Tetrahedron: *Asymmetry* 25 (2014) 610–616

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

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

Asymmetric total synthesis of all four isomers of 6-acetoxy-5-hexadecanolide: the major component of mosquito oviposition attractant pheromones

Hong-Bo Dong, Ming-Yan Yang, Xiao-Teng Zhang, Ming-An Wang *

Department of Applied Chemistry, China Agricultural University, Beijing 100193, PR China

ARTICLE INFO

Article history:
Received 18 January 2014
Accepted 3 March 2014
Available online 2 April 2014

ABSTRACT

An asymmetric total synthesis of (5*S*,6*R*)-(+)-*erythro*-6-acetoxy-5-hexadecanolide **1a** has been accomplished from readily available hex-5-yn-1-ol via Shi's asymmetric epoxidation as the key step, in eight steps with an overall yield of 33.5%. In addition, the stereoselective synthesis of all four isomers of 6-acetoxy-5-hexadecanolide **1a**–**1d** were obtained via Sharpless asymmetric dihydroxylation and Mitsunobu reaction as the key steps with overall yields of 16.5–21.2%, respectively.

1. Introduction

The mosquito oviposition attractant pheromones were first isolated by Laurence and Pickett from apical droplets formed on the egg of the mosquito *Culex pipens fatigans* in 1979,[1] which is distributed worldwide and can be a vector for filarial disease and malaria as well as having the ability to transmit the West Nile virus in hot climates.[2] The absolute configuration of the only natural active pheromone isomer was identified as (−)-(5*R*,6*S*)-6-acetoxy-5-hexadecanolide **1b** (Fig. 1).[1b] Recently, the crystal and solution structures of an odorant-binding protein from the southern house mosquito complexed with the oviposition pheromone **1b** (CquiOBP1·**1b** complex, 3OGN in the protein data bank) have been reported, which showed that CquiOBP binds **1b** in an unprecedented fashion using both a small central cavity for the lactone head group and a long hydrophobic channel for its tail.[3] Due to its biological importance and application in the control of harmful insects,[4,5] the asymmetric synthesis of this pheromone has attracted great attention. The first synthesis of compounds **1a** and **1b** was reported in 1982.[6] Since then, numerous stereoselective syntheses of natural (−)-*erythro*-6-acetoxy-5-hexadecanolide **1b** and unnatural isomers **1a**, (+)- and (−)-*threo*-6-acetoxy-5-hexadecanolides **1c** and **1d** have been reported,[7] with δ-gluconolactone,[7a] (2*R*,3*S*)-1,2-epoxy-4-penten-3-ol,[7d] L-(+)-tartaric acid,[7e] (*R*)-2,3-cyclohexylideneglyceraldehyde,[7h] D-ribose,[7k] and so on being used as chiral sources. However, a more efficient and inexpensive asymmetric total synthetic approach of this pheromone with high overall yield is still required.

Shi's asymmetric epoxidations[8] and Sharpless asymmetric dihydroxylations[9] are efficient methods to introduce two stereogenic centers at the same time, which have provided several new protocols for obtaining chiral compounds in an environmentally friendly manner. The application of Sharpless AE or AD reactions in the synthesis of this pheromone has been reported using 1-tridecen-3-ol, 2-tridecen-1-ol, 1,2-cyclohexanediol, and δ-valerolactone as starting materials.[7l,10] Herein we report the asymmetric total synthesis of (5*S*,6*R*)-(+)-*erythro*-6-acetoxy-5-hexadecanolide **1a** via Shi's asymmetric epoxidation of (*E*)-olefin alcohol **7** and the stereoselective synthesis of 6-acetoxy-5-hexadecanolides **1a**–**1d** via Sharpless asymmetric dihydroxylation of (*E*)-olefin acid **8** as the key steps using very efficient synthetic routes with high overall yields.

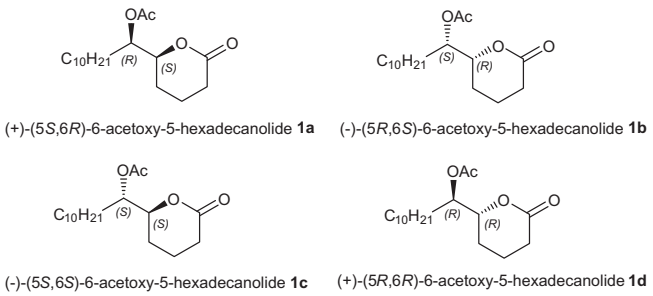


Figure 1. Structures of compounds **1a**, **1b**, **1c,** and **1d**.

* Corresponding author. Tel.: +86 106 273 4093.
E-mail address: wangma@cau.edu.cn (M.-A. Wang).

http://dx.doi.org/10.1016/j.tetasy.2014.03.006
0957-4166/

To the best of our knowledge, although these two methods have found application in a number of syntheses,[11] this would be the first use of these methods to asymmetrically synthesize four isomers of 6-acetoxy-5-hexadecanolide **1a**–**1d** by key intermediate (*E*)-olefin alcohol **7** and (*E*)-olefin acid **8**; these strategies could be used to synthesize various lactones with the desired configurations and side chains with α-hydroxy or α-acyloxy groups with high enantiomeric purity.

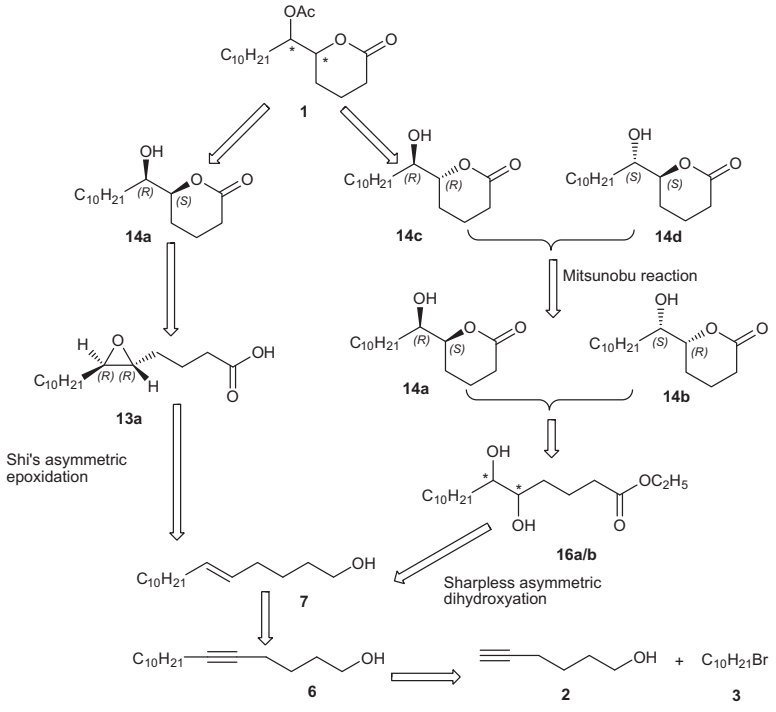
2. Results and discussion

The *retro*-synthetic analysis of 6-acetoxy-5-hexadecanolide isomers **1** by Shi's asymmetric epoxidation and Sharpless asymmetric dihydroxylation is shown in Scheme 1. Compound (+)-(5*R*,6*S*)-6-acetoxy-5-hexadecanolide **1a** was envisaged from the intramolecular cyclization of epoxy carboxyl acid compound **13a**, wherein the terminal carboxyl acid attacks the epoxide from the other side of epoxy group to afford a six-membered lactone. Compound **13a** was easily obtained from the intermediate of Shi's asymmetric epoxidation and oxidation of the terminal olefin alcohol **7**. Compound **7** could be prepared from $LiAlH_4$ reduction of **6**, which was made from the commercially available hex-5-yn-1-ol **2** and 1-bromodecane **3** in very simple steps including THP protection, a coupling reaction, and methanolysis of the THP ether. The four isomers of **1** were easily obtained from **14a** to **14d**, which could be directly prepared from two vicinal diols **16a** and **16b** or by configuration inversion via a Mitsunobu reaction. The vicinal diols **16a** and **16b** were readily synthesized by Sharpless dihydroxylation and oxidation of **7**.

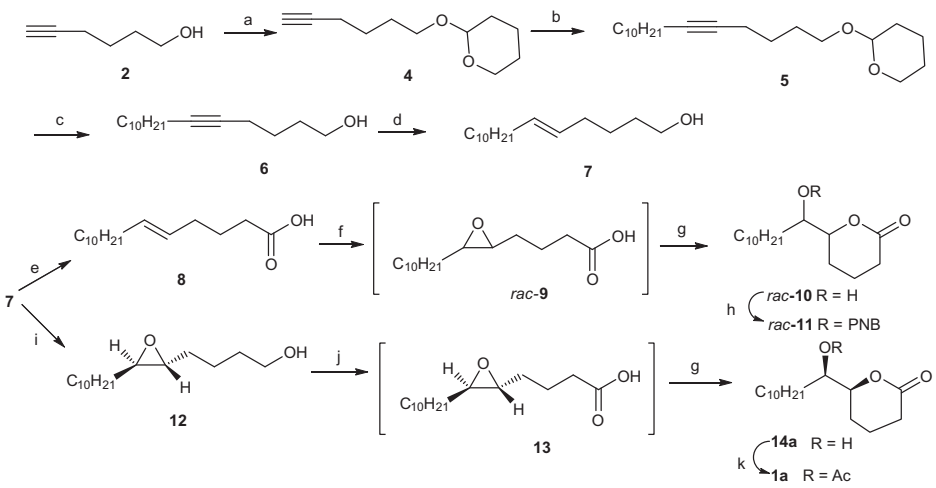
As shown in Scheme 2, our synthetic strategy started from commercially available hex-5-yn-1-ol **2**. The hydroxy group of hex-5-yn-1-ol was protected as a THP ether to give compound **4**. Treatment of **4** with 1-iododecane (readily furnished from 1-bromodecane **3** and NaI in refluxing acetone) in the presence of *n*-BuLi and hexamethylphosphoramide (HMPA) afforded a coupled product **5**. Accordingly, compound **5** was treated with *p*-toluenesulfonic acid in CH_3OH to yield compound **6**.[12] Reduction of the alkyne **6** by $LiAlH_4$ in diglyme at 160 °C directly furnished the (*E*)-olefin alcohol **7** in 83% yield.[13]

With the key intermediate **7** in hand, it was oxidized with pyridinium dichromate (PDC) in dimethylformamide (DMF) under an argon atmosphere to give the desired *trans*-acid **8** in 58% yield.[14] Epoxidation of compound **8** in CH_2Cl_2–water solvent system with peracetic acid in the presence of Na_2CO_3 yielded *rac*-**9**, which automatically cyclized to afford a racemic mixture (5*R*,6*R*) and (5*S*,6*S*) *rac*-**10** in the presence of catalytic quantity of camphorsulfonic acid.[15] In an effort to promote the application of the above procedure, we next sought to exploit the Shi's asymmetric epoxidation procedure for the enantioselective conversion of key intermediate acid **8** to compound **14a**. We attempted to use the Shi's asymmetric epoxidation procedure[16] for the enantioselective conversion of carboxylic acid **8** into lactone **14a** via epoxide **13**, which was the key reaction to introduce the two stereogenic centers into the molecule. The cyclization of **13** into lactone **14a** was attempted under typical basic asymmetric epoxidation conditions (pH = 10).[17,18] The application of Shi's epoxidation conditions and then warming the mixture to react at ambient temperature only gave the corresponding carboxylic acid salts of **13**, which could not be cyclized to chiral lactone **14a** in situ.

We next carried out Shi's asymmetric epoxidation with olefin alcohol **7** to obtain epoxide compound **12** in 88% yield **and** with high enantioselectivity {$[\alpha]_D^{25}$ = +26.7 (*c* 0.52, $CHCl_3$)} under rapid and mild conditions (Fig. 2),[10b,19] followed by oxidation of the terminal alcohol with $NaIO_4$ in the presence of $RuCl_3$ to afford the key intermediate (5*R*,6*R*)-acid **13**. Next, cyclization of (5*R*,6*R*)-acid **13** occurred in the presence of a catalytic amount of (+)-camphorsulfonic acid to yield (5*S*,6*R*)-lactone **14a** with 95.9% ee; the ee value was determined by chiral HPLC (Chiralpak AD column) of the *p*-nitrobenzoate derivative. Finally, the total synthesis of (+)-(5*S*,6*R*)-6-acetoxy-5-hexadecanolide **1a** was achieved by acetylation of (5*S*,6*R*)-lactone **14a** using Ac_2O under the catalysis of DMAP in 89% yield.



Scheme 1. Retrosynthetic analysis of **1** via Shi's epoxidation and Sharpless dihydroxylation.



Scheme 2. Preparation of **1a**. Reagents and conditions: (a) 3,4-dihydro-2*H*-pyran, CSA, CH_2Cl_2, rt, 4 h; (b) *n*-BuLi, 1-iododecane, THF/HMPA, −78 to 0 °C, overnight; (c) PTSA, CH_3OH, rt, 2 h; (d) $LiAlH_4$, THF/diglyme, 160 °C, 13 h; (e) PDC, DMF, rt, overnight; (f) CH_3COOOH, Na_2CO_3, CH_2Cl_2/H_2O, 1 h; (g) CSA, CH_2Cl_2, rt, 8 h; (h) PNBC, DMAP, CH_2Cl_2, rt, 4 h; (i) oxone, D-fructose-derived catalyst **18**, buffer, CH_3CN/H_2O, 0 °C, 3 h; (j) $NaIO_4$, $RuCl_3{\cdot}H_2O$, CCl_4/H_2O, rt, 1 h; (k) Ac_2O, DMAP, CH_2Cl_2, rt, 4 h.

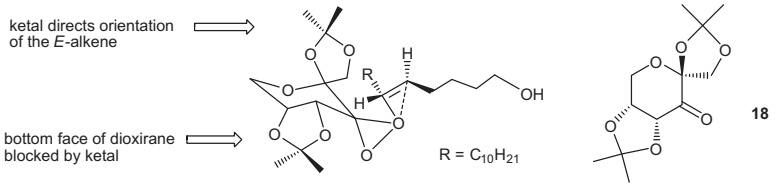
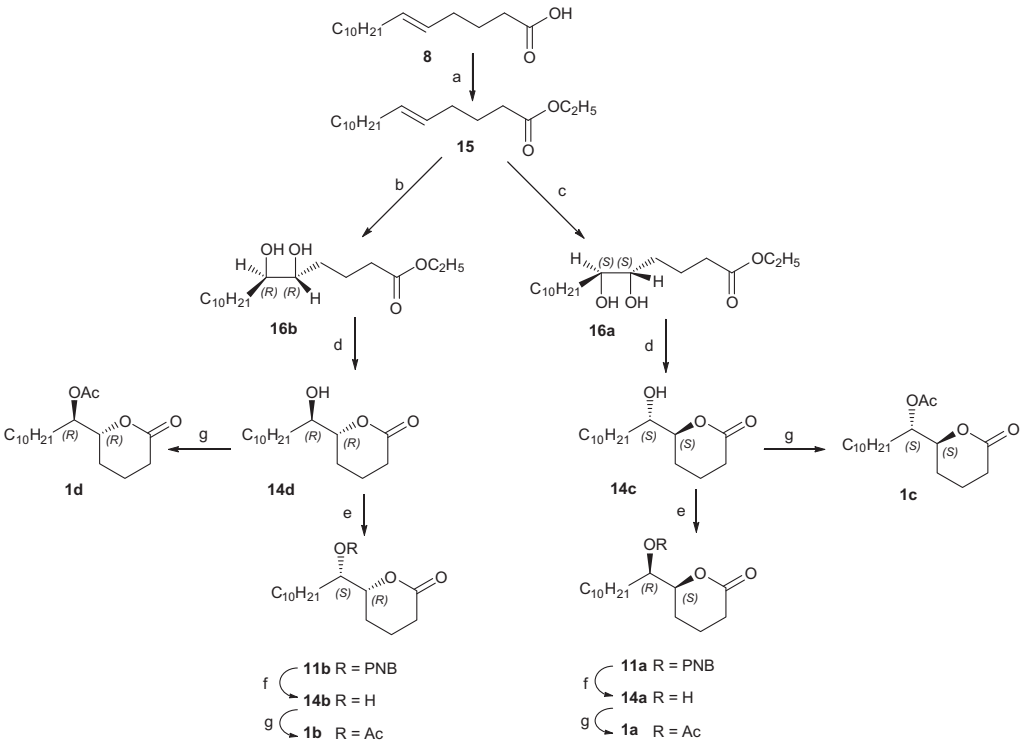


Figure 2. Shi' model and the structure of catalyst **18**.



Scheme 3. Preparation of **1a**–**1d**. Reagents and conditions: (a) H_2SO_4, CH_3CH_2OH, 78 °C, 5 h; (b) AD-mix-β, methanesulfonamide, *t*-BuOH/H_2O, 0 °C, 60 h; (c) AD-mix-α, methanesulfonamide, *t*-BuOH/H_2O, 0 °C, 60 h; (d) (i) NaOH, H_2O, CH_3CH_2OH, 60 °C, 2 h; (ii) CH_2Cl_2, TsOH, rt, 2.5 h; (e) Ph_3P, DEAD, PNBA, THF, rt, 4 h; (f) K_2CO_3, CH_3OH, rt, 10 min; (g) Ac_2O, DMAP, CH_2Cl_2, rt, 4 h.

This synthetic sequence is simple, inexpensive, and is environmentally friendly; however we could only obtain the inactive (5*S*,6*R*)-isomer **1a**. In order to obtain the active (5*R*,6*S*)-isomer and the other two *threo* isomers, we decided to use Sharpless asymmetric dihydroxylation to prepare the four isomers of *erythro*- and *threo*-6-acetoxy-5-hexadecanolide **1a**–**1d**. Our synthetic strategy for the four isomers of 6-acetoxy-5-hexadecanolide from the acid **8** is shown in Scheme 3.

The key intermediate (*E*)-olefin ester **15** was easily obtained from acid **8** in 84% yield. The following Sharpless asymmetric dihydroxylation reactions gave two vicinal diols **16a** and **16b** respectively, which were hydrolyzed by NaOH and then cyclized in the presence of TsOH to afford (5*S*,6*S*)-lactone **14c** and (5*R*,6*R*)-lactone **14d** without any change of stereogenic centers.[20,21] Next, **14c** and **14d** were acetylated with acetic anhydride and DMAP in CH_2Cl_2 at room temperature to produce unnatural products *threo*-(5*R*,6*R*)- and *threo*-(5*S*,6*S*)-6-acetoxy-5-hexadecanolide **1c** and **1d** in 82% and 88% yields. Compounds **14c** and **14d** were transferred and inverted the C-6 configuration using typical Mitsunobu reaction conditions to afford the *p*-nitrobenzoates of (5*S*,6*R*)-lactone **11a** and (5*R*,6*S*)-lactone **11b** in 83% and 90% yields, with high enantioselectivities in 97.9% and 98.7% ee [the ee values were determined by chiral HPLC (Chiralpak AD column)], respectively.[22,23] Hydrolysis of esters **11a** and **11b** with K_2CO_3 in MeOH yielded (5*S*,6*R*)-lactone **14a** and (5*R*,6*S*)-lactone **14b** in good yields. The reaction of (5*S*,6*R*)-lactone **14a** and (5*R*,6*S*)-lactone **14b** with acetic anhydride and DMAP in CH_2Cl_2 at room temperature produced the corresponding natural products *erythro*-(5*S*,6*R*)- and *erythro*-(5*R*,6*S*)-6-acetoxy-5-hexadecanolides **1a** and **1b** in 90% and 96% yields, respectively. All of the products were characterized by their ^{1}H NMR, ^{13}C NMR, high resolution mass spectra and specific rotation values, and these data were consistent with those reported in the literature.

3. Conclusion

In conclusion, we have developed a concise and convergent approach for the total synthesis of (+)-(5*S*,6*R*)-6-acetoxy-5-hexadecanolide **1a** in 33.5% overall yield with Shi's asymmetric epoxidation as the key step. The stereoselective synthesis of (+)-(5*S*,6*R*)-6-acetoxy-5- hexadecanolide **1a**, (−)-(5*R*,6*S*)-6-acetoxy-5-hexadecanolide **1b**, (+)-(5*R*,6*R*)-6-acetoxy-5-hexadecanolide **1c**, and (−)-(5*S*,6*S*)-6-acetoxy-5-hexadecanolide **1d** were successfully achieved in 16.5%, 18.0%, 21.2%, and 22.1% overall yields by utilizing Sharpless asymmetric dihydroxylation and Mitsunobu reactions as the key steps. The two synthetic sequences presented are simple, inexpensive, and amenable for the synthesis of a number of lactones with the side chain having α-hydroxy or α-acyloxy groups with high enantiomeric purity.

4. Experimental

4.1. General

Melting points were measured on a Yanagimoto apparatus and are uncorrected. ^{1}H NMR (300 MHz), and ^{13}C NMR (75 MHz) spectra were recorded on Bruker DPX 300 NMR Spectrometer with $CDCl_3$ as solvent and tetramethylsilane as internal standard. HR-MS were obtained on Bruker Apex II mass spectrometer using nitrobenzoyl alcohol and sodium chloride as matrix. The optical rotations were measured on a Perkin–Elmer 241MC instrument. HPLC analyses were performed on an Agilent LC 1100 instrument equipped with a chiral Chiralpak AD column, eluent: hexane/isopropanol (90:10), flow rate: 1.0 mL/min, UV detection wavelength: 254 nm.

4.2. 2-(Hex-5-ynyloxy)tetrahydro-2*H*-pyran 4

To a cold (0 °C) mixture of hex-5-yn-1-ol **2** (1.91 g, 19.5 mmol), and 3,4-dihydro-2*H*-pyran (1.96 mL, 21.5 mmol,) in dry CH_2Cl_2 (25 mL) was added camphorsulfonic acid (5 mg, CSA). The reaction mixture was warmed to room temperature and stirred for 4 h. The reaction was then quenched with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, and concentrated to give pure 1-hex-5-ynyloxy-tetrahydropyran **7** 3.47 g as a colorless oil, 98% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.58 (t, J = 3.5 Hz, 1H), 3.85–3.72 (m, 2H), 3.52–3.37 (m, 2H), 2.25–2.20 (m, 2H), 1.95 (t, J = 2.6 Hz, 1H), 1.74–1.49 (m, 10H), which were identical with that in the literature.[22]

4.3. Hexadec-5-yn-1-ol 6

To a solution of 2-(hex-5-ynyloxy)tetrahydro-2*H*-pyran **4** (1.82 g, 10 mmol) in THF (50 mL) was added *n*-BuLi (2.5 M in hexane, 6 mL, 15 mmol) at −78 °C and then allowed to warm to −20 °C. After 2 h of stirring, the mixture was cooled to −78 °C and hexamethylphosphoric triamide (HMPA, 20 mL) was added. The resulting mixture was transferred into a solution of 1-iododecane (3.48 g, 13 mmol, readily furnished from 1-bromodecane **3** and NaI in refluxing acetone) in THF (25 mL) at −78 °C via a cannula, and then warmed to room temperature and stirred overnight. The reaction was quenched with saturated NH_4Cl at 0 °C, and the mixture was extracted with Et_2O. The ether layer was washed with saturated $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (50:1 V/V petroleum ether/EtOAc) to give a colorless oil **5**.

Compound **5** was dissolved in MeOH (25 mL) at room temperature and *p*-toluenesulfonic acid (150 mg, PTSA) was added. The solution was stirred at room temperature for 2 h, the reaction was quenched with $NaHCO_3$, filtered, and MeOH was removed under reduced pressure. Water (25 mL) was added to this residue, extracted with ethyl acetate, and the organic phase was washed with brine. The solution was dried over anhydrous Na_2SO_4, filtered, and the solvent was removed under vacuum. Purification by flash column chromatography (silica gel column, gradient elution with 10–20% EtOAc/petroleum ether) afforded compound **6** (1.74 g) as a colorless oil in 73% yield. ^{1}H NMR ($CDCl_3$) δ: 3.63 (t, J = 6.3 Hz, 2H), 2.19–2.08 (m, 4H), 1.84 (s, 1H), 1.67–1.32 (m, 6H), 1.32–1.24 (m, 14H), 0.85 (t, J = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 80.64, 79.65, 62.34, 31.84, 31.80, 29.52, 29.49, 29.26, 29.09, 28.83, 25.33, 22.61, 18.67, 18.47, 14.01. HR-MS (ESI): calcd for $[C_{16}H_{31}O]^+$, 239.2369; found, 239.2370.

4.4. (*E*)-Pentadec-4-en-1-ol 7

A mixture of THF (6 mL), diglyme (54 mL), and $LiAlH_4$ (1.52 g, 40 mmol) was stirred and heated to 130 °C at which point a low boiling fraction was distilled off using a Dean-Stark trap. A solution of alkynol **6** (2.38 g, 10 mmol) in diglyme (10 mL) was slowly added to the above stirred mixture at 0 °C. The temperature was then raised and kept at 160 °C for 13 h. The reaction mixture was cooled and slowly quenched with ice-water. The resulting slurry was filtered through a pad of Celite and the remaining solid was washed extensively with CH_2Cl_2. The combined CH_2Cl_2 solution was worked up. The residue was purified by silica gel flash chromatography and eluted with AcOEt–hexane (1:5) to afford

(*E*)-pentadec-4-en-1-ol **7** (2.0 g) as a white solid in 83%. Mp 21.8–22.0 °C ^{1}H NMR ($CDCl_3$) δ: 5.42–5.37 (m, 2H), 3.64 (br s, 2H), 2.04–1.93 (m, 4H), 1.62–1.52 (m, 2H), 1.46–1.25 (m, 19H), 0.87 (t, J = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 130.84, 129.72, 62.73, 32.54, 32.24, 32.17, 31.87, 29.59, 29.48, 29.30, 29.15, 25.68, 22.63, 14.03. HR-MS (ESI): calcd for $[C_{16}H_{33}O]^+$, 241.2526; found, 241.2528.

4.5. (*E*)-Hexadec-5-enoic acid 8

A mixture of (*E*)-pentadec-4-en-1-ol **7** (1.2 g, 5 mmol), PDC (7.0 g, 18.7 mmol), and DMF (20 mL) was stirred at ambient temperature overnight. The brown mixture was then poured into H_2O (100 mL) and extracted with Et_2O. The combined organic extracts were dried, concentrated, and purified by flash chromatography (AcOEt/hexane = 1:5 v/v) to afford (*E*)-hexadec-5-enoic acid **8** 0.73 g in 58% yield as a colorless oil. ^{1}H NMR ($CDCl_3$): 11.20 (br, 1H), 5.46–5.31 (m, 2H), 2.34 (t, J = 7.5 Hz, 2H), 2.07–1.93 (m, 4H), 1.74–1.64 (m, 2H), 1.26 (br, 16H), 0.87 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$): 180.05, 131.91, 128.61, 33.32, 32.54, 31.91, 31.80, 29.63, 29.53, 29.51, 29.33, 29.18, 24.45, 22.67, 14.08. HR-MS (ESI): calcd for $[C_{16}H_{30}O_2Na]^+$, 277.2138; found, 277.2138.

4.6. (5*S*,6*R*)- and (5*R*,6*S*)-6-hydroxy-5-hexadecanolide *rac*-10

To a solution of acid **8** (0.28 g, 1.1 mmol) in CH_2Cl_2 (10 mL) was added a peracetic acid solution (2.1 mL = 3 × 0.7 mL) and anhydrous Na_2CO_3 (0.72 g = 3 × 0.24 g) in three portions. The reaction mixture was stirred for 1.5 h at room temperature. After the reaction was finished as detected by TLC, the mixture was diluted with saturated $Na_2S_2O_3$ (10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with brine (3 × 10 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo to give a white solid compound *rac*-**9**. Compound *rac*-**9** was dissolved in CH_2Cl_2 (20 mL) at room temperature and CSA (5 mg) was added. The mixture was stirred at ambient temperature overnight. After the reaction was finished, the organic phase was washed with 5% Na_2CO_3 solution and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Flash chromatography on silica gel (3:1 V/V petroleum ether/EtOAc) afforded a white solid *rac*-**10** 0.22 g in 74% yield. Mp 67.0–67.8 °C. ^{1}H NMR ($CDCl_3$) δ: 4.28–4.22 (m, 1H), 3.82 (br, 1H), 2.60–2.42 (m, 2H), 2.08 (br, 1H), 1.89–1.75 (m, 4H), 1.53–1.26 (m, 18H), 0.88 (t, J = 6.7 Hz, 3H). It was identical to that in the literature.[5]

4.7. 4-((2*R*,3*R*)-3-Decyloxiran-2-yl)butan-1-ol 12

To a 100 mL three-necked flask were added a buffer [0.05 M $Na_2B_4O_7{\cdot}10H_2O$ in 4×10^{-4} M aqueous Na_2(EDTA)] (20 mL), acetonitrile (30 mL), (*E*)-pentadec-4-en-1-ol **7** (0.48 g, 2 mmol), tetrabutylammonium hydrogen sulfate (0.075 g, 0.02 mmol), and ketone **18** (0.167 g, 0.67 mmol). The reaction mixture was cooled with an ice-water bath. A solution of oxone (1.7 g, 2.76 mmol) in aqueous Na_2(EDTA) (4×10^{-4} M 13 mL) and a solution of K_2CO_3 (1.6 g, 11.6 mmol) in water (13 mL) were added dropwise through two separate addition funnels over a period of 3 h. The epoxidation reaction mixture was then allowed to warm up to room temperature and extracted with EtOAc (3 × 30 mL), worked up, purified by silica gel flash chromatography, and eluted with petroleum ether/EtOAc = 5:1 to give a white solid 4-((2*R*,3*R*)-3-decyloxiran-2-yl)butan-1-ol **12** 0.45 g in 88% yield. Mp 36.8–37.4 °C. $[\alpha]_D^{25}$ = +26.7 (c 0.52, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 3.61 (t, J = 6.1 Hz, 2H), 2.75 (s, 1H), 2.68 (t, J = 4.5 Hz, 2H), 1.62–1.26 (m, 24H), 0.88 (t, J = 6.5 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 62.20, 58.83, 58.72, 32.27, 31.96, 31.80, 31.69, 29.49, 29.45, 29.35, 29.21, 25.92, 22.56, 22.25, 13.97. HR-MS (ESI): calcd for $[C_{16}H_{32}O_2Na]^+$, 279.2295; found, 279.2290.

4.8. (5*S*,6*R*)-6-Hydroxy-5-hexadecanolide 14a

A mixture of compound **12** (0.256 g, 1 mmol), $NaIO_4$ (1.5 g, 7 mmol), H_2O (20 mL) and CCl_4 (15 mL) was stirred for 5 min. Next, $RuCl_3{\cdot}H_2O$ (5 mg) was added, the black slurry was stirred for 1 h at ambient temperature. The mixture was diluted with water (20 mL) and extracted with CH_2Cl_2. The organic phase was combined and worked up. The residue was purified by silica gel column chromatography and eluted with AcOEt–petroleum ether (1:3) to afford compound **13** 0.225 g in 83% yield as a white solid.

Compound **13** was dissolved in CH_2Cl_2 (15 mL) at room temperature and CSA (5 mg) was added. The mixture was stirred at room temperature for 8 h, washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, and the solvent removed under vacuum. The residue was purified by silica gel flash chromatography and eluted with AcOEt–petroleum ether (1:3) to afford a white solid, which was recrystallized in hexane to give compound **14a** 0.195 g in 72% yield for two steps. Mp 67.0–67.5 °C. $[\alpha]_D^{25}$ = +12.0 (c 0.42, $CHCl_3$) {lit.[7m] $[\alpha]_D^{25}$ = +12.7 (c 0.74, $CHCl_3$)}. ^{1}H NMR ($CDCl_3$) δ: 4.28–4.22 (m, 1H), 3.81 (br, 1H), 2.60–2.42 (m, 2H), 2.21 (br, 1H), 1.98–1.73 (m, 4H), 1.53–1.42 (m, 3H), 1.26 (br, 16H), 0.88 (t, J = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 171.69, 83.41, 72.30, 31.81, 31.73, 29.71, 29.50, 29.47, 29.44, 29.22, 25.78, 22.58, 21.18, 18.26, 14.00. HR-MS (ESI): calcd for $[C_{16}H_{30}O_3Na]^+$, 293.2087; found, 293.2086. Compound **14a** was reacted with *p*-nitrobenzoyl chloride to form *p*-nitrobenzoate derivative **11a**; the ee value was determined to be 95.9% with the retention time of 19.580 min in the HPLC profile.

4.9. (5*S*,6*R*)-6-Acetoxy-5-hexadecanolide 1a

A mixture of **14a** (0.31 g, 1.15 mmol), Ac_2O (0.33 mL, 3.5 mmol) and 4-(dimethylamino)pyridine (DMAP) (0.42 g, 3.4 mmol) in dry CH_2Cl_2 (10 mL) was stirred at room temperature for 4 h. Next, the mixture was quenched with $NaHCO_3$ solution and extracted with CH_2Cl_2. The combined extracts were dried over $MgSO_4$, filtered, the solvent removed, and purified by silica gel column chromatography (petroleum ether/AcOEt 6:1) to give **1a** 0.32 g in 89% yield as a colorless oil. $[\alpha]_D^{25}$ = +38.0 (c 0.60, $CHCl_3$) {lit.[7m] $[\alpha]_D^{25}$ = +36.4 (c 1.2, $CHCl_3$)}. ^{1}H NMR ($CDCl_3$) δ: 5.01–4.95 (m, 1H), 4.35 (ddd, J = = 3.3, 4.5, 13.1 Hz, 1H), 2.65–2.50 (m, 1H), 2.48–2.41 (m, 1H), 2.09 (s, 3H), 1.96–1.89 (m, 3H), 1.70–1.61 (m, 3H), 1.26 (br, 16H), 0.88 (t, J = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 170.62, 170.15, 80.27, 74.02, 31.65, 29.38, 29.36, 29.32, 29.30, 29.20, 29.16, 29.06, 25.02, 23.20, 22.43, 20.74, 18.01, 13.85. HR-MS (ESI): calcd for $[C_{18}H_{32}O_4Na]^+$, 335.2193; found, 335.2196.

4.10. (*E*)-Ethyl hexadec-5-enoate 15

(*E*)-Hexadec-5-enoic acid **8** (1.1 g, 0.44 mmol) was dissolved in ethanol (60 mL) and 0.2 mL of concentrated H_2SO_4 were added. After 5 h at reflux, the solvent was evaporated and the residue was purified by silica gel column chromatography (100:1 V/V petroleum ether/EtOAc) to give **15** (1.0 g, 84%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 5.37–5.24 (m, 2H), 4.04 (q, J = 7.1 Hz, 2H), 2.21 (t, J = 7.5 Hz, 2H), 1.97–1.86 (m, 4H), 1.66–1.55 (m, 2H), 1.17 (br, 20H), 0.81 (t, J = 6.5 Hz, 3H); ^{13}C NMR δ: 173.55, 131.56, 128.77, 59.99, 33.54, 32.49, 31.84, 29.56, 29.48, 29.45, 29.27, 29.10, 24.71, 22.60, 14.14, 13.98. HR-MS (ESI): calcd for $[C_{18}H_{35}O_2]^+$, 283.2632; found, 283.2635.

4.11. (5*R*,6*R*)-6-Hydroxy-5-hexadecanolide 14d

Compound **15** (0.846 g, 3 mmol) was added to a cold (0 °C) solution of AD-mix-β (1.5 g/mmol, 4.5 g) and $MeSO_2NH_2$ (0.31 g, 3.2 mmol) in *tert*-butyl alcohol and water (1:1, 60 mL). The mixture was stirred at 0 °C for 60 h, then quenched by $Na_2S_2O_3$ and extracted with EtOAc. The solvents were removed under reduced pressure to give crude product **16b**.

Compound **16b** was dissolved in methanol (10 mL) and aqueous NaOH (3 M, 10 mL). After being stirred at 60 °C for 2 h, the mixture was cooled to 0 °C, acidified with 3 M HCl, and extracted with ethyl acetate. The solvents were removed under reduced pressure and the residue was dissolved in 50 mL of CH_2Cl_2. Next, 30 mg of *p*-toluenesulfonic acid were added, and the mixture was stirred at ambient temperature overnight. Work-up was carried out and followed by column chromatography (silica gel, petroleum ether/EtOAc, 3:1) to give a white solid, which was recrystallized from hexane to give compound **14d** 0.65 g, 80% yield. Mp 69.5–71.0 °C, $[\alpha]_D^{25} = -10.5$ (*c* 1.2, $CHCl_3$) {lit.[7n] $[\alpha]_D = -10.2$ (*c* 0.87, $CHCl_3$)}. ^{1}H NMR ($CDCl_3$) δ: 4.22–4.16 (m, 1H), 3.58–3.54 (m, 1H), 2.64–2.39 (m, 3H), 1.96–1.71 (m, 4H), 1.56–1.26 (m, 18H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 171.38, 83.13, 73.24, 32.58, 31.80, 29.57, 29.49, 29.47, 29.45, 29.21, 25.36, 24.07, 22.57, 18.35, 13.99. HR-MS (ESI): calcd for $[C_{16}H_{30}O_3Na]^+$, 293.2087; found, 293.2088.

4.12. (5*S*,6*S*)-6-Hydroxy-5-hexadecanolide 14c

Dihydroxylation of compound **15** with AD-mix-α was carried out in the same procedure as for compound **14d** to obtain a white solid **14c** in 87% yield. Mp 69.0–70.0 °C, $[\alpha]_D^{25} = +9.8$ (*c* 0.73, $CHCl_3$). {lit.[7n] $[\alpha]_D = +11.5$ (*c* 0.74, $CHCl_3$)}. ^{1}H NMR ($CDCl_3$) δ: 4.22–4.15 (m, 1H), 3.58–3.55 (m, 1H), 2.61–2.45 (m, 2H), 2.21 (d, *J* = 5.9 Hz, 1H), 1.96–1.84 (m, 4H), 1.56–1.26 (m, 18H), 0.88 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 171.36, 83.13, 73.26, 32.59, 31.80, 29.58, 29.50, 29.48, 29.46, 29.22, 25.37, 24.08, 22.57, 18.36, 14.00. HR-MS (ESI): calcd for $[C_{16}H_{30}O_3Na]^+$, 293.2087; found, 293.2085.

4.13. (5*R*,6*R*)-6-Acetoxy-5-hexadecanolide 1c

The procedure was the same as for compound **1a** in Section 4.9 from compound **14c** to obtain a light yellow oil compound **1c** in 92% yield. $[\alpha]_D^{25} = +14.6$ (*c* 0.12, $CHCl_3$). {lit.[7m] $[\alpha]_D^{25} = +13.7$ (*c* 0.6, $CHCl_3$)}. ^{1}H NMR ($CDCl_3$) δ: 4.99 (ddd, *J* = 3.7, 5.6, 8.0 Hz, 1H), 4.39–4.33 (m, 1H), 2.66–2.41 (m, 2H), 2.10 (s, 3H), 1.99–1.82 (m, 3H), 1.70–1.61 (m, 3H), 1.25 (br s, 16H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 170.70, 170.49, 79.66, 73.78, 31.78, 29.82, 29.52, 29.44, 29.42, 29.33, 29.27, 29.19, 25.22, 24.00, 22.55, 20.83, 18.28, 13.98. HR-MS (ESI): calcd for $[C_{18}H_{33}O_4]^+$, 313.2373; found, 313.2368.

4.14. (5*S*,6*S*)-6-Acetoxy-5-hexadecanolide 1d

The procedure was the same as for compound **1c** in Section 4.13 from compound **14d** to obtain a light yellow oil compound **1d** in 88% yield. $[\alpha]_D^{25} = -13.7$ (*c* 0.10, $CHCl_3$). {lit.[7m] $[\alpha]_D^{25} = -11.5$ (*c* 0.7, $CHCl_3$)}. ^{1}H NMR ($CDCl_3$) δ: 5.01–4.95 (m, 1H), 4.39–4.33 (m, 1H), 2.60–2.45 (m, 2H), 2.09 (s, 3H), 1.94–1.81 (m, 3H), 1.70–1.61 (m, 3H), 1.25 (br s, 16H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 170.71, 170.49, 79.66, 73.78, 31.78, 29.82, 29.51, 29.44, 29.42, 29.33, 29.27, 29.19, 25.21, 24.00, 22.55, 20.83, 18.28, 13.98. HR-MS (ESI): calcd for $[C_{18}H_{33}O_4]^+$, 313.2373; found, 313.2369.

4.15. (5*R*,6*S*)-6-Hydroxy-5-hexadecanolide 4-nitrobenzoate 11b

Under a nitrogen atmosphere, 25 mL of dry THF were added into a 50 mL round-bottomed flask. It was then cooled to 0 °C, after which triphenylphosphine (1.05 g, 4 mmol) and DEAD (0.59 g, 4 mmol) were added, followed by compound **14d** (0.27 g, 1 mmol) and *p*-nitrobenzoic acid (0.20 g, 1.2 mmol). The mixture was stirred at room temperature for 4 h. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel (10:1–5:1 (v/v) petroleum ether/EtOAc) to afford 377 mg (90% yield) of (5*R*,6*S*)-6-hydroxy-5-hexadecanolide *p*-nitrobenzoate compound **11b** as a light yellow oil. $[\alpha]_D^{25} = +10.8$ (*c* 0.44, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ: 8.32–8.28 (m, 2H), 8.24–8.19 (m, 2H), 5.31–5.25 (m, 1H), 4.54–4.48 (m, 1H), 2.60–2.47 (m, 2H), 2.03–1.98 (m, 2H), 1.89–1.71 (m, 4H), 1.32–1.23 (m, 16H), 0.86 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 170.53, 164.04, 150.63, 135.22, 130.77, 123.54, 80.33, 76.01, 31.78, 29.50, 29.44, 29.41, 29.33, 29.30, 29.27, 29.19, 25.28, 23.55, 22.57, 18.23, 14.00. HR-MS (ESI): calcd for $[C_{23}H_{34}NO_6]^+$ 420.2381; found, 420.2378. The ee value of compound **11b** was determined to be 97.9% with a retention time of 21.185 min in the HPLC profile.

4.16. (5*S*,6*R*)-6-Hydroxy-5-hexadecanolide *p*-nitrobenzoate 11a

The procedure was the same as compound **11b** in Section 4.15 from compound **14c** to afford a light yellow oil **11a** in 83% yield. $[\alpha]_D^{25} = -11.2$ (*c* 0.23, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ: 8.32–8.28 (m, 2H), 8.25–8.20 (m, 2H), 5.32–5.26 (m, 1H), 4.56–4.50 (m, 1H), 2.67–2.48 (m, 2H), 2.06–1.99 (m, 2H), 1.91–1.73 (m, 4H), 1.41–1.23 (m, 16H), 0.85 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 170.52, 164.02, 150.61, 135.21, 130.75, 123.52, 80.31, 75.99, 31.77, 29.49, 29.42, 29.40, 29.32, 29.29, 29.25, 29.18, 25.26, 23.52, 22.55, 18.22, 13.99. HRMS (ESI): calcd for $[C_{23}H_{34}NO_6]^+$ 420.2381; found, 420.2378. The ee value of compound **11a** was determined to be 98.7% with the retention time 19.895 min in the HPLC profile.

4.17. (5*R*,6*S*)-6-Hydroxy-5-hexadecanolide 14b

At first, 15 mL of CH_3OH, K_2CO_3 (0.35 g, 2.5 mmol) and compound **11b** (0.21 g, 0.5 mmol) were added to a 50 mL round-bottomed flask. The mixture was stirred for 10 min at room temperature and then filtered. The solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel (4:1 (v/v) hexanes/EtOAc) to afford 0.23 g of (5*R*,6*S*)-6-hydroxy-5-hexadecanolide **14b** in 87% yield as a white solid. Mp 67.4–68.0 °C, $[\alpha]_D^{25} = -12.5$ (*c* 0.75, $CHCl_3$) {lit.[7g] $[\alpha]_D^{25} = -12.7$ (*c* 1.0, $CHCl_3$)}. ^{1}H NMR ($CDCl_3$) δ: 4.28–4.22 (m, 1H), 3.81 (br, 1H), 2.66–2.57 (m, 1H), 2.51–2.39 (m, 1H), 2.03 (d, *J* = 4.2 Hz, 1H), 2.00–1.75 (m, 4H), 1.51–1.42 (m, 3H), 1.26 (br, 15H), 0.88 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 171.71, 83.43, 72.36, 31.85, 31.72, 29.74, 29.54, 29.50, 29.48, 29.27, 25.82, 22.63, 21.18, 18.30, 14.05. HR-MS (ESI): calcd for $[C_{16}H_{30}O_3Na]^+$, 293.2087; found, 293.2089.

4.18. (5*S*,6*R*)-6-Hydroxy-5-hexadecanolide 14a

The procedure was the same as for compound **14b** in Section 4.17 from compound **18a** to obtain a white solid **14a** in 90% yield. Mp 68.0–68.2 °C, $[\alpha]_D^{25} = +11.6$ (*c* 0.24, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ: 4.28–4.22 (m, 1H), 3.82 (br, 1H), 2.60–2.42 (m, 2H), 2.17 (br, 1H), 1.98–1.75 (m, 4H), 1.53–1.42 (m, 3H), 1.26 (br, 15H), 0.88 (t, *J* = 6.7 Hz, 3H), which were identical with that in Section 4.8.

4.19. (5*R*,6*S*)-6-Acetoxy-5-hexadecanolide 1b

A mixture of **14b** (95 mg, 0.35 mmol), Ac_2O (0.1 mL, 1.1 mmol), and 4-(dimethylamino)pyridine (140 mg, 1.1 mmol) in dry CH_2Cl_2 (5 mL) was stirred at room temperature for 4 h, then the mixture was quenched with a $NaHCO_3$ solution and extracted with CH_2Cl_2. The combined extracts were dried over $MgSO_4$, filtered, and the solvent removed. The residue was purified by silica gel column chromatography and deleted with hexane/AcOEt (6:1) to give **1b** 98 mg in 90% yield as a light yellow oil. $[\alpha]_D^{25} = -37.4$ (*c* 0.65, $CHCl_3$) {lit.[7g] $[\alpha]_D^{25} = -36.8$ (*c* 1.55, $CHCl_3$)}. ^1H NMR ($CDCl_3$) δ: 5.01–4.95 (m, 1H), 4.36 (ddd, *J* = 3.3, 6.3, 9.3 Hz, 1H), 2.63–2.41 (m, 2H), 2.07 (s, 3H), 1.99–1.83 (m, 3H), 1.71–1.61 (m, 3H), 1.25 (br, 16H), 0.87 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 170.62, 170.18, 80.30, 74.07, 31.69, 29.42, 29.39, 29.35, 29.33, 29.24, 29.19, 29.09, 25.06, 23.26, 22.46, 20.78, 18.05, 13.89. HR-MS (ESI): calcd for $[C_{16}H_{30}O_3Na]^+$, 335.2193; found, 335.2191.

4.20. (5*S*,6*R*)-6-Acetoxy-5-hexadecanolide 1a

The procedure was the same as for compound **1b** in Section 4.19 from compound **14a** to obtain a light yellow oil **1a** (105 mg) in 96% yield as a colorless oil. $[\alpha]_D^{25} = +36.8$ (*c* 0.60, $CHCl_3$). ^1H NMR (300 MHz) δ: 5.01–4.95 (m, 1H), 4.36 (ddd, *J* = 3.2, 6.4, 9.3 Hz, 1H), 2.59–2.39 (m, 2H), 2.08 (s, 3H), 1.97–1.89 (m, 3H), 1.68–1.61 (m, 3H), 1.26 (br, 16H), 0.87 (t, *J* = 6.7 Hz, 3H), which were identical with that in Section 4.9.

Acknowledgements

This project was co-founded by the National Key Technologies R&D Program (No. 2011BAE06B04), Natural Science Foundation of China (No. 21172254), and National Hi-Tech R&D Program of China (2011AA10A202).

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