Representative Experimental Procedures and Spectral Data

Methyl (3*R*)-3-methyl-2-(phenylsulfonyl)pent-4-enoate (2a). Wilkinson's catalyst (468 mg, 0.5 mmol) was weighed into a flame-dried, 250 ml 1 neck round-bottom flask, and suspended in anhydrous THF (40 ml) under an argon atmosphere. The resulting suspension was immediately sonicated for ca. 2 minutes, then warmed to 30 °C. Trimethyl phosphite (0.24 ml, 2.0 mmol) was added to the catalyst, which resulted in the deep red solution becoming a pale-yellow solution. The resulting homogeneous catalyst was then stirred at this temperature for an additional *ca*. 30 minutes. Sodium hydride (765.9 mg, 19.1 mmol, 60% dispersion in mineral oil) was suspended in a mixture of anhydrous THF/DMF (5.25:1, 42 ml), and the methyl phenylsulfonylacetate (4.293 g, 20.0 mmol) in anhydrous THF (10 ml) added dropwise *via* Teflon® cannula over *ca*. 10 minutes at ambient temperature. The resulting anion was then added to the catalyst using a Teflon® cannula, followed by the allylic carbonate **(*R*)-1a** (1.291 g, 9.9 mmol, 95% *ee*) from a tared syringe. The reaction mixture was stirred at 30 °C for *ca*. 1 hour (t.l.c. control) before being quenched with aqueous 1N NaOH solution and stirred for *ca*. 30 minutes. The reaction mixture was then partitioned between aqueous 1N NaOH solution and diethyl ether. The organic layers were combined, washed with saturated NaCl solution, dried (Na_2SO_4), filtered and concentrated *in vacuo* to afford a viscous oil. Purification by flash chromatography (SiO_2, eluting with 20% ethyl acetate/hexane) afforded the *allylic alkylation product* **2a** (2.560 g, 96%) as an off-white semi-solid: GLC analysis (using a Hewlett-Packard HP-1 column*) 2°:1°* = 36:1; Chiral capillary GLC analysis on the desulfonylated product **2a** (using a Astec CHIRALDEX™ G-TA column) *ee* = 93%; IR ($CHCl_3$) ($CHCl_3$) 3069 (w), 2954 (w), 1743 (s), 1586 (w), 1448 (m), 1327 (m), 1144 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91-7.87 (m, 2H), 7.68-7.63 (m, 1H), 7.57-7.51 (m, 2H), 5.79 (ddd, *J* = 17.1, 10.2, 8.2 Hz, 0.42H), 5.67 (ddd, *J* = 17.1, 10.2, 8.4 Hz, 0.58H), 5.10 (dt, *J* = 17.2, 1.1 Hz, 0.42H), 5.08 (dt, *J* = 10.2, 0.9 Hz, 0.42H), 5.06 (dt, *J* = 17.2, 1.2 Hz, 0.58H), 5.00 (ddd, *J* = 10.2, 1.2, 0.6 Hz, 0.58H), 3.95 (d, *J* = 8.7 Hz, 0.42H), 3.90 (d, *J* = 9.3 Hz, 0.58H), 3.59 (s, 1.29H), 3.45 (s, 1.79H), 3.10-2.96 (m, 1H), 1.34 (d, *J* = 6.8 Hz, 1.79H), 1.10 (d, *J* = 6.9 Hz, 1.29H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.11 (e), 166.08 (e), 138.79 (o), 138.30 (e), 138.15 (e), 138.11 (o), 134.38 (o), 134.35 (o), 129.54 (o), 129.29 (o), 129.15 (o), 129.01 (o), 116.99 (e), 116.60 (e), 75.87 (o), 75.43 (o), 52.86 (o), 52.65 (o), 37.61 (o), 37.24 (o), 18.85 (o), 18.49 (o); HRMS (EI, M^+) calcd for $C_{13}H_{16}O_4S$ 268.0769, found 268.0783

(3*S*,4*R*)-4-Methyl-3-(phenylsulfonyl)-3,4,5-trihydrofuran-2-one 5. The allylic alkylation product **2a** (2.409 g, 9.0 mmol) was dissolved in of MeOH/DCM (1:1, 180 ml), then cooled with stirring to –78 °C. Ozone was bubbled through for the solution *ca*. 20 minutes until a light-blue color developed. The excess ozone was then flushed from the reaction mixture using nitrogen for *ca*. 30 minutes. Sodium borohydride (1.370 g, 36.2 mmol) was then added in a single portion, and the resulting reaction mixture stirred for an additional *ca*. 3.5 hours at –78 °C. The reaction was then quenched by the careful addition of saturated aqueous NH_4Cl (10 ml), and the reaction allowed to warm to room temperature. The reaction mixture was then partitioned between saturated aqueous NH_4Cl solution and diethyl ether. The organic layers were combined, washed with saturated aqueous NaCl solution, dried (Na_2SO_4), filtered then concentrated *in vacuo* to afford a viscous oil. Purification by flash chromatography (SiO_2, gradient elution with 30-40% ethyl acetate/hexane) furnished the *γ-lactone* **5** (1.989 g, 92%) as an off-white semi-solid: mp 84-88 °C (recrystallized from 30% ethyl acetate/hexane); IR ($CHCl_3$) 2972 (w), 2919 (w), 1790 (s), 1774 (s), 1586 (w), 1449 (m), 1325 (s), 1313 (s), 1153 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.97-7.94 (m, 2H), 7.72 (t, J = 7.5 Hz, 1H), 7.62-7.58 (m, 2H), 4.55 (dd, A of ABX, J_{AB} = 8.9, J_{AX} = 7.6 Hz, 1H), 3.90 (dd, B of ABX, J_{AB} = 8.9, J_{BX} = 5.2 Hz, 1H), 3.73 (d, J = 5.8 Hz, 1H), 3.36-3.26 (m, 1H), 1.32 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.19 (e), 136.95 (e), 134.90 (o), 129.57 (o), 129.41 (o), 73.38 (e), 70.19 (o), 32.38 (o), 18.81 (o); HRMS ($M+H^+$) calcd for $C_{11}H_{13}O_4S$ 241.0535, found 241.0527.

(3*S*,4*R*)-3,4-Dimethyl-3-(phenylsulfonyl)-3,4,5-trihydrofuran-2-one. Lithium hexamethyldisilylazide (4.40 ml, 4.4 mmol, 1M in tetrahydrofuran) in anhydrous THF (25 ml) was cooled with stirring to –78 °C. The γ-lactone **5** (0.967 g, 4.0 mmol) in anhydrous THF (10 ml) was then added dropwise *via* Teflon® cannula over *ca*. 20 minutes. The enolate was then allowed to form over *ca*. 1 hour, then methyl iodide (0.75 ml, 12.0 mmol, freshly filtered through basic Al_2O_3) was added. The reaction mixture was warmed to room temperature where it was stirred for an additional *ca*. 16 hours. The reaction was then quenched by the addition of saturated aqueous $NaHCO_3$ (1 ml), and partitioned between 1:1 saturated aqueous NaCl/$Na_2S_2O_3$ solution and diethyl ether. The organic layers were combined, dried (K_2CO_3), filtered and concentrated *in vacuo* to afford a viscous oil. Purification by flash chromatography (SiO_2, eluting with 30% ethyl acetate/hexane) furnished the γ-lactone (0.962 mg, 94%) as an off-white semi-solid: mp 78-83 °C

(recrystallized from 30% ethyl acetate/hexane); IR ($CHCl_3$) 2985 (w), 2922 (w), 1775 (s), 1586 (w), 1448 (m), 1320 (m), 1310 (s), 1158 (m), 1139 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93-7.90 (m, 2H), 7.71 (t, J = 7.5 Hz, 1H), 7.60-7.56 (m, 2H), 4.62 (dd, A of ABX, J_{AB} = 8.8, J_{AX} = 7.7 Hz, 1H), 3.84 (dd, B of ABX, J_{AB} = 8.8, J_{BX} = 6.0 Hz, 1H), 3.51-3.42 (m, 1H), 1.40 (s, 3H), 1.20 (d, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.43 (e), 134.83 (o), 134.51 (e). 131.09 (o), 128.99 (o), 72.54 (e), 70.29 (e), 34.30 (o), 14.54 (o), 14.36 (o); HRMS (EI, M^+) calcd for $C_{12}H_{14}O_4S$ 254.0613, found 254.0620.

(3*S*,4*S*)-3,4-Dimethyl-3-prop-2-enyl-3,4,5-trihydrofuran-2-one 6a. Naphthalene (0.386 mg, 3.0 mmol, recrystallized from diethyl ether) was dissolved in anhydrous THF (10 ml) under an atmosphere of argon. Lithium metal (17.6 mg, 2.5 mmol) was added and the reaction mixture sonicated for *ca*. 1 hour. The resulting dark-green solution was then stirred for an additional *ca*. 2 hours at room temperature. The freshly prepared lithium naphthalenide (8.0 ml, 2.0 mmol, approx. 0.25M in tetrahydrofuran) was then cooled with stirring to –90 °C. The lactone (126.8 mg, 0.5 mmol) in anhydrous THF (2 ml) was added dropwise *via* Teflon® cannula to the sodium naphthalenide solution (dark-green persists after addition) and the enolate allowed to form over *ca*. 1 hour (t.l.c. control). Allyl iodide (0.19 ml, 2.1 mmol, freshly filtered through basic Al_2O_3) was then added which resulted in the complete dissipation of the dark-green color. The reaction mixture was maintained at –90 °C for *ca*. 19 hours, then quenched by the addition of methanol (0.2 ml). The reaction mixture was then partitioned between 1:1 saturated aqueous $NaHCO_3/Na_2S_2O_3$ solution and diethyl ether. The combined organic layers were washed with saturated aqueous NaCl solution, dried (K_2CO_3), filtered and concentrated *in vacuo* to afford a yellow oil. Purification by flash chromatography (SiO_2, gradient elution with 5-20% gradient of diethyl ether/pentane) afforded the γ-lactones **6a/b** (63.3 mg, 83%) as a colorless oil: GLC analysis (using a Hewlett-Packard HP-1 column, 95 °C to 115 °C, 1.0 °C/min) *ds* = 10:1; $[\alpha]_D^{18}$ = 18.9 (c = 1.0, $CHCl_3$); IR ($CHCl_3$) 2974 (w), 2907 (w), 1765 (s), 1641 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.75 (dddd, J = 16.9, 10.3, 8.3, 6.5 Hz, 1H), 5.15-5.08 (m, 2H), 4.32 (dd, A of ABX, J_{AB} = 8.9, J_{AX} = 7.7 Hz, 1H), 3.76 (dd, B of ABX, J_{AB} = 9.0, J_{BX} = 9.5 Hz, 1H), 2.55-2.45 (m, 1H), 2.41 (ddt, J = 14.0, 6.5, 1.3 Hz, 1H), 2.23 (ddt, J = 14.0, 8.3, 0.9 Hz, 1H), 1.06 (s, 3H), 0.96 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.79 (e), 133.26 (o), 119.37 (e). 71.43 (e), 44.92 (e), 41.04 (e), 36.67 (o), 17.13 (o), 11.63 (o); HRMS (CI, M^+) calcd for $C_9H_{14}O_2$ 154.0994, found 154.1004.