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Formal synthesis of Cladospolide C & *epi*-Cladospolide C using *R*-(+)-γ-valerolactone as a chiral synthon☆

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ABSTRACT

The formal synthesis of Cladospolide-C and its analog is achieved by using enantiopure (*R*)-γ−valerolactone **10**. The significant points of this synthesis are the stereoselective dihydroxylation of α, β-unsaturated ester **16** using Sharpless protocol, Wittig olefination of γ −valerolactol **6** with triphenylphosphonium iodide salt **7**, one pot selective oxidation of **22** and subsequent C2-homologation with good *E*/*Z* ratio.

1. Introduction

Cladospolides A–D and *iso*-Cladospolide B comprise a family of fungal secondary metabolites isolated from the fermented broth of cultures that were obtained from either marine or soil fungi [1–4]. Among these, cladospolides A (**1**) and B (**2**) were first isolated from the culture filtrate of the fungus *Cladosporium cladosporiolides* FI-113 by Isogai and co-workers [1]. In 1995, Fukada et al., isolated cladospolide C (**4**) along with cladospolides A and B from *Cladosporium tenuissium* [2]. Later in 2000, Ireland and co-workers isolated **2** from *Cladosporium herbarum* together with *iso*-cladospolide B (**3**) from the fungal strain I96S215 [3]. Cladospolide D (**5**) was isolated in 2001 from the fermentation broth of *Cladosporium* sp. FT0012 [4a]. Structurally, cladospolides A–C are γ, δ-dihydroxy- α, β-unsaturated 12-membered macrolides, whereas Cladospolide D (**5**) is a δ-hydroxy-γ-Oxo-α,β-unsaturated 12-membered lactone (Fig. 1).

Furthermore, Cladospolides A and C possess an (*E*)-olefin geometry, whereas Cladospolides B and D have a (*Z*)-olefin geometry. In contrast to Cladospolides A–D, *iso*-Cladospolide B (**3**) is a butenolide that is γ-substituted by an aliphatic group. Although the Cladospolides are fungal metabolites, they are plant-growth regulators. For example, Cladospolides A–C inhibit the shoot elongation of rice seedlings [4b].

The biological properties of Cladospolide C (**4**) suggest that it is a gibberellin synthesis inhibitor. Unlike the other members, Cladospolide D (**5**) shows antimicrobial activity against *Mucor* recemosus and *Pyricularia oryzae*. Given their fascinating structural diversities and biological profiles, the Cladospolide family members have generated considerable interest in the synthetic community. Accordingly, various strategies have been developed that utilize diverse key reactions [5–9].The absolute and relative stereochemistry for the Cladospolides A, B, and C have been confirmed by several total syntheses from known chiral starting materials [5–9]. For instance, Cladospolides A-C have been prepared by Banwell from 1-hepten-2-ol and *cis*-2, 3-dihydroxychlorobenzene which can be prepared in optically pure form *via* enzymatic resolution and biotransformation [10], whereas others have followed chiron approach using carbohydrate sources [11]. Synthesis of Cladospolide A was reported by Mori and Maemoto in 1987 [12]. Despite their rather intriguing biological profiles, the Cladospolides have only received limited attention as synthetic targets.

In continuation of our pursuit of synthesizing structurally

☆ This article is dedicated to Dr. J. S. Yadav Former Director CSIR-IICT On the occasion of his 70th birthday.

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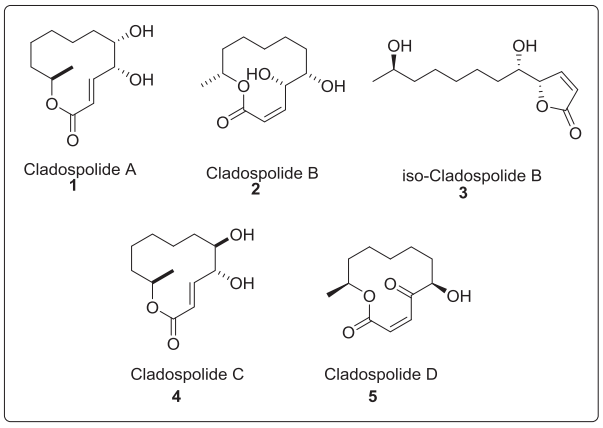


Fig. 1. Structures of Cladospolides A–D and *iso*-Cladospolide B.

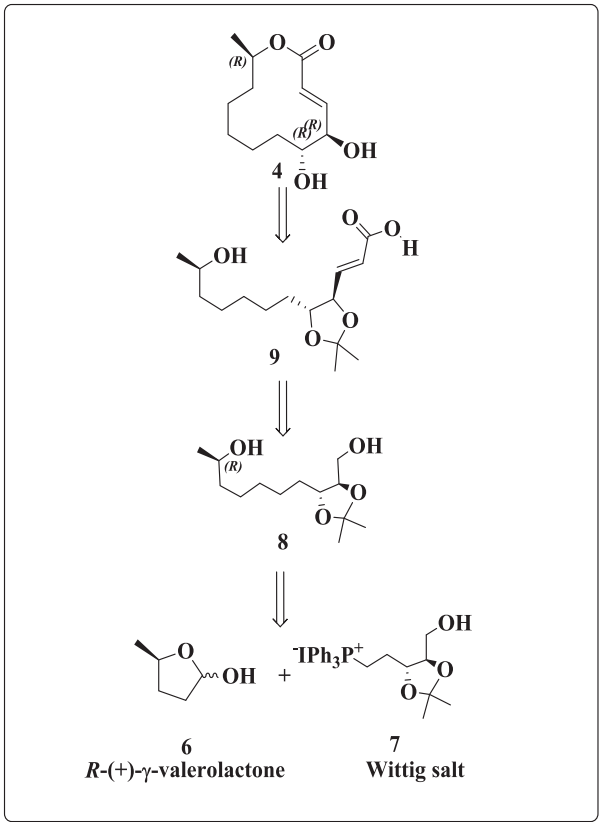
complex molecules beginning with optically pure γ-Valerolactone, herein we report the formal synthesis of Cladospolide C (**4**) from γ-Lactone.

γ-Lactone is very good chiral synthon in the synthesis of natural products [13]. A variety of methods are in practice for the synthesis of optically pure γ-lactones. Though a number of reports available in the literature for the synthesis of optically pure γ-Valerolactone (**10**) [14], we chose to prepare the latter from D-alanine (**11**) *via* D-Lactic acid (**12**) [15].

2. Retrosynthetic approach

The retrosynthetic approach for synthesis of Cladospolide C (**4**) is described in Scheme 1. Accordingly Cladospolide C (**4**) can be achieved by Yamaguchi lactonization of the α, β-unsaturated *seco*-acid **9.** The *seco*-acid **9** is obtained by selective oxidation, a two carbon homologation using Wittig ylide and saponification of the ester. The *seco* acid **9**is traced to intermediate diol **8** which is formed as a result of hydrogenation of the double bond that formed *via* Wittig reaction of corresponding triphenylphosphonium salt (**7**) and lactol (**6**). Compound **6** can be traced from *R*-(+)-γ-Valerolactone (**10**) further compound **7** can be traced from commercial available 1, 3-propanediol **(17).**

The retrosynthetic approach for the synthesis of Wittig salt 7 from 1, 3-propanediol (17) is described in the Scheme 2. The Wittig salt (7) was obtained by phosphorylation of Iodo alcohol 13. The intermediate iodo alcohol 13 was obtained from hydroxy ester 14 *via* halogenation under Appel condition followed by $NaBH_4$ reduction. The hydroxy ester 14 can be traced from α, β-unsaturated ester 16 by means of Asymmetric Sharpless dihydroxylation. The α, β-unsaturated ester 16 can be traced from 1, 3-propanediol (17) by selective mono TBDMS protection followed by C2-homologation.



Scheme 1. Retrosynthetic approach for Cladospolide C (**4**) *via* Wittig olefination.

3. Results and discussion

The synthesis began with reduction of *R*-γ-Valerolactone (10) to corresponding *R*-γ-Valerolactol (6) and this key intermediate was used in synthesis of cladospolides as shown in Scheme 3. The synthesis of *R*-γ-Valerolactone (10) was described in literature [15].

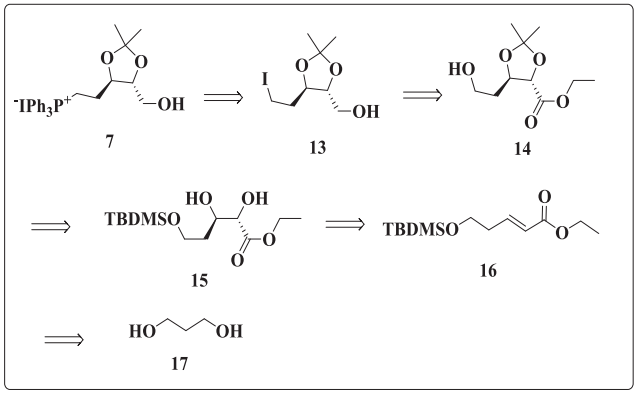
3.1. Reagents and conditions

a) $NaNO_2$, H_2SO_4; 2 h, 58%; b) (i) MeOH, H_2SO_4, rt, 24 h; (ii) TBDMSCl/Imidazole, DCM, 25–35 °C, 12 h, 95%; (iii) DiBAL-H, DCM, −70 ± 5 °C, 2 h; (iv) C2- Wittig (21), 72%; (v) H_2, Pd/C, Ethyl acetate 40 Psi, 4 h, 95% d) *p*TSA, MeOH, 25–35 °C, 24 h, 90%; c) DIBAL-H, DCM, −78 °C, 0.5 h.

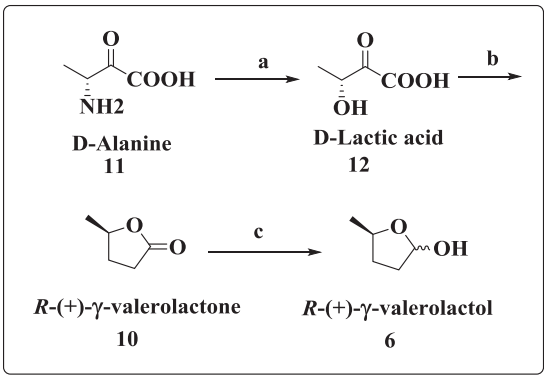
We began synthesis of Wittig salt 7 starting from 1,3 propanediol (17) as described in Scheme 4. The 1,3 propanediol (17) was selectively protected as silyl ether using NaH to afford mono protected diol 18 with good yield [16]. The primary alcohol was then oxidized to aldehyde using PCC which was homologated further with C2- Wittig salt 21 to afford α, β unsaturated ester 16 with >95% *trans* configuration as indicated by ^{1}H NMR [17].

3.2. Reagents and conditions

a) TBDMSCl, NaH, THF, 0–25 °C, 2 h, 90%; b) PCC/NaOAc, DCM, 25 °C, 4 h; C2-wittig (21), 24 h, 82%; c) $(DHQ)_2PHAL$ (15a) or $(DHQD)_2PHAL$ (15b) $K_3Fe(CN)_6$, $K_2OsO_4{\cdot}2H_2O$, K_2CO_3, $NaHCO_3$,



Scheme 2. Retrosynthesis of 7 (Wittig salt) from 1, 3-Propanediol (**17**).



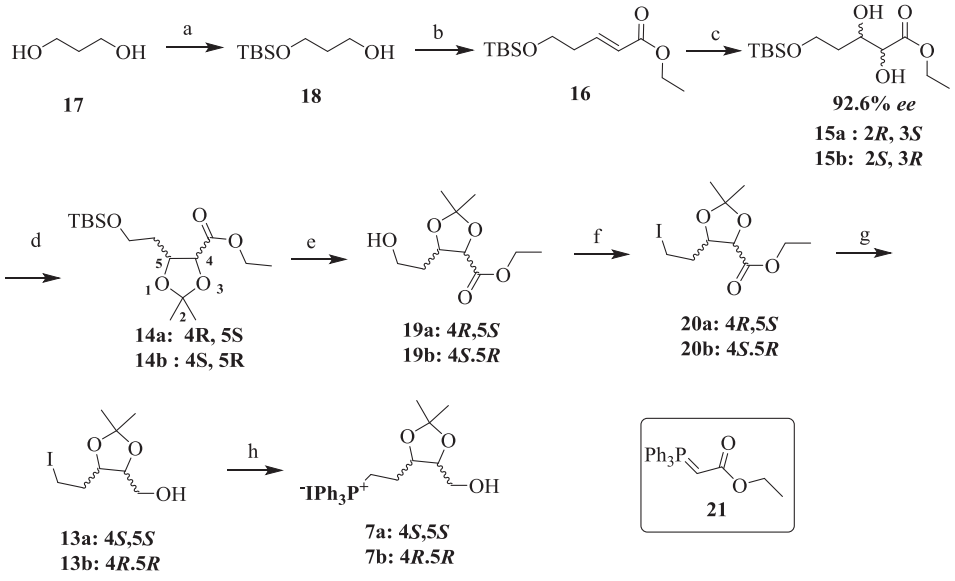
Scheme 3. Synthesis of R-γ-valerolactol (**6**) from R-γ-Valerolactone (**10**).

$MeSO_2NH_2$, *t*-Butanol: H_2O (2:3), 24 h, 5 °C, 94%; d) P*p*TS, Acetone, 2, 2-dimethoxy propane, 24 h, 25 °C, 90%; e) TBAF, THF, 0–5 °C, 12 h, 95%; f) I_2, TPP, imidazole, DCM, rt, 2 h, 82%; g) $NaBH_4$, MeOH: THF (1: 4), 5 °C, 4 h, 89%; h) TPP, ACN, reflux, 12 h, 88%.

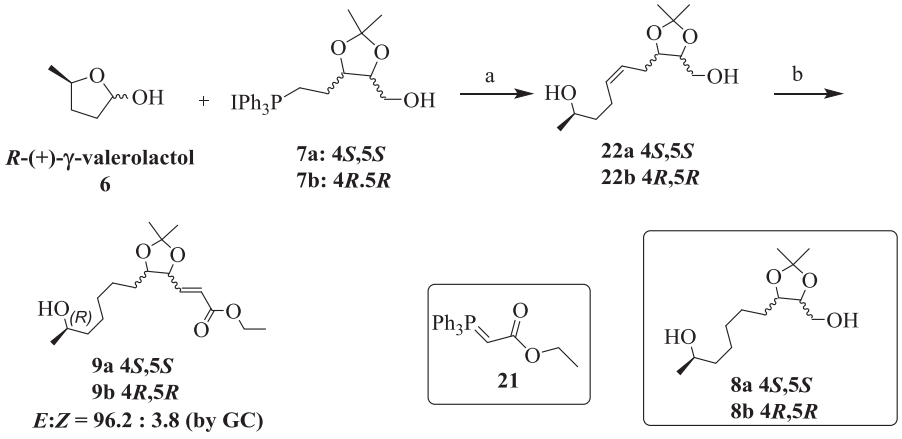
The α, β unsaturated ester 16 was then converted into a chiral diol *via* Sharpless asymmetric dihydroxylation. Both the enantiomers 15a and 15b were synthesized by using a suitable reagent system [17b,c]. Thus obtained stereogenic centers as secondary diols in compound 15a and 15b were protected separately using 2,2 dimethoxy propane in an acetone and catalytic amount of P*p*TS to afford 14a in good yields [17c]. The compound 14a was desilylated with TBAF to afford hydroxy ester 19a [18].

The hydroxy ester 19a was subjected to Mitsunobu mediated halogenation in presence of iodine and triphenylphosphine to afford the corresponding iodo ester 20a [19]. The iodo ester 20a was then treated with $NaBH_4$ in a MeOH:THF (1:4) to afford the corresponding iodo alcohol 13a. The iodo alcohol 13a was finally converted to corresponding Wittig salt 7a and its antipode 13b was traced from 7b in similar fashion.

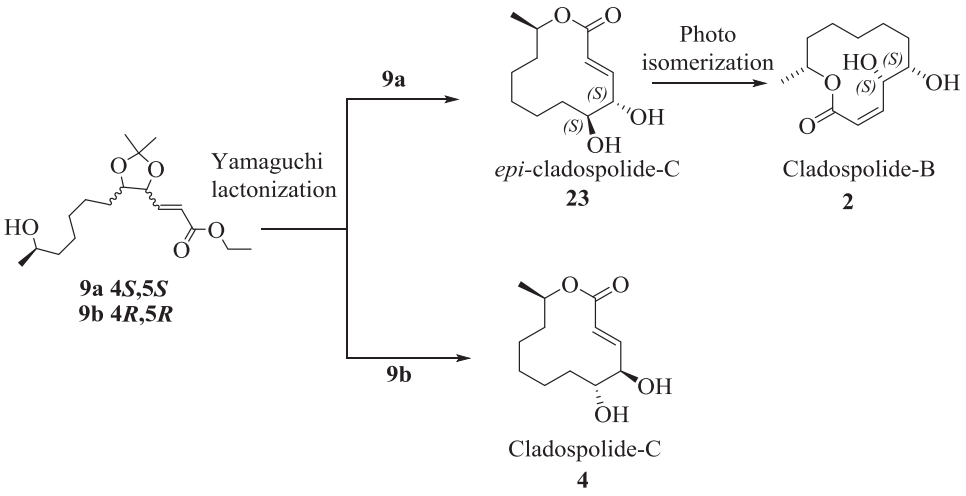
Now the stage is set to synthesize the title compound Cladospolide C (4) using Wittig salt 7 and Lactol 6 *via* Wittig olefination as mentioned in Scheme 5 The obtained lactol 6 (Scheme 3) was treated with Wittig salt 7a (Scheme 4) under Wittig olefination condition [20] to afford corresponding ene-diol 22a. Ene-diol 22a was then subjected to catalytic hydrogenation at 40 psi using $Pd(OH)_2$ as catalyst at ambient temperature to afford the corresponding saturated diol 8a [21].



Scheme 4. Synthesis of Wittig salt (**7a**) & (**7b**) starting from 1, 3 propanediol (**17**).



Scheme 5. Wittig olefination of Lactol **6** & Wittig salt **7**.



Scheme 6. Formal synthesis of Cladospolide C (**4**) & *epi*-Cladospolide C (**23**).

3.3. Reagents and conditions

a) NaHMDS, THF, −78 °C, 86%; b) (i) H_2-Pd(OH)$_2$, 40 psi, ethylacetate, rt, 98%; (ii) BAIB/TEMPO, DCM, 2 h, C2-Wittig (21), rt, 94%.

This step afforded the ideal structural frame work to expedite the final molecule formal synthesis *via* selective oxidation. Thus compound 8a was subjected to one pot selective oxidation and concomitant C2-ylide extension under BAIB/TEMPO [22] conditions to afford 9a with good *E*-selectivity and yield. Diastereomer 9b traced from 8b in similar fashion with *E*:*Z* ratio (96.2 : 3.8) estimated by GC [23].

The *epi*-cladospolide C (23) was synthesized formally from Compound 9a and similarly titled Cladospolide-C (4) was synthesized formally from 9b (Scheme 6) using the reported procedure [24]. Cladospolide B (2) can be synthesized formally from *epi*-Cladospolide-C (23) using reported procedure [25].

4. Conclusion

In summary, formal synthesis of Cladospolide C (4) and *epi*-Cladospolide C (23) has been developed with good yields. The route of synthesis developed for these macrolides utilize fairly inexpensive reagents and operationally friendly processes. This strategy can be utilized for the stereoselective synthesis of other macrolides. The application of this methodology for the synthesis of other biologically active complex macrolides is currently underway.

5. Experimental section

5.1. General information

All reagents were used as received from commercial sources without further purification or prepared as described in the literature. Reactions were monitored by thin layer chromatography (TLC) performed on Merck TLC silica gel 60 F254 aluminium plates. Visualization of the spots on the TLC plates was achieved by exposure to UV radiation (254 nm) or by using an appropriate TLC staining reagent (such as PMA, anisaldehyde and ninhydrin). Chromatographic purification of products was carried out by flash column chromatography on silica gel (60–120 mesh or 100–200 mesh or 230–400 mesh as the case required). Melting points were determined using a Differential Scanning Calorimeter (DSC, Q-2000, TA) apparatus. Infrared spectra were recorded on a Perkin-Elmer 1650 Fourier transform spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 400 MHz spectrometer. Chemical shifts (δ) in ppm are reported relative to Me_4Si (= 0 ppm) by using residual solvent signals as internal reference [$CDCl_3$: $\delta = 7.26$ ppm (^{1}H NMR) and 77.0 ppm (^{13}C NMR); CD_3OD: $\delta = 3.31$ ppm (^{1}H NMR) and 49.2 ppm (^{13}C NMR); DMSO-d_6:$\delta = 2.50$ ppm (^{1}H NMR) and 39.5 ppm (^{13}C NMR)]. LRMS data were recorded on an Agilent 1200 Series liquid chromatography module hyphenated to a 6430 Triple Quad LC/MS system. HRMS spectra were recorded on Micromass LCT Premier mass spectrometer equipped with an ESI lockspray source for accurate mass values.

5.2. Experimental procedures

5.2.1. Synthesis of 3-(tert-butyldimethylsilyloxy) propan-1-ol (**18**)

To a stirred solution of 1, 3-propane diol (17) (3.0 g, 39.42 mmol) in dry THF (40 mL) at 0 °C was added oil free NaH (0.95 g, 39.42 mmol, 1.0 equiv.) in portions over 15 min. The reaction mixture was stirred at room temperature for 30 min, then cooled to 0 °C after which TBDMSCl (5.94 g, 39.42 mmol, 1.0 equiv.) was added. The reaction mixture was stirred at room temperature for 2 h. It was then quenched with ice cold water (10 mL) and the solution extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4), and concentrated. The residue was purified by silica gel column chromatography to give 18 (6.75 g, 90%). Analytical data: Colorless oil.; IR ($CHCl_3$, cm^{-1}): 3373, 2955, 2930, 2858, 1472, 1256, 1087, 965, 836, 774.; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.078 (s, 6H), 0.90 (s, 9H), 1.75 (m, 2H), 2.55 (t, $J = 4.9$ Hz, 1H), 3.78 (m, 4H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ −5.53 (2C), 18.13, 25.63, 25.83, 25.90, 34.19, 62.27, 62.79.; HRMS (ESI+): Calcd. for $C_9H_{22}O_2Si$ + H: 191.1466 found: 191.1467.

5.2.2. Synthesis of (E)-Ethyl 5-(tert-butyldimethylsilyloxy) pent-2-enoate (**16**)

To a mixture of PCC (5.1 g, 23.64 mmol, 1.5 equiv.) and NaOAc (1.94 g, 23.64 mmol, 1.5 equiv.) in dry CH_2Cl_2 (60 mL) was added a solution of alcohol (18) (3.0 g, 5.76 mmol) in CH_2Cl_2 (15 mL) at 0 °C. The reaction mixture was stirred for 4 h at rt and then diluted with petroleum ether/EtOAc (7: 3, 80 mL). The slurry was stirred and filtered through a pad of silica gel and Celite. The residue was washed 3 to 4 times with petroleum ether/EtOAc (7: 3) and filtered. The filtrate was concentrated to give virtually pure aldehyde, which was used directly in the next reaction. To a stirred solution of

aldehyde (4.05 g, 18.07 mmol) in dry DCM (60 mL) at 0 °C was added C2-Wittig (6.04 g, 1.1 equivalents ylide). The mixture was stirred at room temperature for 24 h at rt, solvent was removed under vacuum and crude residue was purified by silica gel column chromatography using petroleum ether/EtOAc (9: 1) as eluent to afford 16 (3.34 g, 82% overall two stages). Colorless oil.; IR ($CHCl_3$, cm^{-1}): 3054, 2930, 2897, 2856, 1724, 1655, 1472, 1464, 1448, 1388, 1367, 1313, 1257, 1176, 1097, 1043, 980, 867, 837, 776, 668.; ^1H NMR (400 MHz, $CDCl_3$): δ 0.04 (s, 6H), 0.89 (s, 9H), 1.26 (t, $J = 7.3$ Hz, 3H), 2.38–2.43 (m, 2H), 3.70 (t, $J = 6.8$ Hz, 2H), 4.15 (q, $J = 7.3$ Hz, 2H), 5.85 (dt, $J = 15.6$ & 1.5 Hz, 1H), 6.91 (dt, $J = 15.6$ & 1.5 Hz, 1H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ −5.35, 14.23, 25.63, 25.85, 35.67, 60.14, 61.55, 122.93, 145.83, 166.48.; HRMS (ESI+): Calcd. for $C_{13}H_{26}O_3Si$ + H: 259.1729 found: 259.1721.

*5.2.3. Synthesis of (2S, 3R)-ethyl5-(tert-butyldimethylsilyloxy)-2, 3-dihydroxypentanoate (**15a**)*

To a mixture of $K_3Fe(CN)_6$ (11.46 g, 34.82 mmol, 3.0 equiv.), K_2CO_3 (4.81 g, 34.82 mmol, 3.0 equiv.), $MeSO_2NH_2$ (1.10 g, 11.60 mmol, 1.0 equiv.), $NaHCO_3$ (2.92 g, 34.82 mmol, 3.0 equiv.), $(DHQ)_2PHAL$ (90.4 mg, 0.116 mmol, 1 mol %), $K_2OsO_4 \cdot 2H_2O$ (17.1 mg, 46.4 mmol, 0.4 mol %), *t*-BuOH (40 mL), and water (60 mL) were added. The mixture was stirred for 5 min and cooled to 0 °C in an ice bath. To the cooled mixture, a solution of the α, β-unsaturated ester 16 (3.0 g, 11.60 mmol) in *t*-BuOH (20 mL) was added. The reaction mixture was stirred at 0 °C for 24 h. It was then quenched with solid Na_2SO_3 (6 g) and stirred for 30 min. The solution was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (9: 1 to 3: 2) as eluent to afford 15a (3.2 g, 94%). Similarly antipode 15b synthesized from 16 using above procedure using $(DHQD)_2PHAL$ (2.9 g, 85%).

*5.2.3.1. Compound **15a**.* Viscous oil.; $[\alpha]_D^{20} = +3.00$ (c 0.5, $CHCl_3$).; IR ($CHCl_3$, cm^{-1}): 3472, 3020, 2957, 2931, 2859, 1737, 1472, 1388, 1258, 1217, 1129, 1097, 1026, 838, 759, 669.; ^1H NMR (400 MHz, $CDCl_3$): δ 0.074 (s, 6H), 0.89 (s, 9H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.71–1.77 (m, 1H), 1.90–1.99 (m, 1H), 3.20 (d, $J = 7.1$ Hz, 1H, OH), 3.25 (d, $J = 4.9$ Hz, 1H, OH), 3.81–3.93 (m, 2H), 4.05 (dd, $J = 3.5$, 1.9 Hz, 1H), 4.16–4.20 (m, 1H), 4.25 (q, $J = 7.1$ Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ −5.56 (2C), 14.14, 18.14, 25.82 (3C), 35.26, 61.59, 61.81, 72.09, 73.67, 173.16.; HRMS (ESI+): Calcd. for $C_{13}H_{28}O_5Si$ + H: 293.1784 found: 293.1770.

*5.2.3.2. Compound **15b**.* Viscous oil.; $[\alpha]_D^{25} = -3.24$ (c 0.5, $CHCl_3$).; IR ($CHCl_3$, cm^{-1}): 3479, 3019, 2956, 2930, 2885, 1736, 1471, 1369, 1250, 1210, 1096, 837, 758, 667.; ^1H NMR ($CDCl_3$, 400 MHz): δ 0.067 (s, 6H), 0.88 (s, 9H), 1.28–1.31 (t, $J = 7.0$ Hz, 3H), 1.70–1.75 (m, 1H), 1.91–1.97 (m, 1H), 3.19–3.26 (m, 1H), 3.81–3.91 (m, 2H), 4.04–4.06 (m, 1H), 4.16–4.18 (m, 1H), 4.24–4.30 (q, $J = 7.4$ & 14.5 Hz, 2H).; ^{13}C NMR ($CDCl_3$, 100 MHz): δ-5.54, −5.52, 14.14, 18.14, 25.82, 35.24, 61.61, 61.82, 72.11, 73.67, 173.18.; HRMS (ESI+): Calcd. for $C_{13}H_{28}O_5Si$ + H: 293.1784 found: 293.1775.

*5.2.4. Synthesis of ethyl (4R,5S)-5-(2-((tert-butyldimethylsilyl)oxy) ethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate (**14a**)*

To a solution of diol 15a (3.0 g, 10.26 mmol) in dry acetone (50 mL) was added 2, 2-dimethoxy propane (3.78 mL, 30.77 mmol, 3.0 equiv.) followed by *p*-TsOH (5 mg). The reaction mixture was stirred at room temperature for 12 h. Solid $NaHCO_3$ (0.5 g) was then added and stirred for 15 min. The solution was filtered through a pad of silica gel and washed with EtOAc and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (9: 1 to 4: 1) as eluent to afford 14a (3.07 g, 90%). Similarly antipode 15b was synthesized from 14b using above procedure to afford (2.71 g. 88%).

*5.2.4.1. Compound **14a**.* Colorless oil.; $[\alpha]_D^{20} = -1.0$ (c 0.5, $CHCl_3$).; IR ($CHCl_3$, cm^{-1}): 2988, 2955, 2930, 2858, 1758, 1472, 1382, 1372, 1257, 1217, 1192, 1168, 1102, 1036, 939, 837, 776, 759, 667.; ^1H NMR (400 MHz, $CDCl_3$): δ 0.039 (s, 6H), 0.871 (s, 9H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.42 (s, 3H), 1.44 (s, 3H), 1.80–1.89 (m, 1H), 1.96–2.06 (m, 1H), 3.72–3.82 (m, 2H), 4.17–4.29 (m, 4H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ −5.45, 14.12, 18.20, 25.8, 27.13, 36.46, 59.38, 61.22, 75.98, 78.96, 110.66, 170.69.; HRMS (ESI+): Calcd. for $C_{16}H_{32}O_5Si$ + H: 293.1784 found: 293.1788.

*5.2.4.2. Compound **14b**.* Colorless oil.; $[\alpha]_D^{25} = +1.41$ (c 0.5, $CHCl_3$).; IR ($CHCl_3$, cm^{-1}): 3021, 2991, 2931, 2884, 1752, 1472, 1484, 1383, 1372, 1256, 1216, 110, 811, 837, 758, 667; ^1H NMR ($CDCl_3$, 400 MHz): δ 0.041 (s, 6H), 0.87 (s, 9H), 1.26–1.29 (t, $J = 7.0$ Hz, 3H), 1.42 (s, 3H), 1.45 (s, 3H), 1.80–1.87 (m, 1H), 1.97–2.03 (m, 1H), 3.70–3.80 (m, 2H), 4.17–4.28 (m, 4H).; ^{13}C NMR ($CDCl_3$, 100 MHz): δ −5.44, −5.39, 14.15, 18.23, 25.64, 25.85, 27.15, 36.48, 59.40, 61.27, 75.98, 78.96, 110.68, 170.73.; HRMS (ESI+): Calcd. for $C_{16}H_{32}O_5Si$ + H: 293.1784 found: 293.1786.

*5.2.5. Synthesis of ethyl(4S, 5R)-5-(2-hydroxyethyl)-2, 2-dimethyl-1, 3-dioxolane-4-carboxylate (**19a**)*

To a solution of 14a (8.0 g, 0.024 mol) in THF (40 mL) at 0 °C was added TBAF (1.0 M solution in THF, 28.91 mL, 0.028 mol) drop wise. The resulting brown solution was stirred for 12 h at 0–5 °C. up on consumption of starting material as indicated by TLC, the solvent was removed in vacuum, and the crude residue was purified by flash column chromatography (hexanes/EtOAc) to afford diol 19a (5.0 g, 95%). Similarly antipode 19b was synthesized from 14b using above procedure to afford (4.71 g. 94%).

*5.2.5.1. Compound **19a**.* Colorless oil.; $[\alpha]_D^{25} = -1.76$ (c 0.9, $CHCl_3$).; IR ($CHCl_3$, cm^{-1}): 3501, 2939, 2988, 1755, 1466, 1373, 1214, 1098, 880, 872.; ^1H NMR (400 MHz, $CDCl_3$): δ1.26 (t, $J = 7.12$ Hz, 3H), 1.42 (s, 3H), 1.46 (s, 3H), 1.89–2.18 (m 2H), 3.8 (t, $J = 5.76$ Hz, 2H), 4.19 (m, 4H).;^{13}C NMR (100 MHz, $CDCl_3$): δ 14.09, 25.50, 27.00, 35.76, 59.97, 61.52, 77.72, 78.92, 110.97, 170.73.; HRMS (ESI+): Calcd. for $C_{10}H_{18}O_5$+H: 219.1232 found: 219.1243.

*5.2.5.2. Compound **19b**.* Colorless oil.; $[\alpha]_D^{25} = +1.27$ (c 0.5, $CHCl_3$).; IR ($CHCl_3$, cm^{-1}):3520, 3018, 2992, 2939, 1749, 1456, 1383, 1216, 1099, 755, 667.;^1H NMR ($CDCl_3$, 400 MHz): δ 1.25–1.29 (t, $J = 7.0$ Hz, 3H), 1.41 (s, 3H), 1.44 (s, 3H), 1.89–1.95 (m, 1H), 1.96–2.07 (m, 1H), 2.39 (bs, 1H), 3.77–3.81 (q, $J = 5.3$ & 10.1 Hz, 2H), 4.18–4.28 (m, 4H).; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.12, 25.52, 27.02, 35.79, 59.95, 61.56, 76.7, 78.94, 110.99, 170.77.; HRMS (ESI+): Calcd. for $C_{10}H_{18}O_5$ + H: 219.1232 found: 219.1240.

*5.2.6. Synthesis of ethyl (4R, 5S)-5-(2-iodoethyl)-2, 2-dimethyl-1, 3-dioxolane-4-carboxylate (**20a**)*

To the solution of PPh_3 (7.07 g, 0.027 mol) in anhydrous CH_2Cl_2 (22.5 mL) under N_2, was added 1H-imidazole (1.82 g, 0.027 mol) and then with I_2 (6.78 g, 0.027 mol). A solution of 19a (4.5 g, 0.020 mol) in anhydrous CH_2Cl_2 (22.5 mL) was added, and the mixture was stirred at r. t. for 2 h. Evaporation of the solvent gave a crude product, which was filtered through a short silica-gel column (Hexane/Ethylacetate 9 : 1; R_f: 0.5) to give pure 20a (5.5 g, 82%). Similarly antipode 20b synthesized from 19b using above procedure (5.8 g. 83%).

*5.2.6.1. Compound **20a**.* Yellow oil.; $[\alpha]_D^{25} = -3.08$ (c 0.5, $CHCl_3$).; IR ($CHCl_3$, cm^{-1}): 2988, 2908, 2937, 1759, 1731, 1445, 1352, 1200, 1036,

854.; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.289 (t, J = 7.16 Hz, 3H), 1.43 (s, 3H), 1.45 (s, 3H), 2.13–2.21 (m 1H), 2.27–2.35 (m, 1H), 3.21–3.35 (m, 2H), 4.12–4.28 (m, 4H).;^{13}C NMR (100 MHz, $CDCl_3$): δ 0.51, 14.19, 25.60, 27.06, 37.74, 61.53, 78.37, 78.68, 111.25, 170.33.; HRMS (ESI+): Calcd. for $C_{10}H_{17}O_4I$ + H: 329.0250 found: 329.0235.

*5.2.6.2. Compound **20b**.* Yellow oil.; $[\alpha]_D^{25}$ = + 3.52 (c 0.51, $CHCl_3$).; IR ($CHCl_3$, cm^{-1}): 3020, 2989, 2938, 2906, 1756, 1732, 1445, 1372, 1238, 1035, 853, 757, 667.; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.28–1.31 (t, J = 7.0 Hz, 3H), 1.42 (s, 3H), 1.44 (s, 3H), 2.14–2.19 (m, 1H), 2.20–2.32 (m, 1H), 3.20–3.34 (m, 2H), 4.11–4.20 (m, 2H), 4.20–4.27 (m, 2H).; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 0.59, 14.22, 25.62, 27.08, 37.74, 61.56, 78.37, 78.68, 111.26, 170.35.; HRMS (ESI+): Calcd. for $C_{10}H_{17}O_4I$ + H: 329.0250 found: 329.0257.

*5.2.7. Synthesis of ((4S, 5S)-5-(2-iodoethyl)-2, 2-dimethyl-1, 3-dioxolan-4-yl) methanol **13a***

To the solution of 20a (5.0 g, 0.015 mol) in MeOH (10.0 mL) and THF (40.0 mL) at 0–10 °C was added $NaBH_4$ (0.855 g, 0.022 mol) lot wise (H_2 evolution) under inert atmosphere. After complete addition temperature was allowed to come to 25–35 °C and maintained for 1–2 h by TLC monitoring. Upon absence of starting material, reaction mass was cooled to 0–10 °C and quenched with saturated ammonium solution and product was extracted with 2X65 mL ethyl acetate, combined organic layers evaporated and the residue was purified by silica gel column chromatography using petroleum ether/EtOAc (9: 1 to 7: 3) as eluent to afford 13a (3.9 g, 89%). Similarly antipode 13b synthesized from 20b using above procedure (3.71 g. 84%).

*5.2.7.1. Compound **13a**.* Pale yellow oil.; $[\alpha]_D^{25}$ = −7.99 (c 0.5, $CHCl_3$).; IR ($CHCl_3$, cm^{-1}): 3436, 2985, 2933, 2876, 1437, 1371, 1218, 1090, 847.; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40 (s, 6H), 1.92 (bs, 1H), 2.07–2.12 (m, 2H), 3.20–3.26 (m, 1H), 3.29–3.35 (m, 1H), 3.61–3.64 (m, 1H), 3.75–3.81 (m, 2H), 39.9–3.98 (m, 1H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ 1.00, 26.99, 27.28, 37.43, 61.75, 80.60, 81.12, 109.19.; HRMS (ESI+): Calcd. for $C_8H_{15}O_3I$ + H: 287.0144 found: 287.0146.

*5.2.7.2. Compound **13b**.* Pale yellow oil.; $[\alpha]_D^{25}$ = + 5.06 (c 0.5, $CHCl_3$).; IR ($CHCl_3$, cm^{-1}): 3435, 2985, 2933, 2876, 1437, 1371, 1218, 1049, 1089, 847.;^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.39 (s, 3H), 2.03–2.12 (m, 3H), 3.19–3.34 (m, 2H), 3.61–3.63 (m, 1H), 3.74–3.80 (m, 2H), 3.80–3.97 (m, 2H).; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 1.09, 26.99, 27.28, 37.40, 61.75, 77.34, 80.63, 109.20.; HRMS (ESI+): Calcd. for $C_8H_{15}O_3I$ + H: 287.0144 found: 287.0147.

*5.2.8. Synthesis of ((4S, 5S)-5-(2-(iodotriphenyl-l5-phosphanyl) ethyl)-2, 2-dimethyl-1, 3-dioxolan-4-yl) methanol (**7a**)*

To the solution of 13a (3.5 g, 0.012 mol) in Acetonitrile (35 mL) was added TPP (6.41 g, 0.024 mol) and reflux for 12 h solvent was evaporated and obtained crude residue was purified by column chromatography by using 5% MeOH/DCM to afford 7a (5.9 g, 88%). Similarly antipode 7b synthesized from 13b using above procedure to afford (6.1 g, 90%).

*5.2.8.1. Compound **7a**.* Waxy solid.; $[\alpha]_D^{20}$ = −1.66 (c 0.5, $CHCl_3$).; IR ($CHCl_3$, cm^{-1}): 3377, 2987, 2934, 2880, 2247, 2198, 1587, 1483, 1376, 1216, 1110, 1053, 909, 721, 687, 642.; ^{1}H NMR (400 MHz, $CDCl_3$): δ1.32 (s, 3H), 1.34 (s, 3H), 1.81–1.92 (m 1H), 2.22–2.32 (m, 1H), 3.56–3.67 (m, 1H), 3.73–3.75 (m, 1H), 3.83–3.95 (m, 4H), 4.38–4.42 (m, 1H), 7.68–7.83 (m, 15H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.34, 19.86, 26.58, 26.62, 26.87, 27.10, 62.13, 78.73, 78.89, 79.98, 108.68, 117.46, 118.32, 130.51, 130.63, 133.59, 133.69, 135.19, 135.22.; HRMS (ESI+): Calcd. for $C_{26}H_{30}O_3P$-I: 421.1933 found: 421.1930.

*5.2.8.2. Compound **7b**.* Waxy solid.; $[\alpha]_D^{25}$ = + 4.92 (c 0.5, $CHCl_3$).; IR ($CHCl_3$, cm^{-1}): 3368, 3059, 3014, 2966, 2937, 1588, 1438, 1216, 1113, 1060, 762, 724, 662.; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.30 (s, 3H), 1.32 (s, 3H), 1.80–1.88 (m, 1H), 2.01–2.27 (m, 1H), 3.41–3.60 (m, 1H), 3.67–3.87 (m, 3H), 4.33–4.38 (m, 1H), 7.67–7.82 (m, 15H).; ^{13}C NMR ($CDCl_3$, 100 MHz): 19.32, 19.85, 26.54, 26.59, 26.89, 27.12, 61.95, 78.53, 78.69, 80.03, 108.73, 117.35, 118.21, 130.57, 130.70, 133.57, 133.67, 135.27, 135.30.; HRMS (ESI+): Calcd. for $C_{26}H_{30}O_3P$ − I: 421.1933 found: 421.1928.

*5.2.9. Synthesis of (R, Z)-7-((4S, 5S)-5-(hydroxymethyl)-2, 2-dimethyl-1, 3-dioxolan-4-yl) hept-5-en-2-ol (**22a**)*

To the solution of 7a (5.3 g, 9.7 mmol) in THF (25 mL) was added 1.0 M NaHMDS (35.29 mL, 35.2 mmol) at −30 °C under N_2 atmosphere (yellow suspension to orange colored solution). for 15–30 min. The solution of lactol 6 (0.9 g, 8.8 mmol) was added as a solution in THF (10 mL) at −30 °C to above orange colored reaction mass, maintained addition 1–2 h, then quenched with sat. NH_4Cl (45 mL) and allowed to come to rt and stirred for 1–2 h. The product was extracted with 3 × 45 mL of ethyl acetate solvent was evaporated and obtained crude residue was purified by column chromatography to afford 22a(1.85 g, 86%). Similarly antipode 22bwas synthesized from 7b using above procedure to afford (1.75 g, 82%).

*5.2.9.1. Compound **22a**.* Viscous oil.; $[\alpha]_D^{20}$ = - 3.5 (c 0.2, $CHCl_3$).; IR ($CHCl_3$, cm^{-1}): 3413, 2984, 2927, 2250, 1650, 1455, 1375, 1217, 1164, 1055, 904, 842, 725, 648.; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17–1.18 (d, J = 6.2 Hz, 3H), 1.39 (s, 3H), 1.41 (s, 3H), 1.47–1.53 (m 2H), 2.06–2.28 (m, 2H), 2.29–2.49 (m, 3H), 3.46 (bs, 1H), 3.61–3.64 (m, 1H), 3.73–3.82 (m, 3H), 3.89–3.95 (m, 1H), 5.43–5.56 (m, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.28, 124.63, 108.70, 80.86, 66.77, 62.07, 38.45, 27.17, 26.95, 23.70, 23.52.; GC-MS (ES): 229 [M^+-15].

*5.2.9.2. Compound **22b**.* Viscous oil.; $[\alpha]_D^{20}$ = +3.0(c 0.2, $CHCl_3$).; IR ($CHCl_3$, cm^{-1}): 3429, 3015, 2989, 2932, 1634, 1373, 1216, 1057, 843, 755, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ1.17–1.19 (d, J = 6.2 Hz, 3H), 1.40 (s, 3H), 1.42 (s, 3H), 1.47–1.53 (m 2H), 2.06–2.51 (m, 5H), 3.58–3.65 (m, 2H), 3.73–3.80 (m, 3H), 3.89–3.96 (m, 1H), 5.43–5.56 (m, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.31, 124.67, 108.72, 80.85, 66.75, 62.02, 38.44, 27.19, 26.96, 23.77, 23.53.; GC-MS (ES): 229 [M^+-15].

*5.2.10. Synthesis of (R)-7-((4S, 5S)-5-(hydroxymethyl)-2, 2-dimethyl-1, 3-dioxolan-4-yl) heptan-2-ol (**8a**)*

To a solution of 22a(1.8 g, 7.3 mmol) in ethyl acetate (36 mL) at rt added 20% $Pd(OH)_2$ by wt. and hydrogenated for 4 h at 40psi, upon completion of reaction catalyst was removed by filtration, thus obtained filtrate was evaporated to afford 8a (1.75 g, 96%). Similarly antipode 8b was synthesized from 22busing above procedure to afford (1.88 g, 98%).

*5.2.10.1. Compound **8a**.* Colorless oil.; $[\alpha]_D^{20}$ = + 2.33 (c 0.2, $CHCl_3$).; IR ($CHCl_3$, cm^{-1}): 3450, 2988, 2965, 2933, 2860, 1438, 1457, 1379, 1243, 1050, 756, 666.; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16–1.18 (d, J = 6.2 Hz, 3H), 1.33–2.12 (m, 18H), 3.56–3.60 (m, 1H), 3.69–3.89 (m 4H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.49, 25.55, 25.57, 25.95, 27.01, 27.37, 29.59, 32.93, 39.16, 61.97, 68.05, 81.43, 108.57.; HRMS (ESI+): Calcd. for $C_{13}H_{27}O4$+H: 247.1909 found: 247.1899.

*5.2.10.2. Compound **8b**.* Colorless oil.; $[\alpha]_D^{20}$ = −3.11 (c 0.2, $CHCl_3$).; IR ($CHCl_3$, cm^{-1}): 3435, 3018, 2990, 2934, 2860, 1458, 1372, 1215, 770, 669.; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16–1.17 (d, J = 6.2 Hz, 3H), 1.33–1.79 (m, 18H), 3.56–3.60 (m, 1H), 3.69–3.80 (m 3H), 3.84–3.87 (m, 1H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.47, 25.55,

25.94, 27.01, 27.36, 29.56, 32.91, 61.99, 68.05, 81.46, 108.58.; GC-MS (ES): 231 [M^+-15].

*5.2.11. Synthesis of ethyl (E)-3-{(4S, 5S)-5-[(R)-6-hydroxyheptyl]-2, 2-dimethyl-1, 3-dioxolan-4-yl}acrylate (**9a**)*

To diol 8a (175 mg, 0.71 mmol) in CH_2Cl_2 (3 mL) at 0 °C were added BAIB (263 mg, 0.81 mmol) and TEMPO (10 mg, 0.06 mmol). After stirring at room temperature for 2 h, the mixture was cooled to 0 °C, and (ethoxycarbonylmethylene) triphenylphosphorane (21) (320 mg, 0.92 mmol) was added. The stirring was continued for another 2 h at room temperature. After completion of the reaction, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography (hexanes/EtOAc) to afford α, β-unsaturated ester 9a (210 mg, 94%). Similarly diastereomer 9b synthesized from 8b using above procedure to afford (195 mg, 88%).

*5.2.11.1. Compound **9a**.* Pale yellow liquid.; $[\alpha]_D^{20} = +10$ (c 0.1, $CHCl_3$).; IR ($CHCl_3$, cm^{-1}): 3504, 2984, 2933, 2860, 2250, 1716, 1660, 1459, 1373, 1240, 1168, 1103, 1036, 907, 725, 647.; ^1H NMR (400 MHz, $CDCl_3$): δ 6.82–6.87 (dd, $J = 5.8$, 15.6 Hz, 1H), 6.08–6.12 (d, $J = 15.6$ Hz, 1H), 4.16–4.23 (m, 2H), 4.11–4.15 (m, 1H), 3.67–3.82 (m, 2H), 1.27–1.62 (m, 19H), 1.16–1.18 (d, $J = 6.16$ Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.02, 144.11, 122.73, 109.34, 80.21, 68.03, 60.59, 39.15, 31.96, 29.54, 27.24, 26.63, 25.91, 25.54, 23.49, 14.18.; GC-MS (ES): 299 [M^+-15].

*5.2.11.2. Compound **9b**.* Pale yellow liquid., $[\alpha]_D^{20} = -7.9$ (c 0.1, $CHCl_3$).; IR ($CHCl_3$, cm^{-1}): 3528, 3018, 2988, 2936, 2881, 1717, 1662, 1459, 1371, 1216, 1035, 756, 668.; ^1H NMR (400 MHz, $CDCl_3$): δ 6.82–6.88 (dd, $J = 5.7$, 15.8 Hz, 1H), 6.08–6.12 (dd, $J = 1.4$ Hz, 15.6 Hz, 1H), 4.11–4.23 (m, 3H), 3.69–3.80 (m, 2H), 1.40–1.64 (m, 19H), 1.16–1.18 (d, $J = 6.2$ Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.05, 144.11, 122.74, 109.336, 80.58, 80.56, 68.04, 60.62, 39.16, 31.95, 29.55, 27.26, 25.94, 25.54, 23.49, 14.21.; GC-MS (ES): 299 [M^+-15].

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Appendix A. Supplementary data

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