Supporting Information

Formal Enantioselective Synthesis of (+)-Compactin

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General Procedures. All anhydrous solvents were used as received from either Aldrich or Acros. All glassware was flame dried under a nitrogen atmosphere. Purification by flash chromatography used 230-400 mesh silica gel. ¹H and ¹³C spectra were recorded on a Bruker AMX500 in (CD₃)₂CO or CDCl₃.

Trimethylsilyl Series:

3-(Trimethylsilyl)prop-2-yn-1-ol: To a solution of propargyl alcohol **8** (10 mL, 171 mmol) in Et₂O (180 mL) at 0 °C was added *n*-BuLi (137 mL of 2.5 M in hexanes) dropwise and the mixture was stirred 1 hour at rt. At 0 °C, chlorotrimethylsilane (53 mL, 417.6 mmol) was added dropwise and the mixture was stirred 16 hours at room temperature. The Et₂O was distilled off and the resulting solution was refluxed for 3 hours. After cooling to room temperature Et₂O (100 mL) was added followed by aq. 0.5 M sulphuric acid (50 mL) dropwise and the mixture was stirred 1 ¼ h at rt. The layers were separated and the aqueous layer was extracted with Et₂O (3x). The combined organic layer was washed with water (3x), brine and dried over anhydrous Na₂SO₄, filtrated and concentrated *in vacuo*. The crude product was distilled under reduced pressure (83-88 °C, ~8 mm of Hg) to give 3-(trimethylsilyl)prop-2-yn-1-ol (10.8 g, 49% yield) as a colorless oil.

(2E)-3-(Trimethylsilyl)prop-2-en-1-ol (9a): To a solution of 3-(trimethylsilyl)prop-2-yn-1-ol (10.8 g, 84.3 mmol) in Et₂O (100 mL) at 0 °C was added dropwise a solution of *bis*(2-methoxyethoxy)aluminium hydride (40 mL, 140 mmol) and stirred at 0 °C for 10 minutes and at rt for 1 hour. The reaction was quenched with the dropwise addition of aq. H₂SO₄ 1 M (110 mL) and the aluminium salt residue was filtered off. The two layers were separated and the aqueous layer was extracted with EtOAc/Et₂O (1:1, 2x). The combined organic layer was washed with water (2x), brine and dried over anhydrous MgSO₄, filtrated and concentrated *in vacuo*. The crude product was distilled under reduce pressure (76-81 °C, ~8 mm of Hg) to afford the desired *trans*-allylic alcohol **9a** (6.48 g, 59% yield) as a colorless oil. ¹H NMR (500MHz, (CD₃)₂CO) δ 6.18 (dt, *J* = 18.8, 4.1 Hz, 1H), 5.90 (dt, *J* = 18.8, 1.9 Hz, 1H), 4.08 (m, 2 H), 3.78 (t, *J* = 5.7 Hz, 1H), 0.04 (s, 9 H); ¹³C NMR (500MHz, (CD₃)₂CO) δ 147.6, 127.9, 65.1, -1.1 ppm.

(2E)-3-(Trimethylsilyl)acrylaldehyde (7a): To alcohol **9a** (4.6 g, 35.38 mmol) in CH₂Cl₂ (150 mL) was added MnO₂ (30 g, 353 mmol) and the mixture was refluxed for 6 hours. The solution was filtered to remove the MnO₂ and the solution was concentrated *in vacuo*. Purification of the crude product by flash chromatography (Et₂O/hexanes, 15:85) of over silica gel gave the desired aldehyde **7a** (4.07 g, 90% yield) as a colorless oil. ¹H NMR (500MHz, (CD₃)₂CO) δ 9.50 (d, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 18.8 Hz, 1H), 6.46 (dd, *J* = 18.8, 7.5 Hz, 1H), 0.18 (s, 9 H); ¹³C NMR (500MHz, (CD₃)₂CO) δ 194.9, 158.6, 145.0, -2.0 ppm.

(3S)-3-[(2R)-5-Oxo-2,5-dihydrofuran-2-yl]-3-(trimethylsilyl)propanal (11a): In a flask charged with (2*S*,5*S*)-2-(1',1'-Dimethylethyl)-3-methyl-5-phenylmethyl-4-imidazolidinone (**10**) (1.42 g, 5.78 mmol) was added chloroform (140 mL), water (2.6 mL, 144.4 mmol), dichloroacetic acid (475 µL, 5.79 mmol) and aldehyde **7a** (3.69 g, 28.77 mmol) at -40 °C. The solution was stirred 10 minutes and 2-(trimethylsilyloxy)furan (**6**) (5.8 mL, 34.48 mmol) was added in one portion. The resulting solution was stirred at -40 °C for 15 hours. The reaction mixture was filtered cold through a short celite pad and washed with ether. The solution was concentrated *in vacuo*. The resulting residue was purified by flash chromatography (EtOAc/Hex, 40:60)

and the desired adduct **11a** was obtained (5.82 g, 95% yield, >30:1 syn:anti, the e.e. could only be determined after the next chemical transformation) as a yellow oil. ^1H NMR (500MHz, $(\text{CD}_3)_2\text{CO}$) δ 9.69 (s, 1 H), 7.51 (dd, $J = 5.7, 1.4$ Hz, 1H), 6.08 (dd, $J = 5.7, 1.9$ Hz, 1H), 5.35 (m, 1 H), 2.48-2.32 (m, 2 H), 1.89 (m, 1 H), 0.12 (s, 9 H); ^{13}C NMR (500MHz, $(\text{CD}_3)_2\text{CO}$) δ 202.2, 173.0, 158.7, 121.9, 84.6, 38.9, 23.2, -2.1 ppm; HRMS (+ESI): calcd for $\text{C}_{10}\text{H}_{17}\text{O}_3\text{Si}$ $[\text{M}+\text{H}]^+$ 213.09361, found 213.09415; $[\alpha]_{\text{D}}^{25} = -79.6^\circ$ [$c = 1.17$, CHCl_3].

(5R)-5-[(1S)-4,4-Dibromo-1-(trimethylsilyl)but-3-en-1-yl]furan-2(5H)-one (5a): To a flask containing CBr_4 (1.75 g, 5.28 mmol), Ph_3P (1.37 g, 5.22 mmol) and zinc (0.35 g, 5.35 mmol) was added CH_2Cl_2 (40 mL) and the suspension was stirred at rt for 24 hours in the dark. The aldehyde **11a** (392 mg, 1.85 mmol) in CH_2Cl_2 (15 mL) was added dropwise at 0 °C and the mixture was stirred 2 days at rt. The zinc was filtered off, water was added, and the aqueous layer was extracted with Et_2O (3x). The combined organic layer was dried over anhydrous MgSO_4 , filtered and concentrated *in vacuo*. The crude product obtained was purified by flash chromatography (Et_2O /hexanes, 1:1) over silica gel and afford the desired *gem*-dibromide **5a** (664 mg, 98% yield, 82% ee) as a yellow oil. Measurement of enantioselectivity was conducted at this stage by chiral HPLC (Chiral Pak OD colum, $\lambda_{\text{max}} = 227$ nm, 10% *i*-PrOH in Hexanes (isocratic), flow = 1 mL/min., $R_t = 8.31$ min., area = 77.2% (major enantiomer), $R_t = 7.10$ min., area = 7.7% (minor enantiomer). ^1H NMR (500MHz, $(\text{CD}_3)_2\text{CO}$) δ 7.71 (dd, $J = 5.7, 1.4$ Hz, 1H), 6.53 (t, $J = 7.2$ Hz, 1H), 6.14 (dd, $J = 5.7, 2.1$ Hz, 1H), 3.35 (t, $J = 1.6$ Hz, 1H), 2.16-1.99 (m, 2H), 1.54 (m 1H), 0.15 (s, 9H); ^{13}C NMR (500MHz, $(\text{CD}_3)_2\text{CO}$) δ 173.1, 158.7, 140.6, 121.6, 89.5, 84.9, 28.8, 14.4, -1.9 ppm; HRMS (+ESI): calcd for $\text{C}_{11}\text{H}_{17}\text{O}_2\text{Br}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 366.93542, found 366.93591; $[\alpha]_{\text{D}}^{25} = -88.6^\circ$ [$c = 0.83$, CHCl_3].

(3aS,7S,7aR)-4-Bromo-7-(trimethylsilyl)-3a,6,7,7a-tetrahydro-1-benzofuran-2(3H)-one (12a): To the *gem*-dibromide **5a** (5.46 g, 14.83 mmol) in EtOAc (450 mL) at reflux was added dropwise a solution of *n*- Bu_3SnH (4.15 mL, 15.40 mmol) and AIBN (0.98 g, 5.98 mmol) in EtOAc (50 mL) over a period of 1 hour. After refluxing the reaction mixture 3 ½ hours, an additional amount of AIBN (119 mg, 0.72 mmol) and *n*- Bu_3SnH

(0.8 mL, 2.97 mmol) in EtOAc (20 mL) was added dropwise to bring the reaction to completion and the mixture was refluxed another 1 ½ hour. The reaction was quenched by the addition of water and the aqueous layer was extracted with EtOAc (2x). The combined organic layer was washed with an aqueous solution of 10% KF (3x) and dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography (EtOAc/hexanes, 1:9, then 2:8) over silica gel to afford the desired lactone **12a** (1.74 g, 41% yield) as a pale yellow oil. ¹H NMR (500MHz, (CD₃)₂CO) δ 6.38 (dd, *J* = 6.1, 1.4 Hz, 1H), 5.02 (d, *J* = 5.3 Hz, 1H), 3.29 (m, 1H), 2.97 (dd, *J* = 17.4, 8.9 Hz, 1H), 2.53 (d, *J* = 17.4 Hz, 1H), 2.19-2.08 (m, 2H), 1.16 (m, 1H), 0.09 (s, 9H); ¹³C NMR (500MHz, (CD₃)₂CO) δ 175.5, 133.5, 123.9, 81.5, 44.5, 35.7, 24.1, 23.5, -2.6 ppm; HRMS (+ESI): calcd for C₁₁H₁₈O₂Br₁Si [M+H]⁺ 289.02459, found 289.02540; [α]_D²⁵ = -31.6° [*c* = 1.03, CHCl₃].

(3a*R*,7*S*,7a*R*)-7-(Trimethylsilyl)-4-vinyl-3a,6,7,7a-tetrahydro-1-benzofuran-2(3*H*)-one (14a): To lactone **12a** (850 mg, 2.94 mmol), *tetrakis*(triphenylphosphine) palladium (0) (374 mg, 0.323 mmol) and tributylvinyltin (2.6 mL, 8.90 mmol) was added DMF (17 mL) and the reaction mixture was stirred at 57 °C for 5 ½ hours. The reaction was quenched with water and the aqueous layer was extracted with Et₂O (3x). The combined organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography (EtOAc/hexanes, 10:90, then 15:85,) over silica gel to afford the desired product **14a** (614 mg, 89 % yield) as a yellow oil. ¹H NMR (500MHz, (CD₃)₂CO) δ 6.30 (dd, *J* = 17.8, 11.0 Hz, 1H), 6.09 (m, 1H), 5.08-4.97 (m, 3H), 3.28 (m, 1H), 3.05 (dd, *J* = 17.4, 9.3 Hz, 1H), 2.26 (d, *J* = 17.4 Hz, 1H), 2.12-2.09 (m, 2H), 0.97-0.93 (m, 1H), 0.09 (s, 9H); ¹³C NMR (500MHz, (CD₃)₂CO) δ 176.6, 138.9, 136.2, 132.8, 112.0, 80.8, 36.0, 35.4, 25.1, 21.1, -2.4 ppm; HRMS (+ESI): calcd for C₁₃H₂₁O₂Si [M+H]⁺ 237.13011, found 237.13053; [α]_D²⁵ = -90.7° [*c* = 1.00, CHCl₃].

Diethyl [(3*S*,3a*R*,7*S*,7a*R*)-2-oxo-7-(trimethylsilyl)-4-vinyl-2,3,3a,6,7,7a-hexahydro-1-benzofuran-3-yl]phosphonate (15a): To a stirred solution of LDA (prepared *in situ* from diisopropylamine (770 μL, 4.77 mmol) and *n*-butyl lithium in hexanes (2.50 M, 1.9 mL, 4.77 mmol) in Et₂O (20 mL) at 0 °C) that was cooled to -78 °C was added dropwise a

solution of lactone **14a** (900 mg, 3.81 mmol) in Et₂O (5 mL) and the reaction mixture was stirred for 1h. HMPA (660 μ L, 3.81 mmol) was added and the reaction was stirred another 5 minutes at that temperature. Diethyl phosphorochloridite (700 μ L, 4.77 mmol) was added and the resulting mixture was allowed to warm to 0 °C and was stirred another 1 hour at rt. The reaction was again cooled to 0 °C and 1 equivalent of aq. 30% H₂O₂ was added and the reaction was stirred another 10 minutes. Water was added and the product was extracted with Et₂O (2x), and the combined organic phase was dried over anhydrous Na₂SO₄. After concentration *in vacuo*, the crude product was purified by flash chromatography (3:7 to 4:6, EtOAc/hexanes) over silical gel to afford the desired phosphonate **15a** (1.15 g, 81 % yield) as a yellow oil. ¹H NMR (500MHz, (CD₃)₂CO) δ 6.28 (dd, *J* = 17.9, 11.3 Hz, 1H), 6.14 (br d, *J* = 4.1 Hz, 1H), 5.42 (d, *J* = 17.9 Hz, 1H), 5.25 (d, *J* = 5.6 Hz, 1H), 5.01 (d, *J* = 11.3 Hz, 1H), 4.19 (m, 4H), 3.52 (br dd, *J* = 16.9, 3.4 Hz, 1H), 2.92 (d, *J* = 23.0 Hz, 1H), 2.46 (m, 2H), 1.33 (m, 6H), 2.06 (m, 1H), 0.10 (s, 9H); ¹³C NMR (500MHz, (CD₃)₂CO) δ 171.6, 138.4, 134.9, 133.9, 113.2, 80.5, 63.6, 48.2, 47.1, 38.8, 24.4, 22.8, 20.9, 16.6, -2.5 ppm; HRMS (+ESI): calcd for C₁₇H₃₀O₅SiP [M+H]⁺ 373.15905, found 373.15947; [α]_D²⁵ = -31.0° [*c* = 1.00, CHCl₃].

(3Z,3aS,7S,7aR)-3-Ethylidene-7-(trimethylsilyl)-4-vinyl-3a,6,7,7a-tetrahydro-1-benzofuran-2(3H)-one (4a): To phosphonate **15a** (270 mg, 0.724 mmol) in benzene (7 mL) and acetaldehyde (400 μ L, 7.24 mmol) at 0 °C was added portionwise solid NaH 60 % w/w in mineral oil (110 mg, 2.75 mmol) and the resulting suspension was stirred at rt for one hour. The reaction was quenched with water and the aqueous layer was extracted with Et₂O (3x). The combined organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. Purification of the crude product by flash chromatography (EtOAc/hexanes, 2:8) over silica gel gave the desired unsaturated (*Z*)-*exo*- α,β -unsaturated lactone **4a** (160 mg, 85% yield) as a yellow oil. ¹H NMR (500MHz, (CD₃)₂CO) δ 6.47 (m, 1H), 6.29 (dd, *J* = 17.7, 11.1 Hz, 1H), 6.13 (dd, *J* = 6.9, 2.3 Hz, 1H), 5.29 (d, *J* = 17.7 Hz, 1H), 5.04-5.26 (m, 2H), 3.90 (d, *J* = 6.1 Hz, 1H), 2.16-1.98 (m, 5H), 0.89 (m, 1H), 0.10 (s, 9H); ¹³C NMR (500MHz, (CD₃)₂CO) δ 170.1, 139.4, 138.7,

136.6, 131.8, 130.1, 112.8, 78.8, 40.9, 26.5, 21.2, 14.1, -2.3 ppm; $[\alpha]_D^{25} = +32.5^\circ$ [$c = 1.00$, CHCl_3].

Vinyl magnesium bromide preparation. To magnesium turnings (1.22 g, 50 mmol) was added dry THF (95 mL) and vinylbromide (10.7 g, 100 mmol) and the suspension was gently heated with a heat gun until the reaction was initiated. Occasional cooling with an ice bath was required to maintain a gentle reflux. After consumption of most of the magnesium turnings, the reaction was heated at 40 °C for ½ h and was afforded a ~ 0.5 M solution of vinylmagnesium bromide in THF.

(3*S*,3*aR*,7*S*,7*aR*)-3-[(1*S*)-1-Methylprop-2-en-1-yl]-7-(trimethylsilyl)-4-vinyl-3*a*,6,7,7*a*-tetrahydro-1-benzofuran-2(3*H*)-one (3*a*): To $\text{CuBr}\cdot\text{Me}_2\text{S}$ (2.4 g, 11.7 mmol) at -40 °C was added directly the freshly prepared solution of vinylmagnesium bromide (~0.5 M in THF, 54.8 mL, 27.4 mmol) and the resulting black suspension was warmed to 0 °C and stirred 30 minutes at that temperature. A solution of the (*Z*)-*exo*- α,β -unsaturated lactone **4a** (307 mg, 1.17 mmol) in THF (4 mL) was added dropwise at -40 °C and the reaction mixture was warmed to 0 °C and stirred for an additional 30 minutes. Another 10 equivalent of cuprate reagent was prepared separately and added at 0 °C to drive the reaction to completion. The reaction was warmed to rt and stirred an additional hour and quenched by the addition of a sat. aq. solution of NH_4Cl . The aqueous layer was extracted with Et_2O (2x) and the combined organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated *in vacuo*. Purification of the crude residue by flash chromatography (EtOAc /hexanes, 15:85) over silica gel afforded the desired Michael addition product **3a** (110 mg, 47% yield) as a colorless oil. ^1H NMR (500MHz, $(\text{CD}_3)_2\text{CO}$) δ 6.32 (dd, $J = 17.8, 11.1$ Hz, 1H), 6.14 (br t, $J = 4.8$ Hz, 1H), 5.90 (m, 1H), 5.33 (d, $J = 17.0$ Hz, 1H), 5.18-5.00 (m, 4H), 3.09 (d, $J = 5.9$ Hz, 1H), 2.84 (m, 1H), 2.36 (d, $J = 4.1$ Hz, 1H), 2.18-2.05 (m, 2H), 1.26 (d, $J = 7.0$ Hz, 3H), 0.92 (m, 1H), 0.12 (s, 9H); ^{13}C NMR (500MHz, $(\text{CD}_3)_2\text{CO}$) δ 176.3, 140.0, 138.5, 135.6, 132.1, 115.8, 111.2, 78.8, 52.6, 41.3, 40.3, 24.4, 20.0, 18.4, -3.2 ppm; HRMS (+ESI): calcd for $\text{C}_{17}\text{H}_{27}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 291.17714, found 291.17748; $[\alpha]_D^{25} = -39.3^\circ$ [$c = 1.33$, CHCl_3].

(1R,2R,6S)-2-[(1S,2S)-1-(Hydroxymethyl)-2-methylbut-3-en-1-yl]-6-(trimethylsilyl)-3-vinylcyclohex-3-en-1-ol (16a): A solution of LAH in THF (1.0 M, 140 μ L, 0.144 mmol) was added dropwise to a solution of the lactone **3a** (21 mg, 0.072 mmol) in THF (1 mL) at 0 °C and then stirred 2 hours at room temperature. The reaction was carefully quenched with aq. 10 % HCl and the aqueous layer was extracted with EtOAc (3x). The combined organic layer was dried with anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. The crude diol was purified by flash chromatography (EtOAc/hexanes, 2:8) over silica gel afforded the desired diol **16a** (14 mg, 67% yield) as a colorless oil. ¹H NMR (500MHz, (CD₃)₂CO) δ 6.26 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.99 (t, *J* = 2.8 Hz, 1H), 5.90-5.82 (m, 1H), 5.13 (dd, *J* = 9.4, 7.9 Hz, 1H), 5.10 (br s, 2H), 4.94 (dd, *J* = 10.2, 1.9 Hz, 1H), 4.86 (dd, *J* = 10.9, 1.5 Hz, 1H), 4.33 (br s, 1H), 4.25 (br s, 1H), 3.59 (br s, 1H), 3.48 (br d, *J* = 10.8 Hz, 1H), 2.81 (br s, 1H), 2.73-2.67 (m, 1H), 2.37 (br t, *J* = 15.1 Hz, 1H), 1.98-1.92 (m, 2H), 1.10 (d, *J* = 6.7 Hz, 3H), 0.88 (dd, *J* = 12.8, 9.2 Hz, 1H), 0.03 (s, 9H); ¹³C NMR (500MHz, (CD₃)₂CO) δ 143.8, 139.1, 136.7, 128.2, 113.0, 111.7, 64.0, 58.9, 44.7, 44.6, 35.8, 28.6 (embedded in acetone signal), 21.7, 18.6, -3.1 ppm; HRMS (+ESI): calcd for C₁₇H₃₀O₂SiNa [M+Na]⁺ 317.18989, found 317.19073; [α]_D²⁵ = + 51.2° [*c* = 0.83, CHCl₃].

(1R,2S,7S,8S,8aR)-8-(Hydroxymethyl)-7-methyl-2-(trimethylsilyl)-1,2,3,7,8,8a-hexahydronaphthalen-1-ol (17a): To the diol **16a** (12 mg, 0.04 mmol) and Grubbs 2nd generation catalyst (7 mg, 0.008 mmol) was added CH₂Cl₂ (2 mL) and the reaction mixture was refluxed for 30 minutes. The solution was concentrated *in vacuo* and the crude diene was purified by flash chromatography (EtOAc/hexanes, 3:7) over silica gel to afford the desired decalin **17a** (9.0 mg, 85% yield). ¹H NMR (500MHz, (CD₃)₂CO) δ 5.92 (d, *J* = 9.6 Hz, 1H), 5.65 (dd, *J* = 9.6, 5.8 Hz, 1H), 5.59 (br t, *J* = 2.5 Hz, 1H), 4.36 (t, *J* = 3.9 Hz, 1H), 4.30 (br s, 1H), 3.89-3.84 (m, 1H), 3.73 (d, *J* = 5.4 Hz, 1H), 3.70-3.65 (m, 1H), 2.50-2.43 (m, 1H), 2.31-2.24 (m, 2H), 2.04-2.16 (m, 1H), 1.98-1.90 (m, 1H), 1.01 (dd, *J* = 12.8, 5.6 Hz, 1H), 0.89 (d, *J* = 7.0 Hz, 3H), 0.05 (s, 9H); ¹³C NMR (500MHz, (CD₃)₂CO) δ 134.0, 131.9, 129.1, 124.6, 65.6, 64.1, 40.4, 40.2, 33.2, 27.6, 21.7, 14.2, -3.1 ppm; HRMS (+ESI): calcd for C₁₅H₂₆O₂SiNa [M+Na]⁺ 289.15913, found 289.15943; [α]_D²⁵ = -268.6° [*c* = 0.43, CHCl₃].

(1S,7S,8S,8aR)-8-(Hydroxymethyl)-7-methyl-1,2,3,7,8,8a-hexahydronaphthalen-1-ol (2a): To diol **17a** (9.0 mg) was added TBAF (29 mg, 0.108 mmol), 18-Crown-6 (30 mg, 0.110 mmol), potassium *t*-butoxide (22 mg, 0.196 mmol) followed by DMSO:H₂O (19:1, 750 μ L) and the reaction mixture was stirred 2 hours at 75 °C and then 2 hours at 80 °C. The reaction was quenched with a few drops of aq. 10% HCl and brine was added. The aqueous layer was extracted with EtOAc (3x), the combined organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. The crude diol was purified by flash chromatography (EtOAc/hexanes, 1:1) over silica gel and afforded the desired final product **2a** (2.0 mg, 31% yield) as a colorless solid. $[\alpha]_D^{25} = -199^\circ$ [*c* = 0.20, CHCl₃].

NMR in deuterated chloroform:

¹H NMR (500MHz, CDCl₃) δ 5.96 (d, *J* = 9.6 Hz, 1H), 5.68 (dd, *J* = 9.3, 5.9 Hz, 1H), 5.61 (br s, 1H), 4.28 (br s, 1H), 3.83 (dd, *J* = 10.1, 8.5 Hz, 1H), 3.72 (dd, *J* = 10.2, 3.0 Hz, 1H), 2.47 (m, 1H), 2.33 (m, 2H), 2.12 (m, 1H), 2.02 (m, 2H), 1.73 (m, 1H), 0.88 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (500MHz, CDCl₃) δ 133.6, 132.5, 128.6, 124.0, 65.5, 65.4, 40.5, 38.6, 33.3, 28.5, 20.4, 14.8 ppm.

NMR in deuterated acetone:

¹H NMR (500MHz, *d*₆-Me₂CO) δ 5.90 (d, *J* = 9.7 Hz, 1H), 5.64 (dd, *J* = 9.2, 6.0 Hz, 1H), 5.47 (br s, 1H), 4.16 (br s, 1H), 4.13 (br s, 1H), 3.85 (br t, *J* = 8.7 Hz, 1H), 3.74 (d, *J* = 3.6 Hz, 1H), 3.61 (dd, *J* = 10.2, 5.0 Hz, 1H), 2.47 (m, 1H), 2.35 (m, 1H), 2.25 (br d, *J* = 12.4 Hz, 1H), 2.04-1.86 (m, 3H), 1.64 (m, 1H), 0.87 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (500MHz, *d*₆-Me₂CO) δ 134.2, 132.2, 128.9, 123.6, 64.0, 63.5, 40.0, 38.1, 32.6, 28.9, 20.3, 14.1 ppm.

Benzyltrimethylsilyl Series:

(2E)-3-[Benzyl(dimethyl)silyl]prop-2-en-1-ol (9a): To catalyst *bis*(1.5-cyclooctadiene)rhodium(I)tetrafluoroborate hydrate (130 mg, 0.3 mmol) and Ph₃P (160 mg, 0.6 mmol) in degassed Me₂CO (200 mL) was added propargylic alcohol (**8**) (4.1 mL, 68.9 mmol) followed by benzyltrimethylsilane (9.4 g, 62.6 mmol) and the

reaction mixture was stirred at room temperature for 18 hours. The reaction mixture was concentrated *in vacuo* and the crude product was purified by flash chromatography (Et₂O/Hex, 35:65) over silica gel to provide the desired *trans*-allylic alcohol **9a** (10.50 g, 85 % yield) as a colorless oil. ¹H NMR (500MHz, (CD₃)₂CO) δ 7.22 (t, *J* = 7.7 Hz, 2H), 7.09-7.04 (m, 3H), 6.22 (dt, *J* = 4.0, 18.8 Hz, 1H), 5.94 (br t, *J* = 1.8, 17.9 Hz, 1H), 4.14-4.10 (m, 2H), 3.83 (t, *J* = 5.7 Hz, 1H (OH)), 2.09 (s, 2H), 0.05 (s, 6H); ¹³C NMR (500MHz, (CD₃)₂CO) δ 148.0, 140.0, 128.2, 128.0, 125.1, 123.9, 64.3, 25.5, -4.0 ppm; HRMS (+ESI): calcd for C₁₂H₁₉OSi [M+H]⁺ 207.12020, found 207.11997.

(2E)-3-[Benzyl(dimethyl)silyl]acrylaldehyde (7b): To alcohol **9b** (10.5 g, 50 mmol) was added CH₂Cl₂ (250 mL) followed by MnO₂ (43.5 g, 500 mmol) and the suspension was refluxed for 5 hours. The MnO₂ was filtered off and the solution was concentrated *in vacuo*. Purification of the crude product by flash chromatography (Et₂O/Hex, 2:8) over silica gel of the crude product afforded the desired aldehyde **7b** (7.3 g, 72 % yield) as a colorless oil. ¹H NMR (500MHz, (CD₃)₂CO) δ 9.53 (d, *J* = 7.5 Hz, 1H), 7.33-7.22 (m, 3H), 7.11 (m, 3H), 6.48 (dd, *J* = 7.5, 18.8 Hz, 1H), 2.34 (s, 2H), 0.20 (s, 6H); ¹³C NMR (500MHz, (CD₃)₂CO) δ 193.9, 156.1, 145.0, 139.0, 128.2 (2 carbons), 124.3, 24.3, -4.7 ppm; HRMS (+ESI): calcd for C₁₂H₁₇OSi [M+H]⁺ 205.10442, found 205.10432.

(3S)-3-[Benzyl(dimethyl)silyl]-3-[(2R)-5-oxo-2,5-dihydrofuran-2-yl]propanal (11b): In a flask charged with (2*S*,5*S*)-2-(1',1'-Dimethylethyl)-3-methyl-5-phenylmethyl-4-imidazolidinone (**10**) (1.76 g, 7.17 mmol) was added chloroform (175 mL), water (3.2 mL, 178.9 mmol), dichloroacetic acid (600 μL, 7.17 mmol) and aldehyde **7b** (7.3 g, 35.78 mmol) at -40 °C. The solution was stirred 10 minutes before the addition of 2-(trimethylsilyloxy)furan (**6**) (9.0 mL, 53.78 mmol) in one portion. The resulting solution was stirred at -40 °C for 18 hours. The reaction mixture was filtered cold through a short celite pad which was washed with Et₂O. The solution was concentrated *in vacuo* and the crude residue was purified by flash chromatography (Et₂O/Hex, 6:4, then 7:3, then 9:1) over silica gel to afford the desired adduct **11b** (6.20 g, 60 % yield, >30:1 syn:anti, the e.e. could only be determined after the next chemical transformation) as a yellow oil. ¹H NMR (500MHz, (CD₃)₂CO) δ 9.68 (s, 1H), 7.48 (dd, *J* = 5.7, 1.4 Hz, 1H), 7.24 (t, *J* = 7.6

Hz, 2H), 7.11-7.08 (m, 3H), 6.10 (dd, $J = 5.7, 1.8$ Hz, 1H), 5.39 (t, $J = 1.7$ Hz, 1H), 2.46-2.41 (m, 2H), 2.31 (s, 2H), 2.05-2.01 (m, 1H), 0.15 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (500MHz, $(\text{CD}_3)_2\text{CO}$) δ 201.1, 172.2, 157.9, 139.5, 128.3, 128.2, 124.3, 121.1, 83.6, 37.9, 24.0, 21.0, -4.7, -4.8 ppm; HRMS (+ESI): calcd for $\text{C}_{16}\text{H}_{21}\text{O}_3\text{Si}$ $[\text{M}+\text{H}]^+$ 289.12557, found 289.12545; $[\alpha]_{\text{D}}^{25} = -37.2^\circ$ [$c = 2.93$, CHCl_3].

(5R)-5-[(1S)-1-[Benzyl(dimethyl)silyl]-4,4-dibromobut-3-en-1-yl]furan-2(5H)-one (5b): To CBr_4 (13.3 g, 40.0 mmol), Ph_3P (10.5 g, 40.0 mmol) and zinc (2.6 g, 40.0 mmol) was added CH_2Cl_2 (200 mL) and the mixture was stirred at room temperature for 18 hours in the dark. The reaction mixture was then cooled to 0°C and aldehyde **11b** (6.2 g, 21.5 mmol) in CH_2Cl_2 (50 mL) was added dropwise and the mixture was stirred another 18 hours at rt. The zinc was filtered off and water was added. The aqueous layer was extracted with Et_2O (2x) and the combined organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated *in vacuo*. Purification of the crude product by flash chromatography (EtOAc /hexanes, 3:7) gave the desired *gem*-dibromide **5b** (8.5 g, 89 % yield, 70% ee) as a yellow oil. Measurement of enantioselectivity was conducted at this stage by chiral HPLC (Chiral Pak AD column, $\lambda_{\text{max}} = 220$ nm, 5% EtOH in Hexanes, flow = 1 mL/min., $R_t = 9.47$ min., area = 81.7% (major enantiomer), $R_t = 11.62$ min., area = 14.2% (minor enantiomer). ^1H NMR (500MHz, $(\text{CD}_3)_2\text{CO}$) δ 7.72 (d, $J = 5.7$ Hz, 1H), 7.26 (t, $J = 7.6$ Hz, 2H), 7.14-7.08 (m, 3H), 6.53 (t, $J = 7.2$ Hz, 1H), 6.17 (dd, $J = 5.7, 2.0$ Hz, 1H), 5.40 (br d, $J = 1.1$ Hz, 1H), 2.34 (s, 2H), 2.18-2.00 (m, 2H), 1.65 (m, 1H), 0.16 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (500MHz, $(\text{CD}_3)_2\text{CO}$) δ 172.3, 157.8, 139.8, 139.5, 128.3 (2C), 124.3, 120.8, 89.0, 83.9, 28.2, 27.9, 24.1, -4.5 (2C) ppm; HRMS (+ESI): calcd for $\text{C}_{17}\text{H}_{21}\text{O}_2\text{Br}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 442.96671, found 442.96721; $[\alpha]_{\text{D}}^{25} = -56.6^\circ$ [$c = 3.13$, CHCl_3].

(3aS,7S,7aR)-7-[Benzyl(dimethyl)silyl]-4-bromo-3a,6,7,7a-tetrahydro-1-benzofuran-2(3H)-one (12b): To *gem*-dibromide **5b** (8.5 g, 19.1 mmol) in EtOAc (200 mL) at reflux was added dropwise a solution of *n*- Bu_3SnH (5.6 mL, 20.01 mmol) and AIBN (1.3 g, 7.64 mmol) in EtOAc (200 mL) over a period of 1 hour. After this time an additional amount of AIBN (630 mg, 3.82 mmol) in EtOAc (20 mL) was added dropwise to the

reaction mixture which was stirred another additional ½ hour at reflux. The reaction was cooled to 0 °C and an aq. 10% KF solution was added to the reaction mixture and the slurry generated was stirred for ½ hour. The solid was filtered off and rinsed with EtOAc. This process was repeated twice and the organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography over silica gel (EtOAc/hexanes, 2:8, then 3:7) to provide the desired lactone **12b** (2.83 g, 40% yield) as a colorless oil. ¹H NMR (500MHz, (CD₃)₂CO) δ 7.24 (t, *J* = 7.7 Hz, 2H), 7.12-7.07 (m, 3H), 6.39 (t, *J* = 3.8 Hz, 1H), 5.07 (dd, *J* = 5.3, 1.4 Hz, 1H), 3.32 (m, 1H), 3.01 (dd, *J* = 17.4, 8.8 Hz, 1H), 2.57 (d, *J* = 17.4 Hz, 1H), 2.28 (s, 2H), 2.16-2.11 (m, 2H), 1.29-1.23 (m, 1H), 0.10 (s, 3H), 0.09 (s, 3H); ¹³C NMR (500MHz, (CD₃)₂CO) δ 174.6, 139.7, 132.6, 128.2, 128.1, 124.1, 123.0, 80.6, 43.7, 34.9, 23.8, 22.8, 22.1, -5.0, -5.1 ppm; HRMS (+ESI): calcd for C₁₇H₂₂O₂BrSi [M+H]⁺ 365.05607, found 365.05670; [α]_D²⁵ = -9.8° [c = 1.33, CHCl₃].

The more polar reduced product **13b** (2.88 g, 41% yield) was also obtained and characterized. ¹H NMR (500MHz, (CD₃)₂CO) δ 7.71 (dd, *J* = 5.7, 1.3 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.14-7.08 (m, 3H), 6.33 (d, *J* = 6.9 Hz, 1H), 6.24 (q, *J* = 6.9 Hz, 1H), 6.14 (dd, *J* = 5.7, 2.0 Hz, 1H), 5.39 (d, *J* = 1.5 Hz, 1H), 2.34 (s, 2H), 2.31-2.12 (m, 2H), 1.62-1.57 (m, 1H), 0.15 (s, 3H), 0.14 (s, 3H); ¹³C NMR (500MHz, (CD₃)₂CO) δ 172.3, 157.8, 139.6, 135.5, 128.3, 128.2, 124.2, 120.8, 108.6, 84.2, 24.6, 24.3, 24.2, -4.5 (2C) ppm; HRMS (+ESI): calcd for C₁₇H₂₂O₂BrSi [M+H]⁺ 365.05598, found 365.05670.

(3a*R*,7*S*,7a*R*)-7-[Benzyl(dimethyl)silyl]-4-vinyl-3a,6,7,7a-tetrahydro-1-benzofuran-2(3*H*)-one (14b): To lactone **12b** (2.8 g, 7.67 mmol), *tetrakis*(triphenylphosphine) palladium (0) (890 mg, 0.767 mmol) and tributylvinyltin (6.7 mL, 23.0 mmol) was added DMF (50 mL) and the reaction mixture was stirred at 65 °C for 5 hours. Water was added and the aqueous layer was extracted with Et₂O (2x). The combined organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. Purification of the crude product by flash chromatography (EtOAc/hexanes, 1:9, then 15:85) over silica gel gave the desired diene **14b** (1.52 g, 64 % yield) as a yellowish oil. ¹H NMR (500MHz, (CD₃)₂CO) δ 7.24 (t, *J* = 7.6 Hz, 2H), 7.12-7.07 (m, 3H), 6.33 (dd, *J* = 17.8, 11.0 Hz, 1H), 6.11 (t, *J* = 4.3 Hz, 1H), 5.12 (d, *J* = 5.8 Hz, 1H), 5.06 (d, *J* = 16.0 Hz, 1H), 5.02 (d,

$J = 10.5$ Hz, 1H), 3.31 (t, $J = 7.4$ Hz, 1H), 3.09 (dd, $J = 17.4, 9.3$ Hz, 1H), 2.31 (d, $J = 16.5$ Hz, 1H), 2.29 (s, 2H), 2.18-2.12 (m, 2H), 1.06 (t, $J = 8.8$ Hz, 1H), 0.10 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (500MHz, $(\text{CD}_3)_2\text{CO}$) δ 175.8, 139.9, 138.0, 135.3, 131.9, 128.2 (2C), 124.1, 111.3, 79.9, 35.2, 34.5, 23.9, 23.0, 20.4, -5.0, -5.1 ppm; HRMS (+ESI): calcd for $\text{C}_{19}\text{H}_{25}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 313.16103, found 313.16183; $[\alpha]_{\text{D}}^{25} = -28.0^\circ$ [$c = 1.00$, CHCl_3].

Diethyl {(3*S*,3*aR*,7*S*,7*aR*)-7-[benzyl(dimethyl)silyl]-2-oxo-4-vinyl-2,3,3*a*,6,7,7*a*-hexahydro-1-benzofuran-3-yl}phosphonate (15b**):** A solution of lactone **14b** (1.51 g, 4.13 mmol) in Et_2O (10 mL) was added dropwise to a stirred solution at -78°C of LDA (1.25 eq., prepared *in situ* from diisopropylamine (760 μL , 5.38 mmol) and *n*-butyl lithium in hexanes (2.4 M, 2.2 mL, 5.17 mmol) in Et_2O (20 mL) at 0°C). After 1 hour HMPA (720 μL , 4.13 mmol) was added and the reaction mixture was stirred 10 minutes after which was added diethyl chlorophosphite (780 μL , 5.38 mmol). The resulting mixture was warmed to 0°C and stirred for 1 hour at rt. The reaction mixture was again cooled to 0°C , aq. 30% H_2O_2 (470 μL , 4.13 mmol) was added dropwise and the reaction mixture was stirred for another 15 minutes. The reaction mixture was poured in water, extracted with Et_2O (2x) and concentrated *in vacuo*. The crude product was purified by flash chromatography (EtOAc /hexanes, 4:6) over silica gel to afford the desired phosphonate **15b** (1.45 g, 70% yield) as a colorless solid. ^1H NMR (500MHz, $(\text{CD}_3)_2\text{CO}$) δ 7.21 (t, $J = 7.6$ Hz, 2H), 7.09-7.37 (m, 3H), 6.28 (dd, $J = 17.9, 11.3$ Hz, 1H), 6.12 (br t, $J = 4.0$ Hz, 1H), 5.42 (d, $J = 17.9$ Hz, 1H), 5.27 (d, $J = 5.5$ Hz, 1H), 5.02 (d, $J = 11.3$ Hz, 1H), 4.25-4.14 (m, 4H), 3.53 (dd, $J = 17.4, 5.0$ Hz, 1H), 2.94 (d, $J = 23.0$ Hz, 1H), 2.25 (s, 2H), 2.13-2.09 (m, 2H), 1.37-1.31 (m, 6H), 1.10 (t, $J = 8.8$ Hz, 1H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (500MHz, $(\text{CD}_3)_2\text{CO}$) δ 171.7, 140.6, 138.4, 135.0, 134.9, 133.8, 129.1, 125.0, 113.3, 80.5, 63.8 (br), 48.4, 47.1, 38.7, 24.7, 23.3, 21.1, 16.7 (br), -5.0, -5.1 ppm; HRMS (+ESI): calcd for $\text{C}_{23}\text{H}_{34}\text{O}_5\text{PSi}$ $[\text{M}+\text{H}]^+$ 449.18909, found 449.19077; $[\alpha]_{\text{D}}^{25} = +1.5^\circ$ [$c = 1.03$, CHCl_3].

(3*Z*,3*aS*,7*S*,7*aR*)-7-[Benzyl(dimethyl)silyl]-3-ethylidene-4-vinyl-3*a*,6,7,7*a*-tetrahydro-1-benzofuran-2(3*H*)-one (4b**):** To the phosphonolactone **15b** (560 mg, 1.11 mmol) in benzene (25 mL) at 0°C was added acetaldehyde (630 μL , 11.1 mmol) followed by NaH

(60 % w/w in mineral oil, 19.3 mg, 0.483 mmol) in 3 portions. The reaction mixture was stirred at room temperature for ½ hour. More acetaldehyde (320 uL, 5.55 mmol) was added and the reaction was heated at 40 °C for ½ hour before being diluted with EtOAc. The organic layer was washed with water and the organic layer was dried with anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography (EtOAc/hexanes, 2:8) over silica gel to afford the desired (*Z*)-*exo*- α,β -unsaturated lactone **4b** (340 mg, 90% yield) as a pale yellow oil. ¹H NMR (500MHz, (CD₃)₂CO) δ 7.24 (br t, *J* = 7.5 Hz, 2H), 7.12-7.06 (m 3H), 6.51 (dd, *J* = 14.5, 7.2 Hz, 1H), 6.33 (dd, *J* = 17.6, 11.1 Hz, 1H), 6.14 (br m, 1H), 5.32 (d, *J* = 17.7 Hz, 1H), 5.09-5.05 (m, 2H), 3.94 (br d, *J* = 5.2 Hz, 1H), 2.12 (s, 2H), 2.12-2.05 (m, 5H), 1.00 (m, 1H), 0.12 (s, 3H), 0.11 (s, 3H); ¹³C NMR (500MHz, (CD₃)₂CO) δ 169.3, 140.0, 138.7, 137.8, 135.8, 130.8, 129.2, 128.2 (2C), 124.1, 112.0, 77.9, 39.9, 24.5, 24.0, 20.5, 13.3, -4.9, -5.0 ppm; HRMS (+ESI): calcd for C₂₁H₂₇O₂Si [M+H]⁺ 339.17677, found 339.17748; [α]_D²⁵ = +36.4° [*c* = 1.87, CHCl₃].

(3*S*,3*aR*,7*S*,7*aR*)-7-[Benzyl(dimethyl)silyl]-3-[(1*S*)-1-methylprop-2-en-1-yl]-4-vinyl-3*a*,6,7,7*a*-tetrahydro-1-benzofuran-2(3*H*)-one (3b): To CuBrMe₂S (2.0 g, 9.76 mmol) at -40 °C was added directly the freshly prepared solution of vinylmagnesium bromide (~0.5 M in THF, 19.5 mmol) and the resulting black suspension was stirred 10 minutes at that temperature. A solution of the (*Z*)-*exo*- α,β -unsaturated lactone **4b** (330 mg, 0.976 mmol) in THF (4 mL) was added dropwise at -40 °C and the reaction mixture was warmed to 0 °C and stirred an additional 30 minutes. TLC analysis indicated completion of the reaction and the reaction mixture was quenched by the addition of a saturated aqueous solution of NH₄Cl. The aqueous layer was extracted with Et₂O (2x) and the combined organic layer was dried with anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. Purification of the crude residue by flash chromatography (EtOAc/hexanes, 15:85) over silica gel afforded the desired Michael addition product **3b** (266 mg, 75% yield) as a colorless oil. ¹H NMR (500MHz, (CD₃)₂CO) δ 7.24 (br t, *J* = 7.4 Hz, 2H), 7.11-7.07 (m, 3H), 6.32 (dd, *J* = 17.7, 11.1 Hz, 1H), 6.12 (br s, 1H), 5.90 (m, 1H), 5.33 (d, *J* = 16.9 Hz, 1H), 5.17 (d, *J* = 10.0 Hz, 1H), 5.12 (d, *J* = 17.9 Hz, 1H), 5.04-4.99 (m, 2H), 3.07 (d, *J* = 5.8 Hz, 1H), 2.88-2.80 (m, 1H), 2.37 (d, *J* = 4.1 Hz, 1H), 2.27 (s, 2H),

2.16-2.08 (m, 2H), 1.26 (d, $J = 7.0$ Hz, 3H), 1.04-0.94 (m, 1H), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (500MHz, $(\text{CD}_3)_2\text{CO}$) δ 176.3, 140.0, 139.9, 138.4, 135.5, 131.9, 128.2, 128.1, 124.1, 115.9, 111.2, 78.8, 52.6, 41.3, 40.2, 24.0, 23.2, 20.1, 18.3, -4.9 (2C) ppm; HRMS (+ESI): calcd for $\text{C}_{23}\text{H}_{31}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 367.20802, found 367.20878; $[\alpha]_{\text{D}}^{25} = -11.3^\circ$ [$c = 1.20$, CHCl_3].

(1R,2R,6S)-6-[Benzyl(dimethyl)silyl]-2-[(1S,2S)-1-(hydroxymethyl)-2-methylbut-3-en-1-yl]-3-vinylcyclohex-3-en-1-ol (16b): To a solution of lactone **3b** (228 mg, 0.622 mmol) in THF (6 mL) at 0 °C was added dropwise a solution of LAH in THF (1.0 M, 1.25 mL, 1.25 mmol) and the reaction mixture was stirred for 1 hour at room temperature. The reaction was carefully quenched at 0 °C with aq. 10 % HCl and the aqueous layer was extracted with EtOAc (3x). The combined organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography (EtOAc/hexanes, 15:85) over silica gel to afford the desired diol **16b** (175 mg, 76% yield) as a colorless oil. ^1H NMR (500MHz, $(\text{CD}_3)_2\text{CO}$) δ 7.22 (br t, $J = 7.6$ Hz, 2H), 7.09-7.04 (m, 3H), 6.29 (dd, $J = 17.3, 10.9$ Hz, 1H), 6.01 (m, 1H), 5.90 (m, 1H), 5.27 (s, 1H), 5.19 (br s, 1H), 5.19 (s, 1H), 7.49 (dd, $J = 10.3, 2.0$ Hz, 1H), 4.91 (dd, $J = 10.9, 1.6$ Hz, 1H), 4.41 (br s, 1H), 4.32 (br s, 1H), 3.67-3.61 (m, 1H), 3.55-3.51 (m, 1H), 2.89 (br s, 1H), 2.85-2.70 (m, 1H), 2.44 (br t, $J = 15.3$ Hz, 1H), 2.24 (d, $J = 5.4$ Hz, 2H), 2.09-1.93 (m, 2H), 1.14 (d, $J = 6.6$ Hz, 3H), 1.01 (dd, $J = 12.8, 4.9$ Hz, 1H), 0.06 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (500MHz, $(\text{CD}_3)_2\text{CO}$) δ 143.8, 140.7, 139.0, 136.7, 128.1 (2C), 128.0, 123.7, 113.1, 111.8, 64.0, 58.9, 44.7, 44.5, 35.8, 27.6, 24.3, 21.8, 18.7, -4.8, -4.9 ppm; HRMS (+ESI): calcd for $\text{C}_{23}\text{H}_{35}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 371.23929, found 371.24008; $[\alpha]_{\text{D}}^{25} = +38.9^\circ$ [$c = 0.90$, CHCl_3].

(1R,2S,7S,8S,8aR)-2-[Benzyl(dimethyl)silyl]-8-(hydroxymethyl)-7-methyl-1,2,3,7,8,8a-hexahydronaphthalen-1-ol (17b): To diol **16b** (160 mg, 0.432 mmol) in CH_2Cl_2 (10 mL) was added Grubbs 2nd generation catalyst (73 mg, 0.0865 mmol) and the reaction mixture was refluxed for 15 minutes. The mixture was concentrated *in vacuo* and the crude product was purified by flash chromatography (EtOAc/hexanes, 2:8, then 25:75) over silica gel to afford the desired decalin **17b** (105 mg, 71% yield) along with

the minor undesired diastereomer (15 mg, 10%) which was generated during the Michael conjugate addition and could be separated at this stage. ^1H NMR (500MHz, $(\text{CD}_3)_2\text{CO}$) δ 7.22 (br t, $J = 6.7$ Hz, 2H), 7.21-7.04 (m, 3H), 5.94 (d, $J = 9.6$ Hz, 1H), 5.67 (dd, $J = 9.6$, 5.8 Hz, 1H), 5.59 (m, 1H), 4.40 (t, $J = 4.0$ Hz, 1H), 4.32 (br s, 1H), 3.87 (m 1H), 3.83 (dd, $J = 5.4$, 0.9 Hz, 1H), 3.69 (m, 1H), 2.49 (dd, $J = 12.2$, 6.0 Hz, 1H), 2.39-2.23 (m, 4H), 2.09-2.01 (m, 1H), 2.00-1.91 (m, 1H), 1.12 (dd, $J = 12.7$, 5.7 Hz, 1H), 0.89 (d, $J = 7.0$ Hz, 3H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (500MHz, $(\text{CD}_3)_2\text{CO}$) δ 140.7, 134.0, 132.0, 129.0, 128.1, 128.0, 124.5, 123.7, 65.6, 64.1, 40.4, 40.1, 33.2, 26.2, 24.3, 21.8, 14.3, -4.8, -5.1 ppm; HRMS (+ESI): calcd for $\text{C}_{21}\text{H}_{31}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 343.20809, found 343.20878; $[\alpha]_{\text{D}}^{25} = -127.9^\circ$ [$c = 0.57$, CHCl_3].

(1S,7S,8S,8aR)-8-(hydroxymethyl)-7-Methyl-1,2,3,7,8,8a-hexahydronaphthalen-1-ol (2a): To diol **17b** (68 mg, 0.199 mmol) was added TBAF (165 mg, 0.627 mmol), 18-Crown-6 (171 mg, 0.647 mmol) and potassium *t*-butoxide (124 mg, 1.10 mmol) followed by DMSO:H₂O (19:1, 2 ml) and the reaction mixture was stirred overnight at 60 °C. The reaction mixture was diluted with EtOAc (~ 100 ml) and was washed with water (2x). The organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. Purification of the crude diol by flash chromatography (EtOAc/hexanes, 1:1) over silica gel afforded the desired final compound **2a** (14 mg, 36% yield) as a colorless solid ($[\alpha]_{\text{D}}^{25} = -208^\circ$ [$c = 0.25$, CHCl_3]). The NMR data proved identical to that obtained from the desilylation reaction of diol **17a**.