Supporting Information

Synthesis of a Broad Array of Highly Functionalized, Enantiomerically Pure Cyclohexanecarboxylic Acid Derivatives by Microbial Dihydroxylation of Benzoic Acid and Subsequent Oxidative and Rearrangement Reactions.

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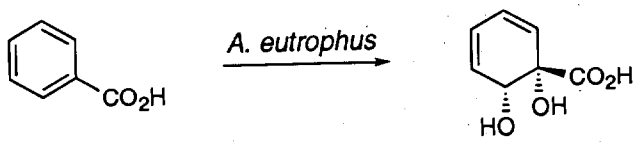
Microbial Dihydroxylation of Benzoic Acid



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Preparation of Glycerol Stock Solutions

Alcaligenes eutrophus B9 cells[1] (lyophilized powder, 20 mg) were suspended in nutrient broth (5 mL, prepared by dissolving 8 g of Difco Bacto© Nutrient Broth in 1 L of nanopure water followed by sterilization in an autoclave at 125 °C) in a 20-mL sterile culture tube. Aqueous sodium succinate solution (16.7 μL of a 2.5 M aqueous solution, 5 mM final concentration) was added, and the culture tube was shaken at 250 rpm at 30 °C until cell growth became apparent (3 d). An aliquot (250 μL) of the cellular suspension was then transferred to 5 mL of Hutner's mineral base medium (HMB, see paragraph below) containing sodium succinate (16.7 μL of a 2.5 M aqueous solution, 5 mM final concentration) in a 20-mL sterile culture tube. The culture tube was shaken at 250 rpm for 2 d at 30 °C, whereupon an aliquot (250 μL) of the fermentation solution was subcultured in a sterile Erlenmeyer flask containing 50 mL of HMB and aqueous sodium succinate solution (167 μL of a 2.5 M solution, 5 mM final concentration). The flask was

shaken at 250 rpm for 24 h at 30 °C. The resulting solution was used directly for the preparation of glycerol stock solutions. Thus, a portion of the subcultured cellular suspension (5 mL) was diluted with an equal volume of sterile glycerol, and the resulting solution was divided equally into ten 2-mL sterile Eppendorf tubes. The individual stock solutions were then stored at –80 °C.

Hutner's Mineral Base Medium

Hutner's mineral base medium (HMB) was prepared as follows. Solid potassium hydroxide (400 mg) was dissolved in 500 mL of nanopure water in a 2-L Erlenmeyer flask. Nitrilotriacetic acid (200 mg), magnesium sulfate (283 mg), calcium chloride dihydrate (67 mg), ammonium molybdate (0.2 mg), iron (II) sulfate (2.0 mg), Hutner's Metals 44 solution (1 mL, see paragraph below), ammonium sulfate (1.0 g), potassium dihydrogen phosphate (2.72 g) and sodium monohydrogen phosphate heptahydrate (5.36 g) were added sequentially. The solution was diluted to a total volume of 1 L and the pH was adjusted to 6.8 with concentrated hydrochloric acid. The medium was sterilized by filtration or by heating in an autoclave.

Hutner's Metals 44 solution was prepared as follows. Concentrated sulfuric acid (100 μL) was added to nanopure water (50 mL) in a 250-mL Erlenmeyer flask. Solid EDTA (0.50 g), zinc sulfate heptahydrate (2.20 g), iron (II) sulfate heptahydrate (1.0 g), copper (I) sulfate (0.39 g), cobalt (II) nitrate hexahydrate (50 mg) and sodium tetraborate decahydrate (36 mg) were then added in sequence, followed by 50 mL of nanopure water.

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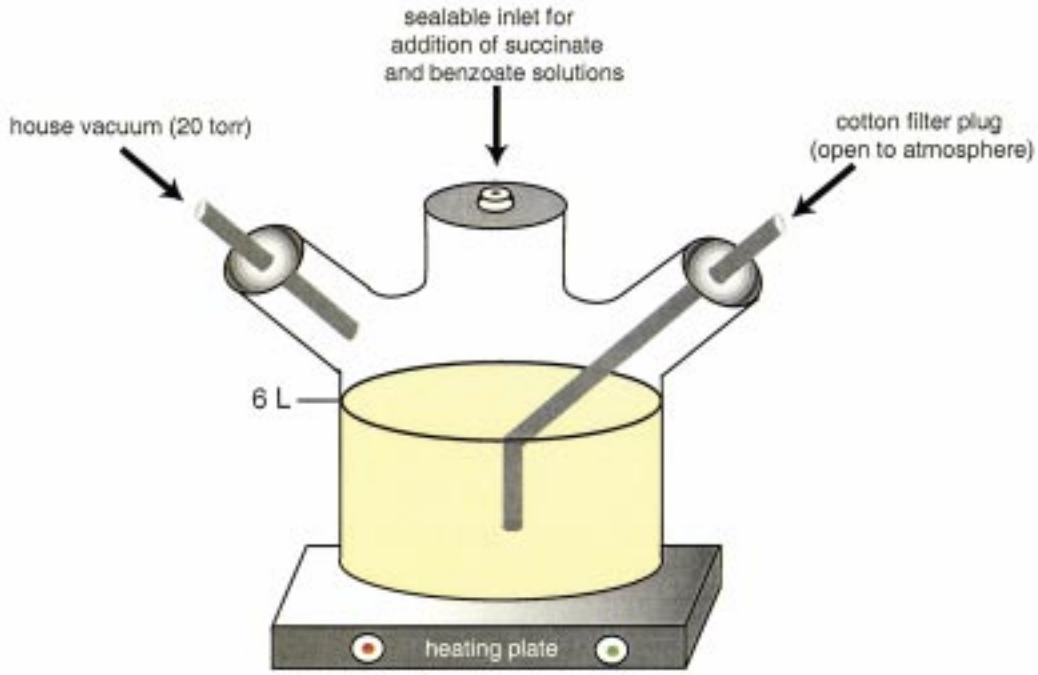
[1] We gratefully acknowledge Prof. George D. Hegeman (Indiana University) for a generous gift of *Alcaligenes eutrophus* B9 cells.

Cellular Dihydroxylation of Sodium Benzoate

Medium Scale

A sterile pipette tip was streaked across the surface of a frozen glycerol stock solution to produce small shards (ca. 10 mg). The frozen shards were added to a sterile 125 mL Erlenmeyer flask containing HMB (25 mL) and aqueous sodium succinate solution (140 μL of a 1.5 M solution, 5 mM final concentration). The flask was shaken at 250 rpm for 2 days at 30 °C. An aliquot (10 mL) of the white, heterogeneous solution was transferred using a sterile pipette to a mammalian cell growth jar containing HMB (6 L) and aqueous sodium succinate solution (20 mL of a 1.5 M solution, 5 mM final concentration). The jar was warmed on a hot plate to an internal temperature of 30 °C; cotton-filtered air was sparged through the medium. After 2 days, the white, heterogeneous solution was treated with aqueous sodium benzoate solution (18 mL of a 1.0 M solution) and aqueous sodium succinate solution (10 mL of a 1.5 M solution), inducing dihydroxylation. The resulting mixture was aerated vigorously for 6 hours at an internal temperature of 30 °C. After induction, sufficient aqueous sodium benzoate solution (24 to 48 mL of a 1.0 M solution, depending on the rate of consumption) was added hourly to maintain a concentration of 10-20 mM (determined by UV absorbance at 225 nm). Aqueous sodium succinate solution (10 mL of a 1.5 M solution) was added every fourth hour. These additions proceeded over 18 hours, then the solution was aerated overnight at an internal temperature of 30 °C, to ensure complete conversion. The fermentation broth was centrifuged, in portions, at 6000 rpm (Sorvall GS-3 rotor, model SLA-3000) to remove cellular material. The supernatant was concentrated to a volume of 400 mL using a rotary evaporator (bath temperature <45 °C). The concentrate

was cooled to 0 °C and then acidified to pH 3.0 using concentrated aqueous hydrochloric acid. The acidified aqueous solution was extracted repeatedly with ethyl acetate (8 × 500 mL, 4 × 800 mL, 8 × 1 L). The ethyl acetate extracts were dried over sodium sulfate before concentration using a rotary evaporator (bath temperature <45 °C), providing a pale yellow solid residue. Trituration of the residue with dichloromethane (2 × 200 mL) followed by drying *in vacuo* afforded pure (1*S*,2*R*)-1,2-dihydroxycyclohexa-3,5-diene-1-carboxylic acid as a white powder (38 g, 74%).



Apparatus Construction and Sterilization

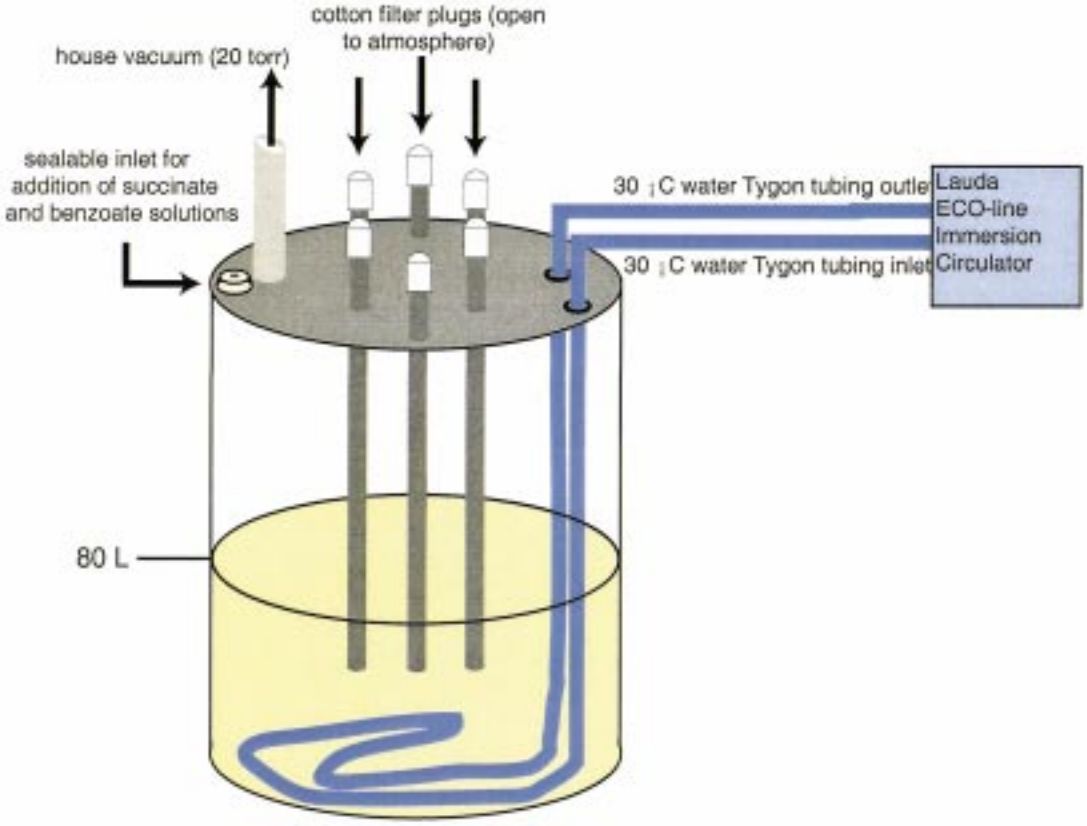
A 15-L mammalian cell growth jar was assembled and the stirring device was removed. Holes (3/8" diameter) were drilled through the 2 end caps and 2 lengths of Tygon tubing (1/2" diameter) were forced through the holes. One length of tubing was suspened above what would be the level of the fermentation broth and was connected to an outlet to the house vacuum. The other tube was placed 2" above the bottom of the jar and was fitted with a cotton plug on the exterior end.

Absolute ethanol (1 L) was added through the port for solutions and the jar was shaken to ensure that all of the internal parts had been in contact with the ethanol. The ethanol was drained through the solutions port and the apparatus was washed 3 times with 1 L of nanopure water by a similar procedure. At this point, the apparatus was ready for use.

Large Scale

A sterile pipette tip was streaked across the surface of a frozen glycerol stock solution to produce small shards (ca. 10 mg). The frozen shards were added to a sterile, baffled 2 L Erlenmeyer flask containing HMB (500 mL) and aqueous sodium succinate solution (1.67 mL of a 1.5 M stock solution, 5 mM final concentration). The flask was shaken at 250 rpm for 24 h at 30 °C. The white, heterogeneous solution was added to a large scale fermentor (see included diagram and description) containing HMB (80 L) and aqueous sodium succinate solution (267 mL of a 1.5 M stock solution, 5 mM final concentration). The solution was warmed to an internal temperature of 30 °C by circulating warm water through a 30' coil of Tygon tubing (1/2" diameter); cotton-filtered air was sparged through the medium. After 24 h the white, heterogeneous solution was treated with aqueous sodium benzoate solution (240 mL of a 1.0 M solution) and aqueous sodium succinate solution (133 mL of a 1.5 M solution), inducing dihydroxylation. The resulting mixture was then aerated vigorously for 6 hours at an internal temperature of 30 °C. After induction, sufficient aqueous sodium benzoate solution (160 to 400 mL of a 1.0 M solution, depending on the rate of consumption) was added hourly to maintain a concentration of 10-20 mM (determined by UV absorbance at 225 nm). Aqueous sodium succinate solution (135 mL of a 1.5 M solution) was added when the rate of oxidation slowed (determined by UV absorbance at 225 nm). The fermentation mixture was maintained at pH 6.8 (monitored every hour) by periodic additions (every other hour after the first 4 hours) of aqueous sodium dihydrogen phosphate solution (2.0 M solution). These additions proceeded over 22 h, then the

solution was aerated overnight at an internal temperature of 30 °C to maximize conversion. The fermentation broth was centrifuged, in portions, at 2000 rpm (bench top centrifuge) to remove the majority of cellular material. The supernatant was concentrated to a volume of 20 L using a large scale rotary evaporator (bath temperature <45 °C). The concentrate was then centrifuged, in portions, at 6000 rpm (Sorvall GS-3 rotor, model SLA-3000) to remove any residual cellular material. The supernatant was further concentrated to 6 L using a large scale rotary evaporator (bath temperature <45 °C), and the concentrate was divided into three 2-L portions. The light grey solutions were cooled to 0 °C and acidified to pH 3.0 using concentrated hydrochloric acid. The acidified aqueous solutions were each extracted repeatedly with ethyl acetate (approximately 60 L) until less than 50 mg of material was isolated per 1-L ethyl acetate extract. The ethyl acetate extracts were dried over sodium sulfate, then were concentrated using a large scale rotary evaporator (bath temperature <45 °C), providing a light brown residue. Trituration of the residue with dichloromethane (2 L) followed by drying *in vacuo* afforded pure (1*S*,2*R*)-1,2-dihydroxycyclohexa-3,5-diene-1-carboxylic acid as a white powder mp 95-96 °C dec (210 g, 30%). The dichloromethane wash was concentrated, providing a brown residue. This residue was dissolved in a minimal amount of ethyl acetate and the resulting solution was cooled to –20 °C to induce precipitation of a light yellow solid, which was collected by filtration. Trituration of the solid with dichloromethane (2 x 250 mL) followed by drying *in vacuo* provide additional (1*S*,2*R*)-1,2-dihydroxycyclohexa-3,5-diene-1-carboxylic acid as an off-white powder (60 g, 9%) .



Apparatus Construction and Sterilization

A sealable, food grade 55-gal drum was purchased from Lab Safety (item # 1A-3973). The cover was removed and the two prefabricated sealable inlets were used for the addition of succinate and benzoate solutions and connection to the house vacuum (7/8" O.D., 3/8" I.D. vacuum tubing was secured by forcing it into the 3/4" bung hole). Six 1" holes were drilled through the cover and six 35" lengths of PVC pipe (1" diameter), fitted with cotton plugs on the exterior, were placed through the holes. In addition, two 1/2" holes were drilled through the lid and a 35' length of Tygon tubing (1/2" diameter) was run through these, coiled on the bottom of the drum and connected to a Lauda ECO-line Immersion Circulator (set to 30 ¡C) filled with water.

The cover was secured. Absolute ethanol (8 L) was added through the solutions bung hole and the drum was shaken to ensure that all of the internal parts had been in contact with the ethanol. The ethanol was drained through the solutions bung hole and the apparatus was washed 3 times with 4 L of nanopure water by a similar procedure. At this point, the apparatus was ready for use.

2. White solid: mp 54-55 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.19 (dd, 1H, *J* = 9.5, 5.0 Hz), 5.98 (m, 1H), 5.86 (m, 1H), 5.79 (m, 1H), 4.88 (br d, 1H, *J* = 10.0 Hz), 3.92 (s, 3H), 3.57 (s, 1H), 2.61 (d, 1H, *J* = 10.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.6, 132.1, 127.0, 124.8, 122.9, 74.1, 71.2, 54.0; FTIR (neat film): cm^{-1} 3444 (s), 3041 (w), 1735 (s), 1436 (m), 1256 (s), 1087 (s), 1038 (s); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_8H_{10}O_4$, 170.0579; found, 170.0583.

3. Colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.05 (m, 2H), 5.92 (m, 1H), 5.70 (dd, 1H, *J* = 9.0, 1.5 Hz), 4.85 (dd, 1H, *J* = 4.0, 1.0 Hz), 1.39 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.9, 124.5, 124.4, 123.9, 123.8, 107.4, 79.1, 72.8, 26.7, 25.1; FTIR (neat film): cm^{-1} 3500 (bs), 1736 (s), 1373 (s), 1213, (s), 1165 (s), 1040 (s); HRMS-CI (*m/z*): $[M+NH_4]^+$ calcd for $C_{10}H_{16}NO_4$, 214.1079; found, 214.1086.

4. Colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.11 (m, 2H), 6.02 (m, 1H), 5.82 (m, 1H), 4.97 (d, 1H, *J* = 4.5 Hz), 3.79 (s, 3H), 1.44 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.1, 124.7, 124.5, 124.0, 124.0, 106.7, 79.4, 72.7, 52.9, 26.8, 25.1; FTIR (neat film): cm^{-1} 3041 (m), 2977 (s), 2956 (m), 2924 (m), 1750 (s), 1735 (s), 1453 (m), 1432 (m), 1384 (s), 1368 (s), 1251 (s), 1214 (s), 1166 (s), 1081 (s), 1044 (s), 885 (m), 805 (m), 710 (m); HRMS-CI (*m/z*): $[M+NH_4]^+$ calcd for $C_{11}H_{18}NO_4$, 228.1236; found, 228.1241.

5 (R = TMS). Pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.11 (dd, 1H, *J* = 9.6, 5.2 Hz), 5.90 (m, 1H), 5.78 (dd, 1H, *J* = 9.6, 0.8 Hz), 5.64 (dt, 1H, *J* = 9.6, 0.8 Hz), 4.92 (m, 1H), 3.79 (s, 3H), 3.41 (s, 1H), 0.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.4, 132.1, 126.8, 124.9, 122.8, 74.7, 72.5, 53.2, 0.16; FTIR (neat film): cm^{-1} 3542 (s), 3050 (m), 1747 (s), 1731 (s), 1253 (s), 1111 (s), 1049 (s); HRMS-FAB (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{18}O_4NaSi$, 265.0872; found, 265.0880.

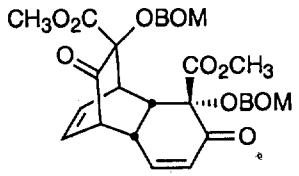
6 (R = TMS). Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (m, 5H), 6.21 (ddd, 1H, *J* = 10.4, 4.8, 0.8 Hz), 5.89 (m, 3H), 5.05 (m, 1H), 4.95 (d, 1H, *J* = 7.2 Hz), 4.87 (d, 1H, *J* = 7.2 Hz), 4.72 (d, 1H, *J* = 11.6 Hz), 4.66 (d, 1H, *J* = 11.6 Hz), 3.76 (s, 3H), 0.14 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.4, 138.5, 134.3, 128.5, 127.9, 127.8, 127.6, 124.2, 122.5, 91.5, 79.4, 72.9, 70.3, 52.9, 0.43; FTIR (neat film): cm^{-1} 3030 (m), 1752 (s), 1730 (s), 1251 (s), 1120 (s), 1038 (m); HRMS-FAB (*m/z*): $[M+Na]^+$ calcd for $C_{19}H_{26}O_5NaSi$, 385.1447; found, 385.1460.

6 (R = H). Colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (m, 5H), 6.27 (ddd, 1H, *J* = 10.0, 3.5, 1.0 Hz), 5.95 (m, 3H), 4.97 (d, 1H, *J* = 7.0 Hz), 4.93 (br d, 1H, *J* = 10.0 Hz), 4.81 (d, 1H, *J* = 7.0 Hz), 4.70 (d, 1H, *J* = 12.0 Hz), 4.62 (d, 1H, *J* = 12.0 Hz), 3.82 (s, 3H), 3.39 (d, 1H, *J* = 10.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0, 137.5, 133.8, 128.8, 128.7, 128.1, 128.0, 123.0, 122.4, 90.9, 78.6, 71.7, 70.5, 53.2; FTIR (neat film): cm^{-1} 3466 (m), 3041 (w), 1741 (s), 1251 (s), 1103 (s), 1022 (s); HRMS-FAB (*m/z*): $[M+Na]^+$ calcd for $C_{16}H_{18}O_5Na$, 313.1052; found, 313.1056.

7. Yellow solid: mp 84-84 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (m, 5H), 6.97 (ddd, 1H, *J* = 9.6, 6.0, 1.2 Hz), 6.54 (br dd, 1H, *J* = 10.0, 6.0 Hz), 6.26 (br d, 1H, *J* = 9.6 Hz), 6.01 (d, 1H, *J* = 10.0 Hz), 4.96 (d, 1H, *J* = 8.0 Hz), 4.81 (d, 1H, *J* = 8.0 Hz), 4.59 (d, 1H, *J* = 11.6 Hz), 4.43 (d, 1H, *J* = 11.6 Hz), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.5, 167.4, 140.0, 137.4, 134.8, 128.6, 128.4, 128.2, 128.0, 126.5, 92.0, 80.1, 71.1, 53.6; FTIR (neat film): cm^{-1} 3030 (w), 1763 (s), 1670 (s), 1223 (s), 1049 (s); HRMS-CI (*m/z*): $[M+NH_4]^+$ calcd for $C_{16}H_{20}O_5N$, 306.1342; found, 306.1342.

Diels–Alder Dimer of 7.



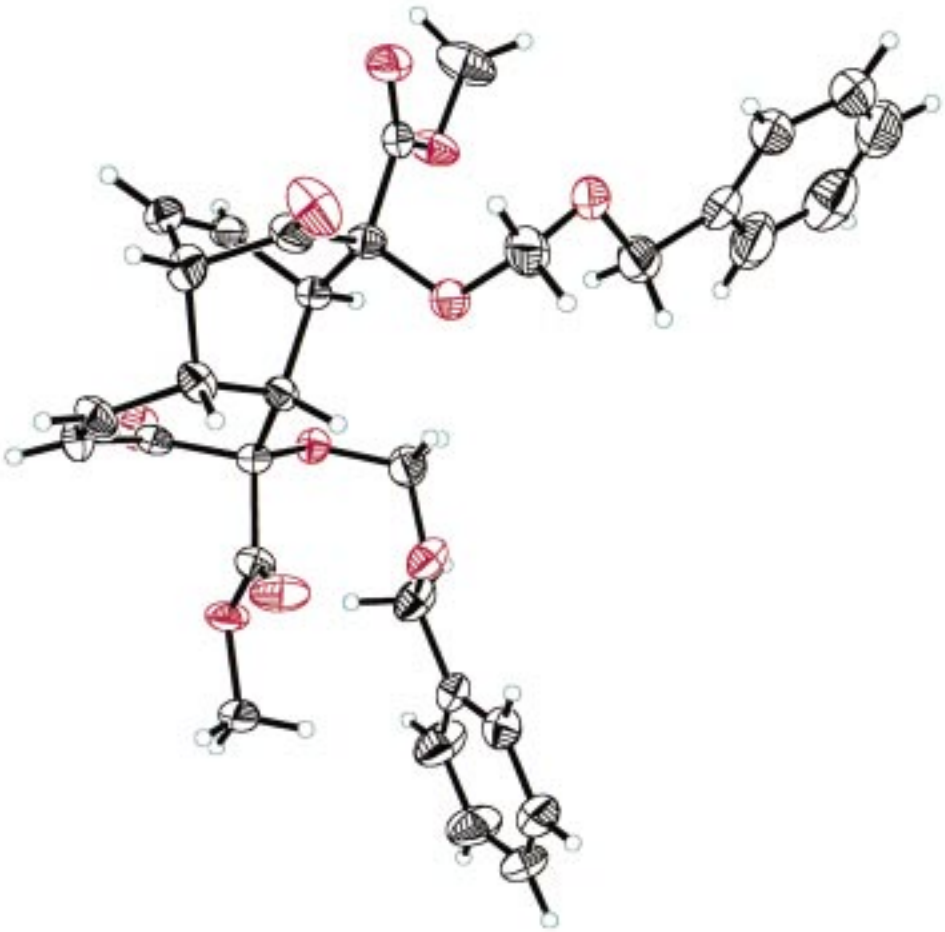


Table 1. Crystal data and structure refinement for Diels–Alder Dimer of **7**.

Identification code	amh211t	
Empirical formula	C32 H32 O10	
Formula weight	576.58	
Temperature	213(2) K	
Wavelength	0.71073 ≈	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 6.6635(11) ≈	_= 90∞.
	b = 12.877(2) ≈	_= 97.035(3)∞.

	c = 16.937(3) ≈ _ = 90∞.
Volume	1442.3(4) ≈^{3}
Z	2
Density (calculated)	1.328 Mg/m^3
Absorption coefficient	0.099 mm^{-1}
F(000)	608
Crystal size	0.5 x 0.1 x 0.4 mm^3
Theta range for data collection	1.21 to 28.36∞.
Index ranges	-8<=h<=8, -15<=k<=16, -22<=l<=19
Reflections collected	9666
Independent reflections	5661 [R(int) = 0.0530]
Completeness to theta = 28.36∞	96.3 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5661 / 1 / 381
Goodness-of-fit on F^2	1.142
Final R indices [I>2sigma(I)]	R1 = 0.0704, wR2 = 0.1604
R indices (all data)	R1 = 0.0933, wR2 = 0.1776
Absolute structure parameter	0.6(15)
Largest diff. peak and hole	0.301 and -0.318 e.≈$^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (≈^{2}x 10^3) for Diels–Alder Dimer of **7**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	6177(5)	9205(2)	6835(2)	41(1)
O(2)	9255(4)	8534(2)	7196(2)	37(1)
O(3)	2997(4)	7490(3)	6587(2)	46(1)
O(4)	6536(4)	6857(2)	7628(2)	34(1)
O(5)	6976(5)	8147(3)	8609(2)	43(1)
O(6)	7004(5)	3490(2)	6610(2)	44(1)
O(7)	9766(5)	3045(2)	6055(2)	34(1)
O(8)	10818(4)	4959(2)	4947(2)	34(1)
O(9)	11013(4)	5079(2)	6496(1)	24(1)
O(10)	11340(4)	4026(2)	7634(2)	35(1)

C(1)	6636(5)	7333(3)	6870(2)	25(1)
C(2)	4564(6)	7237(3)	6359(2)	31(1)
C(3)	4698(6)	6723(4)	5564(2)	34(1)
C(4)	6354(6)	7277(3)	5192(2)	32(1)
C(5)	8140(6)	7255(3)	5626(2)	28(1)
C(6)	8179(5)	6735(3)	6428(2)	22(1)
C(7)	7391(5)	5601(3)	6335(2)	23(1)
C(8)	5427(6)	5575(3)	5745(2)	28(1)
C(9)	5554(6)	5047(3)	4962(2)	32(1)
C(10)	7277(6)	4752(3)	4703(2)	29(1)
C(11)	9212(5)	4873(3)	5210(2)	25(1)
C(12)	9054(5)	4847(3)	6106(2)	22(1)
C(13)	7295(6)	8478(3)	6964(2)	26(1)
C(14)	10099(8)	9562(4)	7318(4)	56(1)
C(15)	5640(8)	7451(4)	8205(3)	43(1)
C(16)	8652(10)	7640(4)	9057(3)	60(2)
C(17)	9778(9)	8362(4)	9652(2)	48(1)
C(18)	11724(10)	8138(6)	9957(3)	66(2)
C(19)	12755(10)	8761(6)	10555(4)	71(2)
C(20)	11763(12)	9573(6)	10848(3)	71(2)
C(21)	9834(10)	9802(5)	10558(3)	60(2)
C(22)	8822(9)	9202(4)	9952(3)	50(1)
C(23)	8449(6)	3720(3)	6295(2)	27(1)
C(24)	9509(8)	1987(3)	6314(3)	43(1)
C(25)	11249(7)	5025(4)	7337(2)	35(1)
C(26)	13174(6)	3489(4)	7532(3)	39(1)
C(27)	13296(7)	2493(4)	8002(2)	35(1)
C(28)	14866(8)	1803(5)	7923(3)	55(1)
C(29)	15033(9)	894(4)	8350(4)	59(2)
C(30)	13683(10)	659(4)	8872(3)	59(2)
C(31)	12090(9)	1330(4)	8945(3)	53(1)
C(32)	11910(7)	2250(4)	8512(2)	42(1)

Table 3. Bond lengths [≈] and angles [∞] for Diels–Alder Dimer of **7**.

O(1)-C(13)	1.200(5)
O(2)-C(13)	1.319(5)
O(2)-C(14)	1.443(6)
O(3)-C(2)	1.203(5)
O(4)-C(15)	1.428(5)
O(4)-C(1)	1.432(5)
O(5)-C(15)	1.383(6)
O(5)-C(16)	1.429(6)
O(6)-C(23)	1.194(4)
O(7)-C(23)	1.333(5)
O(7)-C(24)	1.448(5)
O(8)-C(11)	1.213(4)
O(9)-C(25)	1.416(5)
O(9)-C(12)	1.421(4)
O(10)-C(25)	1.379(5)
O(10)-C(26)	1.433(5)
C(1)-C(13)	1.542(6)
C(1)-C(2)	1.542(5)
C(1)-C(6)	1.548(5)
C(2)-C(3)	1.513(6)
C(3)-C(4)	1.515(6)
C(3)-C(8)	1.575(6)
C(4)-C(5)	1.320(6)
C(5)-C(6)	1.513(5)
C(6)-C(7)	1.553(5)
C(7)-C(8)	1.546(5)
C(7)-C(12)	1.558(5)
C(8)-C(9)	1.502(5)
C(9)-C(10)	1.334(5)
C(10)-C(11)	1.467(5)
C(11)-C(12)	1.535(5)
C(12)-C(23)	1.549(5)
C(16)-C(17)	1.503(8)
C(17)-C(18)	1.367(8)

C(17)-C(22)	1.383(7)
C(18)-C(19)	1.404(9)
C(19)-C(20)	1.362(10)
C(20)-C(21)	1.351(9)
C(21)-C(22)	1.391(7)
C(26)-C(27)	1.506(6)
C(27)-C(32)	1.375(6)
C(27)-C(28)	1.391(7)
C(28)-C(29)	1.372(7)
C(29)-C(30)	1.371(8)
C(30)-C(31)	1.386(8)
C(31)-C(32)	1.391(7)

C(13)-O(2)-C(14)	116.5(4)
C(15)-O(4)-C(1)	117.0(3)
C(15)-O(5)-C(16)	112.3(4)
C(23)-O(7)-C(24)	114.5(3)
C(25)-O(9)-C(12)	116.1(3)
C(25)-O(10)-C(26)	114.0(3)
O(4)-C(1)-C(13)	111.1(3)
O(4)-C(1)-C(2)	109.4(3)
C(13)-C(1)-C(2)	111.1(3)
O(4)-C(1)-C(6)	109.0(3)
C(13)-C(1)-C(6)	109.2(3)
C(2)-C(1)-C(6)	106.9(3)
O(3)-C(2)-C(3)	123.6(4)
O(3)-C(2)-C(1)	123.4(4)
C(3)-C(2)-C(1)	112.9(3)
C(2)-C(3)-C(4)	106.8(4)
C(2)-C(3)-C(8)	106.7(3)
C(4)-C(3)-C(8)	107.5(3)
C(5)-C(4)-C(3)	114.3(4)
C(4)-C(5)-C(6)	115.1(3)
C(5)-C(6)-C(1)	105.9(3)
C(5)-C(6)-C(7)	110.9(3)
C(1)-C(6)-C(7)	106.3(3)

C(8)-C(7)-C(6)	109.6(3)
C(8)-C(7)-C(12)	113.4(3)
C(6)-C(7)-C(12)	111.7(3)
C(9)-C(8)-C(7)	116.4(3)
C(9)-C(8)-C(3)	107.6(3)
C(7)-C(8)-C(3)	108.8(3)
C(10)-C(9)-C(8)	124.3(4)
C(9)-C(10)-C(11)	120.5(3)
O(8)-C(11)-C(10)	123.2(3)
O(8)-C(11)-C(12)	122.3(3)
C(10)-C(11)-C(12)	114.5(3)
O(9)-C(12)-C(11)	106.5(3)
O(9)-C(12)-C(23)	110.4(3)
C(11)-C(12)-C(23)	106.0(3)
O(9)-C(12)-C(7)	113.2(3)
C(11)-C(12)-C(7)	111.7(3)
C(23)-C(12)-C(7)	108.8(3)
O(1)-C(13)-O(2)	125.6(4)
O(1)-C(13)-C(1)	124.4(4)
O(2)-C(13)-C(1)	110.0(3)
O(5)-C(15)-O(4)	112.8(4)
O(5)-C(16)-C(17)	111.5(4)
C(18)-C(17)-C(22)	119.0(5)
C(18)-C(17)-C(16)	119.7(5)
C(22)-C(17)-C(16)	121.1(5)
C(17)-C(18)-C(19)	120.6(6)
C(20)-C(19)-C(18)	119.0(6)
C(21)-C(20)-C(19)	121.2(6)
C(20)-C(21)-C(22)	120.0(6)
C(17)-C(22)-C(21)	120.1(6)
O(6)-C(23)-O(7)	124.8(4)
O(6)-C(23)-C(12)	124.7(3)
O(7)-C(23)-C(12)	110.5(3)
O(10)-C(25)-O(9)	114.0(3)
O(10)-C(26)-C(27)	109.8(3)
C(32)-C(27)-C(28)	119.0(4)

C(32)-C(27)-C(26)	121.9(4)
C(28)-C(27)-C(26)	119.0(4)
C(29)-C(28)-C(27)	120.5(5)
C(30)-C(29)-C(28)	120.7(5)
C(29)-C(30)-C(31)	119.3(5)
C(30)-C(31)-C(32)	120.1(5)
C(27)-C(32)-C(31)	120.3(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\approx^2$x 10^3) for Diels–Alder Dimer of **7**. The anisotropic displacement factor exponent takes the form: $-2\_^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	48(2)	28(2)	44(2)	-1(1)	-5(1)	10(1)
O(2)	32(2)	23(2)	54(2)	-7(1)	1(1)	-4(1)
O(3)	23(2)	54(2)	59(2)	-22(2)	5(1)	4(1)
O(4)	47(2)	30(2)	28(1)	-1(1)	15(1)	3(1)
O(5)	61(2)	36(2)	29(1)	-3(1)	1(1)	10(2)
O(6)	38(2)	28(2)	70(2)	9(2)	19(2)	-5(1)
O(7)	50(2)	17(1)	38(2)	0(1)	15(1)	6(1)
O(8)	26(2)	43(2)	34(1)	2(1)	7(1)	-3(1)
O(9)	19(1)	28(2)	25(1)	1(1)	0(1)	5(1)
O(10)	35(2)	41(2)	32(1)	11(1)	10(1)	12(1)
C(1)	22(2)	22(2)	32(2)	0(2)	3(2)	1(2)
C(2)	29(2)	27(2)	37(2)	-6(2)	3(2)	4(2)
C(3)	21(2)	43(3)	34(2)	-2(2)	-10(2)	11(2)
C(4)	41(2)	28(2)	28(2)	3(2)	4(2)	6(2)
C(5)	39(2)	20(2)	27(2)	1(2)	9(2)	1(2)
C(6)	16(2)	22(2)	28(2)	0(2)	1(1)	-2(1)
C(7)	25(2)	22(2)	22(2)	-2(2)	8(1)	-3(1)
C(8)	24(2)	30(2)	30(2)	-7(2)	7(2)	-2(2)
C(9)	26(2)	29(2)	40(2)	-10(2)	-1(2)	-5(2)
C(10)	26(2)	36(2)	24(2)	-5(2)	0(2)	-2(2)
C(11)	26(2)	17(2)	32(2)	-3(2)	5(2)	2(2)

C(12)	21(2)	19(2)	26(2)	1(2)	4(1)	0(1)
C(13)	32(2)	26(2)	20(2)	-2(2)	2(1)	1(2)
C(14)	55(3)	31(3)	82(4)	-15(3)	6(3)	-18(2)
C(15)	52(3)	45(3)	36(2)	-5(2)	20(2)	2(2)
C(16)	92(4)	46(3)	38(2)	-4(2)	-10(3)	25(3)
C(17)	75(4)	42(3)	26(2)	10(2)	2(2)	3(3)
C(18)	80(4)	77(5)	40(3)	11(3)	5(3)	17(3)
C(19)	64(4)	91(6)	56(3)	18(4)	-5(3)	-12(4)
C(20)	103(5)	65(4)	43(3)	4(3)	2(3)	-28(4)
C(21)	92(5)	43(3)	43(3)	-3(2)	3(3)	-7(3)
C(22)	75(4)	37(3)	37(2)	0(2)	3(2)	-9(3)
C(23)	24(2)	23(2)	35(2)	-3(2)	4(2)	-1(2)
C(24)	74(3)	20(2)	35(2)	-1(2)	7(2)	2(2)
C(25)	35(2)	36(2)	33(2)	-2(2)	-1(2)	8(2)
C(26)	34(2)	47(3)	36(2)	12(2)	7(2)	9(2)
C(27)	42(2)	36(2)	25(2)	4(2)	-1(2)	2(2)
C(28)	55(3)	56(3)	57(3)	23(3)	19(3)	20(3)
C(29)	68(4)	41(3)	70(4)	18(3)	13(3)	21(3)
C(30)	96(5)	33(3)	47(3)	16(2)	-1(3)	5(3)
C(31)	81(4)	43(3)	37(2)	7(2)	16(3)	-3(3)
C(32)	54(3)	41(3)	33(2)	0(2)	9(2)	-4(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($\approx^2$x 10^{3}) for Diels–Alder Dimer of **7**.

	x	y	z	U(eq)
H(3)	3390	6746	5217	41
H(4)	6130	7607	4694	39
H(5)	9303	7542	5449	34
H(6)	9549	6759	6729	26
H(7)	7036	5377	6859	27
H(8)	4376	5216	6009	34
H(9)	4339	4916	4633	39

H(10)	7251	4464	4192	35
H(14A)	9657	9991	6859	85
H(14B)	11563	9518	7389	85
H(14C)	9643	9866	7789	85
H(15A)	4480	7834	7938	52
H(15B)	5139	6977	8589	52
H(16A)	9575	7382	8693	72
H(16B)	8163	7042	9336	72
H(18)	12378	7560	9765	79
H(19)	14110	8621	10750	86
H(20)	12432	9980	11259	85
H(21)	9176	10368	10765	72
H(22)	7485	9368	9747	60
H(24A)	9692	1960	6891	65
H(24B)	10503	1544	6109	65
H(24C)	8161	1748	6117	65
H(25A)	12492	5391	7544	42
H(25B)	10114	5386	7533	42
H(26A)	14339	3929	7713	46
H(26B)	13208	3334	6967	46
H(28)	15820	1960	7576	66
H(29)	16084	428	8282	71
H(30)	13837	49	9179	71
H(31)	11129	1163	9287	63
H(32)	10837	2707	8567	51

Table 6. Torsion angles [∞] for Diels–Alder Dimer of **7**

C(15)-O(4)-C(1)-C(13)	42.8(4)
C(15)-O(4)-C(1)-C(2)	-80.1(4)
C(15)-O(4)-C(1)-C(6)	163.3(3)
O(4)-C(1)-C(2)-O(3)	51.2(5)
C(13)-C(1)-C(2)-O(3)	-71.8(5)
C(6)-C(1)-C(2)-O(3)	169.2(4)
O(4)-C(1)-C(2)-C(3)	-124.8(4)

C(13)-C(1)-C(2)-C(3)	112.2(4)
C(6)-C(1)-C(2)-C(3)	-6.9(5)
O(3)-C(2)-C(3)-C(4)	133.8(5)
C(1)-C(2)-C(3)-C(4)	-50.2(4)
O(3)-C(2)-C(3)-C(8)	-111.5(5)
C(1)-C(2)-C(3)-C(8)	64.6(4)
C(2)-C(3)-C(4)-C(5)	58.3(5)
C(8)-C(3)-C(4)-C(5)	-55.9(5)
C(3)-C(4)-C(5)-C(6)	-3.1(5)
C(4)-C(5)-C(6)-C(1)	-57.8(4)
C(4)-C(5)-C(6)-C(7)	57.2(4)
O(4)-C(1)-C(6)-C(5)	177.9(3)
C(13)-C(1)-C(6)-C(5)	-60.5(4)
C(2)-C(1)-C(6)-C(5)	59.7(4)
O(4)-C(1)-C(6)-C(7)	59.9(4)
C(13)-C(1)-C(6)-C(7)	-178.5(3)
C(2)-C(1)-C(6)-C(7)	-58.3(4)
C(5)-C(6)-C(7)-C(8)	-46.1(4)
C(1)-C(6)-C(7)-C(8)	68.5(3)
C(5)-C(6)-C(7)-C(12)	80.4(4)
C(1)-C(6)-C(7)-C(12)	-164.9(3)
C(6)-C(7)-C(8)-C(9)	111.7(4)
C(12)-C(7)-C(8)-C(9)	-13.9(5)
C(6)-C(7)-C(8)-C(3)	-10.0(4)
C(12)-C(7)-C(8)-C(3)	-135.6(3)
C(2)-C(3)-C(8)-C(9)	179.6(3)
C(4)-C(3)-C(8)-C(9)	-66.1(4)
C(2)-C(3)-C(8)-C(7)	-53.5(4)
C(4)-C(3)-C(8)-C(7)	60.8(4)
C(7)-C(8)-C(9)-C(10)	-10.7(6)
C(3)-C(8)-C(9)-C(10)	111.7(5)
C(8)-C(9)-C(10)-C(11)	4.0(7)
C(9)-C(10)-C(11)-O(8)	-154.4(4)
C(9)-C(10)-C(11)-C(12)	27.5(6)
C(25)-O(9)-C(12)-C(11)	-175.7(3)
C(25)-O(9)-C(12)-C(23)	-61.0(4)

C(25)-O(9)-C(12)-C(7)	61.2(4)
O(8)-C(11)-C(12)-O(9)	7.7(5)
C(10)-C(11)-C(12)-O(9)	-174.2(3)
O(8)-C(11)-C(12)-C(23)	-110.0(4)
C(10)-C(11)-C(12)-C(23)	68.2(4)
O(8)-C(11)-C(12)-C(7)	131.7(4)
C(10)-C(11)-C(12)-C(7)	-50.1(4)
C(8)-C(7)-C(12)-O(9)	162.6(3)
C(6)-C(7)-C(12)-O(9)	38.2(4)
C(8)-C(7)-C(12)-C(11)	42.4(4)
C(6)-C(7)-C(12)-C(11)	-82.1(4)
C(8)-C(7)-C(12)-C(23)	-74.2(4)
C(6)-C(7)-C(12)-C(23)	161.3(3)
C(14)-O(2)-C(13)-O(1)	1.4(6)
C(14)-O(2)-C(13)-C(1)	-179.4(4)
O(4)-C(1)-C(13)-O(1)	-104.9(4)
C(2)-C(1)-C(13)-O(1)	17.1(5)
C(6)-C(1)-C(13)-O(1)	134.8(4)
O(4)-C(1)-C(13)-O(2)	75.9(4)
C(2)-C(1)-C(13)-O(2)	-162.1(3)
C(6)-C(1)-C(13)-O(2)	-44.4(4)
C(16)-O(5)-C(15)-O(4)	-62.5(5)
C(1)-O(4)-C(15)-O(5)	-82.5(5)
C(15)-O(5)-C(16)-C(17)	-165.0(4)
O(5)-C(16)-C(17)-C(18)	-160.0(5)
O(5)-C(16)-C(17)-C(22)	26.0(7)
C(22)-C(17)-C(18)-C(19)	-1.3(8)
C(16)-C(17)-C(18)-C(19)	-175.4(5)
C(17)-C(18)-C(19)-C(20)	2.4(9)
C(18)-C(19)-C(20)-C(21)	-1.9(9)
C(19)-C(20)-C(21)-C(22)	0.4(9)
C(18)-C(17)-C(22)-C(21)	-0.2(7)
C(16)-C(17)-C(22)-C(21)	173.8(5)
C(20)-C(21)-C(22)-C(17)	0.7(8)
C(24)-O(7)-C(23)-O(6)	-9.0(6)
C(24)-O(7)-C(23)-C(12)	170.9(3)

O(9)-C(12)-C(23)-O(6)	120.5(4)
C(11)-C(12)-C(23)-O(6)	-124.5(4)
C(7)-C(12)-C(23)-O(6)	-4.3(5)
O(9)-C(12)-C(23)-O(7)	-59.5(4)
C(11)-C(12)-C(23)-O(7)	55.5(4)
C(7)-C(12)-C(23)-O(7)	175.7(3)
C(26)-O(10)-C(25)-O(9)	71.0(5)
C(12)-O(9)-C(25)-O(10)	75.2(4)
C(25)-O(10)-C(26)-C(27)	169.6(3)
O(10)-C(26)-C(27)-C(32)	-6.7(6)
O(10)-C(26)-C(27)-C(28)	173.7(4)
C(32)-C(27)-C(28)-C(29)	-0.2(8)
C(26)-C(27)-C(28)-C(29)	179.3(5)
C(27)-C(28)-C(29)-C(30)	-1.3(10)
C(28)-C(29)-C(30)-C(31)	2.6(9)
C(29)-C(30)-C(31)-C(32)	-2.3(9)
C(28)-C(27)-C(32)-C(31)	0.5(7)
C(26)-C(27)-C(32)-C(31)	-179.0(5)
C(30)-C(31)-C(32)-C(27)	0.8(8)

Symmetry transformations used to generate equivalent atoms:

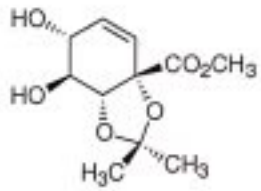
White solid: mp 115-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (m, 10H), 6.32 (m, 1H), 6.26 (dd, 1H, *J* = 10.0, 3.6 Hz), 6.10 (dd, 1H, *J* = 10.0, 1.2 Hz), 5.93 (m, 1H), 5.31 (d, 1H, *J* = 7.2 Hz), 5.23 (d, 1H, *J* = 7.2 Hz), 5.04 (d, 2H, *J* = 6.8 Hz), 4.66 (m, 3H), 4.57 (d, 1H, *J* = 11.6 Hz), 3.95 (br d, 1H, *J* = 8.0 Hz), 3.78 (br d, 1H, *J* = 6.8 Hz), 3.56 (s, 3H), 3.55 (s, 3H), 3.48 (m, 1H), 3.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.2, 193.3, 169.3, 168.2, 144.0, 137.4, 134.1, 131.3, 129.2, 128.6, 128.5, 128.3, 128.2, 128.1, 91.8, 91.6, 81.2, 79.4, 70.6, 70.4, 53.8, 53.3, 52.3, 40.9, 40.5, 36.9; FTIR (neat film): cm^{-1} 3030 (w), 1746 (s), 1712 (s), 1454 (w), 1255 (s) 1053 (s); HRMS-FAB (*m/z*): $[M+Na]^+$ calcd for $C_{32}H_{32}O_{10}Na$, 599.1893; found, 599.1912.

8. White solid: mp 87-91 °C; ^{1}H NMR (400 MHz, CD_3OD): δ 6.23 (dd, 1H, *J* = 9.6, 3.9 Hz), 5.92 (dd, 1H, *J* = 9.6, 1.9 Hz), 4.40 (d, 1H, *J* = 1.3 Hz), 3.58 (dd, 1H, *J* = 4.4, 1.3 Hz), 3.49 (m, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ 175.8, 135.1, 128.8, 75.4, 70.9, 57.5, 50.3; FTIR (neat film): cm^{-1} 3381 (s), 1738 (s), 1608 (m), 1255 (m), 1230 (m), 1084 (m); HRMS-CI (*m/z*): $[M + NH_4]^+$ calcd for $C_7H_8O_5$, 190.0715; found, 190.0707.

9. White solid: mp 89-91 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.18 (dd, 1H, *J* = 10.4, 4.4 Hz), 5.84 (dt, 1H, *J* = 10.0, 1.2 Hz), 5.17 (m, 1H), 3.78 (s, 3H), 3.65 (dd, 1H, *J* = 3.6, 2.0 Hz), 3.39 (m, 1H), 1.47 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 130.6, 124.8, 112.1, 79.2, 73.5, 53.1, 49.8, 45.9, 27.6, 25.7; FTIR (neat film): cm^{-1} 2976 (m), 2926 (m), 1738 (s), 1447 (w), 1431 (w), 1386 (m), 1371 (m), 1265 (s), 1235 (m), 1175 (m), 1084 (m); HRMS-CI (*m/z*): $[M+NH_4]^+$ calcd for $C_{11}H_{14}O_5$, 244.1185; found, 244.1178.

10. White solid: mp 129-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.86 (dd, 1H, *J* = 10.3, 1.8, Hz), 5.57 (ddd, 1H, *J* = 10.3, 2.6,1.5 Hz), 4.57 (m, 1H), 4.39 (dt, 1H, *J* = 8.4, 2.2 Hz), 4.00 (bs, 2H), 3.88 (dd, 2H, *J* = 8.4, 2.6 Hz), 3.77 (s, 3H), 1.41 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 132.7, 125.4, 111.5, 82.4, 78.7, 73.5, 68.5, 53.3, 27.6, 26.4; FTIR (neat film): cm^{-1} 3435 (vs), 1735 (s), 1377 (m), 1260 (s), 1070 (s); HRMS-CI (*m/z*): $[M + NH_4]^+$ calcd for $C_{11}H_{16}O_6$, 262.1291; found, 262.1296.

11.



11

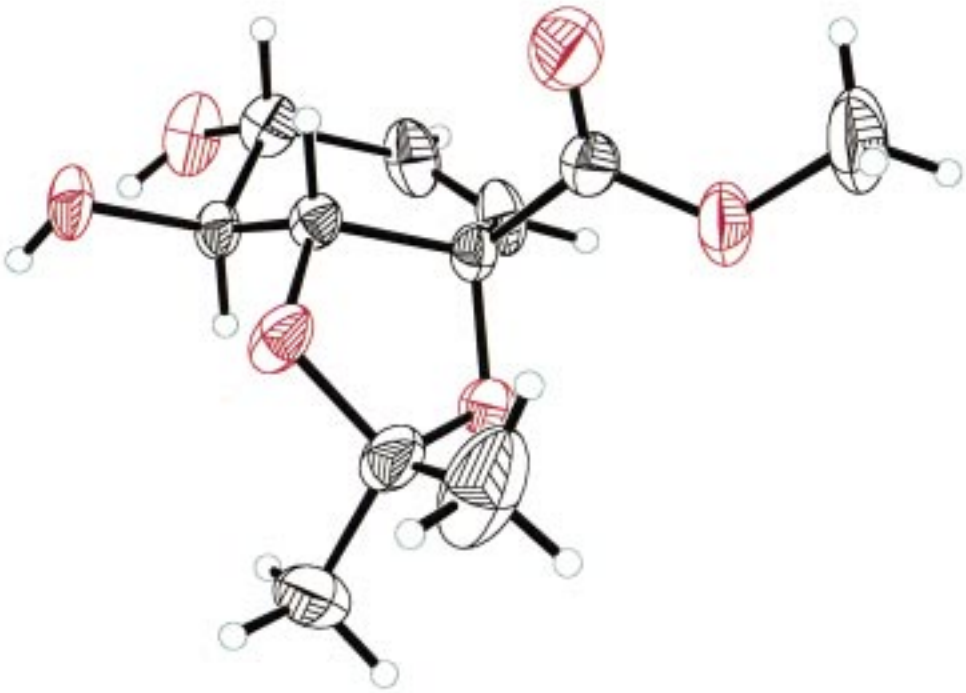


Table 1. Crystal data and structure refinement for **11**.

Identification code	amh23t	
Empirical formula	C11 H16 O6	
Formula weight	244.24	
Temperature	213(2) K	
Wavelength	0.71073 ≈	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 12.1580(13) ≈	α= 90∞.
	b = 7.3088(8) ≈	β= 107.945(2)∞.
	c = 14.6111(16) ≈	γ = 90∞.

Volume	1235.2(2) $\AA^3$
Z	4
Density (calculated)	1.313 Mg/m^3
Absorption coefficient	0.107 mm^{-1}
F(000)	520
Crystal size	0.15 x 0.2 x 0.6 mm^3
Theta range for data collection	1.46 to 28.28°.
Index ranges	-15<=h<=16, -9<=k<=9, -16<=l<=19
Reflections collected	8070
Independent reflections	5216 [R(int) = 0.0696]
Completeness to theta = 28.28°	95.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5216 / 1 / 317
Goodness-of-fit on F^2	1.087
Final R indices [I>2sigma(I)]	R1 = 0.0638, wR2 = 0.1631
R indices (all data)	R1 = 0.0674, wR2 = 0.1666
Absolute structure parameter	-1.4(11)
Largest diff. peak and hole	0.349 and -0.295 $e.\AA^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($\AA^2$x 10^3) for **11**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1A)	6629(2)	4190(3)	5868(2)	35(1)
O(2A)	8514(2)	3249(3)	6374(2)	36(1)
O(3A)	9188(1)	1510(3)	4854(1)	34(1)
O(4A)	7274(2)	464(4)	3187(1)	46(1)
O(5A)	6740(3)	-104(4)	6925(2)	69(1)
O(6A)	5340(2)	1979(4)	6659(2)	50(1)
O(1B)	1744(2)	1391(3)	9862(2)	39(1)
O(2B)	1754(3)	3852(3)	8894(2)	53(1)
O(3B)	921(2)	3123(3)	6841(1)	35(1)
O(4B)	455(2)	-712(3)	6363(1)	38(1)
O(5B)	4369(2)	977(6)	9304(2)	74(1)

O(6B)	3966(2)	569(4)	10660(2)	58(1)
C(1A)	6614(2)	2257(4)	5730(2)	26(1)
C(2A)	7864(2)	1831(3)	5770(2)	24(1)
C(3A)	8007(2)	1876(4)	4768(2)	25(1)
C(4A)	7201(2)	449(4)	4139(2)	33(1)
C(5A)	5985(2)	898(5)	4100(2)	42(1)
C(6A)	5724(2)	1764(5)	4796(2)	38(1)
C(7A)	6272(3)	1224(4)	6525(2)	35(1)
C(8A)	4877(4)	1045(8)	7341(4)	80(2)
C(9A)	7760(2)	4721(4)	6449(3)	43(1)
C(10A)	7811(4)	4970(8)	7483(3)	79(2)
C(11A)	8074(4)	6425(6)	5976(5)	81(2)
C(1B)	2369(2)	834(4)	9232(2)	31(1)
C(2B)	2052(2)	2320(4)	8436(2)	33(1)
C(3B)	1072(2)	1728(4)	7555(2)	28(1)
C(4B)	1370(2)	-79(4)	7181(2)	32(1)
C(5B)	1589(3)	-1503(4)	7957(2)	39(1)
C(6B)	2010(3)	-1076(4)	8878(2)	40(1)
C(7B)	3693(2)	831(5)	9731(2)	37(1)
C(8B)	5202(4)	645(9)	11186(3)	80(2)
C(9B)	1596(3)	3324(5)	9796(2)	43(1)
C(10B)	2520(5)	4307(6)	10585(2)	66(1)
C(11B)	379(5)	3753(8)	9777(6)	102(2)

Table 3. Bond lengths [≈] and angles [∞] for **11**.

O(1A)-C(1A)	1.427(3)
O(1A)-C(9A)	1.429(3)
O(2A)-C(2A)	1.430(3)
O(2A)-C(9A)	1.440(3)
O(3A)-C(3A)	1.427(3)
O(4A)-C(4A)	1.420(3)
O(5A)-C(7A)	1.184(4)
O(6A)-C(7A)	1.329(4)
O(6A)-C(8A)	1.456(4)

O(1B)-C(1B)	1.421(3)
O(1B)-C(9B)	1.424(4)
O(2B)-C(2B)	1.408(4)
O(2B)-C(9B)	1.442(4)
O(3B)-C(3B)	1.429(3)
O(4B)-C(4B)	1.436(3)
O(5B)-C(7B)	1.179(4)
O(6B)-C(7B)	1.308(3)
O(6B)-C(8B)	1.463(4)
C(1A)-C(6A)	1.501(4)
C(1A)-C(2A)	1.535(3)
C(1A)-C(7A)	1.546(4)
C(2A)-C(3A)	1.528(3)
C(3A)-C(4A)	1.529(3)
C(4A)-C(5A)	1.499(4)
C(5A)-C(6A)	1.316(5)
C(9A)-C(10A)	1.504(6)
C(9A)-C(11A)	1.529(6)
C(1B)-C(6B)	1.506(4)
C(1B)-C(2B)	1.551(3)
C(1B)-C(7B)	1.550(4)
C(2B)-C(3B)	1.523(3)
C(3B)-C(4B)	1.515(4)
C(4B)-C(5B)	1.501(4)
C(5B)-C(6B)	1.321(5)
C(9B)-C(11B)	1.504(5)
C(9B)-C(10B)	1.520(5)

C(1A)-O(1A)-C(9A)	108.7(2)
C(2A)-O(2A)-C(9A)	110.18(19)
C(7A)-O(6A)-C(8A)	115.7(3)
C(1B)-O(1B)-C(9B)	108.8(2)
C(2B)-O(2B)-C(9B)	110.4(2)
C(7B)-O(6B)-C(8B)	115.6(3)
O(1A)-C(1A)-C(6A)	109.9(2)
O(1A)-C(1A)-C(2A)	103.10(19)

C(6A)-C(1A)-C(2A)	114.5(2)
O(1A)-C(1A)-C(7A)	111.8(2)
C(6A)-C(1A)-C(7A)	106.3(2)
C(2A)-C(1A)-C(7A)	111.4(2)
O(2A)-C(2A)-C(3A)	111.8(2)
O(2A)-C(2A)-C(1A)	103.24(19)
C(3A)-C(2A)-C(1A)	111.26(18)
O(3A)-C(3A)-C(2A)	108.63(18)
O(3A)-C(3A)-C(4A)	111.5(2)
C(2A)-C(3A)-C(4A)	108.7(2)
O(4A)-C(4A)-C(5A)	108.7(2)
O(4A)-C(4A)-C(3A)	111.2(2)
C(5A)-C(4A)-C(3A)	108.4(2)
C(6A)-C(5A)-C(4A)	123.1(2)
C(5A)-C(6A)-C(1A)	122.7(2)
O(5A)-C(7A)-O(6A)	124.7(3)
O(5A)-C(7A)-C(1A)	124.9(3)
O(6A)-C(7A)-C(1A)	110.3(2)
O(1A)-C(9A)-O(2A)	105.7(2)
O(1A)-C(9A)-C(10A)	111.3(3)
O(2A)-C(9A)-C(10A)	109.7(3)
O(1A)-C(9A)-C(11A)	106.4(3)
O(2A)-C(9A)-C(11A)	108.7(3)
C(10A)-C(9A)-C(11A)	114.6(4)
O(1B)-C(1B)-C(6B)	109.4(2)
O(1B)-C(1B)-C(2B)	103.1(2)
C(6B)-C(1B)-C(2B)	114.4(2)
O(1B)-C(1B)-C(7B)	112.4(2)
C(6B)-C(1B)-C(7B)	108.0(2)
C(2B)-C(1B)-C(7B)	109.6(2)
O(2B)-C(2B)-C(3B)	112.2(2)
O(2B)-C(2B)-C(1B)	104.0(2)
C(3B)-C(2B)-C(1B)	112.6(2)
O(3B)-C(3B)-C(4B)	110.5(2)
O(3B)-C(3B)-C(2B)	107.8(2)
C(4B)-C(3B)-C(2B)	109.9(2)

O(4B)-C(4B)-C(5B)	108.4(2)
O(4B)-C(4B)-C(3B)	111.7(2)
C(5B)-C(4B)-C(3B)	109.8(2)
C(6B)-C(5B)-C(4B)	121.9(3)
C(5B)-C(6B)-C(1B)	123.3(3)
O(5B)-C(7B)-O(6B)	124.5(3)
O(5B)-C(7B)-C(1B)	122.9(2)
O(6B)-C(7B)-C(1B)	112.5(2)
O(1B)-C(9B)-O(2B)	106.1(3)
O(1B)-C(9B)-C(11B)	108.1(3)
O(2B)-C(9B)-C(11B)	109.5(4)
O(1B)-C(9B)-C(10B)	111.7(3)
O(2B)-C(9B)-C(10B)	106.9(3)
C(11B)-C(9B)-C(10B)	114.1(4)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\approx^2$x 10^3) for **11**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2\, a^{*2}U^{11} + \ldots + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1A)	20(1)	29(1)	53(1)	2(1)	9(1)	3(1)
O(2A)	20(1)	38(1)	42(1)	-14(1)	0(1)	5(1)
O(3A)	17(1)	51(1)	34(1)	10(1)	8(1)	7(1)
O(4A)	33(1)	75(2)	26(1)	-5(1)	6(1)	8(1)
O(5A)	85(2)	62(2)	84(2)	38(2)	60(2)	29(2)
O(6A)	47(1)	60(2)	59(1)	11(1)	36(1)	7(1)
O(1B)	39(1)	35(1)	49(1)	5(1)	24(1)	4(1)
O(2B)	84(2)	32(1)	32(1)	3(1)	4(1)	2(1)
O(3B)	23(1)	42(1)	33(1)	13(1)	-1(1)	-3(1)
O(4B)	31(1)	40(1)	36(1)	-4(1)	3(1)	3(1)
O(5B)	32(1)	145(3)	46(1)	27(2)	13(1)	17(2)
O(6B)	43(1)	94(2)	29(1)	6(1)	0(1)	18(1)
C(1A)	20(1)	29(1)	31(1)	1(1)	9(1)	1(1)
C(2A)	19(1)	27(1)	24(1)	-1(1)	3(1)	1(1)

C(3A)	16(1)	31(1)	26(1)	3(1)	4(1)	2(1)
C(4A)	28(1)	39(2)	26(1)	-5(1)	3(1)	1(1)
C(5A)	22(1)	63(2)	35(1)	-8(1)	2(1)	-13(1)
C(6A)	18(1)	58(2)	37(1)	2(1)	6(1)	-6(1)
C(7A)	40(1)	34(1)	37(1)	0(1)	20(1)	2(1)
C(8A)	83(3)	93(4)	93(3)	27(3)	70(3)	18(3)
C(9A)	24(1)	36(2)	68(2)	-15(1)	10(1)	1(1)
C(10A)	52(2)	112(4)	70(3)	-51(3)	13(2)	3(2)
C(11A)	49(2)	33(2)	169(5)	-3(2)	46(3)	-7(2)
C(1B)	29(1)	37(1)	25(1)	6(1)	7(1)	3(1)
C(2B)	27(1)	34(1)	32(1)	9(1)	1(1)	-3(1)
C(3B)	17(1)	33(1)	30(1)	6(1)	5(1)	-1(1)
C(4B)	20(1)	43(2)	31(1)	2(1)	6(1)	2(1)
C(5B)	38(1)	31(1)	46(2)	3(1)	8(1)	7(1)
C(6B)	42(2)	34(2)	42(2)	10(1)	9(1)	8(1)
C(7B)	32(1)	50(2)	26(1)	7(1)	6(1)	10(1)
C(8B)	53(2)	113(4)	50(2)	-5(2)	-20(2)	26(3)
C(9B)	47(2)	37(2)	51(2)	4(1)	22(1)	6(1)
C(10B)	108(3)	47(2)	34(2)	-3(1)	11(2)	-1(2)
C(11B)	72(3)	69(3)	189(7)	14(4)	73(4)	29(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (≈^{2}x 10 ^{3}) for **11**.

	x	y	z	U(eq)
H(3A)	9404	2212	4497	51
H(4A)	7792	1180	3157	68
H(3B)	385	3812	6861	52
H(4B)	233	140	5974	56
H(2A)	8099	622	6072	29
H(3A1)	7796	3104	4483	30
H(4A1)	7408	-781	4423	39
H(5A)	5380	545	3554	50

H(6A)	4949	2086	4704	46
H(8A1)	4902	-267	7249	120
H(8A2)	4084	1426	7237	120
H(8A3)	5338	1355	7992	120
H(10D)	7238	5865	7523	119
H(10E)	8575	5394	7852	119
H(10F)	7652	3812	7741	119
H(11D)	7996	6163	5308	121
H(11E)	8866	6773	6311	121
H(11F)	7560	7420	6009	121
H(2B)	2743	2613	8241	39
H(3B1)	351	1592	7729	33
H(4B1)	2080	79	6993	38
H(5B)	1421	-2734	7783	47
H(6B)	2089	-2012	9335	48
H(8B1)	5630	-21	10832	121
H(8B2)	5340	96	11816	121
H(8B3)	5454	1910	11260	121
H(10A)	2532	3828	11207	98
H(10B)	2350	5606	10558	98
H(10C)	3269	4115	10494	98
H(11A)	-158	3008	9292	153
H(11B)	219	5036	9626	153
H(11C)	293	3491	10402	153

Table 6. Torsion angles [∞] for **11**.

C(9A)-O(1A)-C(1A)-C(6A)	-152.2(2)
C(9A)-O(1A)-C(1A)-C(2A)	-29.8(3)
C(9A)-O(1A)-C(1A)-C(7A)	90.0(3)
C(9A)-O(2A)-C(2A)-C(3A)	102.8(3)
C(9A)-O(2A)-C(2A)-C(1A)	-16.9(3)
O(1A)-C(1A)-C(2A)-O(2A)	28.0(2)
C(6A)-C(1A)-C(2A)-O(2A)	147.3(2)
C(7A)-C(1A)-C(2A)-O(2A)	-92.1(2)

O(1A)-C(1A)-C(2A)-C(3A)	-92.1(2)
C(6A)-C(1A)-C(2A)-C(3A)	27.3(3)
C(7A)-C(1A)-C(2A)-C(3A)	147.9(2)
O(2A)-C(2A)-C(3A)-O(3A)	63.9(3)
C(1A)-C(2A)-C(3A)-O(3A)	178.7(2)
O(2A)-C(2A)-C(3A)-C(4A)	-174.59(19)
C(1A)-C(2A)-C(3A)-C(4A)	-59.7(3)
O(3A)-C(3A)-C(4A)-O(4A)	-61.9(3)
C(2A)-C(3A)-C(4A)-O(4A)	178.4(2)
O(3A)-C(3A)-C(4A)-C(5A)	178.7(2)
C(2A)-C(3A)-C(4A)-C(5A)	59.0(3)
O(4A)-C(4A)-C(5A)-C(6A)	-149.0(3)
C(3A)-C(4A)-C(5A)-C(6A)	-28.0(4)
C(4A)-C(5A)-C(6A)-C(1A)	-4.9(5)
O(1A)-C(1A)-C(6A)-C(5A)	120.9(3)
C(2A)-C(1A)-C(6A)-C(5A)	5.4(4)
C(7A)-C(1A)-C(6A)-C(5A)	-117.9(3)
C(8A)-O(6A)-C(7A)-O(5A)	-1.0(6)
C(8A)-O(6A)-C(7A)-C(1A)	175.6(3)
O(1A)-C(1A)-C(7A)-O(5A)	-135.8(3)
C(6A)-C(1A)-C(7A)-O(5A)	104.2(4)
C(2A)-C(1A)-C(7A)-O(5A)	-21.0(4)
O(1A)-C(1A)-C(7A)-O(6A)	47.5(3)
C(6A)-C(1A)-C(7A)-O(6A)	-72.4(3)
C(2A)-C(1A)-C(7A)-O(6A)	162.3(2)
C(1A)-O(1A)-C(9A)-O(2A)	19.9(3)
C(1A)-O(1A)-C(9A)-C(10A)	-99.2(4)
C(1A)-O(1A)-C(9A)-C(11A)	135.3(3)
C(2A)-O(2A)-C(9A)-O(1A)	-0.7(3)
C(2A)-O(2A)-C(9A)-C(10A)	119.4(3)
C(2A)-O(2A)-C(9A)-C(11A)	-114.5(3)
C(9B)-O(1B)-C(1B)-C(6B)	-149.9(2)
C(9B)-O(1B)-C(1B)-C(2B)	-27.8(3)
C(9B)-O(1B)-C(1B)-C(7B)	90.1(3)
C(9B)-O(2B)-C(2B)-C(3B)	108.5(3)
C(9B)-O(2B)-C(2B)-C(1B)	-13.4(3)

O(1B)-C(1B)-C(2B)-O(2B)	24.9(3)
C(6B)-C(1B)-C(2B)-O(2B)	143.5(3)
C(7B)-C(1B)-C(2B)-O(2B)	-95.0(3)
O(1B)-C(1B)-C(2B)-C(3B)	-96.8(3)
C(6B)-C(1B)-C(2B)-C(3B)	21.8(3)
C(7B)-C(1B)-C(2B)-C(3B)	143.3(2)
O(2B)-C(2B)-C(3B)-O(3B)	68.0(3)
C(1B)-C(2B)-C(3B)-O(3B)	-175.1(2)
O(2B)-C(2B)-C(3B)-C(4B)	-171.5(2)
C(1B)-C(2B)-C(3B)-C(4B)	-54.6(3)
O(3B)-C(3B)-C(4B)-O(4B)	-62.6(3)
C(2B)-C(3B)-C(4B)-O(4B)	178.6(2)
O(3B)-C(3B)-C(4B)-C(5B)	177.0(2)
C(2B)-C(3B)-C(4B)-C(5B)	58.2(3)
O(4B)-C(4B)-C(5B)-C(6B)	-152.5(3)
C(3B)-C(4B)-C(5B)-C(6B)	-30.1(4)
C(4B)-C(5B)-C(6B)-C(1B)	-3.5(5)
O(1B)-C(1B)-C(6B)-C(5B)	122.9(3)
C(2B)-C(1B)-C(6B)-C(5B)	7.9(4)
C(7B)-C(1B)-C(6B)-C(5B)	-114.5(3)
C(8B)-O(6B)-C(7B)-O(5B)	5.9(6)
C(8B)-O(6B)-C(7B)-C(1B)	-176.9(3)
O(1B)-C(1B)-C(7B)-O(5B)	-155.7(4)
C(6B)-C(1B)-C(7B)-O(5B)	83.5(4)
C(2B)-C(1B)-C(7B)-O(5B)	-41.7(5)
O(1B)-C(1B)-C(7B)-O(6B)	27.1(4)
C(6B)-C(1B)-C(7B)-O(6B)	-93.7(3)
C(2B)-C(1B)-C(7B)-O(6B)	141.1(3)
C(1B)-O(1B)-C(9B)-O(2B)	20.4(3)
C(1B)-O(1B)-C(9B)-C(11B)	137.8(4)
C(1B)-O(1B)-C(9B)-C(10B)	-95.8(3)
C(2B)-O(2B)-C(9B)-O(1B)	-3.1(3)
C(2B)-O(2B)-C(9B)-C(11B)	-119.6(4)
C(2B)-O(2B)-C(9B)-C(10B)	116.2(3)

Symmetry transformations used to generate equivalent atoms:

White solid: mp 105-106 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.03 (dd, 1H, *J* = 10.0, 2.8 Hz), 5.76 (dd, 1H, *J* = 10.4, 2.0 Hz), 4.67 (d, 1H, *J* = 6.4 Hz), 4.19 (m, 1H), 3.91 (m, 1H), 3.82 (s, 3H), 2.88 (d, 1H, *J* = 5.2 Hz), 2.49 (d, 1H, *J* = 6.8 Hz), 1.51 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 134.2, 124.2, 112.4, 82.3, 79.5, 74.1, 69.0, 53.2, 28.3, 26.5; FTIR (neat film): cm^{-1} 3433 (bs), 2986 (m), 2943 (m), 1731 (s), 1436 (m), 1376 (m), 1256 (s), 1218 (s), 1164 (m), 1088 (s), 1028 (s); HRMS-CI (*m/z*): $[M+NH_4]^+$ calcd for $C_{11}H_{16}O_6$, 262.1279; found, 262.1299.

12. White solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.37 (m, 2H), 5.27 (m, 1H), 4.73 (dd, 1H, *J* = 7.0, 4.0 Hz), 4.35 (dd, 1H, *J* = 7.0, 0.7 Hz), 3.57 (s, 1H), 1.39 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 135.4, 127.2, 114.7, 78.3, 77.8, 76.5, 74.0, 25.8, 25.6; FTIR (neat film): cm^{-1} 3436 (s), 1766 (vs), 1372 (m), 1204 (s), 1145 (s), 1066 (m); HRMS-CI (*m/z*): $[M + NH_4]^+$ calcd for $C_{10}H_{12}O_5$, 230.1027; found, 230.1027.

13. White foam: (1.5:1 diastereomeric ratio, asterisk denotes minor diastereomer); ^{1}H NMR (500 MHz, benzene-d_6): δ 8.25* (d, 1H, *J* = 8.5 Hz), 8.10 (d, 1H, *J* = 8.0 Hz), 7.14 (s, 1H), 6.88* (s, 1H), 6.42 (d, 1H, *J* = 9.0 Hz), 6.37* (d, 1H, *J* = 8.0 Hz), 6.28* (d, 1H, *J* = 1.0 Hz), 6.27 (d, 1H, *J* = 1.0 Hz), 5.94 (d, 1H, *J* = 10 Hz), 5.88* (d, 1H, *J* = 10.0 Hz), 5.83* (dd, 1H, *J* = 3.5, 1.0 Hz), 5.75 (ddd, 1H, *J* = 9.5, 3.5, 1.0 Hz), 4.96 (d, 1H, *J* = 3.5 Hz), 4.76* (dd, 1H, *J* = 3.0, 1.0 Hz), 3.29 (s, 2H), 3.27 (s, 3H), 3.11 (s, 3H), 3.23* (s, 3H), 3.22* (s, 3H), 3.17* (s, 3H); FTIR (neat film): cm^{-1} 3000 (m), 1749 (s), 1737 (s), 1607 (s), 1587 (s), 1508 (s), 1267 (s), 1209 (s); HRMS-FAB (*m/z*): $[M+Na]^+$ calcd for $C_{17}H_{18}O_7Na$, 357.1100; found, 357.0950.

14. White crystalline solid: mp 137-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.37 (dd, 1H, *J* = 10.3, 4.8 Hz), 6.11 (ddd, 1H, *J* = 10.3, 4.4, 1.1 Hz), 4.92 (d, 1H, *J* = 4.4 Hz), 4.76 (d, 1H, *J* = 3.7 Hz), 4.62 (m, 1H), 1.54 (s, 3H), 1.43 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 134.2, 123.1, 113.1, 87.5, 78.3, 73.5, 40.5, 27.5, 26.4; FTIR (neat film): cm^{-1} 1838 (vs), 1380 (m), 1203 (m), 1115 (s); HRMS-CI (*m/z*): $[M + NH_4]^+$ calcd for $C_{10}H_{11}BrO_4$, 292.018; found, 292.0199.

15. White solid: mp 55-59 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.14 (ddd, 1H, *J* = 10.3, 3.7,1.8 Hz), 5.95 (ddd, 1H, *J* = 10.3, 2.6, 1.1 Hz), 4.99 (dd, 1H, *J* = 2.6, 1.8 Hz), 3.89 (s, 3H), 3.68 (d, 1H, *J* = 3.7 Hz), 3.43 (m, 1H), 1.41 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 133.1, 123.8, 113.2, 80.6, 73.4, 53.4, 51.8, 47.3, 28.5, 27.4; FTIR (neat film): cm^{-1} 1741 (s), 1370 (m), 1251 (m), 1060 (s); HRMS-CI (*m/z*): $[M + NH_4]^+$ calcd for $C_{11}H_{14}O_5$, 244.1180; found, 244.1185.

16. Colorless oil: ^{1}H NMR (5:1 isomeric ratio, asterisk denotes minor isomer peaks, 400 MHz, $CDCl_3$): δ 5.93* (m, 2H), 5.89 (dt, 1H, *J* = 10.6, 1.8 Hz), 5.69 (dt, 1H, *J* = 10.3, 1.8 Hz), 4.97* (m, 2H), 4.58 (dd, 1H, *J* = 3.7, 1.5 Hz), 4.28 (m, 2H), 3.84 (s, 3H), 3.84* (s, 3H), 3.54 (bs, 1H), 2.86 (bs, 1H), 1.44* (s, 3H), 1.43 (s, 3H), 1.39 (s, 3H), 1.37* (s, 3H); FTIR (neat film): cm^{-1} 3455 (vs), 1741 (s), 1374 (m), 1261 (s), 1060 (s); HRMS-CI (*m/z*): $[M + NH_4]^+$ calcd for $C_{11}H_{16}O_6$, 262.1291; found, 262.1297.

18. Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.14 (dd, 1H, *J* = 10.0, 4.0 Hz), 5.85 (dd, 1H, *J* = 10.0, 1.6 Hz), 4.50 (d, 1H, *J* = 1.6 Hz), 3.45 (dd, 1H, *J* = 4.4, 1.6 Hz), 3.35 (dt, 1H, *J* = 4.0, 1.6 Hz), 0.81 (s, 9H), 0.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.9, 133.9, 127.3, 77.1, 71.8, 55.7, 52.4, 48.0, 2.25, 0.41; FTIR (neat film): cm^{-1} 2960 (s), 2900 (w), 1756 (s), 1730 (s), 1433 (w), 1247 (s), 1171 (s), 1126 (m), 1106 (m), 1076 (m), 1041 (m), 900 (s), 840 (s); HRMS-CI (*m/z*): $[M+NH_4]^+$ calcd for $C_{14}H_{30}NO_5Si_2$, 348.1663; found, 348.1667.

19. Colorless oil: ^{1}H NMR (400 MHz, benzene-d_6): δ 5.70 (dd, 1H, *J* = 9.6, 4.0, 1.2 Hz), 5.41 (ddd, 1H, *J* = 10.0, 2.8, 1.2 Hz), 4.82 (d, 1H, *J* = 4.0 Hz), 4.27 (dt, 1H, *J* = 4.0, 1.2 Hz), 3.28 (s, 3H), 2.95 (dd, 1H, *J* = 2.8, 0.8 Hz), 0.24 (s, 9H), 0.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 137.4, 123.5, 68.9, 67.4, 60.3, 52.6, 52.5, 0.44, 0.26; FTIR (neat film): cm^{-1} 2950 (s), 2889 (w), 1755 (s), 1735 (s), 1433 (m), 1383 (w), 1282 (m), 1247 (s), 1186 (m), 1142 (s), 1111 (m), 1056 (s), 945 (m), 910 (m), 870 (s), 840 (s), 749 (m); HRMS-EI (*m/z*): $[M^+]$ calcd for $C_{14}H_{26}O_5Si_2$, 330.1319; found, 330.1317.

21. Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.92 (m, 2H), 4.63 (d , 1H, J = 4.4 Hz), 4.42 (m, 1H), 3.78 (s, 3H), 3.31 (dd, 1H, J = 2.8, 1.2 Hz), 0.90 (s, 9H), 0.89 (s, 9H), 0.08 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 138.7, 122.6, 69.3, 68.4, 59.7, 52.5, 52.0, 25.9, 25.7, 18.3, 18.2, -4.18, -4.27, -4.45, -5.21; FTIR (neat film): cm^{-1} 2954 (s), 2929 (s), 2887, (m), 2857 (s), 1759 (m), 1736 (s), 1473 (m), 1256 (w), 1253 (s), 1150 (s), 1111 (m), 1057 (s), 940 (m), 861 (s), 832 (s), 773 (s); HRMS-EI (*m/z*): [M^+] calcd for $C_{20}H_{38}O_5Si_2$, 414.2258; found, 414.2239.