Synthesis of 2,6 Dideoxysugars via Ring Closing Olefinic Metathesis

Peter R. Andreana, Jason S. McLellan, Yongchen Chen, Peng George Wang*

Department of Chemistry, Wayne State University, Detroit, Michigan

*pwang@chem.wayne.edu

Experimental Section for Supporting Information

General Methods. Solvents were distilled from the appropriate drying agents before use. The RCM reactions, unless stated otherwise, were all carried out under a positive pressure of argon and were monitored by TLC on silica gel 60 F₂₅₄ (0.25 mm, E. Merck). Spots were detected by using an iodine chamber or from *p*-anisaldehyde stain. The dihydroxylation reactions were carried out at room temperature in the fume hood. All solvents were evaporated under reduced pressure and below 60 °C (bath). Organic solutions of crude products were dried over anhydrous Na₂SO₄ or MgSO₄. Column chromatography was performed with silica gel 60 (40-60µm). The ratio between silica gel and crude product ranged from 100 to 50:1 (w/w). Optical rotations were measured on a Perkin-Elmer 241MC Polarimeter at 23 ± 5 °C. The GC results were obtained on an Agilent 6850 Series GC System. A ChiralDEXTM Capillary GC Column from Alltech in Deerfield, IL. Cat No 71123 was used to obtain ee.'s. The chiral column was Type B-PH which corresponds to a β-cyclodextrin permethylated hydroxypropyl stationary phase. It was 30 m x 0.32 mm in size. ¹H NMR spectra were recorded at 499.753 MHz or 400.078 MHz. ¹³C NMR spectra were recorded at either 125.674 or 100.609 MHz and ¹³C NMR spectra are referenced to CDCl₃ (77.00, CDCl₃) or CD₃OD (47.81, CD₃OD).

General Procedure for the synthesis of Allylic Acids. Magnesium turnings (10 g) were washed with 1 M HCl (200 mL), methanol (200 mL), distilled water (200 mL) and acetone (200 mL). They were then allowed to dry overnight in a 90 °C oven. The magnesium turnings and a few crystals of iodine were then added to 400 mL freshly distilled THF (dry) in a three necked, 1 L round bottom flask equipped with a stir bar, condenser and air trap. The allyl chloride was diluted by twice its volume with THF in a dropping funnel. 50 mL of the diluted allyl chloride was initially added which invoked the mixture to reflux (if the mixture did not reflux after 50 mL addition, more allyl chloride was added (20 mL) and then the vessel was gently heated with a heat gun). The allyl chloride was added drop wise maintaining a gentle reflux until complete consumption. The reaction was then allowed to stir for 30 min under argon and then the temperature was adjusted to -78 °C (using dry ice/acetone). The reaction then turned a milky color and was allowed to stir at -78 °C for 30 min. At this point the argon was removed and replaced with a steady stream of CO₂. The reaction was saturated with CO₂ ca. 1 hr and then the temperature was slowly allowed to increase to 0 °C by removing the cold bath. Once the reaction reached 0 °C, it was then cooled back to -78 °C only this time with a steady stream of CO₂ accompanying it. Once at 0 °C the reaction was saturated once again with CO₂ ca. 10 min. and then the reaction was allowed to warm to 10 °C. The pH was then adjusted to 10 - 11 with cold 2 M NaOH and extracted with diethyl ether three times. The mixture was then acidified with cold 4 M HCl to pH 2 - 3

and extracted three times with diethyl ether. The organic solvent was concentrated under reduced pressure to yield pure homoallyl acid.

Important spectral data for new compounds **4a-4c**.

But-3-enoic acid (**4a**). ^1H NMR (500 MHz, CDCl_3) δ 5.96-5.88 (m, 1H), 5.22 (d, 1H, $J = 1.5$ Hz), 5.20-5.19 (m, 1H), 3.15 (dt, 2H, $J = 1.5, 6.5$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 129.66, 119.42, 38.98; HRMS calcd for $\text{C}_4\text{H}_6\text{O}_2$ (M^+) 86.0368, found 86.0374.

2-Methyl-but-3-enoic acid (**4b**). ^1H NMR (500 MHz, CD_3OD) δ (tdd, 1H, $J = 7.5, 7.5, 7.5$ Hz), 5.06-5.15 (dddd, 2H, $J = 1, 1.9, 10.5, 17.5$ Hz), 3.11 (m, 1H), 1.23 (d, 3H, $J = 7.0$); ^{13}C NMR (125 MHz, CD_3OD) δ 177.10, 137.72, 114.85, 43.69, 16.09; HRMS calcd for $\text{C}_5\text{H}_8\text{O}_2$ (M^+) 100.0524, found 100.0522.

3-Methyl-but-3-enoic acid (**4c**). ^1H NMR (500 MHz, CDCl_3) δ 4.96 (t, 1H, $J = 1.5$ Hz), 4.89 (s, 1H), 3.08 (s, 2H), 1.84 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 177.97, 138.12, 115.60, 43.31, 22.62; HRMS calcd for $\text{C}_5\text{H}_8\text{O}_2$ (M^+) 100.0524, found 100.0523.

General procedure for the synthesis of esters. The acids (**4a-4c**) 2 g and the alcohol, 1 mol eq., are dissolved in 30 mL of dry chloroform. *p*-TsOH (1 mol %) is added. The reaction vessel is equipped with an inverse Dean Stark trap partially filled with 4 Å MS and fitted with a condenser. The reaction is heated to reflux and allowed to stir overnight. The product is then concentrated under reduced pressure. Silica gel column chromatography (hexanes:ethyl acetate, 15:1) is then used to purify the ester.

Important spectral data for new compounds **6a** through **6j**.

But-3-enoic acid allyl ester (**6a**). ^1H NMR (500 MHz, CDCl_3) δ 5.98-5.88 (m, 2H), 5.34-5.16 (m, 4H), 4.6 (dd, 2H, $J = 1.0, 3.5$ Hz), 3.12 (dd, 2H, $J = 1.0, 4.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 171.45, 132.25, 130.37, 118.93, 118.60, 65.57, 39.32; MS ES^+ m/z (M^+) 125.92.

2-Methyl-but-3-enoic acid allyl ester (**6b**). ^1H NMR (300 MHz, CDCl_3) δ 5.98-5.84 (m, 2H), 5.34-5.08 (m, 4H), 4.58 (dd, 2H, $J = 1.2, 5.4$ Hz), 3.22-3.13 (m, 1H), 1.27 (d, 3H, $J = 6.9$ Hz); ^{13}C NMR (75.5 MHz, CDCl_3) δ 174.32, 137.26, 132.36, 118.29, 116.22, 65.40, 43.90, 16.90; HRMS calcd for $\text{C}_8\text{H}_{12}\text{O}_2$ (M^+) 140.0837, found 140.0838.

3-Methyl-but-3-enoic acid allyl ester (**6c**). ^1H NMR (500 MHz, CDCl_3) δ 5.92-5.87 (m, 1H), 5.29 (d, 1H, $J = 17.5$ Hz), 5.21 (d, 2H, $J = 10.5$ Hz), 4.86 (d, 2H, $J = 29$ Hz), 4.57 (d, 2H, $J = 5.5$ Hz), 3.04 (s, 2H), 1.79 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.19, 138.64, 132.31, 118.46, 114.96, 65.44, 43.57, 22.63; HRMS calcd for $\text{C}_8\text{H}_{12}\text{O}_2$ (M^+) 140.0837, found 140.0833.

But-3-enoic acid 2-methyl-allyl ester (**6d**). ^1H NMR (500 MHz, CDCl_3) δ 5.97-5.92 (m, 1H), 5.19 (dd, 1H, $J = 1.5, 6.5$ Hz), 5.17 (t, 1H, $J = 1.5$ Hz), 4.95 (dd, 2H, $J = 1.5, 22$ Hz), 4.52 (s, 2H), 3.14 (dt, 2H, $J = 1.5, 7.5$ Hz), 1.75 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.47, 140.05, 130.40, 118.92, 113.22, 68.12, 39.37, 19.73; MS ES^+ m/z (M^+) 140.02.

2-Methyl-but-3-enoic acid 2-methyl-allyl ester (**6e**). ^1H NMR (400 MHz, CDCl_3) δ 5.95-5.86 (m, 1H), 5.14-5.06 (m, 2H), 4.90 (d, 2H, $J = 21.2$ Hz), 4.47 (s, 2H), 3.16 (m, 1H), 1.71 (s, 3H), 1.26 (d, 3H, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 174.19,

140.11, 137.25, 116.17, 112.91, 67.89, 43.94, 19.60, 16.86. HRMS calcd for $C_9H_{14}O_2$ (M⁺) 154.0994, found 154.0994.

3-Methyl-but-3-enoic acid 2-methyl-allyl ester (**6f**). ¹H NMR (400 MHz, CDCl₃) δ 4.95-4.84 (m, 4H), 4.49 (s, 2H), 3.06 (s, 2H), 1.80 (s, 3H), 1.73 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.23, 140.06, 138.64, 115.01, 113.16, 68.04, 43.62, 22.67, 19.68; HRMS calcd for $C_9H_{14}O_2$ (M⁺) 154.0994, found 154.0998.

General procedure for the Lindlar's reduction (6g-6j). The propargylic esters were dissolved in methylene chloride (20 mL/g) and 15 mol% of Lindlar's catalyst was added. The reaction vessel was charged with H₂ (g) at 1 atm (balloon) and stirred for 2-4 hrs. The reaction was monitored via TLC (hexanes:ethylacetate, 10:1) until completion and then it was passed through a thin pad of Celite® to remove the catalyst. The ester was then concentrated under reduced pressure.

(*S*) But-3-enoic acid 1-methyl-allyl ester (**6g**). ¹H NMR (500 MHz, CDCl₃) δ 5.92-5.90 (m, 1H), 5.88-5.80 (m, 1H), 5.36-5.32 (m, 1H), 5.26-5.21 (dd, 1H, *J* = 1.5, 19.0 Hz), 5.16-5.10 (m, 3H), 3.06 (dt, 2H, *J* = 1.0, 7.0 Hz), 1.29 (d, 3H, *J* = 6.5 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 168.89, 135.35, 127.14, 119.83, 117.72, 74.19, 37.12, 18.86. MS ES⁺ *m/z* (M⁺) 140.11.

$[\alpha]_D^{23} = -10^\circ$ (*c* = 1.0, CHCl₃).

ee. = 94% GC conditions: Temp. ramp – 70 °C → 140 °C @ 1 °C/min

Injector Temp – 150 °C

Detector Temp – 200 °C

He(g) flow rate – 0.75 mL/min

(*S*) 3-Methyl-but-3-enoic acid 1-methyl-allyl ester (**6h**). ¹H NMR (500 MHz, CDCl₃) δ 5.86-5.79 (m, 1H), 5.38-5.33 (m, 1H), 5.23 (d, 1H, *J* = 17.0 Hz), 5.11 (d, 1H, *J* = 10.5 Hz), 4.86 (d, 2H, *J* = 27.5 Hz), 3.02 (s, 2H), 1.8 (s, 3H), 1.3 (s, 3H, *J* = 6.5 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 170.79, 138.81, 137.75, 116.04, 114.77, 71.35, 43.91, 22.61, 20.05; HRMS calcd for $C_9H_{14}O_2$ (M⁺) 154.0994, found 154.1110.

$[\alpha]_D^{23} = -13^\circ$ (*c* = 0.7, CHCl₃).

ee. = 96% GC conditions: Temp. ramp – 50 °C → 140 °C @ 1 °C/min

Injector Temp – 150 °C

Detector Temp – 200 °C

He(g) flow rate – 0.50 mL/min

(*R*) But-3-enoic acid 1-methyl-allyl ester (**6i**). ¹H NMR (500 MHz, CDCl₃) δ 5.91-5.88 (m, 1H), 5.85-5.78 (m, 1H), 5.36-5.31 (m, 1H), 5.24-5.19 (dd, 1H, *J* = 1.5, 19.0 Hz), 5.16-5.10 (m, 3H), 3.06 (dt, 2H, *J* = 1.0, 7.0 Hz), 1.29 (d, 3H, *J* = 6.5 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 170.89, 137.75, 130.54, 118.63, 116.02, 71.39, 39.59, 20.06; MS ES⁺ *m/z* (M⁺) 140.02.

$[\alpha]_D^{23} = +12^\circ$ (*c* = 1.0, CHCl₃).

ee. = 96% GC conditions: Temp. ramp – 70 °C → 140 °C @ 1 °C/min

Injector Temp – 150 °C

Detector Temp – 200 °C

He(g) flow rate – 0.75 mL/min

(*R*) 3-Methyl-but-3-enoic acid 1-methyl-allyl ester (**6j**). ¹H NMR (500 MHz, CDCl₃) δ 5.86-5.79 (m, 1H), 5.38-5.33 (m, 1H), 5.23 (d, 1H, *J* = 17.0 Hz), 5.11 (d, 1H, *J*

= 10.5 Hz), 4.86 (d, 2H, J = 27.5 Hz), 3.02 (s, 2H), 1.8 (s, 3H), 1.3 (s, 3H, J = 6.5 Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 170.79, 138.81, 137.75, 116.04, 114.77, 71.35, 43.91, 22.61, 20.05; HRMS calcd for $\text{C}_9\text{H}_{14}\text{O}_2$ (M^+) 154.0994, found 154.0982.

$[\alpha]_{\text{D}}^{23}$ = +15° (c = 1.0, CHCl_3).

ee = 98% GC conditions: Temp. ramp – 50 °C → 140 °C @ 1 °C/min

Injector Temp – 150 °C

Detector Temp – 200 °C

$\text{He}_{(\text{g})}$ flow rate – 0.50 mL/min

General Procedure for RCM. A 2 L, three necked round bottom flask was charged with 1.7 L of either methylene chloride or chloroform (dry). 2.0 g of ester was added along with 0.3 mol eq. of $\text{Ti}(\text{OiPr})_4$ and the mix was refluxed for 1.5 hrs. A stream of argon was then introduced at a very slow rate. 0.9 mol% of Grubbs' second generation catalyst **2** was then introduced and the mixture was allowed to reflux for 6 hrs. If after the aforementioned time frame elapsed and the reaction was not complete, an additional 0.2 mol% of Grubbs' second generation catalyst was added. When Grubbs' first generation catalyst **1** was used, 3 mol% was added and the procedure remained the same. Upon completion of the ring closing metathesis reaction (as indicated by TLC, hexanes:ethylacetate, 4:1; iodine stain), the β,γ -unsaturated δ -lactone was concentrated under low pressure and then allowed to pass through a thin pad of silica gel to remove the $\text{Ti}(\text{OiPr})_4$. Column chromatography ensued (hexanes:ethylacetate) to remove small traces of cross metathesis product (<1% w/w) and yield the final product.

Important spectral data for new compounds **8a** through **8j**.

3,6-Dihydro-pyran-2-one (**8a**). ^1H NMR (500 MHz, CDCl_3) δ 5.88-5.80 (m, 2H), 4.86-4.84 (m, 2H), 3.03-3.01 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 168.97, 122.57, 122.03, 69.20, 30.33; DEPT 69.20 (CH_2), 30.33 (CH_2); HRMS for $\text{C}_5\text{H}_6\text{O}_2$ (M^+) 98.0368, found 98.0372.

3-Methyl-3,6-dihydro-pyran-2-one (**8b**). ^1H NMR (400 MHz, CDCl_3) δ 5.82-5.78 (m, 1H), 5.71-5.67 (m, 1H), 4.76-4.74 (m, 2H), 2.97-2.93 (m, 1H), 1.24 (d, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 172.71, 128.74, 122.28, 68.61, 35.11, 17.47; DEPT 68.61 (CH_2); HRMS calcd for $\text{C}_6\text{H}_8\text{O}_2$ (M^+) 112.0524, found 112.0522.

4-Methyl-3,6-dihydro-pyran-2-one (**8c**). ^1H NMR (500 MHz, CDCl_3) δ 5.57-5.55 (m, 1H), 4.81-4.79 (m, 2H), 2.94 (s, 2H), 1.75 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.66, 130.81, 116.29, 68.91, 35.07, 21.64; DEPT 68.91 (CH_2), 35.07 (CH_2); HRMS for $\text{C}_6\text{H}_8\text{O}_2$ (M^+) 112.0524, found 112.0527.

5-Methyl-3,6-dihydro-pyran-2-one (**8d**). ^1H NMR (500 MHz, CDCl_3) δ 5.42-5.41 (m, 1H), 4.65 (s, 2H), 2.94-2.93 (m, 2H), 1.64 (d, 3H, J = 1 Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 169.34, 130.03, 116.04, 72.08, 29.96, 18.10; DEPT 72.08 (CH_2), 29.96 (CH_2); HRMS for $\text{C}_6\text{H}_8\text{O}_2$ (M^+) 112.0524, found 112.0526.

3,6-Dimethyl-3,6-dihydro-pyran-2-one (**8e**). ^1H NMR (400 MHz, CDCl_3) δ 5.84-5.74 (m, 2H), 5.15-4.96 (m, 1H), 3.18-2.97 (m, 1H), 1.43 (t, 3H, J = 6.8), 1.36 (t, 3H, J = 7.6 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 172.91, 128.10, 126.99, 75.48, 34.30, 21.83, 17.78; HRMS calcd for $\text{C}_7\text{H}_{10}\text{O}_2$ (M^+) 126.0681, found 126.06781.

4,5-Dimethyl-3,6-dihydro-pyran-2-one (**8f**). ^1H NMR (400 MHz, CDCl_3) δ 4.68 (s, 2H), 2.96 (s, 2H), 1.71 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.30, 122.31, 121.98, 72.49, 35.54, 17.84, 14.17; DEPT 72.49 (CH_2), 35.54 (CH_2); HRMS calcd for $\text{C}_7\text{H}_{10}\text{O}_2$ (M^+) 126.0681, found 126.0685.

(*S*) 6-Methyl-3,6-dihydro-pyran-2-one (**8g**). ^1H NMR (400 MHz, CDCl_3) δ 5.83 (s, 2H), 5.11-5.06 (m, 1H), 3.06-3.04 (m, 2H), 1.46 (d, 3H, $J = 6.4$); ^{13}C NMR (100 MHz, CDCl_3) δ 168.30, 128.04, 121.36, 76.24, 29.91, 22.00; DEPT 76.24 (CH_2); HRMS calcd for $\text{C}_6\text{H}_8\text{O}_2$ (M^+) 112.0524, found 112.05236.
 $[\alpha]_{\text{D}}^{23} = +37^\circ$ ($c = 0.5$, CHCl_3).

(*S*) 4,6-Dimethyl-3,6-dihydro-pyran-2-one (**8h**). ^1H NMR (500 MHz, CDCl_3) δ 5.47 (q, 1H, $J = 1.5$ Hz), 4.97-4.95 (m, 1H), 2.89 (s, 2H), 1.72 (s, 3H), 1.36 (d, 3H, $J = 7.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 170.00, 130.11, 121.99, 75.97, 34.59, 22.11, 21.61; DEPT 34.59 (CH_2); MS ES^+ m/z (M^+) 127.26.
 $[\alpha]_{\text{D}}^{23} = +40^\circ$ ($c = 0.2$, CHCl_3).

(*R*) 6-Methyl-3,6-dihydro-pyran-2-one (**8i**). ^1H NMR (500 MHz, CDCl_3) δ 5.77-5.76 (m, 2H), 5.03-4.99 (m, 1H), 2.98-2.95 (m, 2H), 1.38-1.36 (m, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.35, 127.98, 121.32, 76.21, 29.84, 21.89; DEPT 29.84 (CH_2); HRMS for $\text{C}_6\text{H}_8\text{O}_2$ (M^+) 112.0524, found 112.0523.
 $[\alpha]_{\text{D}}^{23} = -38.5^\circ$ ($c = 0.5$, CHCl_3).

(*R*) 4,6-Dimethyl-3,6-dihydro-pyran-2-one (**8j**). ^1H NMR (500 MHz, CDCl_3) δ 5.57 (q, 1H, $J = 1.5$ Hz), 5.03-4.99 (m, 1H), 2.95 (s, 2H), 1.87 (s, 3H), 1.39 (d, 3H, $J = 7.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 169.88, 129.85, 121.57, 75.80, 35.02, 22.41, 21.68; DEPT 35.02 (CH_2); HRMS for $\text{C}_7\text{H}_{10}\text{O}_2$ (M^+) 126.0681 found 126.06807.
 $[\alpha]_{\text{D}}^{23} = -42^\circ$ ($c = 0.2$, CHCl_3).

General Procedure for Asymmetric Dihydroxylation. In a 25 mL round bottom flask was added a 1:1 mix of 1.5 M KH_2PO_4 pH=10.1/ i BuOH (10 mL) and freshly crushed 3 mol eq. of $\text{K}_3\text{Fe}(\text{CN})_6$. The resulting reddish/orange solution was stirred until complete homogeneity (heating may have been required). 5 mol% of chiral ligand and 100 mg of the β,γ -unsaturated δ -lactone was added. The mixture was then cooled to -4°C (ice + salt) whereby 4 mol% of $\text{K}_2\text{OsO}_2(\text{OH})_4$ was added quickly. The reaction was monitored via TLC (ethylacetate/methanol; 5:2) until all the starting olefin was depleted (2-16 hrs). The pH was checked every 3 hrs and maintained at 10.1 through the addition of 2 N NaOH (cold). The top layer was siphoned off by using either a micropipette or separatory funnel. The dihydroxylated product was reduced under low pressure and purified by column chromatography using ethylacetate and methanol as the mobile phase.

Important spectral data for new compounds **9a** through **9j**.

4(*R*),5(*S*)-Dihydroxy-tetrahydro-pyran-2-one (**9a**). ^1H NMR (500 MHz, CD_3OD) δ 4.43-4.41 (tt, 1H, $J = 2.5, 2.5$ Hz), 4.37-4.35 (s, 1H, $J = 1.5$ Hz), 3.77-3.67 (qd, 2H, $J = 4.0, 13.0, 23.5$ Hz), 2.93-2.89 (dd, 1H, $J = 7.0, 11.0$ Hz) 2.39-2.35 (dd, 1H, $J = 2.5, 15.0$ Hz); ^{13}C NMR (125 MHz, CD_3OD) δ 177.47, 88.99, 68.52, 61.34, 37.97; DEPT 61.34 (CH_2), 37.97 (CH_2); HRMS for $\text{C}_5\text{H}_8\text{O}_4$ ($\text{M} + \text{H}^+$) 132.0423, found 133.05008.
 $[\alpha]_{\text{D}}^{23} = -13.3^\circ$ ($c = 1.0$, MeOH).

$ee.$ = 95% GC conditions: Temp. ramp – $150^\circ\text{C} \rightarrow 240^\circ\text{C}$ @ $1^\circ\text{C}/\text{min}$

Injector Temp – 200 °C
 Detector Temp – 200 °C
 He_(g) flow rate – 2.00 mL/min

The hydroxyl groups were converted to trifluoroacetates according to referenced protocol for GC analysis.¹

4(*S*),5(*R*)-Dihydroxy-tetrahydro-pyran-2-one (**9b**). ¹H NMR (500 MHz, CD₃OD) δ 4.47-4.44 (m, 1H), 4.40-4.38 (d, 1H, *J* = 1.5 Hz), 3.83-3.80 (qd, 2H, *J* = 3.5, 12.5, 24.0, Hz), 2.95-2.91 (dd, 1H, *J* = 7.0, 10.5 Hz), 2.40-2.36 (dd, 1H, *J* = 3.0, 15.0 Hz); ¹³C NMR (125 MHz, CD₃OD) δ 178.47, 89.00, 67.46, 60.53, 38.13; DEPT 60.53 (CH₂), 38.13 (CH₂); HRMS for C₅H₈O₄ (M + H)⁺ 132.0423, found 133.04825. $[\alpha]_D^{23}$ = +12.7° (*c* = 1.0, MeOH).

ee. = 91% GC conditions: Temp. ramp – 150 °C → 240 °C @ 1 °C/min

Injector Temp – 200 °C
 Detector Temp – 200 °C
 He_(g) flow rate – 2.00 mL/min

The hydroxyl groups were converted to trifluoroacetates according to referenced protocol for GC analysis (see footnote 1).

4(*R*),5(*S*)-Dihydroxy-6(*S*)-methyl-tetrahydro-pyran-2-one (**9c**). ¹H NMR (500 MHz, CD₃OD) δ 4.42-4.40 (dt, 1H, *J* = 2.0, 7.0 Hz), 4.18 (t, 1H, *J* = 2.5 Hz), 3.93-3.88 (qd, 1H, *J* = 2.5, 7.0 Hz), 2.94-2.89 (dd, 1H, *J* = 7.0, 17.5 Hz), 2.36-2.32 (dd, 1H, *J* = 2.0, 18.0 Hz), 1.25 (d, 3H, *J* = 6.5 Hz); ¹³C NMR (125 MHz, CD₃OD) δ 167.47, 91.00, 69.20, 67.00, 37.88, 18.38; DEPT 37.88 (CH₂); HRMS for C₆H₁₀O₄ (M⁺) 146.0579, found 146.0583.

4(*S*),5(*R*)-Dihydroxy-6(*S*)-methyl-tetrahydro-pyran-2-one (**9d**). ¹H NMR (500 MHz, CD₃OD) δ 4.52-4.50 (dt, 1H, *J* = 2.0, 7.0 Hz), 4.18 (t, 1H, *J* = 2.5 Hz), 3.93-3.88 (qd, 1H, *J* = 2.5, 7.0 Hz), 2.94-2.89 (dd, 1H, *J* = 7.0, 17.5 Hz), 2.36-2.32 (dd, 1H, *J* = 2.0, 18.0 Hz), 1.25 (d, 3H, *J* = 6.5 Hz); ¹³C NMR (125 MHz, CD₃OD) δ 167.47, 92.05, 69.20, 67.00, 38.06, 17.74; DEPT 37.88 (CH₂); MS ES⁺ *m/z* (M⁺) 146.23.

4(*R*),5(*S*)-Dihydroxy-4,6(*S*)-dimethyl-tetrahydro-pyran-2-one (**9e**). ¹H NMR (500 MHz, CDCl₃) δ 4.15 (s, 1H), 4.05 (t, 1H, *J* = 3.5 Hz), 2.85 (d, 1H, *J* = 15.0 Hz), 2.48 (d, 1H, *J* = 15.0 Hz), 1.53 (s, 3H), 1.35 (d, 3H, *J* = 7.0 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 177.47, 92.35, 66.40, 44.24, 22.60, 20.65; DEPT 44.24 (CH₂); HRMS for C₇H₁₂O₄ (M⁺) 160.0736, found 160.0732.

4(*S*),5(*R*)-Dihydroxy-4,6(*S*)-dimethyl-tetrahydro-pyran-2-one (**9f**). ¹H NMR (500 MHz, CDCl₃) δ 4.38 (p, 1H, *J* = 3.5), 4.15 (s, 1H), 2.92 (d, 1H, *J* = 12.0 Hz), 2.56 (d, 1H, *J* = 12.0 Hz), 2.05 (s, 3H), 1.45 (d, 3H, *J* = 7.0 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 176.47, 94.99, 70.42, 44.29, 22.65, 21.22; DEPT 44.29 (CH₂); MS ES⁺ *m/z* (M⁺) 160.13.

4(*S*),5(*R*)-Dihydroxy-6(*R*)-methyl-tetrahydro-pyran-2-one (**9g**). ¹H NMR (500 MHz, CD₃OD) δ 4.45-4.43 (dt, 1H, *J* = 2.0, 7.0 Hz), 4.21 (t, 1H, *J* = 2.5 Hz), 3.93-3.89 (qd, 1H, *J* = 2.5, 7.0 Hz), 2.93-2.90 (dd, 1H, *J* = 7.0, 17.0 Hz), 2.36-2.34 (dd, 1H, *J* = 2.0, 18.0 Hz), 1.28 (d, 3H, *J* = 6.5 Hz); ¹³C NMR (125 MHz, CD₃OD) δ 167.87, 91.12, 69.20, 67.05, 37.88, 18.59; DEPT 37.88 (CH₂); HRMS for C₆H₁₀O₄ (M⁺) 146.0579, found 146.0587.

¹ Koenig, W. A.; Mischnick-Luebbecke, P.; Brassat, B.; Lutz, S.; Wenz, G.; *Carbohydr. Res.* **1988**, *183*, 11-18.

4(*R*),5(*S*)-Dihydroxy-6(*R*)-methyl-tetrahydro-pyran-2-one (**9h**). ^1H NMR (500 MHz, CD_3OD) δ 4.54 (dt, 1H, $J = 2.0, 7.0$ Hz), 4.18 (t, 1H, $J = 2.5$ Hz), 3.95-3.90 (qd, 1H, $J = 2.5, 7.0$ Hz), 2.94-2.89 (dd, 1H, $J = 7.0, 17.5$ Hz), 2.36-2.32 (dd, 1H, $J = 2.0, 18.0$ Hz), 1.30 (d, 3H, $J = 6.5$ Hz); ^{13}C NMR (125 MHz, CD_3OD) δ 167.47, 92.05, 69.20, 67.00, 38.06, 17.74; DEPT 37.88 (CH_2); HRMS for $\text{C}_6\text{H}_{10}\text{O}_4$ (M^+) 146.0579, found 146.0574.

4(*S*),5(*R*)-Dihydroxy-4,6(*R*)-dimethyl-tetrahydro-pyran-2-one (**9i**). ^1H NMR (500 MHz, CD_3OD) δ 4.23 (s, 1H), 4.14 (t, 1H, $J = 4.0$ Hz), 2.94 (d, 1H, $J = 17.0$ Hz), 2.43 (d, 1H, $J = 14.5$ Hz), 1.68 (s, 3H), 1.30 (d, 3H, $J = 7.0$ Hz); ^{13}C NMR (125 MHz, CD_3OD) δ 178.47, 94.23, 69.32, 44.38, 22.70, 21.08; DEPT 44.38 (CH_2); MS ES^+ m/z ($\text{M} + 1$) $^+$ 161.09.

4(*R*),5(*S*)-Dihydroxy-4,6(*R*)-dimethyl-tetrahydro-pyran-2-one (**9j**). ^1H NMR (500 MHz, CDCl_3) δ 4.22 (t, 1H, $J = 3.0$), 4.19 (s, 1H), 2.87 (d, 1H, $J = 12.0$ Hz), 2.54 (d, 1H, $J = 12.0$ Hz), 2.14 (s, 3H), 1.35 (d, 3H, $J = 7.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 178.47, 91.99, 70.58, 44.54, 22.63, 21.02; DEPT 44.54 (CH_2); HRMS for $\text{C}_7\text{H}_{12}\text{O}_4$ (M^+) 160.0736, found 160.0733.

General Procedure for Borohydride Reduction. A 50 mL round bottom flask was charged with 25 mL of 1.0 M AcOH/AcONa pH 5.2 and 100 mg of dihydroxylated lactone. 3.5 mol eq. of $\text{Na}(\text{CN})\text{BH}_3$ was added and the reaction mixture stirred at room temperature for 16 hrs. TLC (17:3:1, ethylacetate/methanol/water) confirmed completion of reduction. The reaction was then lyophilized and subjected to column chromatography using the solvent system as stated above. The fractions were then collected and concentrated under reduced pressure followed by lyophilization to yield the 2,6-dideoxysugar.

Important spectral data for new compounds **10a** through **10j**.

2-Deoxy-L-ribose (**10a**). Mixture of α/β anomers. Selected data for α anomer. ^1H NMR (500 MHz, D_2O) δ 5.13 (t, 1H, $J = 3.5$), 3.98-3.93 (dt, 1H, $J = 3.5, 10.0$ Hz), 3.81-3.79 (dd, 1H, $J = 2.5, 12.5$ Hz), 3.69 (d, 1H, $J = 2.0$ Hz), 3.54-3.50 (dd, 1H, $J = 6.5, 15.5$ Hz), 1.85-1.79 (dq, 1H, $J = 3.5, 6.5$ Hz), 1.65-1.61 (dt, 1H, $J = 3.5, 9.5$ Hz); ^{13}C NMR (125 MHz, D_2O) δ 91.71, 67.36, 64.61, 62.86, 33.70; DEPT 62.86 (CH_2); HRMS for $\text{C}_5\text{H}_{10}\text{O}_4$ (M^+) 134.0579 found 134.0663.

2-Deoxy-D-ribose (**10b**). Mixture of α/β anomers. Selected data for α anomer. ^1H NMR (400 MHz, D_2O) δ 5.19 (t, 1H, $J = 3.0$), 3.95-3.91 (dt, 1H, $J = 3.0, 9.0$ Hz), 3.81-3.78 (dd, 1H, $J = 2.0, 12.0$ Hz), 3.71 (d, 1H, $J = 2.0$ Hz), 3.54-3.50 (dd, 1H, $J = 6.0, 15.0$ Hz), 1.85-1.79 (q, 1H, $J = 3.0$ Hz), 1.68-1.65 (t, 1H, $J = 3.0$ Hz); ^{13}C NMR (100 MHz, D_2O) δ 91.83, 67.43, 64.53, 62.84, 33.67; DEPT 62.84 (CH_2); HRMS for $\text{C}_5\text{H}_{10}\text{O}_4$ (M^+) 134.0579 found 134.0571.

L-Digitoxose (**10c**). Mixture of α/β anomers. Selected data for α anomer. ^1H NMR (500 MHz, D_2O) δ 5.25-5.20 (t, 1H, $J = 2.5$ Hz), 4.28 (ddd, 1H, $J = 2.0, 2.5, 4.0$ Hz), 3.98-3.95 (qd, 1H, $J = 3.0, 7.5$ Hz), 3.68 (dd, 1H, $J = 7.0, 17.0$ Hz), 2.01-1.97 (dd, 2H, $J = 2.0, 18.0$ Hz), 1.15 (d, 3H, $J = 6.5$ Hz); ^{13}C NMR (125 MHz, D_2O) δ 91.03, 69.90, 67.20, 64.51, 32.06, 15.38; DEPT 32.06 (CH_2); MS ES^+ m/z 171.13 ($\text{M} + \text{Na}$) $^+$. $[\alpha]_{\text{D}}^{23} = -43^\circ$ ($c = 1.0, \text{D}_2\text{O}$).

2-Deoxy-L-fucose (**10d**). Mixture of α/β anomers. Selected data for α anomer. ^1H NMR (500 MHz, D_2O) δ 5.37-5.32 (t, 1H, $J = 3.5$ Hz), 4.15 (dq, 1H, $J = 2.0, 7.0$ Hz), 4.08-4.05 (dd, 1H, $J = 3.0, 6.5$ Hz), 3.68 (d, 1H, $J = 7.0$ Hz), 1.83-1.81 (dd, 2H, $J = 2.0, 18.0$ Hz), 1.20 (d, 3H, $J = 7.0$ Hz); ^{13}C NMR (125 MHz, D_2O) δ 93.51, 70.82, 69.57, 66.54, 34.56, 17.88; DEPT 34.56 (CH_2); MS ES^+ m/z 149.16 ($\text{M} + \text{H}$) $^+$. $[\alpha]_{\text{D}}^{23} = -45^\circ$ ($c = 1.0$, D_2O).

L-olivomycopyranose (**10e**). Mixture of α/β anomers. Selected data for α anomer. ^1H NMR (500 MHz, D_2O) δ 5.33 (bs, 1H), 4.18 (d, 1H, $J = 7.0$ Hz), 4.10 (m, 1H), 3.28 (s, 1H), 1.95 (ddd, 1H, $J = 2.0, 2.5, 7.0$ Hz), 1.84 (qd, 1H, $J = 2.0, 18.0$ Hz), 1.35 (d, 3H, $J = 7.0$ Hz), 1.23 (s, 3H); ^{13}C NMR (125 MHz, D_2O) δ 91.23, 73.57, 67.78, 63.42, 44.52, 22.66, 15.71; DEPT 44.52 (CH_2); HRMS for $\text{C}_7\text{H}_{14}\text{O}_4$ (M^+) 162.0892 found 162.0889. $[\alpha]_{\text{D}}^{23} = -17^\circ$ ($c = 1.0$, D_2O).

L-mycarose (**10f**). Mixture of α/β anomers. Selected data for α anomer. ^1H NMR (500 MHz, D_2O) δ 4.97 (dd, 1H, $J = 2.5, 10.0$ Hz), 3.81 (dq, 1H, $J = 7.0, 10.0$ Hz), 3.46 (ddd, 1H, $J = 2.0, 4.0, 10.0$ Hz), 2.12 (dd, 1H, $J = 2.0, 14.0$ Hz), 2.03 (dd, 1H, $J = 5.0, 15.0$ Hz), 1.25 (d, 3H, $J = 9.0$ Hz), 1.20 (s, 3H); ^{13}C NMR (125 MHz, D_2O) δ 91.45, 78.26, 68.14, 61.14, 41.65, 21.03, 19.85; DEPT 41.65 (CH_2); MS ES^+ m/z 163.23 ($\text{M} + \text{H}$) $^+$. $[\alpha]_{\text{D}}^{23} = -27^\circ$ ($c = 1.0$, D_2O).

D-Digitoxose (**10g**). Mixture of α/β anomers. Selected data for α anomer. ^1H NMR (500 MHz, D_2O) δ 5.23 (bs, 1H), 4.35 (dd, 1H, $J = 2.0, 4.0$ Hz), 3.98-3.94 (qd, 1H, $J = 3.0, 7.0$ Hz), 3.72 (dd, 1H, $J = 7.0, 17.0$ Hz), 2.01 (dd, 2H, $J = 2.0, 18.0$ Hz), 1.21 (d, 3H, $J = 6.0$ Hz); ^{13}C NMR (125 MHz, D_2O) δ 91.21, 69.72, 67.41, 64.51, 32.06, 15.38; DEPT 32.06 (CH_2); MS ES^+ m/z 171.08 ($\text{M} + \text{Na}$) $^+$. $[\alpha]_{\text{D}}^{23} = +43^\circ$ ($c = 1.0$, D_2O).

2-Deoxy-D-fucose (**10h**). Mixture of α/β anomers. Selected data for α anomer. ^1H NMR (400 MHz, D_2O) δ 5.15 (bs, 1H), 3.95 (q, 1H, $J = 7.0$ Hz), 3.88-3.84 (ddd, 1H, $J = 3.0, 7.0, 12.0$ Hz), 3.49 (d, 1H, $J = 2.0$ Hz), 1.78 (m, 1H), 1.65 (d, 1H, $J = 7.0$ Hz), 1.10 (d, 3H, $J = 7.0$ Hz); ^{13}C NMR (100 MHz, D_2O) δ 92.79, 71.21, 69.58, 65.98, 33.33, 17.58; DEPT 33.33 (CH_2); MS ES^+ m/z 149.33 ($\text{M} + \text{H}$) $^+$. $[\alpha]_{\text{D}}^{23} = +48^\circ$ ($c = 1.0$, D_2O).

D-mycopyranose (**10i**). Mixture of α/β anomers. Selected data for α anomer. ^1H NMR (500 MHz, D_2O) δ 5.25 (t, 1H, $J = 3.0$ Hz), 4.02 (dd, 1H, $J = 3.5, 7.0$ Hz), 3.90 (m, 1H), 3.38 (d, 1H, $J = 2.0$ Hz), 1.84 (ddd, 1H, $J = 2.5, 3.0, 7.0$ Hz), 1.77 (qd, 1H, $J = 2.5, 17.5$ Hz), 1.25 (d, 3H, $J = 7.0$ Hz), 1.15 (s, 3H); ^{13}C NMR (125 MHz, D_2O) δ 93.33, 76.02, 68.67, 64.44, 41.32, 20.03, 16.04; DEPT 41.32 (CH_2); HRMS for $\text{C}_7\text{H}_{14}\text{O}_4$ (M^+) 162.0892, found 162.0883. $[\alpha]_{\text{D}}^{23} = +28^\circ$ ($c = 1.0$, D_2O).

2,6-dideoxy-3-methyl- L-lyxose (**10j**). Mixture of α/β anomers. Selected data for α anomer. ^1H NMR (500 MHz, D_2O) δ 4.93 (bs, 1H), 3.95 (m, 1H), 3.42 (dd, 1H, $J = 2.0, 10.0$ Hz), 2.18 (dd, 1H, $J = 2.0, 13.5$ Hz), 1.98 (dd, 1H, $J = 5.0, 15.0$ Hz), 1.28 (d, 3H, $J = 9.0$ Hz), 1.22 (s, 3H); ^{13}C NMR (125 MHz, D_2O) δ 92.31, 76.01, 68.29, 61.11, 42.03, 20.03, 17.95; DEPT 42.03 (CH_2); MS ES^+ m/z 171.19 ($\text{M} + \text{Na}$) $^+$. $[\alpha]_{\text{D}}^{23} = +14^\circ$ ($c = 1.0$, D_2O).

std menthol
res=0.7Hz
sw probe
April 1 99
lock freq=1.470
new shima

expt s2pol

SAMPLE		DEC. & VT	
solvent	CDCl3	dn	H1
file	exp	dn	0
ACQUISITION		dm	nmh
sfreq	499.753	dmf	c
tn	H1	dpr	200
at	1.928	PROCESSING	
np	32000	wtfile	9
sw	8297.0	proc	ft
fb	4600	fn	not used
bs	4	math	f
ss	1		
tpwr	60	warr	n
pw	5.3	warp	
dl	1.500	whs	
tof	0	wnt	wft
nt	16	DISPLAY	
ct	12	sp	-1654.3
alock	n	wp	8297.0
gain	not used	vs	50
FLAGS		sc	0
il	n	wc	250
in	n	hnm	33.19
dp	y	is	313.55
hs	nm	rfl	1654.3
		rtp	0
		th	5
		ins	100.000
		nm	cdc ph

std menthol
res=0.7Hz
sw probe
April 1 99
lock freq=1.470
new shima

expt s2pol

SAMPLE		DEC. & VT	
solvent	CDCl3	dn	H1
file	exp	dn	0
ACQUISITION		dm	nmh
sfreq	499.758	dmf	c
tn	H1	dpr	200
at	1.928	PROCESSING	
np	32000	wtfile	9
sw	8297.0	proc	ft
fb	4600	fn	not used
bs	4	math	f
ss	1		
tpwr	60	warr	n
pw	5.3	warp	
dl	1.500	whs	
tof	0	wnt	wft
nt	16	DISPLAY	
ct	16	sp	-1654.3
alock	n	wp	8297.0
gain	not used	vs	22
FLAGS		sc	0
il	n	wc	250
in	n	hnm	33.19
dp	y	is	313.55
hs	nm	rfl	1654.3
		rtp	0
		th	5
		ins	100.000
		nm	cdc ph

std menthol
res=0.78s
sw:probe
April 1 '99
lock freq=1.470
new shims

exp1 s2pul

SAMPLE DEC. & VT

SAMPLE	dn	def	hl
solvent	CDCl3	def	0
file	exp	dm	nm
ACQUISITION	dm		
sfreq	499.751	dmf	200
tn	hl	dwr	9
at	1.928	PROCESSING	
np	32000	wtfile	
sw	8297.0	proc	ft
fb	4600	fn	not used
bs	4	math	f
ss	1		
tpwr	60	warr	n
pw	5.3	warp	
d1	2.500	wha	
tof	0	wnt	wft
nt	16	DISPLAY	
ct	4	sp	1854.2
clock	n	wp	8297.0
gain	not used	vs	23
FLAGS	ac		0
il	n	wc	250
in	n	hwm	0.65
dp	y	ls	313.55
hs	nn	rfl	1854.2
	zfp		0
	th		5
	lms		100.000
	ns	ode	ph

Unity 500 spectrometer

proton spectrum

exp1 s2pul

SAMPLE DEC. & VT

SAMPLE	dn	def	hl
solvent	CDCl3	def	0
file	exp	dm	nm
ACQUISITION	dm		
sfreq	400.078	dmf	200
tn	hl	dwr	10
at	1.205	PROCESSING	
np	16000	wtfile	
sw	6641.4	proc	ft
fb	1600	fn	not used
bs	4	math	f
ss	2		
tpwr	58	warr	n
pw	4.8	warp	
d1	2.500	wha	
tof	0	wnt	wft
nt	16	DISPLAY	
ct	16	sp	11.7
clock	n	wp	4005.4
gain	not used	vs	82
FLAGS	ac		0
il	n	wc	250
in	n	hwm	16.02
dp	y	ls	244140.62
hs	nn	rfl	1288.1
	zfp		0
	th		28
	lms		2.900
	ns	ode	ph

Mercury 400 spectrometer

std menthol
res=0.7Hz
sw probe
April 1 99
lock freq=1.470
new shims

expt alpul

SAMPLE DEC. & VT H1
solvent CDCl3 dof 0
file exp dm mm
ACQUISITION dm c
afreq 499.751 dmf 200
tm H1 dper 9
at 1.928 PROCESSING
np 32000 wtf file
sw 8297.0 proc ft
fb 4600 fa not used
bs 4 math f
ss 1
tpwr 60 werr n
pw 5.3 wexp
dl 2.500 wbs
tof 0 wnt wtt
nt 16
et 8 sp DISPLAY
clock n wp -1654.2
gain not used vs 8297.0
FLAG ac 0
il n wc 250
in n hnm 0.63
dp y ls 313.55
hs nm rfi 1654.2
rfp 0
th 5
fns 100.000
nm cdc ph

Unity 500 spectrometer

std menthol
res=0.7Hz
sw probe
April 1 99
lock freq=1.470
new shims

expt alpul

SAMPLE DEC. & VT H1
solvent CDCl3 dof 0
file exp dm mm
ACQUISITION dm c
afreq 499.751 dmf 200
tm H1 dper 9
at 1.928 PROCESSING
np 32000 wtf file
sw 8297.0 proc ft
fb 4600 fa not used
bs 4 math f
ss 1
tpwr 60 werr n
pw 5.3 wexp
dl 1.500 wbs
tof 0 wnt wtt
nt 16
et 8 sp DISPLAY
clock n wp -1654.2
gain not used vs 8297.0
FLAG ac 0
il n wc 250
in n hnm 0.63
dp y ls 313.55
hs nm rfi 1654.2
rfp 0
th 5
fns 100.000
nm cdc ph

Unity 500 spectrometer

Proton spectrum

expt s2pol

SAMPLE DEC. & VT

solvent	CDCL3	dn	not used
file	exp	dper	0
ACQUISITION	dot	0	0
sfreq	300.079	dm	nm
tn	01	dms	0
at	1.600	daf	200
np	16000	PROCESSING	
sw	5000.0	wtfile	
fb	2600	proc	ft
bs	4	fn	not used
ss	2		
tpwr	58	warr	n
pw	5.0	wexp	n
dl	1.500	wha	n
tof	451.0	wnt	wit
nt	16		
ct	12		
clock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-972.2		
wp	5000.0		
vs	26		
ss	0		
ws	250		
hnm	20.00		
ia	299.98		
rfl	972.2		
rfp	0		
th	38		
ins	100.000		
na	ph		

Unity 300 spectrometer

std menthol
res=0.7Hz
sw probe
April 1 89
lock freq=1.470
new shims

expt s2pol

SAMPLE DEC. & VT

solvent	CDCL3	dn	0
file	exp	dm	nm
ACQUISITION	dot	0	0
sfreq	499.751	dms	200
tn	01	dper	0
at	1.928	PROCESSING	
np	32000	wtfile	
sw	8297.0	proc	ft
fb	4600	fn	not used
bs	4	math	c
ss	1		
tpwr	60	warr	n
pw	5.3	wexp	n
dl	1.500	wha	n
tof	0	wnt	wit
nt	16		
ct	12	DISPLAY	
clock	n	sp	-1654.2
gain	not used	wp	8297.0
FLAGS		vs	33
il	n	sq	0
in	n	wu	250
dp	y	hnm	0.65
hs	na	ia	312.55
		rfl	1654.2
		rfp	0
		th	5
		ins	100.000
		na	cdc ph

Unity 300 spectrometer

std methol
res=0.7Hz
av probe
April 1 99
lock freq=1.470
new shima

expt a2pul

SAMPLE DEC. 4 VT

solvent	CDCL3	dof	H1
file	exp	dm	nmn
ACQUISITION	dm	o	
sfreq	499.751	dmf	200
tn	H1	dpwr	9
at	1.928	PROCESSING	
np	32000	wtfile	
sw	8237.0	proc	ft
fb	4600	fn	not used
hs	4	math	c
ss	1		
tpwr	60	warr	n
pw	5.3	wexp	
dl	1.500	wha	
tot	0	wt	wt
nt	16	DISPLAY	
ct	16	sp	-1654.2
clock	n	wp	8237.0
gain	not used	vs	28
PLAGS	sc		0
il	n	wc	250
in	n	hnm	0.65
dp	y	is	313.55
hs	dm	rfl	1654.2
		rtp	0
		th	5
		ins	100.000
		nm	cdc ph

Unity 500 spectrometer

proton spectrum

expt a2pul

SAMPLE DEC. 4 VT

solvent	CDCL3	dof	H1
file	exp	dm	nmn
ACQUISITION	dm	o	
sfreq	400.078	dmf	200
tn	H1	dpwr	30
at	1.205	PROCESSING	
np	16000	wtfile	
sw	6641.4	proc	ft
fb	3600	fn	not used
hs	4	math	c
ss	2		
tpwr	38	warr	o
pw	3.9	wexp	
dl	2.500	wha	
tot	0	wt	wt
nt	16	DISPLAY	
ct	16	sp	-1288.1
clock	n	wp	6641.4
gain	not used	vs	140
PLAGS	sc		0
il	n	wc	250
in	n	hnm	0.13
dp	y	is	313.55
hs	dm	rfl	1288.1
		rtp	0
		th	5
		ins	100.000
		nm	cdc ph

Mercury 400 spectrometer

std menthol
res=0.7Hz
sw probe
April 199
lock freq=1.470
new shims

expt 22pol

SAMPLE DEC. & VT H1
solvent CDCL3 dnf 0
file exp dnf sun
ACQUISITION dnf 0
freq 499.750 dnf 200
tn H1 dnf 9
at 1.928 PROCESSING
up 32000 wfile
sw 8297.0 proc ft
fb 4800 fn not used
bs 4 meth f
ss 1
tper 60 verr n
pw 5.3 wexp
di 1.500 vbs
tof 0 vnt wlt
nt 16 DISPLAY
et 8 sp -1654.3
alock n vp 8297.0
gain not used ve 29
FLAGS eo 0
il n ve 250
in n hnm 0.65
dp y la 313.55
hs nn rfi 1654.3
rfp 0
ch 9
ins 100.000
nm cdc ph

std menthol
res=0.7Hz
sw probe
April 199
lock freq=1.470
new shims

expt 22pol

SAMPLE DEC. & VT H1
solvent CDCL3 dnf 0
file exp dnf sun
ACQUISITION dnf 0
freq 499.751 dnf 200
tn H1 dnf 9
at 1.928 PROCESSING
up 32000 wfile
sw 8297.0 proc ft
fb 4800 fn not used
bs 4 meth f
ss 1
tper 60 verr n
pw 5.3 wexp
di 1.500 vbs
tof 0 vnt wlt
nt 16 DISPLAY
et 8 sp -1654.2
alock n vp 8297.0
gain not used ve 29
FLAGS eo 0
il n ve 250
in n hnm 0.65
dp y la 313.55
hs nn rfi 1654.2
rfp 0
ch 9
ins 100.000
nm cdc ph

std methol
res=0.7Hz
sw probe
April 1 99
lock freq=1.470
new shims

expl s2pul

SAMPLE		DEC. & VT		H1
solvent	CDCl3	dof		0
file	exp	dm		nmn
ACQUISITION		dm		0
afreq	499.750	dmf		200
tn	H1	dpwr		9
at	1.928	PROCESSING		
np	32000	wtfile		
sw	8297.0	proc		ft
rb	4600	fn		not used
bs	4	math		f
ss	1			
tpwr	60	werr		n
pw	5.3	wexp		
d1	1.500	wba		
tof	0	wnt		wft
nt	16	DISPLAY		
ct	16	sp		-1654.3
alock	n	wp		8297.0
gain	not used	va		25
FLAGS		ac		0
il	n	wc		250
in	n	hrm		0.65
dp	y	is		313.55
hs	nm	rfl		1654.3
		rpf		0
		th		5
		ins		100.000
		nm	cdc	ph

Unity 500 spectrometer

std methol
res=0.7Hz
sw probe
April 1 99
lock freq=1.470
new shims

expl s2pul

SAMPLE		DEC. & VT		H1
solvent	CD3OD	dof		0
file	exp	dm		nmn
ACQUISITION		dm		0
afreq	499.753	dmf		200
tn	H1	dpwr		9
at	1.928	PROCESSING		
np	32000	wtfile		
sw	8297.0	proc		ft
rb	4600	fn		not used
bs	4	math		f
ss	1			
tpwr	60	werr		n
pw	5.3	wexp		
d1	2.500	wba		
tof	0	wnt		wft
nt	16	DISPLAY		
ct	16	sp		-1654.2
alock	n	wp		8297.0
gain	not used	va		464
FLAGS		ac		0
il	n	wc		250
in	n	hrm		33.19
dp	y	is		313.55
hs	nm	rfl		1654.2
		rpf		0
		th		5
		ins		100.000
		nm	cdc	ph

Unity 500 spectrometer

std menthol
res=0.7Hz
sw probe
April 1 99
lock freq=1.470
new shima

expt s2pul

SAMPLE		DEC. & VT	
solvent	CD3OD	dof	0
file	exp	dm	nmn
ACQUISITION		dmn	c
afreq	499.753	dmf	200
tn	hl	dpwr	9
at	1.928	PROCESSING	
np	32000	wtfile	
sw	8297.0	proc	ft
fb	4600	fn	not used
bs	4	math	f
ss	1		
tpwr	60	warr	n
pw	5.3	wexp	
dl	2.500	wbs	
tof	0	wnt	wft
nt	16	DISPLAY	
ct	16	sp	-1654.2
clock	n	wp	8297.0
gain	not used	vs	464
FLAGS		sc	0
il	n	sc	250
in	n	hnm	33.19
dp	y	ie	313.55
hs	nn	rfl	1654.2
		rfp	0
		th	5
		lms	100.000
		nm	cdc ph

Unity 500 spectrometer

std menthol
res=0.7Hz
sw probe
April 1 99
lock freq=1.470
new shima

expt s2pul

SAMPLE		DEC. & VT	
solvent	CD3OD	dof	-70.1
file	exp	dm	ynn
ACQUISITION		dmn	c
afreq	499.753	dmf	200
tn	hl	dpwr	6
at	1.928	PROCESSING	
np	32000	lb	0.50
sw	8297.0	wtfile	
fb	4600	proc	ft
bs	4	fn	not used
ss	1	math	f
tpwr	60		
pw	5.3	warr	n
dl	1.000	wexp	
tof	0	wbs	
nt	16	wnt	wft
ct	16	DISPLAY	
clock	n	sp	-1654.2
gain	not used	wp	8297.0
FLAGS		vs	29
il	n	sc	0
in	n	sc	250
dp	y	hnm	33.19
hs	nn	ie	313.55
		rfl	1654.2
		rfp	0
		th	5
		lms	100.000
		nm	cdc ph

Unity 500 spectrometer

Unity 500 spectrometer

Unity 500 spectrometer

std menthol
res=0.7Hz
av probe
April 1 99
lock freq=1.470
new shime

expt s7pul

SAMPLE		DEC. 4 VT	Xi
solvent	CDCl3	def	-70.1
file	exp	da	yya
ACQUISITION			
sfreq	499.753	def	200
ta	NI	dpr	6
at	1.928	PROCESSING	
ap	32000	lb	0.50
sv	8297.0	wtfile	
fb	4600	proc	ft
bs	4	fn	not used
es	1	math	f
tpwr	40		
pw	5.3	werr	a
di	1.000	wamp	
tol	0	wha	
nt	16	vnt	wft
ct	16	DISPLAY	
alock	n	sp	-1654.3
gain	not used	wp	8297.0
FLAGS			
li	n	ac	0
in	n	ec	250
dp	y	hama	33.19
he	no	ie	311.55
		zfl	1654.3
		rtp	0
		th	5
		ins	100.000
		na	cdc ph

std manthol
res=0.7Hz
sw probe
April 1 99
lock freq=1.470
new shine

expt a2pul

SAMPLE		DEC. & VT	
solvent	CD3OD	d1	H1
file	exp	dof	-74.2
ACQUISITION		dmm	yyu
sfreq	499.753	daf	c
tn	H1	dpr	200
at	1.928	PROCESSING	
sp	32000	lb	0.50
sw	8297.0	etfile	
fb	4600	proc	ft
hs	4	fn	not used
ss	1	math	f
tpwr	60		
pw	5.3	wavr	n
d1	1.000	wexp	
tof	0	wbe	
nt	16	wnt	wit
ot	16	DISPLAY	
alock	n	sp	-1654.2
gain	not used	wp	8297.0
FLAGS		vs	55
il	n	ac	0
in	n	ec	250
du	y	hxxm	33.19
hs	nn	is	313.55
		rfl	1654.2
		rfp	0
		th	5
		ins	100.000
		ms	cdc ph

Unity 500 spectrometer

Unity 500 spectrometer

std menthol
res=0.7Hz
sw probe
April 1 99
lock freq=1.470
new shine

exp1 s2pel

SAMPLE		DESC. & VT		
solvent	CDCl3	dn	def	H1
file	exp	dn	nm	
ACQUISITION				
freq	499.758	dnf		100
tn	H1	dpwr		9
at	1.928	PROCESSING		
np	32000	wtfile		
sv	8297.0	proc		ft
fb	4600	fn	not used	
be	4	math		f
ss	1			
tpwr	60	werr		n
pw	5.3	wexp		
dl	1.500	whs		
tof	0	wnt		wft
nt	16	DISPLAY		
ct	16	sp	-1654.3	
alock	n	wp	8297.0	
gain	not used	vs	158	
FLAGS				
il	n	vc	250	
in	n	hmm	33.19	
dp	y	is	784.55	
hs	nn	rfl	1654.3	
		rtp	0	
		th	5	
		ins	1.000	
		nm	cdc	ph

Unity 500 spectrometer

std menthol
res=0.7Hz
sw probe
April 1 99
lock freq=1.470
new shine

exp1 s2pel

SAMPLE		DESC. & VT		
solvent	CDCl3	dn	def	H1
file	exp	dn	nm	
ACQUISITION				
freq	499.758	dnf		100
tn	H1	dpwr		9
at	1.928	PROCESSING		
np	32000	wtfile		
sv	8297.0	proc		ft
fb	4600	fn	not used	
be	4	math		f
ss	1			
tpwr	60	werr		n
pw	5.3	wexp		
dl	1.500	whs		
tof	0	wnt		wft
nt	16	DISPLAY		
ct	16	sp	-1654.3	
alock	n	wp	8297.0	
gain	not used	vs	158	
FLAGS				
il	n	vc	250	
in	n	hmm	33.19	
dp	y	is	784.55	
hs	nn	rfl	1654.3	
		rtp	0	
		th	5	
		ins	1.000	
		nm	cdc	ph

Unity 500 spectrometer

std menthol
res=0.7Hz
sv probe
April 1 99
lock freq=1.470
new shine

expi s2pul

SAMPLE		DEC. & VT	
solvent	CD3OD	def	-70.1
file	exp	da	yyr
ACQUISITION			
afreq	499.753	daf	200
ta	EL	dpwr	6
at	1.938	PROCESSING	
up	32000	lb	0.50
sv	8297.0	wtfile	
fb	4600	proc	ft
ba	4	fn	not used
sa	1	math	f
tpwr	60		
pw	5.3	warr	n
dl	1.000	wexp	
tof	0	ebe	
nt	16	emt	wft
ct	16	DISPLAY	
alock	n	sp	-1654.2
gain	not used	up	8297.0
FLAGS			
il	n	sc	0
in	n	wo	250
dp	y	hmm	33.19
hs	nn	ls	313.55
		rfl	1654.2
		rfp	0
		th	5
		lms	100.000
	nm	cdc	ph

Unity 500 spectrometer

std menthol
res=0.7Hz
sw probe
April 1 99
lock freq=1.470
new shima

expl s2pol

SAMPLE		DEC. & VT		H1
solvent	CD3OD	dof	-70.1	
file	exp	dm	ym	
ACQUISITION				
sfreq	499.753	dmf	200	
tn	h1	dpwr	6	
et	1.928	PROCESSING		
np	32000	lb	0.50	
sw	8297.0	wtfile		
fb	4600	proc	ft	
bs	4	fn	not used	
ss	1	math	f	
tpwr	60			
pw	5.3	warr	n	
dl	1.000	wexp		
tof	0	wbe		
nt	16	wnt	wft	
ct	16	DISPLAY		
alock	n	sp	-1654.2	
gain	not used	vp	8297.0	
FLAGS		va	29	
il	n	ac	0	
in	n	uc	250	
dp	y	hmm	33.19	
hs	na	ie	313.55	
		rfl	1654.2	
		rtp	0	
		th	5	
		ins	100.000	
		nm	cdc ph	

Unity 500 spectrometer

std menthol
res=0.7Hz
sw probe
April 1 99
lock freq=1.470
new shima

expl s2pol

SAMPLE		DEC. & VT		H1
solvent	CD3OD	dof	-70.1	
file	exp	dm	ym	
ACQUISITION				
sfreq	499.753	dmf	200	
tn	h1	dpwr	6	
et	1.928	PROCESSING		
np	32000	lb	0.50	
sw	8297.0	wtfile		
fb	4600	proc	ft	
bs	4	fn	not used	
ss	1	math	f	
tpwr	60			
pw	5.3	warr	n	
dl	1.000	wexp		
tof	0	wbe		
nt	16	wnt	wft	
ct	16	DISPLAY		
alock	n	sp	-1654.2	
gain	not used	vp	8297.0	
FLAGS		va	29	
il	n	ac	0	
in	n	uc	250	
dp	y	hmm	33.19	
hs	na	ie	313.55	
		rfl	1654.2	
		rtp	0	
		th	5	
		ins	100.000	
		nm	cdc ph	

Unity 500 spectrometer

std menthol
res=0.7Hz
sw probe
April 1 99
lock freq=1.470
new shims

expl s2pol

SAMPLE		DEC. & VT	
solvent	CD3OD	dof	0
file	exp	dim	nmn
ACQUISITION	dim	c	
afreq	499.753	dmf	200
tn	H1	qper	9
at	1.924	PROCESSING	
np	32000	wtfile	
sw	8297.0	proc	ft
fb	4600	fn	not used
bs	4	math	t
ss	1		
tpwr	40	warr	n
pw	5.3	wamp	
di	2.500	vas	
tof	0	wat	wfc
nt	16	DISPLAY	
ct	16	sp	-1654.2
clock	n	vp	8297.0
gain	not used	ve	464
FLAGS	sc		0
il	n	wo	250
in	n	hnm	33.19
dp	y	is	313.55
hs	nn	rfl	1654.2
		rtp	0
		th	5
		ina	100.000
		nm	cdc ph

Unity 500 spectrometer

std methanol
res=0.7Hz
sp probe
April 1 99
lock freq=1.470
new shine
expt s2pui

duffy 320 spectrometer

std menthol
res=0.7Hz
sw probe
April 1 99
lock freq=1.470
new shima

Crity 300 spectrometer

expl s2pul

SAMPLE DEC. 6 VT
solvent D2O dnf H1
file exp dm nna
ACQUISITION dm c
freq 499.733 dmf 200
tn H1 dper 9
at 1.928 PROCESSING
np 32000 wtfite ft
sw 8297.0 proc not used
fb 4600 fm
bs 4 math f
ss 1
tpwr 60 werr n
pw 5.3 wexp
dl 2.500 wba
tof 0 wnt wft
nt 16
ct 16 sp -1654.3
alock n wp 8297.0
gain not used vs 464
FLAGS sc 0
il n wc 250
in n hnm 33.19
cp y is 313.55
hs nm rfi 1654.2
rfp 0
th 5
ins 100.000
nm odc ph

std menthol
res=0.7Hz
sw probe
April 1 99
lock freq=1.470
new shima

Crity 300 spectrometer

expl s2pul

SAMPLE DEC. 6 VT
solvent D2O dnf H1
file exp dm yrn
ACQUISITION dm c
freq 499.733 dmf 200
tn H1 dper 6
at 1.928 PROCESSING
np 32000 lb 0.50
sw 8297.0 wtfite ft
fb 4600 proc not used
bs 4 fm
ss 1 math f
tpwr 60
pw 3.7 werr n
dl 1.000 wexp
tof 0 wba
nt 16 wnt wft
ct 16
alock n sp -1654.3
gain not used wp 8297.0
FLAGS vs 34
il n sc 0
in n wc 250
cp y hnm 33.19
hs nm is 313.55
rfi 1654.3
rfp 0
th 5
ins 100.000
nm odc ph

proton spectrum

expt1 s2pul

SAMPLE		DEC. & VT		H1
	dn			
solvent	D2O	def		0
file	exp	dm		mm
ACQUISITION				
streq	400.079	dmf		200
tn	H1	qpr		30
at	1.205	PROCESSING		
sp	16000	wtfile		
sv	6641.4	proc		ft
fb	3600	fn	not used	
bs	4	meth		f
ss	3			
tpwr	50	warr		n
pw	4.0	warp		
dl	2.500	whs		
tof	0	wnt		wft
nt	16	DISPLAY		
et	8	sp	-1288.1	
alock	n	wp	6641.4	
gain	not used	vs	550	
FLAGS				
il	n	wo	350	
in	n	hmm	0.23	
dp	y	ls	313.55	
hs	nn	rfl	1288.1	
		rtp	0	
		th	5	
		ina	100.000	
		nm	cdc ph	

Mercury 400 spectrometer

HO
HO-OH
2-deoxy-D-fucose

std methanol
res=0.7Hz
sw probe
April 1 99
lock freq=1.470
new shine

expt1 s2pul

SAMPLE		DEC. & VT		H1
	dn			
solvent	D2O	def		0
file	exp	dm		mm
ACQUISITION				
streq	499.733	dmf		200
tn	H1	qpr		3
at	1.028	PROCESSING		
sp	32000	wtfile		
sv	8297.0	proc		ft
fb	4600	fn	not used	
bs	4	meth		f
ss	1			
tpwr	50	warr		n
pw	5.7	warp		
dl	2.500	whs		
tof	0	wnt		wft
nt	16	DISPLAY		
et	8	sp	-1654.3	
alock	n	wp	8297.0	
gain	not used	vs	1204	
FLAGS				
il	n	wo	350	
in	n	hmm	0.65	
dp	y	ls	313.55	
hs	nn	rfl	1654.3	
		rtp	0	
		th	5	
		ina	100.000	
		nm	cdc ph	

Unity 500 spectrometer

HO
HO-OH
HO
D-mycarose

RUN# 173

AREAX

RT	AREA	TYPE	WIDTH	AREAX
4.296	514784960	SHB	.994	98.54272
10.870	88384	PB	.193	.01128
21.605	141106	PU	.427	.02781
23.216	119365	UU	.376	.02285

RUN# 160

RT	AREA	TYPE	WIDTH	AREA%
3.655	512058640	>SPB	.989	91.69622
21.670	44540400	BB	.565	7.97730
23.281	963033	PB	.190	.17245

* RUN # 188
START

RUN# 188

RT	AREA	TYPE	WIDTH	AREA%
3.196	712752960	>SBB	1.377	91.67856
7.260	1130631	TBB	.511	.20974
20.664	1010909	PU	.569	.20620
23.461	27720360	UV	.902	6.66406
37.090	749003	UB	.439	.09644

* RUN # 183
START

RUN# 183

AREAX

RT	AREA	TYPE	WIDTH	AREAX
3.888	540489600	>SPB	1.238	91.98982
6.996	3278798	TBB	.451	.47097
20.526	198111	PP	.220	.02046
21.224	60075	PP	.240	.00863
32.569	1193455	UB	.314	.17143
35.185	961531	PB	.255	.13812

* RUN # 175
START

RUN# 175

AREAX

RT	AREA	TYPE	WIDTH	AREAX
3.940	69984	UU	.189	.01085
4.190	285425	UH	.115	.04428
4.263	603100160	>SNB	1.164	93.56781
10.761	2842954	PV	.439	.44107
32.653	36007296	PV	1.320	5.58634
35.294	383935	UP	.435	.13714

* RUN # 185

START

RUN# 185

AREAX

RT	AREA	TYPE	WIDTH	AREAX
1.927	86232704	PD	.544	13.80536
3.803	59836	BH	.118	.00902
3.905	542443520	>SHB	1.048	81.80970
32.160	521619	PV	.693	.07067
35.185	24225904	UB	1.381	3.65368

* RUN # 212

START

RUN# 212

AREAX

RT	AREA	TYPE	WIDTH	AREAX
1.221	590520320	>SPB	1.141	99.75472
27.221	234218	BU	.278	.05381
28.578	264310	PP	.337	.05855

* RUN # 207
START

RUN# 207

AREAX

RT	AREA	TYPE	WIDTH	AREAX
1.446	485882400	>SBB	.938	98.92784
8.487	86464	PU	.260	.01760
11.490	105669	UU	.299	.02151
27.744	3141960	PU	.489	.63971
28.565	77845	PU	.218	.01621

* RUN# 210
START

RUN# 210

AREAX

RT	AREA	TYPE	WIDTH	AREAX
1.455	450878720	>SBB	.871	99.87776
27.490	12210	BU	.078	.00481
28.502	264310	PP	.337	.05955