The Supporting Information has been revised and is available with the correction linked to this paper (*Org. Lett.* **2014**, *16* (5), 1534).

Supporting Information

Enantioselective Total Synthesis of (–)-Erinacine B

Hideaki Watanabe, Masashi Takano, Akinori Umino, Toshiya Ito, and Hiroyuki Ishikawa, and Masahisa Nakada*

Department of Chemistry, School of Science and Engineering, Waseda University

3-4-1, Ohkubo, Shinjuku, Tokyo 169-8555, Japan

mnakada@waseda.jp

Phone & Fax: +813-5286-3240

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General Information. ^1H and ^{13}C NMR spectra were recorded on a JEOL AL-400 spectrometer or Bruker AVANCE 600 spectrometer. ^1H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) with the solvent resonances as internal standards. The following abbreviations were used to explain the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; band, several overlapping signals; b, broad. IR spectra were recorded on a JASCO FT/IR-8300. Optical rotations were measured using a 2 ml cell with a 1 dm path length on a JASCO DIP-1000. Melting points (mp) are uncorrected, recorded on a Yamato capillary melting point apparatus. Chiral HPLC analysis was performed on a JASCO PU-980 and UV-970. Mass spectra and elemental analyses were provided at the Materials Characterization Central Laboratory, Waseda University. All reactions were carried out under an argon atmosphere with dry, freshly distilled solvents under anhydrous conditions, unless otherwise noted. All reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and phosphomolybdic acid and heat as developing agents. E. Merck silica gel (60, particle size 0.040-0.063 mm) was used for flash chromatography. Preparative thin-layer chromatography (PTLC) separations were carried out on self-made 0.3 mm E. Merck silica gel plates (60F-254).

Materials. THF was distilled from sodium/benzophenone ketyl. Toluene was distilled from sodium. Methylene chloride (CH_2Cl_2), benzene, and DMF were distilled from CaH_2 under reduced pressure, and all other reagents were purchased from Aldrich, TCI, or Kanto Chemical Co. Ltd.

(-)-(3a*S*,5a*R*,6*S*)-6-(4-methoxybenzyloxy)-2,3,3a,4,5,5a,6,7,8,9-decahydro-3a,5a-dimethylcyclopenta[*a*]naphthalen-1-one (13a)

A solution of the alcohol **13** (1.57 g, 4.22 mmol) in CH₂Cl₂ (80 mL) and pyridine (1.54 mL, 19.0 mmol) was treated with SOCl₂ (0.649 mL, 8.45 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 2 h. Saturated aqueous NaHCO₃ solution (30 mL) was added, and the mixture was extracted with CH₂Cl₂ (2 × 20 mL). The organic extract was dried over Na₂SO₄, filtered, and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate=10/1) to afford a mixture of isomers (1.37 g, 91%, unconjugated enone:conjugated enone=3.5:1). A solution of this mixture (656 mg, 1.85 mmol) and DBU (1.10 mL, 7.39 mmol) in toluene (20 mL) was refluxed for 1 d. The volatiles were removed under reduced pressure and the residue was purified by flash chromatography (hexane/ethyl acetate=10/1) to afford **13a** (606 mg, 92 %) as a clear colorless oil.

R_f = 0.45 (hexane / ethyl acetate = 4 / 1); ¹H NMR (400 MHz, CDCl₃) δ 7.23 (2H, d, *J*=8.6 Hz), 6.85 (2H, d, *J*=8.6 Hz), 4.51 (1H, d, *J*=11.4 Hz), 4.27 (1H, d, *J*=11.4 Hz), 3.99 (1H, d, *J*=13.2 Hz), 3.80 (3H, s), 3.33 (1H, s), 2.56-2.48 (1H, m), 2.46-2.37 (1H, m), 2.24-2.16 (1H, m), 1.90-1.71 (5H, m), 1.70-1.61 (2H, m), 1.52-1.44 (2H, m), 1.13 (3H, s), 1.07 (3H, m), 1.06-1.00 (1H, m); ¹³C NMR (100 MHz, CDCl₃) δ 208.4, 158.3, 153.0, 137.6, 130.9, 128.7, 113.4, 83.4, 70.4, 55.3, 42.5, 40.6, 36.9, 35.3, 33.4, 29.2, 25.9, 25.2, 23.6, 22.8, 21.6; IR (neat) ν_{max} 1704, 1626, 1516, 1250, 1072, 822 cm⁻¹; HRMS(FAB) [M+H]⁺ calculated for C₂₃H₃₁O₃: 355.2273, found: 355.2273; [α]_D²⁵ -139.8 (c 1.03, CHCl₃).

(-)-(3a*S*,5a*R*,6*S*)-2,3,3a,4,5,5a,6,7,8,9-decahydro-6-hydroxy-3a,5a-dimethylcyclopenta[*a*]naphthalen-1-one (8)

To a solution of ketone **13a** (433 mg, 1.22 mmol) in CH₂Cl₂/*t*-BuOH/H₂O (8/1/1, 10 mL) was added DDQ (416 mg, 1.83 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched by a mixture of saturated aqueous NaHCO₃ solution (10 mL), saturated aqueous Na₂S₂O₃ solution (10 mL), and Et₂O (10 mL). The phases were separated and the aqueous layer was extracted with Et₂O (3 × 10 mL). The combined organic layer was washed with brine (10 mL), dried (Na₂SO₄), filtered, and concentrated under reduced

pressure. The residue was purified by flash chromatography (hexane/ethyl acetate=20/1) to afford ketone **8** (286 mg, 100 %) as a white solid.

R_f = 0.16 (hexane / ethyl acetate = 4 / 1); mp 95.1-96.5 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.97-3.91 (1H, m), 3.68-3.62 (1H, m), 2.49-2.38 (2H, m), 2.28-2.18 (1H, m), 2.08-1.98 (1H, m), 1.91-1.78 (2H, m), 1.75-1.63 (4H, m), 1.57-1.44 (3H, m), 1.18-1.10 (1H, m), 1.16 (3H, s), 1.13 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 208.3, 151.4, 139.7, 76.4, 42.9, 40.5, 36.6, 35.4, 33.2, 29.2, 28.3, 26.0, 24.8, 22.5, 21.2; IR (KBr) ν_{max} 3496, 1694, 1617 cm^{-1} ; HRMS(FAB) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{15}\text{H}_{23}\text{O}_2$: 235.1698, found: 235.1690; $[\alpha]_{\text{D}}^{19}$ -264.8 (c 1.01, CHCl_3).

(+)-(3a*S*,5a*R*,6*S*,9a*R*,9b*S*)-decahydro-6-hydroxy-3a,5a-dimethyl-2*H*-cyclopenta[*a*]naphthalen-1(9b*H*)-one (14)

To a solution of ketone **8** (100 mg, 0.427 mmol) in THF (10 mL) was added a solution of SmI_2 (0.1 M solution in THF, 10.0 mL, 1.00 mmol) and HMPA (0.696 mL, 4.00 mmol) at -15 °C via a cannula. After the addition, the mixture was allowed to warm to room temperature and stirred for 1 h, and then was quenched by air and a mixture of saturated aqueous NaHCO_3 solution (10 mL) and saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution (10 mL). The aqueous layer was extracted with Et_2O (2×20 mL), dried over Na_2SO_4 , filtered, and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate=8/1) to afford hydroxyl ketone **14** (94.4 mg, 94 %) as a white solid.

R_f = 0.21 (hexane / ethyl acetate = 4 / 1); mp 108.3-109.2 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.31 (1H, dd, $J=2.4, 2.4$ Hz), 2.46-2.32 (2H, m), 2.26-2.16 (1H, m), 2.05-1.81 (3H, m), 1.78-1.71 (1H, m), 1.69-1.53 (6H, m), 1.51 (1H, br), 1.41-1.34 (1H, m), 1.31-1.24 (1H, m), 1.21 (3H, s), 0.98-1.92 (1H, m), 0.74 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 221.6, 75.4, 58.8, 39.7, 38.6, 36.3, 35.4, 34.7, 30.1, 29.2, 29.0, 26.2, 25.5, 21.1, 18.1; IR (KBr) ν_{max} 3490 1715 cm^{-1} ; HRMS(FAB) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{15}\text{H}_{25}\text{O}_2$: 237.1855, found: 237.1850; $[\alpha]_{\text{D}}^{23}$ +96.0 (c 1.01, CHCl_3).

(+)-(3a*S*,5a*R*,6*S*,9a*R*,9b*S*)-dodecahydro-3a,5a-dimethyl-1-oxo-1*H*-cyclopenta[*a*]naphthalen-6-yl-3,5-dinitrobenzoate (14a)

A mixture of hydroxyl ketone **14** (17.0 mg, 0.072 mmol), DMAP (13.2 mg, 0.108 mmol), 3, 5-dinitrobenzoyl chloride (19.8 mg, 0.086 mmol) in CH₂Cl₂ (5.0 mL) was refluxed for 6 h. The reaction was quenched with saturated aqueous NH₄Cl solution (10 mL) and the mixture was extracted with CH₂Cl₂ (2 × 5.0 mL). The combined organic layer was dried over Na₂SO₄, filtered, and evaporated. The residue was purified by preparative TLC (hexane/ethyl acetate=4/1) to afford **14a** (28.8 mg, 93 %) as a white solid.

R_f = 0.33 (hexane / ethyl acetate = 4 / 1); mp 196.8-197.1 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.24 (1H, t, *J*=2.2 Hz), 9.19 (2H, d, *J*=2.2 Hz), 4.89 (1H, dd, *J*=2.4, 2.4 Hz), 2.60-2.47 (1H, m), 2.47-2.37 (1H, m), 2.31-2.22 (1H, m), 2.22-2.17 (1H, m), 2.02-1.84 (1H, m), 1.82-1.54 (8H, m), 1.29-1.26 (1H, m), 1.26 (3H, s), 1.12-1.04 (1H, m), 0.92 (3H, s); ¹³C NMR (100 MHz, CDCl₃) δ 220.8, 161.5, 148.7, 129.1, 122.2, 100.5, 81.0, 58.5, 39.6, 38.4, 36.1, 36.1, 35.2, 30.2, 28.8, 26.2, 25.9, 25.1, 21.9, 17.9; IR (KBr) ν_{max} 1717, 1546 cm⁻¹; HRMS(FAB) [M+H]⁺ calculated for C₂₂H₂₇N₂O₇: 431.1818, found: 431.1803; [α]_D¹⁹ +118.1 (c 1.28, CHCl₃).

CIFF file of **14a** is available. See Supporting Information.

(-)-(1R,3aS,5aR,6S,9aR,9bS)-dodecahydro-3a,5a-dimethyl-1-(prop-1-en-2-yl)-1H-cyclopenta[a]naphthalene-1,6-diol (14b**)**

To a solution of **14** (667 mg, 3.06 mmol) and CeCl₃ (anhydrous) (1.88 g, 7.64 mmol) in THF (30.0 mL) was added a solution of a solution of isopropenyl lithium (0.764 M solution in Et₂O, 10.0 mL, 7.64 mmol) at -78 °C via a cannula. After the addition, the reaction mixture was stirred for 2 h, and then quenched by saturated aqueous NH₄Cl solution

(10 mL). The mixture was filtered through a plug of Celite[®], and the aqueous layer was extracted with Et₂O (2 × 10 mL), dried over Na₂SO₄, filtered, and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate=9/1) to afford **14b** (663 mg, 84 %) as a white solid and starting material **14** (55.0 mg, 8.2 %).

R_f = 0.41 (hexane / ethyl acetate = 4 / 1); mp 110.2-112.1 °C; ¹H NMR (400 MHz, CDCl₃) δ 5.05 (1H, s), 4.78 (1H, s), 3.32 (1H, br), 2.17-2.05 (1H, m), 2.05-1.90 (2H, m), 1.88-1.77 (3H, m), 1.83 (3H, s), 1.75-1.65 (1H, m), 1.63-1.44 (6H, m), 1.31-1.19 (2H, m), 1.14 (3H, s), 1.06 (3H, s), 0.96-0.86 (1H, m); ¹³C NMR (100 MHz, CDCl₃) δ 152.0, 108.9, 85.5, 76.6, 53.9, 40.7, 40.2, 39.8, 37.1, 34.9, 33.5, 30.6, 28.3, 28.3, 25.4, 21.6, 20.2, 20.0; IR (neat) $\nu_{\max}$ 3388, 2936, 1638, 1458, 1388, 1218 cm⁻¹; HRMS(FAB) [M]⁺ calculated for C₁₈H₃₀O₂: 278.2246, found: 278.2256; [α]_D²⁶ -53.3 (c 0.99, CHCl₃).

(-)-(1*S*,3*aS*,5*aR*,6*S*,9*aR*,9*bS*)-dodecahydro-1-isopropyl-3*a*,5*a*-dimethyl-1*H*-cyclopenta[*a*]naphthalene-1,6-diol (14c)

A mixture of diol **14b** (663 mg, 2.38 mmol), Pd/C (10 % Pd, 300 mg) and EtOAc (15 mL) was stirred under H₂ atmosphere (1 atm) at room temperature for 1.5 h. After completion of the reaction, the mixture was filtered through a plug of Celite[®], and the filtrate was concentrated. The residue was purified by flash chromatography (hexane/ethyl acetate=10/1) to afford **14c** (632 mg, 95 %) as a white solid.

R_f = 0.41 (hexane / ethyl acetate = 4 / 1); mp 125.1-125.9 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.33 (1H, s), 2.21 (1H, ddd, J =12.8, 7.2, 2.8 Hz), 1.92-1.72 (6H, m), 1.63-1.43 (5H, m), 1.30-1.12 (5H, m), 1.08 (3H, s), 1.03 (3H, s), 0.95 (3H, d, J =6.8 Hz), 0.91 (3H, d, J =6.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 86.2, 76.7, 53.6, 41.4, 39.9, 38.6, 37.2, 34.8, 33.5, 31.3, 30.4, 28.6, 27.5, 26.5, 21.8, 20.7, 19.2, 17.7; IR (KBr) $\nu_{\max}$ 3365, 1474, 1385 cm⁻¹; HRMS(FAB) [M+Na]⁺ calculated for C₁₈H₃₂O₂Na: 303.2300, found: 303.2286; [α]_D³¹ -1.97 (c 1.00, CHCl₃).

(+)-(1*S*,3*aS*,5*aR*,9*aR*,9*bS*)-decahydro-1-hydroxy-1-isopropyl-3*a*,5*a*-dimethyl-1*H*-cyclopenta[*a*]naphthalen-6(9*bH*)-one (15)

To a solution of **14c** (370 mg, 1.32 mmol) in CH₂Cl₂ (15 mL) was added Dess-Martin periodinane (1.03 g, 2.43 mmol) portionwise, and the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched by adding Et₂O (20 mL), saturated aqueous NaHCO₃ solution (20 mL), and saturated aqueous Na₂S₂O₃ solution (20 mL) successively. The organic layer was separated, washed with brine (20 mL), dried over Na₂SO₄, and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate=10/1) to afford **15** (335 mg, 91 %) as a white solid. *R*_f = 0.53 (hexane / ethyl acetate = 4 / 1); mp 108.2-109.9 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.65 (1H, ddd, *J*=15.8, 6.8, 6.8 Hz), 2.25-2.10 (2H, m), 2.09-1.99 (1H, m), 1.98-1.90 (1H, m), 1.89-1.82 (2H, m), 1.80-1.72 (3H, m), 1.65-1.40 (6H, m), 1.30-1.19 (1H, m), 1.23 (3H, s), 1.02 (3H, s), 0.97 (3H, d, *J*=6.8 Hz), 0.93 (3H, d, *J*=6.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 216.8, 85.6, 54.2, 48.0, 43.5, 41.2, 39.8, 38.4, 37.9, 34.0, 30.8, 28.9, 27.4, 27.1, 25.7, 20.1, 19.1, 17.6; IR (KBr) ν_{max} 2545, 1700, 1375 cm⁻¹; HRMS(FAB) [M+H]⁺ calculated for C₁₈H₃₁O₂: 279.2324, found: 279.2323; [α]_D²⁵ +26.4 (c 0.99, CHCl₃).

(–)-(3aS,5aR,9aR,9bS)-3a,4,5,5a,7,8,9,9a-octahydro-1-isopropyl-3a,5a-dimethyl-3H-cyclopenta[a]naphthalen-6(9bH)-one (15a)

A solution of **15** (243 mg, 0.874 mmol) in CH₂Cl₂ (20 mL) and pyridine (0.354 mL, 4.37 mmol) was treated with SOCl₂ (0.134 mL, 1.75 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 2 h. The reaction was quenched with saturated aqueous NaHCO₃ solution (10 mL), and the mixture was extracted with CH₂Cl₂ (2 × 10 mL). The combined organic layer was dried over Na₂SO₄, filtered, and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate=10/1) to afford **15a** (228 mg, 100 %) as a clear colorless oil.

*R*_f = 0.64 (hexane / ethyl acetate = 4 / 1); ¹H NMR (400 MHz, CDCl₃) δ 5.28 (1H, s), 2.57 (1H, sept, *J*=6.4 Hz), 2.63-2.50 (1H, m), 2.38 (1H, br), 2.24-2.15 (2H, m), 2.02-1.82 (3H, m), 1.79-1.39 (7H, m), 1.12 (3H, d, *J*=6.4 Hz), 1.12 (3H, s), 1.11 (3H, s), 1.03 (3H, d, *J*=6.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 215.7, 154.1, 121.1, 55.5, 49.6, 46.6,

44.4, 42.3, 38.2, 30.9, 29.7, 29.3, 27.5, 27.3, 24.5, 23.7, 21.4, 17.6; IR (neat) $\nu_{\max}$ 2948, 2865, 1706, 1700, 1451 cm^{-1} ; HRMS(FAB) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{18}\text{H}_{29}\text{O}$: 261.2218, found: 261.2208; $[\alpha]_{\text{D}}^{22.8} -18.0$ (c 0.10, CHCl_3).

(-)-(3aR,5aR,9aR)-2,3,3a,4,5,5a,7,8,9,9a-decahydro-1-isopropyl-3a,5a-dimethylcyclopenta[a]naphthalen-6-one
(7)

A solution of **15a** (481 mg, 1.85 mmol) and *p*-TsOH (351 mg, 1.85 mmol) in benzene (20 mL) was refluxed for 4 h. The volatiles were removed under reduced pressure and the residue was purified by flash chromatography (hexane/ethyl acetate=10/1) to afford ketone **7** (481 mg, 100 %) as a clear colorless oil.

R_f = 0.64 (hexane / ethyl acetate = 4 / 1); ^1H NMR (400 MHz, CDCl_3) δ 3.09 (1H, sept, $J=6.8$ Hz), 2.64 (1H, ddd, $J=7.2, 7.2, 6.1$ Hz), 2.50-2.40 (1H, m), 2.34-2.22 (3H, m), 2.18-1.97 (3H, m), 1.78 (1H, ddd, $J=7.2, 7.2, 4.4$ Hz), 1.70-1.37 (6H, m), 1.06 (3H, s), 1.03 (3H, d, $J=6.8$ Hz), 0.99 (3H, s), 0.96 (3H, d, $J=6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 216.1, 141.5, 135.2, 50.9, 48.5, 46.7, 39.0, 37.8, 36.7, 30.1, 28.9, 26.8, 26.6, 25.9, 23.8, 22.4, 21.6, 17.1; IR (neat) $\nu_{\max}$ 2946, 2862, 1700, 1452 cm^{-1} ; HRMS(FAB) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{18}\text{H}_{29}\text{O}$: 261.2218, found: 261.2218; $[\alpha]_{\text{D}}^{25} -13.9$ (c 0.18, CHCl_3).

(-)-(3aR,5aR,9aR)-methyl-3,3a,4,5,5a,8,9,9a-octahydro-6-hydroxy-1-isopropyl-3a,5a-dimethyl-2H-cyclopenta[a]naphthalene-7-carboxylate (7a)

To a solution of ketone **7** (78.7 mg, 0.302 mmol) in THF (3.0 mL) was added LHMDs (1.07 M in hexanes, 0.424 mL, 0.453 mmol) at -78 °C. The mixture was stirred at 0 °C for 0.5 h before the addition of cyano methyl formate (36.0 μL , 0.453 mmol). The mixture was stirred at -78 °C for 1 h. The reaction was quenched by saturated aqueous NH_4Cl solution (10 mL) and Et_2O (10 mL). The phases were separated and the aqueous layer was extracted with Et_2O (3×10 mL). The combined organic layer was washed with brine (10 mL), dried (Na_2SO_4), filtered, and concentrated under

reduced pressure. The residue was purified with flash chromatography (hexane/ethyl acetate=40/1) to afford the enol ester **7a** (75.8 mg, 79 %) as a colorless oil.

R_f = 0.45 (hexane / ethyl acetate = 10 / 1); ^1H NMR (400 MHz, CDCl_3) δ 12.37 (1H, s), 3.76 (3H, s), 3.00 (1H, sept, J =6.8 Hz), 2.35-2.26 (2H, m), 2.25-2.17 (2H, m), 2.13-2.01 (1H, m), 1.99-1.85 (2H, m), 1.78-1.66 (1H, m), 1.65-1.56 (1H, m), 1.55-1.37 (4H, m), 1.00 (3H, s), 0.95 (3H, s), 0.90 (3H, d, J =6.8 Hz), 0.89 (3H, d, J =6.8 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 178.7, 173.7, 140.3, 136.1, 94.6, 51.4, 48.3, 43.1, 41.5, 39.3, 37.1, 31.8, 28.6, 26.3, 24.0, 23.5, 22.7, 22.1, 21.6, 18.0; IR (neat) ν_{max} 2956, 2864, 1658, 1614, 1440, 1360, 1240 cm^{-1} ; HRMS(FAB) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{20}\text{H}_{31}\text{O}_3$: 319.2273 found: 319.2274; $[\alpha]_{\text{D}}^{27}$ -168.1 (c 1.05, CHCl_3).

(-)-(3a*R*,5a*R*,9a*R*)-methyl-3,3a,4,5,5a,6,7,8,9,9a-decahydro-7-iodomethyl-1-isopropyl-3a,5a-dimethyl-6-oxo-2*H*-cyclopenta[*a*]naphthalene-7-carboxylate (7b**)**

To a solution of compound **7a** (75.8 mg, 0.238 mmol) in THF (2.0 mL) was added TBAF (1.0 M in THF, 0.357 mL, 0.357 mmol) and CH_2I_2 (23.0 μL , 0.286 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched by saturated aqueous NH_4Cl solution (5.0 mL) and ether (5.0 mL). The phases were separated and the aqueous layer was extracted with ether (3 $\times$ 5.0 mL). The combined organic layer was washed with brine (10 mL), dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (hexane/ethyl acetate=20/1) to afford iodomethyl ester **7b** (72.5 mg, 66 %, dr=4.2:1) as a colorless oil.

Major product:

R_f = 0.38 (hexane / ethyl acetate = 10 / 1); ^1H NMR (400 MHz, CDCl_3) δ 3.78 (3H, s), 3.57 (1H, d, J =10.2 Hz), 3.54 (1H, d, J =10.2 Hz), 3.02 (1H, sept, J =6.6 Hz), 2.71-2.51 (2H, m), 2.35-2.16 (3H, m), 2.11-1.99 (1H, m), 1.95-1.80 (2H, m), 1.71-1.37 (4H, m), 1.34-1.22 (1H, m), 1.01 (3H, s), 1.00 (3H, d, J =6.6 Hz), 0.95 (3H, d, J =6.6 Hz), 0.94 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 210.1, 170.0, 141.8, 134.9, 58.0, 53.0, 49.8, 48.1, 40.5, 39.1, 36.1, 32.1, 30.0, 28.9, 26.6, 23.5, 22.3, 21.4, 20.6, 17.1, 9.2; IR (neat) ν_{max} 1754, 1734, 1508, 1216 cm^{-1} ; HRMS(FAB) $[\text{M}+\text{H}]^+$ calculated for HRMS(FAB) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{32}\text{O}_3\text{I}$: 459.1396 found: 459.1393; $[\alpha]_{\text{D}}^{24}$ -92.9 (c 1.04, CHCl_3).

Minor product:

$R_f = 0.43$ (hexane / ethyl acetate = 10 / 1) ^1H NMR (400 MHz, CDCl_3) δ 3.83 (1H, d, $J=10.5$ Hz), 3.72 (3H, s), 3.26 (1H, d, $J=10.5$ Hz), 3.07 (1H, sept, $J=6.8$ Hz), 2.87-2.81 (1H, m), 2.49-2.36 (2H, m), 2.32-2.24 (2H, m), 2.05-1.99 (1H, m), 1.84-1.24 (7H, m), 1.00 (3H, d, $J=6.8$ Hz), 0.98 (3H, s), 0.95 (3H, d, $J=6.8$ Hz), 0.90 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 208.6, 169.1, 142.4, 134.4, 97.1, 58.2, 52.3, 48.2, 46.2, 38.9, 36.3, 35.8, 30.5, 30.5, 30.5, 28.9, 26.4, 23.6, 22.4, 21.6, 16.0; IR (neat) ν_{max} 1736, 1704, 1542, 1216 cm^{-1} ; HRMS(FAB) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{32}\text{O}_3$: 459.1396 found: 459.1393; $[\alpha]_{\text{D}}^{23} -95.7$ (c 0.93, CHCl_3).

(–)-(3a*R*,5a*R*,8*R*,10a*R*)-methyl-2,3,3a,4,5,5a,6,7,8,9,10,10a-dodecahydro-1-isopropyl-3a,5a-dimethyl-6-oxocyclohepta[*e*]indene-8-carboxylate (16**)**

To a solution of **7b** (120 mg, 0.262 mmol) in THF (10 mL) was added a solution of SmI_2 (0.2 M solution in THF, 3.28 mL, 0.655 mmol) and HMPA (0.456 mL, 2.62 mmol) at -78°C via a cannula. After the addition, the reaction mixture was stirred for 1 h, and then quenched by air and a mixture of saturated aqueous NaHCO_3 solution (10 mL) and saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution (10 mL). The aqueous layer was extracted with CH_2Cl_2 (2×10 mL), dried over Na_2SO_4 , filtered, and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate=10/1) to afford ketone **16** (70.2 mg, 81 %) as a colorless oil.

$R_f = 0.43$ (hexane / ethyl acetate = 4 / 1); ^1H NMR (400 MHz, CDCl_3) δ 3.70 (3H, s), 3.06 (1H, dd, $J=11.7$, 6.6 Hz), 2.95 (1H, sept, $J=6.6$ Hz), 2.93-2.80 (2H, m), 2.64 (1H, d, $J=9.5$ Hz), 2.32-2.26 (2H, m), 2.18-1.96 (3H, m), 1.8-1.78 (1H, m), 1.76-1.43 (3H, m), 1.30-1.18 (1H, m), 1.08 (3H, s), 1.03 (3H, s), 0.98 (3H, d, $J=6.6$ Hz), 0.96 (3H, d, $J=6.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 215.0, 174.9, 140.5, 136.4, 53.7, 51.9, 48.9, 43.6, 39.3, 38.8, 38.1, 36.0, 33.0, 30.3, 28.4, 26.9, 26.4, 24.1, 21.5, 14.5, 14.4; IR (neat) ν_{max} 2956, 1738, 1700, 1456, 1174, 1084 cm^{-1} ; HRMS(FAB) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{21}\text{H}_{30}\text{O}_3\text{Na}$: 355.2249, found: 355.2266; $[\alpha]_{\text{D}}^{25} -46.0$ (c 3.01, CHCl_3).

(–)-(3a*R*,5a*R*,7*E*,10a*R*)-methyl-2,3,3a,4,5,5a,6,9,10,10a-decahydro-1-isopropyl-3a,5a-dimethyl-6-oxocyclohepta[*e*]indene-8-carboxylate (16a**)**

To a solution of ketone **16** (18.0 mg, 0.0541 mmol) and triethylamine (30.2 μL , 0.217 mmol) in CH_2Cl_2 (2.0 mL) was added trimethylsilyl trifluoromethanesulfonate (24.9 μL , 0.108 mmol) at 0 $^\circ\text{C}$, and stirring was continued for 2 h. Saturated aqueous NaHCO_3 solution (10 mL) was added to quench the reaction at 0 $^\circ\text{C}$, and the aqueous layer was extracted with CH_2Cl_2 (2×5.0 mL). The combined organic layer was dried over Na_2SO_4 , filtered, and evaporated. To a solution of the dried residue in THF (2.0 mL) was added PhSeCl (12.4 mg, 0.0650 mmol) at -78 $^\circ\text{C}$. The mixture was stirred at -78 $^\circ\text{C}$ for 15 min before the addition of pyridine (8.8 μL , 0.108 mmol) and 30% H_2O_2 (12.3 μL , 0.108 mmol). The mixture was allowed to warm to 0 $^\circ\text{C}$ and stirred for 1 h. The reaction was quenched by saturated aqueous NaHCO_3 solution (5.0 mL) and ether (5.0 mL). The phases were separated and the aqueous layer was extracted with ether (3×5.0 mL). The combined organic layer was washed with brine (10 mL), dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (hexane/ethyl acetate=10/1) to afford **16a** (16.1 mg, 90 %) as a clear liquid and starting material **16** (1.5 mg, 8.3 %).

R_f = 0.29 (hexane / ethyl acetate = 10 / 1); ^1H NMR (400 MHz, CDCl_3) δ 6.98 (1H, s), 3.80 (3H, s), 2.93 (1H, sept, J =6.6 Hz), 2.75-2.50 (3H, m), 2.37-2.17 (3H, m), 2.05-1.82 (2H, m), 1.66-1.41 (3H, m), 1.34-1.24 (2H, m), 1.10 (3H, s), 1.04 (3H, s), 1.00 (3H, d, J =6.6 Hz), 0.98 (3H, d, J =6.6 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 210.4, 167.8, 140.8, 138.1, 136.4, 136.2, 54.8, 52.5, 49.3, 42.6, 37.8, 35.8, 33.4, 29.8, 28.6, 27.1, 25.6, 24.0, 21.9, 21.6, 15.2; IR (neat) ν_{max} 3748, 2960, 2364, 1724, 1680, 1546, 1238 cm^{-1} ; HRMS(FAB) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{21}\text{H}_{30}\text{O}_3\text{Na}$: 353.2093, found: 353.2097; $[\alpha]_{\text{D}}^{24}$ -170.0 (c 0.81, CHCl_3).

(-)-(3aR,5aR,8E,10aR)-methyl-2,3,3a,4,5,5a,6,7,10,10a-decahydro-1-isopropyl-3a,5a-dimethyl-6-oxocyclohepta[e]indene-8-carboxylate (6**)**

A solution of **16a** (16.1 mg, 0.0487 mmol) and DBU (10.0 μL , 0.0672 mmol) in benzene (2.0 mL) was refluxed for 6 h. The volatiles were removed under reduced pressure and the residue was purified by flash chromatography (hexane/ethyl acetate=10/1) to afford **6** (15.8 mg, 98 %) as a colorless oil.

$R_f = 0.26$ (hexane / ethyl acetate = 10 / 1); ^1H NMR (400 MHz, CDCl_3) δ 7.07-7.03 (1H, m), 3.99-3.91 (1H, m), 3.75 (3H, s), 3.51 (1H, d, $J=14.1$ Hz), 3.26 (1H, d, $J=14.1$ Hz), 2.90 (1H, sept, $J=6.8$ Hz), 2.85-2.64 (2H, m), 2.35-2.28 (2H, m), 1.98-1.89 (1H, m), 1.70-1.61 (1H, m), 1.60-1.50 (2H, m), 1.30-1.22 (2H, m), 1.11 (3H, s), 1.04 (3H, s), 1.01 (3H, d, $J=6.8$ Hz), 0.97 (3H, d, $J=6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 211.2, 167.2, 142.4, 140.8, 134.8, 125.2, 54.9, 52.3, 49.3, 39.3, 38.0, 37.0, 36.0, 32.8, 30.8, 28.5, 27.0, 24.1, 21.8, 21.6, 12.7; IR (neat) ν_{max} 2936, 2364, 1716, 1650, 1438, 1246, 1136 cm^{-1} ; HRMS(FAB) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{21}\text{H}_{30}\text{O}_3\text{Na}$: 353.2093, found: 353.2087; $[\alpha]_{\text{D}}^{24} -83.6$ (c 0.70, CHCl_3).

(–)-(3a*R*,5a*R*,6*R*,8*E*,10a*R*)-2,3,3a,4,5,5a,6,7,10,10a-decahydro-8-hydroxymethyl-1-isopropyl-3a,5a-dimethylcyclohepta[*e*]inden-6-ol (5)

To a solution of keto ester **6** (15.8 mg, 0.0478 mmol) in CH_2Cl_2 (2.0 mL) at -78°C was added DIBAL-H (0.191 mL, 1.0 M in hexanes, 0.191 mmol) dropwise over 5 min. After 2 h, the mixture was quenched with MeOH (20 μL) and saturated Rochelle's salt (5.0 mL), and then was extracted with CH_2Cl_2 (3×5.0 mL). The combined organic layer was dried over Na_2SO_4 , concentrated, and the residue was purified by flash chromatography to afford **5** (14.0 mg, 96 %, ($\text{dr}=10:1$)) as a white solid. The separated undesired diastereomer was easily recycled by a sequence of Dess-Martin oxidation and DIBAL-H reduction.

$R_f = 0.19$ (hexane / ethyl acetate = 1 / 1); mp 111.5 - 112.7°C ; ^1H NMR (400 MHz, CDCl_3) δ 5.90 (1H, dd, $J=8.5$, 2.7 Hz), 4.03 (2H, s), 3.38 (1H, d, $J=9.5$ Hz), 2.88 (1H, sept, $J=6.8$ Hz), 2.72-2.58 (2H, m), 2.41 (1H, d, $J=11.5$ Hz), 2.31-2.18 (4H, m), 1.69-1.17 (6H, m), 1.04 (3H, s), 0.99 (3H, d, $J=6.8$ Hz), 0.97 (3H, d, $J=6.8$ Hz), 0.95 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 138.9, 138.8, 137.7, 129.0, 78.2, 68.2, 49.4, 46.2, 43.7, 37.5, 36.1, 35.6, 33.1, 28.1, 27.1, 24.4, 21.4, 11.3; IR (neat) ν_{max} 3752, 3620, 3468, 3276, 2932, 2364, 1654, 1508, 1216 cm^{-1} ; HRMS(FAB) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{20}\text{H}_{32}\text{O}_2\text{Na}$: 327.2300, found: 327.2301; $[\alpha]_{\text{D}}^{24} -93.6$ (c 0.65, CHCl_3).

(–)-(3a*R*,5a*R*,6*R*,8*R*,10a*R*)-2,3,3a,4,5,5a,6,7,10,10a-dodecahydro-8,9-epoxy-8-hydroxymethyl-1-isopropyl-3a,5a-dimethylcyclohepta[*e*]inden-6-ol (5a)

To a solution of **5** (12.1 mg, 0.0397 mmol) and VO(acac)₂ (2.1 mg, 7.95×10⁻³ mmol) in toluene (1.5 mL) at -40 °C was added TBHP (19.9 μL, 4.0 M in toluene, 0.0795 mmol) dropwise over 5 min. After 3 h, the mixture was quenched by adding Et₂O (5.0 mL), saturated aqueous NaHCO₃ solution (5.0 mL), and saturated aqueous Na₂S₂O₃ solution (5.0 mL) successively and was extracted with Et₂O (3 × 5.0 mL). The organic layer was separated, washed with brine (10 mL), dried over Na₂SO₄, and evaporated. The crude **5a** was used for the next step without further purification.

R_f = 0.14 (hexane / ethyl acetate = 1 / 1); mp 134.3-135.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.86 (1H, dd, *J*=12.4, 4.9 Hz), 3.72 (1H, dd, *J*=12.4, 8.5 Hz), 3.50-3.43 (1H, m), 3.17 (1H, dd, *J*=7.1, 7.1 Hz), 2.82 (1H, sept, *J*=6.8 Hz), 2.42 (1H, dd, *J*=12.9, 6.8 Hz), 2.33-2.22 (4H, m), 2.04-1.90 (2H, m), 1.85-1.74 (1H, m), 1.72-1.68 (1H, m), 1.67-1.62 (1H, m), 1.62-1.43 (2H, m), 1.36-1.32 (1H, m), 1.07 (3H, s), 1.00 (3H, d, *J*=6.8 Hz), 0.96 (3H, d, *J*=6.8 Hz), 0.79 (3H, s); ¹³C NMR (150 MHz, CDCl₃) δ 140.0, 137.8, 77.8, 63.4, 60.8, 57.5, 49.7, 45.8, 39.6, 36.9, 35.8, 35.5, 35.0, 30.6, 28.1, 27.1, 24.1, 22.1, 21.2, 9.5; IR (neat) ν_{max} 3748, 3408, 2176, 1870, 1654, 1508, 1458, 1184 cm⁻¹; HRMS(FAB) [M+Na]⁺ calculated for C₂₀H₃₂O₃Na: 343.2249, found: 343.2234; [α]_D³⁷ -125.8 (c 0.13, CHCl₃).

(-)-(3aR,5aR,8R,10aR)-2,3,3a,4,5,5a,10,10a-decahydro-8,9-epoxy-8-(tert-butyldiphenylsilyloxymethyl)-1-isopropyl-3a,5a-dimethylcyclohepta[e]inden-6(7H)-one (17)

To a solution of crude **5a** (12.7 mg, 0.0397 mmol) and imidazole (4.0 mg, 0.0594 mmol) in CH₂Cl₂ (1.5 mL) was added TBDPSCl (12.4 μL, 0.0475 mmol) at room temperature. After 3 h, the mixture was quenched by saturated aqueous NH₄Cl solution (5.0 mL), and extracted with CH₂Cl₂ (3 × 5.0 mL). The organic layer was separated, washed with brine (10 mL), dried over Na₂SO₄, and evaporated. To a solution of the crude product in CH₂Cl₂ (1.5 mL) was added Dess-Martin periodinane (33.6 mg, 0.0792 mmol) portionwise, and the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched by adding Et₂O (10 mL), saturated aqueous NaHCO₃ solution (10 mL) and saturated aqueous Na₂S₂O₃ solution (10 mL). The aqueous layer was extracted with Et₂O (3 × 5.0 mL). The organic layer was separated, washed with brine (10 mL), dried over Na₂SO₄, and evaporated. The residue was

purified by flash chromatography (hexane/ethyl acetate=20/1) to afford epoxy ketone **17** (17.6 mg, 80% (3 steps)) as a colorless oil.

R_f = 0.50 (hexane / ethyl acetate = 6 / 1); ^1H NMR (400 MHz, CDCl_3) δ 7.65-7.28 (10H, m), 3.62 (1H, d, J =12.5 Hz), 3.59 (1H, d, J =12.5 Hz), 3.27 (1H, d, J =12.2 Hz), 2.94 (1H, dd, J =6.6, 3.7 Hz), 2.82 (1H, sept, J =6.8 Hz), 2.78 (1H, d, J =12.0 Hz), 2.76 (1H, d, J =12.2 Hz), 2.37 (1H, dd, J =15.1, 6.6 Hz), 2.25 (1H, d, J =7.6 Hz), 2.24 (1H, d, J =7.6 Hz), 1.89-1.78 (1H, m), 1.59-1.34 (5H, m), 1.26-1.11 (1H, m), 1.03 (3H, s), 0.99 (9H, s), 0.95 (3H, d, J =6.8 Hz), 0.91 (3H, d, J =6.8 Hz), 0.90 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 210.3, 141.2, 135.7, 135.6, 135.5, 129.8, 129.8, 127.7, 66.3, 60.2, 58.6, 53.6, 49.4, 40.5, 40.3, 37.6, 35.7, 31.9, 29.5, 28.4, 27.1, 26.8, 24.3, 21.9, 21.5, 19.3, 14.2 IR (neat) ν_{max} 2936, 1698, 1592, 1465, 1428, 1376, 1248, 1114 cm^{-1} ; HRMS(FAB) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{36}\text{H}_{48}\text{O}_3\text{SiNa}$: 579.3270, found: 579.3256; $[\alpha]_{\text{D}}^{31}$ -28.4 (c 0.88, CHCl_3).

(-)-(3a*R*,5a*R*,9*R*,10a*R*,*Z*)-8-(*tert*-butyldiphenylsilyloxymethyl)-1-isopropyl-3a,5a-dimethyl-6-oxo-2,3,3a,4,5,5a,6,9,10,10a-decahydrocyclohepta[*e*]inden-9-yl benzoate (18**)**

A solution of epoxy ketone **17** (17.0 mg, 0.0305 mmol) and DBU (10.0 μL , 0.0672 mmol) in benzene (2.0 mL) was stirred for 1 d at 50 $^\circ\text{C}$. The volatiles were removed under reduced pressure and the residue was passed through a short silica gel column (hexane/ethyl acetate=4/1) to afford crude product, which was dissolved in $(\text{CH}_2\text{Cl}_2)_2$ (1.5 mL) and was treated with pyridine (4.9 μL , 0.0611 mmol), DMAP (0.37 mg, 3.05×10^{-3} mmol), and benzoic anhydride (10.4 mg, 0.0458 mmol) at 50 $^\circ\text{C}$ for 1 d. The reaction was quenched with saturated aqueous NaHCO_3 solution (5.0 mL), and the aqueous layer was extracted with CH_2Cl_2 (3×5.0 mL). The combined organic layer was dried over Na_2SO_4 , filtered, and evaporated. The residue was purified by preparative TLC (hexane/ethyl acetate=6/1) to afford **18** (15.7 mg, 78 %) as a colorless oil.

R_f = 0.44 (hexane / ethyl acetate = 6 / 1); ^1H NMR (400 MHz, CDCl_3) δ 7.90-7.30 (15H, m), 6.42 (1H, s), 5.59 (1H, dd, J =6.6, 6.6 Hz), 4.35 (1H, d, J =15.4 Hz), 4.32 (1H, d, J =15.4 Hz), 2.91 (1H, d, J =10.2 Hz), 2.88 (1H, sept, J =6.6 Hz), 2.64 (1H, dd, J =12.2, 6.6 Hz), 2.35-2.28 (2H, m), 2.25-2.15 (1H, m), 1.83-1.73 (1H, m), 1.70-1.47 (4H, m), 1.45-1.38 (1H, m), 1.20 (3H, s), 1.12 (3H, s), 1.07 (9H, s), 0.97 (3H, d, J =6.6 Hz), 0.97 (3H, d, J =6.6 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 210.3, 141.2, 135.7, 135.6, 135.5, 129.8, 129.8, 127.7, 66.3, 60.2, 58.6, 53.6, 49.4, 40.5, 40.3, 37.6, 35.7,

31.9, 29.5, 28.4, 27.1, 26.8, 24.3, 21.9, 21.5, 19.3, 14.2 IR (neat) $\nu_{\max}$ 2936, 2860, 1722, 1680, 1452, 1428, 1374, 1272, 1218, 1108, 1028 cm^{-1} ; HRMS(FAB) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{43}\text{H}_{52}\text{O}_4\text{SiNa}$: 683.3533, found: 683.3564; $[\alpha]_{\text{D}}^{25}$ -69.0 (c 0.79, CHCl_3).

(–)-(3a*R*,5a*R*,6*S*,9*R*,10a*R*,*Z*)-8-(*tert*-butyldiphenylsilyloxymethyl)-6-hydroxy-1-isopropyl-3a,5a-dimethyl-2,3,3a,4,5,5a,6,9,10,10a-decahydrocyclohepta[e]inden-9-yl benzoate (19)

To a solution of ketone **18** (15.0 mg, 0.0227 mmol) in CH_2Cl_2 (1.0 mL) was added a solution of $\text{BH}_3\cdot\text{SMe}_2$ (90 %, 2.4 μL , 0.0227 mmol) and (*R*)-CBS catalyst (1.0 M solution in toluene, 5.7 μL , 5.67×10^{-3} mmol) in CH_2Cl_2 (100 mL) via a cannula at -40°C . After the addition, the reaction mixture was stirred for 2 h, and then was quenched by adding 50 μL of MeOH. After adding saturated aqueous NH_4Cl solution (10 mL) to the mixture, stirring was continued at room temperature for 1 h. The aqueous layer was extracted with CH_2Cl_2 (3×5.0 mL), dried over Na_2SO_4 , filtered, and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate=6/1) to afford alcohol **19** (14.3 mg, 95 %) as an oil.

R_f = 0.24 (hexane / ethyl acetate = 6 / 1); ^1H NMR (400 MHz, CDCl_3) δ 7.93-7.28 (15H, m), 6.20 (1H, d, J =8.8 Hz), 6.01 (1H, d, J =6.8 Hz), 4.35 (1H, d, J =14.6 Hz), 4.23 (1H, d, J =14.6 Hz), 4.01 (1H, d, J =6.8 Hz), 3.12 (1H, d, J =12.0 Hz), 2.86 (1H, sept, J =6.8 Hz), 2.32-2.22 (3H, m), 2.19-2.08 (1H, m), 1.68-1.42 (5H, m), 1.35-1.18 (1H, m), 1.11 (3H, s), 1.06 (9H, s), 0.96 (3H, d, J =6.8 Hz), 0.91 (3H, d, J =6.8 Hz), 0.84 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 165.6, 139.5, 138.4, 135.5, 135.5, 133.6, 133.4, 132.8, 130.4, 129.7, 129.6, 128.3, 127.9, 127.7, 127.6, 76.3, 73.9, 64.1, 49.4, 42.1, 39.9, 38.0, 36.9, 33.8, 30.8, 29.7, 28.6, 26.8, 24.4, 21.8, 21.7, 19.2, 16.7 IR (neat) $\nu_{\max}$ 3480, 2936, 2864, 1718, 1452, 1318, 1274, 1114 cm^{-1} ; HRMS(FAB) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{43}\text{H}_{54}\text{O}_4\text{SiNa}$: 685.3689, found: 685.3679; $[\alpha]_{\text{D}}^{23}$ -46.3 (c 0.72, CHCl_3).

(+)-(2*S*,3*R*,4*S*,5*R*)-3,4,5-tris(4-methoxybenzyloxy)-tetrahydro-2-phenylthio-2*H*-pyran (20)

To a suspension of NaH (60 %, 19.8 mg, 0.495 mmol) and TBAI (4.6 mg, 0.0124 mmol) in THF (1.0 mL) was added a solution of phenyl 1-thio- β -D-xylopyranoside (30.0 mg, 0.124 mmol) in THF (2×0.5 mL) via a cannula at 0 °C. To this reaction mixture was added *p*-methoxybenzyl chloride (77.6 μ L, 0.495 mmol) at 0 °C, and the reaction mixture was stirred at 50 °C for 3 h. The reaction was quenched with saturated aqueous NH₄Cl solution (10 mL), and the aqueous layer was extracted with Et₂O (2×5.0 mL). The residue was purified by flash chromatography (hexane/ethyl acetate=6/1) to afford **20** (61.5 mg, 82 %) as a colorless oil.

R_f = 0.30 (hexane / ethyl acetate = 4 / 1); ¹H NMR (400 MHz, CDCl₃) δ 7.54-7.16 (11H, m), 6.92-6.79 (6H, m), 4.86-4.51 (7H, m), 4.34-3.96 (1H, m), 3.81 (3H, s), 3.80 (3H, s), 3.79 (3H, s), 3.66-3.49 (2H, m), 3.44-3.36 (1H, m), 3.24-3.14 (1H, m); ¹³C NMR (100 MHz, CDCl₃) δ 159.3, 159.2, 133.8, 131.8, 131.4, 130.7, 130.3, 130.2, 129.8, 129.7, 129.5, 129.4, 128.9, 127.4, 113.8, 113.7, 88.4, 85.0, 80.1, 77.4, 75.3, 75.1, 72.9, 67.5, 55.2; IR (neat) $\nu_{\max}$ 3008, 1614, 1588, 1516, 1250 cm⁻¹; HRMS(FAB) [M+Na]⁺ calculated for C₃₅H₃₈O₇Na: 625.2236, found: 625.2247; [α]_D²⁵ +45.9 (*c* 1.44, CHCl₃).

(3aR,5aR,6S,9R,10aR,Z)-6-[(2S,3R,4S,5R)-3,4,5-tris(4-methoxybenzyloxy)-tetrahydro-2H-pyran-2-yloxy]-8-hydroxymethyl-1-isopropyl-3a,5a-dimethyl-2,3,3a,4,5,5a,6,9,10,10a-decahydrocyclohepta[e]inden-9-yl benzoate (21)

To a mixture of **19** (14.2 mg, 0.0214 mmol), **20** (19.4 mg, 0.0321 mmol), and MS 4A (30.0 mg) in Et₂O (0.5 mL) was added MeOTf (7.3 μ L 0.0642 mmol) at room temperature. After the addition, the reaction mixture was stirred for 2 d. The reaction was quenched with saturated aqueous NaHCO₃ solution (5.0 mL), and the aqueous layer was extracted with CH₂Cl₂ (3×5.0 mL), dried over Na₂SO₄, filtered, and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate=6/1) to afford crude product (19.5 mg) and starting material **19** (3.0 mg, 20 %). To a solution of this crude product (19.5 mg) in THF (1.0 mL) was added HF·Py (25.0 μ L, 0.791 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 10 h. The reaction was quenched by saturated

aqueous NaHCO₃ solution (10 mL) and CH₂Cl₂ (5.0 mL). The phases were separated and the aqueous layer was extracted with CH₂Cl₂ (3 × 3.0 mL). The combined organic layer was washed with brine (5.0 mL), dried (Na₂SO₄), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (hexane/ethyl acetate=2/1) to afford **21** (15.2 mg, 77 %, a mixture of anomeric isomers ($\alpha/\beta=1/3.5$)) as a clear colorless oil.

R_f = 0.10 (hexane / ethyl acetate = 2 / 1); ¹H NMR (400 MHz, CDCl₃) δ (β -glycoside): 8.08-7.09 (11H, m), 6.89-6.78 (6H, m), 6.11 (1H, br), 5.91 (1H, d, $J=6.3$ Hz), 4.95-4.46 (6H, m), 4.73 (2H, s), 4.39 (1H, d, $J=7.1$ Hz), 4.26-4.11 (1H, m), 3.82-3.75 (1H, m), 3.79 (3H, s), 3.79 (3H, s), 3.79 (3H, s), 3.67-3.50 (3H, m), 3.46-3.39 (1H, m), 3.11-2.79 (3H, m), 2.36-2.19 (4H, m), 1.74-1.40 (5H, m), 0.99 (3H, s), 0.97 (3H, d, $J=6.8$ Hz), 0.92 (3H, d, $J=6.8$ Hz), 0.88 (3H, s); δ (α -glycoside): 8.08-7.09 (11H, m), 6.89-6.78 (6H, m), 6.11 (1H, br), 5.76 (1H, d, $J=5.4$ Hz), 4.95-4.46 (7H, m), 4.73 (2H, s), 4.26-4.11 (1H, m), 3.82-3.75 (1H, m), 3.79 (3H, s), 3.79 (3H, s), 3.79 (3H, s), 3.67-3.50 (3H, m), 3.46-3.39 (1H, m), 3.11-2.79 (3H, m), 2.36-2.19 (4H, m), 1.74-1.40 (5H, m), 0.99 (3H, s), 0.95 (3H, d, $J=6.8$ Hz), 0.91 (3H, d, $J=6.8$ Hz), 0.88 (3H, s); IR (neat) $\nu_{\max}$ 3482, 1722, 1516, 1076 cm⁻¹; HRMS(FAB) [M+Na]⁺ calculated for C₅₆H₆₈O₁₁Na: 939.4659, found: 939.4696.

(3aR,5aR,6S,9R,10aR,E)-6-[(2S,3R,4S,5R)-3,4,5-tris(4-methoxybenzyloxy)-tetrahydro-2H-pyran-2-yloxy]-8-formyl-1-isopropyl-3a,5a-dimethyl-2,3,3a,4,5,5a,6,9,10,10a-decahydrocyclohepta[e]inden-9-yl benzoate (21a)

To a solution of **21** (15.0 mg, 0.0163 mmol) in CH₂Cl₂ (1.0 mL) was added Dess-Martin periodinane (13.9 mg, 0.0327 mmol) portionwise, and the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched by adding Et₂O (5.0 mL), saturated aqueous NaHCO₃ solution (5.0 mL), and saturated aqueous Na₂S₂O₃ solution (5.0 mL) successively. The organic layer was separated, washed with brine (5.0 mL), dried over Na₂SO₄, and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate=3/1) to afford aldehyde **21a** (14.3 mg, 96 %, a mixture of anomeric isomers ($\alpha/\beta=1/3.5$)) as a colorless oil.

R_f = 0.40 (hexane / ethyl acetate = 2 / 1); ¹H NMR (400 MHz, CDCl₃) δ (β -glycoside): 9.50 (1H, s), 8.02-7.17 (11H, m), 6.99 (1H, d, $J=5.4$ Hz), 6.92-6.83 (6H, m), 6.20-6.13 (1H, m), 4.89-4.48 (7H, m), 4.34 (1H, d, $J=7.6$ Hz), 3.90-3.71 (3H, m), 3.81 (3H, s), 3.80 (6H, s), 3.67-3.35 (2H, m), 2.99-2.67 (3H, m), 2.35-2.24 (2H, m), 2.12-1.89 (2H, m),

1.79-1.38 (5H, m), 1.02 (3H, s), 0.98 (3H, d, $J=6.3$ Hz), 0.96 (3H, s), 0.95 (3H, d, $J=6.3$ Hz); δ (α -glycoside): 9.32 (1H, s), 8.02-7.17 (11H, m), 6.92-6.83 (6H, m), 6.81 (1H, d, $J=8.3$ Hz), 6.20-6.13 (1H, m), 4.89-4.48 (7H, m), 4.86 (1H, d, $J=4.1$ Hz), 3.90-3.71 (3H, m), 3.81 (3H, s), 3.80 (6H, s), 3.67-3.35 (2H, m), 2.99-2.67 (3H, m), 2.35-2.24 (2H, m), 2.12-1.89 (2H, m), 1.79-1.38 (5H, m), 1.02 (3H, s), 0.98 (3H, d, $J=6.3$ Hz), 0.96 (3H, s), 0.95 (3H, d, $J=6.3$ Hz); IR (neat) $\nu_{\max}$ 2928, 1726, 1702, 1516, 1252 cm^{-1} ; HRMS(FAB) $[M+Na]^+$ calculated for $C_{56}H_{66}O_{11}Na$: 939.4659, found: 937.4498.

(3a*R*,5a*R*,6*S*,9*R*,10a*R*,*E*)-6-[(2*S*,3*R*,4*S*,5*R*)-3,4,5-trihydroxytetrahydro-2*H*-pyran-2-yloxy]-8-formyl-1-isopropyl-3a,5a-dimethyl-2,3,3a,4,5,5a,6,9,10,10a-decahydrocyclohepta[*e*]inden-9-yl benzoate (22**)**

To a solution of aldehyde **21a** (14.3 mg, 0.0156 mmol) in CH_2Cl_2 (1.0 mL) was added TFA (0.10 mL) at -20°C . After the addition, the reaction mixture was stirred for 2 h. The reaction mixture was quenched by adding saturated aqueous NaHCO_3 solution (10 mL). The aqueous layer was extracted with EtOAc (4×5.0 mL), dried over Na_2SO_4 , filtered, and evaporated. The residue was purified by preparative TLC (ethyl acetate) to afford triol **22** (8.7 mg, 100 %, a mixture of anomeric isomers) as an oil.

R_f = 0.12 (ethyl acetate); ^1H NMR (400 MHz, CDCl_3) δ (β -glycoside): 9.45 (1H, s), 8.00-7.37 (5H, m), 7.06 (1H, d, $J=5.3$ Hz), 6.10 (1H, dd, $J=6.6, 6.6$ Hz), 4.61 (1H, d, $J=5.4$ Hz), 4.26 (1H, d, $J=5.3$ Hz), 3.79 (1H, dd, $J=11.5, 5.4$ Hz), 3.67-3.60 (1H, m), 3.58-3.45 (2H, m), 3.03 (1H, d, $J=10.8$ Hz), 2.85-2.61 (3H, m), 2.33-2.18 (3H, m), 2.14-2.06 (1H, m), 1.82-1.73 (1H, m), 1.65-1.56 (1H, m), 1.54-1.34 (3H, m), 1.03 (3H, s), 0.96 (3H, d, $J=6.3$ Hz), 0.95 (3H, s), 0.94 (3H, d, $J=6.3$ Hz); δ (α -glycoside): 9.49 (1H, s), 8.00-7.37 (5H, m), 6.84 (1H, d, $J=5.4$ Hz), 6.17 (1H, dd, $J=7.3, 7.3$ Hz), 4.87 (1H, d, $J=3.4$ Hz), 4.26 (1H, d, $J=5.4$ Hz), 3.79 (1H, dd, $J=11.5, 3.4$ Hz), 3.67-3.60 (1H, m), 3.58-3.45 (2H, m), 3.03 (1H, d, $J=10.8$ Hz), 2.85-2.61 (3H, m), 2.33-2.18 (3H, m), 2.14-2.06 (1H, m), 1.82-1.73 (1H, m), 1.65-1.56 (1H, m), 1.54-1.34 (3H, m), 1.03 (3H, s), 0.96 (3H, d, $J=6.3$ Hz), 0.95 (3H, s), 0.94 (3H, d, $J=6.3$ Hz); IR (neat) $\nu_{\max}$ 3384, 2928, 2856, 1726, 1704, 1464, 1268, 1110 cm^{-1} ; HRMS(FAB) $[M+Na]^+$ calculated for $C_{32}H_{42}O_8Na$: 577.2777, found: 577.2750.

(–)-erinacine B

To a solution of triol **22** (8.7 mg, 0.0156 mmol) and LiBr (0.68 mg, 7.81×10^{−3} mmol) in THF (2.0 mL) was added TEA (6.5 μL, 0.0469 mmol) and the reaction mixture was stirred at room temperature for 1 d. The reaction was quenched with brine (5.0 mL), and the aqueous layer was extracted with EtOAc (4 × 5.0 mL). The combined organic layer was dried over Na₂SO₄, filtered, and evaporated. The residue was purified by preparative TLC (hexane/ethyl acetate=1/2) to afford (–)-**erinacine B** (5.0 mg, 74 %, a single isomer) as a white solid.

R_f = 0.15 (hexane / ethyl acetate = 1 / 1); mp 124.8-126.6 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.56 (1H, s), 6.98 (1H, m), 5.14 (1H, d, *J*=9.7 Hz), 4.58 (1H, d, *J*=8.4 Hz), 4.03 (1H, dd, *J*=11.7, 5.9 Hz), 3.82 (1H, d, *J*=9.7 Hz), 3.69 (1H, m), 3.60 (1H, dd, *J*=8.8, 8.8 Hz), 3.35 (1H, dd, *J*=11.7, 10.6 Hz), 3.20 (1H, dd, *J*=8.8, 8.4 Hz), 2.75 (1H, m), 2.72 (2H, m), 2.30 (1H, m), 2.26 (2H, m), 1.69 (1H, m), 1.62 (1H, m), 1.58 (2H, m), 1.50 (2H, m), 1.02 (3H, s), 0.99 (3H, s), 0.98 (3H, d, *J*=6.2 Hz), 0.97 (3H, d, *J*=6.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 193.1, 156.8, 142.2, 140.3, 135.8, 98.4, 79.3, 75.0, 71.2, 71.1, 70.7, 66.7, 49.4, 41.7, 41.6, 38.1, 36.3, 29.7, 28.4, 27.7, 27.1, 24.4, 21.9, 21.4, 16.4; IR (neat) ν_{max} 3421, 1691, 1616, 1458, 1377 cm^{−1}; HRMS(FAB) [M+H]⁺ calculated for C₂₅H₃₇O₆: 455.2590, found: 433.2578; [α]_D²³ −34.6 (*c* 0.18, MeOH).

DFILE C:\Documents and Settings#\n
COMNT 06.02.10-eri-isomerization
DATIM Fri Feb 10 14:37:20 2006

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EXMOD NON

OBFREQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz

POINT 32768
FREQU 7992.01 Hz

SCANS 16
ACQTM 4.1001 sec

PD 2.9000 sec
PW1 6.60 usec

IRNUC 1H

CTEMP 25.9 c

SLVNT CDCL3

EXREF 0.00 ppm

BF 0.12 Hz

RGAIN 14

DFILE
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OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27247.90 Hz
SCANS 128
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PD 1.7940 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 22.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 24

DFILE C:\Documents and Settings\#1
COMNT 06.02.14-er i-cleavage.of. M
DATIM Tue Feb 14 11:13:56 2006

OBNUC 1H
EXMOD NON

OBFREQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz

POINT 32768
FREQU 7992.01 Hz

SCANS 16

ACQTM 4.1001 sec
PD 2.9000 sec
PW1 6.60 usec

IRNUC 1H

CTEMP 26.7 c

SLVNT CDCL3

EXREF 0.00 ppm

BF 0.12 Hz
RGAIN 18

DFILE F:\Ytakano\Ynmt10Feb28.als
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DATIM Fri Jan 28 23:59:24 2005
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EXMOD BCM
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OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 128
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 4.80 usec
IRNUC 1H
CTEMP 25.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 26

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COMNT 06.02.15-er i-1.4-red. (Sml2
DATIM Wed Feb 15 16:17:43 2006

OBNUC 1H
EXMOD NON

OBFREQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz

POINT 32768
FREQU 7992.01 Hz

SCANS 16

ACQTM 4.1001 sec
PD 2.9000 sec

PW1 6.60 usec

IRNUC 1H

CTEMP 27.0 c

SLVNT CDCL3

EXREF 0.00 ppm

BF 1.00 Hz

RGAIN 19

DF ILE F:\Ytakano\Ynmt10Feb012005. a

COMNT

DATIM Tue Feb 01 18:34:15 2005

OBNUC 13C

EXMOD BCM

OBFREQ 100.40 MHz

OBSET 125.00 KHz

OBFIN 10500.00 Hz

POINT 32768

FREQ 27173.90 Hz

SCANS 128

ACQTM 1.2059 sec

PD 1.7940 sec

PW1 4.80 usec

IRNUC 1H

CTEMP 26.5 c

SLVNT CDCL3

EXREF 77.00 ppm

BF 1.00 Hz

RGAIN 26

DFILE F:\Ytakano date\mnt002Feb01

COMNT

DATIM Tue Feb 01 23:45:09 2005

OBNUC 1H

EXMOD NON

OBFREQ 399.65 MHz

OBSSET 124.00 KHz

OBFIN 10500.00 Hz

POINT 32768

FREQ 8000.00 Hz

SCANS 16

ACQTM 4.0960 sec

PD 2.9040 sec

PW1 6.70 usec

IRNUC 1H

CTEMP 26.1 c

SLVNT CDCL3

EXREF 0.00 ppm

BF 0.12 Hz

RGAIN 14

14a

DFILE
COMNT
DATIM Tue Feb 01 23:53:54 2005
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 128
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 4.80 usec
IRNUC 1H
CTEMP 26.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 26

14a

DFILE C:\Documents and Settings\#
COMNT 06.07.07-er i-566-isopropen
DATIM Fri Jul 07 20:52:41 2006

OBNUC 1H
EXMOD NON

OBFREQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz

POINT 32768
FREQ 7992.01 Hz

SCANS 16

ACQTM 4.1001 sec
PD 2.9000 sec

PW1 6.60 usec

IRNUC 1H

CTEMP 23.2 C

SLVNT CDCL3

EXREF 0.00 ppm

BF 0.12 Hz

RGAIN 20

14b

DFILE C:\Documents and Settings\#1
COMNT 060921 isopropenyl e11 carl
DATIM Thu Sep 21 18:26:18 2006

OBNUC 13C
EXMOD BCM

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OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz

SCANS 64

ACQTM 1.2083 sec
PD 1.7920 sec
PW1 4.60 usec

IRNUC 1H

CTEMP 24.6 c

SLVNT CDCL3

EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 24

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 DATIM 1H
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 EXMOD 399.65 MHz
 OBFREQ 124.00 KHz
 OBSET 10500.00 Hz
 OBF IN 32768
 POINT 7992.01 Hz
 FREQU 16
 SCANS 4.1001 sec
 ACQTM 2.9000 sec
 PD 6.60 usec
 PW1 1H
 IRNUC 27.6 c
 CTEMP CDCL3
 SLVNT 0.00 ppm
 EXREF 0.12 Hz
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 RGAIN

COMNT
DATIM Tue May 10 11:36:48 2005
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OBFIN 10500.00 Hz
POINT 32768
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PD 1.7940 sec
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IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 24

DFILE C:\Documents and Settings#\r
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DATIM Fri Mar 10 12:36:41 2006

OBNUC 1H
EXMOD NON

OBFREQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz

POINT 32768
FREQU 7992.01 Hz

SCANS 16

ACQTM 4.1001 sec
PD 2.9000 sec

PW1 6.60 usec

IRNUC 1H

CTEMP 28.7 c

SLVNT CDCL3

EXREF 0.00 ppm

BF 0.12 Hz

RGAIN 22

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COMNT
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EXMOD BCM
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OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 128
ACQTM 1.2059 sec
PD 1.7940 sec
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IRNUC 1H
CTEMP 27.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 24

DFILE F:\eri NMR\060718 dehydrox
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DATIM Tue Jul 18 15:04:15 2006

OBNUC 1H
EXMOD NON

OBFREQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz

POINT 32768
FREQU 7992.01 Hz

SCANS 16

ACQTM 4.1001 sec
PD 2.9000 sec

PW1 6.60 usec

IRNUC 1H

CTEMP 21.8 c

SLVNT CDCL3

EXREF 0.00 ppm

BF 1.20 Hz

RGAIN 20

COMNT
 DATIM Sat May 14 22:33:43 2005
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 EXMOD BCM
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 OBSET 125.00 KHz
 OBFIN 10500.00 Hz
 POINT 32768
 FREQU 27173.90 Hz
 SCANS 128
 ACQTM 1.2059 sec
 PD 1.7940 sec
 PW1 4.80 usec
 IRNUC 1H
 CTEMP 26.2 C
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 24

DFILE C:\Documents and Settings#\n
COMNT 06.03.14-eri-isomerization
DATIM Tue Mar 14 10:55:30 2006

OBNUC 1H
EXMOD NON

OBFREQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz

POINT 32768
FREQU 7992.01 Hz

SCANS 16

ACQTM 4.1001 sec
PD 2.9000 sec

PW1 6.60 usec

IRNUC 1H

CTEMP 25.5 c

SLVNT CDCL3

EXREF 0.00 ppm

BF 1.00 Hz

RGAIN 13

COMNT
DATIM Tue May 17 14:12:54 2005
OBNUC 13C
EXMOD BCM
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POINT 32768
FREQU 27173.90 Hz
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ACQTM 1.2059 sec
PD 1.7940 sec
PW1 7.00 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 24

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 06.03.14-eri-C02Me
 Tue Mar 14 18:11:20 2006
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 NON
 399.65 MHz
 124.00 KHz
 10500.00 Hz
 32768
 7992.01 Hz
 16
 4.1001 sec
 2.9000 sec
 6.60 usec
 1H
 24.9 c
 CDCL3
 0.00 ppm
 0.12 Hz
 16
 RGAIN

DF IL E C:\Documents and Settings#\1
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 PD 1.7920 sec
 PW1 4.60 usec
 IRNUC 1H
 CTEMP 25.4 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 25

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C:\Documents and Settings\
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Mon Mar 27 14:52:03 2006
1H
NON
399.65 MHz
124.00 KHz
10500.00 Hz
32768
7992.01 Hz
16
4.1001 sec
2.9000 sec
6.60 usec
1H
25.4 c
CDCL3
0.00 ppm
0.12 Hz
17

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C:\Documents and Settings\H
 06.03.27-er i-iodomethyl-ma
 Mon Mar 27 15:06:04 2006
 13C
 BCM

EXMOD
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 OBSET 125.00 KHz
 OBFIN 10500.00 Hz
 POINT 32768
 FREQU 27118.64 Hz
 SCANS 256
 ACQTM 1.2083 sec
 PD 1.7920 sec
 PW1 4.60 usec
 IRNUC 1H
 CTEMP 25.1 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 25

DF IL
 COMNT
 DATIM
 OBNUC
 EXMOD
 OBFRQ
 OBSET
 OBFIN
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 PW1
 IRNUC
 CTEMP
 SLVNT
 EXREF
 BF
 RGAIN

DFILE C:\Documents and Settings\#1
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OBNUC 1H
 EXMOD NON

OBFRC 399.65 MHz
 OBSET 124.00 KHz
 OBFIN 10500.00 Hz

POINT 32768
 FREQU 7992.01 Hz

SCANS 16

ACQTM 4.1001 sec
 PD 2.9000 sec

PW1 6.60 usec

IRNUC 1H

CTEMP 24.6 c

SLVNT CDCL3

EXREF 0.00 ppm

BF 0.12 Hz

RGAIN 19

C:\Documents and Settings\#1
 06.03.27-er i-iodomethyl-m
 Mon Mar 27 15:28:44 2006
 13C
 BCM
 100.40 MHz
 125.00 KHz
 10500.00 Hz
 32768
 27118.64 Hz
 256
 1.2083 sec
 1.7920 sec
 4.60 usec
 1H
 23.9 c
 CDCL3
 77.00 ppm
 0.12 Hz
 25

DF IL
 COMNT
 DATIM
 OBNUC
 EXMOD
 OBFREQ
 OBSET
 OBFIN
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 PW1
 IRNUC
 CTEMP
 SLVNT
 EXREF
 BF
 RGA IN

C:\Documents and Settings\H
06.04.18-er i-ring-expansion
Wed Apr 19 17:25:31 2006

DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFREQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

1H
NON

399.65 MHz
124.00 KHz
10500.00 Hz
32768
7992.01 Hz
16
4.1001 sec
2.9000 sec
6.60 usec
25.5 c
CDCL3
0.00 ppm
0.12 Hz
18

DFILE C:\Documents and Settings#\n
COMNT 06.07.03-er i-567-ring-expa
DATIM Mon Jul 03 17:37:44 2006

OBNUC 13C
EXMOD BCM

OBFREQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz

POINT 32768
FREQU 27118.64 Hz

SCANS 128

ACQTM 1.2083 sec

PD 1.7920 sec

PW1 4.60 usec

IRNUC 1H

CTEMP 22.9 c

SLVNT CDCL3

EXREF 77.00 ppm

BF 0.12 Hz

RGAIN 24

DF IL F:¥NMR¥eri A, B. C¥0-2
 COMNT
 DATIM Wed May 17 19:05:29 2006
 OBNUC 1H
 EXMOD NON
 OBF RQ 399.65 MHz
 OBSE 124.00 KHz
 OBF IN 10500.00 Hz
 POIN 32768
 FREQU 7992.01 Hz
 SCANS 16
 ACQTM 4.1001 sec
 PD 2.9000 sec
 PW1 6.60 usec
 IRNUC 1H
 CTEMP 24.0 c
 SLVNT CDCL3
 EXREF 7.24 ppm
 BF 0.12 Hz
 RGAIN 16

DF IL E F:\NMR\eri A, B. C\0-2
 COMNT
 DATIM Wed May 17 19:02:41 2006
 OBNUC 13C
 EXMOD BCM
 OBFRQ 100.40 MHz
 OBSET 125.00 KHz
 OBF IN 10500.00 Hz
 POINT 32768
 FREQU 27118.64 Hz
 SCANS 401
 ACQTM 1.2083 sec
 PD 1.7920 sec
 PW1 4.60 usec
 IRNUC 1H
 CTEMP 24.3 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.00 Hz
 RGAIN 25

DFILE F:\NMR\eri\eri A, B, C\0-3
COMNT 06.04.27-eri-isomerization
DATIM Thu Apr 27 22:08:19 2006

OBNUC 1H
EXMOD NON

OBFREQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz

POINT 32768
FREQU 7992.01 Hz

SCANS 16

ACQTM 4.1001 sec
PD 2.9000 sec

PW1 6.60 usec

IRNUC 1H

CTEMP 25.1 C

SLVNT CDCL3

EXREF 0.00 ppm

BF 0.12 Hz

RGAIN 22

DF IL E F:¥NMR¥eri¥eri A, B. C¥0-3
 COMNT
 DATIM Fri May 19 11:22:33 2006
 OBNUC 13C
 EXMOD BCM
 OBF RQ 100.40 MHz
 OBSE T 125.00 KHz
 OBF IN 10500.00 Hz
 POIN T 32768
 FREQU 27118.64 Hz
 SCANS 400
 ACQTM 1.2083 sec
 PD 1.7920 sec
 PW1 4.60 usec
 IRNUC 1H
 CTEMP 24.6 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.00 Hz
 RGAIN 25

DFILE F:\NMR\eri\eri A, B. C\1-d
COMNT
DATIM Sun Apr 16 17:16:43 2006
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7992.01 Hz
SCANS 32
ACQTM 4.1001 sec
PD 2.9000 sec
PW1 6.60 usec
IRNUC 1H
CTEMP 24.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 21

DFILE F:\NMR\eri\eri A, B. C\1-d
COMNT
DATIM Fri May 19 19:37:23 2006
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 400
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 4.60 usec
IRNUC 1H
CTEMP 24.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 25

DF IL E F:\NMR\eri\eri A, B. C\2-er
 COMNT 06.05.17-eri-567-epoxydat
 DATIM Wed May 17 11:03:22 2006
 OBNUC 1H
 EXMOD NON
 OBFRQ 399.65 MHz
 OBSET 124.00 KHz
 OBFIN 10500.00 Hz
 POINT 32768
 FREQU 7992.01 Hz
 SCANS 32
 ACQTM 4.1001 sec
 PD 2.9000 sec
 PW1 6.60 usec
 IRNUC 1H
 CTEMP 24.2 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 21

DATIM 13C

OBNUC 13C
EXMOD 150.91 MHz
OBFREQ 8.59 KHz
OBSET 3.80 Hz
OBFIN 65536
POINT 34722.22 Hz
FREQ 8
SCANS 0.0000 sec
ACQTM 0.0000 sec
PD 10.00 usec
PW1 0.0 c
IRNUC 77.00 ppm
CTEMP 0.12 Hz
SLVNT 0
EXREF
BF
RGAIN

DF IL E F:\NMR\eri\eri A, B. C\4-D
 COM NT
 DAT IM Mon Sep 11 21:09:56 2006
 OBNUC 1H
 EXMOD NON
 OBFRQ 399.65 MHz
 OBSET 124.00 KHz
 OBF IN 10500.00 Hz
 POIN T 32768
 FREQU 7992.01 Hz
 SCANS 16
 ACQTM 4.1001 sec
 PD 2.9000 sec
 PW1 6.60 usec
 IRNUC 1H
 CTEMP 24.5 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 15

DFILE F:\NMR\eri\eri A, B. C\4-D
COMNT
DATIM Mon Sep 11 21:06:55 2006
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 128
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 4.60 usec
IRNUC 1H
CTEMP 24.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 25

DFILE F:\NMR\eri\eri A, B. C\6-B-

COMNT
DATIM Thu Sep 14 10:45:28 2006
OBNUC 1H
EXMOD NON
OBFREQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7992.01 Hz
SCANS 16
ACQTM 4.1001 sec
PD 2.9000 sec
PW1 6.60 usec
IRNUC 1H
CTEMP 24.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 18

DF IL E F:\NMR\eri\eri A, B. C\6-B-
 COM NT
 DAT IM Thu Sep 14 10:41:51 2006
 OBNUC 13C
 EXMOD BCM
 OBFRQ 100.40 MHz
 OBSET 125.00 KHz
 OBF IN 10500.00 Hz
 POIN T 32768
 FREQU 27118.64 Hz
 SCANS 280
 ACQTM 1.2083 sec
 PD 1.7920 sec
 PW1 4.60 usec
 IRNUC 1H
 CTEMP 24.4 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.00 Hz
 RGAIN 25

DFILE F:\NMR\eri\eri A, B. C\7-B
COMNT
DATIM Wed Sep 06 13:08:14 2006
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7992.01 Hz
SCANS 16
ACQTM 4.1001 sec
PD 2.9000 sec
PW1 6.60 usec
IRNUC 1H
CTEMP 25.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 21

DFIL F:\NMR\eri A, B. C\7-B
 COMNT
 DATIM Thu Sep 14 20:17:26 2006
 OBNUC 13C
 EXMOD BCM
 OBFRQ 100.40 MHz
 OBSET 125.00 KHz
 OBFIN 10500.00 Hz
 POINT 32768
 FREQU 27118.64 Hz
 SCANS 256
 ACQTM 1.2083 sec
 PD 1.7920 sec
 PW1 4.60 usec
 IRNUC 1H
 CTEMP 26.2 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.00 Hz
 RGAIN 25

DFILE F:\NMR\eri\sugar\2-SPH tri
COMNT
DATIM Thu Sep 14 10:24:20 2006
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7992.01 Hz
SCANS 16
ACQTM 4.1001 sec
PD 2.9000 sec
PW1 6.60 usec
IRNUC 1H
CTEMP 24.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 17

DF IL E F:\NMR\eri\sugar\2-SPH tri
 COMNT
 DATIM Thu Sep 14 10:21:30 2006
 OBNUC 13C
 EXMOD BCM
 OBFRQ 100.40 MHz
 OBSET 125.00 KHz
 OBF IN 10500.00 Hz
 POINT 32768
 FREQU 27118.64 Hz
 SCANS 256
 ACQTM 1.2083 sec
 PD 1.7920 sec
 PW1 4.60 usec
 IRNUC 1H
 CTEMP 25.1 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.00 Hz
 RGA IN 25

DF IL E F:\NMR\eri\eri A, B. C\9-B
 COM NT
 DAT IM Mon Sep 18 12:47:25 2006
 OBNUC 1H
 EXMOD NON
 OBFRQ 399.65 MHz
 OBSET 124.00 KHz
 OBF IN 10500.00 Hz
 POIN T 32768
 FREQU 7992.01 Hz
 SCANS 16
 ACQTM 4.1001 sec
 PD 2.9000 sec
 PW1 6.60 usec
 IRNUC 1H
 CTEMP 24.9 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 16

DF IL E F:\NMR\eri\eri A, B. C\10-1
 COM NT
 DAT IM Tue Sep 19 14:01:02 2006
 OBNUC 1H
 EXMOD NON
 OBFRQ 399.65 MHz
 OBSET 124.00 KHz
 OBF IN 10500.00 Hz
 POIN T 32768
 FREQU 7992.01 Hz
 SCANS 16
 ACQTM 4.1001 sec
 PD 2.9000 sec
 PW1 6.20 usec
 IRNUC 1H
 CTEMP 25.5 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 1.00 Hz
 RGAIN 17

DFILE F:\NMR\eri\eri A, B. C\11-1-1
 COMNT
 DATIM Wed Sep 20 09:41:28 2006
 OBNUC 1H
 EXMOD NON
 OBFREQ 399.65 MHz
 OBSET 124.00 KHz
 OBFIN 10500.00 Hz
 POINT 32768
 FREQU 7992.01 Hz
 SCANS 18
 ACQTM 4.1001 sec
 PD 2.9000 sec
 PW1 6.60 usec
 IRNUC 1H
 CTEMP 24.6 c
 SLVNT CD3OD
 EXREF 0.00 ppm
 BF 1.00 Hz
 RGAIN 18

22

DFILE F:\NMR\eri\eri A, B. C\eri
COMNT
DATIM Thu Sep 21 09:19:54 2006
OBNUC 1H
EXMOD NON
OBFREQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQ 7992.01 Hz
SCANS 32
ACQTM 4.1001 sec
PD 2.9000 sec
PW1 6.60 usec
IRNUC 1H
CTEMP 24.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 20

DFILE F:\NMR\eri\eri A, B. C\eri in
 COMNT
 DATIM Thu Sep 21 09:11:22 2006
 OBNUC 13C
 EXMOD BCM
 OBFRQ 100.40 MHz
 OBSET 125.00 KHz
 OBFIN 10500.00 Hz
 POINT 32768
 FREQU 27118.64 Hz
 SCANS 2048
 ACQTM 1.2083 sec
 PD 1.7920 sec
 PW1 4.60 usec
 IRNUC 1H
 CTEMP 24.7 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 2.00 Hz
 RGAIN 25