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A common and versatile synthetic route to (–) and (+) pentenomycin I, (+) halopentenomycin I and dehydropentenomycin

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ABSTRACT

A versatile and stereoselective total synthesis of (+) and (–) pentenomycin I, (+) halopentenomycins I and dehydropentenomycin from a common chiral polyhydroxylated cyclopentene through oxidation and protection/deprotection has been described. Stereoselective hydroxymethylation, stereoselective Grignard reaction and ring closing metathesis are the key features of our approach.

1. Introduction

Cyclopentenones and their congeners[1] are widely used as chiral building blocks in organic synthesis and have been used for the synthesis of a large number of natural and unnatural products such as punaglandins **1**,[2] xanthocidin **2**,[3] untenone A **3**,[4] and (–) pentenomycin I **4**,[5] prostaglandins,[6] cyclopentanoid monoterpenoids,[7] carbocyclic nucleosides,[8] etc. (Fig. 1). In addition, a diverse range of natural products for example didemnenone **6**, parthenin **7**, tricycloclavulone **8**, etc.[9–11] contain cyclopentenone structural entities as important segments in their basic core structures (Fig. 1). Generally such molecules bearing cyclopentenone framework exert their biological effects through highly reactive α, β unsaturated carbonyl center which behaves as an excellent Michael acceptor toward various cellular nucleophiles.[12] Moreover, the highly oxygenated cyclopentanoid analogues are of increasing interest among the synthetic chemists because of their promising biological activity profiles[13] such as glycosidase inhibitor,[13a–g] aminoglycosidase antibiotic,[13h] anticancers,[13i–l] etc. In particular, pentenomycin, a cyclopentanoid class of antibiotics, exhibits moderate to strong activity against both Gram-positive and Gram-negative bacteria.[5a] It was isolated by Umino and co-workers in 1973 from culture strains of *Streptomyces eurythermus*.[5b,c] The assemblage of a variety of reactive functional groups along with the quaternary chiral center makes the molecule interesting for its synthesis. In addition, pentenomycin congeners with interesting biological properties have generated renewed interest in the chemistry of cyclopentanoid within past few years.[14–19] Various synthetic methods such as ring closing metathesis,[14] 1,3-dipolar nitrone alkene cycloaddition,[15] Pauson–Khand reaction,[16] Diels–Alder cycloaddition followed by decarbonylation[17] etc. have been reported regarding the total synthesis of pentenomycin including both racemic as well as enantiopure forms. Recently, Rao's group[18] have reported the synthesis of both natural (–) and unnatural (+) pentenomycin I using Tebbe olefination and intramolecular aldol condensation as their key steps.

Although many successful synthetic methods have been reported for the total synthesis of pentenomycin,[19] however, there is a still demand to synthesize both the isomers of pentenomycin I from a single precursor. On this line, dehydropentenomycin **5** (Fig. 1) is a closely related member of the pentenomycin family and has reasonable antibiotic potency.[20a,b] However a limited literature is available for the total synthesis of dehydropentenomycin.[20c] Therefore, we wish to report herein the total synthesis of both natural (–) and unnatural (+) pentenomycin I, dehydropentenomycin and halo derivatives of unnatural (+) pentenomycin I from a polyoxygenated cyclopentene as the common chiral building block, which has been synthesized from easily available starting material D-ribose *via* stereoselective hydroxymethylation, stereoselective Grignard reaction and ring closing metathesis as key steps.

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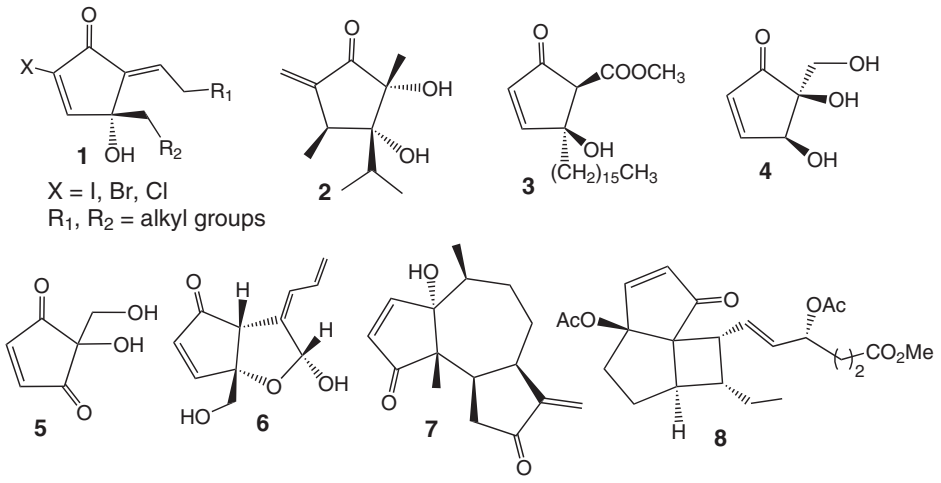


Fig. 1. Naturally occurring biomolecules: punaglandins **1**, xanthocidin **2**, untenone-A **3**, (−) pentenomycin I **4**, dehydropentenomycin **5**, didemnenone **6**, parthenin **7**, tricycloclavulone **8**.

2. Result and discussion

As a part of our ongoing research for the exploration of novel carbocyclic nucleoside template, and inspiration from the extensive and pioneering work of Jeong and co-workers,[21] we devised a common synthetic strategy for the total synthesis of both (+) and (−) pentenomycin I, (+) halopentenomycin I as well as dehydropentenomycin as shown in Scheme 1.

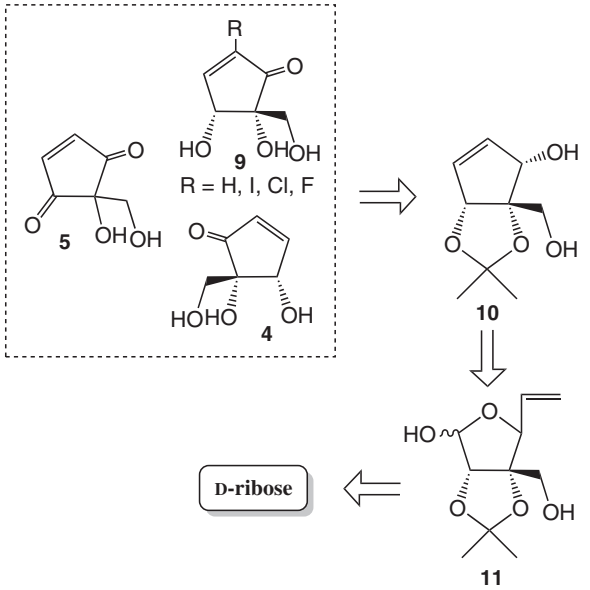
The carbocyclic framework **10** was envisioned as being a versatile synthetic building block towards the synthesis of pentenomycin analogues and dehydropentenomycin *via* oxidation, functional group transformations and deprotection. The carbocyclic framework **10** in turn could be obtained from the lactol **11** using Wittig and RCM reaction. The lactol **11** can be prepared from D-ribose *via* protection, stereoselective hydroxymethylation, stereoselective Grignard followed by oxidative cleavage.

A unified and general approach for chiral cyclopentenol **10** was commenced with the protection of D-ribose to 2,3 acetonide protected D-ribose **12** by treatment with catalytic amount of conc. H_2SO_4 in acetone. It was followed by stereoselective aldol condensation[22] using 37% aqueous formaldehyde in methanol to yield hydroxymethylated compound **13** which established a quarternary chiral center at the desired position with very good yield.

The hydroxymethylated compound **13** was subjected to a stereoselective Grignard reaction with vinyl magnesium bromide in THF under –78 °C to yield the ring opened polyhydroxylated alkene **14**. The stereoselectivity of Grignard reaction may be explained *via* the Felkin–Anh cyclic chelate transition model as shown in Fig. 2. This chelate transition state explains the β-attack of nucleophile from the less hindered face providing a single stereoisomer in a predominant amount. It was observed that Grignard reaction on acetonide protected D-ribose without hydroxymethylated chain[23] and with hydroxymethylated chain conserves the steroselectivity.

It was directly used for next step without purification due to its high polar nature. The ring opened Grignard adduct **14** was subjected to oxidative cleavage with sodium *m*-periodate in order to yield the desired lactol intermediate **11**. Wittig olefination of lactol **11** with methyl triphenylphosphonium ylide gave the diene **15** in a satisfactory yield which set the stage for ring closing metathesis.[24] Cyclization proceeded smoothly on the substrate **15** by employing Grubbs' second generation catalyst providing the cyclopentenol **10** in quantitative yield (Scheme 2). The structure of cyclopentenol **10** has been deduced through ^1H and ^{13}C NMR and HRMS. The stereochemical structure of compound **10** was confirmed with the help of single crystal X-ray structure (Fig. 3).

Selective allylic oxidation of **10** afforded the cyclopentenone **17** in a good yield. Then acetonide deprotection was accomplished by



Scheme 1. Retrosynthetic analysis.

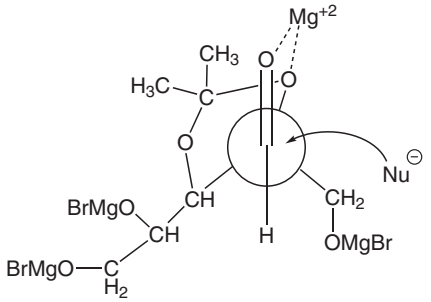
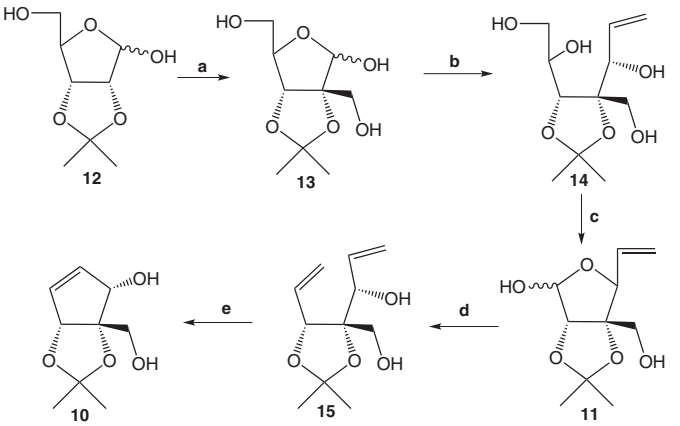
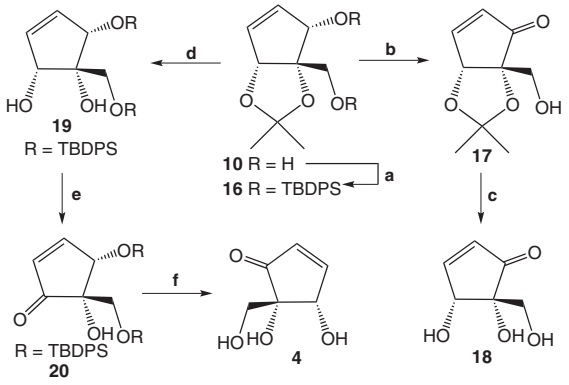


Fig. 2. Felkin–Anh cyclic chelate transition model.



Reagents and condtions: (a) 37% aq. HCHO, K_2CO_3, methanol, reflux, 72 h, 90%; (b) Vinyl magnesium bromide, THF, -78 °C-rt, 24 h; (c) $NaIO_4$ (0.65 M), CH_2Cl_2, 0 °C-rt, 1.5 h, 61% for two steps; (d) CH_3PPh_3Br, *t*-BuOK, THF, 0 °C-rt, 5 h, 75%; (e) Grubbs' second generation catalyst, CH_2Cl_2, rt, 24 h, 93%

Scheme 2. Synthesis of cyclopentenol **10**.



Reagents and condtions: (a) TBDPSCl, Imidazole, N,N-Dimethylformamide, 0 °C-rt, 24 h, 96%; (b) MnO_2, Toluene, 90 °C, reflux, 24 h, 77%; (c) 50% aq TFA, 0 °C-rt, 30 min, 82%; (d) TFA:THF:H_2O (5:4:3), 0 °C, 1.5 h, 93%; (e) PDC, CH_2Cl_2, rt, 5 h, 65%; (f) TBAF, AcOH, THF, 0 °C-rt, 1.5 h, 65%

Scheme 3. Synthesis of (+) pentenomycin I, **18** and (−) pentenomycin I, **4**.

trifluoroacetic acid and water to achieve synthesis of (+) pentenomycin I **18** with good yield.

A simple functional group transformation was envisioned for natural (−) pentenomycin I **4** from the common precursor **10** as per above mentioned strategy. Compound **10** was protected with TBDPSCl and imidazole to yield the disilyl ether **16**. After that a selective acetonide deprotection was accomplished under mild acidic condition in order to get the cyclopentenol **19** in a good yield. PDC oxidation in dry dichloromethane led to the cyclopentenone **20** followed by deprotection with TBAF culminated the natural (−) pentenomycin I **4** in a good yield (Scheme 3).

In order to achieve the halo analogues of (+) pentenomycin I, compound **10** was selectively protected as its mono silyl ether **21** and subsequently oxidized by PDC to give **22**. The compound **22** was subjected to electrophilic fluorination in the presence of *N*-fluorobenzenesulfonimide and n-butyllithium which resulted in decomposition of product. However, in the presence of bis-acetoxyiodobenzene and pyridinium hydrochloride the chloro derivative **23** was isolated with poor yield. Hence, the cyclopentenone **17** was directly converted to the chloro analogue **25** effectively using the same reagents. The chloro analogue **25** was then subjected to acetonide deprotection to yield the (+) chloropentenomycin I **27**. On the contrary, the iodinated product **24** was obtained in a quite good yield from the compound **22** upon treatment with iodine and pyridine in THF. Then, subsequent desilylation of compound **24** followed by acetonide deprotection led to (+) iodopentenomycin I **28** (Scheme 4).

On the other hand, total synthesis of dehydropentenomycin **5** was achieved from the same common intermediate **10** through manipulation of a few protection/deprotection steps. The mono-TBDPS protected cyclopentenol **21** was subjected to acetonide deprotection under mild acidic conditions to yield the triol **29** (Scheme 5). Then the dioxidation was investigated by several oxidizing agents such as (i) PDC, CH_2Cl_2, 4 Å MS, rt, 2 h, 14%;[25] (ii) MnO_2, CH_2Cl_2, rt-reflux, decomposed;[26] (iii) PCC, CH_2Cl_2, 4 Å MS, rt, 3.5 h, 9%;[27] (iv) CrO_3, pyridine, acetic anhydride, CH_2Cl_2, 0 °C–rt, 1.5 h, 35%;[28] (V) DMP, CH_2Cl_2, 0 °C–rt, 1.5 h, decomposed;[29] (vi) $(COCl)_2$, DMSO, CH_2Cl_2, Et_3N, –78 °C–rt, 2 h, 25%;[30] etc. to provide the dienone **31**. However, all our efforts were futile and only a trace amount of product was isolated.

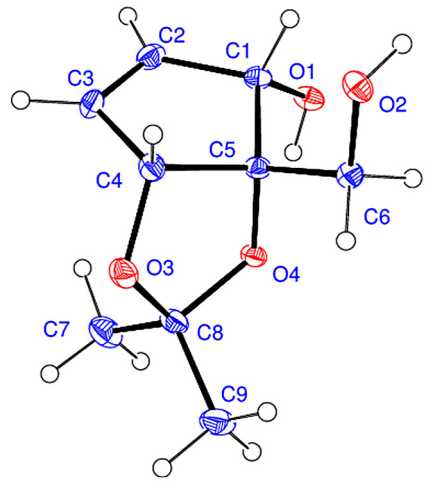
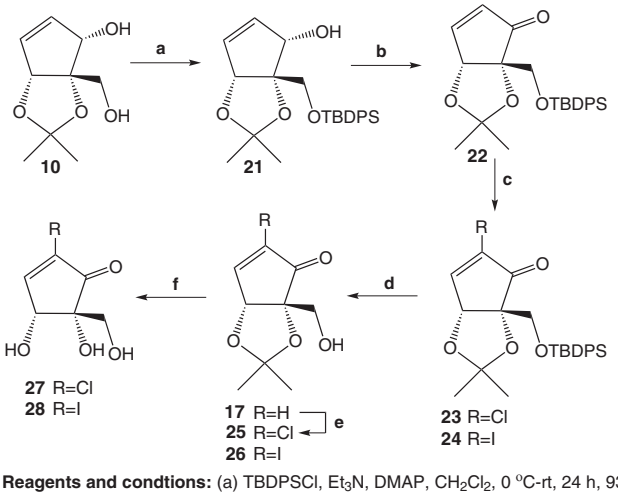
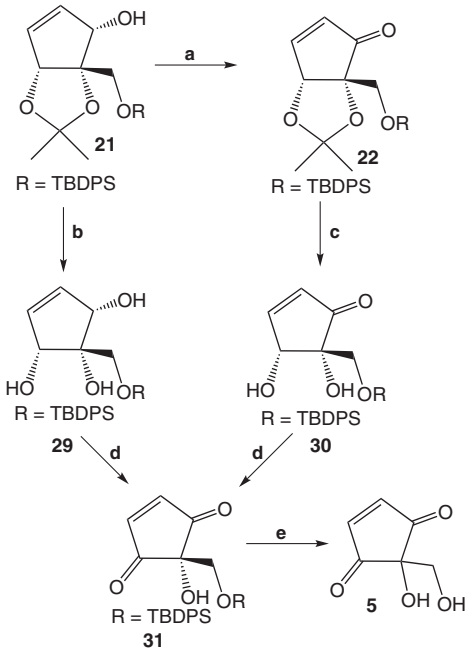


Fig. 3. X-ray crystal structure of cyclopentenol **10** (30% ellipsoid probability).



Reagents and condtions: (a) TBDPSCl, Et_3N, DMAP, CH_2Cl_2, 0 °C-rt, 24 h, 93%; (b) PDC, CH_2Cl_2, rt, 24 h, 79%; (c) i. for **23;** BAIB, Py.HCl, CH_2Cl_2, rt, 6 h, 5% ii. for **24;** I_2, Pyridine, THF, 0 °C-rt, 2 h, 90%; (d) for **26**; TBAF, AcOH, THF, 0 °C-rt, 2.5 h, 68%; (e) BAIB, Py.HCl, CH_2Cl_2, rt, 6 h, 15% (f) i. for **27;** TFA:THF:H_2O (2.5:1:1), 0 °C-rt, 12 h, 27% ii. for **28;** TFA:THF:H_2O (2:1:1), 0 °C-rt, 2 h, 60%.

Scheme 4. Synthesis of (+) chloropentenomycin **I**, **27** and (+) iodopentenomycin **I**, **28**.



Reagents and condtions: (a) PDC, CH_2Cl_2, rt, 24 h, 79%; (b) TFA:THF:H_2O (4:3:3), 0 °C, 1.5-2 h, 93%; (c) TFA:THF:H_2O (3:1:1), 0 °C, 3.5 h, 64% (bsr); (d) PDC, CH_2Cl_2, rt, 5 h, 38% (e) TBAF, AcOH, THF, 0 °C-rt, 4.5 h, 85%

Scheme 5. Synthesis of dehydropentenomycin, **5**.

At this juncture, we thought to explore the oxidation in a step wise manner. Towards this, first the mono-TBDPS protected product **21** was oxidized in PDC in dichloromethane to the cyclopentenone **22** which after acetonide deprotection provided the diol **30** in a good yield. The allylic alcohol oxidation was then carried out with several oxidizing agents such as (i) PCC, CH_2Cl_2, 4 Å MS, rt, 3.5 h, 15%; (ii) CrO_3, pyridine, acetic anhydride, CH_2Cl_2, 0 °C–rt, 1.5 h, 12%; (iii) MnO_2, CH_2Cl_2, rt-reflux, 35%; (iv) PDC, CH_2Cl_2, 4 Å MS, rt, 5 h, 38% to yield the same dienone **31** (Scheme 5). The low yield of oxidation may be attributed to the unstable nature of the dienone **31**. Finally, the TBDPS deprotection with TBAF buffered in acetic acid offered dehydropentenomycin **5** in a good yield.

3. Conclusion

The work described here presents a short and versatile approach for the total synthesis of both (+) and (−) isomers of pentenomycin I, (+) halopentenomycin I as well as dehydropentenomycin from a common polyhydroxylated cyclopentene intermediate *via* simple protection and/or deprotection and functional group interconversion. The common intermediate has been achieved *via* stereoselective hydroxymethylation, stereoselective Grignard reaction and ring closing metathesis as pivotal steps. The intrinsic flexibility of this approach may be employed to construct other cyclopentenone derivatives with multi hydroxyl groups and functionalized carbocycle templates for modified nucleoside derivatives.

4. Experimental section

4.1. General remarks

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without purification. All reactions were carried out under ambient atmosphere unless otherwise mentioned. Tetrahydrofuran (THF) was freshly distilled under argon atmosphere from sodium benzophenone ketyl. Dichloromethane was freshly distilled from P_2O_5 under argon atmosphere. All reactions were monitored by analytical thin layer chromatography (TLC) on aluminium precoated Merck silica gel plates (EM-60-F254). TLC visualization was accompanied using UV lamp (254 nm) or charring solution (ethanolic *p*-anisaldehyde). Column chromatography was generally performed on silica gel (100–200 mesh). Melting points were recorded in BUCHI M-560 instrument and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer ^1H NMR (400 MHz), ^{13}C NMR (100 MHz). Chemical shifts for ^1H NMR were reported as δ values (in parts per million) and coupling constants were in hertz (Hz). ^1H NMR spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm) or with TMS (δ 0.00 ppm) as internal standard. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.0 ppm, middle peak). IR spectra were obtained on NaCl plates (film) with a Bruker Tensor 27 FT-IR and selected absorbance are reported in cm^{-1}. High resolution (HR) mass spectrometry data were acquired by an Agilent 6520 (Q-TOF) mass spectrometer using MeOH as solvent. Optical rotations were measured in an Anton Paar MCP 100 Polarimeter. Single crystal X-ray structures were determined by Bruker D8 Venture diffractometer equipped with CMOS detector.

4.2. Synthesis of ((3aR,6aR)-4-hydroxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole-3a,6-diyl)dimethanol (*13*)

The hydroxymethylated compound (**13**) was prepared according to the reported procedure.[22]

4.3. (3aS,6aS)-6a-(Hydroxymethyl)-2,2-dimethyl-6-vinyltetrahydrofuro[3,4-d][1,3]dioxol-4-ol (*11*)

To a stirred suspension of hydroxymethylated compound **13** (2.61 g, 11.86 mmol) in dry THF (8 mL) was added vinyl magnesium bromide (65.25 mL, 65.25 mmol, 1.0 M solution in THF) at –78 °C and stirred at 0 °C for 1 h. Then it was stirred for 24 h at room temperature. It was then refluxed at 60 °C for 2.5 h to ensure the completion of reaction. The reaction mixture was quenched by slow addition of saturated ammonium chloride solution at 0 °C and the resulting precipitate was removed through a celite pad. The filtrate was evaporated under reduced pressure to give a crude oil **14** which was directly used for the next step without further purification.

To the stirred suspension of **14** (2.94 g, 11.85 mmol) in methylene chloride (50 mL), an aqueous solution of $NaIO_4$ (48.94 mmol, 0.65 M solution) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 1.5 h. After the addition of water, the mixture was extracted with methylene chloride. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure to give a crude product. It was then purified by silica gel column chromatography using hexane and ethyl acetate (4:1) as eluent to give the lactol **11** (1.38 g, 61% for two steps).

4.4. (−)-(S)-1-((4S,5R)-4-(Hydroxymethyl)-2,2-dimethyl-5-vinyl-1,3-dioxolan-4-yl)prop-2-en-1-ol (*15*)

To the stirred suspension of CH_3PPh_3Br (60.28 g, 168.74 mmol) in dry THF (150 mL), was added potassium *tert*-butoxide (18.93 g, 168.74 mmol) at 0 °C and the mixture was stirred at the same temperature for 20 minutes. Then it was brought to room temperature and stirred for 1 h to give a yellow suspension. To this stirred solution was added the lactol **11** (8.1 g, 37.46 mmol) in THF (50 mL) at 0 °C and the reaction mixture was stirred at room temperature for 5 h. Then the reaction mixture was partitioned between water (100 mL) and ethyl acetate (150 mL × 4) and the organic layer was

dried over Na_2SO_4, filtered and evaporated in vacuo. The residue was purified by silica gel column chromatography using hexane and ethyl acetate (5:1) as the eluent to give the diene **15** (5.95 g, 75%) as a colourless oil; $[\alpha]_D^{25}$ –93.848 (*c* 1.75, $CHCl_3$); R_f 0.5 (hexane:EtOAc, 1:2); IR (film)ν_{max}/cm^{-1}: 3423, 2988, 2937, 1377, 1248, 1218, 1178, 1117, 1043; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 (3H, s), 1.47 (3H, s), 2.16 (2H, br s), 3.65 (1H, d, *J* = 12 Hz), 3.79 (1H, d, *J* = 12 Hz), 4.33 (1H, d, *J* = 8 Hz), 4.73 (1H, d, *J* = 8 Hz), 5.26 (3H, td, *J* = 12 Hz, 4 Hz), 5.54 (1H, d, *J* = 16 Hz), 6.05–6.16 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.3, 28.1, 62.3, 72.7, 80.2, 84.4, 108.7, 116.7, 118.2, 132.7, 136.4; HRMS (ESI) (*m*/*z*): calcd for $C_{11}H_{18}O_4$ $[M + Na]^+$ 237.1102; found 237.0995.

*4.5. (+)-(3aS,4S,6aR)-3a-(Hydroxymethyl)-2,2-dimethyl-4,6a-ldihydro-3aH-cyclopenta[d][1,3]dioxol-4-ol (**10**)*

To the stirred solution of diene **15** (5.95 g, 27.76 mmol), in dry methylene chloride (60 mL) was added Grubbs' second generation catalyst (235 mg, 1 mol %) at room temperature. The reaction mixture was stirred for 24 h and evaporated in vacuo to give a brown residue. This residue was directly applied to silica gel column chromatography and purified by using hexane and ethyl acetate (3:1) as the eluent to give the cyclopentenol **10** (4.85 g, 93%) as a white crystalline solid; mp 50.4–53.2 °C; $[\alpha]_D^{25}$ +20.833 (*c* 0.09, $CHCl_3$); R_f 0.5 (hexane:EtOAc, 1:1); IR (KBr)ν_{max}/cm^{-1}: 3418, 3062, 2990, 2936, 2875, 1458, 1376, 1351, 1312, 1239, 1217, 1179, 1099, 1048; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (3H, s), 1.43 (3H, s), 3.01 (2H, br s), 3.73 (2H, s), 4.41 (1H, s), 4.90 (1H, s), 5.89 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.8, 29.1, 64.4, 75.4, 85.8, 89.4, 113.4, 132.7; HRMS (ESI) (*m*/*z*): calcd for $C_9H_{14}O_4$ $[M + Na]^+$ 209.0789; found 209.0786.

*4.6. (–)-(3aR,6aR)-3a-(Hydroxymethyl)-2,2-dimethyl-3aH-cyclopenta[d][1,3]dioxol-4(6aH)-one (**17**)*

To a stirred solution of cyclopentenol **10** (330 mg, 1.77 mmol) in dry toluene was added activated MnO_2 powder (4.80 g, 46.93 mmol) at room temperature under inert atmosphere and refluxed for 24 h at 90 °C. The reaction mixture was filtered in a celite pad and the filtrate was evaporated in vacuo to give the crude product. It was then applied on silica gel column chromatography and purified by using hexane and ethyl acetate (4:1) as the eluent to give the cyclopentenone **17** (250 mg, 77%) as a white crystalline solid; mp 67.7–69.6 °C; $[\alpha]_D^{25}$ –18.568 (*c* 0.1, $CHCl_3$); R_f 0.5 (hexane:EtOAc, 1:1); IR (KBr)ν_{max}/cm^{-1}: 3423, 2991, 2937, 1723, 1587, 1459, 1374, 1346, 1274, 1245, 1215, 1168, 1123, 1073; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28 (3H, s), 1.40 (3H, s), 2.50 (1H, s), 3.80 (2H, t, *J* = 12 Hz), 5.19 (1H, d, *J* = 4 Hz), 6.25 (1H, d, *J* = 8 Hz), 7.64 (1H, dd, *J* = 4 Hz, 8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.5, 28.7, 61.5, 81.4, 84.5, 115.4, 134.8, 160.9, 204.9; HRMS (ESI) (*m*/*z*): calcd for $C_9H_{12}O_4$ $[M + Na]^+$ 207.0633; found 207.0628.

*4.7. (+) Pentenomycin I (**18**)*

To the compound **17** (140 mg, 0.76 mmol) in H_2O (1 mL) trifluoroacetic acid (2 mL) was added dropwise at 0 °C and stirred at room temperature for 30 min. Then TFA was removed in vacuo under reduced pressure to give a colourless syrup and it was purified by column chromatography using methylene chloride and methanol (9:1) as eluent to give (+) pentenomycin I **18** (90 mg, 82%) as a colourless syrup; $[\alpha]_D^{25}$ +21.8 (*c* 0.35, MeOH) (lit.[14b] $[\alpha]_D$ +30.1 (c 0.1, EtOH); R_f 0.3 (CH_2Cl_2:CH_3OH, 10:1); IR (KBr)ν_{max}/cm^{-1}: 3417, 2929, 2851, 1750, 1715,1643, 1405, 1344, 1147, 1114, 1073, 1039, 1026; ^{1}H NMR (400 MHz, D_2O): δ 3.63 (2H, dd, *J* = 12 Hz, 24 Hz), 4.73 (1H, s), 6.35 (1H, d, *J* = 8 Hz), 7.75 (2H, dd, *J* = 4 Hz, 8 Hz); ^{13}C NMR (100 MHz, D_2O): δ 63.2, 71.6, 76.2, 133.4, 164.5, 209.8; HRMS (ESI) (*m*/*z*): calcd for $C_6H_8O_4$ $[M + Na]^+$ 167.0320; found 167.0313.

*4.8. (–)-tert-Butyl(((3aR,4S,6aR)-4-((tert-butyldiphenylsilyl)oxy)-2,2-dimethyl-4,6a-dihydro-3aH-cyclopenta[d][1,3]dioxol-3a-yl)methoxy)diphenylsilane (**16**)*

To a stirred solution of cyclopentenol **10** (520 mg, 2.79 mmol) in dry DMF (12 mL), imidazole (951 mg, 13.96 mmol) was added at 0 °C. To this solution TBDPSCl (2.2 mL, 8.40 mmol) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 24 h. Solvent was removed in vacuo and the reaction mixture was partitioned between water and diethyl ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and solvent was removed in vacuo to give the crude product which was purified by silica gel column chromatography using hexane and ethyl acetate (10:0.1) as eluent to give the di-TBDPS protected product **16** (1.798g, 96%) as a colourless viscous oil; $[\alpha]_D^{25}$ –19.697 (*c* 0.06, $CHCl_3$); R_f 0.7 (hexane:EtOAc, 9:1); IR (film)ν_{max}/cm^{-1}: 3070, 3051, 2957, 2932, 2892, 2858, 1468, 1427, 1364, 1243, 1211, 1190, 1110, 1060, 1005; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (9H, s), 1.11 (9H, s), 1.46 (3H, s); 1.55 (3H, s); 3.48 (1H, d, *J* = 8 Hz); 3.61 (1H, d, *J* = 6 Hz); 4.56 (1H, s); 4.91 (1H, s); 5.72 (1H, d, *J* = 8 Hz); 5.93 (1H, d, *J* = 4 Hz); 7.24–7.44 (12H, m); 7.52 (2H, d, *J* = 8 Hz); 7.61(2H, d, *J* = 4 Hz); 7.74(4H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.2, 19.3, 26.8, 26.9, 28.8, 29.1, 65.4, 76.3, 85.9, 89.2, 113.3, 127.58, 127.63, 127.67, 129.7, 132.6, 133.2, 133.3, 133.7, 134.3, 135.6, 135.7, 135.9, 136.1, 137.1; HRMS (ESI) (*m*/*z*): calcd for $C_{41}H_{50}O_4Si_2$ $[M + Na]^+$ 685.3145; found 685.3138.

*4.9. (+)-(1R,2R,5S)-5-(tert-Butyldiphenylsilyloxy)-1-((tert-butyldiphenylsilyloxy)methyl) cyclopent-3-ene-1,2-diol (**19**)*

To a stirred suspension of compound **16** (3.63 g, 5.48 mmol) in THF (4 mL) was added water (3 mL) followed by dropwise addition of trifluoroacetic acid (5 mL) at 0 °C and stirred for 1.5 h. The solution was neutralized by addition of sodium bicarbonate at 0 °C and partitioned between water and ethyl acetate. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and solvent was removed in vacuo to give the crude product which was purified by silica gel column chromatography using hexane and ethyl acetate (5:0.25) as eluent to give the di-TBDPS protected product **19** (3.2 g, 93%) as a white crystalline solid; mp 87–91.5 °C; $[\alpha]_D^{25}$ +1.814 (*c* 0.32, $CHCl_3$); R_f 0.5 (hexane:EtOAc, 10:1); IR (film)ν_{max}/cm^{-1}: 3483, 3070, 3051, 2957, 2932, 2892, 2859, 1783, 1468, 1427, 1391, 1362, 1336, 1171, 1111, 1053, 1002; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (9H, s), 1.10 (9H, s), 2.79 (1H, br s); 3.62 (1H, d, *J* = 12 Hz); 3.73 (1H, d, *J* = 8 Hz); 4.58 (1H, s); 4.85 (1H, s); 5.48 (1H, d, *J* = 8 Hz); 5.87 (1H, d, *J* = 4 Hz); 7.32–7.48 (12H, m); 7.59 (4H, dd, *J* = 8 Hz, 12 Hz); 7.68 (4H, t, *J* = 4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.25, 19.34, 26.8, 26.9, 64.4, 75.2, 79.4, 127.7, 127.8, 127.9, 128.0, 129.7, 129.8, 130.1, 130.2, 132.2, 132.4, 133.1, 133.2, 135.61, 135.64, 135.8, 135.2, 136.0; HRMS (ESI) (*m*/*z*): calcd for $C_{38}H_{46}O_4Si_2$ $[M + Na]^+$ 645.2832; found 645.2828.

*4.10. (+)-(4S,5S)-4-(tert-Butyldiphenylsilyloxy)-5-((tert-butyldiphenylsilyloxy)methyl)-5-hydroxycyclopent-2-enone (**20**)*

To a stirred solution of diol **19** (232 mg, 0.372 mmol) in dichloromethane (10 mL) was added pyridinium dichromate (560 mg, 1.48 mmol) and 4 Å molecular sieves (500 mg) at room temperature and stirred under inert atmosphere for 5 h. The reaction mixture was filtered in celite pad and the filtrate was dried under vacuo to give the crude product. It was then purified by silica gel column chromatography using hexane and ethyl acetate (5:0.2) as eluent to give the cyclopentenone **20** (150 mg, 65%) as a colourless viscous oil; $[\alpha]_D^{25}$ +8.653 (*c* 0.08, $CHCl_3$); R_f 0.6 (hexane:EtOAc, 10:1); IR (film)ν_{max}/cm^{-1}: 3492, 3070, 2956, 2929, 2857, 1729, 1467, 1427,

1363, 1338, 1110, 1054, 1002; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.78 (9H, s), 1.07 (9H, s), 3.50 (1H, d, J = 8 Hz); 3.53 (1H, s); 3.97 (1H, d, J = 4 Hz); 4.99 (1H, q, J = 4 Hz); 6.26 (1H, dd, J = 4 Hz, 8 Hz); 7.03 (1H, d, J = 4 Hz); 7.25–7.49 (16H, m); 7.64 (2H, d, J = 8 Hz); 7.67 (2H, d, J = 4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.2, 19.4, 26.7, 27.0, 64.9, 73.8, 74.3, 127.9, 128.3, 128.3, 129.89, 129.94, 130.7, 131.8, 132.6, 132.8, 132.9, 135.0, 135.6, 135.7, 135.8, 135.9, 160.6, 206.5; HRMS (ESI) (m/z): calcd for $C_{38}H_{44}O_4Si_2$ $[M + Na]^+$ 643.2675; found 643.2684.

4.11. (–) Pentenomycin I (**4**)

A buffered solution was prepared by addition of glacial acetic acid (0.03 mL, 0.587 mmol) to a solution of TBAF (0.340 mL, 1.17 mmol). Then a stirred solution of cyclopentenone **20** (731 mg, 1.17 mmol) in THF (10 mL) was treated with the previously prepared buffer solution at 0 °C and stirred at rt for 1.5 h. Solvent was removed in vacuo and the crude product was directly applied to silica gel column chromatography and it was purified by using methylene chloride and methanol (9:1) as eluent to give **4** (110 mg, 65%) as a colourless syrup; $[\alpha]_D^{25}$ –23.396 (*c* 0.27, MeOH) (lit.[14b] $[\alpha]_D$ –30.2 (c 0.29, EtOH); R_f 0.3 (CH_2Cl_2:CH_3OH, 10:1); ^{1}H NMR (400 MHz, D_2O): δ 3.63 (2H, dd, J = 12 Hz, 24 Hz), 4.73 (1H, s), 6.35 (1H, d, J = 8 Hz), 7.75 (2H, dd, J = 4 Hz, 8 Hz).

4.12. (+)-(3a*S*,4*S*,6a*R*)-3a-((tert-Butyldiphenylsilyloxy)methyl)-2,2-dimethyl-4,6a-dihydro-3aH-cyclopenta[d][1,3]dioxol-4-ol (**21**)

To a stirred solution of cyclopentenol **10** (1.54 g, 8.3 mmol) in dichloromethane (15 mL) was added triethyl amine (3 mL, 20 mmol) dropwise at 0 °C under inert atmosphere. Then TBDPSCl solution (2.39 mL, 9.13 mmol) was added dropwise at 0 °C followed by a catalytic amount of DMAP and stirred for 24 h at rt. The reaction mixture was partitioned between water and ethyl acetate, organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and solvent was removed under reduced pressure to provide the crude product. It was then purified by silica gel column chromatography and it was purified by using hexane and ethyl acetate (5:0.25) as eluent to give a the mono-TBDPS protected product **21** (3.29 g, 93%) as a colourless viscous oil; $[\alpha]_D^{25}$ +11.799 (*c* 0.1, $CHCl_3$); R_f 0.3 (hexane:EtOAc, 9:1); IR (film)ν_{max}/cm^{-1}: 3449, 3069, 2932, 2858, 1467, 1427, 1374, 1110; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (9H, s), 1.36 (9H, s), 1.38 (1H, s); 2.68 (1H, br s); 3.77 (2H, s); 4.59 (1H, s); 5.03 (1H, s); 5.92 (2H, q, J = 4 Hz); 7.36–7.44 (m, 6H); 7.63–7.65 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.5, 26.9, 29.0, 29.3, 64.5, 75.0, 86.1, 89.3, 113.4, 127.9, 130.01, 130.03, 132.9, 133.1, 133.3, 135.75, 135.81, 137.4; HRMS (ESI) (m/z): calcd for $C_{25}H_{32}O_4Si$ $[M + Na]^+$ 447.1967; found 447.1965.

4.13. (–)-(3a*R*,6a*R*)-3a-(((tert-Butyldiphenylsilyl)oxy)methyl)-2,2-dimethyl-3aH-cyclopenta[d][1,3]dioxol-4(6aH)-one (**22**)

To a stirred solution of the cyclopentenol **21** (250 mg, 0.588 mmol) in dichloromethane was added pyridinium dichromate (886 mg, 2.35 mmol) and 4 Å molecular sieves (100 mg) at room temperature and stirred under inert atmosphere for overnight. The reaction mixture was filtered in celite pad and the filtrate was dried under vacuo to give the crude product. It was then purified by silica gel column chromatography using hexane and ethyl acetate (5:0.15) as eluent to give the cyclopentenone **22** (197 mg, 79%) as a colourless viscous oil; $[\alpha]_D^{25}$ –0.671 (*c* 0.30, $CHCl_3$); R_f 0.7 (hexane:EtOAc, 10:1); IR (film)ν_{max}/cm^{-1}: 3071, 3050, 2995, 2957, 2932, 2891, 2858, 1731, 1589, 1471, 1427, 1381, 1372, 1343, 1270, 1245, 1214, 1180, 1111, 1046; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.01 (9H, s); 1.35 (3H, s); 1.39 (3H, s); 3.83 (1H, d, J = 10 Hz); 4.10 (1H, d, J = 10 Hz); 5.32 (1H, s); 6.39 (1H, d, J = 5 Hz) 7.40–7.48 (6H, m); 7.63–7.67 (4H, m); 7.72 (1H, dd, J = 5 Hz, 10 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 19.2, 26.7, 28.5, 28.6, 63.1, 82.1, 84.2, 115.3, 127.8, 127.9, 129.92, 129.94, 132.3, 132.9, 135.3, 135.5, 135.7, 160.2, 204.7; HRMS (ESI) (m/z): calcd for $C_{25}H_{30}O_4Si$ $[M + Na]$+ 445.1811; found 445.1806.

4.14. (+)-(3a*R*,6a*R*)-3a-((tert-Butyldiphenylsilyloxy)methyl)-5-iodo-2,2-dimethyl-3aH-cyclopenta[d][1,3]dioxol-4(6aH)-one (**24**)

To a stirred solution of cyclopentenone **22** (1.5 g, 3.54 mmol) in THF (15 mL) was added iodine (1.35 g, 5.31 mmol) at room temperature under inert atmosphere. To this solution, pyridine (0.286 mL, 3.54 mmol) was added at 0 °C and the reaction mixture was stirred at rt for 2 h. The reaction mixture was diluted with water. The organic layer was extracted with methylene chloride, washed with brine, dried over anhydrous Na_2SO_4, filtered and solvent was evaporated to give the crude product. It was then purified by silica gel column chromatography using hexane and ethyl acetate (5:0.2) as eluent to give the iodo substituted cyclopentenone **24** (1.75 g, 90%) as a colourless viscous oil; $[\alpha]_D^{25}$ +27.442 (*c* 0.2, $CHCl_3$); R_f 0.8 (hexane:EtOAc, 20:1); IR (film)ν_{max}/cm^{-1}: 3070, 2991, 2932, 2858, 1740, 1570, 1466, 1427, 1376, 1316, 1260, 1212, 1108, 1043, 1009; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (9H, s); 1.29 (3H, s), 1.35 (3H, s); 3.79 (1H, d, J = 8 Hz); 4.12 (1H, d, J = 8 Hz); 5.19 (1H, d, J = 4 Hz); 7.38–7.45 (6H, m); 7.56–7.61 (4H, m); 8.06 (1H, d, J = 4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.2, 26.7, 28.2, 28.4, 63.5, 81.9, 83.3, 106.4, 115.5, 127.9, 129.9, 132.0, 135.5, 135.7, 165.3, 199.5; HRMS (ESI) (m/z): calcd for $C_{25}H_{29}IO_4Si[M + Na]^+$ 571.0777; found 571.0772.

4.15. (+)-(3a*R*,6a*R*)-3a-(Hydroxymethyl)-5-iodo-2,2-dimethyl-3aH-cyclopenta[d][1,3]dioxol-4(6aH)-one (**26**)

A buffer solution was prepared by addition of acetic acid (0.05 mL, 0.9 mmol) to TBAF (1M solution in THF, 1.82 mL, 1.82 mmol). To a stirred solution of the compound **24** (1 g, 1.82 mmol) was added the previously prepared buffer solution dropwise at 0 °C and stirred at room temperature for 2.5 h. Solvent was removed in vacuo and the crude product was directly applied to silica gel column chromatography. Then it was purified by using hexane and ethyl acetate (4:1) as eluent to give the iodocyclopentenone **26** (382 mg, 68%) as a yellow viscous oil; $[\alpha]_D^{25}$ +23.622 (*c* 0.1, $CHCl_3$) R_f 0.3 (hexane:EtOAc, 6:1); IR (film)ν_{max}/cm^{-1}: 3450, 3065, 2990, 2935, 2875, 1733, 1568, 1457, 1377, 1318, 1243, 1213, 1159, 1111, 1078, 1054; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (3H, s); 1.45 (3H, s); 2.49 (1H, br s); 3.88 (2H, q, J = 12 Hz); 5.22 (1H, d, J = 4 Hz); 8.07 (1H, d, J = 4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.3, 28.6, 61.5, 82.4, 105.4, 115.7, 166.0, 199.3; HRMS (ESI) (m/z): calcd for $C_9H_{11}IO_4[M + Na]^+$ 332.9599; found 332.9594.

4.16. (+) Iodopentenenomycin I (**28**)

The compound **26** (380 mg, 1.22 mmol) was treated with THF, water and trifluoroacetic acid in 1:1:2 proportion at 0 °C and stirred at rt for 2 h. Then TFA was removed in vacuo under reduced pressure to give a colourless syrup and it was purified by column chromatography using methylene chloride and methanol (20:1) as eluent to give (+) iodopentenomycin I **28** (195 mg, 60%) as a yellow crystalline solid; mp 87.0–92.7 °C; $[\alpha]_D^{25}$ +15.714 (*c* 0.07, MeOH); R_f 0.4 (CH_2Cl_2:CH_3OH, 10:1); IR (film)ν_{max}/cm^{-1}: 3282, 2931, 2879, 1730, 1632, 1570, 1447, 1402, 1371, 1266, 1193, 1159, 1096, 1065, 1003; ^{1}H NMR (400 MHz, D_2O): δ 3.66 (1H, d, J = 12 Hz); 3.75 (1H, d, J = 12 Hz); 4.78 (1H, d, J = 4 Hz); 8.25 (1H, d, J = 4 Hz); ^{13}C NMR (100 MHz, D_2O): δ 63.3, 72.9, 74.7, 102.8, 169.9, 204.8; HRMS (ESI) (m/z): calcd for $C_6H_7O_4I$ $[M + Na]^+$ 292.9286; found 292.9274.

*4.17. (+)-(3a*R*,6a*R*)-5-Chloro-3a-(hydroxymethyl)-2,2-dimethyl-3aH-cyclopenta[d][1,3]dioxol-4(6aH)-one (**25**)*

To a stirred solution of cyclopentenone **17** (287 mg, 1.558 mmol) in dichloromethane (10 mL) were added bis-acetoxyiodobenzene (602.2 mg, 1.87 mmol) and pyridinium hydrochloride (432.1 mg, 3.74 mmol) at room temperature and stirred for 6 h. Pyridine was removed in vacuo and after the addition of water, the mixture was extracted with methylene chloride. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure to give a crude product. It was then purified by silica gel column chromatography using hexane and ethyl acetate (6:1) as eluent to give the chloro derivative **25** (51 mg, 15%) as a colourless viscous oil; $[\alpha]_D^{25}$ +23.952 (*c* 0.16, $CHCl_3$); R_f 0.8 (hexane:EtOAc, 1:1); IR (film)ν_{max}/cm^{-1}: 3472, 3075, 2992, 2938, 2878, 1740, 1592, 1458, 1376, 1321, 1269, 1243, 1215,1164, 1096, 1053; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (3H, s), 1.47 (3H, s); 1.99 (1H, s); 3.89 (2H, s); 5.24 (1H, d, *J* = 4 Hz); 7.58 (1H, d, *J* = 4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.5, 28.7, 61.6, 78.9, 84.4, 115.7, 137.9, 153.4, 196.7; HRMS (ESI) (*m*/*z*): calcd for $C_9H_{11}O_4Cl$ $[M + Na]^+$ 241.0243; found 241.0242.

*4.18. (+) Chloropentenenomycin I (**27**)*

The compound **25** (100 mg, 0.457 mmol) was treated with THF, water and trifluoroacetic acid in 1:1:2.5 proportion at 0 °C and stirred at rt for 12 h. Then TFA was removed in vacuo under reduced pressure to give a colourless syrup and it was purified by column chromatography using methylene chloride and methanol (20:1) as eluent to give (+) chloropentenomycin I **27** (22 mg, 27%) as a colourless viscous oil; $[\alpha]_D^{25}$ +25.714 (*c* 0.07, MeOH); R_f 0.8 (CH_2Cl_2:CH_3OH, 10:1); IR (film)ν_{max}/cm^{-1}: 3417, 1727, 1637, 1276, 1073; ^{1}H NMR (400 MHz, D_2O): δ 3.70 (1H, d, *J* = 12 Hz); 3.79 (1H, d, *J* = 12 Hz); 4.82 (1H, d, *J* = 4 Hz); 7.81(1H, d, *J* = 4 Hz); ^{13}C NMR (100 MHz, D_2O): δ 63.4, 69.7, 76.3, 136.4, 157.5, 201.9; HRMS (ESI) (*m*/*z*): calcd for $C_6H_7O_4Cl$ $[M + Na]^+$ 200.9930; found 200.9925.

*4.19. (+)-(1*R*,2*S*,3*S*)-2-(((*tert*-Butyldiphenylsilyl)oxy)methyl) cyclopent-4-ene-1,2,3-triol (**29**)*

The cyclopentenol **21** (3.29 g, 7.74 mmol) was treated with THF, water and trifluoroacetic acid in 3:3:4 proportion at 0 °C and stirred for 1.5–2 h. The reaction mixture was neutralized by addition of $NaHCO_3$ and partitioned between water and ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and solvent was removed under reduced pressure to provide the crude product. It was then purified by silica gel column chromatography and it was purified by using hexane and ethyl acetate (3:1) as eluent to give the triol **29** (3.29 g, 93%) as a white crystalline solid; mp 110.4–111.6 °C; $[\alpha]_D^{25}$ +0.744 (*c* 0.1, $CHCl_3$); R_f 0.3 (hexane:EtOAc, 1:1); IR (film)ν_{max}/cm^{-1}: 3468, 3390, 3132, 3052, 2955, 2923, 2892, 2857, 2745, 2713; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (9H, s); 2.68 (2H, br s); 3.74 (2H, s); 4.48 (2H, s); 5.84 (2H, s); 7.36–7.44 (6H, m); 7.64–7.66 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.4, 27.1, 66.8, 76.3, 79.9, 128.0, 130.1, 133.1, 134.3, 135.8; HRMS (ESI) (m/z): calcd for $C_{22}H_{28}O_4Si$ $[M + Na]^+$ 407.1654; found 407.1651.

*4.20. (+)-(4*R*,5*R*)-5-(((*tert*-Butyldiphenylsilyl)oxy)methyl)-4,5-dihydroxycyclopent-2-enone (**30**)*

The cyclopentenone **22** (2.58 g, 6.1 mmol) was treated with THF, water and trifluoroacetic acid in 1:1:3 proportion at 0 °C and stirred for 3.5 h. The reaction mixture was neutralized by addition of $NaHCO_3$ and partitioned between water and ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and solvent was removed under reduced pressure to provide the crude product. It was then purified by silica gel column chromatography using hexane and ethyl acetate (3:1) as eluent to give the diol **30** (652 mg, 64% (bsr)) as a white crystalline solid; mp 55.7–57.2 °C; $[\alpha]_D^{25}$ +11.682 (*c* 0.1, $CHCl_3$); R_f 0.5 (hexane:EtOAc, 4:1); IR (film)ν_{max}/cm^{-1}: 3372, 3074, 3036, 3012, 2958, 2936, 2894, 2860, 1721, 1592; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.02 (9H, s); 3.05 (1H, s); 3.41 (1H, s); 3.74 (1H, d, *J* = 10 Hz); 3.85 (1H, d, *J* = 10 Hz); 4.85 (1H, s); 6.36 (1H, d, *J* = 5 Hz); 7.39–7.48 (6H, m); 7.60–7.65(4H, m); 7.68 (1H, dd, *J* = 5 Hz, 10 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 19.2, 26.7, 65.3, 72.5, 74.7, 127.85, 127.89, 130.0, 132.3, 132.6, 133.9, 135.57, 135.62, 162.8, 206.4; HRMS (ESI) (*m*/*z*): calcd for $C_{22}H_{26}O_4Si$ $[M + Na]^+$ 405.1498; found 405.1499.

*4.21. (+)-(3a*R*,6a*R*)-3a-(((*tert*-Butyldiphenylsilyl)oxy)methyl)-2,2-dimethyl-3aH-cyclopenta[d][1,3]dioxol-4(6aH)-one (**31**)*

To a stirred solution of the cyclopentenol **30** (976.9 mg, 2.553 mmol) in dichloromethane were added pyridinium dichromate (3.843 g, 10.21 mmol) and 4 Å molecular sieves (100 mg) at room temperature and stirred under inert atmosphere for 5 h. The reaction mixture was filtered in celite pad and the filtrate was dried under vacuo to give the crude product. It was then purified by silica gel column chromatography using hexane and ethyl acetate (3:1) as eluent to give the cyclopentenone **31** (368.9 mg, 38%) as a yellow crystalline solid; mp 129.9–131.4 °C; $[\alpha]_D^{25}$ +2.077 (*c* 0.09, $CHCl_3$); R_f 0.5 (hexane:EtOAc, 3:1); IR (KBr)ν_{max}/cm^{-1}: 3482, 3063, 3028, 2957, 2928, 2892, 2858, 1756, 1708, 1465, 1427, 1385, 1360, 1331, 1117; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.91 (9H, s); 3.01 (1H, d, *J* = 10 Hz); 3.84 (2H, s); 7.35–7.43 (6H, m); 7.45 (2H, s); 7.49–7.51 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 19.1, 26.6, 63.5, 74.1, 127.9, 130.1, 131.8, 135.5, 149.7, 202.5; HRMS (ESI) (m/z): calcd for $C_{22}H_{24}O_4Si$ $[M + Na]^+$ 403.1341; found 403.1340.

*4.22. Dehydropentenomycin (**5**)*

A buffered solution was prepared by addition of glacial acetic acid (0.022 mL, 0.383 mmol) to a solution of TBAF (0.228 mL, 0.784 mmol). Then a stirred solution of cyclopentenone **31** (300 mg, 0.788 mmol) in THF (10 mL) was treated with the previously prepared buffer solution at 0 °C and stirred at rt for 4.5 h. Solvent was removed in vacuo and the crude product was directly applied to silica gel column chromatography and it was purified by using methylene chloride and methanol (8:1) as eluent to give dehydropentenomycin **5** (95 mg, 85%) as a yellow viscous liquid; R_f 0.5 (CH_2Cl_2:CH_3OH, 10:1); IR (film)ν_{max}/cm^{-1}: 3384, 2937, 1754, 1707, 1638, 1331, 1126, 1055, 1033; ^{1}H NMR (400 MHz, acetone-d_6): δ 3.79 (2H, d, *J* = 5.2 Hz); 4.28 (1H, t, *J* = 5.2 Hz); 5.17 (1H, s); 7.51(2H, s); ^{13}C NMR (100 MHz, acetone-d_6): δ 63.6, 74.1, 149.6, 205.2; HRMS (ESI) (*m*/*z*): calcd for $C_6H_6O_4$ $[M + Na]^+$ 165.0163; found 165.0154.

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Appendix: Supplementary material Spectral data and X-ray crystallographic data

Supplementary data to this article can be found online at doi:10.1016/j.carres.2015.08.003.

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