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Efficient resolution of some monoprotected derivatives of Corey lactone

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General

Solvents were purified and dried before use by standard procedures. Reagents were generally of the best quality commercial grade and used without further purification unless otherwise indicated. All reactions were carried in oven-dried glassware. TLC was performed using Sorbfil STC-1A 110 μm layer, silica gel 5–17 precoated foil plates. Column chromatography was carried out using 210–280 mesh silica gel. Optical rotations were measured using sodium D line at 589 nm on a Perkin Elmer, Model 241 MC polarimeter. IR (infrared spectra) was recorded on a Shimadzu IRPrestige-21 spectrometer as a Nujol mull or as neat thin films on KBr plates. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker AM-300 (300 MHz for ^{1}H and 75.47 MHz for ^{13}C) as solutions in $CDCl_3$ (Aldrich Chemical Company; spectra grade). Mass spectra were recorded on a Shimadzu LCMS QP-2010EV (APCI) spectrometer. Elemental analyses were carried on a Euro EA 3000 CHNS-analyzer. Melting points were measured on a Mel-Temp apparatus and are uncorrected.

Hemiacylal **3** colorless crystals with mp 116.5−117 ºC, $[\alpha]_D^{20} = -110.3$ (*c* 1.00, EtOH) was synthesized according to the literature.[18] Literature data for enantiopure **3**[7c]: $[\alpha]_D^{28} = -102.0$ (*c* 2%, EtOH), mp 117−118 ºC (acetone).

(±)-(3a*RS*,*4SR*,5*RS*,6a*SR*)-4-{[*tert*-Butyl(dimethyl)silyloxy]methyl}-5-hydroxy-hexahydro-2*H*-cyclopenta[*b*]furan-2-one 2a. Yield 94%; colorless crystals; mp 96−98 ºC; R_f 0.20 (hexane–ethyl acetate, 7:3); IR (Nujol mull) 3385, 2944, 2899, 1759, 1465, 1255, 1226, 1109, 1089, 1008 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3/CHCl_3$): δ 0.02 (s, 6H, $SiMe_2$), 0.85 (s, 9H, Si-CMe_3), 1.97 (m, 2H, 4-H, 6-H^{endo}), 2.38 (m, 1H, 6-H^{exo}), 2.49 (dd, J = 17.8, 2.0 Hz, 1H, 3-H^{endo}), 2.61 (m, 2H, 3a-H, OH), 2.75 (dd, J = 17.8, 10.0 Hz, 1-H, 3-H^{exo}), 3.57 (dd, J = 10.0, 6.5 Hz, 1H, CH_2O), 3.65 (dd, J = 10.0, 5.0 Hz, 1H, CH_2O), 4.09 (q, J = 6.4 Hz, 1H, 5-H), 4.89 (td, J = 6.9, 2.8 Hz, 1H, 6a-H); ^{13}C NMR (75 MHz $CDCl_3/CHCl_3$): δ -1.05 ($SiMe_2$), 18.07 (Si-$\underline{C}Me_3$), 25.73 (Si-C$\underline{Me}_3$), 35.35 (C3), 39.54 (C3a), 40.72 (C6), 55.26 (C4), 63.83 (CH_2O), 75.38 (C5),

83.99 (C6a), 177.41(C2). MS (APCI), *m/z* (%): 287 [MH^+] (100), 269 [$M–H_2O]^+$ (18.9), 233 (14.4), 231 (9.0).

(±)-(3a*RS*,4*SR*,5*RS*,6a*SR*)-5-Hydroxy-4-[(triisopropylsilyloxy)methyl]hexahydro-2*H*-cyclopenta[*b*]furan-2-one 2b. Yield 85%; colorless crystals; mp 43−43.5 ºC; R_f 0.33 (hexane–ethyl acetate, 7:3); IR (Nujol mull) 3448, 3433, 2941, 2866, 1772, 1475, 1176, 1107, 1037 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3/CHCl_3$): δ 1.03 (s, 3H, Si-CH), 1.05 (s, 18H, 6Me), 1.98 (m, 2H, 4-H, 6-H^{endo}), 2.34 (br s, 1H, OH), 2.47 (m, 2H, 3-H^{endo}, 6-H^{exo}), 2.62 (m, 1H, 3a-H), 2.77 (dd, J = 17.8, 10.0 Hz, 1H, 3-H^{exo}), 3.68 (dd, J = 10.0, 6.6 Hz, 1H, CH_2O), 3.81 (dd, J = 10.0, 5.0 Hz, 1H, CH_2O), 4.15 (q, J = 6.4 Hz, 1H, 5-H), 4.91 (td, J = 6.9, 2.8 Hz, 1H, 6a-H); ^{13}C NMR (75 MHz $CDCl_3/CHCl_3$): δ 11.71 (Si-<u>C</u>HMe_2), 17.90 (Si-CH<u>Me</u>$_2$), 35.26 (C3), 39.45 (C3a), 40.75 (C6), 55.31 (C4), 64.49 (CH_2O), 75.62 (C5), 83.75 (C6a), 177.15 (C2). MS (APCI), *m/z* (%): 329 [MH^+] (47.7), 311 [$M–H_2O]^+$ (100).

(±)-[(3a*RS*,4*SR*,5*RS*,6a*SR*)-5-Hydroxy-2-oxohexahydro-2*H*-cyclopenta[*b*]furan-4-yl]methyl benzoate 2c. Yield 80%; colorless oily substance; R_f 0.40 (hexane–ethyl acetate, 1:1); IR (film) 3385, 3034, 1749, 1703, 1454, 1375, 1355, 1278, 1116, 1101, 1037, 709 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3/CHCl_3$): δ 2.09 (m, 2H, OH, 6-H^{endo}), 2.27 (m, 1H, 4-H), 2.46 (m, 1H, 6-H^{exo}), 2.61 (dd, J = 17.6, 1.9 Hz, 1H, 3-H^{endo}), 2.75 (m, 1H, 3a-H), 2.87 (dd, J = 17.6, 9.9 Hz, 1H, 3-H^{exo}), 4.19 (m, 1H, 5-H), 4.30 (dd, J = 11.6, 5.8 Hz, 1H, CH_2O), 4.43 (dd, J = 11.6, 6.1 Hz, 1H, CH_2O), 4.98 (td, J = 6.9, 2.5 Hz, 1H, 6a-H), 7.46 (m, 2H, Ph), 7.59 (m, 1H, Ph), 8.00 (d, J = 7.2 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3/CHCl_3$): 35.48 (C3), 40.13 (C3a), 40.40 (C6), 53.00 (C4), 64.66 (CH_2O), 74.14 (C5), 83.64 (C6a), 128.59 ($2C_{Ph}^{m}$), 129.55 ($1C_{Ph}^{i}$), 129.55 ($2C_{Ph}^{o}$), 133.42 ($1C_{Ph}^{p}$), 166.69 (Ph<u>C</u>O), 177.40 (C2). MS (APCI), *m/z* (%): 277 [MH^+] (66.7), 259 [$M–H_2O]^+$ (100).

(–)-(3a*R*,4*S*,5*R*,6a*S*)-4-{[*tert*-Butyl(dimethyl)silyloxy]methyl}-5-{[(1*S*,2*R*,5*R*)-6,6-dimethyl-4-oxo-3-oxabicyclo[3.1.0]hex-2-yl]oxy}hexahydro-2*H*-cyclopenta[*b*]furan-2-one 4a. Yield 30%; $[\alpha]_D^{22} = -93.65$ (*c* 3.50, $CHCl_3$); colorless crystals; mp 116−117 ºC; R_f 0.35 (hexane–ethyl acetate, 7:3); IR (Nujol mull) 1768, 1460, 1377, 1352, 1188, 1149, 1118, 1103, 1080, 1056 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3/CHCl_3$): δ 0.02 (s, 6H, $SiMe_2$), 0.86 (s, 9H, Si-CMe_3), 1.13 (s, 3H, Me), 1.15 (s, 3H, Me), 1.97 (d, J = 5.5 Hz, 1H, 1'-H), 2.01 (d, J = 5.8 Hz, 1H, 5'-H), 2.11-2.30 (m, 3H, 4-H, 6-H^{endo}, 6-H^{exo}), 2.54 (m, 1H, 3-H^{endo}), 2.84 (m, 2H, 3a-H, 3-H^{exo}), 3.56 (m, 2H, CH_2O), 4.26 (m, 1H, 5-H), 5.02 (t, J = 5.8 Hz, 1H, 6a-H), 5.15 (s, 1H, 2'-H); ^{13}C NMR (75 MHz, $CDCl_3/CHCl_3$): δ -0.35 ($SiMe_2$), 14.98 (Me), 18.04 (Si-<u>C</u>Me_3), 24.48 (C6'),

25.23 (Me), 25.75 (Si-C<u>Me</u>$_3$), 29.77 (C1'), 35.17 (C5'), 35.95 (C3), 37.36 (C6), 40.00 (C3a), 55.56 (C4), 63.33 (CH_2O), 81.76 (C5), 85.08 (C6a), 98.83 (C2'), 173.22 (C4'), 177.29 (C2). MS (APCI), *m/z* (%): 411 [MH^+] (100), 393 [$M–H_2O]^+$ (8.3), 365 (30.6), 367 [$M–CO_2]^+$ (13.9).

(–)-(3a*S*,4*R*,5*S*,6a*R*)-4-{[*tert*-Butyl(dimethyl)silyloxy]methyl}-5-{[(1*S*,2*R*,5*R*)-6,6-dimethyl-4-oxo-3-oxabicyclo[3.1.0]hex-2-yl]oxy}hexahydro-2*H*-cyclopenta[*b*]furan-2-one 5a. Yield 26%; $[\alpha]_D^{22} = -37.95$ (*c* 3.50, $CHCl_3$); colorless crystals; mp 112−113 ºC; R_f 0.25 (hexane–ethyl acetate, 7:3); IR (Nujol mull) 1772, 1463, 1379, 1188, 1170, 1151, 1119, 1105, 1081, 1057 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3/CHCl_3$): δ 0.04 (s, 6H, $SiMe_2$), 0.88 (s, 9H, Si-CMe_3), 1.14 (s, 3H, Me), 1.16 (s, 3H, Me), 1.99 (d, *J* = 5.8 Hz, 1H, 1'-H), 2.02 (d, *J* = 5.2 Hz, 1H, 5'-H), 2.09 (m, 1H, 4-H), 2.20-2.40 (m, 2H, 6-H^{endo}, 6-H^{exo}), 2.45 (dd, *J* = 17.8, 2.0 Hz, 1H, 3-H^{endo}), 2.67 (m, 1H, 3a-H), 2.82 (dd, *J* = 17.8, 10.1 Hz, 1H, 3-H^{exo}), 3.52 (dd, *J* = 10.2, 5.5 Hz, 1H, CH_2O), 3.61 (dd, *J* = 10.5, 5.0 Hz, 1H, CH_2O), 4.18 (m, 1H, 5-H), 4.94 (td, *J* = 6.3, 1.8 Hz, 1H, 6a-H), 5.14 (s, 1H, 2'-H); ^{13}C NMR (75 MHz, $CDCl_3/CHCl_3$): δ -1.02 ($SiMe_2$) 15.03 (Me), 18.13 (Si-<u>C</u>Me_3), 24.43 (C6'), 25.28 (Me), 25.78 (Si-C<u>Me</u>$_3$), 30.04 (C1'), 35.17 (C5'), 35.81 (C3), 39.36 (C6), 39.42 (C3a), 54.32 (C4), 62.52 (CH_2O), 81.35 (C5), 84.36 (C6a), 100.24 (C2'), 173.72 (C4'), 176.75 (C2). MS (APCI), *m/z* (%): 411 [MH^+] (100), 393 [$M–H_2O]^+$ (8.9), 365 (31.5), 367 [$M–CO_2]^+$ (13.2).

(–)-(3a*R*,4*S*,5*R*,6a*S*)-5-{[(1*S*,2*R*,5*R*)-6,6-Dimethyl-4-oxo-3-oxabicyclo[3.1.0]hex-2-yl]oxy}-4-[(triisopropylsilyloxy)methyl]hexahydro-2*H*-cyclopenta[*b*]furan-2-one 4b. Yield 33%; $[\alpha]_D^{20} = -106.8$ (*c* 1.50, $CHCl_3$); colorless crystals; mp 87−88 ºC; R_f 0.43 (hexane–ethyl acetate, 7:3); IR (Nujol mull) 2852, 1768, 1462, 1377, 1352, 1168, 1116, 1099, 1058, 1039 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3/CHCl_3$): δ 1.02 (s, 3H, Si-CH), 1.03 (s, 18H, 6Me), 1.13 (s, 3H, Me), 1.15 (s, 3H, Me), 1.97 (d, *J* = 5.5 Hz, 1H, 1'-H), 2.01 (d, *J* = 5.8 Hz, 1H, 5'-H), 2.14-2.32 (m, 3H, 4-H, 6-H^{endo}, 6-H^{exo}), 2.55 (d, *J* = 15.3 Hz, 1H, 3-H^{endo}), 2.79-2.97 (m, 2H, 3a-H, 3-H^{exo}), 3.67 (m, 2H, CH_2O), 4.30 (m, 1H, 5-H), 5.04 (t, *J* = 5.8 Hz, 1H, 6a-H), 5.16 (s, 1H, 2'-H); ^{13}C NMR (75 MHz, $CDCl_3/CHCl_3$): δ 11.52 (Si-<u>C</u>HMe_2), 14.79 (Me), 17.72 (Si-CH<u>Me</u>$_2$), 24.26 (C6'), 25.04 (Me), 29.58 (C1'), 34.97 (C5'), 35.81 (C3), 37.11 (C6), 39.66 (C3a), 55.67 (C4), 63.57 (CH_2O), 81.56 (C5), 84.88 (C6a), 98.64 (C2'), 172.98 (C4'), 177.09 (C2). MS (APCI), *m/z* (%): 453 [MH^+] (100), 435 [$M–H_2O]^+$ (8.0), 370 (14.5), 329 (43.5), 311 [$M–C_7H_{10}O_3]^+$ (13.0).

(–)-(3a*S*,4*R*,5*S*,6a*R*)-5-{[(1*S*,2*R*,5*R*)-6,6-Dimethyl-4-oxo-3-oxabicyclo[3.1.0]hex-2-yl]oxy}-4-[(triisopropylsilyloxy)methyl]hexahydro-2*H*-cyclopenta[*b*]furan-2-one 5b. Yield 30%; $[\alpha]_D^{26} = -19.6$ (*c* 0.475, $CHCl_3$); colorless oily substance; R_f 0.38 (hexane–ethyl acetate,

7:3); IR (film) 2866, 1770, 1462, 1380, 1344, 1166, 1118, 1107, 1070, 1041 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3/CHCl_3$): δ 1.02 (s, 3H, Si-CH), 1.03 (s, 18H, 6Me), 1.12 (s, 3H, Me), 1.13 (s, 3H, Me), 1.97 (d, J = 5.7 Hz, 1H, 1'-H), 2.00 (d, J = 5.7 Hz, 1H, 5'-H), 2.11 (m, 1H, 4-H), 2.25 (m, 1H, 6-H^{endo}), 2.36 (m, 1H, 6-H^{exo}), 2.45 (dd, J = 17.3, 1.2 Hz, 1H, 3-H^{endo}), 2.74 (m, 1H, 3a-H), 2.82 (dd, J = 17.3, 10.2 Hz, 1H, 3-H^{exo}), 3.61 (dd, J = 10.2, 5.8 Hz, 1H, CH_2O), 3.70 (dd, J = 10.2, 5.0 Hz, 1H, CH_2O), 4.22 (m, 1H, 5-H), 4.93 (td, J = 6.5, 2.1 Hz, 1H, 6a-H), 5.14 (s, 1H, 2'-H); ^{13}C NMR (75 MHz, $CDCl_3/CHCl_3$): δ 11.81 (Si-<u>C</u>HMe_2), 15.02 (Me), 17.98 (Si-CH<u>Me</u>$_2$), 24.46 (C6'), 25.29 (Me), 30.12 (C1'), 35.22 (C5'), 35.78 (C3), 39.19 (C3a), 39.31 (C6), 54.56 (C4), 62.71 (CH_2O), 81.37 (C5), 84.35 (C6a), 100.51 (C2'), 173.15 (C4'), 176.95 (C2). MS (APCI), *m/z* (%): 453 [MH^+] (100), 435 [M–H_2O]$^+$ (8.3), 370 (14.2), 329 (44.0), 311 [M–$C_7H_{10}O_3$]$^+$ (13.3).

(–)-((3a*R*,4*S*,5*R*,6a*S*)-5-{[(1*S*,2*R*,5*R*)-6,6-Dimethyl-4-oxo-3-oxabicyclo[3.1.0]hex-2-yl]oxy}-2-oxohexahydro-2*H*-cyclopenta[*b*]furan-4-yl)methyl benzoate 4c. Yield 40%; $[\alpha]_D^{20} = -122.5$ (*c* 5.8, $CHCl_3$); colorless crystals; mp 135−136 ºC; R_f 0.48 (hexane–ethyl acetate, 1:1); IR (Nujol mull) 3072, 2852, 1768, 1716, 1463, 1455, 1379, 1336, 1279, 1186, 1171, 1099, 1071, 1042 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3/CHCl_3$): δ 1.12 (s, 3H, Me), 1.14 (s, 3H, Me), 1.96 (d, J = 5.5 Hz, 1H, 1'-H), 2.01 (d, J = 5.7 Hz, 1H, 5'-H), 2.21 (m, 1H, 6-H^{exo}), 2.35 (m, 1H, 6-H^{endo}), 2.60 (m, 2H, 4-H, 3-H^{endo}), 2.86 (m, 2H, 3a-H, 3-H^{exo}), 4.23 (m, 2H, CH_2O), 4.36 (m, 1H, 5-H), 5.07 (t, J = 5.7 Hz, 1H, 6a-H), 5.16 (s, 1H, 2'-H), 7.43 (m, 2H, Ph), 7.56 (m, 1H, Ph), 7.97 (d, J = 7.2 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3/CHCl_3$): δ 15.03 (Me), 24.55 (C6'), 25.26 (Me), 29.71 (C1'), 35.20 (C5'), 35.76 (C3), 36.96 (C6) 40.28 (C3a), 52.52 (C4), 64.57 (CH_2O), 80.70 (C5), 83.97 (C6a), 99.08 (C2'), 128.59 ($2C_{Ph}^{m}$), 129.55 ($1C_{Ph}^{i}$), 129.55 ($2C_{Ph}^{o}$), 133.37 ($1C_{Ph}^{p}$), 166.24 (Ph<u>C</u>O), 173.00 (C4'), 176.76 (C2). MS (APCI), *m/z* (%): 401 [MH^+] (100).

(–)-((3a*S*,4*R*,5*S*,6a*R*)-5-{[(1*S*,2*R*,5*R*)-6,6-Dimethyl-4-oxo-3-oxabicyclo[3.1.0]hex-2-yl]oxy}-2-oxohexahydro-2*H*-cyclopenta[*b*]furan-4-yl)methyl benzoate 5c. Yield 37%; $[\alpha]_D^{20} = -34.77$ (*c* 6.75, $CHCl_3$); colorless viscous substance; R_f 0.44 (hexane–ethyl acetate, 1:1); IR (film) 3072, 2852, 1772, 1720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3/CHCl_3$): δ 1.09 (s, 3H, Me), 1.11 (s, 3H, Me), 1.93 (d, J = 5.7 Hz, 1H, 1'-H), 1.99 (d, J = 5.7 Hz, 1H, 5'-H), 2.26 (m, 1H, 6-H^{endo}), 2.39 (m, 1H, 4-H), 2.52 (m, 1H, 6-H^{exo}), 2.54 (dd, J = 17.8, 1.6 Hz, 1H, 3-H^{endo}), 2.72 (m, 1H, 3a-H), 2.86 (dd, J = 17.8, 9.8 Hz, 1H, 3-H^{exo}), 4.17 (q, J = 5.9 Hz, 1H, 5-H), 4.34 (d, J = 6.1 Hz, 2H, CH_2O), 4.96 (td, J = 6.7, 2.4 Hz, 1H, 6a-H), 5.13 (s, 1H, 2'-H), 7.45 (m, 2H, Ph), 7.59 (m, 1H, Ph), 7.99 (d, J = 7.6 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3/CHCl_3$): δ 14.97

(Me), 24.45 (C6'), 25.26 (Me), 29.88 (C1'), 35.18 (C5'), 35.32 (C3), 39.37 (C6), 39.72 (C3a), 50.85 (C4), 64.10 (CH_2O), 81.56 (C5), 83.18 (C6a), 100.86 (C2'), 128.63 ($2C_{Ph}^{m}$), 129.54 ($1C_{Ph}^{i}$), 129.54 ($2C_{Ph}^{o}$), 133.50 ($1C_{Ph}^{p}$), 166.29 (PhCO), 172.82 (C4'), 176.22 (C2). MS (APCI), *m/z* (%): 401 [MH^+] (100).

(+)-(5-{[(1*S*,2*R*,5*R*)-6,6-Dimethyl-4-oxo-3-oxabicyclo[3.1.0]hex-2-yl]oxy}-2-oxo-hexahydro-2*H*-cyclopenta[*b*]furan-4-yl)methyl benzoate 6c *(2'-epimer)*. Yield ~11%; colorless viscous substance; R_f 0.36 (hexane–ethyl acetate, 1:1); ^{1}H NMR (300 MHz, $CDCl_3/CHCl_3$): δ 1.13 (s, 3H, Me), 1.36 (s, 3H, Me), 1.99 (d, J = 6.0 Hz, 1H, 1'-H), 2.03 (d, J = 4.0 Hz, 1H, 5'-H), 2.30 (m, 2H, 6-H^{endo}, 4-H), 2.58 (m, 2H, 3-H^{endo}, 6-H^{exo}), 2.85 (m, 2H, 3a-H, 3-H^{exo}), 4.25 (m, 2H, CH_2O), ~4.30~4.40 (m, 1H, 5-H), 5.05 (m, 1H, 6a-H), 5.67 (d, J = 4.2 Hz, 1H, 2'-H), 7.45 (m, 2H, Ph), 7.58 (m, 1H, Ph), 7.99 (d, J = 7.3 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3/CHCl_3$): δ 17.72 (Me), 25.48 (C6'), 25.88 (Me), 31.80 (C1'), 32.65 (C5'), 35.67 (C3), 37.22 (C6), 40.40 (C3a), 52.38 (C4), 64.40 (CH_2O), 101.71 (C2'), 128.58 ($2C_{Ph}^{m}$), 129.36 ($1C_{Ph}^{i}$), 129.52 ($2C_{Ph}^{o}$), 133.40 ($1C_{Ph}^{p}$), 166.26 (PhCO), 172.09 (C4'), 176.36 (C2).

(–)-(3a*R*,4*S*,5*R*,6a*S*)-4-{[*tert*-Butyl(dimethyl)silyloxy]methyl}-5-hydroxyhexahydro-2*H*-cyclopenta[*b*]furan-2-one 2a. Produced from **4a**, yield 68%; $[\alpha]_D^{20} = -14.7$ (*c* 1.05, $CHCl_3$); ee > 98%; {Lit.[7b], $[\alpha]_D^{20} = +14.2$ (c 1.008, $CHCl_3$); ee ≥ 99%, Lit.[2e], $[\alpha]_D^{20} = -14.7$ (c 0.9, $CHCl_3$)}.

(+)-(3a*S*,4*R*,5*S*,6a*R*)-4-{[*tert*-Butyl(dimethyl)silyloxy]methyl}-5-hydroxyhexahydro-2*H*-cyclopenta[*b*]furan-2-one 2a. Produced from **5a**, yield 64%; $[\alpha]_D^{20} = +14.2$ (*c* 1.05, $CHCl_3$); ee > 98%.

(–)-(3a*R*,4*S*,5*R*,6a*S*)-5-Hydroxy-4-[(triisopropylsilyloxy)methyl]hexahydro-2*H*-cyclopenta[*b*]furan-2-one 2b. Produced from **4b**, yield 70%; $[\alpha]_D^{24} = -10.1$ (*c* 1.725, $CHCl_3$); ee > 97%.

(+)-(3a*S*,4*R*,5*S*,6a*R*)-5-Hydroxy-4-[(triisopropylsilyloxy)methyl]hexahydro-2*H*-cyclopenta[*b*]furan-2-one 2b. Produced from **5b**, yield 71%; $[\alpha]_D^{24} = +10.0$ (*c* 1.725, $CHCl_3$); ee > 97%.

(–)-[(3a*R*,4*S*,5*R*,6a*S*)-5-Hydroxy-2-oxohexahydro-2*H*-cyclopenta[*b*]furan-4-yl]methyl benzoate 2c. Produced from **4c**, Yield 85%; $[\alpha]_D^{20} = -12.1$ (*c* 3.0, CH_3OH); ee > 96.5%.

(+)-[(3a*S*,4*R*,5*S*,6a*R*)-5-Hydroxy-2-oxohexahydro-2*H*-cyclopenta[*b*]furan-4-yl]methyl benzoate 2c. Produced from **5c**, Yield 86%; $[\alpha]_D^{20} = +12.5$ (*c* 3.0, CH_3OH); ee > 96.5%.

(–)-(1*R*,4*R*,5*S*,1'*R*,4'*R*,5'*S*)-4,4'-Oxybis(6,6-dimethyl-3-oxabicyclo[3.1.0]hexan-2-one) 7. Yield ~7~5%; $[\alpha]_D^{22} = -253.0$ (*c* 0.205, CH_3OH); colorless crystals; mp 194-196 ºC; IR (Nujol mull) 1772, 1458, 1352, 1165, 1109, 1076, 1039 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3/CHCl_3$): δ 1.17 (s, 6H, 2Me), 1.18 (s, 6H, 2Me), 2.04 (d, J = 5.5 Hz, 2H, 1-H, 1'-H), 2.11 (d, J = 5.6 Hz, 2H, 5-H, 5'-H), 5.50 (s, 2H, 4-H, 4'-H); ^{13}C NMR (75 MHz, $CDCl_3/CHCl_3$): δ 14.97 (Me), 24.91 (C6, C6'), 25.33 (Me), 29.42 (C1, C1'), 34.98 (C5, C5'), 97.18 (C4, C4'), 172.67 (C2, C2'). Found (%): C, 63.05; H, 6.70. Calc. for $C_{14}H_{18}O_5$ (%): C, 63.09; H, 6.76.