Supporting Information:

Stereoselective *C*-Glycosidation with Achiral and Enantioenriched Allenylsilanes

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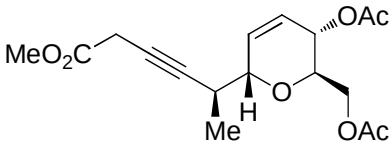
General Information:

All reactions were carried out in oven or flame dried glassware under an atmosphere of argon and using standard techniques for handling air sensitive materials. All solvents were reagent grade. Trimethylsilyltrifluoromethanesulfonate was freshly distilled before use. All other reagents were purchased from Aldrich of Alfa Aesar and used as supplied. All reactions were magnetically stirred and monitored by thin layer chromatography using Macherey-Nagel 0.20 mm silica gel 60 plates. Flash chromatography was performed with silica gel 60 (particle size 0.032-0.063mm) provided by Sorbent Technologies. Yields refer to chromatographically and spectroscopically pure compounds unless otherwise noted. ^{1}H NMR spectra were recorded using an internal deuterium lock at ambient temperature on a Varian 400MHz spectrometer. An internal reference of 7.24 was used for δ_H $CDCl_3$. Data are presented as follows: chemical shift (on a δ scale relative to $\delta_{TMS} = 0$), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, br = broad), coupling constant (*J*/Hz), and integration. Carbon-13 NMR spectra were recorded on a Varian 75 MHz spectrometer. An internal reference of δ_C 77.00 was used for $CDCl_3$. All 2D spectra were recorded on a Varian 400MHz spectrometer. Infrared spectra were recorded on a Nexus 670 FT-IR spectrophotometer. Optical rotations were recorded on an Autopol III digital polarimeter at 589 nm and reported as follows: $[\alpha]_D^{20}$, concentration (*c* in g/100mL) and solvent. High resolution mass spectra were obtained on a Waters Q-TOF mass spectrometer in the Boston University Mass Spectrometry Laboratory.

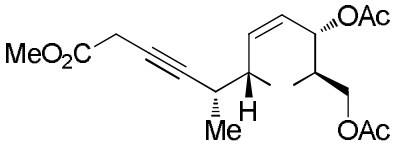
Experimental Procedures:



2a

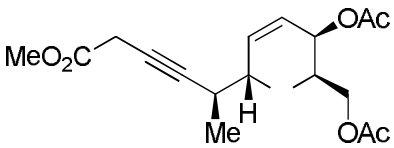
S*-methyl 5-((2*S*,5*S*,6*R*)-5-acetoxy-6-(acetoxymethyl)-5,6-dihydro-2*H*-pyran-2-yl)hex-3-ynoate (2a):** A solution of Tri-O-acetyl-D-glucal (0.163 g, 0.6 mmol) and *R*-methyl 3-(dimethyl(phenyl)silyl)hexa-3,4-dienoate (R*$_a$-1**) (0.130 g, 0.5 mmol) in acetonitrile (1.0 mL) was chilled to -40 °C. Trimethylsilyltrifluoromethanesulfonate (0.097 mL, 0.5 mmol) was added slowly, and the reaction was stirred 1 hour at -40 °C. The reaction was quenched with saturated sodium bicarbonate, and extracted with ethyl acetate (2 X 5 mL). The combined organic layers were washed with water, dried with magnesium sulfate, filtered and evaporated. Purification over silica gel (gradient elution, 80:20 to 70:30 hexanes: ethyl acetate) yields **2a** (0.128 g., 0.378 mmol, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.29 (d, J=10.4, 1H), 5.82 (d, J=10.4, 1H), 5.13 (m, 1H), 4.14 (m, 2H), 4.00 (m, 1H), 3.88 (m, 1H), 3.72 (s, 3H), 3.25 (d, J=2.0, 2H), 2.70 (m, 1H), 2.07 (s, 3H), 2.06 (s, 3H), 1.26 (d, J=6.8, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.7, 170.3, 168.9, 131.7, 124.4, 84.3, 75.0,

74.2, 69.9, 64.9, 62.9, 52.4, 30.0, 25.7, 21.0, 20.7, 17.8; IR (film) υ_{max} 2955, 1743, 1371, 1232, 1194 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{17}H_{22}O_7$ [M+Na^+] 361.1263, found: 361.1254; $[\alpha]_D^{20}$ -6.2 (c 3.2, CH_2Cl_2).



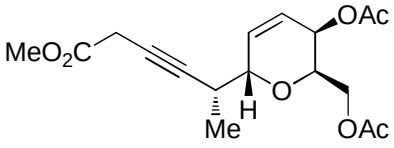
2b

R*-methyl 5-((2*S*,5*S*,6*R*)-5-acetoxy-6-(acetoxymethyl)-5,6-dihydro-2*H*-pyran-2-yl)hex-3-ynoate (2a):** Same procedure as **2a** using *S*-methyl 3-(dimethyl(phenyl)silyl)hexa-3,4-dienoate (S*$_a$-1**) (0.130 g, 0.5 mmol) gives **2b** (0.109 g., 0.322 mmol, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.05 (d, J=11.6, 1H), 5.93 (m, 1H), 5.03 (s, 1H), 4.26 (m, 1H), 4.21 (m, 2H), 4.13 (m, 1H), 3.71 (s, 3H), 3.26 (d, J=2.0, 2H), 2.79 (m, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 1.18 (d, J=6.8, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.8, 170.5, 169.0, 131.2, 124.4, 84.4, 74.0, 72.9, 71.6, 64.6, 62.3, 52.5, 30.3, 25.8, 21.0, 20.8, 16.1; IR (film) υ_{max} 2955, 1741, 1371, 1232, 1193 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{17}H_{22}O_7$ [M+Na^+] 361.1263, found: 361.1269; $[\alpha]_D^{20}$ +79.1 (c 1.1, CH_2Cl_2).



3a

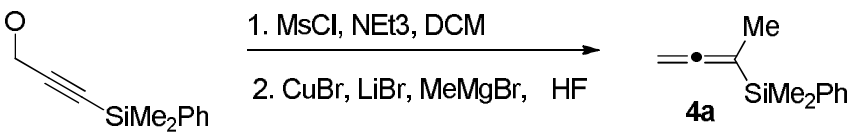
***S*-methyl 5-((2*S*,5*R*,6*R*)-5-acetoxy-6-(acetoxymethyl)-5,6-dihydro-2*H*-pyran-2-yl)hex-3-ynoate (3a):** Same procedure as **2a** using Tri-O-acetyl-D-galactal (0.163 g, 0.6 mmol) gives **3a** (0.117 g., 0.346 mmol, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.42 (dd, J=2.8, 7.6, 1H), 6.03 (m, 1H), 5.03 (m, 1H), 4.16 (m, 2H), 4.07 (m, 2H), 3.71 (s, 3H), 3.25 (d, J=2.4, 2H), 2.70 (m, 1H), 2.06 (s, 3H), 2.05 (s, 3H), 1.25 (d, J=6.8, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6, 170.5, 168.9, 133.7, 122.3, 84.2, 75.8, 74.3, 68.4, 63.4, 63.0, 52.5, 28.9, 25.7, 20.9, 20.7, 17.8; IR (film) υ_{max} 2956, 1731, 1369, 1223, 1191 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{17}H_{22}O_7$ [M+Na^+] 361.1263, found: 361.1278; $[\alpha]_D^{20}$ -159.8 (c 3.6, CH_2Cl_2).



3b

R*-methyl 5-((2*S*,5*R*,6*R*)-5-acetoxy-6-(acetoxymethyl)-5,6-dihydro-2*H*-pyran-2-yl)hex-3-ynoate (3b):** Same procedure as **3a** using *S*-methyl 3-(dimethyl(phenyl)silyl)hexa-3,4-dienoate (S*$_a$-1**) (0.130 g, 0.5 mmol) gives **3b** (0.082 g., 0.247 mmol, 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.05 (s, 2H), 5.16 (d, J=3.2, 1H), 4.58 (m, 1H), 4.19 (m, 3H), 3.70 (s, 3H), 3.23 (d, J=2.4, 2H), 2.72 (m, 1H), 2.06 (s, 3H), 2.04 (s, 3H), 1.24 (d, J=6.8, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.8, 170.5, 168.9, 132.2, 123.8, 84.5, 74.1, 74.1, 69.5, 64.0, 62.5, 52.5, 30.4, 25.8, 20.9, 20.8, 17.0; IR (film) υ_{max} 2956, 1742, 1372, 1232, 1197 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{17}H_{22}O_7$ [M+Na^+] 361.1263, found: 361.1274; $[\alpha]_D^{20}$ -46.8 (c 3.2, CH_2Cl_2).

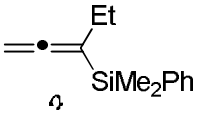
Preparation of Achiral Allenylsilanes (4a-c):



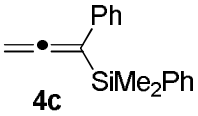
4a

Buta-2,3-dien-2-yldimethyl(phenyl)silane (4a): A solution of 3-(dimethyl(phenyl)silyl)-prop-2-yn-1-ol (1.90 g., 10 mmol) and triethylamine (1.21 g., 12 mmol) in DCM (10mL) was chilled

to -50 °C. Methanesulfonyl chloride (0.85 mL, 11 mmol) was added slowly, and the reaction was warmed to room temperature and stirred 45 minutes. The reaction was quenched with water, extracted with DCM (3 X 15 mL), washed with water, dried with magnesium sulfate, filtered and the solvents were removed under vacuum. A solution of copper bromide (1.72 g., 12 mmol) and lithium bromide (1.04 g., 12 mmol) in THF (10 mL) was chilled to 0 °C. MeMgBr (1.4M in THF, 8.57 mL, 12 mmol) was added slowly and the reaction was stirred 15 min at 0 °C. A solution of the crude mesylate in THF (10 mL) was then added, and the reaction was stirred 12 hours warming from 0 °C to room temperature. The reaction was quenched with sat NH_4Cl, extracted with ether (3 X 15 mL), washed with water, dried with magnesium sulfate, filtered and the solvents were removed under vacuum. Purification over silica gel (98:2 hexanes: ethyl acetate) yields **4a** (1.45 g., 7.68 mmol, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (m, 2H), 7.35 (m, 3H), 4.32 (m, 2H), 1.65 (m, 3H), 0.36 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.8, 137.8, 133.8, 129.1, 127.8, 88.0, 67.9, 15.5, -3.4; IR (film) υ_{max} cm^{-1} 3069, 2960, 2917, 1932, 1250, 1112.

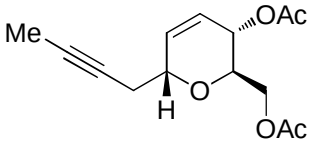


Dimethyl(penta-1,2-dien-3-yl(phenyl)silane (4b): Same procedure as **4a** using ethyl magnesium bromide (3.0M in diethyl ether, 4.0 mL, 12 mmol) yields **4b** (1.27 g., 6.28 mmol, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (m, 2H), 7.34 (m, 3H), 4.42 (m, 2H), 1.91 (m, 2H), 0.99 (t, J=7.6, 3H), 0.36 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.1, 138.1, 133.8, 129.0, 127.7, 95.1, 70.0, 22.0, 13.4, -3.1; IR (film) υ_{max} cm^{-1} 3069, 2963, 2931, 1926, 1250, 1112.



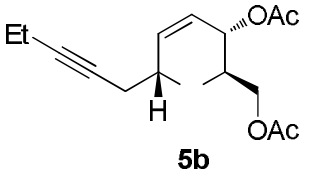
4c

Dimethyl(phenyl)(1-phenylpropa-1,2-dien-1-yl)silane (4c): Same procedure as **4a** using phenyl magnesium bromide (1.8M in THF, 6.67 mL, 12 mmol) yields **4c** (1.75 g., 6.99 mmol, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (m, 2H), 7.41 (m, 1H), 7.34 (m, 3H), 7.19 (m, 3H), 7.11 (m, 1H), 4.75 (s, 2H), 0.45 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 212.3, 138.2, 136.5, 133.9, 129.2, 128.4, 127.9, 127.8, 126.2, 97.0, 71.2, -1.9; IR (film) υ_{max} cm^{-1} 3066, 2959, 1917, 1490, 1251, 1111.



5a

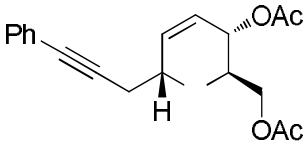
((2*R*,3*S*,6*R*)-3-acetoxy-6-(but-2-yn-1-yl)-3,6-dihydro-2*H*-pyran-2-yl)methyl acetate (5a): Same procedure as **2a** using Buta-2,3-dien-2-yldimethyl(phenyl)silane (**4a**) (0.094 g, 0.5 mmol) gives **5a** (0.124 g., 0.466 mmol, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.08 (d, J=10.4, 1H), 5.83 (d, J=10.4, 1H), 5.10 (m, 1H), 4.31 (m, 1H), 4.24 (m, 1H), 4.12 (m, 1H), 3.97 (m, 1H), 2.46 (m, 2H), 2.08 (s, 3H), 2.06 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.8, 170.3, 131.2, 124.0, 78.4, 74.4, 70.4, 70.3, 64.7, 62.6, 24.1, 21.0, 20.7, 3.4; IR (film) υ_{max} 2921, 1742, 1371, 1234, 1047 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{14}H_{18}O_5$ [M+Na^+] 289.1052, found: 289.1062; $[\alpha]_D^{20}$ +20.0 (c 6.0, CH_2Cl_2).



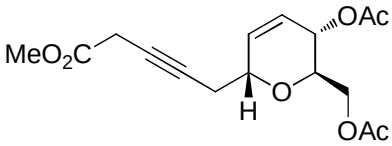
5b

((2*R*,3*S*,6*R*)-3-acetoxy-6-(pent-2-yn-1-yl)-3,6-dihydro-2*H*-pyran-2-yl)methyl acetate (5b): Same procedure as **2a** using Dimethyl(penta-1,2-dien-3-yl(phenyl)silane (**4b**) (0.101 g, 0.5 mmol) gives **5b** (0.124 g., 0.442 mmol, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.08 (d, J=10.8, 1H), 5.83 (d, J=10.4, 1H), 5.11 (m, 1H), 4.32 (m, 1H), 4.24 (m, 1H), 4.12 (m, 1H), 3.99 (m, 1H), 2.48 (m, 2H), 2.14 (q, J=7.6, 2H), 2.08 (s, 3H), 2.06 (s, 3H), 1.10 (t, J=7.6, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.8, 170.4, 131.1, 124.0, 84.2, 74.6, 70.4,

70.3, 64.7, 62.6, 24.2, 21.0, 20.7, 14.0, 12.3; IR (film) υ_{max} 2976, 2939, 1743, 1371, 1233, 1047 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{15}H_{20}O_5$ [M+Na^+] 303.1208, found: 303.1215; $[\alpha]_D^{20}$ +35.5 (c 1.8, CH_2Cl_2).

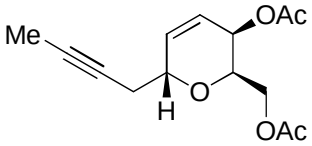


((2*R*,3*S*,6*R*)-3-acetoxy-6-(phenylprop-2-yn-1-yl)-3,6-dihydro-2*H*-pyran-2-yl)methyl acetate (5c): Same procedure as **2a** using Dimethyl(phenyl)(1-phenylpropa-1,2-dien-1-yl)silane (**4c**) (0.101 g, 0.5 mmol) gives **5c** (0.089 g., 0.271 mmol, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (m, 2H), 7.27 (m, 3H), 6.14 (d, J=10.4, 1H), 5.88 (d, J=10.4, 1H), 5.14 (m, 1H), 4.47 (m, 1H), 4.27 (m, 1H), 4.15 (m, 1H), 4.06 (m, 1H), 2.76 (m, 2H), 2.07 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.8, 170.4, 131.9, 131.6, 128.2, 127.9, 124.4, 123.3, 85.3, 82.9, 70.5, 70.2, 64.7, 62.6, 24.9, 21.0, 20.8; IR (film) υ_{max} 2918, 1743, 1370, 1231, 1046 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{19}H_{20}O_5$ [M+Na^+] 351.1208, found: 351.1216; $[\alpha]_D^{20}$ +30.0 (c 1.0, CH_2Cl_2).



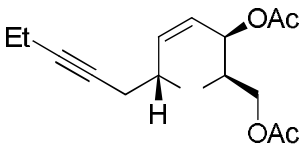
5d

Methyl 5-((2*R*,5*S*,6*R*)-5-acetoxy-6-(acetoxymethyl)-5,6-dihydro-2*H*-pyran-2-yl)pent-3-ynoate (5d): Same procedure as **2a** using Methyl 3-(dimethyl(phenyl)silyl)penta-3,4-dienoate (**4d**) (0.123 g, 0.5 mmol) gives **5d** (0.106 g., 0.327 mmol, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.09 (d, J=10.4, 1H), 5.84 (d, J=10.4, 1H), 5.12 (m, 1H), 4.36 (m, 1H), 4.24 (m, 1H), 4.13 (m, 1H), 3.97 (m, 1H), 3.72 (s, 3H), 3.25 (d, J=2.4, 2H), 2.54 (m, 2H), 2.08 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.8, 170.4, 168.9, 131.8, 124.3, 79.1, 74.0, 70.3, 70.2, 64.7, 62.5, 52.5, 25.8, 24.2, 21.0, 20.8; IR (film) υ_{max} 2956, 1740, 1372, 1229, 1045 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{16}H_{20}O_7$ [M+Na^+] 347.1107, found: 347.1107; $[\alpha]_D^{20}$ +29.1 (c 2.4, CH_2Cl_2).



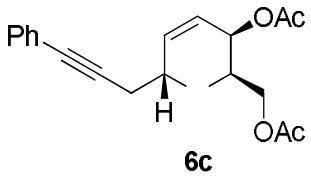
6a

((2*R*,3*R*,6*R*)-3-acetoxy-6-(but-2-yn-1-yl)-3,6-dihydro-2*H*-pyran-2-yl)methyl acetate (6a): Same procedure as **5a** using Tri-O-acetyl-D-galactal (0.163 g, 0.6 mmol) gives **6a** (0.109 g., 0.409 mmol, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.17 (m, 1H), 6.01 (m, 1H), 5.07 (d, J=4.8, 1H), 4.40 (m, 1H), 4.17 (m, 3H), 2.44 (m, 2H), 2.06 (s, 3H), 2.05 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6, 170.4, 133.9, 122.5, 78.0, 74.3, 71.3, 68.5, 63.5, 62.7, 23.2, 20.8, 20.7, 3.4; IR (film) υ_{max} 2921, 1734, 1372, 1230, 1094 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{14}H_{18}O_5$ [M+Na^+] 289.1052, found: 289.1066; $[\alpha]_D^{20}$ -152.0 (c 2.5, CH_2Cl_2).



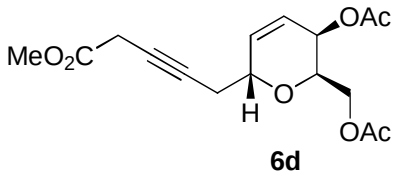
6b

((2*R*,3*R*,6*R*)-3-acetoxy-6-(pent-2-yn-1-yl)-3,6-dihydro-2*H*-pyran-2-yl)methyl acetate (6b): Same procedure as **5b** using Tri-O-acetyl-D-galactal (0.163 g, 0.6 mmol) gives **6b** (0.121 g., 0.432 mmol, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.18 (m, 1H), 6.01 (m, 1H), 5.07 (d, J=4.8, 1H), 4.41 (m, 1H), 4.18 (s, 3H), 2.46 (m, 2H), 2.14 (q, J=7.6, 2H), 2.06 (s, 3H), 2.05 (s, 3H), 1.10 (t, J=7.6, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6, 170.4, 133.8, 122.4, 84.1, 74.5, 71.2, 68.5, 63.4, 62.6, 23.2, 20.8, 20.7, 14.0, 12.3; IR (film) υ_{max} 2975, 2934, 1742, 1371, 1232, 1094 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{15}H_{20}O_5$ [M+Na^+] 303.1208, found: 303.1207; $[\alpha]_D^{20}$ -100.0 (c 3.8, CH_2Cl_2).



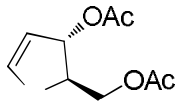
6c

((2*R*,3*R*,6*R*)-3-acetoxy-6-(phenylprop-2-yn-1-yl)-3,6-dihydro-2*H*-pyran-2-yl)methyl acetate (6c): Same procedure as **5c** using Tri-O-acetyl-D-galactal (0.163 g, 0.6 mmol) gives **6c** (0.064 g., 0.195 mmol, 39% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 2H), 7.28 (m, 3H), 6.26 (m, 1H), 6.08 (m, 1H), 5.12 (d, J=4.8, 1H), 4.56 (m, 1H), 4.23 (m, 3H), 2.76 (m, 2H), 2.07 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.8, 170.5, 133.7, 131.6, 128.2, 128.0, 123.3, 122.9, 85.2, 82.9, 71.1, 68.7, 63.5, 62.7, 24.0, 20.9, 20.8; IR (film) υ_{max} 2925, 1735, 1370, 1228, 1094 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{19}H_{20}O_5$ [M+Na$^+$] 351.1208, found: 351.1201; $[\alpha]_D^{20}$ -22.9 (c 6.1, CH_2Cl_2).

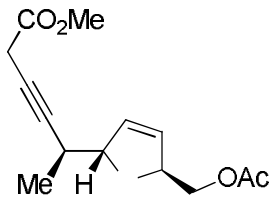


6d

Methyl 5-((2*R*,5*R*,6*R*)-5-acetoxy-6-(acetoxymethyl)-5,6-dihydro-2*H*-pyran-2-yl)pent-3-ynoate (5d): Same procedure as **5d** using Tri-O-acetyl-D-galactal (0.163 g, 0.6 mmol) gives **6d** (0.102 g., 0.314 mmol, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.18 (m, 1H), 6.04 (m, 1H), 5.08 (d, J=5.2, 1H), 4.44 (m, 1H), 4.19 (s, 3H), 4.19 (s, 3H), 3.25 (d, J=1.6, 2H), 2.52 (m, 2H), 2.06 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.7, 170.5, 168.9, 133.6, 122.8, 79.1, 74.0, 70.9 68.6, 63.4, 62.7, 52.5, 25.8, 23.3, 20.9, 20.8; IR (film) υ_{max} 2955, 1734, 1370, 1228, 1093 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{16}H_{20}O_7$ [M+Na$^+$] 347.1107, found: 347.1113; $[\alpha]_D^{20}$ -77.7 (c 2.7, CH_2Cl_2).



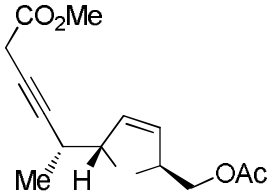
((2*R*,3*S*)-3-acetoxy-2,3-dihydrofuran-2-yl)methyl acetate (7): Acetic anhydride (11.23 g., 110 mmol) was added to a solution of D-Ribose (3.0 g., 20 mmol) and pyridine (9.49 g., 120 mmol) in DCM (20 mL). The resulting solution was stirred for 12 hours at room temperature. The reaction was quenched with water (20 mL), extracted with DCM (3X 20 mL), washed with water, dried with magnesium sulfate, filtered and the solvents were removed under vacuum. The crude product was filtered through a plug of silica, washed with 20% ethyl acetate in hexanes, concentrated and used crude for the next step. The crude ribose tetra-acetate was mixed in HBr (33 wt % in acetic acid, 10.36 mL, 60 mmol), and stirred 5 hours at room temperature. The reaction was diluted with MeCN (20 mL), and sodium acetate (3.28 g., 40 mmol), ammonium chloride (3.21 g., 60 mmol), and zinc dust (3.93 g., 40 mmol) are added sequentially. The reaction is stirred for 2 hours at room temperature, then quenched with water, extracted with ethyl acetate (3X25 mL), washed with water, dried with magnesium sulfate, filtered and the solvents are removed under vacuum. Purification over silica gel (gradient elution, 95:5 to 85:15 hexanes: ethyl acetate) yields **7** (1.33 g., 6.64 mmol, 33 % yield from D-Ribose).



?a

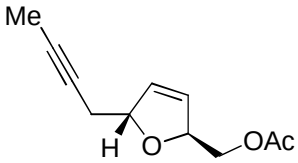
(*S*)-methyl 5-((2*S*,5*S*)-5-(acetoxymethyl)-2,5-dihydrofuran-2-yl)hex-3-ynoate (8a): Same procedure as **2a** using ((2*R*,3*S*)-3-acetoxy-2,3-dihydrofuran-2-yl)methyl acetate (**7**) (0.120 g, 0.6 mmol) gives **8a** (0.055 g., 0.203 mmol, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.99 (d, J=10.4, 1H), 5.91 (d, J=10.8, 1H), 5.28 (m, 1H), 4.20 (m, 2H), 3.71 (s, 3H), 3.47 (m, 1H), 3.25 (s, 2H), 2.73 (m, 1H), 2.05 (s, 3H), 1.13 (d, J=7.2, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5, 169.1, 130.7, 126.6, 84.3,

75.8, 73.7, 65.7, 64.9, 52.5, 30.6, 25.8, 21.0, 15.5; IR (film) υ_{max} 2976, 2938, 1736, 1372, 1231, 1174 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{14}H_{18}O_5$ [M+Na^+] 289.1052, found: 289.1061; $[\alpha]_D^{20}$ +56.5 (c 2.3, CH_2Cl_2).



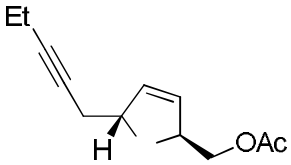
8b

(*R*)-methyl 5-((2*S*,5*S*)-5-(acetoxymethyl)-2,5-dihydrofuran-2-yl)hex-3-ynoate (8a): Same procedure as **2b** using ((2*R*,3*S*)-3-acetoxy-2,3-dihydrofuran-2-yl)methyl acetate (**7**) (0.120 g, 0.6 mmol) gives **8b** (0.048 g., 0.180 mmol, 36% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.20 (d, J=10.4, 1H), 5.89 (d, J=10.4, 1H), 5.19 (m, 1H), 4.08 (dd, J=4.8, 6.8, 1H), 3.96 (m, 1H), 3.71 (s, 3H), 3.53 (dd, J=4.8, 6.4, 1H), 3.26 (d, J=2.4, 2H), 2.59 (m, 1H), 2.05 (s, 3H), 1.21 (d, J=6.8, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6, 169.1, 132.3, 124.9, 84.4, 76.3, 73.8, 64.9, 64.6, 52.5, 30.5, 25.8, 21.0, 17.1; IR (film) υ_{max} 2956, 1732, 1371, 1230, 1128 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{14}H_{18}O_5$ [M+Na^+] 289.1052, found: 289.1049; $[\alpha]_D^{20}$ +47.2 (c 2.8, CH_2Cl_2).



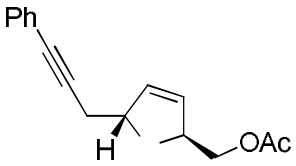
9a

((2*S*,5*R*)-5-(but-2-yn-1-yl)-2,5-dihydrofuran-2-yl)methyl acetate (9a): Same procedure as **5a** using ((2*R*,3*S*)-3-acetoxy-2,3-dihydrofuran-2-yl)methyl acetate (**7**) (0.120 g, 0.6 mmol) gives **9a** (0.090 g., 0.436 mmol, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.03 (d, J=10.4, 1H), 5.87 (d, J=10.0, 1H), 5.23 (m, 1H), 4.21 (m, 1H), 4.11 (dd, J=5.2, 6.4, 1H), 3.54 (dd, J=4.8, 6.8, 1H), 2.36 (m, 2H), 2.06 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5, 132.8, 124.8, 77.9, 74.5, 72.3, 65.2, 64.7, 24.7, 21.0, 3.5; IR (film) υ_{max} 2921, 1737, 1372, 1235, 1094 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{11}H_{14}O_3$ [M+Na^+] 217.0841, found: 217.0845; $[\alpha]_D^{20}$ +112.1 (c 3.3, CH_2Cl_2).



9b

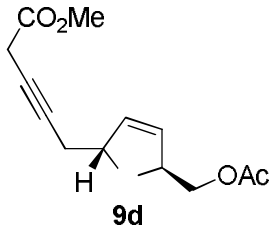
((2*S*,5*R*)-5-(pent-2-yn-1-yl)-2,5-dihydrofuran-2-yl)methyl acetate (9b): Same procedure as **5b** using ((2*R*,3*S*)-3-acetoxy-2,3-dihydrofuran-2-yl)methyl acetate (**7**) (0.120 g, 0.6 mmol) gives **9b** (0.092 g., 0.442 mmol, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.05 (d, J=10.4, 1H), 5.87 (d, J=10.4, 1H), 5.22 (m, 1H), 4.21 (m, 1H), 4.11 (dd, J=5.2, 6.4, 1H), 3.54 (dd, J=4.8, 6.8, 1H), 2.39 (m, 2H), 2.15 (q, J=7.2, 2H), 2.05 (s, 3H), 1.10 (t, J=7.6, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5, 132.9, 124.7, 84.1, 74.7, 72.3, 65.1, 64.7, 24.7, 21.0, 14.1, 12.4; IR (film) υ_{max} 2975, 2936, 1738, 1373, 1236, 1094 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{12}H_{16}O_3$ [M+Na^+] 231.0997, found: 231.0997; $[\alpha]_D^{20}$ +113.3 (c 3.0, CH_2Cl_2).



9c

((2*S*,5*R*)-5-(3-phenylprop-2-yn-1-yl)-2,5-dihydrofuran-2-yl)methyl acetate (9c): Same procedure as **5c** using ((2*R*,3*S*)-3-acetoxy-2,3-dihydrofuran-2-yl)methyl acetate (**7**) (0.120 g, 0.6 mmol) gives **9c** (0.057 g., 0.222 mmol, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 2H), 7.27 (m, 3H), 6.13 (d, J=10.4, 1H), 5.92 (d, J=10.4, 1H), 5.25 (m, 1H), 4.34 (m, 1H), 4.16 (dd, J=5.2, 6.8, 1H), 3.59 (dd, J=5.2, 6.4, 1H), 2.66 (m, 2H), 2.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5,

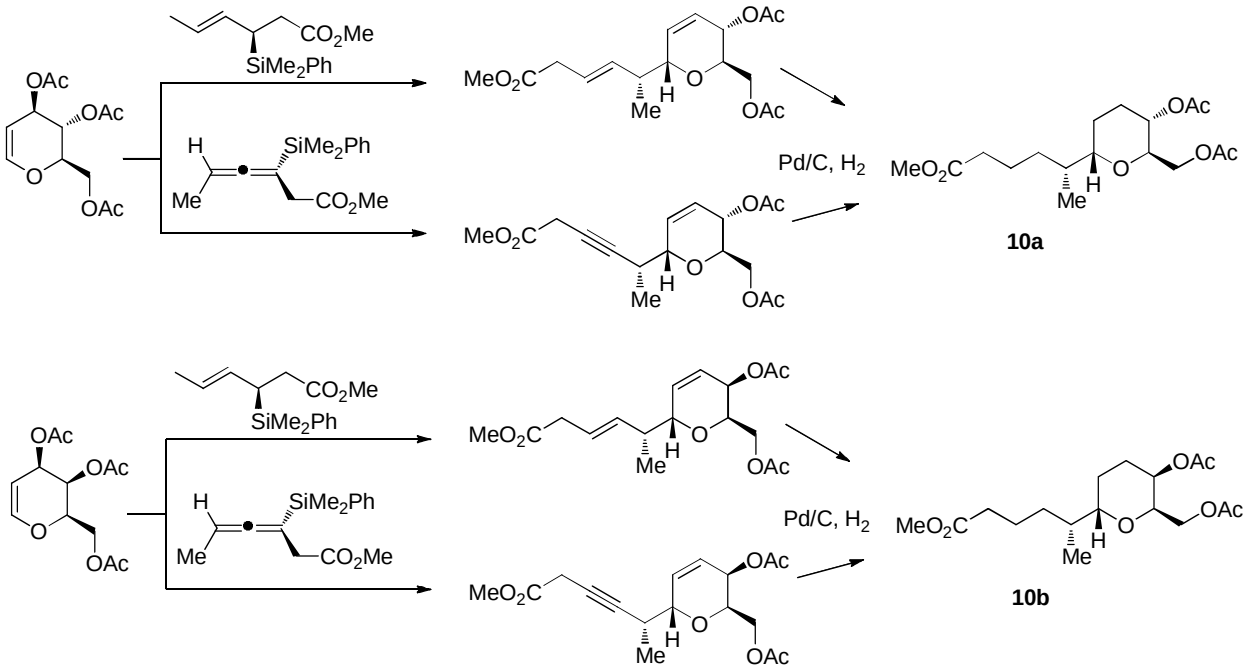
132.7, 131.6, 128.2, 127.9, 125.0, 123.3, 85.3, 82.7, 72.0, 65.2, 64.6, 25.3, 21.0; IR (film) υ_{max} 2929, 1736, 1490, 1372, 1236, 1094 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{16}H_{16}O_3$ [M+H^+] 257.1178, found: 257.1184; $[\alpha]_D^{20}$ +36.5 (c 4.2, CH_2Cl_2).



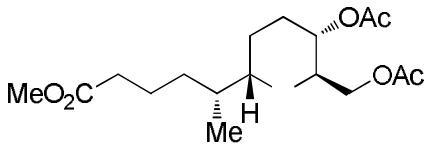
9d

methyl 5-((2*R*,5*S*)-5-(acetoxymethyl)-2,5-dihydrofuran-2-yl)pent-3-ynoate (9d): Same procedure as **5d** using ((2*R*,3*S*)-3-acetoxy-2,3-dihydrofuran-2-yl)methyl acetate (**7**) (0.120 g, 0.6 mmol) gives **9d** (0.068 g., .0269 mmol, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.05 (d, J=10.4, 1H), 5.88 (d, J=10.4, 1H), 5.22 (m, 1H), 4.26 (m, 1H), 4.11 (dd, J=4.8, 6.4, 1H), 3.72 (s, 3H), 3.54 (dd, J=4.8, 6.4, 1H), 3.26 (d, J=2.0, 2H), 2.45 (m, J=2H), 2.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6, 169.0, 132.6, 125.0, 79.2, 73.8, 71.9, 65.1, 64.6, 52.5, 25.8, 24.7, 21.1; IR (film) υ_{max} 2955, 1736, 1372, 1235, 1093 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{13}H_{16}O_5$ [M+Na^+] 275.0895, found: 275.0890; $[\alpha]_D^{20}$ +110.0 (c 1.0, CH_2Cl_2).

Confirmation of the relative and absolute stereochemistry of the products:



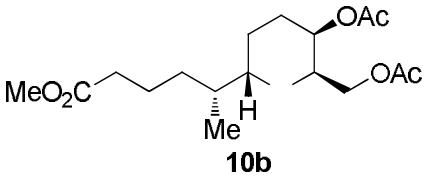
The products of the *C*-glycosidation reactions with the (*R*)-enatiomer of the crotylsilane, which was previously reported by our lab were compared to the products obtained with the (S_a)-enantiomer of the allenylsilane. After hydrogenation both reaction products were identical by NMR analysis and optical rotation. This sequence was carried out to assign the stereochemistry of both diastereomers, derived from glucal and galactal.



10a

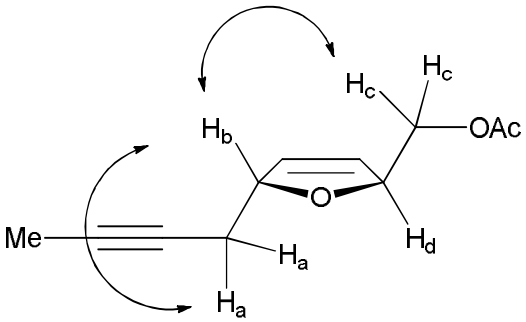
***R*-methyl 5-((2*S*,5*S*,6*R*)-5-acetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)hexanoate (10a):** ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.71 (m, 1H), 4.32 (q, J=7.2, 1H), 4.05 (dd, J=4.4, 6.8, 1H), 3.89 (m, 1H), 3.65 (s, 3H), 3.35 (m, 1 H), 2.28 (m, 2H), 2.06 (s, 3H), 2.05 (s, 3H), 1.85 (m, 1H), 1.68 (m, 7H), 1.07 (m, 1H), 0.84 (d, J=6.4, 3H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 174.0, 170.8, 170.3, 75.3, 72.0, 67.6, 62.2, 51.4, 34.6, 34.4, 31.7, 24.4, 23.3, 22.2, 21.2, 20.8, 15.2; IR (film) υ_{max} 2954, 1737, 1368, 1232, 1040 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{17}H_{28}O_7$ [M+Na$^+$] 367.1733, found: 367.1729; $[\alpha]_D^{20}$ +15.5 (from alkyne c 4.5, CH_2Cl_2), +15.4 (from alkene c 4.2, CH_2Cl_2).



10b

***R*-methyl 5-((2*S*,5*R*,6*R*)-5-acetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)hexanoate (10b):** ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.93 (m, 1H), 4.39 (m, 1H), 4.06 (m, 2H), 3.64 (s, 3H), 3.40 (m, 1 H), 2.82 (m, 2H), 2.05 (s, 6H), 1.81 (m, 6H), 1.50 (m, 2H), 1.09 (m, 1H), 0.84 (d, J=6.4, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.0, 170.8, 170.2, 74.6, 68.3, 61.1, 51.4, 34.3, 34.2, 31.9, 24.0, 23.8, 22.1, 21.0, 20.8, 15.4; IR (film) υ_{max} 2955, 1737, 1372, 1232, 1049 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{17}H_{28}O_7$ [M+Na$^+$] 367.1733, found: 367.1729; $[\alpha]_D^{20}$ +14.5 (from alkyne c 3.2, CH_2Cl_2), +14.6 (from alkene c 2.6, CH_2Cl_2).



The relative stereochemistry of the dihydrofuran products was determined using NOESY. Proton H_b shows distinct correlation to H_a and H_c, but does not show a correlation to proton H_d. These measurements confirm the expected addition to the nucleophile to the α-face of the oxonium ion.