Tetrahedron 66 (2010) 3159–3164

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis of (−)-galantinic acid via iterative hydrolytic kinetic resolution and tethered aminohydroxylation

Abhishek Dubey, Shruti V. Kauloorkar, Pradeep Kumar *

Division of Organic Chemistry, National Chemical Laboratory, Homi Bhabha Road, Pune 411008, Maharashtra, India

ARTICLE INFO

Article history:
Received 6 January 2010
Received in revised form 25 February 2010
Accepted 26 February 2010
Available online 6 March 2010

Keywords:
Iterative hydrolytic kinetic resolution
Tethered aminohydroxylation
1,3-Diol
1,2-Aminoalcohol
Selectivity

ABSTRACT

A new synthetic strategy for (−)-galantinic acid is reported using iterative hydrolytic kinetic resolution and tethered aminohydroxylation as the key steps.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

(−)-Galantinic acid **1**, a nonproteinogenic amino acid, is a key component of the peptide antibiotic galantin I **2**, isolated from a culture broth of *Bacillus pulvifaciens*.[1] The originally proposed tetrahydropyranoid structure **3** of galantinic acid was later shown to be incorrect by total synthesis and was revised to **1** by Sakai and Ohfune[2] who also reported its first total synthesis[3](Fig. 1). The syntheses known for galantinic acid derive the asymmetry from chiral pool starting materials, such as serine aldehyde and mannitol etc.[4a–f] However, synthetic approaches involving achiral substrate as starting materials are rather scarce.[4g–h]

As a part of our research programme aimed at developing enantioselective synthesis of biologically active aminoalcohols,[5] we became interested in devising a new route to (−)-galantinic acid based on synthetic protocol developed by us for 1,3-diol[6] using

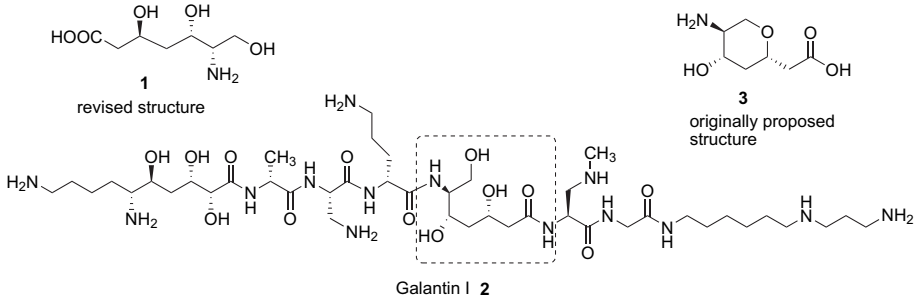


Figure 1. Structures of galantinic acid **1**, galantin I **2** and originally proposed structure of galantinic acid **3**.

potent biological activity and unique structure with an array of functionalities makes galantinic acid an attractive synthetic target of considerable interest. Various methods for its synthesis have been reported in the literature.[4] Most of the enantioselective hydrolytic kinetic resolution[7] (HKR) and also by tethered aminohydroxylation (TA).[8] The tethered aminohydroxylation has emerged as a powerful method of preparing vicinal aminoalcohols in a regio- and stereoselective manner. This method overcomes the problem of low regioselectivity mainly encountered during the asymmetric aminohydroxylation,[9] a recent discovery of Sharpless to introduce amine and alcohol functionality in a single step in

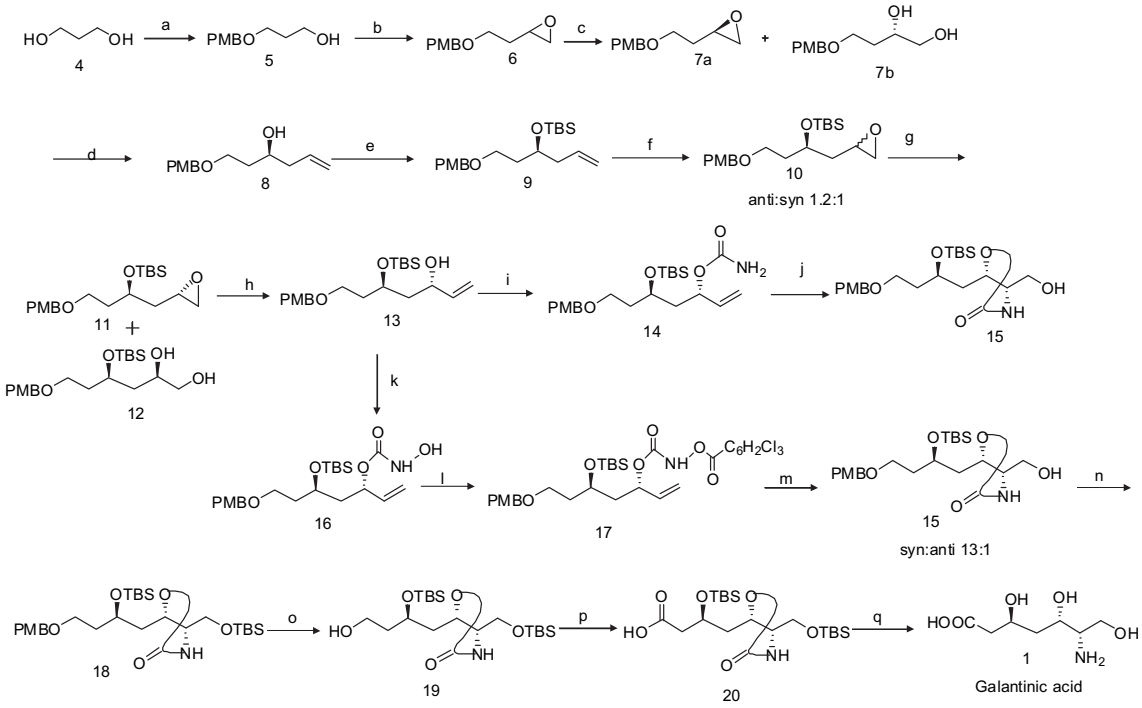
* Corresponding author. Tel.: +91 20 25902050; fax: +91 20 25902629.
E-mail address: pk.tripathi@ncl.res.in (P. Kumar).

0040-4020/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2010.02.093

enantio- and stereoselective way. Herein, we report a new synthesis of (−)-galantinic acid employing iterative hydrolytic kinetic resolution and tethered aminohydroxylation as the key steps.

2. Results and discussion

The synthesis of (−)-galantinic acid started from commercially available 1,3-propanediol **4** as illustrated in Scheme 1. Thus selective mono hydroxy protection of **4** with *p*-methoxybenzyl chloride in the presence of NaH gave the mono protected diol **5** in 86% yield, which was oxidized to the corresponding aldehyde under Swern oxidation conditions[10] followed by Corey–Chaykovsky reaction[11] with dimethylsulfoxonium methylide to afford the racemic epoxide **6** in 71% yield. Epoxide **6** was subjected to Jacobsen HKR[7] using (*R*,*R*)-Salen–Co^{III}–OAc complex as a catalyst to give the methanol furnished the carbamate **14** in 95% yield. The carbamate **14** was subjected to TA[8] using *tert*-butyl hypochlorite as the oxidant, potassium osmate, NaOH, diisopropylethylamine and propanol as the solvent. However, we could isolate only 15% of the protected aminoalcohol **15** along with starting material and unidentified side products as major compounds. The limited life time of *N*-chlorocarbamates, produced in situ by the action of NaOH and *t*-BuOCl on a primary carbamate and chlorination of the alkene unit as a competing side reaction in the TA reaction may be responsible for lowering the yield.[8e] Therefore, we turned our attention on replacement of the chlorine of the *N*-chlorocarbamate by *N*-O–CO-R group. Accordingly, alcohol **13** was reacted with CDI in pyridine, followed by the addition of hydroxylamine hydrochloride, to afford the hydroxycarbamate **16** in excellent yield. The resulting hydroxycarbamate **16** was then treated with 2,4,6-tri-



Scheme 1. Reagents and conditions: (a) PMBCl, NaH, TBAI, 0 °C, DMF, 6 h, 86%; (b) (i) Oxalyl chloride, DMSO, Et_3N, −78 °C, 4 h; (ii) Trimethylsufoxonium iodide, DMSO, NaH, 0 °C, 5 h, 71%; (c) (*R*,*R*)-Salen–Co^{III}–(OAc) (0.5 mol %), distd H_2O (0.60 equiv), 0 °C, 24 h, (47% for **7a**, 48% for **7b**); (d) Vinylmagnesium bromide, CuI, THF, −40 °C, 4 h, 90%; (e) TBSCl, imidazole, DCM, 6 h, 95%; (f) *m*CPBA, DCM, 0 °C, 10 h, 88% (g) (*S*,*S*)-Salen–Co^{III}–(OAc) (0.5 mol %), distd H_2O (0.55 equiv), THF (0.55 equiv), 0 °C, 22 h, (48% for **11**); (h) $(CH_3)_3S^+I^-$, *n*-BuLi, −20 °C, 4 h, 85%; (i) $Cl_3CCONCO$, K_2CO_3, CH_2Cl_2:CH_3OH (1.5:1), 4 h, 95%; (j) NaOH, *t*-BuOCl, $^iPr_2EtN$, potassium osmate, 2.5 h, 15%; (k) CDI, pyridine, $NH_2OH.HCl$, 40 °C, 85%; (l) 2,4,6-trichlorobenzoyl chloride, Et_3N, 0 °C, 1 h, 90%; (m) $K_2OsO_4.2H_2O$, *t*-BuOH: H_2O (3:1), 40 ml/mmol; 3 h, 75%; (n) TBSCl, imidazole, DCM, 2 h, 85%; (o) DDQ, THF: H_2O (18:1), 0 °C, 3 h, 93%; (p) (i) Oxalyl chloride, DMSO, Et_3N, −78 °C, 1.5 h; (ii) $NaClO_2$, DMSO, NaH_2PO_4, 12 h, 73% for two step; (q) (i) K_2CO_3, methanol, 0 °C, 6 h; (ii) acidified with 2 N HCl, 55% for two steps.

enantiopure epoxide **7a** in 47% yield (>98% ee), which was easily isolated from the more polar diol **7b** by column chromatography. With enantiomerically pure epoxide in hand our next aim was to construct the 1,3-*anti*-diol. Thus epoxide **7a** was treated with vinylmagnesium bromide in the presence of CuI to give the homoallylic alcohol **8** in 90% yield.[6] The hydroxyl group was protected as TBS ether followed by epoxidation with *m*CPBA to give **10** in 88% yield. The epoxide was found to be a mixture of two diastereomers (*anti*/*syn* 1.2:1). To construct diastereomerically pure epoxide[6] by means of Jacobsen HKR, the epoxide **10** was treated with (*S*,*S*)-Salen–Co^{III}–OAc complex (0.5 mol %) and water in (0.55 equiv) in THF (0.55 equiv) to afford the epoxide **11** as a single diastereomer (as determined from ^1H and ^{13}C NMR spectral analysis). Epoxide **11** was treated with excess of dimethylsulfonium methylide[12] (generated from trimethylsulphonium iodide and *n*-BuLi) to furnish the allylic alcohol **13** in 85% yield. Alcohol **13** was then reacted with trichloroacetyl isocyanate in CH_2Cl_2 to give the corresponding isocyanate, which on treatment with aq K_2CO_3 and chlorobenzoyl chloride to give **17** in 90% yield. Compound **17** was subjected to tethered aminohydroxylation under modified and optimized reaction conditions. Thus by increasing the dilution of reaction from 20 ml/mmol to 40 ml/mmol and slow addition of potassium osmate to the solution of **17** in *t*-BuOH/H_2O, we could get the protected aminoalcohol **15** in 75% yield with complete regio- and very good diastereoselectivity (*syn*/*anti* 13:1, determined from ^1H NMR). The diastereomeric mixture could easily be separated by column chromatography. The key step in the TA as depicted in Figure 2 is the intramolecular addition of the RN═Os═O fragment across the alkene leading to *syn* or *anti* relative stereochemistry. Between the two possible conformations **A** and **B** of tethered [3+2] cycloaddition, equilibrium is more shifted toward the conformation **A** over **B**, due to steric interaction between bulky R group and alkene in **B** thus leading to major *syn* product.

With required framework in hand our next task was to protect the newly generated alcohol with TBS chloride to give the TBS ether **18** in 85% yield. The PMB group was removed by DDQ to afford the

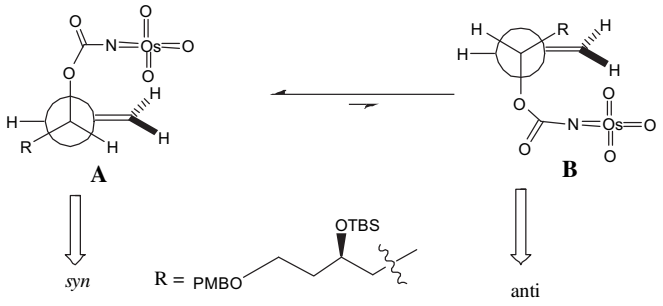


Figure 2. Depicts the origin of steroselectivity.

alcohol **19** in 93% yield. The alcohol was oxidized to the aldehyde under Swern oxidation conditions followed by subsequent oxidation using $NaClO_2$ to give the acid **20** in 73% yield. This was further subjected to hydrolysis with K_2CO_3 in methanol to furnish the crude aminoalcohol. Subsequent acidification by 2 N HCl produced (−)-galantinic acid **1** in 55% yield from two steps. The physical and spectroscopic data of **1** were in complete agreement with those described in literature.[2] The overall yield of the target compound **1** was found to be 1.52% from fifteen steps.

3. Conclusion

We have developed a new synthetic approach to (−)-galantinic acid using iterative hydrolytic kinetic resolution and tethered aminohydroxylation as key steps.

4. Experimental

4.1. General

All reactions were carried out under argon or nitrogen in oven-dried glassware using standard gas-light syringes, cannulas, and septa. Melting points are uncorrected. Solvents and reagents were purified and dried by standard methods prior to use. Optical rotations were measured at room temperature sodium D line on JASCO-181 digital polarimeter. IR spectra were recorded on an FTIR instrument. ^{1}H NMR spectra were recorded at 200 MHz, 400 MHz, and 500 MHz and are reported in parts per million (delta) downfield relative to $CDCl_3$ as internal standard and ^{13}C NMR spectra were recorded at 50 MHz, 100 MHz, and 125 MHz and are assigned in parts per million (delta) relative to $CDCl_3$. Column chromatography was performed on silica gel (100–200 and 230–400 mesh) using a mixture of petroleum ether and ethyl acetate as the eluent. Microanalytical data were obtained using a Carlo–Erba CHNS-0 EA 1108 elemental analyzer. Enantiomeric excess was determined using chiral HPLC.

*4.1.1. 3-(4-Methoxybenzyloxy)propan-1-ol (**5**).* To a solution of 1,3-propanediol **4** (5.0 g, 65.71 mmol) in dry DMF (200 mL) was added sodium hydride (60%, 2.90 g, 72.28 mmol) at 0 °C. The reaction mixture was then stirred at room temperature for 30 min after which it was again cooled to 0 °C. To this was added slowly *p*-methoxybenzyl chloride (11.32 g, 10.75 mL, 72.28 mmol) and tetra *n*-butylammonium iodide (2.6 g, 6.57 mmol) with further stirring for 6 h at the same temperature. The reaction was quenched with addition of cold water at 0 °C. The two phases were separated and the aqueous phase was extracted with EtOAc (3×100 mL). The combined organic layers were washed with water (3×100 mL), brine, dried over Na_2SO_4, and concentrated. The residual oil was purified by silica gel column chromatography using petroleum ether/EtOAc (6:4) as eluent to furnish the mono-PMB protected alcohol **5** (11.09 g, 86%) as colorless oil; Anal. Calcd for $C_{11}H_{16}O_3$ (196.24): C, 67.32; H, 8.22%; found: C, 67.41; H, 8.19%; R_f (80% EtOAc/pet. ether) 0.51; IR (neat, cm^{-1}): ν_{max} 3410, 2940, 2863, 1612, 1513, 1249, 1175, 1098; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.22–2.27 (2H, m), 2.82 (1H, br s), 4.02 (2H, t, J=5.27 Hz), 4.15 (2H, t, J=5.67 Hz), 4.20 (3H,s), 4.85 (2H, s), 7.28 (2H, d, J=10 Hz), 7.65 (2H, d, J=9.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 32.2, 55.2, 61.5, 68.7, 72.8, 113.8 (2-carbons), 129.2 (2-carbons), 130.2, 159.2; MS (ESI) m/z: 219 [M+Na]$^+$.

*4.1.2. 2-(2-(4-Methoxybenzyloxy)ethyl)oxirane (**6**).* (i) Swern oxidation. To a solution of oxalyl chloride (3.33 mL, 38.21 mmol) in dry CH_2Cl_2 (50 mL) at −78 °C was added dropwise dry DMSO (5.42 mL, 76.43 mmol) in CH_2Cl_2 (20 mL). After 30 min, alcohol **5** (5.0 g, 25.47 mmol) in CH_2Cl_2 (20 mL) was added over 10 min giving copious white precipitate. After stirring for 1 h at −78 °C, the reaction mixture was brought to −60 °C and Et_3N (15.62 mL, 112.24 mmol) was added slowly and stirred for 30 min allowing the reaction mixture to warm to room temperature. The reaction mixture was then diluted with water (100 mL) and CH_2Cl_2. The organic layer was separated and washed with water and brine, dried over Na_2SO_4, and passed through short pad of Celite. The filtrate was concentrated to give the aldehyde (4.70 g, 95%) as pale yellow oil, which was used as such for the next step without purification.

(ii) To a solution of trimethylsulfoxonium iodide (7.98 g, 36.29 mmol) in dry DMSO was added NaH (0.87 g, 36.29 mmol). After 1 h, aldehyde (4.7 g, 24.19 mmol) dissolved in THF was added at 25 °C. After stirring for 5 h ice was added to the reaction mixture and the reaction mixture was extracted with water, brine, dried over Na_2SO_4. Solvent was removed under pressure and the crude product was purified by silica gel column chromatography using petroleum ether/EtOAc (95:5) to get pure epoxide **6** (3.77 g, 71%) as colorless liquid; Anal. Calcd for $C_{12}H_{16}O_3$ (208.25): C, 69.21; H, 7.74%; found: C, 69.24; H, 7.70%; R_f (20% EtOAc/pet. ether) 0.72; IR (neat, cm^{-1}): ν_{max} 3490, 2940, 2863, 1612, 1513, 1249, 1175, 1098; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.70–1.91 (2H, m), 2.53–2.57 (1H, m), 2.78–2.83 (1H, m), 3.07–3.11 (1H, m), 3.62 (2H, t, J=6.95 Hz), 3.83 (3H, s), 4.48 (2H, s), 6.88–6.93 (2H, d, J=8.72 Hz), 7.29–7.31 (2H, d, J=8.72 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 32.8, 47.0, 50.0, 55.1, 66.6, 72.6, 113.7 (2-carbons), 129.2 (2-carbons), 130.2 159.1; MS (ESI) m/z: 231 [M+Na]$^+$.

*4.1.3. (R)-2-(2-(4-Methoxybenzyloxy)ethyl)oxirane (**7a**).* Racemic epoxide (±)-**6** (8.0 g, 38.41 mmol), THF (583 μL) were added to (*S*,*S*)-Salen–Co^{III}–OAc catalyst (127 mg, 0.192 mmol, 0.5 mol %) and the solution was cooled to 0 °C. Every 5 min, H_2O (50 μL) was added until 414 μL (0.60 equiv, 23.04 mmol) had been added; after another 5 min the ice bath was removed and the reaction was stirred at room temperature for 24 h. The reaction mixture was concentrated and purified through silica gel column chromatography using petroleum ether/EtOAc (95:5) as eluent to furnish the epoxide (*R*)-**7a** as a single stereoisomer as a yellow colored liquid. Continued chromatography with petroleum ether/EtOAc (6:4) provided the diol (*S*)-**7b** as a brown colored liquid as a single enantiomer. (*R*)-**7a**: Yield: 3.84 g, 48%; $[\alpha]_D^{25}$ −12.98 (*c* 1, $CHCl_3$); HPLC: Chiracel OD-H column (2-propanol/petroleum ether=4:96, flow rate 0.5 mL/min, λ=220 nm). Retention time (min): 18.59 (major) and 19.4 (minor). The racemic standard was prepared in the same way with racemic epoxide, ee>98%.

*4.1.4. (S)-1-(4-Methoxybenzyloxy)hex-5-en-3-ol (**8**).* A round bottomed flask was charged with copper(I)iodide (0.274 mg, 1.44 mmol), gently heated under vacuum and slowly cooled with a flow of argon and THF (20 mL) was added. This suspension was cooled to −40 °C, stirred and vinylmagnesium bromide (1 M in THF, 28.8 mL, 28.8 mmol) was added to it. A solution of epoxide (*R*)-**7a**

(3.0 g, 14.40 mmol) in THF (15 mL) was added to the above reagent and the mixture was stirred at −40 °C for 4 h. After consumption of starting material, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl. The water layer was extracted with EtOAc (3×50 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated. Purification of crude product by silica gel column chromatography using petroleum ether/EtOAc (9:1) as eluent afforded (*S*)-**8** (3.06 g, 90%) as a colorless liquid; Anal. Calcd for $C_{14}H_{20}O_3$ (236.31): C, 71.16; H, 8.53%; found: C, 71.21; H, 8.47%; R_f (30% EtOAc/pet. ether) 0.69; $[\alpha]_D^{25}$ −5.98 (*c* 1.35, $CHCl_3$); IR (neat, cm^{-1}): ν_{max} 3386, 1640, 1603, 1493, 1453, 1243; ^1H NMR (200 MHz, $CDCl_3$): δ 1.74–1.80 (2H, m), 2.21–2.28 (2H, m), 2.74 (1H, br s), 3.56–3.76 (2H, m), 3.81 (3H, s), 3.84–3.93 (1H, m), 4.46 (2H, s), 5.06–5.17 (2H, m), 5.74–5.94 (1H, m), 6.88 (2H, d, *J*=8.72 Hz), 7.26 (2H, d, *J*=8.72 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 35.8, 41.9, 55.2, 68.7, 70.5, 72.9, 113.8 (2-carbons), 117.5, 129.3 (2-carbons), 130.0 134.9, 159.2; MS (ESI) *m*/*z*: 259 $[M+Na]^+$.

*4.1.5. (S)-tert-Butyl(1-(4-methoxybenzyloxy)hex-5-en-3-yloxy)-dimethylsilane (**9**).* To a stirred solution of alcohol **8** (5 g, 21.86 mmol) in CH_2Cl_2 was added imidazole (2.88 g, 42.37 mmol). To this solution *t*-butyl dimethylchlorosilane (4.78 g, 31.77 mmol) was added at 0 °C and the reaction was stirred at room temperature for 6 h. The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl and extracted with CH_2Cl_2. The extract was washed with brine, dried over Na_2SO_4, and concentrated. Purification of crude product by silica gel column chromatography using petroleum ether/EtOAc (95:5) as eluent afforded (*S*)-**9** (7.04 g, 95%); as a colorless liquid; Anal. Calcd for $C_{20}H_{34}O_3Si$ (350.57): C, 68.52; H, 9.78%; found: C, 68.49; H, 9.73%; R_f (10% EtOAc/pet. ether) 0.78; $[\alpha]_D^{25}$ +16.12 (*c* 1.65, $CHCl_3$); IR (neat, cm^{-1}): ν_{max} 1641, 1606, 1491, 1462; ^1H NMR (200 MHz, $CDCl_3$): δ 0.05 (3H, s), 0.06 (3H, s), 0.89 (9H, s), 1.63–1.80 (2H, m), 2.19–2.26 (2H, m), 3.51 (2H, t, *J*=6.32 Hz), 3.81 (3H, s), 3.84–3.95 (1H, m), 4.43 (2H, Abq, *J*=11.5 Hz), 4.48–5.09 (2H, m), 5.71–5.92 (1H, m), 6.89 (2H, d, *J*=8.71 Hz), 7.27 (2H, d, *J*=8.72 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ −4.7, −4.4, 18.1, 25.9 (3-carbons), 36.7, 42.3, 55.2, 66.7, 68.9, 72.6, 113.7 (2-carbons), 116.9, 129.3 (2-carbons), 130.7, 134.9, 159.1; MS (ESI) *m*/*z*: 373 $[M+Na]^+$.

*4.1.6. tert-Butyl((R)-4-(4-methoxybenzyloxy)-1-((S)-oxiran-2-yl)butan-2-yloxy)dimethylsilane (**10**).* To a stirred solution of olefin **9** (5 g, 14.26 mmol) in CH_2Cl_2 (100 mL) at 0 °C was added *m*-CPBA (50%) (5.41 g, 6.38 mmol). The reaction mixture was stirred at room temperature for 10 h and quenched by saturated $NaHCO_3$ solution, extracted with CH_2Cl_2, washed with satd $NaHCO_3$ and brine, dried over Na_2SO_4, concentrated and purified by silica gel column chromatography using petroleum ether/EtOAc (9:1) as eluent to yield the epoxide **10** as a colorless liquid in diastereomeric mixture (*anti*/*syn*=1.2:1). Yield: 4.6 g, 88%.

*4.1.7. tert-Butyl((R)-4-(4-methoxybenzyloxy)-1-((S)-oxiran-2-yl)butan-2-yloxy)dimethylsilane (**11**).* A solution of epoxide **10** (4 g, 10.92 mmol) and (*S*,*S*)-Salen–Co^{III}–OAc (0.036 g, 0.055 mmol) in THF (0.4 mL) was stirred at 0 °C for 5 min, and then distilled water (108 μL, 6.01 mmol) was added. After stirring for 24 h, it was concentrated and purified by silica gel column chromatography using petroleum ether/EtOAc (9:1) as eluent to afford **11** (1.84 g, 46%) as a yellow colored liquid, Continued chromatography with pet. ether/EtOAc (3:2) provided the diol **12** as a brown colored liquid as a single diastereomer. Compound **11**: Anal. Calcd for $C_{20}H_{34}O_4Si$ (366.57): C, 52.67; H, 9.2%; found: C, 52.74; H, 9.11%; R_f (20% EtOAc/pet. ether) 0.68; $[\alpha]_D^{25}$ −14.0 (*c* 1, $CHCl_3$); IR (neat, cm^{-1}): ν_{max} 2960, 2860, 1470, 1410, 1340, 1250, 1095, 1035, 840, 780; ^1H NMR (200 MHz, $CDCl_3$): 0.06 (3H, s), 0.08 (3H, s), 0.89 (9H, s), 1.62–1.72 (2H, m), 1.77–1.90 (2H, m), 2.43–2.51 (1H, m), 2.74–2.82 (1H, m), 2.98–3.11 (1H, m), 3.51 (2H, t, *J*=6.44 Hz), 3.81 (3H, s), 4.04–4.11 (1H, m), 4.42 (2H, Abq, *J*=11.54 Hz), 6.88 (2H, d, *J*=8.72 Hz), 7.26 (2H, d, *J*=8.72 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ −4.9, −4.7, 18.0, 25.8 (3-carbons), 37.7, 40.6, 47.7, 49.7, 55.2, 66.3, 67.5, 72.6, 113.8 (2-carbons), 129.3 (2-carbons), 130.5, 159.1; MS (ESI) *m*/*z*: 389 $[M+Na]^+$, 405$[M+K]^+$.

*4.1.8. (3S,5R)-5-(tert-Butyldimethylsilyloxy)-7-(4-methoxybenzyloxy)-hept-1-en-3-ol (**13**).* To a stirred solution of dry THF was added trimethylsulfoniumiodide (13.91 g, 68.19 mmol) at −20 °C. The reaction mixture was stirred for 20 min followed by addition of *n*-BuLi (42.6 ml, 1.6 M, 68.19 mmol). After 40 min, epoxide **11** (5.0 g, 13.63 mmol) in THF was added dropwise. The reaction mixture was stirred at −20 °C for 3 h and quenched by saturated solution of ammonium chloride. The two phases were separated and the aqueous phase was extracted with EtOAc (3×50 mL). The combined organic layers were washed with water (3×50 mL), brine, dried over Na_2SO_4 and concentrated. The residual oil was purified by silica gel column chromatography using petroleum ether/EtOAc (8:2) as eluent to furnish the allylic alcohol **13** (4.41 g, 85%) as colorless oil; Anal. Calcd for $C_{21}H_{36}O_4Si$ (380.59): C, 66.27; H, 9.53%; found: C, 66.32; H, 9.47%; R_f (30% EtOAc/pet. ether) 0.69; $[\alpha]_D^{25}$ −5.25 (*c* 1.3, $CHCl_3$); IR (neat, cm^{-1}): ν_{max} 3430, 3018, 2957, 2931, 2859, 1652, 1471, 1379, 1256, 1212, 1101, 1036, 971, 869, 758; ^1H NMR (200 MHz, $CDCl_3$): δ 0.09 (3H, s), 0.11 (3H, s), 0.9 (9H, s), 1.63–1.73 (2H, m), 1.85–1.97 (2H, m), 2.44–2.94 (1H, br s), 3.5 (2H, t, *J*=6.44 Hz), 3.81 (3H, s), 4.06–4.31 (2H, m), 4.43 (2H, Abq, *J*=11.49 Hz), 5.04–5.29 (2H, m), 5.76–5.92 (1H, m), 6.88 (2H, d, *J*=8.71 Hz), 7.25 (2H, d, *J*=8.72 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ −4.7, −4.3, 17.9, 25.8 (3-carbons), 36.4, 42.4, 55.2, 68.4, 68.6, 69.6, 72.3, 113.8, 113.9, 129.3 (2-carbons), 130.4, 140.0, 141.1, 159.2; MS (ESI) *m*/*z*: 403 $[M+23]^+$.

*4.1.9. (3S,5R)-5-(tert-Butyldimethylsilyloxy)-7-(4-methoxybenzyloxy)-hept-1-en-3-yl carbamate (**14**).* Trichloroacetyl isocyanate (0.594 g, 0.37 mL, 3.15 mmol) was added dropwise to a solution of the alcohol **13** (1.0 g, 2.62 mmol) in dry dichloromethane 3.93 mL (1.5 mL/mmol) at 0 °C. After stirring for 2 h, or until TLC showed no starting material present, the mixture was concentrated under reduced pressure. The residue was dissolved in methanol 5.24 mL (2 mL/mmol), cooled to 0 °C and an aqueous potassium carbonate solution (1.09 g, 7.86 mmol, 2 mL/mmol) was added. The cooling bath was removed and the mixture was allowed to stir for 4 h, by which time TLC showed complete conversion. Methanol was evaporated under reduced pressure and the aqueous residue was extracted with dichloromethane (25 mL×3). The combined organics were washed with brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure to yield the crude carbamate, which was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (7:3) as eluent to give carbamate **14** (1.05 g, 95%) as colorless oil; Anal.. Calcd for $C_{22}H_{37}NO_5Si$ (423.62): C, 62.38; H, 8.80; N, 3.31%; found: C, 62.32; H, 8.75; N, 3.3%; R_f (30% EtOAc/pet. ether) 0.44; $[\alpha]_D^{25}$ −5.0 (*c* 1, $CHCl_3$); IR (neat, cm^{-1}); IR (neat, cm^{-1}): ν_{max} 3370, 1692, 1308, 1276, 1140, 974, 771, 699; ^1H NMR (200 MHz, $CDCl_3$): δ 0.04 (3H, s), 0.06 (3H, s), 0.88 (9H, s), 1.67–1.86 (4H, m), 3.52 (2H, t, *J*=6.69 Hz), 3.81 (3H, s), 3.87–3.98 (1H, m), 4.42 (2H, s), 4.80 (1H, br s), 5.12–5.30 (3H, m), 5.71–5.90 (1H, m), 6.88 (2H, d, *J*=8.33), 7.26 (2H, d, *J*=8.72 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ −4.9, −4.6, 18.0, 25.8 (3-carbons), 37.6, 42.1, 55.2, 66.2, 66.4, 72.5, 72.6, 113.7 (2-carbons), 115.7, 129.2 (2-carbons), 130.5, 136.9, 156.3, 159; MS (ESI) *m*/*z*: 446.63 $[M+Na]^+$.

*4.1.10. (3S,5R)-5-(tert-Butyldimethylsilyloxy)-7-(4-methoxybenzyloxy)hept-1-en-3-yl hydroxycarbamate (**16**).* *N*,*N*-Carbodiimidazole

(1.70 g, 10.50 mmol) was added to the alcohol **13** (2.0 g, 5.25 mmol) in pyridine at 40 °C. Hydroxylamine hydrochloride (0.803 g, 11.56 mmol) was added after complete adduct formation between alcohol and CDI (~4 h). The reaction was stirred for 24 h at 40 °C, quenched with 1 M HCl, partitioned and aqueous layer extracted with diethyl ether and ethyl acetate. The combined organic layer was washed with water and brine, dried. The solvent was azeotropically removed with toluene. The crude product was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (8:2) as eluent to give hydroxylamine **16** (1.96 g, 85%) as colorless oil; Anal.. Calcd for $C_{22}H_{37}NO_6Si$ (439.62): C, 60.11; H, 8.48; N, 3.19%; found: C, 60.17; H, 8.56; N, 3.2%; R_f (40% EtOAc/pet. ether) 0.48; $[\alpha]_D^{25}$ −11.40 (*c* 1, $CHCl_3$); IR (neat, cm^{-1}): ν_{max} 3253, 1700, 1516, 1306, 1256, 1138, 971, 771, 694; ^1H NMR (200 MHz, $CDCl_3$): δ 0.03 (3H, s), 0.05 (3H, s), 0.88 (9H, s), 1.71–1.88 (4H, m), 3.52 (2H, t, *J*=6.31 Hz), 3.81 (3H, s), 3.85–3.97 (1H, m), 4.41 (2H, ABq, *J*=11.49 Hz), 5.14–5.33 (3H, m), 5.75–5.86 (1H, m), 6.88 (2H, d, *J*=8.69 Hz), 7.25 (2H, d, *J*=8.69 Hz), 7.35 (1H, br s,); ^{13}C NMR (50 MHz, $CDCl_3$): δ −4.6, −4.5, 18.0, 25.8 (3-carbons), 36.6, 41.9, 55.2, 66.3, 66.4, 72.6, 73.8, 113.7 (2-carbons), 117.0, 129.5 (2-carbons), 130.2, 136.2, 158.4, 159.1; MS (ESI) *m*/*z*: 462 $[M+Na]^+$, 478 $[M+K]^+$.

*4.1.11. (3S,5R)-5-(tert-Butyldimethylsilyloxy)-7-(4-methoxybenzyloxy)hept-1-en-3-yl-2,4,6-trichlorobenzoyloxycarb-amate (**17**).* To an ice-cold solution of hydroxycarbamate **16** (1.0 g, 2.27 mmol) in Et_2O (4:1; 5 ml/mmol) was added Et_3N (0.348 mL, 2.50 mmol), before the addition of the 2,4,6-trichlorobenzoyl chloride (0.355 mL, 2.27 mmol) in small portions. The reaction was quenched with HCl (1 M aq soln, 25 mL) and the aqueous layer was extracted with Et_2O (3×20 ml). The combined organic layers were washed sequentially with water (30 ml), $NaHCO_3$ (aq satd soln, 30 ml) and brine (30 ml), dried ($NaSO_4$), filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography using petroleum ether/ethyl acetate (97:3) as eluent to give *O*-trichlorobenzoyl substituted hydroxylamine **17** (1.32 g, 90%) as pale yellow oil; Anal. Calcd for $C_{29}H_{38}Cl_3NO_7Si$ (647.06): C, 53.83; H, 5.92; N, 2.16%; found: C, 53.56; H, 6.21; N, 2.26%; R_f (10% EtOAc/pet. ether) 0.64; $[\alpha]_D^{25}$ −3.19 (*c* 1.2, $CHCl_3$); IR (neat, cm^{-1}): ν_{max} 3425, 2965, 1760, 1740, 1652, 1471, 1101, 1036, 971, 869, 758; ^1H NMR (200 MHz, $CDCl_3$): δ 0.04 (3H, s), 0.05 (3H, s), 0.88 (9H, s), 1.66–1.87 (4H, m), 3.52 (2H, t, *J*=6.57 Hz), 3.80 (3H, s), 3.87–4.02 (1H, m), 4.41 (2H, ABq, *J*=11.89 Hz), 5.14–5.45 (3H, m), 5.72–5.88 (1H, m), 6.87 (2H, d, *J*=8.46 Hz), 7.25 (2H, d, *J*=8.46 Hz), 7.38–7.40 (2H, m), 8.4 (1H, br s); ^{13}C NMR (50 MHz, $CDCl_3$): δ −4.9, −4.4, 17.9, 25.8 (3-carbons), 37.5, 42.0, 55.2, 66.0, 66.2, 72.5, 75.3, 113.7 (2-carbons), 117.3, 128.2 (2-carbons), 129.1 (2-carbons), 130.4, 133.6, 135.5, 135.8, 137.6, 155.1, 159.0, 163; MS (ESI) *m*/*z*: 670 $[M+Na]^+$.

*4.1.12. (4R,5R)-5-((R)-2-(tert-Butyldimethylsilyloxy)-4-(4-methoxybenzyloxy)butyl)-4-(hydroxymethyl)oxazolidin-2-one (**15**).* To a solution of *O*-trichlorobenzoyl substituted hydroxycarbamate **17** (0.50 g, 0.772 mmol) in *tert*-butanol and water 30 mL (3:1, 40 mL/mmol) was added dropwise a solution of potassium osmate dihydrate (5 mg, 0.015 mmol, 2 mol%) in water (5 mL). The reaction was quenched by addition of sodium sulphite (200 mg/mmol) and the solvent azeotropically removed with toluene. The crude product was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (6:4) as eluent to afford the aminohydroxylated product **15** (0.25 g, 75%) as colorless syrupy oil; Anal. Calcd for $C_{22}H_{37}NO_6Si$ (439.62): C, 60.11; H, 8.48; N, 3.19%; found: C, 60.18; H, 8.41; N, 3.11%; R_f (60% EtOAc/pet. ether) 0.44; $[\alpha]_D^{25}$ −27.33 (*c* 1.3, $CHCl_3$); IR (neat, cm^{-1}): ν_{max} 3386, 2930, 1698, 1490, 1435, 1285, 1072, 818, 768; ^1H NMR (500 MHz, $CDCl_3$): δ 0.07 (3H, s), 0.08 (3H, s), 0.87 (9H, s), 1.64–1.90 (4H, m), 3.13–3.34 (1H, br s), 3.46–3.64 (5H, m), 3.80 (3H, s), 4.04–4.09 (1H, m), 4.36–4.56 (3H, m), 6.59–6.66 (1H,br s), 6.88 (d, *J*=8.71 Hz, 2H), 7.25 (d, *J*=8.71 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): −4.8, −4.5, 18.0, 25.8 (3-carbons), 37.8, 43.0, 55.2, 59.6, 63.5, 65.9, 66.1, 72.6, 75.9, 113.8 (2-carbons), 129.3 (2-carbons), 130.3, 159.1, 159.5; MS (ESI) *m*/*z*: 462 $[M+Na]^+$.

*4.1.13. (4R,5R)-5-((R)-2-(tert-Butyldimethylsilyloxy)-4-(4-methoxybenzyloxy)butyl)-4-((tert-butyldimethylsilyloxy)methyl)oxazolidin-2-one (**18**).* To a stirred solution of alcohol **15** (0.20 g, 0.454 mmol) in CH_2Cl_2 was added imidazole (46 mg, 0.682 mmol). To this solution *tert*-butyl dimethylchlorosilane (102 mg, 0.682 mmol) was added at 0 °C and the reaction was stirred at room temperature for 6 h. The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl and extracted with CH_2Cl_2. The extract was washed with brine, dried (Na_2SO_4), concentrated, and purified using silica gel chromatography of crude product using EtOAc/petroleum ether (2:8) as eluent to give the protected aminohydroxylated product **21** (0.214 g, 85%) as a thick colorless liquid; Anal. Calcd for $C_{28}H_{51}NO_6Si_2$ (553.38): C, 60.72; H, 9.28; N, 2.53%; found: C, 60.67; H, 9.35; N, 2.47%; R_f (30% EtOAc/pet. ether) 0.50; $[\alpha]_D^{25}$ −33.33 (*c* 1, $CHCl_3$); IR (neat, cm^{-1}): ν_{max} 3289, 2900, 1690, 1101, 1044, 971, 869, 769; ^1H NMR (500 MHz, $CDCl_3$): δ 0.06–0.07 (12H, m), 0.87–0.88 (18H, m), 1.59–1.95 (4H, m), 3.42–3.59 (5H, m), 3.81 (3H, s), 4.02–4.14 (1H, m), 4.4 (2H, ABq, *J*=11.5 Hz), 4.46–4.45 (1H, m), 5.85 (1H, br s) 6.88 (2H, d, *J*=8.69 Hz), 7.25 (2H, d, *J*=8.69 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): −5.6 (2-carbons), −4.8, −4.5, 18.0, 18.1, 25.7 (3-carbons), 25.8 (3-carbons), 37.9, 43.2, 55.2, 59.2, 64.4, 65.9, 66., 72.6, 76.2, 113.7 (2-carbons), 129.2 (2-carbons), 130.4, 159.1, 159.3; MS (ESI) *m*/*z*: 576 $[M+Na]^+$.

*4.1.14. (4R,5R)-5-((R)-2-(tert-Butyldimethylsilyloxy)-4-hydroxybutyl)-4-((tert-butyldimethylsilyloxy)methyl)oxazolidin-2-one (**19**).* To a stirring solution of PMB ether **18** (200 mg, 0.374 mmol) in CH_2Cl_2/H_2O (20:1) was added DDQ (170 mg, 0.749 mmol). The resulting mixture was stirred for 3 h at 0 °C. The mixture was poured into saturated aqueous $NaHCO_3$ and further diluted with CH_2Cl_2. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2×10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated. The solvents were removed under reduced pressure to give the crude product mixture as yellow oil. Silica gel column chromatography of the crude product using petroleum ether/EtOAc (1:1) as eluent gave **19** (0.145 g, 93%) as a colorless solid; Anal. Calcd for $C_{20}H_{43}NO_5Si_2$ (433.73): C, 55.38; H, 9.99; N, 3.23%; found: C, 55.32; H, 10.02; N, 3.2%; R_f (60% EtOAc/pet. ether) 0.40; mp: 63 °C; $[\alpha]_D^{25}$ −30.18 (*c* 1, $CHCl_3$); IR (neat, cm^{-1}): ν_{max} 3251, 2929, 1688, 1451, 1101; ^1H NMR (400 MHz, $CDCl_3$): δ 0.05 (6H, s), 0.11 (3H, s), 0.12 (3H, s), 0.88–0.89 (18H, m), 1.66–1.72 (1H, m), 1.77–1.83 (1H, m), 1.85–1.92 (2H, m), 2.27 (1H, br s), 3.47–3.50 (1H, m), 3.59–3.60 (2H, m), 3.70–3.74 (1H, m), 3.79–3.84 (1H, m), 4.15–4.20 (1H, m), 4.50–4.54 (1H, m), 6.14 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$): −5.6 (2-carbons), −4.9, −4.5, 17.9, 18.1, 25.7 (3-carbons), 25.8 (2-carbons), 39.2, 42.6, 59.2, 59.3, 64.3, 67.1, 76.2, 159.3; MS (ESI) *m*/*z*: 456 $[M+Na]^+$.

*4.1.15. (S)-3-(tert-Butyldimethylsilyloxy)-4-((4R,5R)-4-((tert-butyldimethylsilyloxy)methyl)-2-oxooxazolidin-5-yl)butanoic acid (**20**).* A solution of oxalyl chloride (0.087 g, 0.060 mL, 0.691 mmol) in dry CH_2Cl_2 (10 mL) at −78 °C was added dropwise dry DMSO (0.108 g, 0.098 mL, 1.38 mmol) in CH_2Cl_2 (2 mL). After 30 min, alcohol **19** (200 mg, 0.461 mmol) in CH_2Cl_2 (3 mL) was added over 10 min giving a copious white precipitate. After stirring for 1 h at −78 °C the reaction mixture was brought to −60 °C and Et_3N (0.205 g, 0.282 mL, 2.02 mmol) was added slowly and stirred for 30 min allowing the reaction mixture to warm to room temperature. The

reaction mixture was poured into water (10 mL) and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2×15 mL) and combined organic layers were washed with water (3×10 mL), brine (20 mL), dried (Na_2SO_4) and passed through short pad of silica gel. The filtrate was concentrated to give the aldehyde (180 mg) as pale yellow syrup, which was used as such for the next step without further purification.

A solution of 79% $NaClO_2$ (56 mg, 0.625 mmol) in 1.0 mL of water was added dropwise a stirred solution of above crude aldehyde (180 mg, 0.416 mmol) in 0.5 mL of DMSO and NaH_2PO_4 (37 mg, 0.312 mmol) in 1.0 mL of water over a period of 5 min at room temperature. The mixture was left overnight at room temperature, then 5% aqueous solution of $NaHCO_3$ was added. The aqueous phase was extracted three times with CH_2Cl_2 and washed with brine, dried (Na_2SO_4), and concentrated. Silica gel column chromatography of the crude product using petroleum ether/EtOAc (2:8) as eluent gave the acid **20** (0.150 g, 73%) as a yellowish solid; Anal. Calcd for $C_{20}H_{41}NO_6Si_2$ (439.62): C, 53.65; H, 9.23; N, 3.13%; found: C, 53.56; H, 9.2; N, 3.18%; R_f (90% EtOAc/pet. ether) 0.37; mp: 68 °C; $[\alpha]_D^{25}$ −13.45 (*c* 0.5, $CHCl_3$); IR (neat, cm^{-1}): ν_{max} 3400, 2957, 1730, 1652; NMR (200 MHz, $CDCl_3$): δ 0.06–0.13 (12H, m), 0.88 (18H, s), 1.79–1.96 (2H, m), 2.55–2.65 (2H, m), 3.47–3.55 (1H, m), 3.60–3.62 (2H, m), 4.36–4.52 (1H, m), 4.54–4.61 (1H, m), 6.09 (1H, br s), 9.82 (1H, br s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): −5.3 (2-carbons), −4.6, −4.3, 18.1, 18.3, 26 (6-carbons), 39.5, 45.8, 59.4, 64.6, 67.3, 76.5, 159.6, 178.5.

*4.1.16. (3S,5S,6S)-6-Amino-3,5,7-trihydroxyheptanoic acid (−)-galantinic acid (**1**).* To a stirred solution of TA product **20** (100 mg, 0.223 mmol) in methanol (3 mL) was added potassium carbonate (92 mg, 0.67 mmol) and the reaction mixture was stirred until completion of the starting material (almost 6 h) and methanol was removed in vacuo. Water was added to the crude product and extracted with ethyl acetate (3×3 mL) and dried over sodium sulfate and concentrated to near dryness, which was subsequently treated with 2 N HCl to afford crude crystals of **1**. These were recrystallized from H_2O/MeOH to give pure (−)-galantinic acid **1** (23 mg, 55%); mp: 128 °C (lit.[3] 125 −130 °C); $[\alpha]_D^{25}$ −29.7 (*c*, 0.5, H_2O); (lit.[2] $[\alpha]_D^{25}$ −29.4); ^1H NMR (500 MHz, $CDCl_3$): δ 1.51–1.83 (2H, m), 2.37 (1H, dd, *J*=5.8, 13.65 Hz), 2.49 (1H dd, *J*=6.5, 13.86 Hz), 3.13 (1H dt, *J*=7.0, 12.25 Hz), 3.61 (1H, q, *J*=8.32, 14.91 Hz), 3.91–4.21 (3H, m); MS (ESI) *m*/*z*: 194 $[M+H]^+$.

Acknowledgements

A.D. thanks CSIR, New Delhi for the award of Senior Research Fellowship. We thank Dr. Ganesh Pandey, Head, organic division, NCL for his support and encouragement.

References and notes

1. Shoji, J.; Sakajaki, R.; Koizumi, K.; Matsurra, S. J. *J. Antibiot.* **1975**, *28*, 122–125.
2. Sakai, N.; Ohfune, Y. *Tetrahedron Lett.* **1990**, *31*, 4151–4154.
3. Sakai, N.; Ohfune, Y. *J. Am. Chem. Soc.* **1992**, *114*, 998–1010.
4. (a) Ikota, N. *Heterocycles* **1991**, *32*, 521–528; (b) Kumar, J. S. R.; Datta, A. *Tetrahedron Lett.* **1999**, *40*, 1381–1384; (c) Kiyooka, S.; Goh, K.; Nakamura, Y.; Takesue, H.; Hena, M. A. *Tetrahedron Lett.* **2000**, *41*, 6599–6603; (d) Moreau, X.; Campagne, J. *Tetrahedron Lett.* **2001**, *42*, 4467–4469; (e) Bethuel, Y.; Gademann, K. *Synlett* **2006**, 1580–1582; (f) Nagaiah, K.; Sreenu, D.; Purnima, K. V.; Rao, R. S.; Yadav, J. S. *Synlett* **2009**, 1386–1392; (g) Raghavan, S.; Ramakrishna Reddy, S. *J. Org. Chem.* **2003**, *68*, 5754–5757; (h) Pandey, S. K.; Kandula, S. R.; Kumar, P. *Tetrahedron Lett.* **2004**, *45*, 5877–5879.
5. (a) Fernandes, R. A.; Kumar, P. *Eur. J. Org. Chem.* **2000**, 3447–3449; (b) Kandula, S. V.; Kumar, P. *Tetrahedron Lett.* **2003**, *44*, 1957–1958; (c) Kondekar, N. B.; Subba Rao, K. V.; Kumar, P. *Tetrahedron Lett.* **2004**, *45*, 5477–5479; (d) Kumar, P.; Bodas, M. S. *J. Org. Chem.* **2005**, *70*, 360–363; (e) Pandey, S. K.; Pandey, M.; Kumar, P. *Tetrahedron Lett.* **2008**, *49*, 3297–3299; (f) Dubey, A.; Kumar, P. *Tetrahedron Lett.* **2009**, *50*, 3425–3427 and references cited therein.
6. Kumar, P.; Gupta, P.; Naidu, S. V. *Chem.—Eur. J.* **2006**, *12*, 1397–1402.
7. (a) Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. *Science* **1997**, *277*, 936–938; (b) Schaus, S. E.; Brandes, B. D.; Larrow, J. F.; Tokunaga, M.; Hansen, K. B.; Gould, A. E.; Furrow, M. E.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2002**, *124*, 1307–1315; (c) For various application of HKR in synthesis of bioactive compounds, see review: Kumar, P.; Naidu, S. V.; Gupta, P. *Tetrahedron* **2007**, *63*, 2745–2785 account (d) Kumar, P.; Gupta, P. *Synlett* **2009**, 1367–1382.
8. (a) Donohoe, T. J.; Johnson, P. D.; Helliwell, M.; Keenan, M. *Chem. Commun.* **2001**, *3*, 2078–2079; (b) Donohoe, T. J.; Johnson, P. D.; Cowley, A.; Keenan, M. *J. Am. Chem. Soc.* **2002**, *124*, 12934–12935; (c) Donohoe, T. J.; Johnson, P. D.; Pye, R. J. *Org. Biomol. Chem.* **2003**, *1*, 2025–2028; (d) Donohoe, T. J.; Johnson, P. D.; Pye, R. J.; Keenam, M. *Org. Lett.* **2004**, *6*, 2583–2585; (e) Donohoe, T. J.; Carole, J. R.; William, G.; Johannes, K.; Emile, R. *Org. Lett.* **2007**, *7*, 1725–1728.
9. (a) Li, G.; Chang, H. T.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **1996**, *35*, 451–454; (b) Brien, P. O. *Angew. Chem., Int. Ed.* **1999**, *38*, 326–329 and references cited therein.
10. For reviews on the Swern oxidation, see: (a) Tidwell, T. T. *Synthesis* **1990**, 857–870; (b) Tidwell, T. T. *Org. React.* **1990**, *39*, 297–572.
11. Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353–1364.
12. Alcaraz, L.; Harnett, J. J.; Mioskowski, C.; Martel, J. P.; Le Gall, T.; Shin, D.-S.; Falck, J. R. *Tetrahedron Lett.* **1994**, *35*, 5449–5452.