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First stereoselective total synthesis of triumfettamide

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ABSTRACT

The first total synthesis of triumfettamide (**1**) is described. The asymmetric syntheses of two highly functionalized units—α-hydroxylated C17 monounsaturated fatty acid unit (**2**) and C26 phytosphingosine (**3**) have been accomplished involving Sharpless asymmetric dihydroxylation, Sharpless kinetic resolution, regioselective epoxide opening, regioselective DIBAL-H reduction of acetal, Wittig olefination as the key steps. Finally N-acylation of phytosphingosine **3** with (2*R*,6*Z*)-2-hydroxy-6-heptadecenoic acid **2** followed by DDQ deprotection of PMB, provided target compound **1**.

1. Introduction

Phytoceramides (Fig. 1) are a unique class of secondary metabolites, which play essential roles in cell growth, survival and cell death. This class of compounds is composed of phytosphingosine base[1] and fatty acid linked by an amide bond. These are abundant in yeast, plants[2] and also in mammals.[3] They exhibit a wide spectrum of biological activities.[4] One important application of phytoceramides is in cosmetic industries as they play important roles in human stratum corneum.[5] They are involved in skin permeability and antimicrobial barrier homeostatic functions.[6]

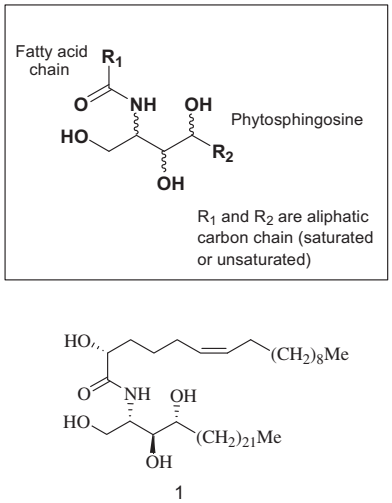

Fig. 1. Structure of phytoceramide and triumfettamide (**1**).

Triumfettamide **1** (Fig. 1), is a phytoceramide, which was isolated from *Triumfetta cordofolia A.* RICH,[7] a wild shrub, which is localized in the tropical Africa. This species is used as folk medicine for the treatment of diahorrea, dysentery and cholera. Its crushed stems are used to treat wounds and aqueous extracts of its stems and leaves are also employed as laxative, dystocia etc. We have long been engaged in the synthesis of bioactive natural products[8] having chiral 2-amino alcohol moiety and in continuation of our research work on synthesis of naturally occurring bioactive sphingolipids,[9] we report herein a concise and convergent synthesis of triumfettamide **1** involving Sharpless asymmetric dihydroxylation,[10] Sharpless kinetic resolution,[11] regioselective DIBAL-H reduction of acetal,[12] regioselective epoxide opening[13] and Wittig olefination[14] as the key steps. To the best of our knowledge, no total synthesis of **1** has been reported till date.

2. Results and discussion

2.1. Synthetic approach

Retrosynthetic analysis of triumfettamide **1** is depicted in Scheme 1. We envisioned completion of the synthesis of

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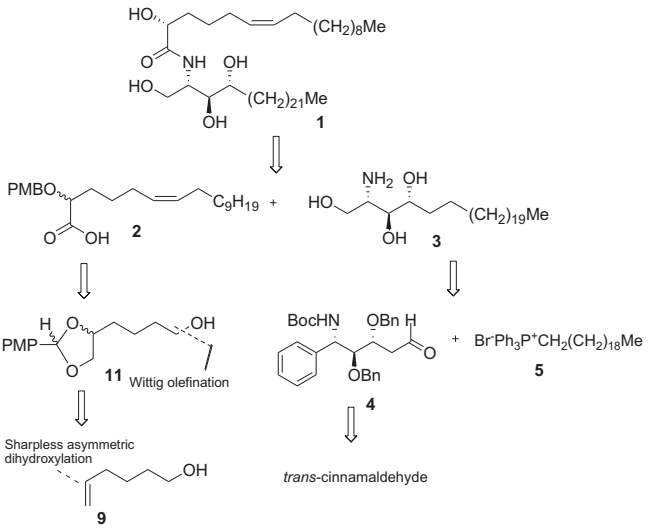
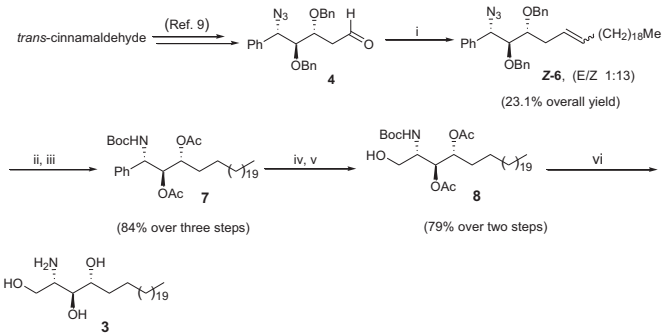


Scheme 1. Retrosynthesis of triumfettamide.

triumfettamide **1** occurring through N-acylation between C26 phytosphingosine **3** and (2*R*,6*Z*)-2-hydroxy-6-heptadecenoic acid **2**. The synthesis was designed with several key principles in mind, first we planned creation of chiral hydroxyl group at α-position of fatty acid **2** occurring through Sharpless asymmetric dihydroxylation[10] reaction of commercially available hex-5-en-1-ol **9**. The C-1 carbonyl groups of oxidized products of **11a** and **11b** would be elongated through Wittig olefination resulting *Z*-olefin of the required hydrocarbon chain. Reductive opening of acetal **12a**–**b** with DIBAL-H could be used for the formation of terminal primary alcohol, which in turn would be converted to carboxylic acid (Scheme 1). The C26 phytosphingosine part could be synthesized from aldehyde **4** through Wittig olefination with phosphonium salt **5**. Finally aldehyde **4** could be obtained from *trans*-cinnamaldehyde.

2.2. Synthesis of C26 D-*ribo*-phytosphingosine

Recently we have reported a stereoselective synthetic route to C18 D-*ribo*-phytospingosine starting from a cheap and commercially available *trans*-cinnamaldehyde.[9] Using the same synthetic route we synthesized the important intermediate aldehyde **4** from *trans*-cinnamaldehyde (Scheme 2). At this step different alkyl chains of varied length can be linked to construct phytosphingosines of different alkyl chain backbones. Here we used C20 phosphonium salt to get C26 phytosphingosine **3**.

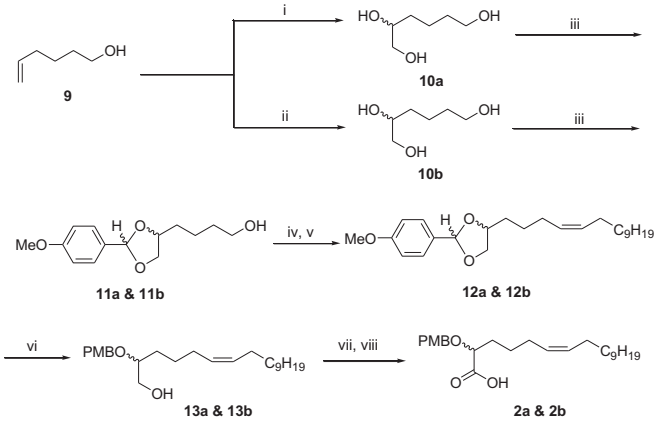


Scheme 2. Synthesis of C20 D-*ribo*-phytosphingosine. Reagents and conditions: (i) $Br^{-}Ph_3P^{+}CH_2(CH_2)_{18}Me$ (**5**), *n*-BuLi, THF, −40 °C to rt, 5 h; (ii) 10% Pd/C, H_2, EtOAc, rt; $(Boc)_2O$, Et_3N, DCM, rt; (iii) Ac_2O, pyridine, DMAP, 2 h,; (iv) $NaIO_4$, $RuCl_3\cdot H_2O$, CCl_4/CH_3CN/H_2O (2:2:3), 0 °C to rt, 8 h; (v) $BH_3\cdot Me_2S$, THF, −78 °C to rt, 6 h; (vi) pyridine, MeOH, rt, 4 h; TFA, rt, 2.5 h, 95% yield, 98% ee.

Wittig olefination of the aldehyde **4** with Wittig salt ($Br^{-}Ph_3P^{+}CH_2C_{19}H_{39}$) **5** using *n*-BuLi as base in dry THF at low temperature furnished the *Z*-olefin **6** contaminated with its *E*-isomer in the ratio of 13:1 in 23% overall yield starting from *trans*-cinnamaldehyde. Catalytic hydrogenation of compound **6** with 10% Pd/C in EtOAc[15] at room temperature reduced the azide and double bond as well as deprotected the benzyl groups. This on *N*-Boc protection with $(Boc)_2O$, Et_3N in DCM[16] followed by acetylation of the diol with Ac_2O in pyridine using DMAP[17] as catalyst gave the protected amino diol **7**. Phenyl ring cleavage to carboxylic group on treatment with $RuCl_3\cdot 3H_2O$, $NaIO_4$, in CH_3CN/CCl_4/H_2O solvent system[18] followed by $BH_3\cdot Me_2S$ reduction in dry THF[19] at room temperature provided the aminotriol **8**. Finally base catalysed deprotection of two O-Ac of **8** using Et_3N in MeOH[20] at room temperature followed by acid catalysed *N*-Boc deprotection (TFA/DCM at room temperature)[16] furnished the phytosphingosine **3**.

2.3. Synthesis of (2*R*,6*Z*)-2-hydroxy-6-heptadecenoic acid

As illustrated in Scheme 3, we began the synthesis of (2*R*,6*Z*)-2-hydroxy-6-heptadecenoic acid by subjecting hex-5-en-1-ol **9** to Sharpless asymmetric dihydroxylation[13] using AD-mix-α (and AD-mix-β) to provide the triols **10a**–**b** in 96% yield with 99% ee (as determined by chiral column HPLC) as colourless gum. The triol **10a**–**b** was protected as benzylidene acetals by reaction with dimethoxy acetal *p*-anisaldehyde and catalytic CSA giving compounds **11a**–**b** as a mixture of two diastereomers (1:1) in 96% yield.[21]



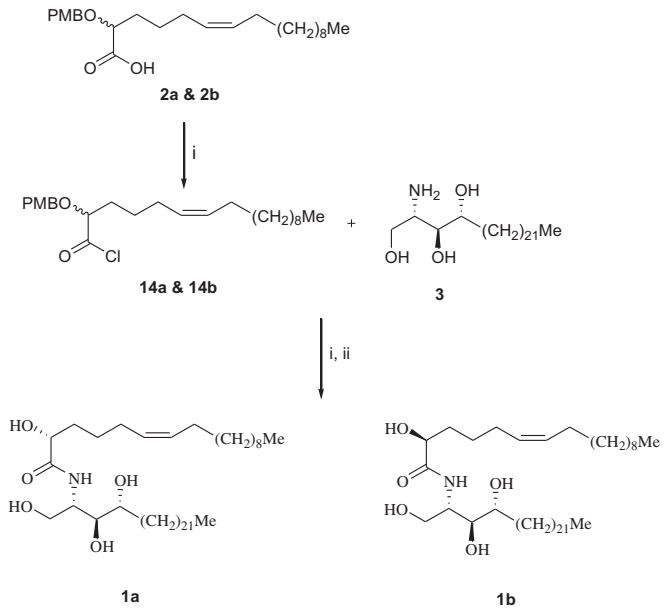
Scheme 3. Synthesis of (2*R*,6*Z*)-2-hydroxy-6-heptadecenoic acid. Reagents and conditions: (i) AD-mix-α, *t*-BuOH/H_2O (1:1), 0 °C, 96%; (ii) AD-mix-β, *t*-BuOH/H_2O (1:1), 0 °C, 96%; (iii) *p*-methoxybenzyl-dimethyl acetal, CSA, DCM, rt, 91%; (iv) Dess–Martin periodinane, $NaHCO_3$, DCM, rt; (v) $Br^{-}Ph_3P^{+}CH_2(CH_2)_9Me$, *n*-BuLi, THF, −45 °C to rt, 89% over two steps; (vi) DIBAL-H, DCM, −78 °C, 96%; (vii) Dess–Martin periodinane, $NaHCO_3$, DCM, rt; (viii) $NaClO_2$, $NaHPO_4$, *t*-BuOH, H_2O, H_2O_2, 87% over two steps.

Dess–Martin periodinane oxidation[22] of the terminal hydroxyl group of diastereomers **11a**–**b** provided the corresponding aldehydes, which were subjected to Wittig olefination using $Br^{-}Ph_3PCH_2(CH_2)_9Me$ in the presence of *n*-BuLi at −45 °C to furnish **12a**–**b** in 89% yield with major *Z*-olefin contaminated with its *E*-isomers in the ratio of 12.3:1. Regioselective reduction of acetal **12a**–**b** with DIBAL-H in DCM[12] at −78 °C provided the compound **13a**–**b** in 96% yield. Finally the terminal hydroxyl group of **13a**–**b** were oxidised to aldehyde using Dess–Martin periodinane followed by Pinnick oxidation[23] ($NaClO_2$, $NaHPO_4$, H_2O_2, *t*-BuOH/H_2O) to provide the PMB protected α-hydroxyl fatty acids **2a**–**b**.

2.4. Synthesis of triumfettamide

With phytosphingosine **3**, and fatty acids **2a**–**b** in hand, we performed the N-acylation by first converting the fatty acids **2a**–**b**

to their corresponding acid chlorides and then treated with **3** in presence of base (Scheme 4). Exposure of **2a**–**b** to $SOCl_2$ under reflux condition[24] provided the corresponding acid chlorides **14a**–**b**, which on treatment with amine **3** in THF/NaOAc (aq) 8 M (1:1) system,[16] followed by PMB deprotection with DDQ in DCM/MeOH[25] furnished the target compounds **1a**–**b** in 70% yield over three steps (Scheme 3). We compared the spectroscopic data recorded for the synthetic Triumfettamide **1a** and **1b** with the reported natural product **1**. A comparison of the optical rotations further corroborates this assignment. Natural **1** and synthetic **1a** show optical rotations $[\alpha]_D^{20}$ −7.36 (*c* 0.095, C_5H_5N)[7] and $[\alpha]_D^{20}$ −6.1 (*c* 0.108, C_5H_5N), which is almost identical, while the isomer **1b**has $[\alpha]_D^{20}$ +1.7 (*c* 0.112, C_5H_5N).



Scheme 4. Synthesis of triumfettamide through N-acylation of C26 D-*ribo*-phytosphingosine with fatty acid. Reagents and conditions: (i) $SOCl_2$, reflux, 90 min; (ii) NaOAc (aq), THF, 2 h, rt; (iii) DDQ, DCM–MeOH, 2 h, rt.

3. Conclusions

A concise and convergent synthetic route for the synthesis of triumfettamide has been developed. The synthesis of novel chiral α-hydroxy fatty acid fragment was accomplished using Sharpless asymmetric dihydroxylation and regioselective DIBAL-H reduction of acetal. Wittig olefination was successfully applied to introduce aliphatic alkyl chains. The overall yield of the target compounds **1a** and the isomer **1b** are 6.5% and 6.1% starting from commercially available and inexpensive *trans*-cinnamaldehyde and hex-5-en-1-ol.

4. Experimental section

4.1. General

The following solvents and reagents were dried prior to use: CH_2Cl_2 (from P_2O_5), Et_2O, and THF (freshly distilled from sodium/benzophenone). Analytical thin layer chromatography (TLC) was performed using Merck silica gel 60 F254 precoated plates. Flash chromatography (CombiFlash) was performed with Merck silica gel (230–400 mesh), column chromatography was performed with Merck silica gel (100–200 mesh) Moisture sensitive reactions were conducted under a dry nitrogen and argon atmosphere. NMR spectroscopic data were obtained with Bruker DPX-300 NMR machine. IR spectra were recorded on a Perkin–Elmer 1640 FT-IR spectrometer, and $CHCl_3$ was used as the sole solvent unless otherwise indicated. Mass spectra were recorded on WATERS Micromass ZQ 4000 (ESI Probe) spectrometer. Optical rotations were recorded on Perkin–Elmer 343 polarimeter. All solvents were distilled at their boiling point and commercially available chemicals were used directly without purification. All analytical data were recorded at Analytical Chemistry Division (CSIR-NEIST, Jorhat-6, Assam, India).

4.2. Chemical procedures and characterisation data

*4.2.1. Preparation of phosphonium salt **5**.* In a round bottom flask, fitted with a condenser was taken Ph_3P (0.723 g, 2.76 mmol) and heated until it melted (85 °C) under N_2 atmosphere. Then bromoeicosane (1 g, 2.76 mmol) was added and stirred for 24 h at the same temperature. The salt was washed with Hexane under refluxed condition to remove the left over Ph_3P. Then the solvent was removed under vacuum and dried to get white powdery solid (1.4 g, 2.20 mmol, mp 76–79 °C, 80% yield).

*4.2.2. Compound **6**.* To a stirred solution of Wittig salt **5** (0.542 g, 0.870 mmol) in dry THF (10 mL) at −15 °C was added dropwise a 1.6 M solution of *n*-BuLi in Hexane (0.54 mL, 0.870 mmol) and continued to stir for 20 min. Then crude aldehyde **4** (0.290 mmol) was added and continued stirring for 15 min at the same temperature. The mixture was allowed to attain at room temperature and stirred for 4 h. The reaction was quenched with saturated aqueous NH_4Cl solution and extracted with ether. The combined organic extracts were washed with water, brine and dried. Evaporation of the solvent gave a residue, which was purified by column chromatography (2% EtOAc/Hexane) to give **6** (0.126 g, 0.185 mmol, 64% over two steps) as a colourless oil; Elemental analysis calcd. Found: C, 79.40; H, 9.58; N, 6.21. $C_{45}H_{65}N_3O_2$ requires C, 79.48; H, 9.63; N, 6.18; O, 4.17; R_f (5% EtOAc/Hexane) 0.70; $[\alpha]_D^{20}$ +21.4 (*c* 1.09, $CHCl_3$); IR ν_{max} (film) 2924, 2852, 2102, 1456, 772 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 7.56–7.14 (15H, m, aromatics), 5.50–5.48 (2H, m, *CH*=C*H*), 4.61–4.55 (4H, m, benzyl protons), 4.31 (1H, d, *J*=10.3 Hz, C*H*N_3), 4.12–4.10 (1H, m, 2C*H*), 3.92–3.90 (1H, m, 3C*H*), 2.13–2.10 (1H, m, 4C*H*), 2.03–1.98 (3H, m, 4C*H* & 7CH_2), 1.23–1.03 (34H, m, $(CH_2)_{17}$), 0.89 (3H, t, *J*=6.3 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6, 136.8, 130.9, 129.0, 128.8, 127.4, 125.6, 84.3, 74.4, 73.0, 58.8, 33.3, 30.5, 30.1, 29.9, 29.8, 29.6, 27.1, 23.1, 14.0; MS (ESI, positive ion): *m*/*z* (%)=679.1 (100) $[M^+]$.

*4.2.3. Compound **7**.* To a solution of *E*/*Z*-**6** (0.110 g, 0.161 mmol) in ethyl acetate (8 mL) was added 10% Pd/C (30 mg) and stirred under hydrogen for 6 h. After completing the reaction, it was filtered and the filtrate was evaporated to give a residue, which was used directly in the subsequent reaction without further purification. To the stirred solution of the crude amine in DCM (6 mL) were added Et_3N (0.024 g, 0.241 mmol) and di-*tert*-butyldicarbonate (0.042 g, 0.193 mmol) successively at room temperature and continued to stir for 5 h. Then the reaction mixture was diluted with DCM and washed with saturated aqueous NH_4Cl and separated the organic phase. The organic layer was dried and concentrated in vacuo to give the crude product. To the above crude product in pyridine (1.5 mL) were added DMAP (catalytic amount) and acetic anhydride (0.15 mL, 0.805 mmol) successively at room temperature and stirred for 3 h under N_2 atmosphere. After completing the reaction, ice-cooled 6 N HCl solution was added to the reaction mixture at 0 °C and extracted with ethyl acetate. The combined organic extracts were washed with saturated aqueous $NaHCO_3$ solution, water and then brine. Then it was dried and evaporated to give a residue, which was purified by flash chromatography to compound **7** (0.089 g, 0.136 mmol, 84% over three steps) as colourless oil; Elemental analysis calcd. Found: C, 72.74; H, 10.50; N, 2.09. $C_{40}H_{69}NO_6$

requires C, 72.79; H, 10.54; N, 2.12; O, 14.55; R_f (5% EtOAc/Hexane) 0.68; $[\alpha]_D^{20}$ +27.3 (*c* 1.12, $CHCl_3$); IR ν_{max} (film) 3351, 2965, 2935, 2875, 1744, 1713, 1221, 1169, 758, 701 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 7.33–7.21 (5H, m, aromatic), 5.35 (2H, m, N*H* & C*H*OAc protons), 5.12 (1H, m, C*H*NHAc), 4.95 (1H, m, C*H*OAc), 1.87 (6H, br s, CH_3CO), 1.66–1.60 (2H, m, CH_2), 1.41 (9H, s, $C(CH_3)_3$), 1.26 (40H, br s, $(CH_2)_{20}$), 0.91 (3H, t, *J*=7.5 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 169.9, 154.9, 138.7, 128.4, 127.6, 127.1, 79.9, 74.7, 72.2, 54.3, 32.8, 31.9, 30.6, 29.6, 29.5, 29.4, 29.3, 28.7, 28.3, 28.1, 22.6, 20.8, 20.6, 18.3, 14.0; MS (ESI, positive ion): *m*/*z* (%)=659.0 (100) [M^+].

4.2.4. Compound ***8***. To a solution of compound **7** (80 mg, 0.121 mmol) in $CCl_4/CH_3CN/H_2O$ (2:2:3) (1.5 mL) was added $NaIO_4$ (310 mg, 1.45 mmol) slowly at 0 °C. After stirring for 30 min at 0 °C, $RuCl_3 \cdot 3H_2O$ (0.05 equiv) was added and the temperature was raised to room temperature and continued stirring for overnight. The reaction mixture was filtered and washed the solid with DCM three times. The combined filtrate was dried and concentrated in vacuum to give carboxylic acid residue, which was used directly in the subsequent step without further purification. To a stirred solution of the crude organic acid in dry THF (1.5 mL) was added $BH_3 \cdot Me_2S$ (0.04 mL, 0.181 mmol) at −78 °C and continued to stir for 10 min at the same temperature. Then it was allowed to attain at 20 °C and stirred for 2 h under inert atmosphere. The reaction was quenched with methanol and the resulting mixture was concentrated in vacuum giving a residue, which was purified by flash chromatography to give **8**, as a colourless oil, (58 mg, 0.095 mmol, 79% over two steps); Elemental analysis calcd. Found: C, 68.45; H, 11.05; N, 2.24. $C_{35}H_{67}NO_7$ requires C, 68.48; H, 11.00; N, 2.28; O, 18.24; R_f (30% EtOAc/Hexane) 0.40; $[\alpha]_D^{20}$ +17.1 (*c* 1.06, $CHCl_3$); IR ν_{max} (film) 3384 (br), 2924, 1746, 1713, 1019, 702 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 5.24 (1H, br s, N*H*), 5.11 (1H, m, 3C*H*), 5.03 (1H, m, 4C*H*), 4.98 (1H, m, 2C*H*), 3.75 (1H, m, $1CH_a$), 3.56 (1H, m, $1CH_b$), 1.96 (6H, s, CH_3CO), 1.56 (2H, m, $5CH_2$), 1.37 (9H, s, $C(CH_3)_3$), 1.25 (40H, br s, $(CH_2)_{20}$), 0.87 (3H, t, *J*=7.5 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 169.6, 154.9, 79.7, 74.5, 71.9, 65.3, 50.1, 32.8, 31.9, 30.5, 29.7, 29.5, 29.4, 29.1, 28.7, 28.5, 28.3, 28.1, 22.5, 20.8, 20.6, 18.5, 14.1; MS (ESI, positive ion): *m*/*z* (%)=613.0 (100) [M^+].

4.2.5. Compound ***3***. To a solution of **8** (0.080 g, 0.130 mmol) in methanol (1.5 mL) was added Et_3N (0.065 g, 0.650 mmol) at room temperature and continued to stir for 3.5 h. Then the solvent was removed under vacuo to give a residue. To the residue dissolved in DCM (1.5 mL) was added TFA (1 mL) at 0 °C and stirred at room temperature for 45 min. The reaction mixture was concentrated under vacuum and the residue was dissolved in methanol followed by evaporation under vacuum. This process was repeated to remove excess TFA. The crude product was purified by flash chromatography to furnish **3** (0.052 g, 0.122 mmol, 94%) as white solid; Elemental analysis calcd. Found: C, 72.60; H, 12.86; N, 3.21. $C_{26}H_{55}NO_3$ requires C, 72.67; H, 12.90; N, 3.26; O, 11.17; R_f (MeOH/EtOAc/Hexane, 1:10:10) 0.30; $[\alpha]_D^{20}$ +5.8 (*c* 1.05, C_5H_5N); mp 106 °C; IR ν_{max} (film) (KBr) 3319 (br), 2918, 2850, 1051 cm^{-1}; ^1H NMR (300 MHz CD_3OD) δ 3.75 (1H, dd, *J*=10.6, 4.2 Hz, $1CH_a$), 3.57 (1H, m, $1CH_b$), 3.51 (1H, m, 4C*H*), 3.33–3.30 (1H, m, 3C*H*), 3.02–2.97 (1H, m, 2C*H*), 1.73 (1H, m, $5CH_a$), 1.60 (1H, m, $5CH_b$), 1.33–1.51 {40H, m, $(CH_2)_{20}$}, 0.90 (3H, t, *J*=7.0 Hz, CH_3); ^{13}C NMR (75 MHz, CD_3OD) δ 76.4, 74.3, 65.5, 54.6, 33.6, 33.0, 31.1, 30.0, 29.9, 29.7, 29.6, 27.3, 26.9, 23.2, 14.0; MS (ESI, positive ion): *m*/*z* (%)=429.0 (100) [M^+].

4.2.6. Compound ***10a***. To a stirred solution of AD-mix-α (4.2 g) in 20 mL of 1:1 *t*-BuOH/H_2O at 0 °C was added hex-5-en-1-ol (0.300 g, 2.99 mmol) and continued to stir for 16 h at the same temperature. Solid sodium metabisulfite (2.5 g) was added to quench the reaction and allowed to attain at room temperature and stirred for 1 h. Then the mixture was extracted with ethyl acetate and dried. Evaporation of the solvent gave a residue, which was purified by column chromatography to give triol, **10a** (0.385 g, 2.87 mmol, 96%) as a colourless gum; Elemental analysis calcd. Found: C, 53.68; H, 10.50. $C_6H_{14}O_3$ requires C, 53.71; H, 10.52; O, 35.77; R_f (EtOAc/MeOH, 9:1) 0.16; $[\alpha]_D^{20}$ −8.2 (*c* 1.08, MeOH); IR ν_{max} (film) (KBr) 3388, 2935, 2861, 1642, 1372, 1056, 772; ^1H NMR (300 MHz CD_3OD) δ 3.61 (2H, m, $1CH_2$), 3.46 (2H, m, $6CH_2$), 3.33 (1H, m, 2C*H*), 1.92 (2H, br s, O*H*), 1.41–1.31 (4H, m, CH_2), 1.19 (2H, m, CH_2); ^{13}C NMR (75 MHz, CD_3OD) δ 76.8, 71.6, 64.0, 33.5, 32.9, 20.7; MS (ESI, positive ion): *m*/*z* (%)=134.0 (100) [M^+].

4.2.7. Compound ***10b***. Compound **10b** was synthesized following the procedure described for the synthesis of compound **10a** using AD-mix-β as the catalyst. Colourless gum; (0.380 g, 2.84 mmol, 96%); Elemental analysis calcd. Found: C, 53.67; H, 10.55. $C_6H_{14}O_3$ requires C, 53.71; H, 10.52; O, 35.77; R_f (EtOAc/MeOH, 9:1) 0.16; $[\alpha]_D^{20}$ +8.0 (*c* 1.03, MeOH); IR ν_{max} (film) (KBr) 3387, 2935, 2862, 1642, 1372, 1056, 771; ^1H NMR (300 MHz CD_3OD) δ 3.61 (2H, m, $1CH_2$), 3.46 (2H, m, $6CH_2$), 3.32 (1H, m, 2C*H*), 1.96 (2H, br s, O*H*), 1.39–1.32 (4H, m, CH_2), 1.18 (2H, m, CH_2); ^{13}C NMR (75 MHz, CD_3OD) δ 76.8, 71.6, 64.1, 33.5, 32.9, 21.0; MS (ESI, positive ion): *m*/*z* (%)=134.0 (100) [M^+].

4.2.8. Compound ***11a***. To a stirred solution of triol (**10a**) (0.350 g, 2.60 mmol) in DCM (10 mL) were added CSA (0.025 g) and *p*-methoxybenzyldimethyl acetal (0.56 mL, 3.9 mmol) successively at room temperature and continued to stir for 3 h. Then triethyl amine was added to the reaction mixture and stirred for 10 min. Evaporation of the solvent under reduced pressure gave a residue, which was purified by column chromatography to give a 1:1 diastereomeric mixture of **11a** (0.596 g, 2.36 mmol, 91%) as colourless oil; Elemental analysis calcd. Found: C, 66.63; H, 7.94. $C_{14}H_{20}O_4$ requires C, 66.65; H, 7.99; O, 25.37; R_f (EtOAc/Hexane, 3:7) 0.4; IR ν_{max} (film) 3418, 2938, 2866, 1615, 1518, 1249, 1075, 1033, 830; ^1H NMR (300 MHz $CDCl_3$) δ 7.39 (2H, d, *J*=8.1 Hz, aromatic), 6.92 (2H, d, *J*=8.7 Hz, aromatic), 5.86 (0.5H, s, benzylidene acetal proton), 5.75 (0.5H, s, benzylidene acetal proton), 4.27–4.18 (2H, m, CH_2), 4.11 (1H, m, C*H*), 3.81 (3H, s, CH_3O), 3.71–3.60 (2H, m, CH_2), 1.76–1.48 (6H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.4, 160.2, 130.4, 129.8, 128.7, 127.8, 113.7, 113.4, 108.5, 103.8, 102.9, 76.3, 76.0, 62.2, 55.5, 55.2, 33.1, 33.0, 32.4, 32.2, 22.0, 21.7; MS (ESI, positive ion): *m*/*z* (%)=252.0 (100) [M^+].

4.2.9. Compound ***11b***. Compound **11b** was synthesized following the procedure described for the synthesis of compound **11a**. Colourless oil; (0.602 g, 2.39 mmol, 92%); Elemental analysis calcd. Found: C, 66.60; H, 7.93. $C_{14}H_{20}O_4$ requires C, 66.65; H, 7.99; O, 25.37; R_f (EtOAc/Hexane, 3:7) 0.4; IR ν_{max} (film) 3418, 2938, 2866, 1615, 1518, 1249, 1075, 1033, 830; ^1H NMR (300 MHz $CDCl_3$) δ 7.39 (2H, d, *J*=8.1 Hz, aromatic), 6.92 (2H, d, *J*=8.7 Hz, aromatic), 5.87 (0.5H, s, benzylidene proton), 5.76 (0.5H, s, benzylidene proton), 4.27–4.18 (2H, m, CH_2), 4.11 (1H, m, C*H*), 3.81 (3H, s, CH_3O), 3.71–3.60 (2H, m, CH_2), 1.76–1.48 (6H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.4, 160.2, 130.4, 129.8, 128.7, 127.8, 113.7, 113.4, 108.5, 103.8, 102.9, 76.3, 76.0, 62.2, 55.5, 55.2, 33.1, 33.0, 32.4, 32.2, 22.0, 21.7; MS (ESI, positive ion): *m*/*z* (%)=252.0 (100) [M^+].

4.2.10. Compound ***12a***. To a stirred solution of alcohol **11a** (0.150 g, 0.594 mmol) in DCM (6 mL) were added $NaHCO_3$ (0.499 g, 5.94 mmol) and 15% Dess–Martin periodinane solution in DCM (2.4 mL, 0.891 mmol) at room temperature and continued to stir for 2 h. Then the reaction was quenched with saturated $Na_2S_2O_5$ and saturated $NaHCO_3$ aqueous solution and extracted with DCM. The combined organic extracts were dried and evaporated to give the aldehyde, which was used for the next step without further purification. $Br^-Ph_3P^+CH_2(CH_2)_9Me$ (0.886 g, 1.78 mmol) was dissolved

in THF (15 mL) and to it 1.6 M solution of ^{n}BuLi in Hexane (1.2 mL, 1.78 mmol) was added at −15 °C and stirred for 30 min at the same temperature and then the above crude aldehyde in THF (2 mL) was added at −45 °C and stirred for 3 h at room temperature. After completing the reaction saturated aqueous NH_4Cl solution was added and extracted with diethyl ether. The combined organic extracts were washed with water, brine and dried. Evaporation of the solvent gave a residue, which was purified by column chromatography to give the compound **12a** (0.205 g, 0.528 mmol, 89%) as colourless oil in the ratio of 1:1 diastereomeric mixture; Elemental analysis calcd. Found: C, 77.23; H, 10.32. $C_{25}H_{40}O_3$ requires C, 77.27; H, 10.38; O, 12.35; R_f (EtOAc/Hexane 1:9) 0.56; IR ν_{max} (film) 3003, 2925, 2854, 1615, 1517, 1081, 827; ^{1}H NMR (300 MHz $CDCl_3$) δ 7.42 (2H, d, J=8.7 Hz, aromatic), 6.91 (2H, d, J=8.7 Hz, aromatic), 5.86 (0.5H, s, benzylidene acetal proton), 5.75 (0.5H, s, benzylidene acetal proton), 5.39–5.33 (2H, m, C*H*=C*H*), 4.25 (2H, m, CH_2), 4.07 (1H, m, C*H*), 3.81 (3H, s, CH_3O), 2.12–1.98 (4H, m, CH_2), 1.65–1.54 (8H, m, CH_2), 1.26 (12H, br s, $(CH_2)_6$), 0.90 (3H, t, J=6.3 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.4, 160.2, 130.6, 130.0, 129.0, 128.0, 127.8, 113.7, 103.9, 102.9, 70.7, 70.0, 33.0, 32.9, 32.6, 31.9, 29.7, 29.5, 29.3, 27.2, 27.0, 25.8, 22.6, 14.0; MS (ESI, positive ion): m/z (%)=388.1 (100) [M^+].

*4.2.11. Compound **12b**.* Compound **12b** was synthesized following the procedure described for the synthesis of compound **12a**. Colourless oil (0.200 g, 0.516 mmol, 87%); Elemental analysis calcd. Found: C, 77.22; H, 10.33. $C_{25}H_{40}O_3$ requires C, 77.27; H, 10.38; O, 12.35; R_f (EtOAc/Hexane 1:9) 0.56; IR ν_{max} (film) 3003, 2926, 2854, 1615, 1518, 1249, 826; ^{1}H NMR (300 MHz $CDCl_3$) δ 7.42 (2H, d, J=8.7 Hz, aromatic), 6.90 (2H, d, J=8.7 Hz, aromatic), 5.85 (0.5H, s, benzylidene acetal proton), 5.74 (0.5H, s, benzylidene acetal proton), 5.40–5.36 (2H, m, C*H*=C*H*), 4.23 (2H, m, CH_2), 4.02 (1H, m, C*H*), 3.81 (3H, s, CH_3O), 2.12–1.98 (4H, m, CH_2), 1.64–1.55 (8H, m, CH_2), 1.26 (12H, br s, $(CH_2)_6$), 0.90 (3H, t, J=6.3 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.3, 160.1, 130.5, 130.0, 129.1, 128.0, 127.6, 113.4, 103.7, 102.8, 70.8, 70.2, 33.1, 33.0, 32.4, 31.5, 29.6, 29.4, 29.1, 27.0, 26.9, 25.7, 22.5, 14.2; MS (ESI, positive ion): m/z (%)=388.0 (100) [M^+].

*4.2.12. Compound **13a**.* To a stirred solution of acetal **12a** (0.150 g, 0.386 mmol) in DCM (5 mL) was added 20% DIBAL in toluene solution (0.78 mL, 1.54 mmol) at −78 °C and continued to stir for 30 min under N_2 atmosphere. The reaction mixture was allowed to warm at 0 °C and stirred for 1 h and another 1 h at room temperature. After completing the reaction (monitored by TLC), it was quenched at 0 °C by adding acetone (1 mL), methanol (1 mL) and saturated aqueous NH_4Cl solution (1 mL). The whole mixture was diluted with diethyl ether and extracted with diethyl ether and dried. Evaporation of the solvent gave a residue, which was purified by column chromatography to furnish **13a** (0.144 g, 0.370 mmol, 96%) as clear oil; Elemental analysis calcd. Found: C, 76.80; H, 10.87. $C_{25}H_{42}O_3$ requires C, 76.87; H, 10.84; O, 12.29; R_f (EtOAc/Hexane 1:4) 0.4; $[\alpha]_D^{20}$ +8.9 (c 0.88, $CHCl_3$). IR ν_{max} (film) 3420, 3003, 2925, 2854, 1613, 1514, 1464, 1248, 1038, 771; ^{1}H NMR (300 MHz $CDCl_3$) δ 7.29 (2H, d, J=8.1 Hz, aromatic), 6.91 (2H, d, J=8.7 Hz, aromatic), 5.39–5.32 (2H, m, C*H*=C*H*), 4.58 (1H, d, J=11.1 Hz, benzyl proton), 4.48 (1H, d, J=11.4 Hz, benzyl proton), 3.80 (3H, s, CH_3O), 3.68 (1H, m, C*H*), 3.51–3.48 (2H, m, CH_2), 2.05–1.97 (6H, m, CH_2), 1.60 (4H, m, CH_2), 1.26 (14H, br s, $(CH_2)_7$), 0.90 (3H, t, J=6.3 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.2, 130.5, 129.4, 129.1, 113.9, 79.3, 71.2, 64.2, 55.2, 31.9, 30.4, 29.7, 29.5, 29.3, 27.2, 25.4, 22.7, 14.1; MS (ESI, positive ion): m/z (%)=390.0 (100) [M^+].

*4.2.13. Compound **13b**.* Compound **13b** was synthesized following the procedure described for the synthesis of compound **13a**. Clear oil; (0.143 g, 0.366 mmol, 95%); Elemental analysis calcd. Found: C, 76.79; H, 10.81. $C_{25}H_{42}O_3$ requires C, 76.87; H, 10.84; O, 12.29; R_f (EtOAc/Hexane 1:4) 0.41; $[\alpha]_D^{20}$ −9.1 (c 1.02, $CHCl_3$); IR ν_{max} (film) 3420, 3003, 2925, 2854, 1613, 1514, 1464, 1248, 1038, 771; ^{1}H NMR (300 MHz $CDCl_3$) δ 7.30 (2H, d, J=8.1 Hz, aromatic), 6.92 (2H, d, J=8.7 Hz, aromatic), 5.40–5.34 (2H, m, C*H*=C*H*), 4.58 (1H, d, J=11.1 Hz, benzyl proton), 4.48 (1H, d, J=11.4 Hz, benzyl proton), 3.80 (3H, s, CH_3O), 3.68 (1H, m, C*H*), 3.51–3.48 (2H, m, CH_2), 2.05–1.97 (6H, m, CH_2), 1.60 (4H, m, CH_2), 1.26 (14H, br s, $(CH_2)_7$), 0.90 (3H, t, J=6.3 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.3, 130.4, 129.4, 129.2, 113.9, 79.4, 71.2, 64.1, 55.2, 31.9, 30.4, 29.7, 29.5, 29.3, 27.2, 25.4, 22.7, 14.1; MS (ESI, positive ion): m/z (%)=390.0 (100) [M^+].

*4.2.14. Compound **2a**.* To a stirred solution of alcohol **13a** (0.100 g, 0.256 mmol) in DCM (5 mL) were added $NaHCO_3$ (0.215 g, 2.56 mmol) and 15% Dess–Martin periodinane solution in DCM (1.1 mL, 0.384 mmol) at room temperature and continued to stir for 2 h. Then the reaction was quenched with saturated $Na_2S_2O_5$ and saturated $NaHCO_3$ aqueous solution and extracted with DCM. The combined organic extracts were dried and evaporated to give the aldehyde, which was used for the next step without further purification. The above crude aldehyde was dissolved in ^{t}BuOH (5 mL) and to it H_2O_2 (0.83 mL) was added at 0 °C. Then a solution of $NaClO_2$ (0.031 g, 0.768 mmol) and NaH_2PO_4 (0.092 g, 0.768 mmol) in H_2O (5 mL) was added dropwise and continued to stir for 1 h. After completing the reaction it was quenched with saturated aqueous NH_4Cl solution and extracted with ethyl acetate. Then the combined organic extracts were washed with brine and dried with Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by column chromatography to furnish compound **2a** (0.090 g, 0.222 mmol, 87%) as white waxy solid; mp: 49–51 °C; Elemental analysis calcd. Found: C, 74.21; H, 9.95. $C_{25}H_{40}O_4$ requires C, 74.22; H, 9.97; O, 15.82; R_f ($CHCl_3$/MEOH 19:1) 0.23; $[\alpha]_D^{20}$ −6.9 (c 1.06, $CHCl_3$); IR ν_{max} (film) 3420, 2925, 2854, 1708, 1465, 1294, 1016, 741; ^{1}H NMR (300 MHz $CDCl_3$) δ 7.20 (2H, d, J=7.5 Hz, aromatic), 6.90 (2H, d, J=8.4 Hz, aromatic), 5.36–5.16 (2H, m, C*H*=C*H*), 4.67 (1H, d, J=9.6 Hz, benzylic proton), 4.47 (1H, d, J=11.1 Hz, benzylic proton), 3.99 (1H, m, C*H*), 3.80 (3H, s, CH_3O), 2.05–1.97 (4H, m, CH_2), 1.82 (2H, m, CH_2), 1.50 (4H, m, CH_2), 1.25 (14H, br s, $(CH_2)_7$), 0.87 (3H, t, J=6.9 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.5, 159.5, 132.0, 130.7, 129.8, 129.1, 128.7, 128.0, 113.9, 94.7, 72.1, 55.2, 32.2, 31.9, 29.7, 29.5, 29.3, 27.2, 26.7, 25.2, 25.0, 22.7, 14.1; MS (ESI, positive ion): m/z (%)=404.0 (100) [M^+].

*4.2.15. Compound **2b**.* Compound **2b** was synthesized following the procedure described for the synthesis of compound **2a**. White waxy solid; (0.088 g, 0.217 mmol, 85%); mp: 49–51 °C; Elemental analysis calcd. Found: C, 74.20; H, 9.95. $C_{25}H_{40}O_4$ requires C, 74.22; H, 9.97; O, 15.82; R_f ($CHCl_3$/MEOH 19:1) 0.23; $[\alpha]_D^{20}$ +7.1 (c 1.04, $CHCl_3$); IR ν_{max} (film) 3421, 2925, 2854, 1709, 1467, 1294, 1016, 742; ^{1}H NMR (300 MHz $CDCl_3$) δ 7.22 (2H, d, J=7.5 Hz, aromatic), 6.91 (2H, d, J=8.4 Hz, aromatic), 5.36–5.16 (2H, m, C*H*=C*H*), 4.67 (1H, d, J=9.6 Hz, benzylic proton), 4.47 (1H, d, J=11.1 Hz, benzylic proton), 3.99 (1H, m, C*H*), 3.80 (3H, s, CH_3O), 2.06–1.99 (4H, m, CH_2), 1.82 (2H, m, CH_2), 1.50 (4H, m, CH_2), 1.22 (14H, br s, $(CH_2)_7$), 0.86 (3H, t, J=6.9 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.6, 159.8, 132.1, 130.7, 129.8, 129.1, 128.7, 128.0, 113.9, 94.7, 72.1, 55.2, 32.2, 31.9, 29.7, 29.5, 29.3, 27.2, 26.7, 25.2, 22.9, 14.1; MS (ESI, positive ion): m/z (%)=404.0 (100) [M^+].

*4.2.16. Compound **1a**.*[7] Compound **2a** (0.024 g, 0.058 mmol) dissolved in $SOCl_2$ (0.2 mL, 1.62 mmol) was refluxed for 90 min. After completing the reaction the excess $SOCl_2$ was removed under reduced pressure to give the crude acid chloride. Then the crude acid chloride was dissolved in dry THF (0.5 mL) and added with vigorous stirring to a solution of amine **3** (0.025 g, 0.058 mmol) in THF/NaOAc (aq) 8 M (1:1, 1.5 mL). After vigorous stirring for 2 h, the

reaction mixture was allowed to stand and the phases were separated. The aqueous phase was extracted with THF and the combined organic extract was dried with sodium sulfate and evaporated under reduced pressure to give a residue. Again the residue was dissolved in CH_2Cl_2–MeOH (10:1, 1 mL) and to it DDQ (0.015 g, 0.069 mmol) was added. Then the mixture was stirred for 1.5 h at room temperature. After completing the reaction the mixture was diluted with CH_2Cl_2 and washed with minimum amount of saturated aqueous $NaHCO_3$ solution and again extracted the aqueous phase with DCM (3×5 mL). Evaporation of the combined organic solvent gave a residue, which was purified by column chromatography (CH_2Cl_2/MeOH 1:19) to furnish the compound **1a** (0.028 g, 0.040 mmol, 70%) as white solid; mp 130–132 °C; Elemental analysis calcd. Found: C, 74.21; H, 12.29; N, 2.03. $C_{43}H_{85}NO_5$ requires C, 74.19; H, 12.31; N, 2.01; O, 11.49; R_f (10% MeOH/CH_2Cl_2) 0.31; $[\alpha]_D^{20}$ −6.1 (*c* 0.108, C_5H_5N); IR ν_{max} (film) (KBr) 3400, 3201, 1642, 1612, 1541, 1073; ^{1}H NMR (300 MHz CD_3OD) δ 8.21 (1H, d, *J*=8.1 Hz, N*H*), 5.39–5.30 (2H, m, C*H*=C*H*), 4.77–4.63 (1H, m, C*H*), 4.43–4.39 (1H, m, C*H*), 4.13 (1H, dd, *J*=10.6, 5.1 Hz, CH_a), 4.07 (1H, dd, *J*=10.3, 5.0 Hz, CH_b), 3.88–3.75 (1H, m, C*H*), 3.68–3.67 (1H, m, C*H*), 1.99–1.95 (4H, m, CH_2), 1.75–1.70 (2H, m, CH_2), 1.48–1.43 (4H, m, CH_2), 1.31 (56H, br s, $(CH_2)_{28}$), 0.86 (6H, t, *J*=7.0 Hz, CH_3); ^{13}C NMR (75 MHz, CD_3OD): δ 174.6, 130.6, 130.3, 76.5, 72.5, 72.1, 61.6, 53.0, 36.5, 34.0, 33.8, 33.5, 32.0, 29.9, 27.1, 24.0, 23.1, 21.1, 13.8; MS (ESI, positive ion): *m*/*z* (%)=695.1 (100) [M^+].

*4.2.17. Compound **1b**.* Compound **1b** was synthesized following the procedure described for the synthesis of compound **1a**. White solid; (0.027 g, 0.039 mmol, 68%); mp 127 °C; Elemental analysis calcd. Found: C, 74.20; H, 12.27; N, 2.01. $C_{43}H_{85}NO_5$ requires C, 74.19; H, 12.31; N, 2.01; O, 11.49; R_f (10% MeOH/CH_2Cl_2) 0.31; $[\alpha]_D^{20}$ +1.7 (*c* 0.112, C_5H_5N); IR ν_{max} (film) (KBr) 3402, 3201, 1642, 1621, 1541, 1071; ^{1}H NMR (300 MHz CD_3OD) δ 8.1 (1H, d, *J*=8.1 Hz, N*H*), 5.33–5.40 (2H, m, C*H*=C*H*), 4.58–4.76 (1H, m, C*H*), 4.21–4.30 (1H, m, C*H*), 4.20 (1H, dd, *J*=10.6, 5.1 Hz, CH_a), 4.15 (1H, dd, *J*=10.3, 5.0 Hz, CH_b), 3.90 (1H, m, C*H*), 3.86 (1H, m, C*H*), 1.88–1.90 (3H, m, C*H* & CH_2), 1.65–1.76 (5H, m, C*H* & CH_2), 1.49 (1H, m, CH_2), 1.32 (56H, br s, $(CH_2)_{28}$), 0.85 (6H, t, *J*=7.0 Hz, CH_3); ^{13}C NMR (75 MHz, CD_3OD): δ 175.1, 131.3, 76.8, 72.5, 72.0, 61.8, 54.0, 36.6, 34.0, 33.8, 33.1, 32.0, 29.8, 27.5, 24.0, 23.1, 21.1, 13.7; MS (ESI, positive ion): *m*/*z* (%)=695.0 (100) [M^+].

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.08.068.

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