Supporting Information

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Stereoselective Total Synthesis of the Proposed Structure of 2-Epibotcinolide

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S1	General Information
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General Information. ¹H and ¹³C NMR spectra were recorded with tetramethylsilane (TMS), chloroform (in chloroform-*d*), benzene (in benzene-*d*₆) or methanol (in methanol-*d*₄) as internal standard. Column chromatography was performed on silica gel 60 (Merck) or Wakogel B5F. Thin layer chromatography was performed on Wakogel B5F.

All reactions were carried out under argon atmosphere in dried glassware, unless otherwise noted. Dichloromethane was distilled from diphosphorus pentoxide, then calcium hydride, and dried over MS 4Å, benzene and toluene were distilled from diphosphorus pentoxide, and dried over MS 4 Å, and THF and diethyl ether were distilled from sodium/benzophenone immediately prior to use. All reagents were purchased from Tokyo Kasei Kogyo Co., Ltd., Kanto Chemical Co., Inc. or Aldrich Chemical Co., Inc., and used without further purification unless otherwise noted.

Methyl (*R*)-2-(*tert*-butyldimethylsiloxy)propanoate: To a suspension of sodium hydride (60% in oil, 5.50 g, 137 mmol) in THF (170 mL) at 0 °C was added a solution of methyl (*R*)-lactate (**3**) (13.0 g, 125 mmol) in THF (30 mL). After the reaction mixture had been stirred for 10 min at 0 °C, *t*-butylchlorodimethylsilane (22.5 g, 150 mmol) in THF (50 mL) was added. The reaction mixture was stirred for 50 min at room temperature and then the solvent was removed by distillation under reduced pressure. Dichloromethane (200 mL) and water (20 mL) was added to the residue and the mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by distillation to afford **methyl (*R*)-2-(*tert*-butyldimethylsiloxy)propanoate** (22.4 g, 82%) as a colorless oil: IR (neat): 1754 cm^{-1} ; ^1H NMR (CDCl_3): 4.28 (q, $J = 6.6$ Hz, 1H, 2-H), 3.66 (s, 3H, OMe), 1.34 (d, $J = 6.6$ Hz, 3H, 3-H), 0.85 (s, 9H, TBS), 0.04 (s, 3H, TBS), 0.02 (s, 3H, TBS); ^{13}C NMR (CDCl_3): 174.5 (1), 68.3 (2), 51.8 (OMe), 25.7 (TBS), 21.3 (3), 18.3 (TBS), -5.1 (TBS), -5.3 (TBS); HR MS: calcd for $\text{C}_{10}\text{H}_{22}\text{O}_3\text{SiNa}$ ($\text{M} + \text{Na}^+$) 241.1230, found 241.1240.

(*R*)-2-(*tert*-Butyldimethylsiloxy)propanal (4**):** To a solution of **methyl (*R*)-2-(*tert*-butyldimethylsiloxy)propanoate** (5.69 g, 26.1 mmol) in dichloromethane (104.4 mL) at -78 °C was added DIBAL in hexanes (1.0 M, 52.2 mL, 52.2 mmol). The reaction mixture was stirred for 5 h at -78 °C and then DIBAL in hexanes (1.0 M, 13.0 mL, 13.0 mmol) was added to the mixture. After the reaction mixture had been stirred for 30 min at -78 °C, methanol was added. The mixture was allowed to warm to room temperature and then saturated aqueous potassium sodium tartrate was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, dried over sodium sulfate. After evaporation of the solvent, the crude product was purified by distillation to afford aldehyde **4** (4.51 g, 92%) as a colorless oil: IR (neat): 1741 cm^{-1} ; ^1H NMR (CDCl_3): 9.59 (d, $J = 1.5$ Hz, 1H, 1-H), 4.08 (dq, $J = 6.9, 1.5$ Hz, 1H, 2-H), 1.26 (d, $J = 6.9$ Hz, 3H, 3-H), 0.90 (s, 9H, TBS), 0.07 (s, 3H, TBS), 0.07 (s, 3H, TBS); ^{13}C NMR (CDCl_3): 204.2 (1), 73.8 (2), 25.7 (TBS),

18.5 (3), 18.2 (TBS), -4.8 (TBS), -4.8 (TBS); HR MS: calcd for $C_9H_{20}O_2SiNa$ ($M + Na^+$) 211.1125, found 211.1134.

S-Ethyl (2*S*,3*S*,4*R*)-4-(*tert*-butyldimethylsiloxy)-3-hydroxy-2-methylpentanethioate (7): To tin(II) trifluoromethanesulfonate (214 mg, 0.510 mmol) at room temperature were added a solution of (*S*)-1-methyl-2-(1-naphthylaminomethyl)pyrrolidine (146 mg, 0.610 mmol) in dichloromethane (1 mL), dibutyltin diacetate (197 mg, 0.560 mmol) and dichloromethane (1 mL). After the reaction mixture had been stirred for 5 min at room temperature, a solution of (*Z*)-1-ethylthio-1-trimethylsiloxy-1-propene (**5**) (97.6 mg, 0.510 mmol) in dichloromethane (1 mL) and a solution of aldehyde **4** (87.8 mg, 0.470 mmol) in dichloromethane (0.5 mL) were added at -78 °C. The reaction mixture was stirred for 12 h at -78 °C and then saturated aqueous sodium hydrogencarbonate was added. The mixture was filtered through a short pad of Celite, and the filtrate was extracted with dichloromethane. The organic layer was washed with brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford a mixture of aldol **7** (119 mg, 83%) as a colorless oil: IR (neat): 3543, 1681 cm^{-1} ; 1H NMR (C_6D_6): 3.95 (ddd, $J = 2.4, 5.4, 5.9$ Hz, 1H, 3-H), 3.86 (dq, $J = 5.9, 5.9$ Hz, 1H, 4-H), 3.07 (dq, $J = 5.4, 7.0$ Hz, 1H, 2-H), 2.66 (q, $J = 7.3$ Hz, 2H, SEt), 2.60 (d, $J = 2.4$ Hz, 1H, OH), 1.39 (d, $J = 7.0$ Hz, 3H, 2-Me), 1.28 (d, $J = 5.9$ Hz, 3H, 5-H), 1.01 (t, $J = 7.3$ Hz, 3H, SEt), 0.98 (s, 9H, TBS), 0.05 (s, 3H, TBS), 0.05 (s, 3H, TBS); ^{13}C NMR (C_6D_6): 203.0 (1), 76.5 (3), 69.2 (4), 50.2 (2), 25.9 (TBS), 23.2 (SEt), 19.0 (5), 18.1 (TBS), 14.8 (SEt), 13.0 (2-Me), -4.1 (TBS), -4.9 (TBS); HR MS: calcd for $C_{14}H_{30}O_3SSiNa$ ($M + Na^+$) 329.1577, found 329.1567.

S-Ethyl (2*S*,3*S*,4*R*)-3,4-di(*tert*-butyldimethylsiloxy)-2-methylpentanethioate: To a solution of aldol **7** (3.06 g, 9.98 mmol) in dichloromethane (80 mL) at 0 °C were added 2,6-lutidine (2.14 g, 20.0 mmol) in dichloromethane (20 mL) and *t*-butyldimethylsilyl trifluoromethanesulfonate (3.44 mL, 15.0 mmol). The reaction mixture was stirred for 2 h at 0 °C and then saturated aqueous ammonium chloride was added. The mixture was extracted with dichloromethane, and

the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford **S-ethyl (2*S*,3*S*,4*R*)-3,4-di(*tert*-butyldimethylsiloxy)-2-methylpentanethioate** (3.97 g, 95%) as a colorless oil: IR (neat): 1685 cm⁻¹; ¹H NMR (CDCl₃): 3.89 (dd, *J* = 4.0, 5.9 Hz, 1H, 3-H), 3.69 (dq, *J* = 4.0, 6.2 Hz, 1H, 4-H), 2.85 (q, *J* = 7.3 Hz, 2H, SEt), 2.85 (dq, *J* = 5.9, 7.0 Hz, 1H, 2-H), 1.24 (t, *J* = 7.3 Hz, 3H, SEt), 1.17 (d, *J* = 7.0 Hz, 3H, 2-Me), 1.12 (d, *J* = 6.2 Hz, 3H, 5-H), 0.88 (s, 9H, TBS), 0.88 (s, 9H, TBS), 0.09 (s, 3H, TBS), 0.04 (s, 3H, TBS), 0.04 (s, 3H, TBS), 0.02 (s, 3H, TBS); ¹³C NMR (CDCl₃): 202.6 (1), 78.7 (3), 70.3 (4), 51.4 (2), 26.1 (TBS), 25.9 (TBS), 23.1 (SEt), 18.7 (5), 18.4 (TBS), 18.1 (TBS), 14.7 (SEt), 12.9 (2-Me), -3.9 (TBS), -4.4 (TBS), -4.6 (TBS), -4.7 (TBS); HR MS: calcd for C₂₀H₄₄O₃SSi₂Na (M+Na⁺) 443.2442, found 443.2470.

(2*S*,3*S*,4*R*)-3,4-di(*tert*-Butyldimethylsiloxy)-2-methylpentanal (8): To a mixture of **S-ethyl (2*S*,3*S*,4*R*)-3,4-di(*tert*-butyldimethylsiloxy)-2-methylpentanethioate** (8.47 g, 20.2 mmol) and 10% palladium on activated carbon (1.06 g, 1.00 mmol) in acetone (50.4 mL) at 0 °C was added triethylsilane (4.83 mL, 30.2 mmol). The reaction mixture was stirred for 90 min at 0 °C and then it was filtered through a short pad of Celite eluting with ethyl acetate. After evaporation of the solvent, the crude product was purified by column chromatography to afford aldehyde **8** (7.24 g, quant.) as a colorless oil: IR (neat): 1728 cm⁻¹; ¹H NMR (CDCl₃): 9.74 (s, 1H, 1-H), 3.98 (dd, *J* = 3.0, 6.3 Hz, 1H, 3-H), 3.70 (dq, *J* = 6.3, 6.0 Hz, 1H, 4-H), 2.75 (dq, *J* = 3.0, 6.9 Hz, 1H, 2-H), 1.18 (d, *J* = 6.0 Hz, 3H, 5-H), 1.09 (d, *J* = 6.9 Hz, 3H, 2-Me), 0.87 (s, 9H, TBS), 0.86 (s, 9H, TBS), 0.09 (s, 3H, TBS), 0.08 (s, 3H, TBS), 0.06 (s, 3H, TBS), -0.02 (s, 3H, TBS); ¹³C NMR (CDCl₃): 205.1 (1), 76.2 (3), 70.0 (4), 49.5 (2), 25.9 (TBS), 25.8 (TBS), 20.6 (5), 18.2 (TBS), 17.9 (TBS), 7.5 (2-Me), -4.0 (TBS), -4.1 (TBS), -4.2 (TBS), -4.9 (TBS); HR MS: calcd for C₁₈H₄₀O₃Si₂Na (M+Na⁺) 383.2408, found 383.2408.

Ethyl (E)-(4*R*,5*S*,6*R*)-5,6-di(*tert*-butyldimethylsiloxy)-2,4-dimethyl-2-heptenoate: To a solution of aldehyde **8** (3.69 g, 10.2 mmol) in toluene (102 mL) at room temperature was added (carbethoxymethylene)triphenylphosphorane (4.82 g, 13.3

mmol). The reaction mixture had been stirred for 6.5 h at 100 °C and then the solvent was removed by distillation under reduced pressure. The crude product was purified by column chromatography to afford **ethyl (E)-(4R,5S,6R)-5,6-di(tert-butyldimethylsiloxy)-2,4-dimethyl-2-heptenoate** (4.33 g, 95%) and its geometric isomer (24.5 mg, 0.5%) as colorless oils.

Ethyl (E)-(4R,5S,6R)-5,6-di(tert-butyldimethylsiloxy)-2,4-dimethyl-2-heptenoate: IR (neat): 1714 cm⁻¹; ¹H NMR (CDCl₃): 6.65 (dq, *J* = 10.2, 1.5 Hz, 1H, 3-H), 4.22 (dq, *J* = 10.5, 7.2 Hz, 1H, OEt), 4.14 (dq, *J* = 10.5, 7.2 Hz, 1H, OEt), 3.68 (dq, *J* = 3.9, 6.0 Hz, 1H, 6-H), 3.40 (dd, *J* = 3.9, 6.0 Hz, 1H, 5-H), 2.68 (ddq, *J* = 6.0, 10.2, 6.6 Hz, 1H, 4-H), 1.83 (d, *J* = 1.5 Hz, 3H, 2-Me), 1.29 (t, *J* = 7.2 Hz, 3H, OEt), 1.07 (d, *J* = 6.0 Hz, 3H, 7-H), 1.01 (d, *J* = 6.6 Hz, 3H, 4-Me), 0.92 (s, 9H, TBS), 0.88 (s, 9H, TBS), 0.09 (s, 3H, TBS), 0.06 (s, 3H, TBS), 0.05 (s, 3H, TBS), 0.04 (s, 3H, TBS); ¹³C NMR (CDCl₃): 168.2 (1), 145.4 (3), 126.6 (2), 80.8 (5), 70.3 (6), 60.4 (OEt), 36.3 (4), 26.2 (TBS), 26.0 (TBS), 18.5 (7), 18.5 (TBS), 18.2 (TBS), 15.2 (4-Me), 14.3 (OEt), 12.5 (2-Me), -3.5 (TBS), -4.3 (TBS), -4.6 (TBS), -4.7 (TBS); HR MS: calcd for C₂₃H₄₈O₄Si₂Na (M+Na⁺) 467.2983, found 467.2943.

(E)-(4R,5S,6R)-5,6-Di(tert-butyldimethylsiloxy)-2,4-dimethyl-2-hepten-1-ol: To a solution of **ethyl (E)-(4R,5S,6R)-5,6-di(tert-butyldimethylsiloxy)-2,4-dimethyl-2-heptenoate** (4.33 g, 9.73 mmol) in THF (97.3 mL) at 0 °C was added L-Selectride® in THF (1.0 M, 29.2 mL, 29.2 mmol). The reaction mixture was stirred for 5 h at room temperature and then saturated aqueous ammonium chloride was added at 0 °C. The mixture was extracted with ethyl acetate, and the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford **(E)-(4R,5S,6R)-5,6-di(tert-butyldimethylsiloxy)-2,4-dimethyl-2-hepten-1-ol** (3.59 g, 92%) as a colorless oil: IR (neat): 3337 cm⁻¹; ¹H NMR (CDCl₃): 5.27 (dq, *J* = 9.9, 1.5 Hz, 1H, 3-H), 3.98 (s, 2H, 1-H), 3.74 (dq, *J* = 3.3, 6.0 Hz, 1H, 6-H), 3.34 (dd, *J* = 3.3, 7.2 Hz, 1H, 5-H), 2.51 (ddq, *J* = 7.2, 9.9, 6.6 Hz, 1H, 4-H), 1.66 (d, *J* = 1.5 Hz, 3H, 2-Me), 1.06 (d, *J* = 6.0 Hz, 3H, 7-H), 0.95 (d, *J* = 6.6 Hz, 3H, 4-Me), 0.90 (s, 9H, TBS), 0.85 (s, 9H, TBS), 0.08 (s, 3H, TBS), 0.04 (s, 3H, TBS), 0.04 (s, 3H, TBS), 0.03 (s, 3H, TBS); ¹³C NMR (CDCl₃): 133.8 (2), 130.4 (3), 81.6 (5), 70.3 (6), 68.9 (1), 35.4 (4), 26.2 (TBS), 26.0 (TBS),

18.5 (TBS), 18.2 (TBS), 18.1 (7), 16.6 (4-Me), 13.9 (2-Me), -3.5 (TBS), -4.4 (TBS), -4.5 (TBS), -4.6 (TBS); HR MS: calcd for $C_{21}H_{46}O_3Si_2Na$ ($M+Na^+$) 425.2878, found 425.2896.

(E)-(4R,5S,6R)-5,6-Di(tert-butyldimethylsiloxy)-2,4-dimethyl-2-heptenal (9): To a mixture of MS 4Å (3.60 g) and **(E)-(4R,5S,6R)-5,6-di(tert-butyldimethylsiloxy)-2,4-dimethyl-2-hepten-1-ol** (2.46 g, 6.11 mmol) in dichloromethane (61 mL) at room temperature was added NMO (2.15 g, 18.3 mmol). After the reaction mixture had been stirred for 5 min at room temperature, TPAP (107.5 mg, 0.310 mmol) was added at 0 °C. The reaction mixture was stirred for 2 h at 0 °C and then it was filtered through a pre-cooled short pad of silica gel eluting with eluant (hexane/ethyl acetate=2/1). Evaporation of the solvent gave aldehyde **9** (2.45 g, quant.) as a colorless oil. The product was instantly used in the following coupling reaction without further purification.

9: IR (neat): 1695, 1684 cm^{-1} ; 1H NMR (C_6D_6): 9.43 (s, 1H, 1-H), 6.07 (dq, $J = 10.3, 1.4$ Hz, 1H, 3-H), 3.68 (dq, $J = 3.8, 6.2$ Hz, 1H, 6-H), 3.45 (dd, $J = 3.8, 6.5$ Hz, 1H, 5-H), 2.79 (ddq, $J = 6.5, 10.3, 6.8$ Hz, 1H, 4-H), 1.74 (d, $J = 1.4$ Hz, 3H, 2-Me), 1.11 (d, $J = 6.2$ Hz, 3H, 7-H), 1.05 (s, 9H, TBS), 1.00 (d, $J = 6.8$ Hz, 3H, 4-Me), 0.96 (s, 9H, TBS), 0.19 (s, 3H, TBS), 0.10 (s, 3H, TBS), 0.04 (s, 3H, TBS); ^{13}C NMR (C_6D_6): 193.8 (1), 156.0 (3), 138.7 (2), 80.9 (5), 70.8 (6), 36.8 (4), 26.4 (TBS), 26.1 (TBS), 18.7 (TBS), 18.7 (TBS), 18.7 (7), 15.4 (4-Me), 9.6 (2-Me), -3.3 (TBS), -4.2 (TBS), -4.3 (TBS), -4.6 (TBS); HR MS: calcd for $C_{21}H_{44}O_3Si_2Na$ ($M+Na^+$) 423.2721, found 423.2735.

S-Ethyl (E)-(2S,3R,6S,7S,8R)-7,8-di(tert-butyldimethylsiloxy)-3-hydroxy-2,4,6-trimethyl-4-nonenethioate (10a) and S-Ethyl (E)-(2R,3S,6S,7S,8R)-7,8-di(tert-butyldimethylsiloxy)-3-hydroxy-2,4,6-

trimethyl-4-nonenethioate (10b): To a solution of LHMDs in THF (1.0 M, 12.8 mL, 12.8 mmol) at -78 °C was added a solution of *S*-ethyl propanethioate (1.52 g, 12.8 mmol) in THF (34 mL). After the reaction mixture had been stirred for 20 min, a solution of the crude aldehyde **9** (2.57 g, 6.42 mmol) in THF (30 mL) was added at -78 °C. The reaction mixture was stirred for 3 h at -78 °C and then saturated aqueous ammonium chloride was added. The mixture was extracted with ethyl acetate, and the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford aldols **10a** (1.66 g, 49.9%), **10b** (681 mg, 20.4%), **10c** (299 mg, 8.9%) and **10d** (282 mg, 8.4%) as colorless oils.

10a: IR (neat): 3517, 1682 cm⁻¹; ¹H NMR (CDCl₃): 5.30 (dq, *J* = 5.3, 0.9 Hz, 1H, 5-H), 4.14 (d, *J* = 9.3 Hz, 1H, 3-H), 3.75 (dq, *J* = 3.3, 6.0 Hz, 1H, 8-H), 3.36 (dd, *J* = 3.3, 6.9 Hz, 1H, 7-H), 2.92 (dq, *J* = 15.0, 7.5 Hz, 1H, SEt), 2.91 (dq, *J* = 15.0, 7.5 Hz, 1H, SEt), 2.82 (dq, *J* = 9.3, 7.2 Hz, 1H, 2-H), 2.51 (ddq, *J* = 5.3, 6.9, 6.9 Hz, 1H, 6-H), 1.61 (d, *J* = 0.9 Hz, 3H, 4-Me), 1.27 (t, *J* = 7.5 Hz, 3H, SEt), 1.06 (d, *J* = 6.0 Hz, 3H, 9-H), 1.02 (d, *J* = 7.2 Hz, 3H, 2-Me), 0.93 (d, *J* = 6.9 Hz, 3H, 6-Me), 0.91 (s, 9H, TBS), 0.88 (s, 9H, TBS), 0.10 (s, 3H, TBS), 0.06 (s, 3H, TBS), 0.05 (s, 3H, TBS), 0.04 (s, 3H, TBS); ¹³C NMR (CDCl₃): 203.6 (1), 133.7 (5), 133.2 (4), 81.4 (7), 80.2 (3), 70.3 (8), 51.9 (2), 35.4 (6), 26.2 (TBS), 26.0 (TBS), 23.3 (SEt), 18.5 (TBS), 18.2 (TBS), 18.1 (9), 16.6 (6-Me), 15.3 (2-Me), 14.5 (SEt), 10.9 (4-Me), -3.5 (TBS), -4.4 (TBS), -4.5 (TBS), -4.6 (TBS); HR MS: calcd for C₂₆H₅₄O₄SSi₂Na (M+Na⁺) 541.3179, found 541.3196.

10b: IR (neat): 3480, 1682 cm⁻¹; ¹H NMR (CDCl₃): 5.29 (dq, *J* = 10.2, 0.9 Hz, 1H, 5-H), 4.12 (d, *J* = 8.4 Hz, 1H, 3-H), 3.72 (dq, *J* = 2.4, 6.3 Hz, 1H, 8-H), 3.36 (dd, *J* = 2.4, 7.5 Hz, 1H, 7-H), 2.91 (dq, *J* = 15.0, 7.5 Hz, 1H, SEt), 2.90 (dq, *J* = 15.0, 7.5 Hz, 1H, SEt), 2.84 (dq, *J* = 8.4, 6.9 Hz, 1H, 2-H), 2.44 (ddq, *J* = 7.5, 10.2, 6.6 Hz, 1H, 6-H), 1.61 (d, *J* = 0.9 Hz, 3H, 4-Me), 1.26 (t, *J* = 7.5 Hz, 3H, SEt), 1.06 (d, *J* = 6.9 Hz, 3H, 2-Me), 1.03 (d, *J* = 6.3 Hz, 3H, 9-H), 0.96 (d, *J* = 6.6 Hz, 3H, 6-Me), 0.91 (s, 9H, TBS), 0.87 (s, 9H, TBS), 0.10 (s, 3H, TBS), 0.06 (s, 3H, TBS), 0.03 (s, 3H, TBS), 0.02 (s, 3H, TBS); ¹³C NMR (CDCl₃): 203.5 (1), 133.2 (4), 133.0 (5), 81.5 (7), 80.1 (3), 70.6 (8), 51.4 (2), 36.2 (6), 26.2 (TBS), 26.0 (TBS), 23.3 (SEt), 18.6 (TBS), 18.3 (TBS), 17.5 (9), 17.3 (6-Me), 15.5 (2-Me), 14.5 (SEt), 11.0 (4-Me), -3.5 (TBS), -4.4 (TBS), -4.6 (TBS), -4.7 (TBS); HR MS: calcd for C₂₆H₅₄O₄SSi₂Na (M+Na⁺) 541.3174, found 541.3174.

10c: ^1H NMR (CDCl_3): 5.43 (dq, $J = 9.9, 1.2$ Hz, 1H, 5-H), 4.33 (d, $J = 3.3$ Hz, 1H, 3-H), 3.74 (dq, $J = 3.0, 6.0$ Hz, 1H, 8-H), 3.37 (dd, $J = 3.0, 7.5$ Hz, 1H, 7-H), 2.95-2.77 (m, 1H, 2-H), 2.89 (dq, $J = 15.0, 7.5$ Hz, 1H, SEt), 2.88 (dq, $J = 15.0, 7.5$ Hz, 1H, SEt), 2.48 (ddq, $J = 7.5, 9.9, 6.6$ Hz, 1H, 6-H), 1.59 (d, $J = 1.2$ Hz, 3H, 4-Me), 1.26 (t, $J = 7.5$ Hz, 3H, SEt), 1.14 (d, $J = 6.9$ Hz, 3H, 2-Me), 1.04 (d, $J = 6.0$ Hz, 3H, 9-H), 0.95 (d, $J = 6.6$ Hz, 3H, 6-Me), 0.91 (s, 9H, TBS), 0.89 (s, 9H, TBS), 0.10 (s, 3H, TBS), 0.07 (s, 3H, TBS), 0.06 (s, 3H, TBS), 0.05 (s, 3H, TBS).

10d: ^1H NMR (CDCl_3): 5.37 (dq, $J = 9.9, 1.2$ Hz, 1H, 5-H), 4.29 (d, $J = 4.5$ Hz, 1H, 3-H), 3.76 (dq, $J = 2.7, 6.0$ Hz, 1H, 8-H), 3.39 (dd, $J = 2.7, 7.5$ Hz, 1H, 7-H), 2.93-2.79 (m, 1H, 2-H), 2.87 (q, $J = 7.5$ Hz, 2H, SEt), 2.44 (ddq, $J = 7.5, 9.9, 6.6$ Hz, 1H, 6-H), 1.60 (d, $J = 1.2$ Hz, 3H, 4-Me), 1.25 (t, $J = 7.5$ Hz, 3H, SEt), 1.17 (d, $J = 6.9$ Hz, 3H, 2-Me), 1.04 (d, $J = 6.0$ Hz, 3H, 9-H), 0.93 (d, $J = 6.6$ Hz, 3H, 6-Me), 0.91 (s, 9H, TBS), 0.88 (s, 9H, TBS), 0.11 (s, 3H, TBS), 0.07 (s, 3H, TBS), 0.04 (s, 3H, TBS), 0.03 (s, 3H, TBS).

(E)-(2R,3R,6R,7S,8R)-7,8-Di(tert-butyldimethylsiloxy)-2,4,6-trimethyl-4-nonen-1,3-diol: To a solution of aldol **10a** (16.8 mg, 32.4 μmol) in toluene (0.65 mL) at 0 $^\circ\text{C}$ was added Red-Al[®] in toluene (65%, 0.05 mL, 0.162 mmol). The reaction mixture was stirred for 3 h at 0 $^\circ\text{C}$ and then methanol and saturated aqueous potassium sodium tartrate were added. The mixture was extracted with ethyl acetate and the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford **(E)-(2R,3R,6R,7S,8R)-7,8-di(tert-butyldimethylsiloxy)-2,4,6-trimethyl-4-nonen-1,3-diol** (10.7 mg, 72%) as a colorless oil.

(E)-(2R,3R,6R,7S,8R)-1,3-(Isopropylidenedioxy)-7,8-di(tert-butyldimethylsiloxy)-2,4,6-trimethyl-4-nonene (11a): To a solution of **(E)-(2R,3R,6R,7S,8R)-7,8-di(tert-butyldimethylsiloxy)-2,4,6-trimethyl-4-**

nonen-1,3-diol (10.7 mg, 23.2 μ mol) in acetone dimethylacetal (0.23 mL) and dichloromethane (0.23 mL) at 0 °C was added CSA (0.5 mg, 2.3 μ mol). The reaction mixture was stirred for 1.5 h at room temperature and then saturated aqueous sodium hydrogencarbonate was added at 0 °C. The mixture was extracted with dichloromethane and the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford acetone **11a** (11.7 mg, quant.) as a colorless oil: ^1H NMR (C_6D_6): 5.27 (dq, $J = 9.7, 1.4$ Hz, 1H, 5-H), 4.00 (dq, $J = 2.4, 6.2$ Hz, 1H, 8-H), 3.76 (d, $J = 10.0$ Hz, 1H, 3-H), 3.72 (dd, $J = 11.6, 4.9$ Hz, 1H, 1-H), 3.54 (dd, $J = 2.4, 8.1$ Hz, 1H, 7-H), 3.42 (dd, $J = 11.6, 11.1$ Hz, 1H, 1-H), 2.63 (ddq, $J = 8.1, 9.7, 6.8$ Hz, 1H, 6-H), 1.85 (dddq, $J = 4.9, 10.0, 11.1, 6.8$ Hz, 1H, 2-H), 1.69 (d, $J = 1.4$ Hz, 3H, 4-Me), 1.58 (s, 3H, acetonide-Me), 1.44 (s, 3H, acetonide-Me), 1.24 (d, $J = 6.2$ Hz, 3H, 9-H), 1.14 (s, 9H, TBS), 1.13 (d, $J = 6.8$ Hz, 3H, 6-Me), 1.06 (s, 9H, TBS), 0.46 (d, $J = 6.8$ Hz, 3H, 2-Me), 0.32 (s, 3H, TBS), 0.26 (s, 3H, TBS), 0.16 (s, 3H, TBS), 0.15 (s, 3H, TBS).

(E)-(2S,3S,6R,7S,8R)-7,8-Di(*tert*-butyldimethylsiloxy)-2,4,6-trimethyl-4-nonen-1,3-diol: To a solution of aldol **10b** (37.3 mg, 71.9 μ mol) in toluene (1.4 mL) at 0 °C was added Red-Al[®] in toluene (65%, 0.09 mL, 0.288 mmol). The reaction mixture was stirred for 2 h at 0 °C and then methanol and saturated aqueous potassium sodium tartrate were added. The mixture was extracted with ethyl acetate and the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford **(E)-(2S,3S,6R,7S,8R)-7,8-di(*tert*-butyldimethylsiloxy)-2,4,6-trimethyl-4-nonen-1,3-diol** (29.0 mg, 88%) as a colorless oil.

(E)-(2S,3S,6R,7S,8R)-1,3-(Isopropylidenedioxy)-7,8-di(*tert*-butyldimethylsiloxy)-2,4,6-trimethyl-4-nonene (11b): To a solution of **(E)-(2S,3S,6R,7S,8R)-7,8-di(*tert*-butyldimethylsiloxy)-2,4,6-trimethyl-4-**

nonen-1,3-diol (29.0 mg, 62.9 μ mol) in acetone dimethylacetal (0.6 mL) and dichloromethane (0.6 mL) at 0 °C was added CSA (1.5 mg, 6.3 μ mol). The reaction mixture was stirred for 1.5 h at room temperature and then saturated aqueous sodium hydrogencarbonate was added at 0 °C. The mixture was extracted with dichloromethane and the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford acetone **11b** (28.8 mg, 91%) as a colorless oil: ^1H NMR (C_6D_6): 5.35 (dq, J = 9.7, 1.4 Hz, 1H, 5-H), 3.92 (dq, J = 2.2, 6.2 Hz, 1H, 8-H), 3.81 (d, J = 10.3 Hz, 1H, 3-H), 3.71 (dd, J = 11.3, 5.1 Hz, 1H, 1-H), 3.56 (dd, J = 2.2, 8.4 Hz, 1H, 7-H), 3.42 (dd, J = 11.3, 11.3 Hz, 1H, 1-H), 2.56 (ddq, J = 8.4, 9.7, 5.4 Hz, 1H, 6-H), 1.89 (dddq, J = 5.1, 10.3, 11.3, 6.8 Hz, 1H, 2-H), 1.70 (d, J = 1.4 Hz, 3H 4-Me), 1.57 (s, 3H, acetone-Me), 1.38 (s, 3H, acetone-Me), 1.19 (d, J = 6.2 Hz, 3H, 9-H), 1.13 (d, J = 5.4 Hz, 3H, 6-Me), 1.12 (s, 9H, TBS), 1.04 (s, 9H, TBS), 0.53 (d, J = 6.8 Hz, 3H, 2-Me), 0.34 (s, 3H, TBS), 0.24 (s, 3H, TBS), 0.15 (s, 3H, TBS), 0.14 (s, 3H, TBS).

(2S,3R,4S)-3-Benzylloxymethoxy-2,4-dimethyl-4-[(1R,2R,3S,4R)-3,4-di(*tert*-butyldimethylsiloxy)-1-hydroxy-2-methylpentan-1-yl]butanolide (12) and (2S,3R,4R)-3-benzylloxymethoxy-2,4-dimethyl-4-[(1S,2R,3S,4R)-3,4-di(*tert*-butyldimethylsiloxy)-1-hydroxy-2-methylpentan-1-yl]butanolide (12''): To a solution of **10a** (50.0 mg, 0.080 mmol) in pyridine (0.8 mL) at 0 °C was added osmium tetroxide (265 mg, 0.802 mmol). After the reaction mixture was stirred for 30 h at 60 °C, it was diluted with hexane and saturated with dried hydrogen sulfide gas. After the mixture was filtered through a short pad of Celite, and evaporation of the solvent, the crude product was purified by thin layer

chromatography to afford diols **12** (8.5 mg, 17%) and **12''** (7.6 mg, 16%) as pale yellow oils.

12: ^1H NMR (CDCl_3): 7.36-7.30 (m, 5H, Ph), 4.77 (d, $J = 6.9$ Hz, 1H, BOM), 4.73 (d, $J = 6.9$ Hz, 1H, BOM), 4.64 (br s, 2H, BOM), 4.49 (d, $J = 7.5$ Hz, 1H, 3-H), 3.94 (dq, $J = 3.6, 7.2$ Hz, 1H, 8-H), 3.91-3.89 (m, 1H, 5-H), 3.53 (dd, $J = 3.6, 3.6$ Hz, 1H, 7-H), 3.28 (dq, $J = 7.5, 7.5$ Hz, 1H, 2-H), 2.20 (br dq, $J = 3.6, 8.1$ Hz, 1H, 6-H), 1.34 (s, 3H, 4-Me), 1.24 (d, $J = 8.1$ Hz, 3H, 6-Me), 1.21 (d, $J = 7.2$ Hz, 3H, 9-H), 1.07 (d, $J = 7.5$ Hz, 3H, 2-Me), 0.89 (s, 9H, TBS), 0.89 (s, 9H, TBS), 0.10 (s, 3H, TBS), 0.09 (s, 3H, TBS), 0.09 (s, 3H, TBS), 0.07 (s, 3H, TBS).

12'': ^1H NMR (CDCl_3): 7.36-7.30 (m, 5H, Ph), 4.83 (d, $J = 6.6$ Hz, 1H, BOM), 4.78 (d, $J = 6.6$ Hz, 1H, BOM), 4.68 (d, $J = 11.9$ Hz, 1H, BOM), 4.62 (d, $J = 11.9$ Hz, 1H, BOM), 4.20 (d, $J = 6.9$ Hz, 1H, 3-H), 4.01 (dd, $J = 1.7, 5.6$ Hz, 1H, 7-H), 3.90 (d, $J = 7.8$ Hz, 1H, 5-H), 3.74 (dq, $J = 5.6, 6.3$ Hz, 1H, 8-H), 2.96 (dq, $J = 6.9, 7.2$ Hz, 1H, 2-H), 2.25 (ddq, $J = 1.7, 7.8, 7.5$ Hz, 1H, 6-H), 1.40 (s, 3H, 4-Me), 1.29 (d, $J = 7.5$ Hz, 3H, 6-Me), 1.17 (d, $J = 6.3$ Hz, 3H, 9-H), 0.96 (d, $J = 7.2$ Hz, 3H, 2-Me), 0.87 (s, 9H, TBS), 0.87 (s, 9H, TBS), 0.10 (s, 3H, TBS), 0.09 (s, 3H, TBS), 0.06 (s, 3H, TBS), 0.05 (s, 3H, TBS).

(2S,3R,4S)-3-Benzylloxymethoxy-2,4-dimethyl-4-[(1R,2R,3S,4R)-1,3,4-trihydroxy-2-methylpentan-1-yl]butanolide: To a solution of diol **12** (3.1 mg, 5.1 μmol) in THF (0.2 mL) at 0 °C was added hydrogen fluoride-pyridine (hydrogen fluoride/pyridine = *ca.* 7/3, 9 drops). The reaction mixture was stirred for 15.5 h at room temperature and then saturated aqueous sodium hydrogencarbonate was added at 0 °C. The mixture was extracted with ethyl acetate, and the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford **(2S,3R,4S)-3-benzylloxymethoxy-2,4-dimethyl-4-**

[(1*R*,2*R*,3*S*,4*R*)-1,3,4-hydroxy-2-methylpentan-1-yl]butanolide (2.0 mg, quant.) as a colorless oil.

(2*S*,3*R*,4*S*)-3-Benzylloxymethoxy-2,4-dimethyl-4-[(1*R*,2*R*,3*S*,4*R*)-1,3-[(*R*)-benzylidenedioxy]-4-hydroxy-2-methylpentan-1-yl]butanolide: To a solution of (2*S*,3*R*,4*S*)-3-benzylloxymethoxy-2,4-dimethyl-4-[(1*R*,2*R*,3*S*,4*R*)-1,3,4-trihydroxy-2-methylpentan-1-yl]butanolide (2.2 mg, 5.7 μ mol) in benzaldehyde dimethylacetal (0.11 mL) at 0 °C was added CSA (0.13 mg, 0.5 μ mol). The reaction mixture was stirred for 2 h at room temperature and then saturated aqueous sodium hydrogencarbonate was added at 0 °C. The mixture was extracted with ethyl acetate and the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford (2*S*,3*R*,4*S*)-3-benzylloxymethoxy-2,4-dimethyl-4-[(1*R*,2*R*,3*S*,4*R*)-1,3-[(*R*)-benzylidenedioxy]-4-hydroxy-2-methylpentan-1-yl]butanolide (2.1 mg, 78%) as a colorless oil: ^1H NMR (C_6D_6): 7.60-6.97 (m, 10H, Ph*2), 5.25 (s, 1H, benzylidene), 4.45 (d, $J = 12.0$ Hz, 1H, BOM), 4.40 (d, $J = 6.9$ Hz, 1H, BOM), 4.39 (d, $J = 12.0$ Hz, 1H, BOM), 4.35 (d, $J = 6.9$ Hz, 1H, BOM), 4.23 (d, $J = 7.2$ Hz, 1H, 3-H), 3.58 (dq, $J = 8.7, 6.3$ Hz, 1H, 8-H), 3.44 (d, $J = 1.8$ Hz, 1H, 5-H), 3.21 (dd, $J = 1.8, 8.7$ Hz, 1H, 7-H), 2.98 (dq, $J = 7.2, 7.5$ Hz, 1H, 2-H), 2.11 (ddq, $J = 1.8, 1.8, 6.9$ Hz, 1H, 6-H), 1.40 (d, $J = 6.9$ Hz, 3H, 6-Me), 1.27 (s, 3H, 4-Me), 1.14 (d, $J = 6.3$ Hz, 3H, 9-H), 1.08 (d, $J = 7.5$ Hz, 3H, 2-Me).

Determination of the stereochemistry of benzylidene acetal derived from **12**

***S*-Ethyl (E)-(2*S*,3*R*,6*R*,7*S*,8*R*)-3-(benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-2,4,6-trimethyl-4-nonenethioate:** To a solution of aldol **10a** (1.01 g, 1.94 mmol) in dichloromethane (19.4 mL) at 0 °C were added diisopropylethylamine (4.9 mL, 29.1 mmol) and benzyloxymethyl chloride (2.7 mL, 19.4 mmol). The reaction mixture was stirred for 11 h at 60 °C and then saturated aqueous ammonium chloride was added at 0 °C. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford ***S*-ethyl (E)-(2*S*,3*R*,6*R*,7*S*,8*R*)-3-(benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-2,4,6-trimethyl-4-nonenethioate** (1.19 g, 96%) as a colorless oil: IR (KBr): 1690 cm⁻¹; ¹H NMR (CDCl₃): 7.34-7.26 (m, 5H, Ph), 5.37 (dq, *J* = 10.0, 1.1 Hz, 1H, 5-H), 4.61 (d, *J* = 11.6 Hz, 1H, BOM), 4.54 (s, 2H, BOM), 4.34 (d, *J* = 11.6 Hz, 1H, BOM), 4.25 (d, *J* = 10.0 Hz, 1H, 3-H), 3.77 (dq, *J* = 2.4, 6.2 Hz, 1H, 8-H), 3.39 (dd, *J* = 2.4, 7.9 Hz, 1H, 7-H), 3.01-2.80 (m, 3H, SEt, 2-H), 2.48 (ddq, *J* = 7.9, 10.0, 6.8 Hz, 1H, 6-H), 1.54 (d, *J* = 1.1 Hz, 3H, 4-Me), 1.27 (t, *J* = 7.5 Hz, 3H, SEt), 1.02 (d, *J* = 6.2 Hz, 3H, 9-H), 0.98 (d, *J* = 7.3 Hz, 3H, 2-Me), 0.95 (d, *J* = 6.8 Hz, 3H, 6-Me), 0.91 (s, 9H, TBS), 0.85 (s, 9H, TBS), 0.10 (s, 3H, TBS), 0.06 (s, 3H, TBS), 0.01 (s, 3H, TBS), 0.00 (s, 3H, TBS); ¹³C NMR (CDCl₃): 202.4 (1), 137.9 (Ph), 136.5 (5), 129.5 (4), 128.2 (Ph), 128.2 (Ph), 127.4 (Ph), 90.3 (BOM), 83.3 (3), 81.4 (7), 70.6 (8), 69.0 (BOM), 50.8 (2), 36.4 (6), 26.2 (TBS), 26.0 (TBS), 23.3 (SEt), 18.6 (TBS), 18.3 (TBS), 17.7 (6-Me), 17.2 (9), 15.1 (2-Me), 14.8 (SEt), 10.5 (4-Me), -3.5 (TBS), -4.6 (TBS), -4.7 (TBS), -4.8 (TBS); HR MS: calcd for C₃₄H₆₂O₅SSi₂Na (M+Na⁺) 661.3749, found 661.3731.

(E)-(2*R*,3*R*,6*R*,7*S*,8*R*)-3-(Benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-2,4,6-trimethyl-4-nonen-1-ol: To a solution of ***S*-ethyl (E)-(2*S*,3*R*,6*R*,7*S*,8*R*)-3-(benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-2,4,6-trimethyl-4-nonenethioate** (1.19 g, 1.87 mmol) in toluene (18.7 mL) at 0 °C was added Red-Al[®] in toluene (65%, 2.24 mL, 7.46 mmol). After the reaction mixture had been stirred for 2 h at 0 °C, methanol was added. The

mixture was allowed to warm to room temperature and then saturated aqueous potassium sodium tartrate was added. The mixture was extracted with ethyl acetate, and the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford **(E)-(2R,3R,6R,7S,8R)-3-(benzyloxymethoxy)-7,8-di(tert-butyldimethylsiloxy)-2,4,6-trimethyl-4-nonen-1-ol** (1.00 g, 92%) as a colorless oil: IR (neat): 3461 cm^{-1} ; ^1H NMR (CDCl_3): 7.34-7.28 (m, 5H, Ph), 5.26 (dq, $J = 10.3, 1.1$ Hz, 1H, 5-H), 4.74 (d, $J = 11.9$ Hz, 1H, BOM), 4.65 (d, $J = 6.8$ Hz, 1H, BOM), 4.62 (d, $J = 6.8$ Hz, 1H, BOM), 4.52 (d, $J = 11.9$ Hz, 1H, BOM), 3.85 (d, $J = 9.7$ Hz, 1H, 3-H), 3.78 (dq, $J = 2.4, 6.2$ Hz, 1H, 8-H), 3.66 (d, $J = 5.1$ Hz, 2H, 1-H), 3.39 (dd, $J = 2.4, 8.4$ Hz, 1H, 7-H), 2.48 (ddq, $J = 8.4, 10.3, 6.5$ Hz, 1H, 6-H), 1.97 (dtq, $J = 9.7, 5.1, 7.0$ Hz, 1H, 2-H), 1.55 (d, $J = 1.1$ Hz, 3H, 4-Me), 1.03 (d, $J = 6.2$ Hz, 3H, 9-H), 0.94 (d, $J = 6.5$ Hz, 3H, 6-Me), 0.91 (s, 9H, TBS), 0.87 (s, 9H, TBS), 0.73 (d, $J = 7.0$ Hz, 3H, 2-Me), 0.11 (s, 3H, TBS), 0.06 (s, 3H, TBS), 0.03 (s, 3H, TBS), 0.02 (s, 3H, TBS); ^{13}C NMR (CDCl_3): 137.6 (Ph), 135.0 (5), 130.7 (4), 128.3 (Ph), 127.7 (Ph), 127.6 (Ph), 90.7 (BOM), 87.4 (3), 81.5 (7), 70.6 (8), 69.6 (BOM), 67.4 (1), 37.1 (2), 36.3 (6), 26.2 (TBS), 26.0 (TBS), 18.5 (TBS), 18.2 (TBS), 17.6 (6-Me), 17.1 (9), 13.8 (2-Me), 10.7 (4-Me), -3.5 (TBS), -4.6 (TBS), -4.8 (TBS), -4.8 (TBS); HR MS: calcd for $\text{C}_{32}\text{H}_{60}\text{O}_5\text{Si}_2\text{Na}$ ($\text{M}+\text{Na}^+$) 603.3871, found 603.3871.

(E)-(2R,3R,6R,7S,8R)-1-Acetoxy-3-(benzyloxymethoxy)-7,8-di(tert-butyldimethylsiloxy)-2,4,6-trimethyl-4-nonene (13): To a solution of **(E)-(2R,3R,6R,7S,8R)-3-(benzyloxymethoxy)-7,8-di(tert-butyldimethylsiloxy)-2,4,6-trimethyl-4-nonen-1-ol** (997 mg, 1.72 mmol) in pyridine (17.2 mL) at 0 °C were added DMAP (314 mg, 2.57 mmol) and acetic anhydride (0.41 mL, 4.29 mmol). The reaction mixture was stirred for 1 h at 0 °C and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with ethyl acetate, and the organic layer was washed with saturated aqueous copper(II) sulfate, saturated aqueous sodium hydrogencarbonate, water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography (eluant; hexane/ethyl acetate=20/1) to afford acetate **13** (999 mg, 93%) as a colorless oil: IR (neat): 1742 cm^{-1} ; ^1H NMR (CDCl_3): 7.36-7.22 (m, 5H, Ph), 5.29 (dq, $J = 10.3, 1.4$ Hz, 1H, 5-H),

4.68 (d, $J = 12.1$ Hz, 1H, BOM), 4.63 (d, $J = 6.8$ Hz, 1H, BOM), 4.58 (d, $J = 6.8$ Hz, 1H, BOM), 4.46 (d, $J = 12.1$ Hz, 1H, BOM), 4.32 (dd, $J = 10.8, 3.2$ Hz, 1H, 1-H), 4.13 (dd, $J = 10.8, 6.1$ Hz, 1H, 1-H), 3.81 (d, $J = 10.3$ Hz, 1H, 3-H), 3.80 (dq, $J = 2.4, 6.5$ Hz, 1H, 8-H), 3.40 (dq, $J = 8.1, 2.4$ Hz, 1H, 7-H), 2.49 (dddq, $J = 8.1, 10.3, 6.8$ Hz, 1H, 6-H), 2.03 (dddq, $J = 3.2, 6.1, 10.3, 7.0$ Hz, 1H, 2-H), 1.97 (s, 3H, Ac), 1.53 (d, $J = 1.4$ Hz, 3H, 4-Me), 1.04 (d, $J = 6.5$ Hz, 3H, 9-H), 0.95 (d, $J = 6.8$ Hz, 3H, 6-Me), 0.91 (s, 9H, TBS), 0.87 (s, 9H, TBS), 0.80 (d, $J = 7.0$ Hz, 3H, 2-Me), 0.11 (s, 3H, TBS), 0.07 (s, 3H, TBS), 0.03 (s, 3H, TBS), 0.02 (s, 3H, TBS); ^{13}C NMR (CDCl_3): 171.2 (Ac), 138.0 (Ph), 135.2 (5), 130.6 (4), 128.2 (Ph), 127.5 (Ph), 127.4 (Ph), 90.7 (BOM), 82.6 (3), 81.5 (7), 70.7 (8), 69.2 (BOM), 66.5 (1), 36.4 (6), 35.0 (2), 26.2 (TBS), 26.0 (TBS), 20.8 (Ac), 18.6 (TBS), 18.2 (TBS), 17.6 (6-Me), 17.2 (9), 14.0 (2-Me), 10.7 (4-Me), -3.5 (TBS), -4.6 (TBS), -4.7 (TBS), -4.8 (TBS); HR MS: calcd for $\text{C}_{34}\text{H}_{62}\text{O}_6\text{Si}_2\text{Na}$ ($\text{M}+\text{Na}^+$) 645.3977, found 645.3977.

(2R,3R,4S,5R,6R,7S,8R)-1-Acetoxy-3-(benzyloxymethoxy)-7,8-di(tert-butyltrimethylsiloxy)-4,5-dihydroxy-2,4,6-trimethylnonane (14) and (2R,3R,4R,5S,6R,7S,8R)-1-Acetoxy-3-(benzyloxymethoxy)-7,8-di(tert-butyltrimethylsiloxy)-4,5-dihydroxy-2,4,6-trimethylnonane (14''): To a solution of acetate **13** (536 mg, 0.860 mmol) in pyridine (3.0 mL) at 0 °C was added osmium tetroxide (346 mg, 1.36 mmol). After the reaction mixture was stirred for 48 h at room temperature, it was diluted with hexane and saturated with dried hydrogen sulfide gas. After the mixture was filtered through a short pad of Celite, and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford diols **14** (168 mg, 30%) and **14''** (200 mg, 35%) as pale yellow oils.

14: IR (neat): 3502, 1739 cm^{-1} ; ^1H NMR (CDCl_3): 7.35-7.32 (m, 5H, Ph), 4.82 (d, $J = 6.4$ Hz, 1H, BOM), 4.77 (d, $J = 6.4$ Hz, 1H, BOM), 4.70 (d, $J = 12.2$ Hz, 1H, BOM), 4.58 (d, $J = 12.2$ Hz, 1H, BOM), 4.36 (dd, $J = 11.0, 4.2$ Hz, 1H, 1-H), 3.97-3.83 (m, 2H, 1-H, 8-H), 3.94 (d, $J = 1.6$ Hz, 3-H), 3.65 (d, $J = 2.1$ Hz, 1H, 5-OH), 3.57 (dd, $J = 6.8, 3.0$ Hz, 1H, 7-H), 3.56 (d, $J = 2.1$ Hz, 1H, 5-H), 2.77 (s, 1H, 4-OH), 2.33-2.22 (m, 1H, 2-H), 2.05-2.00 (m, 1H, 6-H), 2.04 (s, 3H, Ac), 1.16 (d, $J = 6.5$ Hz, 3H, 9-H), 1.13 (d, $J = 7.3$ Hz, 3H, 2-Me), 1.13 (s, 3H, 4-Me), 1.05 (d, $J = 7.3$ Hz, 3H, 6-Me), 0.90 (s, 9H, TBS), 0.89 (s, 9H, TBS), 0.09 (s, 3H, TBS), 0.07 (s, 3H, TBS); ^{13}C NMR (CDCl_3): 171.2 (Ac),

137.5 (Ph), 128.5 (Ph), 127.7 (Ph), 127.7 (Ph), 97.5 (BOM), 87.7 (5), 81.2 (7), 71.2 (3), 70.5 (8), 70.5 (BOM), 67.4 (1), 38.4 (4), 33.1 (2), 26.1 (TBS), 25.9 (TBS), 21.0 (Ac), 21.0 (6), 20.0 (9), 18.7 (4-Me), 18.7 (TBS), 18.3 (TBS), 18.1 (2-Me), 10.5 (6-Me), -3.7 (TBS), -4.5 (TBS), -4.5 (TBS), -4.8 (TBS); HR MS: calcd for $C_{34}H_{64}O_8Si_2Na$ ($M+Na^+$) 679.4032, found 679.4022.

14'': IR (neat): 3448, 1741 cm^{-1} ; 1H NMR ($CDCl_3$): 7.38-7.28 (m, 5H, Ph), 4.93 (d, $J = 6.6$ Hz, 1H, BOM), 4.76 (d, $J = 6.6$ Hz, 1H, BOM), 4.73 (d, $J = 12.0$ Hz, 1H, BOM), 4.63 (d, $J = 12.0$ Hz, 1H, BOM), 4.35 (dd, $J = 11.1, 4.2$ Hz, 1H, 1-H), 4.05 (dd, $J = 2.1, 5.1$ Hz, 1H, 7-H), 3.88 (dq, $J = 11.1, 8.7$ Hz, 1H, 1-H), 3.81 (dq, $J = 5.1, 6.0$ Hz, 1H, 8-H), 3.70 (d, $J = 2.4$ Hz, 1H, 3-H), 3.55 (br s, 1H, 5-OH), 3.40 (d, $J = 6.6$ Hz, 1H, 5-H), 3.33 (br s, 1H, 4-OH), 2.21-2.17 (m, 2H, 2-H, 6-H), 2.05 (s, 3H, Ac), 1.22 (s, 3H, 4-Me), 1.18 (d, $J = 6.0$ Hz, 3H, 9-H), 1.11 (d, $J = 6.6$ Hz, 3H, 2-Me), 1.03 (d, $J = 6.9$ Hz, 3H, 6-Me), 0.90 (s, 9H, TBS), 0.88 (s, 9H, TBS), 0.11 (s, 3H, TBS), 0.11 (s, 3H, TBS), 0.06 (s, 3H, TBS), 0.06 (s, 3H, TBS); HR MS: calcd for $C_{34}H_{64}O_8Si_2Na$ ($M + Na^+$) 679.4032, found 679.4029.

Determination of the relative stereochemistry of **14** and **12**

(2*R*,3*R*,4*R*,5*R*,6*R*,7*S*,8*R*)-3-(Benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-2,4,6-trimethylnonan-1,4,5-triol: To a solution of diol **14** (1.2 mg, 1.8 μ mol) in methanol (0.1 mL) at 0 °C was added potassium carbonate (0.5 mg, 3.6 μ mol). The reaction mixture was stirred for 1.5 h at room temperature and then saturated aqueous ammonium chloride was added at 0 °C. The mixture was extracted with ethyl acetate and the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford **(2*R*,3*R*,4*R*,5*R*,6*R*,7*S*,8*R*)-3-(benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-2,4,6-trimethylnonan-1,4,5-triol**: (1.1 mg, quant.) as a colorless oil: 1H NMR (C_6D_6): 7.36-7.29 (m, 5H, Ph), 4.86 (s, 2H, BOM), 4.72 (d, $J = 12.0$ Hz, 1H, BOM), 4.60 (d, $J = 12.0$ Hz, 1H, BOM), 4.00-3.89 (m, 1H, 3-H), 3.93 (dq, $J = 3.5, 6.5$ Hz, 1H, 8-H), 3.69 (dd, $J = 11.3, 4.0$ Hz, 1H, 1-H), 3.66 (dd, J

= 11.3, 6.3 Hz, 1H, 1-H), 3.60 (d, J = 4.5 Hz, 1H, 5-H), 3.57 (dd, J = 3.5, 4.5 Hz, 1H, 7-H), 2.21-2.09 (m, 1H, 2-H), 2.08-1.98 (m, 1H, 6-H), 1.18 (d, J = 6.5 Hz, 3H, 9-H), 1.15 (s, 3H, 4-Me), 1.09 (d, J = 7.0 Hz, 3H, 2-Me), 1.05 (d, J = 7.5 Hz, 3H, 6-Me), 0.90 (s, 9H, TBS), 0.89 (s, 9H, TBS), 0.09 (s, 3H, TBS), 0.08 (s, 3H, TBS), 0.07 (s, 3H, TBS), 0.07 (s, 3H, TBS).

(2*R*,3*R*,4*R*,5*R*,6*R*,7*S*,8*R*)-3-(Benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-2,4,6-trimethylnonan-1,4,5-triol: To a solution of hydroxy lactone **12** (1.7 mg, 2.8 μ mol) in THF (0.4 mL) at 0 °C was added lithium aluminum hydride (0.3 mg, 7.0 μ mol). The reaction mixture was stirred for 40 min at 0 °C and then methanol and saturated aqueous potassium sodium tartrate were added at 0 °C. The mixture was extracted with ethyl acetate and the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford **(2*R*,3*R*,4*R*,5*R*,6*R*,7*S*,8*R*)-3-(benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-2,4,6-trimethylnonan-1,4,5-triol** (0.7 g, 41%) as a colorless oil.

Determination of the relative stereochemistry of **14''** and **12''**

(2*R*,3*R*,4*S*,5*S*,6*R*,7*S*,8*R*)-3-(Benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-2,4,6-trimethylnonan-1,4,5-triol: To a solution of diol **14''** (5.0 mg, 7.6 μ mol) in methanol (0.1 mL) at 0 °C was added potassium carbonate (2.1 mg, 15.2 μ mol). The reaction mixture was stirred for 1.5 h at room temperature and then saturated aqueous ammonium chloride was added at 0 °C. The mixture was extracted with ethyl acetate and the organic layer was washed with water and brine, dried

over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford **(2*R*,3*R*,4*S*,5*S*,6*R*,7*S*,8*R*)-3-(benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-2,4,6-trimethylnonan-1,4,5-triol** (4.1 mg, 87%) as a colorless oil: ^1H NMR (C_6D_6): 7.36-7.32 (m, 5H, Ph), 4.94 (d, $J = 6.6$ Hz, 1H, BOM), 4.84 (d, $J = 6.6$ Hz, 1H, BOM), 4.72 (d, $J = 12.0$ Hz, 1H, BOM), 4.67 (d, $J = 12.0$ Hz, 1H, BOM), 4.01 (dd, $J = 2.0, 4.7$ Hz, 1H, 7-H), 3.82 (dq, $J = 4.7, 6.3$ Hz, 1H, 8-H), 3.70 (d, $J = 3.0$ Hz, 1H, 5-H), 3.67 (dd, $J = 11.4, 6.9$ Hz, 1H, 1-H), 3.59 (dd, $J = 11.4, 4.1$ Hz, 1H, 1-H), 3.46 (d, $J = 7.2$ Hz, 1H, 3-H), 2.20-2.05 (m, 2H, 2-H, 6-H), 1.23 (s, 3H, 4-Me), 1.18 (d, $J = 6.3$ Hz, 3H, 9-H), 1.07 (d, $J = 6.9$ Hz, 3H, 6-Me), 1.02 (d, $J = 7.2$ Hz, 3H, 2-Me), 0.90 (s, 9H, TBS), 0.88 (s, 9H, TBS), 0.11 (s, 3H, TBS), 0.11 (s, 3H, TBS), 0.06 (s, 3H, TBS), 0.05 (s, 3H, TBS).

(2*R*,3*R*,4*S*,5*S*,6*R*,7*S*,8*R*)-3-(Benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-2,4,6-trimethylnonan-1,4,5-triol: To a solution of hydroxy lactone **12''** (2.7 mg, 4.4 μmol) in THF (0.4 mL) at 0 °C was added lithium aluminum hydride (0.4 mg, 11.0 μmol). The reaction mixture was stirred for 2 h at 0 °C and then methanol and saturated aqueous potassium sodium tartrate were added at 0 °C. The mixture was extracted with ethyl acetate and the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford **(2*R*,3*R*,4*S*,5*S*,6*R*,7*S*,8*R*)-3-(benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-2,4,6-trimethylnonan-1,4,5-triol** (0.7 g, 26%) as a colorless oil.

(2*R*,3*R*,4*R*,5*R*,6*R*,7*S*,8*R*)-1-Acetoxy-3-(benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-4,5-(cyclohexylidenedioxy)-2,4,6-trimethylnonane:

To a solution of diol **14** (85.4 mg, 0.130 mmol) and 1-methoxycyclohexene (233 mg, 2.08 mmol) in dichloromethane (1.6 mL) at room temperature was added CSA (12.1 mg, 52.0 μ mol). The reaction mixture was stirred for 8 h at room temperature and then saturated aqueous sodium hydrogencarbonate was added at 0 °C. The mixture was extracted with dichloromethane and the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford **(2*R*,3*R*,4*R*,5*R*,6*R*,7*S*,8*R*)-1-acetoxy-3-(benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-4,5-(cyclohexylidenedioxy)-2,4,6-trimethylnonane** (92.5 mg, 97%) as a colorless oil: IR (neat): 1741 cm^{-1} ; ^1H NMR (C_6D_6): 7.40 (d, J = 7.3 Hz, 2H, Ph), 7.23 (dd, J = 7.3, 7.3 Hz, 2H, Ph), 7.12 (dd, J = 7.3, 7.3 Hz, 1H, Ph), 4.86 (d, J = 6.5 Hz, 1H, BOM), 4.82 (dd, J = 10.8, 4.6 Hz, 1H, 1-H), 4.79 (d, J = 6.5 Hz, 1H, BOM), 4.76 (d, J = 12.2 Hz, 1H, BOM), 4.52 (d, J = 12.2 Hz, 1H, BOM), 4.29 (dd, J = 10.8, 10.8 Hz, 1H, 1-H), 4.11 (d, J = 1.9 Hz, 1H, 5-H), 3.93 (dq, J = 5.7, 5.7 Hz, 1H, 8-H), 3.73 (dd, J = 5.7, 3.8 Hz, 1H, 7-H), 3.57 (d, J = 2.7 Hz, 3-H), 2.56 (dddq, J = 2.7, 4.6, 10.8, 6.8 Hz, 1H, 2-H), 2.33 (ddq, J = 1.9, 3.8, 6.8 Hz, 1H, 6-H), 1.79-1.60 (m, 10H, *c*-Hex), 1.77 (s, 3H, Ac), 1.40 (s, 3H, 4-Me), 1.32 (d, J = 6.8 Hz, 3H, 2-Me), 1.28 (d, J = 5.7 Hz, 3H, 9-H), 1.26 (d, J = 6.8 Hz, 3H, 6-Me), 1.12 (s, 9H, TBS), 1.02 (s, 9H, TBS), 0.30 (s, 3H, TBS), 0.26 (s, 3H, TBS), 0.14 (s, 3H, TBS), 0.12 (s, 3H, TBS); ^{13}C NMR (C_6D_6): 170.3 (Ac), 138.3 (Ph), 128.6 (Ph), 127.9 (Ph), 127.9 (Ph), 107.9 (acetal), 97.6 (BOM), 88.7 (3), 86.1 (4), 83.1 (5), 82.2 (7), 70.8 (BOM), 70.6 (8), 67.5 (1), 39.0 (*c*-Hex), 37.2 (*c*-Hex), 35.9 (6), 34.6 (2), 26.6 (TBS), 26.2 (TBS), 25.5 (*c*-Hex), 24.4 (*c*-Hex), 24.2 (*c*-Hex), 20.6 (Ac), 20.2 (9), 19.6 (4-Me), 18.8 (TBS), 18.3 (TBS), 18.1 (2-Me), 10.3 (6-Me), -3.2 (TBS), -3.8 (TBS), -4.1 (TBS), -4.5 (TBS); HR MS: calcd for $\text{C}_{40}\text{H}_{72}\text{O}_8\text{Si}_2\text{Na}$ ($\text{M}+\text{Na}^+$) 759.4658, found 759.4640.

(2*R*,3*R*,4*R*,5*R*,6*R*,7*S*,8*R*)-3-(Benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-4,5-(cyclohexylidenedioxy)-2,4,6-trimethylnonan-1-ol:

To a solution of **(2*R*,3*R*,4*R*,5*R*,6*R*,7*S*,8*R*)-1-acetoxy-3-**

(benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-4,5-(cyclohexylidenedioxy)-2,4,6-trimethylnonane (67.9 mg, 92.1 μ mol) in methanol (1.3 mL) at 0 °C was added potassium carbonate (25.4 mg, 0.184 mmol). The reaction mixture was stirred for 12 h at room temperature and then water was added at 0 °C. The mixture was extracted with ethyl acetate and the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography and reprecipitation from dichloromethane/hexane to afford **(2*R*,3*R*,4*R*,5*R*,6*R*,7*S*,8*R*)-3-(benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-4,5-(cyclohexylidenedioxy)-2,4,6-trimethylnonanol** (57.5 mg, 90%) as a colorless oil: IR (neat): 3437 cm^{-1} ; ^1H NMR (C_6D_6): 7.35 (d, J = 7.0 Hz, 2H, Ph), 7.22 (dd, J = 7.0, 7.0 Hz, 2H, Ph), 7.12 (dd, J = 7.0, 7.0 Hz, 1H, Ph), 4.89 (d, J = 6.8 Hz, 1H, BOM), 4.87 (d, J = 6.8 Hz, 1H, BOM), 4.68 (d, J = 12.2 Hz, 1H, BOM), 4.47 (d, J = 12.2 Hz, 1H, BOM), 4.18 (d, J = 1.9 Hz, 1H, 5-H), 3.92 (dq, J = 5.3, 5.9 Hz, 1H, 8-H), 3.89 (dd, J = 4.3, 6.5 Hz, 2H, 1-H), 3.78 (dd, J = 3.2, 5.3 Hz, 1H, 7-H), 3.62 (d, J = 4.9 Hz, 1H, 3-H), 3.02 (t, J = 6.5 Hz, 1H, OH), 2.36 (ddq, J = 1.9, 3.2, 7.0 Hz, 1H, 6-H), 2.22 (dtq, J = 4.9, 4.3, 7.3 Hz, 1H, 2-H), 1.76-1.57 (m, 10H, *c*-Hex), 1.36 (s, 3H, 4-Me), 1.30 (d, J = 5.9 Hz, 9-H), 1.27 (d, J = 7.0 Hz, 6-Me), 1.24 (d, J = 7.3 Hz, 2-Me), 1.13 (s, 9H, TBS), 1.03 (s, 9H, TBS), 0.32 (s, 3H, TBS), 0.28 (s, 3H, TBS), 0.15 (s, 3H, TBS), 0.13 (s, 3H, TBS); ^{13}C NMR (C_6D_6): 138.1 (Ph), 128.7 (Ph), 127.9 (Ph), 127.8 (Ph), 107.9 (acetal), 97.7 (BOM), 88.5 (3), 86.3 (4), 82.5 (5), 82.4 (7), 70.8 (8), 70.6 (BOM), 65.2 (1), 39.0 (*c*-Hex), 37.5 (2), 37.0 (*c*-Hex), 35.8 (6), 26.6 (TBS), 26.2 (TBS), 25.4 (*c*-Hex), 24.5 (*c*-Hex), 24.2 (*c*-Hex), 20.5 (4-Me), 20.4 (9), 18.8 (TBS), 18.3 (TBS), 16.8 (2-Me), 10.1 (6-Me), -3.1 (TBS), -3.8 (TBS), -4.1 (TBS), -4.5 (TBS); HR MS: calcd for $\text{C}_{38}\text{H}_{70}\text{O}_7\text{Si}_2\text{Na}$ ($\text{M}+\text{Na}^+$) 717.4552, found 717.4534.

(2*S*,3*R*,4*R*,5*R*,6*R*,7*S*,8*R*)-3-(Benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-4,5-(cyclohexylidenedioxy)-2,4,6-trimethylnonanal: To a mixture of MS 4Å (115.5 mg) and **(2*R*,3*R*,4*R*,5*R*,6*R*,7*S*,8*R*)-3-(benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-4,5-(cyclohexylidenedioxy)-2,4,6-trimethylnonanol** (132.8 mg, 0.191 mmol) in

dichloromethane (3.8 mL) at room temperature was added NMO (70.0 mg, 0.598 mmol). After the reaction mixture had been stirred for 5 min at room temperature, TPAP (7.7 mg, 22.2 μ mol) was added at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and then it was filtered through a pre-cooled short pad of silica gel eluting with eluant (hexane/ethyl acetate=2/1). Evaporation of the solvent gave **(2*S*,3*R*,4*R*,5*R*,6*R*,7*S*,8*R*)-3-(benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-4,5-(cyclohexylidenedioxy)-2,4,6-trimethylnonanal** (131 mg, 99%) as a colorless oil. The product was instantly used in the following coupling reaction without further purification.

(2*S*,3*R*,4*R*,5*R*,6*R*,7*S*,8*R*)-3-(Benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-4,5-(cyclohexylidenedioxy)-2,4,6-trimethylnonanal: ^1H NMR (C_6D_6): 10.06 (d, $J = 1.4$ Hz, 1H, 1-H), 7.36-7.13 (m, 5H, Ph), 4.77 (d, $J = 6.9$ Hz, 1H, BOM), 4.72 (d, $J = 6.9$ Hz, 1H, BOM), 4.63 (d, $J = 12.2$ Hz, 1H, BOM), 4.43 (d, $J = 12.2$ Hz, 1H, BOM), 4.02 (d, $J = 3.0$ Hz, 1H, 5-H), 3.92 (dq, $J = 4.6, 5.9$ Hz, 1H, 8-H), 3.76 (d, $J = 2.4$ Hz, 1H, 3-H), 3.68 (dd, $J = 3.2, 4.6$ Hz, 1H, 7-H), 2.94 (ddq, $J = 1.4, 2.4, 7.3$ Hz, 1H, 2-H), 2.25 (ddq, $J = 3.0, 3.2, 6.8$ Hz, 1H, 6-H), 1.68-1.60 (m, 10H, *c*-Hex), 1.37 (s, 3H, 4-Me), 1.33 (d, $J = 7.3$ Hz, 3H, 2-Me), 1.26 (d, $J = 5.9$ Hz, 3H, 9-H), 1.24 (d, $J = 6.8$ Hz, 3H, 6-Me), 1.09 (s, 9H, TBS), 1.01 (s, 9H, TBS), 0.24 (s, 3H, TBS), 0.24 (s, 3H, TBS), 0.12 (s, 3H, TBS), 0.11 (s, 3H, TBS).

(2*S*,3*R*,4*R*,5*R*,6*R*,7*S*,8*R*)-3-(Benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-4,5-(cyclohexylidenedioxy)-2,4,6-trimethylnonanoic acid (15): To a solution of the crude **(2*S*,3*R*,4*R*,5*R*,6*R*,7*S*,8*R*)-3-(benzyloxymethoxy)-7,8-di(*tert*-butyldimethylsiloxy)-4,5-(cyclohexylidenedioxy)-2,4,6-trimethylnonanal** (131 mg, 0.189 mmol), *t*-butyl alcohol (1.9 mL), water (0.51 mL) and 2-methyl-2-butene (0.16 mL, 1.53 mmol) at room temperature was added sodium dihydrogen phosphate (22.8 mg, 0.191 mmol). The reaction mixture was stirred for 15 min at room temperature and then sodium chlorite (86.4 mg, 0.955 mmol) was added. After the reaction mixture was stirred for 12 h at room temperature, the solution was acidified

(pH=6) by 1 M hydrochloric acid at 0 °C. The mixture was extracted with diethyl ether, and the organic layer was dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford carboxylic acid **15** (123 mg, 92%) as a colorless oil: IR (neat): 1710 cm⁻¹; ¹H NMR (C₆D₆): 7.39 (d, *J* = 7.0 Hz, 2H, Ph), 7.25 (dd, *J* = 7.0, 7.3 Hz, 2H, Ph), 7.15 (dd, *J* = 7.3, 7.3 Hz, 1H, Ph), 4.91 (d, *J* = 6.8 Hz, 1H, BOM), 4.86 (d, *J* = 6.8 Hz, 1H, BOM), 4.77 (d, *J* = 12.1 Hz, 1H, BOM), 4.55 (d, *J* = 12.1 Hz, 1H, BOM), 4.07 (d, *J* = 2.7 Hz, 1H, 5-H), 4.02 (d, *J* = 4.3 Hz, 1H, 3-H), 3.93 (dq, *J* = 4.9, 6.0 Hz, 1H, 8-H), 3.71 (dd, *J* = 3.5, 4.9 Hz, 1H, 7-H), 3.21 (dq, *J* = 4.3, 7.0 Hz, 1H, 2-H), 2.32 (ddq, *J* = 2.7, 3.5, 5.9 Hz, 1H, 6-H), 1.77-1.62 (m, 6H, *c*-Hex), 1.51 (d, *J* = 7.0 Hz, 3H, 2-Me), 1.40 (s, 3H, 4-Me), 1.40-1.24 (m, 4H, *c*-Hex), 1.26 (d, *J* = 6.0 Hz, 3H, 9-H), 1.25 (d, *J* = 5.9 Hz, 3H, 6-Me), 1.11 (s, 9H, TBS), 1.02 (s, 9H, TBS), 0.28 (s, 3H, TBS), 0.25 (s, 3H, TBS), 0.14 (s, 3H, TBS), 0.12 (s, 3H, TBS); ¹³C NMR (C₆D₆): 178.4 (1), 138.2 (Ph), 128.6 (Ph), 128.1 (Ph), 128.0 (Ph), 108.6 (acetal), 96.8 (BOM), 85.8 (3), 85.6 (4), 84.0 (5), 81.9 (7), 70.8 (BOM), 70.7 (8), 43.2 (2), 38.9 (*c*-Hex), 36.5 (*c*-Hex), 35.5 (6), 26.5 (TBS), 26.2 (TBS), 25.4 (*c*-Hex), 24.4 (*c*-Hex), 24.2 (*c*-Hex), 20.3 (9), 19.3 (4-Me), 18.8 (TBS), 18.3 (TBS), 15.3 (2-Me), 10.4 (6-Me), -3.2 (TBS), -3.8 (TBS), -4.1 (TBS), -4.5 (TBS); HR MS: calcd for C₃₈H₆₈O₈Si₂Na (M+Na⁺) 731.4345, found 731.4320.

(2*S*,3*R*,4*R*,5*R*,6*R*,7*S*,8*R*)-3-(Benzyloxymethoxy)-7-(*tert*-butyldimethylsiloxy)-4,5-(cyclohexylidenedioxy)-8-hydroxy-2,4,6-trimethylnonanoic acid (16): To a solution of carboxylic acid **15** (123.3 mg, 0.174 mmol) in THF (1.2 mL) at 0 °C was added hydrogen fluoride-pyridine (hydrogen fluoride/pyridine = *ca.* 7/3, 0.35 mL). After the reaction mixture was stirred for 5 h at room temperature, the solution was acidified (pH=6) by 1 M hydrochloric acid at 0 °C. The mixture was extracted with diethyl ether and the organic layer was dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford seco-acid **16** (52.8 mg, 51%), dihydroxycarboxylic acid (14.0 mg, 17%) and recovered carboxylic acid **15** (16.2 mg, 13%) as colorless oils.

16: IR (neat): 3445, 1715 cm^{-1} ; ^1H NMR (C_6D_6): 7.36 (d, $J = 7.3$ Hz, 2H, Ph), 7.22 (dd, $J = 7.3, 7.8$ Hz, 2H, Ph), 7.12 (dd, $J = 7.8, 7.8$ Hz, 1H, Ph), 4.82 (d, $J = 6.5$ Hz, 1H, BOM), 4.76 (d, $J = 6.5$ Hz, 1H, BOM), 4.69 (d, $J = 12.1$ Hz, 1H, BOM), 4.49 (d, $J = 12.1$ Hz, 1H, BOM), 4.11 (d, $J = 2.2$ Hz, 1H, 5-H), 3.92 (d, $J = 3.5$ Hz, 1H, 3-H), 3.81 (dq, $J = 6.5, 5.9$ Hz, 1H, 8-H), 3.57 (dd, $J = 1.9, 6.5$ Hz, 1H, 7-H), 3.14 (dq, $J = 3.5, 7.3$ Hz, 1H, 2-H), 2.24 (ddq, $J = 1.9, 2.2, 7.3$ Hz, 1H, 6-H), 1.68-1.54 (m, 6H, *c*-Hex), 1.50 (d, $J = 7.3$ Hz, 3H, 2-Me), 1.36-1.22 (m, 4H, *c*-Hex), 1.33 (s, 3H, 4-Me), 1.29 (d, $J = 5.9$ Hz, 3H, 9-H), 1.29 (d, $J = 7.3$ Hz, 3H, 6-Me), 1.03 (s, 9H, TBS), 0.18 (s, 3H, TBS), 0.13 (s, 3H, TBS); ^{13}C NMR (C_6D_6): 177.0 (1), 138.0 (Ph), 128.6 (Ph), 128.1 (Ph), 127.6 (Ph), 108.7 (acetal), 96.6 (BOM), 85.7 (4), 85.0 (3), 82.9 (5), 81.4 (7), 70.7 (BOM), 70.3 (8), 42.8 (2), 38.6 (*c*-Hex), 36.8 (6), 36.2 (*c*-Hex), 26.3 (TBS), 25.2 (*c*-Hex), 24.3 (*c*-Hex), 24.2 (*c*-Hex), 20.3 (9), 19.5 (4-Me), 18.5 (TBS), 15.8 (2-Me), 11.7 (6-Me), -3.8 (TBS), -3.9 (TBS); HR MS: calcd for $\text{C}_{32}\text{H}_{54}\text{O}_8\text{SiNa}$ ($\text{M}+\text{Na}^+$) 617.3480, found 617.3466.

(2*S*,3*R*,4*R*,5*R*,6*R*,7*S*,8*R*)-3-(Benzyloxymethoxy)-7-(*tert*-butyldimethylsiloxy)-4,5-(cyclohexylidenedioxy)-2,4,6-trimethylnonan-8-olide (17) and its dimer (17-dimer): To a solution of MNBA (33.4 mg, 97.0 μmol), DMAP (23.3 mg, 0.191 mmol) in dichloromethane (9.0 mL) at room temperature was added a solution of seco-acid **16** (18.6 mg, 31.3 μmol) in dichloromethane (6.5 mL). After the reaction mixture had been stirred for 4 h at room temperature, saturated aqueous sodium hydrogencarbonate was added at 0 °C. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford lactone **17** (12.7 mg, 71%) and diolide **17-dimer** (1.4 mg, 7%) as colorless oils.

17: IR (neat): 1734 cm^{-1} ; ^1H NMR (C_6D_6): 7.35-7.10 (m, 5H, Ph), 5.36 (dq, $J = 8.4, 6.6$ Hz, 1H, 8-H), 5.01 (d, $J = 6.8$ Hz, 1H, BOM), 4.85 (d, $J = 6.8$ Hz, 1H, BOM), 4.77 (d, $J = 1.8$ Hz, 1H, 5-H), 4.71 (d, $J = 12.0$ Hz, 1H, BOM), 4.47 (d, $J = 12.0$ Hz, 1H, BOM), 3.87 (d, $J = 0.9$ Hz, 1H, 3-H), 3.68 (dd, $J = 8.4, 8.7$ Hz, 1H, 7-H), 3.14 (dq, $J = 0.9, 7.5$ Hz, 1H, 2-H), 2.18 (ddq, $J = 1.8, 8.7, 7.2$ Hz, 1H, 6-H), 1.83-1.56 (m, 10H, *c*-Hex), 1.33 (s, 3H, 4-Me), 1.32 (d, $J = 6.6$ Hz, 3H, 9-H), 1.28 (d, $J = 7.5$ Hz, 3H, 2-Me), 1.24 (d, $J = 7.2$ Hz, 3H, 6-Me), 0.99 (s, 9H, TBS), 0.14 (s, 3H, TBS), -0.04 (s, 3H, TBS); ^{13}C NMR (C_6D_6): 173.8 (1), 138.6 (Ph), 128.6 (Ph), 127.8 (Ph), 127.8 (Ph), 106.3 (acetal), 97.8 (BOM), 87.0 (4), 87.0 (3), 80.4 (7), 77.9 (5), 74.8 (8), 69.9 (BOM), 43.7 (2), 39.4 (*c*-Hex), 38.0 (6), 36.4 (*c*-Hex), 26.2 (TBS), 25.6 (*c*-Hex), 24.6 (*c*-Hex), 24.3 (*c*-Hex), 21.3 (4-Me), 19.0 (9), 18.3 (TBS), 16.2 (2-Me), 13.4 (6-Me), -3.2 (TBS), -4.0 (TBS); HR MS: calcd for $\text{C}_{32}\text{H}_{52}\text{O}_7\text{SiNa}$ ($\text{M}+\text{Na}^+$) 599.3375, found 599.3375.

Determination of the relative stereochemistry of lactone **17**

17-dimer: IR (neat): 1730 cm^{-1} ; ^1H NMR (C_6D_6): 7.35-7.12 (m, 10H, Ph), 5.25 (dq, $J = 6.3, 6.6$ Hz, 2H, 8-H), 5.18 (d, $J = 6.9$ Hz, 2H, BOM), 4.95 (d, $J = 6.9$ Hz, 2H, BOM), 4.80 (d, $J = 12.2$ Hz, 2H, BOM), 4.69 (d, $J = 2.4$ Hz, 2H, 5-H), 4.44 (d, $J = 12.2$ Hz, 2H, BOM), 3.71 (dd, $J = 6.3, 9.0$ Hz, 2H, 7-H), 3.67 (d, $J = 3.9$ Hz, 2H, 3-H), 2.69 (dq, $J = 3.9, 7.5$ Hz, 2H, 2-H), 2.07 (ddq, $J = 2.4, 9.0, 7.2$ Hz, 2H, 6-H), 1.69-1.64 (m, 20H, *c*-Hex), 1.49 (d, $J = 7.5$ Hz, 6H, 2-Me), 1.37 (d, $J = 6.6$ Hz, 6H, 9-H), 1.26 (d, $J = 7.2$ Hz, 6H, 6-Me), 1.09 (s, 6H, 4-Me), 0.98 (s, 18H, TBS), 0.14 (s, 6H, TBS), -0.01 (s, 6H, TBS); ^{13}C NMR (C_6D_6): 174.2 (1), 138.7 (Ph), 128.7 (Ph), 128.6 (Ph), 127.6 (Ph), 106.0 (acetal), 99.0 (BOM), 87.3 (4), 84.3 (3), 80.7 (7), 77.8 (5), 75.5 (8), 70.5 (BOM), 42.2 (2), 39.3 (*c*-Hex), 38.4 (6), 36.5 (*c*-Hex), 26.2 (TBS), 25.5 (*c*-Hex), 24.5 (*c*-Hex), 24.3 (*c*-Hex), 20.6 (4-Me), 19.1 (9),

18.3 (TBS), 16.3 (2-Me), 13.4 (6-Me), -3.3 (TBS), -4.0 (TBS); HR MS: calcd for $C_{64}H_{104}O_{14}Si_2Na$ ($M+Na^+$) 1175.6863, found 1175.6839.

18

(2*S*,3*R*,4*R*,5*R*,6*R*,7*S*,8*R*)-7-(*tert*-Butyldimethylsiloxy)-4,5-(cyclohexylidenedioxy)-3-hydroxy-2,4,6-trimethylnonan-8-olide: To a solution of lactone **17** (9.10 mg, 15.8 μ mol) in ethanol (0.32 mL) at room temperature was added palladium(II) hydroxide (1.8 mg, 12.6 μ mol). The reaction mixture was stirred for 15 h at room temperature under hydrogen atmosphere. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford hydroxy lactone **18** (7.3 mg, quant.) as a colorless oil: IR (neat): 3436, 1726 cm^{-1} ; 1H NMR (C_6D_6): 5.33 (dq, $J = 8.4, 6.6$ Hz, 1H, 8-H), 4.64 (d, $J = 1.6$ Hz, 1H, 5-H), 3.80 (br d, $J = 3.9$ Hz, 1H, 3-H), 3.65 (dd, $J = 8.4, 9.0$ Hz, 1H, 7-H), 3.03 (br q, $J = 7.6$ Hz, 1H, 2-H), 2.70 (br d, $J = 3.9$ Hz, 1H, OH), 2.16 (ddq, $J = 1.6, 9.0, 7.6$ Hz, 1H, 6-H), 1.69-1.55 (m, 10H, *c*-Hex), 1.30 (d, $J = 6.6$ Hz, 3H, 9-H), 1.21 (d, $J = 7.6$ Hz, 3H, 6-Me), 1.21 (d, $J = 7.6$ Hz, 3H, 2-Me), 1.18 (s, 3H, 4-Me), 0.99 (s, 9H, TBS), 0.14 (s, 3H, TBS), -0.03 (s, 3H, TBS); HR MS: calcd for $C_{24}H_{44}O_6SiNa$ ($M+Na^+$) 479.2799, found 479.2798.

19

(2*S*,4*S*,5*R*,6*R*,7*S*,8*R*)-7-(*tert*-Butyldimethylsiloxy)-4,5-(cyclohexylidenedioxy)-2,4,6-trimethyl-3-oxononan-8-olide (**19**): To a mixture of MS $4\text{\AA}$ (26.3 mg) and hydroxy lactone **18** (20.0 mg, 43.8 μ mol) in dichloromethane (0.88 mL) at room temperature was added NMO (15.3 mg, 0.131 mmol). After the reaction mixture had been stirred for 5 min at room temperature, TPAP (6.1 mg, 17.5 μ mol) was added at 0 $^{\circ}C$. The reaction mixture was stirred for 3 h at 0 $^{\circ}C$ and then it was filtered through a pre-cooled short pad of Silica gel 60N [spherical, neutral, Kanto Chem. Co., Inc.] with eluant (hexane/ethyl acetate=2/1). 1H NMR

spectra of the crude product shows the residue is a mixture of ketolactones **19** and its diastereomer 2-*epi*-**19** (**19**/2-*epi*-**19**=78/22).

19: ^1H NMR (C_6D_6): 5.14 (dq, $J = 7.0, 6.2$ Hz, 1H, 8-H), 4.66 (d, $J = 4.3$ Hz, 1H, 5-H), 3.63 (q, $J = 7.3$ Hz, 1H, 2-H), 3.52 (dd, $J = 7.0, 7.6$ Hz, 1H, 7-H), 2.22 (ddq, $J = 4.3, 7.6, 6.5$ Hz, 1H, 6-H), 2.02-1.59 (m, 10H, *c*-Hex), 1.42 (s, 3H, 4-Me), 1.30 (d, $J = 7.3$ Hz, 3H, 2-Me), 1.19 (d, $J = 6.5$ Hz, 3H, 6-Me), 1.17 (d, $J = 6.2$ Hz, 3H, 9-H), 0.96 (s, 9H, TBS), 0.08 (s, 3H, TBS), -0.02 (s, 3H, TBS).

2-*epi*-**19**

(2*R*,4*S*,5*R*,6*R*,7*S*,8*R*)-7-(*tert*-Butyldimethylsiloxy)-4,5-(cyclohexylidenedioxy)-2,4,6-trimethyl-3-oxononan-8-olide (2-*epi*-**19**): The crude mixture of ketolactones **19** and 2-*epi*-**19** (**19**/2-*epi*-**19**=78/22) was purified by thin layer chromatography to afford a mixture of ketolactones **19** and its diastereomer 2-*epi*-**19** (16.4 mg, 82%, **19**/2-*epi*-**19**=8/92) as a colorless oil.

2-*epi*-**19**: IR (neat): 1752, 1720 cm^{-1} ; ^1H NMR (C_6D_6): 4.93 (dq, $J = 6.6, 8.1$ Hz, 1H, 8-H), 4.17 (d, $J = 3.6$ Hz, 1H, 5-H), 3.40 (dd, $J = 8.1, 8.4$ Hz, 1H, 7-H), 3.28 (q, $J = 6.9$ Hz, 1H, 2-H), 2.33-2.27 (m, 1H, *c*-Hex), 2.11 (ddq, $J = 3.6, 8.4, 7.5$ Hz, 1H, 6-H), 1.93-1.69 (m, 9H, *c*-Hex), 1.34 (d, $J = 6.9$ Hz, 3H, 2-Me), 1.31 (s, 3H, 4-Me), 1.23 (d, $J = 7.5$ Hz, 3H, 6-Me), 1.09 (d, $J = 6.6$ Hz, 3H, 9-H), 0.95 (s, 9H, TBS), 0.04 (s, 3H, TBS), -0.10 (s, 3H, TBS); HR MS: calcd for $\text{C}_{24}\text{H}_{42}\text{O}_6\text{SiNa}$ ($\text{M}+\text{Na}^+$) 477.2643, found 477.2642.

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(2*R*,3*S*,4*R*,5*R*,6*R*,7*S*,8*R*)-7-(*tert*-Butyldimethylsiloxy)-4,5-(cyclohexylidenedioxy)-3-hydroxy-2,4,6-trimethylnonan-8-olide: To a mixture of ketolactones **19** and 2-*epi*-**19** (16.4 mg, 36.1 μmol , **19**/2-*epi*-**19**=8/92) in methanol (0.72 mL) at 0 $^\circ\text{C}$ was added sodium borohydride (5.4 mg, 0.144 mmol). The

reaction mixture was stirred for 2 h at 0 °C and then saturated aqueous ammonium chloride was added. The mixture was extracted with ethyl acetate, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford hydroxy lactone **20** (11.7 mg, 77% from 2-*epi*-**19**) and hydroxy lactone **18** (0.7 mg, 50% from **19**) as colorless oils.

20; IR (neat): 3421, 1734 cm^{-1} ; ^1H NMR (C_6D_6): 5.21 (dq, $J = 6.5, 7.8$ Hz, 1H, 8-H), 4.53 (d, $J = 2.2$ Hz, 1H, 5-H), 3.62 (dd, $J = 7.8, 9.2$ Hz, 1H, 7-H), 3.58 (dd, $J = 3.8, 5.1$ Hz, 1H, 3-H), 2.61 (dq, $J = 3.8, 7.6$ Hz, 1H, 2-H), 2.32 (d, $J = 5.1$ Hz, 1H, OH), 2.01 (ddq, $J = 2.2, 9.2, 7.3$ Hz, 1H, 6-H), 1.74-1.51 (m, 10H, *c*-Hex), 1.41 (d, $J = 7.6$ Hz, 3H, 2-Me), 1.28 (d, $J = 6.5$ Hz, 3H, 9-H), 1.24 (d, $J = 7.3$ Hz, 3H, 6-Me), 1.08 (s, 3H, 4-Me), 0.97 (s, 9H, TBS), 0.12 (s, 3H, TBS), 0.04 (s, 3H, TBS); HR MS: calcd for $\text{C}_{24}\text{H}_{44}\text{O}_6\text{SiNa}$ ($\text{M}+\text{Na}^+$) 479.2799, found 479.2801.

Determination of the relative stereochemistry of hydroxy lactone **20**

(2*R*,3*S*,4*R*,5*R*,6*R*,7*S*,8*R*)-7-(*tert*-Butyldimethylsiloxy)-4,5-(cyclohexyldenedioxy)-2,4,6-trimethyl-3-(tetrahydro-2*H*-pyran-2-yloxy)nonan-8-olide: To a solution of hydroxy lactone **20** (5.3 mg, 11.6 μmol) and 3,4-dihydro-2*H*-pyran (2.00 mg, 23.2 μmol) in dichloromethane (0.12 mL) at room temperature was added CSA (0.3 mg, 1.16 μmol). The reaction mixture had been stirred for 1 h at room temperature and then saturated aqueous sodium hydrogencarbonate was

added at 0 °C. The mixture was extracted with dichloromethane and the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford **(2*R*,3*S*,4*R*,5*R*,6*R*,7*S*,8*R*)-7-(tert-butyldimethylsiloxy)-4,5-(cyclohexylidenedioxy)-2,4,6-trimethyl-3-(tetrahydro-2*H*-pyran-2-yloxy)nonan-8-olide** (5.4 mg, 86%) as a colorless oil: IR (neat): 1733 cm⁻¹; ¹H NMR (C₆D₆): 5.24 (dq, *J* = 7.8, 6.6 Hz, 1H, 8-H), 4.98 (dd, *J* = 2.1, 8.4 Hz, 1H, THP), 4.69 (d, *J* = 2.1 Hz, 1H, 5-H), 4.07 (d, *J* = 3.6 Hz, 1H, 3-H), 3.85 (dt, *J* = 11.1, 4.1 Hz, 1H, THP), 3.71 (dd, *J* = 7.8, 9.3 Hz, 1H, 7-H), 3.25 (dt, *J* = 11.1, 2.4 Hz, 1H, THP), 2.78 (dq, *J* = 3.6, 7.2 Hz, 1H, 2-H), 2.09 (ddq, *J* = 2.1, 9.3, 7.2 Hz, 1H, 6-H), 1.97 (d, *J* = 13.2 Hz, 1H, THP), 1.81 (t, *J* = 6.0 Hz, 2H, *c*-Hex), 1.72-1.59 (m, 8H, THP, *c*-Hex), 1.68 (d, *J* = 7.2 Hz, 3H, 2-Me), 1.41-1.26 (m, 5H, THP, *c*-Hex), 1.36 (d, *J* = 6.6 Hz, 3H, 9-H), 1.27 (d, *J* = 7.2 Hz, 3H, 6-Me), 1.13 (s, 3H, 4-Me), 0.98 (s, 9H, TBS), 0.13 (s, 3H, TBS), -0.07 (s, 3H, TBS); HR MS: calcd for C₂₉H₅₂O₇SiNa (M+Na⁺) 563.3375, found 563.3375.

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(2*R*,3*S*,4*R*,5*R*,6*R*,7*S*,8*R*)-4,5-(Cyclohexylidenedioxy)-7-hydroxy-2,4,6-trimethyl-3-(tetrahydro-2*H*-pyran-2-yloxy)nonan-8-olide (21): To a solution of **(2*R*,3*S*,4*R*,5*R*,6*R*,7*S*,8*R*)-7-(tert-butyldimethylsiloxy)-4,5-(cyclohexylidenedioxy)-2,4,6-trimethyl-3-(tetrahydro-2*H*-pyran-2-yloxy)nonan-8-olide** (7.2 mg, 13.3 μmol) in THF (0.27 mL) at 0 °C was added a solution of TBAF in THF (1.0 M, 0.03 mL, 30 μmol). After the reaction mixture had been stirred for 3 h at 0 °C, saturated aqueous ammonium chloride was added. The mixture was extracted with ethyl acetate, and the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford hydroxy lactone **21** (5.6 mg, 98%) as a colorless oil: IR (neat): 3446, 1725 cm⁻¹; ¹H NMR (C₆D₆): 5.12 (dq, *J* = 8.4, 6.5 Hz, 1H, 8-H), 4.95 (dd, *J* = 2.0, 8.0 Hz, 1H, THP), 4.50 (d, *J* = 2.4 Hz, 1H, 5-H), 4.05 (d, *J* = 4.1 Hz, 1H, 3-H), 3.84 (dd, *J* = 10.8, 2.2 Hz, 1H, THP), 3.28 (dd, *J* = 8.4, 8.4 Hz, 1H, 7-H), 3.24 (dd, *J* = 10.8, 2.7 Hz, 1H, THP), 2.75 (dq, *J* = 4.1, 7.3 Hz, 1H, 2-H), 1.95-1.88 (m, 2H, 6-H, THP), 1.80-1.59 (m, 10H, THP, *c*-Hex), 1.63 (d, *J* = 7.3 Hz, 3H, 2-Me), 1.37-1.26 (m, 5H,

THP, *c*-Hex), 1.32 (d, $J = 6.5$ Hz, 3H, 9-H), 1.13 (d, $J = 7.3$ Hz, 3H, 6-Me), 1.11 (s, 3H, 4-Me); HR MS: calcd for $C_{23}H_{38}O_7Na$ ($M+Na^+$) 449.2510, found 449.2516.

(*E*)-(R)-4-(tert-Butyldimethylsiloxy)-2-octenoic acid (28): IR (neat): 1698, 1656 cm^{-1} ; 1H NMR ($CDCl_3$): 7.05 (ddd, $J = 0.8, 4.6, 15.7$ Hz, 1H, 3-H), 5.99 (ddd, $J = 0.7, 1.9, 15.7$ Hz, 1H, 2-H), 4.35-4.30 (m, 1H, 4-H), 1.59-1.51 (m, 2H, 5-H), 1.34-1.25 (m, 4H, 6-H, 7-H), 0.96-0.87 (m, 3H, 8-H), 0.91 (s, 9H, TBS), 0.06 (s, 3H, TBS), 0.04 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): 172.0 (1), 135.5 (3), 119.4 (2), 71.5 (4), 36.9 (5), 26.9 (6), 25.8 (TBS), 25.6 (TBS), 22.7 (7), 14.0 (8), -4.6 (TBS), -4.9 (TBS); HR MS: calcd for $C_{14}H_{28}O_3SiNa$ ($M+Na^+$) 295.1700, found 295.1693.

(2*R*,3*S*,4*R*,5*R*,6*R*,7*S*,8*R*)-4,5-(Cyclohexylidenedioxy)-2,4,6-trimethyl-3-(tetrahydro-2*H*-pyran-2-yloxy)nonan-8-olid-7-yl (E)-(R)-4-(tert-butyldimethylsiloxy)-2-octenoate: To a solution of the side chain **28** (3.6 mg, 14.2 μ mol) in dichloromethane (0.1 mL) were added MNBA (10.2 mg, 29.6 μ mol), a solution of DMAP (0.2 mg, 2.0 μ mol) in dichloromethane (0.05 mL) and triethylamine (6.0 mg, 59.1 μ mol) in dichloromethane (0.05 mL). After the reaction mixture had been stirred for 10 min, a solution of hydroxy lactone **21** (3.7 mg, 8.7 μ mol) in dichloromethane (0.1 mL) was added. The reaction mixture had been stirred for 3.5 h at room temperature and then saturated aqueous ammonium chloride was added at 0 °C. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford the title coupling product **(2*R*,3*S*,4*R*,5*R*,6*R*,7*S*,8*R*)-4,5-(cyclohexylidenedioxy)-2,4,6-trimethyl-3-(tetrahydro-2*H*-pyran-2-yloxy)nonan-8-olid-7-yl (E)-(R)-4-(tert-butyldimethylsiloxy)-2-octenoate** (5.1 mg, 86%) as a colorless oil: IR (neat): 1732, 1717 cm^{-1} ; 1H NMR (C_6D_6): 7.20

(dd, $J = 4.8, 15.6$ Hz, 1H, 3'-H), 6.34 (dd, $J = 1.5, 15.6$ Hz, 1H, 2'-H), 5.52-5.45 (m, 2H, 7-H, 8-H), 4.95 (dd, $J = 1.8, 7.8$ Hz, 1H, THP), 4.74 (d, $J = 2.4$ Hz, 1H, 5-H), 4.13-4.08 (m, 1H, 4'-H), 4.06 (d, $J = 3.6$ Hz, 1H, 3-H), 3.84 (br d, $J = 11.7$ Hz, 1H, THP), 3.23 (dt, $J = 11.7, 2.4$ Hz, 1H, THP), 2.76 (dq, $J = 3.6, 7.5$ Hz, 1H, 2-H), 2.32-2.21 (m, 1H, 6-H), 1.89 (d, $J = 10.5$ Hz, 1H, THP), 1.67-1.50 (m, 9H, THP, *c*-Hex), 1.62 (d, $J = 7.5$ Hz, 3H, 2-Me), 1.48-1.39 (m, 18H, 6-Me, 9-H, 5'-H, 6'-H, 7'-H, *c*-Hex), 1.10 (s, 3H, 4-Me), 1.01 (s, 9H, TBS), 0.87 (t, $J = 7.2$ Hz, 3H, 8'-H), 0.08 (s, 3H, TBS), 0.06 (s, 3H, TBS); HR MS: calcd for $C_{37}H_{64}O_9SiNa$ ($M+Na^+$) 703.4212, found 703.4227.

(2*R*,3*S*,4*R*,5*R*,6*R*,7*S*,8*R*)-4,5-(Cyclohexylidenedioxy)-3-hydroxy-2,4,6-trimethylnonan-8-olid-7-yl (E)-(R)-4-hydroxy-2-octenoate (29): To a solution of **(2*R*,3*S*,4*R*,5*R*,6*R*,7*S*,8*R*)-4,5-(cyclohexylidenedioxy)-2,4,6-trimethyl-3-(tetrahydro-2*H*-pyran-2-yloxy)nonan-8-olid-7-yl (E)-(R)-4-(*tert*-butyldimethylsiloxy)-2-octenoate** (4.6 mg, 6.8 μ mol) in THF (0.14 mL) at 0 °C was added hydrogen fluoride·pyridine (hydrogen fluoride/pyridine = *ca.* 7/3, 3 drops). The reaction mixture was stirred for 3 h at room temperature and then saturated aqueous sodium hydrogencarbonate was added at 0 °C. The mixture was extracted with ethyl acetate and the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford diol **29** (2.8 mg, 85%) as a colorless oil: IR (neat): 1732, 1719 cm^{-1} ; 1H NMR (C_6D_6): 7.05 (dd, $J = 4.2, 15.6$ Hz, 1H, 3'-H), 6.20 (dd, $J = 1.8, 15.6$ Hz, 1H, 2'-H), 5.51-5.38 (m, 2H, 7-H, 8-H), 4.65 (d, $J = 2.1$ Hz, 1H, 5-H), 3.83-3.75 (m, 1H, 4'-H), 3.57 (dd, $J = 3.9, 4.5$ Hz, 1H, 3-H), 2.61 (dq, $J = 3.9, 7.5$ Hz, 1H, 2-H), 2.30 (d, $J = 4.5$ Hz, 1H, 3-OH), 2.29-2.11 (m, 1H, 6-H), 1.76-1.49 (m, 4H, *c*-Hex), 1.43-1.10 (m, 12H, 5'-H, 6'-H, 7'-H, *c*-Hex), 1.37 (d, $J = 7.5$ Hz, 3H, 2-Me), 1.25 (d, $J = 7.2$ Hz, 3H, 6-Me), 1.24 (d, $J = 6.0$ Hz, 3H, 9-H), 1.08 (s, 3H, 4-Me), 0.83 (t, $J = 6.9$ Hz, 3H, 8'-H); 1H NMR (CD_3OD): 6.90 (dd, $J = 4.5, 15.6$ Hz, 1H, 3'-H), 5.93 (dd, $J = 1.8, 15.6$ Hz, 1H, 2'-H), 4.89 (dq, $J = 6.3, 6.0$ Hz, 1H, 8-H), 4.84 (dd, $J = 6.3, 9.6$ Hz, 1H, 7-H), 4.26 (d,

$J = 2.4$ Hz, 1H, 5-H), 4.16-4.10 (m, 1H, 4'-H), 3.56 (d, $J = 3.6$ Hz, 1H, 3-H), 2.61 (dq, $J = 3.6, 7.2$ Hz, 1H, 2-H), 1.81 (ddq, $J = 2.4, 9.6, 7.2$ Hz, 1H, 6-H), 1.55-1.39 (m, 10H, *c*-Hex), 1.36-1.11 (m, 6H, 5'-H, 6'-H, 7'-H), 1.21 (d, $J = 7.2$ Hz, 3H, 2-Me), 1.17 (d, $J = 6.0$ Hz, 3H, 9-H), 0.98 (s, 3H, 4-Me); 0.80 (t, $J = 6.9$ Hz, 3H, 8'-H) 0.77 (d, $J = 7.2$ Hz, 3H, 6-Me); ^{13}C NMR (C_6D_6): 174.3 (1), 165.7 (1'), 152.2 (3'), 119.3 (2'), 106.0 (acetal), 86.4 (4), 79.0 (3), 76.2 (8), 75.9 (5), 72.0 (7), 70.8 (4'), 41.5 (2), 39.1 (*c*-Hex), 36.4 (6), 36.1 (5'), 36.0 (*c*-Hex), 27.6 (6'), 25.4 (*c*-Hex), 24.3 (*c*-Hex), 24.0 (*c*-Hex), 22.8 (4-Me), 19.6 (7'), 18.5 (9), 15.6 (2-Me), 14.1 (8'), 11.9 (6-Me); ^{13}C NMR (CDCl_3): 174.5 (1), 165.7 (1'), 151.5 (3'), 119.3 (2'), 105.9 (acetal), 85.9 (4), 78.6 (3), 76.0 (8), 75.3 (5), 72.0 (7), 71.1 (4'), 41.0 (2), 38.7 (*c*-Hex), 36.4 (6), 35.7 (5'), 35.4 (*c*-Hex), 27.3 (6'), 25.1 (*c*-Hex), 24.0 (*c*-Hex), 23.7 (*c*-Hex), 22.5 (4-Me), 19.4 (7'), 18.6 (9), 15.5 (2-Me), 14.0 (8'), 11.4 (6-Me); HR MS: calcd for $\text{C}_{26}\text{H}_{42}\text{O}_8\text{Na}$ ($\text{M}+\text{Na}^+$) 505.2772, found 505.2783.

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(1*R*,2*R*,3*S*,4*R*)-1,4-Dihydroxy-1-[(2*R*,3*S*,4*S*)-3-hydroxy-2,4-dimethylbutanolid-4-yl]-2-methylpentan-3-yl (E)-(R)-4-hydroxy-2-octenoate (23): To a solution of diol **29** (1.5 mg, 3.1 μmol) in dichloromethane (0.15 mL) at -45°C was added a solution of boron tribromide in dichloromethane (1.0 M, 2 drops, *ca.* 10 μmol). The reaction mixture was stirred for 1.5 h at -45°C and then it was filtered through a pre-cooled short pad of silica gel eluting with ethyl acetate. After evaporation of the solvent, the crude product was purified by thin layer chromatography to afford γ -lactone **30** (0.6 mg, 48%) as a colorless oil: IR (neat): 3437, 1732, 1728 cm^{-1} ; ^1H NMR (CD_3OD): 6.89 (dd, $J = 5.0, 15.5$ Hz, 1H, 3'-H), 5.96 (dd, $J = 2.0, 15.5$ Hz, 1H, 2'-H), 4.53 (dd, $J = 6.0, 7.5$ Hz, 1H, 7-H), 4.21 (d, $J = 7.0$ Hz, 1H, 3-H), 4.19-4.13 (m, 1H, 4'-H), 3.84 (dq, $J = 6.0, 6.0$ Hz, 1H, 8-H), 3.64 (d, $J = 1.5$ Hz, 1H, 5-H), 3.08 (dq, $J = 7.0, 7.0$ Hz, 1H, 2-H), 2.35 (ddq, $J = 1.5, 7.5, 7.5$ Hz, 1H, 6-H), 1.33 (s, 3H, 4-Me), 1.31-1.17 (m, 6H, 5'-H, 6'-H, 7'-H), 1.08 (d, $J = 6.0$ Hz, 3H, 9-H), 1.07 (d, $J = 7.0$ Hz, 3H, 2-Me), 0.94 (d, $J = 7.5$ Hz, 3H, 6-Me), 0.85 (t, $J = 7.0$ Hz, 3H, 8'-H); HR MS: calcd for $\text{C}_{20}\text{H}_{34}\text{O}_8\text{Na}$ ($\text{M}+\text{Na}^+$) 425.2146, found 425.2159.

(2*R*,3*S*,4*R*,5*R*,6*R*,7*S*,8*R*)-4,5-(Isopropylidenedioxy)-3-hydroxy-2,4,6-trimethylnonan-8-olid-7-yl (*E*)-(R)-4-hydroxy-2-octenoate:

^1H NMR (CD_3OD): 7.03 (dd, $J = 4.8, 15.6$ Hz, 1H, 3'-H), 6.06 (dd, $J = 1.2, 15.6$ Hz, 1H, 2'-H), 5.01 (dq, $J = 6.6, 7.2$ Hz, 1H, 8-H), 4.83 (dd, $J = 6.6, 7.2$ Hz, 1H, 7-H), 4.43 (d, $J = 2.4$ Hz, 1H, 5-H), 4.28-4.24 (m, 1H, 4'-H), 3.68 (d, $J = 3.6$ Hz, 1H, 3-H), 2.74 (dq, $J = 3.6, 7.2$ Hz, 1H, 2-H), 1.95 (ddq, $J = 2.4, 7.2, 7.2$ Hz, 1H, 6-H), 1.40 (s, 3H, acetonide), 1.37 (s, 3H, acetonide), 1.35 (d, $J = 7.2$ Hz, 3H, 2-Me), 1.31-1.29 (m, 6H, 5'-H, 6'-H, 7'-H), 1.19 (d, $J = 7.2$ Hz, 3H, 9-H), 1.11 (s, 3H, 4-Me), 0.93 (t, $J = 7.2$ Hz, 3H, 8'-H), 0.88 (d, $J = 7.2$ Hz, 3H, 6-Me); ^{13}C NMR (CD_3OD): 176.4 (1), 167.4 (1'), 154.1 (3'), 119.8 (2'), 106.7 (acetonide), 87.8 (4), 80.0 (3), 77.5 (8), 76.8 (5), 73.1 (7), 71.6 (4'), 43.1 (2), 37.2 (5'), 36.9 (6), 29.1 (acetonide-Me), 28.7 (6'), 26.7 (acetonide-Me), 23.6 (4-Me), 20.3 (7'), 18.3 (9), 15.9 (2-Me), 14.4 (8'), 11.9 (6-Me); HR MS: calcd for $\text{C}_{23}\text{H}_{38}\text{O}_8\text{Na}$ ($\text{M}+\text{Na}^+$) 465.2459, found 465.2451.

(1*S*,2*R*,3*S*,4*R*)-1,4-Dihydroxy-1-[(2*R*,3*S*,4*R*)-3-hydroxy-2,4-dimethylbutanolid-4-yl]-2-methylpentan-3-yl (*E*)-(R)-4-hydroxy-2-octenoate:

a colorless oil: IR (neat): 3418, 1747, 1716 cm^{-1} ; ^1H NMR (CD_3OD): 6.89 (dd, $J = 5.0, 15.5$ Hz, 1H, 3'-H), 5.96 (dd, $J = 1.5, 15.5$ Hz, 1H, 2'-H), 5.22 (dd, $J = 2.0, 7.0$ Hz, 1H, 7-H), 4.21 (d, $J = 6.5$ Hz, 1H, 3-H), 4.19-4.15 (m, 1H, 4'-H), 3.77 (dq, $J = 7.0, 6.5$ Hz, 1H, 8-H), 3.33 (d, $J = 5.0$ Hz, 1H, 5-H), 3.09 (dq, $J = 6.5, 7.5$ Hz, 1H, 2-H), 2.35 (ddq, $J = 2.0, 5.0, 7.5$ Hz, 1H, 6-H), 1.54-1.46 (m, 2H, 5'-H), 1.39-1.22 (m, 4H, 6'-H, 7'-H), 1.32 (s, 3H, 4-Me), 1.10 (d, $J = 6.5$ Hz, 3H, 9-H), 1.09 (d, $J = 7.5$ Hz, 3H, 2-Me), 1.04 (d, $J = 7.5$ Hz, 3H, 6-Me); 0.87 (t, $J = 7.0$ Hz, 3H, 8'-H); ^{13}C NMR (CD_3OD): 181.8 (1), 168.2 (1'), 152.8 (3'), 120.9 (2'),

93.6 (4), 78.3 (5), 77.7 (3), 74.3 (7), 71.6 (4'), 68.5 (8), 41.9 (2), 37.3 (5'), 36.3 (6), 28.7 (6'), 23.6 (9), 19.7 (7'), 17.7 (4-Me), 14.3 (8'), 13.8 (6-Me), 9.2 (2-Me); HR MS: calcd for $C_{20}H_{34}O_8Na$ ($M+Na^+$) 425.2146, found 425.2173.

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ACQTM 0.0000 sec
PD 0.0000 sec
PW1 11.70 usec
IRNUC OFF
CTEMP 22.9 c
SLVNT C6D6
EXREF 7.20 ppm
BF 0.25 Hz
RGAIN 813

F:\NMR(ALS)\RS-43-TM.als
rs-43-tm

DFILE F:\NMR(ALS)\RS-43-TM.ε
COMNT rs-43-tm
DATIM 2006/Sep/06 12:12:54
OBNUC 1H
EXMOD ZG30
OBFRQ 300.01 MHz
OBSET 0.00 KHz
OBFIN 1842.92 Hz
POINT 32768
FREQU 6172.84 Hz
SCANS 16
ACQTM 0.0000 sec
PD 0.0000 sec
PW1 11.70 usec
IRNUC OFF
CTEMP 22.9 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.25 Hz
RGAIN 1024

F:\NMR(ALS)\RS-42-TM.als
rs-42-tm

DFILE F:\NMR(ALS)\RS-42-TM.ε
COMNT rs-42-tm
DATIM 2006/Sep/06 12:06:00
OBNUC 1H
EXMOD ZG30
OBFRQ 300.01 MHz
OBSET 0.00 KHz
OBFIN 1842.92 Hz
POINT 32768
FREQU 6172.84 Hz
SCANS 16
ACQTM 0.0000 sec
PD 0.0000 sec
PW1 11.70 usec
IRNUC OFF
CTEMP 22.9 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.25 Hz
RGAIN 912

C:\WINNR98\DATA\AutoINON EI_FT.als
 194 Cyclohex
 DFIL 194 Cyclohex
 COM1 194 Cyclohex
 DATI Wed Aug 31 18:13:07 2005
 EXMOD NON
 OBNUC 1H
 OBFRQ 270.05 MHz
 OBSET 112.00 KHz
 OBFIN 5800.0 Hz
 POINT 32768
 FREQU 5405.4 Hz
 CLPNT 1
 TODAT 1
 CLFRQ 100.0 Hz
 SCANS 8
 ACQTM 6.062 sec
 PD 0.935 sec
 FW1 6.0 us
 FW2 10.0 us
 FW3 10.0 us
 FI1 1.000 ms
 FI2 1.000 ms
 FI3 1.00 ms
 TRNUC 1H
 CTEMP 22.0 C
 SILVNT C6D6
 EXREF 7.20 ppm
 CLEXP 0.00
 RGAIN 13
 ORATN 511
 LOOP1 1

C:\Documents and Settings\A-E\ffjXfNfgbfv\4, @, .E\NMR\cyclohexilidene-CHO\AutolNON_E1_FT.als
176 CHO

DFILE C:\Documents and Settj
COMNT 176 CHO
DATIM Mon Aug 01 19:34:24 20
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.00 Hz
POINT 32768
FREQU 5405.40 Hz
SCANS 16
ACQTM 6.0621 sec
PD 0.9350 sec
PW1 6.00 usec
IRNUC 1H
CTEMP 22.0 C
SLVNT C6D6
EXREF 7.20 ppm
BF 0.12 Hz
RGAIN 17

E:\cyclohexilidene-COOH\Auto1NON_E1_FT.als
26 COOH

DFILE E:\cyclohexilidene-COOH
 COMNT 26 COOH
 DATIM Tue Oct 11 13:49:28 2004
 OBNUC 1H
 EXMOD NON
 OBFRQ 270.05 MHz
 OBSET 112.00 KHz
 OBFIN 5800.00 Hz
 POINT 32768
 FREQU 5405.40 Hz
 SCANS 8
 ACQTM 6.0621 sec
 PD 0.9350 sec
 PW1 6.00 usec
 IRNUC 1H
 CTEMP 22.3 c
 SLVNT C6D6
 EXREF 7.26 ppm
 BF 0.12 Hz
 RGAIN 12

C:\WINNR98\TEMPDATA\Auto2BCM_EI_FT.als
28-1 9-membered lacton

C:\WINNR98\TEMPDATA\Auto2BCM_EI_F
28-1 9-membered lacton
Sat Oct 15 14:29:10 2005
BCM
13C

67.80 MHz
135.00 KHz
5200.0 Hz
32768
18348.6 Hz
1
1
500.0 Hz
480
1.786 sec
1.211 sec
3.8 us
10.0 us
10.0 us
1.000 ms
1.000 ms
1.00 ms
1H
22.1 c
CGD6
128.00 ppm
0.00
26
511
1
LOOP1

D:\WINNMR95\DATA\Auto\1MON_E1_FT.a1
 dimer from cyclohex.
 Thu Feb 02 11:48:51 2006

IRNUC 1H
 EXMOD NON
 OBPRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6020.4 Hz
 SCANS 24
 ACQTM 5.443 sec
 PD 1.554 sec
 PW1 5.4 us
 IRNUC 1H
 CTEMP 20.2 c
 SLVNT C6D6
 EXREF 7.20 ppm
 BF 0.12 Hz
 RGAIN 16

C:\Documents and Settings\Å-4-E\ffXfNfgfbfv\12,0,,E\NMR\Ketolactone\H.als
186 ketolactone

C:\Documents and Settj
186 ketolactone
Wed Aug 24 19:49:13 20
1H
NON
270.05 MHz
112.00 KHz
5800.00 Hz
32768
5405.40 Hz
40
6.0621 sec
0.9350 sec
6.00 usec
1H
21.9 c
C6D6
7.20 ppm
0.12 Hz
22
RGAIN

C:\Documents and Settings\Å-Å-E\ffxfNfgbfv\Å-Å-E\NMR\NaBH4\191-3-H..als
191-3 NaBH4

DFILE	C:\Documents and Settj
COMNT	191-3 NaBH4
DATIM	Sat Aug 27 17:25:34 20
OBNUC	1H
EXMOD	NON
OBFRQ	270.05 MHz
OBSET	112.00 KHz
OBFIN	5800.00 Hz
POINT	32768
FREQU	5405.40 Hz
SCANS	48
ACQTM	6.0621 sec
PD	0.9350 sec
PW1	6.00 usec
IRNUC	1H
CTEMP	20.9 C
SLVNT	C6D6
EXREF	7.20 ppm
BF	0.12 Hz
RGAIN	22

E:\THP\NON.als
38-1 THP TM

DFILE E:\THP\NON.als
COMNT 38-1 THP TM
DATIM Mon Oct 24 12:30:23 20
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6020.40 Hz
SCANS 40
ACQTM 5.4428 sec
PD 1.5539 sec
PW1 5.40 usec
IRNUC 1H
CTEMP 20.7 C
SLVNT C6D6
EXREF 7.20 ppm
BF 0.12 Hz
RGAIN 17

E:\tbf\non.als
No.43-2 TBAF TM

DFILE E:\tbf\non.als
COMNT No.43-2 TBAF TM
DATIM Wed Oct 26 21:01:40 20
OBNUC 1H
EXMOD NON
OBFREQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.00 Hz
POINT 32768
FREQU 5405.40 Hz
SCANS 40
ACQTM 6.0621 sec
PD 0.9350 sec
PW1 6.00 usec
IRNUC 1H
CTEMP 23.0 c
SLVNT C6D6
EXREF 7.20 ppm
BF 0.12 Hz
RGAIN 20

C:\WINMR95\DATA\Auto1\NON_EI_FT.als
 33
 DATEM Tue May 16 15:12:42 2006
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 6020.4 Hz
 SCANS 8
 ACQTM 5.443 sec
 PD 1.554 sec
 PWI 5.4 us
 IIRNUC 1H
 CTMP 21.2 C
 SLUNT CDCL3
 EXREF 7.26 ppm
 RF 0.12 Hz
 RGAIN 9

E:\hitomi\cooh-2.als
COOH

E:\hitomi\cooh-2.als
COOH
Wed Aug 09 15:09:45 20
13C
BCM
75.45 MHz
124.00 KHz
1840.00 Hz
32768
20408.10 Hz
1016
1.6056 sec
1.3944 sec
4.10 usec
1H
22.0 c
CDCL3
77.00 ppm
1.20 Hz
22
RGAIN

C:\Documents and Settings\A-E\ffXfNfgbfv\,4,0,,E\NMR\deTBSdeTHP\single-isomer-non.als
No.68 deTHP & deTBS single isomer

DFILE C:\Documents and Settj
COMNT No.68 deTHP & deTBS sj
DATIM Wed Nov 30 22:15:40 20
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6020.40 Hz
SCANS 64
ACQTM 5.4428 sec
PD 1.5539 sec
PW1 5.40 usec
IRNUC 1H
CTEMP 20.4 C
SLVNT C6D6
EXREF 7.20 ppm
BF 0.12 Hz
RGAIN 18

F:\yk-final.als
BBr3

DFILE F:\yk-final.als
COMNT BBr3
DATIM Sat Apr 15 07:47:04 20
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 3600
ACQTM 3.2768 sec
PD 3.7232 sec
PW1 6.25 usec
IRNUC 1H
CTEMP 23.2 c
SLVNT CD3OD
EXREF 4.80 ppm
BF 0.12 Hz
RGAIN 17

Current Data Parameters
 NAME komiyama
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20060412
 Time_ 22.49
 INSTRUM av600
 PROBHD 5 mm CPDUL 13C
 PULPROG zg30
 TD 40960
 SOLVENT MeOD
 NS 64
 DS 2
 SWH 8389.262 Hz
 FIDRES 0.204516 Hz
 AQ 2.4413257 sec
 RG 22.6
 DW .59.600 usec
 DE 6.00 usec
 TE 297.9 K
 D1 1.0000000 sec
 MCREST 0.0000000 sec
 MCWRK 0.0150000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 14.40 usec
 PL1 -5.80 dB
 SF01 600.1337060 MHz
 F2 - Processing parameters
 SI 327.68 MHz
 SF 600.1337060 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

C:\suzuki\NMR(ALS)\suzuki fin\suzuki-final-H.Auto1non_E1_FT.als
rs-35plus

DFILE C:\suzuki\NMR(ALS)\suz
COMNT rs-35plus
DATIM Sat Sep 02 21:49:52 20
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 32
ACQTM 3.2768 sec
PD 3.7232 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 24.0 c
SLVNT CD3OD
EXREF 4.80 ppm
BF 0.12 Hz
RGAIN 23

C:\suzuki\NMR(ALS)\suzuki fin\Suzuki-Fin-Auto3bcm_E1_FT.als
Suzuki-fin

DFILE C:\suzuki\NMR(ALS)\suz
COMNT Suzuki-fin
DATIM Mon Sep 04 06:28:09 20
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 127958.00 Hz
POINT 32768
FREQU 33898.30 Hz
SCANS 36000
ACQTM 0.9667 sec
PD 2.0333 sec
FW1 5.25 usec
IRNUC 1H
CTEMP 25.5 c
SLVNT CD3OD
EXREF 49.00 ppm
BF 1.20 Hz
RGAIN 30