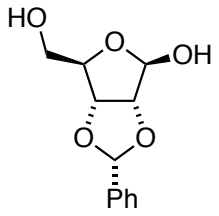
Alkynylation of Pentose Derivatives with Stereochemical Fidelity: Implications for the Regioselectivity of Alkynyl Diol Cycloisomerizations to Cyclic Enol Ethers

Frank E. McDonald,* Dian Ding, Andrew J. Ephron,† and John Bacsa
Department of Chemistry, Emory University, Atlanta, Georgia 30322, United States
e-mail: fmcdona@emory.edu

SUPPORTING INFORMATION: Experimental details and characterization data

General experimental: Proton and carbon NMR spectra were recorded on MERCURY 300 (300 MHz), INOVA-400 (400 MHz), VNMR 400 (400 MHz), INOVA-500 (500 MHz), INOVA-600 (600 MHz), or a BRUKER 600 (600 MHz) instrument equipped with cryogen probe. NMR spectra were recorded in solutions of deuterated chloroform ($CDCl_3$) with the residual chloroform (7.27 ppm for ^1H NMR and 77.23 ppm for ^{13}C NMR) taken as the internal standard, or in deuterated dimethyl sulfoxide (DMSO-d_6) and were reported in parts per million (ppm). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublet; ddd, doublet of doublet of doublet; dt, doublet of triplet; m, multiplet. IR spectra were collected on a Nicolet iS10 from Thermo Scientific and reported in units of cm^{-1}. Mass spectra (high resolution ESI and APCI) were recorded on a Finnigan LTQ FTMS Mass spectrometer. Optical rotations were measured using a Perkin-Elmer 341 polarimeter (concentration in g/100mL). X-ray crystallographic characterization was conducted on a Bruker APEX-II CCD diffractometer. Melting points were measured on a Barnstead Model 1001 Capillary Melting Point Apparatus. Thin layer chromatography (TLC) was performed on pre-coated glass-backed plates purchased from Whatman (silica gel 60F254; 0.25mm thickness). Flash column chromatography was carried out with silica gel 60 (230-400 mesh ASTM) from Silicycle. All reactions were carried out with anhydrous solvents in oven-dried or flame-dried and argon-charged glassware unless otherwise specified. All anhydrous solvents were purchased from Sigma-Aldrich. Other solvents used in extraction procedures and chromatography were used as received from commercial suppliers without prior purification.



5

Preparation of 2,3-benzylidene-protected ribofuranose 5: In a 500 mL round-bottom flask, D-ribofuranose (**4**, 10.0 g, 66.6 mmol) was dissolved in DMF (45 mL). Then, distilled benzaldehyde (27.2 mL, 266 mmol) and camphorsulfonic acid (CSA, 7.74 g, 33.3 mmol) were added. The reaction mixture was stirred for three days under a balloon of argon, then quenched with triethylamine (30 mL), diluted with dichloromethane (70 mL), filtered through Celite, and concentrated by rotary evaporation. The solution was then filtered through silica gel, eluting with ethyl acetate, and reconcentrated. Then, the solution was diluted with dichloromethane, and washed with water (3 x 100 mL) to remove DMF. The combined aqueous layers were extracted with dichloromethane (3 x 100 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The resulting solid was purified by silica gel flash column chromatography (3:2 EtOAc:Hexane → pure EtOAc), yielding **5** as a white solid, as a 5 : 1 mixture of diastereomers (7.25 g, 30.4 mmol, 46% yield). A pure sample of the major diastereomer was isolated by a second chromatographic purification.

On a larger scale, D-ribofuranose (**4**, 20.4 g, 133 mmol) was converted into compound **5** (10.97 g, 46.1 mmol, 35% yield of a 5 : 1 mixture of diastereomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.43 – 7.37 (m, 3H), 5.78 (s, 1H), 5.58 (d, *J* = 6.7 Hz, 1H), 4.94 (dq, *J* = 6.2, 0.6 Hz, 1H), 4.70 (d, *J* = 6.2 Hz, 1H), 4.65 – 4.58 (m, 1H), 4.30 (d, *J* = 6.7 Hz, 1H), 3.85 – 3.75 (m, 2H), 3.23 (dd, *J* = 7.3, 3.1 Hz, 1H), 1.64 (s, 2H).

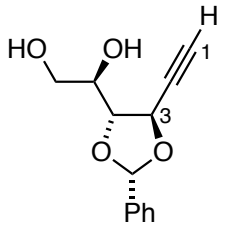
^{13}C NMR (126 MHz, $CDCl_3$) δ 135.7, 130.0, 128.7, 126.9, 105.8, 102.5, 87.5, 82.6, 63.6.

FT-IR ν_{max}/cm^{-1} 3391 (OH), 2939 (CH).

HRMS Anal. Calcd. for $C_{12}H_{14}O_5Na$ (M+23) 261.07343; found: 261.07334.

Melting point 102.6 – 104.3 °C.

Optical rotation $[\alpha]_D^{20}$ -23.1 (c 0.31, $CHCl_3$).



7

Preparation of alkynyl diol 7: In a 1 L 3-neck flask, compound **5** (9.0 g, 41 mmol) was dissolved in methanol (250 mL). Potassium carbonate (11 g, 82 mmol) was added, and the mixture was stirred under argon atmosphere. A reflux condenser was attached, and the solution was heated to 65 °C. The Ohira-Bestmann reagent **6** (15.75 g, 82 mmol)[1] was dissolved in methanol (120 mL), and this solution was added *via* syringe pump over 12 hours, and then stirred for 12 additional hours. The reaction mixture was quenched with 1M aqueous acetic acid (82 mL). The solution was then concentrated by rotary evaporation. The concentrated solution was extracted with dichloromethane (3 x 100 mL). The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated. The resulting solid was purified by silica gel flash column chromatography (1:1→3:1 EtOAc:Hexane), yielding alkynyl diol **7** as an oil (4.58 g, 20.6 mmol, 51% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 2H), 7.43 – 7.38 (m, 3H), 6.02 (s, 1H), 4.97 (dd, *J* = 5.0, 2.1 Hz, 1H), 4.25 (dd, *J* = 5.8, 5.0 Hz, 1H), 3.91 (dd, *J* = 5.8, 3.6 Hz, 1H), 3.85 (dd, *J* = 11.4, 3.6 Hz, 1H), 3.76 (dd, *J* = 11.4, 5.7 Hz, 1H), 2.79 (s, 1H), 2.62 (d, *J* = 2.1 Hz, 1H). 1.57 (br, 1H).

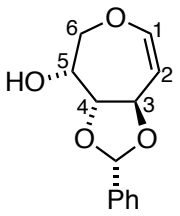
^{13}C NMR (151 MHz, $CDCl_3$) δ 135.9, 130.0, 128.6, 126.8, 103.8, 83.3, 81.2, 75.5, 71.8, 67.5, 63.3.

FT-IR ν_{max}/cm^{-1} 3279 (OH), 2926 (CH).

HRMS Anal. Calcd. for $C_{13}H_{14}O_4Na$ (M+23) 257.07849; found: 235.07843.

Optical rotation $[\alpha]_D^{20}$ -19.3 (c 0.33, $CHCl_3$).

[1] Pietruszka, J.; Witt, A. Synthesis of the Bestmann-Ohira Reagent. *Synthesis* **2006**, 4266-4268.



8, D-*arabino*

Preparation of D-*arabino*-septanose glycal 8: In a 500 mL Schlenk flask, alkynyl diol **7** (4.58 g, 20.6 mmol) was dissolved in toluene (200 mL). Then 1,4-diazabicyclo[2.2.2]octane (DABCO, 4.62 g, 41.2 mmol) and tungsten hexacarbonyl (1.81 g, 5.15 mmol) were added. The flask was transferred to a Rayonet photoreactor, a reflux condensor was added, and the mixture was stirred under a steady flow of argon. The reaction mixture was irradiated with 350 nm light for 12 hours, without using the cooling fan, so that the reaction mixture warmed to approximately 55 °C. The solution was then transferred to a 500 mL round bottom flask, and concentrated by rotary evaporation. The resulting yellow oil was purified by silica gel flash column chromatography (1:3→1:1 EtOAc:Hexane), yielding septanose glycal **8** as a white solid (1.43 g, 6.43 mmol, 31% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.48 (m, 2H), 7.44 – 7.39 (m, 3H), 6.41 (dd, *J* = 6.3, 2.1 Hz, 1H), 6.15 (s, 1H), 5.30 (dd, *J* = 6.3, 1.8 Hz, 1H), 5.02 (dt, *J* = 9.7, 1.8 Hz, 1H), 4.58 (dddd, *J* = 7.8, 5.8, 3.9, 1.9 Hz, 1H), 4.28 (dd, *J* = 12.5, 5.3 Hz, 1H), 4.06 (dd, *J* = 9.7, 3.9 Hz, 1H), 3.79 (dd, *J* = 12.5, 8.0 Hz, 1H), 2.42 (d, *J* = 2.0 Hz, 1H).

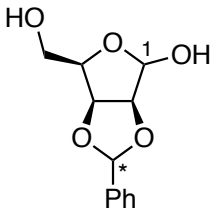
^{13}C NMR (126 MHz, $CDCl_3$) δ 148.6, 138.7, 129.4, 128.6, 126.3, 109.3, 104.4, 82.0, 72.9, 71.7, 66.0.

FT-IR ν_{max}/cm^{-1} 3444 (OH), 2884 (CH).

HRMS Anal. Calcd. for $C_{13}H_{15}O_4$ (M+1) 235.09649; found: 235.09640.

Melting point 87.5 – 88.6 °C.

Optical rotation $[\alpha]_D^{20}$ -46.0 (c 0.19, $CHCl_3$).



10a-10b (1 : 1 dr)*

Preparation of 2,3-benzylidene-protected lyxofuranose 10a and 10b: In a 250 mL oven-dried round bottom flask, D-lyxofuranose (**9**, 5.00 g, 33.3 mmol) was dissolved in DMF (17 mL). Then, distilled benzaldehyde (13.6 mL, 133 mmol) and CSA (3.87 g, 16.7 mmol) were added. The reaction mixture was stirred for 16 hours under a balloon of argon, then quenched with triethylamine (15 mL), diluted with dichloromethane (35 mL), filtered through Celite, and concentrated by rotary evaporation. The solution was filtered through silica gel eluting with ethyl acetate, and reconcentrated. Then, the solution was diluted with dichloromethane and washed with water (3 x 30 mL) to remove DMF. The combined aqueous layers were extracted with dichloromethane (3 x 100 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The resulting solid was purified by silica gel flash column chromatography (1:1→3:1 EtOAc:Hexane), yielding **10a** and **10b** as a white solid, as an 1:1 mixture of inseparable diastereomers (4.07 g, 17.4 mmol, 52% yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.47 – 7.36 (m, 5H), 6.52 (d, J = 4.3 Hz, 0.5H), 6.46 (d, J = 4.3 Hz, 0.5H), 5.79 (s, 0.5H), 5.72 (s, 0.5H), 5.32 (d, J = 4.4 Hz, 0.5H), 5.26 (d, J = 4.3 Hz, 0.5H), 4.85 (dd, J = 5.5, 3.7 Hz, 0.5H), 4.82 – 4.74 (m, 1.5H), 4.59 (d, J = 5.5 Hz, 0.5H), 4.53 (d, J = 6.2 Hz, 0.5H), 4.11 (dddd, J = 12.3, 6.8, 5.7, 3.5 Hz, 1H), 3.72 (ddt, J = 29.0, 10.9, 5.4 Hz, 1H), 3.60 (dddd, J = 11.1, 8.9, 6.3, 3.3 Hz, 1H).

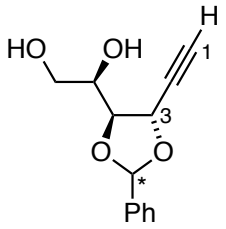
^{13}C NMR (126 MHz, $CDCl_3$) δ 136.2, 135.5, 130.1, 129.8, 128.5, 128.5, 127.0, 126.6, 106.33, 106.31, 105.65, 105.61, 101.2, 100.7, 86.2, 85.3, 81.0, 80.6, 80.0, 61.2.

FT-IR ν_{max}/cm^{-1} 3334, 3198 (OH), 2924 (CH).

HRMS Anal. Calcd. for $C_{12}H_{14}O_5Na$ (M+23) 261.07343; found: 261.07334.

Melting Point 98.5 – 99.4 °C.

Optical rotation $[\alpha]_D^{20}$ +25.2 (c 0.36, $CHCl_3$).



11a-11b (1 : 1 dr)*

Preparation of alkynyl diol 11a and 11b: In a 250 mL 3-neck flask, compound **10a-10b** (1.3 g, 5.5 mmol) was dissolved in methanol (28 mL). Potassium carbonate (1.50 g, 10.9 mmol) was added, and the mixture was stirred under argon atmosphere. A reflux condenser was attached, and the solution was heated to 65 °C. The Ohira-Bestmann reagent **6** (2.10 g, 10.9 mmol) was dissolved in methanol (16 mL), and this solution was added *via* syringe pump over 12 hours, and then stirred for 12 additional hours. The reaction mixture was quenched with 1M aqueous acetic acid (22 mL). The solution was then concentrated by rotary evaporation. The concentrated solution was extracted with dichloromethane (3 x 30 mL). The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated. The resulting solid was purified by silica gel flash column chromatography (1:1→3:1 EtOAc:Hexane), yielding **11a** and **11b** as a clear, colorless oil, as a 1:1 mixture of diastereomers (558 mg, 2.37 mmol, 43% yield). A small quantity of each diastereomer was purified for NMR characterization.

Alkynyl diol 11a (less polar diastereomer):

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.40 – 7.36 (m, 3H), 6.00 (s, 1H), 4.88 (dd, *J* = 5.9, 2.1 Hz, 1H), 4.30 (dd, *J* = 6.0, 3.7 Hz, 1H), 3.82-3.80 (m, 1H), 3.75 (d, *J* = 4.8 Hz, 1H), 2.63 (d, *J* = 2.1 Hz, 1H), 2.38 (br, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 135.7, 129.9, 128.5, 126.7, 104.0, 83.8, 80.6, 75.6, 70.4, 67.3, 64.0.

Alkynyl diol 11b (more polar diastereomer):

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.40 – 7.37 (m, 3H), 6.00 (s, 1H), 4.85 (dd, *J* = 7.7, 2.0 Hz, 1H), 4.12 (dd, *J* = 7.7, 2.4 Hz, 1H), 3.82 (dd, *J* = 8.6, 4.3 Hz, 1H), 3.78 (t, *J* = 5.4 Hz, 1H), 2.58 (d, *J* = 2.1 Hz, 1H), 2.48 (br, 2H).

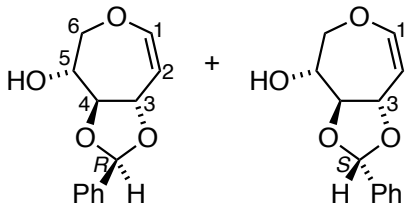
^{13}C NMR (151 MHz, $CDCl_3$) δ 136.7, 129.7, 128.4, 126.7, 105.3, 82.4, 78.8, 75.8, 69.7, 68.2, 64.5.

Alkynyl diol 11a-11b mixture:

FT-IR ν_{max}/cm^{-1} 3450 (OH), 3284 (CH alkyne), 2889 (CH alkane).

HRMS Anal. Calcd. for $C_{13}H_{15}O_4$ (M+1) 235.09628; found: 235.09649.

Optical rotation $[\alpha]_D^{20}$ +5.5 (c 0.86, $CHCl_3$).



12a D-*xylo* **12b**

Preparation of D-*xylo*-septanose glycals 12a and 12b

In a 50 mL Schlenk flask, the alkynyl diols **11a-11b** (558 mg, 2.37 mmol) were dissolved in toluene (20 mL). Then DABCO (570 mg, 4.7 mmol) and tungsten hexacarbonyl (230 mg, 0.593 mmol) were added. The flask was then transferred to a Rayonet photoreactor, a reflux condensor was added, and the mixture was stirred under a steady flow of argon. The reaction mixture was irradiated with 350 nm light for 12 hours**,** without using the cooling fan, so that the reaction mixture warmed to approximately 55 °C. The solution was then transferred to a 50 mL round bottom flask, and concentrated by rotary evaporation. The resulting yellow oil was purified by silica gel flash column chromatography (1:5→1:1 EtOAc:Hexane), yielding 1:1 mixture of diastereomers **12a** and **12b** (278 mg, 1.19 mmol, 50% yield). Some of the chromatography fractions yielded the separated diastereomers, affording **12a** (53.9 mg, 0.23 mmol) and **12b** (59.4 mg, 0.25 mmol).

Septanose glycal 12a (less polar diastereomer):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.40 – 7.36 (m, 3H), 6.42 (dd, *J* = 6.4, 2.0 Hz, 1H), 6.11 (s, 1H), 5.19 (dd, *J* = 6.5, 1.6 Hz, 1H), 4.66 (dt, *J* = 9.7, 1.8 Hz, 1H), 4.27 (dt, *J* = 7.4, 2.6 Hz, 1H), 4.17 (dd, *J* = 13.4, 2.1 Hz 1H), 4.16 (dd, *J* = 9.2, 7.5 Hz 1H), 4.03 (dd, *J* = 13.3, 3.2 Hz, 1H), 2.41 (br, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.2, 138.3, 129.4, 128.5, 126.3, 107.1, 104.6, 86.0, 75.4, 73.5, 72.7.

FT-IR ν_{max}/cm^{-1} 3456 (OH), 2919, 2852 (CH).

HRMS Anal. Calcd. for $C_{13}H_{15}O_4$ (M+1) 235.09649; found: 235.09643.

melting point 84.6 – 85.4 °C.

optical rotation $[\alpha]_D^{20}$ -10.0 (c 0.21, $CHCl_3$).

Septanose glycal 12b (more polar diastereomer):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.40-7.38 (m, 3H), 6.45 (dd, *J* = 6.5, 2.0 Hz, 1H), 6.08 (s, 1H), 5.25 (dd *J* = 6.4, 1.4 Hz, 1H), 4.72 (dt, *J* = 9.7, 1.8 Hz, 1H), 4.18 (dt, *J* = 10.4, 3.6 Hz, 1H), 4.13 (ddd, *J* = 13.2, 2.4, 1.1 Hz, 1H), 4.08 (dd, *J* = 13.4, 3.1 Hz, 1H), 4.05 (dd, *J* = 9.7, 7.5 Hz, 1H), 2.25 (d, 4.8 Hz, 1H).

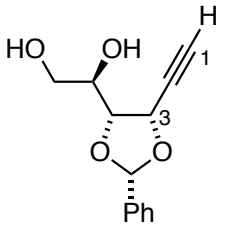
^{13}C NMR (126 MHz, $CDCl_3$) δ 151.3, 149.7, 129.4, 128.4, 126.5, 106.1, 104.4, 84.0, 75.6, 74.9, 73.3.

FT-IR ν_{max}/cm^{-1} 3537 (OH), 2912 (CH).

HRMS Anal. Calcd. for $C_{13}H_{15}O_4$ (M+1) 235.09649; found: 235.09654.

Melting Point 80.8 **–** 81.3 °C.

Optical rotation $[\alpha]_D^{20}$ +30.0 (c 0.16, $CHCl_3$).



14, D-*ribo*

Preparation of alkynyldiol 14: In a 50 mL round-bottom flask, *i*-Pr_2NH (0.95 mL, 6.76 mmol) was dissolved in THF (6 mL) and cooled to -78 °C. *n*-BuLi (1.58 M in hexanes, 4.30 mL, 6.76 mmol) was slowly added, and the resulting mixture was stirred for 20 min at -78 °C. A solution of $TMSCHN_2$ (2.0 M in hexanes, 1.27 mL, 2.54 mmol) was then added dropwise at -78 °C, and this mixture stirred for 20 minutes to generate a solution of lithium trimethylsilyldiazomethane (**13**). In a separate flask, the benzylidene-protected ribofuranose **5** (400 mg, 1.7 mmol) was dissolved in THF (2 mL), and this solution was added to the cold solution of **13**. The resulting mixture was stirred at -78 °C for 1 h, and then warmed to 65 °C for 2 h. The reaction mixture was quenched with crushed ice and saturated aqueous ammonium chloride. The aqueous layer was extracted with ethyl acetate, and the combined organic extracts were dried over Na_2SO_4 and concentrated by rotary evaporation. The crude product was a red residue containing a mixture of terminal alkynyl diol and trimethylsilyl-substituted alkyne, which was dissolved in methanol (0.65 mL) and aqueous potassium carbonate (10% w/w, 0.65 mL) and stirred for 2 h. This mixture was carefully neutralized with aqueous 1M HCl. The aqueous layer was extracted with ethyl acetate, and the combined organic extracts were dried over Na_2SO_4 and concentrated by rotary evaporation. Purification by flash chromatography (2:1 Ether/Hexane → 1:1 EtOAc/Hexane) afforded alkynyl diol **14** as a yellow oil (182 mg, 0.78 mmol, 46% yield).

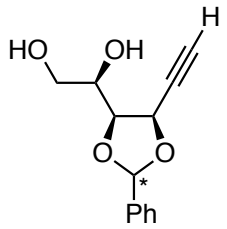
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.42 – 7.37 (m, 3H), 5.83 (s, 1H), 5.02 (dd, *J* = 6.3, 2.2 Hz, 1H), 4.22 (dd, *J* = 8.7, 6.3 Hz, 1H), 4.16 (ddd, *J* = 8.6, 5.1, 3.0 Hz, 1H), 3.92 (dd, *J* = 11.6, 3.0 Hz, 1H), 3.81 (dd, *J* = 11.6, 5.1 Hz, 1H), 2.98 (br, 1H), 2.71 (d, *J* = 2.2 Hz, 1H), 2.44 (br, 1H).

^{13}C NMR (151 Hz, $CDCl_3$) δ 136.3, 129.9, 128.6, 127.2, 105.3, 79.4, 78.9, 77.0, 71.2, 68.6, 64.0.

FT-IR ν_{max}/cm^{-1} 3394 (OH), 3285 (CH alkyne), 2926 (CH alkane).

HRMS Anal. Calcd. for $C_{13}H_{14}O_4Na$ (M+23) 257.07843; found: 257.07813.

Optical rotation $[\alpha]_D^{20}$ +0.9 (c 0.60, $CHCl_3$).



15a-15b (1 : 1 dr at acetal)*

Preparation of alkynyldiols 15a and 15b: In a 100 mL round-bottom flask, *i*-Pr_2NH (2.47 mL, 17.64 mmol) was dissolved in THF (14.8 mL) and cooled to -78 °C. *n*-BuLi (1.45 M in hexane, 12.17 mL, 17.64 mmol) was slowly added, and the resulting mixture was stirred for 20 min at -78 °C. A solution of $TMSCHN_2$ (2.0 M in hexanes, 3.78 mL, 7.56 mmol) was then added dropwise at -78 °C, and this mixture stirred for 20 minutes to generate a solution of lithium trimethylsilyldiazomethane (**13**). In a separate flask, the benzylidene-protected lyxofuranose **10a-10b** (1.15 g, 4.85 mmol) was dissolved in THF (5.8 mL), and this solution was added to the cold solution of **13**. The resulting mixture was stirred at -78 °C for 1 h, and then warmed to 65 °C for 3 h. The reaction mixture was quenched with crushed ice and saturated aqueous ammonium chloride. The aqueous layer was extracted with ethyl acetate, and the combined organic extracts were dried over Na_2SO_4 and concentrated by rotary evaporation. The crude product was a red residue containing a mixture of terminal alkynyl diol and trimethylsilyl-substituted alkyne, which was dissolved in methanol (1.68 mL) and aqueous potassium carbonate (10% w/w, 1.68 mL) and stirred for 2 h. This mixture was carefully neutralized with aqueous 1M HCl. The aqueous layer was extracted with ethyl acetate, and the combined organic extracts were dried over Na_2SO_4 and concentrated by rotary evaporation. Purification by flash chromatography (5:3 Hexane/EtOAc) afforded **15a-15b** as a brown oil, a 1:1 mixture of diastereomers (555 mg, 2.37 mmol, 49% yield). A second silica gel flash column chromatography (2:1 Pentane/Hexane) provided some fractions of each of the pure diastereomers, which were characterized by proton NMR.

Alkynyl diol 15a (less polar diastereomer):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H), 7.41 – 7.33 (m, 3H), 6.22 (s, 1H), 5.05 (dd, *J* = 6.3, 2.2 Hz, 1H), 4.30 (ddd, *J* = 7.0, 6.1, 1.0 Hz, 1H), 4.14 (td, *J* = 6.1, 3.8 Hz, 1H), 3.80 (dd, *J* = 11.6, 3.7 Hz, 1H), 3.72 (dd, *J* = 11.7, 5.4 Hz, 1H), 2.69 (d, *J* = 2.3, 1H).

Alkynyl diol 15b (more polar diastereomer):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 2H), 7.43 – 7.38 (m, 3H), 5.85 (s, 1H), 4.95 (dd, *J* = 6.6, 2.2 Hz, 1H), 4.29 (t, *J* = 6.6 Hz, 1H), 4.18 (ddd, *J* = 6.5, 5.3, 3.7 Hz, 1H), 3.85 (dd, *J* = 11.7, 3.8 Hz, 1H), 3.77 (dd, *J* = 11.6, 5.3 Hz, 1H), 2.68 (d, *J* = 2.2 Hz, 1H).

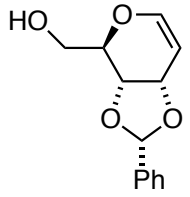
Alkynyl diol 15a-15b mixture:

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.1, 136.1, 130.1, 129.8, 128.68, 128.66, 127.4, 126.6, 104.9, 103.8, 78.7, 78.3, 77.7, 77.3, 71.9, 71.6, 67.9, 67.6, 63.49, 63.48.

FT-IR ν_{max}/cm^{-1} 3386 (OH), 3286 (CH alkyne), 2930 (CH alkane).

HRMS Anal. Calcd. for $C_{13}H_{15}O_4Na$ (M+23) 257.07843; found: 257.07813.

Optical rotation $[\alpha]_D^{20}$ -8.3 (c 0.42, $CHCl_3$).



16

Preparation of pyranose glycal 16: In a 25 mL Schlenk flask topped with a reflux condensor, alkynyl diol **14** (102.6 mg, 0.438 mmol) was dissolved in toluene (3.5 mL). DABCO (98 mg, 0.88 mmol) and $W(CO)_6$ (385 mg, 0.110 mmol) were added. The flask was then transferred to a Rayonet photoreactor, a reflux condensor was added, and the mixture was stirred under a steady flow of argon. The reaction mixture was irradiated with 350 nm light for 30 hours**,** without using the cooling fan, so that the reaction mixture warmed to approximately 55 ^oC. The resulting mixture was concentrated by rotary evaporation. Purification by flash chromatography (hexane/EtOAc 1:1) afforded compound **16** as a brown oil (62.2 mg, 0.263 mmol, 58% yield).

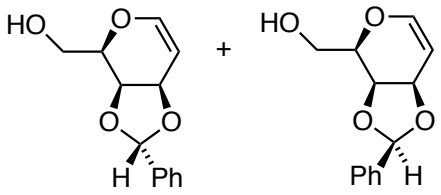
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H), 7.42 – 7.35 (m, 3H), 6.71 (d, *J* = 6.0 Hz, 1H), 5.85 (s, 1H), 5.26 (dd, *J* = 5.9, 4.7, 1H), 4.50 (ddd, *J* = 5.8, 4.6, 1.1 Hz, 1H), 4.15 (dd, *J* = 10.0, 6.0 Hz, 1H), 4.06 (dd, *J* = 12.2, 4.0 Hz, 1H), 3.88 (dt, *J* = 11.6, 5.4 Hz, 1H), 3.56 (ddd, *J* = 10.0, 5.3, 2.7 Hz, 1H), 2.03 (br, 1H).

^{13}C NMR (151 Hz, $CDCl_3$) δ 148.6, 136.6, 129.7, 128.6, 127.0, 103.3, 98.8, 76.2, 70.1, 69.9, 61.9.

FT-IR ν_{max}/cm^{-1} 3423 (OH), 2924, 2883 (CH).

HRMS Anal. Calcd. for $C_{13}H_{14}O_4Na$ (M+23) 257.07843; found: 257.07814.

Optical rotation $[\alpha]_D^{20}$ +195.1 (c 1.15, $CHCl_3$).



17a **17b**

Preparation of pyranose glycals 17a and 17b

In a 25 mL Schlenk flask, alkynyl diols **15a-15b** (81.9 mg, 0.346 mmol) were dissolved in toluene (2.6 mL). Then DABCO (77.6 mg, 0.692 mmol) and $W(CO)_6$ (49 mg, 0.14 mmol) were added. The flask was then transferred to a Rayonet photoreactor, a reflux condensor was added, and the mixture was stirred under a steady flow of argon. The reaction mixture was irradiated with 350 nm light for 27 hours**,** without using the cooling fan, so that the reaction mixture warmed to approximately 55 °C. The resulting mixture was concentrated by rotary evaporation. Purification by flash chromatography (4:1 Hexane/EtOAc) afforded **17a-17b** as a thick white oil, as a mixture of two separable diastereomers **17a** (13 mg, 0.055 mmol, 16% yield) and **17b** (20 mg, 0.085 mmol, 25% yield).

Pyranose glycal 17a (less polar diastereomer):

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.41 – 7.36 (m, 3H), 6.75 (d, *J* = 6.2 Hz, 1H), 6.01 (s, 1H), 5.07 (dd, *J* = 6.4, 3.0 Hz, 1H), 4.87 (ddd, *J* = 6.2, 3.1, 1.1 Hz, 1H), 4.45 (d, *J* = 6.3 Hz, 1H), 4.05 (t, *J* = 5.6 Hz, 1H), 4.01 (dd, *J* = 11.8, 8.1 Hz, 1H), 3.90 (ddd, *J* = 11.6, 8.2, 3.6 Hz, 1H), 2.23 (br d, 8.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.7, 137.2, 129.7, 128.6, 126.9, 102.5, 99.7, 76.0, 73.8, 70.1, 63.6.

FT-IR ν_{max}/cm^{-1} 3422 (OH), 2923, 2854 (CH).

HRMS Anal. Calcd. for $C_{13}H_{14}O_4Na$ (M+23) 257.07843; found: 257.07814.

Optical rotation $[\alpha]_D^{20}$ -2.6 (c 0.34, $CHCl_3$).

Pyranose glycal 17b (more polar diastereomer):

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2H), 7.42 – 7.33 (m, 3H), 6.50 (d, *J* = 6.2 Hz, 1H), 5.94 (s, 1H), 4.95 (ddd, *J* = 6.3, 3.1, 1.4 Hz, 1H), 4.80 (dd, *J* = 6.8, 3.1 Hz, 1H), 4.44 (dt, *J* = 6.8, 1.5 Hz, 1H), 4.12 (ddd, *J* = 7.3, 4.0, 1.7 Hz, 1H), 4.07 (dd, *J* = 11.5, 7.3 Hz, 1H), 3.90 (d, *J* = 11.7 Hz, 1H), 2.07 (br, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.2, 137.4, 129.7, 128.5, 127.3, 105.6, 102.3, 75.0, 74.9, 68.6, 63.1.

FT-IR ν_{max}/cm^{-1} 3404 (OH), 2923, 2853 (CH).

HRMS Anal. Calcd. for $C_{13}H_{14}O_4Na$ (M+23) 257.07843; found: 257.07814.

Optical rotation $[\alpha]_D^{20}$ -43.6 (c 0.41, $CHCl_3$).

X-Ray Diffraction Analysis of 8 and 12a: Single colourless prism-shaped crystals of compound **8** were recrystallised from a mixture of pentane and THF by vapor diffusion, and a suitable crystal 0.60×0.59×0.17 mm^3 was selected for diffraction analysis. Single colourless plate-shaped crystals of compound **12a** were obtained by vapor diffusion using THF as the solvent and pentane as the precipitant, and a suitable crystal 0.61×0.40×0.16 mm^3 was selected for diffraction analysis. Each crystal was mounted on a loop with paratone oil on an Bruker APEX-II CCD diffractometer. Each crystal was kept at a steady T = 100(2) K during data collection. The structures were solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The models were refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

The main crystallographic data and thermal ellipsoid diagrams for **8** and **12a** are given in Table S1, Figures S1 and S2. CCDC 1902793 (compound **8**) and 1902792 (compound **12a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data for compounds **8** and **12a**

	8	**12a**
Formula	$C_{13}H_{14}O_4$	$C_{26}H_{30}O_9$
$D_{calc.}$/ g cm^{-3}	1.347	1.377
μ/mm^{-1}	0.100	0.868
Formula Weight	234.24	486.50
Colour	colourless	colourless
Shape	prism	plate
Size/mm^3	0.60×0.59×0.17	0.61×0.40×0.16
T/K	100(2)	100(2)
Crystal System	monoclinic	monoclinic
Flack Parameter	0.0(5)	-0.02(6)
Hooft Parameter	-0.2(3)	0.03(3)
Space Group	$P2_1$	$C2$
a/Å	9.8806(3)	8.7488(2)
b/Å	11.2155(4)	6.9938(2)
c/Å	10.4580(4)	19.1850(5)
α/°	90	90
β/°	94.618(3)	91.649(2)
γ/°	90	90
V/Å^3	1155.14(7)	1173.39(5)
Z	4	2
Z'	2	0.5
Wavelength/Å	0.710730	1.541838
Radiation type	MoK_α	CuK_α
Θ_{min}/°	1.954	2.304
Θ_{max}/°	30.505	66.575
Measured Refl.	15137	4674
Independent Refl.	5771	1937
Reflections with I > 2(I)	5261	1914
R_{int}	0.0291	0.0087
Parameters	307	165
Restraints	77	6
Largest Peak	0.363	0.131
Deepest Hole	-0.210	-0.147
GooF	1.059	1.060
wR_2 (all data)	0.1049	0.0763
wR_2	0.1019	0.0761
R_1 (all data)	0.0476	0.0283
R_1	0.0424	0.0280

Figure S1. Thermal ellipsoid diagram for compound **8**

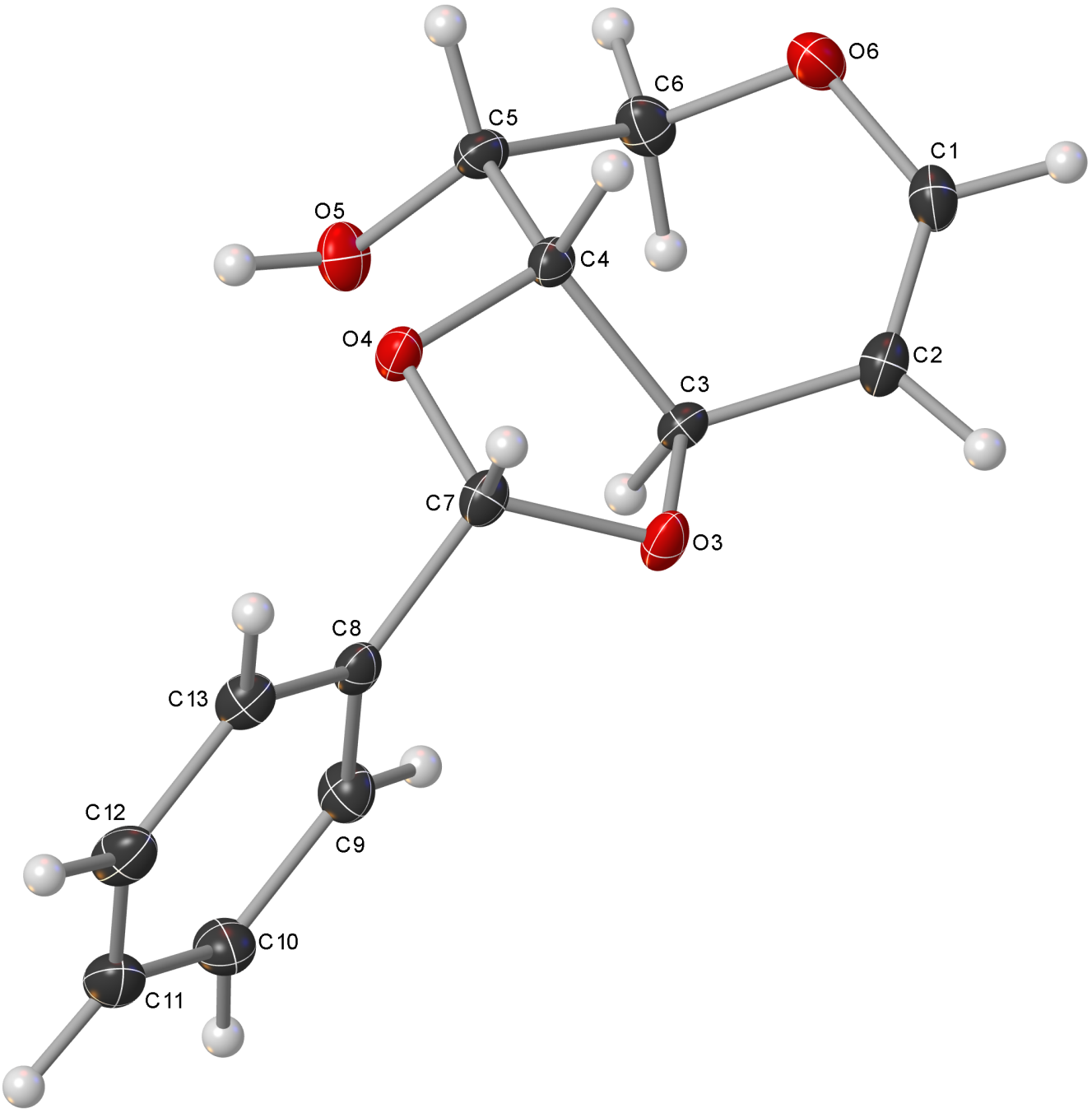


Figure S2. Thermal ellipsoid diagram for compound **12a**

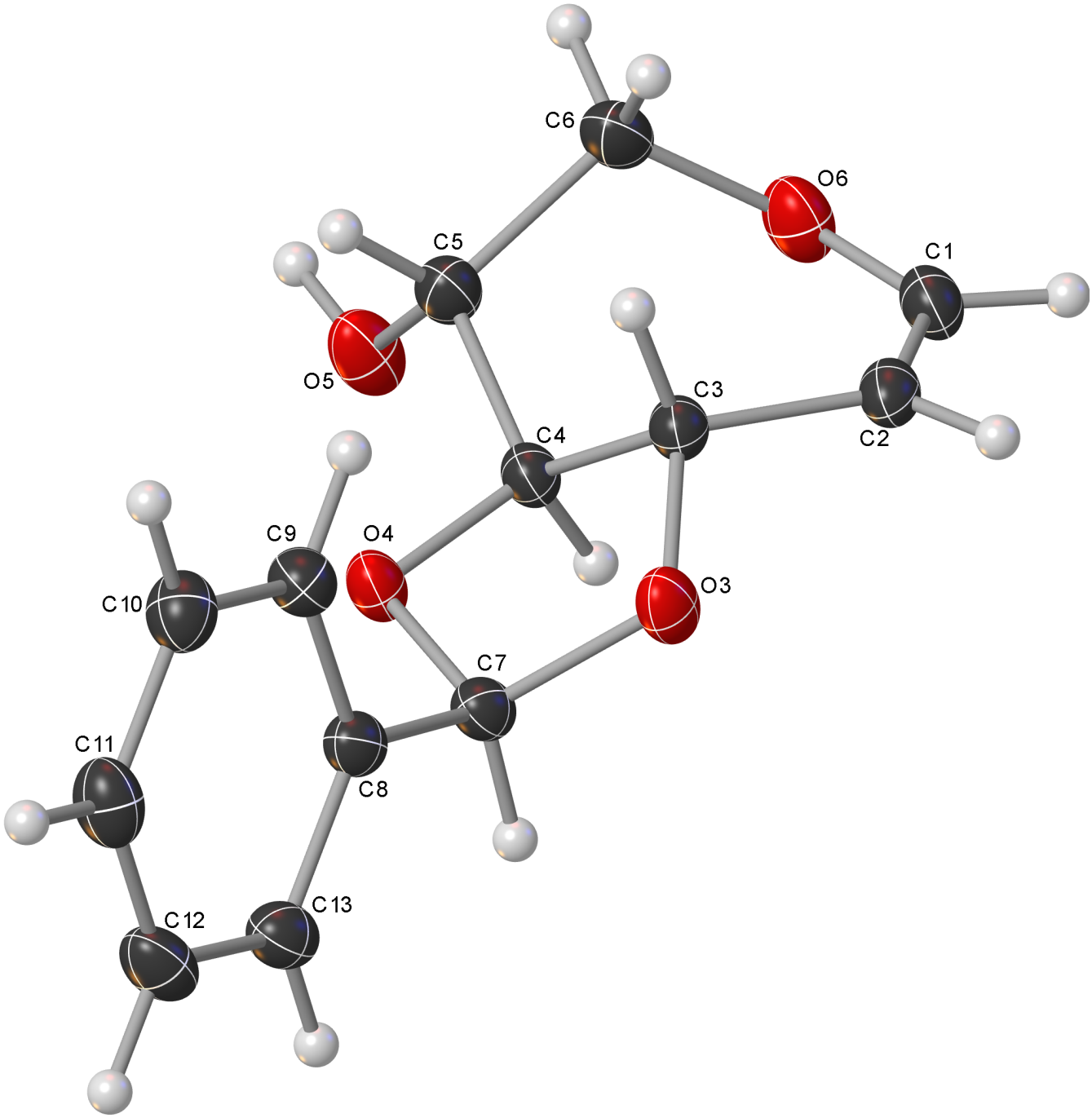


Table S2. Chemical shifts and coupling constants for alkynyl diols **7, 11a-11b, 14,** and **15a-15b.** The chemical shifts for hydrogens at C5 (**bold**) are particularly diagnostic, to distinguish diastereomers at C3.

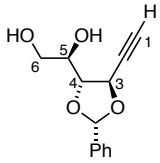
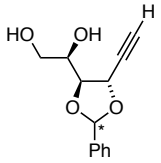
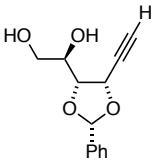
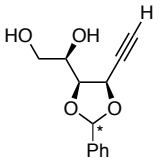
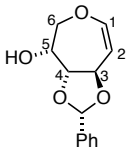
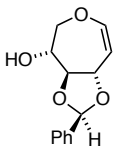
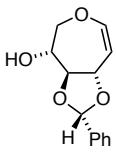
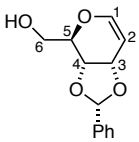
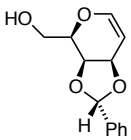
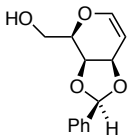
	arabino	*xylo*		*ribo*	*lyxo*	
						
carbon	**7**	**11a-11b** (1 : 1 dr at acetal)*		**14**	**15a-15b** (1 : 1 dr at acetal)*	
1	2.62, d (2.1 Hz)	2.63, d (2.1 Hz)	2.58, d (2.1 Hz)	2.71, d (2.2 Hz)	2.69, d (2.3 Hz)	2.68, d (2.2 Hz)
3	4.97, dd (5.0, 2.1 Hz)	4.88, dd (5.9, 2.1 Hz)	4.85, dd (7.7, 2.0 Hz)	5.02, dd (6.3, 2.2 Hz)	5.05, dd (6.3, 2.2 Hz)	4.95, dd (6.6, 2.2 Hz)
4	4.25, dd (5.8, 5.0 Hz)	4.30, dd (6.0, 3.7 Hz)	4.12, dd (7.7, 2.4 Hz)	4.22, dd (8.7, 6.3 Hz)	4.30, ddd (7.0, 6.1, 1.0 Hz)	4.29, t (6.6 Hz)
5	**3.91**, dd (5.8, 3.6 Hz)	**3.82–3.80**, m	**3.82**, dd (8.6, 4.3 Hz)	**4.16**, ddd (8.6, 5.1, 3.0 Hz)	**4.14**, td (6.1, 3.8 Hz)	**4.18**, ddd (6.5, 5.3, 3.7 Hz)
6a	3.85, dd (11.4, 3.6 Hz)	3.75, d (2H) (4.8 Hz)	3.78, t (2H) (5.4 Hz)	3.92, dd (11.6, 3.0 Hz)	3.80, dd (11.6, 3.7 Hz)	3.85, dd (11.7, 3.8 Hz)
6b	3.76, dd (11.4, 5.7 Hz)			3.81, dd (11.6, 5.1 Hz)	3.72, dd (11.7, 5.4 Hz)	3.77, dd (11.6, 5.3 Hz)
acetal	6.02, s	6.00, s	6.00, s	5.83, s	6.22, s	5.85, s
phenyl, 2H	7.52-7.45, m	7.51-7.47, m	7.53-7.47, m	7.54-7.49, m	7.50-7.42, m	7.59-7.55, m
phenyl, 3H	7.43-7.38, m	7.40-7.36, m	7.40-7.37, m	7.42-7.37, m	7.41-7.33, m	7.43-7.38, m

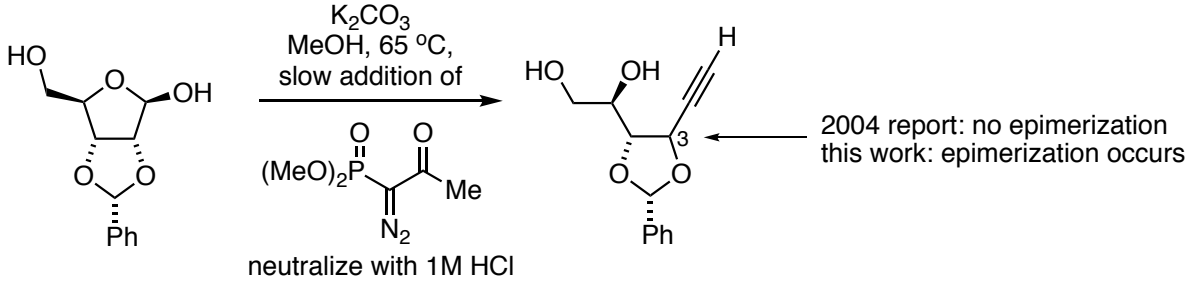
Table S3. Chemical shifts and coupling constants for septanose glycals **8** and **12a-12b,** and pyranose glycals **16** and **17a-17b**, with diagnostic coupling constants for hydrogens at C3, C4, and C5 **(bold)**.

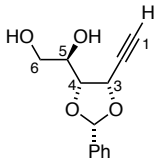
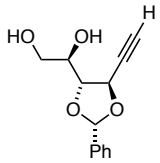
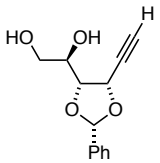
	septanose glycals			pyranose glycals		
	arabino	*xylo*		*ribo*	*lyxo*	
						
carbon	**8**	**12a**	**12b**	**16**	**17a**	**17b**
1	6.41, dd (6.3, 2.1 Hz)	6.42, dd (6.4, 2.0 Hz)	6.45, dd (6.5, 2.0 Hz)	6.71, d (6.0 Hz)	6.75, d (6.2 Hz)	6.50, d (6.2 Hz)
2	5.30, dd (6.3, 1.8 Hz)	5.19, dd (6.5, 1.6 Hz)	5.25, dd (6.4, 1.4 Hz)	5.26, dd (5.9, 4.7 Hz)	4.87, ddd (6.2, 3.1, 1.1 Hz)	4.95, ddd (6.3, 3.1, 1.4 Hz)
3	5.02, dt (**9.7**, 1.8 Hz)	4.66, dt (**9.7**, 1.8 Hz)	4.72, dt (**9.7**, 1.8 Hz)	4.50, ddd (**5.8**, 4.6, 1.1 Hz)	5.07, dd (**6.4**, 3.0 Hz)	4.80, dd (**6.8**, 3.1 Hz)
4	4.06, dd (**9.7**, **3.9** Hz)	4.16, dd (**9.2**, **7.5** Hz)	4.05, dd (**9.7**, **7.5** Hz)	4.15, dd (**10.0**, **6.0** Hz)	4.45, d (**6.3** Hz)	4.44, d t (**6.8**, **1.5** Hz)
5	4.58, dddd (7.8, 5.6, **3.9**, 1.9 Hz)	4.27, dt (**7.4**, 2.6 Hz)	4.18, td (**7.1**, 3.0 Hz)	3.56, ddd (**10.0**, 5.3, 2.7 Hz)	4.01 dd (11.8, 8.1 Hz)	4.12, dd (7.3, 4.0, **1.7** Hz)
6a	4.28, dd (12.5, 5.3 Hz)	4.17, dd (13.4, 2.1 Hz)	4.13, ddd (13.2, 2.4, 1.1 Hz)	4.06, dd (12.2, 4.0 Hz)	4.05, t (5.6 Hz)	4.07, dd (11.5, 7.3 Hz)
6b	3.79, dd (12.5, 8.0 Hz)	4.03, dd (13.3, 3.2 Hz)	4.08, dd (13.4, 3.1 Hz)	3.88, dd (12.1, 4.9 Hz)	3.90, ddd (11.6, 8.2, 3.6 Hz)	3.90, d (11.7 Hz)
acetal	6.15, s	6.11, s	6.08, s	5.85, s	6.01, s	5.94, s
phenyl, 2H	7.51-7.48, m	7.50-7.45, m	7.49-7.47, m	7.50-7.42, m	7.50-7.44, m	7.51-7.44, m
phenyl, 3H	7.44-7.39, m	7.40-7.36, m	7.40-7.38, m	7.42-7.35, m	7.42-7.33, m	7.41-7.36, m

Data comparisons between structures from *Org. Lett.* 2004, *6*, 3877-3800, and this work:

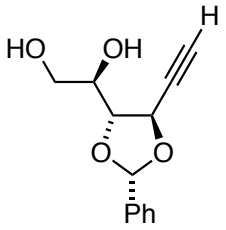
1) Benzylidene-protected substrates and products:

a) Reassignment of stereochemistry of the alkynyl diol from Ohira-Bestmann alkynylation of benzylidene-protected D-ribofuranose, labeled compound **10** in 2004 publication:

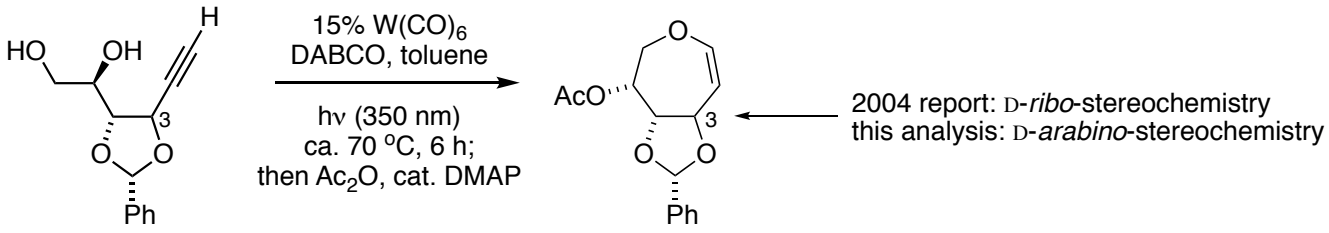


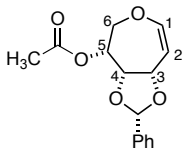
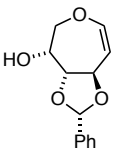
	compound **10** in 2004 publication	structures described in this work	
		 **7**	 **14**
^{1}H NMR data:	data reported in 2004 publication	data from this work	
1	2.64, d (2.2 Hz)	2.62, d (2.1 Hz)	2.71, d (2.2 Hz)
3	4.98, dd (4.8, 2.0 Hz)	4.97, dd (5.0, 2.1 Hz)	5.02, dd (6.3, 2.2 Hz)
4	4.26, t (5.6 Hz)	4.25, dd (5.8, 5.0 Hz)	4.22, dd (8.7, 6.3 Hz)
5	3.92, app dt (5.6, 3.9 Hz)	3.91, dd (5.8, 3.6 Hz)	4.16, ddd (8.6, 5.1, 3.0 Hz)
6a	3.85, dd (11.5, 3.6 Hz)	3.85, dd (11.4, 3.6 Hz)	3.92, dd (11.6, 3.0 Hz)
6b	3.76, dd (11.8, 5.6 Hz)	3.76, dd (11.4, 5.7 Hz)	3.81, dd (11.6, 5.1 Hz)
acetal	6.03, s	6.02, s	5.83, s
phenyl, 2H	7.49, m	7.52-7.45, m	7.54-7.49, m
phenyl, 3H	7.41, m	7.43-7.38, m	7.42-7.37, m
$[\alpha]_D$	-20.9 (c 0.88, MeOH)	-19.3 (c 0.33, $CHCl_3$)	+0.9 (c 0.60, $CHCl_3$)

Conclusion: Based on the similarities with compound **7** and differences from compound **14** in this work, we must reassign the stereochemistry for the compound labeled **10** in the 2004 publication, to the structure below.



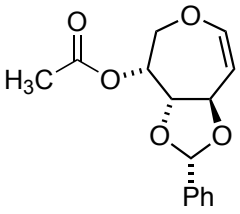
b) Reassignment of stereochemistry of the septanose glycal from tungsten-catalyzed cycloisomerization of the alkynyldiol compound labeled as **10** followed by acetylation of the crude product mixture, labeled compound **11** in 2004 publication:



	compound **11** in 2004 publication 	structure described in this work, confirmed by X-ray crystallography  **8**, D-*arabino*
^{1}H NMR data:	data reported in 2004 publication	data from in this work
1	6.43, dd (6.2, 2.4 Hz)	6.41, dd (6.3, 2.1 Hz)
2	5.69, app dt (6.2, 3.8 Hz)	5.30, dd (6.3, 1.8 Hz)
3	4.97 dt (**10.0**, 2.4, 1.9 Hz)	5.02, dt (**9.7**, 1.8 Hz)
4	4.06, dd (**9.5**, **3.3** Hz)	4.06, dd (**9.7**, **3.9** Hz)
5	5.42, dd (6.2, **2.4** Hz)	4.58, dddd (7.8, 5.6, **3.9**, 1.9 Hz)
6a	4.15, dd (12.9, 3.8 Hz)	4.28, dd (12.5, 5.3 Hz)
6b	3.95, dd (12.9, 6.7 Hz)	3.79, dd (12.5, 8.0 Hz)
acetal	6.16, s	6.15, s
phenyl, 2H	7.47, m	7.51-7.48, m
phenyl, 3H	7.38, m	7.44-7.39, m

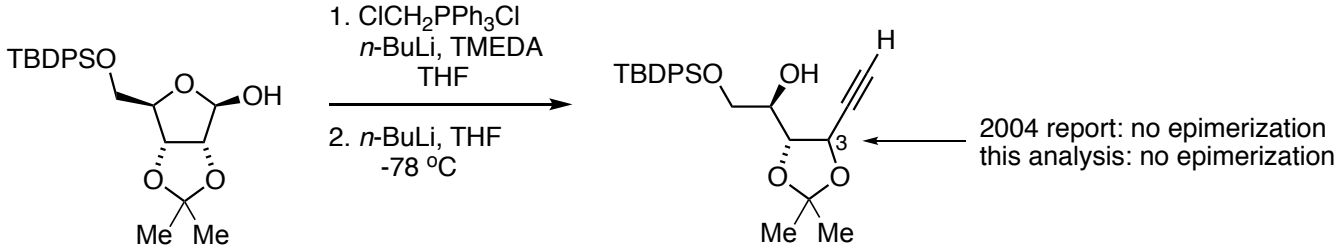
Despite the difference in structures (acetate ester at O5 vs. alcohol), the coupling constants are very similar, especially the diagnostic $^3J_{H3,H4}$ and $^3J_{H4,H5}$.

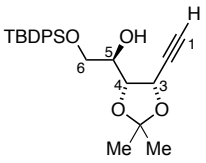
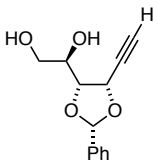
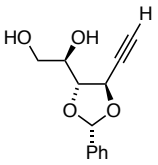
Conclusion: We must reassign the stereochemistry for the compound labeled **11** in the 2004 publication, to the structure below.



2) Compounds arising from Wittig chloromethylenation and dehydrohalogenation:

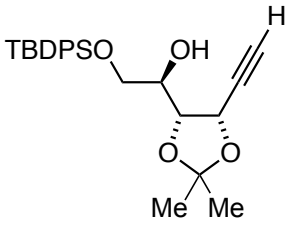
a) Confirmation of stereochemistry of the alkynyl alcohol labeled compound **4** in 2004 publication:



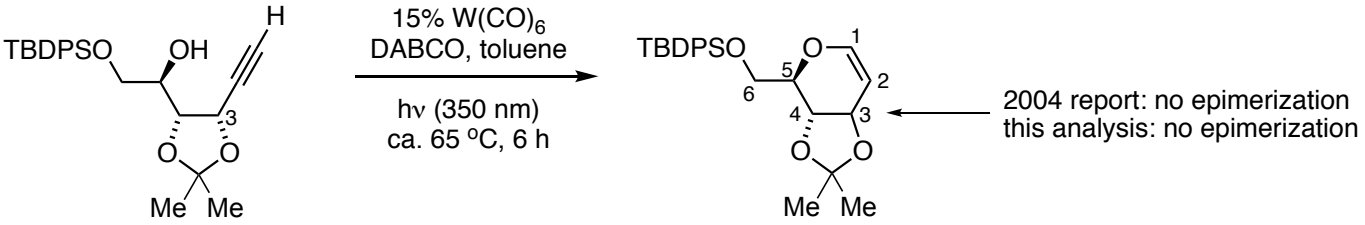
	compound **4** in 2004 publication	comparison with structures described in this work	
		 **14**	 **7**
^{1}H NMR data:	data reported in 2004 publication	data from this work	
1	2.57, d (2.0 Hz)	2.71, d (2.2 Hz)	2.62, d (2.1 Hz)
3	4.95 dd (5.8, 2.2 Hz)	5.02, dd (6.3, 2.2 Hz)	4.97, dd (5.0, 2.1 Hz)
4	4.17, dd (8.8, 5.6 Hz)	4.22, dd (8.7, 6.3 Hz)	4.25, dd (5.8, 5.0 Hz)
5	**4.08**, m	**4.16**, ddd (8.6, 5.1, 3.0 Hz)	**3.91**, dd (5.8, 3.6 Hz)
6a	3.95, dd (10.6, 3.0 Hz)	3.92, dd (11.6, 3.0 Hz)	3.85, dd (11.4, 3.6 Hz)
6b	3.90, dd (10.4, 4.4 Hz)	3.81, dd (11.6, 5.1 Hz)	3.76, dd (11.4, 5.7 Hz)

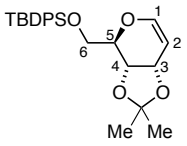
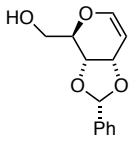
Despite the different protective groups, the relative chemical shifts for the hydrogens at C5 are closer to compound **14** than compound **7**. This follows the trend observed with other alkyne substrates with dioxolane protective groups, in which diastereomers bearing a *cis*-relationship at H3 and H4 exhibit chemical shifts for H5 downfield of 4.0 ppm, whereas substrates with a *trans*-relationship have chemical shifts for H5 upfield of 4.0 ppm.

Conclusion: This confirms the stereochemistry of the compound labeled **4** in the 2004 publication.



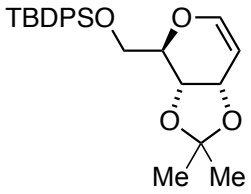
b) Confirmation of stereochemistry of the pyranose glycal labeled compound **6** in 2004 publication:



	compound **6** in 2004 publication 	comparison with structure described in this work  **16**
^{1}H NMR data:	data reported in 2004 publication	data from this work
1	6.66, d (6.0 Hz)	6.71, d (6.0 Hz)
2	5.10, dd (5.8, 4.6 Hz)	5.26, dd (5.9, 4.7 Hz)
3	4.64, t (**5.0** Hz)	4.50, ddd (**5.8**, 4.6, 1.1 Hz)
4	4.11, dd (**9.8**, **5.4** Hz)	4.15, dd (**10.0**, **6.0** Hz)
5	3.49, ddd (**9.6**, 5.2, 2.4 Hz)	3.56, ddd (**10.0**, 5.3, 2.7 Hz)
6a	4.03, dd (11.4, 2.2 Hz)	4.06, dd (12.2, 4.0 Hz)
6b	3.93, dd (11.6, 4.8 Hz)	3.88, dd (12.1, 4.9 Hz)

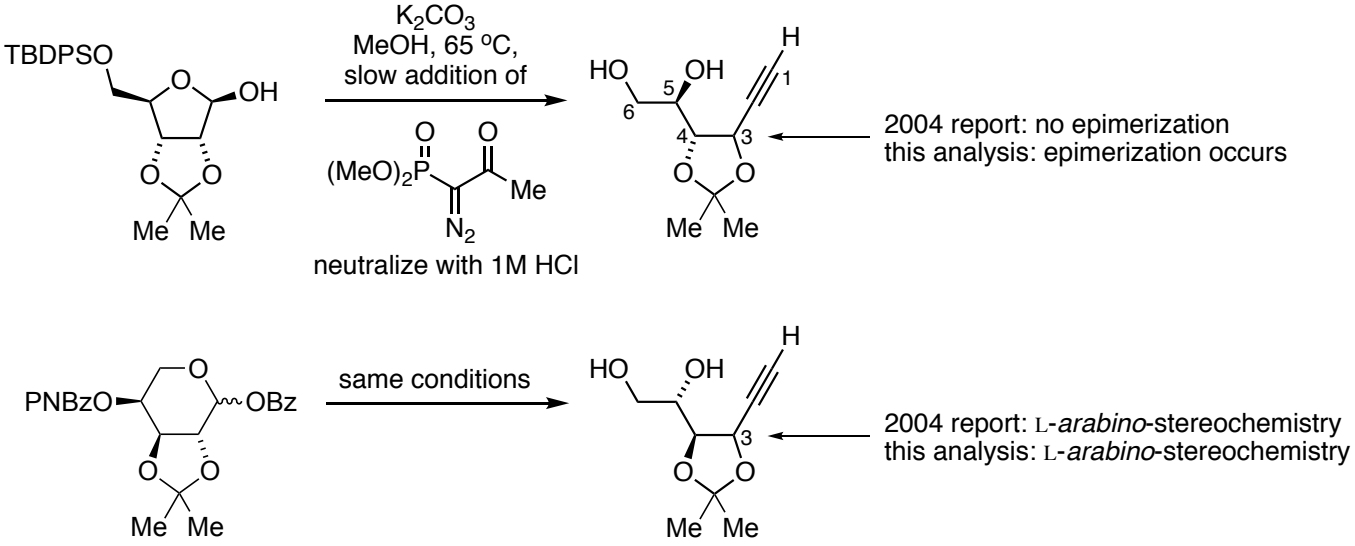
Despite the different protective groups, the coupling constants are similar, especially the diagnostic $^3J_{H3,H4}$ and $^3J_{H4,H5}$.

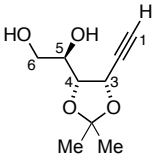
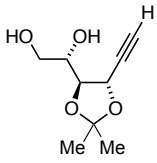
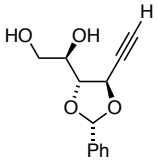
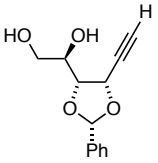
Conclusion: This confirms the stereochemistry of the compound labeled **6** in the 2004 publication.



3) Compounds arising from Ohira-Bestmann alkynylations of acetonide-protected D-ribofuranose and L-arabinopyranose derivatives:

a) Reassignment of stereochemistry of the alkynyl alcohol labeled compound **5** in 2004 publication, and confirmation of stereochemistry of the alkynyl alcohol labeled compound **16** in 2004 publication:

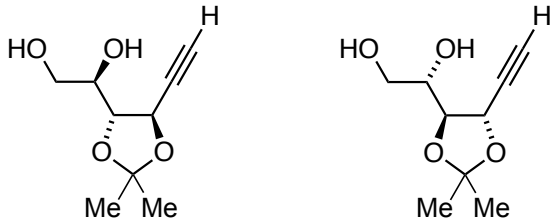


	compound **5** in 2004 publication	compound **16** in 2004 publication	structures described in this work	
			 **7**	 **14**
^{1}H NMR data:	data reported in 2004 publication		data from this work	
1	2.56, d (1.8 Hz)	2.55, d (2.0 Hz)	2.62, d (2.1 Hz)	2.71, d (2.2 Hz)
3	4.66, dd (6.0, 1.8 Hz)	4.67, dd (6.6, 1.8 Hz)	4.97, dd (5.0, 2.1 Hz)	5.02, dd (6.3, 2.2 Hz)
4	4.08, t (6.3 Hz)	4.11, dd (6.6, 5.4 Hz)	4.25, dd (5.8, 5.0 Hz)	4.22, dd (8.7, 6.3 Hz)
5	**3.81**, m	**3.85**, m	**3.91**, dd (5.8, 3.6 Hz)	**4.16**, ddd (8.6, 5.1, 3.0 Hz)
6a	3.74, dt (12.0, 3.6 Hz)	3.74, m	3.85, dd (11.4, 3.6 Hz)	3.92, dd (11.6, 3.0 Hz)
6b	3.63, dd (11.4, 6.6 Hz)	3.66, d (11.4, 6.2 Hz)	3.76, dd (11.4, 5.7 Hz)	3.81, dd (11.6, 5.1 Hz)
Me	1.46, s	1.48, s	na	na
Me	1.39, s	1.40, s	na	na

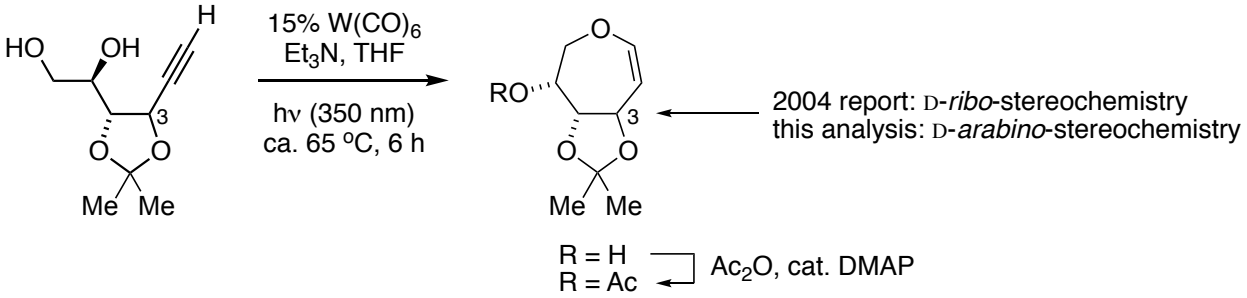
Side-by-side comparison of the ^{1}H NMR data reported in 2004 shows close correlation for all resonances, suggesting that both of those compounds are the same structure, or enantiomers based on the sources of the respective starting materials. The ^{13}C NMR data for both compounds from the 2004 publication (not depicted here) are also consistent within 0.2 ppm for all

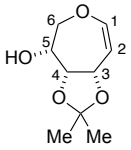
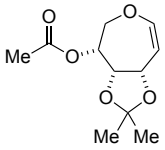
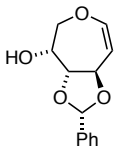
resonances. In comparing the acetonides with the benzylidene-protected alkynyl diols **7** and **14**, the relative chemical shifts for the hydrogens at C5 are closer to compound **7** than to compound **14**, exhibiting chemical shifts for H5 upfield of 4.0 ppm, consistent with other dioxolane substrates with a *trans*-relationship at H3 and H4 with chemical shifts for H5 upfield of 4.0 ppm.

Conclusions: We must reassign the stereochemistry for the compound labeled **5** in the 2004 publication, to the structure on the left. This also confirms the stereochemistry for the compound labeled **16** in the 2004 publication, shown below to the right. These compounds are antipodes.



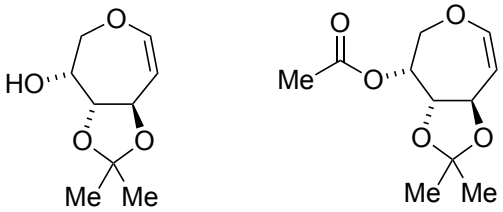
b) Reassignment of stereochemistry of the septanose glycal from tungsten-catalyzed cycloisomerization of the alkynyldiol compound labeled as compound **5** into the alcohol **8,** R = H, followed by acetylation of the crude product mixture to provide the acetate ester **9**, R = Ac, with compound numbering used in the 2004 publication:



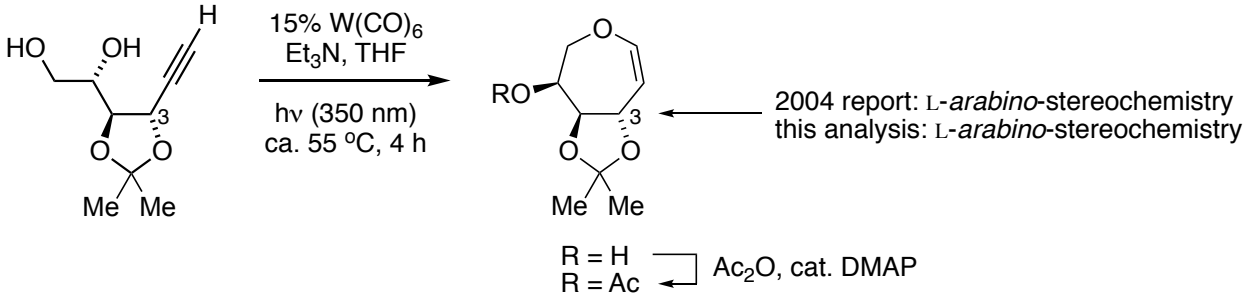
	compound **8** in 2004 publication	compound **9** in 2004 publication	structure described in this work, confirmed by X-ray crystallography
			 **8**, D-*arabino*
^{1}H NMR data:	data reported in 2004 publication		data from this work
1	6.36, dd (6.4, 2.0 Hz)	6.36, dd (6.0, 2.4 Hz)	6.41, dd (6.3, 2.1 Hz)
2	5.16, dd (6.4, 2.0 Hz)	5.29, dd (6.2, 2.2 Hz)	5.30, dd (6.3, 1.8 Hz)
3	4.87, dt (**10.0**, 2.0 Hz)	4.89 dt (**9.4**, 2.2 Hz)	5.02, dt (**9.7**, 1.8 Hz)
4	3.85, dd (**9.6**, **4.0** Hz)	3.82, dd (**9.6**, **3.6** Hz)	4.06, dd (**9.7**, **3.9** Hz)
5	4.39, dt (8.4, **4.3** Hz)	5.48, dt (6.4, **3.6** Hz)	4.58, dddd (7.8, 5.6, **3.9**, 1.9 Hz)
6a	4.22, dd (12.4, 5.2 Hz)	4.03, dd (12.8, 4.0 Hz)	4.28, dd (12.5, 5.3 Hz)
6b	3.75, dd (12.4, 8.0 Hz)	3.89, dd (12.8, 6.2 Hz)	3.79, dd (12.5, 8.0 Hz)

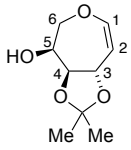
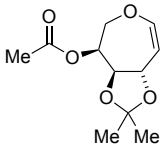
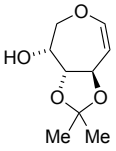
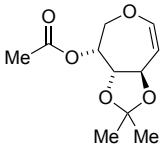
Despite the different protective groups, the coupling constants are similar for all three compounds, especially the diagnostic $^3J_{H3,H4}$ and $^3J_{H4,H5}$.

Conclusions: We must reassign the stereochemistry for the compounds labeled **8** and **9** in the 2004 publication, to the structures below.



c) Confirmation of stereochemistry of the septanose glycal labeled compound **17-OH** (R = H) and **17** (R = Ac) in 2004 publication:



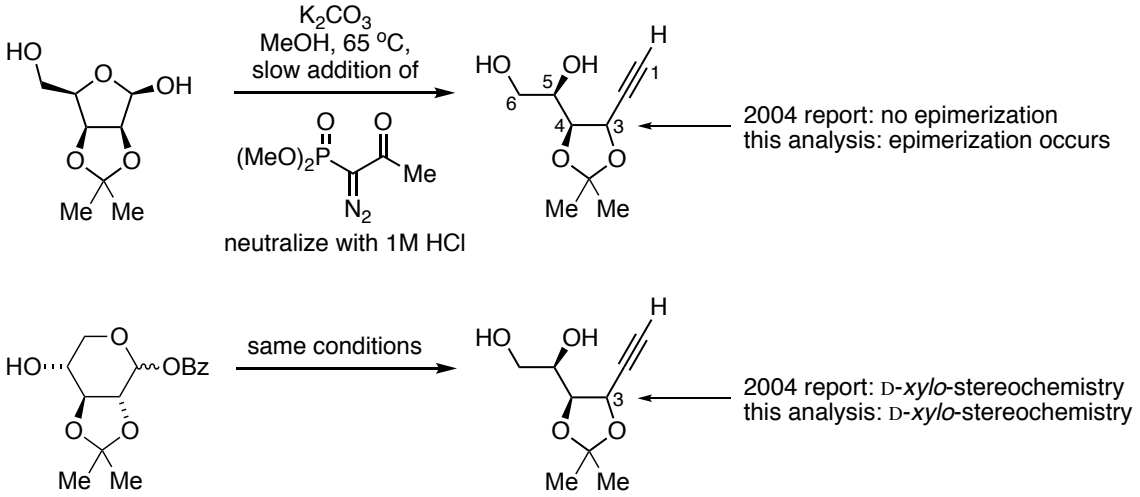
	compound **17-OH** in 2004 publication	compound **17** in 2004 publication	2004 structures corrected in analysis on page S-25 compound **8**	compound **9**
				
^{1}H NMR data:	data reported in 2004 publication			
1	6.36, dd (6.2, 2.2 Hz)	6.39, dd (6.4, 2.4 Hz)	6.36, dd (6.4, 2.0 Hz)	6.36, dd (6.0, 2.4 Hz)
2	5.16, dd (6.2, 1.8 Hz)	5.32, dd (6.0, 2.0 Hz)	5.16, dd (6.4, 2.0 Hz)	5.29, dd (6.2, 2.2 Hz)
3	4.87, app d (**9.6** Hz)	4.92, dt (**9.6**, 2.2 Hz)	4.87, dt (**10.0**, 2.0 Hz)	4.89 dt (**9.4**, 2.2 Hz)
4	3.84, dd (**9.6**, **4.0** Hz)	3.85, dd (**9.6**, **3.6** Hz)	3.85, dd (**9.6**, **4.0** Hz)	3.82, dd (**9.6**, **3.6** Hz)
5	4.38, dt (8.3, **4.2** Hz)	5.51, dt (6.4, **3.6** Hz)	4.39, dt (8.4, **4.3** Hz)	5.48, dt (6.4, **3.6** Hz)
6a	4.20, dd (12.4, 5.2 Hz)	4.06, dd (13.0, 4.2 Hz)	4.22, dd (12.4, 5.2 Hz)	4.03, dd (12.8, 4.0 Hz)
6b	3.75, m	3.93, dd (13.2, 6.0 Hz)	3.75, dd (12.4, 8.0 Hz)	3.89, dd (12.8, 6.2 Hz)
acetyl	na	2.13, s	na	2.10, s
Me	1.45, s	1.44, s	1.46, s	1.41, s
Me	1.43, s	1.40, s	1.44, s	1.36, s
$[\alpha]_D$	not reported	+52.86 (c 0.69, $CHCl_3$)	-66.47 (c 0.73, $CHCl_3$)	-77.89 (c 1.62, $CHCl_3$)

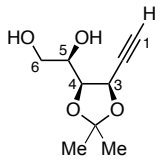
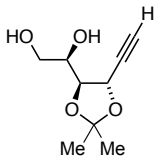
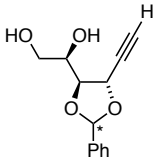
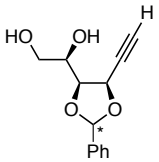
Side-by-side comparison of the ^{1}H NMR data reported in 2004 shows close correlation for all resonances, and therefore also correlates with the structure of compound **8** in this work, which was determined by X-ray crystallography. The ^{13}C NMR data for both of the acetates from the 2004 publication (not depicted here) are also consistent within 0.2 ppm for all resonances. The optical rotations for the acetates exhibit opposite signs, consistent with the compounds being enantiomers, although the magnitudes are different.

Conclusion: Despite the inconsistent magnitudes of the optical rotations, the remaining data confirms the stereochemistry of the compound labeled **17** in the 2004 publication. Compound **9** and compound **17** are antipodes.

4) Compounds arising from Ohira-Bestmann alkynylations of acetonide-protected D-lyxofuranose and D-xylopyranose derivatives:

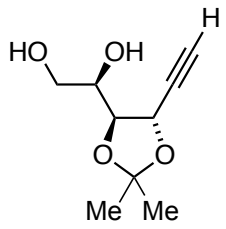
a) Reassignment of stereochemistry of the alkynyl alcohol labeled compound **12** in 2004 publication, and confirmation of stereochemistry of the alkynyl alcohol labeled compound **14** in 2004 publication:



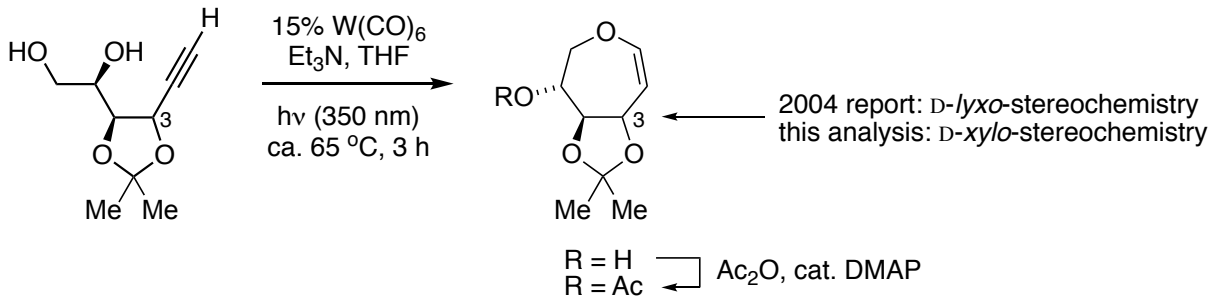
	compound **12** in 2004 publication 	compound **14** in 2004 publication 	structures described in this work  **11a-11b** (1 : 1 dr at acetal)*		 **15a-15b** (1 : 1 dr at acetal)*	
^{1}H NMR data:	data reported in 2004 publication		data from this work			
1	2.55, d (1.8 Hz)	2.55, d (1.8 Hz)	2.63, d (2.1 Hz)	2.58, d (2.1 Hz)	2.69, d (2.3 Hz)	2.68, d (2.2 Hz)
3	4.61, dd (7.5, 2.1 Hz)	4.62, dd (7.8, 1.8 Hz)	4.88, dd (5.9, 2.1 Hz)	4.85, dd (7.7, 2.0 Hz)	5.05, dd (6.3, 2.2 Hz)	4.95, dd (6.6, 2.2 Hz)
4	4.07, dd (8.1, 2.7 Hz)	4.09, dd (7.8, 3.0 Hz)	4.30, dd (6.0, 3.7 Hz)	4.12, dd (7.7, 2.4 Hz)	4.30, ddd (7.0, 6.1, 1.0 Hz)	4.29, t (6.6 Hz)
5			**3.82–3.80**, m	**3.82**, dd (8.6, 4.3 Hz)	**4.14**, td (6.1, 3.8 Hz)	**4.18**, ddd (6.5, 5.3, 3.7 Hz)
6a	**3.73, m (3H)**	**3.74, m (3H)**	3.75, d (2H) (4.8 Hz)	3.78, t (2H) (5.4 Hz)	3.80, dd (11.6, 3.7 Hz)	3.85, dd (11.7, 3.8 Hz)
6b					3.72, dd (11.7, 5.4 Hz)	3.77, dd (11.6, 5.3 Hz)
Me	1.46, s	1.47, s	na	na	na	na
Me	1.41, s	1.42, s	na	na	na	na
$[\alpha]_D$	-21.64 (c 1.65, $CHCl_3$)	-20.27 (c 1.18, $CHCl_3$)	+5.5 (c 0.86, $CHCl_3$)		-8.3 (c 0.42, $CHCl_3$)	

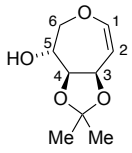
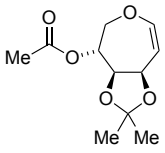
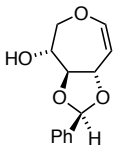
Side-by-side comparison of the ^{1}H NMR data reported in 2004 shows close correlation for all resonances, suggesting that both of those compounds are the same structure. The ^{13}C NMR data for both compounds from the 2004 publication (not depicted here) are also consistent within 0.1 ppm for all resonances. The optical rotations for both compounds are similar. The hydrogens at H5 and H6 overlap in these acetonide-protected compounds, but none of these hydrogens exhibit chemical shifts downfield of 4.0 ppm. This is consistent with the H5 chemical shifts in other dioxolane alkynyl diols including **11a-11b** with a *trans*-relationship at H3 and H4, and quite different from benzylidene-protected **15a-15b** with a *cis*-relationship at H3 and H4 and chemical shifts downfield of 4.0 ppm.

Conclusions: The structures for compounds labeled **12** and **14** in the 2004 publication are identical. Therefore we must reassign the stereochemistry for the compound labeled **12** in the 2004 publication. This also confirms the stereochemistry for the compound labeled **14** in the 2004 publication.



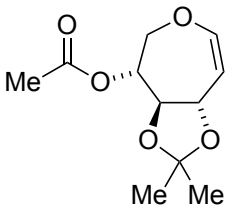
b) Reassignment of stereochemistry of the septanose glycal from tungsten-catalyzed cycloisomerization of the alkynyldiol compound labeled as compound **12** into the alcohol **13-OH,** R = H, followed by acetylation of the crude product mixture to provide the acetate ester **13**, R = Ac, with compound numbering used in the 2004 publication:



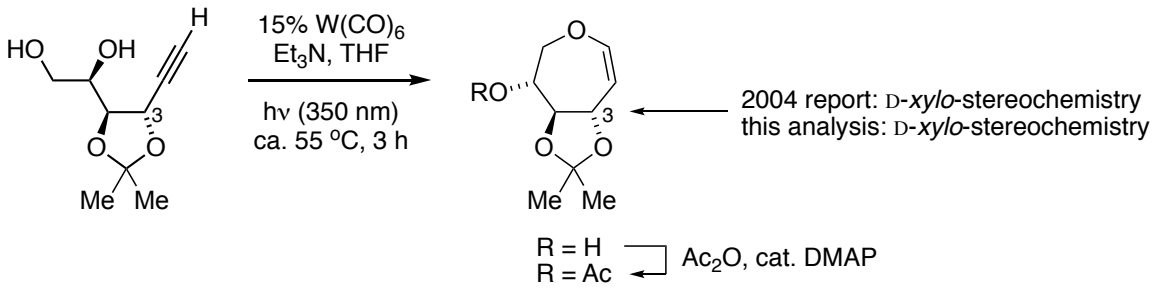
	compound **13-OH** in 2004 publication 	compound **13** in 2004 publication 	structure described in this work, confirmed by X-ray crystallography  **12a**
^{1}H NMR data:	data reported in 2004 publication		data from this work
1	6.37, dd (6.6, 1.8 Hz)	6.38, dd (6.2, 1.8 Hz)	6.42, dd (6.4, 2.0 Hz)
2	5.08, dd (6.6, 1.4 Hz)	5.05, dd (6.2, 1.4 Hz)	5.19, dd (6.5, 1.6 Hz)
3	4.54, d (**9.6** Hz)	4.64 dt (**9.6**, 1.6 Hz)	4.66, dt (**9.7**, 1.8 Hz)
4	3.92, dd (**9.6**, **7.2** Hz)	4.18, dd (**10.0**, **7.6** Hz)	4.16, dd (**9.2**, **7.5** Hz)
5	4.06, m (2H)	5.15, dd (**7.7**, 2.0 Hz)	4.27, dt (**7.4**, 2.6 Hz)
6a		4.23, dd (14.0, 1.2 Hz)	4.17, dd (13.4, 2.1 Hz)
6b	3.99, dd (13.6, 3.6 Hz)	4.01, dd (14.0, 2.8 Hz)	4.03, dd (13.3, 3.2 Hz)

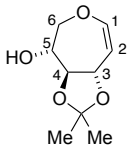
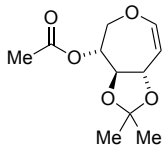
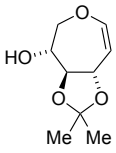
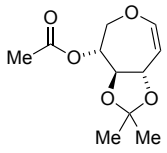
Despite the different protective groups, the coupling constants are similar for all three compounds, especially the diagnostic $^3J_{H3,H4}$ and $^3J_{H4,H5}$.

Conclusions: We must reassign the stereochemistry for the compound labeled **13** in the 2004 publication, to the structure below.



c) Confirmation of stereochemistry of the septanose glycal labeled compound **15-OH** (R = H) and **15** (R = Ac) in 2004 publication:



	compound **15-OH** in 2004 publication	compound **15** in 2004 publication	2004 structures corrected in analysis on page S-29 compound **13-OH**	compound **13**
				
^{1}H NMR data:	data reported in 2004 publication			
1	6.35, dd (6.4, 2.0 Hz)	6.38, dd (6.4, 2.0 Hz)	6.37, dd (6.6, 1.8 Hz)	6.38, dd (6.2, 1.8 Hz)
2	5.05, dd (6.4, 1.6 Hz)	5.05, dd (6.6, 1.4 Hz)	5.08, dd (6.6, 1.4 Hz)	5.05, dd (6.2, 1.4 Hz)
3	4.52, dt (**9.8**, 1.8 Hz)	4.65, dt (**10.0**, 1.6 Hz)	4.54, d (**9.6** Hz)	4.64 dt (**9.6**, 1.6 Hz)
4	3.90, dd (**9.8**, **7.4** Hz)	4.18, dd (**9.6**, **7.6** Hz)	3.92, dd (**9.6**, **7.2** Hz)	4.18, dd (**10.0**, **7.6** Hz)
5	3.98, m (3H)	5.15, dd (**7.8**, 1.8 Hz)	4.06, m (2H)	5.15, dd (**7.7**, 2.0 Hz)
6a		4.23, dd (14.0, 1.2 Hz)		4.23, dd (14.0, 1.2 Hz)
6b		4.01, dd (14.4, 2.8 Hz)	3.99, dd (13.6, 3.6 Hz)	4.01, dd (14.0, 2.8 Hz)
acetyl	na	2.16, s	na	2.15, s
Me	1.41, s	1.45, s	1.46, s	1.45, s
Me	1.40, s	1.43, s	1.44, s	1.43, s
$[\alpha]_D$	-8.67 (c 0.98, $CHCl_3$)	-65.25 (c 0.36, $CHCl_3$)	-10.65 (c 1.11, $CHCl_3$)	-65.65 (c 0.63, $CHCl_3$)

Side-by-side comparison of the ^{1}H NMR data reported in 2004 shows close correlation for all resonances, and therefore also correlates with the structure of compound **12a** in this work, which was determined by X-ray crystallography. The ^{13}C NMR data for the alcohols from the 2004 publication (not depicted here) are also consistent within 0.3 ppm for all resonances, and most ^{13}C resonances for the acetates from the 2004 publication are consistent within 0.6 ppm, although two differences are apparent, which may be erroneous data recording. The optical rotations for both the alcohols and the acetates are consistent with regard to sign and magnitude.

Conclusion: The structures for compounds labeled **13** and **15** in the 2004 publication are identical. The data confirms the stereochemistry of the compound labeled **15**.