Supporting Information

for


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Preparation of 2-(R)-2-But-3-enyloxybut-3-en-1-ol (7b)

Following the protocol for allyl alcohol, butadiene monooepoxide (4) and 3-butenol (5b) were converted into alcohol 7b with the following quantities of reagents and solvents: Pd$_2$dba$_3$·CHCl$_3$ (5.2 mg, 5.0 μmol), (S,S)-9b (11.8 mg, 15 μmol), DMAP (6.2 mg, 50 μmol), a 1.0 M solution of Et$_3$B in THF (5.0 μL, 5.0 μmol), 3-butenol (172 μL, 2.0 mmol), butadiene monooepoxide (81 μL, 1.0 mmol), CH$_2$Cl$_2$ (10 mL). The reaction time in this case was 4 h. Flash chromatography of the crude material (silica gel, 4:1 pentane-ether) afforded 116 mg (82%) of 7b as a colorless oil in 90% ee (separated by chiral GLC, Cyclosil B column, isothermal 100°C, (S)-(+)isomer$_{rt}$ = 11.97 min, (R)-(−)-isomer$_{rt}$ = 12.20 min), [α]$_D$ = -50.0° (c 2.20, CHCl$_3$). IR: 3431, 3079, 2869, 1844, 1734, 1642, 1424, 1397, 1223, 1102, 993, 926, 854 cm$^{-1}$; $^1$H NMR (300 MHz): δ 2.09 (br s, 1H), 2.28-2.35 (m, 2H), 3.32-3.40 (m, 1H), 3.46-3.66 (m, 3H), 3.77-3.83 (m, 1H), 5.01 (d, 1H, $J = 11$ Hz), 5.10 (d, 1H, $J = 17$ Hz), 5.23 (d, 1H, $J = 10$ Hz), 5.28 (d, 1H, $J = 17$ Hz), 5.60-5.84 (m, 2H); $^{13}$C NMR (75 MHz): δ 34.2, 65.3, 67.9, 81.7, 116.6, 118.7, 135.2, 135.2. Anal. Calcd. for C$_8$H$_{14}$O$_2$: C, 67.57; H, 9.92. Found C, 67.36; H, 9.80.
Preparation of 2-(R)-2-Pent-4-enyloxy-but-3-en-1-ol (7c)

Following the protocol for allyl alcohol, butadiene monoepoxide (4) and 4-pentenol (5c) were converted into alcohol 7c with the following quantities of reagents and solvents: Pd_{2}db_{a}·CHCl_{3} (5.2 mg, 5.0 μmol), (S,S)-9b (11.8 mg, 15 μmol), DMAP (6.2 mg, 50 μmol), a 1.0 M solution of Et_{3}B in THF (5.0 μL, 5.0 μmol), 4-pentenol (207 μL, 2.0 mmol), butadiene monoepoxide (81 μL, 1.0 mmol), CH_{2}Cl_{2} (10 mL). The reaction time in this case was 4 h. Flash chromatography of the crude material (silica gel, 4:1 pentane-ether) afforded 131 mg (84%) of 7c as a colorless oil in 90% ee (separated by chiral GLC, Cyclosil B column, isothermal 120°C, (S)-(+-isomer_{rt} = 9.33 min, (R)-(−)-isomer_{rt} = 9.68 min), [α]_{D} = -33.2° (c 2.86, CHCl_{3}). IR: 3439, 1641, 1422, 1327, 1103, 993, 926 cm^{-1}; 1H NMR (300 MHz) δ 1.66 (quint, 2H, J = 7 Hz), 2.07-2.26 (m, 3H), 3.28-3.61 (m, 4H), 3.75-3.81 (m, 1H), 4.94 (d, 1H, J = 11 Hz), 5.00 (d, 1H, J = 17 Hz), 5.24 (d, 1H, J = 9 Hz), 5.28 (d, 1H, J = 17 Hz), 5.60-5.83 (m, 2H). 13C NMR (75.5 MHz) δ 28.9, 30.4, 65.2, 68.2, 81.6, 114.8, 118.7, 135.4, 138.2. Anal. Calc’d. for C_{9}H_{16}O_{2}: C, 69.19; H, 10.32. Found: C, 69.23; H, 10.14.

Preparation of 2-(R)-2-Hex-5-enyloxy-but-3-en-1-ol (7d)

Following the protocol for allyl alcohol, butadiene monoepoxide (4) and 5-hexenol (5d) were converted into alcohol 113 with the following quantities of reagents and solvents: Pd_{2}db_{a}·CHCl_{3} (5.2 mg, 5.0 μmol), (±)-9a (10.4 mg, 15 μmol), DMAP (6.2 mg, 50 μmol), a 1.0 M solution of Et_{3}B in THF (5.0 μL, 5.0 μmol), 5-hexenol (240 μL, 2.0 mmol), butadiene monoepoxide (81 μL, 1.0 mmol), CH_{2}Cl_{2} (10 mL). The reaction time in this case was 4 h. Flash chromatography of the crude material (silica gel, 4:1 pentane-ether) afforded ~135 mg (80%) of 7d as a colorless oil. (enantiomers separated by chiral GLC, Cyclosil B column isothermal 120°C, (S)-(+-isomer_{rt} = 15.52 min, (R)-(−)-isomer_{rt} = 16.21 min). IR: 3441, 1641, 1458, 1423, 1403, 1325, 1103, 993, 927, 911 cm^{-1}; 1H NMR (300 MHz) δ 1.36-1.43 (m, 2H), 1.50-1.58 (m, 2H), 1.97-2.04 (m, 2H), 2.50 (br s, 1H), 3.24-3.31 (m, 1H), 3.43-3.53 (m, 3H), 3.71-3.75 (m, 1H), 4.89 (d, 1H, J = 11 Hz), 4.94 (d, 1H, J = 19 Hz), 5.20 (d, 1H, J = 9 Hz), 5.24 (d, 1H, J = 17 Hz), 5.57-5.78 (m, 2H); 13C NMR (75.5 MHz) δ 25.3, 29.1, 33.4, 65.1, 68.6, 81.6, 114.5, 118.4, 135.4, 138.5. Anal. Calc’d. for C_{10}H_{18}O_{2}: C, 70.55; H, 10.66. Found: C, 70.66; H, 10.43.
Preparation of 2-phenyl-2-vinylepoxide 10b

To a 0 °C solution of freshly prepared vinylmagnesium bromide (0.67 M in THF, 48 mL, 32 mmol) was added a solution of 2-chloroacetophenone (4.52 g, 29.2 mmol) in THF (15 mL) over 30 min. After the addition, the mixture was stirred at 0 °C for 15 min, allowed to warm over 30 min, diluted with sat aq NH₄Cl (100 mL), and extracted with ether (2x150 mL). The organic layer was stirred over 1 N NaOH (100 mL) for 3 hr, and then separated. The aqueous layer was extracted with ether (2x150 mL), and the combined organic layers were dried (Na₂SO₄), and concentrated to give a yellow oil. Some chlorohydrin remained, and the residue was dissolved in ether (50 mL) and stirred over 1 N NaOH (50 mL) for 3 hr, and worked up as above to provide 10b as a reddish oil, which was used without further purification (3.895 g, 26.6 mmol, 91%): ¹H NMR (300 MHz) δ 7.30-7.42 (m, 5H), 6.05 (dd, J=10.6, 17.2 Hz, 1H), 5.33 (dd, J=1.2, 10.6 Hz, 1H), 5.25 (dd, J=1.2, 17.2 Hz, 1H), 3.10 (d, J=5.7 Hz, 1H), 3.03 (d, J=5.7 Hz, 1H); ¹³C NMR (75 MHz) δ 137.3, 128.2, 127.8, 127.0, 119.0, 56.7; IR (film) 3061, 2988, 1689, 1640, 1603, 1496, 1448, 1411, 928 cm⁻¹.

Preparation of Enantioenriched 2-phenyl-2-vinylepoxide (10b)

A solution of 12 (0.141 g, 0.690 mmol, 94% ee), pyridine (0.22 mL, 2.7 mmol), DMAP (12.0mg, 0.098 mmol), and TsCl (0.394 g, 2.07 mmol) in CH₂Cl₂ (1.5 mL) was stirred overnight, and then heated at 50 °C overnight. The mixture was diluted with 1 N HCl (10 mL), extracted with CH₂Cl₂ (2x10 mL), dried (K₂CO₃), concentrated and purified by flash chromatography (10% ether/pet. ether) to provide the corresponding tosylate as a yellow gum (0.241 g, 0.672 mmol, 97%).

A solution of the tosylate (27.1 mg, 0.0756 mmol), SeO₂ (10.2 mg, 0.0919 mmol), and AcOH (6.5 mL, 0.16 mmol) in DME (0.4 mL) was heated to 90 °C for 90 min, evaporated, and purified by flash chromatography (20% ether/pet. ether) to provide the corresponding alcohol as a clear oil (14.0 mg, 0.0440 mmol, 58%). To a solution of the alcohol in ether (0.5 mL) was added 1 N NaOH (0.2mL), and the mixture was stirred for 2 hr, separated, dried (Na₂SO₄), concentrated and purified by flash chromatography (10% ether/pet. ether) to provide 10b as a clear film (1 mg, 0.007 mmol, 16%). Chiral GC analysis indicated 90% ee (Cyclosil-B, 110 °C).
Preparation of 2-(R)-2-Methyl-2-But-enyloxy-2-methyl-but-3-en-1-ol (11b)

Following the general procedure, isoprene monoepoxide (10a) and 3-butenol (5b) were converted into alcohol 11b with the following quantities of reagents and solvents: Pd$_2$dba$_3$·CHCl$_3$ (10.4 mg, 10 µmol), (S,S)-9a (20.8 mg, 30 µmol), DMAP (6.2 mg, 50 µmol), a 1.0 M solution of Et$_3$B in THF (10 µL, 10 µmol), 3-butenol (172 µL, 2.0 mmol), isoprene monoepoxide (99 µL, 1.0 mmol), CH$_2$Cl$_2$ (10 mL). The reaction time in this case was 3 h, while the reaction temperature was 40°C. Flash chromatography of the crude material (silica gel, 4:1 pentane-ether) afforded 260 mg (83%) of 11b as a colorless oil in 96% ee (separated by chiral GLC, Cyclosil B column, isothermal 80°C, (R)-(−)-isomer$_{rt}$ = 34.78 min, (S)-(+)−isomer$_{rt}$ = 36.66 min), [α]$_D$ = -10.6° (c 2.29, CHCl$_3$). IR: 3453, 2929, 1642, 1415, 1203, 1120, 1069, 997, 923 cm$^{-1}$; $^1$H NMR (300 MHz): δ 1.26 (s, 3H), 2.01 (br s, 1H), 2.24-2.30 (m, 2H), 3.24-3.48 (m, 4H), 5.01 (d, 1H, J = 11 Hz), 5.06 (d, 1H, J = 18 Hz), 5.16-5.26 (m, 2H), 5.72-5.86 (m, 2H); $^{13}$C NMR (75 MHz): δ 18.4, 34.7, 61.7, 69.2, 77.6, 116.3, 116.5, 135.3, 139.9. Anal. Calcd. for C$_9$H$_{16}$O$_2$: C, 69.19; H, 10.32; found C, 69.30; H, 10.15.

Preparation of 2-(R)-2-Methyl-2-pent-4-enyloxy-but-3-en-1-ol (11c)

Following the general procedure, isoprene monoepoxide (10a) and 4-pentenol (5c) were converted into alcohol 11c with the following quantities of reagents and solvents: Pd$_2$dba$_3$·CHCl$_3$ (10.4 mg, 10 µmol), (S,S)-9a (20.8 mg, 30 µmol), DMAP (6.2 mg, 50 µmol), a 1.0 M solution of Et$_3$B in THF (10 µL, 10 µmol), 4-pentenol (207 µL, 2.0 mmol), isoprene monoepoxide (99 µL, 1.0 mmol), CH$_2$Cl$_2$ (10 mL). The reaction time in this case was 2 h, while the reaction temperature was 40°C. Flash chromatography of the crude material (silica gel, 4:1 pentane-ether) afforded 147 mg (86%) of 11c as a colorless oil in 91% ee (separated by chiral GLC, Cyclosil B column, isothermal 110°C, (R)-(−)-isomer$_{rt}$ = 18.84 min, (S)-(+)−isomer$_{rt}$ = 19.86 min), [α]$_D$ = -12.0° (c 2.54, CHCl$_3$). IR: 3449, 1641, 1450, 1415, 1371, 1121, 1072, 913 cm$^{-1}$; $^1$H NMR (300 MHz) δ 1.25 (s, 3H), 1.61 (quint, 2H, J = 7 Hz), 2.06-2.13 (m, 3H), 3.28-3.33 (m, 2H), 3.38 (d, 1H, J = 11 Hz), 3.45 (d, 1H, J = 11 Hz), 4.94 (d, 1H, J = 11 Hz), 4.99 (d, 1H, J = 17 Hz), 5.20 (d, 1H, J = 18 Hz), 5.23 (d, 1H, J = 11 Hz), 5.74-5.83 (m, 2H).
Conversion of Recovered Epoxide 10b to (S-2-Phenylglycidol (13)).

A stream of O₃ was bubbled through a solution of 10b (0.202 g, 1.38 mmol) recovered from the above formation of 12 in MeOH (4 mL) at -78 °C for 5 min. The solution was purged with O₂, and NaBH₄ (52.6 mg, 1.39 mmol) was then added and stirred 30 min. The mixture was diluted with sat aq NaHCO₃ (10 mL), extracted with CH₂Cl₂ (2x10 mL), washed with brine (5 mL), dried (Na₂SO₄), concentrated and purified by flash chromatography (25% EtOAc/pet. ether) to provide 13 as a light yellow oil (0.153 g, 1.02 mmol, 74%). ¹H NMR spectrum agreed with literature data. Chiral HPLC analysis indicated 41% ee (Chiracel OJ, 90:10 Hept:IPA, 1.0 mL/min tᵣ(-)-isomer=7.42 min, tᵣ(+)-isomer=9.07 min); [α]₂⁴D –9.45 (c 2.47, EtOH).

General Procedure for Preparation of Acetate-Protected Substrates

To a stirred solution of the alcohol in CH₂Cl₂ (1 mL per mmol alcohol) was added pyridine (1.2 equiv), DMAP (0.05 equiv), and acetic anhydride (1.2 equiv). Stirring was continued for 3-18 h, at which time the solvent was removed in vacuo, and the crude material was purified by flash chromatography on silica gel. Any remaining traces of solvent or moisture were removed under reduced pressure (vacuum pump).

Preparation of 2-(R)-2-But-3-enyloxybut-3-enyl acetate (16a)

Following the general procedure, the alcohol 7b was converted into acetate 16a using the following quantities of reagents and solvents: compound 7b (110 mg, 0.77 mmol), pyridine (75 μL, 0.93 mmol), DMAP (5 mg, 0.04 mmol), acetic anhydride (88 μL, 0.93 mmol), CH₂Cl₂ (1 mL). The reaction time in this case was 6 h. Flash chromatography of the crude material (silica gel, 10:1 pentane-ether) afforded 131 mg (92%) of 16a as a colorless oil. IR: 1746, 1643, 1428, 1381, 1233, 1102, 1044, 993, 929 cm⁻¹; ¹H NMR (300 MHz) δ 2.03 (s, 3H), 2.26-2.33 (m, 2H), 3.34-3.42 (m, 1H), 3.51-3.59 (m, 1H), 3.90-3.94 (m, 1H), 3.99-4.08 (m, 2H), 4.99 (d, 1H, J = 11 Hz), 5.04 (d, 1H, J = 19 Hz), 5.24 (d, 1H, J = 19 Hz), 5.29 (d, 1H, J = 19 Hz), 5.62-5.83 (m, 2H); ¹³C NMR (75.5 MHz) δ 20.9, 34.1, 66.1, 68.3, 78.7, 116.3, 118.7, 134.8, 135.0, 170.8.
Preparation of 2-((R)-2-Pent-4-enyloxy-but-3-enyl acetate (16c)

Following the general procedure, the alcohol 7c was converted into acetate 16c using the following quantities of reagents and solvents: compound 7c (200 mg, 1.28 mmol), pyridine (124 µL, 1.54 mmol), DMAP (8 mg, 0.06 mmol), acetic anhydride (145 µL, 1.54 mmol), CH₂Cl₂ (2 mL). The reaction time in this case was 3 h. Flash chromatography of the crude material (silica gel, 10:1 pentane-ether) afforded 226 mg (89%) of 16c as a colorless oil. IR: 1746, 1642, 1425, 1381, 1233, 1103, 1042, 994, 929 cm⁻¹; ¹H NMR (300 MHz) δ 1.59-1.70 (m, 2H), 2.02-2.13 (m, 5H), 3.32-3.40 (m, 1H), 3.47-3.55 (m, 1H), 4.00-4.10 (m, 2H), 4.93 (d, 1H, J = 11 Hz), 4.99 (d, 1H, J = 11 Hz), 5.24 (d, 1H, J = 11 Hz), 5.29 (d, 1H, J = 18 Hz), 5.63-5.83 (m, 2H); ¹³C NMR (75.5 MHz) δ 20.9, 28.8, 30.2, 66.2, 68.3, 78.7, 114.7, 118.6, 135.0, 138.2, 170.9.

Preparation of 2-((R)-2-But-3-enyloxy-2-methyl-but-3-enyl acetate (16b)

Following the general procedure, the alcohol 11b was converted into acetate 16b using the following quantities of reagents and solvents: compound 11b (150 mg, 0.96 mmol), pyridine (93 µL, 1.15 mmol), DMAP (6 mg, 0.05 mmol), acetic anhydride (109 µL, 1.15 mmol), CH₂Cl₂ (1 mL). The reaction time in this case was 4 h. Flash chromatography of the crude material (silica gel, 10:1 pentane-ether) afforded 180 mg (95%) of 16b as a colorless oil. IR: 1747, 1642, 1415, 1382, 1369, 1242, 1072, 916 cm⁻¹; ¹H NMR (300 MHz) δ 1.23 (s, 3H), 2.01 (s, 3H), 2.192.25 (m, 2H), 3.29-3.34 (m, 2H), 3.95 (d, 1H, J = 11 Hz), 4.01 (d, 1H, J = 11 Hz), 4.95 (d, 1H, J = 11 Hz), 5.00 (d, 1H, J = 19 Hz), 5.19 (d, 1H, J = 18 Hz), 5.19 (d, 1H, J = 11 Hz), 5.68-5.77 (m, 2H); ¹³C NMR (75.5 MHz) δ 19.8, 20.8, 34.7, 62.0, 68.7, 76.0, 116.1, 116.4, 135.2, 139.5, 170.7.

Preparation of 2-((R)-2-Methyl-2-pent-4-enyloxy-but-3-enyl acetate (16d)

Following general procedure, the alcohol 11c was converted into acetate 16d using the following quantities of reagents and solvents: compound 11c (250 mg, 1.46 mmol), pyridine (143 µL, 1.75 mmol), DMAP (9 mg, 0.07 mmol), acetic anhydride (166 µL, 1.75 mmol), CH₂Cl₂ (2 mL). The reaction time in this case was 3 h. Flash chromatography of the crude material (silica gel, 10:1 pentane-ether) afforded 286 mg (92%) of 16d as a colorless oil. IR: 1747, 1641, 1415, 1381, 1369, 1241, 1074, 1046,
Preparation of 2-\((R)\)-2-Hex-5-enyloxy-but-3-enyl acetate (18)

Following the general procedure, the alcohol 7d was converted into acetate 18 using the following quantities of reagents and solvents: compound 7d (120 mg, 0.70 mmol), pyridine (68 μL, 0.85 mmol), DMAP (4 mg, 0.04 mmol), acetic anhydride (80 μL, 0.85 mmol), CH₂Cl₂ (1 mL). The reaction time in this case was 18 h. Flash chromatography of the crude material (silica gel, 10:1 pentane-ether) afforded 135 mg (90%) of 18 as a colorless oil. IR: 1746, 1641, 1437, 1381, 1386, 1233, 1104, 1042, 929, 911 cm⁻¹; ¹H NMR (300 MHz) δ 1.21 (s, 3H), 1.55 (quint, 2H, J = 7 Hz), 1.97-2.06 (m, 5H), 3.23-3.28 (m, 2H), 3.93 (d, 1H, J = 11 Hz), 3.99 (d, 1H, J = 11 Hz), 4.87 (d, 1H, J = 10 Hz), 4.93 (d, 1H, J = 17 Hz), 5.15 (d, 1H, J = 18 Hz), 5.16 (d, 1H, J = 11 Hz), 5.66-5.77 (m, 2H); ¹³C NMR (75.5 MHz) δ 19.8, 20.8, 29.3, 30.1, 61.6, 68.6, 75.8, 114.4, 116.2, 138.2, 139.7, 170.6.

Preparation of Epoxide 22

A solution of TFPAA in CH₂Cl₂ (20 mL, 11.6 mmol) prepared in situ from urea-hydrogen peroxide and TFAA was added over 30 min to a suspension of 14b and Na₂HPO₄ (4.82g, 33.9 mmol) in CH₂Cl₂ (20 mL), and stirred another 10 min. The mixture was diluted with 1 M Na₂SO₃ (15 mL) and brine (10 mL), extracted with CH₂Cl₂ (3x25 mL), dried (Na₂SO₄), and purified by flash chromatography (60% ether/pet. ether) to give 22 as a clear oil (0.335 g, 2.57 mmol, 61%); [α]²⁴_D 22.7 (c 1.00, CH₂Cl₂). IR (film) 3447, 2927, 1750, 1457 cm⁻¹; ¹H NMR (300 MHz) δ 4.05 (d, J=10.7 Hz, 1H), 3.70-3.80 (m, 4H), 3.58 (d, J=2.9 Hz, 1H), 2.18 (br s, 1H), 1.18 (s, 3H); ¹³C NMR (75 MHz) δ 80.3, 66.1, 66.0, 59.8, 55.1, 17.8.

Preparation of Silyl Ether 24

To a solution of alcohol 22 (0.600 g, 4.61 mmol) and imidazole (0.473 g, 6.96 mmol) in CH₂Cl₂ (9 mL) was added TBDMSCl (0.835 g, 5.54 mmol). The reaction
mixture was stirred 30 min, diluted with ether (75 mL), washed with water (20 mL) and 
brine (20 mL), dried (Na₂SO₄), and concentrated to give a clear oil. Flash 
chromatography (5% ether/pet. ether) provided 18 as a clear oil (0.934 g, 3.82 mmol, 
83%); [α]²⁴ D 24.9 (c 1.00, CH₂Cl₂). IR (film) 2956, 2858, 1472 cm⁻¹; ¹H NMR (300 
MHz) δ 3.98 (d, 10.7 Hz, 1H), 3.68-3.75 (m, 3H), 3.57 (d, J=3.0 Hz, 1H), 3.48 (d, J=9.3 
Hz, 1H), 1.19 (s, 3H), 0.91 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ¹³C NMR (75 MHz) δ 
80.9, 66.1, 65.1, 59.6, 59.0, 25.8, 18.2, 18.1, -5.5, -5.6.

Preparation of (2S, 3S)-2-Methyl-t-butyldimethylsiloxy-3-hydroxy-2, 3-dihydrofuran 
(26a)

To a solution of diethyl amine (0.93 mL, 9.0 mmol) in ether (9 mL) at 0 °C was 
added n-butyllithium (1.5 M in hex, 5.5 mL, 8.2 mmol), and the solution stirred 10 min. 
HMPA (0.95 mL, 5.5 mmol) was added and stirring continued 2 min. A solution of 24 
(0.669 g, 2.74 mmol) in ether (2.5 mL) was added dropwise. After stirring 3.5 hr, the 
reaction mixture was diluted with ether (40 mL), washed with water (2x10 mL) and brine 
(15 mL), dried (Na₂SO₄), concentrated and purified by flash chromatography (5% 
ether/pet. ether) to provide 43 as a white waxy solid (0.521 g, 2.13 mmol, 78%); mp 30-
33 °C; [α]²⁴ D 37.0 (c 1.00, CH₂Cl₂). IR (film) 3441, 2930, 1615, 1472 cm⁻¹; ¹H NMR 
(300 MHz) δ 6.46 (s, 1H), 5.05 (s, 1H), 4.60 (d, J=7.9 Hz, 1H), 3.91 (d, J=10.5 Hz, 1H), 
3.82 (d, J=10.5 Hz, 1H), 3.38 (d, J=7.9 Hz, 1H), 1.23 (s, 3H), 0.89 (s, 9H), 0.09 (s, 6H); 
¹³C NMR (75 MHz) δ 148.6, 103.3, 86.9, 81.0, 66.2, 25.7, 22.0, 18.1, -5.4, -5.6. HRMS 
m/z calcd for C₁₂H₂₃O₂Si, 227.1467. Found, 227.1460.

Preparation of (2S, 3S)-2-Methyl-t-butyldimethylsiloxy-3-acetoxy-2, 3-dihydrofuran (27)

To a solution of 26a (60.5 mg, 0.248 mmol) in ether (1.2 mL) at -78 °C was 
added n-butyllithium (1.5 M in hexanes, 0.34 mL, 0.54 mmol). After stirring 15 min, the 
cooling bath was removed, and acetic anhydride (70 µL, 0.74 mmol) was added. After 
30 min, the mixture was diluted with water (5 mL), extracted with CH₂Cl₂ (7 mL), dried 
(Na₂SO₄), and concentrated to provide crude 27 as a yellow oil (74 mg, 0.26 mmol, 
~quant.) which was used directly: ¹H NMR (300 MHz) δ 6.53 (d, J=2.7 Hz, 1H), 5.54 
(d, J=2.7 Hz, 1H), 5.02 (t, J=2.7 Hz, 1H), 3.79 (d, J=10.2 Hz, 1H), 3.66 (d, J=10.2 Hz,
Glycosylation of 6-Chloropurine to 28

A solution of Pd2dba3.CHCl3 (1.8 mg, 0.0017 mmol) and ligand A (2.3 mg, 0.014 mmol) in CH2Cl2 (0.30 mL) was stirred for 20 min, and added to a mixture of 27 (18 mg, 0.062 mmol), Et3N (25 μL, 0.18 mmol), and 6-chloropurine (11.4 mg, 0.091 mmol). After stirring overnight, the reaction was concentrated, and the product purified by flash chromatography (20% EtOAc/pet. ether) to give a 2:1 mixture of purines 28 as a clear film (10.7 mg, 0.0281 mmol, 45%). Major: 1H NMR (300 MHz) δ 8.76 (s, 1H), 8.47 (s, 1H), 7.19 (s, 1H), 6.39 (dd, J=1.7, 6.1 Hz, 1H), 6.01 (d, J=6.1 Hz, 1H), 3.68 (s, 2H), 1.39 (s, 3H), 0.88 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H).

Preparation of (2R)-2-t-Butyldiphenylsiloxymethyl-2, 5-dihydrofuran (29)

To a solution of 14a (26.2 mg, 0.262 mmol) and imidazole (26.8 mg, 0.394 mmol) in DMF (0.80 mL) was added TBDPSCl (82 μL, 0.315 mmol). The reaction mixture was stirred 2 hr, and then diluted with ether (12 mL) and washed with water (5 mL), and brine (5 mL). The organic layer was dried (Na2SO4) and concentrated to give a yellow oil, which was purified by flash chromatography (5% ether/pet. ether) to give 29 as a clear film which solidified upon cooling (56.4 mg, 0.167 mmol, 64%), mp 40-42 °C; [α]24D 69.3 (c 1.0, CH2Cl2). IR (film) 3071, 2930, 2857, 1590, 1472, 1428, 1112, 1084 cm⁻¹; 1H NMR (300 MHz) 7.66-7.70 (m, 4H), 7.30-7.48 (m, 6H), 5.95 (dq, J=2.0, 6.3 Hz, 1H), 5.82 (m, 1H), 4.90 (m, 1H), 4.65 (m, 2H), 3.70 (dd, J=1.7, 4.9 Hz, 2H), 1.05 (s, 9H); 13C NMR (75 MHz) δ 135.6, 133.6, 129.5, 127.7, 127.6, 127.3, 86.8, 75.6, 66.5, 26.8, 19.2. Anal.: Calcd for C21H26O2Si: C, 74.49; H, 7.76. Found: C, 74.32; H, 7.59.

Preparation of (2R)-2-t-Butyldiphenylsiloxymethyl-2, 3-dihydrofuran (30)

A solution of 29 (8.4 mg, 0.025 mmol) and H2Ru(CO)(PPh3)3 (1.2 mg, 0.0013 mmol) in toluene (0.25 mL) was heated at 100 °C for 2 hr. The reaction mixture was concentrated and purified by flash chromatography (3% ether/pet. ether) to provide 30 as a clear film (7.0 mg, 0.021 mmol, 83%), possessing 1H and 13C NMR data in agreement with those published,14 [α]24D –49.6 (c 1.0, CH2Cl2). 1H NMR (300 MHz) δ 7.67-7.70 (m, 4H), 7.35-7.45 (m, 6H), 6.27 (q, J=2.4 Hz, 1H), 4.84 (q, J=2.4 Hz, 1H), 4.66 (dddd, J=4.9, 5.7, 7.4, 10.5 Hz, 1H), 3.75 (dd, J=5.7, 10.7 Hz, 1H), 3.68 (dd, J=4.9, 10.7 Hz,
1H), 2.64 (qt, J=2.4, 10.5, 15.2 Hz, 1H), 2.47 (qt, J=2.4, 7.4, 15.2 Hz, 1H), 1.09 (s, 9h); 
\(^{13}\)C NMR (75 MHz) \(\delta\) 145.18, 135.6, 129.6, 127.6, 99.0, 81.2, 65.9, 31.2, 26.0, 19.3.

Preparation of (2\textit{R})-\textit{t}-Butyldiphenylsiloxymethyl-2, 3-dihydrofuran (31)

A solution of TBAF (1 M in THF, 0.11 mL, 0.11 mmol) was added to a solution of 30 (30 mg, 0.09 mmol) in 2:1 ether:THF (0.8 mL). After stirring 30 min, the reaction was concentrated and the product was purified by flash chromatography (35% ether/pentane) to provide 31 as a clear film (6.2 mg, 0.027 mmol, 31%). \(^1\)H NMR spectrum agreed with literature data.\(^{21}\) Chiral GC analysis indicated 89% ee (\textit{R})-isomer (Cyclosil-B, 70 °C; \(t_R(\text{S})=26.6\) min; \(t_R(\text{R})=29.7\) min).

Preparation of Uridine Analog 43.

To a solution of 35 (25.2 mg, 0.0715 mmol) in dioxane (0.5 mL) was added PhSeCl (17.6 mg, 0.0919 mmol). After stirring for 45 min, bis(trimethylsilyl)uracil (37.3 mg, 0.145 mmol) was added, followed by InCl\(_3\) (24.2 mg, 0.109 mmol). The reaction mixture was stirred for 3 hr, diluted with sat aq NaHCO\(_3\) (7 mL), and extracted with CH\(_2\)Cl\(_2\) (2x7 mL). The combined organic layers were dried (Na\(_2\)SO\(_4\)), concentrated, and purified by flash chromatography (30% EtOAc/pet. ether) to give an impure mixture of selenides as a yellow film (38 mg). This mixture was dissolved in THF (0.8 mL), and pyridine (12 \(\mu\)L) and 30% H\(_2\)O\(_2\) (16 \(\mu\)L) was added. The mixture was stirred for 45 min, concentrated, and purified by flash chromatography (40% EtOAc/pet. ether) to afford a 5:1 mixture of C-1' isomers of 38 as a clear film (19.7 mg, 0.0426 mmol, 60%). 38\(\alpha\): mp 137-141 °C. [\(\alpha\)]\(^{24}\)\(_D\) 1.74 (c 1.0, CH\(_2\)Cl\(_2\)). IR (film) 3192, 1693, 1458 cm\(^{-1}\); \(^1\)H NMR (300 MHz) \(\delta\) 8.60 (br s, 1H), 7.57-7.65 (m, 4H), 7.35-7.47 (m, 6H), 7.01 (s, 1H), 6.26 (dd, \(J=2.0, 5.9\) Hz, 1H), 5.76 (dd, \(J=1.2, 5.9\) Hz, 1H), 5.09 (dd, \(J=2.0, 8.1\) Hz, 1H), 3.80 (d, \(J=11.2\) Hz, 1H), 3.72 (d, \(J=11.2\) Hz, 1H), 1.27 (s, 3H), 1.07 (s, 9H); \(^{13}\)C NMR (75 MHz) \(\delta\) 163.1, 150.7, 140.8, 139.6, 135.6, 135.5, 135.3, 133.1, 132.4, 130.1, 130.0, 127.9, 127.8, 127.7, 125.0, 102.4, 92.0, 89.9, 68.9, 27.0, 23.4, 19.4. To a solution of 38 (15.2 mg, 0.0329 mmol) in THF (0.30 mL) was added TBAF (1.0 M in THF, 36 \(\mu\)L, 0.036 mmol). The resultant solution was stirred 2 hr, concentrated, and purified by flash chromatography (4% MeOH/CH\(_2\)Cl\(_2\)) to afford 43 as a white solid (7.0 mg, 0.0312 mmol, 95%); mp 154-157 °C, [\(\alpha\)]\(^{24}\)\(_D\) –38.9 (c 0.45, MeOH). IR (film) 3400, 1694, 1468, 1269, 1251, 1083 cm\(^{-1}\); \(^1\)H NMR (CD\(_3\)OD, 500 MHz) \(\delta\) 7.95 (d, \(J=8.0\) Hz, 1H), 6.93 (s, 1H).
6.34 (dd, J=2.0, 6.0 Hz, 1H), 5.84 (dd, J=1.2, 6.0 Hz, 1H), 5.62 (d, J=8.0 Hz, 1H), 3.62 (d, J=12.2 Hz, 1H), 3.55 (d, J=12.2 Hz, 1H), 1.26 (s, 3H); 13C NMR (CD3OD, 125 MHz) δ 166.4, 152.8, 143.5, 141.0, 125.9, 102.2, 93.9, 90.8, 67.7, 23.2; HRMS m/z calcd for C10H12N2O4: 224.0797. Found: 224.0800.

Preparation of 6-Chloropurine Analog 44.

To a solution of 35 (35.5 mg, 0.101 mmol) in dioxane (0.5 mL) was added PhSeCl (25.0 mg, 0.131 mmol). After stirring 45 min, a solution of (TMS)-6-chloropurine (0.5 M in dioxane, 0.40 mL, 0.20 mmol) was added followed by InCl3 (2.3 mg, 0.010 mmol). The reaction mixture was stirred for 3 hr, diluted with sat aq NaHCO3 (5 mL), and extracted with CH2Cl2 (2x7 mL). The combined organic layers were dried (Na2SO4), concentrated, and purified by flash chromatography (20% EtOAc/pet. ether) to give an impure mixture of selenides as a yellow film (20 mg). This mixture was dissolved in THF (1 mL), and pyridine (16 µL) and 30% H2O2 (25 µL) were added. The mixture was stirred for 45 min, concentrated, and purified by flash chromatography (25% EtOAc/pet. ether) to afford an inseparable 2.5:1 mixture of 39 as a clear film (12.6 mg, 0.0398 mmol, 40%). 39: 1H NMR δ 8.73 (s, 1H), 8.08 (s, 1H), 7.57 (t, J=8.0 Hz, 4H), 7.26-7.45 (m, 6H), 7.14 (s, 1H), 6.45 (dd, J=1.7, 5.9 Hz, 1H), 6.01 (d, 5.9 Hz, 1H), 3.67 (s, 2H), 1.44 (s, 3H), 1.05 (s, 9H). 35: 1H NMR (300 MHz) δ 8.79 (s, 1H), 8.18 (s, 1H), 7.65-7.70 (m, 4H), 7.26-45 (m, 6H), 7.14 (s, 1H), 6.39 (dd, J=1.8, 5.9 Hz, 1H), 6.08 (d, J=5.9 Hz, 1H), 3.69 (ab, J=10.5 Hz, 2H), 1.40 (s, 3H), 1.08 (s, 9H). To a solution of a 1:1 mixture of 39 (0.157 mg, 0.312 mmol) in THF (3 mL) was added TBAF (1.0 M in THF, 0.34 mL, 0.34 mmol). The resultant solution was stirred 45 min, concentrated, and purified by flash chromatography (2% MeOH/CH2Cl2) to afford a 1:1 mixture of 1'-isomeric products (85.1 mg). Further purification by preparative HPLC (80:20 EtOAc:Hex, 20 mL/min) gave the desired 44 (30.8 mg, 0.115 mmol, 37%) and 44 (32.0 mg, 0.120 mmol, 38%) isomers as white foams.

44: mp 109-111 °C. [α]24D –68.5 (c 1.0, CH2Cl2). IR (film) 3362, 2930, 1592, 1563, 1396, 1335, 1194, 1085 cm⁻¹. 1H NMR (500 MHz) δ 0.75 (s, 1H), 8.45 (s, 1H), 7.13 (t, J=1.4 Hz, 1H), 6.44 (dd, J=1.7, 5.9 Hz, 1H), 6.02 (dd, J=1.2, 5.9 Hz, 1H), 3.78 (d, J=12.0 Hz, 1H), 3.74 (d, J=12.0 Hz, 1H), 1.39 (s, 3H); 13C NMR (125 MHz) δ 151.9, 151.2,
151.1, 144.6, 140.1, 132.0, 123.9, 94.0, 89.1, 67.4, 22.8; Chiral HPLC analysis indicates 90% ee (Chiralpak AS, 90:10 hept:IPA, 0.70 mL/min, tR(+ isomer)=16.6 min, tR(- isomer)=19.7 min). Anal calcd for C_{11}H_{11}N_{4}O_{2}:  C, 49.53; H, 4.17; N, 21.01. Found: C, 49.70; H, 4.32; N, 21.03. 44β: mp 146 °C (dec). [α]_{24}^{D} 75.4 (c 1.0, CH_{2}Cl_{2}). IR (film) 3380, 2929, 1591, 1397, 1336, 1187, 1084, 949 cm^{-1}; ^1H NMR (500 MHz) δ 8.80 (s, 1H), 8.20 (s, 1H), 7.20 (t, J=1.4 Hz, 1H), 6.43 (dd, J=1.4, 6.0 Hz, 1H), 6.16 (dd, J=1.2, 6.0 Hz, 1H), 3.72 (d, J=11.9 Hz, 1H), 3.65 (J=11.9 Hz, 1H), 1.40 (s, 3H); ^13C NMR (125 MHz) δ 152.3, 151.5, 151.2, 142.8, 139.6, 132.0, 124.0, 93.5, 88.6, 67.9, 22.5.

Preparation of Adenosine Analogs 47.

A solution of 44α (29.0 mg, 0.109 mmol) in NH_{3}/MeOH (sat’d at 0°C, 0.5 mL) was heated in a sealed vial to 60 °C for 17 hr. The mixture was concentrated and purified by flash chromatography (5% MeOH/CH_{2}Cl_{2}) to afford known 47 as a white powder (9.7 mg, 0.039 mmol, 36%): mp 161-163 °C; [α]_{24}^{D} –67.3 (c 0.5, MeOH) [Lit^{17} for enantiomer: mp 164 °C; [α]_{24}^{D} 94.2 (c 0.6, MeOH)]. ^1H NMR (DMSO-d_{6}, 500 MHz) δ 8.17 (s, 1H), 8.13 (s, 1H), 7.25 (br s, 2H), 6.94 (s, 1H), 6.40 (d, J=5.9 Hz, 1H), 6.06 (d, J=5.9 Hz, 1H), 5.10 (t, J=5.2 Hz, 1H), 3.49 (dd, d=5.2, 11.6 Hz, 1H), 3.41 (dd, J=5.9, 11.6 Hz, 1H), 1.25 (s, 3H).

Ent-47. A solution of ent-39 (40.2 mg, 0.0796 mmol) in NH_{3}/MeOH (sat’d at 0 °C, 0.5 mL) was heated in a sealed vial to 60 °C for 18 hr. The mixture was concentrated and purified by flash chromatography (5% MeOH/CH_{2}Cl_{2}) to afford 49 as a clear film (28.8 mg, 0.0593 mmol, 74%). This film was dissolved in THF (0.6 mL) and treated with TBAF (1.0 M in THF, 66 µL, 0.066 mmol). The resultant solution was stirred 90 min, concentrated, and purified by flash chromatography (6 to 8% MeOH/CH_{2}Cl_{2}) to afford ent-47 as a white solid (12.1 mg, 0.0489 mmol, 83%): [α]_{24}^{D} 73.4 (c 0.6, MeOH).