Progressive-Convergent Elucidation of Stereochemistry in Complex Polyols.

The Absolute Configuration of (–)-Sagittamide A.

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Scheme S1: Synthesis of *xyl*o-Alkenes

a) In° , $\text{CH}_2=\text{CHCH}_2\text{Br}$, water, 93%, dr 1.3:1 *syn:anti*; *b*) pyridine, Tr-Cl, reflux, 45%; *c*) PPTS, acetone, $\text{CH}_3\text{C}(\text{OCH}_3)_2\text{CH}_3$, **S20**: 33%, **S21**: 15%; *d*) SiO_2 -HPLC, 19:1 hexanes:EtOAc; *e*) 1 atm H_2 , Pd/C, $\text{CF}_3\text{CH}_2\text{OH}$, **S22**: 91%, 3h, **S23**: 63%, 8h; *f*) i. oxalyl-Cl, DMSO, CH_2Cl_2 , ii. NEt_3 , iii. NaHCO_3 , *g*) i. **15**, DME, NaHMDS, -78°C , ii. aldehyde, **S24**:**S25**: 1.8:1, 46% two steps, **S26**:**S27**: 1.6:1, 25% two steps; *h*) i. **14**, THF, NaHMDS, -78°C , ii. aldehyde, **S25**: 30% two steps, **S27**: 34% two steps.

Scheme S2: Synthesis of *xylo*-Models S34-S39

a) AD-Mix- β , *t*-BuOH, H₂O, NH₂SO₂Me, 0°C-RT, **S28**: *dr*: 3.5:1, 79%, **S31**: *dr* >20:1, 84%; b) AD-Mix- α , *t*-BuOH, H₂O, NH₂SO₂Me, 0°C-RT, **S29**:**S30** *dr* 1.4:1, 92%, **S32**:**S33** *dr* 2.4:1, 84%; f) i. 2% TMS-Cl, MeOH, ii. Ac₂O, pyridine, iii. CH₂N₂, ether, CH₂Cl₂ **S34**: 36%, **S35**: 15%, **S36**: 9%, **S37**: 17%, **S38**: 28%, **S39**: 30%.

Figure S1: $\Delta\delta$ of xylo-Models S34-S39. ^{13}C NMR $\Delta\delta$ values (δ 1 - δ model) of xylo-Models S34-S39 (125MHz, d_6 -DMSO, T = 298 K).

Scheme S3: Synthesis of Olefination Reagents **14** and **15**

a) TMS-Cl, NaI, MeCN, 90%; *b*) isobutylene, ether, H_2SO_4 , 67%; *c*) PPh_3 , K_2CO_3 , MeCN, reflux, 70%; *d*) i. KH, THF, 1-phenyl-1H-tetrazole-5-thiol, ii. **S53**, 54%; *e*) $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, H_2O_2 , EtOH, 96%.

Scheme S4: Synthesis of *ribo*-Alkenes

a) In° , $\text{CH}_2=\text{CHCH}_2\text{Br}$, H_2O *dr* 1.4:1 *syn:anti*; b) pyridine, Tr-Cl, reflux 53% two steps; c) CSA, acetone, $\text{CH}_3\text{C}(\text{OCH}_3)_2\text{CH}_3$ **10**: 38%, **11**: 20%; d) SiO_2 -HPLC 19:1 hexanes:EtOAc; e) 1 atm H_2 , 10% Pd/C, $\text{CF}_3\text{CH}_2\text{OH}$, **S42**: 69%, **S43**: 35%; f) i. oxalyl-Cl, DMSO, CH_2Cl_2 , ii. TEA, iii. NaHCO_3 ; g) i. **15**, DME, NaHMDS, -78°C , ii. RCHO **12:13** *dr* 3.0:1, 25%; h) i. **14**, THF, NaHMDS, -78°C , ii. RCHO, **13**: 16% two steps; i) i. **15**, DME, NaHMDS, -78°C , ii. RCHO **S44:S45** *dr* 2.0:1, 69%.

Scheme S5: Synthesis of *ribo*-Models 2-9

OsO₄, NMO, acetone, H₂O **16:17** *dr* 4.9:1, 85%, **S46:S47** *dr* 1.4:1, 95%, **S48:S49** *dr* 9.8:1, 87%, **S50:S51** *dr* 1.7:1, 93%; *b*) i. 2% TMS-Cl, MeOH, ii. CH₂N₂, ether/MeOH, iii. Ac₂O, pyridine 6h **2**: 48%, **3**: 22%, **4**: 23%, **5**: 25%, **6**: 56%, **7**: 85%, **8**: 30%, **9**: 26%.

Table S1: Dihydroxylation of *ribo*-Model Alkenes and Assignment of Configuration

	Alkene	Conditions ^c	Yield	dr	Major configuration	Major isomer
1	12	<i>c</i>	85%	4.9:1 ^a	(5 <i>S</i> ,6 <i>R</i>)	16
2	12	<i>d</i>	86%	1:3.8 ^a	(5 <i>R</i> ,6 <i>S</i>)	17
3	12	<i>e</i>	87%	1:2.2 ^a	(5 <i>R</i> ,6 <i>S</i>)	17
4	13	<i>c</i>	86%	9.8:1 ^b	(5 <i>S</i> ,6 <i>S</i>)	S48
5	13	<i>d</i>	>98%	1:2.2 ^b	(5 <i>R</i> ,6 <i>R</i>)	S49
6	13	<i>e</i>	92%	4.2:1 ^a	(5 <i>S</i> ,6 <i>S</i>)	S48
7	S44	<i>c</i>	95%	1.4:1 ^a	(5 <i>S</i> ,6 <i>R</i>)	S46
8	S44	<i>d</i>	>98%	>20:1 ^a	(5 <i>S</i> ,6 <i>R</i>)	S46
9	S44	<i>e</i>	79%	1:3.3 ^a	(5 <i>R</i> ,6 <i>S</i>)	S47
10	S45	<i>c</i>	93%	1:1.7 ^a	(5 <i>S</i> ,6 <i>S</i>)	S50
11	S45	<i>d</i>	55%	~1:1 ^a		—
12	S45	<i>e</i>	>95%	1.8:1 ^a	(5 <i>R</i> ,6 <i>R</i>)	S51

a, *dr* from ¹H NMR of crude product. *b*, *dr* from isolated yield. *c*, OsO₄, NMO, acetone. *d*, AD-mix- α ; *e*, AD-mix- β .

Scheme S6: Synthesis of the Hexabenzoates

a) i. CH₂N₂, ether, MeOH; ii. NH₃, MeOH; *b*) i. *p*-BrBzCl, pyridine, DMAP, ii. *N,N*-dimethyl-3-aminopropylamine; **17**: 13% *three steps*. *d*) i. 2% TMS-Cl, MeOH, ii. CH₂N₂, ether/MeOH, iii. *p*-BrBzCl, pyridine, DMAP 60 °C **18**: 15%, **S55**: 35%, **19**: 25%, **S56**: 17% *three steps*.

Table S2: Selected ^{13}C NMR δ 's of compounds **1-9** (125 MHz, d_6 -DMSO, 298 K).

C #	δ_c								
	1	2	3	4	5	6	7	8	9
3	22.2	21.1	20.9	21.0	21.0	21.1	20.8	21.2	20.9
4	29.6	30.3	30.2	30.4	30.4	28.5	29.7	28.3	29.4
5	72.0	70.0	70.7	70.6	71.2	71.7	70.1	72.0	70.7
6	70.8	70.6	70.9	69.5	69.4	70.6	70.1	71.2	70.5
7	68.1	71.3	70.7	71.0	71.2	68.0	71.1	70.1	68.9
8	67.2	71.3	71.1	71.3	71.3	67.2	68.9	70.0	69.6
9	69.6	70.6	69.0	70.3	71.2	69.6	70.3	71.1	71.8
10	70.6	69.9	71.1	71.9	72.2	70.2	68.4	71.9	71.5
11	31.2	33.1	33.1	31.2	31.7	33.4	33.2	31.3	32.3

J-Based Analysis of Sagittamide A (1):

A basis set of $^3J_{\text{HH}}$ and $^2,^3J_{\text{CH}}$ values were obtained by homonuclear 2D COSY and heteronuclear HSQMBC NMR experiments of **1** (Table S3), and used to predict an all *syn*-provisional assignment of relative configuration for C6-C9 in **1**. The large $^3J_{\text{HH}}$ between H6/H7 ($J=8.4$ Hz) and H8/H9 ($J=10.0$ Hz) indicated that the protons must be *anti* with respect to one another, and in both cases nOe were observable between H5/H8 and H7/H10 placing the C5/C8 and C7/C10 *gauche* to each other and assigning the conformation between C6/C7 and C8/C9 (Fig. S2). A small $^3J_{\text{HH}}$ between H7/H8 ($J=1.5$ Hz) placed these protons *gauche* to one another. Large $^2J_{\text{CH}}$ and $^3J_{\text{CH}}$ couplings between C8/H7 ($J=-4.0$ Hz) and C6/H8 ($J=-4.4$ Hz) respectively, measured from an HSQMBC spectrum, put the carbon chains *gauche* to one another (Fig. S1.). Combination of these relationships gives the provisional relative stereochemistry of C6 through C9 in **1** as all *syn*.

Figure S2: Relative Conformations of Sagittamide A.

Table S3: Scalar Couplings from ^1H NMR and HSQMBC of **1**

Carbon #	$^3J_{\text{HH}}^{\text{a}}$ H, Hz		$^2J_{\text{CH}}$ H, Hz		$^3J_{\text{CH}}$ H, Hz
5	H ₄	− ^b	H ₆	4.0	H ₇ − ^c
6	H ₅	4.0	H ₇	8.2	H ₈ +7.4
7	H ₆	8.4	H ₈	1.6	^d
8	H ₇	1.4	H ₉	9.8	H ₆ −4.4
9	H ₈	10.0	H ₁₀	2.0	^d
10	H ₉	1.6	H ₁₁	6.8	^d

^a Spectra measured in *d*₆-DMSO at 600 MHz. ^b Unresolved.

^c Need $^3J_{\text{H4,H5}}$ to calculate. ^d Not observed.

Synthesis of the all *syn xylo*-series of models **S34-S39** followed by analysis of ^{13}C chemical shifts belied the prediction from the *J*-based analysis. Reexamination of the data revealed that second-order effects biased the *measured* heteronuclear couplings of H6, H7, and H9 from the HSQMBC spectrum, which affected the calculation of $^2J_{\text{CH}}$ and $^3J_{\text{CH}}$ values utilized for assignment. In addition, lack of dispersion of chemical shifts, even at 600 MHz, gave equivocal assignments of the critical nOe's between the pairs H9/H10 as and H7/H10. The ambiguities were resolved by synthesis of models and comparison of their respective ^{13}C NMR spectra with those of sagittamide A (**1**, see text).

Experimental:

IR, UV, CD and optical rotations were measured using a Mattson Galaxy Series FTIR 3000, a Hewlett-Packard 8452A diode array spectrophotometer, Jasco J-810, and a Jasco DIP-370 digital polarimeter, respectively. ^1H NMR and ^{13}C NMR spectra were measured in CDCl_3 , $(\text{CD}_3)_2\text{SO}$ or CD_3OD from Cambridge Isotope Laboratories on a 600 MHz (Bruker with cryoprobe), 500 MHz (Bruker), 600 MHz (Varian), 400 MHz (Varian Inova 400), or 300 MHz (Varian Mercury) using standard manufacturer's software, and referenced to residual protiated solvent signal (δ_{H} 7.24, δ_{C} 77.00 ppm in CDCl_3 , δ_{H} 2.50, δ_{C} 45.45 ppm in $(\text{CD}_3)_2\text{SO}$; δ_{H} 3.30, δ_{C} 49.00 ppm in CD_3OD). HRMS were run by either University of California, Riverside mass spectrometry facility or University of California, San Diego mass spectrometry facility. Normal-phase HPLC was carried out on a Rainin Rabbit HP systems using 100 Å Si 10×250 mm or 25×250 mm columns from Microsorb with UV and refractive index detection.

General Allylation Procedure:¹

D-(+)-Xylose (0.7686 g, 5.12 mmol) was dissolved in water (50.0 ml) and followed by the addition of indium (0.8277 g, 7.21 mmol) and allyl-bromide (1.35 ml, 16.4 mmol). The biphasic solution was stirred rapidly and aliquots of allyl-bromide were added at 1 hour (0.75 ml) and at 2 hours (1.0 ml). After 10 hours the aqueous solution was washed with ethyl acetate and extracted four times with n-butanol. The combined n-butanol partitions were concentrated in vacuo to give **S18** as 1.5339 g clear glass still containing butanol. ^1H NMR of the crude mixture shows a 1.4:1 *syn:anti* ratio with 7% remaining xylose.²

¹ Paquette, L. A.; Mitzel, T. M. *J. Am. Chem. Soc.* **1996**, *118*, 1931-1937.

² The *syn* and *anti* assignments for **S18** were made by peracetylation and SiO_2 -HPLC separation and comparison of the H5 and H6 chemical shifts to the *gluco*-analogs. Kim, E.; Gordon, D. M.;

(2R,3S,4S)-1,2,3,4,5-pentahydroxy-oct-7-ene (S18)

93% as a pale foam, (1.4:1 *syn:anti*) ^1H NMR (300 MHz, CD_3OD): δ 5.86 (m, 2H), 5.07 (m, 4H), 4.04 (m, 2H), 3.8-3.5 (m, 10H), 2.49 (m, 1H), 2.35 (m, 2H), 2.18 (m, 1H) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ 135.8 (C-7), 135.5 (C-7), 117.7 (C-8), 117.6 (C-8), 74.9 (CH), 74.3 (CH), 73.1 (CH), 72.8 (CH), 72.6 (CH), 72.6 (CH), 71.8 (CH), 69.7 (CH), 63.7 (C-1), 63.5 (C-1), 38.7 (C-6), and 38.5 (C-6) ppm.

(2R,3R,4S)-1,2,3,4,5-pentahydroxy-oct-7-ene (S40)

95% as a clear glass, (1.7:1 *syn:anti*) ^1H NMR (400 MHz, CDCl_3): δ 5.90 (ddd, 2H), 5.15 (dm, 2H), 5.08 (dm, 2H), 3.95-3.55 (m, 12H), 2.48 (ddd, 1H, s), 2.36 (m, 2H, a), 2.27 (m, 1H, s) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 135.7, 135.4, 116.3, 116.1, 75.1, 73.4, 73.2, 73.16, 72.8, 72.5, 72.3, 70.3, 63.2, 63.0, 38.2, 37.0 ppm.

General Tritylation Procedure:³

Dissolve alcohol **S18** (1.1721 g, 6.10 mmol) in anhydrous THF (60 mL) and add triphenylmethyl chloride (1.86 g, 6.67 mmol) and anhydrous pyridine (1.35 mL, 16.69 mmol). Heat solution to reflux 16 h. Solution was cooled to r.t. and diluted with 75 mL water and extracted three times with 75 mL ethyl acetate. The combined organics were washed with brine, dried over Na_2SO_4 and concentrated in vacuo to a yellow oil which was purified by silica

Schmid, W.; Whitesides, G. M. *J. Org. Chem.* **1993**, 58, 5500-5507. Mirrington, R. N.; Schmalzl, K. J. *J. Org. Chem.* **1972**, 37, 2877-2881.

³ Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*; 3rd ed.; John Wiley & Sons, Inc., 1999.

chromatography eluting with DCM, and 19:1 DCM:MeOH to yield the protected alcohol **S19** as 1.19 g (45%) pale yellow glass in a 5:4 mix of diastereomers.

(2*R*,3*S*,4*S*)-1-*O*-trityl-2,3,4,5-tetrahydroxyl-7-octenol (**S19**)

45% as a pale glass (5:4 *syn:anti*) ¹H NMR (400 MHz, CD₃OD): δ 7.46 (m, *o*- or *m*-Ph), 7.27 (m, *o*- or *m*-Ph), 7.20 (m, *p*-Ph), 5.90 (ddt, *J*=17.2, 10.4, 7.0 Hz, H-7), 5.84 (ddt, *J*= 17.2, 10.4, 7.0 Hz, H-7), 5.07 (dm, *J*= 17.2 Hz, H-8, H-8'), 5.02 (dm, *J*=9.0 Hz, H-8'), 4.99 (dm, *J*= 10.0 Hz, H-8'), 4.01 (dd, *J*=4.4, 2.0 Hz, 1H), 3.91 (td, *J*= 5.2, 4.0 Hz, 1H), 3.89 (t, *J*= 5.0, 1H), 3.85 (t, *J*= 4.0 Hz, 1H), 3.76 (ddd, *J*= 7.6, 5.2, 3.6 Hz, 1H), 3.67 (td, *J*= 4.0, 3.2 Hz, 1H), 3.46 (t, *J*= 4.0 Hz, 1H), 3.37 (dd, *J*= 7.6, 2.0 Hz, 1H), 3.32 (dd, *J*=9.2, 4.4 Hz, H-1), 3.28 (dd, *J*=4.8, ? Hz, H-1), 3.19 (t, *J*= 6.0 Hz, H-1'), 3.16 (dd, *J*= 6.0, 5.6 Hz, H-1'), 2.46 (dm, *J*= 14.4 Hz, H-6), 2.33 (m, H-6), 2.27 (m, H-6'), 2.16 (dm, *J*= 14.4 Hz, H-6') ppm. ¹³C NMR (100 MHz, CD₃OD): δ 145.5 (*i*-Ph), 145.4 (*i*-Ph), 136.6 (C-7), 136.3 (C-7), 129.92 (*o*- or *m*-Ph), 129.90 (*o*- or *m*-Ph), 128.7 (*p*-Ph), 128.0 (*p*-Ph), 117.4 (C-8), 117.3 (C-8), 87.9 (C-Ph₃), 87.8 (C-Ph₃), 79.4 (CH), 75.8 (CH), 74.3 (CH), 73.9 (CH), 73.1 (CH), 72.6 (CH), 72.32 (CH), 72.28 (CH), 70.8 (CH), 66.3 (C-1), 66.1 (C-1), 39.2 (C-6), and 39.0 (C-6) ppm.

(2*R*,3*R*,4*S*)-2,3,4,5-tetrahydroxy-1-*O*-trityl-1-oxo-oct-7-ene (**S41**)

(5.49 g, 53% over 2 steps). ¹H NMR (400 MHz, CDCl₃): δ 7.5 (m, *o*- or *m*-Ph), 7.25 (m, *o*- or *m*-Ph and *p*-Ph), 5.95 (m, H-7), 5.15 (m, H-8, H-8'), 4.3-3.5 (m, H-1, H-1', H-2, H-3, H-4, H-5), 2.83 (m, H-6), 2.35 (m, H-6') ppm.

General Procedure for Acetonide Protection of Tetrol:

Tetrol **S19** (0.83 g, 1.91 mmol) was dissolved in 60 mL of 1:1 acetone:2,2-dimethoxypropane. (*R*)-camphorsulfonic acid (88.5 mg, 0.381 mmol) was added and the solution stirred at r.t. for 16 min. NaHCO₃ (1.3965 g) was added to neutralize acid and solution was diluted with 100 mL water then extracted three times with 100 mL ethyl acetate. The combined organics were washed with brine, dried over Na₂SO₄ and concentrated in vacuo to give a pale yellow glass. Initial purification of di-isopropylidene by silica flash chromatography eluting with 5% EtOAc:hexanes was followed by silica HPLC in 5% EtOAc:Hexanes to separate isomers. Yield **S20**: 207.1 mg (22% *syn* isomer) and **S21**: 168.6 mg (18% *anti* isomer).⁴

(2*R*,3*S*,4*S*,5*R*)- 2,3:4,5-di-*O*-isopropylidene-1-*O*-trityl-1,2,3,4,5-pentaoxo-7-octene (**S20**) 22% as a clear glass. ¹H NMR (300 MHz, CDCl₃): δ 7.43 (m, *o*- or *m*-Ph), 7.26 (m, *o*- or *m*-Ph and *p*-Ph), 5.76 (ddd, *J*= 17.2, 10.4, 6.9 Hz, H-7), 5.03 (m, H-8, H-8'), 4.27 (dt, *J*= 7.8, 4.9 Hz, H-2), 4.06 (dt, *J*= 8.4, 5.9 Hz, H-5), 3.87 (dd, *J*= 7.8, 2.6 Hz, H-3), 3.70 (dd, *J*= 8.4, 2.6 Hz, H-4), 3.29 (dd, *J*= 9.8, 4.9 Hz, H-1), 3.19 (dd, *J*= 9.6, 4.9 Hz, H-1'), 2.29 (m, H-6, H-6'), 1.41 (s, 2 Me), 1.40 (s, Me), 1.38 (s, Me) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 143.7 (*i*-Tr), 133.5 (C-7), 128.7 (*o*- or *m*-Ph) 127.8 (*o*- or *m*-Ph), 127.1 (*p*-Ph), 117.7 (C-8), 109.4 (C-Me₂), 108.7 (C-Me₂), 86.7 (C-Ph₃), 79.3 (C-4), 77.3 (C-3), 76.1 (C-2), 75.9 (C-5), 63.8 (C-1), 37.0 (C-6), 27.4 (Me), 27.3 (Me), 26.7 (Me), 26.6 (Me) ppm. IR (NaCl): ν 3064, 2984, 2935, 1379, 1248, 1168, 1076 cm⁻¹. MS (FAB) calc'd for C₃₃H₃₈O₅Na [M+Na]⁺ 537.2617, found 537.2639. [α_D]^{25°} +17.5 [c 0.42, CHCl₃].

⁴ Assignment of C4-C5 configuration in **10** and **11** was determined by the formation of *syn, syn* 1,3-dioxanes in **11**. Rychnovsky, S. D.; Rogers, B.; Yang, G. *J. Org. Chem.* **1993**, 58, 3511-3515.

(2*R*,3*S*,4*S*,5*S*)-2,3:4,5-di-*O*-isopropylidene-1-*O*-trityl-1,2,3,4,5-pentaoxo-7-octene (**S21**) 18% as a clear glass. ¹H NMR (400 MHz, CDCl₃): δ 7.42 (m, *o*- or *m*-Ph), 7.25 (m, *o*- or *m*-Ph and *p*-Ph), 5.80 (m, H-7), 5.09 (ddd, *J*= 17.2, 1.6, 1.6 Hz, H-8), 5.03 (ddd, *J*=10.3, 2.8, 1.6 Hz, H-8'), 4.21 (dt, *J*=12.0, 6.4 Hz, H-5), 4.15 (dt, *J*=7.4, 4.0 Hz, H-2), 3.97 (dd, *J*= 6.4, 1.6 Hz, H-4), 3.89 (dd, *J*=6.4, 1.6 Hz, H-3), 3.24 (d, *J*= 4.0 Hz, H-1, H-1'), 2.58 (dddt, *J*= 14.5, 8.1, 6.4, 1.6 Hz, H-6), 2.38 (dddt, *J*= 14.5, 7.4, 6.0, 1.2 Hz, H-6'), 1.50 (s, Me), 1.45 (s, Me), 1.40 (s, Me), 1.34 (s, Me) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 143.7 (*i*-Ph), 134.6 (C-7), 128.7 (*o*- or *m*-Ph), 127.8 (*o*- or *m*-Ph), 127.0 (*p*-Ph), 117.1 (C-8), 109.3 (C-Me₂), 108.4 (C-Me₂), 86.7 (C-Ph₃), 76.6 (C-3), 76.4 (C-2), 76.3 (C-5), 75.3 (C-4), 63.3 (C-1), 34.3 (C-6), 27.2 (Me), 227.1 (Me), 26.7 (Me), 25.5 (Me) ppm. IR (NaCl): ν 3064, 2984, 1451, 1380, 1207, 1076 cm⁻¹. MS (FAB) calc'd for C₃₃H₃₈O₅Na [M+Na]⁺ 537.2617, found 537.2625. [α_D]^{25°} +15.2 [c 0.32, CHCl₃].

(2*R*,3*R*,4*S*,5*R*)-2,3:4,5-di-*O*-isopropylidene-1-*O*-trityl-1,2,3,4,5-pentaoxo-oct-7-ene (**10**) 2.08 g, 38% colorless glass ¹H NMR (300 MHz, CDCl₃): δ 7.54 (m, *o*- or *m*-Ph), 7.30 (m, *o*- or *m*-Ph and *p*-Ph), 5.91 (ddd, *J*= 16.2, 9.6, 6.3, H-7), 5.14 (dm, *J*= 16.2 Hz, H-8), 5.09 (dm, *J*= 9.6 Hz, H-8'), 4.45 (td, *J*= 6.0, 3.3 Hz, H-2), 4.07 (dd, *J*= 9.0, 6.0 Hz, H-3), 3.99 (td, *J*= 7.8, 3.3 Hz, H-5), 3.66 (dd, *J*= 9.0, 7.8 Hz, H-4), 3.41 (dd, *J*= 10.2, 3.3 Hz, H-1), 3.28 (dd, *J*= 10.2, 6.0 Hz, H-1'), 2.62 (dddt, *J*= 14.7, 6.5, 3.0, 1.5 Hz, H-6), 2.25 (dt, *J*= 14.7, 7.8 Hz, H-6'), 1.56 (s, Me), 1.44 (s, Me), 1.28 (s, Me), 1.18 (s, Me) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 144.0 (*i*-Ph), 134.5 (C-8), 128.9 (*o*- or *m*-Ph), 127.7 (*o*- or *m*-Ph), 126.9 (*p*-Ph), 117.0 (C-7), 109.2 (C-Me₃), 108.7 (C-Me₃), 86.6 (C-Ph₃), 80.5 (C-4), 78.5 (C-3), 77.5 (C-2), 76.6 (C-4), 63.0 (C-1), 37.3 (C-6), 27.5 (Me), 27.1 (Me), 26.9 (Me), 25.5 (Me) ppm. IR (NaCl): ν 3066, 2985, 2937, 1450, 1381,

1064 cm^{-1} . MS (FAB) calc'd for $\text{C}_{33}\text{H}_{38}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$ 537.2617, found 537.2640. $[\alpha_D]^{30^\circ}$ +11.49 [c 2.01, CHCl_3].

(2*R*,3*R*,4*S*,5*S*)-2,4:3,5-di-*O*-isopropylidene-1-*O*-trityl-1,2,3,4,5-pentaoxo-oct-7-ene (**11**) 1.07 g, 20% colorless glass. ^1H NMR (300 MHz, CDCl_3): δ 7.54 (m, *o*- or *m*-Ph), 7.30 (m, *o*- or *m*-Ph and *p*-Ph), 5.91 (ddd, J = 17.7, 9.8, 6.3 Hz, H-7), 5.13 (dm, J = 17.7 Hz, H-8), 5.10 (dm, J = 9.8 Hz, H-8') 3.87 (m, H-2, H-5, and H-3 or H-4), 3.47 (ddd, J = 9.3, 4.7, 4.7 Hz, H-3 or H-4), 3.27 (dd, J = 9.9, 1.8 Hz, H-1), 3.17 (dd, J = 9.9, 3.0 Hz, H-1), 2.49 (dddt, J = 14.7, 4.5, 3.0, 1.8 Hz, H-6), 2.22 (dt, J = 14.7, 7.2 Hz, H-6'), 1.51 (s, Me), 1.496 (s, Me) 1.494 (s, Me), 1.36 (s, Me) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 144.2(*i*-Ph), 134.1(C-8), 128.8 (*o*- or *m*-Ph), 127.6 (*o*- or *m*-Ph), 126.8 (*p*-Ph), 117.0 (C-7), 99.9 (C-Me₂), 99.7 (C-Me₂), 86.1 (C-Ph₃), 72.0 (C-2, C-3, C-4 or C-5), 71.7(C-2, C-3, C-4 or C-5), 70.5 (C-3 or C-4), 67.8(C-2, C-3, C-4 or C-5), 63.0 (C-1), 35.5(C-6), 29.44 (Me), 29.38 (Me), 19.84 (Me), 19.79 (Me) ppm. IR (NaCl): ν 3060, 2991, 2939, 1630, 1598, 1482, 1215, 1065 cm^{-1} . MS (FAB) calc'd for $\text{C}_{33}\text{H}_{38}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$ 537.2617, found 537.2629. $[\alpha_D]^{27^\circ}$ +6.57 [c 2.82, CHCl_3].

General Procedure for Detritylation:

After drying three times from toluene to remove chlorinated solvents dissolve trityl-ether **S20** (207.1 mg, 0.402 mmol) in trifluoroethanol (25 mL) and add 10% palladium on carbon (97.7 mg, 0.0918 mmol). Evacuate flask and place under hydrogen atmosphere three times and stir under hydrogen for 3 hours. Filter reaction mixture through Celite to remove palladium on carbon and concentrate in vacuo. Residue was purified by silica chromatography eluting with 19:1 EtOAc:hexanes then 1:1 EtOAc:hexanes. Alcohol **S22** was collected as a pale yellow oil (100.5 mg, 91%).

(2*R*,3*S*,4*S*,5*R*)- 1-hydroxy-2,3:4,5-di-*O*-isopropylidene-2,3,4,5-tetraoxo-octane (**S22**) 91% as a colorless glass (100.5 mg) ^1H NMR (400 MHz, CDCl_3): δ 4.17 (td, $J = 8.3, 3.0$ Hz, H-3), 4.04 (m, H-5), 3.91 (dd, $J = 8.3, 2.6$ Hz, H-2), 3.83 (dt, $J = 12.0, 1.0$ Hz, H-1), 3.61 (m, H-1'), 3.59 (dd, $J = 8.2, 2.0$ Hz, H-4), 2.04 (br, OH), 1.52 (m, H-6, H-6', H-7'), 1.41 (s, Me), 1.40 (m, H-7), 1.40 (s, Me), 1.38 (s, Me), 1.36 (s, Me), and 0.92 (t, $J = 7.2$ Hz, H-8) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 109.4 (C-Me₂), 108.7 (C-Me₂), 79.3 (C-5), 77.4 (C-6), 76.9 (C-4), 75.4 (C-7), 61.4 (C-8), 35.0 (C-3), 27.5 (Me), 27.2 (Me), 26.7 (Me), 26.5 (Me), 19.3 (C-2), and 14.1 (C-1) ppm. IR (NaCl): ν 2473, 2986, 2934, 2874, 1708, 1457, 1380, 1251, 1167, 1126, 1032, 990, 879 cm^{-1} . UV CHCl_3 λ_{max} (log ϵ) 200 (3.76), 222 (3.81), 240 (3.81) nm. MS (ESI) calc'd for $\text{C}_{14}\text{H}_{27}\text{O}_5$ $[\text{M}+\text{H}]^+$ 275.1858, found 275.1855. $[\alpha_D]^{20} +32.5$ [c 5.38, CHCl_3].

(2*R*,3*S*,4*S*,5*S*)- 1-hydroxy-2,3:4,5-di-*O*-isopropylidene-2,3,4,5-tetraoxo-octane (**S23**) as a white wax (56.9 mg, 63%). ^1H NMR (300 MHz, CDCl_3): δ 4.21 (ddd, $J = 10.2, 6.6, 3.6$ Hz, H-5), 4.05 (dt, $J = 8.5, 2.0$ Hz, H-3), 3.96 (dd, $J = 6.6, 2.0$ Hz, H-4), 3.85 (dd, $J = 8.5, 1.5$ Hz, H-2), 3.82 (dm, $J = 3.6$ Hz, H-1), 3.58 (ddd, $J = 11.7, 8.4, 3.3$ Hz, H-1), 1.97 (dd, $J = 8.4, 4.2$ Hz, OH), 1.79 (m, H-6, H-7), 1.49 (s, Me), 1.43 (s, Me), 1.39 (s, Me), 1.34 (s, Me), 0.94 (t, $J = 7.2$ Hz, H-8) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 109.4 (C-Me₂), 108.4 (C-Me₂), 77.4 (C-3), 76.9 (C-5), 75.0 (C-4), 74.9 (C-2), 60.8 (C-1), 31.6 (C-6), 27.2 (Me), 27.0 (Me), 26.7 (Me), 25.5 (Me), 20.1 (C-7), 14.0 (C-8) ppm. IR (NaCl): ν 3478, 2985, 2960, 2936, 2874, 1457, 1379, 1255, 1215, 1167, 1116, 1033, 900, 857 cm^{-1} . MS (EI) calc'd for $\text{C}_{14}\text{H}_{26}\text{O}_5$ $[\text{M}]^+$ 274.1780, found 274.1780. $[\alpha_D]^{26} +48.8$ [c 5.69, CH_2Cl_2].

(2*R*,3*R*,4*S*,5*R*)-1-hydroxy-2,3:4,5-di-*O*-isopropylidene -2,3,4,5-tetraoxo-octane (S42)

69% as a clear glass (0.517 g). ^1H NMR (600 MHz, CDCl_3): δ 4.35 (dt, $J = 7.8, 5.7$ Hz, H-2), 4.09 (dd, $J = 9.6, 6.0$ Hz, H-3), 3.97 (td, $J = 8.1, 2.8$ Hz, H-5), 3.83 (m, H-1), 3.77 (m, H-1'), 3.67 (dd, $J = 9.9, 7.5$ Hz, H-4), 2.91 (dd, $J = 9.0, 5.4$ Hz, OH), 1.74 (m, H-6), 1.53 (m, H-6', H-7), 1.43 (m, H-7'), 1.40 (s, Me), 1.39 (s, Me), 1.35 (s, Me), 1.33 (s, Me), and 0.93 (t, $J = 7.2$, H-8) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ 109.2 (C-Me₂), 108.9 (C-Me₂), 81.2 (C-5), 78.9 (C-3), 77.7 (C-2), 77.2 (C-4), 60.6 (C-1), 35.7 (C-6), 27.7 (Me), 27.4 (Me), 26.9 (Me), 25.2 (Me), 19.3 (C-7), and 14.1 (C-8) ppm. IR (NaCl): ν 3509, 2987, 2939, 1366, 1213, 1049 cm^{-1} . MS (FAB) calc'd for $\text{C}_{14}\text{H}_{27}\text{O}_5$ $[\text{M}+\text{H}]^+$ 275.1858, found 275.1859. $[\alpha_D]^{20} +1.03$ [c 0.37, CHCl_3].

(2*R*,3*R*,4*S*,5*S*)-1-hydroxy-2,4:3,5-di-*O*-isopropylidene -2,3,4,5-tetraoxo-octane (S43)

35% as a clear glass ^1H NMR (600 MHz, CDCl_3): δ 3.79 (dt, $J = 9.6, 4.4$ Hz, H-2), 3.71 (dd, $J = 11.7, 3.3$ Hz, H-1), 3.70 (td, $J = 9.0, 3.0$ Hz, H-5), 3.61 (dd, $J = 11.7, 4.5$ Hz, H-1'), 3.58 (t, $J = 9.6$ Hz, H-3), 3.37 (t, $J = 9.3$ Hz, H-4), 1.95 (br s, OH), 1.63 (m, H-6), 1.49 (s, Me), 1.47 (s, Me), 1.45 (m, H-7), 1.38 (s, Me), 1.36 (s, Me), 1.32 (m, H-6', H-7'), and 0.89 (t, $J = 6.9$ Hz, H-8) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ 100.0 (C-Me₂), 99.9 (C-Me₂), 72.3 (C-2□), 71.9 (C-5), 71.0 (C-4), 68.0 (C-3), 62.3 (C-1), 33.5 (C-6), 29.5 (Me), 29.4 (Me), 20.1 (Me), 20.0 (Me), 17.9 (C-7), and 14.0 (C-8) ppm. IR (NaCl): ν 3520, 2991, 2939, 1656, 1377, 1215, 1059, 843 cm^{-1} . MS (EI) calc'd for $\text{C}_{14}\text{H}_{26}\text{O}_5$ $[\text{M}]^+$ 274.1780, found 274.1773 $[\alpha_D]^{20} +10.32$ [c 2.87, CHCl_3].

General Procedure for Aldehyde Formation:⁵

Oxalyl chloride (18.0 μ L, 0.21 mmol) was dissolved in dichloromethane (0.5 mL) and cooled to -78° C. Dimethylsulfoxide (28.5 μ L, 0.40 mmol) in 40 μ L dichloromethane was added and allowed to stir for 2 minutes. Primary alcohol **S22** (15.5 mg, 56.5 μ mol) was added and the solution stirred at -78° C for 30 minutes. Triethylamine (200 μ L, 1.43 mmol) was added and the solution was stirred for 30 minutes. Aqueous NaHCO₃ (1.0 mL) was added while the solution was still cold and allowed to stir at -78°C for 10 minutes before warming. Once mixture was warm enough to melt aqueous layer the solution was partitioned between aqueous NaHCO₃ and CH₂Cl₂ and the aqueous layer washed a second time with CH₂Cl₂. The combined organics were dried over Na₂SO₄ and conc. in vacuo to give the crude aldehyde 15.0 mg (95%).

5-iodo-valeric acid, t-butyl ester (S52**)⁶**

5-iodo-valeric acid⁷ (21.25 g, 0.0933 mol) was dissolved in ether (25.0 mL) and placed in a pressure vessel. Concentrated sulfuric acid (1.0 mL) was added and the vessel cooled to -78 °C. Isobutylene (~22 mL) was condensed into the cooled vessel and the vessel was sealed before warming to RT and stirring for 20 h. The vessel was then cooled to -78 °C before opening and the reaction quenched by addition of solid NaHCO₃. The solution was diluted with sat'd NaHCO₃ solution (250 mL) and water (100 mL) then extracted with ether (3x 350 mL). The combined organics were dried over Na₂SO₄ and concentrated in vacuo to a yellow oil **S52** (17.76 g, 67%). ¹H NMR (300 MHz, CDCl₃): δ 3.16 (t, J = 6.6 Hz, H-2), 2.21 (t, J = 7.1 Hz, H-5), 1.82

⁵ Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480-2482.

⁶ Denmark, S. E.; Beutner, G. L. *J. Am. Chem. Soc.* **2003**, *125*, 7800-7801.

⁷ Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *J. Org. Chem.* **1979**, *44*, 1247-1251.

(m, H-3), 1.66 (m, H-4), and 1.41 (s, *t*-Bu) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 172.5 (C-1), 80.3 (C-Me₃) 32.7 (C-2 or C-4), 31.2 (C-2 or C-4), 28.7 (3 Me), 25.9 (C-3), and 6.04 (C-5) ppm.

5-(triphenylphosphonium)-valeric acid, *t*-butyl ester iodide⁸ (**14**)

S52 (5.9813 g, 21.1 mmol) and triphenylphosphine (6.1037 g, 23.3 mmol) were dissolved in anhydrous MeCN (80.0 mL) anhydrous K_2CO_3 (6.240 g, 45.2 mmol) was suspended with stirring. The heterogenous mixture was heated to reflux for 18 h then cooled. The solid K_2CO_3 was removed by filtration and the solution concentrated in vacuo to ~10 mL and triturated with ether until yellow oil becomes a white gummy solid and no triphenylphosphine remains. **14** was isolated as a sticky white glass (8.10 g, 70%). A small amount later crystallized from THF (mp = 92-93 °C).

^1H NMR (300 MHz, CD_3OD): δ 7.77 (m, Ph), 3.47 (m, H-5), 2.30 (t, J = 6.9 Hz, H-2), 1.83 (p, J = 7.2 Hz, H-3), 1.70 (m, H-4), and 1.37 (s, *t*-Bu) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 174.1 (C-1), 136.3 (*p*-Ph, J = 2.8 Hz), 134.9 (*o*- or *m*-Ph, J = 10.3 Hz), 131.6 (*o*- or *m*-Ph, J = 12.5 Hz), 119.9 (*i*-Ph, J = 85.9 Hz), 81.7 (C-Me₃), 35.4 (C-2), 28.3 (3 Me), 27.5 (C-4, J = 17.6 Hz), 22.9 (C-3), 22.2 (C-5) ppm. MS (FAB) calc'd for $\text{C}_{27}\text{H}_{32}\text{O}_2\text{P}$ $[\text{M-I}]^+$ 419.2140, found 419.2134.

5-thio-(1'-phenyl-5'-thiotetrazole)-valeric acid, *t*-butyl ester⁹ (**S53**)

Wash 35% KH in oil (4.1632 g, 36.3 mmol) three times with anhydrous hexanes, then suspend in anhydrous THF (30.0 mL) and cool to -78 °C. 1-Phenyl-5-thiotetrazole (6.3807 g, 35.8 mmol) in THF (30.0 mL) was added and the solution was allowed to warm slowly until all

⁸ Allevi, P.; Ciuffreda, P.; Tarocco, G.; Anastasia, M. *Tetrahedron: Asymmetry* **1995**, 6, 2357-2364.

⁹ Blakemore, P. R.; Cole, W. J.; Kocienski, P. J.; Morley, A. *Synlett* **1998**, 26-28.

solid dissolved. The yellow solution was then recooled to -78 °C and **S52** (6.5686 g, 23.1 mmol) was added as a solution in THF (15.0 mL). The solution was maintained at -78 °C for 30 min then allowed to warm to RT overnight. After 18 h the solution was diluted with water (300 mL) and the aqueous layer extracted with DCM (3x 300 mL). The combined organics were dried over brine then Na₂SO₄ and concentrated in vacuo to a yellow oil which was purified by silica chromatography eluting with 30% EtOAc/70% hexanes to yield **S53** as a pale yellow oil (4.20 g, 54%). ¹H NMR (300 MHz, CDCl₃): δ 7.54 (br m, Ph), 3.38 (t, *J* = 7.1 Hz, H-2), 2.24 (t, *J* = 7.2 Hz, H-5), 1.83 (m, H-3), 1.72 (m, H-4), and 1.41 (s, *t*-Bu) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 172.5 (C-1), 130.08 (*p*-Ph), 129.8 (*o*- or *m*-Ph), 123.8 (*o*- or *m*-Ph), 80.4 (C-Me₃) 34.7 (C-2 or C-4), 32.9 (C-2 or C-4), 28.4 (C-5), 28.1 (3 Me), 23.9 (C-3) ppm. IR (NaCl): ν 3071, 2976, 1725, 1593, 1503, 1160 cm⁻¹. MS (FAB) calc'd for C₁₆H₂₃N₄O₂S [M+H]⁺ 335.1542, found 335.1543.

5-sulfonyl-(1'-phenyl-5'-sulfonyltetrazole)-valeric acid, *t*-butyl ester¹⁰ (**15**)

Ammonium molybdate tetrahydrate (1.3028 g, 1.05 mmol) dissolved in 30% hydrogen peroxide (14.2686 g, 126 mmol) to give a bright yellow solution. **S53** (3.66 g, 9.99 mmol) was added as a solution in EtOH (60 mL). Stir at RT 18 h then heat to reflux until NMR aliquot shows complete reaction. Cool to Rt then dilute with water (300 mL) and extract aqueous layer with EtOAc (3x 350 mL). The combined organic layers were dried with brine, then Na₂SO₄ and concentrated in vacuo to give **15** as a pale yellow oil (3.8492 g, 96%). ¹H NMR (300 MHz, CDCl₃): δ 7.68 (m, *o*- or *m*-Ph), 7.60 (m, *o*- or *m*-Ph and *p*-Ph), 3.74 (dt, *J* = 7.8, 2.0 Hz, H-2), 2.28 (dt, *J* = 7.4, 2.4 Hz, H-5), 1.99 (p, *J* = 7.4 Hz, H-3), 1.78 (p, *J* = 7.4 Hz, H-4), and 1.43 (s, *t*-Bu) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 171.9 (C-1), 153 (C-5'), 133.0 (*i*-Ph), 131.5 (*p*-Ph),

¹⁰ Fuerstner, A.; Feyen, F.; Prinz, H.; Waldmann, H. *Tetrahedron* **2004**, *60*, 9543-9558.

129.7 (*o*- or *m*-Ph), 125.04 (*o*- or *m*-Ph), 80.7 (C-Me₃), 55.7 (C-5) 34.6 (C-2), 28.1 (3 Me), 23.5 (C-3 or C-4), and 21.6 (C-3 or C-4) ppm. IR (NaCl): ν 3072, 2978, 2933, 2879, 1726, 1595, 1342, 1153, 763 cm⁻¹. MS (EI) calc'd for C₁₆H₂₆N₅O₄S [M+NH₄]⁺ 384.1722, found 394.1709.

General Procedure for Formation of *Z*-alkenes:¹¹

After drying four times from anhydrous THF/toluene **14** was dissolved in anhydrous THF to form a 25 mg/mL solution. 3.5 mL of the **14** solution (87.5 mg, 0.160 mmol) was cooled to -78 °C and 2.0 M NaHMDS in THF (0.11 mL, 0.22 mmol) was added. The orange solution was stirred for 40 min and aldehyde (39.3 mg, 0.144) in 0.25 mL THF was added and the solution was allowed to warm to RT over 16 h. The resulting yellow solution was diluted with water (10.0 mL) and extracted with DCM (3x 5.0 mL). The combined organic layers were dried over brine then Na₂SO₄ and concentrated in vacuo to a yellow oil, which was purified by silica chromatography eluting with a gradient of 2.5% EtOAc/97.5% hexanes, 5% EtOAc/95% hexanes, to 20% EtOAc/80%hexanes. Yield **S25** 16.3 mg, (30% over 2 steps) of colorless oil.

(5*Z*,7*R*,8*S*,9*S*,10*R*)-7,8:9,10-di-*O*-isopropylidene-7,8,9,10-tetraoxo-tridec-5-enoic acid, *t*-butyl ester (**S25**) as colorless oil (16.3 mg, 30% over 2 steps).

¹H NMR (400 MHz, CDCl₃): δ 5.67 (dt, *J*= 11.0, 8.0 Hz, H-5), 5.38 (ddt, *J*= 11.0, 8.6, 1.5 Hz, H-6), 4.79 (td, *J*= 8.6, 0.8 Hz, H-7), 4.02 (ddd, *J*= 8.4, 6.4, 5.2 Hz, H-10), 3.53 (dd, *J*= 8.6, 2.4 Hz, H-8), 3.45 (dd, *J*=8.4, 2.4 Hz, H-9), 2.21 (t, *J*= 7.8 Hz, H-2), 2.20 (m, H-2', H-4), 2.12 (hep. d, *J*= 7.2, 1.2 Hz, H-4'), 1.65 (m, H-3, H-3'), 1.46 (m, H-11, H-11'), 1.41 (s, *t*-Bu), 1.40 (m, H-12), 1.39 (s, Me), 1.37 (s, Me), 1.37 (s, Me), 1.36 (m, H-12'), and 0.91 (t, *J*= 6.8 Hz, H-13) ppm.

¹¹ Crombie, L.; Hemesley, P.; Pattenden, G. *J. Chem. Soc. Sect. C: Org.* **1969**, 1024-1027.

^{13}C NMR (75 MHz, CDCl_3): δ 172.7 (C-1), 135.8 (C-5), 126.5 (C-6), 109.1 (C-Me₂), 108.5 (C-Me₂), 80.1 (C-Me₃), 79.4 (C-8), 78.5 (C-9), 76.9 (C-10), 73.0 (C-7), 35.0 (C-2), 34.9 (C-12), 28.1 (3 Me), 27.5 (3 Me), 27.4 (C-4), 27.2 (Me), 26.53 (Me), 26.48 (Me), 24.9 (C-3), 19.3 (C-11), and 14.13 (C-13) ppm. IR (NaCl): ν 2983, 2934, 2872, 1732, 1457, 1369, 1249, 1167, 1057, 891 cm^{-1} . MS (FAB) calc'd for $\text{C}_{23}\text{H}_{40}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$ 435.2723, found 435.2710. $[\alpha_D]^{25} +31.4$ [c 1.21, CH_2Cl_2].

(5*Z*,7*R*,8*S*,9*S*,10*S*)-7,8:9,10-di-*O*-isopropylidene-7,8,9,10-tetraoxo-tridec-5-enoic acid, *t*-butyl ester (**S27**) as a colorless glass (3.2 mg, 34% over 2 steps).

^1H NMR (400 MHz, CDCl_3): δ 5.66 (dtd, J = 10.8, 7.2, <1.0 Hz, H-5), 5.36 (ddt, J = 10.8, 9.0, 1.2 Hz, H-6), 4.68 (td, J =9.0, 1.2 Hz, H-7), 4.15 (ddd, J = 10.0, 6.5, 3.6 Hz, H-10), 3.85 (dd, J = 6.5, 2.0 Hz, H-9), 3.50 (dd, J =9.0, 2.0 Hz, H-8), 2.24 (dt, J =7.6, 1.2 Hz, H-2), 2.21 (m, H-4), 2.12 (hep. d, J = 7.2, 1.6 Hz, H-4'), 1.75 (m, H-11), 1.66 (pent. J = 7.2 Hz, H-3, H-3'), 1.54 (s, Me), 1.50 (s, Me), 1.45 (m, H-11', H-12, H-12'), 1.42 (s, *t*-Bu), 1.40 (s, Me), 1.33 (s, Me), and 0.93 (t, J =7.2 Hz, H-13) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 172.8 (C-1), 135.7 (C-5), 126.8 (C-6), 109.4 (C-Me₂), 108.3 (C-Me₂), 80.1 (C-Me₃), 79.3 (C-8), 76.7 (C-10), 74.6 (C-9), 73.3 (C-7), 35.0 (C-2), 31.8 (C-11), 28.1 (3 Me), 27.3 (Me), 27.1 (Me), 27.0 (Me), 26.9 (Me), 25.6 (Me), 25.0 (C-3), 20.0 (C-12), and 14.1 (C-13) ppm. IR (NaCl): ν 2982, 2935, 2872, 1731, 1378, 1253, 1217, 1151, 1061 cm^{-1} . MS (FAB) calc'd for $\text{C}_{23}\text{H}_{40}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$ 435.2723, found 435.2717. $[\alpha_D]^{25} -1.9$ [c 0.32, CH_2Cl_2].

(5*Z*,7*R*,8*R*,9*S*,10*R*)-7,8:9,10-di-*O*-isopropylidene-7,8,9,10-tetraoxo-tridec-5-enoic acid, *t*-butyl ester (**13**) as a colorless glass (193.0 mg, 0.468 mmol, 51%)

^1H NMR (400 MHz, CDCl_3): δ 5.60 (dt, $J=11.2, 7.4$ Hz, H-5), 5.51 (dd, $J=11.0, 9.4$ Hz, H-6), 4.93 (dd, $J= 9.0, 5.8$ Hz, H-7), 3.98 (dd, $J= 9.0, 5.8$ Hz, H-8), 3.93 (td, 7.6, 3.2 Hz, H-10), 3.58 (dd, $J= 9.0, 7.4$ Hz, H-9), 2.19 (td, $J=7.6, 2.7$ Hz, H-2), 2.13 (dt, $J= 7.2, 7.0$ Hz, H-2'), 1.67 (m, H-3, H-3', H-11, H-11'), 1.45 (m, H-12, H-12'), 1.42 (s, Me), 1.40 (s, 3Me), 1.32 (s, Me), 1.30 (s, 2 Me), and 0.91 (t, $J= 7.0$ Hz, H-13) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 172.9 (C-1), 133.9 (C-5), 125.5 (C-6), 108.65 (C-Me₂), 108.58 (C-Me₂), 80.6 (C-10), 80.0 (C-Me₃), 79.7 (C-8), 77.6 (C-9), 73.6 (C-7), 35.9 (C-2), 34.9 (C-11), 28.1 (3 Me), 28.0 (C-4), 27.4 (Me), 27.4 (Me), 27.0 (Me), 25.5 (Me), 24.7 (C-3), 19.3 (C-12), and 14.1 (C-13) ppm. IR (NaCl): ν 2986, 2870, 1730, 1450, 1366, 1150, 1055 cm^{-1} . MS (EI) calc'd for $\text{C}_{23}\text{H}_{40}\text{O}_6$ $[\text{M}]^+$ 412.2824, found 412.2826. $[\alpha]_{\text{D}}^{30}$ -3.24 [c 0.93, CHCl_3].

General Procedure for Formation of *E*-Alkenes:¹²

Dissolve **15** (200.5 mg, 5.47 mmol) in anhydrous DME (4.0 mL) and cool to -78 $^{\circ}\text{C}$; add 2.0 M NaHMDS in THF (0.26 mL, 0.52 mmol) and warm until all solid dissolves. Recool bright yellow solution to -78 $^{\circ}\text{C}$ and add aldehyde (56.3 mg, 2.07 mmol) in 1.0 mL DME. Allow solution to warm slowly to RT over 12 h. Dilute pale yellow solution with water (60 mL) and extract aqueous layer with DCM (3x 35 mL). The combined organics were dried over brine, then Na_2SO_4 , and the dried in vacuo to a yellow oil. Purification by elution through a silica cartridge (12 g) eluting with 2.5% EtOAc/97.5%hexanes then 5%EtOAc/95%hexanes gives the mixed alkene **S24** and **S25** (de 1.8:1 *E:Z*) as a colorless oil (39.0 mg, 46%). The diastereomers were separable by silica HPLC eluting with 5% EtOAc/95%hexanes.

¹² Blakemore, P. R.; Cole, W. J.; Kocienski, P. J.; Morley, A. *Synlett* **1998**, 26-28. Baudin, J. B.; Julia, S. A.; Ruel, O.; Wang, Y. *Tetrahedron Lett.* **1990**, 31, 213-216. Kocienski, P. J.; Lythgoe, B.; Ruston, S. *J. Chem. Soc., Perkin Trans. 1* **1978**, 829-834.

(5*E*,7*R*,8*S*,9*S*,10*R*)-7,8:9,10-di-*O*-isopropylidene-7,8,9,10-tetraoxo-tridec-5-enoic acid, *t*-butyl ester (**S24**) as a colorless oil (25.1 mg, 29.6%).

¹H NMR (300 MHz, CDCl₃): δ 5.84 (dt, *J*= 15.2, 7.0 Hz, H-5), 5.44 (ddt, *J*= 15.2, 8.3, 1.4 Hz, H-6), 4.39 (t, *J*= 8.3 Hz, H-7), 4.01 (m, H-10), 3.61 (dd, *J*=8.3, 3.2 Hz, H-8), 3.56 (dd, *J*=8.3, 3.2 Hz, H-9), 2.22 (t, *J*=7.5 Hz, H-2, H-2'), 2.01 (ddd, *J*=14.5, 7.0, 1.2 Hz, H-4, H-4'), 1.70 (dd, *J*=14.5, 7.5, H-3, H-3'), 1.52 (m, H-11, H-11', H-12, H-12'), 1.44 (s, *t*-Bu), 1.44 (s, Me), 1.42 (s, Me), 1.41 (s, Me), 1.39 (s, Me), and 0.94 (t, *J*=6.8 Hz, H-13) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 172.7 (C-1), 136.2 (C-5), 127.2 (C-6), 109.0 (C-Me₂), 108.8 (C-Me₂), 79.9 (C-8), 79.3 (C-9), 78.4 (C-7), 76.9 (C-10), 35.2 (C-11), 34.8 (C-2), 31.6 (C-4), 28.1 (3 Me), 27.5 (Me), 27.2 (Me), 26.6 (Me), 26.5 (Me), 24.2 (C-3), 19.3 (C-12), and 14.1 (C-13) ppm. IR (NaCl): ν 2983, 2934, 2873, 1732, 1379, 1251, 1220, 1167 cm⁻¹. MS (FAB) calc'd for C₂₃H₄₀O₆Na [M+Na]⁺ 435.2723, found 435.2707. [α_D]²⁶ +29.0 [c 1.63, CH₂Cl₂].

(5*E*,7*R*,8*S*,9*S*,10*S*)-7,8:9,10-di-*O*-isopropylidene-7,8,9,10-tetraoxo-tridec-5-enoic acid, *t*-butyl ester (**S26**) as a colorless glass (*dr* 1.6:1 *E*:*Z*, 16.2 mg, 25%).

¹H NMR (400 MHz, CDCl₃): δ 5.83 (dt, *J*= 15.4, 6.8 Hz, H-5), 5.40 (ddm, *J*= 15.4, 8.4, <1.0 Hz, H-6), 4.29 (t, *J*= 8.4 Hz, H-7), 4.17 (ddd, *J*=9.6, 6.4, 4.0 Hz, H-10), 3.90 (dd, *J*= 6.4, 2.0 Hz, H-9), 3.53 (dd, *J*= 8.4, 2.0 Hz, H-8), 2.19 (t, *J*=7.6 Hz, H-2), 2.05 (q, *J*= 7.2 Hz, H-4), 1.74 (m, H-11), 1.66 (m, H-3, H-3', H-12, H-12'), 1.57 (s, Me), 1.50 (m, H-11'), 1.50 (s, Me), 1.42 (s, *t*-Bu), 1.40 (s, Me), 1.35 (s, Me), and 0.94 (t, *J*= 7.2 Hz, H-13) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 172.8 (C-1), 136.3 (C-5), 127.3 (C-6), 109.2 (C-Me₂), 108.4 (C-Me₂), 80.2 (C-Me₃), 79.1 (C-8), 78.9 (C-7), 76.8 (C-10), 74.7 (C-9), 34.9 (C-2), 31.66 (C-4 or C-11), 31.63 (C-4 or C-11), 28.1 (3

Me), 27.3 (Me), 27.0 (Me), 26.9 (Me), 25.7 (Me), 24.3 (C-3), 20.0 (C-12), and 14.1 (C-13) ppm.

IR (NaCl): ν 2982, 2934, 2872, 1731, 1459, 1378, 1255, 1216, 1152, 1059, 969 cm^{-1} . MS (FAB)

calc'd for $\text{C}_{23}\text{H}_{40}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$ 435.2723, found 435.2707. $[\alpha_D]^{24} +23.1$ [c 0.45, CH_2Cl_2].

(5*E*,7*R*,8*R*,9*S*,10*R*)-7,8:9,10-di-*O*-isopropylidene-7,8,9,10-tetraoxo-tridec-5-enoic acid, *t*-butyl ester (**12**) as a colorless glass (*dr* 3.0:1 *E:Z*, 25%).

^1H NMR (400 MHz, CDCl_3): δ 5.73 (dt, J = 15.2, 6.5 Hz, H-5), 5.54 (dd, J = 15.2, 7.6 Hz, H-6), 4.61 (t, J = 13.2 Hz, H-7), 3.97 (dd, J = 8.8, 6.2 Hz, H-8), 3.91 (td, J = 7.8, 3.1 Hz, H-10), 3.56 (dd, J = 9.2, 7.6 Hz, H-9), 2.20 (td, J = 9.2, 6.7 Hz, H-2, H-2'), 2.10 (m, H-4, H-4'), 1.69 (m, H-3, H-3', H-11), 1.45 (m, H-11', H-12, H-12'), 1.42 (s, Me), 1.41 (s, 3 Me), 1.32 (s, 2 Me), 1.31 (s, Me), and 0.91 (t, J = 7.0 Hz, H-13) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 173.1 (C-1), 133.7 (C-5), 126.1 (C-6), 108.6 (C-Me₂), 108.5 (C-Me₂), 80.7 (C-10), 80.0 (C-Me₃), 79.8 (C-8), 78.9 (C-7), 77.6 (C-9), 35.9 (C-11), 34.7 (C-2), 31.5 (C-4), 28.1 (3 Me), 27.8 (Me), 27.4 (Me), 27.1 (Me), 25.4 (Me), 24.2 (C-3), 19.3 (C-12), and 14.1 (C-13) ppm. IR (NaCl): ν 2986, 2933, 1735, 1377, 1213, 1049 cm^{-1} . MS (EI) calc'd for $\text{C}_{23}\text{H}_{40}\text{O}_6$ $[\text{M}]^+$ 412.2824, found 412.2815. $[\alpha_D]^{29} +3.74$ [c 0.67, CHCl_3].

(5*E*,7*R*,8*R*,9*S*,10*S*)-7,9:8,10-di-*O*-isopropylidene-7,8,9,10-tetraoxo-tridec-5-enoic acid, *t*-butyl ester (**S44**) as an amorphous solid (*dr* 2.0:1, 69%).

^1H NMR (400 MHz, CDCl_3): δ 5.70 (dtd, J = 15.2, 7.3, 1.2 Hz, H-5), 5.38 (ddt, J = 15.2, 6.4, 1.6 Hz, H-6), 4.09 (td, J = 6.4, 2.0 Hz, H-7), 3.66 (m, H-10), 3.34 (dd, J = 6.0, 2.2 Hz, H-8, H-9), 2.16 (m, H-2, H-2'), 2.07 (m, H-4, H-4'), 1.63 (m, H-3, H-3', H-11, H-11'), 1.48 (s, Me), 1.43 (s, Me), 1.40 (s, 3 Me), 1.37 (s, Me), 1.33 (s, Me), 1.28 (m, H-12, H-12'), and 0.92 (t, J = 7.2 Hz, H-

13) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 172.9 (C-1), 134.3 (C-5), 128.5 (C-6), 99.9 (C-Me₂), 99.7 (C-Me₂), 79.9 (C-Me₃), 72.8 (C-7), 71.9 (C-10), 71.5 (C-8 or C-9), 71.4 (C-8 or C-9), 35.5 (C-2), 33.5 (C-11), 31.6 (C-4), 29.53 (Me), 29.50 (Me), 28.1 (3 Me), 24.1 (C-3), 19.9 (Me), 19.8 (Me), 17.9 (C-12), and 14.0 (C-13) ppm. IR (NaCl): ν 2997, 2939, 1725, 1376, 1160 cm^{-1} . MS (EI) calc'd for $\text{C}_{23}\text{H}_{40}\text{O}_6$ $[\text{M}]^+$ 412.2824, found 412.2816. $[\alpha_D]^{30^\circ}$ -14.38 [c 1.26, CHCl_3].

(5*Z*,7*R*,8*R*,9*S*,10*S*)-7,9:8,10-di-*O*-isopropylidene-7,8,9,10-tetraoxo-tridec-5-enoic acid, *t*-butyl ester (**S45**) as an amorphous solid

^1H NMR (400 MHz, CDCl_3): δ 5.63 (dtd, J = 10.8, 7.6, 0.8 Hz, H-5), 5.29 (ddt, J =10.8, 8.2, 1.4 Hz, H-6), 4.45 (tm, J = 8.2, 1.2 Hz, H-7), 3.67 (ddt, J = 8.2, 6.6, 2.4 Hz, H-10), 3.37 (dt, J = 8.8, 6.6 Hz, H-8, H-9), 2.20 (t, J = 7.6 Hz, H-2, H-2'), 2.11 (m, H-4, H-4'), 1.63 (m, H-3, H-3'), 1.52 (s, Me), 1.43 (s, Me), 1.42 (m, H-11, H-11', H-12), 1.41 (s, 3 Me), 1.37 (s, Me), 1.32 (s, Me), 1.30 (m, H-12'), and 0.88 (t, J = 7.2 Hz, H-13) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 173.0 (C-1), 135.2 (C-5), 127.4 (C-6), 99.9 (C-Me₂), 99.7 (C-Me₂), 79.9 (C-Me₃), 71.7 (C-10), 71.6 (C-7 or C-8), 71.3 (C-7 or C-8), 68.5 (C-7), 34.9 (C-2), 33.5 (C-11), 29.6 (Me), 29.4 (Me), 28.1 (3 Me), 27.6 (C-4), 24.7 (C-3), 19.5 (Me), 19.8 (Me), 17.9 (C-12), and 14.0 (C-13) ppm. IR (NaCl): ν 2992, 2939, 1725, 1371, 1150, 1076, 906 cm^{-1} . MS (EI) calc'd for $\text{C}_{23}\text{H}_{40}\text{O}_6$ $[\text{M}]^+$ 412.2824, found 412.2816. $[\alpha_D]^{30^\circ}$ -14.47 [c 0.51, CHCl_3].

General Procedures for Synthesis of the Diols:

Method A:¹³ Mix potassium ferricyanide (102.4 mg, 0.311 mmol) potassium carbonate (43.1 mg, 0.311 mmol), DHQ(D)₂PHAL (2.0 mg, 2.57 μ mol) and dissolve in *t*-BuOH (500 μ L) and water (500 μ L). Add OsO₄ (2.5% w/w in *t*-BuOH) (10.0 μ L, 0.798 μ mol) and stir biphasic mixture at RT for 20 min. Cool to 0 °C (some inorganic salts ppt) and add NH₂SO₂CH₃ (15.3 mg, 0.161 mmol) and add alkene (41.2 mg, 0.0999 mmol) in *t*-BuOH (150 μ L). Stir the mixture vigorously for 2 hours at 0 °C then allow it to warm to RT and continue stirring for 48 hours. Add additional potassium ferricyanide (110.3 mg, 0.335 mmol), potassium carbonate (80.0 mg, 0.579 mmol), DHQ(D)₂PHAL (4.8 mg, 6.16 μ mol), NH₂SO₂CH₃ (15.9 mg, 0.167 mmol), OsO₄ (20.0 μ L, 0.160 μ mol), and water (500 μ L) and stir for 9 h. Add sodium bisulfite (524.3 mg, 5.04 mmol), mixture bubbles upon addition of bisulfite, and stir at RT for 45 min and yellow-orange solution turns blue-purple. Dilute with water (3 mL) and extract with DCM (3x 2.0 mL). The organic layer was washed with 2N KOH, dried over brine then Na₂SO₄, and conc. in vacuo to give a clear oil. The residue was purified by silica chromatography eluting with 50% EtOAc/50%hexanes to give the mixed diol as a clear oil (38.1 mg, 85.4%). The diastereomers were separable by SiO₂-HPLC eluting with 2:1 hexane:EtOAc.

Method B:¹⁴ Dissolve alkene (1.5 mg, 3.64 μ mol) and *N*-methyl-morpholine-*N*-oxide (5.1 mg, 43.5 μ mol) in acetone (100 μ L) and water (50 μ L). Add OsO₄ (2.5% w/w in *t*-BuOH) (2.0 μ L, 0.0160 μ mol) and stir at room temperature. After 24 hours add additional NMO (11.7 mg, 99.8 μ mol), and stir for another 24 h. Quench reaction by adding Na₂S₂O₄ (40.0 mg, 231.1

¹³ Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483-2547.

¹⁴ Van Rheenen, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, 1973-1976.

μmol) and stir for an hour. Dilute with water (2 mL) and extract with DCM (3x 2.0 mL). The organic layer was dried over brine then Na_2SO_4 , and conc. in vacuo to give a clear oil. The residue was purified by silica chromatography eluting with 50% EtOAc/50%hexanes to give the mixed diol as a clear oil (1.2 mg, 74%). The diastereomers were separable by SiO_2 -HPLC eluting with 2:1 hexane:EtOAc.

Method A DHQD₂PHAL:

(5*R*,6*S*,7*R*,8*S*,9*S*,10*R*)-5,6-dihydroxy-7,8:9,10-di-*O*-isopropylidene-5,6,7,8,9,10-hexaoxo-tridecanoic acid, *t*-butyl ester (**S28**) as a colorless glass (*dr* 3.5:1, 79%).

^1H NMR (400 MHz, CDCl_3): δ 4.12 (dd, J = 2.8, 1.6 Hz, H-7), 4.09 (m, H-10), 4.04 (m, H-8), 3.78 (ddt, J = 7.8, 5.4, 2.6 Hz, H-5), 3.58 (dd, J = 8.4, 1.6 Hz, H-9), 3.38 (ddd, J = 10.2, 2.0, 1.4 Hz, H-6), 2.83 (d, J = 2.4 Hz, OH-5), 2.56 (d, J = 10.4 Hz, OH-6), 2.25 (m, H-2, H-2'), 1.74 (m, H-3, H-4, H-4'), 1.63 (m, H-3', H-11), 1.52 (m, H-11', H-12), 1.45 (m, H-12'), 1.42 (s, *t*-Bu), 1.40 (s, Me), 1.39 (s, Me), 1.39 (s, Me), 1.36 (s, Me), and 0.93 (t, J = 7.2 Hz, H-13) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 173.0 (C-1), 109.9 (C-Me₂), 108.7 (C-Me₂), 80.2 (C-Me₃), 80.0 (C-5), 78.8 (C-7), 76.8 (C-8), 75.2 (C-10), 73.3 (C-6), 69.6 (C-9), 35.2 (C-11), 35.0 (C-2), 28.1 (3 Me), 27.5 (Me), 27.1 (Me), 26.8 (Me), 26.5 (Me), 21.2 (C-3), 19.3 (C-12), and 14.1 (C-13) ppm. IR (NaCl): ν 3465, 2983, 2934, 2874, 1731, 1458, 1368, 1251, 1218, 1166, 890 cm^{-1} . MS (FAB) calc'd for $\text{C}_{23}\text{H}_{43}\text{O}_8$ $[\text{M}+\text{H}]^+$ 447.2958, found 447.2973. $[\alpha_D]^{26} +35.8$ [c 0.97, CH_2Cl_2].

Method A DHQ₂PHAL: as a colorless glass (*dr* 1.4:1 **S29:S30**, 92%,)

(5*R*,6*R*,7*R*,8*S*,9*S*,10*R*)-5,6-dihydroxy-7,8:9,10-di-*O*-isopropylidene-5,6,7,8,9,10-hexaoxo-tridecanoic acid, *t*-butyl ester (**S29**)

^1H NMR (400 MHz, CDCl_3): δ 4.12 (dd, J = 7.8, 6.6 Hz, H-7), 4.08 (dd, J =7.8, 2.2 Hz, H-8), 4.06 (dt, J = 8.2, 4.0 Hz, H-10), 3.84 (dd, J = 8.2, 2.2 Hz, H-9), 3.73 (ddd, J = 9.0, 6.6, 3.6 Hz, H-5), 3.64 (td, J = 6.6, 3.6 Hz, H-7), 2.72 (dd, J = 3.6, 1.2 Hz, OH-5 and OH-6), 2.27 (td, J = 7.0, 1.2 Hz, H-2, H-2'), 1.79 (m, H-3, H-3', H-4), 1.67 (m, H-4', H-11, H-11'), 1.55 (m, H-12, H-12'), 1.43 (s, *t*-Bu), 1.39 (3 Me), 1.38 (Me), and 0.93 (t, J = 7.0 Hz, H-13) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 173.5 (C-1), 109.4 (C-Me₂), 108.6 (C-Me₂), 79.5 (C-9), 77.8 (C-7, C-8, or C-10), 77.6 (C-7, C-8 or C-10), 77.2 (C-7, C-8 or C-10), 74.5 (C-6), 72.8 (C-5), 35.2 (C-2 or C-11), 35.1 (C-2 or C-11), 31.0 (C-4), 28.1 (3 Me), 27.5 (Me), 27.2 (Me), 26.7 (Me), 26.65 (Me), 20.4 (C-3), 19.3 (C-12), and 14.2 (C-13) ppm. IR (NaCl): ν 3459, 2983, 2935, 2874, 1731, 1379, 1251, 1167 cm^{-1} . MS (FAB) calc'd for $\text{C}_{23}\text{H}_{43}\text{O}_8$ $[\text{M}+\text{H}]^+$ 447.2958, found 447.2953. $[\alpha]_{\text{D}}^{28} +28.6$ [*c* 1.55, CH_2Cl_2].

(5*S*,6*S*,7*R*,8*S*,9*S*,10*R*)-5,6-dihydroxy-7,8:9,10-di-*O*-isopropylidene-5,6,7,8,9,10-hexaoxo-tridecanoic acid, *t*-butyl ester (**S30**)

^1H NMR (400 MHz, CDCl_3): δ 4.29 (dd, J = 8.4, 1.6 Hz, H-7), 4.13 (dd, J = 8.4, 2.4 Hz, H-8), 4.06 (td, J =11.6, 3.6 Hz, H-10), 3.63 (br m, J =7.2 Hz, H-5), 3.59 (dd, J = 8.4, 2.4 Hz, H-9), 3.38 (ddd, J = 7.6, 6.0, 1.6 Hz, H-6), 2.60 (d, J =10.4, OH-6), 2.34 (d br, J = 8.0 Hz, OH-5), 2.27 (t, J =7.0 Hz, H-2, H-2'), 1.84 (m, H-3), 1.68 (m, H-3', H-4, H-4'), 1.53 (m, H-11, H-11', H-12), 1.45 (m, H-12'), 1.43 (s, *t*-Bu), 1.41 (s, Me), 1.39 (s, Me), 1.39 (s, Me) 1.36 (s, Me), and 0.92 (t, J = 7.0 Hz, H-13) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 173.1 (C-1), 109.7 (C-Me₂), 108.7 (C-Me₂), 80.3 (C-Me₃), 79.0 (C-9), 76.9 (C-10), 76.8 (C-7), 75.5 (C-8), 73.6 (C-5), 70.4 (C-6), 35.2 (C-2), 35.0 (C-11), 33.1 (C-4), 28.1 (3 Me), 27.5 (Me), 27.1 (Me), 26.8 (Me), 26.5 (Me), 21.1

(C-3), 19.3 (C-12), and 14.1 (C-13) ppm. IR (NaCl): ν 3492, 2934, 2874, 1731, 1380, 1250, 1166 cm^{-1} . $[\alpha_D]^{29} +35.0$ [c 0.92, CH_2Cl_2].

Method A DHQD₂PHAL:

(5*R*,6*S*,7*R*,8*S*,9*S*,10*S*)-5,6-dihydroxy-7,8:9,10-di-*O*-isopropylidene-5,6,7,8,9,10-hexa-*oxo*-tridecanoic acid, *t*-butyl ester (**S31**) as a colorless glass (*dr* >20:1, 84%).

¹H NMR (400 MHz, CDCl_3): δ 4.24 (ddd, J = 10.0, 6.6, 3.6, H-10), 4.05 (dd, J =9.2, <1.0 Hz, H-8), 4.01 (dd, J = 9.2, 1.2 Hz, H-7), 3.97 (br d, J = 6.6 Hz, H-9), 3.79 (m, H-5), 3.35 (br d, J =10.4, H-6), 2.90 (br s, OH-5), 2.55 (d, J = 10.4 Hz, OH-6), 2.24 (t, J =7.2 Hz, H-2, H-2'), 1.74 (m, H-11), 1.59 (m, H-3, H-4, H-4', H-11'), 1.56 (s, Me), 1.49 (s, Me), 1.45 (m, H-3', H-12, H-12'), 1.42 (s, *t*-Bu), 1.38 (s, Me), 1.34 (s, Me), and 0.95 (t, J = 7.2 Hz, H-13) ppm. ¹³C NMR (100 MHz, CDCl_3): δ 173.0 (C-1), 109.8 (C-Me₂), 108.5 (C-Me₂), 80.2 (C-Me₃), 80.1 (C-7), 76.9 (C-10), 75.2 (C-8), 74.3 (C-9), 73.4 (C-5), 69.0 (C-6), 35.2 (C-2), 32.5 (C-4), 28.1 (3 Me), 27.1 (Me) 26.9 (Me), 26.6 (Me), 25.5 (Me), 21.2 (C-3), 20.2 (C-12), and 14.0 (C-13) ppm. IR (NaCl): ν 3456, 2981, 2873, 1730, 1457, 1368, 1256, 1215, 1167, 1116 cm^{-1} . MS (FAB) calc'd for $\text{C}_{23}\text{H}_{43}\text{O}_8$ $[\text{M}+\text{H}]^+$ 447.2958, found 447.2945. $[\alpha_D]^{26} +26.8$ [c 0.42, CH_2Cl_2].

Method A DHQ₂PHAL: as a colorless glass (*dr* 2.4:1 **S32:S33**, 84%)

(5*R*,6*R*,7*R*,8*S*,9*S*,10*S*)-5,6-dihydroxy-7,8:9,10-di-*O*-isopropylidene-5,6,7,8,9,10-hexa-*oxo*-tridecanoic acid, *t*-butyl ester (**S32**)

¹H NMR (400 MHz, CDCl_3): δ 4.32 (dd, J = 6.8, 1.0 Hz, H-9), 4.21 (ddd, J = 10.0, 6.8, 4.0 Hz, H-10), 3.98 (t, J = 7.6 Hz, H-7), 3.92 (dd, J = 7.6, 1.0 Hz, H-8), 3.75 (ddt, J = 8.8, 6.0, 2.2 Hz, H-5), 3.63 (ddd, J = 7.6, 6.0, 4.0 Hz, H-6), 2.78 (d, J =2.2 Hz, OH-5), 2.59 (d, J = 4.0 Hz, OH-6), 2.27

(m, H-2, H-2'), 1.83 (m, H-11), 1.75 (m, H-3, H-3'), 1.62 (m, H-11', H-12), 1.55 (m, H-4, H-4'), 1.38 (m, H-12'), 1.50 (s, Me), 1.43 (s, *t*-Bu, Me), 1.36 (s, Me), 1.34 (s, Me), and 0.95 (t, $J=6.8$ Hz, H-13) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 173.7 (C-1), 109.5 (C-Me₂), 108.2 (C-Me₂), 80.6 (C-Me₃), 78.6 (C-8), 77.6 (C-7), 76.8 (C-10), 75.7 (C-9), 74.9 (C-6), 73.9 (C-5), 34.9 (C-2), 31.6 (C-11), 30.7 (C-4), 28.1 (3 Me), 27.1 (Me), 27.0 (Me), 26.7 (Me), 25.5 (Me), 20.3 (C-3), 20.0 (C-12), and 14.1 (C-13) ppm. IR (NaCl): ν 3454, 2981, 2962, 2935, 2916, 2873, 1730, 1379, 1367, 1255, 1215, 1167, 1153, 1115, 1066, 1034 cm^{-1} . MS (FAB) calc'd for $\text{C}_{23}\text{H}_{43}\text{O}_8$ $[\text{M}+\text{H}]^+$ 447.2958, found 447.2968. $[\alpha_D]^{30} +19.2$ [c 0.24, CH_2Cl_2].

(5*S*,6*S*,7*R*,8*S*,9*S*,10*S*)-5,6-dihydroxy-7,8:9,10-di-*O*-isopropylidene-5,6,7,8,9,10-hexaoxo-tridecanoic acid, *t*-butyl ester (**S33**)

^1H NMR (400 MHz, CDCl_3): δ 4.22 (ddd, $J=10.0, 6.8, 3.6$ Hz, H-10), 4.15 (dd, $J=9.0, 1.2$ Hz, H-8), 4.04 (dd, $J=9.0, 1.0$ Hz, H-7), 3.94 (dd, $J=6.8, 1.2$ Hz, H-9), 3.65 (m, $J=9.2, 2.8$ Hz, H-5), 3.36 (ddd, $J=10.4, 5.2, 1.2$ Hz, H-6), 2.65 (d, $J=10.4$ Hz, OH-6), 2.34 (d, $J=9.2$ Hz, OH-5), 2.27 (t, $J=7.2$ Hz, H-2, H-2'), 1.81 (m, H-4), 1.75 (m, H-3, H-3'), 1.65 (m, H-4', H-11, H-11'), 1.45 (m, H12, H12'), 1.49 (s, Me), 1.43 (s, *t*-Bu), 1.41 (s, Me), 1.38 (s, Me), 1.33 (s, Me), and 0.94 (t, $J=7.2$ Hz, H-13) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 173.1 (C-1), 109.7 (C-Me₂), 108.4 (C-Me₂), 80.3 (C-Me₃), 76.9 (C-10), 76.8 (C-8), 75.2 (C-7), 74.4 (C-9), 74.0 (C-5), 69.7 (C-6), 35.2 (C-2), 33.1 (C-11), 31.6 (C-4), 28.1 (3 Me), 27.1 (Me), 27.0 (Me), 26.7 (Me), 25.5 (Me), 21.3 (C-3), 20.2 (C-12), and 14.1 (C-13) ppm. IR (NaCl): ν 3475, 2981, 2962, 2935, 2875, 1730, 1458, 1379, 1367, 1255, 1215, 1167, 1151, 1117, 1066, 1034 cm^{-1} . MS (FAB) calc'd for $\text{C}_{23}\text{H}_{43}\text{O}_8$ $[\text{M}+\text{H}]^+$ 447.2958, found 447.2948. $[\alpha_D]^{31} +41.8$ [c 0.11, CH_2Cl_2].

Method B: as a colorless glass (*dr* 4.9:1 **16:17**, 85%)

(5*S*,6*R*,7*R*,8*R*,9*S*,10*R*)-5,6-dihydroxy-7,8:9,10-di-*O*-isopropylidene-5,6,7,8,9,10-hexaoxo-tridecanoic acid, *t*-butyl ester (**16**)

¹H NMR (500 MHz, CDCl₃): δ 4.35 (dd, *J*=9.5, 5.5 Hz, H-7), 4.09 (dd, *J*= 9.5, 5.8 Hz, H-8), 4.02 (td, *J*= 8.0, 2.7 Hz, H-10), 3.74 (br m, H-5), 3.67 (m, H-6), 3.66 (dd, *J*= 9.8, 7.8 Hz, H-9), 2.26 (t, *J*= 7.3 Hz, H-2, H-2'), 1.78 (m, H-3), 1.65 (m, H-11, H'11', H-4, H-4'), 1.52 (m, H3', H-12, H-12'), 1.42 (s, 3Me), 1.40 (s, Me), 1.37 (s, Me), 1.36 (s, Me), 1.30 (s, Me), and 0.92 (t, *J*= 7.3 Hz, H-13) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 173.2 (C-1), 109.4 (C-Me₂), 109.1 (C-Me₂), 81.1 (C-10), 80.1 (C-Me₃), 79.2 (C-8), 77.1(C-7), 77.0 (C-9), 71.3 (C-5), 70.3 (C-6), 35.8 (C-4 or C-11), 35.5 (C-2), 33.3 (C-4 or C-11), 28.1 (3 Me), 27.9 (Me), 27.4 (Me), 26.8 (Me), 25.4 (Me), 21.6 (C-3), 19.2 (C-12), and 14.1 (C-13) ppm. IR (NaCl): ν 3481, 2940, 1735, 1366, 1155 cm⁻¹. MS (EI) calc'd for C₂₃H₄₃O₈ [M+H]⁺ 447.2958, found 447.2958. [α_D]^{25°} -13.51 [c 2.65, CHCl₃].

(5*R*,6*S*,7*R*,8*R*,9*S*,10*R*)-5,6-dihydroxy-7,8:9,10-di-*O*-isopropylidene-5,6,7,8,9,10-hexaoxo-tridecanoic acid, *t*-butyl ester (**17**)

¹H NMR (500 MHz, CDCl₃): δ 4.27 (dd, *J*= 6.0, 4.0 Hz, H-7), 4.04 (dd, *J*= 9.0, 6.0 Hz, H-8), 3.92 (td, *J*= 7.5, 3.0 Hz, H-10), 3.87 (t, *J*= 8.0 Hz, H-9), 3.81 (br s, H-6), 3.73 (m, H-5), 2.72 (br d, OH), 2.24 (t, *J*= 7.0 Hz, H-2, H-2'), 1.75 (m, H-3, H-4), 1.58 (m, H-3', H-11), 1.46 (m, H-4', H-11', H-12, H-12') 1.44 (s, Me), 1.423 (s, Me), 1.417 (s, 3 Me), 1.36 (s, Me), 1.33 (s, Me), and 0.92 (t, *J*= 7.3 Hz, H-13) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 173.1 (C-1), 109.0 (C-Me₂), 108.9 (C-Me₂), 81.3 (C-10), 80.1 (C-Me₃), 78.9 (C-8), 78.6 (C-7), 77.2 (C-9), 72.2 (C-5), 70.3 (C-6), 35.8 (C-4 or C-11), 35.4 (C-2), 32.9 (C-4 or C-11), 28.1 (3 Me), 27.4 (Me), 27.3 (Me), 27.1(Me), 25.1 (Me), 21.2 (C-3), 19.3 (C-12), and 14.1 (C-13) ppm. IR (NaCl): ν 3499, 2939,

1730 1366, 1150, 1055 cm^{-1} . MS (EI) calc'd for $\text{C}_{23}\text{H}_{43}\text{O}_8$ $[\text{M}+\text{H}]^+$ 447.2958, found 447.2943.
 $[\alpha_D]^{30^\circ} +13.14$ [c 0.47, CHCl_3].

Method B: as a colorless glass (*dr 1.4:1* **S46:S47**, 95%)

(5*S*,6*R*,7*R*,8*R*,9*S*,10*S*)-5,6-dihydroxy-7,9:8,10-di-*O*-isopropylidene-5,6,7,8,9,10-hexaoxo-tridecanoic acid, *t*-butyl ester (**S46**)

^1H NMR (300 MHz, CDCl_3): δ 3.88 (dd, $J=9.3, 4.8$ Hz, H-6 or H-9), 3.75 (m, H-5 and H-10), 3.72 (t, $J=9.3$ Hz, H-7 or H-8), 3.60 (dd, $J=5.0, 1.4$ Hz, H-7 or H-8), 3.41 (t, $J=9.5$ Hz, H-6 or H-9), 2.26 (t, $J=7.1$ Hz, H-2, H-2'), 1.8-1.5 (m, H-3, H-3', H-4, H-4', H-11, H-11'), 1.52 (s, Me), 1.51 (s, Me), 1.44 (s, 3 Me), 1.39 (s, 2 Me), 1.32 (m, H-12, H-12'), and 0.91 (t, $J=7.1$ Hz, H-13) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 173.0 (C-1), 100.4 (C-Me₂) 100.3 (C-Me₂), 80.1 (C-Me₃), 74.3 (C-7 or C-8), 72.7 (C-6 or C-9), 71.9 (C-7 or C-8), 70.8 (C-6 or C-9), 69.9 (C-5 or C-10), 69.4 (C-5 or C-10), 35.4 (C-2), 33.4 (C-4 or C-11), 32.9 (C-4 or C-11), 29.4 (Me), 29.3 (Me), 28.1 (3 Me), 21.5 (C-3), 20.0 (Me), 19.7 (Me), 17.8 (C-12), and 14.0 (C-13) ppm. IR (NaCl): ν 3509, 2939, 1730, 1361, 1150 cm^{-1} . MS (EI) calc'd for $\text{C}_{23}\text{H}_{43}\text{O}_8$ $[\text{M}+\text{H}]^+$ 447.2958, found 447.2957. $[\alpha_D]^{24^\circ} -9.42$ [c 1.04, CHCl_3].

(5*R*,6*S*,7*R*,8*R*,9*S*,10*S*)-5,6-dihydroxy-7,9:8,10-di-*O*-isopropylidene-5,6,7,8,9,10-hexaoxo-tridecanoic acid, *t*-butyl ester (**S47**)

^1H NMR (400 MHz, CDCl_3): δ 3.83 (m, H-7), 3.80 (t, $J=9.6$ Hz, H-8), 3.73 (m, H-10), 3.71 (m, H-5), 3.54 (br s, H-6), 3.37 (br t, 8.6 Hz, H-9), 2.25 (t, $J=6.9$ Hz, H-2, H-2'), 1.8-1.5 (m, H-3, H-3', H-4, H-4', H-11, H-11'), 1.51 (s, 2 Me), 1.44 (s, 3 Me), 1.39 (s, Me), 1.37 (s, Me), 1.32 (m,

H-12, H-12'), and 0.91 (t, J = 7.1 Hz, H-13) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 173.2 (C-1), 100.4 (C-Me₂), 100.3 (C-Me₂), 80.3 (C-Me₃), 75.4 (C-7), 73.0 (H-10), 72.1 (H-5), 71.4 (H-9), 70.2 (C-6), 66.9 (C-8), 35.6 (C-2), 33.7 (C-11), 32.9 (C-4), 29.7 (Me), 29.6 (Me), 28.3 (Me), 21.5 (C-3), 20.3 (Me), 20.1 (Me), 18.1 (C-12), and 14.2 (C-13) ppm. IR (NaCl): ν 3472, 2939, 1730, 1366, 1150, 1086 cm^{-1} . MS (EI) calc'd for $\text{C}_{23}\text{H}_{43}\text{O}_8$ $[\text{M}+\text{H}]^+$ 447.2958, found 447.2951. $[\alpha_D]^{28^\circ}$ -2.67 [c 0.36, CHCl_3].

Method B: as a colorless glass (*dr* 9.8:1 **S48:S49**, 87%)

(5*R*,6*R*,7*R*,8*R*,9*S*,10*R*)-5,6-dihydroxy-7,8:9,10-di-*O*-isopropylidene-5,6,7,8,9,10-hexaoxo-tridecanoic acid, *t*-butyl ester (**S48**)

^1H NMR (400 MHz, CDCl_3): δ 4.18 (dd, J = 8.8, 5.6 Hz, H-7), 4.12 (dd, J = 9.6, 5.6 Hz, H-8), 4.02 (td, J = 7.8, 6.7 Hz, H-10), 3.84 (m, H-6), 3.78 (m, H-5), 3.69 (dd, J = 9.6, 7.6 Hz, H-9), 2.73 (br s, OH), 2.25 (t, J = 7.4 Hz, H-2, H-2'), 1.85 (m, H-3), 1.68 (m, H-3', H-4, H-4', H-11, H-11'), 1.50 (m, H-12, H-12'), 1.42 (s, 3Me), 1.40 (s, Me), 1.38 (s, Me), 1.35 (s, Me), 1.31 (s, Me), and 0.92 (t, J = 7.0 Hz, H-13) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 173.2 (C-1), 109.5 (C-Me₂), 109.4 (C-Me₂), 81.0 (C-10), 79.9 (C-Me₃), 79.6 (C-8), 79.0 (C-7), 77.0 (C-9), 72.9 (C-5), 70.6 (C-6), 35.8 (C-2 or C-11), 35.6 (C-2 or C-11), 30.5 (C-4), 28.1 (3Me), 27.7 (Me), 27.4 (Me), 26.8 (Me), 25.3 (Me), 21.2 (C-3), 19.1 (C-12), and 14.0 (C-13) ppm. IR (NaCl): ν 3499, 2939, 1730, 1371, 1213, 1055 cm^{-1} . MS (EI) calc'd for $\text{C}_{23}\text{H}_{43}\text{O}_8$ $[\text{M}+\text{H}]^+$ 447.2955, found 447.2958. $[\alpha_D]^{28^\circ}$ -0.26 [c 0.15, CHCl_3].

(5*S*,6*S*,7*R*,8*R*,9*S*,10*R*)-5,6-dihydroxy-7,8:9,10-di-*O*-isopropylidene-5,6,7,8,9,10-hexaoxo-tridecanoic acid, *t*-butyl ester (**S49**)

^1H NMR (400 MHz, CDCl_3): δ 4.38 (dd, J = 6.0, 4.4 Hz, H-8), 4.11 (dd, J = 9.2, 6.0 Hz, H-9), 3.94 (td, J = 7.6, 2.9 Hz, H-10), 3.87 (dd, J = 9.2, 7.6 Hz, H-7), 3.84 (br m, H-6), 3.54 (td, 8.0, 2.4 Hz, H-5), 2.70 (br s, OH), 2.27 (t, J = 7.1 Hz, H-2), 1.75 (m, H-3, H-3', H-4, H-11, H-11'), 1.45 (m, H-12, H-4'), 1.45 (s, Me), 1.43 (s, 3 Me), 1.38 (s, Me), 1.36 (s, Me), 1.34 (s, Me), and 0.92 (t, J = 7.2 Hz, H-13) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 173.2 (C-1), 108.9 (C-Me₂), 108.4 (C-Me₂), 81.2 (C-10), 80.1 (C-Me₃), 78.9 (C-9), 77.5 (C-8), 77.1 (C-7), 73.4 (C-5), 71.0 (C-6), 35.8 (C-4 or C-11), 35.3 (C-2), 33.7 (C-4 or C-11), 28.1 (3 Me), 27.4 (Me), 27.3 (Me), 26.9 (Me), 25.0 (Me), 20.9 (C-3), 19.2 (C-12), and 14.1 (C-13) ppm. IR (NaCl): ν 3474, 2936, 1723, 1366, 1150, 1050 cm^{-1} . MS (EI) calc'd for $\text{C}_{23}\text{H}_{43}\text{O}_8$ $[\text{M}+\text{H}]^+$ 447.2958, found 447.2953. $[\alpha]_{\text{D}}^{20} +2.92$ [c 0.47, CHCl_3].

Method B: as a colorless glass (*dr* 1.7:1 **S51:S50**, 93%)

(5*R*,6*R*,7*R*,8*R*,9*S*,10*S*)-5,6-dihydroxy-7,9:8,10-di-*O*-isopropylidene-5,6,7,8,9,10-hexaoxo-tridecanoic acid, *t*-butyl ester (**S50**)

^1H NMR (600 MHz, CDCl_3): δ 3.92 (dd, J = 9.6, 3.6 Hz, H-7), 3.80 (t, J = 9.6 Hz, H-8), 3.74 (td, J = 8.4, 3.0 Hz, H-10), 3.61 (br s, H-5 and H-6), 3.41 (t, J = 9.0 Hz, H-9), 2.94 (br s, OH), 2.72 (br s, OH), 2.24 (t, J = 7.5 Hz, H-2, H-2'), 1.84 (m, H-3), 1.66 (m, H-3', H-4, H-11), 1.53 (s, Me), 1.50 (s, Me), 1.45 (m, H-4, H-12), 1.43 (s, 3 Me), 1.38 (s, 2 Me), 1.31 (m, H-11', H-12'), and 0.90 (t, J = 7.2 Hz, H-13) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ 173.1 (C-1), 100.3 (C-Me₂), 100.2 (C-Me₂), 80.0 (C-Me₃), 75.3 (H-5 or H-6), 72.0 (C-7, C-10, and C-5 or C-6), 70.7 (C-9), 68.2 (C-8), 35.6 (C-2), 33.3 (C-11), 32.6 (C-4), 29.5 (Me), 29.3 (Me), 28.1 (3 Me), 21.3 (C-3), 20.0 (Me), 19.9 (Me), 17.8 (C-12), and 14.0 (C-13) ppm. IR (NaCl): ν 3451, 2960, 1730, 1377,

1165, 1065 cm^{-1} . MS (EI) calc'd for $\text{C}_{23}\text{H}_{43}\text{O}_8$ $[\text{M}+\text{H}]^+$ 447.2958, found 447.2948. $[\alpha_D]^{30^\circ}$ -4.59 [c 0.69, CHCl_3].

(5*S*,6*S*,7*R*,8*R*,9*S*,10*S*)-5,6-dihydroxy-7,9:8,10-di-*O*-isopropylidene-5,6,7,8,9,10-hexaoxo-tridecanoic acid, *t*-butyl ester (**S51**)

^1H NMR (600 MHz, CDCl_3): δ 3.99 (dd, J = 9.3, 2.1 Hz, H-7), 3.81 (t, J =9.6 Hz, H-8), 3.72 (td, J = 8.4, 3.0 Hz, H-10), 3.62 (dtd, J = 15.9, 7.5, 3.0 Hz, H-5), 3.53 (ddd, J = 9.5, 6.6, 2.6 Hz, H-6), 3.39 (t, J = 9.3 Hz, H-9), 2.50 (d, J = 10.2 Hz, 6-OH), 2.45 (d, J =7.8 Hz, 5-OH), 2.26 (t, J = 7.2 Hz, H-2), 1.83 (m, H3), 1.68 (m, H-3, H-3'), 1.503 (s, Me), 1.501 (s, Me), 1.45 (m, H-4, H-4', H-11, H-11', H-12) 1.43 (s, 3 Me), 1.38 (s, Me), 1.36 (s, Me), 1.32 (m, H12'), and 0.90 (t, J = 7.2 Hz, H-13) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ 173.1 (C-1), 100.1 (C-Me₂), 100.0 (C-Me₂), 80.2 (C-Me₃), 72.7 (C-5), 72.3 (C-7), 71.9 (C-10), 71.3 (C-9), 70.5 (C-6), 66.6 (C-8), 35.3 (C-2), 33.4 (C-4 or C-11), 33.2 (C-4 or C-11), 29.5 (Me), 29.4 (Me), 28.1 (3 Me), 21.2 (C-3), 20.0 (Me), 19.9 (Me), 17.9 (C-12), and 14.0 (C-13) ppm. IR (NaCl): ν 3477, 2928, 1730, 1371, 1150, 1050 cm^{-1} . MS (EI) calc'd for $\text{C}_{23}\text{H}_{43}\text{O}_8$ $[\text{M}+\text{H}]^+$ 447.2958, found 447.2951. $[\alpha_D]^{29^\circ}$ -3.14 [c 0.29, CHCl_3].

General Procedure for Synthesis of the Hexaacetate:

The diol was dissolved in anhydrous MeOH containing 2% chlorotrimethylsilane to a concentration of 10 mg/mL and stirred at RT for 2 h. The solution was then dried in vacuo and the residue redissolved in MeOH containing 2% chlorotrimethylsilane (to 10 mg/mL) and stirred at RT for an additional 2h before drying in vacuo and redrying from MeOH to remove traces of acid. The residue was dissolved in MeOH and treated with an excess of diazomethane in ether.

The resulting methyl ester was dissolved in a solution of 1:1 acetic anhydride:pyridine (25 mg/mL) and allowed to stir at RT for 6-12 hours before concentration in vacuo. The residual salts were removed by elution through a plug of silica with 50% EtOAc/hexanes and the crude acetates purified by SiO₂-HPLC eluting with 25% EtOAc/hexanes. A variable amount of C5-C8 tetrahydrofuran side product also was apparent.

(5*R*,6*S*,7*R*,8*R*,9*S*,10*R*)-5,6,7,8,9,10-hexa-*O*-acetoxy-5,6,7,8,9,10-hexaoxo-tridecanoic acid, methyl ester (**S34**) as a clear glass (36%, *three steps*).

¹H NMR (600 MHz, *d*₆-DMSO): δ 5.19 (d, *J*= 6.6 Hz, H-7, H-8), 5.06 (pent, *J*= 2.7 Hz, H-6, H-9), 4.96 (m, H-5, H-10), 3.57 (s, Me), 2.26 (dt, *J*= 6.6, 3.0 Hz, H-2, H-2'), 2.07 (s, 4 OAc), 2.051 (s, OAc), 2.045 (s, OAc), 1.40 (m, H-3, H-3', H-4, H-4', H-11), 1.34 (m, H-11'), 1.15 (m, *J*=7.2, H-12, H-12'), 0.81 (t, *J*= 7.2 Hz, H-13) ppm. ¹³C NMR (125 MHz, *d*₆-DMSO): δ 173.8 (C-1), 171.09 (OAc), 171.07 (OAc), 170.77 (OAc), 170.74 (OAc), 170.52 (OAc), 170.46 (OAc), 71.1 (C-6 or C-9), 71.0 (C-6 or C-9), 70.54 (C-5 or C-10), 70.45 (C-5 or C-10), 69.2 (C-7 or C-8), 69.1 (C-7 or C-8), 51.9 (OMe), 33.3 (C-2), 33.2 (C-11), 30.3 (C-4), 21.6 (2 OAc), 21.3 (2 OAc), 21.2 (2 OAc), 20.8 (C-3), 18.6 (C-12), and 14.3 (C-13) ppm. IR (NaCl): ν 2962, 2917, 2848, 1742, 1376, 1219, 1027 cm⁻¹. MS (EI) calc'd for C₂₆H₄₁O₁₄ [M+H]⁺ 577.2496, found 577.2511. [α_D]²⁹ +38.3 [c 0.26, CH₂Cl₂].

(5*R*,6*R*,7*R*,8*R*,9*S*,10*R*)-5,6,7,8,9,10-hexa-*O*-acetoxy-5,6,7,8,9,10-hexaoxo-tridecanoic acid, methyl ester (**S35**) as a clear glass (9%, *three steps*).

¹H NMR (600 MHz, *d*₆-DMSO): δ 5.30 (d, *J*= 8.4 Hz, H-7), 5.21 (d, *J*=8.4 Hz, H-9), 5.17 (m, H-10), 4.98 (dd, *J*=8.4, 2.4 Hz, H-8), 4.92 (dd, *J*= 8.4, 2.4 Hz, H-6), 4.80 (dm, *J*=8.4, <1.5 Hz, H-

5), 3.58 (s, OMe), 2.28 (t, $J=6.3$ Hz, H-2), 2.14 (s, OAc), 2.08 (s, OAc), 2.04 (s, OAc), 1.99 (s, OAc), 1.98 (s, OAc), 1.97 (s, OAc), 1.54 (m, H-3, H-4, H-4'), 1.44 (m, H-3', H-11), 1.34 (ddd, $J=14.4, 5.4, 5.4$ Hz, H-11'), 1.22 (m, H-12), 1.15 (m, H-12'), and 0.83 (t, $J=7.2$ Hz, H-13) ppm. ^{13}C NMR (125 MHz, d_6 -DMSO): δ 173.9 (C-1), 171.0 (OAc), 170.9 (2 OAc), 170.6 (OAc), 170.3 (OAc), 170.2 (OAc), 72.0 (C-5), 71.1 (C-8), 70.8 (C-10), 70.3 (C-6), 68.9 (C-7), 68.6 (C-9), 51.8 (OMe), 33.6 (C-2), 33.2 (C-11), 28.2 (C-4), 21.5 (OAc), 21.43 (OAc), 21.41 (2 OAc), 21.2 (2 OAc), 21.2 (C-3), 18.7 (C-12), and 14.4 (C-13) ppm. IR (NaCl): ν 3058, 2962, 2916, 2848, 1754, 1372, 1216, 1027 cm^{-1} . MS (FAB) calc'd for $\text{C}_{26}\text{H}_{41}\text{O}_{14}$ $[\text{M}+\text{H}]^+$ 577.2496, found 577.2484. $[\alpha_D]^{29} +67.2$ [c 0.15, CH_2Cl_2].

(5*S*,6*S*,7*R*,8*R*,9*S*,10*R*)-5,6,7,8,9,10-hexa-*O*-acetoxy-5,6,7,8,9,10-hexaoxo-tridecanoic acid, methyl ester (**S36**) as a clear glass (15%, *three steps*).

^1H NMR (600 MHz, d_6 -DMSO): δ 5.25 (t, $J=5.1$ Hz, H-8), 5.16 (t, $J=5.1$ Hz, H-6), 5.12 (t, $J=5.1$ Hz, H-7), 5.06 (t, $J=5.1$ Hz, H-9), 4.99 (dt, $J=8.4, 5.1$ Hz, H-10), 4.69 (m, H-5), 3.58 (s, OMe), 2.29 (dd, $J=13.2, 6.6$ Hz, H-2, H-2'), 2.08 (s, 2 OAc), 2.06 (s, OAc), 2.05 (s, OAc), 2.03 (s, OAc), 1.95 (s, OAc), 1.51 (m, H-3, H-4, H-4'), 1.39 (m, H-3', H-11, H-11'), 1.21 (m, H-12), 1.15 (m, H-12'), and 0.81 (t, $J=7.2$ Hz, H-13) ppm. ^{13}C NMR (125 MHz, d_6 -DMSO): δ 173.9 (C-1), 171.0 (OAc), 170.9 (OAc), 170.74 (OAc), 170.73 (OAc), 170.5 (OAc), 170.4 (OAc), 71.4 (C-6), 71.1 (C-7 and C-10), 70.7 (C-5), 68.9 (C-9), 68.7 (C-8), 51.5 (OMe), 33.6 (C-2), 32.9 (C-11), 28.9 (C-4), 21.5 (2 OAc), 21.4 (OAc), 21.3 (OAc), 21.21 (OAc), 21.20 (OAc), 21.0 (C-3), 18.5 (C-12), and 14.3 (C-13) ppm. IR (NaCl): ν 2961, 2916, 2848, 1754, 1372, 1221, 1027 cm^{-1} . MS (FAB) calc'd for $\text{C}_{26}\text{H}_{41}\text{O}_{14}$ $[\text{M}+\text{H}]^+$ 577.2496, found (poor ionization). $[\alpha_D]^{30} +22.0$ [c 0.02, CH_2Cl_2].

(5*R*,6*S*,7*R*,8*R*,9*S*,10*S*)-5,6,7,8,9,10-hexa-*O*-acetoxy-5,6,7,8,9,10-hexaoxo-tridecanoic acid, methyl ester (**S37**) as a clear glass (17%, *two steps*).

¹H NMR (600 MHz, *d*₆-DMSO): δ 5.26 (t, *J*= 4.8 Hz, H-8), 5.16 (t, *J*= 4.8 Hz, H-9), 5.10 (t, *J*= 4.8 Hz, H-6), 5.06 (t, *J*= 4.8 Hz, H-7), 4.99 (m, H-5), 4.70 (m, H-10), 3.57 (s, OMe), 2.27 (dd, *J*= 12.6, 6.0 Hz, H-2, H-2'), 2.07 (2 OAc), 2.06 (2 OAc), 2.04 (OAc), 1.93 (OAc), 1.50 (m, H-11), 1.43 (m, H-3, H-3', H-4, H-4'), 1.40 (m, H-11'), 1.30 (m, H-12), 1.16 (hep., *J*=7.2 Hz, H-12'), and 0.85 (t, *J*= 7.2 Hz, H-13) ppm. ¹³C NMR (125 MHz, *d*₆-DMSO): δ 173.8 (C-1), 171.1 (OAc), 170.9 (OAc), 170.8 (OAc), 170.7 (OAc), 170.5 (OAc), 170.4 (OAc), 71.7 (C-9), 71.02 (C-5), 70.96 (C-6), 70.7 (C-10), 68.9 (C-8), 68.8 (C-7), 52.2 (OMe), 33.4 (C-2), 31.3 (C-11), 30.2 (C-4), 21.50 (OAc), 21.45 (OAc), 21.4 (OAc), 21.3 (OAc), 21.2 (OAc), 21.2 (OAc), 20.8 (C-3), 18.7 (C-12), and 14.3 (C-13) ppm. IR (NaCl): ν 2960, 2917, 2850, 1744, 1374, 1220, 1027 cm⁻¹. MS (FAB) calc'd for C₂₆H₄₁O₁₄ [M+H]⁺ 577.2496, found 577.2498. [α_D]²⁵ +69.7 [c 0.073, CH₂Cl₂].

(5*R*,6*R*,7*R*,8*R*,9*S*,10*S*)-5,6,7,8,9,10-hexa-*O*-acetoxy-5,6,7,8,9,10-hexaoxo-tridecanoic acid, methyl ester (**S38**) as a clear glass (28%, *two steps*).

¹H NMR (600 MHz, *d*₆-DMSO): δ 5.29 (t, *J*= 5.4 Hz, H-8), 5.21 (t, *J*= 5.4 Hz, H-9), 5.17 (t, *J*= 5.4 Hz, H-7), 4.93 (t, *J*= 5.4 Hz, H-6), 4.87 (m, H-5), 4.78 (m, H-10), 3.58 (s, OMe), 2.30 (m, *J*= 6.6, 2.4 Hz, H-2, H-2'), 2.07 (s, OAc), 2.06 (s, OAc), 2.05 (s, OAc), 1.99 (s, OAc), 1.97 (s, OAc), 1.95 (s, OAc), 1.64 (m, H-4), 1.53 (m, H-3, H-4', H-11), 1.45 (m, H-3', H-11'), 1.32 (m, H-12), 1.19 (m, H-12'), and 0.85 (t, *J*= 7.5 Hz, H-13) ppm. ¹³C NMR (125 MHz, *d*₆-DMSO): δ 173.9 (C-1), 170.84 (OAc), 170.78 (OAc), 170.68 (OAc), 170.67 (OAc), 170.4 (OAc), 170.3

(OAc), 71.5 (C-9), 71.3 (C-5), 70.9 (C-6 and C-10), 69.9 (C-7), 68.7 (C-8), 52.2 (OMe), 33.6 (C-2), 31.6 (C-11), 28.9 (C-4), 21.6 (OAc), 21.51 (OAc), 21.48 (OAc), 21.42 (OAc), 21.36 (OAc), 21.32 (OAc), 20.7 (C-3), 18.7 (C-12), and 14.4 (C-13) ppm. IR (NaCl): ν 2959, 2873, 2849, 1748, 1436, 1371, 1220, 1031 cm^{-1} . MS (FAB) calc'd for $\text{C}_{26}\text{H}_{41}\text{O}_{14}$ $[\text{M}+\text{H}]^+$ 577.2496, found 577.2520. $[\alpha_D]^{26} +57.3$ [c 0.129, CH_2Cl_2].

(5*S*,6*S*,7*R*,8*R*,9*S*,10*S*)-5,6,7,8,9,10-hexa-*O*-acetoxo-5,6,7,8,9,10-hexaoxo-tridecanoic acid, methyl ester (**S39**) as a clear glass (30%, *two steps*).

^1H NMR (600 MHz, d_6 -DMSO): δ 5.19 (m, H-6, H-9), 5.14 (s, H-7, H-8), 4.79 (m, H-5 or H-10), 4.75 (m, H-5 or H-10), 3.58 (s, OMe), 2.30 (m, H-2, H-2'), 2.12 (s, 2 OAc), 1.99 (s, 2 OAc), 1.96 (s, OAc), 1.95 (s, OAc), 1.51 (m, H-3, H-4, H-4', H-11), 1.46 (m, H-3', H-11'), 1.27 (m, H-12), 1.17 (hep., $J=7.6$ Hz, H-12'), and 0.84 (t, $J=7.6$ Hz, H-13) ppm. ^{13}C NMR (125 MHz, d_6 -DMSO): δ 173.9 (C-1), 170.9 (OAc), 170.84 (OAc), 170.80 (OAc), 170.6 (OAc), 170.3 (2 OAc), 71.2 (C-6 or C-9), 70.9 (C-6 or C-9), 70.3 (C-5 or C-10), 70.2 (C-5 or C-10), 68.4 (C-7 and C-8), 52.2 (OMe), 32.40 (C-2 or C-11), 32.36 (C-2 or C-11), 29.2 (C-4), 21.5 (2 OAc), 21.31 (2 OAc), 21.26 (2 OAc), ~ 20.5 (C-3), ~ 18.5 (C-12), and 14.5 (C-13) ppm. IR (NaCl): ν 2960, 2939, 2877, 1747, 1436, 1372, 1216, 1030 cm^{-1} . MS (FAB) calc'd for $\text{C}_{26}\text{H}_{41}\text{O}_{14}$ $[\text{M}+\text{H}]^+$ 577.2496, found 577.2484. $[\alpha_D]^{26} +128$ [c 0.041, CH_2Cl_2].

(5*S*,6*R*,7*R*,8*S*,9*S*,10*R*)-5,6,7,8,9,10-hexa-*O*-acetoxo-5,6,7,8,9,10-hexaoxo-tridecanoic acid, methyl ester (**2**) as a colorless glass (48%, *three steps*).

^1H NMR (600 MHz, d_6 -DMSO): δ 5.15 (dt, $J=8.4$, <1.0 Hz, H-7 and H-8), 4.98 (d, $J=8.4$ Hz, H-5, H-6, H-9, and H-10), 3.57 (s, OMe), 2.29 (m, H-2, H-2'), 2.131 (s, OAc), 2.125 (s, OAc),

1.96 (s, 3 OAc), 1.96 (s, OAc), 1.44 (m, H-3, H-3', H-4, H-4', H-11), 1.39 (m, H-11'), 1.21 (m, H-12, H-12'), and 0.84 (t, $J = 7.2$ Hz, H-13) ppm. ^{13}C NMR (125 MHz, d_6 -DMSO): δ 173.9 (C-1), 170.9 (OAc), 170.8 (OAc), 170.51 (OAc), 170.49 (OAc), 170.0 (2 OAc), 71.34 (C-7 or C-8), 71.26 (C-7 or C-8), 70.63 (C-6 or C-9), 70.59 (C-6 or C-9), 70.0 (C-5 or C-10), 69.9 (C-5 or C-10), 52.2 (OMe), 33.6 (C-2), 33.1 (C-11), 30.3 (C-4), 21.4 (4 OAc), 21.3 (2 OAc), 21.1 (C-3), 18.8 (C-12), and 14.5 (C-13) ppm. ^1H NMR (600 MHz, CDCl_3): δ 5.23 (ddd, $J = 9.0, 4.0, 2.6$ Hz, 2H), 5.06 (ddd, $J = 9.3, 3.3, 1.5$ Hz, 2H), 5.04 (m, 2H), 3.64 (s, OMe), 2.29 (dt, $J = 7.4, 7.2$ Hz, H-2, H-2'), 2.19 (s, OAc), 2.18 (s, OAc), 2.03 (s, 2 OAc), 2.02 (s, OAc), 2.01 (s, OAc), 1.58 (m, 2H), 1.49 (m, 2H), 1.45 (m, 1H), 1.40 (m, 1H), 1.27 (m, 2H), and 0.88 (t, $J = 7.2$ Hz, H-13) ppm. IR (NaCl): ν 2971, 1746, 1371, 1218, 1033 cm^{-1} . MS (EI) calc'd for $\text{C}_{26}\text{H}_{41}\text{O}_{14}$ $[\text{M}+\text{H}]^+$ 577.2496, found 577.2486. $[\alpha_D]^{27} +1.47$ [c 0.93, CHCl_3].

(5*R*,6*S*,7*R*,8*S*,9*S*,10*R*)-5,6,7,8,9,10-hexa-*O*-acetoxy-5,6,7,8,9,10-hexaoxo-tridecanoic acid, methyl ester (**3**) as a colorless glass (22%, *three steps*).

^1H NMR (600 MHz, d_6 -DMSO): δ 5.23 (m, H-6 or H-9), 5.22 (m, H-7 and H-8), 5.06 (ddd, $J = 6.8, 4.2, 1.8$ Hz, H-5 or H-10), 5.03 (m, H-10 or H-5), 4.92 (dd, $J = 7.4, 2.4$ Hz, H-9 or H-6), 3.58 (s, OMe), 2.32 (t, $J = 6.0$ Hz, H-2), 2.17 (OAc), 2.06 (OAc), 2.03 (OAc), 2.02 (OAc), 2.01 (OAc), 1.93 (OAc), 1.48 (m, H-3, H-3', H-4, H-4', H-11), 1.39 (m, H-11'), 1.23 (m, H-12, H-12'), and 0.84 (t, $J = 7.5$ Hz, H-13) ppm. ^{13}C NMR (125 MHz, d_6 -DMSO): δ 173.8 (C-1), 171.0 (OAc), 170.9 (OAc), 170.7 (OAc), 170.5 (OAc), 170.3 (OAc), 170.1 (OAc), 71.12 (C-8 or C-7 and C-10 or C-5), 70.9 (C-6 or C-9), 70.7 (C-5 or C-10), 70.6 (C-7 or C-8), 69.0 (C-9 or C-6), 52.2 (OMe), 33.4 (C-2), 33.1 (C-11), 30.2 (C-4), 21.7 (OAc), 21.4 (2 OAc), 21.3 (OAc), 21.2 (2 OAc), 20.9 (C-3), 18.9 (C-12), and 14.5 (C-13) ppm. ^1H NMR (600 MHz, CDCl_3): δ 5.34 (dd,

$J=6.0, 3.0$ Hz, 1H), 5.32 (dd, $J=6.6, 4.2$ Hz, 1H), 5.27 (dd, $J=8.4, 2.4$ Hz, 1H), 5.14 (ddd, $J=7.8, 5.0, 2.7$ Hz, 1H), 5.09 (m, 1H), 5.01 (dd, $J=8.1, 3.3$ Hz, 1H), 3.64 (s, OMe), 2.31 (t, $J=7.2$ Hz, H-2, H-2'), 2.21 (s, OAc), 2.11 (s, OAc), 2.08 (s, OAc), 2.06 (s, OAc), 2.04 (s, OAc), 1.98 (s, OAc), 1.56 (m, 4H), 1.43 (m, 1H), 1.38 (m, 1H), 1.28 (m, 2H), and 0.88 (t, $J=7.2$ Hz, H-13) ppm. IR (NaCl): ν 2933, 1747, 1375, 1224, 1020 cm^{-1} . MS (EI) calc'd for $\text{C}_{26}\text{H}_{41}\text{O}_{14}$ $[\text{M}+\text{H}]^+$ 577.2496, found 577.2501. $[\alpha_D]^{26^\circ} +24.53$ [c 0.11, CHCl_3].

(5*S*,6*R*,7*R*,8*S*,9*S*,10*S*)-5,6,7,8,9,10-hexa-*O*-acetoxy-5,6,7,8,9,10-hexaoxo-tridecanoic acid, methyl ester (**4**) as a clear glass (23%, *three steps*).

^1H NMR (600 MHz, d_6 -DMSO): δ 5.20 (dd, $J=8.7, 2.7$ Hz, H-7), 5.19 (br s, H-8 and H-9), 5.05 (dd, $J=8.4, <1.0$ Hz, H-6), 5.00 (m, H-5), 4.90 (dt, $J=9.6, 1.5$ Hz, H-10), 3.57 (s, OMe), 2.29 (t, $J=6.0$ Hz, H-2, H-2'), 2.12 (s, OAc), 2.07 (s, OAc), 2.04 (s, OAc), 1.99 (s, OAc), 1.97 (s, OAc), 1.96 (s, OAc), 1.51 (m, H-11), 1.44 (m, H-3, H-3', H-4, H-4', H-11, H-11'), 1.29 (m, H-12), 1.17 (m, H-12), and 0.83 (t, $J=7.2$ Hz, H-13) ppm. ^{13}C NMR (125 MHz, d_6 -DMSO): δ 173.9 (C-1), 170.9 (OAc), 170.8 (OAc), 170.6 (OAc), 170.3 (OAc), 170.1 (OAc), 71.9 (C-10), 71.3 (C-8), 71.0 (C-7), 70.6 (C-5), 70.3 (C-9), 69.5 (C6), 52.2 (OMe), 33.5 (C2), 31.2 (C11), 30.4 (C4), 21.5 (OAc), 21.43 (OAc), 21.36 (2 OAc), 21.31 (2 OAc), 21.0 (C-3), 18.8 (C-12), and 14.4 (C-13) ppm. ^1H NMR (600 MHz, CDCl_3): δ 5.28 (dd, $J=8.7, 2.7$ Hz, 1H), 5.25 (dd, $J=7.8, 3.6$ Hz, 1H), 5.20 (dd, $J=8.4, 2.4$ Hz, 1H), 5.07 (td, $J=6.7, 2.6$ Hz, 1H), 4.98 (dt, $J=10.2, 3.0$ Hz, 1H), 3.64 (s, OMe), 2.29 (ddd, $J=15.9, 10.8, 7.2$ Hz, 2H), 2.19 (s, OAc), 2.11 (s, OAc), 2.08 (s, OAc), 2.04 (s, OAc), 2.03 (s, OAc), 2.02 (s, OAc), 1.58 (m, 3H), 1.50 (m, 2H), 1.43 (m, 1H), 1.34 (m, 1H), 1.22 (m, 1H), and 0.86 (t, $J=7.2$ Hz, H-13) ppm. IR (NaCl): ν 2965, 1746, 1429, 1371,

1223, 1033 cm^{-1} . MS (EI) calc'd for $\text{C}_{26}\text{H}_{41}\text{O}_{14}$ $[\text{M}+\text{H}]^+$ 577.2496, found 577.2493. $[\alpha_{\text{D}}]^{29^\circ}$ - 35.49 $[\text{c } 0.47, \text{CHCl}_3]$.

(5*R*,6*S*,7*R*,8*S*,9*S*,10*S*)-5,6,7,8,9,10-hexa-*O*-acetoxy-5,6,7,8,9,10-hexaoxo-tridecanoic acid, methyl ester (**5**) as a clear glass (25%, *three steps*).

^1H NMR (600 MHz, d_6 -DMSO): δ 5.25 (dd, J = 6.6, 3.6 Hz, H-9), 5.22 (dd, J = 6.6, 3.6 Hz, H-8), 5.14 (dd, J = 7.5, 3.3 Hz, H-7), 5.03 (dd, J = 7.8, 3.6 Hz, H-6), 5.00 (m, H-5), 4.93 (dt, J = 9.0, 4.1 Hz, H-10), 3.57 (s, OMe), 2.30 (t, J = 6.6 Hz, H-2), 2.08 (s, OAc), 2.07 (s, OAc), 2.019 (s, OAc), 2.016 (s, OAc), 1.98 (s, OAc), 1.47 (m, H-3, H-3', H-4, H-4', H-11, H-11'), 1.29 (m, H-12), 1.19 (m, H-12), and 0.83 (t, J =7.5 Hz, H-13) ppm. ^{13}C NMR (125 MHz, d_6 -DMSO): δ 173.9 (C-1), 171.1 (OAc), 170.9 (OAc), 170.7 (OAc), 170.6 (OAc), 170.2 (OAc), 170.0 (OAc), 72.2 (C-10), 71.28 (C-8), 71.24 (C-9), 71.18 (C-5 and C-7), 69.4 (C-6), 52.3 (OMe), 33.5 (C-2), 31.7 (C-11), 30.4 (C-4), 21.7 (OAc), 21.5 (OAc), 21.4 (2 OAc), 21.3 (2 OAc), 21.0 (C-3), 19.0 (C-12), and 14.3 (C-13) ppm. ^1H NMR (600 MHz, CDCl_3): δ 5.36 (m, 2H), 5.26 (dd, J = 7.2, 3.6 Hz, 1H), 5.15 (dd, J = 7.2, 3.6 Hz, 1H), 5.11 (m, 1H), 5.03 (dt, J = 8.4, 4.2 Hz, 1H), 3.65 (s, OMe), 2.34 (m, H-2, H-2'), 2.12 (s, OAc), 2.11 (s, OAc), 2.06 (s, OAc), 2.05 (s, OAc), 2.04 (s, OAc), 2.01 (s, OAc), 1.57 (m, 6H), 1.38 (m, 1H), 1.27 (m, 1H), and 0.90 (t, J = 7.2 Hz, H-13) ppm. IR (NaCl): ν 2970, 2880, 1746, 1371, 1218, 1023 cm^{-1} . MS (EI) calc'd for $\text{C}_{26}\text{H}_{41}\text{O}_{14}$ $[\text{M}+\text{H}]^+$ 577.2496, found 577.2490. $[\alpha_{\text{D}}]^{30^\circ}$ -5.52 $[\text{c } 0.42, \text{CHCl}_3]$.

(5*R*,6*R*,7*R*,8*S*,9*S*,10*R*)-5,6,7,8,9,10-hexa-*O*-acetoxy-5,6,7,8,9,10-hexaoxo-tridecanoic acid, methyl ester (**6**) (56%, *3 steps*)

^1H NMR (500 MHz, d_6 -DMSO): δ 5.32 (d, $J=10.0$ Hz, H-8), 5.02 (m, H-6), 5.01 (m, H-7), 5.00 (m, H-9), 4.84 (m, H-5 and H-10), 3.57 (s, OMe), 2.28 (t, $J=6.5$ Hz, H-2), 2.07 (s, OAc), 2.04 (s, OAc), 2.00 (s, 2 OAc), 1.98 (s, 2 OAc), 1.60 (m, H-4), 1.52 (m, H-4', H-3), 1.40 (m, H-3'), 1.31 (m, H-11, H-11'), 1.20 (m, H-12, H-12'), and 0.82 (t, $J=7.3$, H-13). ppm. ^{13}C NMR (125 MHz, d_6 -DMSO): δ 173.9 (C-1), 170.83 (OAc), 170.77 (OAc), 170.67 (OAc), 170.55 (OAc), 170.42 (OAc), 170.13 (OAc), 71.7 (C-5), 70.6 (C-6), 70.2 (C-10), 69.6 (C-9), 68.0 (C-7), 67.2 (C-8), 52.2 (OMe), 33.6 (C-2), 33.4 (C-11), 28.5 (C-4), 21.6 (OAc), 21.52 (2 OAc), 21.49 (OAc), 21.43 (OAc), 21.39 (OAc), 21.1 (C-3), 18.9 (C-12), and 14.6 (C-13) ppm. ^1H NMR (600 MHz, CD_3OD): δ 5.30 (dd, $J=8.7, 2.7$ Hz, 1H), 5.26 (dd, $J=7.2, 3.6$ Hz, 1H), 5.20 (dd, $J=7.2, 3.0$ Hz, 1H), 5.16 (dd, $J=8.4, 3.0$ Hz, 1H), 5.01 (ddd, $J=7.8, 5.4, 2.6$ Hz, 1H), 5.00 (dt, $J=9.0, 3.6$ Hz, 1H), 3.64 (s, OMe), 2.32 (t, $J=7.0$ Hz, 2H), 2.16 (s, OAc), 2.09 (s, OAc), 2.07 (s, OAc), 2.03 (s, OAc), 2.02 (s, OAc), 1.98 (s, OAc), 1.62 (m, 3H), 1.54 (m, 1H), 1.45 (m, 2H), 1.30 (m, 2H), and 0.90 (t, $J=7.2$ Hz, 3H) ppm. IR (NaCl): ν 2960, 2881, 1741, 1371, 1218, 1033 cm^{-1} . MS (EI) calc'd for $\text{C}_{26}\text{H}_{40}\text{O}_{14}$ $[\text{M}]^+$ 576.2413, found 576.2422. $[\alpha_D]^{28} +25.22$ [c 0.21, CHCl_3].

(5*S*,6*S*,7*R*,8*S*,9*S*,10*R*)-5,6,7,8,9,10-hexa-*O*-acetoxo-5,6,7,8,9,10-hexaoxo-tridecanoic acid, methyl ester (**7**) as a clear glass (85%, *three steps*).

^1H NMR (500 MHz, d_6 -DMSO): δ 5.24 (dd, $J=13.5, <2.0$ Hz, H-7 or H-8), 5.20 (dd, $J=12.5, <2.0$ Hz, H-6), 5.16 (m, H-9), 5.12 (m, H-10), 5.05 (dd, $J=11.5, 10.5$ Hz, H-7 or H-8), 4.87 (br t, H-5), 3.57 (s, OMe), 2.29 (q, $J=5.5$ Hz, H-2, H-2'), 2.10 (s, Me), 2.08 (s, OAc), 2.00 (s, OAc), 1.99 (s, OAc), 1.98 (s, OAc), 1.96 (s, OAc), 1.50 (m, H-3, H-4), 1.45 (m, H-3', H-4', H-11), 1.32 (m, H-11', H-12), 1.21 (hex, $J=7.0$ Hz, H-12'), and 0.85 (t, $J=7.0$ Hz, H-13) ppm. ^{13}C NMR (125 MHz, d_6 -DMSO): δ 173.9 (C-1), 170.9 (OAc), 170.7 (OAc), 170.61 (OAc), 170.55 (OAc),

170.5 (OAc), 170.3 (OAc), 71.1 (C-9), 70.3 (C-6), 70.14 (C-7 or C-8), 70.06 (C-5), 68.9 (C-7 or C-8), 68.4 (C-10), 52.2 (OMe), 33.6 (C-2), 33.3 (C-11), 29.7 (C-4), 21.53 (2 OAc), 21.45 (OAc), 21.4 (OAc), 21.33 (OAc), 21.28 (OAc), 20.8 (C-3), 18.8 (C-12), and 14.5 (C-13) ppm. ^1H NMR (600 MHz, CD_3OD): δ 5.34 (dd, J = 7.8, 3.0 Hz, 1H), 5.30 (dd, J = 5.4, 3.0 Hz, 1H), 5.26 (ddd, J = 7.8, 5.4, 2.4 Hz, 1H), 5.24 (dd, J = 6.9, 2.7 Hz, 1H), 5.16 (dd, J = 6.9, 5.7 Hz, 1H), 4.98 (m, 1H), 3.64 (s, OMe), 2.32 (m, 2H), 2.11 (s, OAc), 2.07 (s, OAc), 2.04 (s, OAc), 2.03 (s, OAc), 2.02 (s, OAc), 2.00 (s, OAc), 1.63 (m, 2H), 1.54 (m, 3H), 1.42 (m, 2H), 1.30 (m, 2H), and 0.91 (t, J = 7.2 Hz, 3H) ppm. IR (NaCl): ν 2960, 2880, 1746, 1435, 1371, 1218, 1023 cm^{-1} . MS (EI) calc'd for $\text{C}_{26}\text{H}_{40}\text{O}_{14}$ $[\text{M}]^+$ 576.2413, found 576.2408. $[\alpha]_{\text{D}}^{30}$ -3.28 [c 0.35, CHCl_3].

(5*R*,6*R*,7*R*,8*S*,9*S*,10*S*)-5,6,7,8,9,10-hexa-*O*-acetoxy-5,6,7,8,9,10-hexaoxo-tridecanoic acid, methyl ester (**8**) as a colorless glass (30%, *three steps*).

^1H NMR (600 MHz, d_6 -DMSO): δ 5.16 (m, H-6, H-7, H-8 and H-9), 4.89 (m, H-5 and H-10), 3.57 (s, OMe), 2.28 (t, J = 6.0 Hz, H-2, H-2'), 2.05 (s, 2 OAc), 2.039 (s, OAc), 2.035 (s, OAc), 1.99 (s, OAc), 1.98 (s, OAc), 1.50 (m, H-3, H-3', H-4, H-11), 1.43 (m, H-4', H-11'), 1.28 (m, H-12), 1.19 (m, H-12'), and 0.82 (t, J = 7.5 Hz, H-13) ppm. ^{13}C NMR (125 MHz, d_6 -DMSO): δ 174.0 (C-1), 170.9 (2 OAc), 170.4 (OAc), 170.2 (OAc), 72.0 (C-5 or C-10), 71.9 (C-5 or C-10), 71.2 (C-6, C-7, C-8 or C-9), 71.1 (C-6, C-7, C-8 or C-9), 70.1 (C-6, C-7, C-8 or C-9), 70.0 (C-6, C-7, C-8 or C-9), 52.2 (OMe), 33.6 (C-2), 31.3 (C-11), 28.7 (C-4), 21.5 (2 OAc), 21.4 (4 OAc), 21.2 (C-3), 18.8 (C-12), and 14.4 (C-13) ppm. ^1H NMR (600 MHz, CDCl_3): δ 5.27 (m, 2H), 5.24 (m, 2H), 4.95 (tt, J = 10.2, 3.0, 2H), 3.65 (s, OMe), 2.28 (td, J = 7.1, 5.3 Hz, H-2, H-2'), 2.112 (s, OAc), 2.110 (s, OAc), 2.090 (s, OAc), 2.085 (s, OAc), 2.03 (s, OAc), 2.02 (s, OAc), 1.63 (m, 2H), 1.56 (m, 3H), 1.44 (m, 1H), 1.33 (m, 1H), 1.22 (m, 1H), and 0.86 (t, J = 7.2 Hz, H-13) ppm.

IR (NaCl): ν 2965, 1745, 1368, 1208, 1031 cm^{-1} . MS (EI) calc'd for $\text{C}_{26}\text{H}_{41}\text{O}_{14}$ $[\text{M}+\text{H}]^+$ 577.2496, found 577.2504. $[\alpha_D]^{26^\circ} +2.60$ [c 0.35, CHCl_3].

(5*S*,6*S*,7*R*,8*S*,9*S*,10*S*)-5,6,7,8,9,10-hexa-*O*-acetoxy-5,6,7,8,9,10-hexaoxo-tridecanoic acid, methyl ester (**9**) as a colorless glass (26%, *three steps*).

^1H NMR (600 MHz, d_6 -DMSO): δ 5.26 (dd, $J=6.0, 2.4$ Hz, H-7), 5.18 (dd, $J=6.6, 2.4$ Hz, H-6), 5.11 (t, $J=5.4$ Hz, H-8), 5.06 (t, $J=5.1$ Hz, H-9), 4.94 (td, $J=7.2, 5.1$ Hz, H-10), 4.85 (td, $J=6.0, 4.0$ Hz, H-5), 3.51 (s, OMe), 2.29 (t, $J=6.0$ Hz, H-2), 2.035 (s, 2 OAc), 2.034 (s, 2 OAc), 2.00 (s, OAc), 1.99 (s, OAc), 1.58 (m, H-4), 1.54 (m, H-3, H-4, H-4'), 1.50 (m, H-11, H-11'), 1.44 (m, H-3'), 1.28 (m, H-12), 1.19 (m, H-12'), and 0.84 (t, $J=7.5$ Hz, H-13) ppm. ^{13}C NMR (125 MHz, d_6 -DMSO): δ 173.9 (C-1), 170.65 (2 OAc), 170.52 (OAc), 170.47 (OAc), 170.29 (OAc), 170.22 (OAc), 71.8 (C-9), 71.5 (C-10), 70.7 (C-5), 70.5 (C-6), 69.6 (C-8), 68.9 (C-7), 52.2 (OMe), 33.6 (C-2), 32.3 (C-11), 29.4 (C-4), 21.52 (OAc), 21.49 (OAc), 21.45 (OAc), 21.38 (OAc), 21.35 (OAc), 21.32 (OAc), 20.9 (C-3), 18.7 (C-12), and 14.4 (C-13) ppm. ^1H NMR (600 MHz, CD_3OD): δ 5.38 (dd, $J=6.3, 3.3$ Hz, 1H), 5.31 (dd, $J=6.9, 3.3$ Hz, 1H), 5.19 (dd, $J=6.0, 4.8$ Hz, 1H), 5.16 (t, $J=5.1$ Hz, 1H), 5.052 (dt, $J=7.8, 4.8$ Hz, 1H), 4.96 (td, $J=7.5, 2.6$ Hz, 1H), 3.65 (s, OMe), 2.32 (m, 2H), 2.072 (s, OAc), 2.065 (s, OAc), 2.06 (s, OAc), 2.05 (s, OAc), 2.029 (s, OAc), 2.027 (s, OAc), 1.65 (m, 2H), 1.55 (m, 4H), 1.36 (m, 1H), 1.28 (m, 1H), and 0.91 (t, $J=7.2$ Hz, 3H) ppm. IR (NaCl): ν 2965, 2870, 1741, 1366, 1218, 1039 cm^{-1} . MS (EI) calc'd for $\text{C}_{26}\text{H}_{41}\text{O}_{14}$ $[\text{M}+\text{H}]^+$ 577.2496, found 577.2511. $[\alpha_D]^{30^\circ} -33.75$ [c 0.53, CHCl_3].

General Procedure for Benzoylation:

The acetone (10.0 mg, 0.0224 mmol) was dissolved in anhydrous MeOH containing 2% chlorotrimethylsilane (5.0 mL) and stirred at RT for 2 min. The solution was then dried in vacuo and the residue redissolved in MeOH containing 2% chlorotrimethylsilane (5.0 mL) and stirred at RT for an additional 2 h. The residue was redried from MeOH and then dissolved in 0.5 mL MeOH and excess diazomethane in ether was added and allowed to stand for 1 hour. The solution was dried and the residue redried from anhydrous toluene. The residue was dissolved in anhydrous pyridine and *p*-bromobenzoylchloride (125.0 mg, 0.570 mmol) and DMAP (1.0 mg, 0.0082 mmol) were added and stirred at RT for 12 hours. 3-(*N,N*-dimethylamino)-propylamine (125 μ l) was added and allowed to stir for 10 minutes before concentrating mixture in vacuo. The bright orange oil was purified first by silica chromatography eluting with 30% EtOAc/hexanes then by silica chromatography eluting with 10% ether/hexanes followed by 30% ether hexanes to give the hexabenzoyl ester and the tetrabenzoyl ester- C5-C8 tetrahydrofuran.

(5*R*,6*R*,7*R*,8*S*,9*S*,10*R*)-5,6,7,8,9,10-hexa-*O*-(*p*-bromo-benzoyl)-5,6,7,8,9,10-hexaoxo-tridecanoic acid, methyl ester (**18**) (15% over 3 steps)

¹H NMR (600 MHz, CDCl₃): δ 8.05 (d, *J* = 9.0 Hz, 2 Ph), 7.93 (d, *J* = 8.4 Hz, 2 Ph), 7.87 (d, *J* = 8.4 Hz, 2 Ph), 7.80 (d, *J* = 8.4 Hz, 2 Ph), 7.64 (d, *J* = 8.4 Hz, 2 Ph), 7.59 (d, *J* = 8.4 Hz, 2 Ph), 7.57 (m, 8 Ph), 7.51 (d, *J* = 8.4 Hz, 2 Ph), 7.35 (d, *J* = 8.4 Hz, 2 Ph), 5.90 (dd, *J* = 9.3, 2.4 Hz, H-9), 5.86 (m, H-6 and H-7), 5.65 (dd, *J* = 9.0, 2.4 Hz, H-8), 5.32 (td, *J* = 5.4, 2.4 Hz, H-10), 5.17 (dt, *J* = 10.2, 2.7 Hz, H-5), 3.46 (s, OMe), 2.08 (m, H-2, H-2'), 1.73 (m, H-4), 1.65 (m, H-4'), 1.50 (m, H-11, H-3), 1.37 (m, H-3'), 1.26 (m, H-12), 1.17 (m, H-12'), and 0.72 (t, *J* = 7.2 Hz, H-13) ppm. ¹³C NMR (150 MHz, CDCl₃): δ 173.1 (C-1), 164.8 (-CO₂R), 164.7 (2 -CO₂R), 164.6 (2 -

CO₂R), 164.4 (-CO₂R), 132.10 (2 *o*- or *m*-Ph), 132.09 (2 *o*- or *m*-Ph), 131.99 (2 *o*- or *m*-Ph), 131.93 (2 *o*- or *m*-Ph), 131.80 (2 *o*- or *m*-Ph), 131.73 (4 *o*- or *m*-Ph), 131.5 (2 *o*- or *m*-Ph), 131.40 (2 *o*- or *m*-Ph), 131.37 (2 *o*- or *m*-Ph), 131.2 (2 *o*- or *m*-Ph), 130.9 (2 *o*- or *m*-Ph), 129.4 (*i*- or *p*-Ph), 129.1 (*i*- or *p*-Ph), 129.0 (*i*- or *p*-Ph), 128.9 (*i*- or *p*-Ph), 128.4 (*i*- or *p*-Ph), 128.3 (*i*- or *p*-Ph), 128.2 (*i*- or *p*-Ph), 128.04 (*i*- or *p*-Ph), 127.96 (*i*- or *p*-Ph), 127.73 (*i*- or *p*-Ph), 127.68 (*i*- or *p*-Ph), 127.4 (*i*- or *p*-Ph), 72.4 (C-5), 71.9 (C-9), 71.55 (C-10), 71.53 (C-6 or C-7), 71.0 (C-6 or C-7), 69.9 (C-8), 51.5 (OMe), 33.1 (C-2), 32.8 (C-11), 27.7 (C-4), 20.6 (C-3), 18.5 (C-12), and 13.6 (C-13) ppm. IR (NaCl): ν 2960, 2870, 1725, 1588, 1255, 1096, 1028, 838, 754 cm⁻¹. CD (CH₃CN) λ_{max} ($\Delta\epsilon$): 256 (-10.5), 237 (+7.3), 210 (+11.9).

(5*S*,6*R*,7*R*,8*S*,9*S*,10*R*)-6,7,9,10-tetra-*O*-(*p*-bromo-benzyol)-5,8-cyclo-5,6,7,8,9,10-hexaoxo-tridecanoic acid, methyl ester (**S55**) (37% over 3 steps)

¹H NMR (400 MHz, CDCl₃): δ 7.76 (d, *J* = 8.8 Hz, 2 Ph), 7.75 (d, *J* = 8.8 Hz, 2 Ph), 7.70 (d, *J* = 8.4 Hz, 2 Ph), 7.50 (d, *J* = 8.8 Hz, 2 Ph), 7.46 (d, *J* = 8.4 Hz, 2 Ph), 7.43 (d, *J* = 8.4 Hz, 2 Ph), 7.35 (d, *J* = 2.4 Hz, 4 Ph), 5.80 (dd, *J* = 7.2, 4.8 Hz, H-7), 5.69 (t, *J* = 4.2 Hz, H-6), 5.62 (dd, *J* = 5.6, 4.0 Hz, H-9), 5.58 (dt, *J* = 6.4, 5.4 Hz, H-10), 4.45 (t, *J* = 6.6 Hz, H-8), 4.23 (m, H-5), 3.59 (s, OMe), 2.27 (t, *J* = 6.8 Hz, H-2), 1.71 (m, H-3, H-3', H-4, H-11, H-11'), 1.58 (m, H-4, H-12), 1.38 (m, H-12'), and 0.88 (t, *J* = 7.4 Hz, H-13) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 173.5 (C-1), 165.0 (-CO₂R), 164.9 (-CO₂R), 164.5 (-CO₂R), 164.0 (-CO₂R), 131.9 (2 *o*- or *m*-Ph), 131.8 (2 *o*- or *m*-Ph), 131.7 (2 *o*- or *m*-Ph), 131.5 (2 *o*- or *m*-Ph), 131.10 (4 *o*- or *m*-Ph), 131.08 (2 *o*- or *m*-Ph), 130.7 (2 *o*- or *m*-Ph), 128.8 (*i*- or *p*-Ph), 128.6 (*i*- or *p*-Ph), 128.43 (*i*- or *p*-Ph), 128.35 (*i*- or *p*-Ph), 127.9 (*i*- or *p*-Ph), 127.8 (*i*- or *p*-Ph), 127.3 (*i*- or *p*-Ph), 79.3 (C-5), 77.8 (C-8), 74.3 (C-9), 74.0 (C-7), 73.3 (C-6), 72.8 (C-10), 51.5 (OMe), 33.5 (C-2), 33.2 (C-11), 28.6 (C-4), 21.1 (C-3),

18.4 (C-12), and 13.8 (C-13) ppm. IR (NaCl): ν 2960, 1730, 1588, 1260, 1091, 754 cm^{-1} . MS (FAB) calc'd for $\text{C}_{42}\text{H}_{39}\text{O}_{11}\text{Br}_4$ $[\text{M}+\text{H}]^+$ 1034.9235, found 1034.9220. CD (CH_3CN) λ_{max} ($\Delta\epsilon$): 253 (-39.7), 236 (+22.8), 214 (+4.8).

(5*S*,6*S*,7*R*,8*S*,9*S*,10*R*)-5,6,7,8,9,10-hexa-*O*-(*p*-bromo-benzoyl)-5,6,7,8,9,10-hexaoxo-tridecanoic acid, methyl ester (**19**) (25% over 3 steps)

^1H NMR (600 MHz, CDCl_3): δ 7.92 (d, J = 8.4 Hz, 2 Ph), 7.79 (d, J = 8.4 Hz, 2 Ph), 7.77 (d, J = 8.4 Hz, 2 Ph), 7.67 (d, J = 8.4 Hz, 2 Ph), 7.60 (d, J = 8.4 Hz, 2 Ph), 7.58 (d, J = 8.4 Hz, 2 Ph), 7.56 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2 Ph), 7.48 (d, J = 8.4 Hz, 2 Ph), 7.46 (d, J = 8.4 Hz, 2 Ph), 7.38 (d, J = 8.4 Hz, 2 Ph), 7.32 (d, J = 8.4 Hz, 2 Ph), 5.97 (dd, J = 7.8, 1.8 Hz, H-9), 5.94 (dd, J = 5.4, 3.6 Hz, H-6), 5.86 (t, J = 3.6 Hz, H-7), 5.82 (dd, J = 8.4, 4.2 Hz, H-8), 5.61 (m, H-10), 5.51 (q, J = 6.0 Hz, H-5), 3.58 (s, OMe), 2.30 (m, H-2, H-2'), 1.8 (m, H-4), 1.62 (m, H-4', H-11, H-11', H-3, H-3') 1.35 (m, H-12, H-12'), and 0.90 (t, J = 7.2 Hz, H-13) ppm. IR (NaCl): ν 2934, 2923, 2855, 1725, 1582, 1250, 1091, 843 cm^{-1} . CD (CH_3CN) λ_{max} ($\Delta\epsilon$): 258 (+11.2), 236 (-7.5), 211 (-6.1).

(5*R*,6*S*,7*R*,8*S*,9*S*,10*R*)-6,7,9,10-tetra-*O*-(*p*-bromo-benzyol)-5,8-cyclo-5,6,7,8,9,10-hexaoxo-tridecanoic acid, methyl ester (**S56**) (17% over 3 steps)

^1H NMR (600 MHz, CDCl_3): δ 7.86 (d, J =8.4, 2 Ph), 7.69 (d, J = 8.7, 4 Ph), 7.61 (d, J = 8.4 Hz, 2 Ph), 7.49 (d, J = 8.7 Hz, 2 Ph), 7.46 (d, J = 8.7 Hz, 2 Ph), 7.42 (d, J = 8.4 Hz, 2 Ph), 7.39 (d, J = 8.4 Hz, 2 Ph), 5.74 (dd, J = 5.3, 2.9 Hz, H-9), 5.65 (ddd, J = 11.1, 5.4, 3.0 Hz, H-10), 5.58 (d, J = 3.0 Hz, H-7), 5.43 (d, J = 3.6 Hz, H-6), 4.23 (dd, J = 5.1, 3.3 Hz, H-8), 4.08 (tt, J = 4.8, 3.0, H-5), 3.58 (s, OMe), 2.27 (m, H-2, H-2'), 1.63 (m, 3H), 1.52 (m, 3H), 1.35 (m, H-12), 1.24 (m, H-12'), and

0.87 (t, $J = 7.4$ Hz, H-13) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ 173.5 (C-1), 164.9 (2 $-\text{CO}_2\text{R}$), 164.5 ($-\text{CO}_2\text{R}$), 164.0 ($-\text{CO}_2\text{R}$), 131.9 (2 *o*- or *m*-Ph), 131.8 (2 *o*- or *m*-Ph), 131.63 (2 *o*- or *m*-Ph), 131.61 (2 *o*- or *m*-Ph), 131.4 (2 *o*- or *m*-Ph), 131.2 (2 *o*- or *m*-Ph), 131.11 (2 *o*- or *m*-Ph), 131.99 (2 *o*- or *m*-Ph), 128.8 (*i*- or *p*-Ph), 128.73 (*i*- or *p*-Ph), 128.70 (*i*- or *p*-Ph), 128.4 (*i*- or *p*-Ph), 128.2 (*i*- or *p*-Ph), 128.0 (*i*- or *p*-Ph), 127.8 (*i*- or *p*-Ph), 127.6 (*i*- or *p*-Ph), 82.2 (C-H), 80.7 (C-H), 79.0 (C-H), 78.1 (C-H), 73.0 (C-H), 72.9 (C-H), 51.5 (OMe), 33.6 (C-2 or C-11), 33.2 (C-2 or C-11), 27.8 (C-4), 21.5 (C-3), 18.5 (C-12), and 13.8 (C-13) ppm. IR (NaCl): ν 2930, 1732, 1590, 1260, 1091, 1006, 846 cm^{-1} . MS (FAB) calc'd for $\text{C}_{42}\text{H}_{39}\text{O}_{11}\text{Br}_4$ $[\text{M}+\text{H}]^+$ 1034.9235, found 1034.9212. CD (CH_3CN) λ_{max} ($\Delta\epsilon$): 251 (+10.3), 231 (+1.3), 214 (+5.4).

(2'*S*)-*N*-valyl-(2''*S*)-*N*-(δ -valeroamide)-(5*S*,6*S*,7*S*,8*R*,9*R*,10*S*)-5,6,7,8,9,10-hexa-*O*-(*p*-bromobenzoyl)-5,6,7,8,9,10-hexaoxo-hexaeicosoic-diamide (**17**)

Sagittamide A (**1**) (3.4 mg, 3.44 μmol) was dissolved in 0.5 mL MeOH and excess diazomethane in ether was added and allowed to stand for 1 hour. The solution was dried and the residue was dissolved in anhydrous MeOH sat'd with NH_3 (3.0 mL) and stirred at RT for 24 hours dried and retreated for a second 24 hours when MS showed no remaining acetates. The residue was redried from anhydrous toluene then dissolved in anhydrous pyridine (2.0 mL) and *p*-bromobenzoylchloride (136.5 mg, 0.622 mmol) and DMAP (2.2 mg, 0.018 mmol) were added and stirred at 40° C for 9.5 hours. 3-(*N,N*-dimethylamino)-propylamine (150 μL) was added and allowed to stir for 10 minutes before concentrating mixture in vacuo. The bright orange oil was purified first by silica chromatography eluting with EtOAc then by silica chromatography eluting with 10% ether/hexanes, 30% ether hexanes, ether, EtOAc to give the hexabenzoate **17** (0.8 mg, 13% over 4 steps).

^1H NMR (600 MHz, CDCl_3): δ 7.87 (d, J = 8.4 Hz, 2 Ph), 7.82 (d, J = 8.4 Hz, 2 Ph), 7.74 (d, J = 8.4 Hz, 2 Ph), 7.63 (d, J = 8.4 Hz, 2 Ph), 7.580 (d, J = 8.4 Hz, 2 Ph), 7.575 (d, J = 8.4 Hz, 4 Ph), 7.45 (d, J = 8.4 Hz, 2 Ph), 7.44 (d, J = 8.4 Hz, 2 Ph), 7.43 (d, J = 8.4 Hz, 2 Ph), 7.35 (d, J = 8.4 Hz, 2 Ph), 7.29 (d, J = 8.4 Hz, 2 Ph), 6.61 (s, NH), 6.03 (d, J = 7.8 Hz, NH), 5.98 (br s, NH), 5.79 (d, J = 10.2 Hz, 1H), 5.72 (d, J = 6.5 Hz, 1H), 5.69 (t, J = 5.7 Hz, 1H), 5.61 (dd, J = 7.2, 2.4 Hz, 1H), 5.56 (m, 1H), 5.31 (m, 1H), 4.41 (dd, J = 8.4, 4.9 Hz, 1H), 3.63 (s, OMe), 3.45 (m, 3H), 2.30 (m, 2H), 2.20 (m, 2H), 2.03 (m, 1H), 1.6-1.4 (m, 8H), 1.23 (br s, 22H), 0.81 (d, J = 7.2 Hz, 3H), and 0.78 (d, J = 7.2 Hz, 3H). CD (CH_3CN) λ_{max} ($\Delta\epsilon$): 257 (+13.7), 241 (-9.7), 212 (-2.8).

400 MHz in CDCl₃
10

75 MHz in CDCl₃
10

600 MHz in CDCl_3
S42

150 MHz in CDCl₃
S42

100 MHz in CDCl_3
13

75 MHz in CDCl₃
S48

600 MHz in d_6 -DMSO
2

Current Data Parameters
NAME SL-021106
EXPNO 9
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060212
Time 8.34
INSTRUM spect
PROBHD 5 mm TXI Z-GRD
PULPROG zg
TD 32768
SOLVENT DMSO
NS 64
DS 0
SWH 9615.385 Hz
FIDRES 0.293438 Hz
AQ 1.7040380 sec
RG 10
DW 52.000 usec
DE 6.00 usec
TE 298.1 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 6.00 usec
PL1 -6.00 dB
SFO1 600.1628214 MHz

F2 - Processing parameters
SI 32768
SF 600.1600064 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

125 MHz in d_6 -DMSO 2

600 MHz in d_6 -DMSO
3

Current Data Parameters
NAME SL-021106
EXPNO 13
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060212
Time 16.43
INSTRUM spect
PROBHD 5 mm TXI Z-GRD
PULPROG zg
TD 32768
SOLVENT DMSO
NS 128
DS 0
SWH 9615.385 Hz
FIDRES 0.293438 Hz
AQ 1.7040380 sec
RG 10
DW 52.000 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 6.00 usec
PL1 -6.00 dB
SFO1 600.1628214 MHz

F2 - Processing parameters
SI 32768
SF 600.1600058 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

125 MHz in d_6 -DMSO
3

600 MHz in d_6 -DMSO
4

```

Current Data Parameters
NAME          SL-021106
EXPNO         1
PROCNO        1

F2 - Acquisition Parameters
Date_         20060211
Time          12.46
INSTRUM       spect
PROBHD        5 mm TXI Z-GRD
PULPROG       zg
TD            32768
SOLVENT       DMSO
NS            64
DS            0
SWH           9615.385 Hz
FIDRES       0.293438 Hz
AQ           1.7040380 sec
RG           10
DE           52.000 usec
TE           297.9 K
D1           1.00000000 sec
MCWREST      0.00000000 sec
MCWPK        0.01500000 sec

===== CHANNEL f1 =====
NUC1          1H
P1            6.00 usec
PL1          -6.00 dB
SFO1         600.1628214 MHz

F2 - Processing Parameters
SI           32768
SF          600.1600061 MHz
WDW          EM
SSB          0
LB           0.30 Hz
GB           0
PC           1.00
  
```

125 MHz in d_6 -DMSO
4

600 MHz in d_6 -DMSO

5

Current Data Parameters
NAME SL-021106
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060211
Time 22.02
INSTRUM spect
PROBHD 5 mm TXI Z-GRD
PULPROG zg
TD 32768
SOLVENT DMSO
NS 64
DS 0
SWH 9615.385 Hz
FIDRES 0.293438 Hz
AQ 1.7040380 sec
RG 10
DM 52.000 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

==== CHANNEL f1 =====
NUC1 1H
P1 6.00 usec
PL1 -6.00 dB
SFO1 600.1628214 MHz

F2 - Processing parameters
SI 32768
SF 600.1600064 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

125 MHz in d_6 -DMSO

5

500 MHz in d_6 -DMSO 6

125 MHz in d_6 -DMSO
6

600 MHz in CD₃OD
7

600 MHz in d_6 -DMSO **8**

125 MHz in d_6 -DMSO
8

600 MHz in d_6 -DMSO
9

Current Data Parameters
NAME SL-021106
EXPNO 21
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060215
Time 8.11

INSTRUM spect
PROBHD 5 mm TXI 2-GR
PULPROG zg
TD 32768
SOLVENT DMSO
NS 64

DS 0
SWH 9615.385 Hz
FIDRES 0.293438 Hz
AQ 1.7040380 sec

RG 10
DW 52.000 usec

DE 6.00 usec
TE 298.1 K

D1 1.00000000 sec
MCREST 0.00000000 sec

MCWRK 0.01500000 sec

===== CHANNEL f1 =====

NUC1 1H

P1 6.00 usec

PL1 -6.00 dB

SFO1 600.1628214 MHz

F2 - Processing parameters

SI 32768

SF 600.1600061 MHz

WDW EM

SSB 0

LB 0.30 Hz

GB 0

PC 1.00

125 MHz in d_6 -DMSO
9

600 MHz in d_6 -DMSO

S34

Current Data Parameters
NAME SL-051606
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050516
Time 9.33
INSTRUM spect
PROBHD 5 mm TXI Z-GRD
PULPROG zg
TD 32768
SOLVENT DMSO
NS 64
DS 0
SWH 9615.385 Hz
FIDRES 0.293438 Hz
AQ 1.7040380 sec
RG 10
DW 52.000 usec
DE 6.00 usec
TE 295.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCMRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 ^1H
P1 6.00 usec
PL1 -6.00 dB
SFO1 600.1628214 MHz

F2 - Processing parameters
SI 32768
SF 600.1600046 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

125 MHz in d_6 -DMSO
S34

600 MHz in d_6 -DMSO
S35

Current Data Parameters
NAME SL-051606
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050516
Time 14.47
INSTRUM spect
PROBHD 5 mm TXI Z-GRD
PULPROG zg
TD 32768
SOLVENT DMSO
NS 128
DS 8
SWH 9615.385 Hz
FIDRES 0.293438 Hz
AQ 1.7040380 sec
RG 10
DW 52.000 usec
DE 6.00 usec
TE 295.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 6.00 usec
PL1 -6.00 dB
SFO1 600.1628214 MHz

F2 - Processing parameters
SI 32768
SF 600.1600049 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

125 MHz in d_6 -DMSO
S35

600 MHz in d_6 -DMSO

S36

```

Current Data Parameters
NAME          SL-051606
EXPNO         9
PROCNO        1

F2 - Acquisition Parameters
Date_         20050516
Time_         22.21
INSTRUM       spect
PROBHD        5 mm TXI Z-GRD
PULPROG       zg
TD            32768
SOLVENT       DMSO
NS            128
DS            8
SWH           9615.385 Hz
FIDRES        0.293438 Hz
AQ            1.7040380 sec
RG            10
DE           52.000 usec
TE           295.0 K
D1            1.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

===== CHANNEL f1 =====
NUC1          1H
P1            6.00 usec
PL1          -6.00 dB
SFO1         600.1628214 MHz

F2 - Processing parameters
SI           32768
SF          600.1600041 MHz
WDW          EM
SSB          0
LB           0.30 Hz
GB           0
PC           1.00
  
```

125 MHz in d_6 -DMSO
S36

Current Data Parameters
NAME SCL_051305
EXPNO 9
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050515
Time 11.46
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 40960
SOLVENT CDCl3
NS 24772
DS 2
SWH 27777.777 Hz
FIDRES 0.678168 Hz
AQ 0.7373480 sec
RG 8192
DW 18.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.50000000 sec
d11 0.03000000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 5.00 usec
PL1 3.00 dB
SFO1 125.7652853 MHz

===== CHANNEL f2 =====
CPDPRG2 garp
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 22.00 dB
SFO2 500.1120004 MHz

F2 - Processing parameters
SI 65536
SF 125.7526997 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

600 MHz in d_6 -DMSO
S37

```

Current Data Parameters
NAME          ST-053005
EXPNO         1
PROCNO        1

F2 - Acquisition Parameters
Date_         20050530
Time          19.11
INSTRUM       spect
PROBHD        5 mm TXI Z-GRD
PULPROG       zg
TD            32768
SOLVENT       DMSO
NS            128
DS            0
SWH           9615.385 Hz
FIDRES       0.293438 Hz
AQ           1.7040380 sec
RG           10
DE           52.000 usec
TE           295.1 K
D1           1.00000000 sec
MCREST       0.00000000 sec
MCWRR       0.01500000 sec

===== CHANNEL f1 =====
NUC1          1H
P1           6.00 usec
PL1          -6.00 dB
SFO1         600.1628214 MHz

F2 - Processing parameters
SI           32768
SF           600.159935 MHz
WDW          EM
SSB          0
LB           0.30 Hz
GB           0
PC           1.00
  
```

125 MHz in d_6 -DMSO
S37

Current Data Parameters
NAME SCL_053105
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050531
Time 17.30
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 40960
SOLVENT CDCl3
NS 23872
DS 2
SWH 27777.777 Hz
FIDRES 0.678168 Hz
AQ 0.7373480 sec
RG 8192
DW 18.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.50000000 sec
d11 0.03000000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 5.00 usec
PL1 3.00 dB
SFO1 125.7652853 MHz

===== CHANNEL f2 =====
CPDPRG2 garp
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 22.00 dB
SFO2 500.1120004 MHz

F2 - Processing parameters
SI 65536
SF 125.7526993 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

600 MHz in d_6 -DMSO
S38

```

Current Data Parameters
NAME          SL-053005
EXPNO         5
PROCNO        1

F2 - Acquisition Parameters
Date_         20050531
Time          8.02
INSTRUM       spect
PROBHD        5 mm TXI Z-GRD
PULPROG       zg
TD            32768
SOLVENT       DMSO
NS            128
DS            0
SWH           9615.385 Hz
FIDRES        0.293438 Hz
AQ            1.7040380 sec
RG            10
DW            52.000 usec
DE            6.00 usec
TE            295.0 K
D1            1.00000000 sec
MCREST        0.00000000 sec
MCWPRK        0.01500000 sec

===== CHANNEL f1 =====
NUC1          1H
P1            6.00 usec
PL1           -6.00 dB
SFO1          600.1628214 MHz

F2 - Processing parameters
SI            32768
SF            600.1599923 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
  
```

125 MHz in d_6 -DMSO
S38

600 MHz in d_6 -DMSO
S39

Current Data Parameters
NAME SL-053005
EXPNO 9
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050531
Time 17.54
INSTRUM spect
PROBHD 5 mm TXI Z-GRD
PULPROG zg
TD 32768
SOLVENT DMSO
NS 256
DS 0
SWH 9615.385 Hz
FIDRES 0.293438 Hz
AQ 1.7040380 sec
RG 10
DM 52.000 usec
DE 6.00 usec
TE 295.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 6.00 usec
PL1 -6.00 dB
SFO1 600.1628214 MHz

F2 - Processing parameters
SI 32768
SF 600.159923 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

125 MHz in d_6 -DMSO
S39

R = *p*-BrBz

600 MHz in CDCl₃

18

R = *p*-BrBz

600 MHz in CDCl₃
19

R = *p*-BrBz

300 MHz in CDCl₃
20