydroxylation of a monosubstituted allylic amine and then 2) lactonization of the resulting amino diol unit under acidic condition[17,18]. These studies attempted the OsO_4-catalyzed dihydroxylation of vinyl glycine analogues, but most of the results showed low or mixed diastereoselecti- vities. For example, the *N*-Cbz protected vinyl glycine methyl ester, which is an analog of **7**, provided only a modest *anti* selectivity (5 : 1) or reversed syn selectivity (1 : 1.3 to 1 : 12.2) in several different osmylation conditions[18]. Therefore, the *anti* selectivity obtained by the current method is a noteworthy result when compared with previous results. Indeed, controlling the acyclic conformation of an allylic amine by a bulky OBO ester group successfully provided the desired stereochemical outcome with a good diastereoselectivity and chemical yield.

4. Conclusion

We demonstratedthe efficient and stereoselective synthesis of (2*S*, 3*R*)-3-hydroxyhomoserine lactone using the *anti* selective dihydroxylation of a protected vinyl glycine analog. The target product **1** was synthesized in 7 steps in 34% overall yield from commercially available *N*-Cbz-L-serine **2**. The high selectivity was achieved without the use of chiral agents and therefore the OBO ester group in the monosubstituted allylic amine proved to be a useful stereodirecting group in the OsO_4-catalysed dihydroxylation. Our synthetic route for **1** compared favorably with several previously reported techniques; moreover, it is anticipated that the current method could be applied in the synthesis of other important bioactive compounds.

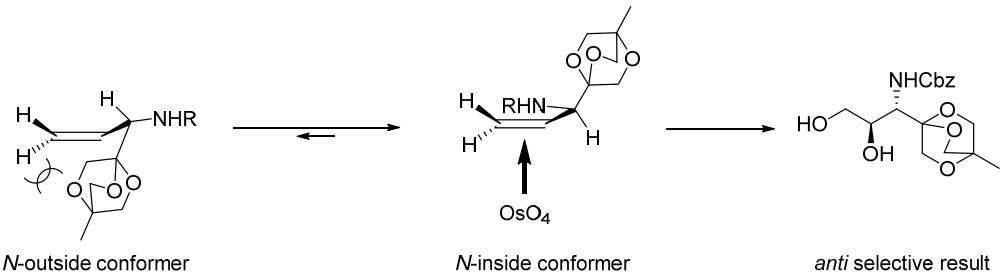
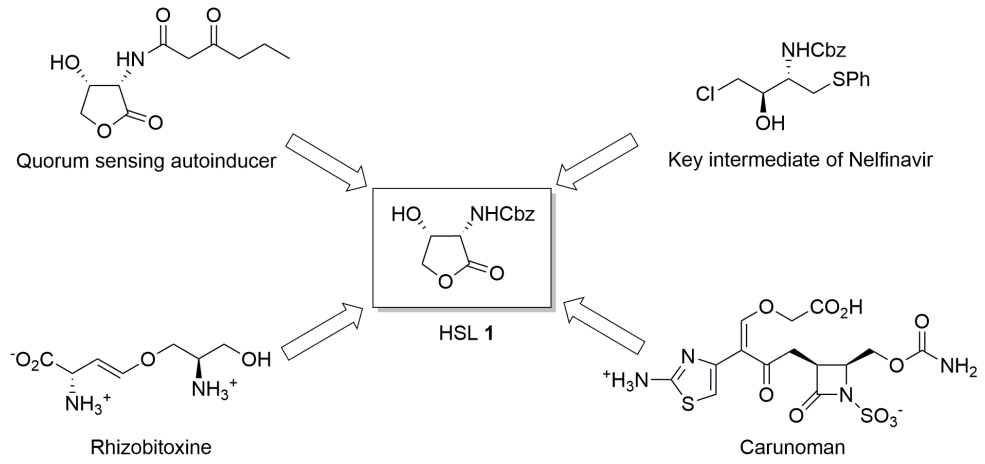


Figure 1. Probable transition state model (R = Cbz).



Scheme 4. Biologically active compounds prepared from HSL.

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References

1. C.-X. Ye, Y. Y. Melcamu, H.-H. Li, J.-T. Cheng, T.-T. Zhang, Y.-P. Ruan, X. Zheng, X. Lu, and P.-Q. Huang, Dual catalysis for enantioselective convergent synthesis of enantiopure vicinal amino alcohols, *Nat. Commun.*, **9**, 410-418 (2018).
2. M. M. Heravi, T. B. Lashaki, B. Fattahi, and V. Zadsirjan, Application of asymmetric Sharplessaminohydroxylation in total synthesis of natural products and some synthetic complex bio-active molecules, *RSC Adv.*, **8**, 6634-6659 (2018).
3. O. K. Karjalainen and A. M. P. Koskinen, Diastereoselective synthesis of vicinal amino alcohols, *Org. Biomol. Chem.*, **10**, 4311-4326 (2012).
4. J. Jeon, N. Shin, and Y. G. Kim, Stereocontrolled dihydroxylation reactions of acyclic allylic amines, *Appl. Chem. Eng.*, **25**, 437-446 (2014).
5. J. S. Oh, D. Y. Park, B. S. Song, J. G. Bae, S. W. Yoon, and Y. G. Kim, *anti* Selective dihydroxylation by the ketimine derivatives of the allylic amine in monosubstituted olefins, *Tetrahedron Lett.*, **43**, 7209-7212 (2002).
6. J. S. Oh, J. Jeon, D. Y. Park, and Y. G. Kim, Stereoselective dihydroxylation reactions of reactions of γ-amino-α,β-unsaturated esters via their aryl ketimine derivatives, *Chem. Commun.*, **41**, 770-771 (2005).
7. J. Jeon, S.-K. Hong, J. S. Oh, and Y. G. Kim, Stereoselective synthesis of protected (2*R*,3*R*,4*S*)-4,7-diamino-2,3-dihydroxyheptanoic acid: A novel amino acid of callipeltins A and D, *J. Org. Chem.*, **71**, 3310-3313 (2006).
8. J. Jeon, J. H. Lee, J.-W. Kim, and Y. G. Kim, *syn*-Selective dihydroxylation of γ-amino-α,β-unsaturated (*Z*)-esters from D-serine: Stereoselective synthesis of D-iminolyxitol, *Tetrahedron: Asymmetry*, **18**, 2448-2453 (2007).
9. J. Jeon, N. Shin, J. H. Lee, and Y. G. Kim, Efficient stereoselective synthesis of (2*S*,3*S*,4*S*)-3,4-dihydroxyglutamic acid, *Appl. Chem. Eng.*, **25**, 392-395 (2014).
10. J. Jeon, M. Shin, J. W. Yoo, J. S. Oh, J. G. Bae, S. H. Jung, and Y. G. Kim, Highly *anti*-selective dihydroxylation of 1,2-dialkyl substituted (*Z*)-allylic amines: Stereoselective synthesis of a D-*ribo*-phytosphingosine derivative, *Tetrahedron Lett.*, **48**, 1105-1108 (2007).
11. J. Jeon, S.-H Kim, J. H. Lee, and Y. G. Kim, *anti*-Selective dihydroxylations of monosubstituted allylic amine and γ-amino-α,β-unsaturated (*E*)-esters by bulky alkyl groups, *Bull. Korean Chem. Soc.*, **30**, 1003-1008 (2009).
12. M. A. Blaskovich and G. A. Lajoie, Synthesis of a chiral serine aldehyde equivalent and its conversion to chiral α-amino acid derivatives, *J. Am. Chem. Soc.*, **115**, 5021-5030 (1993).
13. M. A. Blaskovich, G. Evindar, N. G. W. Rose, S. Wilkinson, Y. Luo, and G. A. Lajoie, Stereoselectivesynthesis of *threo* and *erythro* β-hydroxyand β-disubstituted-β-hydroxy α-amino acids, *J. Org.*

Chem., **63**, 3631-3646 (1998).
14. D. B. Hansen, X. Wan, P. J. Carroll, and M. M. Joullié, Stereoselectivesynthesis of four stereoisomers of β-methoxytyrosine, a component of callipeltin A, *J. Org. Chem.*, **70**, 3120-3126 (2005).
15. K. N. Houk, H. Y. Duh, Y. D. Wu, and S. R. Moses, Steric models for stereoselectivity of nitrile oxide cycloadditions to chiral alkenes, *J. Am. Chem. Soc.*, **108**, 2754-2755 (1986).
16. M. Koh, *anti-Selective dihydroxylation of an OBO ester derivative of vinyl glycine: Application to stereoselective synthesis of (2S,3R)-3-hydroxyhomoserine lactone*, Ph. D. Dissertation, Seoul National University, Seoul, Republic of Korea (2009).
17. M. C. Pirrung, D. S. Nunn, and A. T. McPhail, Synthesis and absolute configuration of hydroxythreonine, a biosynthetic precursor of rhizobitoxine in pseudomonas, *Bioorg. Med. Chem. Lett.*, **3**, 2095-2098 (1993).
18. J. A. Olsen, R. Severinsen, T. B. Rasmussen, M. Hentzer, M. Givskov, and J. Nielsen, Synthesis of new 3- and 4-substituted analogues of acyl homoserine lactone quorum sensing autoinducers, *Bioorg. Med. Chem. Lett.*, **12**, 325-328 (2002).
19. M. Ikunaka, J. Matsumoto, Y. Fujima, and Y. Hirayama, An enantioselective synthesis of (2*S*,3*R*)-3-(N-benzyloxycarbonyl)amino-1-chloro-4-phenylthiobutan-2-ol, a central intermediate of Nelfinavir, *Org. Process Res. Dev.*, **6**, 49-53 (2002).
20. V. P. Vassilev, T. Uchiyama, T. Kajimoto, and C.-H. Wong, An efficient chemo-enzymatic synthesis of α-amino-β-hydroxy-γ-butyrolactone, *Tetrahedron Lett.*, **28**, 5063-5064 (1995).