Stereoselective Synthesis of γ-Butyrolactones Subunit of Polycavernoside A

Sudhakar Kadari,* Hemasri Yerrabelly,* Thirupathi Gogula, Yadaiah Goud Erukala, Jayaprakash Rao Yerrabelly, and Prem Kumar Begari

Department of Chemistry, Osmania University, Hyderabad, Telangana 500007, India
*E-mail: sudhakarou@osmania.ac.in; hemay2@yahoo.com
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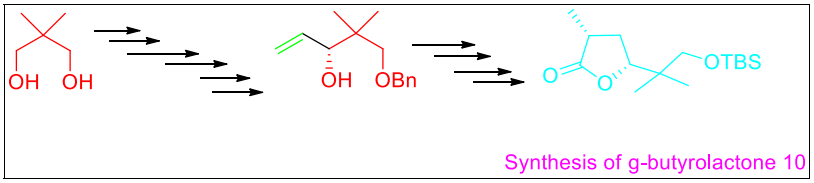

An efficient and versatile linear synthesis of γ-butyrolactone subunit of polycavernolide A has been reported in 14.2% overall yield with 10 linear steps by employing Sharpless asymmetric epoxidation, ring-closing metathesis, and diastereoface selective hydrogenation.

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INTRODUCTION

The red alga *Polycavernosa tsudai* is a delicacy widely consumed in the Far East. When several Guam natives died suddenly following its ingestion in April 1991, immediate attempts were launched to identify the responsible toxin. Shortly thereafter, Yasumoto and co-workers succeeded in characterizing polycavernoside A [1] (Fig. 1) as one of the principal risk factors. The proposed macrolactone disaccharide structure was confirmed via the first total synthesis by Murai et al., which furthermore established the absolute stereochemistry [2]. Despite the molecular complexity of polycavernoside, the lactone moiety has proved to be essential for the biological activity.

Lactone rings constitute structural features of a wide range of natural products that display important biological activities such as anti-HIV, antifungal, antibacterial, and antitumor properties. Among them, six-membered lactone, five-membered lactone, and macrolide lactone moieties are relatively common in various types of natural products [3]. In recent years, synthesis of novel heterocycles has gained considerable attention due to their potential role in organic synthesis for the formation of bioactive natural products and their semisynthetic derivatives [4–8]. γ-Butyrolactones have been utilized as intermediates for synthetic transformations, and much attention has been paid to their synthesis. To the best of our knowledge, this is the first report for the preparation of γ-butyrolactones using ring-closing metathesis (RCM).

Previously, synthesis of γ-butyrolactones subunit of polycavernoside A was achieved by novel ene reaction followed by intramolecular oxidative cyclization methodology and reduction of exo-methylene C–C double bond producing the syn-disubstituted lactone as a single diastereoisomer [9]. Our strategy relies on Sharpless asymmetric epoxidation, reductive elimination, RCM, and stereoselective hydrogenation to synthesize γ-butyrolactones subunit of polycavernoside A (Scheme 1).

RESULTS AND DISCUSSION

γ-Butyrolactones subunit can be synthesized from readily available 2,2-dimethyl-1,3-propane diol, 1. The selective monobenzylation of the diol was achieved by treatment with one equivalent of NaH and BnBr to afford **2** in 80% yield. The free primary hydroxy group was oxidized under Swern condition to afford crude aldehyde which without further purification immediately subjected to Wittig-Horner homologation to obtain α, β-unsaturated ester **3** along with minor amount of *cis* diastereomer in a 9:1 ratio as a separable mixture. Compound **3** was treated with DIBAL-H in CH_2Cl_2 at 0°C to provide the desired *trans* known [10] allyl alcohol **4**. Sharpless asymmetric epoxidation of **4** with D-(+)-DET, Ti $(OiPr)_4$, molecular sieves in dry CH_2Cl_2, TBHP, at −20°C for 6 h afforded the epoxy alcohol **5** in 80% of yield [11]. Compound **5** was confirmed from ^{1}H NMR spectrum wherein the protons attached to the epoxide ring resonated as multiplet at δ 3.03 for one proton and at δ 2.87 (d, J = 2.2 Hz, 1H) for one proton while the remaining protons resonated at their respective chemical shifts. In ESI-MS, $[M + H]^+$ peaks observed at *m/z* 237 further supported the formation of the product **5**.

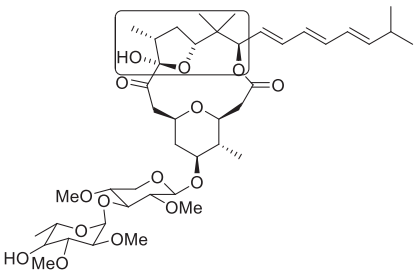


Figure 1. Polycavernoside A.

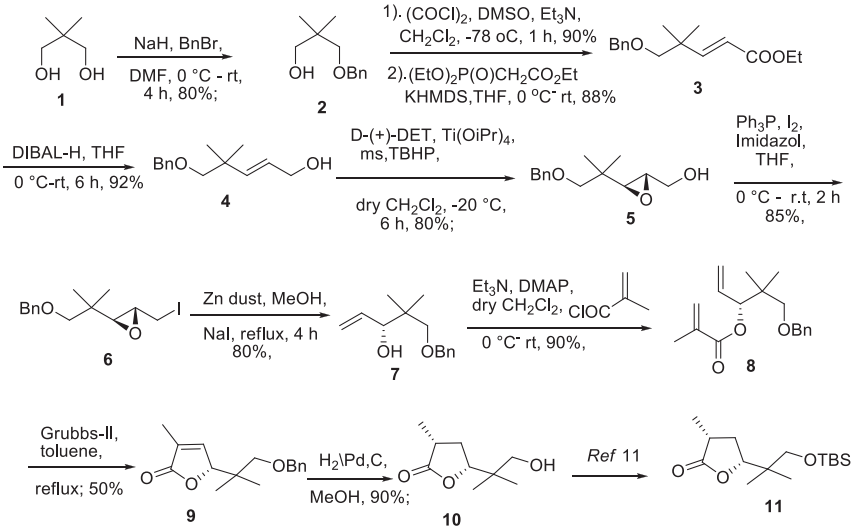
Compound **5** was converted to its iodo derivative **6** by treating with triphenylphosphine, imidazole, and iodine in ether and acetonitrile (8:2) [12]. Product structure was established from its ^{1}H NMR spectrum where the chemical shift of epoxy protons was resonated at δ 2.93 ppm (dd, J = 9.4, 2.3 Hz, 1H) and δ 2.74 ppm (d, J = 2.1 Hz, 1H) and other protons were resonated at expected regions and further supported by its ESI-MS, which showed $[M + Na]^+$ peaks at *m/z* 369. Then the compound **6** was converted into allylic alcohol **7** with zinc dust and sodium iodide in methanol at reflux for 4 h to furnish **7** in 80% yield [13].

Compound **7** structure was confirmed from its ^{1}H NMR spectrum in which terminal double bond protons were resonated at δ 5.79–6.02 (m, 1H) and δ 5.08–5.37 (m, 2H), while the remaining protons were observed at their respective chemical shifts. Esterification of compound **7** with methacryloyl chloride and triethyl amine in CH_2Cl_2 at 0°C to room temperature afforded corresponding bis-olefine **8** [14]. The ^{1}H NMR, ^{13}C NMR, and mass spectroscopy clearly indicates the presence of bis olefin. In ^{1}H NMR, the resonance due to terminal double bond proton appeared at δ 6.08 ppm as a doublet for one proton, at δ 5.83 as a multiplet for two protons, at δ 5.53 as a multiplet for two protons, and with the other required protons confirmed the product. Further, the formation of the product was supported by ESI-MS, which showed $[M + Na]^+$ peaks at *m/z* 311.

In order to construct the lactone ring, compound **8** was subjected to RCM using Grubbs' 2nd generation catalyst in refluxing toluene for 8 h under nitrogen atmosphere to afford α, β-unsaturated γ-lactone **9** [15]. In ^{1}H NMR, terminal olefinic proton peaks disappeared and resonance due to α, β-unsaturated double bond proton appeared at δ 7.06 ppm as a doublet for one proton indicating the cyclization and rest of the protons appeared at their respective chemical shifts. Further, the formation of the product was supported by ESI-MS, which showed $[M + Na]^+$ peaks at *m/z* 283.

Diastereoface selective reduction of olefin **9** with simaltaneous debenzylation with Pd\C under hydrogen atmosphere afforded **10**. The alcohol was protected as its TBDPS-ether with TBDPSCl and imidazole in dry CH_2Cl_2 to yield **11**. In ^{1}H NMR, the presence of compound **11**, δ 7.60–7.66 multiplet for four protons and δ 7.46–7.35 multiplet for six protons, indicates the presence of TBDPS protection and the resonance of methyl peak at δ 1.26 ppm (d, J = 7.0 Hz, 3H), while the remaining protons at their respective chemical shifts further support the structure. In addition, the product formation was supported by ESI-MS, which showed $[M + Na]^+$ peaks at *m/z* 433.

Scheme 1. Synthesis of g-butyrolactone **10**.



Compound **11** was identical with reported compound in literature [16].

CONCLUSION

In summary, we have reported a stereoselective synthesis (10 steps, 14.2% overall yields) of γ-butyrolactones subunit of polycavernoside A, relying on Sharpless assymitric epoxidation, reductive elimination, RCM, and diastereo face selective hydrogenation. Current efforts are now directed towards the synthesis of polycavernoside A.

EXPERIMENTAL PART

Silica gel (60–120 mesh) for column chromatography was purchased from M/s Acme Synthetic Chemicals (Mumbai, India), and pre-coated TLC plates (Silica gel 60F254) were purchased from Merck (Darmstadt, Germany). All the chemicals, reagents, and solvents were purchased from M/s SD Fine Chemicals (Mumbai, India) and were of the highest grade of purity. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker 400 and 100 MHz, respectively, and TMS was used as an internal standard. Chemical shifts relative to TMS as internal standards were given as δ values in ppm. Mass spectra were recorded using electron spray ionization on Waters e2695 Seperators module (Waters, Milford, MA, USA) mass spectrometer. IR spectra were recorded on a Fourier transform infrared, USA (Perkin-Elmer model 337) instrument. The melting points were determined on a Barnstead Electro Thermal 9200 Instrument.

(*E*)-Ethyl 5-(benzyloxy)-4,4-dimethylpent-2-enoate (3). To a stirred solution of oxalyl chloride (0.37 mL, 3.36 mmol) in CH_2Cl_2 (5 mL) at −78°C, DMSO (0.32 mL, 4.93 mmol) was added followed by compound **2** (1.0 g, 2.24 mmol) in CH_2Cl_2 (5 mL), and the contents were stirred for 1 h at −78°C. Later, the reaction mixture was quenched with Et_3N (0.94 mL, 6.72 mmol) and diluted with CH_2Cl_2 (25 mL). The combined organic layers were washed with brine (1 × 15 mL), dried (Na_2SO_4), and concentrated, and the residue was passed through a pad of silica gel to give the corresponding aldehyde (0.89 g, 90%), which was used as such for further reaction. To a stirred solution of $(Ph)_3PCH_2CO_2Et$ (0.56 mL, 2.66 mmol), 18-crown-6 (2.47 g, 9.36 mmol) in anhydrous THF (10 mL) at −0°C followed by KHMDS (0.67 g, 2.93 mmol) was added and stirred the reaction mixture for 30 min. To the reaction mixture, the aldehyde (0.80 g, 1.80 mmol) dissolved in THF (5 mL) was added. The reaction mixture was stirred for 4 h and quenching with aq NH_4Cl and extracted into EtOAc. The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated, and the residue was purified over silica gel (EtOAc: n-Hexane, 1:9) to give the product **3** (0.79 g, 88%, for two steps) as colorless syrup. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23–7.44 (*m*, 5 H); 7.02 (d, *J* = 16.0, 1H); 5.81 (d, *J* = 16.0, 1H); 4.51 (s, 2H); 4.18 (q, *J* = 7.0, 2H); 3.26 (s, 2H); 1.29 (t, *J* = 7.0, 3H); 1.09 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 166.5; 160.0; 137.6; 128.2; 127.4; 125.0; 115.1; 83.1; 72.3; 61.1; 35.8; 23.0; 14.5. IR (neat) ν_{max}: 3425, 2966, 2929, 2860, 1719, 1650, 1456, 1307, 1181, 1101, 738 cm^{-1}. Mass (ESI-MS) *m/z*: 285 $(M + Na)^+$.

(*E*)-5-(benzyloxy)-4,4-dimethylpent-2-en-1-ol (4). To a stirred solution of **3** (1.60 g, 3.20 mmol) in anhydrous ether (10 mL) DIBAL-H (5.68 mL, 8.00 mmol, 20% solution in toluene) was added dropwise at 0°C and stirred at rt for 6 h and diluted with methanol, sodium potassium tartrate, and extracted with EtOAc. The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated, and the residue was purified over silica gel (EtOAc: n-Hexane, 1:3) to afford **4** (1.42 g, 92%) as thick syrup. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22–7.40 (m, 5H); 6.08 (d, *J* = 12.5, 1H); 5.72–5.92 (m, 1H); 5.53–5.58 (m, 1H); 5.18–5.39 (m, 2H); 4.51 (s, 1H); 4.46 (d, *J* = 3.2, 1H); 4.01 (s, 1H); 3.14–3.32 (m, 2H); 1.92–1.82 (m, 3H); 0.94–1.18 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 166.2; 138.5; 136.6; 133.2; 128.2; 127.3; 125.0; 118.1; 78.5; 76.3; 73.2; 38.5; 21.1; 20.7; 18.2. IR (neat) ν_{max}: 3420, 2906, 2860, 1650, 1456, 1254, 1181, 1080, 720 cm^{-1}. Mass (ESI-MS) *m/z*: 243 $(M + Na)^+$.

(*2S*, *3S*)-3-(1-(benzyloxy)-2-methylpropan-2-yl) oxiran-2-yl) methanol (5). To a stirred solution of D-(+)-DET (2.78 g, 13.50 mmol) and molecular sieves (4 A°, 5 g) in CH_2Cl_2 at −23°C was added $Ti(OiPr)_4$ (3.08 g, 10.80 mmol). The resulting mixture was stirred at −23°C for 10 min, and a solution of compound **9** (12.0 g, 54.0 mmol) in CH_2Cl_2 was added. After 30 min, TBHP (27.0 mL, 4 M solution in toluene, 108.1 mmol) was added and stirred for 4 h at the same temperature. The reaction mixture was quenched by the addition of brine solution (68 mL, containing 10% NaOH), saturated Na_2SO_4 and Et_2O. The resulting mixture was stirred at room temperature for 2 h. Filtration through a pad of celite followed by concentration and purification by column chromatography using silica gel (100–200 mesh, 30% EtOAc/hexane) afforded the pure compound **5** (10.2 g, 80%) as colorless oil. R_f = 0.3 (30% EtOAc/hexane). ^{1}H NMR (300 MHz, $CDCl_3$): 7.19–7.42 (m, 6H); 4.48 (s, 2H); 3.83 (d, *J* = 12.3, 1H); 3.55 (m, 1H); 3.21 (dd, *J* = 8.9, 15.9, 2H); 3.03 (m, 1H); 2.87 (d, *J* = 2.3, 1H); 0.91 (d, *J* = 3.0, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 138.4; 128.2; 127.4; 127.4; 127.3; 73.2; 62.1; 60.9; 55.3; 35.0; 20.9; 20.6. IR (neat) ν_{max}: 3437, 2965, 2865, 1739, 1456, 1096, 740 cm^{-1}. Mass (ESI-MS) *m/z*:

259 $(M + Na)^+$. Optical rotation: $[\alpha]_D^{25}$ − 14 [c 0.5, $(CHCl_3)$].

(*2S*, *3R*)-2-(1-(benzyloxy)-2-methylpropan-2-yl)-3-(iodomethyl) oxirane (6). To a solution of alcohol **5** (210 mg, 0.96 mmol) in THF (6 mL) were added imidazole (138 mg, 2.0 mmol), triphenylphosphine (530 mg, 2.0 mmol), and iodine (490 mg, 1.92 mmol) at 0°C, allowed the reaction mixture to warm to room temperature, and stirred for 2 h. The reaction was quenched with saturated aqueous Na_2SO_3. The resultant mixture was diluted with EtOAc, washed with water and brine, dried (Na_2SO_4), and concentrated under reduced pressure. Purification of the residue by column chromatography gave iodide **6** (290 mg, 95%) as a colorless clear oil. R_f = 0.4 (SiO_2, 10% EtOAc in hexane). ^{1}H NMR (300 MHz, $CDCl_3$): 7.16–7.40 (m, 6H); 4.48 (s, 2H); 3.09–3.29 (m, 4H); 2.93 (dd, *J* = 2.3, 9.4, 2H); 2.74 (d, *J* = 2.1, 1H); 0.94 (s, 3H); 0.90 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 138.6; 128.4; 127.6; 127.5; 76.9; 73.4; 67.7; 55.5; 35.6; 21.1; 20.8; 5.6. IR (neat) ν_{max}: 3447, 2963, 2861, 1599, 1454, 1102, 739 cm^{-1}. Mass (ESI-MS) *m/z*: 369 $(M + Na)^+$. Optical rotation: $[\alpha]_D^{25}$ + 44 [c 1, $(CHCl_3)$].

(*R*)-5-(benzyloxy)-4,4-dimethylpent-1-en-3-ol (7). Compound **6** was dissolved in methanol (40 mL) and stirred with zinc dust (6.77 g) for 4 h. The methanol was then removed under reduced pressure, and water (30 mL) was added. The mixture was extracted with dichloromethane (3 × 30 mL), and the combined organic layers were dried (Na_2SO_4), and the solvent was removed under reduced pressure. Purification of the crude by column chromatography on silica yielded **7** (2.65 g, 80%) as a white solid. R_f = 0.2 (SiO_2, 80% EtOAc in hexane). ^{1}H NMR (300 MHz, $CDCl_3$): 7.23–7.44 (m, 6H); 5.79–6.02 (m, 1H); 5.08–5.37 (m, 2H); 4.51 (s, 2 H); 3.96 (d, *J* = 6.4, 1H); 3.41 (d, *J* = 8.7, 1H); 3.29 (d, *J* = 8.7, 1H); 0.96 (s, 3H); 0.9 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 137.8; 137.4; 128.4; 127.7; 127.5; 116.3; 79.9; 79.2; 73.5; 38.2; 22.6; 19.9. IR (neat) ν_{max}: 3292, 2862, 2361, 1612, 1513, 1461, 1361, 1247, 1176, 1097, 1034, 822, 642 cm^{-1}. Mass (ESI-MS) *m/z*: 243 $(M + Na)^+$. Optical rotation: $[\alpha]_D^{25}$ + 14 [c 0.5, $(CHCl_3)$].

(*R*)-5-(benzyloxy)-4,4-dimethylpent-1-en-3-yl methacrylate (8). To a stirred solution of compound **7** (0.40 g, 0.78 mmol), triethyl amine (0.14 mL, 1.56 mmol) in CH_2Cl_2 (5 mL) was added catalytic amount of sssDMAP and methacryloyl chloride (0.07 mL, 1.09 mmol) dropwise at 0°C and stirred at room temperature for 10 h. The reaction mixture was treated with water (1 × 15 mL) and extracted into CH_2Cl_2 (2 × 15 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, EtOAc: n-Hexane, 1:9) to afford the acrylate **8** (0.39 g, 90%) as thick yellow syrup. ^{1}H NMR (300 MHz, $CDCl_3$): 7.23–7.44 (m, 6H); 6.08 (d, *J* = 12.0, 1H); 5.83 (m, 1H); 5.53–5.58 (m, 2H); 4.51 (s, 2H); 3.96 (d, *J* = 6.4); 3.41 (d, *J* = 8.7, 1H); 3.29 (d, *J* = 8.7, 1H); 0.96 (s, 3H); 0.92 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 166.8; 138.3; 137.8; 133.4; 128.9; 128.6; 124.9; 118.2; 79.9; 78.4; 73.4; 38.2; 21.3; 21.6; 18.4. IR (neat) ν_{max}: 3511, 2968, 2932, 2859, 1720, 1453, 1292, 1165, 1102, 933, 741 cm^{-1}. Mass (ESI-MS) *m/z*: 311 $(M + Na)^+$. Optical rotation: $[\alpha]_D^{25}$ + 35 [c 0.02, $(CHCl_3)$].

(*S*)-5-(1-(benzyloxy)-2-methylpropan-2-yl)-3-methylfuran-2(5*H*)-one (9). A solution of **8** (0.41 g, 0.72 mmol) and Grubbs' 2nd generation catalyst (0.06 g, 0.07 mmol) in anhydrous CH_2Cl_2 (15 mL) was stirred at reflux for 8 h. After completion of the reaction, solvent was removed under reduced pressure, and the residue purified by column chromatography (silica gel, EtOAc: n-Hexane, 1:4) to afford **9** (0.33 g, 50%) as thick syrup. ^{1}H NMR (300 MHz, $CDCl_3$): 7.2–7.44 (m, 6H); 7.06 (t, *J* = 1.5, 1H); 4.92 (t, *J* = 1.9, 1H); 4.51 (dd, *J* = 12.3, 25.9, 2H); 3.41 (d, *J* = 9.1, 1H); 3.23 (d, *J* = 9.1, 1H); 1.91 (t, *J* = 1.9, 3H); 0.95 (s, 3H); 0.92 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 179.3; 137; 130.8; 128.7; 128.2; 127.3; 82.1; 76.3; 73.3; 38.6; 20; 19.6; 18.4. IR (neat) ν_{max}: 3427, 2933, 2880, 1720.9, 1454, 1452, 1383, 1247, 1220, 1097, 1032, 991, 738, 698 cm^{-1}. Mass (ESI-MS) *m/z*: 283 $(M + Na)^+$. Optical rotation: $[\alpha]_D^{25}$ + 11.6 [c 0.5, $(CHCl_3)$].

(*3R*, *5S*)-5-(1-hydroxy-2-methylpropan-2-yl)-3-methyl-dihydrofuran-2(3*H*)-one (10). To a solution of **9** (0.1 g, 0.28 mmol) in methanol (1 mL) was added 10% Pd–C under the hydrogen atmosphere, and the mixture was stirred for 6 h. Then the reaction mixture was filtered through a celite pad, and filtrate was evaporated under reduced pressure to obtain a residue, which was subjected to chromatography (silica gel 60–120 mesh, EtOAc: n-Hexane, 3.6:6.4) to afford **10** (0.06 g) yield of 90%. ^{1}H NMR (300 MHz, $CDCl_3$): 4.38 (dd, *J* = 5.5, 11.1, 1H); 3.55 (d, *J* = 10.9, 1H); 3.43 (d, *J* = 10.9, 1H); 2.50–2.88 (m, 2H); 2.32–2.36 (m, 1H); 1.27 (d, *J* = 7.2, 3H); 0.92 (d, *J* = 4.9, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 177.2; 84.4; 73.2; 38.3; 34.7; 32.2; 21.6; 16.6. IR (neat) ν_{max}: 3501, 2960, 2942, 2850, 1725, 1353, 1292, 1165, 1102, 933, 741 cm^{-1}. Mass (ESI-MS) *m/z*: 433 $(M + Na)^+$. Optical rotation: $[\alpha]_D^{25}$ + 30 [(c 0.8, $CHCl_3$)].

(*3R*, *5S*)-5-(1-(tert-butyldiphenylsilyloxy)-2-methylpropan-2-yl)-3-methyl-dihydrofuran-2(3*H*)-one (11). To a stirred solution of **10** (3.5 g, 22.15 mmol) in anhydrous CH_2Cl_2 (30 mL) was added imidazole (4.19 g, 66.45 mmol) followed by *tert*-butyldiphenylsilyl chloride (24.36 mL, 13.6 mmol) at 0°C, and the reaction mixture allowed to stir at room temperature for 5 h. Then, reaction mixture was quenched with saturated aq. NH_4Cl solution (25 mL) and extracted with CH_2Cl_2 washed with water (40 mL),

brine (40 mL), the combined organic layers were dried over (Na_2SO_4), concentrated, and the crude residue was purified by column chromatography (60–120 silica gel 1:20 (EtOAc: n-Hexane, 1:9) to afford product **11** (7.54 g) in 86% yield as a pale-yellow liquid. ^{1}H NMR (300 MHz, CDCl3): δ 7.66–7.60 (m, 4H), 7.46–7.35 (m, 6H), 4.45 (dd, *J* = 5.6, 11.1 Hz, 1H), 3.55 (d, *J* = 9.9 Hz, 1H), 3.40 (d, *J* = 9.9 Hz, 1H), 2.67 (ddq, *J* = 7.0, 8.6, 12.5 Hz, 1H), 2.23 (ddd, *J* = 5.6, 8.6, 12.5 Hz, 1H), 1.68 (q, *J* = 12.2 Hz, 1H), 1.26 (d, *J* = 7.0 Hz, 3H), 1.07 (s, 9H), 0.93 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (75 MHz, CDCl3): δ 179.5, 135.6 (4C), 133.4, 133.3, 129.7 (2C), 127.7 (4C), 81.6, 69.7, 38.5, 36.0, 31.9, 26.9 (3C), 19.6, 19.4, 19.2, 14.9; IR (neat) ν_{max}: 3395, 3029, 2960, 2911, 2859, 1725, 1453, 1396, 1259, 1086, 1028, 761, 705 cm^{-1}. Mass (ESI-MS) *m/z*: 433 $(M + Na)^+$. Optical rotation: $[\alpha]_D^{25}$ + 42.11 [c 0.5, ($CHCl_3$)].

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SUPPORTING INFORMATION

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