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P. Srihari [a], K. Ravindar [a], R. Somaiah [a] & J. S. Yadav [a]
[a] Organic Division I, Indian Institute of Chemical Technology, Hyderabad, India

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First Concise Total Synthesis of 5-Epi-prelactone B

P. Srihari, K. Ravindar, R. Somaiah, and J. S. Yadav

Organic Division I, Indian Institute of Chemical Technology, Hyderabad, India

Abstract: First short total synthesis of 5-epi-prelactone B has been achieved involving Sharpless asymmetric epoxidation and intramolecular hydride transfer reaction for formation of the aldol product by nonaldol chemistry as the key steps.

Keywords: Aldol, δ-lactones, prelactone B, Sharpless asymmetric epoxidation, Wittig reaction

INTRODUCTION

δ-Lactones, specifically β-hydroxy-δ-lactones, are structural components of many bioactive natural products. Prelactones[1–4] **4**–**7** isolated from various polyketide macrolide-producing microorganisms are a subgroup of this class of compounds and have received attained much attention because of their structural motifs, which represent useful building blocks for the synthesis of complex structures such as bafilomycins,[5,6] concanomycin,[7,8] hygrolidin,[9] and compactin[10] (see Fig. 1).

Prelactone B was isolated from *Streptomyces griseus*[4] (strain Tu 2599 ana 18) and represents an early metabolite in the biosynthesis of polyketide antibiotics. It has been used as a standard for investigations concerning the mechanism of polyketide synthase (PKS). Because of the importance of this class of compound, several syntheses of prelactone B[11] and epi-prelactones[12] have been well reported. As part of an academic program, we were

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Address correspondence to P. Srihari, Organic Division I, Indian Institute of Chemical Technology, Hyderabad 500007, India. E-mail: srihari@iict.res.in

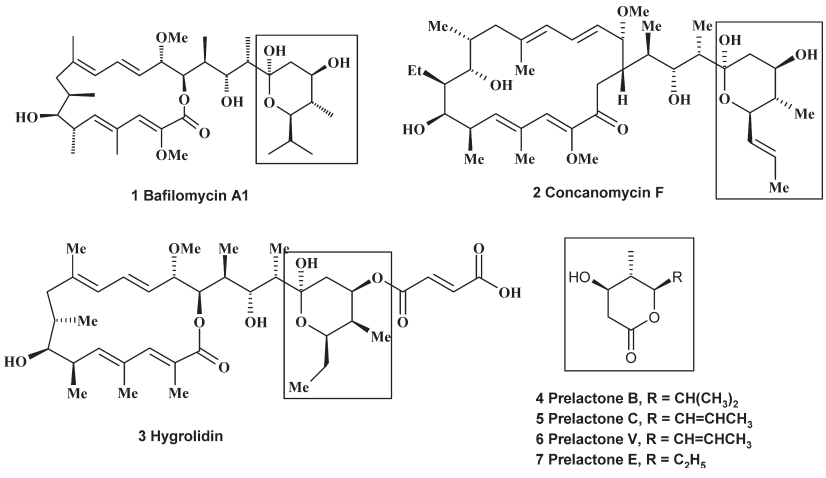


Figure 1. Few biologically active compounds with β-hydroxy δ-lactone motifs.

interested in the synthesis of compounds containing β-hydroxy-δ-lactone moieties and have investigated various strategies that lead to the development of two different routes for the synthesis of β-hydroxy-δ-lactones, resulting in multigram synthesis of prelactone B[13] and total synthesis of prelactone B, C, and V.[14] In continuation of our work on β-hydroxy-δ-lactones, herein we report the first total synthesis of 5-epi-prelactone B by employing Sharpless asymmetric epoxidation and an intramolecular hydride transfer reaction to get the aldol product **10** (by nonaldol chemistry) for the synthesis of 5-epi-prelactone B as the key steps. Our retrosynthetic analysis is depicted in Fig. 2.

RESULTS AND DISCUSSION

The synthesis of 5-epi-prelactone starts with the commercially available isobutyraldehyde, which was subjected to the Wittig reaction with (1-(ethoxycarbonyl)ethyl)triphenylphosphonium bromide) to exclusively get the trans ester **11**. The ester **11**, on reduction with DIBAL-H,[15] afforded allyl alcohol **12** and was then subjected to Sharpless asymmetric epoxidation[16] with D(−)-diethyl tartarate (DET), tert-butyl hydroperoxide (TBHP), and Ti(^{i}PrO)$_4$ to get the chiral epoxy alcohol **13** in 90% yield with 96% ee. The epoxy alcohol was treated with

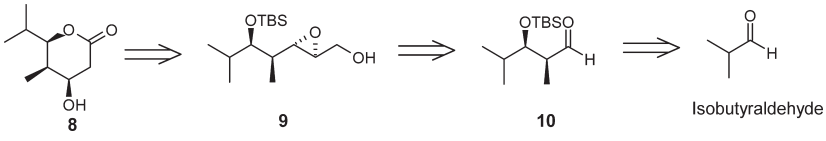
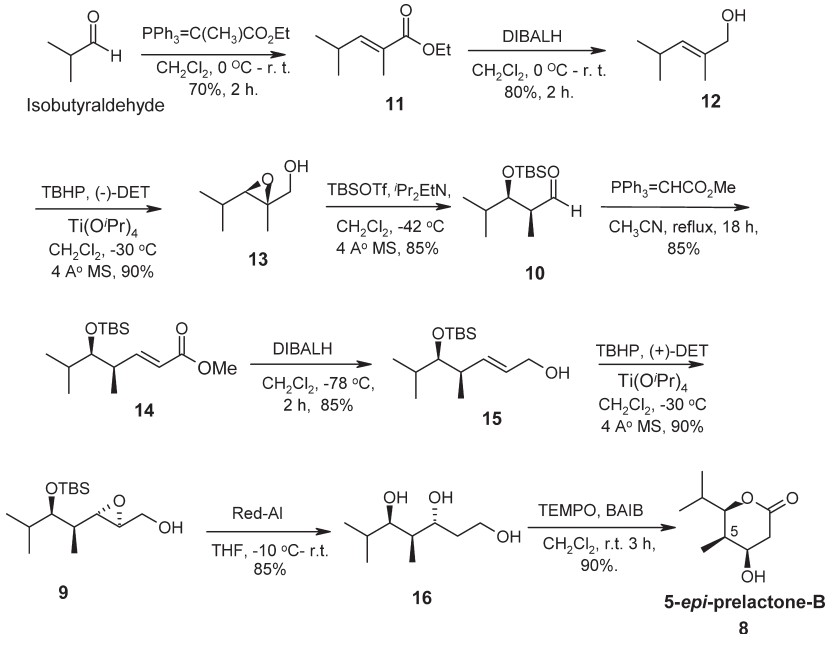


Figure 2. Retrosynthesis.



Scheme 1.

TBSOTf in the presence of Hunig's base for the intramolecular hydride tranfer from the methylene group of the in situ formed silyl ether of the epoxy alcohol to get the TBS protected aldehyde **10**.[17] The resulting aldehyde **10** was subjected to the Wittig reaction with (methoxycarbonylmethyl)triphenylphosphonium bromide to afford the trans homologated product **14** in 85% yield. The compound **14** was treated with DIBAL-H to reduce the conjugated ester to allyl alcohol **15**. The allyl alcohol **15**, upon Sharpless asymmetric epoxidation with L(+)-DET, TBHP, and Ti(^{i}PrO)$_4$ in DCM at -30 °C, gave chiral epoxy alcohol **9**. The chiral epoxy alcohol, on treatment with sodium bis(2-methoxyethoxy)aluminum hydride, underwent a one-pot epoxide opening and also desilylation to afford the 1,3,5-triol **16** (Scheme 1). Selective oxidation[18] of the primary alcohol with (diacetoxyiodo)benzene (BAIB) in the presence of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) afforded the target molecule 5-epi-prelactone B. The stereochemistry of the product was also reconfirmed by NMR studies from the coupling constant values.

CONCLUSION

In conclusion, an efficient short synthesis of 5-epi-prelactone B has been described in an overall yield of 21% from nine steps. The synthetic strategy applied is amenable for multigram scale synthesis and also provides access

to other prelactones and their derivatives by maneuvering the substrates and reagents. Studies to evaluate of their biological activity are currently under progress.

EXPERIMENTAL

All the solvents were dried and distilled prior to use. Column chromatography was performed using silica gel 60–120 mesh. IR spectra were recorded on a Perkin-Elmer infrared spectrophotometer as KBr wafers, neat, or in $CHCl_3$ as a thin film. ^1H and ^{13}C NMR were recorded on a Varian Gemini 200 or Bruker Avance 300-MHz instrument using TMS as an internal standard. Mass spectra were recorded on Micromass VG 7070H mass spectrometer for electron impact (EI), VG Autospec mass spectrometer for fast atom bombardment mass spectroscopy (FABMS), and micromass Quatro LC-triple quadrupole mass spectrometer for electron spray ionization (ESI) analysis. The optical rotations were recorded on a Jasco DIP-360 digital polarimeter at 25 °C.

(*E*)-Ethyl 2,4-dimethylpent-2-enoate (11)

Ethoxycarbonylmethylenetriphenylphosphorane (19.6 g, 45 mmol) to the mixture of the isobutyraldehyde (3.0 g, 41 mmol) in CH_2Cl_2 (50 mL) was added at 0 °C, and the mixture was allowed to stirr for 2 h at room temperature. Then CH_2Cl_2 was removed under reduced pressure; this crude product was purified by column chromatography to afford the pure ester as a colorless oil. Yield 4.5 g (70%); R_f 0.80 (EtOAc/hexane 10:90); IR (KBr): ν_{max}, 2922, 2852, 1738, 1461, 1375, 1098, 759 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.51 (d, 1H, $J = 9.0$ Hz), 4.16 (q, 2H, $J = 7.0$, 14.3 Hz), 2.66–2.56 (m, 1H), 1.81 (s, 3H, $J = 1.0$ Hz), 1.30 (t, 3H, $J = 7.0$ Hz), 1.03 (d, 6H, $J = 7.0$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.1, 148.3, 125.7, 60.49, 28.0, 22.0, 14.4, 12.3. EIMS: 157 $[M+H]^+$.

(*E*)-2,4-Dimethylpent-2-en-1-ol (12)

A solution of ester **11** (2.5 g, 16.8 mmol) in CH_2Cl_2 (100 mL) was treated with DIBAL-H [28% (w/v) in toluene, 35.2 mL, 35 mmol] in a dropwise fashion at 0 °C. After stirring for 2 h at 0 °C, a saturated solution of aqueous potassium sodium tartarate (50 mL) was added, and the mixture was extracted with Et_2O (3 × 25 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated. The crude product was purified by column chromatography to afford alcohol **12** as colorless oil. Yield 1.46 g (80%); R_f 0.60 [EtOAc/hexane 10:90]; IR (KBr): ν_{max}, 3421, 2922, 2852, 1735, 1627, 1461, 787 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 5.19–5.23

(d, 1H, $J = 9.0$ Hz), 3.93 (s, 2H), 2.59–2.46 (m, 1H), 1.66 (s, 3H), 0.95 (d, 6H, $J = 7.0$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.2, 132.5, 69.0, 26.9, 22.8, 13.7; EIMS: 115 $[M+ H]^+$.

((2*R*,3*R*)-3-Isopropyl-2-methyloxiran-2-yl)methanol (13)

D-(−)-diethyltartarate (2.9 mL, 17 mmol) was added to a suspension of 4 Å MS (2 g) in 100 mL of CH_2Cl_2 followed by addition of Ti(*i*-PrO)$_4$ (4.14 mL, 13 mmol) at −30 °C. The suspension was stirred at −30 °C for 30 min. A solution of allyl alcohol **12** (2.0 g, 17 mmol) was added dropwise, The mixture was stirred at −30 °C for 1 h, then *tert*-butylhydroperoxide (TBHP, 2.32 mL, 24 mmol) was added dropwise. The resulting mixture was stirred for 1 h at −30 °C, then warmed to 0 °C and poured into cooled (0 °C) Fe_2SO_4 (38.0 g) and tartaric acid (11.0 g) in water (180 mL). The resulting mixture was stirred for 15 min, and the aqueous phase was saturated with solid NaCl and extracted with CH_2Cl_2 (5 × 50 ml). Emulsions formed in some of the extractions were dispersed by filtration through Celite®. The organic phases were combined and dried over Na_2SO_4, filtered through Celite, concentrated under reduced pressure, and purified by column chromatography to afford epoxy alcohol **13** as colorless oil. Yield 2.05 g (90%); R_f 0.40 (EtOAc/hexane 20:80); $[\alpha]_D^{25}$ +15.9 (c 1.0 $CHCl_3$); IR (KBr): ν_{max} 3443, 3923, 2853, 1626, 1460, 1383, 1083 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.63 (dd, 1H, $J = 12.0$, 4.5 Hz), 3.51 (dd, 1H, $J = 12.0$, 8.3 Hz), 2.65 (d, 1H, $J = 9.8$ Hz), 1.99 (dd, 1H, $J = 8.3$, 5.2 Hz), 1.54 (m, 1H), 1.29 (s, 3H), 1.10 (d, 3H, $J = 6.7$ Hz), 0.95 (d, 3H, $J = 6.7$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 65.9, 65.5, 61.5, 27.5, 20.0, 18.3, 13.9; HRMS calcd. for $C_7H_{14}O_2Na$; 153.0891; found: 153.0896.

(2*S*,3*R*)-3-(*tert*-Butyldimethylsilyloxy)-2,4-dimethylpentanal (10)

A solution of epoxy alcohol **13** (2.0 g, 15 mmol) and *N,N*-diisopropylethyl amine (3.66 mL, 21 mmol) in CH_2Cl_2 was added to a cooled (−40 °C) suspension of 4 Å MS (2.5 g) in 100 mL of CH_2Cl_2. Then tert-butyldimethyl trifluoromethane sulfonate (TBSOTf, 4.6 mL, 99 mmol) was added dropwise over 15 min. The resulting solution was stirred for 1 h at −40 °C, then quenched by addition of pH 7.0 buffer (25 mL) and allowed to warm to room temperature. The mixture was diluted with pentane, and the phases were separated. The organic phases were washed with saturated copper(II) sulfate two times and brine, then dried over Na_2SO_4, filtered through Celite, and concentrated under reduced pressure to give the aldehyde **10** as clear yellow oil. Yield 3.19 g (85%); R_f 0.60 (EtOAc/Hexane 10:90); $[\alpha]_D^{25}$ +39.5 (c 1.30 CH_2Cl_2); IR (KBr): $\nu_{max,}$ 2960, 2933, 2884, 2860, 1727, 1473, 1464, 1254, 1141, 1103, 1048, 1030, 1006, 837, 775, 667; ^{1}H NMR

(300 MHz, $CDCl_3$) δ 9.78 (d, 1H, $J = 0.7$ Hz), 3.90 (dd, 1H, $J = 5.4$, 3.8 Hz), 2.50 (m, 1H), 1.81 (m, 1H), 1.09 (d, 3H, $J = 7.1$ Hz), 0.92 (d, 3H, $J = 6.9$ Hz), 0.89 (d, 3H, $J = 6.8$ Hz), 0.88 (s, 9H), 0.07 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.4, 76.4, 50.6, 32.2, 29.7, 25.9, 19.7, 18.2, 8.6, −4.0, −4.2; HRMS: calcd. for $C_9H_{19}O_2Si$ (M^+-C_4H_9) 187.1154; found: 187.1151.

(4*R*,5*R*,*E*)-Methyl-5-(*tert*-butyldimethylsilyloxy)-4,6-dimethylhept-2-enoate (14)

A mixture of aldehyde **10** (2.5 g, 10 mmol) and methyl(triphenylphosphoranylidine)acetate (3.82 g, 11 mmol) in 50 mL of dry CH_3CN was heated to reflux for 18 h. The mixture was concentrated, diluted with 50 ml of CH_2Cl_2 and 80 mL of hexane, and filtered through a Celite pad to remove the polar impurities. The solution was removed under reduced pressure and then purified by column chromatography to afford the pure ester **14** as a colorless oil. Yield 2.61 g (85%); R_f 0.80 (EtOAc/hexane 10:90); $[\alpha]_D^{25}$ +34.0° (c 1.50 CH_2Cl_2); IR (KBr): ν_{max}, 2957, 2920, 2856, 1726, 1658, 1435, 1332, 1251, 1178, 1060, 837, 772 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.01 (dd, 1H, $J = 15.7$, 7.8 Hz), 5.77 (dd, 1H, $J = 15.7$, 1.3 Hz), 3.70 (s, 3H), 3.36 (t, 1H, $J = 4.8$ Hz), 2.48 (m, 1H), 1.71 (m, 1H), 1.03 (d, 3H, $J = 6.8$ Hz), 0.89 (s, 9H), 0.86 (d, 3H, $J = 5.7$ Hz), 0.85 (d, 3H, $J = 6.7$ Hz), 0.03 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.2, 153.2, 119.7, 80.0, 51.3, 40.9, 32.0, 26.1, 20.3, 18.4, 17.5, 15.1, −3.7, −3.8; HRMS m/z calcd. for $C_{12}H_{23}O_3Si$ (M^+-C_4H_9) 243.1416; found: 243.1412.

(4*R*,5*R*,*E*)-5-(*tert*-Butyldimethylsilyloxy)-4,6-dimethylhept-2-en-1-ol (15)

A solution of ester **14** (2.5 g, 8.3 mmol) in CH_2Cl_2 (100 mL) was treated with DIBAL-H (1.0 M in hexane 18.3 mL, 18 mmol) in a dropwise fashion at −78 °C. After stirring for 2 h at −78 °C, a saturated solution of aqueous potassium sodium tartarate (50 mL) was added and extracted with Et_2O (3 × 25 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated. The crude product was purified by column chromatography to afford alcohol **15** as a colorless oil; yield 1.46 g (80%); R_f 0.40 (EtOAc/hexane 10:90); yield 1.92 g (85%); $[\alpha]_D^{25}$ +10.6° (c 0.5 $CHCl_3$); IR (KBr): ν_{max}, 3445, 2921, 2862, 1729, 1629, 1459, 1280, 1117 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.71–5.48 (m, 2H), 4.11–4.0 (m, 2H), 3.29–3.24 (m, 1H), 2.41–2.29 (m, 1H), 1.82–1.66 (m, 1H), 0.98 (d, 3H, $J = 6.7$ Hz), 0.93–0.83 (m, 15H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.5, 127.8, 81.0, 64.2, 40.8, 31.9, 26.4, 20.7, 17.8, 16.2, −3.3, −3.5; ESIMS: 273 [M+ H]$^+$.

((2*S*,3*S*)-3-(2*R*,3*R*)-3-(*tert*-Butyldimethylsilyloxy)-4-methylpentan-2-yl)oxiran-2-yl)methanol (9)

L-(+)-diethyltartarate (1.25 mL, 7.3 mmol) was added to a suspension of 4 Å MS (2.5 g) in 100 mL of CH_2Cl_2 followed by addition of Ti(*i*-PrO)$_4$ (1.78 mL, 5.9 mmol) at −30 °C. The suspension was stirred at −30 °C for 30 min. A solution of allyl alcohol **15** (2.0 g, 7.3 mmol) was added dropwise; the resulting mixture was stirred for 1 h at −30 °C. Then *tert*-butyl hydro peroxide (TBHP, 1.0 mL, 10 mmol) was added dropwise. The mixture was stirred at −30 °C for 1 h, then warmed to 0 °C and poured into a precooled (0 °C) solution of Fe_2SO_4 (38.0 g) and tartaric acid (11.0 g) in water (180 mL). The resulting mixture was stirred for 15 min, and the aqueous phase was saturated with solid NaCl and extracted with CH_2Cl_2 (5 × 50 mL). The organic phases were dried over Na_2SO_4, filtered through Celite, concentrated under reduced pressure, and purified by column chromatography to afford epoxy alcohol **9** as colorless oil. Yield 2.05 g (90%); R_f 0.40 (EtOAc/hexane 20:80); $[\alpha]_D^{25}$ −16.60° (c 2.0 $CHCl_3$); IR (KBr): ν_{max}, 3442, 3921, 2852, 1625, 1462, 1379, 1081 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.87 (dd, 1H, J = 12.8, 4.5), 3.60 (dd, 1H, J = 12.0, 4.50 Hz), 3.64–3.50 (m, 2H), 2.90–2.82 (m, 2H), 1.85–1.70 (m, 1H), 1.57–1.45 (m, 1H), 1.05–0.82 (m, 18H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 77.8, 61.8, 58.7, 58.4, 39.0, 32.2, 26.1, 19.5, 18.8, 10.7, −3.7, −4.1; ESIMS: 289 [M+ H]$^+$.

(3*R*,4*R*,5*R*)-4,6-Dimethylheptane-1,3,5-triol (16)

A solution of epoxy alcohol **9** (2.0 g, 6.9 mmol) in THF (100 mL) was treated with Red-Al [65% (w/v) in toluene, 9.2 mL, 20.8 mmol] in a dropwise fashion at −10 °C. After stirring for 8 h at −10 °C, a saturated solution of aqueous potassium sodium tartarate (40 mL) was added, and the mixture was extracted with Et_2O (3 × 25 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated. The crude product was purified by column chromatography to afford triol **16** as a colorless oil; yield 1.03 g (85%); R_f 0.15 (EtOAc/hexane 50:50); yield 1.92 g (85%); $[\alpha]_D^{25}$ −1.40° (c 1.25 $CHCl_3$); IR (KBr): ν_{max}, 3475, 2966, 2920, 1460, 1272, 1010 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.16 (br s, 1H), 3.94–3.76 (m, 3H), 3.57–3.49 (m, 1H), 3.35 (br s, 2H), 1.94–1.80 (m, 1H), 1.72–1.57 (m, 2H), 1.28–1.22 (m, 1H), 1.01 (d, 3H, J = 6.4 Hz), 0.98 (d, 3H, J = 6.9 Hz), 0.81 (d, 3H, J = 6.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 80.1, 74.7, 62.7, 39.1, 36.8, 31.4, 19.9, 19.0, 10.4; ESIMS: 177 [M+ H]$^+$.

(4*R*,5*R*,6*R*)-4-Hydroxy-6-isopropyl-5-methyl-tetrahydropyran-2-one (8)

Bis-acetoxyiodobenzene (BAIB, 7.32 g, 22.7 mmol) and 2,2,6,6-tetramethyl-piperidinooxy (TEMPO, 0.16 g, 1.0 mmol) were added sequentially to the

stirred solution of triol **16** (1.0 g, 5.6 mmol) in CH_2Cl_2 (10 mL) at room temperature. After stirring for 3.0 h, saturated aqueous $Na_2S_2O_3$ and Et_2O (25 mL) were added. The separated organic phase was washed with saturated aqueous $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography to provide lactone **8** as a colorless viscous oil; yield 0.8 g (90%); R_f 0.50 (EtOAc/hexane 50:50); yield 1.92 g (85%); $[\alpha]_D^{20} = +48.0$ (c 1.75 $CHCl_3$); IR (KBr): ν_{max} 3473, 2970, 2924, 1715, 1463, 1272, 1006 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.15 (m, 1H), 3.69 (dd, 1H, $J = 10.2$, 2.2 Hz), 2.80 (dd, 1H, $J = 18.1$, 7.1 Hz), 2.40 (dd, 1H, $J = 18.1$, 10.5 Hz), 2.25 (m, 1H), 1.92 (m, 1H), 1.10 (d, 3H, $J = 6.4$ Hz), 0.92 (d, 6H, $J = 7.1$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.13, 86.63, 67.33, 35.34, 34.89, 29.72, 20.07, 18.13, 3.73; ESIMS: 173 $[M^+ + H]$. HRMS: calcd. for $C_9H_{16}O_3Na$ $[m/z]$: 195.0997; found: 195.1000.

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