Stereodivergent Approach to the Asymmetric Synthesis of Bacillariolides. A Formal Synthesis of ent-Bacillariolide II

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Supporting Information

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Experimental Section

Melting points were taken in open capillaries in sulfuric acid bath and are uncorrected. Petroleum ether refers to the fraction having bp 60-80 ^{o}C. A usual workup of the reaction mixture consists of extraction with ether, washing with brine, drying over Na_2SO_4, and removal of the solvent in vacuo. Column chromatography was carried out with silica gel (60-120 mesh). Peak positions in ^{1}H and ^{13}C NMR spectra are indicated in ppm downfield from internal TMS in δ units. NMR spectra were taken in $CDCl_3$ at 300 MHz for ^{1}H and 75 MHz for ^{13}C. ^{13}C peaks assignment is based on DEPT experiment. IR spectra were recorded as neat for liquids and in KBr for solids. Unless otherwise indicated, all reactions were carried out under a blanket of N_2.

tert-Butyl (3R)-3-[(2S)-1,4-dioxaspiro[4.5]dec-2-yl]pent-4-enoate 4b. A solution of the ester **4a** (1.60 g, 5.97 mmol) in ethanol (10 mL) was heated with KOH (1.67 g, 29.82 mmol) and water (5 mL) at 80^{o}C for 2 h. Removal of ethanol in vacuo followed by acidification of the residual mass with cold 6N HCl afforded the corresponding acid (1.40 g). To a magnetically stirred solution of this acid (1.40 g, 5.83 mmol) in THF (7 mL), 4-dimethylaminopyridine (570 mg, 4.6 mmol), t-butanol (3.4 mL, 35 mmol) were added. A solution of 1,3-Dicyclohexylcarbodiimide (DCC) (1.8 g, 8.75 mmol) in dichloromethane (7mL) was added slowly to the reaction mixture at 0 ^{o}C. Stirring was continued for 30 min at 0 ^{o}C and 16 h at rt. Precipitated solid mass was then filtered and the filtrate was concentrated in vacuo. The residue was extracted with ether. The ether extract was washed with 0.5 N HCl (2×2 mL), saturated $NaHCO_3$ (2 mL) solution and dried. Evaporation of ether followed by column chromatography (ether-petroleum ether 1:19) of the residual mass afforded the ester **4b** (1.49 g, 81%): [α] $^{25}_{D}$ +15.1 (*c* 0.13, $CHCl_3$); IR 1732 cm^{-1}; ^{1}H NMR δ 1.42 (9H, s, CH_3), 1.57-1.73 (10H, m, CH_2), 2.30 (1H, dd, *J* = 9.6, 15.3, CH_2), 2.45 (1H, dd, *J* = 4.8, 15.3, CH_2), 2.73 (1H, m, CH), 3.63 (1H, t, *J* = 7.8, OCH_2), 3.96 (1H, t, *J* = 7.3, OCH_2), 4.12 (1H, dd, *J* = 6.6, 11.6, OCH), 5.12 (2H, m, $=CH_2$), 5.74 (1H, m, =CH-); ^{13}C NMR δ 23.6 (CH_2), 23.8 (CH_2), 25.0 (CH_2), 27.9 (CH_3), 34.6 (CH_2), 35.7 (CH_2), 36.9 (CH_2), 42.8 (CH), 66.2 (OCH_2), 77.0 (OCH), 80.3 (C), 109.4 (C), 117.3 (CH_2), 136.2 (CH), 171.3 (CO); Anal. Calcd for $C_{17}H_{28}O_4$: C, 68.89: H,

9.52. Found: C, 69.18; H, 9.72. HRMS (ESI) calcd for $C_{17}H_{28}O_4Na$ m/z $(M+Na)^+$ 319.1875, found 319.1852 m/z.

tert-Butyl(3S)-3-[(2S)-1,4-dioxaspiro[4.5]dec-2-yl]pent-4-enoate 2b. Following the above procedure, the ester **2a** (3.60 g, 13.4 mmol) was converted to the tert-butyl ester **2b** (2.73 g, 76%): $[\alpha]^{25}_D$ +12.8 (*c* 0.21, $CHCl_3$); IR 1732 cm^{-1}; ^1H NMR δ 1.39 (9H, s, CH_3), 1.59-1.66 (10H, m, CH_2), 2.27 (1H, dd, *J* = 9.5, 15.0, CH_2), 2.43 (1H, dd, *J* = 5.1, 15.0, CH_2), 2.70 (1H, m, CH), 3.62 (1H, t, *J* = 7.7, OCH_2), 3.94 (1H, t, *J* = 7.6, OCH_2), 4.09 (1H, dd, *J* = 6.7, 11.5, OCH), 5.07 (2H, m, $=CH_2$), 5.72 (1H, m, =CH-); ^{13}C NMR δ 23.7 (CH_2), 23.8 (CH_2), 25.0 (CH_2), 27.0 (CH_3), 34.9 (CH_2), 36.3 (CH_2), 37.5 (CH_2), 44.0 (CH), 67.4 (OCH_2), 77.0 (OCH), 80.2 (C), 109.7(C), 117.4 (CH_2), 136.6 (CH), 171.4 (CO); Anal. Calcd for $C_{17}H_{28}O_4$: C, 68.89: H, 9.52. Found: C, 68.81; H, 9.89. HRMS (ESI) calcd for $C_{17}H_{28}O_4Na$ m/z $(M+Na)^+$ 319.1875, found 319.1855 m/z.

tert-Butyl (3S)-2-allyl-3-[(2S)-1,4-dioxaspiro[4.5]dec-2-yl]pent-4-enoate 7b. A solution of the ester **4b** (1.46 g, 4.93 mmol) in THF (5 mL) was added dropwise to a magnetically stirred solution of LDA [prepared from diisopropylamine (1.7 mL, 12.3 mmol) in anhydrous THF (2.5 mL) and nBuLi (9.0 mL, 9.86 mmol, 1.1 M in hexane] at –78 ^oC. The reaction mixture was then slowly raised to –30 ^oC and stirred at that temperature for 1 h. The reaction mixture was again cooled to –78 ^oC and to it HMPA (1 mL) followed by allyl bromide (0.52 mL, 5.92 mmol) were added dropwise. The reaction mixture was allowed to attain rt and stirred for 5 h. After quenching with saturated aqueous NH_4Cl solution (1 mL), the reaction mixture was worked up in the usual way to afford after column chromatography (ether-petroleum ether 1:19) 1:1 diastereomeric mixture of diene **7b** and its cis-diastereoisomer (1.38g, 83%) as a liquid: $[\alpha]^{25}_D$ +13.7 (*c* 0.29, $CHCl_3$); IR 1724 cm^{-1}; ^1H NMR δ (of the mixture of diastereomers) 1.33 (9H, s, CH_3), 1.38 (9H, s, CH_3), 1.43-1.54 (20H, m, CH_2), 2.14-2.30 (4H, m, CH_2), 2.29 (2H, m, CH), 2.46 (2H, m, CH), 3.54 (1H, t, *J* = 7.8, OCH_2), 3.60 (1H, t, *J* = 7.9, OCH_2), 3.87 (1H, t, *J* = 7.6, OCH_2), 3.97 (1H, t, *J* = 7.6, OCH_2), 4.08 (1H, m, OCH), 4.18 (1H, q, *J* = 6.0, OCH), 4.91-5.21 (8H, m, $=CH_2$), 5.61-5.78 (4H, m, =CH-); ^{13}C NMR δ 23.67 (CH_2), 23.69 (CH_2), 23.8 (CH_2), 25.0 (CH_2), 25.0 (CH_2), 27.0 (CH_3), 34.4 (CH_2), 34.6 (CH_2), 34.8 (CH_2), 35.0 (CH_2), 35.1 (CH_2),35.6 (CH_2), 35.8 (CH_2), 47.3 (CH), 47.4 (CH), 48.2 (CH), 48.7 (CH), 66.7 (OCH_2), 66.9 (OCH_2), 74.6 (OCH), 75.2 (OCH), 80.4 (C), 80.5

(C), 109.1 (C), 109.3 (C), 116.4 (CH_2), 116.7 (CH_2), 118.9 (CH_2), 119.5 (CH_2), 134.4 (CH), 134.6 (CH), 135.2 (CH), 135.2 (CH), 172.7 (CO), 173.9 (CO); Anal. Calcd for $C_{20}H_{32}O_4$: C, 71.39: H, 9.59. Found: C, 71.25; H, 9.68. HRMS (ESI) calcd for $C_{20}H_{32}O_4Na$ m/z $(M+Na)^+$ 359.2198, found 359.2147 m/z.

tert-Butyl (3R)-2-allyl-3-[(2S)-1,4-dioxaspiro[4.5]dec-2-yl]pent-4-enoate 13. Following the above procedure, the ester **2b** (970 mg, 3.28 mmol) was allylated with allyl bromide (0.34 mL, 3.93 mmol) to afford a 1:1 diastereomeric mixture of the diene **13** (930 mg, 84%) as a colorless liquid: $[\alpha]$ $^{25}_D$ +16.5 (*c* 0.17, $CHCl_3$); IR 1728 cm^{-1}; ^1H NMR δ (of the mixture of diastereomers) 1.43 (9H, s, CH_3), 1.44 (9H, s, CH_3), 1.53-1.60 (20H, m, CH_2), 2.20-2.31 (4H, m, CH_2), 2.29 (1H, m, CH), 2.60 (2H, m, CH), 2.83 (1H, m, CH), 3.54 (1H, t, *J* = 7.7, OCH_2), 3.65 (1H, dd, *J* = 6.6, 8.1, OCH_2), 3.93 (2H, m, OCH_2), 4.04-4.15 (2H, m, OCH), 4.98-5.16 (8H, m, $=CH_2$), 5.49-5.83 (4H, m, =CH-); ^{13}C NMR δ 24.20 (CH_2), 24.22 (CH_2), 24.30 (CH_2), 24.33 (CH_2), 25.52 (CH_2), 25.53 (CH_2), 28.48 (CH_3), 28.51 (CH_3), 32.8 (CH_2),35.1 (CH_2), 35.6 (CH_2), 35.6(CH_2), 36.7 (CH_2), 36.9 (CH_2), 46.6 (CH), 47.5 (CH), 50.6 (CH), 51.1 (CH), 67.9 (OCH_2), 68.7 (OCH_2), 75.8 (OCH), 77.0 (OCH), 80.7 (C), 80.8 (C), 110.1 (C), 110.2 (C), 116.6 (CH_2), 116.9 (CH_2), 119.41 (CH_2), 119.44 (CH_2), 134.5 (CH), 134.8 (CH), 136.2 (CH), 136.6 (CH), 173.3 (CO), 173.7 (CO); Anal. Calcd for $C_{20}H_{32}O_4$: C, 71.39: H, 9.59. Found: C, 71.45; H, 9.70. HRMS (ESI) calcd for $C_{20}H_{32}O_4Na$ m/z $(M+Na)^+$ 359.2198, found 359.2182 m/z.

tert-Butyl(2S)-2-[(2S)-1,4-dioxaspiro[4.5]dec-2-yl]cyclopent-3-ene-1-carboxylate 9b. A solution of the dienes **7b** (1.30g, 3.87 mmol) in anhydrous benzene (52 mL) was degassed by bubbling Ar through it. To it was added Grubbs' catalyst **8** (190 mg, 0.23 mmol) in one portion. The resulting pink solution was stirred at 60 ^oC for 36 h. The solvent was removed under reduced pressure and the dark residue was purified by column chromatography (ether-petroleum ether 1:19) to afford a 1:1 diastereomeric mixture of cyclopentene **9b** and its cis-diastereoisomer (1.03 g, 86%) as a colorless liquid: $[\alpha]$ $^{25}_D$ -50.7 (*c* 0.54, $CHCl_3$); IR 1726 cm^{-1}; ^1H NMR δ (of the mixture of diastereomers) 1.45 (9H, s, CH_3), 1.46 (9H, s, CH_3), 1.62 (20H, m, CH_2), 2.47-2.65 (4H, m, CH_2), 2.69-2.77 (2H, m, CH), 3.04-3.15 (2H, m, CH), 3.66-3.72 (2H, m, OCH_2), 4.03 (2H, m, OCH_2), 4.04 (1H, m, OCH), 4.24 (1H, m, OCH), 5.66-5.84 (4H, m, =CH-); ^{13}C

NMR δ 24.17 (CH_2), 24.29 (CH_2), 24.36 (CH_2), 24.41 (CH_2), 25.55 (CH_2), 25.57 (CH_2), 28.40 (CH_3), 28.43 (CH_3), 35.16 (CH_2), 35.25 (CH_2), 36.04 (CH_2), 36.6 (CH_2), 36.9 (CH_2), 37.0 (CH_2), 45.5 (CH), 46.3 (CH), 52.0 (CH), 53.8 (CH), 67.6 (OCH_2), 68.6 (OCH_2), 76.2 (OCH), 78.6 (OCH), 80.7 (C), 80.9 (C), 109.5 (C), 109.9 (C), 130.4 (CH), 130.5 (CH), 130.6 (CH), 131.6 (CH), 173.6 (CO), 175.2 (CO); Anal. Calcd for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 70.16; H, 8.76. HRMS (ESI) calcd for $C_{18}H_{28}O_4Na$ m/z $(M+Na)^+$ 331.1885, found 331.1905 m/z.

tert-Butyl(2R)-2-[(2S)-1,4-dioxaspiro[4.5]dec-2-yl]cyclopent-3-ene-1-carboxylate 14. Following the above procedure, the dienes **13** (900 mg, 2.68 mmol) were ring closed with Grubbs' catalyst **8** (132 mg, 0.16mmol) to afford a 1:1 diastereomeric mixture of the cyclopentene derivatives **14** (760 mg, 92%): $[\alpha]^{25}_D$ +75.5 (*c* 0.17, $CHCl_3$); IR 1724 cm^{-1}; ^1H NMR δ (of the mixture of diastereomers) 1.37 (9H, s, CH_3), 1.39 (9H, s, CH_3), 1.54 (20H, m, CH_2), 2.39 (1H, dd, *J* = 8.9, 16.8, CH_2), 2.56 (4H, dt, *J* = 2.1, 7.4, CH_2), 2.77 (1H, q, *J* = 6.5, CH), 3.04-3.17 (2H, m, CH), 3.45 (1H, dd, *J* = 7.2, 8.0, OCH_2), 3.47 (1H, t, *J* = 7.6, OCH_2), 3.87 (1H, t, *J* = 7.3, OCH_2), 3.96 (1H, dd, *J* = 6.4, 7.9, OCH_2), 4.03 (1H, q, *J* = 6.2, OCH), 4.13 (1H, q, *J* = 6.5, OCH), 5.45 (2H, m, =CH-), 5.66 (1H, m, =CH-), 5.79 (1H, m, =CH-); ^{13}C NMR δ 23.5 (CH_2), 23.6 (CH_2), 23.8 (CH_2), 23.9 (CH_2), 25.00 (CH_2), 25.02 (CH_2), 27.90 (CH_3), 27.93 (CH_3), 34.65 (CH_2), 34.70 (CH_2), 35.4 (CH_2), 36.0 (CH_2), 36.02 (CH_2), 36.22 (CH_2), 44.8 (CH), 45.2 (CH), 51.1 (CH), 52.8 (CH), 66.0 (OCH_2), 66.5 (OCH_2), 74.8 (OCH), 77.3 (OCH), 80.1 (C), 80.3 (C), 108.7 (C), 109.3 (C), 128.3 (CH), 129.1 (CH), 131.1 (CH), 132.1 (CH), 173.2 (CO), 174.8 (CO); Anal. Calcd for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 70.21; H, 9.06. HRMS (ESI) calcd for $C_{18}H_{28}O_4Na$ m/z $(M+Na)^+$ 331.1885, found 331.1851 m/z.

Ethyl(1R, 2S)-2-[(2S)-1,4-dioxaspiro[4.5]dec-2-yl]-1-(phenylseleno) cyclopent-3-ene-1-carboxylate 11. A solution of the ester **10a** (160 mg, 0.57 mmol) in THF (1.5 mL), was added dropwise to a magnetically stirred solution of LDA [prepared from diisopropylamine (0.16 mL, 1.14 mmol) in anhydrous THF (1 mL) and nBuLi (0.82 mL, 1.14 mmol, 1.4 M in hexane] at –78 ^oC. The reaction mixture was then slowly raised to –30 ^oC and stirred at that temperature for 1 h. The reaction mixture was then again cooled to –78 ^oC and to it HMPA (0.2 mL) followed by addition of a solution of phenylselenium bromide (200 mg, 0.86 mmol) in THF (1 mL). The reaction mixture was allowed to attain

–30 ^{o}C and stirred for 2 h. After quenching with saturated aqueous NH_4Cl (1 mL), usual work up of the reaction mixture afforded 2.5:1 mixture of **11** and its diastereomer. The mixture was chromatographed (ether-petroleum ether 1:19) to afford **11** (156 mg, 63%): IR 1726 cm^{-1}; ^{1}H NMR δ 1.21 (3H, t, *J* = 6.9, CH_3), 1.48 (10H, m, CH_2), 2.39 (1H, d, *J* = 2.5, CH_2), 2.45 (1H, br s, CH), 2.82 (1H, br s, CH_2), 3.66 (1H, dd, *J* = 6.3, 8.1, OCH_2), 3.96 (1H, dd, *J* = 6.9, 8.1, OCH_2), 4.13 (2H, q, *J* = 7.1, OCH_2), 4.51 (1H, m, OCH), 5.77 (1H, m, =CH-), 5.92 (1H, m, =CH-), 7.29 (3H, m, ArH), 7.58 (2H, m, ArH); ^{13}C NMR δ 13.9 (CH_3), 23.3 (CH_2), 23.6 (CH_2), 25.0 (CH_2), 34.4 (CH_2), 35.6 (CH_2), 42.1 (CH_2), 55.2 (CH), 57.5 (C), 60.7(OCH_2) 66.6 (OCH_2), 74.9 (OCH), 109.2 (C), 127.7 (CH), 129.3 (CH), 129.3 (CH), 130.0 (CH), 131.6 (CH), 132.2 (C), 137.6 (CH), 137.6 (CH), 172.3 (CO).

tert-Butyl (1R, 2S)-2-[(2S)-1,4-dioxaspiro[4.5]dec-2-yl]-1-(phenylthio) cyclopent-3-ene-1-carboxylate 10b. A solution of the ester **9b** (1.0g, 3.25 mmol) in THF (4 mL), was added dropwise to a magnetically stirred solution of LDA [prepared from diisopropylamine (0.77 mL, 5.52 mmol) in anhydrous THF (2 mL) and nBuLi (3.1 mL, 4.88 mmol, 1.6 M in hexane] at –78 ^{o}C. The reaction mixture was then slowly raised to –30 ^{o}C and stirred at that temperature for 1 h. The reaction mixture was then again cooled to –78 ^{o}C and to it HMPA (1 mL) followed by addition of a solution of diphenyldisulphide (1.06 g, 4.88 mmol) in THF (2 mL). The reaction mixture was allowed to attain –30 ^{o}C and stirred for 2 h. After quenching with saturated aqueous NH_4Cl (1 mL). Usual work up of the mixture followed by column chromatography (ether-petroleum ether 1:19) afforded the substituted cyclopentene **10b** (1.04g, 77%): [α] $^{25}_{D}$ -110.5 (*c* 0.38, $CHCl_3$); IR 1720 cm^{-1}; ^{1}H NMR δ 1.45 (9H, s, CH_3), 1.49 (10H, m, CH_2), 2.40 (1H, dd, *J* = 1.4, 17.4, CH_2), 2.75 (1H, br s, CH), 3.31 (1H, ddd, *J* = 2.0, 4.1, 17.4, CH_2), 3.74 (1H, dd, *J* = 6.3, 8.3, OCH_2), 3.98 (1H, dd, *J* = 6.0, 8.5, OCH_2), 4.51 (1H, m, OCH), 5.74 (1H, m, =CH-), 5.96 (1H, m, =CH-), 7.32 (3H, m, ArH), 7.48 (2H, m, ArH); ^{13}C NMR δ 23.6 (CH_2), 23.8 (CH_2), 25.1 (CH_2), 27.8 (CH_3), 34.6 (CH_2), 35.6 (CH_2), 42.1 (CH_2), 55.6 (CH), 63.1 (C), 66.7 (OCH_2), 75.2 (OCH), 81.2 (C), 109.3 (C), 124.1 (C), 127.3 (CH), 128.4 (CH), 128.4 (CH), 128.9 (CH), 131.5 (CH), 136.0 (CH), 136.0 (CH), 170.6 (CO); Anal. Calcd for $C_{24}H_{32}O_4S$: C, 69.20; H, 7.74. Found: C, 69.57;

H, 7.65. HRMS (ESI) calcd for $C_{24}H_{32}O_4SNa$ m/z $(M+Na)^+$ 439.1919, found 439.1924 m/z.

tert-Butyl (1R, 2S)-2-[(2S)-1,4-dioxaspiro[4.5]dec-2-yl]-1-(methylsulfanyl) cyclopent-3-ene-1-carboxylate 10c. Following the above procedure, the cyclopentene **14** (630 mg, 2.05 mmol) was allowed to react with dimethyldisulfide (0.23 mL, 2.46 mmol). After quenching with saturated aqueous NH_4Cl (1 mL), usual work up of the reaction mixture afforded 1:1 mixture of **10c** and its diastereomer. The mixture was chromatographed (ether-petroleum ether 1:19) to afford **10c** (310 mg, 43%): IR 1715 cm^{-1}; ^1H NMR δ 1.50 (9H, s, CH_3), 1.51 (10H, m, CH_2), 2.12 (3H, s, CH_3), 2.35 (1H, dd, *J* = 2.6, 17.4, CH_2), 2.76 (1H, d, *J* = 1.9, CH), 3.16 (1H, dd, *J* = 4.1, 17.4, CH_2), 3.73 (1H, dd, *J* = 6.1, 8.4, OCH_2), 4.00 (1H, dd, *J* = 6.6, 8.4, OCH_2), 4.59 (1H, dd, *J* = 5.1, 11.5, OCH), 5.70 (1H, m, =CH-), 5.89 (1H, m, =CH-); ^{13}C NMR δ 13.7 (SCH_3), 24.1 (CH_2), 24.4 (CH_2), 25.6 (CH_2), 28.4 (CH_3), 35.2 (CH_2), 36.1 (CH_2), 42.5 (CH_2), 55.5 (CH), 59.9 (C), 67.2 (OCH_2), 75.8 (OCH), 81.7 (C), 109.9 (C), 127.9 (CH), 132.0 (CH), 170.9 (CO).

tert-Butyl (1R, 2S)-2-[(2S)-1,4-dioxaspiro[4.5]dec-2-yl]-1-(phenylthio) cyclopent-3-ene-1-carboxylate 15. Following the above procedure, the cyclopentene **14** (360 mg, 1.17 mmol) was allowed to react with diphenyldisulfide (382 mg, 1.75 mmol) to afford the cyclopentene derivative **15** (412 mg, 85%): $[\alpha]\ ^{25}_D$ +113.9 (*c* 0.18, $CHCl_3$); IR 1714 cm^{-1}; ^1H NMR δ 1.42 (9H, s, CH_3), 1.53 (10H, m, CH_2), 2.52 (1H, dd, *J* = 1.9, 18.0, CH_2), 3.00 (1H, dd, *J* = 2.0, 18.0, CH_2), 3.23 (1H, m, CH), 3.38 (1H, t, *J* = 7.7, OCH_2), 3.75 (1H, t, *J* = 7.8, OCH_2), 4.42 (1H, dd, *J* = 6.0, 12.8, OCH), 5.69 (1H, m, =CH-), 5.83 (1H, m, =CH-), 7.27 (3H, m, ArH), 7.43 (2H, m, ArH); ^{13}C NMR δ 24.10 (CH_2), 24.13 (CH_2), 25.5 (CH_2), 28.2 (CH_3), 35.2 (CH_2), 36.3 (CH_2), 42.9 (CH_2), 56.8 (CH), 62.5 (C), 65.3 (OCH_2), 75.1 (OCH), 82.4 (C), 109.2 (C), 128.8 (CH), 128.9 (CH), 128.9 (CH), 129.0 (CH), 131.0 (CH), 132.9 (C), 135.5 (CH), 135.5 (CH), 171.2 (CO); Anal. Calcd for $C_{24}H_{32}O_4S$: C, 69.20; H, 7.74. Found: C, 69.32; H, 7.93. HRMS (ESI) calcd for $C_{24}H_{32}O_4SNa$ m/z $(M+H)^+$ 417.2094, found 417.2030 m/z.

(3R,3aR,6aS)-3-(hydroxymethyl)-6a-(phenylthio)-3,3a,6,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-1-one 12. A solution of cyclopentene derivative **10b** (500 mg, 1.20 mmol) in aqueous trifluoroacetic acid (80%, 5 mL) was stirred at 80 ^oC for 2 h. The reaction mixture was diluted with EtOAc (20 mL) and washed with 3% NaOH solution

(w/v) several times to make it alkaline (pH paper). The organic layer was separated and usual workup afforded a liquid which was chromatographed (ether-petroleum ether 3:7) to afford the substituted lactone **12** (240 mg, 76%): $[\alpha]^{25}_{D}$ + 6.1 (*c* 0.45, $CHCl_3$); IR 1765, 3417 cm^{-1}; ^1H NMR δ 2.11 (1H, br s, OH), 2.75 (1H, ddd, *J* = 2.2, 4.5, 17.2, CH_2), 3.05 (1H, ddd, *J* = 2.0, 4.0, 17.1, CH_2), 3.62 (1H, td, *J* = 2.1, 6.4, CH), 3.68 (2H, d, *J* = 6.0, OCH_2), 4.08 (1H, q, *J* = 6.0, OCH), 5.62 (1H, m, =CH-), 5.85 (1H, m, =CH-), 7.40 (3H, m, ArH), 7.62 (2H, m, ArH); ^{13}C NMR δ 43.9 (CH_2), 55.9 (CH), 59.4 (C), 62.3 (OCH_2), 80.7 (OCH), 126.6 (CH), 129.1 (CH), 129.1 (CH), 129.3 (C), 130.0 (CH), 132.7 (CH), 136.0 (CH), 177.9 (CO); Anal. Calcd for $C_{14}H_{14}O_3S$: C, 64.10; H, 5.38. Found: C, 64.25; H, 5.10. HRMS (ESI) calcd for $C_{14}H_{14}O_3S$ m/z $(M+H)^+$ 263.0736, found 263.0786.

(3R, 3aS, 6aR)-3-(hydroxymethyl)-6a-(phenylthio)-3,3a, 6, 6a-tetrahydro-1*H*-cyclopenta[*c*] furan-1-one 16. Following the above procedure, the cyclopentene ester **15** (217 mg, 0.52 mmol) was transformed to the substituted lactone **16** (107 mg, 78%): $[\alpha]^{25}_{D}$ + 22.4 (*c* 0.25, $CHCl_3$); IR 1764, 3411 cm^{-1}; ^1H NMR δ 2.69 (1H, br s, OH), 2.80 (1H, ddd, *J* = 2.0, 4.1, 17.5, CH_2), 2.96 (1H, ddd, *J* = 2.0, 4.0, 17.5, CH_2), 3.34 (1H, dd, *J* = 2.1, 4.3, CH), 3.48 (2H, d, *J* = 6.0, OCH_2), 4.27 (1H, dt, *J* = 2.7, 6.0, OCH), 5.67 (1H, m, =CH-), 5.77 (1H, m, =CH), 7.40 (3H, m, ArH), 7.57 (2H, m, ArH); ^{13}C NMR δ 45.3 (CH_2), 55.4 (CH), 58.2 (C), 64.4 (OCH_2), 84.0 (OCH), 129.6 (CH), 129.6 (CH), 129.6 (CH), 130.3 (CH), 130.9 (C), 131.3 (CH), 136.34 (CH), 136.4 (CH), 136.4 (CH), 178.6 (CO); Anal. Calcd for $C_{14}H_{14}O_3S$: C, 64.10; H, 5.38. Found: C, 63.93; H, 5.45. HRMS (ESI) calcd for $C_{14}H_{14}O_3S$ m/z $(M+H)^+$ 263.0736, found 263.0695.

(3R, 3aS, 6aR)-3-(hydroxymethyl)-3,3a, 6,6a-tetrahydro-1*H*-cyclopenta[*c*] furan-1-one 3. A solution of the substituted lactone **12** (225 mg, 0.86 mmol) in anhydrous benzene (2 mL) was degassed by bubbling Ar and tributyltinhydride (0.35 mL, 1.29 mmol) was added to it. 2,2'-Azobisisobutyronitrile (AIBN) (5 mg) was added to it at 80 ^oC and refluxed for 4 h. Solvent removed under vacuo and white solid was purified by column chromatography (ether-petroleum ether 4:6) to afford the white solid lactone **3** (120 mg, 90%); mp 102-104 ^oC; $[\alpha]^{25}_{D}$ +36.7 (*c* 0.14, $CHCl_3$); IR 1760, 3398 cm^{-1}; ^1H NMR δ 2.74 (1H, ddd, *J* = 4.4, 8.3, 17.2, CH_2), 2.81 (1H, ddd, *J* = 2.0, 3.9, 17.2, CH_2), 3.30 (1H, dt, *J* = 1.6, 8.0, CH), 3.64 (1H, m, CH), 3.82 (2H, m, OCH_2), 4.73 (1H, dt, *J* = 4.8, 6.8, OCH), 5.63 (1H, m, =CH-), 5.90 (1H, m, =CH-); ^{13}C NMR δ 36.1 (CH_2), 43.6

(CH), 48.3 (CH), 62.8 (OCH_2), 82.3 (OCH), 126.5 (CH), 133.7 (CH), 180.2 (CO); Anal. Calcd for $C_8H_{10}O_3$: C, 62.33; H, 6.54. Found: C, 61.98; H, 6.74. HRMS (ESI) calcd for $C_8H_{10}O_3$ m/z $(M+H)^+$ 155.0703, found 155.0626 m/z.

(3R, 3aR, 6aS)-3-(hydroxymethyl)-3,3a,6,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-1-one 1. Following the above procedure, the substituted lactone **16** (90 mg, 0.34 mmol) on reaction with tributyltinhydride (0.14 mL, 0.53 mmol) was transformed to the lactone derivative **1** (48 mg, 91%) as colorless viscous liquid: $[\alpha]^{25}_D$ +29.8 (*c* 0.15, $CHCl_3$); IR 1759, 3408 cm^{-1}; ^1H NMR δ 2.62 (2H, dd, *J* = 2.4, 4.7, CH_2), 3.26 (1H, td, *J* = 5.2, 8.0, CH), 3.47 (1H, dd, *J* = 2.0, 8.0, CH), 3.75 (1H, dd, *J* = 3.8, 12.3, OCH_2), 3.92 (1H, dd, *J* = 2.9, 12.3, OCH_2), 4.4 (1H, m, OCH), 5.67 (1H, m, =CH-), 5.84 (1H, m, =CH-); ^{13}C NMR δ 28.4 (CH_2), 37.0 (CH), 49.4 (CH), 65.0 (OCH_2), 84.5 (OCH), 130.6 (CH), 132.6 (CH), 181.9 (CO); Anal. Calcd for $C_8H_{10}O_3$: C, 62.33; H, 6.54. Found: C, 62.54; H, 6.20. HRMS (ESI) calcd for $C_8H_{10}O_3$ m/z $(M+H)^+$ 177.0528, found 177.0559 m/z.

(3R, 3aS, 6aR)-3-(tert-Butyl-dimethyl-silanyloxymethyl)-3,3a,6,6a-tetrahydro-cyclopenta[*c*]furan-1-one 22. To a magnetically stirred solution of **3** (115 mg, 0.75 mmol) in dichloromethane (2 mL), triethylamine (0.21 mL, 1.5 mmol), DMAP (5 mg), imidazole (5 mg) were added. t-Butyldimethylsilyl chloride (168 mg, 1.12 mmol) was added to it at 0 ^oC in portion and stirred 10 h at room temperature. After evaporation of the solvent the residual mass was chromatographed (ether-petroleum ether 1:19) to afford the silylether **22** (158 mg, 79%) as white solid crystals: mp 76-78 ^oC; $[\alpha]^{25}_D$ -3.95 (*c* 1.07, $CHCl_3$); IR 1774 cm^{-1}; ^1H NMR δ -0.02 (6H, s, CH_3), 0.80 (9H, s, CH_3), 2.69 (1H, ddd, *J* = 4.8, 8.2, 17.1, CH_2), 2.75(1H, dd, *J* = 1.9, 17.1, CH_2), 3.12 (1H, dt, *J* = 1.8, 8.3, CH), 3.53 (1H, m, CH), 3.61 (1H, dd, *J* = 6.5, 10.5, OCH_2), 3.78 (1H, dd, *J* = 6.3, 10.8, OCH_2), 4.53 (1H, q, *J* = 6.6, OCH), 5.60 (1H, m, =CH-), 5.81 (1H, m, =CH-); ^{13}C NMR δ -5.2 (CH_3), 18.5 (C), 26.1 (CH_3), 36.6 (CH_2), 43.5 (CH), 49.1 (CH), 62.1 (OCH_2), 81.6 (OCH), 126.5 (CH), 133.9 (CH), 180.5 (CO); HRMS (ESI) calcd for $C_{14}H_{24}O_3Si$ m/z $(M+H)^+$ 269.1567, found 269.1526 m/z.

(3R, 3aR, 6aS)-3-(tert-Butyl-dimethyl-silanyloxymethyl)-3,3a,6,6a-tetrahydro-cyclopenta[*c*]furan-1-one 17. Following the above procedure, the alcohol **1** (340 mg, 2.21 mmol) in CH_2Cl_2 (3.5 mL) was treated with t-Butyldimethylsilyl chloride (496 mg, 3.31 mmol) to afford the silylether **17** (484 mg, 82%): $[\alpha]^{25}_D$ +4.6 (*c* 0.15, $CHCl_3$); IR

1764 cm^{-1}; ^1H NMR δ -0.01 (6H, s, CH_3), 0.82 (9H, s, CH_3), 2.66 (2H, m, CH_2), 3.05 (1H, dt, *J* = 3.8, 7.6, CH), 3.34 (1H, m, CH), 3.67 (1H, dd, *J* = 2.0, 11.1, OCH_2), 3.81 (1H, dd, *J* = 2.6, 11.1, OCH_2), 4.30 (1H, m, CH), 5.60 (1H, m, =CH-), 5.77 (1H, m, =CH-); ^{13}C NMR δ -5.6 (CH_3), 18.1 (C), 25.7 (CH_3), 36.7 (CH_2), 42.8 (CH), 49.4 (CH), 65.0 (OCH_2), 83.3 (OCH), 130.4 (CH), 132.0 (CH), 181.0 (CO); HRMS (ESI) calcd for $C_{14}H_{24}O_3Si$ m/z $(M+H)^+$ 269.1567, found 269.1539 m/z.

(1aR, 1bS, 2R, 4aR, 5aS)-2-(tert-Butyl-dimethyl-silanyloxymethyl)hexahydro-4*H*-oxireno[3,4]cyclopenta[1,2-*c*]furan-4-one 23. To a magnetically stirred cold (0 ^oC) solution of **22** (150 mg, 0.56 mmol) in 1,2-dichloroethane (2 mL), *m*-CPBA (192 mg, 1.12 mmol) was added in one portion. After stirring at rt for 6 h the reaction mixture was cooled to 0 ^oC and quenched by adding saturated Na_2SO_3 solution, extracted with ether (20 mL) and washed with ice-cold 2% NaOH solution (w/v) (3x2 mL) and dried. After evaporation of the solvent the residual mass was found to be a 7:1 mixture of the epoxide **23** and its diastereoisomer. The mixture was chromatographed (ether-petroleum ether 3:17) to afford the pure epoxide **23** (105 mg, 66%): $[\alpha]^{25}_D$ -3.5 (*c* 0.20, $CHCl_3$); IR 1770 cm^{-1}; ^1H NMR δ 0.04 (6H, s, CH_3), 0.88 (9H, s, CH_3), 2.02 (1H, dd, *J* = 8.6, 14.6, CH_2), 2.55 (1H, d, *J* = 14.6, CH_2), 2.94 (2H, m, OCH), 3.55 (1H, d, *J* = 1.8, CH), 3.61 (1H, t, *J* = 2.0, CH), 3.94 (1H, dd, *J* = 7.8, 10.3, OCH_2), 4.10 (1H, dd, *J* = 6.2, 10.2, OCH_2), 4.64 (1H, td, J = 6.1, 7.7, OCH); ^{13}C NMR δ -5.6 (CH_3), 18.1 (C), 25.7 (CH_3), 30.6 (CH_2), 41.6 (CH), 42.6 (CH), 56.7 (OCH), 57.5 (OCH), 62.7 (OCH_2), 79.0 (OCH), 178.4 (CO); HRMS (ESI) calcd for $C_{14}H_{24}O_4Si$ m/z $(M+H)^+$ 285.1517, found 285.1506 m/z.

(1aR, 1bR, 2R, 4aS, 5aS)-2-(tert-Butyl-dimethylsilanyloxymethyl)hexanhdro-4*H*-oxireno[3,4]cyclopenta[1,2-*c*]furan-4-one 18. Following the above procedure, the cyclopentene derivative **17** (570 mg, 2.13 mmol) was treated with *m*-CPBA (733 mg, 4.26 mmol) to afford a liquid mass. After evaporation of the solvent the residual mass was found to be a 7:1 mixture of the epoxide **18** and its diastereoisomer. The crude mass obtained was chromatographed (ether-petroleum ether 3:17) to afford the pure epoxide **18** (370 mg, 61%): $[\alpha]^{25}_D$ +3.8 (*c* 0.21, $CHCl_3$); IR 1768 cm^{-1}; ^1H NMR δ -0.06 (6H, s, CH_3), 0.8 (9H, s, CH_3), 2.02 (1H, dd, *J* = 9.6, 14.7, CH_2), 2.44 (1H, d, *J* = 14.7, CH_2), 2.77 (1H, d, *J* = 9.0, OCH), 3.00 (1H, t, *J* = 9.0, OCH), 3.58 (1H, m, CH), 3.61 (1H, m, CH), 3.70 (1H, dd, *J* = 1.9, 11.2, OCH_2), 3.84 (1H, dd, *J* = 2.7, 11.1, OCH_2), 4.67 (1H, m, OCH);

^{13}C NMR δ -5.7 (CH_3), 18.2 (C), 25.8 (CH_3), 31.1 (CH_2), 41.6 (CH), 42.6 (CH), 58.5 (OCH), 59.6 (OCH), 65.0 (OCH_2), 80.3 (OCH), 179.4 (CO); HRMS (ESI) calcd for $C_{14}H_{24}O_4Si$ m/z $(M+H)^+$ 285.1517, found 285.1508 m/z.

(3R, 3aS, 4S, 6aS)-4-Hydroxy-3-(tert-butyl-dimethyl-silanyloxymethyl)-3,3a,4,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-1-one 19. $NaBH_4$ (80 mg, 2.11 mmol) was added in small portions to a magnetically stirred solution of diphenyldiselenide (330 mg, 1.06 mmol) in absolute ethanol (2 mL). After addition of the epoxide **18** (200 mg, 0.70 mmol) in absolute ethanol (2 mL) the reaction mixture was refluxed for 12 h. The solution was cooled to 0 ^oC and THF (2 mL) was added to it. Then 30% H_2O_2 (1.9 mL, 21.1 mmol) was added dropwise and stirred for another 12 h at rt. Usual workup of the reaction mixture followed by column chromatography (ether-petroleum ether 3:7) afforded the alcohol **19** (76 mg, 38%): $[\alpha]^{25}_D$ -26.8 (*c* 0.23, $CHCl_3$); IR 1759, 3352 cm^{-1}; ^{1}H NMR δ -0.02 (6H, s, CH_3), 0.81 (9H, s, CH_3), 2.50 (1H, br s, OH), 3.05 (1H, dt, *J* = 4.5, 7.9, CH), 3.58 (1H, d, *J* = 8.4, CH), 3.69 (1H, dd, *J* = 3.0, 11.1, OCH_2), 3.79 (1H, dd, *J* = 3.9, 10.8, OCH_2), 4.80 (1H, dd, *J* = 4.2, 7.2, OCH), 4.91 (1H, d, *J* = 7.5, OCH), 5.86 (2H, br s, =CH-); ^{13}C NMR δ -5.52 (CH_3), -5.50 (CH_3), 18.2 (C), 25.6 (CH_3), 43.9 (CH), 52.6 (CH), 64.9 (OCH_2), 77.0 (OCH), 78.2 (OCH), 129.6 (CH), 136.2 (CH), 176.3 (CO); HRMS (ESI) calcd for $C_{14}H_{24}O_4Si$ m/z $(M+H)^+$ 285.1517, found 285.1520 m/z.

(3R, 3aS, 4S, 6aS)-4-Hydroxy-3-(tert-butyl-dimethyl-silanyloxymethyl)hexahydro-1*H*-cyclopenta[*c*]furan-1-one 20. A solution of the alcohol **19** (20 mg, 0.07 mmol) in dry ethanol (2 mL) containing Pd-C (10%) (5 mg) was stirred under hydrogen atmosphere at room temperature for 12 h. The mixture was filtered, concentrated under vacuum to afford a colorless liquid which on column chromatography (ether-petroleum ether 3:17) afforded **21** (7 mg, 35%) : $[\alpha]^{25}_D$ -73.0 (*c* 0.10, $CHCl_3$); IR 1747, 1778 cm^{-1}; -0.005 (6H, s, CH_3), 0.81 (9H, s, CH_3), 2.26 (4H, m, CH_2), 2.85 (1H, d, *J* = 9.3, CH), 3.37 (1H, t, *J* = 9.3, CH), 3.66 (1H, dd, *J* = 2.2, 11.4, OCH_2), 3.86 (1H, dd, *J* = 1.8, 11.4, OCH_2), 4.51 (1H, m, OCH); ^{13}C NMR δ -5.8 (CH_3), -5.7 (CH_3), 18.0 (C), 24.0 (CH_2), 25.6 (CH_3), 36.5 (CH_2), 42.6 (CH), 50.4 (CH), 65.0 (OCH_2), 81.0 (OCH), 179.5 (CO), 217.7 (CO); HRMS (ESI) calcd for $C_{14}H_{24}O_4SiNa$ m/z $(M+Na)^+$ 285.1517, found 285.1473 m/z. and **20** (11 mg, 55%): $[\alpha]^{25}_D$ -8.6 (*c* 0.50, $CHCl_3$); IR 1747, 3454 cm^{-1}; ^{1}H

NMR δ 0.04 (6H, s, CH_3), 0.86 (9H, s, CH_3), 1.60 (1H, m, CH_2), 1.96 (3H, m, CH_2), 2.21 (1H, br s, OH), 2.80 (1H, dt, *J* = 2.6, 8.1, CH), 3.05 (1H, dt, *J* = 3.3, 9.2, CH), 3.65 (1H, dd, *J* = 3.3, 11.1, OCH_2), 3.84 (1H, dd, *J* = 3.3, 11.1, OCH_2), 4.32 (1H, dd, *J* = 6.6, 11.7, OCH), 4.75 (1H, dd, *J* = 2.7, 5.4, OCH); ^{13}C NMR δ -5.63 (CH_3), -5.53 (CH_3), 18.2 (C), 25.7 (CH_3), 26.8 (CH_2), 34.3 (CH_2), 44.3 (CH), 45.9 (CH), 65.1 (OCH_2), 73.9 (OCH), 78.4 (OCH), 180.9 (CO); HRMS (ESI) calcd for $C_{14}H_{26}O_4SiNa$ m/z $(M+Na)^+$ 309.1498, found 309.1540 m/z.

(3R, 3aS, 5R, 6aR)-5-Hydroxy-3-(tert-butyldimethyl-silanyloxymethyl)hexahydro-1*H*-cyclopenta[*c*]furan-1-one 24. The epoxide **23** (225 mg, 0.79 mmol) and tert-butylmercaptan (0.71mL, 6.3 mmol) were dissolved in anhydrous THF (2.5 mL) and from a dropping funnel was added titanocene monochloride [prepared from titanocene dichloride (235 mg, 0.94 mmol) and activated Zn (247 mg, 3.78 mmol)] dissolved in anhydrous THF (15 mL). The reaction mixture was stirred at rt for 2 h and then quenched by adding saturated NaH_2PO_4 (2 mL). Usual work up followed by column chromatography (ether-petroleum ether 2:3) afforded the alcohol **24** (122 mg, 54%): mp 118-120 ^oC; $[\alpha]^{25}_D$ +4.04 (*c* 1.10, $CHCl_3$); IR 1743, 3433 cm^{-1}; ^{1}H NMR δ 0.08 (6H, s, CH_3), 0.89 (9H, s, CH_3), 1.79 (1H, dd, *J* = 4.2, 12.0, CH_2), 1.96 (2H, m, CH_2), 2.20 (1H, m, CH_2), 2.25 (1H, br s, OH), 2.98 (1H, m, CH), 3.04 (1H, dd, *J* = 3.6, 12.0, CH), 3.82 (1H, dd, *J* = 6.3, 10.8, OCH_2), 3.95 (1H, dd, *J* = 5.7, 10.8, OCH_2), 4.32 (1H, m, OCH), 4.60 (1H, dd, *J* = 6.3, 12.9, OCH); ^{13}C NMR δ -5.5 (CH_3), -5.4 (CH_3), 18.2 (C), 25.8 (CH_3), 34.8 (CH_2), 39.2 (CH), 39.5 (CH_2), 44.5 (CH), 62.3 (OCH_2), 72.6 (OCH), 80.2 (OCH), 180.6 (CO); HRMS (ESI) calcd for $C_{14}H_{26}O_4Si$ m/z $(M+Na)^+$ 309.1498, found 309.1491 m/z.

(3R, 3aR, 4S, 6aR)-4-Hydroxy-3-(tert-butyl-dimethyl-silanyloxymethyl)hexahydro-1*H*-cyclopenta[*c*]furan-1-one 25. To a magnetically stirred solution of diphenyldiselenide (439 mg, 1.41 mmol) in absolute ethanol (2mL), sodium borohydride (94 mg, 2.46 mmol) was added in portions and stirring was continued until the bright yellow solution turned colorless. A solution of the epoxide **23** (200 mg, 0.70 mmol) in absolute ethanol (2 mL) was added dropwise to the the reaction mixture and then refluxed at 60 ^oC for 12 h. The solution was cooled to 0 ^oC and quenched with saturated aqueous NH_4Cl solution. The reaction mixture was worked up in the usual way to afford

orange oily liquid. A solution of this liquid in anhydrous benzene (3 mL) was degassed by bubbling Ar gas and tributyltinhydride (TBTH) (0.22 mL, 0.82 mmol) was added to it. 2,2'-Azobisisobutyronitrile (AIBN) (5 mg) was added to it at 80 ^{o}C and refluxed for 4 h. Solvent removed under vacuo and white solid was purified by column chromatography (ether-petroleum ether 3:7) to afford the alcohol **25** (80 mg, 40%): $[\alpha]^{25}_{D}$ + 8.0 (*c* 0.23, $CHCl_3$); IR 1741, 3431 cm^{-1}; ^{1}H NMR δ 0.09 (6H, s, CH_3), 0.88 (9H, s, CH_3), 1.56 (1H, q, *J* = 11.0, CH_2), 1.98 (2H, m, CH_2), 2.21 (1H, m, CH_2), 2.62 (1H, dt, *J* = 2.5, 8.9, CH), 3.08 (1H, dt, *J* = 4.0, 9.5, CH), 3.99 (1H, dd, *J* = 2.2, 12.0, OCH_2), 4.00 (1H, br s, OH), 4.25 (1H, dd, *J* = 3.5, 12.1, OCH_2), 4.34 (1H, m, OCH), 4.52 (1H, m, OCH); ^{13}C NMR δ -5.9 (CH_3), -5.8 (CH_3), 18.2 (C), 23.7 (CH_2), 25.6 (CH_3), 34.9 (CH_2), 44.6 (CH), 50.6 (CH), 61.6 (OCH_2), 72.3 (OCH), 78.7 (OCH), 179.9 (CO); HRMS (ESI) calcd for $C_{14}H_{26}O_4Si$ m/z $(M+H)^+$ 287.1673, found 287.1609 m/z. and the regioisomeric alcohol **24** (103 mg, 51%).

(3R, 3aR, 4S, 6aR)-3-Hydroxymethyl-4-(methoxymethoxy)hexahydro-1*H*-cyclopenta[*c*]furan-1-one 26. To a magnetically stirred solution of alcohol **25** (10 mg, 0.035 mmol) in dimethoxymethane (200 μL), $BF_3.Et_2O$ (6 μL, 0.042 mmol) was added dropwise at 0 ^{o}C. After complete addition, the reaction mixture was stirred for 0.5 h at 0 ^{o}C. After quenching with saturated $NaHCO_3$ solution, the reaction mixture was worked up in the usual way to afford after column chromatography (ether-petroleum ether 3:17) the ether derivative (6 mg, 52%): $[\alpha]^{25}_{D}$ -7.9 (*c* 0.80, $CHCl_3$); IR 1770 cm^{-1}; ^{1}H NMR δ 0.09 (6H, s, CH_3), 0.91 (9H, s, CH_3), 1.50 (1H, m, CH_2), 2.13 (3H, m, CH_2), 2.75 (1H, m, CH), 3.12 (1H, dd, *J* = 6.9, 9.1, CH), 3.37 (3H, s, OCH_3), 4.01 (1H, dd, *J* = 5.7, 10.7, OCH_2), 4.18 (1H, dd, *J* = 10.7, 6.7, OCH_2), 4.22 (1H, m, OCH), 4.58 (1H, d, *J* = 7.0, OCH_2O), 4.64 (1H, m, OCH), 4.65 (1H, d, J = 7.1, OCH_2O); ^{13}C NMR δ -5.4 (CH_3), -5.3 (CH_3), 18.2 (C), 24.0 (CH_2), 25.8 (CH_3), 32.5 (CH_2), 44.4 (CH), 47.9 (CH), 56.2 (OCH_3), 62.3 (OCH_2), 78.9 (OCH), 80.5 (OCH), 95.1 (OCH_2O), 179.7 (CO); HRMS (ESI) calcd for $C_{16}H_{30}O_5Si$ m/z $(M+H)^+$ 331.1935, found 331.1911 m/z.

To a solution of the above ether derivative (14 mg, 0.042 mmol) in THF (200 μL) at 0 ^{o}C was added $nBu_4N^+F^-$ (27 mg, 0.085 mmol). After stirring for 30 min at 0 ^{o}C the reaction mixture was then concentrated in vacuo and the residue was purified by column chromatography (acetone-petroleum ether 1:4) to afford the white solid lactone **26** (7 mg,

76%): mp 112-113°C; $[\alpha]^{25}_{D}$ +1.20 (*c* 1.00, $CHCl_3$); IR 1762, 3417 cm^{-1}; ^1H NMR δ 1.62 (1H, m, CH_2), 2.11 (3H, m, CH_2), 2.33(1H, br s, OH), 2.83 (1H, ddd, *J* = 4.9, 6.4, 10.4, CH), 3.16 (1H, dt, *J* = 4.5, 9.1, CH), 3.37 (3H, s, OCH_3), 3.93 (1H, m, OCH_2), 4.20 (1H, m, OCH), 4.27 (1H, dd, *J* = 7.5, 12.0, OCH_2), 4.60 (1H, d, *J* = 6.9, OCH_2O), 4.66 (1H, d, *J* = 6.9, OCH_2O), 4.72 (1H, td, *J* = 4.2, 6.9, OCH); ^{13}C NMR δ 24.2 (CH_2), 32.2 (CH_2), 44.6 (CH), 47.1 (CH), 56.3 (OCH_3), 61.9 (OCH_2), 79.1 (OCH), 81.1 (OCH), 95.2 (OCH_2O), 179.4 (CO); HRMS (ESI) calcd for $C_{10}H_{16}O_5Na$ m/z $(M+Na)^+$ 239.0895, found 239.0886 m/z.

X-Ray crystal data for compound 24

Crystal Data, C16H24O4Si, M = 286.44, monoclinic, spacegroup $P2_1$, Z=2, a = 7.577(8), b = 8.208(11), c = 13.461(15)Å, β = 97.80(1)^o , U = 829(2)Å^3 , dcalc = 1.147 g cm^{-3}.

Experimental Details.

Data were measured with MoKα radiation using a Marresearch Image Plate system. The crystal was positioned at 70 mm from the CCD and 100 frames were measured at 2^o intervals with a counting time of 2min. Data analysis was carried out with the XDS program.[1] to provide 2680 independent reflections. The structure was solved using direct methods with the Shelx97 program [2]. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The structure was refined on F^2 using Shelx97 [2] to R1 0.0553, wR2 0.1129 for 2680 reflections with I> 2σ(I). Maximum and minimum residual electron density were 0.195, -0.160 eÅ^{-3}.

The structure is shown in Figure 1. There is an intermolecular hydrogen bond connecting O8-H with O5(1-x,-0.5+y,-z) with dimensions H...O5 2.16Å, O8-H-O5 173^o and O8...O5 2.974

Figure 1 The structure of **24**, with ellipsoids at 25% probability.

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References

[1] XDS program, W.Kabsch, 1988, J.Appl.Cryst. 916.

[2] Shelxl97, G.M.Sheldrick, 1997, program for crystal structure refinement. University of Gottingen.