Supplementary Information for

Synthesis of a Fully Functionalized Protected C1-C11 Fragment

for the Synthesis of the Tedanolides

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(5*S*,6*R*) 2-[(2*S*,3*R*,4*S*,5*S*) 3-Bromo-5-methoxy-2,4-dimethyltetrahydrofuran-2-yl]-6-[(1*S*,2*R*) 1-methyl-2-methanesulfonyloxy)ethyl]-5-methyl-5,6-dihydropyran-2[2*H*]-one 8. To a flame-dried 10 mL round-bottomed flask equipped with a magnetic stirring bar was added anhydrous THF (0.5 mL). After cooling the solvent to 0 °C, NaH (1 mg, 0.05 mmol) and *p*-methoxybenzyl bromide (9 μL, 0.05 mmol) were added. The alcohol **7** (8 mg, 0.016 mmol) was then added to the stirred mixture in THF (0.5 mL, followed by 2 x 0.5 mL rinses). The reaction mixture was allowed to stir for 1 h, at which time it was quenched by the addition of 1M $NaHCO_3$ (5 mL) and extracted with diethyl ether (3 x 5 mL).). The organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by prepar-ative TLC (30% ethyl acetate in hexanes) to afford the pyrone **8** as an oil (7 mg, 94%). R_f = 0.14, 20% EtOAc in hexanes. ^1H NMR (360 MHz, $CDCl_3$) δ 7.01 (dd, *J* = 9.5, 6.6 Hz, 1H), 5.98 (d, *J* = 9.6 Hz, 1H), 4.75 (d, *J* = 4.8 Hz, 1H), 4.62 (d, *J* = 5.8 Hz, 1H), 4.35 (dd, *J* = 10.2, 3.0 Hz, 1H), 3.98 (d, *J* = 11.8 Hz, 1H), 3.38 (s, 3H), 3.19 (s, 3H), 2.89 (m, 1H), 2.37 (m, 2H), 1.45 (s, 3H), 1.32 (d, *J* = 6.5 Hz, 3H), 1.13 (d, *J* = 6.7 Hz, 3H), 1.04 (d, *J* = 7.1 Hz, 3H).

(*Z*) (4*S*,5*R*,6*S*,7*R*) 7-[(2*S*,3*R*,4*S*,5*RS*) 3-Bromo-5-methoxy-2,4-dimethyltetrahydro-furan-2-yl]-1-[(1,1-dimethyl)ethyldimethylsilyloxy]-7-methanesulfonyloxy-5-(4-methoxyphenylmethoxy)-4,6-dimethylhept-2-ene 9.

To a flame-dried 50 mL recovery flask equipped with a magnetic stirring bar was added the *cis*-ester **7** (840 mg, 1.72 mmol) and anhydrous diethyl ether (15 mL). After cooling the solution to -78 °C, 1.5M DIBAL-H (3.45 mL, 5.17 mmol) in toluene was slowly added. The mixture was allowed to stir for 1 h, at which time the reaction mixture was quenched by the addition of Na^+K^+ tartrate (20 mL). After allowing the mixture to stir for 24 h, it was extracted with diethyl ether (3 x 20 mL). The organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude diol [(*Z*) (4*S*,5*R*,6*S*,7*R*) 7-[(2*S*,3*R*,4*S*,5*RS*) 3-bromo-5-methoxy-2,4-dimethyltetrahydrofuran-2-yl]-4,6-dimethyl-7-methanesulfonyloxyhept-2-ene-1,5-diol] was used in the next step without further purification. Diol **a**: R_f = 0.20, 40% EtOAc in hexanes. Diol **b**: R_f = 0.36, 40% EtOAc in hexanes. To a flame-dried 50 mL recovery flask equipped with a magnetic stirring bar was added the above diol (ca. 1.72 mmol) and anhydrous DMF (15 mL). Imidazole (351 mg, 5.16 mmol) and TBSCl (519 mg, 3.44 mmol) were then added to the solution. After stirring the mixture for 2 h, additional imidazole (176 mg, 2.58 mmol) and TBSCl (259 mg, 1.72 mmol) were added. The mixture was allowed to stir for a total of 2.5 h, at which time it was quenched by the addition of H_2O (20 mL) and extracted with diethyl ether (3 x 20 mL). The organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude silyl ether alcohol [(*Z*) (4*S*,5*R*,6*S*,7*R*) 7-[(2*S*,3*R*,4*S*,5*RS*) 3-bromo-5-metho-xy-2,4-dimethyltetrahydrofuran-2-yl]-4,6-dimethyl-1-[(1,1-dimethyl-)ethyldimethylsilyloxy]-7-methanesulfonyloxyhept-2-ene-5-ol] was used in the next step without further purification. Silyl ether **a**: R_f = 0.50, 40% EtOAc in hexanes. Silyl ether **b**: R_f = 0.56, 40% EtOAc in hexanes. To a flame-dried 50 mL recovery flask equipped with a magnetic stirring bar was added the alcohol (ca. 1.72 mmol), anhydrous DMF (10 mL), and anhydrous THF (10 mL). After chilling the solution to 0 °C and placing it in the dark, NaH (124 mg, 5.16 mmol) and PMBBr (0.93 mL, 5.16 mmol) were added. The mixture was allowed to stir for 1 h, at which time the reaction mixture was quenched by the addition of 1M $NaHCO_3$ (10 mL). The quenched reaction was poured into a separa-

tory funnel containing H_2O (10 mL) and extracted with diethyl ether (3 x 20 mL). The organic extracts were dried over K_2CO_3, neutralized with triethylamine (1 mL), filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography twice (5% EtOAc in hexanes, gradient to 20% EtOAc in hexanes) to provide the ether **9** as a pale yellow oil (892 mg, 75% over 3 steps).

S-anomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.52 (ddd, *J* = 11.5, 7.1, 4.9 Hz, 1H), 5.42 (dd, *J* = 10.1, 10.1 Hz, 1H), 4.73 (d, *J* = 6.4 Hz, 1H), 4.73 (s, 1H), 4.61 (d, *J* = 10.4 Hz, 1H), 4.53 (d, *J* = 10.4 Hz, 1H), 4.36 (ddd, *J* = 13.3, 6.9, 1.4 Hz, 1H), 4.25 (ddd, *J* = 13.3, 4.8, 1.6 Hz, 1H), 3.89 (d, *J* = 11.6 Hz, 1H), 3.79 (s, 3H), 3.44 (s, 3H), 3.25 (dd, *J* = 6.1, 6.1 Hz, 1H), 3.07 (s, 3H), 2.78 (m, 1H), 2.39 (m, 1H), 2.27 (m, 1H), 1.41 (s, 3H), 1.13 (d, *J* = 6.8 Hz, 3H), 1.10 (d, *J* = 7.1 Hz, 3H), 1.08 (d, *J* = 6.8 Hz, 3H), 0.90 (s, 9H), 0.08 (s, 3H), 0.08 (s, 3H). ^{13}C NMR (90 MHz, $CDCl_3$) δ 159.4, 133.0, 130.7, 129.9, 129.3, 113.6, 104.6, 88.6, 86.7, 85.0, 75.1, 59.7, 56.3, 55.6, 55.2, 46.4, 38.9, 37.0, 36.0, 25.9, 21.8, 18.3, 16.2, 10.7, 9.8, -5.1, -5.2. $[\alpha]_D^{20}$ = +64.9 (*c* = 2.15, CH_2Cl_2).

R-anomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.53 (ddd, *J* = 11.6, 6.2, 6.2 Hz, 1H), 5.40 (dd, *J* = 10.1, 10.1 Hz, 1H), 4.65 (d, *J* = 2.1 Hz, 1H), 4.61 (d, *J* = 10.4 Hz, 1H), 4.57 (d, *J* = 10.4 Hz, 1H), 4.57 (d, *J* = 5.4 Hz, 1H), 4.32 (ddd, *J* = 13.2, 6.6, 1.4 Hz, 1H), 4.25 (ddd, *J* = 13.2, 5.5, 1.5 Hz, 1H), 3.79 (s, 3H), 3.70 (d, *J* = 10.5 Hz, 1H), 3.38 (s, 3H), 3.26 (dd, *J* = 5.8, 5.8 Hz, 1H), 2.99 (s, 3H), 2.82 (m, 1H), 2.43 (m, 1H), 2.33 (m, 1H), 1.50 (s, 3H), 1.19 (d, *J* = 6.9 Hz, 3H), 1.10 (d, *J* = 6.8 Hz, 3H), 1.08 (d, *J* = 7.1 Hz, 3H), 0.90 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$) δ 159.1, 133.4, 130.6, 129.7, 129.4, 113.7, 108.6, 86.4, 85.8, 85.2, 74.9, 59.6, 56.2, 55.2, 54.5, 48.4, 38.9, 36.6, 35.9, 25.9, 21.3, 18.3, 16.7, 14.1, 9.9, -5.2. IR (neat) 2955, 2934, 1514, 1360, 1250, 1174, 1080, 1005, 936, 839, 777 cm^{-1}. HRMS (FAB, NBA, NaI, *m/z*)

717.2291, calcd for $C_{31}H_{53}BrO_8SiS$ $(M+Na)^+$ 717.2301. $[\alpha]_D^{20}$ = -6.3 (*c* = 2.44, CH_2Cl_2).

***(Z)* (4*S*,5*R*,6*S*,7*R*) 7-[(2*S*,3*R*,4*S*,5*RS*) 3-Bromo-5-methoxy-2,4-dimethyltetrahydrofuran-2-yl]-5-(4-methoxyphenylmethoxy)-4,6-dimethyl-7-(triethylsilyloxy)hept-2-en-1-ol 10.** To a flame-dried 25 mL recovery flask equipped with a magnetic stirring bar was added the mesylate **9** (210 mg, 0.302 mmol) and anhydrous THF (5 mL). After cooling the solution to 0 °C, 0.9M methyllithium (0.67 mL, 0.605 mmol) in diethyl ether was added. The mixture was allowed to stir for 1 h, at which time additional 0.9M methyllithium (0.67 mL, 0.605 mmol) in diethyl ether was added. After stirring for an additional 30 min, the reaction mixture was quenched by the addition of 1M $NaHCO_3$ (10 mL) and extracted with diethyl ether (3 x 10 mL). The organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude alcohol [(*Z*) (1*R*,2*R*,3*R*,4*S*) 1-[(2*S*,3*R*,4*S*,5*RS*) 3-bromo-5-methoxy-2,4-dimethyltetrahydrofuran-2-yl]-7-[(1,1-dimethyl)ethyldimethylsilyloxy]-3-(4-methoxyphenylmethoxy)-2,4-dimethylhept-5-en-1-ol] was used in the next step without further purification.

S-anomer

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 5.51 (ddd, *J* = 11.3, 6.1, 6.1 Hz, 1H), 5.40 (dd, *J* = 9.9, 9.9 Hz, 1H), 4.73 (d, *J* = 5.0 Hz, 1H), 4.59 (d, *J* = 10.5 Hz, 1H), 4.51 (d, *J* = 10.5 Hz, 1H), 4.34 (d, *J* = 11.8 Hz, 1H), 4.27 (m, 2H), 3.80 (s, 3H), 3.53 (bd, *J* = 9.1 Hz, 1H), 3.40 (s, 3H), 3.25 (dd, *J* = 5.7, 5.7 Hz, 1H), 2.77 (m, 1H), 2.43 (d, *J* = 8.1 Hz, 1H), 2.35 (m, 1H), 2.01 (m, 1H), 1.29 (s, 3H), 1.10 (d, *J* = 6.8 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 3H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.90 (s, 9H), 0.07 (s, 6H).

R-anomer

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.53 (ddd, *J* = 11.5, 6.2, 6.2 Hz, 1H), 5.37 (dd, *J* = 10.0, 10.0 Hz, 1H), 4.59 (d, *J* = 5.0 Hz, 1H), 4.57 (s, 2H), 4.26 (m, 2H), 4.15 (d, *J* = 10.9 Hz, 1H), 3.79 (s, 3H), 3.59 (d, *J* = 7.5

Hz, 1H), 3.37 (s, 3H), 3.29 (dd, *J* = 6.9, 4.6 Hz, 1H), 2.81 (m, 1H), 2.63 (d, *J* = 7.6 Hz, 1H), 2.37 (m, 1H), 2.06 (m, 1H), 1.30 (s, 3H), 1.20 (d, *J* = 6.8 Hz, 3H), 1.09 (d, *J* = 6.7 Hz, 3H), 1.02 (d, *J* = 7.0 Hz, 3H), 0.90 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 134.0, 130.6, 129.4, 113.8, 113.8, 109.4, 87.9, 86.6, 74.5, 73.8, 59.5, 55.9, 55.3, 55.2, 46.8, 36.1, 35.9, 25.9, 20.8, 18.3, 16.9, 14.2, 8.0, -5.1, -5.2.

To a flame-dried 25 mL recovery flask equipped with a magnetic stirring bar was added the above alcohol (ca. 0.302 mmol) and anhydrous pyridine (5 mL). TESOTf (0.34 mL, 1.51 mmol) was added, and the mixture was allowed to stir for 3 h. The reaction mixture was then concentrated *in vacuo*, filtered through a plug of silica gel, and rinsed with 20% EtOAc in hexanes. After concentrating the filtrate *in vacuo*, the crude bis silyl ether [(*Z*) (2*S*,3*R*,4*S*,5*RS*) 3-bromo-2-{(1*R*,2*S*,3*R*,4*S*) 7-[(1,1-dimethyl)ethyldimethylsilyloxy]-3-(4-methoxyphenylmethoxy)-2,4-dimethyl-1-triethylsilyloxyhept-5-enyl}-5-methoxy-2,4-dimethyltetrahydrofuran] was used in the next step without further purification. *S*-anomer: R_f = 0.59, 10% EtOAc in hexanes. *R*-anomer: R_f = 0.49, 10% EtOAc in hexanes.

S-anomer

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.54 (dd, *J* = 11.1, 11.1 Hz, 1H), 5.48 (ddd, *J* = 11.1, 6.8, 4.6 Hz, 1H), 4.69 (d, *J* = 5.0 Hz, 1H), 4.55 (d, *J* = 10.6 Hz, 1H), 4.46 (d, *J* = 10.6 Hz, 1H), 4.34 (dd, *J* = 13.7, 7.0 Hz, 1H), 4.19 (dd, *J* = 13.1, 3.7 Hz, 1H), 3.91 (d, *J* = 11.6 Hz, 1H), 3.80 (s, 3H), 3.59 (s, 1H), 3.36 (s, 3H), 3.11 (dd, *J* = 8.4, 3.4 Hz, 1H), 2.66 (m, 1H), 2.38 (m, 1H), 2.15 (m, 1H), 1.31 (s, 3H), 1.10 (d, *J* = 6.7 Hz, 3H), 1.06 (d, *J* = 6.9 Hz, 3H), 1.02 (d, *J* = 6.3 Hz, 3H), 0.97 (t, *J* = 7.6 Hz, 9H), 0.90 (s, 9H), 0.68 (m, 6H), 0.07 (s, 6H).

To a flame-dried 25 mL recovery flask equipped with a magnetic stirring bar was added the above silyl ether (ca. 0.302 mmol) and a solution of 70% HF•pyr in pyridine and THF (1 : 4 : 10, 5 mL). The mixture was allowed to stir for 2 h, at which time it was quenched by the addition of 1M $NaHCO_3$ (5 mL). After extracting with ethyl acetate (3 x 10 mL), the organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The

crude material was purified by column chromatography (10% EtOAc in hexanes, gradient to 20% EtOAc in hexanes) to provide the alcohol **10** as a pale yellow oil (62 mg, 33% over 3 steps).

S-anomer, **10a**

R_f = 0.20, 20% EtOAc in hexanes.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.61 (m, 2H), 4.69 (d, *J* = 5.0 Hz, 1H), 4.56 (d, *J* = 10.6 Hz, 1H), 4.46 (d, *J* = 10.6 Hz, 1H), 4.20 (bd, *J* = 5.7 Hz, 2H), 3.91 (d, *J* = 11.6 Hz, 1H), 3.80 (s, 3H), 3.62 (d, *J* = 1.0 Hz, 1H), 3.37 (s, 3H), 3.15 (dd, *J* = 8.1, 3.6 Hz, 1H), 2.76 (m, 1H), 2.39 (m, 1H), 2.16 (m, 1H), 1.32 (s, 3H), 1.11 (d, *J* = 6.7 Hz, 3H), 1.07 (d, *J* = 6.9 Hz, 3H), 1.03 (d, *J* = 6.8 Hz, 3H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.70 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 136.3, 130.8, 129.0, 127.5, 113.7, 104.1, 88.4, 84.6, 77.7, 74.9, 58.7, 57.0, 55.5, 55.3, 45.7, 38.3, 35.7, 22.0, 15.6, 10.8, 10.2, 7.1, 5.5. $[\alpha]_D^{20}$ = +68.9 (*c* = 0.88, CH_2Cl_2).

R-anomer, **10b**

R_f = 0.29, 20% EtOAc in hexanes.

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 5.57 (m, 2H), 4.56 (d, *J* = 10.6 Hz, 1H), 4.52 (d, *J* = 5.2 Hz, 1H), 4.47 (d, *J* = 10.6 Hz, 1H), 4.20 (bd, *J* = 4.2 Hz, 2H), 3.80 (s, 3H), 3.63 (d, *J* = 10.4 Hz, 1H), 3.58 (d, *J* = 1.5 Hz, 1H), 3.38 (s, 3H), 3.20 (dd, *J* = 7.4, 4.0 Hz, 1H), 2.78 (m, 1H), 2.44 (m, 1H), 2.17 (m, 1H), 1.56 (bs, 1H), 1.42 (s, 3H), 1.18 (d, *J* = 6.9 Hz, 3H), 1.05 (d, *J* = 6.6 Hz, 3H), 1.04 (d, *J* = 6.5 Hz, 3H), 0.99 (t, *J* = 8.0 Hz, 9H), 0.68 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 136.4, 130.8, 129.0, 127.5, 113.7, 108.6, 87.5, 84.7, 77.4, 74.9, 58.7, 56.0, 55.8, 55.2, 48.4, 37.9, 35.5, 21.1, 15.8, 14.4, 10.3, 7.2, 5.5. IR (neat) 3411, 2955, 2878, 1514, 1248, 1127, 1071, 1013, 826, 741 cm^{-1}. HRMS (FAB, NBA, NaI, *m/z*) 637.2513, calcd for $C_{30}H_{51}BrO_6Si$ $(M+Na)^+$ 637.2536. $[\alpha]_D^{20}$ = -4.5 (*c* = 2.55, CH_2Cl_2).

(2*S*,3*R*) 3-(1*R*,2*R*,3*S*,4*R*) {4-[(2*S*,3*R*,4*S*,5*R*) 3-Bromo-5-methoxy-2,4-dimethyltetrahydrofuran-2-yl]-2-(4-methoxyphenylmethoxy)-1,3-dimethyl-4-triethylsilyloxybutyl}oxirane-2-methanol 11b. To a flame-dried 10 mL round-bottomed flask equipped with a magnetic stirring bar was added the alcohol **10b** (43 mg, 0.070 mmol) and anhydrous dichloromethane (0.5 mL). After cooling the solution to 0 °C, $NaHCO_3$ (23 mg, 0.28 mmol) and MCPBA (24 mg, 0.14 mmol) were added. The mixture was allowed to stir for 4 h, at which time the reaction mixture was quenched by the addition of 1M $NaHCO_3$ (5 mL) and extracted with diethyl ether (3 x 5 mL). The organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography (10% EtOAc in hexanes, gradient to 30% EtOAc in hexanes) to provide the epoxy alcohol **11b** as an oil (32 mg desired diastereomer, 84%, 6:1 diastereomeric ratio). R_f = 0.20, 20% EtOAc in hexanes.
^{1}H NMR (360 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.63 (d, *J* = 10.6 Hz, 1H), 4.55 (d, *J* = 10.6 Hz, 1H), 4.51 (d, *J* = 5.1 Hz, 1H), 3.88 (dd, *J* = 12.1, 4.3 Hz, 1H), 3.80 (s, 3H), 3.72 (dd, *J* = 12.0, 6.6 Hz, 1H), 3.61 (d, *J* = 10.5 Hz, 1H), 3.52 (dd, *J* = 10.0, 2.8 Hz, 1H), 3.44 (s, 1H), 3.37 (s, 3H), 3.26 (ddd, *J* = 6.6, 4.4, 4.4 Hz, 1H), 3.11 (dd, *J* = 9.5, 4.4 Hz, 1H), 2.40 (m, 1H), 2.19 (m, 1H), 1.68 (bs, 1H), 1.64 (m, 1H), 1.38 (s, 3H), 1.18 (d, *J* = 6.9 Hz, 3H), 1.14 (d, *J* = 6.8 Hz, 3H), 1.02 (t, *J* = 8.0 Hz, 9H), 0.97 (d, *J* = 6.9 Hz, 3H), 0.73 (m, 6H). ^{13}C NMR (90 MHz, $CDCl_3$) δ 159.1, 130.9, 129.0, 113.7, 108.6, 87.3, 81.8, 75.8, 75.2, 60.7, 59.9, 57.6, 56.0, 55.7, 55.3, 48.1, 37.4, 34.4, 21.0, 14.3, 10.5, 9.9, 7.2, 5.6. IR (neat) 3451, 2955, 2878, 1514, 1456, 1248, 1113, 1038, 1007, 824, 731 cm^{-1}. HRMS (FAB, NBA, NaI, *m/z*) 653.2470, calcd for $C_{30}H_{51}BrO_7Si$ $(M+Na)^+$ 653.2485. $[\alpha]_D^{20}$ = -14.1 (*c* = 1.60, CH_2Cl_2).

(α*S*,2*S*,3*R*,4*R*,5*S*,6*R*) 6-[(2*S*,3*R*,4*S*,5*R*) 3-Bromo-5-methoxy-2,4-dimethyltetrahydrofuran-2-yl]-α-hydroxymethyl-4-(4-methoxyphenylmeth-oxy)-3,5-dimethyltetrahydropyran-2-methanol 13. To a flame-dried 10 mL round-bottomed flask equipped with

a magnetic stirring bar was added the epoxide **11b** (10 mg, 0.016 mmol) and anhydrous methanol (0.5 mL). The solution was chilled to -78 °C before adding BF_3•OEt_2 (6 μL, 0.047 mmol). After 1 h, the reaction temperature was increased to -42 °C, and another portion of BF_3•OEt_2 (6 μL, 0.047 mmol) was added. After 3 h, the reaction temperature was increased to -20 °C, and another portion of BF_3•OEt_2 (6 μL, 0.047 mmol) was added. After 5 h, another portion of BF_3•OEt_2 (6 μL, 0.047 mmol) was added. The reaction mixture was allowed to stir for an additional 1 h, at which time it was quenched by the addition of 1M $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 x 5 mL). The organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by preparative TLC (40% ethyl acetate in hexanes) to afford the tetrahydropyran **13** as an oil (5 mg, 61%). R_f = 0.18, 40% EtOAc in hexanes.

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.63 (s, 2H), 4.59 (d, *J* = 5.0 Hz, 1H), 4.09 (d, *J* = 10.8 Hz, 1H), 3.91 (ddd, *J* = 11.8, 7.2, 4.0 Hz, 1H), 3.80 (s, 3H), 3.73 (ddd, *J* = 11.9, 6.6, 4.7 Hz, 1H), 3.59 (dd, *J* = 6.8, 4.4 Hz, 1H), 3.50 (dd, *J* = 9.2, 1.2 Hz, 1H), 3.38 (s, 3H), 3.26 (ddd, *J* = 6.9, 4.2, 4.2 Hz, 1H), 3.04 (dd, *J* = 9.5, 4.4 Hz, 1H), 2.41 (d, *J* = 9.3 Hz, 1H), 2.38 (m, 1H), 2.16 (m, 1H), 1.76 (m, 2H), 1.34 (s, 3H), 1.19 (d, *J* = 6.9 Hz, 3H), 1.08 (d, *J* = 6.9 Hz, 3H), 1.02 (d, *J* = 6.9 Hz, 3H).

(*Z*) (4*S*,5*R*,6*S*,7*R*) 7-Phenylmethoxy-7-[(2*S*,3*R*,4*S*,5*R*) 3-bromo-5-methoxy-2,4-dimethyltetrahydrofuran-2-yl]-5-(4-methoxyphenylmethoxy)-4,6-dimethylhept-2-en-1-ol 14. To a flame-dried 25 mL recovery flask equipped with a magnetic stirring bar was added the mesylate **9** (245 mg, 0.353 mmol) and anhydrous diethyl ether (5 mL). After cooling the solution to 0 °C, 0.9M methyllithium (0.78 mL, 0.706 mmol) in diethyl ether was added. Periodic addition of 0.9M methyllithium (0.39 mL, 0.353 mmol) in diethyl ether was continued at 1-hour intervals for 3 h. After stirring for an additional 90 minutes at room temperature, the reaction mixture was quenched by the addition of 1M $NaHCO_3$ (10 mL) and extracted with diethyl ether (3 x 20 mL). The organic extracts

were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude alcohol [(*Z*) (1*R*,2*S*,3*R*,4*S*) 1-[(2*S*,3*R*,4*S*,5*R*) 3-bromo-5-methoxy-2,4-dimethyltetrahydrofuran-2-yl]-7-[(1,1-dimethyl)ethyldimethylsilyloxy]-3-(4-methoxyphenylmethoxy)-2,4-dimethyl-hept-5-en-1-ol] was used in the next step without further purification. R_f = 0.52, 20% EtOAc in hexanes. To a flame-dried 25 mL recovery flask equipped with a magnetic stirring bar was added the above alcohol (ca. 0.353 mmol) and anhydrous THF (5 mL). Sodium hydride (25 mg, 1.06 mmol), benzyl bromide (0.13 mL, 1.06 mmol), and TBAI (20 mg) were added. After allowing the mixture to stir for 12 h, additional sodium hydride (25 mg, 1.06 mmol), benzyl bromide (0.13 mL, 1.06 mmol), and TBAI (20 mg) were added. After allowing the mixture to stir for an additional 6 h, more benzyl bromide (0.13 mL, 1.06 mmol) was added. The reaction mixture was allowed to stir for an additional 18 h, at which time it was quenched by the addition of 1M $NaHCO_3$ (10 mL) and extracted with diethyl ether (3 x 20 mL). The organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude ether [(*Z*) (4*S*,5*R*,6*S*,7*R*) 7-phenylmethoxy-7-[(2*S*,3*R*,4*S*,5*R*) 3-bromo-5-methoxy-2,4-dimethyltetrahydrofuran-2-yl)-1-[(1,1-dimethyl)ethyldimethylsilyloxy]-5-(4-methoxyphenylmethoxy)-4,6-dimethyl-hept-2-ene] was used in the next step without further purification. R_f = 0.49, 10% EtOAc in hexanes.

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.31 (m, 5H), 7.28 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.52 (ddd, *J* = 11.4, 6.1, 6.1 Hz 1H), 5.41 (dd, *J* = 10.1, 10.1 Hz, 1H), 4.64 (d, *J* = 11.4 Hz, 1H), 4.56 (m, 3H), 4.52 (d, *J* = 11.4 Hz, 1H), 4.30 (ddd, *J* = 12.9, 6.4, 1.2 Hz, 1H), 4.21 (ddd, *J* = 12.8, 5.4, 1.2 Hz, 1H), 3.89 (d, *J* = 10.6 Hz, 1H), 3.80 (s, 3H), 3.37 (s, 3H), 3.32 (d, *J* = 2.9 Hz, 1H), 3.21 (dd, *J* = 5.5, 5.5 Hz, 1H), 2.81 (m, 1H), 2.39 (m, 1H), 2.27 (m, 1H), 1.43 (s, 3H), 1.16 (d, *J* = 6.9 Hz, 3H), 1.10 (d, *J* = 6.6 Hz, 3H), 1.09 (d, *J* = 7.1 Hz, 3H), 0.89 (s, 9H), 0.06 (s, 3H), 0.06 (s, 3H). ^{13}C NMR (90 MHz, $CDCl_3$) δ 159.1, 138.6, 134.2, 130.9, 129.2, 129.1, 128.3, 127.5, 127.4, 113.8, 108.7, 87.8, 86.4, 83.2, 75.0, 74.7, 59.6, 55.8, 55.3, 54.9, 47.8, 37.7, 36.3, 25.9, 21.9, 18.3, 16.8, 14.3, 9.8, -5.1. IR

(neat) 2932, 2857, 1514, 1456, 1250, 1086, 1005, 837cm^{-1}. HRMS (FAB, NBA, NaI, *m/z*) 727.2981, calcd for $C_{31}H_{43}BrO_6$ $(M+Na)^+$ 727.3005. $[\alpha]_D^{20}$ = -8.6 (*c* = 1.65, CH_2Cl_2).

To a flame-dried 25 mL recovery flask equipped with a magnetic stirring bar was added the above silyl ether (ca. 0.353 mmol) and a solution of 70% HF•pyr in pyridine and THF solution (1 : 4 : 10, 3 mL). The mixture was allowed to stir for 2 h, at which time it was quenched by the addition of 1M $NaHCO_3$ (5 mL). After extracting with ethyl acetate (3 x 10 mL), the organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography (20% EtOAc in hexanes, gradient to 30% EtOAc in hexanes) to provide the alcohol **14** as a pale yellow oil (129 mg, 61% over 3 steps). R_f = 0.12, 20% EtOAc in hexanes.

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.31 (m, 5H), 7.27 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.6 (ddd, *J* = 11.1, 6.7, 6.7 Hz, 1H), 5.50 (dd, *J* = 10.2, 10.2 Hz, 1H), 4.63 (d, *J* = 11.5 Hz, 1H), 4.58 (d, *J* = 11.5 Hz, 1H), 4.56 (m, 3H), 4.16 (bd, *J* = 6.5 Hz, 2H), 3.86 (d, *J* = 10.6 Hz, 1H), 3.79 (s, 3H), 3.37 (s, 3H), 3.31 (d, *J* = 2.7 Hz, 1H), 3.24 (dd, *J* = 5.4, 5.4 Hz, 1H), 2.88 (m, 1H), 2.39 (m, 1H), 2.28 (m, 1H), 1.43 (s, 3H), 1.16 (d, *J* = 6.8 Hz, 3H), 1.10 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (90 MHz, $CDCl_3$) δ 159.1, 138.6, 136.3, 130.7, 129.3, 128.3, 128.0, 127.5, 127.4, 113.8, 108.7, 87.9, 86.2, 83.4, 74.6, 58.6, 55.9, 55.2, 55.1, 47.7, 37.4, 35.9, 21.7, 17.1, 14.3, 10.1 (one high field carbon unresolved). IR (neat) 3426, 2934, 2876, 1615, 1514, 1456, 1248, 1109, 1084, 1036, 1003 cm^{-1}. HRMS (FAB, NBA, NaI, *m/z*) 613.2135, calcd for $C_{31}H_{43}BrO_6$ $(M+Na)^+$ 613.2141. $[\alpha]_D^{20}$ = -18.4 (*c* = 1.10, CH_2Cl_2).

(2*S*,3*R*) 3-(1*R*,2*R*,3*S*,4*R*) {4-Phenylmethoxy-4-[(2*S*,3*R*,4*S*,5*R*) 3-bromo-5-methoxy-2,4-dimethyltetrahydrofuran-2-yl]-2-(4-methoxyphenylmethoxy)-1,3-dimethyl-butyl}oxirane-2-methanol 15. To a flame-dried 10 mL round-bottomed flask equipped with a magnetic stirring bar was added the alcohol **14** (30 mg, 0.051 mmol) and anhydrous dichloromethane (1 mL). After cooling the solution to 0 °C, $NaHCO_3$ (17 mg, 0.20

mmol) and MCPBA (17 mg, 0.10 mmol) were added. The mixture was allowed to stir for 3 h, at which time the reaction mixture was quenched by the addition of 1M $NaHCO_3$ (5 mL) and extracted with diethyl ether (3 x 5 mL). The organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by column chromotography (10% EtOAc in hexanes, gradient to 30% EtOAc in hexanes) to provide the epoxy alcohol **15** as an oil (24 mg desired diastereomer, 90%, 6:1 diastereomeric ratio). R_f = 0.25, 30% EtOAc in hexanes.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, 5H), 7.28 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.66 (d, *J* = 11.5 Hz, 1H), 4.61 (d, *J* = 11.5 Hz, 1H), 4.59 (m, 3H), 3.89 (dd, *J* = 12.1, 4.1 Hz, 1H), 3.84 (d, *J* = 10.6 Hz, 1H), 3.80 (s, 3H), 3.70 (dd, *J* = 12.1, 6.5 Hz, 1H), 3.63 (dd, *J* = 8.3, 3.0 Hz, 1H), 3.36 (s, 3H), 3.28 (bd, *J* = 1.7 Hz, 1H), 3.25 (ddd, *J* = 6.5, 6.5, 4.3 Hz, 1H), 3.06 (dd, *J* = 9.5, 4.4 Hz, 1H), 2.38 (m, 1H), 2.31 (m, 1H), 1.79 (m, 1H), 1.40 (s, 3H), 1.19 (d, *J* = 6.9 Hz, 3H), 1.15 (d, *J* = 6.9 Hz, 3H), 1.02 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 138.4, 130.8, 129.2, 128.3, 127.7, 127.6, 113.7, 108.7, 87.7, 82.8, 82.0, 75.2, 75.1, 60.7, 59.9, 57.5, 55.8, 55.3, 55.2, 47.4, 37.7, 34.8, 21.5, 14.3, 10.9, 10.7. IR (neat) 3445, 2965, 2936, 1514, 1456, 1240, 1107, 1038, 1001 cm^{-1}. HRMS (FAB, NBA, NaI, *m/z*) 629.2098, calcd for $C_{31}H_{43}BrO_7$ $(M+Na)^+$ 629.2090. $[\alpha]_D^{20}$ = -22.8 (*c* = 0.65, CH_2Cl_2).

(2*R*,3*R*,4*R*,5*R*,6*S*,7*R*) 7-Phenylmethoxy-7-[(2*S*,3*R*,4*S*,5*R*) 3-bromo-5-methoxy-2,4-dimethyltetrahydrofuran-2-yl]-2-methoxy-5-(4-methoxyphenylmethoxy)-4,6-dimethylheptane-1,3-diol 17. To a flame-dried 10 mL round-bottomed flask equipped with a magnetic stirring bar was added the epoxide **15** (24 mg, 0.040 mmol) and anhydrous methanol (1 mL). After cooling the solution to 0 °C, BF_3•OEt_2 (5 drops) was added at 3-hour intervals for 6 h. The reaction mixture was allowed to stir for an additional 3 h at room temperature, at which time it was quenched by the addition of 1M $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 x 5 mL). The organic extracts were

dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography (35% EtOAc in hexanes, gradient to 45% EtOAc in hexanes) to provide the diol **17** as an oil (15 mg, 59%). R_f = 0.26, 40% EtOAc in hexanes. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, 5H), 7.24 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.71 (d, *J* = 11.6 Hz, 1H), 4.67 (d, *J* = 11.5 Hz, 1H), 4.59 (d, *J* = 5.0 Hz, 1H), 4.58 (d, *J* = 9.9 Hz, 1H), 4.54 (d, *J* = 9.9 Hz, 1H), 3.94 (dd, *J* = 11.6, 4.4 Hz, 1H), 3.86 (d, *J* = 10.5 Hz, 1H), 3.86 (m, 1H), 3.79 (s, 3H), 3.77 (m, 1H), 3.58 (bd, *J* = 9.2 Hz, 1H), 3.50 (s, 3H), 3.37 (s, 3H), 3.33 (m, 2H), 2.66 (bs, 1H), 2.47 (bs, 1H), 2.38 (m, 1H), 2.29 (m, 1H), 2.13 (m, 1H), 1.41 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 138.6, 131.1, 129.3, 128.3, 127.8, 127.6, 113.7, 108.7, 87.9, 82.4, 80.7, 78.9, 75.5, 75.1, 74.2, 62.7, 58.1, 55.9, 55.5, 55.3, 47.7, 38.1, 37.4, 21.5, 14.3, 11.3, 10.5. IR (neat) 3453, 2936, 1514, 1456, 1248, 1111, 1082, 1040, 1005 cm^{-1}. HRMS (FAB, NBA, NaI, *m/z*) 661.2346, calcd for $C_{32}H_{47}BrO_8$ $(M+Na)^+$ = 661.2352. $[\alpha]_D^{20}$ = +1.6 (*c* = 0.75, CH_2Cl_2).

(2*R*,3*S*) 3-{(1*R*,2*R*,3*S*,4*R*) 4-Phenylmethoxy-4-[(2*S*,3*R*,4*S*,5*R*) 3-bromo-5-methoxy-2,4-dimethyltetrahydrofuran-2-yl]-2-(4-methoxyphenylmethoxy)-1,3-dimethyl-butyl]oxirane-2-methanol 18. To a flame-dried 10 mL round-bottomed flask equipped with a magnetic stirring bar was added the alcohol **14** (26 mg, 0.044 mmol), acetonitrile (1 mL), and 4 x 10^{-4}M EDTA (1 mL). After cooling the solution to 0 °C, to the mixture was added acetone (32 μL, 0.44 mmol), $NaHCO_3$ (11 mg, 0.13 mmol), and Oxone (41 mg, 0.066 mmol). Periodic addition of $NaHCO_3$ (11 mg, 0.13 mmol) and Oxone (41 mg, 0.066 mmol) was continued every 2 h for 6 h. The reaction mixture was allowed to stir for an additional 2 h, at which time the mixture was quenched by the addition of 1M $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 x 5 mL). The organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography (20% EtOAc in hexanes, gradient to 30% EtOAc in hexanes)

to provide the epoxy alcohol **18** as an oil (22 mg total, 82%, 3:1 diastereomeric ratio). R_f = 0.32, 30% EtOAc in hexanes.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 5H), 7.23 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.60 (d, *J* = 11.6 Hz, 1H), 4.55 (d, *J* = 5.0 Hz, 1H), 4.54 (d, *J* = 11.1 Hz, 1H), 4.49 (d, *J* = 11.1 Hz, 1H), 3.79 (m, 2H), 3.79 (s, 3H), 3.52 (m, 1H), 3.45 (dd, *J* = 5.3, 2.9 Hz, 1H), 3.36 (s, 3H), 3.18 (d, *J* = 2.5 Hz, 1H), 3.12 (ddd, *J* = 6.8, 5.4, 4.2 Hz, 1H), 2.92 (dd, *J* = 9.5, 4.1 Hz, 1H), 2.45 (bs, 1H), 2.40 (m, 1H), 2.33 (m, 1H), 1.83 (m, 1H), 1.43 (s, 3H), 1.20 (d, *J* = 6.9 Hz, 3H), 1.17 (d, *J* = 7.0 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 138.4, 129.8, 129.7, 128.3, 127.5, 127.3, 113.9, 108.7, 87.8, 84.2, 83.8, 74.8, 73.7, 60.5, 60.3, 57.4, 55.9, 55.2, 55.1, 47.7, 36.1, 35.9, 21.5, 14.4 (two carbons), 10.6. IR (neat) 3451, 2936, 1514, 1456, 1250, 1109, 1038, 1001 cm^{-1}. HRMS (FAB, NBA, NaI,*m/z*) 629.2113, calcd for $C_{31}H_{43}BrO_7$ $(M+Na)^+$ 629.2090. $[\alpha]_D^{20}$ = +10.9 (*c* = 0.70, CH_2Cl_2).

(2*S*,3*S*,4*R*,5*R*,6*S*,7*R*) 2-(2-Propenyl)-7-phenylmethoxy-7-[(2*S*,3*R*,4*S*,5*R*) 3-bromo-5-methoxy-2,4-dimethyltetrahydrofuran-2-yl]-5-(4-methoxyphenylmethoxy)-4,6-dimethylheptane-1,3-diol 19. To a flame-dried 10 mL round-bottomed flask equipped with a magnetic stirring bar was added the epoxide **18** (4 mg, 0.0066 mmol) and allyl alcohol (0.5 mL). To the stirred solution was added BF_3•OEt_2 (2 drops), and after 1 h, another portion of BF_3•OEt_2 (2 drops) was added. The reaction mixture was allowed to stir for an additional 1 h, at which time the mixture was quenched by the addition of 1M $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 x 5 mL). The organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by preparative TLC (40% EtOAc in hexanes) to provide the diol **19** as an oil (1 mg, 23%). R_f = 0.29, 40% EtOAc in hexanes.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (m, 7H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.94 (ddd, *J* = 16.1, 11.3, 5.7 Hz, 1H), 5.29 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.20 (dd, *J* = 10.3, 1.4 Hz, 1H),

4.66 (d, J = 11.7 Hz, 1H), 4.61 (d, J = 11.7 Hz, 1H), 4.57 (m, 3H), 4.50 (d, J = 10.8 Hz, 1H), 4.20 (dd, J = 12.6, 5.6 Hz, 1H), 4.09 (dd, J = 12.7, 5.8 Hz, 1H), 3.86 (d, J = 10.5 Hz, 1H), 3.79 (s, 6H), 3.77 (m, 1H), 3.54 (dd, J = 11.9, 4.0 Hz, 1H), 3.43 (dd, J = 6.1, 4.6 Hz, 1H), 3.38 (m, 1H), 3.37 (s, 3H), 3.34 (d, J = 2.3 Hz, 1H), 2.39 (m, 2H), 2.00 (m, 1H), 1.44 (s, 3H), 1.15 (d, J = 6.8 Hz, 3H), 1.15 (d, J = 7.1 Hz, 3H), 1.03 (d, J = 7.0 Hz, 3H).

(4*R*) 4-{(1*S*,2*R*,3*R*,4*S*,5*R*) 5-Phenylmethoxy-5-[(2*S*,3*R*,4*S*,5*R*) 3-bromo-5-methoxy-2,4-dimethyltetrahydrofuran-2-yl]-1-hydroxy-3-(4-methoxyphenylmethoxy)-2,4-dimethylpentyl}-1,3-dioxolan-2-one 20. To a flame-dried 10 mL round-bottomed flask equipped with a magnetic stirring bar was added the alcohol **18** (35 mg, 0.058 mmol) and anhydrous dichloromethane (1 mL). To the stirred solution was added triethylamine (0.02 mL, 0.17 mmol), phenyl isocyanate (0.02 mL, 0.17 mmol), and DMAP (1 mg, 0.0058 mmol). The reaction mixture was allowed to stir for 15 min, at which time it was concentrated *in vacuo*. The crude material was purified by column chromatography (10% EtOAc in hexanes, gradient to 20% EtOAc in hexanes) to afford the carbamate [(2*S*,3*S*) 3-[(1*R*,2*R*,3*S*,4*R*) 3-{4-phenylmethoxy-4-[(2*S*,3*R*,4*S*,5*R*) 3-bromo-5-methoxy-2,4-dimethyltetrahydrofuran-2-yl]-2-(4-methoxyphenyl-methoxy)-1,3-dimethylbutyl}-oxirane-2-methyl-*N*-phenylcarbamate] as a colorless oil (40 mg, 95%). R_f = 0.57, 30% EtOAc in hexanes.

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.30 (m, 9H), 7.24 (d, J = 8.7 Hz, 2H), 7.07 (m, 1H), 6.85 (d, J = 8.6 Hz, 2H), 6.69 (bs, 1H), 4.68 (d, J = 11.6 Hz, 1H), 4.61 (d, J = 11.6 Hz, 1H), 4.58 (d, J = 10.9 Hz, 1H), 4.56 (d, J = 4.9 Hz, 1H), 4.51 (d, J = 10.9 Hz, 1H), 4.23 (d, J = 6.4 Hz, 2H), 3.79 (m, 1H), 3.78 (s, 3H), 3.40 (dd, J = 6.5, 3.8 Hz, 1H), 3.35 (s, 3H), 3.23 (d, J = 2.1 Hz, 1H), 3.19 (dd, J = 10.0, 5.9 Hz, 1H), 2.98 (dd, J = 9.3, 4.1 Hz, 1H), 2.39 (m, 2H), 1.77 (m, 1H), 1.45 (s, 3H), 1.23 (d, J = 6.7 Hz, 3H), 1.17 (d, J = 6.6 Hz, 3H), 1.15 (d, J = 6.6 Hz, 3H). ^{13}C NMR (90 MHz, $CDCl_3$) δ 159.3, 152.8, 138.6, 137.5, 130.3, 129.5, 129.0, 128.3, 127.4, 127.1, 123.6, 118.7, 113.8, 108.8, 88.0, 83.4, 83.0, 74.8, 74.4,

63.3, 30.5, 55.8, 55.2, 55.2, 55.1, 47.8, 37.4, 35.8, 21.4, 14.3, 12.8, 10.4. IR (neat) 3324, 2936, 1738, 1603, 1514, 1445, 1248, 1217, 1109, 1030 cm^{-1}. HRMS (FAB, NBA, NaI, *m/z*) 748.2486, calcd for $C_{38}H_{48}BrNO_8$ $(M+Na)^+$ 748.2461. $[\alpha]_D^{20}$ = +9.3 (*c* = 1.75, CH_2Cl_2).

To a flame-dried 10 mL round-bottomed flask equipped with a magnetic stirring bar was added the above carbamate (35 mg, 0.048 mmol) and anhydrous acetonitrile (1 mL). To the stirred solution was added 5% $HClO_4$ (0.5 mL). The reaction mixture was allowed to stir for 4 h, at which time it was quenched by the addition of 1M $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 x 5 mL). The organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*.. The crude material was purified by column chromatography (20% EtOAc in hexanes, gradient to 30% EtOAc in hexanes) to afford the cyclic carbonate **20** as a colorless oil (23 mg, 74%). R_f = 0.24, 30% EtOAc in hexanes. ^1H NMR (360 MHz, $CDCl_3$) δ 7.38 (m, 5H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 4.90 (d, *J* = 12.3 Hz, 1H), 4.61 (m, 2H), 4.56 (d, *J* = 12.3 Hz, 1H), 4.25 (d, *J* = 11.1 Hz, 1H), 4.25 (m, 1H), 4.11 (dd, *J* = 6.7, 6.7 Hz, 1H), 4.05 (dd, *J* = 8.3, 8.3 Hz, 1H), 3.79 (s, 3H), 3.69 (d, *J* = 10.5 Hz, 1H), 3.38 (s, 3H), 3.29 (m, 2H), 3.27 (bs, 1H), 2.43 (m, 1H), 2.34 (m, 1H), 1.83 (m, 1H), 1.47 (s, 3H), 1.23 (d, *J* = 7.1 Hz, 3H), 1.20 (d, *J* = 6.9 Hz, 3H), 1.03 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (90 MHz, $CDCl_3$) δ 159.4, 154.8, 139.0, 130.1, 129.6, 128.4, 127.6, 127.6, 113.9, 108.7, 88.2, 83.3, 82.7, 74.7, 73.8, 73.5, 66.3, 55.9, 55.7, 55.3, 47.8, 38.3, 37.8, 20.9, 14.4, 10.9, 8.9 (one high field carbon unresolved). IR (neat) 3459, 2936, 1798, 1514, 1250, 1175, 1074 cm^{-1}. HRMS (FAB, NBA, NaI, *m/z*) 673.1970, calcd for $C_{32}H_{43}BrO_9$ $(M+Na)^+$ 673.1988. $[\alpha]_D^{20}$ = +32.5 (*c* = 1.10, CH_2Cl_2).

(4*R*) 4-{(1*S*,2*R*,3*R*,4*S*,5*R*) 5-Phenylmethoxy-5-[(2*S*,3*R*,4*S*,5*R*) 3-bromo-5-methoxy-2,4-dimethyltetrahydrofuran-2-yl]-1-methoxy-3-(4-methoxyphenylmethoxy)-2,4-dimethylpentyl}-1,3-dioxolan-2-one 21. To a flame-dried 10 mL round-bottomed flask equipped with a magnetic stirring bar was added the carbonate **20** (9 mg, 0.014 mmol)

and anhydrous dichloromethane (0.5 mL). To the stirred solution was added 2,6-di-*tert*-butylpyridine (0.15 mL, 0.69 mmol) and methyl triflate (0.08 mL, 0.69 mmol). After stirring the reaction mixture at room temperature for 20 h, it was placed in a 30 °C oil bath for an additional 2 d. At this time, dichloromethane (0.5 mL), 2,6-di-tert-butyl-pyridine (0.15 mL, 0.69 mmol) and methyl triflate (0.05 mL, 0.42 mmol) were added. The oil bath was warmed to 45 °C and the reaction mixture was refluxed for an additional 4 d, at which time it was quenched by the addition of 1M $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 x 5 mL). The organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*.. The crude material was purified by preparative TLC (20% EtOAc in hexanes) to afford the methyl ether **21** as an oil (4 mg, 43%). R_f = 0.28, 30% EtOAc in hexanes.

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.38 (m, 5H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 4.88 (d, *J* = 12.3 Hz, 1H), 4.62 (d, *J* = 11.6 Hz, 1H), 4.58 (m, 2H), 4.26 (d, *J* = 11.5 Hz, 1H), 4.22 (ddd, *J* = 7.8, 7.8, 3.6 Hz, 1H), 3.97 (dd, *J* = 8.3, 8.3 Hz, 1H), 3.85 (dd, *J* = 7.1, 7.1 Hz, 1H), 3.79 (s, 3H), 3.68 (d, *J* = 10.5 Hz, 1H), 3.46 (s, 3H), 3.37 (s, 3H), 3.31 (m, 1H), 3.27 (dd, *J* = 5.0, 2.7 Hz, 1H), 2.84 (dd, *J* = 6.8, 3.7 Hz, 1H), 2.42 (m, 1H), 2.36 (m, 1H), 2.00 (m, 1H), 1.47 (s, 3H), 1.19 (d, *J* = 7.1 Hz, 3H), 1.18 (d, *J* = 6.9 Hz, 3H), 1.01 (d, *J* = 7.0 Hz, 3H).

(4*S*) 4-{(1*R*,2*S*,3*S*,4*R*,5*S*) 4-Phenylmethoxy-4-[(2*S*,3*R*,4*S*,5*R*) 3-bromo-5-methoxy-2,4-dimethyltetrahydrofuran-2-yl]-2-(4-methoxyphenylmethoxy)-1,3-dimethyl-butyl}-5-hydroxymethyl-1,3-dioxolan-2-one 22. To a flame-dried 10 mL round-bottomed flask equipped with a magnetic stirring bar was added the carbonate **20** (3 mg, 0.0046 mmol) and anhydrous THF (0.5 mL). The solution was chilled to 0 °C before adding sodium hydride (1 mg, 0.046 mmol) and methyl iodide (3 μL, 0.046 mmol). The reaction mixture was allowed to stir for 1 h, at which time it was quenched by the addition of 1M $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 x 5 mL). The organic

extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by preparative TLC (40% EtOAc in hexanes) to afford the carbonate **22** as an oil (3 mg, 100%). R_f = 0.13, 30% EtOAc in hexanes.

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.35 (m, 5H), 7.24 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.84 (d, *J* = 11.9 Hz, 1H), 4.58 (m, 3H), 4.52 (d, *J* = 10.7 Hz, 1H), 4.35 (d, *J* = 10.7 Hz, 1H), 4.30 (m, 1H), 3.80 (s, 3H), 3.69 (d, *J* = 10.5 Hz, 1H), 3.65 (dd, *J* = 12.7, 3.3 Hz, 1H), 3.37 (s, 3H), 3.33 (m, 3H), 2.38 (m, 2H), 2.04 (m, 1H), 1.47 (s, 3H), 1.18 (d, *J* = 7.1 Hz, 3H), 1.17 (d, *J* = 6.9 Hz, 3H), 1.06 (d, *J* = 6.9 Hz, 3H). IR (neat) 3457, 2936, 1798, 1514, 1250, 1175, 1084, 1005 cm^{-1}.

(2*S*,3*S*,4*R*,5*R*,6*S*,7*R*) 7-Phenylmethoxy-7-[(2*S*,3*R*,4*S*,5*R*) 3-bromo-5-methoxy-2,4-dimethyltetrahydrofuran-2-yl]-3-methoxy-5-(4-methoxyphenylmethoxy)-4,6-dimethylheptane-1,2-diol 23. To a flame-dried 10 mL round-bottomed flask equipped with a magnetic stirring bar was added the carbonate **21** (5 mg, 0.0075 mmol) and 0.5M NaOH in 1:1 dioxane:H_2O (0.5 mL). The reaction mixture was allowed to stir for 30 min, at which time it was quenched by the addition of saturated NH_4Cl (5 mL) and extracted with ethyl acetate (3 x 5 mL). The organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by preparative TLC (50% EtOAc in hexanes) to afford the diol **23** as an oil (4 mg, 83%). R_f = 0.14, 40% EtOAc in hexanes.

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.35 (m, 5H), 7.21 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.77 (d, *J* = 11.9 Hz, 1H), 4.69 (d, *J* = 11.9 Hz, 1H), 4.59 (m, 2H), 4.33 (d, *J* = 11.1 Hz, 1H), 3.80 (s, 3H), 3.77 (m, 1H), 3.61 (m, 1H), 3.55 (m, 1H), 3.47 (m, 2H), 3.44 (s, 3H), 3.40 (d, *J* = 2.3 Hz, 1H), 3.37 (s, 3H), 2.99 (dd, *J* = 7.6, 2.6 Hz, 1H), 2.43 (d, *J* = 7.3 Hz, 1H), 2.40 (m, 1H), 2.34 (m, 1H), 2.17 (m, 1H), 1.91 (m, 1H), 1.44 (s, 3H), 1.20 (d, *J* = 7.0 Hz, 3H), 1.15 (d, *J* = 6.9 Hz, 3H), 1.04 (d, *J* = 7.0 Hz, 3H).

(2*S*,3*R*,4*S*,5*R*) 2-{(2*R*,3*S*,4*R*,5*R*,6*S*,7*R*) 1,6-Bis(phenylmethoxy)-5-methoxy-3-(4-methoxyphenylmethoxy)-2,4-dimethyl-7-[(1,1-dimethyl)-ethyldiphenylsilyloxy]-heptyl}-3-bromo-5-methoxy-2,4-dimethyltetrahydrofuran 24. To a flame-dried 10 mL round-bottomed flask equipped with a magnetic stirring bar was added the diol **23** (4 mg, 0.0063 mmol) and anhydrous DMF (0.5 mL). To the stirred solution was added imidazole (2 mg, 0.019 mmol) and TBDPSCl (3 μL, 0.013 mmol). After allowing the reaction mixture to stir for 1 h, an additional portion of imidazole (2 mg, 0.019 mmol) and TBDPSCl (3 μL, 0.013 mmol) were added. The reaction mixture was allowed to stir for an additional 4 h, at which time it was poured into a separatory funnel containing H_2O (15 mL) and extracted with ethyl acetate (3 x 5 mL). The organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by preparative TLC (10% EtOAc in hexanes) to afford the alcohol [(2*R*,3*S*,4*R*,5*R*,6*S*,7*R*) 7-phenylmethoxy-7-[(2*S*,3*R*,4*S*,5*R*) 3-bromo-5-methoxy-2,4-dimethyltetrahydrofuran-2-yl]-1-[(1,1-dimethyl)ethyldiphenylsilyloxy)-3-methoxy-5-(4-methoxyphenylmethoxy)-4,6-dimethyl-heptan-2-ol] as an oil (4 mg, 72%). R_f = 0.88, 40% EtOAc in hexanes. ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.63 (m, 4H), 7.34 (m, 11H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 4.73 (d, *J* = 11.9 Hz, 1H), 4.69 (d, *J* = 11.9 Hz, 1H), 4.57 (d, *J* = 5.0 Hz, 1H), 4.47 (d, *J* = 10.8 Hz, 1H), 4.38 (d, *J* = 10.8 Hz, 1H), 3.87 (m, 1H), 3.82 (d, *J* = 10.6 Hz, 1H), 3.76 (s, 3H), 3.71 (dd, *J* = 9.7, 6.6 Hz, 1H), 3.59 (dd, *J* = 9.9, 6.5 Hz, 1H), 3.45 (dd, *J* = 7.8, 2.1 Hz, 1H), 3.41 (s, 3H), 3.39 (m, 1H), 3.35 (s, 3H), 3.23 (dd, *J* = 7.9, 1.7 Hz, 1H), 2.39 (d, *J* = 6.3 Hz, 1H), 2.38 (m, 1H), 2.32 (m, 1H), 2.23 (m, 1H), 1.42 (s, 3H), 1.17 (d, *J* = 7.0 Hz, 3H), 1.14 (d, *J* = 6.8 Hz, 3H), 1.04 (d, 3H), 1.03 (s, 9H). To a flame-dried 10 mL round-bottomed flask equipped with a magnetic stirring bar was added the above alcohol (4 mg, 0.0046 mmol) and anhydrous THF (0.5 mL). To the stirred solution was added NaH (0.3 mg, 0.014 mmol), benzyl bromide (2 μL, 0.014 mmol), and TBAI (2 mg, 0.0046 mmol). After allowing the reaction mixture to stir for 2 h, an additional portion of NaH (0.3 mg, 0.014 mmol) and benzyl bromide (2 μL, 0.014

mmol) were added. The reaction mixture was allowed to stir for an additional 18 h, at which time an additional portion of THF (0.5 mL), NaH (0.3 mg, 0.014 mmol), benzyl bromide (2 μL, 0.014 mmol), and TBAI (2 mg, 0.0046 mmol) were added. After stirring for another 24 hours, the reaction mixture was quenched by the addition of 1M $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 x 5 mL). The organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*.. The crude material was purified by preparative TLC (10% EtOAc in hexanes) to afford the desired bis-benzyl ether **24** (2 mg, 45%) and the tris-benzyl ether **25** (2 mg, 53%), both as oils.

Compound **24**. R_f = 0.36, 10% EtOAc in hexanes.

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.66 (m, 4H), 7.34 (m, 16H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 4.63 (d, *J* = 11.7 Hz, 1H), 4.55 (m, 5H), 4.53 (d, *J* = 11.6 Hz, 1H), 3.84 (d, *J* = 10.8 Hz, 1H), 3.83 (m, 2H), 3.78 (s, 3H), 3.71 (m, 1H), 3.49 (s, 3H), 3.42 (dd, *J* = 4.8, 4.8 Hz, 1H), 3.41 (m, 1H), 3.30 (s, 3H), 3.28 (d, *J* = 2.2 Hz, 1H), 2.36 (m, 2H), 2.16 (m, 1H), 1.40 (s, 3H), 1.10 (d, *J* = 7.0 Hz, 3H), 1.08 (d, *J* = 6.9 Hz, 3H), 1.04 (s, 9H), 1.03 (d, *J* = 6.7 Hz, 3H).

^{1}H NMR (360 MHz, C_6D_6) δ 7.82 (m, 4H), 7.40 (m, 5H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.20 (m, 11H), 6.80 (d, *J* = 8.7 Hz, 2H), 4.89 (d, *J* = 11.6 Hz, 1H), 4.72 (d, *J* = 10.9 Hz, 1H), 4.72 (m, 2H), 4.59 (d, *J* = 11.9 Hz, 1H), 4.57 (d, *J* = 11.0 Hz, 1H), 4.37 (d, *J* = 5.1 Hz, 1H), 4.11 (d, *J* = 10.6 Hz, 1H), 4.01 (m, 2H), 3.84 (m, 1H), 3.67 (dd, *J* = 6.1, 3.9 Hz, 1H), 3.64 (dd, *J* = 4.8, 4.8 Hz, 1H), 3.56 (d, *J* = 2.2 Hz, 1H), 3.51 (s, 3H), 3.29 (s, 3H), 3.14 (s, 3H), 2.69 (m, 1H), 2.57 (m, 1H), 2.46 (m, 1H), 1.69 (s, 3H), 1.47 (d, *J* = 7.1 Hz, 3H), 1.27 (d, *J* = 7.0 Hz, 3H), 1.19 (s, 9H), 0.96 (d, *J* = 6.9 Hz, 3H).

Compound **25**. R_f = 0.24, 10% EtOAc in hexanes.

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.28 (m, 17H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.70 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 11.5 Hz, 1H), 4.61 (d, *J* = 11.6 Hz, 1H), 4.57 (d, *J* = 10.9 Hz, 1H), 4.51 (m, 4H), 4.46 (d, *J* = 12.0 Hz, 1H), 3.85 (d, *J* = 10.6 Hz, 1H), 3.79 (m, 1H), 3.78 (s, 3H), 3.65 (dd, *J* = 10.1, 3.9 Hz, 1H), 3.56 (dd, *J* = 10.1, 5.1 Hz, 1H), 3.53 (s, 3H), 3.41

(m, 2H), 3.33 (m, 1H), 3.32 (s, 3H), 2.37 (m, 2H), 2.16 (m, 1H), 1.43 (s, 3H), 1.11 (d, J = 6.8 Hz, 3H), 1.10 (d, J = 7.0 Hz, 3H), 1.05 (d, J = 7.0 Hz, 3H).

^{1}H NMR (360 MHz, C_6D_6) δ 7.43 (d, J = 7.2 Hz, 2H), 7.39 (d, J = 7.3 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 7.2 Hz, 2H), 7.19 (d, J = 7.1 Hz, 2H), 7.19 (d, J = 7.1 Hz, 2H), 7.08 (m, 5H), 6.81 (d, J = 8.7 Hz, 2H), 4.87 (d, J = 11.6 Hz, 1H), 4.75 (d, J = 11.6 Hz, 1H), 4.70 (d, J = 11.0 Hz, 1H), 4.69 (d, J = 11.8 Hz, 1H), 4.58 (d, J = 11.0 Hz, 1H), 4.57 (d, J = 11.8 Hz, 1H), 4.37 (d, J =5.1 Hz, 1H), 4.34 (d, J = 12.1 Hz, 1H), 4.28 (d, J = 12.1 Hz, 1H), 4.10 (d, J = 10.6 Hz, 1H), 3.87 (m, 1H), 3.64 (m, 4H), 3.54 (dd, J = 10.3, 5.0 Hz, 1H), 3.50 (s, 3H), 3.29 (s, 3H), 3.13 (s, 3H), 2.69 (m, 1H), 2.58 (m, 1H), 2.44 (m, 1H), 1.70 (s, 3H), 1.46 (d, J = 7.1 Hz, 3H), 1.31 (d, J = 7.0 Hz, 3H), 0.95 (d, J = 6.9 Hz, 3H).