A Short and Efficient Synthetic Route to Methyl α-Trioxacarcinoside B and Anomerically Activated Derivatives

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Supporting Information

General Experimental Procedures

All reactions were performed in round-bottom fitted with rubber septa under a positive pressure of argon, unless otherwise noted. Air- and moisture-sensitive liquids were transferred via syringe or stainless steel cannula. Organic solutions were concentrated by rotary evaporation (house vacuum, ca. 25–40 Torr) at ambient temperature, unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed using glass plates precoated with silica gel (0.25 mm, 60 Å pore-size, 230–400 mesh, Merck KGA) impregnated with a

fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light, then were stained with either an aqueous sulfuric acid solution of ceric ammonium molybdate (CAM), an acidic solution of *p*-anisaldehyde in ethanol (Anis), or an aqueous sodium hydroxide–potassium carbonate solution of potassium permanganate ($KMnO_4$) then briefly heated with a flameless heat gun. Flash-column chromatography was performed as described by Still et al.,[1] employing silica gel (60 Å, 32–63 μM, standard grade, Dynamic Adsorbents, Inc. and 60 Å, 40–60 μM, standard grade, Agela Technologies).

Materials

Commercial solvents and reagents were used as received with the following exceptions. Tetrahydrofuran, dichloromethane, benzene, and ether were purified by the method of Pangborn et al.[2]

Instrumentation

Proton magnetic resonance (^{1}H NMR) spectra were recorded on Varian INOVA 500 (500 MHz) or 600 (600 MHz) NMR spectrometers at 23 °C. Proton chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to residual protium in the NMR solvent ($CHCl_3$, δ 7.26). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances, br = broad, app = apparent), integration, and coupling constant (*J*) in Hertz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded on Varian INOVA 500 (125 MHz) NMR spectrometers at 23 °C. Carbon chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to the carbon resonances of the NMR solvent ($CDCl_3$, δ 77.0). Infrared (IR) spectra were obtained using a Shimadzu 8400S FT-IR spectrometer and were referenced to a polystyrene standard. Data are represented as follows: frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak, br = broad). Optical rotations were measured on a Jasco DIP-0181 digital polarimeter with a sodium lamp and are reported as follows: $[\alpha]^{T[°C]}_{\lambda}$ (c = g/100 mL, solvent). High-resolution mass spectra were obtained at the Harvard University Mass Spectrometry Facility. High performance liquid chromatography purifications were performed using an Agilent Technologies 1200 Series preparative HPLC system.

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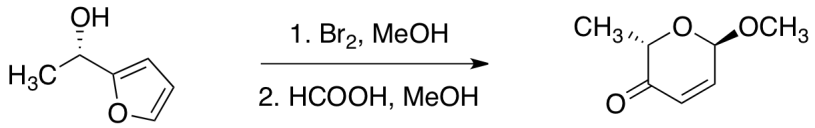
[1] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.
[2] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

Procedures for the Synthesis of Methyl α–Trioxacarcinoside B and Anomerically Activated Derivatives



6 67% **7**

Methyl Acetal 7. [3]

A solution of (*S*)-1-(furan-2-yl)ethanol **6**[4] (20.0 g, 178 mmol, 1 equiv) in methanol (140 mL) and ether (50 mL) was cooled to –78 °C. Bromine (9.46 mL, 184 mmol, 1.03 equiv) was added dropwise by syringe over 35 min. After the addition was complete, the internal temperature was raised to –30 °C and stirring was continued for 30 min. The reaction flask was cooled to –78 °C and the reaction mixture was saturated with dry ammonia (pH 8). The resulting off-white suspension was allowed to warm to 23 °C, then was diluted with ether (300 mL). Precipitates were removed by filtration. The residue was suspended in ether (200 mL) and the resulting suspension was filtered through a plug of activated-neutral aluminum oxide. The filtrate was concentrated and the residue was distilled (80 °C, 5 mmHg). The pale yellow oily distillate was dissolved in methanol (10 mL) and the resulting solution was added to a mixture of formic acid (100 mL) and methanol (5.5 mL) at 23 °C. After 5 min, the reaction mixture was diluted with chloroform (100 mL) and water (100 mL) was added. The layers were separated. The aqueous layer was extracted with chloroform (2 × 100 mL). The organic layers were combined. The combined solution was washed sequentially with saturated aqueous sodium bicarbonate solution (2 x 50 mL) and saturated aqueous sodium chloride solution (100 mL). The washed solution was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated to provide an anomeric mixture of methyl acetals **7** (17 g, 67%, α:β ~ 1.2:1). Separation of the anomers was achieved by medium pressure column chromatography on silica gel (5% ethyl acetate–hexanes). Pure α-anomer **7**

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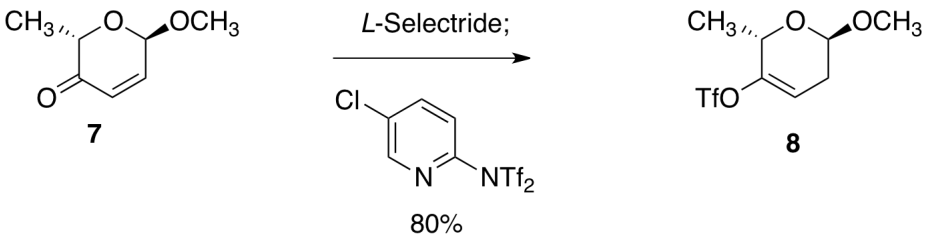
[3] This procedure follows that described by Shan et al.: Shan, M.; Xing, Y.; O'Doherty, G. A. *J. Org. Chem.* **2009**, *74*, 5961–5966.

[4] (*S*)-1-(furan-2-yl)ethanol **6** was prepared in >100-g batches by the reported procedure: Ohkuma, T.; Koizumi, M.; Yoshida, M.; Noyori, R. *Org. Lett.* **2000**, *2*, 1749–1751.

was obtained as a white solid (5.3 g, 20%) Characterization data obtained for **7** were in agreement with values previously reported.[3,5]

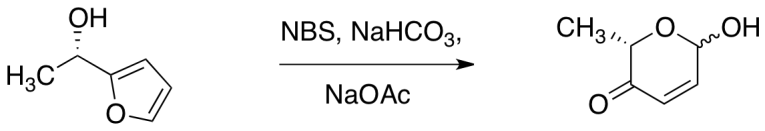


Vinyl Triflate 8.

A 2-L round-bottom flask was charged with a commercial solution of lithium tri-*sec*-butylborohydride in tetrahydrofuran (1.0 M, 43.90 mL, 43.90 mmol, 1.20 equiv). Tetrahydrofuran (834 mL) was added and the resulting clear solution was cooled to –78 °C. A solution of methyl acetal **7** (5.20 g, 36.60 mmol, 1 equiv) in tetrahydrofuran (104 mL, 0.35 M) was added dropwise by cannula over 40 min.[6] After 75 min, *N*-(5-Chloro-2-pyridyl)bis(trifluoromethanesulfonimide) (17.24 g, 43.90 mmol, 1.20 equiv) was added in four equal portions over 5 min. After the addition was complete, the internal temperature of the reaction mixture was maintained at –78 °C for 1 h. The reaction mixture was allowed to warm slowly to an external temperature of –25 °C over 6 h. Methanol (30 mL), water (500 mL) and ether (300 mL) were added in sequence to the pale orange product solution. The layers were separated and the aqueous layer was extracted with ether (3 x 100 mL). The combined organic extracts were filtered and the filtrate was concentrated. The residue was dissolved in pentane–ether (1:1, 500 mL) and the resulting solution was washed in sequence with 10% sodium hydroxide (3 x 100 mL), water (100 mL), saturated aqueous copper sulfate solution (2 x 100 mL), and saturated aqueous sodium chloride solution (200 mL). The washed organic layer was dried over potassium carbonate. The dried solution was filtered and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel (hexanes initially, grading to 5% ethyl acetate–hexanes) to provide pure enol triflate **8** (8.10 g, 80%) as a pale yellow oil. TLC (10% ethyl acetate–hexanes): R_f = 0.40 ($KMnO_4$). $[\alpha]^{23}_D$ –83.4 (*c* 0.80, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 5.73–5.71 (m, 1H), 4.82 (d, *J* = 5.0 Hz, 1H), 4.21–4.35 (m, 1H), 3.43 (s, 3H), 2.64–2.58 (m, 1H), 2.32–2.26 (m, 1H), 1.38 (d,

[5] Du, W.; Hu, Y. *Carbohydrate Research* **2006**, *341*, 725–729.
[6] Paquette, L. A.; Liang, S.; Wang, H. L. *J. Org. Chem.* **1996,** *61*, 3268–3279.

J = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 148.1, 120.0, 118.7 (q, J = 318.4 Hz, CF_3), 112.5, 96.2, 63.1, 55.5, 30.6, 17.3. FTIR (neat), cm^{-1}: 2940 (w), 1421 (m), 1397 (m), 1207 (s), 1140 (s), 1065 (s), 1018 (s). LRMS (CI): Calcd for $(C_8H_{11}F_3O_5S + NH_4)^+$: 294.06. Found: 294.17.



6 90% **28**

Hemiacetal 28.[7]

A 1-L round-bottom flask was charged with a solution of (*S*)-1-(furan-2-yl)ethanol **6**[8] (22.0 g, 196 mmol, 1 equiv) in tetrahydrofuran (370 mL) and water (120 mL). Sodium bicarbonate (27.4 g, 326 mmol, 1.7 equiv) and sodium acetate (26.7 g, 196 mmol, 1.0 equiv) were added. The resulting white suspension was cooled to 0 °C and *N*-bromosuccinimide (34.9 g, 196 mmol, 1.0 equiv) was added in ten equal portions over 40 min. After 1 h, the cooling bath was removed and the reaction flask was allowed to warm to 23 °C. The layers were separated. The aqeuous layer was extracted with ethyl acetate (8 x 100 mL). The combined organic extracts were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue was filtered through a short plug of silica (30% ethyl acetate–hexanes initially, grading to 50% ethyl acetate–hexanes) to provide the pure hemiacetals **28** (22.5 g, 90%, α:β ~ 2:1) as a colorless oil. Characterization data obtained for hemiacetal **28** were in agreement with values previously reported.[7]

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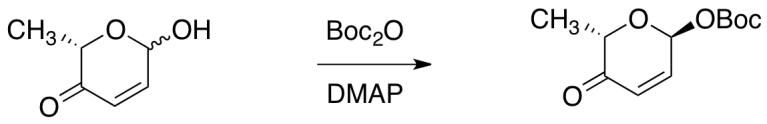
[7] This procedure follows that described by Shan et al.: Shan, M.; Xing, Y.; O'Doherty, G. A. *J. Org. Chem.* **2009**, *74*, 5961–5966.

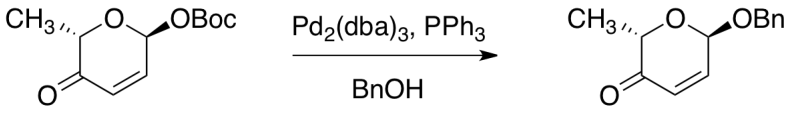
[8] (*S*)-1-(furan-2-yl)ethanol **6** was prepared in >100-g batches by the reported procedure: Ohkuma, T.; Koizumi, M.; Yoshida, M.; Noyori, R. *Org. Lett.* **2000**, *2*, 1749–1751.



28 51% **29**

Boc Acetal 29.[7]

To a solution of hemiacetals **28** (12.0 g, 93.7 mmol, 1 equiv) in dichloromethane (130 mL) was added *N*,*N*-dimethyl-4-aminopyridine (1.14 g, 9.37 mmoL, 0.1 equiv). The mixture was cooled to –78 °C and a solution of di-*tert*-butyl dicarbonate (43.5 mL, 187 mmol, 2 equiv) in dichloromethane (50 mL) was added dropwise. The reaction mixture was allowed to warm slowly to an external temperature of 10 °C over 15 h. The product mixture was diluted with ether (400 mL). The organic layer was washed sequentially with saturated aqueous sodium bicarbonate solution (2 x 50 mL), then brine (50 mL), and the washed solution was dried over sodium sulfate. The dried solution was filtered through a pad of silica gel and the filtrate was concentrated. The anomeric product mixture (α:β ~ 3:1) was purified by flash-column chromatography on silica gel (10% ethyl acetate–hexanes) to afford pure α-anomer **29** (10.8 g, 51%). Characterization data obtained for **29** were in agreement with values previously reported.[7]

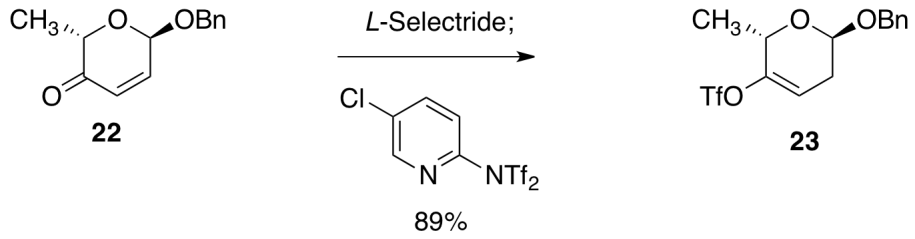


29 65% **22**

Benzyl Acetal 22. [7]

Benzyl alcohol (9.11 mL, 88.0 mmol, 2.0 equiv) was added to an ice-cooled solution of α-anomer **22** (10.0 g, 43.8 mmol, 1 equiv) in dichloromethane (45 mL). Tris(dibenzylideneacetone)dipalladium(0) (100 mg, 110 μmol, 0.002 equiv) and triphenylphosphine (57 mg, 219 μmol, 0.005 equiv) were added sequentially. After 4 h, the orange-yellow reaction mixture was diluted with saturated aqueous sodium bicarbonate solution (250 mL) and ether (300 mL). The layers were separated. The aqueous layer was extracted with ether (3 × 80 mL). The organic layers were combined. The combined solution was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel (hexanes initially, grading to 4% ethyl acetate–hexanes) to provide the pure α-anomer **22** (6.2

g, 65%) as a colorless oil. Characterization data obtained for **22** were in agreement with values previously reported.[7]

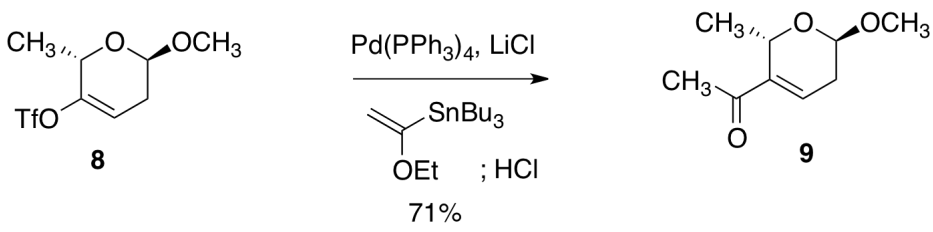


Vinyl Triflate 23.

A 2-L round-bottom flask was charged with a commercial solution of lithium tri-*sec*-butylborohydride in tetrahydrofuran (1.0 M, 31.20 mL, 31.20 mmol, 1.10 equiv). Tetrahydrofuran (600 mL) was added and the resulting clear solution was cooled to –78 °C. A solution of benzyl acetal **22** (6.20 g, 28.4 mmol, 1 equiv) in tetrahydrofuran (81 mL, 0.35 M) was added dropwise via a 250-mL dropping funnel over 30 min.[9] After 60 min, *N*-(5-Chloro-2-pyridyl)bis(trifluoromethanesulfonimide) (12.27 g, 31.20 mmol, 1.10 equiv) was added in three equal portions over 5 min. After the addition was complete, the internal temperature of the reaction mixture was maintained at –78 °C for 1 h. The reaction mixture was allowed to warm slowly to an external temperature of –25 °C over 3 h. Methanol (20 mL), water (300 mL), and ether (400 mL) were added in sequence to the pale orange product solution. The layers were separated and the aqueous layer was extracted with ether (3 x 100 mL). The combined organic extracts were filtered and the filtrate was concentrated. The residue was dissolved in pentane–ether (1:1, 500 mL) and the resulting solution was washed in sequence with 10% sodium hydroxide (3 x 100 mL), water (100 mL), saturated aqueous copper sulfate solution (2 x 100 mL), and saturated aqueous sodium chloride solution (200 mL). The washed organic layer was dried over potassium carbonate. The dried solution was filtered and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel (hexanes initially, grading to 5% ethyl acetate–hexanes) to provide pure enol triflate **23** (8.90 g, 89%) as a pale yellow oil. TLC (10% ethyl acetate–hexanes): R_f = 0.45 (UV, $KMnO_4$). $[\alpha]^{25}_D$ –74.1 (*c* 1.64, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.38–7.31 (m, 5H), 5.78–5.76 (m, 1H), 5.03 (d, *J* = 4.0 Hz, 1H), 4.82 (d, *J* = 10.0 Hz, 1H), 4.58 (d, *J* = 10.0 Hz, 1H), 4.50–4.43 (m, 1H), 2.67–2.62 (m, 1H), 2.39–2.34 (m, 1H), 1.40 (d, *J* = 5.5 Hz, 3H). ^{13}C

[9] Paquette, L. A.; Liang, S.; Wang, H. L. *J. Org. Chem.* **1996,** *61*, 3268–3279.

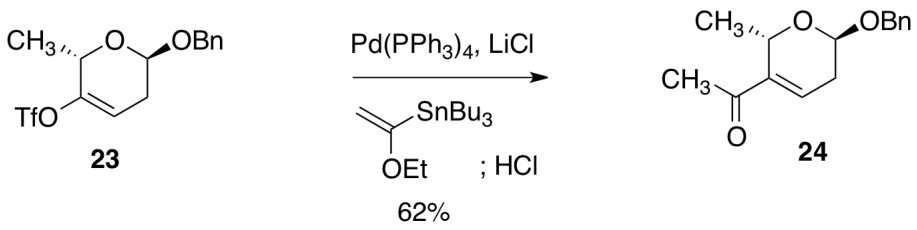
NMR (125 MHz, $CDCl_3$), δ: 147.7, 137.4, 128.5, 127.8, 118.4 (q, J = 319 Hz, CF_3), 112.4, 93.8, 69.2, 63.3, 30.4, 17.1. FTIR (neat), cm^{-1}: 2939 (w), 1419 (s), 1247 (m), 1207 (s), 1139 (s), 1066 (s), 1024 (s). HRMS (ESI): Calcd for $(C_{14}H_{15}F_3O_5S + Na)^+$: 375.0484. Found: 375.0490.



Ketone 9.

A 1-L Schlenk flask charged with anhydrous lithium chloride (2.88 g, 67.9 mmol, 2.50 equiv) was flame-dried under vacuum for 5 min. The flask and its contents were allowed to cool to 23 °C under an atmosphere of dry argon. A solution of vinyltriflate **8** (7.50 g, 27.2 mmol, 1 equiv) in tetrahydrofuran (500 mL) was added and the transfer was quantitated with additional tetrahydrofuran (50 mL). Tributyl(1-ethoxyvinyl)tin (22.93 mL, 67.90 mmol, 2.50 equiv) was added by syringe and the resulting clear solution was deoxygenated by bubbling argon gas below the liquid surface for 30 min using a 19-gauge stainless steel needle. Tetrakis(triphenylphosphine)palladium(0) (1.57 g, 1.36 mmol, 0.05 equiv) was added in one portion and the resulting pale yellow solution was deoxygenated with argon gas for 30 min, as before. The reaction flask was then heated in an oil bath at 80 °C. After 8 h, the heating bath was removed and the dark red product mixture was allowed to cool to 23 °C. The cloudy solution was diluted with pentane (500 mL). The organic layer was washed sequentially with 1.0 M aqueous hydrochloric acid solution (3 x 200 mL), water (200 mL), 30% aqueous ammonium hydroxide solution (2 x 200 mL), 1.0 M sodium hydroxide solution (200 mL), then saturated aqueous sodium chloride solution (500 mL) and the washed solution was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel (pentane initially, grading to 30% ether–pentane) to provide the pure enone **9** (3.30 g, 71%) as a yellow oil. TLC (10% ethyl acetate–hexanes): R_f = 0.13 (UV, $KMnO_4$). $[\alpha]^{23}_D$ –163.5 (*c* 0.40, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 6.79 (br t, J = 3.5 Hz, 1H), 4.86 (app dd, J = 4.0, 2.5 Hz, 1H), 4.69–4.65 (m, 1H), 3.43 (s, 3H), 2.61–2.54 (m, 1H), 2.33–2.31 (m, 1H), 2.28 (s, 3H), 1.36 (d, J = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 197.5, 142.3, 134.5, 95.0, 65.2, 55.2, 30.9,

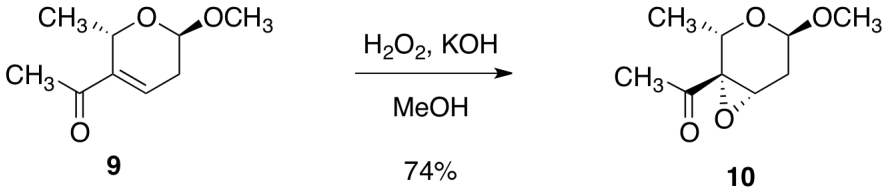
25.6, 19.6. FTIR (neat), cm^{-1}: 2936 (w), 1668 (s), 1363 (m), 1251 (m), 1128 (m), 1063 (s), 1016 (m). LRMS (CI): Calcd for $(C_9H_{14}O_3 + NH_4)^+$: 188.13. Found: 188.18.



Ketone 24.

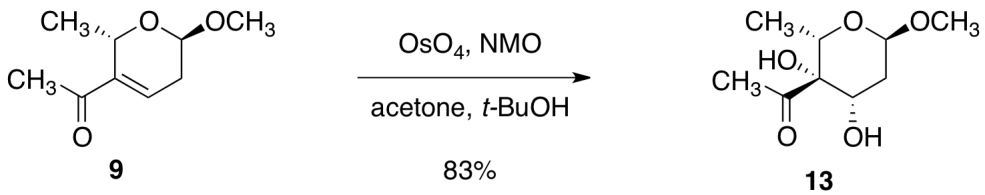
A 1-L Schlenk flask charged with anhydrous lithium chloride (2.65 g, 62.4 mmol, 2.50 equiv) was flame-dried under vacuum for 10 min. The flask and its contents were allowed to cool to 23 °C under an atmosphere of dry argon. A solution of vinyltriflate **23** (8.80 g, 24.9 mmol, 1 equiv) in tetrahydrofuran (350 mL) was added and the transfer was quantitated with additional tetrahydrofuran (50 mL). Tributyl(1-ethoxyvinyl)tin (15.6 mL, 46.2 mmol, 1.85 equiv) was added by syringe and the resulting clear solution was deoxygenated by bubbling argon gas below the liquid surface for 30 min using a 19-gauge stainless steel needle. Tetrakis(triphenylphosphine)palladium(0) (1.44 g, 1.25 mmol, 0.05 equiv) was added in one portion and the resulting pale yellow solution was deoxygenated with argon gas for 30 min, as before. The reaction flask was then heated in an oil bath at 80 °C. After 7 h, the heating bath was removed and the dark red product mixture was allowed to cool to 23 °C. The cloudy solution was diluted with hexane (400 mL). The organic layer was washed sequentially with 1.0 M aqueous hydrochloric acid solution (2 x 100 mL), water (200 mL), 1.0 M sodium hydroxide solution (200 mL), then saturated aqueous sodium chloride solution (300 mL) and the washed solution was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel (hexane initially, grading to 30% ethyl acetate–hexane) to provide the pure enone **24** (3.80 g, 62%) as a pale yellow oil. TLC (10% ethyl acetate–hexanes): R_f = 0.15 (UV, $KMnO_4$). $[\alpha]^{25}_D$ –89.9 (*c* 0.90, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.36–7.28 (m, 5H), 6.80 (br t, *J* = 4.3 Hz, 1H), 5.04 (app dd, *J* = 4.2, 2.4 Hz, 1H), 4.81 (d, *J* = 12.0 Hz, 1H), 4.79–4.73 (m, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 2.61–2.56 (m, 1H), 2.39–2.34 (m, 1H), 2.29 (s, 3H), 1.39 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 197.5, 142.3, 137.5, 134.6, 128.4, 128.0, 127.8, 92.7, 69.2, 65.5, 30.9, 25.6, 19.6. FTIR (neat), cm^{-1}: 2933 (w), 1668 (s), 1385 (m), 1248 (m), 1209 (m), 1124 (m), 1024 (s). HRMS (ESI): Calcd for $(C_{15}H_{18}O_3 + Na)^+$:

269.1148. Found: 269.1150.



Epoxide 10.

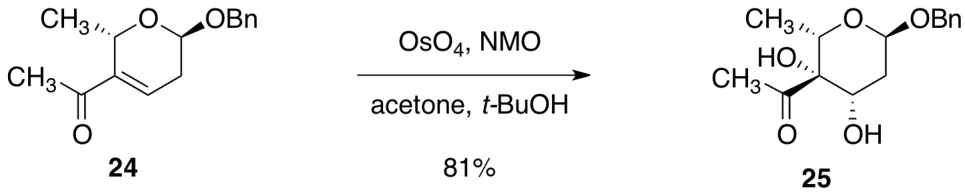
A solution of hydrogen peroxide in water (30% w/w, 420 µL, 4.11 mmol, 2.0 equiv) was added to an ice-cooled solution of enone **9** (350 mg, 2.06 mmol, 1 equiv) in a mixture of methanol (38 mL) and water (4 mL). Potassium hydroxide (923 mg, 16.5 mmol, 8.0 equiv) was added as a solid in one portion at 0 °C. After 1 h, the cooling bath was removed and the reaction flask was allowed to warm to 23 °C. After 18 h, the reaction mixture was diluted with saturated aqueous ammonium chloride solution (100 mL) and chloroform (100 mL). The layers were separated. The aqueous layer was extracted with chloroform (5 × 20 mL). The organic layers were combined. The combined solution was dried over magnesium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel (20% ethyl acetate–hexanes) to provide the pure epoxide **10** (284 mg, 74%) as colorless needles. TLC (20% ethyl acetate–hexanes): R_f = 0.40 ($KMnO_4$). $[\alpha]^{23}_D$ –177.6 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 4.67 (q, *J* = 6.5 Hz, 1H), 4.61 (d, *J* = 5.0 Hz, 1H), 3.45 (d, *J* = 5.0 Hz, 1H), 3.36 (s, 3H), 2.16 (dd, *J* = 10.5, 5.0, 1 Hz, 1H), 2.05 (s, 3H), 1.99 (ddd, *J* = 15.5, 5.5, 1.0 Hz, 1 H), 1.23 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 206.7, 94.6, 62.2, 59.9, 55.0, 53.8, 28.3, 24.0, 16.2. FTIR (neat), cm^{-1}: 2938 (w), 1705 (s), 1420 (w), 1366 (m), 1236 (m), 1130 (s), 1064 (s). HRMS (ESI): Calcd for $(C_9H_{14}O_4 + Na)^+$: 209.0818. Found: 209.0784.



***Cis*-Diol 13.**

A solution of *N*-methylmorpholine-*N*-oxide (2.79 g, 23.8 mmol, 1.50 equiv) in water (36 mL)

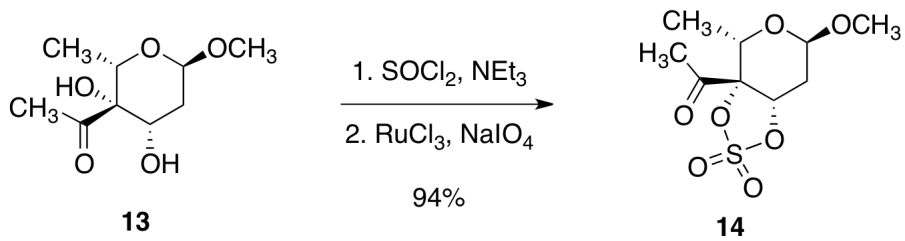
was added to an ice-cooled solution of enone **9** (2.70 g, 15.9 mmol, 1 equiv) in a mixture of acetone (120 mL) and *tert*-butanol (120 mL). A solution of osmium tetroxide (2.5% w/w in *tert*-butanol, 6.97 mL, 0.56 mmol, 0.035 equiv) was added in one portion at 0 °C. After 1 h, the cooling bath was removed and the reaction flask was allowed to warm to 23 °C. After 3 d, 10% aqueous sodium sulfite solution (100 mL) and saturated aqueous sodium chloride solution (100 mL) were added to the product mixture in sequence. The layers were separated. The aqueous layer was extracted with ethyl acetate (10 × 100 mL). The organic layers were combined. The combined solution was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel (30% ethyl acetate–hexanes initially, grading to 40% ethyl acetate–hexanes) to provide the pure *cis*-diol **13** (2.70 g, 83%) as a white solid. TLC (50% ethyl acetate–hexanes): R_f = 0.19 ($KMnO_4$). $[\alpha]^{23}_D$ –121.9 (*c* 0.32, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 4.83 (br d, *J* = 3.5 Hz, 1H), 4.37 (app dq, *J* = 11.5, 5.0 Hz, 1H), 4.14 (q, *J* = 6.5 Hz, 1H), 3.93 (s, OH), 3.38 (s, 3H), 2.31 (s, 3H), 2.06 (ddd, *J* = 12.5, 4.5, 1 Hz, 1H), 1.85 (d, *J* = 5.5 Hz, OH), 1.82 (ddd, *J* = 15.5, 11, 3.5 Hz, 1H), 1.02 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 209.2, 98.5, 82.7, 66.8, 66.0, 55.0, 34.4, 25.1, 14.2. FTIR (neat), cm^{-1}: 3464 (s), 2938 (w), 1709 (s), 1352 (w), 1202 (w), 1123 (w), 1036 (m). HRMS (ESI): Calcd for $(C_9H_{16}O_5 + Na)^+$: 227.0890. Found: 227.0891.



***Cis*-Diol 25.**

A solution of *N*-methylmorpholine-*N*-oxide (2.71 g, 23.1 mmol, 1.50 equiv) in water (35 mL) was added to an ice-cooled solution of enone **24** (3.80 g, 15.4 mmol, 1 equiv) in a mixture of acetone (115 mL) and *tert*-butanol (115 mL). A solution of osmium tetroxide (2.5% w/w in *tert*-butanol, 6.78 mL, 0.54 mmol, 0.035 equiv) was added in one portion at 0 °C. After 10 min, the cooling bath was removed and the reaction flask was allowed to warm to 23 °C. After 3 d, ethyl acetate (400 mL), 10% aqueous sodium sulfite solution (100 mL), and saturated aqueous sodium chloride solution (200 mL) were added to the product mixture in sequence. The layers were separated. The aqueous layer was extracted with ethyl acetate (3 × 150 mL). The organic layers were combined. The combined solution was dried over sodium

sulfate. The dried solution was filtered and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel (30% ethyl acetate–hexanes initially, grading to 50% ethyl acetate–hexanes) to provide the pure *cis*-diol **25** (3.50 g, 81%) as a white solid. TLC (50% ethyl acetate–hexanes): R_f = 0.28 (UV, $KMnO_4$). $[\alpha]^{24}_D$ –84.0 (*c* 1.52, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.39–7.26 (m, 5H), 5.02 (d, *J* = 3.0 Hz, 1H), 4.68 (d, *J* = 12.5 Hz, 1H), 4.52 (d, *J* = 12.5 Hz, 1H), 4.42 (app dt, *J* = 11.0, 5.0 Hz, 1H), 4.15 (q, *J* = 6.5 Hz, 1H), 3.99 (s, OH), 2.40 (d, *J* = 10.5 Hz, OH), 2.26 (s, 3H), 2.07–2.03 (m, 1H), 1.86–1.81 (m, 1H), 0.99 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 209.6, 137.5, 128.3, 127.6, 96.6, 82.8, 69.1, 66.8, 66.4, 34.1, 25.3, 14.1. FTIR (neat), cm^{-1}: 3468 (br), 2939 (w), 1709 (s), 1360 (m), 1215 (m), 1122 (m), 1024 (s). HRMS (ESI): Calcd for $(C_{15}H_{20}O_5 + Na)^+$: 303.1203. Found: 303.1204.

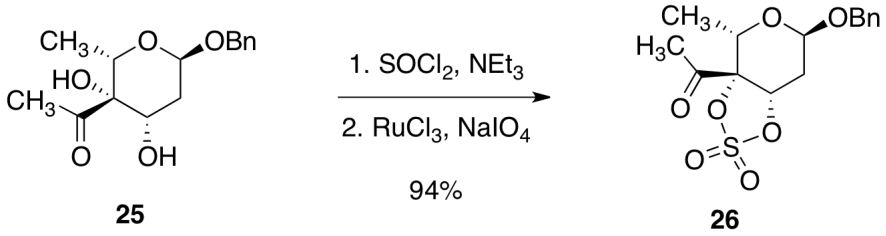


Cyclic Sulfate 14.

To an ice-cooled 0.1 M solution of *cis*-diol **13** (615 mg, 3.01 mmol, 1 equiv) in dichloromethane (30 mL) were added in sequence triethylamine (1.05 mL, 7.53 mmoL, 2.50 equiv) and thionyl chloride (0.33 mL, 4.52 mmol, 1.50 equiv). The resulting orange solution was stirred at 0 °C. After 30 min, the product mixture was diluted with dichloromethane (100 mL). The organic layer was washed sequentially with water (20 mL), then brine (20 mL), and the washed solution was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The cyclic sulfites obtained were oxidized as outlined in the following paragraph directly without purification.

Ruthenium(III) chloride (11 mg, 53 μmol, 0.018 equiv) and sodium periodate (966 mg, 4.52 mmol, 1.50 equiv) were added in sequence to an ice-cooled solution of the unpurified cyclic sulfites (1 equiv) from the previous experiment in a biphasic mixture of carbon tetrachloride (8.6 mL), acetonitrile (8.6 mL), and water (12.9 mL). After 1 h, the mixture was partitioned between saturated aqueous sodium bicarbonate solution (50 mL) and dichloromethane (200 mL). The aqueous layer was extracted with dichloromethane (3 x 20 mL) and the combined organic extracts were dried over sodium sulfate. The dried solution was filtered through a

plug of Celite and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel (10% ethyl acetate–hexanes) to afford the pure cyclic sulfate **14** (755 mg, 94% over two steps) as a colorless oil. TLC (20% ethyl acetate–hexanes): R_f = 0.43 ($KMnO_4$). $[\alpha]^{23}_D$ –83.4 (*c* 0.59, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 4.98 (app t, *J* = 3.0 Hz, 1H), 4.84 (app t, *J* = 6.5 Hz, 1H), 4.16 (q, *J* = 6.0 Hz, 1H), 3.37 (s, 3H), 2.58 (ddd, *J* = 16.5, 7.2, 6 Hz, 1H), 2.42 (s, 3H), 2.06 (ddd, *J* = 15.5, 7.0, 3.0 Hz, 1H), 1.23 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 206.0, 95.8, 91.9, 79.4, 66.1, 55.3, 28.6, 27.5, 14.6. FTIR (neat), cm^{-1}: 2945 (w), 1720 (m), 1400 (s), 1215 (s), 1121 (w), 1053 (w), 972 (s). LRMS (CI): Calcd for $(C_9H_{18}O_7S + NH_4)^+$: 284.08. Found: 284.19.



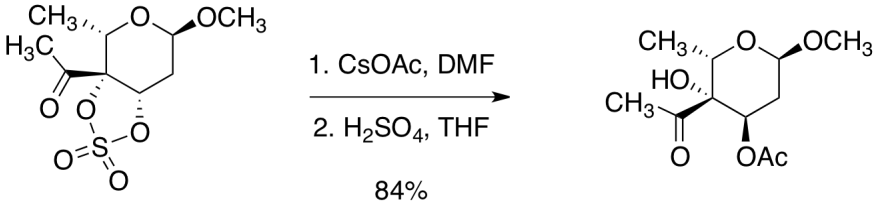
25 **26**

Cyclic Sulfate 26.

To an ice-cooled 0.1 M solution of *cis*-diol **25** (2.00 g, 7.13 mmol, 1 equiv) in dichloromethane (70 mL) were added in sequence triethylamine (2.49 mL, 17.8 mmoL, 2.50 equiv) and thionyl chloride (0.78 mL, 10.70 mmol, 1.50 equiv). The resulting orange solution was stirred at 0 °C. After 30 min, the product mixture was diluted with dichloromethane (200 mL). The organic layer was washed sequentially with water (50 mL), then brine (50 mL), and the washed solution was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The cyclic sulfites obtained were oxidized as outlined in the following paragraph directly without purification.

Ruthenium(III) chloride (148 mg, 0.71 mmol, 0.10 equiv) and sodium periodate (2.29 g, 10.7 mmol, 1.50 equiv) were added in sequence to an ice-cooled solution of the unpurified cyclic sulfites (1 equiv) from the previous experiment in a biphasic mixture of carbon tetrachloride (20 mL), acetonitrile (20 mL), and water (30 mL). After 1 h, the mixture was partitioned between saturated aqueous sodium bicarbonate solution (10 mL) and dichloromethane (300 mL). The aqueous layer was extracted with dichloromethane (3 x 100 mL) and the combined organic extracts were dried over sodium sulfate. The dried solution was filtered through a plug of Celite and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel (10% ethyl acetate–hexanes) to afford the pure cyclic sulfate **26** (2.30 g, 94% over two steps) as a colorless oil. TLC (20% ethyl acetate–hexanes): R_f = 0.52

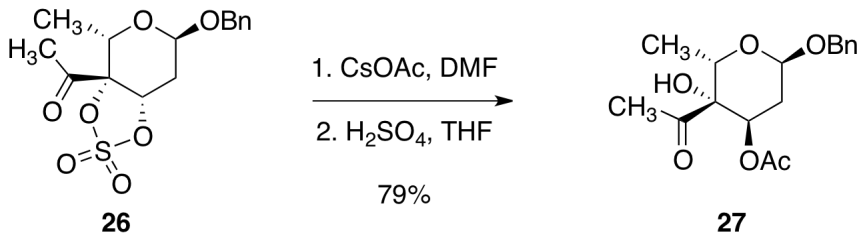
(UV, $KMnO_4$). $[\alpha]^{23}_D$ –83.8 (*c* 1.68, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$), δ: 7.38–7.29 (m, 5H), 5.09 (app t, *J* = 6.5 Hz, 1H), 5.02 (t, *J* = 3.5 Hz, 1H), 4.76 (d, *J* = 12.5 Hz, 1H), 4.59 (d, *J* = 12.5 Hz, 1H), 4.25 (q, *J* = 6.5 Hz, 1H), 2.65–2.60 (m, 1H), 2.45 (s, 3H), 2.22–2.16 (m, 1H), 1.20 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 206.1, 137.3, 128.5, 127.9, 127.8, 94.2, 91.8, 79.4, 69.7, 66.4, 28.7, 27.6, 14.5. FTIR (neat), cm^{-1}: 2933 (w), 1719 (s), 1400 (s), 1362 (m), 1215 (s), 1040 (s), 970 (s). HRMS (ESI): Calcd for $(C_{15}H_{18}SO_7 + Na)^+$: 365.0665. Found: 365.0640.



Methyl 3-Acetyl-α-trioxacarcinoside B 15.

Cesium acetate (404 mg, 2.11 mmol, 1.10 equiv) was added in one portion to a solution of the cyclic sulfate **14** (511 mg, 1.91 mmol, 1 equiv) in dimethylformamide (10 mL) at 23 °C. The resulting pale orange solution was stirred at 23 °C for 15 min. The reaction flask was then heated in an oil bath at 50 °C for 16 h. The heating bath was removed. After cooling to 23 °C the product solution was concentrated. The residue was dissolved in tetrahydrofuran (10 mL) at 23 °C and 20% aqueous sulfuric acid (500 μL) was added to the resulting solution. The turbid mixture was stirred at 23 °C for 1 h. The product solution was partitioned between ether (100 mL) and water (30 mL). The layers were separated and the aqueous layer was extracted with ether (3 x 50 mL). The combined organic extracts were washed with saturated aqueous sodium chloride solution (50 mL) and the washed solution was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel (10% ethyl acetate–hexane initially, grading to 30% ethyl acetate–hexanes) to provide pure methyl 3-acetyl-α-trioxacarcinoside B **15** (395 mg, 84%) as a colorless oil. TLC (30% ethyl acetate–hexanes): R_f = 0.20 ($KMnO_4$). $[\alpha]^{23}_D$ –174.3 (c 0.32, CH_2Cl_2). ^1H NMR (500 MHz, CDCl3), δ: 4.79 (app t, *J* = 3.5 Hz, 1H), 4.75 (dd, *J* = 5.0, 1.5 Hz, 1H), 4.59 (q, *J* = 6.5 Hz, 1H), 3.63 (s, 1H), 3.37 (s, 3H), 2.27 (s, 3H), 2.26–2.21 (m, 1H), 2.06 (s, 3H), 1.99 (ddd, *J* = 15.0, 4.0, 2.0 Hz, 1H), 1.06 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 208.9, 170.1, 97.3, 78.3, 70.7, 63.4, 55.4, 29.2, 26.8, 21.2, 14.2. FTIR (neat), cm^{-1}: 3481 (m), 1943 (m), 1741 (s), 1173 (s), 1371 (s), 1233 (s),

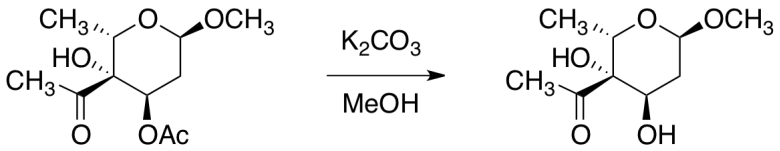
1128 (m), 1033 (s). HRMS (ESI): Calcd for $(C_{11}H_{18}O_6 + Na)^+$: 269.0996. Found: 269.1000.



26 **27**

Benzyl 3-Acetyl-α-trioxacarcinoside B 27.

Cesium acetate (1.55 g, 8.06 mmol, 1.20 equiv) was added in one portion to a solution of the cyclic sulfate **26** (2.30 g, 6.72 mmol, 1 equiv) in dimethylformamide (34 mL) at 23 °C. The resulting pale orange solution was stirred at 23 °C for 15 min. The reaction flask was then heated in an oil bath at 50 °C for 4 h. The heating bath was removed and the product solution was concentrated at 55 °C. The residue was dissolved in tetrahydrofuran (34 mL) at 23 °C and 20% aqueous sulfuric acid (2.5 mL) was added to the resulting solution. The turbid mixture was stirred at 23 °C for 1 h. The product solution was partitioned between ether (200 mL) and water (50 mL). The layers were separated and the aqueous layer was extracted with ether (3 x 70 mL). The combined organic extracts were washed with saturated aqueous sodium chloride solution (100 mL) and the washed solution was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel (20% ethyl acetate–hexane initially, grading to 30% ethyl acetate–hexanes) to provide pure benzyl 3-acetyl-α-trioxacarcinoside B **27** (1.70 g, 79%) as a colorless oil. TLC (20% ethyl acetate–hexanes): R_f = 0.22 (UV, $KMnO_4$). $[\alpha]^{23}_D$ –148.1 (c 1.22, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.39–7.27 (m, 5H), 4.98 (app d, *J* = 4.5 Hz, 1H), 4.81–4.78 (m, 1H), 4.77 (d, *J* = 12.5 Hz, 1H), 4.66 (q, *J* = 6.5 Hz, 1H), 4.50 (d, *J* = 12.5 Hz, 1H), 3.71 (s, OH), 2.29–2.22 (m, 1H), 2.27 (s, 3H), 2.11–2.07 (m, 1H), 2.02 (s, 3H), 1.04 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 208.8, 169.9, 138.0, 128.3, 127.5, 127.3, 95.5, 78.2, 70.7, 69.2, 63.2, 29.1, 26.8, 21.1, 14.2. FTIR (neat), cm^{-1}: 3468 (br), 2916 (m), 1738 (s), 1713 (s), 1371 (m), 1240 (s), 1126 (m), 1062 (s). HRMS (ESI): Calcd for $(C_{17}H_{22}O_6 + Na)^+$: 345.1309. Found: 345.1313.

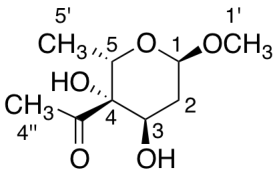


15 **16**

Methyl α-Trioxacarcinoside B 16.

Potassium carbonate (12.4 mg, 0.089 mmol, 0.1 equiv) was added to a solution of methyl 3-acetyl-α-trioxacarcinoside B **15** (220 mg, 0.89 mmol, 1 equiv) in methanol (8.9 mL) at 0 °C. After 30 min, the cooling bath was removed and the reaction mixture was allowed to warm slowly to 23 °C. After 14 h, the product solution was partitioned between saturated aqueous sodium chloride solution (40 mL) and chloroform (100 mL). The layers were separated. The aqueous layer was extracted with chloroform (3 x 30 mL). The combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated, providing methyl α-trioxacarcinoside B **16** (175 mg, 96%) as a white solid. A small sample of the product (~30 mg) was purified by flash-column chromatography on silica gel (20% ethyl acetate–hexanes) for characterization purposes. TLC (50% ethyl acetate–hexanes): R_f = 0.55 ($KMnO_4$). $[\alpha]^{24}_D$ –140.7 (*c* 0.15, $CHCl_3$), $[\alpha]^{24}_D$ –154.2 (*c* 0.34, $CHCl_3$)[10], $[\alpha]^{20}_D$ –60.0 (*c* 0.12, $CHCl_3$)[11], $[\alpha]^{23}_D$ –212.0 (*c* 0.5, $CHCl_3$)[12]. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 4.88 (br d, *J* = 3.0 Hz, 1H), 4.55 (q, *J* = 6.6 Hz, 1H), 4.03 (d, *J* = 9.6 Hz, OH), 3.99 (s, OH), 3.59 (app dt, *J* = 9.6, 3.0 Hz, 1H), 3.44 (s, 3H), 2.39 (s, 3H), 2.31 (ddd, *J* = 14.4, 3.6, 0.6 Hz, 1H), 1.86 (ddd, *J* = 14.4, 3.0, 1.2 Hz, 1H), 1.06 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 210.3, 99.0, 79.4, 70.2, 62.1, 55.5, 31.2, 27.6, 14.4. FTIR (neat), cm^{-1}: 3466 (s), 2926 (s), 1709 (s), 1462 (w), 1354 (w), 1201 (m), 1091 (m), 1036 (s). HRMS (ESI): Calcd for $(C_9H_{16}O_5 + Na)^+$: 227.0889. Found: 227.0895.

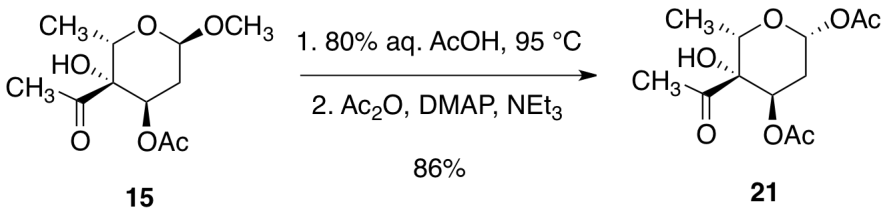
[10] Suami, T.; Nakamura, K.; Hara, J. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1431–1434.
[11] a) Matern, U.; Grisebach, H. *Eur. J. Biochem.* **1972**, *29*, 1–4; b) Matern, U.; Grisebach, H. *Z. Naturforsch.* **1974**, *29c*, 407–413.
[12] Shirahata, K.; Iida, T.; Hirayama, N. *Tennen Yuki Kagobutsu Toronkai Koen Yoshishu* **1981**, *24*, 199–206.



Methyl α–Trioxacarcinoside B (**16**)

Comparison of ^{1}H NMR Spectral Data for Natural and Synthetic Methyl α-Trioxacarcinoside B

	Ref. 11	**Ref. 12**	**Synthetic (this work)**
	100 MHz ($CDCl_3$)	100 MHz ($CDCl_3$)	600 MHz ($CDCl_3$)
CH_3 (1')	3.44 (s)	3.46 (s)	3.44 (s)
H (1e)	4.87 (NR)	4.89 (br d, *J* = 3.7 Hz)	4.88 (br d, *J* = 3.0 Hz)
H (2a)	1.85 (m, *J* = 14.8, 3.0 Hz)	1.86 (ddd, *J* = 14.7, 2.7, 1.5 Hz)	1.86 (ddd, *J* = 14.4, 3.0, 1.2 Hz)
H (2e)	2.33 (m, *J* = 14.8, 3.0 Hz)	2.33 (dt, *J* = 14.7, 3.4 Hz)	2.31 (ddd, *J* = 14.4, 3.6, 0.6 Hz)
H (3e)	3.60 (m, *J* = 9.5, 3.0 Hz)	3.60 (m)	3.59 (app dt, *J* = 9.6, 3.0 Hz)
H (5e)	4.57 (q, *J* = 6.5 Hz)	4.57 (q, *J* = 6.4 Hz)	4.55 (q, *J* = 6.6 Hz)
CH_3 (5')	1.07 (d, *J* = 6.5 Hz)	1.08 (d, *J* = 6.4 Hz)	1.06 (d, *J* = 6.0 Hz)
CH_3 (4")	2.39 (s)	2.40 (s)	2.39 (s)
OH (4')	3.99 (s)	NR	3.99 (s)
OH (3)	4.02 (NR)	NR	4.03 (d, J = 9.6 Hz)

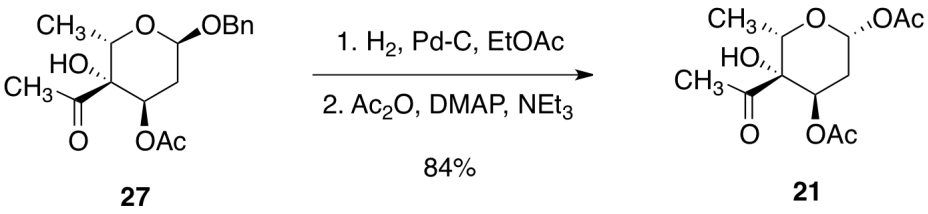


15 **21**

1-*O*-β-Acetyl Glycoside 21.

A solution of methyl 3-acetyl-α-trioxacarcinoside B **15** (250 mg, 1.02 mmol, 1 equiv) in 80% aqueous acetic acid (5 mL) was heated at 95 °C for 2 h. Heating was discontinued and the reaction flask was allowed to cool to 23 °C. The reaction mixture was diluted with ethyl acetate (150 mL) and the resulting solution was carefully poured into a mixture of saturated aqueous sodium chloride (15 mL) and saturated aqueous sodium bicarbonate (15 mL). The layers were separated. The aqueous layer was extracted with ethyl acetate (10 × 30 mL). The organic layers were combined and the combined solution was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The crude hemiacetal obtained in this manner was transformed as outlined in the following paragraph without purification.

Acetic anhydride (144 μL, 1.52 mmol, 1.50 equiv) was added dropwise to a solution of the unpurified hemiacetal (1 equiv) from the previous experiment and triethylamine (354 μL, 2.54 mmol, 2.50 equiv) in dichloromethane (20 mL) at –25 °C. 4-Dimethylaminopyridine (24.8 mg, 0.20 mmol, 0.2 equiv) was added in one portion and the reaction flask was allowed to warm slowly to –10 °C over 90 min. The reaction mixture was partitioned between water (40 mL) and dichloromethane (100 mL). The layers were separated. The aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue was filtered through a plug of silica gel deactivated with triethylamine (20% ethyl acetate–hexanes initially, grading to 30% ethyl acetate–hexane) to provide β-acetoxy glycoside **21** (240 mg, 86%). A small sample of the product (~20 mg) was purified by flash-column chromatography on silica gel deactivated with triethylamine (10% ethyl acetate–hexanes initially, grading to 30% ethyl acetate–hexane) to provide pure 1-*O*-β-acetyl glycoside **21**. See the following experiment for analytical data.

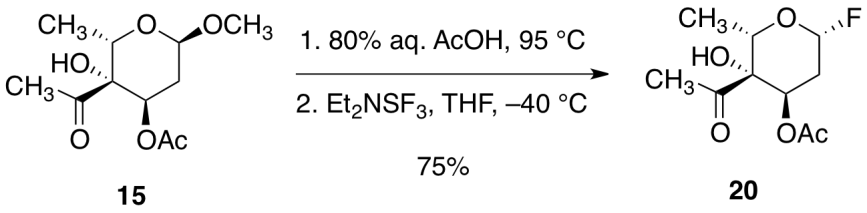


27 **21**

1-*O*-β-Acetyl Glycoside 21.

Palladium on activated charcoal (10% w/w moistened with water, 248 mg, 0.23 mmoL, 0.05 equiv), was added to a solution of benzyl 3-acetyl-α-trioxacarcinoside B **27** (1.50 g, 4.65 mmol, 1 equiv) in ethyl acetate (47 mL) at 23 °C. The resulting black suspension was saturated with hydrogen by bubbling hydrogen gas (1 atm) below the liquid surface for 30 min using a 19-gauge stainless steel needle. The reaction mixture was stirred under a hydrogen atmosphere for 16 h. Ethyl acetate (100 mL) was added and the mixture was filtered through a plug of Celite. The product solution was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The crude hemiacetal obtained in this manner was transformed as outlined in the following paragraph, without additional purification.

Acetic anhydride (658 μL, 6.98 mmol, 1.50 equiv) was added dropwise to a solution of the unpurified hemiacetal (1 equiv) from the previous experiment and triethylamine (1.62 mL, 11.63 mmol, 2.50 equiv) in dichloromethane (93 mL) at –25 °C. 4-Dimethylaminopyridine (114 mg, 0.93 mmol, 0.2 equiv) was added in one portion and the reaction flask was allowed to warm slowly to –10 °C over 90 min. The reaction mixture was partitioned between water (50 mL) and dichloromethane (100 mL). The layers were separated. The aqueous layer was extracted with dichloromethane (3 x 50 mL). The combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel deactivated with triethylamine (10% ethyl acetate–hexanes initially, grading to 30% ethyl acetate–hexane) to provide pure 1-*O*-β-acetyl glycoside **21** (1.07 g, 84%) as an off-white solid. TLC (40% ethyl acetate–hexanes): R_f = 0.52 ($KMnO_4$). $[\alpha]^{22}_D$ –29.2 (*c* 0.26, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 6.01 (dd, *J* = 10.8, 2.4 Hz, 1H), 5.07 (app t, *J* = 3.0 Hz, 1H), 4.49 (q, *J* = 6.6 Hz, 1H), 3.35 (s, OH), 2.24 (s, 3H), 2.16 (ddd, *J* = 14.4, 10.2, 3.0 Hz, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 1.91 (app dt, *J* = 14.4, 3.0 Hz, 1H), 1.09 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 208.4, 169.4, 169.2, 90.5, 76.9, 71.4, 70.8, 30.6, 26.6, 21.0 (2 x CH_3), 14.3. FTIR (neat), cm^{-1}: 3493 (w), 2924 (m), 1748 (s), 1717 (m), 1371 (m), 1232 (s), 1036 (s). HRMS (ESI): Calcd for $(C_{12}H_{18}O_7 + Na)^+$: 297.0945. Found: 297.0854.

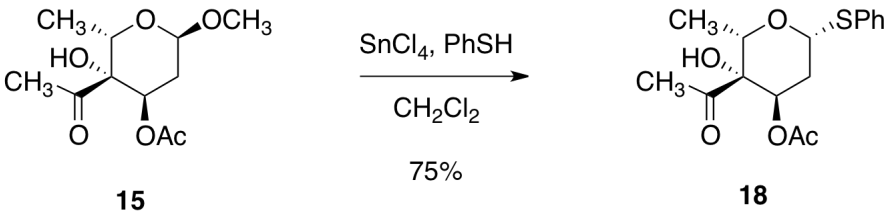


15 **20**

Glycosyl Fluoride 20.

A solution of methyl 3-acetyl-α-trioxacarcinoside B **15** (11.8 mg, 43.0 μmol, 1 equiv) in 80% aqueous acetic acid (1 mL) was heated at 95 °C for 2 h. Heating was discontinued and the reaction flask was allowed to cool to 23 °C. The reaction mixture was diluted with ethyl acetate (50 mL) and the resulting solution was carefully poured into a mixture of saturated aqueous sodium chloride (5 mL) and saturated aqueous sodium bicarbonate (5 mL). The layers were separated. The aqueous layer was extracted with ethyl acetate (10 × 10 mL). The organic layers were combined and the combined solution was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The crude hemiacetal obtained in this manner was transformed as outlined in the following paragraph without purification.

Diethylaminosulfur trifluoride (DAST, 7.40 μL, 56.0 μmol, 1.30 equiv) was added dropwise to a solution of the unpurified hemiacetal (1 equiv) from the previous experiment in tetrahydrofuran (1 mL) at –40 °C. After 20 min, the reaction mixture was partitioned between saturated aqueous sodium chloride solution (10 mL) and dichloromethane (30 mL). The organic layers was separated and dried over anhydrous potassium carbonate. The dried solution was filtered and the filtrate was concentrated to provide the glycosyl fluorides **20** (7.6 mg, 75%, α:β ~ 1:3). TLC (40% ethyl acetate–hexanes): α–**20**: R_f = 0.41 ($KMnO_4$). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 5.70 (dd, *J* = 51.0, 3.0 Hz, 1H), 4.84 (q, *J* = 6.6 Hz, 1H), 4.78 (app t, *J* = 3.0 Hz, 1H), 2.30–2.02 (m, 2H), 2.30 (s, 3H), 2.11 (s, 3H), 1.11 (d, *J* = 6.6 Hz, 3H). β–**20**: R_f = 0.61 ($KMnO_4$). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 5.62 (ddd, *J* = 51.0, 9.0, 3.0 Hz, 1H), 5.15 (app q, *J* = 3.6 Hz, 1H), 4.44 (q, *J* = 6.6 Hz, 1H), 2.76 (s, OH), 2.30–2.02 (m, 2H), 2.26 (s, 3H), 2.08 (s, 3H), 1.17 (d, *J* = 6.6 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$), δ: –132.7 (m, 1F). HRMS (ESI): Calcd for $(C_{10}H_{15}FO_5 + Na)^+$: 257.0796 Found: 257.0815.

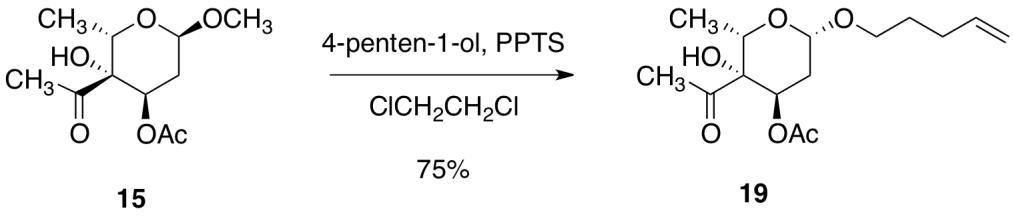


15 **18**

Phenylthioglycoside 18.

Tin(IV) chloride (47 μL, 0.40 mmol, 1.10 equiv) was added dropwise to a solution of thiophenol (56 μL, 0.55 mmol, 1.50 equiv) and methyl 3-acetyl-α-trioxacarcinoside B **15** (90 mg, 0.37 mmol, 1 equiv) in dichloromethane (3.7 mL) at –78 °C. The turbid mixture was stirred at –78 °C for 1 h. Dichloromethane (50 mL), saturated aqueous sodium bicarbonate solution (20 mL), and saturated aqueous sodium-potassium tartrate solution (20 mL) were added in sequence to the pale yellow product solution. The cooling bath was removed and the biphasic mixture was vigorously stirred for 1 h at 23 °C. The layers were separated and the aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic extracts were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel (30% ethyl acetate–hexanes) to provide an anomeric mixture of pure thioglycosides **18** (87 mg, 73%, α:β ~ 1:1.5). The product was purified by flash-column chromatography on silica gel (10% ethyl acetate–hexanes initially, grading to 20% ethyl acetate–hexane) to provide separately the pure anomers, α-**18** (14 mg, 12%) and β-**18** (28 mg, 23%), as colorless oils. α-**18**: TLC (50% ethyl acetate–hexanes): R_f = 0.80 (UV, $KMnO_4$). $[\alpha]^{23}_D$ –262.2 (*c* 0.35, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.51–7.45 (m, 2H), 7.33–7.23 (m, 3H), 5.59 (d, *J* = 5.5 Hz, 1H), 5.09 (q, *J* = 6.5 Hz, 1H), 4.87 (app t, *J* = 3.5 Hz, 1H), 3.72 (s, OH), 2.70 (ddd, *J* = 15.5, 7.0, 3.5 Hz, 1H), 2.32 (s, 3H), 2.21 (s, 3H), 2.19 (ddd, *J* = 15.0, 3.5, 1.5 Hz, 1H), 1.11 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 208.5, 169.5, 136.7, 130.5, 128.9, 127.0, 83.1, 78.0, 70.4, 64.6, 31.1, 26.8, 21.4, 14.3. FTIR (neat), cm^{-1}: 3460 (br), 2928 (w), 1743 (s), 1713 (s), 1371 (s), 1229 (s), 1033 (s). HRMS (ESI): Calcd for $(C_{16}H_{20}O_5S + Na)^+$: 347.0924 Found: 347.0914. β-**18**: TLC (50% ethyl acetate–hexanes): R_f = 0.88 (UV, $KMnO_4$). $[\alpha]^{23}_D$ –78.3 (*c* 0.12, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.53–7.49 (m, 2H), 7.35–7.28 (m, 3H), 5.12 (dd, *J* = 12.0, 2.0 Hz, 1H), 5.07 (t, *J* = 2.5 Hz, 1H), 4.37 (q, *J* = 6.5 Hz, 1H), 3.04 (s, OH), 2.23 (m, 1H), 2.23 (s, 3H), 2.06 (s, 3H), 1.99 (dt, *J* = 14.5, 2.5, 1.5 Hz, 1H), 1.12 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 208.9, 169.5, 131.5, 129.0, 127.7, 94.8, 80.4, 73.2, 70.0, 31.7, 26.5, 21.0, 14.7. FTIR (neat), cm^{-1}: 3472 (br), 2932 (w),

1744 (s), 1715 (s), 1373 (s), 1232 (s), 1030 (s). HRMS (ESI): Calcd for $(C_{16}H_{20}O_5S + Na)^+$: 347.0924 Found: 347.0925.



15 **19**

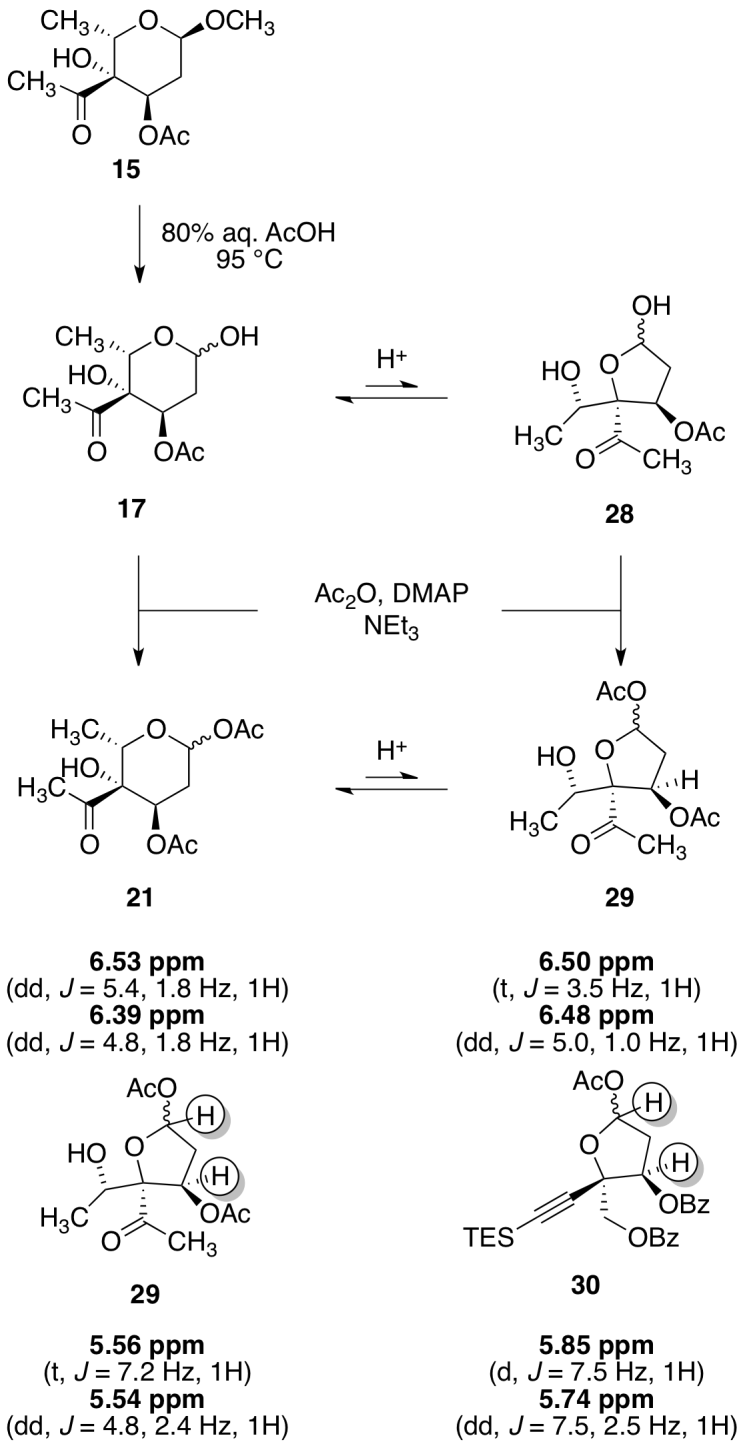
1-*O*-(4'-Pentenyl) Glycoside 19.

Pyridinium *p*-toluenesulfonate (PPTS, 2.0 mg, 8.1 μmol, 0.05 equiv) was added in one portion to a solution of methyl 3-acetyl-α-trioxacarcinoside B **15** (40 mg, 0.16 mmol, 1 equiv) and 4-penten-1-ol (252 μL, 2.44 mmol, 15.0 equiv) in dichloroethane (3 mL) in a 25-mL flask. The flask was sealed with a glas stopper and the stopper was secured with a metal clamp. The reaction flask was heated at 80 °C for 24 h. Heating was discontinued and the reaction flask was allowed to cool to 23 °C. The reaction mixture was diluted with ethyl acetate (50 mL) and the resulting solution was filtered through a plug of Celite. The filtrate was concentrated at 70 °C. The residue was purified by flash-column chromatography on silica gel (30% ethyl acetate–hexanes) to provide an anomeric mixture of pure 1-*O*-(4'-pentenyl) glycosides **19** (36.5 mg, 75%, α:β ~ 1:1). The product was purified by flash-column chromatography on silica gel (5% ethyl acetate–hexanes initially, grading to 20% ethyl acetate–hexane) to provide separately the pure anomers, α-**19** (11 mg, 23%) and β-**19** (13 mg, 27%), as colorless oils. α-**19**: TLC (30% ethyl acetate–hexanes): R_f = 0.49 (Anis). $[\alpha]^{23}_D$ –3.6 (*c* 0.38, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 5.86–5.77 (m, 1H), 5.03 (dd, *J* = 17.0, 2.0 Hz, 1H), 4.97 (br d, *J* = 9.5 Hz, 1H), 4.83 (d, *J* = 4.0 Hz, 1 H), 4.75 (t, *J* = 4.0 Hz, 1H), 4.60 (q, *J* = 6.5 Hz, 1H), 3.70 (dt, *J* = 9.0, 7.0 Hz, 1H), 3.64 (s, OH), 3.36 (dt, *J* = 9.0, 6.5 Hz, 1H), 2.26 (s, 3H), 2.26–2.13 (m, 3H), 2.05 (s, 3H), 2.05–1.97 (m, 1H), 1.73–1.64 (m, 2H), 1.03 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 208.8, 169.9, 138.1, 114.9, 96.1, 78.2, 70.8, 67.0, 63.4, 30.4, 29.2, 28.9, 26.8, 21.2, 14.3. FTIR (neat), cm^{-1}: 3474 (br), 2940 (w), 1742 (s), 1715 (s), 1371 (m), 1240 (s), 1128 (m). HRMS (ESI): Calcd for $(C_{15}H_{24}O_6 + Na)^+$: 323.1465. Found: 323.1408. β-**19**: TLC (30% ethyl acetate–hexanes): R_f = 0.29 (UV, Anis). $[\alpha]^{23}_D$ –133.5 (*c* 0.34, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 5.85–5.77 (m, 1H), 5.11 (app t, *J* = 3.5 Hz, 1 H), 5.02 (dd, *J* = 17.0, 1.5 Hz, 1H), 4.97 (dd, *J* = 10.5, 1.0 Hz, 1H), 4.75 (dd, *J* = 9.5, 2.0 Hz, 1H), 4.30 (q, *J* = 6.5 Hz, 1H), 3.92 (dt, *J* = 9.0, 7.0 Hz, 1H), 3.48

(dt, J = 9.5, 7.0 Hz, 1H), 3.06 (s, OH), 2.23 (s, 3H), 2.12 (app q, J = 7.0 Hz, 2H), 2.05 (s, 3H), 2.04–1.98 (m, 1H), 1.85 (dt, J = 15.0 Hz, 2.0 Hz, 1H), 1.73–1.66 (m, 2H), 1.08 (d, J = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 209.3, 169.5, 138.0, 114.9, 98.3, 70.6, 70.5, 68.7, 32.0, 30.1, 28.8, 26.6, 21.0, 14.4. FTIR (neat), cm^{-1}: 3491 (br), 2941 (w), 1748 (s), 1715 (s), 1371 (m), 1236 (s), 1138 (m). HRMS (ESI): Calcd for $(C_{15}H_{24}O_6 + Na)^+$: 323.1465. Found: 323.1404.

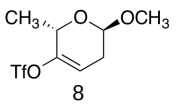
Acid Catalyzed Isomerization

The 1-*O*-acetyl glycosides **21** were obtained with two minor inseparable byproducts when they were prepared from the methyl glycoside **15**. As depicted below, we speculate that these byproducts are the isomeric substances **21** and **29**. These tentative assignments are supported by ^{1}H NMR spectral data of the related molecule **30**,[13] summarized below.



[13] Kohgo, S.; Mitsuya, H.; Ohrui, H. *Biosci. Biotechnol. Biochem.* **2001**, *65*, 1879-1882.

^{1}H and ^{13}C NMR Spectra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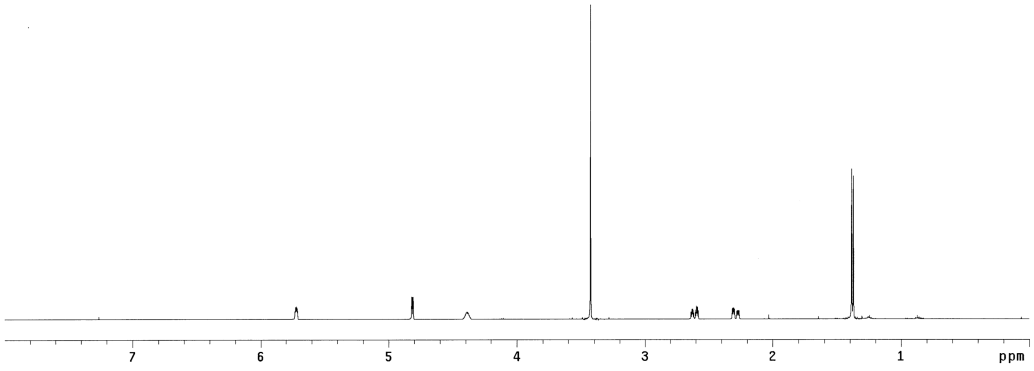
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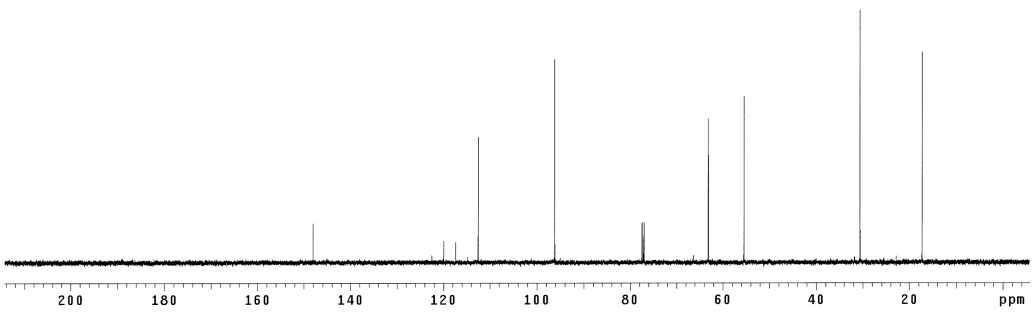
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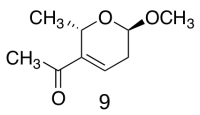
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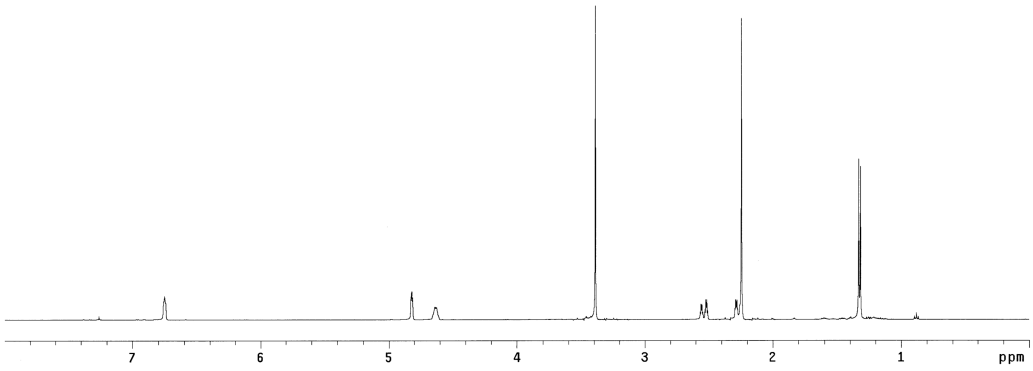
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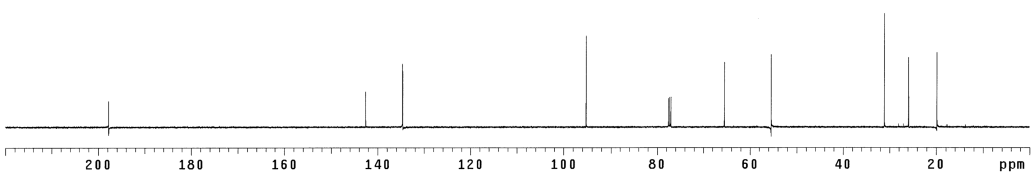
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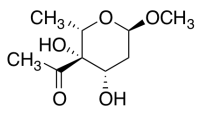
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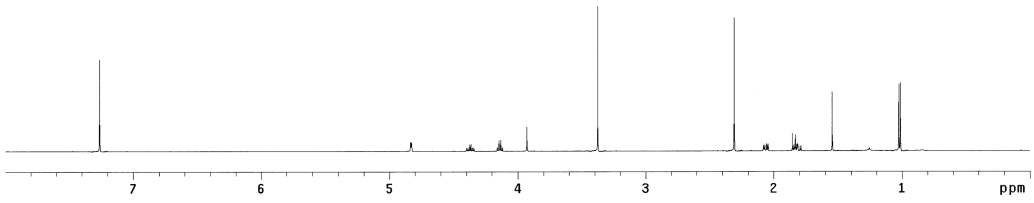
13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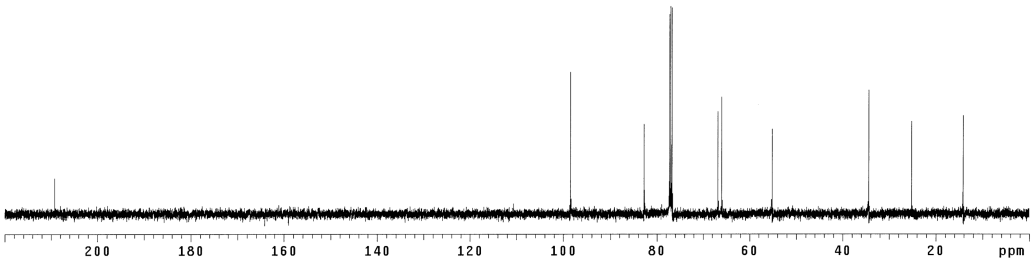
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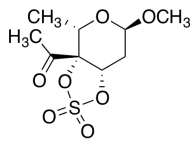
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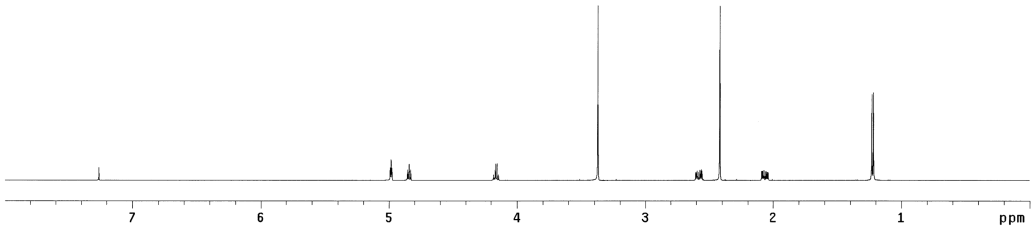
O

14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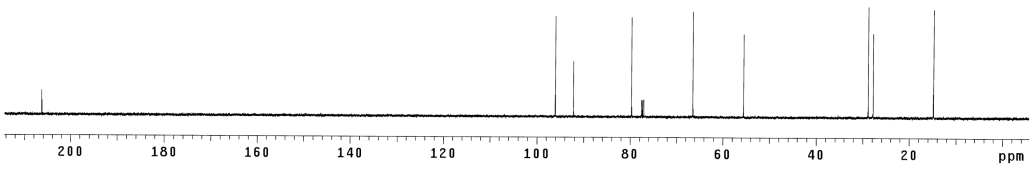
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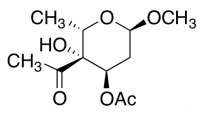
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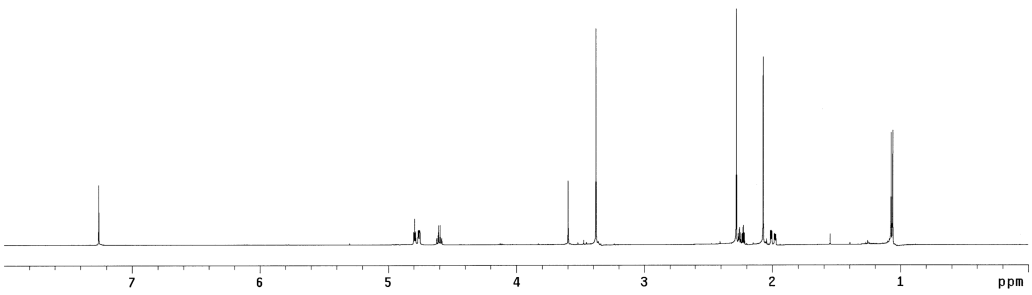
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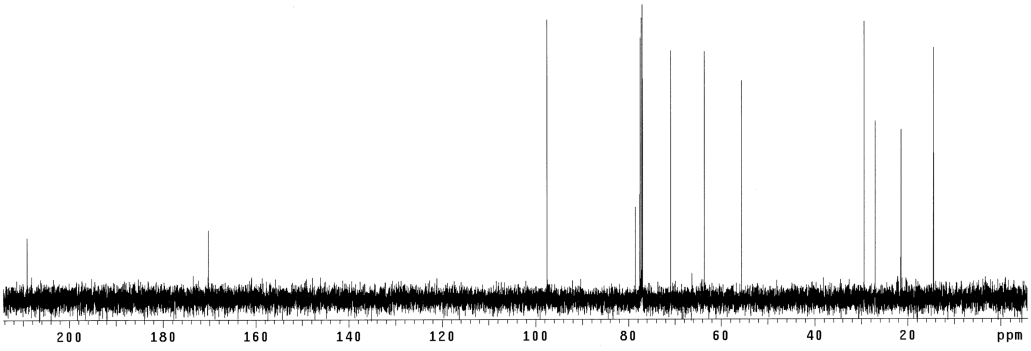
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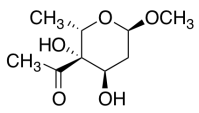
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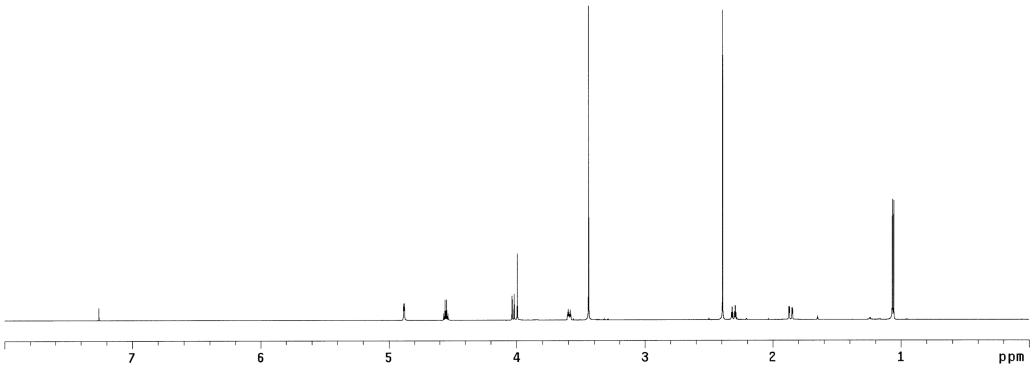
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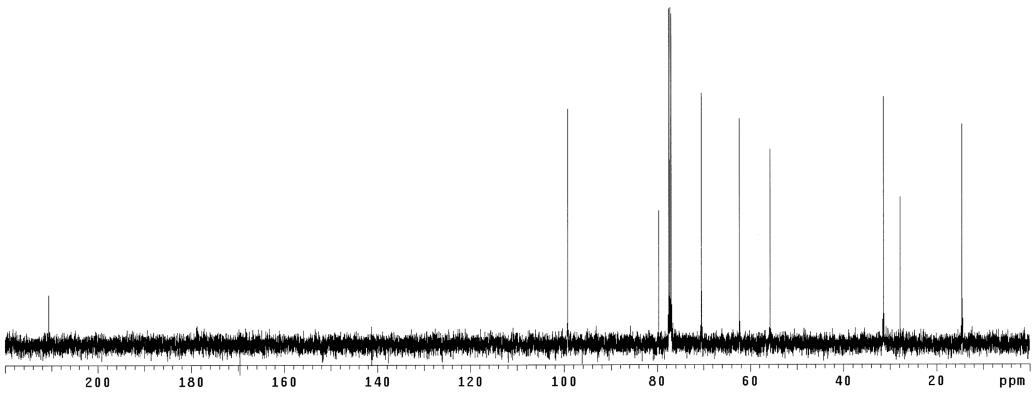
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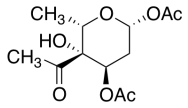
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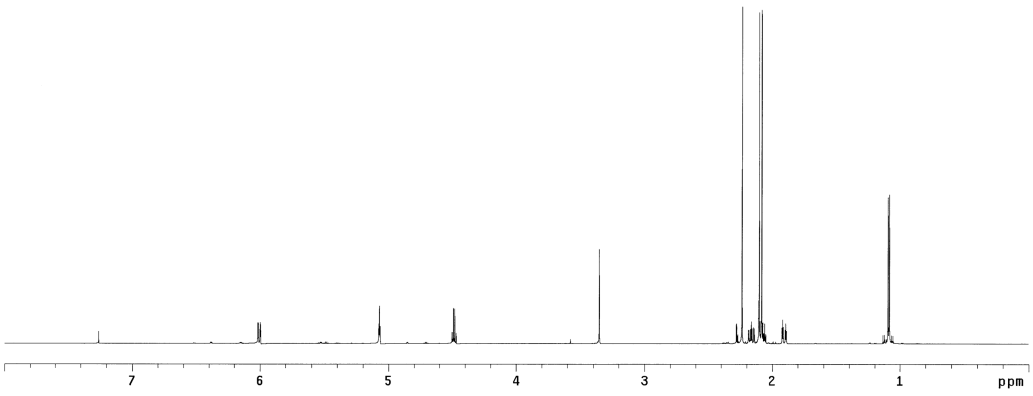
OAc

21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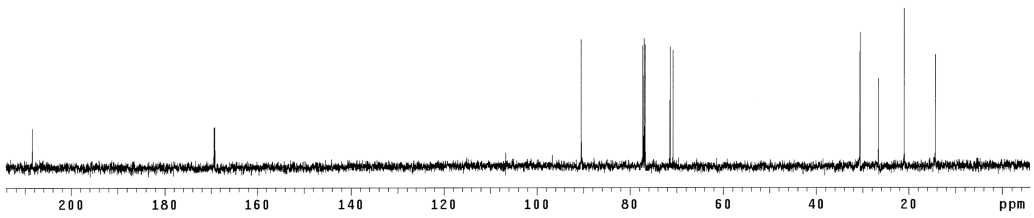
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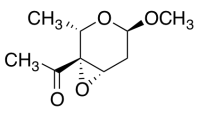
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CH3
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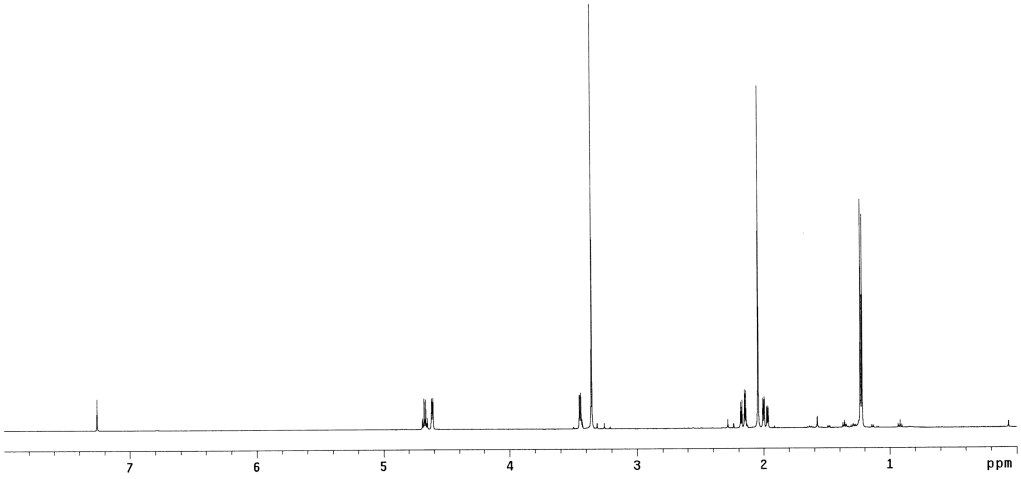
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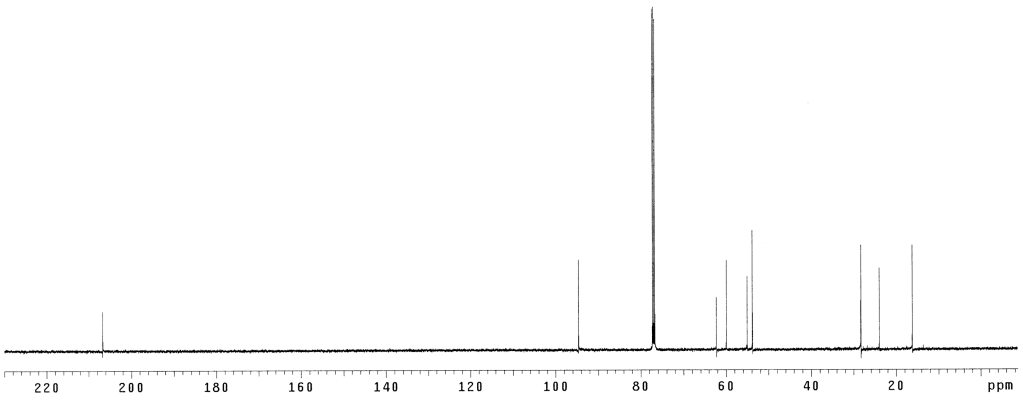
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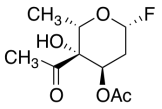
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CH3
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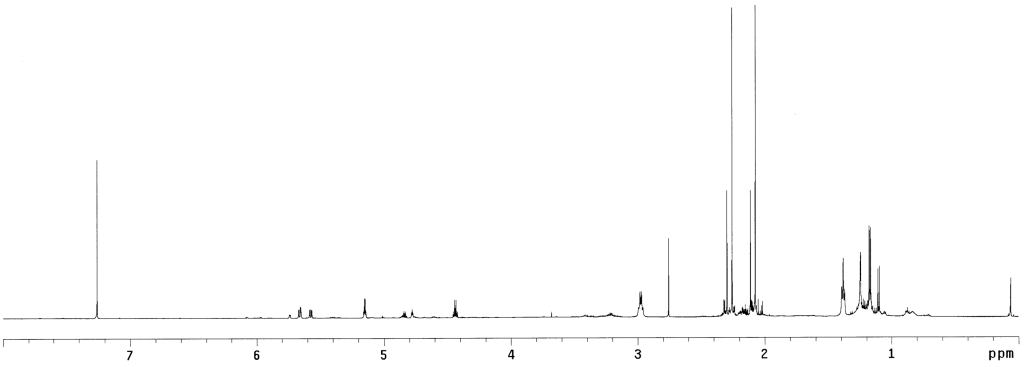
20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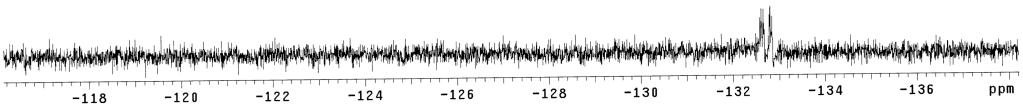
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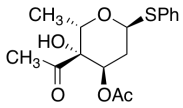
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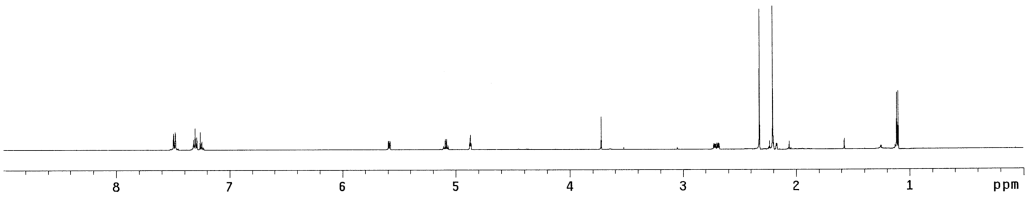
alpha-18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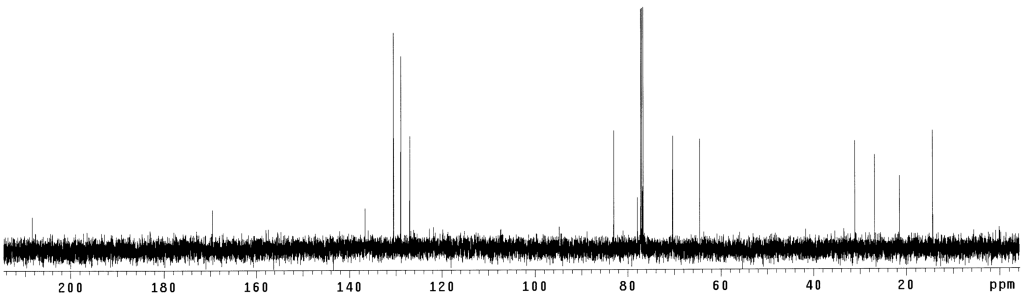
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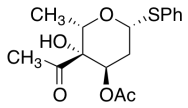
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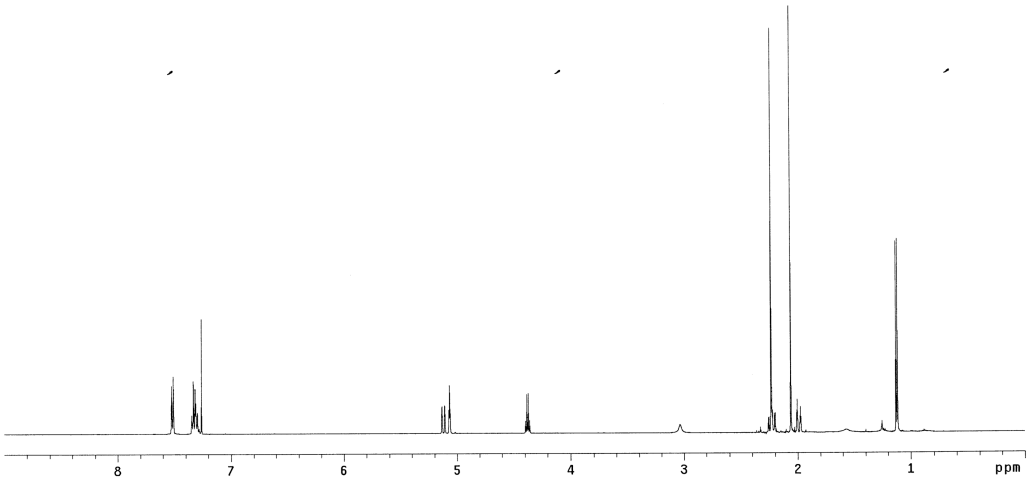
HO
CH3
O
OAc

beta-18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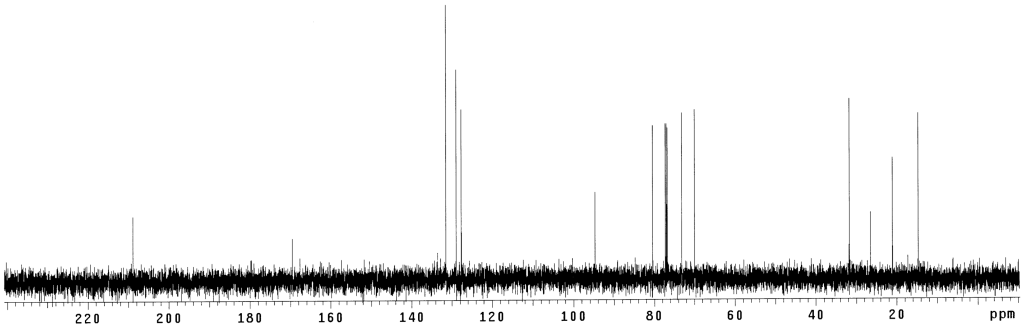
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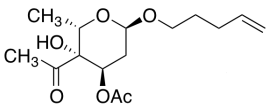
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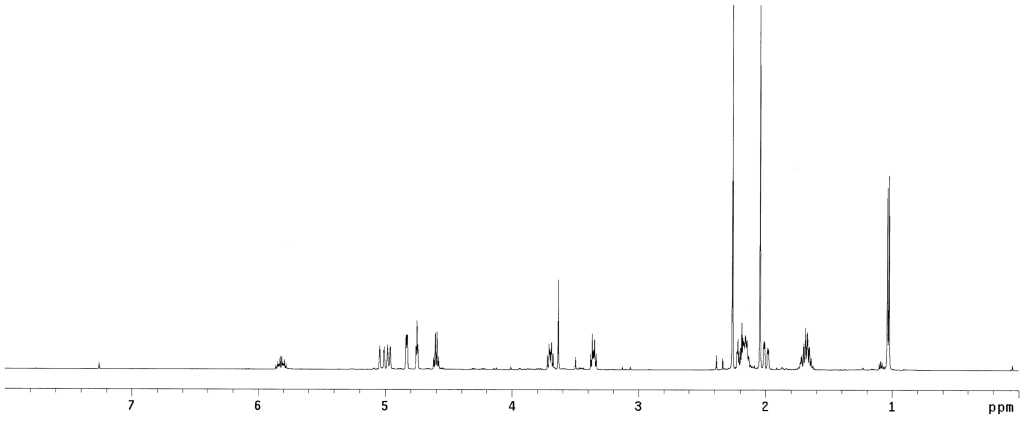
CH3
O
OAc

alpha-19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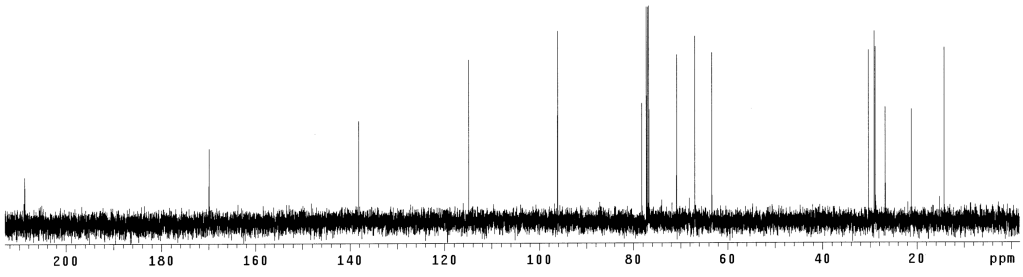
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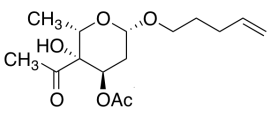
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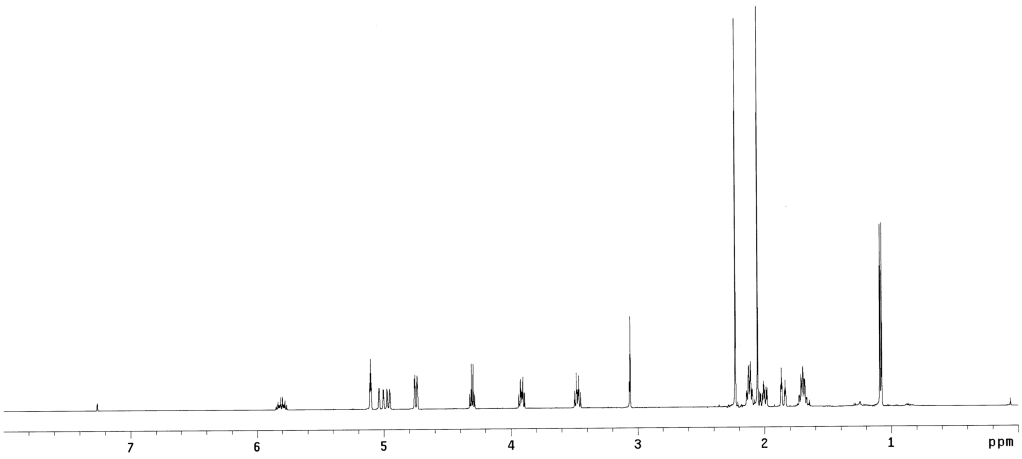
CH3
O
OAc

beta-19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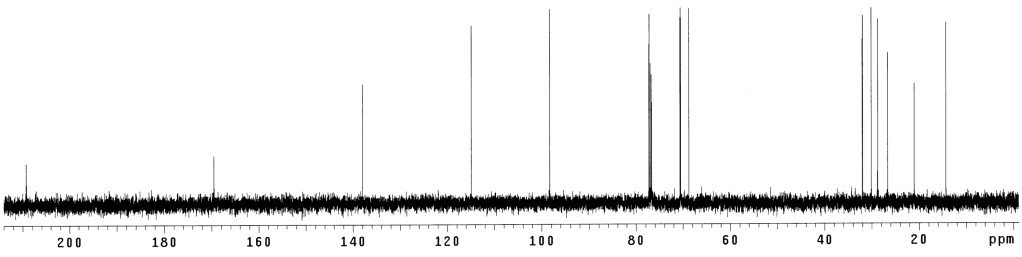
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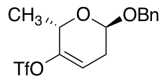

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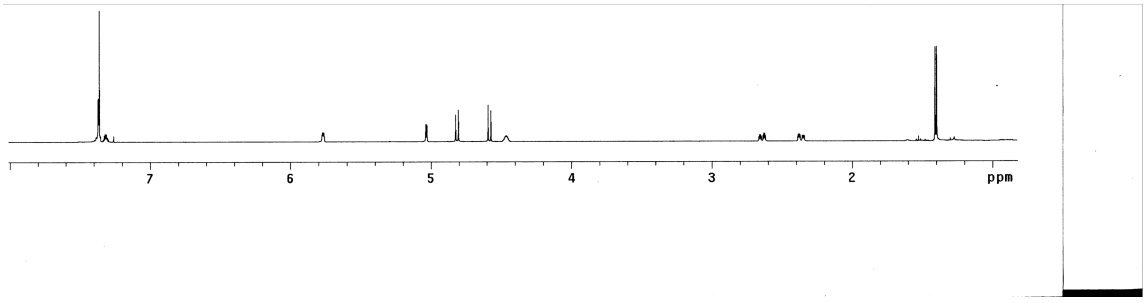

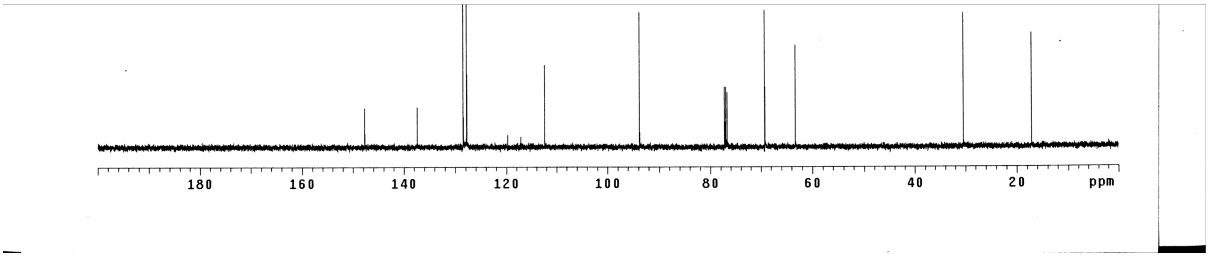

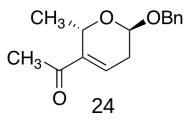
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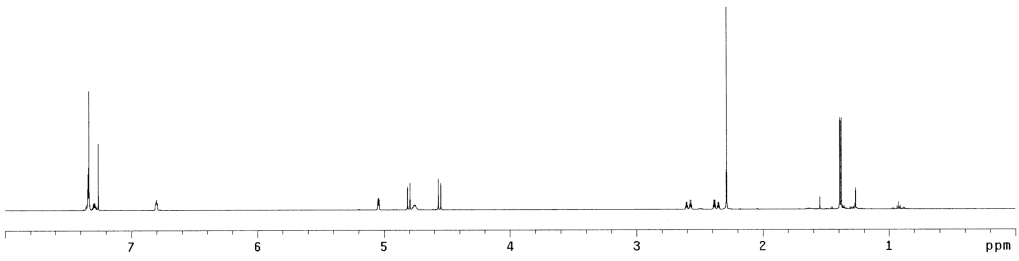
OBn
CH3
O

24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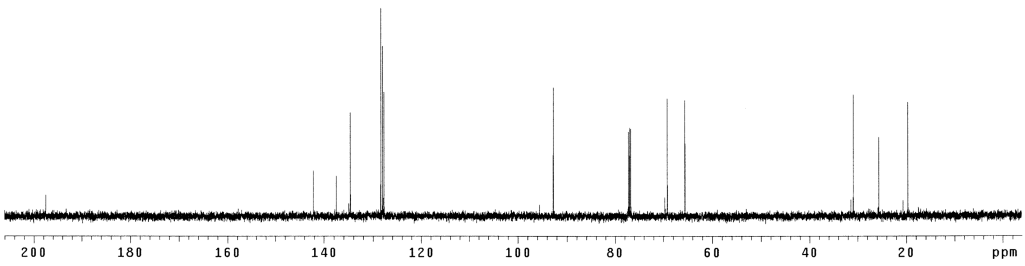
ppm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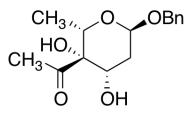
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OBn
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CH3
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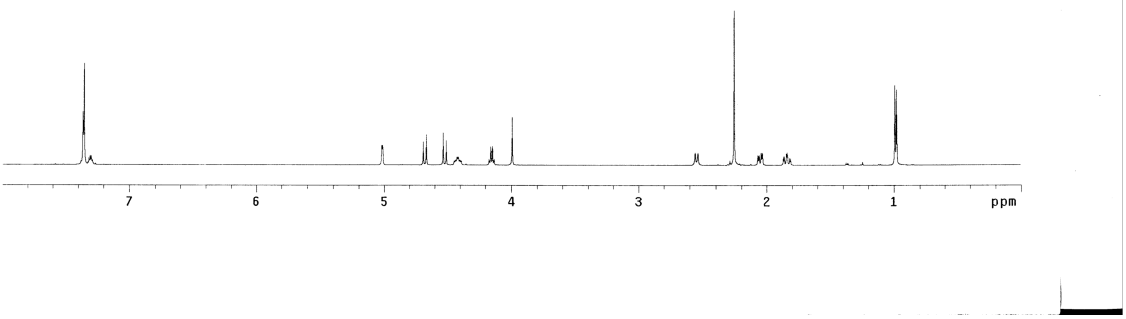
OH

25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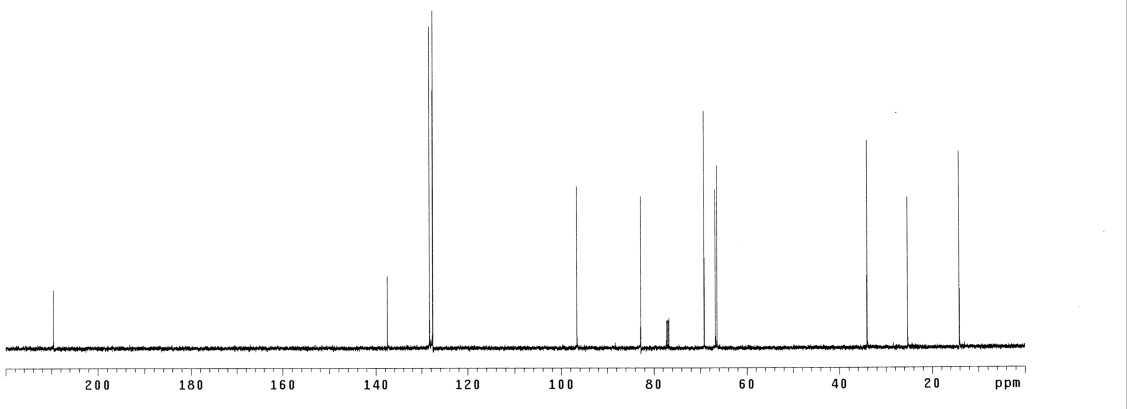
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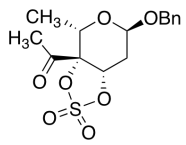
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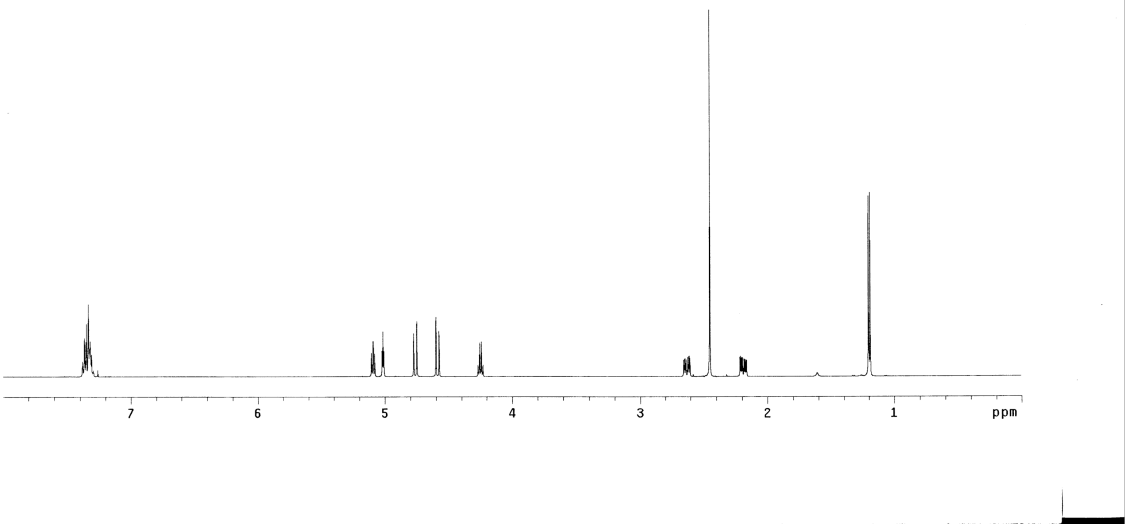
O
OBn
O
O
O
O
S
O
O

26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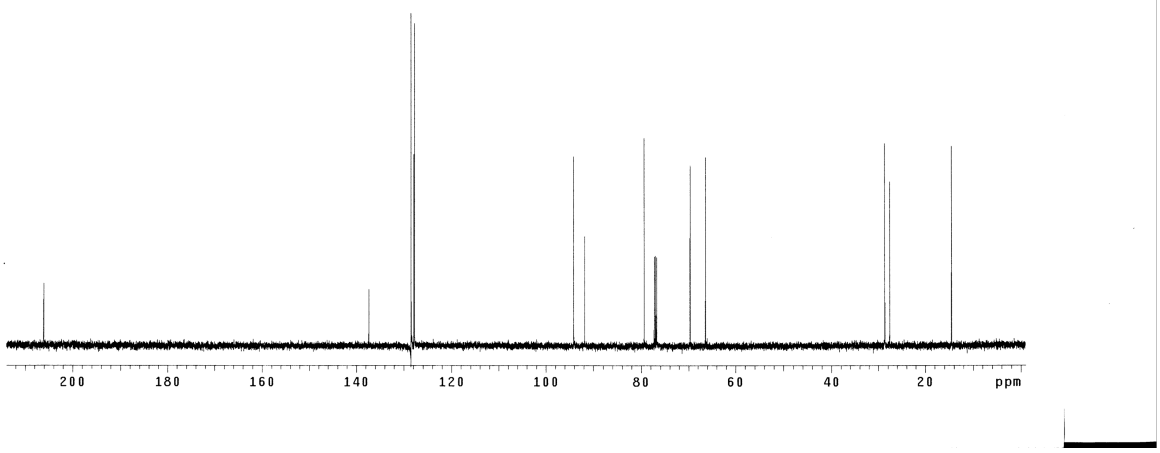
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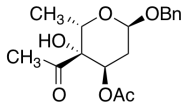
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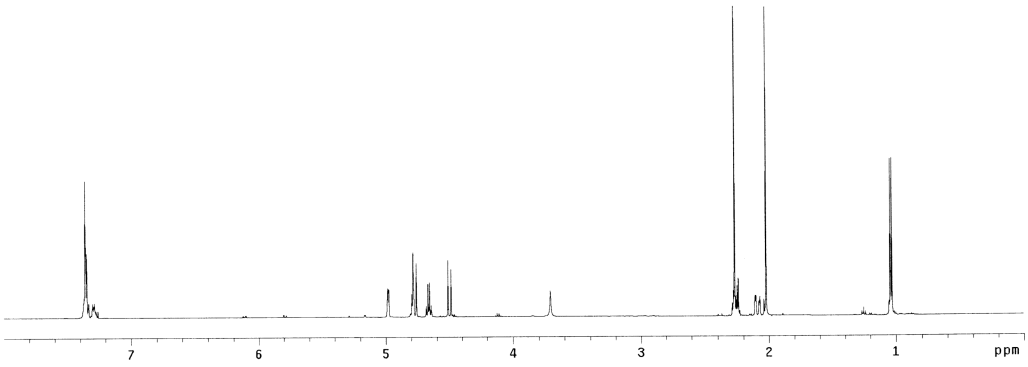
OBn
HO
CH3
O
OAc

27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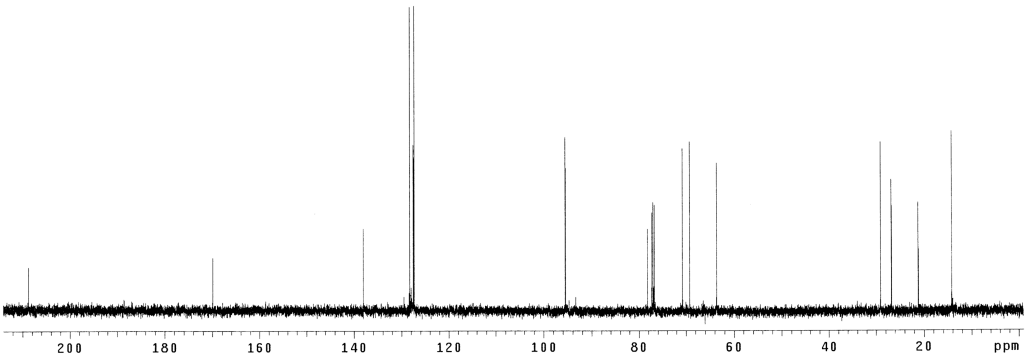
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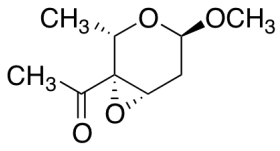
ppm

X-Ray Crystal Structure Data for Epoxide 10

X-Ray Crystallographic Laboratory (Harvard University)



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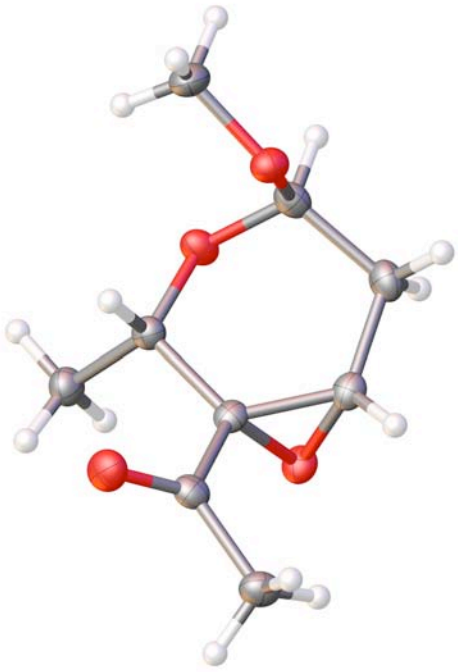

X-Ray Crystallography: Data were collected from a crystal mounted on a Bruker APEX II DUO CCD diffractometer equipped with an Oxford Cryosystems nitrogen flow apparatus using $Cu_{K\alpha}$ radiation (λ=0.71073 Å) at 100 K. The collection method involved 0.5° scans in ω at 28° in 2θ. Data integration to 0.82-Å resolution was carried out using SAINT V7.46 A with reflection spot size optimization.[14] Absorption corrections were made with the program SADABS. [15] The structure was solved by the direct methods procedure and refined by least-squares methods against F2 using SHELXS-97 and SHELXL-97.[15] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on their respective atoms. Crystal data as well as the details of data collection and refinement are summarized in Table S1 and geometric parameters are listed in Table S2. The ORTEP plots of Figure S1 were generated with the SHELXL-97 program,[15] and the graphic depicted in Figure S2 was generated with Accelrys DS Visualizer 2.0.[16]

Table S1. Experimental details

	THMA0115
Crystal data	
Chemical formula	$C_{18}H_{28}O_8$
M_r	372.40
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	296
a, b, c (Å)	8.0667 (2), 8.2677 (2), 14.2711 (3)
β (°)	101.049 (1)
V (Å^3)	934.14 (4)
Z	2
Radiation type	Cu $K\alpha$

[14] Bruker AXS (2009). SMART and SAINTPLUS. Bruker AXS, Madison, Wisconsin
[15] Sheldrick, G. M *Acta Crys*. **2008**, *A64*, 112–122.
[16] Accelrys DS Visualizer v2.0.1.7347, **2007**, Accelrys Software Inc.

μ (mm^{-1})	0.87
Crystal size (mm)	0.26 × 0.24 × 0.20
Data collection	
Diffractometer	CCD area detector diffractometer
Absorption correction	Multi-scan *SADABS*
T_{min}, T_{max}	0.805, 0.845
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17040, 3086, 3060
R_{int}	0.030
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.025, 0.064, 1.09
No. of reflections	3086
No. of parameters	241
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.15, -0.24
Absolute structure	Flack H D (1983), Acta Cryst. A39, 876-881
Flack parameter	-0.07 (10)

Computer programs: *APEX2* v2009.3.0, *SAINT* 7.46A, *SHELXS97*, *SHELXL97*, Bruker *SHELXTL*.[14,15]

Table S2. Selected geometric parameters (Å, º)

O5—C11	1.4155 (15)	O1—C1	1.4202 (16)
O5—C15	1.4379 (15)	O1—C5	1.4305 (16)
O6—C11	1.4077 (16)	O2—C1	1.4059 (16)
O6—C16	1.4260 (18)	O2—C6	1.4343 (16)

O7—C13	1.4414 (16)	O3—C3	1.4434 (16)
O7—C14	1.4469 (15)	O3—C4	1.4460 (14)
O8—C17	1.2146 (17)	O4—C7	1.2177 (16)
C11—C12	1.5134 (18)	C1—C2	1.5190 (18)
C11—H11	0.9800	C1—H1	0.9800
C12—C13	1.5109 (17)	C2—C3	1.5039 (19)
C12—H12A	0.9700	C2—H2A	0.9700
C12—H12B	0.9700	C2—H2B	0.9700
C13—C14	1.4836 (17)	C3—C4	1.4805 (17)
C13—H13	0.9800	C3—H3	0.9800
C14—C15	1.5074 (18)	C4—C7	1.5043 (18)
C14—C17	1.5100 (17)	C4—C5	1.5175 (17)
C15—C19	1.5190 (18)	C5—C9	1.5141 (17)
C15—H15	0.9800	C5—H5	0.9800
C16—H16A	0.9600	C6—H6A	0.9600
C16—H16C	0.9600	C6—H6C	0.9600
C16—H16B	0.9600	C6—H6B	0.9600
C17—C18	1.4955 (19)	C7—C8	1.5022 (18)
C18—H18A	0.9600	C8—H8B	0.9600
C18—H18C	0.9600	C8—H8A	0.9600
C18—H18B	0.9600	C8—H8C	0.9600
C19—H19A	0.9600	C9—H9A	0.9600
C19—H19C	0.9600	C9—H9C	0.9600
C19—H19B	0.9600	C9—H9B	0.9600
C11—O5—C15	114.46 (9)	C1—O1—C5	114.79 (9)
C11—O6—C16	112.98 (11)	C1—O2—C6	112.89 (10)
C13—O7—C14	61.81 (8)	C3—O3—C4	61.65 (8)

O6—C11—O5	112.28 (10)	O2—C1—O1	111.81 (10)
O6—C11—C12	107.20 (10)	O2—C1—C2	107.33 (10)
O5—C11—C12	112.43 (10)	O1—C1—C2	111.20 (10)
O6—C11—H11	108.3	O2—C1—H1	108.8
O5—C11—H11	108.3	O1—C1—H1	108.8
C12—C11—H11	108.3	C2—C1—H1	108.8
C13—C12—C11	112.84 (10)	C3—C2—C1	111.98 (10)
C13—C12—H12A	109.0	C3—C2—H2A	109.2
C11—C12—H12A	109.0	C1—C2—H2A	109.2
C13—C12—H12B	109.0	C3—C2—H2B	109.2
C11—C12—H12B	109.0	C1—C2—H2B	109.2
H12A—C12—H12B	107.8	H2A—C2—H2B	107.9
O7—C13—C14	59.27 (7)	O3—C3—C4	59.26 (8)
O7—C13—C12	116.00 (11)	O3—C3—C2	118.00 (11)
C14—C13—C12	119.55 (11)	C4—C3—C2	119.77 (10)
O7—C13—H13	116.5	O3—C3—H3	116.0
C14—C13—H13	116.5	C4—C3—H3	116.0
C12—C13—H13	116.5	C2—C3—H3	116.0
O7—C14—C13	58.91 (8)	O3—C4—C3	59.09 (7)
O7—C14—C15	115.45 (10)	O3—C4—C7	116.31 (10)
C13—C14—C15	119.60 (10)	C3—C4—C7	118.23 (10)
O7—C14—C17	114.08 (10)	O3—C4—C5	114.89 (10)
C13—C14—C17	118.55 (11)	C3—C4—C5	119.48 (10)
C15—C14—C17	116.79 (10)	C7—C4—C5	116.24 (10)
O5—C15—C14	111.58 (10)	O1—C5—C9	106.39 (10)
O5—C15—C19	105.79 (10)	O1—C5—C4	112.38 (10)
C14—C15—C19	112.61 (11)	C9—C5—C4	110.98 (10)
O5—C15—H15	108.9	O1—C5—H5	109.0

C14—C15—H15	108.9	C9—C5—H5	109.0
C19—C15—H15	108.9	C4—C5—H5	109.0
O6—C16—H16A	109.5	O2—C6—H6A	109.5
O6—C16—H16C	109.5	O2—C6—H6C	109.5
H16A—C16—H16C	109.5	H6A—C6—H6C	109.5
O6—C16—H16B	109.5	O2—C6—H6B	109.5
H16A—C16—H16B	109.5	H6A—C6—H6B	109.5
H16C—C16—H16B	109.5	H6C—C6—H6B	109.5
O8—C17—C18	122.42 (12)	O4—C7—C8	121.57 (12)
O8—C17—C14	119.30 (12)	O4—C7—C4	119.57 (11)
C18—C17—C14	118.29 (11)	C8—C7—C4	118.81 (11)
C17—C18—H18A	109.5	C7—C8—H8B	109.5
C17—C18—H18C	109.5	C7—C8—H8A	109.5
H18A—C18—H18C	109.5	H8B—C8—H8A	109.5
C17—C18—H18B	109.5	C7—C8—H8C	109.5
H18A—C18—H18B	109.5	H8B—C8—H8C	109.5
H18C—C18—H18B	109.5	H8A—C8—H8C	109.5
C15—C19—H19A	109.5	C5—C9—H9A	109.5
C15—C19—H19C	109.5	C5—C9—H9C	109.5
H19A—C19—H19C	109.5	H9A—C9—H9C	109.5
C15—C19—H19B	109.5	C5—C9—H9B	109.5
H19A—C19—H19B	109.5	H9A—C9—H9B	109.5
H19C—C19—H19B	109.5	H9C—C9—H9B	109.5
C16—O6—C11—O5	-62.72 (12)	C6—O2—C1—O1	-63.78 (13)
C16—O6—C11—C12	173.34 (10)	C6—O2—C1—C2	174.01 (10)
C15—O5—C11—O6	-55.61 (13)	C5—O1—C1—O2	-53.04 (14)
C15—O5—C11—C12	65.37 (13)	C5—O1—C1—C2	66.92 (13)

O6—C11—C12—C13	83.22 (12)	O2—C1—C2—C3	76.66 (13)
O5—C11—C12—C13	-40.63 (14)	O1—C1—C2—C3	-45.92 (15)
C14—O7—C13—C12	-110.40 (12)	C4—O3—C3—C2	-109.75 (12)
C11—C12—C13—O7	77.28 (14)	C1—C2—C3—O3	81.43 (13)
C11—C12—C13—C14	9.42 (16)	C1—C2—C3—C4	12.70 (17)
C13—O7—C14—C15	110.61 (11)	C3—O3—C4—C7	-108.60 (11)
C13—O7—C14—C17	-109.98 (12)	C3—O3—C4—C5	110.76 (12)
C12—C13—C14—O7	104.43 (12)	C2—C3—C4—O3	106.81 (13)
O7—C13—C14—C15	-103.56 (12)	O3—C3—C4—C7	105.36 (11)
C12—C13—C14—C15	0.87 (17)	C2—C3—C4—C7	-147.83 (12)
O7—C13—C14—C17	102.38 (12)	O3—C3—C4—C5	-103.01 (12)
C12—C13—C14—C17	-153.19 (11)	C2—C3—C4—C5	3.80 (17)
C11—O5—C15—C14	-52.42 (13)	C1—O1—C5—C9	-169.54 (10)
C11—O5—C15—C19	-175.19 (10)	C1—O1—C5—C4	-47.89 (14)
O7—C14—C15—O5	-48.40 (13)	O3—C4—C5—O1	-55.05 (14)
C13—C14—C15—O5	18.82 (15)	C3—C4—C5—O1	12.10 (16)
C17—C14—C15—O5	173.32 (10)	C7—C4—C5—O1	164.28 (10)
O7—C14—C15—C19	70.39 (14)	O3—C4—C5—C9	63.94 (14)
C13—C14—C15—C19	137.60 (12)	C3—C4—C5—C9	131.10 (12)
C17—C14—C15—C19	-67.89 (14)	C7—C4—C5—C9	-76.73 (13)
O7—C14—C17—O8	-154.94 (11)	O3—C4—C7—O4	-154.76 (12)
C13—C14—C17—O8	138.68 (12)	C3—C4—C7—O4	137.88 (13)
C15—C14—C17—O8	-16.10 (17)	C5—C4—C7—O4	-14.66 (17)
O7—C14—C17—C18	24.58 (15)	O3—C4—C7—C8	27.83 (16)
C13—C14—C17—C18	-41.79 (16)	C3—C4—C7—C8	-39.53 (16)
C15—C14—C17—C18	163.42 (11)	C5—C4—C7—C8	167.93 (11)

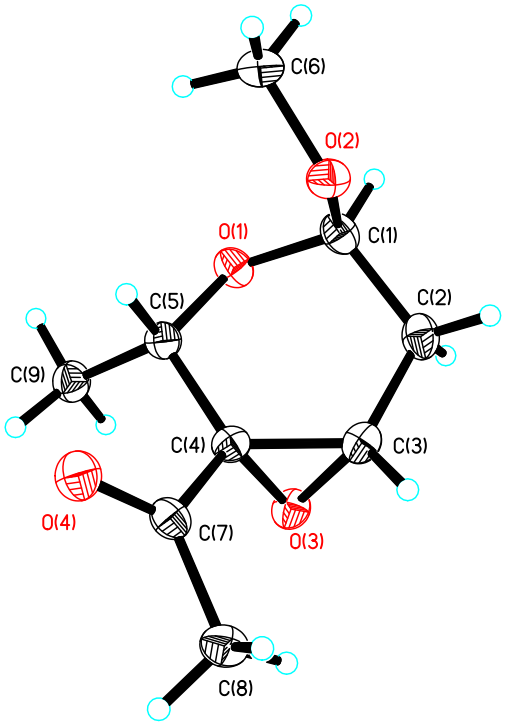

Figure S1a

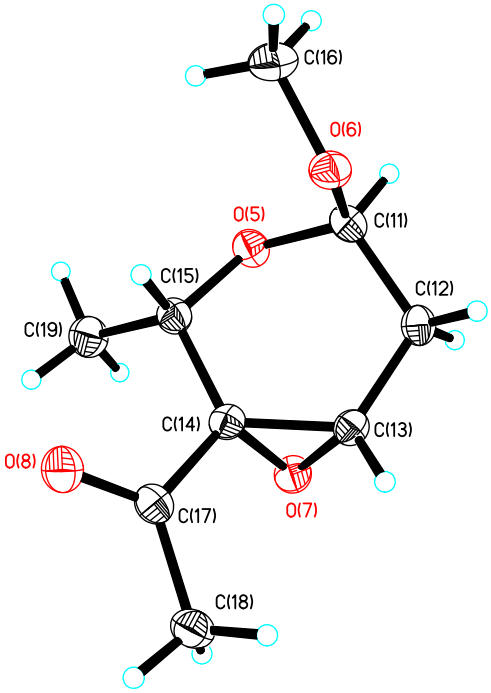

Figure S1b

Figure S1. Perspective views showing 50% probability for two independent molecules.

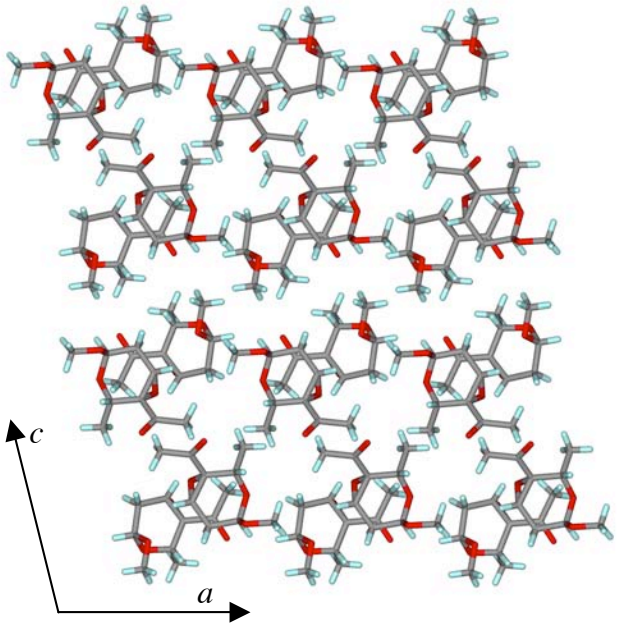

Figure S3. Three-dimensional supramolecular architecture viewed along the *b*-axis direction.