



Just light and heat! Visible-light photoexcitation of the innermost carbonyl of 2,3-diulose triggers an unprecedented Norrish type II photoelimination and uncatalyzed aldol sequential rearrangement through the thermal 5-(enolexo)-exo-trig cyclization of the

acyclic photoenol intermediate. The process involves a pyranosyl ring contraction and the formation of a new type of cyclopentitol derivatives with high diastereoselectivity (see scheme; R = acyl, alkyl, silyl group).

#### **Carbohydrates**

D. Alvarez-Dorta, E. I. León,\* A. R. Kennedy, A. Martín, I. Pérez-Martín, C. Riesco-Fagundo, *E. Suárez*\*..... **IIII**-**I** 

Sequential Norrish Type II Photoelimination and Intramolecular Aldol Cyclization of α-Diketones: Synthesis of Polyhydroxylated Cyclopentitols by **Ring Contraction of Hexopyranose Carbohydrate Derivatives** 



### Sequential Norrish Type II Photoelimination and Intramolecular Aldol Cyclization of α-Diketones: Synthesis of Polyhydroxylated Cyclopentitols by Ring Contraction of Hexopyranose Carbohydrate Derivatives

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**Abstract:** The excitation of the innermost carbonyl of nono-2,3-diulose derivatives by irradiation with visiblelight initiates a sequential Norrish type II photoelimination and aldol cyclization process that finally gives polyfunctionalized cyclopentitols. The rearrangement has been confirmed by the isolation of stable acyclic photoenol intermediates that can be independently cyclized by a thermal 5-(enolexo)-exotrig uncatalyzed aldol reaction with high diastereoselectivity. In this last step, the large deuterium kinetic isotope effect found for the 1,5-hydrogen atom transfer seems to indicate that the aldol reaction runs through a concerted pericyclic mechanism. Owing to the ready availability of pyranose

**Keywords:** carbohydrates • cyclopentitols • diketones • photochemistry • ring contraction sugars of various configurations, this protocol has been used to study the influence of pyranose ring-substituents on the diastereoselectivity of the aldol cyclization reaction. In contrast with other pyranose ring contraction methodologies no transition-metal reagents are needed and the sequential rearrangement occurs simply by using visible light and moderate heating (0 to 60 °C).

#### Introduction

The photochemical behavior of monoketones has attracted a great deal of attention from synthetic and theoretical perspectives, whereas comparatively much less evidence is available on  $\alpha$ -diketones.<sup>[1]</sup> Both types of photoexcited carbonyls exhibit a remarkable regioselectivity of intramolecular 1,5-hydrogen transfer, to give a 1,4-biradical intermediate, which finally evolves following two competitive paths: Norrish type II photoelimination and Norrish–Yang photocyclization.<sup>[2]</sup> Whereas photoelimination is usually the priority process with monoketones,  $\alpha$ -diketones yield almost exclusively 2-hydroxycyclobutanones by photocyclization. Moreover, in  $\alpha$ -diketones the 1,5-hydrogen abstraction apparently occurs only from the external carbonyl, such that the formation of acyl cyclobutanols has never been ob-

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served. The development of synthetic applications of this 1,5-hydrogen atom transfer reaction originated by  $\alpha$ -diketones has been scant.<sup>[3]</sup> This is somewhat surprising since  $\alpha$ -diketones can be selectively activated over other photochemically excitable groups, just by irradiation with visible light (violet-blue interval, ca. 450 nm). We believe this may be due to the lack of direct and general methods for their synthesis, especially on sensitive substrates, and to the instability observed for some aliphatic  $\alpha$ -diketones.

The conversion of carbohydrate derivatives into enantiopure polyfunctionalized cyclopentanes has been extensively documented.<sup>[4]</sup> Two general methodologies are currently used: Ring closing of polyfunctionalized acyclic molecules that most often involves multistep reaction sequences and ring contraction of pyranoside carbohydrate derivatives, which normally require a single synthetic step. These ringcontraction methods represent a highly efficient biomimetic approach to the synthesis of cyclopentanols.<sup>[5]</sup> Several procedures have been published, all of which start from conveniently modified carbohydrate derivatives and in general involve a reductive ring-opening followed by an intramolecular reductive coupling using samarium or zirconium reagents. Representative examples with indication of starting materials and reagents are: Hept-6-enopyranosides ([Cp<sub>2</sub>ZrCl<sub>2</sub>]/BF<sub>3</sub>•OEt<sub>2</sub>)<sup>[6]</sup> or (SmI<sub>2</sub>/[Pd(PPh<sub>3</sub>)<sub>4</sub>]),<sup>[7]</sup> oct-6-enopyranosiduronate (SmI<sub>2</sub>),<sup>[8]</sup> hept-6-ynopyranosides (SmI<sub>2</sub>/  $[Pd(PPh_3)_4]$ ,<sup>[7]</sup> 6-deoxy-6-iodo-hexopyranoside (SmI<sub>2</sub>),<sup>[9]</sup> and glucodialdo-1,5-hexopyranoside (SmI<sub>2</sub>).<sup>[10]</sup>

In connection with our ongoing research programs on the reactivity of  $\alpha$ -diketones<sup>[11]</sup> and intramolecular hydrogen

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Scheme 1. Photochemistry of nono-2,3-diulose 1. INHAT = intramolecular hydrogen atom transfer.

atom transfer (INHAT) promoted by alkoxyl radicals in carbohydrate chemistry,<sup>[12]</sup> we present herein our results on the photochemical reactivity of nono-2,3-diuloses (Scheme 1).<sup>[13]</sup> It is generally accepted that hydrogen atom abstraction by a photoexcited carbonyl closely resembles the hydrogen atom abstraction by alkoxyl radicals.<sup>[1a,b]</sup> Therefore, one would expect that in nono-2,3-diulose 1, in as much as the hydrogen atom at C5 is geometrically inaccessible, the abstraction of H8 may proceed either by the external carbonyl (1,6-HAT) or by the innermost carbonyl (1,5-HAT). Through research conducted in our laboratory we have shown that both types of processes can be carried out with alkoxyl radicals. C-Glycosides possessing 1-hydroxymethyl<sup>[14]</sup> and 1-hydroxyethyl<sup>[15]</sup> tethers cyclized, with the PhI(OAc)<sub>2</sub>/I<sub>2</sub> system, to give 6,8-dioxabicyclo[3.2.1]octane (1,5-HAT) and 2,9dioxabicyclo[3.3.1]nonane (1,6-HAT) derivatives, respectively.

As described in Scheme 1 the reaction of 2,3-diulose 1 proceeded by a sequential Norrish type II photoelimination through the 3,8-biradical I; the intermediate photoenol II subsequently formed was converted into a cyclopentane derivative by a thermal OH- $\beta$ -syn aldol cyclization. Finally, the regenerated  $\alpha$ -diketone reacts with the hydroxyl group at C8 to give the hemiketal 2. Some features of these processes deserve brief comment. Only visible light and moderate heating are necessary for the reaction to take place, in contrast with the other ring contraction methods listed above that require the presence of transition-metal reagents. As mentioned before, Norrish type II photoelimination of  $\alpha$ -diketones is an extremely rare reaction, whereas the uncatalyzed aldol cyclization, in which a photoenol acts as a preformed enolate, is unprecedented to our knowledge. As noted, the stereocenters at C4 and C8 destroyed in the photochemical reaction are regenerated diastereoselectively with inversion of configuration in the aldol cyclization step.

Owing to the ready availability of pyranose sugars of various configurations, this protocol would provide access to highly oxygenated 1,2-*trans* dialkylated cyclopentanes and cyclopentanoid natural products, for example, prostaglandins, brefeldin, and Corey lactone analogues. The synthesis of systems with 1-(hydroxymethyl)cyclopentitol moieties such as trehazoline, calditol, and bacteriohopanoids should be particularly accessible through this methodology. We believe that this protocol is also uniquely suited to study the effect of pyranose ring-substituents on the diastereoselectivity of the aldol cyclization reaction.

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#### **Results and Discussion**

The present contribution is a study of the scope and the selectivity of this reaction, as well as an effort to establish the best conditions for this photoreaction and to demonstrate the mechanism involved. This has been achieved by preparing a variety of 2,3-diuloses belonging to carbohydrates in pyranose and furanose form.

Synthesis of  $\alpha$ -*C*-propynyl glycosides: We based the preparation of these compounds on the  $\alpha$ -ethynylation of sugars by *C*-glycosidation using *n*Bu<sub>3</sub>SnC=CSiMe<sub>3</sub> in the presence of trimethylsilyl triflate (TMSOTf) followed by desilylation of the initial adducts, a methodology well established by the groups of Isobe<sup>[16]</sup> and Dondoni.<sup>[17]</sup> Thus, gluco derivative **6** was obtained from acetate **3** through the silyl intermediate **5** in good yield (Scheme 2). Unfortunately, repeated attempts



Scheme 2. Synthesis of nono-2,3-diuloses by oxidation of non-2-ynitols. a) For the synthesis of **5** from **3**:  $nBu_3SnC=CTMS$  (2 equiv), TMSOTf (2.5 equiv), CH<sub>2</sub>Cl<sub>2</sub>, MS 4 Å, room temperature, 3 h, 66%; for the synthesis of **7** from **3** (Method A): TMSC=CMe (2 equiv), TMSOTf (3 equiv), MeCN, MS 4 Å, 0°C, 2 h, 33%; for the synthesis of **7** from **3** (Method B): n-Bu\_3SnC=CMe (2 equiv), TMSOTf (2 equiv), CH<sub>2</sub>Cl<sub>2</sub>, MS 4 Å, room temperature, 2 h, 82%; for the synthesis of **7** from **4**: n-Bu\_3SnC=CMe (2 equiv), CH<sub>2</sub>Cl<sub>2</sub>, MS 4 Å, room temperature, 2 h, 82%; for the synthesis of **7** from **4**: n-Bu\_3SnC=CMe (2.5 equiv), BF<sub>3</sub>·OEt<sub>2</sub> (2 equiv), CH<sub>2</sub>Cl<sub>2</sub>, MS 4 Å, room temperature, 2 h, 92%; for the synthesis of **7** from **4**: n-Bu\_3SnC=CMe (2.5 equiv), BF<sub>3</sub>·OEt<sub>2</sub> (2 equiv), CH<sub>2</sub>Cl<sub>2</sub>, MS 4 Å, room temperature, 2 h, 92%; c) see text; d) [Pd(PPh\_3)\_4], (0.05 equiv), CUI (0.1 equiv), PhI (1 equiv), piperidine, 80°C, 1 h, 88%; e) O<sub>3</sub> (excess), CH<sub>2</sub>Cl<sub>2</sub>, -78°C, 2 h, then Me<sub>2</sub>S (2.1 equiv), 6 h, dark; f) Daylight-lamp irradiation, C<sub>6</sub>D<sub>6</sub>, 30°C, N<sub>2</sub>, 9 h, then air, 48%, two steps. TMS=trimethylsilyl, OAc= acyl.

to accomplish the alkyne methylation by using several bases (*n*BuLi, LDA, and NaH) and alkylating agents (MeI and MeOTf) under a range of conditions gave none of the desired product 7 and only starting material 6 was recovered in all cases.<sup>[18]</sup> A related attempt at C-glycosidation by treat-

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ment of acetate 3 and commercially available TMSC=CMe was similarly unproductive. After extensive experimentation (see the Supporting Information) the  $\alpha$ -C-propynyl glucoside 7 was obtained with good diastereoselectivity but in an unacceptable maximum yield of 33%. Therefore, an alternative route was sought using  $nBu_3SnC \equiv CMe$  as glycosyl acceptor, which was prepared according to the procedure developed by Logue and Teng.<sup>[19]</sup> The reaction catalyzed by TMSOTf proceeded very smoothly to give 7 in good yield and diastereoselectivity (90%, diastereometic ratio (d.r.)  $\alpha$ /  $\beta$ , 10:1). Alternatively, by using glucopyranosyl fluoride **4** as glycosyl donor and BF3•OEt2 as catalyst the diastereoselectivity was improved since almost only the  $\alpha$ -isomer of the product was detected. All the  $\alpha$ -C-propynyl glycosides shown in Tables 1-4 were prepared by using one of these two methodologies or in some cases by simple functional group modification between them. In general, the fluoride method was preferred in substrates with acid-sensitive protectors (e.g., 15, Table 1), whereas the formation of highly unstable fluorides, as in the furanoses 67-69 (Table 4), prevents its utilization.

For comparative purposes in the photochemical experiments, permethylated 2,6-anhydro-7,8-dideoxy-8-phenyl-Dglycero-L-gulo-oct-7-ynitol (9) was prepared by Sonogashira cross-coupling of alkyne 6 with iodobenzene.<sup>[20]</sup>

Diketones 1, 9 (Scheme 2), 18–24 (Table 1), 38–43 (Table 2), 58–61 (Table 3), and 70–72 (Table 4) were pre-

pared from the corresponding non-2-ynitols by oxidation of the triple bond with ozone (Method A)<sup>[21]</sup> or NaIO<sub>4</sub>/ RuO<sub>2</sub>·xH<sub>2</sub>O (Method B).<sup>[22]</sup>  $\alpha$ -Diketones using benzyl ether as protective groups were better prepared by oxidation of the triple bond with  $NaIO_4/RuO_2 \cdot x H_2O$  than by using the ozone methodology. The  $\alpha$ -diketones obtained as yellow oils are in most cases stable for at least several months when stored at -25°C under nitrogen in the dark and can be purified by rapid silica gel column chromatography, although a significant loss of material was generally observed. In all the  $\alpha$ -diketones the conformation of the pyranose ring was carefully studied by analysis of its vicinal coupling constant values. A chair  ${}^{7}C_{4}$  conformation (equivalent to  ${}^{4}C_{1}$  in the aldose series), in which the H8 and the diketone tether are in a 1,3-diaxial relationship, appears to be essential for the intramolecular hydrogen atom transfer (INHAT) reaction to take place.

In our preliminary experiment, a  $[D_6]$ benzene solution of  $\alpha$ -diketone **1** was irradiated with a daylight lamp (Philips master PL electronic, 23 W/865) at 30 °C until the yellow color faded (3 h). Direct sunlight can also be used but the reaction is usually slower and times are not reproducible. A single diastereomer with a hexahydro-2*H*-cyclopenta[*b*]furan bicyclic structure **2** was formed in 52% yield, and no other isomers were detected by <sup>1</sup>H NMR spectroscopy of the crude reaction mixture (Table 1). With the aim of establishing the excitation behavior of the dicarbonyl system, a solu-

Table 1. Synthesis and photolysis of 2,3-diuloses with α-D-glucopyranose stereochemistry.

α-C-Propynyl glucoside	Method <sup>[b]</sup>	2,3-Diulose	Product
[%] <sup>[a]</sup>		[%] <sup>[a]</sup>	$[\%, d.r.]^{[a,c]}$
		$ \begin{array}{c}                                     $	
<b>7</b> : $R = R^1 = OMe$ (90)	А	1: $R = R^1 = OMe^{[d]}$	<b>2</b> : $R = R^1 = OMe (52)^{[e]}$
<b>11</b> : $R = R^1 = OBn$ (86)	В	<b>18</b> : $R = R^1 = OBn$ (62)	<b>25</b> : $R = R^1 = OBn$ (58)
<b>12</b> : $R = OBn$ , $R^1 = ODPS$	В	<b>19</b> : $R = OBn, R^1 = ODPS$ (64)	<b>26</b> : $R = OBn, R^1 = ODPS$ (65, 5:1)
13: $R = OBn, R^1 = OAc$	В	<b>20</b> : $R = OBn$ , $R^1 = OAc$ (47)	<b>27</b> : $R = OBn$ , $R^1 = OAc$ (67, 1:0.9)
<b>14</b> : $R = OBn, R^1 = N_3$	В	<b>21</b> : $R = OBn, R^1 = N_3$ (59)	<b>28</b> : $R = OBn$ , $R^1 = N_3$ (55, 1.3:1)
<b>15</b> (77)	А	<b>22</b> (67)	<b>29</b> (53, 10:3)
RO <sup>11</sup> , OMe MeO			R <sup>1</sup> O R <sup>1</sup> O Me MeO
<b>16</b> : $R = R^1 = TBS$ (68)	А	<b>23</b> : $R = R^1 = TBS$ (75)	<b>30</b> : $R = R^1 = TBS$ (63)
<b>17</b> : $R = Ac, R^1 = TBS$	А	<b>24</b> : $R = Ac, R^1 = TBS$ (73)	<b>31</b> : $R = Ac, R^1 = TBS$ (62, 10:3)

[a] Yield of the product isolated by using chromatography. [b] Method A:  $O_3$  (excess),  $CH_2Cl_2$ , -78 °C, 2 h, then  $Me_2S$  (2.1 equiv), room temperature, dark. Method B:  $NaIO_4$  (4 equiv),  $RuO_2 \cdot x H_2O$  (8.8 mg),  $CCl_4 / CH_3CN/H_2O$  (1:1:1.5), room temperature, dark. [c] Hemiketal diastereomeric ratio, major isomer shown. [d] Crude product of high purity but could not be purified on chromatography over silica. [e] Yield over three steps. DPS = tert-butyldiphenylsilyl, TBS = tert-butyldimethylsilyl.

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taining the triplet quencher pyrene (13 equiv) was irradiated at 30°C for 12 h. The photoreaction was completely inhibited, confirming that the hydrogen abstraction occurs mainly from the triplet state since cleavage products promoted by the singlet biradical were not detected. Compound 2 is a crystalline solid whose structure and stereochemistry was determined by extensive 1D and 2D NMR studies and confirmed by X-ray crystallographic analysis.<sup>[23]</sup> In particular, the  ${}^{3}J_{H4,H5} =$ 4.7 Hz (calcd 4.1 Hz), HMBC correlations of H4 to C8 and C9, and NOE interactions between the hydroxyl proton and H4 and H9 as well as interactions between 1-Me and H5 and H7 accounted for the  $\beta$ -syn cyclization and the S stereochemistry of the hemiketal. Due to the flexibility of the cyclopentane, weighted average  ${}^{3}J_{\rm H,H}$  for the ring protons were calculated for the more popu-

tion of 1 in  $[D_6]$  benzene con-



lated conformers as determined by pseudorotational analysis.<sup>[24]</sup> Two conformers were obtained with pseudorotational phase angle (P; north- and south-type,  $P_N P_S$ , respectively) and populations, as indicated:  $E_6$  ( $P_N = 346.4^\circ$ , 60%) and  ${}^{6}T_{7}/E_{7}$  ( $P_{s}=189.1^{\circ}$ , 40%; see Table 2S and Figure 1S in the Supporting Information for details). The more stable conformer is in close agreement with the ring conformation in the solid state:  ${}^{7}T_{6}$  ( $P_{N}=358.5^{\circ}$ ). A small but significant  ${}^{4}J_{\rm H5,H7}$  coupling (ca. 1 Hz) can be detected, which is more consistent with the  ${}^{6}T_{7}/E_{7}$  conformation where both hydrogens are pseudoequatorial in a W-type planar arrangement. The X-ray crystallographic structure indicated that the configuration of the hemiketal is stabilized by an intramolecular seven-membered hydrogen bond between the hydroxyl group and the oxygen atom at C9. The reaction was monitored by <sup>1</sup>H NMR spectroscopy but we were unable to detect any photoenol II under these reaction conditions (30 °C); nevertheless, at 0 °C a doublet at  $\delta = 5.56$  ppm (J= 9 Hz) and a broad singlet exchangeable with  $D_2O$  at  $\delta =$ 6.73 ppm assignable to the transient photoenol could be observed.<sup>[25]</sup> Upon warming to room temperature these signals rapidly disappeared completely, the cyclized product 1 being the only one observable after a few minutes.

Unfortunately, the photolysis of phenyl diulose **9** failed completely to undergo the desired 1,5-HAT, instead providing the photoenol **III** as the only intermediate detectable by <sup>1</sup>H NMR spectroscopy (Scheme 2).<sup>[25,26]</sup> This intermediate could not be isolated and was rapidly oxidized during the work-up, presumably by the ambient oxygen, ultimately leading to the degraded lactone **10** in moderate yield. A possible inversion of the pyranose ring in the diketone was discarded by the coupling con-

discarded by the coupling constants, which are undoubtedly consistent with a  ${}^{7}C_{4}$  conformation.

The other 2,3-diuloses belonging to D-glucopyranose series 18-24 (Table 1) with different substituents at C7 and C9, vicinal carbon atoms in the INHAT, were synthesized to determine the influence of steric and electronic effects in both the reactivity of the diradical intermediate I and the diastereoselectivity of the aldol reaction. The reactions involved in this transformation do not seem to be influenced greatly by the steric bulkiness or electronegativity of the protecting groups, similar yields being obtained and only products from OH-β-syn aldol cyclization being observed. The somewhat lower yields obtained in the synthesis of 2 and 29 could be

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more related with the instability of the diulose itself.

The coupling constant  ${}^{3}J_{H4,H5}$  proved to be diagnostic in distinguishing between the OH- $\beta$ -syn and OH- $\alpha$ -syn aldol cyclization (see below,  ${}^{3}J_{H4\alpha,H5\beta}=2-4$  Hz is much smaller than  ${}^{3}J_{H4\beta,H5\beta} = 9-10$  Hz). However, due to the flexibility of the cyclopentane ring the stereochemistries have been confirmed further by nuclear Overhauser effect spectroscopy (NOESY) studies on minimized structures. In those compounds 2 and 29-31 in which the experimental ring coupling constants could be unequivocally determined, a conformational study by pseudorotational analysis has been performed. Two relatively narrow pseudorotational ranges are preferred for these D-glucose-derived cyclopentanes. In the North-type conformations P ranges from 311 to 346° ( ${}^{5}E/{}^{5}T_{6}$ to  $E_6$ ) were observed, whereas P values of 106–189° ( ${}^4T_5$  to  ${}^{6}T_{7}$ ) were found for the conformations positioned in the South region of the pseudorotational wheel (See Table 2S and Figure 1S of the Supporting Information for details).

The next series of reactions explored the photolysis of deoxy-2,3-diuloses **38–43** as described in Table 2. The reactions proceeded analogously to the previously mentioned examples in terms of yield and diastereoselectivity except for 5-deoxy-diulose **38**, which gave a 1:1 diastereomeric mixture of OH- $\beta$ -syn **44** and OH- $\alpha$ -syn **45** aldol cyclization products after heating for 5 h at 60 °C. The photolysis mixture was subjected to acetylation thus allowing for a partial chromatographic separation of acetates **44** and **45**.

The OH- $\beta$ -syn cyclization structure was assigned to **44** by the  ${}^{3}J_{H4\alpha,H5\beta}$ =4.4 Hz and substantiated by the observation of NOESY correlations between 1-Me and H7, and H4 and H6. Moreover, a larger  ${}^{3}J_{H4\beta,H5\beta}$ =9.8 Hz coupling constant

Table 2.	Synthesis and	photolysis of	mono- and di-de	eoxy-2,3-diuloses	in pyranose f	form

Tuble 2. Synthesis and ph	01013515 01 11101	to and a deoxy 2,5 dialoses	in pyranose romi.
$\alpha$ -C-Propynyl glycoside	Method <sup>[b]</sup>	2,3-Diulose	Product
$[\%, d.r.]^{[a]}$		[%] <sup>[a]</sup>	$[\%, d.r.]^{[a,c]}$
DPSO MeO <sup>W</sup> MeO		DPSO MeO <sup>vi</sup> MeO	AcQ DPSO MeO MeO MeO
32 (86) RO RO <sup>11</sup>	В	38 (63) RO RO MON MONE	44 (20) HO RO NO NO NO NO NO NO NO NO NO
<b>33</b> : R = Me (69, 22:1)	А	<b>39</b> : R = Me (65)	<b>46</b> : R = Me (57)
<b>34</b> : R = DPS (87, 14:1)	А	40: R = DPS (77)	<b>47</b> : $R = DPS(75)$
RO O ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		RO O MOME	
<b>35</b> : R = Me (91)	А	<b>41</b> : R = Me (69)	<b>48</b> : R = Me (52)
36: R = DPS	В	<b>42</b> : $R = DPS(71)$	<b>49</b> : R = DPS (61, 10:1)
<b>37</b> : $R = (NO_2)_2Bz$	В	<b>43</b> : $R = (NO_2)_2 Bz (71)^{[d]}$	

[a] Yield of the product isolated by using chromatography. [b] Method A: O<sub>3</sub> (excess), CH<sub>2</sub>Cl<sub>2</sub>, -78 °C, 2 h, then Me<sub>2</sub>S (2.1 equiv), dark. Method B: NaIO<sub>4</sub> (4 equiv), RuO<sub>2</sub>·xH<sub>2</sub>O (8.8 mg), CCl<sub>4</sub>/CH<sub>3</sub>CN/H<sub>2</sub>O (1:1:1.5), room temperature, dark. [c] Hemiketal diastereomeric ratio, major isomer shown. [d] Thermolysis of **43** was never realized. Bz = benzyl.

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and NOESY correlations between 1-Me and H6, and H4 and H7 were consistent with an OH- $\alpha$ -syn cyclication structure for the isomer **45**.

The most unexpected results were found for the deoxy compounds 40–43, which were transformed into the intermediate photoenols 50–53 upon irradiation at 15–35 °C (Scheme 3). Compounds 50–53, which are surprisingly stable



Scheme 3. Synthesis and aldol reactions of stable photoenols **50–53**. a) Daylight-lamp irradiation,  $C_6D_6$ ; b) heat at 40 °C for the synthesis of **47** (78%) from **50**, and at 60 °C for the synthesis of **48** (52%) and **49** (61%) from **51** and **52**, respectively. Thermolysis of **53** was never realized.

at room temperature for extended periods, could be isolated without significant contamination by either the starting material or the respective cyclized product. The oily crude residues did not withstand chromatographic purification over silica gel or alumina but were pure enough to allow complete analytical and spectroscopic characterization. A nuclear Overhauser effect (NOE) interaction between the methyl ketone and the vinyl proton is indicative of the Z configuration for the double bond as shown in Scheme 3. Photoenol **50** obtained by photolysis of **40** at 25 °C cyclized upon heating at 40 °C in light-protected benzene solution for 8 h to afford carbocycle **47**. Photoenols **51** and **52**, which are ther-

mally more stable, were cyclized in the dark at 60 °C to give carbocycles **48** and **49**, respectively.

These thermal experiments, performed with strict exclusion of light, confirm that the aldol reaction proceeded with a high degree of diastereoselectivity, resulting in the exclusive formation of syn-aldols. We did not find any anti-aldol product that (having the  $\alpha$ -diketone moiety unprotected) could have been destroyed by secondary photolysis in the prior illuminated experiments. Several attempts to obtain suitable crystals of the photoenol for X-ray crystallographic analysis by derivatization of the primary alcohol (e.g., 3,5-dinitrobenzoate 53) were unsuccessful.

We next prepared 2,3-diuloses of the D-manno 58 and Dgalacto 59-61 series to evaluate the influence of the C5 and C7 stereochemistry in the diastereoselectivity of the aldol reaction (Table 3). We anticipated on the basis of the previous experiment with 5-deoxy-diulose 38 (Table 2) that the aldol cyclization could show a marked dependence on the stereochemistry of the substituents at C5. This was indeed the case; the photolysis of 58 at 30 °C and subsequent heating at 50 °C led exclusively to the formation of the  $\alpha$ -syn isomer 62, albeit in moderate yield. The crude reaction had to be acetylated to facilitate the purification of 62 from a complex reaction mixture. In the mannose skeleton, an alternative 1,5-HAT reaction of the H5 $\alpha$  proton by the external carbonyl under classical Norrish-Yang conditions is possible. Thus, competitive abstraction of H8 $\alpha$  and H5 $\alpha$  may account for the somewhat lower efficiency of this process but we have been unable to isolate or identify any side products to confirm this hypothesis.

The <sup>1</sup>H NMR spectrum of the permethylated D-galactose model **59** exhibits ring coupling constants that strongly point to a <sup>4</sup>C<sub>7</sub> chair conformation. It was therefore not very surprising that the photochemical reaction gave 2,3,4,6-tetra-*O*-methyl- $\alpha$ -D-galactono-1,5-lactone as the only detectable product in 80% yield. Since in this geometric arrangement the  $\alpha$ -diketone tether and the H8 $\alpha$  are in a 1,3-diequatorial disposition, the 1,5-HAT by the internal carbonyl is impossible. The excited carbonyl preferentially abstracts the axial H4 $\beta$  to give a 3,4-photoenol intermediate (such as III, Scheme 2) which is subsequently and presumably degraded to the lactone by adventitious oxygen during the workup.

The *tert*-butyldiphenylsilyl (DPS) derivative **60** was then synthesized in the hope that an extremely bulky protecting group at the 9-primary alcohol causes a flip of the *C*-glycoside conformation to the  ${}^{7}C_{4}$  chair.<sup>[27]</sup> Fortunately, the ring coupling constants ( ${}^{3}J_{H4,H5}=6.9$ ,  ${}^{3}J_{H5,H6}=8.5$ , and  ${}^{3}J_{H6,H7}=$ 

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able 3.	Synthesis	and j	photolysis	of 2,3-diuloses	with	α-D-manno-	and	α-D-galacto-pyranose	stereochemistry.
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[a] Yield of the product isolated by using chromatography. [b] Method A: O<sub>3</sub> (excess), CH<sub>2</sub>Cl<sub>2</sub>, -78 °C, 2 h, then Me<sub>2</sub>S (2.1 equiv), dark. Method B: NaIO<sub>4</sub> (4 equiv), RuO<sub>2</sub>•xH<sub>2</sub>O (8.8 mg), CCl<sub>4</sub>/CH<sub>3</sub>CN/H<sub>2</sub>O (1:1:1.5), room temperature, dark. [c] Irradiation of **59** led to 2,3,4,6-tetra-*O*-methyl-D-galactono-1,5-lactone exclusively.

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2.6 Hz) confirmed this assumption and the photolysis-heating process on **60** afforded a mixture of two diastereomeric cyclopentitols, which was acetylated and separated into **63** and **64** after careful chromatography (d.r. 1:2). The intermediate photoenol could be fully characterized by monitoring the reaction by using <sup>1</sup>H NMR spectroscopy and subsequent heating at 70 °C was necessary to accomplish the aldol cyclization.

The structure of **63** and **64** as  $\beta$ -syn and  $\alpha$ -syn cyclization isomers, respectively, was assigned on the previously commented basis: The  ${}^{3}J_{\rm H4,H5}$  coupling constant, which is smaller for the  $\beta$ -syn isomer ( ${}^{3}J_{\rm H4\alpha,H5\beta}=2.9$  Hz for **63** versus  ${}^{3}J_{\rm H4\beta,H5\beta}=9.5$  Hz for **64**), and NOESY experiments. To calculate the ring coupling constants and NOE interaction the most populated conformer was determined to be  ${}^{7}T_{6}$  for both isomers (P=6.9 for **63** and 355.8° for **64**) by using pseudorotational analysis (see the Supporting Information for details). Similar results were observed in the reaction of 9-acetyl derivative **61**: a 1:3 mixture of **65** and **66** was obtained in good overall yield (76%), in which the  $\alpha$ -syn isomer was also the major product.

In addition, a number of octo-2,3-diuloses of the pentofuranose series of carbohydrates with D-*ribo* (**70** $\alpha$  and **71** $\beta$ ) and D-*lyxo* (**72**) stereochemistries were next synthesized to study the influence of the furanose ring conformation in the 1,5-HAT reaction (Table 4). The photolysis of the D-*ribo* derivative **70** $\alpha$  led to the lactone **73** in moderate yield, presumably by oxidation of the photoenol intermediate **74a**, as previously observed in diketones **9** and **59** in which photoenolization competes with photoelimination.<sup>[26]</sup> The most populated conformer of **70** $\alpha$  has a phase angle of  $P=256^{\circ}$ 

Table 4. Synthesis and photolysis of 2,3-diuloses with  $\alpha$ -D-*ribo*- and  $\alpha$ -D-*lyxo*furanose stereochemistry.



[a] Yield of the product isolated by using chromatography. [b] Method B: NaIO<sub>4</sub> (4 equiv), RuO<sub>2</sub>·x H<sub>2</sub>O (8.8 mg), CCl<sub>4</sub>/CH<sub>3</sub>CN/H<sub>2</sub>O (1:1:1.5), room temperature, dark. [c] The product was chromatographically unstable.

 $(^{7}T_{\rm o})$ , wherein the  $\alpha$ -diketone tether and the hydrogen at C7 lie in a *syn*-1,3-pseudo-diequatorial relationship. The distance between the oxygen at C3 and the extractable hydrogen at H7 on the minimum energy conformer was calculated as indicative of the 1,5-HAT feasibility. Since it is generally accepted that a narrow range of distances of approx. 2.5– 3.0 Å are required for the reaction to take place, the obtained value of  $d_{\rm C3=O\cdots H7}=4.7$  Å precludes any photochemical hydrogen abstraction.<sup>[28]</sup>

The abstraction at H7 is not geometrically feasible in the D-*ribo* isomer **71** $\beta$ , but the abstraction of H5 by the excited external carbonyl to result in a Yang photocyclization is worthy of consideration. Notwithstanding, the photolysis of **71** $\beta$  gave the same lactone **73** in similar yield, demonstrating that in these sugar derivatives photoenolization also competes favorably with the Yang cyclization.<sup>[26]</sup> In contrast to D-ribo derivative  $70 \alpha$ , the furanose ring of the isomeric Dlyxo 72 adopts a conformation  ${}^{\circ}E$  (P=86°) with the  $\alpha$ -diketone and the H7 in a syn-1,3-pseudo-diaxial relationship. In the global minimum the INHAT distance now possesses an ideal value of 2.53 Å and the photoelimination proceeded smoothly to give 75 presumably by intramolecular hemiketalization of the intermediate photoenol 74b. α,β-Unsaturated ketone 75 could not withstand chromatographic purification but the crude reaction residue was pure enough to allow complete analytical and spectroscopic characterization.

As commented previously, we propose a sequential mechanism for this transformation with two clearly differentiated steps (Scheme 1): A Norrish type II photoelimination of the  $\alpha$ -diketone that opens the pyranose ring leading to the acyclic photoenol **II**, which subsequently undergoes an intramolecular addol cyclization reaction. The photoelimination implies an 1,5-HAT of the H8 by the excited innermost carbonyl of the  $\alpha$ -diketone, followed by  $\beta$ -fragmentation of the 1,4-biradical intermediate **I**. The Norrish type II photoelimination, although very common in monoketones,<sup>[1a]</sup> is extremely rare in  $\alpha$ -diketones, in which only a few synthetically irrelevant examples are documented.<sup>[29]</sup> This reaction has been postulated to occur through a hydrogen abstraction by the innermost carbonyl, which is otherwise completely unreactive from the photochemical point of view.<sup>[30]</sup>

The distance between the carbonyl oxygen and the  $\gamma$ -hydrogen associated with the transition state of the 1,5-HAT has been determined in monoketones to have a critical value of around 2.7 Å.<sup>[31]</sup> It is not surprising, therefore, that the hydrogen abstraction is strongly dependent on the pyranose ring conformation of the  $\alpha$ -*C*-glycoside: favored when a  ${}^{7}C_{4}$  chair is adopted and highly disfavored in  ${}^{4}C_{7}$  arrangements.

As far as we are aware, the uncatalyzed thermal *syn* aldol cyclization in which a Z-photoenol (such as **II**, Scheme 1) acts as a preformed enolate is an unprecedented process.<sup>[32]</sup> According to Baldwin rules<sup>[33]</sup> the 5-(enol*exo*)-*exo-trig* ring closure involved is stereoelectronically favored and may be considered to be a new intramolecular carbonyl-ene cyclization, in which the carbonyl group and the enol can act as

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Scheme 4. Thermal kinetic studies with 50 and [D<sub>1</sub>]50.

enophile and ene unit, respectively (Scheme 4).<sup>[34]</sup> The rearrangement is accompanied by migration of the double bond and a 1,5-shift of the enolic hydrogen.[35] These thermal reactions, studied in detail with more stable deoxy-photoenols 50–52 (Scheme 3), proceeded with low activation energy (40-60 °C). Comparatively, the uncatalyzed carbonyl-ene processes usually require much higher temperatures.<sup>[36]</sup> Surprisingly, the cyclization temperature may be even lower in more substituted pyranose frameworks; for example, permethylated diketone 1 was transformed into 2 by irradiation at 0°C for 12 h in 55% yield. In contrast, the dideoxy photoenol 51 is stable at room temperature and requires 60°C for complete cyclization. This striking steric acceleration effect has been previously observed in an uncatalyzed ene reaction.<sup>[37]</sup> Mechanistic studies of the ene-reaction have demonstrated that a large deuterium kinetic isotope effect (KIE;  $k_{\rm H}/k_{\rm D}$  > 2) indicates that the INHAT is the rate-limiting step and has often been taken as evidence of a concerted mechanism.<sup>[38]</sup> Taking advantage of the ready deuteration of the photoenol, we decided to determine the intramolecular hydrogen-deuterium isotope effect for the thermal reaction of photoenol 50 (Scheme 4). Photoenol 50 was chosen because its cyclization into product 47 proceeded smoothly at a moderate temperature and rate. The value of the reaction rate constants for undeuterated 50  $(k_{\rm H})$  and deuterated  $[D_1]$ 50  $(k_{\rm D})$  were measured by scanning at regular intervals  $[D_6]$  benzene dissolved samples placed in a preheated (40 °C) NMR probe and monitoring integral data for the vinylic proton. The value of KIE obtained  $(k_{\rm H}/k_{\rm D}=3.7)$  appears to indicate a concerted pericylic mechanism.

Models accounting for the observed relative stereochemistry invoke the intermediacy of a Z enolate, intramolecular hydrogen-bonding between the OH and the carbonyl, and a Zimmerman-Traxler-type transition state, which has been frequently used for catalytic intramolecular aldol reactions (Figure 1).<sup>[10,39]</sup> The presence of this hydrogen bond is anticipated to confer additional stability and may help to maintain the five-membered transition state in a prearranged conformation for cyclization. As expected from the models of Figure 1, the major stereoisomer is that in which the two newly created stereogenic centers are *cis* to each other. This is probably very important for the overall yield of the reaction because it permits the internal acetalization of the regenerated  $\alpha$ -diketone moiety avoiding secondary photolysis.<sup>[40]</sup>

The steric influence of the adjacent substituents at C5 and C7 in the stereochemical outcome can also be easily inferred from these models (Figure 1). Interactions with the 5 $\alpha$ -equatorial substituent in D-gluco (1, 18–24, Table 1), 6-deoxy-D-gluco (39–40, Table 2), and 6,7-dideoxy-D-gluco (41–42, Table 2) derivatives afforded exclusively OH- $\beta$ -syn cyclizations. The influence of this substituent is confirmed in the 5-deoxy-D-gluco derivative (38), in which an equimolecular mixture of OH- $\beta$ -syn and OH- $\alpha$ -syn isomers was formed. Inversion of configuration at C5 in D-manno derivative (58) entails a more crowded  $\beta$ -face of the transition-state (TS) ring with exclusive formation of the OH- $\alpha$ -syn cyclization preferentially to a majority of OH- $\alpha$ -syn cyclization products.

Degradation of the masked  $\alpha$ -diketones could be realized under oxidative conditions by using two different methodologies: With periodic acid in methanol (Method A)<sup>[41]</sup> or by β-fragmentation of the alkoxyl radical, generated from the hemiketal alcohol by reaction with the PhI(OAc)<sub>2</sub>/I<sub>2</sub> system (Method B)<sup>[42]</sup> as depicted in Table 5. With method A the vields were excellent with substrates bearing very stable protective groups (e.g., methyl ethers, Table 5, entries 1 and 4) but decreased substantially with easily oxidized (e.g., benzyl ethers, entry 2) or acid-sensitive groups (e.g., silyl ethers, entries 3 and 7). Method B, however, turned out to be more efficient with substrates possessing these sensitive groups, for example, disilyl compound 47 (Table 5, entry 7). The efficiency of both methods is similar with stable protective groups (entry 5). Another observation that emerges from these experiments is that methylation with diazomethane, either of the crude or purified acid, considerably decreases the global yield (compare method A, Table 5, entries 4 and 5 or method B, entries 6 and 7).



Figure 1. Proposed models for the stereochemical course of the aldol reaction. The transition state (TS) of the major isomer is highlighted.

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Table 5. Synthesis of cyclopentitols.

Entry	Substrate	Method $[\%]^{[a,b]}$	Product
	HO R <sup>1</sup> O RO H RO H RO RO RO		AcO CO <sub>2</sub> Me R <sup>10</sup> / <sup>10</sup> / <sub>10</sub> / <sub>10</sub> / <sub>10</sub> OR
1	<b>2</b> : $R = R^1 = Me$	A (85) <sup>[c]</sup>	<b>76</b> : $R = R^1 = Me$
2	<b>25</b> : $R = R^1 = Bn$	A (65) <sup>[c]</sup>	<b>77</b> : $R = R^1 = Bn$
3	26: R=Bn, R <sup>1</sup> =DPS HO, RO, MO, HO, MO, MO, MO, MO, MO, MO, MO, MO, MO, M	A (42) <sup>[c]</sup>	<b>78</b> : $R = Bn$ , $R^1 = DPS$ Aco $CO_2R^1$ RO $NOME$
4	<b>46</b> : R = Me	A (90)	<b>79</b> : $R = Me, R^1 = H$
5	<b>46</b> : R = Me	A (67), <sup>[c]</sup> B (69) <sup>[c]</sup>	<b>80</b> : $R = Me, R^1 = Me$
6	47: R = DPS	B (82)	<b>81</b> : $R = DPS, R^1 = H$
7	47: R = DPS	A (26), <sup>[c]</sup> B (60) <sup>[c]</sup>	<b>82</b> : $R = DPS$ , $R^1 = Me$





Scheme 5. Synthesis of cyclopentitols from 2,3-diuloses in a one-pot, three-step sequence. a) Daylight-lamp irradiation,  $C_6D_6$ ,  $30^{\circ}$ C, 4 h, then  $H_5IO_6$ ·2H<sub>2</sub>O, MeOH, room temperature, 3 h; b) daylight-lamp irradiation,  $C_6D_6$ , 36–40 °C, 2.5 h, then PhI(OAc)<sub>2</sub>, I<sub>2</sub>, *hv*, room temperature, 40 min; c) daylight-lamp irradiation,  $C_6D_6$ , 36–40 °C, 5 h, then  $H_5IO_6$ ·2H<sub>2</sub>O, MeOH, room temperature, 3 h. Product isolated by using silica gel chromatography over three steps.

Another set of experiments in which the crude residue of the photolysis-heating reaction is directly treated with the oxidant reagents is summarized in Scheme 5.  $\alpha$ -Diketones **18**, **22**, and **42** were converted into pure cyclopentanes **83**– **85**, respectively, in good overall yield by using this one-pot, three-step process.

To confirm the structure of the cyclopentane derivatives and to obtain information on their chemical reactivity, a series of short chemical transformations were performed (Scheme 6). The hydrolysis and subsequent methylation with diazomethane of the previously prepared acid **83** afforded the  $\alpha$ -hydroxyester **86** whose relative disposition was



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Scheme 6. Some initial experiments on the reactivity of cyclopentitols. a) KOH, MeOH, room temperature, 24 h; b) PhSO<sub>2</sub>Cl, Py, 0°C, 14 h, 73%, two-step; c) LiAlH<sub>4</sub>, THF, 0°C 4 h, 78%; d) KOH, MeOH, room temperature, 24 h, then CH<sub>2</sub>N<sub>2</sub>, 99%; e) Tf<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, Py, 0°C, 24 h, 93%.

confirmed by dehydration to give the  $\alpha$ , $\beta$ -unsaturated ester **89**. The  $\beta$ -lactone **87** was prepared also using acid **83** as starting material, by treatment with benzenesulfonyl chloride in pyridine after hydrolysis of the acetyl group. The formation of **87** confirms that it does indeed possess the *syn*hydroxy carboxylate arrangement generated during the aldol reaction. Finally, the reduction of **83** with an excess of LiAlH<sub>4</sub> afforded the diol **88** spectroscopically identical to the one synthesized by Chiara et al.<sup>[43]</sup>

#### Conclusion

The new sequential reaction described herein results in the direct formation of densely polyfunctionalized cyclopentitols by ring contraction of hexopyranose carbohydrates. It is worth noting that the reaction proceeds efficiently in a onepot two-step process with no reagents other than light and heat. The easy accessibility of pyranose sugars of various configurations and the possibility of prior structural modifications illustrate the potential of this methodology for the preparation of chiral synthons of cyclopentanoid natural products. To the best of our knowledge, this is the first synthetic application of the Norrish type II photoelimination initiated by the innermost carbonyl of a  $\alpha$ -diketone. The importance of this reaction is that it uniquely generates an acyclic keto-enol system, which is ideally suited for a subsequent 5-(enolexo)-exo-trig intramolecular aldol cyclization. This thermal uncatalyzed aldol reaction in which a Z photoenol acts as a preformed enolate is also unprecedented. The stereochemistry of the cyclization is strongly dependent on the configuration of the sugar-ring substituents; for example, a D-gluco arrangement of the starting material leads exclusively to OH- $\beta$ -syn products, whereas an inverted OH- $\alpha$ -syn cyclization is observed for the D-manno series of carbohydrates.

#### **Experimental Section**

General procedure for the oxidation of *C*-propynyl glycosides to  $\alpha$ -diketones: *Method A*: A solution of *C*-propynyl glycoside (1 equiv) in dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was cooled to -78 °C, ozone was introduced into the solution and the reaction monitored by TLC. Then, nitrogen was bubbled through the solution to expel excess of ozone, dimethyl sulfide (2–10 equiv) was added and the mixture was gradually warmed to room temperature and stirred at this temperature for the specified time in the dark. The mixture was concentrated under reduced pressure to give a yellow residue that, in most cases, can be purified by rapid silica gel chromatography (hexanes/EtOAc mixtures) on a column protected from light with aluminum foil, although a significant loss of material was generally observed.

Method B: NaIO<sub>4</sub> (3–4 equiv) and RuO<sub>2</sub>•xH<sub>2</sub>O (3–12 mg) were added to a solution of C-propynyl glycoside (1 equiv) in CCl<sub>4</sub>/CH<sub>3</sub>CN/H<sub>2</sub>O (17 mL, 1:1:1.5) and the mixture stirred at room temperature for the specified time in the dark. The mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue can be purified by rapid silica gel chromatography (hexanes/EtOAc mixtures) on a column protected from light with aluminum foil, although a significant loss of material was generally observed.

2,6-Anhydro-7,8-dideoxy-1,3,4,5-tetra-O-methyl-8-(trimethylsilyl)-D-glycero-L-gulo-oct-7-ynitol (5): Bu<sub>3</sub>SnC=CTMS (1.49 g, 3.86 mmol) was added to a solution of  $\boldsymbol{3}^{[44]}$  (538 mg, 1.93 mmol) in dry  $CH_2Cl_2$  (8 mL) containing oven-dried powdered 4 Å molecular sieves (1.1 g) and stirred at room temperature under nitrogen for 15 min. Trimethylsilyl trifluoromethanesulfonate (873 µL, 4.83 mmol) was then added dropwise and the stirring continued for 3 h. The mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (32 mL), neutralized with Et<sub>3</sub>N, and filtered through a Celite pad. The filtrated was concentrated under reduced pressure and the residue dissolved in EtOAc and washed with an aqueous saturated solution of KF. The organic layer was dried over Na2SO4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexanes→hexanes/EtOAc 9:1) to give 5 (403 mg, 1.28 mmol, 66%) as an oil:  $[a]_{\rm D} = +130 \,{\rm cm}^3 {\rm g}^{-1} {\rm dm}^{-1}$  (c = 3.53 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 0.18$  (s, 9H), 3.16 (dd, J = 9.3, 9.8 Hz, 1H), 3.23 (dd, J = 5.6, 9.5 Hz, 1 H), 3.39 (s, 3 H), 3.43 (dd, J=9.3, 9.3 Hz, 1 H), 3.46 (s, 3 H), 3.54 (s, 3H), 3.57 (dd, J=10.7, 2.3 Hz, 1H), 3.60 (dd, J=10.7, 3.7 Hz, 1H), 3.63 (s, 3H), 3.82 (ddd, J=10.1, 3.7, 2.3 Hz, 1H), 4.81 ppm (d, J=5.6 Hz, 1 H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = -0.1$  (3×CH<sub>3</sub>), 58.5 (CH<sub>3</sub>), 59.1 (CH<sub>3</sub>), 60.4 (CH<sub>3</sub>), 60.7 (CH<sub>3</sub>), 66.5 (CH), 71.2 (CH<sub>2</sub>), 73.1 (CH), 79.2 (CH), 80.7 (CH), 84.3 (CH), 94.8 (C), 99.7 ppm (C); IR (film): v=2931, 2190, 844 cm<sup>-1</sup>; MS (EI): m/z (%): 316 (<1) [M<sup>+</sup>], 301 (<1); HRMS (EI): m/z: calcd for C<sub>15</sub>H<sub>28</sub>O<sub>5</sub>Si: 316.1706 [M<sup>+</sup>]; found 316.1701; elemental analysis calcd (%) for C15H28O5Si (316.46): C 56.93, H 8.92; found: C 56.92, H 8.95.

#### 2,6-Anhydro-7,8-dideoxy-1,3,4,5-tetra-O-methyl-D-glycero-L-gulo-oct-7-

**ynitol (6):** NaOH (1N, 3.9 mL) was added to a solution of **5** (652 mg, 2.06 mmol) in CH<sub>2</sub>Cl<sub>2</sub>/MeOH (5:1, 72 mL). The mixture was stirred at room temperature for 2 h, neutralized with a solution of HCl 1N and extracted with EtOAc. The organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexanes/EtOAc 70:30) to give **6** (462 mg, 1.89 mmol, 92%) as an oil:  $[\alpha]_D = +132 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1} (c=1.64 \text{ in CHCl}_3); <sup>1</sup>H NMR (500 MHz, CDCl_3): <math>\delta = 2.58$  (d, J = 9.3 Hz, 1H), 3.16 (dd, J = 10.1, 9.0 Hz, 1H), 3.25 (dd, J = 9.5, 5.9 Hz, 1H), 3.39 (s, 3H), 3.47 (dd, J = 9.3, 9.2 Hz, 1H), 3.51 (s, 3H), 3.54 (s, 3H), 3.59 (d, J = 3.4 Hz, 2H), 3.64 (s, 3H), 3.83 (ddd, J = 10.1, 3.0, 3.0 Hz, 1H), 4.84 ppm (dd, J = 5.6, 2.3 Hz, 1H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 5.8.4$  (CH<sub>3</sub>), 58.8 (CH<sub>3</sub>), 60.1 (CH<sub>3</sub>), 60.4 (CH<sub>3</sub>), 65.6 (CH), 70.9 (CH), 73.1 (CH<sub>2</sub>), 77.3

(CH), 77.8 (C), 78.8 (CH), 80.4 (CH), 84.1 ppm (CH); IR (film):  $\tilde{\nu}$ = 3254, 2933, 2112 cm<sup>-1</sup>; MS (EI): m/z (%): 244 (<1) [ $M^+$ ], 199 (7); HRMS (EI): m/z calcd for C<sub>12</sub>H<sub>20</sub>O<sub>5</sub>: 244.1311 [ $M^+$ ]; found: 244.1306; elemental analysis calcd (%) for C<sub>12</sub>H<sub>20</sub>O<sub>5</sub> (244.28): C 59.00, H 8.25; found: C 59.14, H 8.37.

#### 2,6-Anhydro-7,8-dideoxy-1,3,4,5-tetra-O-methyl-8-phenyl-D-glycero-L-

gulo-oct-7-ynitol (8): Compound 6 (310 mg, 1.27 mmol) in piperidine (7 mL) was added to a suspension of  $[Pd(PPh_3)_4]$  (73 mg, 0.06 mmol), CuI (24 mg, 0.13 mmol), and PhI (140 µL, 1.27 mmol) in piperidine (12 mL) at room temperature under nitrogen. The mixture was stirred at 80°C for 1 h, diluted with EtOAc, washed with an aqueous saturated solution of NH<sub>4</sub>Cl, and the organic layer dried and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexanes/EtOAc 7:3) to give 8 (359 mg, 1.12 mmol, 88 %) as a yellowish oil:  $[\alpha]_D = +183 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (c=2.15 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 3.31$  (dd, J = 9.8, 9.2 Hz, 1 H), 3.33 (dd, J = 9.5, 5.6 Hz, 1 H), 3.40 (s, 3 H), 3.51 (s, 3 H), 3.53 (dd, J=9.3, 9.3 Hz, 1 H), 3.55 (s, 3H), 3.606 (d, J=2.3 Hz, 1H), 3.61 (d, J=4.2 Hz, 1H), 3.65 (s, 3H), 3.91 (ddd, J=9.8, 3.9, 2.3 Hz, 1 H), 5.06 (d, J=5.6 Hz, 1 H), 7.30 (m, 3 H), 7.46 ppm (m, 2H);  ${}^{13}$ C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 59.0$  (CH<sub>3</sub>), 59.6 (CH<sub>3</sub>), 60.8 (CH<sub>3</sub>), 61.1 (CH<sub>3</sub>), 67.0 (CH), 71.7 (CH<sub>2</sub>), 73.8 (CH), 79.7 (CH), 81.4 (CH), 83.9 (C), 84.9 (CH), 89.7 (C), 122.7 (C), 128.5 (2×CH), 128.9 (CH), 132.4 ppm (2×CH); IR (film):  $\tilde{\nu}$  = 2931, 2226, 1100 cm<sup>-1</sup>; MS (EI): m/z (%): 305 (<1) [ $M^+$ -Me], 288 (4); HRMS (EI): m/z calcd for  $C_{17}H_{21}O_5$ : 305.1389 [*M*<sup>+</sup>-Me]; found: 305.1396; elemental analysis calcd (%) for  $C_{18}H_{24}O_5$  (320.38): C 67.48, H 7.55; found: C 67.52, H 7.79.

3,7-Anhydro-4,5,6,8-tetra-O-methyl-1-phenyl-D-glycero-D-ido-octos-2ulose (9): Prepared from 8 (82 mg, 0.25 mmol) following the general procedure (Method A) using dimethyl sulfide (40 µL, 0.54 mmol). The mixture was stirred at room temperature in the dark for 6 h and concentrated under reduced pressure to give 9 (106 mg) that was unstable on silica gel and alumina. Notwithstanding, the crude residue (yellow oil) was pure enough to allow spectroscopic characterization. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 2.86$  (s, 3H), 3.22 (s, 3H), 3.34 (s, 3H), 3.39–3.45 (m, 2H), 3.44 (s, 3H), 3.50 (dd, J = 8.6, 8.2 Hz, 1H), 3.64 (m, 2H), 4.65 (ddd, J =9.7, 2.6, 2.6 Hz, 1 H), 5.67 (d, J=7.4 Hz, 1 H), 6.96 (m, 2 H), 7.07 (m, 1 H), 7.98 ppm (m, 2H);  ${}^{13}$ C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 58.5$  (CH<sub>3</sub>), 59.0 (CH<sub>3</sub>), 59.9 (CH<sub>3</sub>), 60.1 (CH<sub>3</sub>), 71.8 (CH<sub>2</sub>), 74.7 (CH), 75.5 (CH), 79.2 (CH), 81.3 (CH), 84.2 (CH), 128.7 (CH), 130.3 (2×CH), 133.1 (C), 133.9  $(2 \times CH)$ , 190.8 (C), 203.7 ppm (C); IR (film):  $\tilde{\nu} = 1716$ , 1672, 1450 cm<sup>-1</sup>; MS (EI): m/z (%): 352 (2) [M<sup>+</sup>], 247 (4), 219 (18); HRMS (EI): m/z calcd for C<sub>18</sub>H<sub>24</sub>O<sub>7</sub>: 352.1522 [M<sup>+</sup>]; found: 352.1527.

**Photolysis of 9**: A deoxygenated solution of crude diketone **9** (106 mg) in dry  $C_6D_6$  (0.7 mL) was placed in a resonance tube and irradiated with a daylight-lamp at 30 °C. The reaction was monitored by <sup>1</sup>H NMR spectroscopy, and complete consumption of starting material was observed after 9 h, leading to exclusive formation of intermediate photoenol **III**. The solution could be concentrated at low temperature under reduced pressure but the photoenol was not stable enough to withstand chromatographic purification (silica gel or alumina). After silica gel column chromatography (hexanes/EtOAc, 75:25) only the known lactone **10**<sup>[45]</sup> (28 mg, 0.12 mmol, 48 % from **8**) could be obtained.

#### 4,8-Anhydro-1-deoxy-5,6,7,9-tetra-O-methyl-D-glycero-D-ido-nono-2,3-

**diulose (1):** Prepared from 7 (69 mg, 0.27 mol) following the general procedure (Method A) using dimethyl sulfide (40  $\mu$ L, 0.54 mmol). The mixture was stirred at room temperature in the dark for 6 h and concentrated under reduced pressure to give 1 (80 mg), which was unstable on silica gel and alumina. Notwithstanding, the crude residue (yellow oil) was pure enough to allow spectroscopic characterization. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =2.25 (s, 3H), 3.16 (dd, *J*=9.8, 7.7 Hz, 1H), 3.29 (dd, *J*=8.2, 7.7 Hz, 1H), 3.35 (s, 3H), 3.37 (s, 3H), 3.49 (s, 3H), 3.51 (dd, *J*=10.6, 4.1 Hz, 1H), 3.55 (s, 3H), 3.59 (dd, *J*=10.6, 2.4 Hz, 1H), 3.64 (dd, *J*=7.9, 7.4 Hz, 1H), 4.18 (ddd, *J*=9.8, 4.2, 2.1 Hz, 1H), 5.48 ppm (d, *J*=7.4 Hz, 1H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$ =23.3 (CH<sub>3</sub>), 59.1 (CH<sub>3</sub>), 59.2 (CH<sub>3</sub>), 59.8 (CH<sub>3</sub>), 60.1 (CH<sub>3</sub>), 71.5 (CH<sub>2</sub>), 72.3 (CH), 74.1 (CH), 78.5 (CH), 80.6 (CH), 82.7 (CH), 197.1 (C), 200.3 ppm (C); IR (film):  $\tilde{\nu}$ =2934, 2933, 1715 cm<sup>-1</sup>; MS (EI): *m/z* (%): 290 (<1) [*M*<sup>+</sup>], 247

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(2); HRMS (EI): m/z calcd for  $C_{13}H_{22}O_7$ : 290.1366 [*M*<sup>+</sup>]; found: 290.1363.

**Photocyclization of 1:** A solution of crude diketone **1** (80 mg) in dry  $C_6D_6$  (1 mL), was placed in a resonance tube and irradiated with a daylight lamp at 30 °C for 3 h. The mixture was concentrated under reduced pressure and the residue purified by silica gel column chromatography (hexanes/EtOAc 7:3), to give (2*S*,3a*S*,4*S*,5*R*,6*S*,6a*R*)-2-hydroxy-4,5,6-trimethoxy-6a-(methoxymethyl)-2-methyltetrahydro-2*H*-cyclopenta[*b*]fur-

an-3(3aH)-one (2) (41 mg, 0.14 mmol, 52 % from 7) as a crystalline solid. M.p. 96.6–97.2 °C (*n*-hexane/EtOAc);  $[a]_{\rm D} = +138 \, {\rm cm}^3 {\rm g}^{-1} {\rm dm}^{-1}$  (c=1.22 in CHCl<sub>3</sub>);  $^{1}$ H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>; note: the hydrogen atoms at C5 and C6 have very similar chemical shifts and as a consequence the coupled hydrogen at C4 appears as a complex signal by virtual coupling. The data of hydrogens at C4-C6 shown below have been calculated by iterative simulation using program DAISY as implemented in Bruker Topspin v. 2.1):  $\delta = 1.64$  (d, J = 0.9 Hz, 3 H), 2.73 (s, 3 H), 3.09 (d, J = 4.7 Hz, 1 H), 3.17 (s, 3H), 3.25 (s, 6H), 3.30 (d, J=10.6 Hz, 1H), 3.49 (d, J=10.3 Hz, 1H), 3.64 (complex signal, d, J=8.2 Hz, 1H), 3.65 (complex signal, dd, J=8.2, 6.3 Hz, 1 H), 3.78 (complex signal, dd, J=6.3, 4.7 Hz, 1 H), 5.21 ppm (d, J=0.6 Hz, 1 H, OH); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =1.41 (d, J=0.9 Hz, 3H), 3.08 (d, J=4.1 Hz, 1H), 3.42 (s, 3H), 3.46 (s, 3H), 3.48 (s, 3H), 3.50 (s, 3H), 3.58 (d, J = 10.4 Hz, 1H), 3.63 (dd, J = 6.1, 1.2 Hz, 1 H), 3.68 (dd, J=6.0, 5.0 Hz, 1 H), 3.70 (ddd, J=5.0, 4.2, 0.9 Hz, 1H), 3.71 (d, J=10.4 Hz, 1H), 5.05 ppm (brd, J=0.9 Hz, 1H, OH); <sup>13</sup>C NMR (100.6 MHz,  $C_6D_6$ ):  $\delta = 21.1$  (CH<sub>3</sub>), 51.2 (CH), 57.5 (CH<sub>3</sub>), 58.1 (CH<sub>3</sub>), 58.7 (CH<sub>3</sub>), 59.0 (CH<sub>3</sub>), 74.2 (CH<sub>2</sub>), 84.2 (CH), 87.6 (C), 88.4 (CH), 90.8 (CH), 99.7 (C), 208.1 ppm (C); IR (film):  $\tilde{v}$  = 3337, 2949, 2836, 1760 cm<sup>-1</sup>; MS (FAB): m/z (%): 290 (2) [ $M^+$ ], 273 (100); HRMS (FAB): m/z: calcd for C<sub>13</sub>H<sub>22</sub>O<sub>7</sub>: 290.1366 [M<sup>+</sup>]; found: 290.1372; elemental analysis calcd (%) for C13H22O7 (290.31): C 53.78, H 7.64; found: C 53.71; H 7.73. Crystal data and structure refinement for compound 2:  $C_{13}H_{22}O_7$ ,  $M_{\tau} = 290.31$ , orthorhombic, space group  $P2_12_12_1$ , a = 7.9261(6) Å, b =9.2758(8) Å, c = 19.6176(17) Å,  $\beta = 90^{\circ}$ , V = 1442.3(2) Å<sup>3</sup>, Z = 4,  $\rho_{calcd} = 1000$ 1.337 mg m<sup>-3</sup>,  $\mu$ (Mo<sub>Ka</sub>)=0.71073 Å, F(000)=624, T=123 (2) K, colorless crystal,  $0.45 \times 0.20 \times 0.12$  mm<sup>3</sup>, collected reflections 12479. The structure was solved by direct method, all hydrogen atoms were refined anisotropically using full-matrix least-squared based  $F_2$  to give  $R_1 = 0.0415$ ,  $wR_2 =$ 0.0689 for 3028 independently observed reflections  $(|F_0| > 2\sigma(|F_0|))$  and 191 parameters.

*Irradiation with pyrene*: A solution of crude diketone **1** (14 mg, 0.048 mmol) and pyrene (126 mg, 0.624 mmol) in dry  $C_6D_6$  (1.2 mL), was placed in a resonance tube and irradiated with a daylight lamp at 30°C for 12 h. No reaction was detected by using <sup>1</sup>H NMR spectroscopy under these conditions.

#### 4,8-Anhydro-5,6,7,9-tetra-O-benzyl-1-deoxy-D-glycero-D-ido-nono-2,3-

diulose (18): Prepared from 11 (70 mg, 0.125 mmol) following the general procedure (Method B) using NaIO4 (107 mg, 0.5 mmol) and RuO2•x H2O (1.1 mg). The reaction mixture was stirred at room temperature in the dark for 1 h. The residue was purified by rapid silica gel column chromatography (hexanes/EtOAc 9:1) to give 18 (46 mg, 0.077 mmol, 62%) as a yellow oil:  $[\alpha]_{\rm D} = +52 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (c=0.65 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.07 (s, 3 H), 3.61 (dd, J = 9.8, 8.0 Hz, 1 H), 3.64 (dd, J=10.9, 3.6 Hz, 1 H), 3.67 (dd, J=10.9, 2.4 Hz, 1 H), 3.73 (dd, J=8.3, 8.0 Hz, 1 H), 3.99 (dd, J=8.3, 7.1 Hz, 1 H), 4.37 (ddd, J=9.8, 3.6, 2.4 Hz, 1 H), 4.45 (d, J = 10.9 Hz, 1 H), 4.46 (d, J = 12.1 Hz, 1 H), 4.49 (d, J = 12.1 Hz, 1 Hz, 1 H), 4.49 (d, J = 12.1 Hz, 1 Hz 10.9 Hz, 1 H), 4.57 (d, J=11.6 Hz, 2 H), 4.69 (d, J=10.9 Hz, 1 H), 4.75 (s, 2H), 5.56 (d, J=7.4 Hz, 1H), 7.09–7.30 ppm (m, 20H); <sup>13</sup>C NMR  $(100.6 \text{ MHz}, \text{ CDCl}_3): \delta = 23.5 \text{ (CH}_3), 68.9 \text{ (CH}_2), 72.4 \text{ (CH}), 73.4 \text{ (CH}_2),$ 74.0 (CH<sub>2</sub>), 74.5 (CH<sub>2</sub>), 74.6 (CH), 74.9 (CH<sub>2</sub>), 77.1 (CH), 78.5 (CH), 81.2 (CH), 127.6-128.4 (20×CH), 136.8 (C), 137.9 (C), 138.1 (C), 138.2 (C), 197.4 (C), 200.7 ppm (C); IR (film):  $\tilde{\nu} = 2928$ , 1721 cm<sup>-1</sup>; MS (EI): m/z(%): 594 (<1)  $[M^+]$ , 503 (2); HRMS (EI): m/z calcd for  $C_{37}H_{38}O_7$ : 594.2618  $[M^+]$ ; found: 594.2622; elemental analysis calcd (%) for C37H38O7 (594.69): C 74.73, H 6.44; found: C 74.80, H 6.29.

**Photocyclization of 18:** A deoxygenated solution of diketone **18** (30 mg, 0.05 mmol) in purified  $CDCl_3$  (0.6 mL), was placed in a resonance tube and irradiated with a daylight lamp at 30 °C for 2 h. The mixture was concentrated under reduced pressure and the residue was purified by silica

chromatography (hexanes/EtOAc 9:1), to gel column give (2S,3aS,4S,5R,6S,6aR)-4,5,6-tris(benzyloxy)-6a-[(benzyloxy)methyl]-2-hydroxy-2-methyltetrahydro-2H-cyclopenta[b]furan-3(3aH)-one (25)(17 mg, 0.029 mmol, 58 %) as a colorless oil:  $[\alpha]_D = +31 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (c = 0.9 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.37$  (s, 3H), 3.21 (m, 1H), 3.77 (d, J=10.6 Hz, 1H), 3.89 (d, J=10.6 Hz, 1H), 3.94 (m, 1H), 4.00 (m, 2H), 4.57-4.76 (m, 8H), 5.09 (s, 1H), 7.23-7.39 ppm (m, 20H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 20.6$  (CH<sub>3</sub>), 51.6 (CH), 71.8 (CH<sub>2</sub>), 72.0 (CH<sub>2</sub>), 72.6 (CH<sub>2</sub>), 73.3 (CH<sub>2</sub>), 74.3 (CH<sub>2</sub>), 82.6 (CH), 85.0 (CH), 87.7 (C), 88.5 (CH), 99.2 (C), 127.7-128.8 (20×CH), 135.9 (C), 137.5 (C), 137.6 (C), 137.8 (C), 208.3 ppm (C); IR (film):  $\tilde{\nu} = 3370, 2918, 1762 \text{ cm}^{-1}$ ; MS (EI): m/z (%): 594 (<1) [ $M^+$ ], 576 (<1); HRMS (EI): m/z calcd for C<sub>37</sub>H<sub>38</sub>O<sub>7</sub>: 594.2618 [*M*<sup>+</sup>]; found: 594.2615; elemental analysis calcd (%) for C<sub>37</sub>H<sub>38</sub>O<sub>7</sub> (594.69): C 74.73, H 6.44; found: C 74.37, H 6.83.

#### 4,8-Anhydro-5,6,7-tri-O-benzyl-9-O-(tert-butyldiphenylsilyl)-1-deoxy-D-

glycero-D-ido-nono-2,3-diulose (19): Prepared from 12 (30 mg, 0.042 mmol) following the general procedure (Method B) using NaIO<sub>4</sub> (36 mg, 0.168 mmol) and RuO2·xH2O (0.5 mg). The reaction mixture was stirred at room temperature in the dark for 1 h. The residue was purified by rapid silica gel column chromatography (hexanes/EtOAc 97:3) to give **19** (20 mg, 0.027 mmol, 64%) as a yellow oil:  $[a]_{\rm D} = +36 \, {\rm cm}^3 {\rm g}^{-1} {\rm dm}^{-1}$  $(c = 1.87 \text{ in CHCl}_3)$ ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 1.07$  (s, 9 H), 2.09 (s, 3H), 3.81 (m, 2H), 3.92 (dd, J=11.7, 3.2 Hz, 1H), 3.95 (dd, J=11.7, 2.1 Hz, 1 H), 4.01 (dd, J = 8.5, 7.2 Hz, 1 H), 4.31 (m, 1 H), 4.58 (d, J =10.9 Hz, 1 H), 4.66 (d, J=10.4 Hz, 2 H), 4.82 (s, 2 H), 4.84 (d, J=11.1 Hz, 1 H), 5.62 (d, J = 7.4 Hz, 1 H), 7.16–7.73 ppm (m, 25 H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ=19.3 (C), 23.6 (CH<sub>3</sub>), 26.5 (3×CH<sub>3</sub>), 62.9 (CH<sub>2</sub>), 72.1 (CH), 74.2 (CH<sub>2</sub>), 74.7 (CH<sub>2</sub>), 75.2 (CH<sub>2</sub>), 75.9 (CH), 76.9 (CH), 79.1 (CH), 81.6 (CH), 127.6-135.8 (25×CH), 133.2-138.2 (5×C), 197.6 (C), 200.7 ppm (C); IR (film):  $\tilde{\nu} = 2928$ , 1713 cm<sup>-1</sup>; MS (EI): m/z (%): 742 (<1)  $[M^+]$ , 685 (<1); HRMS (EI): m/z calcd for  $C_{46}H_{50}O_7Si$ : 742.3326  $[M^+]$ ; found: 742.3345; elemental analysis calcd (%) for C<sub>46</sub>H<sub>50</sub>O<sub>7</sub>Si (742.97): C 74.36, H 6.78; found: C 74.52, H 6.98.

Photocyclization of 19: A deoxygenated solution of diketone 19 (40 mg, 0.054 mmol) in purified CDCl<sub>3</sub> (1.4 mL), was placed in a resonance tube and irradiated with a daylight lamp at room temperature for 3 h. The mixture was concentrated under reduced pressure and the residue purified by silica gel column chromatography (hexanes/EtOAc 9:1) to give (3aS,4S,5R,6S,6aR)-4,5,6-tris(benzyloxy)-6a-[(tert-butyldiphenylsilyl)oxy]methyl-2-hydroxy-2-methyltetrahydro-2H-cyclopenta[b]furan-3(3aH)-one (26) as a mixture of isomers (26 mg, 0.035 mmol, d.r. 5:1, 65%) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>; complex spectrum, only clearly distinguished signals are reported):  $\delta =$  major isomer 1.08 (s, 9 H), 1.44 (s, 3H), 3.29 (d, J=4.5 Hz, 1H), 5.09 ppm (s, 1H); minor isomer 1.02 (s, 9H), 1.49 (s, 3H), 3.31 ppm (d, J=3.7 Hz, 1H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) (complex spectrum, only clearly distinguished signals are reported):  $\delta$  (major isomer) = 19.1 (C), 20.3 (CH<sub>3</sub>), 26.8 (3×CH<sub>3</sub>), 50.9 (CH), 66.0 (CH<sub>2</sub>), 88.8 (C), 99.1 (C), 207.8 ppm (C); δ (minor isomer)=19.2 (C), 22.6 (CH<sub>3</sub>), 26.8 (3×CH<sub>3</sub>), 53.4 (CH), 65.1 (CH<sub>2</sub>), 88.8 (C), 100.1 (C), 210.7 ppm (C); IR (film):  $\tilde{\nu} = 3374$ , 2928, 1765 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 765 (100) [ $M^+$ +Na]; HRMS (ESI<sup>+</sup>): m/z calcd for C<sub>46</sub>H<sub>50</sub>NaO<sub>7</sub>Si: 765.3224 [*M*<sup>+</sup>+Na]; found: 765.3226; elemental analysis calcd (%) for C46H50O7Si (742.97): C 74.36, H 6.78; found: C 74.66, H 6.57.

**9-O-Acetyl-4,8-anhydro-5,6,7-tri-O-benzyl-1-deoxy-D-***glycero-D-ido***-nono-2,3-diulose (20)**: Prepared from **13** (70 mg, 0.136 mmol) following the general procedure (Method B) using NaIO<sub>4</sub> (116 mg, 0.542 mmol) and RuO<sub>2</sub>·*x* H<sub>2</sub>O (1.2 mg). The reaction mixture was stirred at room temperature in the dark for 45 min. The residue was purified by rapid silica gel column chromatography (hexanes/EtOAc 9:1) to give **20** (35 mg, 0.064 mmol, 47%) as a yellow oil:  $[\alpha]_D = +89 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (*c* = 0.62 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 2.05$  (s, 3 H), 2.12 (s, 3 H), 3.49 (dd, *J*=9.8, 7.2 Hz, 1H), 3.80 (dd, *J*=7.9, 7.2 Hz, 1H), 4.07 (dd, *J*=7.8, 7.2 Hz, 1H), 4.21 (dd, *J*=12.2, 4.8 Hz, 1H), 4.33 (dd, *J*=12.2, 2.1 Hz, 1H), 4.45 (ddd, *J*=9.8, 4.8, 2.1 Hz, 1H), 4.503 (d, *J*=10.6 Hz, 1H), 4.506 (d, *J*=11.1 Hz, 1H), 4.59 (d, *J*=10.6 Hz, 1H), 4.74 (d, *J*=10.9 Hz, 1H), 4.76 (d, *J*=11.4 Hz, 1H), 4.81 (d, *J*=11.3 Hz, 1H), 5.57 (d, *J*=7.2 Hz, 1H), 7.10–7.35 ppm (m, 15H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 20.8$ 

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 $\begin{array}{l} ({\rm CH}_3),\ 23.5\ ({\rm CH}_3),\ 63.4\ ({\rm CH}_2),\ 72.6\ ({\rm CH}),\ 72.9\ ({\rm CH}),\ 73.9\ ({\rm CH}_2),\ 74.1\\ ({\rm CH}_2),\ 74.6\ ({\rm CH}_2),\ 76.8\ ({\rm CH}),\ 78.1\ ({\rm CH}),\ 80.2\ ({\rm CH}),\ 127.8{-}128.5\ (15\times {\rm CH}),\ 136.7\ ({\rm C}),\ 137.6\ ({\rm C}),\ 137.9\ ({\rm C}),\ 170.8\ ({\rm C}),\ 197.2\ ({\rm C}),\ 199.6\ {\rm ppm}\ ({\rm C});\\ {\rm IR\ (film):}\ \tilde{\nu}{=}2928,\ 1735\ {\rm cm}^{-1};\ {\rm MS\ (EI):}\ m/z\ (\%):\ 546\ (2)\ [M^+],\ 475\ (1);\\ {\rm HRMS\ (EI):}\ m/z\ {\rm calcd\ for\ C_{32}H_{34}O_8}\ (546.61):\ {\rm C\ 70.31,\ H\ 6.27;\ found:}\\ {\rm C\ 70.34,\ H\ 6.27.} \end{array}$ 

Photocyclization of 20: A deoxygenated solution of diketone 20 (35 mg, 0.064 mmol) in purified CDCl<sub>3</sub> (1 mL), was placed in a resonance tube and irradiated with a daylight lamp at 30 °C for 1 h. The mixture was concentrated under reduced pressure and the residue purified by silica gel column chromatography (hexanes/EtOAc 8:2) to give (3aS,4S,5R,6-S,6aR)-4,5,6-tris(benzyloxy)-6a-(acetyloxy)methyl-2-hydroxy-2-methyltetrahydro-2H-cyclopenta[b]furan-3(3aH)-one (27) a colorless oil as a mixture of isomers (23.5 mg, 0.043 mmol, d.r., 1:0.9, 67 %): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>; complex spectrum, only clearly distinguished signals are reported):  $\delta = 1.35$  (s, 3H), 1.42 (s, 3H), 2.03 (s, 3H), 2.09 (s, 3H), 3.07 (d, J=1.9 Hz, 1 H), 3.11 (d, J=3.2 Hz, 1 H), 3.92 ppm (d, J=5.4 Hz, 1H); <sup>13</sup>C NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>; complex spectrum, only clearly distinguished signals are reported):  $\delta = 20.8$  (CH<sub>3</sub>), 20.9 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>), 22.5 (CH<sub>3</sub>), 52.7 (CH), 54.9 (CH), 65.8 (CH<sub>2</sub>), 65.9 (CH<sub>2</sub>), 87.7 (CH), 87.9 (C), 88.7 (C), 99.3 (C), 100.0 (C), 170.3 (C), 170.4 (C), 206.6 (C), 210.3 ppm (C); IR (film):  $\tilde{\nu} = 3424$ , 2927, 1742 cm<sup>-1</sup>; MS (EI): m/z (%): 546 (<1)  $[M^+]$ , 503 (<1); HRMS (EI): m/z calcd for  $C_{32}H_{34}O_8$ : 546.2254  $[M^+]$ ; found: 546.2273; elemental analysis calcd (%) for C<sub>32</sub>H<sub>34</sub>O<sub>8</sub> (546.61): C 70.31, H 6.27; found: C 70.10, H 6.40.

#### 4,8-Anhydro-9-azido-5,6,7-tri-O-benzyl-1,9-dideoxy-D-glycero-D-ido-

**nono-2.3-diulose** (21): Prepared from 14 (60 mg, 0.121 mmol) following the general procedure (Method B) using NaIO<sub>4</sub> (103 mg, 0.481 mmol) and RuO<sub>2</sub>·x H<sub>2</sub>O (1.1 mg). The reaction mixture was stirred at room temperature in the dark for 30 min. The residue was purified by rapid silica gel column chromatography (hexanes/EtOAc 1:1) to give 21 (38 mg, 0.072 mmol, 59%) as a yellow oil.  $[\alpha]_D = +52 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (c=2.32 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 2.12$  (s, 3H), 3.34 (dd, J = 13.3, 5.0 Hz, 1 H), 3.51 (dd, J=9.8, 7.2 Hz, 1 H), 3.55 (dd, J=13.3, 2.4 Hz, 1 H), 3.77 (dd, J=8.0, 7.4 Hz, 1 H), 4.08 (dd, J=8.2, 7.4 Hz, 1 H), 4.43 (ddd, J= 9.7, 4.6, 2.1 Hz, 1 H), 4.50–4.82 (m, 6 H), 5.60 (d, J=7.2 Hz, 1 H), 7.18– 7.37 ppm (m, 15 H);  ${}^{13}$ C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 23.5$  (CH<sub>3</sub>), 51.7 (CH<sub>2</sub>), 72.6 (CH), 74.0 (CH), 74.1 (CH<sub>2</sub>), 74.3 (CH<sub>2</sub>), 74.7 (CH<sub>2</sub>), 77.7 (CH), 78.2 (CH), 80.2 (CH), 127.8-128.6 (15×CH), 136.7 (C), 137.7 (C), 137.9 (C), 197.2 (C), 199.8 ppm (C); IR (film): v=2925, 2099, 1731, 1715 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 584 (100) [ $M^+$ +MeOH+Na]; HRMS (ESI<sup>+</sup>): m/z calcd for C<sub>31</sub>H<sub>35</sub>N<sub>3</sub>NaO<sub>7</sub>: 584.2373 [ $M^+$ +MeOH+Na]; found: 584.2372. All attempts at obtaining correct elemental analysis for this azide in two different analyzers failed.

Photocyclization of 21: A deoxygenated solution of diketone 21 (31 mg, 0.059 mmol) in purified  $\text{CDCl}_3$  (1.0 mL), was irradiated with a daylight lamp at 30°C for 2 h. The solution was concentrated under reduced pressure and the residue purified by Chromatotron chromatography (Al<sub>2</sub>O<sub>3</sub>, hexanes/EtOAc 8:2) to give the isomeric mixture (3aS,4S,5R,6S,6aR)-6a-(azidomethyl)-4,5,6-tris(benzyloxy)-2-hydroxy-2-methyltetrahydro-2H-cyclopenta[b]furan-3(3aH)-one (28) (17 mg, 0.032 mmol, d.r. 1.3:1, 55%) as a colorless oil: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.36$  (s, 3H), 1.49 (s, 3H), 3.09 (d, J=2.5 Hz, 1H), 3.12 (d, J=3.5 Hz, 1H), 3.46 (d, J=13.6 Hz, 1 H), 3.78 (d, J=10.6 Hz, 1 H), 3.79 (d, J=13.2 Hz, 1 H), 3.89 (d, J=4.4 Hz, 1 H), 3.90 (d, J=12.9 Hz, 1 H), 3.97 (dd, J=3.8, 3.5 Hz, 1 H), 3.99 (dd, J=5.4, 4.7 Hz, 1 H), 4.07 (dd, J=3.8, 3.8 Hz, 1 H), 4.18 (ddd, J= 3.5, 2.4, 1.1 Hz, 1 H), 4.20 (d, J=4.1 Hz, 1 H), 4.41-4.70 (m, 12 H), 7.21-7.38 ppm (m, 30 H);  ${}^{13}$ C NMR (125.7 MHz, CDCl<sub>3</sub>):  $\delta = 21.3$  (CH<sub>3</sub>), 22.6 (CH<sub>3</sub>), 52.8 (CH), 54.7 (CH<sub>2</sub>), 54.7 (CH), 54.9 (CH<sub>2</sub>), 71.6 (CH<sub>2</sub>), 71.9 (CH<sub>2</sub>), 72.3 (CH<sub>2</sub>), 72.7 (CH<sub>2</sub>), 73.2 (CH<sub>2</sub>), 72.2 (CH<sub>2</sub>), 82.5 (CH), 83.6 (CH), 85.1 (CH), 85.3 (CH), 87.9 (CH), 88.4 (C), 88.8 (CH), 90.1 (C), 99.4 (C), 100.3 (C), 127.8-128.7 (30×CH), 136.3 (C), 137.2 (C), 137.3 (C), 137.39 (C), 137.41 (C), 137.5 (C), 207.0 (C), 210.1 ppm (C); IR (film): v= 3414, 2105, 1767 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 552 (100) [ $M^+$ +Na]; HRMS (ESI<sup>+</sup>): m/z calcd for  $C_{30}H_{31}N_3NaO_6$ : 552.2111 [ $M^+$ +Na]; found: 552.2111. All attempts at obtaining a correct elemental analysis for this azide in two different analyzers failed.

4,8-Anhydro-1-deoxy-5,6-di-O-methyl-7,9-O-isopropylidene-D-glycero-Dido-nono-2,3-diulose (22): Prepared from 15 (136.0 mg, 0.50 mmol) following the general procedure (Method A) using dimethyl sulfide (400 µL, 5.4 mmol). The mixture was stirred at room temperature in the dark for 3.5 h and concentrated under reduced pressure. The residue was purified by rapid silica gel column chromatography (hexanes/EtOAc 8:2) to give 22 (102.2 mg, 0.34 mmol, 67%) as a yellow oil:  $[\alpha]_{\rm D} = +107 \, {\rm cm}^3 {\rm g}^{-1} {\rm dm}^{-1}$  $(c = 0.58 \text{ in CHCl}_3)$ ; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.40$  (s, 3 H), 1.48 (s, 3H), 2.28 (s, 3H), 3.34 (dd, J=8.7, 8.6 Hz, 1H), 3.41 (s, 3H), 3.50 (m, 1H), 3.55 (s, 3H), 3.58–3.63 (m, 2H), 3.92 (dd, J=10.7, 5.3 Hz, 1H), 4.13 (ddd, J=10.1, 10.1, 5.3 Hz, 1 H), 5.51 ppm (d, J=7.6 Hz, 1 H); <sup>13</sup>C NMR  $(125.7 \text{ MHz}, \text{CDCl}_3); \delta = 19.0 (\text{CH}_3), 23.4 (\text{CH}_3), 29.0 (\text{CH}_3), 60.0 (\text{CH}_$ 60.3 (CH<sub>3</sub>), 62.5 (CH<sub>2</sub>), 67.3 (CH), 71.9 (CH), 74.0 (CH), 81.1 (CH), 81.2 (CH), 99.3 (C), 197.2 (C), 200.3 ppm (C); IR (CHCl<sub>3</sub>, 0.2 mm): v=2999, 1713 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 357 (100) [ $M^+$ +MeOH+Na]; HRMS (ESI<sup>+</sup>): m/z calcd for C<sub>15</sub>H<sub>26</sub>NaO<sub>8</sub>: 357.1525 [ $M^+$ +MeOH+Na]; found: 357.1526; elemental analysis calcd (%) for C<sub>14</sub>H<sub>22</sub>O<sub>7</sub> (302.32): C 55.62, H 7.33; found: C 55.57, H 7.34.

Photocyclization of 22 to compound 29: A solution of 22 (16.1 mg, 0.053 mmol) in dry C6D6 (0.3 mL), was placed in a resonance tube and irradiated with a daylight lamp at 36-40 °C for 2.5 h. The mixture was concentrated under reduced pressure and the residue purified by silica gel column chromatography (hexanes/EtOAc 7:3) to give a mixture of hemiketal diastereomers 29 (8.5 mg, 0.028 mmol, d.r. 10:3, 53%) (major isomer: (2S,3aS,4S,5R,5aS,9aR)-2-hydroxy-4,5-dimethoxy-2,7,7trimethyltetrahydrofuro[2',3':2,3]cyclopenta[1,2-d][1,3]dioxin-3(2H)-one) as a colorless oil:  $[\alpha]_{\rm D} = +29 \,{\rm cm}^3 {\rm g}^{-1} {\rm dm}^{-1}$  (c=0.50, CHCl<sub>3</sub>); <sup>1</sup>H NMR  $(500 \text{ MHz}, \text{CDCl}_3;): \delta \text{ (major isomer)} = 1.36 \text{ (s, 3 H)}, 1.47 \text{ (s, 3 H)}, 1.48 \text{ (s, 3 H)},$ 3H), 2.99 (d, J=2.2 Hz, 1 H), 3.30 (s, 3H), 3.42 (s, 3H), 3.76 (dd, J=1.6, 1.3 Hz, 1 H), 3.89 (d, J = 12.3 Hz, 1 H), 3.92 (ddd, J = 2.2, 1.6, 1.3 Hz, 1 H), 4.05 (d, J = 12.3 Hz, 1 H), 4.11 ppm (dd, J = 1.3, 1.3 Hz, 1 H); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>): δ (major isomer)=22.3 (CH<sub>3</sub>), 22.8 (CH<sub>3</sub>), 25.5 (CH<sub>3</sub>), 54.9 (CH), 56.0 (CH<sub>3</sub>), 57.2 (CH<sub>3</sub>), 66.4 (CH<sub>2</sub>), 79.0 (CH), 87.9 (CH), 88.0 (C), 88.8 (CH), 99.7 (C), 99.8 (C), 210.8 ppm (C); IR (CHCl<sub>3</sub>, 0.2 mm):  $\tilde{\nu} = 3581$ , 3016, 1770 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 325 (100) [M<sup>+</sup> +Na]; HRMS (ESI<sup>+</sup>): m/z calcd for C<sub>14</sub>H<sub>22</sub>NaO<sub>7</sub>: 325.1263 [ $M^+$ +Na]; found: 325.1252; elemental analysis calcd (%) for C<sub>14</sub>H<sub>22</sub>O<sub>7</sub> (302.32): C 55.62, H 7.33; found: C 55.73, H 7.00.

4,8-Anhydro-7,9-bis-O-(tert-butyldimethylsilyl)-1-deoxy-5,6-di-O-methyl-D-glycero-D-ido-nono-2,3-diulose (23): Prepared from 16 (51 mg, 0.12 mmol) following the general procedure (Method A) using dimethyl sulfide (15 µL, 0.2 mmol). The mixture was stirred at room temperature in the dark for 2 h and concentrated under reduced pressure. The residue was purified by rapid silica gel column chromatography (hexanes/EtOAc 1:1) to give 23 (40 mg, 0.09 mmol, 75%) as a yellow oil:  $[\alpha]_{\rm D} = +$ 74 cm<sup>3</sup> g<sup>-1</sup> dm<sup>-1</sup> (c=0.82 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =0.02 (s, 3H), 0.03 (s, 3H), 0.09 (s, 3H), 0.10 (s, 3H), 0.87 (s, 9H), 0.88 (s, 9H), 2.29 (s, 3 H), 3.17 (dd, J=8.5, 8.2 Hz, 1 H), 3.38 (s, 3 H), 3.51 (s, 3 H), 3.55 (dd, J=8.5, 7.3 Hz, 1 H), 3.58 (dd, J=9.1, 8.2 Hz, 1 H), 3.75 (dd, J=11.7, 3.5 Hz, 1 H), 3.81 (dd, J=11.7, 1.9 Hz, 1 H), 4.02 (ddd, J=9.2, 3.4, 1.9 Hz, 1 H), 5.47 ppm (d, J = 7.2 Hz, 1 H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta =$ -5.4 (CH<sub>3</sub>), -5.1 (CH<sub>3</sub>), -5.0 (CH<sub>3</sub>), -4.1 (CH<sub>3</sub>), 18.1 (C), 18.4 (C), 23.5 (CH<sub>3</sub>), 25.90 (3×CH<sub>3</sub>), 25.95 (3×CH<sub>3</sub>), 58.9 (CH<sub>3</sub>), 60.6 (CH<sub>3</sub>), 62.3 (CH<sub>2</sub>), 69.2 (CH), 72.1 (CH), 77.1 (CH), 81.9 (CH), 83.9 (CH), 197.6 (C), 201.3 ppm (C); IR (film):  $\tilde{\nu}$ =2955, 1711 cm<sup>-1</sup>; MS (EI): m/z (%): 491 (1)  $[M^++H]$ , 433 (87); HRMS (EI): m/z calcd for  $C_{23}H_{47}O_7Si_2$ : 491.2860  $[M^+$ +H]; found: 491.2875; elemental analysis calcd (%) for C<sub>23</sub>H<sub>46</sub>O<sub>7</sub>Si<sub>2</sub> (490.78): C 56.29, H 9.45; found: C 56.30, H 9.45.

**Photocyclization of 23**: A solution of diketone **23** (28 mg, 0.057 mmol) in purified CDCl<sub>3</sub> (0.7 mL), was placed in a resonance tube and irradiated with a daylight lamp at 30 °C for 3 h. The mixture was concentrated under reduced pressure and the residue purified by Chromatotron chromatography (Al<sub>2</sub>O<sub>3</sub>, toluene as eluent) to give (2*S*,3a*S*,4*S*,5*R*,6*S*,6a*R*)-6-[(*tert*-butyldimethylsilyl)oxy]-6a-[(*tert*-butyldimethylsilyl)oxy]methyl-2-hydroxy-4,5-dimethoxy-2-methyltetrahydro-2*H*-cyclopenta[*b*]furan-3(3a*H*)-one (**30**) (17.5 mg, 0.036 mmol, 63%) as a colorless oil:  $[a]_D = +$  54 cm<sup>3</sup>g<sup>-1</sup>dm<sup>-1</sup> (*c*=2.10 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta =$  0.091 (s, 3H), 0.099 (s, 3H), 0.13 (s, 3H), 0.14 (s, 3H), 0.89 (s, 9H), 0.92

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(s, 9H), 1.39 (d, J=0.9 Hz, 3H), 2.95 (d, J=4.4 Hz, 1H), 3.39 (s, 3H), 3.43 (s, 3H), 3.53 (dd, J=5.4, 5.4 Hz, 1H), 3.69 (dd, J=5.0, 4.4 Hz, 1H), 3.77 (d, J=11.4 Hz, 1H), 3.85 (d, J=11.4 Hz, 1H), 3.99 (d, J=5.7 Hz, 1H), 5.11 ppm (d, J=0.9 Hz, 1H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = -5.7$  (CH<sub>3</sub>), -5.6 (CH<sub>3</sub>), -5.1 (CH<sub>3</sub>), -4.8 (CH<sub>3</sub>), 18.0 (C), 18.4 (C), 20.3 (CH<sub>3</sub>), 25.6 (3×CH<sub>3</sub>), 25.8 (3×CH<sub>3</sub>), 51.3 (CH), 57.6 (CH<sub>3</sub>), 58.4 (CH<sub>3</sub>), 65.9 (CH<sub>2</sub>), 81.6 (CH), 72.1 (CH), 84.5 (CH), 89.4 (CH), 90.1 (CH), 98.7 (CH), 208.5 ppm (C); IR (film):  $\bar{\nu}=3368$ , 2931, 1765 cm<sup>-1</sup>; MS (EI): m/z (%): 473 (2) [ $M^+$ -OH], 433 (7); HRMS (EI): m/z calcd for C<sub>23</sub>H<sub>45</sub>O<sub>6</sub>Si<sub>2</sub>: 473.2755 [ $M^+$ -OH]; found: 473.2761; elemental analysis calcd (%) for C<sub>23</sub>H<sub>46</sub>O<sub>7</sub>Si<sub>2</sub> (490.78): C 56.29, H 9.45; found: C 56.21, H 9.22.

#### 7-O-Acetyl-4,8-anhydro-9-O-(tert-butyldimethylsilyl)-1-deoxy-5,6-di-O-

methyl-D-glycero-D-ido-nono-2,3-diulose (24): Prepared from 17 (176.7 mg, 0.46 mmol) following the general procedure (Method A) using dimethyl sulfide (267  $\mu$ L, 3.64 mmol). The mixture was stirred at room temperature in the dark for 2 h and concentrated under reduced pressure. The residue was purified by rapid silica gel column chromatography (hexanes/EtOAc 1:1) to give 24 (139.0 mg, 0.33 mmol, 73%) as a yellow oil:  $[\alpha]_{\rm D} = +76 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1} (c = 0.59 \text{ in CHCl}_3); {}^{1}\text{H NMR} (500 \text{ MHz}, \text{CDCl}_3):$  $\delta = 0.02$  (s, 6H), 0.87 (s, 9H), 2.06 (s, 3H), 2.30 (s, 3H), 3.35 (s, 3H), 3.46 (dd, J=6.8, 6.6 Hz, 1 H), 3.50 (s, 3 H), 3.65 (dd, J=11.4, 4.7 Hz, 1 H), 3.74 (dd, J = 11.4, 3.2 Hz, 1 H), 3.80 (dd, J = 6.8, 6.6 Hz, 1 H), 4.16 (ddd, J = 10.48.8, 4.7, 3.2 Hz, 1 H), 4.96 (dd, J=8.8, 6.6 Hz, 1 H), 5.47 ppm (d, J= 6.6 Hz, 1 H); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>):  $\delta = -5.5$  (2×CH<sub>3</sub>), 18.3 (C), 21.0 (CH<sub>3</sub>), 23.5 (CH<sub>3</sub>), 25.8 (3×CH<sub>3</sub>), 58.9 (CH<sub>3</sub>), 59.6 (CH<sub>3</sub>), 63.0 (CH<sub>2</sub>), 68.8 (CH), 72.9 (CH), 74.6 (CH), 79.6 (2×CH), 169.7 (C), 197.1 (C), 198.5 ppm (C); IR (CHCl<sub>3</sub>, 0.2 mm):  $\tilde{\nu} = 2933$ , 1738, 1715 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 473 (100) [M<sup>+</sup>+MeOH+Na]; HRMS (ESI<sup>+</sup>): m/z calcd for C<sub>20</sub>H<sub>38</sub>NaO<sub>9</sub>Si: 473.2183 [M<sup>+</sup>+MeOH+Na]; found: 473.2182; elemental analysis calcd (%) for  $C_{19}H_{34}O_8Si$  (418.55): C 54.52, H 8.19; found: C 54.53, H 8.19.

Photocyclization of 24: A deoxygenated solution of diketone 24 (41.1 mg, 0.098 mmol) in dry  $C_6D_6$  (0.3 mL), was placed in a resonance tube and irradiated with a daylight lamp at 36-40 °C for 3 h. The solution was concentrated under reduced pressure and the residue purified by silica gel column chromatography (hexanes/EtOAc 7:3) to give a mixture of hemiketal diastereomers 31 (25.4 mg, 0.061 mmol, d.r., 10:3, 62%) (major isomer: (2S,3aS,4S,5R,6S,6aR)-6a-[(tert-butyldimethylsilyl)oxy]methyl-5-ethoxy-2-hydroxy-4-methoxy-2-methyl-3-oxohexahydro-2H-cyclopenta[b]furan-6-yl acetate) as a colorless oil:  $[\alpha]_D = +56 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$ (c = 0.59 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (major isomer) = 0.15 (s, 6H), 0.92 (s, 9H), 1.40 (d, J=1.0 Hz, 3H), 2.08 (s, 3H), 3.11 (dd, J= 2.1, 0.9 Hz, 1 H), 3.34 (s, 3 H), 3.38 (s, 3 H), 3.74 (ddd, J=2.3, 2.3, 0.8 Hz, 1H), 3.77 (d, J=10.7 Hz, 1H), 3.80 (d, J=10.7 Hz, 1H), 3.87 (ddd, J= 2.1, 2.1, 0.9 Hz, 1 H), 4.91 (d, J=1.0 Hz, 1 H), 5.21 ppm (dd, J=2.5, 1.0 Hz, 1 H); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>):  $\delta$  (major isomer) = -5.64  $(CH_3)$ , -5.55  $(CH_3)$ , 18.4 (C), 20.0  $(CH_3)$ , 20.8  $(CH_3)$ , 25.8  $(3 \times CH_3)$ , 52.7 (CH), 57.2 (CH<sub>3</sub>), 57.3 (CH<sub>3</sub>), 64.7 (CH<sub>2</sub>), 80.5 (CH), 86.46 (CH), 86.58 (CH), 90.7 (C), 98.7 (C), 169.6 (C), 207.0 ppm (C); IR (CHCl<sub>3</sub>, 0.2 mm):  $\tilde{\nu}$ =2933, 1766, 1742 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 441 (100) [ $M^+$ +Na]; HRMS (ESI<sup>+</sup>): m/z calcd for C<sub>19</sub>H<sub>34</sub>NaO<sub>8</sub>Si: 441.1921 [ $M^+$ +Na]; found: 441.1920; elemental analysis calcd (%) for  $C_{19}H_{34}O_8Si$  (418.55): C 54.52, H 8.19; found: C 54.55, H 8.14.

**4,8-Anhydro-9**-*O*-(*tert*-butyldiphenylsilyl)-1,5-dideoxy-6,7-di-*O*-methyl-*manno*-nono-2,3-diulose (38): Prepared from 32 (70 mg, 0.155 mmol) following the general procedure (Method B) using NaIO<sub>4</sub> (132 mg, 0.62 mmol) and RuO<sub>2</sub>-x H<sub>2</sub>O (1.1 mg). The reaction mixture was stirred at room temperature in the dark for 1 h. The residue was purified by rapid silica gel column chromatography (hexanes/EtOAc 1:1) to give 38 (47 mg, 0.097 mmol, 63%) as a yellow oil:  $[a]_D = +13 \text{ cm}^3 \text{g}^{-1} \text{ dm}^{-1}$  (*c*= 0.94 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 1.18$  (s, 9H), 1.60 (ddd, J = 13.9, 9.8, 6.0 Hz, 1H), 1.86 (s, 3H), 2.22 (ddd, J = 13.9, 4.4, 3.8 Hz, 1H), 3.11 (s, 3H), 3.23 (dd, J = 7.9, 7.9 Hz, 1H), 3.35 (s, 3H), 3.41 (ddd, J = 9.8, 7.6, 4.4 Hz, 1H), 3.77 (ddd, J = 7.9, 4.4, 2.8 Hz, 1H), 3.98 (dd, J = 11.0, 4.4 Hz, 1H), 4.02 (dd, J = 11.0, 2.8 Hz, 1H), 4.89 (dd, J = 6.0, 3.8 Hz, 1H), 7.21–7.86 pm (m, 10H); <sup>13</sup>C NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 19.5$  (C), 24.4 (CH<sub>3</sub>), 27.0 (3×CH<sub>3</sub>), 28.6 (CH<sub>2</sub>), 56.6 (CH<sub>3</sub>), 59.7 (CH<sub>3</sub>), 63.6 (CH<sub>2</sub>), 72.5 (CH), 77.6 (CH), 78.6 (CH), 79.0 (CH), 127.8–136.2 (10×

CH), 133.8 (C), 134.0 (C), 198.9 (C), 199.9 ppm (C); IR (film):  $\tilde{\nu}$ =2938, 1722 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): *m*/*z* (%): 539 (100) [*M*<sup>+</sup>+MeOH+Na]; HRMS (ESI<sup>+</sup>): *m*/*z* calcd for C<sub>28</sub>H<sub>40</sub>NaO<sub>7</sub>Si: 539.2441 [*M*<sup>+</sup>+MeOH+Na]; found: 539.2440; elemental analysis calcd (%) for C<sub>27</sub>H<sub>36</sub>O<sub>6</sub>Si (484.66): C 66.91, H 7.49; found: C 67.09, H 7.52.

**Photocyclization of 38**: A solution of diketone **38** (48 mg, 0.102 mmol) in dry  $C_6D_6$  (1.0 mL), was placed in a resonance tube and irradiated with a daylight lamp at 30 °C. The reaction was monitored by <sup>1</sup>H NMR spectroscopy, complete consumption of starting material was observed after 9 h. Then, the reaction mixture was heated at 60 °C for 5 h and concentrated under reduced pressure. The residue was solved in CH<sub>2</sub>Cl<sub>2</sub> (0.82 mL) cooled to 0 °C and acetylated by adding Ac<sub>2</sub>O (29 mL, 0.306 mmol) and DMAP (37 mg, 0.306 mmol) followed by stirring at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure and the residue partially resolved by silica gel column chromatography (hexanes/EtOAc 8:2) to give (2*R*,3a,*S*,*S*,*R*,*6*,*S*,6a,*P*)-6a-[(*tert*-butyldiphenyl-silyl)oxy]methyl-5,6-dimethoxy-2-methyl-3-oxohexahydro-2*H*-cyclo-

penta[b]furan-2-yl acetate (**45**) (21 mg, 0.040 mmol, d.r. 1:1, 39%). The sensitive photoenol intermediate was detected by NMR spectroscopy but in this case could not be obtained in pure state. Only clearly distinguished signals from the reaction mixture are reported: <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ ):  $\delta = 1.25$  (s, 9H), 1.75 (s, 3H), 2.85 (s, 3H), 3.00 (s, 3H), 4.70 (d, J = 18.6 Hz, 1H), 4.82 (d, J = 18.6 Hz, 1H), 5.28 (dd, J = 7.5, 7.5 Hz, 1H), 6.66 ppm (br s, 1H, OH); <sup>13</sup>C NMR (125.7 MHz,  $C_6D_6$ ):  $\delta = 19.6$  (C), 22.3 (CH<sub>3</sub>), 27.0 (3×CH<sub>3</sub>), 57.6 (CH<sub>3</sub>), 59.3 (CH<sub>3</sub>), 69.5 (CH<sub>2</sub>), 111.6 (CH), 149.2 (C), 193.9 (C), 207.5 ppm (C).

*Compound* **44**: colorless oil.  $[a]_D = -2 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (*c*=0.54 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =1.06 (s, 9H), 1.55 (s, 3H), 1.75 (s, 3H), 1.99 (dddd, *J*=13.9, 4.4, 4.4, 1.3 Hz, 1H), 2.30 (ddd, *J*=13.9, 10.4, 5.4 Hz, 1H), 3.23 (dd, *J*=10.4, 4.4 Hz, 1H), 3.27 (s, 3H), 3.47 (s, 3H), 3.73 (br d, *J*=4.1 Hz, 1H), 3.85 (d, *J*=10.1 Hz, 1H), 3.88 (ddd, *J*=4.7, 4.7, 4.7 Hz, 1H), 3.91 (d, *J*=10.1 Hz, 1H), 7.36–7.79 ppm (m, 10H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$ =19.3 (C), 20.7 (CH<sub>3</sub>), 23.0 (CH<sub>3</sub>), 26.9 (3×CH<sub>3</sub>), 31.7 (CH<sub>2</sub>), 46.4 (CH), 56.4 (CH<sub>3</sub>), 58.9 (CH<sub>3</sub>), 64.4 (CH<sub>2</sub>), 82.7 (CH), 90.6 (CH), 93.1 (C), 101.9 (C), 127.6–135.8 (10×CH), 133.42 (C), 133.45 (C), 169.5 (C), 209.7 ppm (C); IR (film):  $\bar{\nu}$ =2928, 1766, 1743 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): *m/z* (%): 549 (100) [*M*<sup>+</sup>+Na]; HRMS (ESI<sup>+</sup>): *m/z* calcd for C<sub>29</sub>H<sub>38</sub>NaO<sub>7</sub>Si: 549.2285 [*M*<sup>+</sup>+Na]; found: 549.2285; elemental analysis calcd (%) for C<sub>29</sub>H<sub>38</sub>O<sub>7</sub>Si (526.69): C 66.13, H 7.27; found: C 66.40, H 7.61.

*Compound* **45**: colorless oil,  $[a]_D = -15 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (*c*=0.56 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.07$  (s, 9H), 1.50 (s, 3H), 1.77 (ddd, *J*= 12.8, 9.8, 9.8 Hz, 1H), 1.86 (s, 3H), 2.27 (ddd, *J*=12.9, 6.3, 2.2 Hz, 1H), 3.31 (dd, *J*=10.1, 2.2 Hz, 1H), 3.35 (s, 3H), 3.46 (s, 3H), 3.49 (m, 1H), 3.77 (d, *J*=10.1 Hz, 1H), 3.85 (d, *J*=9.8 Hz, 1H), 3.92 (d, *J*=7.6 Hz, 1H), 7.36–7.69 ppm (m, 10H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 19.3$ (C), 20.5 (CH<sub>3</sub>), 21.9 (CH<sub>3</sub>), 26.9 (3×CH<sub>3</sub>), 30.4 (CH<sub>2</sub>), 46.8 (CH), 57.5 (CH<sub>3</sub>), 59.5 (CH<sub>3</sub>), 65.4 (CH<sub>2</sub>), 84.5 (CH), 84.8 (CH), 88.5 (C), 101.2 (C), 127.7–135.7 (10×CH), 132.9 (C), 133.0 (C), 169.5 (C), 211.0 ppm (C); IR (film):  $\tilde{\nu} = 2931$ , 1768, 1744 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): *m/z* (%): 549 (100) [*M*<sup>+</sup> +Na]; HRMS (ESI<sup>+</sup>): *m/z* calcd for C<sub>29</sub>H<sub>38</sub>NaO<sub>7</sub>Si (526.69): C 66.13, H 7.27; found: C 66.11, H 7.58.

#### 4,8-Anhydro-1,6-dideoxy-5,7,9-tri-O-methyl-D-altro-nono-2,3-diulose

(39): Prepared from 33 (111 mg, 0.486 mmol) following the general procedure (Method A) using dimethyl sulfide (71 µL, 0.970 mmol). The mixture was stirred at room temperature in the dark for 6 h and concentrated under reduced pressure. The residue was purified by rapid silica gel column chromatography (hexanes/EtOAc 7:3→6:4) to give 39 (83 mg, 0.315 mmol, 65%) as a yellow oil:  $[\alpha]_D = +126 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (*c*=1.3 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =1.72 (ddd, *J*=13.2, 8.8, 7.6 Hz, 1H), 2.19 (ddd, *J*=13.2, 5.1, 3.8 Hz, 1H), 2.26 (s, 3H), 3.27 (s, 3H), 3.35 (s, 3H), 3.36 (m, 1H), 3.40 (s, 3H), 3.55 (dd, *J*=10.7, 4.7 Hz, 1H), 3.64 (dd, *J*=10.7, 2.2 Hz, 1H), 3.87 (ddd, *J*=10.7, 6.6, 3.8 Hz, 1H), 4.10 (ddd, *J*=9.2, 4.7, 2.2 Hz, 1H), 5.38 ppm (d, *J*=6.9 Hz, 1H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$ =23.4 (CH<sub>3</sub>), 28.7 (CH<sub>2</sub>), 56.8 (CH<sub>3</sub>), 56.9 (CH<sub>3</sub>),

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59.2 (CH<sub>3</sub>), 72.1 (CH<sub>2</sub>), 73.4 (CH), 74.1 (CH), 74.7 (CH), 75.7 (CH), 197.7 (C), 199.4 ppm (C); IR (film):  $\tilde{\nu}$ =2933, 1716 cm<sup>-1</sup>; MS (EI): *m/z* (%): 260 (<1) [*M*<sup>+</sup>]; HRMS (EI): *m/z*: calcd for: 260.1260 [*M*<sup>+</sup>]; found: 260.1261; elemental analysis calcd (%) for C<sub>12</sub>H<sub>20</sub>O<sub>6</sub> (260.28): C 55.37, H 7.74; found: C 55.52, H 7.73.

**Photocyclization of 39**: *Method A*: A deoxygenated solution of diketone **39** (41 mg, 0.156 mmol) in dry  $C_6D_6$  (0.6 mL), was placed in a resonance tube and irradiated with a daylight lamp at 30 °C for 3 h. The reaction was monitored by <sup>1</sup>H NMR spectroscopy, complete transformation into a mixture of the enol intermediate and the cyclized product **46** was observed. The mixture was heated at 45 °C in the dark for 1 h, concentrated under reduced pressure and the residue purified by Chromatotron chromatography (Al<sub>2</sub>O<sub>3</sub>, hexanes/EtOAc 9:1 $\rightarrow$ 7:3) to give **46** (23 mg, 0.089 mmol, 57%) as a colorless oil.

*Method B*: A deoxygenated solution of diketone **39** (34 mg, 0.131 mmol) in dry  $C_6D_6$  (0.6 mL), was placed in a resonance tube and irradiated with a daylight lamp at 45 °C for 7 h. The reaction was monitored by <sup>1</sup>H NMR spectroscopy, complete transformation into the cyclized product **46** was observed. The mixture was concentrated under reduced pressure and the residue purified by Chromatotron chromatography (Al<sub>2</sub>O<sub>3</sub>, hexanes/ EtOAc 9:1 $\rightarrow$ 7:3 as eluents) to give (2*S*,3a*S*,4*R*,6*S*,6a*R*)-2-hydroxy-4,6-dimethoxy-6a-(methoxymethyl)-2-methyltetrahydro-2*H*-cyclopenta[*b*]fur-

an-3(3aH)-one (46) (20 mg, 0.077 mmol, 59%) as a colorless oil.  $[\alpha]_{\rm D} =$ +139 cm<sup>3</sup>g<sup>-1</sup>dm<sup>-1</sup> (c=1.01 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ = 1.35 (d, J=0.95 Hz, 3 H, OH coupling), 1.95 (ddd, J=14.8, 6.0, 5.4 Hz, 1H), 2.13 (dddd, J=14.5, 3.2, 3.2, 1.3 Hz, 1H), 3.13 (dd, J=1.3, 1.3 Hz, 1 H), 3.35 (s, 3 H), 3.37 (s, 3 H), 3.48 (s, 3 H), 3.75 (d, J = 10.1 Hz, 1 H), 3.76 (dd, J=5.0, 3.4 Hz, 1 H), 3.78 (d, J=10.4 Hz, 1 H), 3.79 (ddd, J=5.7, 2.5, 2.5 Hz, 1 H), 5.35 ppm (d, J=0.9 Hz, 1 H, OH); <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ ):  $\delta = 1.60$  (s, 3H), 1.72 (ddd, J = 14.2, 5.7, 5.7 Hz, 1H), 1.89 (ddd, J=14.2, 4.7, 4.7 Hz, 1 H), 2.70 (s, 3 H), 2.98 (s, 3 H), 3.13 (s, 3 H), 3.18 (d, J=2.8 Hz, 1 H), 3.507 (dd, J=5.0, 5.0 Hz, 1 H), 3.513 (d, J=10.4 Hz, 1 H), 3.54 (d, J=10.4 Hz, 1 H), 3.66 (ddd, J=6.3, 3.8, 2.8 Hz, 1 H), 5.47 ppm (br s, 1H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 21.1$  (CH<sub>3</sub>), 35.4 (CH<sub>2</sub>), 55.8 (CH), 57.3 (CH<sub>3</sub>), 57.8 (CH<sub>3</sub>), 59.5 (CH<sub>3</sub>), 73.9 (CH<sub>2</sub>), 84.5 (CH), 87.5 (CH), 91.2 (C), 98.7 (C), 210.1 ppm (C); <sup>13</sup>C NMR (125.7 MHz,  $C_6D_6$ ):  $\delta = 21.6$  (CH<sub>3</sub>), 35.8 (CH<sub>2</sub>), 55.6 (CH), 56.8 (CH<sub>3</sub>), 57.1 (CH<sub>3</sub>), 58.7 (CH<sub>3</sub>), 74.3 (CH<sub>2</sub>), 83.4 (CH), 87.6 (CH), 91.6 (C), 99.6 (C), 209.6 ppm (C); IR (film):  $\tilde{\nu} = 3348$ , 2936, 1760 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z(%): 283 (100)  $[M^++Na]$ ; HRMS (ESI<sup>+</sup>): m/z calcd for  $C_{12}H_{20}NaO_6$ : 283.1158 [M<sup>+</sup>+Na]; found: 283.1147; elemental analysis calcd (%) for C12H20O6 (260.28): C 55.37, H 7.74; found: C 55.38, H 7.74.

4,8-Anhydro-7,9-bis-O-(tert-butyldiphenylsilyl)-1,6-dideoxy-5-O-methyl-D-altro-nono-2,3-diulose (40): Prepared from 34 (101 mg, 0.15 mmol) following the general procedure (Method A) using dimethyl sulfide (22 µL, 0.3 mmol). The mixture was stirred at room temperature in the dark for 5 h and concentrated under reduced pressure. The residue was purified by rapid silica gel column chromatography (hexanes/EtOAc  $95:5 \rightarrow 9:1$ ) to give **40** (81.4 mg, 0.11 mmol, 77%) as a yellow oil:  $[\alpha]_{\rm D} = +$ 57.9 cm<sup>3</sup>g<sup>-1</sup>dm<sup>-1</sup> (c = 0.95 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta =$ 0.98 (s, 9H), 1.01 (s, 9H), 1.56 (ddd, J=12.6, 9.3, 9.0 Hz, 1H), 1.91 (ddd, J = 12.5, 4.7, 4.7 Hz, 1 H), 2.25 (s, 3 H), 3.10 (s, 3 H), 3.44 (ddd, J = 10.4, 6.9, 4.6 Hz, 1 H), 3.75 (dd, J=11.2, 4.9 Hz, 1 H), 3.82 (ddd, J=10.1, 9.8, 4.5 Hz, 1H), 3.96 (dd, J=11.4, 2.2 Hz, 1H), 4.21 (ddd, J=10.7, 4.9, 2.9 Hz, 1 H), 5.30 (d, J=6.7 Hz, 1 H), 7.27-7.42 (m, 12 H), 7.61-7.64 ppm (m, 8H);  ${}^{13}C$  NMR (125.7 MHz, CDCl<sub>3</sub>):  $\delta = 19.2$  (C), 19.3 (C), 23.5 (CH<sub>3</sub>), 26.8 (6×CH<sub>3</sub>), 34.0 (CH<sub>2</sub>), 56.9 (CH<sub>3</sub>), 63.9 (CH<sub>2</sub>), 66.3 (CH), 72.9 (CH), 75.8 (CH), 78.0 (CH), 127.5 (4×CH), 127.6 (2×CH), 127.7 (2× CH), 129.42 (CH), 129.44 (CH), 129.7 (CH), 129.8 (CH), 133.3 (C), 133.6 (C), 133.9 (C), 134.1 (C), 135.7 (2×CH), 135.76 (2×CH), 135.78 (2× CH), 135.82 (2×CH), 197.9 (C), 200.3 ppm (C); IR (CHCl<sub>3</sub>, 0.2 mm):  $\tilde{\nu}$  = 2933, 1714 cm<sup>-1</sup>; MS (EI): m/z (%): 708 (<1) [ $M^+$ ], 651 (18), 135 (100); HRMS (EI): m/z calcd for C<sub>42</sub>H<sub>52</sub>O<sub>6</sub>Si<sub>2</sub>: 708.3302 [*M*<sup>+</sup>]; found: 708.3286; elemental analysis calcd (%) for C<sub>42</sub>H<sub>52</sub>O<sub>6</sub>Si<sub>2</sub> (709.03): C 71.15, H 7.39; found: C 71.48, H 7.00.

(3Z,5R,7S)-7,9-Bis[(*tert*-butyldiphenylsilyl)oxy]-3-hydroxy-5-methoxy-3nonene-2,8-dione (50): A deoxygenated solution of diketone 40 (56 mg, 0.079 mmol) in purified CDCl<sub>3</sub> (0.6 mL), was placed in a resonance tube and irradiated with a daylight lamp at 15-20 °C. The reaction was monitored by <sup>1</sup>H NMR spectroscopy, complete consumption of starting material 5 was observed after 12 h, leading to exclusive formation of photoenol 50. The solution could be concentrated at low temperature under reduced pressure but 50 was not stable enough to withstand chromatographic purification (silica gel or alumina). Notwithstanding, the crude residue (colorless oil) was pure enough to allow the complete analytical and spectroscopic characterization.  $[\alpha]_{\rm D}\!=\!+32.3~{\rm cm}^3{\rm g}^{-1}{\rm dm}^{-1}~(c\!=\!1.28$  in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta = 0.94$  (s, 9 H), 0.95 (s, 9H), 1.63 (ddd, J=14.3, 6.6, 2.8 Hz, 1H), 2.10 (ddd, J=14.4, 10.6, 2.2 Hz, 1 H), 2.24 (s, 3 H), 3.03 (s, 3 H), 4.20 (d, J=17.7 Hz, 1 H), 4.38 (dd, J=6.3, 2.2 Hz, 1 H), 4.52 (ddd, J=10.8, 8.0, 2.7 Hz, 1 H), 4.53 (d, J=17.9 Hz, 1 H), 5.34 (dd, J=8.2, 1.3 Hz, 1 H), 6.49 (d, J=1.3 Hz, 1 H), 7.16-7.34 (m, 10H), 7.43–7.57 ppm (m, 10H); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta =$ 19.18 (C), 19.21 (C), 23.1 (CH<sub>3</sub>), 26.7 (3×CH<sub>3</sub>), 26.9 (3×CH<sub>3</sub>), 34.5 (CH<sub>2</sub>), 56.7 (CH<sub>3</sub>), 68.3 (CH<sub>2</sub>), 71.1 (CH), 74.6 (CH), 115.6 (CH), 127.6 (2×CH), 127.68 (4×CH), 127.71 (2×CH), 129.67 (CH), 129.69 (CH), 129.86 (CH), 129.88 (CH), 133.6 (C), 133.8 (C), 133.06 (C), 134.12 (C), 135.5 (4×CH), 135.7 (2×CH), 135.8 (2×CH), 148.4 (C), 194.9 (C), 208.6 ppm (C); IR (CHCl<sub>3</sub>, 0.2 mm):  $\tilde{\nu} = 3441$ , 2246, 1733, 1684, 1661 cm<sup>-1</sup>; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\epsilon$ )=271 (sh) (3055), 264 (3841), 261 (3877), 255 (sh) (3441), 227 (5628 mol<sup>-1</sup>m<sup>3</sup> cm<sup>-1</sup>); MS (EI): *m/z* (%): 665 (<1)  $[M^+-Ac]$ , 651 (4), 135 (100); HRMS (ESI<sup>+</sup>): m/z calcd for  $C_{42}H_{52}NaO_6Si_2$ : 731.3200 [*M*<sup>+</sup>+Na]; found: 731.3198; elemental analysis calcd (%) for C42H52O6Si2 (709.03): C 71.15, H 7.39; found: C 71.02, H 7.40

Kinetic studies: The unlabeled photoenol 50 (9.4 mg, 0.013 mmol) was dissolved in [D6]benzene (0.6 mL), transferred to an NMR tube and immediately placed into the preheated probe (40 °C) of a 500 MHz NMR spectrometer to minimize spontaneous cyclization of 50. The integral of vinyl proton at 5.10 ppm (1H, dd, J=8.2, 1.3 Hz) were monitored over 14 h and data were collected every 30 min. The same procedure was carried out for the deuterated photoenol [D<sub>1</sub>]50 (11.5 mg, 0.016 mmol) dissolved in [D<sub>6</sub>]benzene (0.6 mL), prepared by hydroxyl proton exchange with  $D_2O$ . The vinyl proton now appears at 5.11 ppm (1 H, d, J=8.2 Hz). Since  $[D_1]$ **50** was not isotopically pure (contained 11% of unlabeled **50**) the appropriate corrections were introduced during the concentration calculations. The kinetic isotope effect (KIE) value  $(k_{\rm H}/k_{\rm D}=3.7)$  was computed by plotting the selected concentration data against time and fitting the data to a first-order simulation to obtain the rate constants for the cyclization of both **50** ( $k_{\rm H} = 5.42 \times 10^{-5}$ ,  $R^2 = 0.999$ ) and [D<sub>1</sub>]**50** ( $k_{\rm D} = 1.48 \times$  $10^{-5}, R^2 = 0.999$ ).

**Photocyclization of 40**: A deoxygenated solution of diketone **40** (19 mg, 0.027 mmol) in dry C<sub>6</sub>D<sub>6</sub> (0.6 mL), was placed in a resonance tube and irradiated with a daylight lamp at 25 °C for 7 h. The reaction was monitored by <sup>1</sup>H NMR spectroscopy, complete transformation into the enol intermediate **50** was observed. The enol was heated at 40 °C in the dark for 8 h, leading to exclusive formation of carbocycle **47**. The solution was concentrated under reduced pressure and the residue purified by Chromatotron chromatography on alumina (hexanes/EtOAc 9:1) to give (2*S*,3a*S*,4*R*,6*S*,6a*R*)-4-(benzyloxy)-6-[(*tert*-butyldiphenylsilyl)oxy]-6a-

[(tert-butyldiphenylsilyl)oxy]methyl-2-hydroxy-2-methyltetrahydro-2H-cyclopenta[b]furan-3(3aH)-one (47) (14.8 mg, 0.021 mmol, 78%) as a crystalline solid: M.p. 105.7–107.9 °C (MeOH);  $[\alpha]_D = +30.3 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (c = 1.56 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 0.82$  (s, 9H), 1.08 (s, 9H), 1.36 (s, 3H), 1.65 (dddd, J=13.9, 4.6, 4.6, 0.7 Hz, 1H), 1.76 (ddd, J=14.2, 5.7, 5.7 Hz, 1 H), 3.18 (dd, J=2.6, 0.7 Hz, 1 H), 3.26 (s, 3 H), 3.63 (ddd, J = 5.9, 4.7, 2.9 Hz, 1 H), 4.00 (d, J = 11.7 Hz, 1 H), 4.05 (d, J = 11.7 Hz, 1 11.7 Hz, 1H), 4.14 (dd, J=5.4, 5.1 Hz, 1H), 5.38 (s, 1H), 7.24–7.29 (m, 4H), 7.35-7.51 (m, 12H), 7.64-7.67 ppm (m, 4H); <sup>13</sup>C NMR (100.6 MHz,  $CDCl_3$ ):  $\delta = 19.1$  (C), 19.2 (C), 20.7 (CH<sub>3</sub>), 26.7 (3×CH<sub>3</sub>), 26.9 (3×CH<sub>3</sub>), 40.0 (CH<sub>2</sub>), 54.8 (CH), 56.8 (CH<sub>3</sub>), 66.8 (CH<sub>2</sub>), 79.6 (CH), 82.2 (CH), 93.3 (C), 99.0 (C), 127.5 (2×CH), 127.6 (2×CH), 128.0 (2×CH), 128.1 (2× CH), 129.8 (2×CH), 130.1 (CH), 130.3 (CH), 131.4 (C), 131.5 (C), 132.8 (C), 133.5 (C), 135.6 (2×CH), 135.76 (2×CH), 135.81 (2×CH), 135.89  $(2 \times CH)$ , 209.9 ppm (C); IR (CHCl<sub>3</sub>, 0.2 mm):  $\bar{\nu} = 3672$ , 3357, 2932, 1763 cm<sup>-1</sup>; MS (EI): m/z (%): 651 (1)  $[M^+-tBu]$ , 633 (4), 135 (100); HRMS (ESI<sup>+</sup>): m/z calcd for C<sub>42</sub>H<sub>52</sub>NaO<sub>6</sub>Si<sub>2</sub>: 731.3200 [ $M^+$ +Na]; found:

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### 731.3213; elemental analysis calcd (%) for $C_{42}H_{52}O_6Si_2$ (709.03): C 71.15, H 7.39; found: C 71.21, H 7.40.

4,8-Anhydro-6,7-dideoxy-5,9-di-O-methyl-D-arabino-nono-2,3-diulose

(41): Prepared from 35 (25.3 mg, 0.13 mmol) following the general procedure (Method A) using dimethyl sulfide (40 µL, 0.54 mmol). The mixture was stirred at room temperature in the dark for 2 h and concentrated under reduced pressure. The residue was purified by rapid silica gel column chromatography (hexanes/EtOAc 8:2) to give 41 (20.4 mg, 0.09 mmol, 69%) as a yellow oil.  $[a]_D = +116 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (c=2.57 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.48$  (m, 1 H), 1.65 (m, 1 H), 1.75 (m, 1H), 1.97 (m, 1H), 2.27 (s, 3H), 3.27 (s, 3H), 3.38 (s, 3H), 3.39-3.43 (m, 2H), 3.74 (ddd, J=9.2, 6.3, 4.0 Hz, 1H), 4.44 (m, 1H), 5.43 ppm (d, J = 6.3 Hz, 1 H); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>):  $\delta = 23.50$  (CH<sub>2</sub>), 23.54 (CH<sub>2</sub>), 24.1 (CH<sub>2</sub>), 56.9 (CH<sub>3</sub>), 59.2 (CH<sub>3</sub>), 70.6 (CH), 74.1 (CH), 75.0 (CH<sub>2</sub>), 76.3 (CH), 197.8 (C), 200.8 ppm (C); IR (CHCl<sub>3</sub>, 0.2 mm):  $\tilde{\nu} =$ 2934, 1771, 1714, 1099 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 253 (100) [ $M^+$ +Na], 229 (3); HRMS (ESI<sup>+</sup>): *m*/*z* calcd for C<sub>11</sub>H<sub>18</sub>NaO<sub>5</sub>: 253.1052 [*M*<sup>+</sup>+Na]; found: 253.1042; elemental analysis calcd (%) for C<sub>11</sub>H<sub>18</sub>O<sub>5</sub> (230.26): C 57.38, H 7.88; found: C 57.30, H 7.85.

(3E,5R)-3-Hydroxy-5,9-dimethoxy-3-nonene-2,8-dione (51): A deoxygenated solution of diketone 41 (37.0 mg, 0.16 mmol) in purified CDCl<sub>3</sub> (0.3 mL), was placed in a resonance tube and irradiated with a daylight lamp at 30–33 °C. The reaction was monitored by <sup>1</sup>H NMR spectroscopy; complete consumption of starting material was observed after 4.5 h, leading to exclusive formation of intermediate photoenol 51. The solution could be concentrated at low temperature under reduced pressure but 51 was not stable enough to withstand chromatographic purification (silica gel or alumina). Notwithstanding, the crude residue (32.5 mg, 0.14 mmol, 88%) was pure enough to allow the complete analytical and spectroscopic characterization.

*Compound* **51**: colorless oil.  $[a]_D = +19 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (*c*=0.32 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =1.89 (m, 1H), 1.96 (m, 1H), 2.38 (s, 3 H), 2.50 (ddd, *J*=17.4, 8.2, 6.1 Hz, 1H), 2.59 (ddd, *J*=17.4, 8.2, 6.6 Hz, 1H), 3.30 (s, 3H), 3.41 (s, 3H), 4.01 (s, 2H), 4.27 (ddd, *J*=8.3, 7.4, 5.6 Hz, 1H), 5.48 (dd, *J*=8.3, 1.2 Hz, 1H), 6.61 ppm (d, *J*=1.2 Hz, 1H); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>):  $\delta$ =23.1 (CH<sub>3</sub>), 28.2 (CH<sub>2</sub>), 34.6 (CH<sub>2</sub>), 56.9 (CH<sub>3</sub>), 59.3 (CH<sub>3</sub>), 75.1 (CH), 77.6 (CH<sub>2</sub>), 115.5 (CH), 148.8 (C), 194.8 (C), 208.1 ppm (C); IR (CHCl<sub>3</sub>, 0.2 mm):  $\bar{\nu}$ =3435, 2935, 2252, 1731, 1682, 1663, 1350 cm<sup>-1</sup>; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (*ε*)=260 nm (8003 mol<sup>-1</sup>m<sup>3</sup> cm<sup>-1</sup>); MS (EI): *m/z*: calcd for C<sub>11</sub>H<sub>18</sub>O<sub>5</sub>: 230.1154 [*M*<sup>+</sup>]; found: 230.1153; elemental analysis calcd (%) for C<sub>11</sub>H<sub>18</sub>O<sub>5</sub> (230.26): C 57.38, H 7.88; found: C 57.58, H 7.91.

Photocyclization of 41: A deoxygenated solution of diketone 41 (51.2 mg, 0.23 mmol) in dry C<sub>6</sub>D<sub>6</sub> (0.4 mL), was placed in a resonance tube and irradiated with a daylight lamp at 30°C for 4.5 h. The reaction was monitored by <sup>1</sup>H NMR spectroscopy, complete transformation into the intermediate photoenol 51 was observed. The mixture was heated at 60°C in the dark for 7 h, concentrated under reduced pressure and the residue purified by Chromatotron chromatography (Al<sub>2</sub>O<sub>3</sub>, hexanes/EtOAc 8:2) to give (2S,3aS,4R,6aR)-2-hydroxy-4-methoxy-6a-(methoxymethyl)-2methyltetrahydro-2H-cyclopenta[b]furan-3(3aH)-one (48) (26.8 mg, 0.12 mmol, 52%) as a colorless oil:  $[\alpha]_{\rm D} = +101 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (c=0.34 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.37$  (br d, J = 1.4 Hz, 3H), 1.52 (dddd, J=13.5, 12.2, 8.0, 4.5 Hz, 1 H), 1.87 (m, 2 H), 1.94 (dddd, J=13.5, 5.8, 1.6, 1.6 Hz, 1 H), 3.05 (d, J=1.9 Hz, 1 H), 3.32 (s, 3 H), 3.38 (d, J= 9.8 Hz, 1 H), 3.48 (s, 3 H), 3.74 (d, J=9.8 Hz, 1 H), 3.86 ppm (d, J=4.2 Hz, 1 H); <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ ):  $\delta = 1.26-1.35$  (m, 1 H), 1.61 (d, J=0.95 Hz, 3H), 1.58-1.69 (m, 3H), 2.68 (s, 3H), 2.83 (d, J=9.8 Hz, 1H), 2.94 (s, 3H), 3.04 (br s, 1H), 3.24 (d, J=9.5 Hz, 1H), 3.80 (d, J= 4.1 Hz, 1 H), 5.40 ppm (d, J = 1.3 Hz, 1 H, OH);  ${}^{13}C$  NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 20.4 (CH<sub>3</sub>), 29.9 (CH<sub>2</sub>), 33.9 (CH<sub>2</sub>), 55.4 (CH), 56.4 (CH<sub>3</sub>), 59.2 (CH<sub>3</sub>), 77.1 (CH<sub>2</sub>), 85.7 (CH), 90.1 (C), 98.8 (C), 209.5 ppm (C); IR (CHCl<sub>3</sub>, 0.2 mm):  $\tilde{\nu} = 3364$ , 2936, 1762, 1094 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 285 (28) [M<sup>+</sup>+MeOH+Na], 253 (100) [M<sup>+</sup>+Na]; HRMS (ESI<sup>+</sup>): m/z calcd for  $C_{11}H_{18}NaO_5$ : 253.1052 [*M*<sup>+</sup>+Na]; found: 253.1047; elemental analysis calcd (%) for C<sub>11</sub>H<sub>18</sub>O<sub>5</sub> (230.25): C 57.38, H 7.88; found: C 57.43, H 7.87.

## **FULL PAPER**

4,8-Anhydro-9-(tert-butyldiphenylsilyl)-1,6,7-trideoxy-5-O-methyl-D-arabino-nono-2,3-diulose (42): Prepared from 36 (36.7 mg, 0.09 mmol) following the general procedure (Method B) using NaIO<sub>4</sub> (56 mg, 0.26 mmol) and RuO2.\*xH2O (0.25 mg). The reaction mixture was stirred at room temperature in the dark for 30 min. The residue was purified by rapid silica gel column chromatography (EtOAc) to give 42 (28.1 mg, 0.06 mmol, 71%) as a yellow oil:  $[\alpha]_D = +46 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (c=1.53 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ=1.06 (s, 9 H), 1.51 (m, 1 H), 1.66 (m, 1H), 1.88 (m, 1H), 1.96 (m, 1H), 2.29 (s, 3H), 3.27 (s, 3H), 3.66 (dd, J = 10.5, 5.7 Hz, 1H), 3.72 (ddd, J = 5.8, 4.7, 4.1 Hz, 1H), 3.74 (dd, J =10.5, 4.9 Hz, 1 H), 4.33 (m, 1 H), 5.32 (d, J=5.8 Hz, 1 H), 7.40 (m, 6 H), 7.67 ppm (m, 4H);  ${}^{13}$ C NMR (125.7 MHz, CDCl<sub>3</sub>):  $\delta$ =19.2 (C), 23.2 (CH<sub>2</sub>), 23.6 (CH<sub>2</sub>), 23.7 (CH<sub>3</sub>), 26.8 (3×CH<sub>3</sub>), 56.8 (CH<sub>3</sub>), 65.8 (CH<sub>2</sub>), 72.5 (CH), 74.0 (CH), 76.2 (CH), 127.6 (4×CH), 129.6 (2×CH), 133.46 (C), 133.49 (C), 135.6 (4×CH), 198.1 (C), 200.6 ppm (C); IR (CHCl<sub>3</sub>, 0.2 mm):  $\tilde{v} = 2936$ , 1714 cm<sup>-1</sup>; MS (EI): m/z (%): 397 (58)  $[M^+ - tBu]$ , 199 (75); HRMS (EI): *m/z* calcd for C<sub>22</sub>H<sub>25</sub>O<sub>5</sub>Si: 397.1471 [*M*<sup>+</sup>-*t*Bu]; found: 397.1466; elemental analysis calcd (%) for C<sub>26</sub>H<sub>34</sub>O<sub>5</sub>Si (454.63): C 68.69, H 7.54; found: C 68.61, H 7.60.

(3Z,5R)-9-[(tert-Butyldiphenylsilyl)oxy]-3-hydroxy-5-methoxy-3-nonene-2,8-dione (52): A solution of 42 (49.7 mg, 0.11 mmol) in purified CDCl<sub>3</sub> (0.3 mL), was placed in a resonance tube and irradiated with a daylightlamp at 30-35 °C for 3 h. The reaction was monitored by using <sup>1</sup>H NMR spectroscopy to give the photoenol 52 (47.3 mg, 0.1 mmol, 96%) as a yellowish oil that could not withstand chromatographic purification (silica gel or alumina). Nevertheless, the crude residue was pure enough to allow the complete analytical and spectroscopic characterization.  $[\alpha]_{\rm D} =$ +4 cm<sup>3</sup>g<sup>-1</sup>dm<sup>-1</sup> (c=0.47 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta =$ 1.10 (s, 9H), 1.84 (m, 1H), 1.96 (m, 1H), 2.36 (s, 3H), 2.58 (ddd, J=17.8, 8.2, 6.3 Hz, 1 H), 2.67 (ddd, J=17.8, 8.5, 6.3 Hz, 1 H), 3.29 (s, 3 H), 4.19 (s, 2H), 4.26 (ddd, J=8.2, 7.3, 6.0 Hz, 1H), 5.47 (dd, J=8.2, 1.1 Hz, 1H), 6.60 (d, J=1.1 Hz, 1 H), 7.37-7.44 (m, 6 H), 7.64-7.67 ppm (m, 4 H); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>):  $\delta = 19.2$  (C), 23.1 (CH<sub>3</sub>), 26.7 (3×CH<sub>3</sub>), 28.0 (CH<sub>2</sub>), 34.3 (CH<sub>2</sub>), 56.9 (CH<sub>3</sub>), 69.7 (CH<sub>2</sub>), 75.1 (CH), 115.5 (CH), 127.8 (4×CH), 129.9 (2×CH), 132.7 (2×C), 135.5 (4×CH), 148.7 (C), 194.8 (C), 209.6 ppm (C); IR (CHCl<sub>3</sub>, 0.2 mm):  $\tilde{v} = 3435$ , 2933, 2249, 1714, 1681, 1662 cm<sup>-1</sup>; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ )=272 (sh) (2914), 264 (3841), 261 (3877), 255 (sh) (3441), 227 nm (5628 mol<sup>-1</sup> m<sup>3</sup> cm<sup>-1</sup>); MS (EI): m/z (%): 437 (5) [M<sup>+</sup>-OH], 365 (38), 199 (100); HRMS (EI): m/z calcd for  $C_{26}H_{33}O_4Si$ : 437.2148 [*M*<sup>+</sup>-OH]; found: 437.2140; elemental analysis calcd (%) for C26H34O5Si (454.63): C 68.69, H 7.54; found: C 68.83, H 7.30.

Photocyclization of 42: A deoxygenated solution of diketone 42 (58.7 mg, 0.127 mmol) in dry C<sub>6</sub>D<sub>6</sub> (0.3 mL), was irradiated with a daylight lamp at 36-40 °C for 5 h. The reaction was monitored by <sup>1</sup>H NMR spectroscopy, complete transformation into the enol intermediate 52 was observed. The enol was heated at 60 °C in the dark for 2 h, concentrated under reduced pressure and the residue purified by column chromatography (Al<sub>2</sub>O<sub>3</sub>, hexanes/EtOAc 95:5) to give an inseparable mixture of hemiketal diastereomers (35.9 mg, 0.078 mmol, d.r. 10:1, 61%) (major (2S, 3aS, 4R, 6aR)-6a-[(tert-butyldiphenylsilyl)oxy]methyl-2-hyisomer: droxy-4-methoxy-2-methyltetrahydro-2H-cyclopenta[b]furan-3(3aH)-one (49)) as a colorless oil:  $[\alpha]_D = +62 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (c=0.98 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (major isomer) =1.07 (s, 9H), 1.45 (s, 3 H), 1.52 (dddd, J = 12.9, 12.9, 6.9, 4.1 Hz, 1 H), 1.68 (ddd, J = 12.9, 12.9, 6.6 Hz, 1 H), 1.78 (ddd, J=13.2, 6.9, 0.0 Hz, 1 H), 1.86 (dddd, J=13.5, 6.4, 1.3, 1.3 Hz, 1H), 3.10 (d, J=1.9 Hz, 1H), 3.22 (s, 3H), 3.48 (d, J=11.0 Hz, 1 H), 3.86 (br d, J=4.1 Hz, 1 H), 3.99 (d, J=11.0 Hz, 1 H), 5.35 (d, J=0.9 Hz, 1 H), 7.38–7.49 (m, 6 H), 7.66–7.69 ppm (m, 4 H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>;):  $\delta$  (major isomer) = 19.1 (C), 20.3 (CH<sub>3</sub>), 26.8 (3× CH<sub>3</sub>), 30.3 (CH<sub>2</sub>), 33.9 (CH<sub>2</sub>), 55.5 (CH), 56.2 (CH<sub>3</sub>), 69.0 (CH<sub>2</sub>), 85.5 (CH), 91.6 (C), 98.8 (C), 128.0 (2×CH), 128.1 (2×CH), 130.2 (CH), 130.4 (CH), 131.41 (C), 131.45 (C), 135.6 (2×CH), 135.7 (2×CH), 209.3 ppm (C); IR (CHCl<sub>3</sub>, 0.2 mm):  $\tilde{\nu} = 3356$ , 2935, 1762 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 477 (100) [ $M^+$ +Na]; HRMS (ESI<sup>+</sup>): m/z calcd for C<sub>26</sub>H<sub>34</sub>NaO<sub>5</sub>Si: 477.2073 [*M*<sup>+</sup>+Na]; found: 477.2076; elemental analysis calcd (%) for C26H34O5Si (454.63): C 68.69, H 7.54; found: C 68.64, H 7.76.

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4,8-Anhydro-9-O-(3,5-dinitrobenzoyl)-1,6,7-trideoxy-5-O-methyl-D-arabino-nono-2,3-diulose (43): Prepared from 37 (65.5 mg, 0.17 mmol) following the general procedure (Method B) using NaIO<sub>4</sub> (111.1 mg, 0.52 mmol) and  $RuO_2 \cdot x H_2O$  (0.5 mg). The reaction mixture was stirred at room temperature in the dark for 30 min. The residue was purified by rapid silica gel column chromatography (EtOAc) to give 43 (28.1 mg, 0.06 mmol, 71%) as a yellow oil.  $[\alpha]_{\rm D} = +47 \, {\rm cm}^3 {\rm g}^{-1} {\rm dm}^{-1}$  (c=0.59 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.52$  (m, 1H), 1.79–1.88 (m, 2H), 1.94 (m, 1H), 2.28 (s, 3H), 3.28 (s, 3H), 3.88 (ddd, J=7.6, 6.4, 3.6 Hz, 1H), 4.41 (dd, J=11.7, 3.3 Hz, 1H), 4.48 (dd, J=11.7, 7.5 Hz, 1H), 4.61 (m, 1H), 5.38 (d, J=6.4 Hz, 1H), 9.22 ppm (m, 3H); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>): δ=22.2 (CH<sub>2</sub>), 23.1 (CH<sub>2</sub>), 23.5 (CH<sub>3</sub>), 56.9 (CH<sub>3</sub>), 67.9 (CH<sub>2</sub>), 69.4 (CH), 75.0 (CH), 75.8 (CH), 122.4 (CH), 129.6 (2×CH), 133.8 (C), 148.7 (2×C), 162.5 (C), 197.6 (C), 199.2 ppm (C); IR (CHCl<sub>3</sub>, 0.2 mm):  $\tilde{\nu} = 2945$ , 1732 cm<sup>-1</sup>; MS (EI): m/z (%): 410 (3) [M<sup>+</sup>], 378 (4), 340 (14), 339 (85); HRMS (EI): m/z calcd for C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>10</sub>: 410.0961 [M<sup>+</sup> ]; found: 410.0957; elemental analysis calcd (%) for C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>10</sub> (410.33): C 49.76, H 4.42, N 6.83; found: C 49.68, H 4.37, N 6.61.

(5R,6Z)-7-Hydroxy-5-methoxy-2,8-dioxo-6-nonenyl 3,5-dinitrobenzoate (53): A deoxygenated solution of diketone 43 (47.6 mg, 0.12 mmol) in purified CDCl<sub>3</sub> (0.3 mL) was placed in a resonance tube and irradiated with a daylight lamp at 30 °C for 6 h. The reaction was monitored by <sup>1</sup>H NMR spectroscopy and complete transformation into the photoenol intermediate was observed. The solution was concentrated at low temperature under reduced pressure to give 53, which was not stable enough to withstand chromatographic purification (silica gel or alumina). Notwithstanding, the crude residue (yellowish oil) was pure enough to allow the complete analytical and spectroscopic characterization.  $[\alpha]_D = +$  $8 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (c=1.39, CDCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =1.94 (m, 1H), 2.03 (m, 1H), 2.39 (s, 3H), 2.61 (m, 2H), 3.32 (s, 3H), 4.30 (ddd, J=8.2, 7.7, 5.6 Hz, 1H), 5.06 (s, 2H), 5.49 (dd, J=8.2, 1.3 Hz, 1H), 6.65 (d, J=1.3 Hz, 1 H), 9.20 (d, J=2.1 Hz, 2 H), 9.25 ppm (dd, J=2.1, 2.1, 1 H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 23.1$  (CH<sub>3</sub>), 28.3 (CH<sub>2</sub>), 34.7 (CH<sub>2</sub>), 57.0 (CH<sub>3</sub>), 69.3 (CH<sub>2</sub>), 74.9 (CH), 115.1 (CH), 122.7 (CH), 129.7 (2×CH), 133.1 (C), 148.8 (2×C), 148.9 (C), 161.9 (C), 194.7 (C), 201.3 ppm (C); IR (CHCl<sub>3</sub>, 0.2 mm):  $\tilde{v} = 3103$ , 2934, 2258, 1736, 1682, 1664 cm<sup>-1</sup>; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 255 (6229), 236 nm  $(6110 \text{ mol}^{-1}\text{ m}^3\text{ cm}^{-1});$  MS (EI): m/z (%): 410 (<1) [ $M^+$ ], 378 (2), 367 (1), 335 (17); HRMS (EI): *m*/*z*: calcd for C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>10</sub>: 410.0961 [*M*<sup>+</sup>]; found: 410.0967; elemental analysis calcd (%) for C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>10</sub> (410.33): C 49.76, H 4.42, N 6.83; found: C 49.91, H 4.45, N 6.45.

#### 4,8-Anhydro-9-O-(tert-butyldiphenylsilyl)-1-deoxy-5,6,7-tri-O-methyl-D-

glycero-D-talo-nono-2,3-diulosa (58): Prepared from 54 (50 mg, 0.103 mmol) following the general procedure (Method B) using NaIO<sub>4</sub> (88 mg, 0.412 mmol) and RuO<sub>2</sub>•x H<sub>2</sub>O (0.7 mg). The reaction mixture was stirred at room temperature in the dark for 1 h. The residue was purified by rapid silica gel column chromatography (hexanes/EtOAc 1:1) to give **58** (28 mg, 0.055 mmol, 53%) as a yellow oil:  $[\alpha]_{\rm D} = +16 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  $(c=1.50 \text{ in CHCl}_3)$ ; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 1.20$  (s, 9H), 1.86 (s, 3H), 3.18 (s, 3H), 3.19 (s, 3H), 3.33 (s, 3H), 3.43 (dd, J=8.2, 3.2 Hz, 1 H), 3.81 (dd, J = 8.0, 8.0 Hz, 1 H), 4.00 (dd, J = 3.4, 3.4 Hz, 1 H), 4.02– 4.06 (m, 3 H), 5.28 (d, J = 3.4 Hz, 1 H), 7.21–7.89 ppm (m, 10 H); <sup>13</sup>C NMR (100.6 MHz,  $C_6D_6$ ):  $\delta = 19.6$  (C), 24.0 (CH<sub>3</sub>), 27.1 (3×CH<sub>3</sub>), 57.5 (CH<sub>3</sub>), 57.7 (CH<sub>3</sub>), 59.8 (CH<sub>3</sub>), 63.8 (CH<sub>2</sub>), 74.5 (CH), 75.8 (CH), 76.3 (CH), 78.2 (CH), 81.2 (CH), 128.1-132.6 (10×CH), 133.9 (C), 134.2 (C), 198.2 (C), 198.9 ppm (C); IR (film):  $\tilde{\nu} = 2933$ , 1718 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 569 (100) [M<sup>+</sup>+MeOH+Na]; HRMS (ESI<sup>+</sup>): m/z: calcd for  $C_{29}H_{42}NaO_8Si: 569.2547 [M^++MeOH+Na];$  found: 569.2554; elemental analysis calcd (%) for C28H38O7Si (514.68): C 65.34, H 7.44; found: C 65.26, H 7.49.

**Photocyclization of 58**: A deoxygenated solution of diketone **58** (40 mg, 0.078 mmol) in dry C<sub>6</sub>D<sub>6</sub> (1 mL), was placed in a resonance tube and irradiated with a daylight lamp at 30 °C. The reaction was monitored by <sup>1</sup>H NMR spectroscopy, complete transformation of the starting material was accomplished after 18 h. The solution was then heated at 50 °C in the dark for 2 h, and concentrated under reduced pressure. The crude residue in CH<sub>2</sub>Cl<sub>2</sub> (0.7 mL) was acetylated at 0 °C with Ac<sub>2</sub>O (30 µL, 0.778 mmol) and 4-dimethylaminopyridine (DMAP; 28 mg, 0.233 mmol) for 2 h. The

mixture was concentrated under reduced pressure and the residue purified by silica gel column chromatography (hexanes/EtOAc 7:3) to give (2*S*,3*aR*,4*R*,5*R*,6*S*,6*aS*)-6a-[(*tert*-butyldiphenylsilyl)oxy]methyl-4,5,6-trime-thoxy-2-methyl-3-oxohexahydro-2*H*-cyclopenta[*b*]furan-2-yl acetate (**62**) (13 mg, 0.023 mmol, 30%) as a colorless oil. The sensitive photoenol intermediate was detected by NMR spectroscopy but in this case could not be obtained in pure state. Only clearly distinguished signals from the reaction mixture are reported: <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 1.26 (s, 9H), 1.77 (s, 3H), 2.90 (s, 3H), 3.10 (s, 3H), 3.6 (s, 3H), 4.71 (d, *J*=18.3 Hz, 1H), 4.85 (d, *J*=18.5 Hz, 1H), 5.33 (brd, *J*=9.3 Hz, 1H), 6.73 ppm (brs, 1H, OH).

*Compound* **62**:  $[\alpha]_{D} = -4 \text{ cm}^{3} \text{g}^{-1} \text{dm}^{-1}$  (c = 1.00 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.07$  (s, 9H), 1.52 (s, 3H), 1.85 (s, 3H), 3.41 (d, J = 1.9 Hz, 1H), 3.431 (dd, J = 7.9, 4.7 Hz, 1H), 3.434 (s, 3H), 3.46 (s, 3H), 3.52 (s, 3H), 3.72 (d, J = 10.4 Hz, 1H), 3.79 (dd, J = 4.7, 2.1 Hz, 1H), 3.87 (d, J = 10.1 Hz, 1H), 4.19 (d, J = 8.2 Hz, 1H), 7.35–7.70 ppm (m, 10H); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>):  $\delta = 19.3$  (C), 20.4 (CH<sub>3</sub>), 22.4 (CH<sub>3</sub>), 26.8 (3×CH<sub>3</sub>), 51.8 (CH), 57.5 (CH<sub>3</sub>), 58.0 (CH<sub>3</sub>), 60.1 (CH<sub>3</sub>), 64.8 (CH<sub>2</sub>), 79.5 (CH), 82.4 (CH), 85.6 (CH), 88.3 (C), 101.1 (C), 127.6–135.7 (10×CH), 132.9 (C), 133.0 (C), 169.7 (C), 207.7 ppm (C); IR (film):  $\tilde{\nu} = 2921$ , 1763, 1743 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 579 (100) [ $M^+$ +Na]; HRMS (ESI<sup>+</sup>): m/z calcd for C<sub>30</sub>H<sub>40</sub>O<sub>8</sub>Si; 579.2390 [ $M^+$ +Na]; found: 579.2396; elemental analysis calcd (%) for C<sub>30</sub>H<sub>40</sub>O<sub>8</sub>Si (558.72): C 64.72, H 7.24; found: C 66.70, H 7.05.

4,8-Anhydro-1-deoxy-5,6,7,9-tetra-O-methyl-D-glycero-L-gluco-nono-2,3diulose (59): Prepared from 55 (150 mg, 0.581 mmol) following the general procedure (Method A) using dimethyl sulfide ( $85 \,\mu$ L, 1.162 mmol). The mixture was stirred at room temperature in the dark for 3 h and concentrated under reduced pressure. The residue was purified by rapid silica gel column chromatography (hexanes/EtOAc 1:1) to give 59 as a vellow oil (98 mg, 0.338 mmol, 58%), which was unstable on silica gel. However, a small analytical sample could be obtained by rapid silica gel column chromatography (hexanes/EtOAc 7:3).  $[\alpha]_D = -30 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  $(c=2.14 \text{ in CHCl}_3)$ ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 2.35$  (s, 3 H), 3.32 (s, 3H), 3.36 (s, 3H), 3.39-3.56 (m, 3H), 3.44 (s, 3H), 3.51 (s, 3H), 3.83 (dd, J=4.1, 1.9 Hz, 1H), 4.01 (dd, J=2.2, 1.9 Hz, 1H), 4.19 (dd, J=4.7, 4.4 Hz, 1 H), 5.07 ppm (d, J=2.2 Hz, 1 H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 25.6$  (CH<sub>3</sub>), 58.3 (CH<sub>3</sub>), 58.4 (CH<sub>3</sub>), 59.8 (CH<sub>3</sub>), 60.0 (CH<sub>3</sub>), 73.0 (CH<sub>2</sub>), 80.4 (CH), 84.7 (CH), 85.2 (CH), 85.9 (CH), 87.6 (CH), 196.9 (C), 199.7 ppm (C); IR (film):  $\tilde{\nu} = 2931$ , 1728, 1714 cm<sup>-1</sup>; MS (EI): m/z(%): 291 (34)  $[M^++H]$ ; HRMS (EI): m/z calcd for  $C_{13}H_{23}O_7$ : 291.1444  $[M^++H]$ ; found: 291.1414; elemental analysis calcd (%) for C<sub>13</sub>H<sub>22</sub>O<sub>7</sub> (290.31): C 53.78, H 7.64; found: C 53.67, H 7.62.

**Photolysis of 59**: A deoxygenated solution of diketone **59** (25 mg, 0.086 mmol) in dry  $C_6D_6$  (0.6 mL), was placed in a resonance tube and irradiated with a daylight lamp at 30 °C. The reaction was monitored by <sup>1</sup>H NMR spectroscopy, complete consumption of starting material was observed after 2 h, leading to exclusive formation of intermediate photoenol. The solution could be concentrated at low temperature under reduced pressure but the photoenol was not stable enough to withstand chromatographic purification (silica gel or alumina). After silica gel column chromatography (hexanes/EtOAc 40:60) only the known 2,3,4,6-tetra-*O*-methyl-D-galactono-1,5-lactone<sup>[46]</sup> (16 mg, 0.068 mmol, 80%) could be obtained.

4,8-Anhydro-9-O-(tert-butyldiphenylsilyl)-1-deoxy-5,6,7-tri-O-methyl-D-

*glycero*-L-*gluco*-nono-2,3-diulose (60): Prepared from 56 (50 mg, 0.104 mmol) following the general procedure (Method B) using NaIO<sub>4</sub> (89 mg, 0.416 mmol) and RuO<sub>2</sub>-x H<sub>2</sub>O (0.9 mg). The reaction mixture was stirred at room temperature in the dark for 20 min. The residue was purified by rapid silica gel column chromatography (hexanes/EtOAc 4:6) to give 60 (34 mg, 0.066 mmol, 64%) as a yellow oil:  $[a]_D = +$  61 cm<sup>3</sup>g<sup>-1</sup>dm<sup>-1</sup> (c=0.25 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =1.07 (s, 9H), 2.28 (s, 3H), 3.37 (s, 3H), 3.41 (dd, J=8.5, 2.6 Hz, 1H), 3.50 (s, 3H), 3.53 (s, 3H), 3.79 (d, J=2.4 Hz, 1H), 3.81 (d, J=1.1 Hz, 1H), 3.91 (dd, J=2.6, 2.4 Hz, 1H), 3.94 (dd, J=8.5, 6.9 Hz, 1H), 4.44 (m, 1H), 5.38 (d, J=6.9 Hz, 1H), 7.35–7.77 ppm (m, 10H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$ =19.2 (CH<sub>3</sub>), 23.5 (C), 26.9 (3×CH<sub>3</sub>), 57.8 (CH<sub>3</sub>), 59.5 (CH<sub>3</sub>), 60.7 (CH<sub>3</sub>), 61.2 (CH<sub>2</sub>), 71.9 (CH), 74.6 (CH), 75.4 (CH), 78.4 (CH), 81.2

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(CH), 127.7–135.6 (10×CH), 133.3 (C), 133.4 (C), 197.0 (C), 200.1 ppm (C); IR (film):  $\tilde{v}$ =2936, 1716 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 569 (100) [ $M^+$ +MeOH+Na]; HRMS (ESI<sup>+</sup>): m/z calcd for C<sub>29</sub>H<sub>42</sub>NaO<sub>8</sub>Si: 569.2547 [ $M^+$ +MeOH+Na]; found: 569.2556; elemental analysis calcd (%) for C<sub>28</sub>H<sub>38</sub>O<sub>7</sub>Si (514.68): C 65.34, H 7.44; found: C 65.49, H 7.36.

**Photocyclization of 60**: A deoxygenated solution of diketone **60** (28 mg, 0.054 mmol) in dry C<sub>6</sub>D<sub>6</sub> (0.7 mL), was placed in a resonance tube and irradiated with a daylight lamp at 30 °C. The reaction was monitored by <sup>1</sup>H NMR spectroscopy; complete transformation into the enol intermediate was observed after 2.5 h. The solution was heated at 60 °C in the dark for 1.5 h and concentrated under reduced pressure. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (0.6 mL), cooled at 0 °C, and acetylated with Ac<sub>2</sub>O (20  $\mu$ L, 0.163 mmol) and DMAP (20 mg, 0.163 mmol). The solution was stirred at room temperature for 2 h, concentrated under reduced pressure, and the residue purified by silica gel column chromatography (hexanes/EtOAc 7:3) to give (2*S*,3*a*,*A*,*S*,*S*,*6*,*6*,6a*S*)-6a-[(*tert*-butyldiphenylsi-lyl)oxy]methyl-4,5,6-trimethoxy-2-methyl-3-oxohexahydro-2*H*-cyclopen-

ta[b]furan-2-yl acetate (64) and (2R,3aS,4S,5R,6R,6aR)-6a-[(tert-butyldiphenylsilyl)oxy]methyl-4,5,6-trimethoxy-2-methyl-3-oxohexahydro-2H-cyclopenta[b]furan-2-yl acetate (63) (21 mg, 0.038 mmol, d.r. 2:1, 69%). The sensitive photoenol intermediate was detected by NMR spectroscopy but in this case could not be obtained in pure state. Only clearly distinguished signals from the reaction mixture are reported. <sup>1</sup>H NMR  $(400 \text{ MHz}, C_6D_6): \delta = 1.25 \text{ (s, 9 H)}, 1.85 \text{ (s, 3 H)}, 2.89 \text{ (s, 3 H)}, 3.13 \text{ (s, 3 H)},$ 3.15 (s, 3H), 4.68 (d, J=18.3 Hz, 1H), 4.74 (d, J=18.6 Hz, 1H), 5.54 (dd, J=9.0, 1.1 Hz, 1 H), 6.84 ppm (d, J=1.3 Hz, OH); <sup>13</sup>C NMR (100.6 MHz,  $C_6D_6$ ):  $\delta = 19.6$  (C), 22.8 (CH<sub>3</sub>), 27.0 (3×CH<sub>3</sub>), 57.0 (CH<sub>3</sub>), 58.2 (CH<sub>3</sub>), 59.9 (CH<sub>3</sub>), 69.5 (CH<sub>2</sub>), 111.7 (CH), 149.9 (C), 194.6 (C), 206.4 ppm (C). Compound **63**: colorless oil.  $[\alpha]_D = +14 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (*c*=0.28 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 1.08$  (s, 9H), 1.54 (s, 3H), 1.87 (s, 3H), 3.27 (d, J=2.9 Hz, 1 H), 3.36 (s, 3 H), 3.45 (s, 3 H), 3.48 (s, 3 H), 3.70 (d, J=10.3 Hz, 1 H), 3.77 (dd, J=4.2, 4.2 Hz, 1 H), 3.81 (dd, J=4.8, 2.9 Hz, 1H), 3.88 (d, J=10.1 Hz, 1H), 4.06 (d, J=4.0 Hz, 1H), 7.36-7.72 ppm (m, 10H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 19.3$  (C), 20.7 (CH<sub>3</sub>), 22.7 (CH<sub>3</sub>), 26.8 (3×CH<sub>3</sub>), 53.3 (CH), 57.7 (CH<sub>3</sub>), 57.8 (CH<sub>3</sub>), 59.9 (CH<sub>3</sub>), 65.4 (CH<sub>2</sub>), 81.2 (CH), 83.3 (CH), 83.9 (CH), 89.2 (C), 102.0 (C), 127.7–135.7 (10×CH), 132.97 (C), 133.00 (C), 169.8 (C), 207.4 ppm (C); IR (film):  $\tilde{\nu}$ =2930, 1766, 1745 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): *m/z* (%): 579 (100) [*M*<sup>+</sup>+Na]; HRMS (ESI<sup>+</sup>): m/z calcd for C<sub>30</sub>H<sub>40</sub>NaO<sub>8</sub>Si: 579.2390 [M<sup>+</sup>+Na]; found: 579.2393; elemental analysis calcd (%) for  $C_{30}H_{40}O_8Si$  (556.72): C 64.72, H 7.24; found: C 64.75, H 7.16.

*Compound* **64**: colorless oil;  $[a]_{\rm D}$  = +29 cm<sup>3</sup>g<sup>-1</sup>dm<sup>-1</sup> (*c*=0.38 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ=1.06 (s, 9H), 1.59 (s, 3H), 1.63 (s, 3H), 3.14 (d, *J*=9.5 Hz, 1H), 3.47 (s, 3H), 3.50 (s, 3H), 3.58 (s, 3H), 3.71 (dd, *J*=8.2, 3.5 Hz, 1H), 3.92 (d, *J*=11.0 Hz, 1H), 3.94 (d, *J*=3.5 Hz, 1H), 4.00 (d, *J*=11.4 Hz, 1H), 4.07 (dd, *J*=9.5, 8.2 Hz, 1H), 7.35–7.72 ppm (m, 10H); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>): δ=19.4 (C), 20.8 (CH<sub>3</sub>), 22.0 (CH<sub>3</sub>), 26.9 (3×CH<sub>3</sub>), 49.6 (CH), 58.9 (CH<sub>3</sub>), 59.2 (CH<sub>3</sub>), 60.9 (CH<sub>3</sub>), 64.9 (CH<sub>2</sub>), 82.0 (CH), 83.8 (CH), 85.7 (CH), 92.2 (C), 101.9 (C), 127.6–137.8 (10×CH), 129.59 (C), 129.60 (C), 169.5 (C), 205.5 ppm (C); IR (film):  $\tilde{ν}$ =2923, 1766, 1747 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): *m/z* (%): 579 (100) [*M*<sup>+</sup>+Na]; HRMS (EI): *m/z* calcd for C<sub>30</sub>H<sub>40</sub>NaO<sub>8</sub>Si: 579.2490 [*M*<sup>+</sup>+Na]; found: 579.2401; elemental analysis calcd (%) for C<sub>30</sub>H<sub>40</sub>O<sub>8</sub>Si (556.72): C 64.72, H 7.24; found: C 64.35, H 7.11.

#### 9-O-Acetyl-4,8-anhydro-1-deoxy-5,6,7-tri-O-methyl-D-glycero-L-gluco-

**nono-2,3-diulose (61)**: Prepared from **57** (70 mg, 0.244 mmol) following the general procedure (Method B) using NaIO<sub>4</sub> (156 mg, 0.732 mmol) and RuO<sub>2</sub>·*x* H<sub>2</sub>O (1.2 mg). The reaction mixture was stirred at room temperature in the dark for 40 min. The residue was purified by rapid silica gel column chromatography (hexanes/EtOAc 4:6) to give **61** (37 mg, 0.116 mmol, 48%) as a yellow oil.  $[\alpha]_D = +82 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (*c*=0.71 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =2.05 (s, 3H), 2.28 (s, 3H), 3.34 (s, 3H), 3.47 (m, 1H), 3.48 (s, 3H), 3.49 (s, 3H), 3.72 (dd, *J*=3.2, 3.2 Hz, 1H), 3.98 (dd, *J*=6.9, 5.0 Hz, 1H), 4.15 (dd, *J*=12.0, 3.5 Hz, 1H), 4.42–4.51 (m, 2H), 5.39 ppm (d, *J*=5.4 Hz, 1H); <sup>13</sup>C NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ =20.8 (CH<sub>3</sub>), 23.7 (CH<sub>3</sub>), 58.4 (CH<sub>3</sub>), 59.1 (CH<sub>3</sub>), 59.6 (CH<sub>3</sub>), 61.7 (CH<sub>2</sub>), 71.6 (CH), 73.4 (CH), 75.2 (CH), 77.9 (CH), 78.7 (CH), 170.9 (C), 197.1 (C), 198.5 ppm (C); IR (film):  $\tilde{\nu}$ =2936, 1739 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): *m*/*z* 

(%): 373 (100)  $[M^++MeOH+Na]$ , 341 (21)  $[M^++Na]$ ; HRMS (ESI<sup>+</sup>): m/z: calcd for C<sub>15</sub>H<sub>26</sub>NaO<sub>9</sub>: 373.1475  $[M^++MeOH+Na]$ ; found: 373.1465; elemental analysis calcd (%) for C<sub>14</sub>H<sub>22</sub>O<sub>8</sub> (318.32): C 52.82, H 6.97; found: C 52.95, H 6.89.

**Photocyclization of 61**: A deoxygenated solution of diketone **61** (14 mg, 0.044 mmol) in dry C<sub>6</sub>D<sub>6</sub> (0.5 mL), was placed in a resonance tube and irradiated with a daylight lamp at 30 °C. The reaction was monitored by <sup>1</sup>H NMR spectroscopy; complete transformation into the enol intermediate was observed after 2.5 h. The solution was heated at 70 °C in the dark for 3 h and concentrated under reduced pressure. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (0.4 mL), cooled at 0 °C, and acetylated with Ac<sub>2</sub>O (12 µL, 0.132 mmol) and DMAP (16 mg, 0.132 mmol). The solution was stirred at room temperature for 2 h, concentrated under reduced pressure, and the residue purified by silica gel column chromatography (hexanes/EtOAc 7:3) to give (2*S*,3a*R*,4*S*,5*R*,6*R*,6a*S*)-6a-(acetyloxy)methyl-4,5,6-trimethoxy-2-methyl-3-oxohexahydro-2*H*-cyclopenta[*b*]furan-2-yl

acetate (**66**) and (2*R*,3a*S*,4*S*,5*R*,6*R*,6a*R*)-6a-(acetyloxy)methyl-4,5,6-trimethoxy-2-methyl-3-oxohexahydro-2*H*-cyclopenta[*b*]furan-2-yl acetate (**65**) (12 mg, 0.033 mmol, d.r. 3:1, 76% from **61**). The sensitive photoenol intermediate was detected by NMR spectroscopy but in this case could not be obtained in pure state. Only clearly distinguished signals from the reaction mixture are reported: <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 1.79 (s, 3H), 1.87 (s, 3H), 3.13 (s, 3H), 3.14 (s, 3H), 3.24 (s, 3H), 4.92 (d, *J* = 17.5 Hz, 1H), 5.07 (d, *J* = 17.5 Hz, 1H), 5.52 (br d, *J* = 9.3 Hz, 1H), 6.89 ppm (brs, 1H, OH); <sup>13</sup>C NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 20.1 (CH<sub>3</sub>), 22.7 (CH<sub>3</sub>), 57.1 (CH<sub>3</sub>), 58.7 (CH<sub>3</sub>), 60.0 (CH<sub>3</sub>), 67.7 (CH<sub>2</sub>), 111.6 (CH), 150.0 (C), 169.8 (C), 194.6 (C), 202.7 ppm (C).

*Compound* **65**: colorless oil, unstable, and decomposed on standing at room temperature preventing us from obtaining good 1D and 2D NMR spectra.  $[\alpha]_D = +15 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1} (c=0.56 \text{ in CHCl}_3)$ ; <sup>1</sup>H NMR (500 MHz, CDCl}\_3):  $\delta = 1.57$  (s, 3H), 2.04 (s, 3H), 2.11 (s, 3H), 3.29 (d, J=2.8 Hz, 1H), 3.34 (s, 3H), 3.43 (s, 3H), 3.51 (s, 3H), 3.71 (dd, J=4.1, 4.1 Hz, 1H), 3.76 (d, J=4.1 Hz, 1H), 3.82 (dd, J=4.1, 2.8 Hz, 1H), 4.20 (d, J=11.7 Hz, 1H), 4.43 ppm (d, J=11.7 Hz, 1H); <sup>13</sup>C NMR (125.7 MHz, CDCl}\_3):  $\delta = 21.7$  (CH}\_3), 21.86 (CH}\_3), 21.9 (CH}\_3), 54.5 (CH), 58.5 (CH}\_3), 58.7 (CH}\_3), 60.7 (CH}\_3), 67.4 (CH}\_2), 83.2 (CH), 83.8 (CH), 83.8 (PH), (quaternary carbons not observed); IR (film):  $\bar{\nu} = 2922$ , 1766, 1742, 1731 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 383 (100) [ $M^+$ +Na]; found: 383.1322; elemental analysis calcd (%) for C<sub>16</sub>H<sub>24</sub>AO<sub>9</sub> (360.36): C 53.33, H 6.71; found: C 53.43, H 6.46.

*Compound* **66**: colorless oil.  $[a]_D = +25 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (*c*=0.56 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =1.54 (s, 3H), 2.05 (s, 3H), 2.09 (s, 3H), 3.26 (d, *J*=9.1 Hz, 1H), 3.47 (s, 3H), 3.48 (s, 3H), 3.56 (s, 3H), 3.68 (dd, *J*=6.9, 4.1 Hz, 1H), 3.82 (d, *J*=3.8 Hz, 1H), 4.04 (dd, *J*=9.1, 6.9 Hz, 1H), 4.18 (d, *J*=11.7 Hz, 1H), 4.69 ppm (d, *J*=11.7 Hz, 1H); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>):  $\delta$ =20.8 (CH<sub>3</sub>), 20.9 (CH<sub>3</sub>), 21.7 (CH<sub>3</sub>), 50.4 (CH), 58.8 (CH<sub>3</sub>), 59.2 (CH<sub>3</sub>), 60.6 (CH<sub>3</sub>), 64.1 (CH<sub>2</sub>), 83.1 (CH), 83.2 (CH), 85.2 (CH), 89.6 (C), 101.7 (C), 169.8 (C), 170.4 (C), 205.0 ppm (C); IR (film):  $\tilde{ν}$ =2938, 1768, 1744 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): *m/z* (%): 383 (100) [*M*<sup>+</sup> +Na]; HRMS (ESI<sup>+</sup>): *m/z* calcd for C<sub>16</sub>H<sub>24</sub>NaO<sub>9</sub>: 383.1318 [*M*<sup>+</sup>+Na]; found: 383.1324; elemental analysis calcd (%) for C<sub>16</sub>H<sub>24</sub>O<sub>9</sub> (360.36): C 53.33, H 6.71; found: C 53.35, H 6.68.

**4,7-Anhydro-8**-*O-tert*-butyldiphenylsilyl-1-deoxy-5,6-*O*-isopropylidene-D*altro*-octo-2,3-diulosa (70): Prepared from 67 (27 mg, 0.057 mmol) following the general procedure (Method B) using NaIO<sub>4</sub> (37 mg, 0.171 mmol) and RuO<sub>2</sub>·x H<sub>2</sub>O (0.3 mg). The reaction mixture was stirred at room temperature in the dark for 50 min. The residue was purified by rapid silica gel column chromatography (hexanes/EtOAc 97:3) to give 70 (19 mg, 0.039 mmol, 69%) as a yellow oil and the known lactone 73<sup>[47]</sup> (2 mg, 0.005 mmol, 6%).

Compound **70**:  $[\alpha]_D = -4 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (c=1.01 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =1.09 (s, 9H), 1.27 (s, 3H), 1.36 (s, 3H), 2.37 (s, 3H), 3.70 (dd, *J*=11.4, 2.5 Hz, 1H), 3.88 (dd, *J*=11.4, 3.5 Hz, 1H), 4.35 (dd, *J*=2.8, 2.8 Hz, 1H), 4.82 (d, *J*=6.0 Hz, 1H), 5.31 (dd, *J*=5.7, 5.7 Hz, 1H), 5.57 (d, *J*=5.4 Hz, 1H), 7.38–7.65 ppm (m, 10H); <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ =1.08 (s, 3H), 1.13 (s, 9H), 1.35 (s, 3H), 1.99 (s, 3H), 3.39 (dd, *J*=11.0, 3.2 Hz, 1H), 3.66 (dd, *J*=11.4, 3.5 Hz, 1H), 4.31 (dd,

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J=3.5, 2.8 Hz, 1 H), 4.65 (d, J=6.2, 1.1 Hz, 1 H), 5.31 (dd, J=5.7, 5.7 Hz, 1H), 5.66 (d, J = 5.4 Hz, 1H), 7.19–7.70 ppm (m, 10H); <sup>13</sup>C NMR (100.4 MHz, CDCl<sub>3</sub>):  $\delta = 19.1$  (C), 23.6 (CH<sub>3</sub>), 24.8 (CH<sub>3</sub>), 25.7 (CH<sub>3</sub>), 26.9 (3×CH<sub>3</sub>), 65.9 (CH<sub>2</sub>), 82.7 (CH), 83.1 (CH), 84.7 (CH), 85.4 (CH), 113.3 (C), 127.9 (4×CH), 129.9 (CH), 130.0 (CH), 132.5 (C), 132.6 (C), 135.5 (2×CH), 135.6 (2 × CH), 192.2 (C), 197.7 ppm (C);  $^{13}\mathrm{C}\,\mathrm{NMR}$ (100.4 MHz, C<sub>6</sub>D<sub>6</sub>): δ=19.2 (C), 23.1 (CH<sub>3</sub>), 24.9 (CH<sub>3</sub>), 26.0 (CH<sub>3</sub>), 27.0 (3×CH<sub>3</sub>), 65.9 (CH<sub>2</sub>), 83.2 (CH), 83.5 (CH), 84.9 (CH), 85.2 (CH), 113.5 (C), 128.18 (2×CH), 128.21 (2×CH), 130.18, (CH), 130.20 (CH), 133.2 (C), 133.3 (C), 135.9 (2×CH), 136.0 (2×CH), 191.7 (C), 197.4 ppm (C); IR (CHCl<sub>3</sub>, 0.2 mm):  $\tilde{\nu} = 2936$ , 1717 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 537 (100)  $[M^++MeOH+Na]$ , 505 (72)  $[M^++Na]$ ; HRMS (ESI<sup>+</sup>): m/z calcd for C<sub>28</sub>H<sub>38</sub>O<sub>7</sub>NaSi: 537.2285 [M<sup>+</sup>+MeOH+Na]; found: 537.2288; calcd for C<sub>27</sub>H<sub>34</sub>NaO<sub>6</sub>Si [*M*<sup>+</sup>+Na]: 505.2022; found: 505.2025; elemental analysis calcd (%) for C<sub>27</sub>H<sub>34</sub>O<sub>6</sub>Si (482.64): C 67.19, H 7.10; found: C 67.32, H 7.11.

Photolysis of 70: A deoxygenated solution of diketone 70 (21 mg, 0.044 mmol) in dry  $C_6D_6$  (0.6 mL), was placed in a resonance tube and irradiated with a daylight lamp at 30°C for 2 h. The reaction was monitored by <sup>1</sup>H NMR spectroscopy, leading to exclusive formation of the photoenol mixture 74a (4:1). The mixture was concentrated under reduced pressure and the residue purified by silica gel column chromatography (hexanes/EtOAc 9:1) to give known lactone 73 (17 mg, 0.040 mmol, 65%) from the oxidation of the photoenol by oxygen.

Compound 74a: <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ ;):  $\delta$  (major isomer) = 0.99 (s, 9H), 1.23 (s, 3H), 1.36 (s, 3H), 2.46 (s, 3H), 3.22 (dd, J=11.3, 2.2 Hz, 1H), 3.58 (dd, J=11.4, 2.5 Hz, 1H), 4.39 (m, 1H), 4.68 (d, J=6.3 Hz, 1H), 5.62 (d, J = 6.3 Hz, 1H), 6.42 (brs, 1H), 7.18–7.68 ppm (m, 10H);  $\delta$ (minor isomer)=1.00 (s, 9H), 1.27 (s, 3H), 1.46 (s, 3H), 2.37 (s, 3H), 3.26 (dd, J=11.4, 2.5 Hz, 1 H), 3.41 (dd, J=11.4, 2.5 Hz, 1 H), 4.39 (m, 1H), 4.60 (d, J=6.2 Hz, 1H), 5.76 (d, J=6.0 Hz, 1H), 6.06 (br s, 1H), 7.18–7.68 ppm (m, 10 H);  ${}^{13}$ C NMR (125.7 MHz, CDCl<sub>3</sub>;):  $\delta$  (major isomer)=19.1 (C), 25.9 (CH<sub>3</sub>), 26.1 (CH<sub>3</sub>), 26.74 (3×CH<sub>3</sub>), 26.9 (CH<sub>3</sub>), 65.0 (CH<sub>2</sub>), 80.6 (CH), 81.8 (CH), 87.3 (CH), 112.7 (C), 130.4-136.0 (10× CH), 132.5 (C), 133.1 (C), 133.2 (C), 152.2 (C), 191.9 ppm (C); δ (minor isomer)=19.1 (C), 25.6 (CH<sub>3</sub>), 25.7 (CH<sub>3</sub>), 26.7 (3×CH<sub>3</sub>), 26.8 (CH<sub>3</sub>), 65.1 (CH2), 80.8 (CH), 82.0 (CH), 89.1 (CH), 112.9 (C), 130.35-135.99 (10×CH), 132.5 (C), 133.0 (C), 133.2 (C), 152.3 (C), 192.2 ppm (C).

4,7-Anhydro-8-O-tert-butyldiphenylsilyl-1-deoxy-5,6-O-isopropylidene-Dallo-octo-2,3-diulose (71): Prepared from 68 (47 mg, 0.102 mmol) following the general procedure (Method B) using NaIO<sub>4</sub> (73 mg, 0.340 mmol) and RuO2·x H2O (0.6 mg). The reaction mixture was stirred at room temperature in the dark for 2 h. The residue was purified by rapid silica gel column chromatography (hexanes/EtOAc 97:3) to give 71 as a yellow oil  $(33~\text{mg},\,0.069~\text{mmol},\,68\,\%)$  and the known lactone 73 (3 mg, 0.007 mmol, 6%).  $[a]_D = -2 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (c=1.88 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ , 30°C; conformer A):  $\delta = 1.17$  (s, 9H), 1.18 (s, 3H), 1.47 (s, 3H), 1.82 (s, 3H), 3.72 (m, 2H), 4.24 (dd, J=9.8, 5.0 Hz, 1H), 4.46 (d, J=2.5 Hz, 1H), 4.67 (dd, J=6.3, 4.7 Hz, 1H), 5.00 (dd, J=6.6, 3.5 Hz, 1H), 7.21–7.78 (m, 10H); conformer B:  $\delta = 1.13$  (s, 9H), 1.17 (s, 3H), 1.46 (s, 3H), 2.04 (s, 3H), 3.74 (dd, J=11.0, 5.4 Hz, 1H), 3.81 (dd, J=11.0, 4.7 Hz, 1H), 4.33 (m, 1H), 4.63 (dd, J=6.3, 3.2 Hz, 1H), 4.86 (dd, J=6.3, 3.5 Hz, 1H), 5.18 (d, J=3.5 Hz, 1H), 7.21–7.78 ppm (m, 10H); <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ , 70 °C):  $\delta = 1.14$  (s, 9H), 1.19 (s, 3H), 1.45 (s, 3H), 1.86 (s, 3H), 3.74 (dd, J = 11.0, 5.4 Hz, 1H), 3.78 (dd, J = 11.0, 5.1 Hz, 1H), 4.30 (m, 1H), 4.65 (dd, J=6.3, 3.2 Hz, 1H), 4.86 (dd, J=6.3, 3.5 Hz, 1H), 5.10 (d, J = 3.5 Hz, 1 H), 7.22–7.76 ppm (m, 10 H); <sup>13</sup>C (100.6 MHz, C<sub>6</sub>D<sub>6</sub>, 30°C):  $\delta$  (conformer A) = 19.4 (C), 24.0 (CH<sub>3</sub>), 25.5 (CH<sub>3</sub>), 27.03 (CH<sub>3</sub>), 27.4 (3×CH<sub>3</sub>), 64.4 (CH<sub>2</sub>), 82.4 (CH), 82.7 (CH), 85.7 (CH), 86.5 (CH), 114.1 (C), 128.1–136.0 (10×CH), 133.57–133.64 (2×C), 195.3 (C), 197.3 ppm (C);  $\delta$  (conformer B)=19.4 (C), 23.1 (CH<sub>3</sub>), 25.4 (CH<sub>3</sub>), 27.0 (CH<sub>3</sub>), 27.6 (3×CH<sub>3</sub>), 64.7 (CH<sub>2</sub>), 81.6 (CH), 82.0 (CH), 86.3 (CH), 86.9 (CH), 114.1 (C), 128.1-136.0 (10×CH), 133.67-133.64 (2×C), 195.3 (C), 197.3 ppm (C);  ${}^{13}$ C NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>, 70 °C):  $\delta = 19.5$  (C), 24.0 (CH<sub>3</sub>), 25.6 (CH<sub>3</sub>), 27.2 (CH<sub>3</sub>), 27.4 (3×CH<sub>3</sub>), 64.6 (CH<sub>2</sub>), 82.6 (CH), 82.9 (CH), 85.6 (CH), 86.8 (CH), 114.3 (C), 128.09 (2×CH), 128.10 (2×CH), 130.05 (CH), 130.06 (CH), 133.9 (C), 134.0 (C), 136.04 (4×CH), 195.7 (C), 197.5 ppm (C); IR (CHCl<sub>3</sub>, 0.2 mm):  $\nu < \ddot{U} = > = 2936$ , 1721 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 537 (100) [ $M^+$ +MeOH+Na], 505 (38) [ $M^+$ +Na]; HRMS (ESI<sup>+</sup>): m/z calcd for  $C_{28}H_{38}O_7NaSi$ : 537.2285 [M<sup>+</sup> +MeOH+Na]; found: 537.2293; calcd for  $C_{27}H_{34}NaO_6Si [M^++Na]$ : 505.2022; found: 505.2033; elemental analysis calcd (%) for C<sub>27</sub>H<sub>34</sub>O<sub>6</sub>Si (482.64): C 67.19, H 7.10; found: C 67.38, H 7.38.

Photolysis of 71: A deoxygenated solution of diketone 71 (29 mg, 0.061 mmol) in dry C<sub>6</sub>D<sub>6</sub> (0.6 mL), was placed in a resonance tube and irradiated with a daylight lamp at 30 °C for 2 h. The reaction was monitored by <sup>1</sup>H NMR spectroscopy, leading to exclusive formation of the photoenol mixture 74a (3:5). The mixture was concentrated under reduced pressure and the residue purified by silica gel column chromatography (hexanes/EtOAc 9:1) to give the known lactone 73 (12 mg, 0.028 mmol, 64%) from the oxidation of the photoenol by oxygen.

4,7-Anhydro-8-O-tert-butyldiphenylsilyl-1-deoxy-5,6-O-isopropylidene-Dtalo-octo-2,3-diulose (72): Prepared from 69 (70 mg, 0.160 mmol) following the general procedure (Method B) using NaIO<sub>4</sub> (116 mg, 0.540 mmol) and RuO2·xH2O (1 mg). The reaction mixture was stirred at room temperature in the dark for 3 h. The residue was purified by rapid silica gel column chromatography (hexanes/EtOAc 9:1) to give 72 (30 mg, 0.062 mmol, 39%) as a yellow oil.  $[\alpha]_D = +3 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (c=1.14 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.05$  (s, 9 H), 1.32 (s, 3 H), 1.42 (s, 3 H), 2.37 (s, 3 H), 3.93 (dd, J = 10.4, 6.3 Hz, 1 H), 3.99 (dd, J = 10.4, 6.0 Hz, 1 H), 4.08 (ddd, J=6.0, 6.0, 3.5 Hz, 1 H), 4.73 (dd, J=6.0, 3.5 Hz, 1H), 4.94 (dd, J=6.0, 1.3 Hz, 1H), 5.10 (br s, 1H), 7.33-7.71 ppm (m, 10H); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>):  $\delta = 19.2$  (C), 24.5 (CH<sub>3</sub>), 25.3 (CH<sub>3</sub>), 26.3 (CH<sub>3</sub>), 26.8 (3×CH<sub>3</sub>), 61.8 (CH<sub>2</sub>), 80.8 (CH), 82.1 (CH), 83.2 (CH), 84.4 (CH), 113.3 (C), 127.58 (2×CH), 127.63 (2×CH), 129.6 (2× CH), 133.5 (C), 133.6 (C), 135.67 (2×CH), 135.71 (2×CH), 195.6 (C), 198.1 ppm (C); <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ ):  $\delta = 1.12$  (s, 3H), 1.19 (s, 9H), 1.32 (s, 3H), 1.80 (s, 3H), 4.14–4.25 (m, 3H), 4.35 (dd, J = 6.0, 3.5 Hz, 1H), 4.69 (dd, J=6.0, 1.3 Hz, 1H), 5.16 (br s, 1H), 7.21–7.85 (m, 10H); <sup>13</sup>C NMR (100.6 MHz,  $C_6D_6$ ):  $\delta = 19.5$  (C), 23.7 (CH<sub>3</sub>), 25.2 (CH<sub>3</sub>), 26.4 (CH<sub>3</sub>), 27.0 (3×CH<sub>3</sub>), 62.5 (CH<sub>2</sub>), 81.2 (CH), 82.7 (CH), 83.6 (CH), 84.7 (CH), 113.1 (C), 127.97 (2×CH), 128.0 (2×CH), 129.93 (2×CH), 133.9 (C), 134.0 (C), 136.06 (2×CH), 136.12 (2×CH), 195.8 (C), 197.5 ppm (C); IR (CHCl<sub>3</sub>, 0.2 mm):  $\tilde{\nu} = 2933$ , 1719 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 537 (100)  $[M^++MeOH+Na]$ ; 505 (39)  $[M^++Na]$ ; HRMS (ESI<sup>+</sup>): m/z calcd for C<sub>28</sub>H<sub>38</sub>NaO<sub>7</sub>Si [M<sup>+</sup>+MeOH+Na]: 537.2285; found: 537.2287; calcd for  $C_{27}H_{34}NaO_6Si [M^++Na]$ : 505.2022; found: 505.2027; elemental analysis calcd (%) for C<sub>27</sub>H<sub>34</sub>O<sub>6</sub>Si (482.64): C 67.19, H 7.10; found: C 66.80, H 7.51.

Photolysis of 72: A deoxygenated solution of diketone 72 (42.7 mg, 0.09 mmol) in purified CDCl3 (1 mL), was placed in a resonance tube and irradiated with a daylight lamp at 30 °C for 9 h. The reaction was monitored by <sup>1</sup>H NMR spectroscopy, leading to exclusive formation of 75 besides a small amount of photoenol intermediate 74b. The mixture was kept at room temperature in the dark for 14 h for the complete transformation of 74b into 75. The solution could be concentrated at low temperature under reduced pressure to give 75 (41.4 mg) as a hemiketal mixture (10:8). Compound 75 was not stable enough to withstand chromatographic purification (silica gel or alumina). Notwithstanding, the crude residue (colorless oil) was pure enough to allow the complete analytical and spectroscopic characterization.

*Photoenol* **74b**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 2.25$  (s, 3H), 4.26 (d, J =18.8 Hz, 1 H), 4.39 (d, J=18.5 Hz, 1 H), 4.96 (d, J=7.4 Hz, 1 H), 5.37 (dd, J=8.5, 1.3 Hz, 1 H), 5.51 (dd, J=8.7, 7.4 Hz, 1 H), 6.71 (br d, J=1.6 Hz,

Compound 75: <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>; major isomer):  $\delta = 1.11$  (s, 9H), 1.33 (s, 3H), 1.43 (s, 3H), 2.30 (s, 3H), 3.90 (d, J=10.6 Hz, 1H), 4.02 (d, J = 10.6 Hz, 1 H), 4.17 (dd, J = 5.8, 1.3 Hz, 1 H), 4.87 (dd, J = 5.8, 3.2 Hz, 1H), 5.95 (dd, J=3.3, 1.2 Hz, 1H), 7.35–7.76 ppm (m, 10H);  $\delta$  (minor isomer)=1.08 (s, 9H), 1.33 (s, 3H), 1.43 (s, 3H), 2.31 (s, 3H), 3.85 (s, 2H), 4.30 (d, J=6.6 Hz, 1H), 4.70 (dd, J=6.4, 4.0 Hz, 1H), 6.16 (d, J= 4.0 Hz, 1 H), 7.35–7.76 ppm (m, 10 H);  $^{13}$ C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$ (major isomer) = 19.2 (C), 25.9 (CH<sub>3</sub>), 26.5 (CH<sub>3</sub>), 26.7 (CH<sub>3</sub>), 26.80 (3× CH<sub>3</sub>), 66.8 (CH<sub>2</sub>), 69.3 (CH), 73.3 (CH), 98.0 (C), 107.6 (CH), 110.8 (C), 127.6–135.7 (10×CH), 132.4 (C), 132.5 (C), 146.7 (C), 194.61 ppm (C); δ (minor isomer) = 19.3 (C), 25.5 (CH<sub>3</sub>), 26.78 (3×CH<sub>3</sub>), 65.7 (CH<sub>2</sub>), 68.7

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(CH), 72.1 (CH), 97.2 (C), 105.1 (CH), 109.7 (C), 127.6–135.7 (10×CH), 132.6 (C), 132.7 (C), 149.0 (C), 194.57 ppm (C) (isopropylidene methyl atoms not observed); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 262 nm (sh) (2253 mol<sup>-1</sup>m<sup>3</sup>cm<sup>-1</sup>), 259 nm (2374 mol<sup>-1</sup>m<sup>3</sup>cm<sup>-1</sup>), 256 nm (sh) (2274 mol<sup>-1</sup>m<sup>3</sup>cm<sup>-1</sup>), 228 nm (5844 mol<sup>-1</sup>m<sup>3</sup>cm<sup>-1</sup>); IR (CHCl<sub>3</sub>, 0.2 mm):  $\bar{\nu}$ =3520, 2936, 1790, 1727, 1710 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): *m/z* (%): 505 (100) [*M*<sup>+</sup>+Na]; HRMS (ESI<sup>+</sup>): *m/z* calcd for C<sub>27</sub>H<sub>34</sub>NaO<sub>6</sub>Si: 505.2022 [*M*<sup>+</sup> +Na]; found: 505.2019; elemental analysis calcd (%) for C<sub>27</sub>H<sub>34</sub>O<sub>6</sub>Si (482.64): C 67.19, H 7.10; found: C 67.19, H 6.98.

Methyl (1S,2R,3S,4R,5S)-2-acetyloxy-3,4,5-trimethoxy-2-(methoxymethyl)cyclopentane-1-carboxylate (76): H<sub>5</sub>IO<sub>6</sub> (23 mg, 0.101 mmol) was added to a solution of 2 (17 mg, 0.059 mmol) in MeOH (3.5 mL). The mixture was stirred for 2 h at room temperature and concentrated under reduced pressure. A solution of the residue in Et<sub>2</sub>O was treated with diazomethane at 0°C. The mixture was then concentrated under reduced pressure and the residue purified by silica gel column chromatography (hexanes/EtOAc 7:3) to give 76 (16 mg, 0.05 mmol, 85%) as a colorless oil:  $[a]_{\rm D} = +32 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (c=1.35 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.99$  (s, 3H), 3.13 (d, J = 8.8 Hz, 1H), 3.35 (s, 3H), 3.42 (s, 3H), 3.46 (s, 3H), 3.48 (s, 3H), 3.51 (dd, J=5.7, 5.0 Hz, 1H), 3.70 (s, 3H), 3.77 (d, J=9.5 Hz, 1H), 3.89 (brd, J=5.1 Hz, 1H), 3.94 (d, J= 9.8 Hz, 1 H), 4.09 ppm (ddd, J = 8.8, 5.7, 0.6 Hz, 1 H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 21.7 (CH<sub>3</sub>), 51.9 (CH), 52.2 (CH<sub>3</sub>), 58.0 (CH<sub>3</sub>), 58.3 (CH<sub>3</sub>), 58.9 (CH<sub>3</sub>), 59.3 (CH<sub>3</sub>), 70.5 (CH<sub>2</sub>), 84.7 (CH), 86.8 (CH), 86.9 (C), 88.6 (CH), 169.8 (C), 170.7 ppm (C); IR (film): v=3013, 2936, 1740 cm<sup>-1</sup>; MS (EI): m/z (%): 321 (<1) [ $M^+$ +H], 260 (2); HRMS (EI): m/z calcd for C<sub>14</sub>H<sub>25</sub>O<sub>8</sub>: 321.1549; found [M<sup>+</sup>+H]: 321.1558; elemental analysis calcd (%) for  $C_{14}H_{24}O_8$  (320.33): C 52.49, H 7.55; found: C 52.27, H 7.49.

Methyl (1S,2R,3S,4R,5S)-2-acetyloxy-3,4,5-tris(benzyloxy)-2-(benzyloxymethyl)cyclopentane-1-carboxylate (77): H<sub>5</sub>IO<sub>6</sub> (12 mg, 0.054 mmol) was added to a solution of 25 (16 mg, 0.027 mmol) in MeOH (1.6 mL). The mixture was stirred for 1.5 h at room temperature and concentrated under reduced pressure. A solution of the residue in Et<sub>2</sub>O (0.5 mL) was treated with diazomethane at 0°C. The mixture was then concentrated under reduced pressure and the residue purified by silica gel column chromatography (hexanes/EtOAc 90:10) to give 77 (11 mg, 0.018 mmol, 65%) as a colorless oil:  $[\alpha]_{D} = +14 \text{ cm}^{3}\text{g}^{-1}\text{dm}^{-1}$  (c=0.52 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.95$  (s, 3H), 3.37 (d, J = 8.8 Hz, 1H), 3.63 (s, 3H), 3.94 (d, J=9.5 Hz, 1H), 3.96 (dd, J=5.5, 5.5 Hz, 1H), 4.12 (d, J=9.8 Hz, 1 H), 4.29 (br d, J=5.1 Hz, 1 H), 4.48 (dd, J=8.8, 6.0 Hz, 1H), 4.49 (d, J=12.6 Hz, 1H), 4.52 (d, J=12.0 Hz, 1H), 4.55 (d, J= 11.7 Hz, 1 H), 4.58 (d, J=11.7 Hz, 1 H), 4.61 (d, J=11.7 Hz, 1 H), 4.63 (d, J = 11.4 Hz, 1 H), 4.65 (d, J = 11.4 Hz, 1 H), 4.69 (d, J = 11.7 Hz, 1 H), 7.23–7.31 ppm (m, 20 H); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>):  $\delta = 21.7$  (CH<sub>3</sub>), 51.9 (CH<sub>3</sub>), 52.7 (CH), 68.7 (CH<sub>2</sub>), 72.4 (CH<sub>2</sub>), 72.8 (CH<sub>2</sub>), 73.2 (CH<sub>2</sub>), 73.4 (CH<sub>2</sub>), 83.4 (CH), 85.2 (CH), 87.0 (C), 87.1 (CH), 127.39 (CH), 127.43 (2×CH), 127.55 (CH), 127.58 (CH), 127.66 (3×CH), 127.74 (2× CH), 127.8 (2×CH), 128.2 (2×CH), 128.25 (2×CH), 128.3 (4×CH), 138.1 (C), 138.2 (2×C), 138.3 (C), 169.9 (C), 170.7 ppm (C); IR (film):  $\tilde{\nu} = 2928$ , 1738 cm<sup>-1</sup>; MS (FAB): m/z (%): 647 (5) [ $M^+$ +Na]; HRMS (FAB): m/z: calcd for C<sub>38</sub>H<sub>40</sub>NaO<sub>8</sub>: 647.2621 [ $M^+$ +Na]; found: 647.2651; elemental analysis calcd (%) for  $C_{38}H_{40}O_8$  (624.72): C 73.06, H 6.45; found: C 72.65, H 6.82.

Methyl (15,2*R*,35,4*R*,55)-2-acetyloxy-3,4,5-tris(benzyloxy)-2-(*tert*-butyldiphenylsilyloxymethyl)cyclopentano-1-carboxylate (78):  $H_5IO_6$  (15 mg, 0.067 mmol) was added to a solution of 26 (25 mg, 0.034 mmol) in MeOH (2.0 mL). The mixture was stirred for 3 h at room temperature and concentrated under reduced pressure. A solution of the residue in Et<sub>2</sub>O (0.8 mL) was treated with diazomethane at 0°C. The mixture was then concentrated under reduced pressure and the residue purified by silica gel column chromatography (hexanes/EtOAc 90:10) to give 78 (11 mg, 0.014 mmol, 42%) as a colorless oil:  $[\alpha]_D = +17 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1} (c = 0.40 \text{ in CHCl}_3)$ ; <sup>1</sup>H NMR (500 MHz, CDCl\_3):  $\delta = 1.03$  (s, 9H), 1.88 (s, 3H), 3.610 (s, 3H), 3.611 (d, J = 8.8 Hz, 1H), 3.93 (d, J = 10.1 Hz, 1H), 4.13 (dd, J = 7.1 r, 1 Hz, 1H), 4.62 (d, J = 11.7 Hz, 1H), 4.65 (d, J = 12.0 Hz, 1H), 4.67 (d, J = 12.3 Hz, 1H), 4.693 (d, J = 11.0 Hz, 1H), 4.696

(d, J=11.7 Hz, 1 H), 4.74 (d, J=11.7 Hz, 1 H), 7.19–7.4 (m, 21 H), 7.65–7.69 ppm (m, 4 H); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>):  $\delta=19.3$  (C), 21.6 (CH<sub>3</sub>), 26.8 (3×CH<sub>3</sub>), 51.6 (CH), 51.8 (CH<sub>3</sub>), 62.8 (CH<sub>2</sub>), 72.7 (CH<sub>2</sub>), 72.8 (CH<sub>2</sub>), 73.7 (CH<sub>2</sub>), 82.2 (CH), 85.2 (CH), 86.5 (C), 86.7 (CH), 127.4 (CH), 127.5 (3×CH), 127.6 (CH), 127.62 (4×CH), 127.7 (2×CH), 127.9 (2×CH), 128.22 (2×CH), 128.27 (2×CH), 128.31 (2×CH), 129.6 (CH), 129.7 (CH), 135.79 (2×CH), 135.8 (2×CH), 132.9 (C), 138.2 (C), 138.4 (C), 138.6 (C), 169.6 (C), 170.9 ppm (C); IR (CHCl<sub>3</sub>, 0.2 mm):  $\tilde{\nu}=2929$ , 1745 cm<sup>-1</sup>; MS (FAB): m/z (%): 795 (10) [ $M^+$ +Na]; HRMS (FAB): m/z calcd for C<sub>47</sub>H<sub>52</sub>O<sub>8</sub>Si (772.99): C 73.03, H 6.78; found: C 73.16, H 6.99.

Methyl (1S,2R,3S,5R)-2-(acetyloxy)-3,5-dimethoxy-2-(methoxymethyl)cyclopentane-1-carboxylate (80): Method A: A solution of 46 (20.0 mg, 0.08 mmol) in MeOH (5 mL) containing H<sub>5</sub>IO<sub>6</sub> (35.4 mg, 0.16 mmol) was stirred at room temperature for 5 h. The mixture was concentrated under reduced pressure and the residue purified by silica gel column chromatography (EtOAc→EtOAc/MeOH 95:5) to give acid 79 (19.9 mg, 0.072 mmol, 90%) as a colorless oil.  $[\alpha]_D = +16 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (c=0.55 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.80$  (ddd, J = 14.2, 5.0, 5.0 Hz, 1 H), 2.02 (s, 3 H), 2.31 (ddd, J=14.2, 7.3, 5.6 Hz, 1 H), 3.15 (d, J=6.3 Hz, 1H), 3.29 (s, 3H), 3.39 (s, 3H), 3.53 (s, 3H), 3.89 (d, J=10.7 Hz, 1H), 4.19 (dd, J=5.4, 5.0 Hz, 1H), 4.46 (m, 1H), 4.47 ppm (d, J=11.0 Hz, 1H); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>):  $\delta = 21.7$  (CH<sub>3</sub>), 34.3 (CH<sub>2</sub>), 57.6 (CH<sub>3</sub>), 57.8 (CH<sub>3</sub>), 59.6 (CH<sub>3</sub>), 60.0 (CH), 73.4 (CH<sub>2</sub>), 80.7 (CH), 84.1 (CH), 89.2 (C), 169.2 (C), 169.9 ppm (C); IR (film):  $\tilde{\nu} = 3490$ , 2935, 1743 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 299 (100) [ $M^+$ +Na]; HRMS (ESI<sup>+</sup>): m/z calcd for C<sub>12</sub>H<sub>20</sub>O<sub>7</sub>Na: 299.1107 [M<sup>+</sup>+Na]; found: 299.1112; elemental analysis calcd (%) for C<sub>12</sub>H<sub>20</sub>O<sub>7</sub> (276.28): C 52.17, H 7.30; found: C 52.12, H 7.39.

Method A and subsequent diazomethane esterification: A solution of 46 (19 mg, 0.072 mmol) in MeOH (4.5 mL) containing  $H_5IO_6$  (33 mg, 0.145 mmol) was stirred at room temperature for 6 h. The mixture was concentrated under reduced pressure and the residue esterified with a solution of diazomethane in Et2O at 0°C. The solvent was eliminated and the residue purified by silica gel column chromatography (hexanes/ EtOAc 80:20) to give 80 (14 mg, 0.048 mmol, 67%) as a colorless oil:  $[\alpha]_{\rm D} = +35 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1} (c = 0.87 \text{ in CHCl}_3); {}^{1}\text{H NMR} (500 \text{ MHz}, \text{CDCl}_3):$  $\delta = 1.98$  (s, 3 H), 1.71 (ddd, J = 14.5, 3.8, 3.8 Hz, 1 H), 2.40 (ddd, J = 14.2, 8.2, 6.0 Hz, 1 H), 3.04 (d, J=7.3 Hz, 1 H), 3.29 (s, 3 H), 3.33 (s, 3 H), 3.37 (s, 3H), 3.69 (s, 3H), 3.84 (d, J=10.1 Hz, 1H), 3.91 (dd, J=6.0, 3.5 Hz, 1H), 4.19 (d, J=10.1 Hz, 1H), 4.30 ppm (ddd, J=8.1, 8.1, 4.4 Hz, 1H); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>):  $\delta = 21.8$  (CH<sub>3</sub>), 34.6 (CH<sub>2</sub>), 52.0 (CH<sub>3</sub>), 54.8 (CH), 57.4 (CH<sub>3</sub>), 57.9 (CH<sub>3</sub>), 59.1 (CH<sub>3</sub>), 69.6 (CH<sub>2</sub>), 81.2 (CH), 84.0 (CH), 91.0 (C), 169.7 (C), 171.4 ppm (C); IR (film):  $\tilde{\nu}$ =2935, 1737 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 313 (100) [ $M^+$ +Na]; HRMS (ESI<sup>+</sup>): m/z calcd for C<sub>13</sub>H<sub>22</sub>NaO<sub>7</sub>: 313.1263 [M<sup>+</sup>+Na]; found: 313.1261; elemental analysis calcd (%) for C13H22O7 (290.31): C 53.78, H 7.64; found: C 53.61, H 7.72.

Method B and subsequent diazomethane esterification: A solution of **46** (17 mg, 0.065 mmol) in dry  $CH_2Cl_2$  (1.3 mL), containing (diacetoxyiodo)benzene (25 mg, 0.078 mmol) and iodine (17 mg, 0.065 mmol) was irradiated with a 80 W tungsten-filament lamp at room temperature under nitrogen for 2.5 h. The mixture was then poured into water and extracted with  $CH_2Cl_2$ . The organic layer was washed with aqueous sodium thiosulfate, dried, and concentrated under reduced pressure. The residue was esterified with a solution of diazomethane in  $Et_2O$  at 0°C. The solvent was eliminated and the residue purified by silica gel column chromatography (hexanes/EtOAc 8:2) to give **80** (13 mg, 0.045 mmol, 69%). Esterification of the pure acid **79** (15.2 mg, 0.058 mmol) with an excess of diazomethane in  $Et_2O$  at 0°C afforded **80** (9.7 mg, 0.033 mmol, 58%).

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orization of the iodine and the solvent was then evaporated at reduced pressure. The residue was purified by silica gel column chromatography (hexanes/EtOAc 1:1) to give acid 81 (13.0 mg, 0.019 mmol, 82%) as a colorless oil.  $[\alpha]_D = -9 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (c = 0.75 in CHCl<sub>3</sub>); <sup>1</sup>H NMR  $(500 \text{ MHz}, \text{CDCl}_3)$ :  $\delta = 0.75$  (s, 9 H), 1.07 (s, 9 H), 1.47 (ddd, J = 12.9, 8.5, 8.5 Hz, 1 H), 1.83 (s, 3 H), 2.09 (ddd, J = 13.3, 6.9, 6.9 Hz, 1 H), 3.23 (d, J=7.9 Hz, 1 H), 3.31 (s, 3 H), 3.92 (d, J=11.7 Hz, 1 H), 4.29 (ddd, J=8.2, 8.2, 6.9 Hz, 1 H), 4.33 (d, J=11.4 Hz, 1 H), 4.65 (dd, J=8.2, 6.6 Hz, 1 H), 7.19–7.64 ppm (m, 20 H);  ${}^{13}$ C NMR (125.7 MHz, CDCl<sub>3</sub>):  $\delta = 18.9$  (C), 19.2 (C), 21.4 (CH<sub>3</sub>), 26.7 (3×CH<sub>3</sub>), 26.8 (3×CH<sub>3</sub>), 38.4 (CH<sub>2</sub>), 57.8 (CH<sub>3</sub>), 58.8 (CH), 69.2 (CH<sub>2</sub>), 75.5 (CH), 78.9 (CH), 89.00 (C), 127.6-135.8 (20×CH), 131.05 (C), 131.2 (C), 132.5 (C), 133.1 (C), 169.0 (C), 169.7 ppm (C); IR (film):  $\tilde{\nu}$ =2936, 1770, 1742 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z(%): 747 (100) [M++Na]; HRMS (ESI+): m/z calcd for C<sub>42</sub>H<sub>52</sub>NaO<sub>7</sub>Si<sub>2</sub>: 747.3149 [M<sup>+</sup>+Na]; found: 747.3171; elemental analysis calcd (%) for C42H52O7Si2 (725.03): C 69.58, H 7.23; found: C 69.58, H 7.24.

Method B and subsequent diazomethane esterification: A solution of 47 (19.0 mg, 0.027 mmol) in dry CH22Cl2 (0.5 mL), containing (diacetoxyiodo)benzene (10.4 mg, 0.032 mmol) and iodine (6.8 mg, 0.027 mmol) was irradiated with a 80 W tungsten-filament lamp at room temperature under nitrogen for 21 h. Saturated aqueous sodium thiosulfate was then added until complete decolorization of the iodine and the solvent was then evaporated at reduced pressure. The residue was esterified with a solution of diazomethane in  $Et_2O$  at 0 °C. The solvent was eliminated and the residue purified by silica gel column chromatography (hexanes/ EtOAc 9:1) to give 82 (11.9 mg, 0.016 mmol, 60%) as a colorless oil:  $[\alpha]_{\rm D} = +7.6 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1} (c = 1.51 \text{ in CHCl}_3);^{1}\text{H NMR} (500 \text{ MHz, CDCl}_3):$  $\delta = 0.92$  (s, 9 H), 1.10 (s, 9 H), 1.63 (ddd, J = 12.9, 8.2, 7.9 Hz, 1 H), 1.81 (s, 3H), 2.09 (ddd, J=13.0, 7.2, 7.2 Hz, 1H), 3.26 (s, 3H), 3.48 (d, J=7.3 Hz, 1 H), 3.56 (s, 3 H), 4.10 (ddd, J = 7.6, 7.6, 7.6 Hz, 1 H), 4.18 (d, J = 10.8 Hz, 1H), 4.27 (d, J=10.7 Hz, 1H), 4.71 (dd, J=7.9, 6.9 Hz, 1H), 7.26-7.44 (m, 12 H), 7.54–7.58 (m, 4 H), 7.70–7.71 ppm (m, 4 H);  $^{13}C$  NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 19.1$  (C), 19.4 (C), 21.6 (CH<sub>3</sub>), 26.9 ( $6 \times CH_3$ ), 37.8 (CH<sub>2</sub>), 51.6 (CH<sub>3</sub>), 54.0 (CH), 57.2 (CH<sub>3</sub>), 65.0 (CH<sub>2</sub>), 75.7 (CH), 80.0 (CH), 90.2 (C), 127.5 (2×CH), 127.6 (6×CH), 129.58 (CH), 129.62 (CH), 129.68 (CH), 129.72 (CH), 133.0 (C), 131.1 (C), 133.5 (C), 133.8 (C), 135.8 (2×CH), 135.90 (2×CH), 135.92 (2×CH), 135.94 (2×CH), 169.9 (C), 171.5 ppm (C); IR (film):  $\tilde{\nu} = 2933$ , 1737 cm<sup>-1</sup>; MS (EI): m/z(%): 681 (19)  $[M^+-tBu]$ , 135 (100); HRMS (ESI<sup>+</sup>): m/z calcd for C43H54NaO7Si2: 761.3306 [M++Na]; found: 761.3325; elemental analysis calcd (%) for  $C_{43}H_{54}O_7Si_2$  (739.06): C 69.88, H 7.36; found: C 70.07, H 7.42.

Method A and subsequent diazomethane esterification: A solution of **47** (40.7 mg, 0.057 mmol) in MeOH (3.4 mL) containing  $H_{s}IO_{6}$  (26.2 mg, 0.115 mmol) was stirred at room temperature for 20 h. The mixture was concentrated under reduced pressure and the residue esterified with a solution of diazomethane in Et<sub>2</sub>O at 0°C. The solvent was eliminated and the residue purified by silica gel column chromatography (hexanes/ EtOAc 9:1) to give **81** (10.9 mg, 0.015 mmol, 26%). Esterification of pure acid **81** (17.3 mg, 0.024 mmol) with an excess of diazomethane in Et<sub>2</sub>O at 0°C afforded **82** (10.7 mg, 0.014 mmol, 60%).

(1S,2R,3S,4R,5S)-2-Acetyloxy-3,4,5-tris(benzyloxy)-2-(benzyloxymethyl)-

cyclopentanecarboxylic acid (83): A deoxygenated solution of 18 (80 mg, 0.135 mmol) in purified CDCl<sub>3</sub> (2 mL), was placed in a resonance tube and irradiated with a daylight lamp at 30 °C for 4 h. The mixture was concentrated under reduced pressure. The crude residue in EtOH (4 mL) containing  $H_5IO_6$  (61 mg, 0.269 mmol) was stirred at room temperature for 3 h. The mixture was concentrated under reduced pressure and the residue purified by silica gel column chromatography (hexanes/EtOAc 9:1-1:1) to give 83 (48 mg, 0.079 mmol, 58% from 18) as an amorphous solid:  $[\alpha]_D = +11 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (c = 1.87 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.98$  (s, 3 H), 3.26 (d, J = 9.1 Hz, 1 H), 3.91 (dd, J = 6.6, 6.6 Hz, 1H), 3.92 (d, J = 10.7 Hz, 1H), 4.33 (d, J = 10.7 Hz, 1H), 4.35 (d, J 6.3 Hz, 1 H), 4.61 (d, J=11.7 Hz, 2 H), 4.63 (dd, J=9.1, 6.9 Hz, 1 H), 4.66 (d, J=10.7 Hz, 2 H), 4.67 (d, J=11.4 Hz, 1 H), 4.68 (d, J=11.9 Hz, 1 H), 4.73 (d, J=11.0 Hz, 1H), 4.87 (d, J=11.0 Hz, 1H), 7.27-7.37 ppm (m, 20 H);  ${}^{13}$ C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 21.6$  (CH<sub>3</sub>), 56.0 (CH), 71.6 (CH<sub>2</sub>), 72.7 (CH<sub>2</sub>), 73.6 (CH<sub>2</sub>), 73.7 (CH<sub>2</sub>), 74.3 (CH<sub>2</sub>), 82.1 (CH), 85.2

(CH), 85.4 (C), 86.9 (CH), 127.67 (3×CH), 127.71 (CH), 127.9 (3×CH), 128.1 (2×CH), 128.2 (2×CH), 128.3 (2×CH), 128.37 (2×CH), 128.39 (2×CH), 128.6 (CH), 128.8 (2×CH), 135.7 (C), 137.7 (C), 138.0 (C), 138.3 (C), 169.3 (C), 169.9 ppm (C); IR (film):  $\tilde{\nu}$ =2928, 1742, 1731 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): *m/z* (%): 633 (100) [*M*<sup>+</sup>+Na]; HRMS (ESI<sup>+</sup>): *m/z* calcd for C<sub>37</sub>H<sub>38</sub>NaO<sub>8</sub>: 633.2464 [*M*<sup>+</sup>+Na]; found: 633.2463; elemental analysis calcd (%) for C<sub>37</sub>H<sub>38</sub>O<sub>8</sub> (610.69): C 72.77, H 6.27; found: C 72.68, H 6.27.

#### (4aR,5S,6S,7R,7aS)-4a-(Acetyloxy)-6,7-dimethoxy-2,2-dimethylhexahy-

drocyclopenta[d][1,3]dioxine-5-carboxylic acid (84): A deoxygenated solution of diketone 22 (20.0 mg, 0.066 mmol) in dry  $C_6D_6$  (0.3 mL), was placed in a resonance tube and irradiated with a daylight lamp at 36-40°C for 2.5 h. The mixture was concentrated under reduced pressure and the residue dissolved in CH2Cl2 (1.3 mL) and treated with (diacetoxyiodo)benzene (24.6 mg, 0.076 mmol) and iodine (16.1 mg, 0.06 mmol). The mixture was irradiated with an 80 W tungsten-filament lamp at room temperature under nitrogen for 40 min. An excess of solid Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was then added and the solvent concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexanes/ EtOAc 8:2) to give 84 (17.4 mg, 0.054 mmol, 82%, from 22) as an amorphous solid.  $[a]_D = -19 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (c = 0.44 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 1.41$  (s, 3H), 1.60 (s, 3H), 2.00 (s, 3H), 3.39 (s, 3H), 3.46 (s, 3H), 3.48 (d, J=3.2 Hz, 1H), 3.56 (d, J=9.3 Hz, 1H), 4.21 (d, J = 11.9 Hz, 1 H), 4.29 (ddd, J = 9.3, 3.2, 1.1 Hz, 1 H), 4.53 (d, J =11.9 Hz, 1 H), 4.79 ppm (d, J = 1.0 Hz, 1 H); <sup>13</sup>C NMR (100.6 MHz,  $CDCl_3$ ):  $\delta = 19.8$  (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 28.2 (CH<sub>3</sub>), 52.1 (CH), 57.7 (CH<sub>3</sub>), 58.2 (CH<sub>3</sub>), 59.5 (CH<sub>2</sub>), 73.8 (CH), 83.3 (C), 86.8 (CH), 89.9 (CH), 99.1 (C), 170.2 (C), 173.2 ppm (C); IR (CHCl<sub>3</sub>, 0.2 mm):  $\tilde{\nu} = 3504$ , 3016, 1741, 1717 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 341 (100) [ $M^+$ +Na]; HRMS (ESI<sup>+</sup>): m/z calcd for C<sub>14</sub>H<sub>22</sub>NaO<sub>8</sub>: 341.1212 [M<sup>+</sup>+Na]; found: 341.1207; elemental analysis calcd (%) for  $C_{14}H_{22}O_8$  (318.32): C 52.82, H 6.97; found: C 52.86, H 6.92.

(1S,2R,5R)-2-(Acetyloxy)-5-methoxy-2-[(tert-butyldiphenylsilyl)oxy]methyl-1-cyclopentanecarboxylic acid (85) from photocyclization-fragmentation of 42: A deoxygenated solution of 42 (40.8 mg, 0.090 mmol) in dry  $C_6D_6$  (0.3 mL), was placed in a resonance tube and irradiated with a daylight lamp at 36-40 °C for 5 h. The solution was heated to 60 °C for 2 h in the dark and concentrated under reduced pressure. The crude residue in MeOH (3.0 mL), containing H5IO6 (45.4 mg, 0.2 mmol), was stirred at room temperature for 3 h. The mixture was concentrated under reduced pressure and the residue purified by silica gel column chromatography (hexanes/EtOAc 8:2-EtOAc) to give 85 (10.5 mg, 0.022 mmol, 46%) as an amorphous solid.  $[\alpha]_{\rm D} = +1 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1} (c = 0.52 \text{ in CHCl}_3);$ <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 1.10$  (s, 9H), 1.59 (m, 1H), 1.98 (s, 3H), 2.03-2.12 (m, 2H), 2.21 (m, 1H), 3.18 (d, J=6.3 Hz, 1H), 3.38 (s, 3H), 3.78 (d, J = 10.4 Hz, 1 H), 4.386 (d, J = 10.4 Hz, 1 H), 4.387 (ddd, J = 6.3, 6.3, 6.3 Hz, 1 H), 7.38–7.48 (m, 6 H), 7.63–7.67 ppm (m, 4 H); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>):  $\delta = 19.2$  (C), 21.8 (CH<sub>3</sub>), 26.8 (3 × CH<sub>3</sub>), 29.2 (CH<sub>2</sub>), 32.1 (CH<sub>2</sub>), 57.4 (CH<sub>3</sub>), 59.0 (CH), 67.2 (CH<sub>2</sub>), 82.5 (CH), 88.9 (C), 127.9 (2×CH), 128.0 (2×CH), 130.3 (2×CH), 131.6 (C), 131.8 (C), 135.6 (2×CH), 135.7 (2×CH), 169.7 (C), 170.8 ppm (C); IR (CHCl<sub>3</sub>, 0.2 mm):  $\tilde{\nu} = 2938$ , 1739 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 493 (100) [ $M^+$ +Na]; HRMS (ESI<sup>+</sup>): m/z calcd for C<sub>26</sub>H<sub>34</sub>NaO<sub>6</sub>Si: 493.2022 [ $M^+$ +Na]; found: 493.2021; elemental analysis calcd (%) for  $C_{26}H_{34}O_6Si$  (470.63): C 66.35, H 7.28; found: C 66.12, H 7.03.

Methyl (15,2*R*,35,4*R*,55)-3,4,5-tris(benzyloxy)-2-(benzyloxy)methyl]cyclopentanecarboxylate (86): A solution of 83 (19 mg, 0.031 mmol) in methanolic KOH (0.6 mL, 4 mg, 0.078 mmol) was stirred at room temperature for 24 h. The mixture was neutralized with acid resin Dowex 50 W×8 (H<sup>+</sup>), filtered and concentrated under reduced pressure. A solution of the residue in Et<sub>2</sub>O was treated with an excess of diazomethane at 0 °C and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexanes/EtOAc 8:2) to give 86 (18 mg, 0.031 mmol, 99%): colorless oil.  $[\alpha]_D = +2 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (*c* =0.25 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.11 (d, *J* = 8.0 Hz, 1H), 3.64 (s, 3H), 3.69 (d, *J* = 9.5 Hz, 1H), 3.75 (d, *J* = 9.5 Hz, 1H), 3.89 (d, *J* = 3.7 Hz, 1H), 3.94 (dd, *J* = 4.8, 4.0 Hz, 1H), 4.54 (m, 1H), 4.52–4.62 (m, 8H), 7.25–7.35 ppm (m, 20H); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>):  $\delta$  =51.9 (CH<sub>3</sub>), 54.0 (CH), 72.0 (CH<sub>2</sub>), 72.30 (CH<sub>2</sub>), 72.34 (CH<sub>2</sub>), 72.8 (CH<sub>2</sub>), 73.7

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#### (CH<sub>2</sub>), 81.0 (C), 85.1 (CH), 86.6 (CH), 87.2 (CH), 127.6–128.3 (20×CH), 137.9 (C), 138.05 (C), 138.09 (2×C), 172.8 ppm (C); IR (film): $\tilde{\nu}$ =3499, 1732, 1068 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 605 (100) [M<sup>+</sup>+Na]; HRMS (ESI<sup>+</sup>): m/z calcd for C<sub>36</sub>H<sub>38</sub>NaO<sub>7</sub>: 605.2515 [M<sup>+</sup>+Na]; found: 605.2513; elemental analysis calcd (%) for C<sub>36</sub>H<sub>38</sub>O<sub>7</sub> (582.68): C 74.21, H 6.57; found: C 74.42, H 6.60.

#### (1S,2S,3R,4S,5R)-2,3,4-Tris(benzyloxy)-5-(benzyloxy)methyl-6-oxabi-

cyclo[3.2.0]heptan-7-one (87): A solution of 83 (15 mg, 0.025 mmol) in methanolic KOH (0.5 mL, 4 mg, 0.071 mmol) was stirred at room temperature for 24 h, neutralized with acid ion-exchange resin Dowex-50 W×8 (H<sup>+</sup>), filtered and concentrated under reduced pressure. Benzenesulfonyl chloride (16 µL, 0.130 mmol) was added to a solution of the residue in dry pyridine (0.1 mL) and the mixture stirred at 0°C for 14 h. The solution was then poured into ice-water and extracted with Et2O. The residue was purified by silica gel column chromatography (hexanes/EtOAc 8:2) to give 87 (10 mg, 0.018 mmol, 73 %, two-step) as a colorless oil.  $[\alpha]_D = +$  $2 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1}$  (c = 0.50 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.97 (d, J = 12.0 Hz, 1 H), 3.99 (d, J = 11.7 Hz, 1 H), 4.00 (dd, J = 1.5 Hz,  $J_W =$ 1.4 Hz, 1 H), 4.16 (ddd, J=2.4, 2.0 Hz,  $J_W=1.4$  Hz, 1 H), 4.19 (d, J=4.7 Hz, 1 H), 4.22 (dd, J=1.9, 1.9 Hz, 1 H), 4.47 (d, J=12.0 Hz, 1 H), 4.48 (d, J=12.0 Hz, 1 H), 4.52 (d, J=11.7 Hz, 1 H), 4.52 (d, J=12.0 Hz, 1 H), 4.53 (d, J=12.3 Hz, 1 H), 4.57 (d, J=12.0 Hz, 1 H), 4.60 (d, J=12.3 Hz, 1 H), 4.63 (d, J=12.0 Hz, 1 H), 7.22–7.36 ppm (m, 20 H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 60.5$  (CH), 67.6 (CH<sub>2</sub>), 71.1 (CH<sub>2</sub>), 72.1 (CH<sub>2</sub>), 73.0 (CH<sub>2</sub>), 73.8 (CH<sub>2</sub>), 81.4 (CH), 82.9 (CH), 86.8 (CH), 88.1 (C), 127.6-128.5 (20×CH), 137.2 (C), 137.29 (C), 137.34 (C), 137.4 (C), 167.1 ppm (C); IR (film):  $\tilde{v} = 2918$ , 1828, 1087 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): m/z (%): 573 (100)  $[M^++Na]$ ; HRMS (ESI<sup>+</sup>): m/z calcd for  $C_{35}H_{34}NaO_6$ : 573.2253  $[M^+]$ +Na]; found: 573.2249; elemental analysis (%) for C<sub>35</sub>H<sub>34</sub>O<sub>6</sub> (550.64): C 76.34, H 6.22; found: C 76.29, H 6.47.

(1R,2S,3R,4S,5S)-2,3,4-Tris(benzyloxy)-1-(benzyloxy)methyl-5-(hydroxymethyl)cyclopentanol (88): LiAlH<sub>4</sub> (6 mg, 0.082 mmol) was added to a solution of 83 (25 mg, 0.041 mmol) in dry THF (1.6 mL) and the suspension stirred at 0°C under nitrogen for 4 h. A saturated solution of Na<sub>2</sub>SO<sub>4</sub> was then added, the white solid mass precipitate was filtered through Celite, and the solvent concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexanes/ EtOAc 1:1 $\rightarrow$ 4:6) to give **88** (18 mg, 0.032 mmol, 78%) as a colorless oil:  $[\alpha]_{\rm D} = -8.2 \text{ cm}^3 \text{g}^{-1} \text{dm}^{-1} (c = 0.11 \text{ in CHCl}_3); {}^{1}\text{H NMR} (500 \text{ MHz}, \text{CDCl}_3):$  $\delta = 2.21$  (ddd, J = 9.3, 6.0, 3.7 Hz, 1 H), 3.61 (d, J = 9.5 Hz, 1 H), 3.76 (d, J=9.1 Hz, 1 H), 3.79 (dd, J=11.6, 6.0 Hz, 1 H), 3.83 (d, J=4.7 Hz, 1 H), 3.87 (dd, J=11.6, 3.5 Hz, 1 H), 3.91 (dd, J=5.4, 5.4 Hz, 1 H), 4.09 (dd, J= 8.8, 5.4 Hz, 1 H), 4.45-4.73 (m, 8H), 7.25-7.38 ppm (m, 20H); <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ ):  $\delta = 2.24$  (brs, 1H), 2.31 (ddd, J = 4.7, 4.7, 9.5 Hz, 1H), 3.08 (brs, 1H), 3.51 (d, J=9.5 Hz, 1H), 3.68 (d, J=9.5 Hz, 1H), 3.84 (br t, J=4.4 Hz, 2H), 3.93 (d, J=5.4 Hz, 1H), 4.05 (dd, J=5.7, 5.7 Hz, 1H), 4.22 (s, 2H), 4.25 (dd, J=6.0, 8.5 Hz, 1H), 4.54 (d, J=12.0 Hz, 1H), 4.57 (d, J=11.0 Hz, 1 H), 4.57 (d, J=11.0 Hz, 1 H), 4.62 (d, J=11.7 Hz, 1 H), 4.64 (d, J=11.5 Hz, 1H), 4.67 (d, J=11.7 Hz, 1H), 7.05-7.36 ppm (m, 20 H);  ${}^{13}$ C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 49.9$  (CH), 60.5 (CH<sub>2</sub>), 72.2 (CH<sub>2</sub>), 72.6 (CH<sub>2</sub>), 72.6 (CH<sub>2</sub>), 73.1 (CH<sub>2</sub>), 73.9 (CH<sub>2</sub>), 80.6 (C), 82.7 (CH), 86.9 (CH), 87.8 (CH), 127.7-128.5 (20×CH), 137.4 (C), 138.1 (C), 138.2 (C), 138.4 ppm (C);  ${}^{13}$ C NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 50.0 (CH), 60.9 (CH<sub>2</sub>), 72.2 (CH<sub>2</sub>), 72.6 (CH<sub>2</sub>), 72.8 (CH<sub>2</sub>), 73.6 (CH<sub>2</sub>), 73.7 (CH<sub>2</sub>), 80.7 (C), 82.8 (CH), 87.7 (CH), 88.6 (CH), 127.6-128.6 (20×CH), 138.3 (C), 139.0 (C), 139.2 (C), 139.3 ppm (C); IR (film):  $\tilde{\nu} = 3445$ , 2918, 1075 cm<sup>-1</sup>; MS (ESI): m/z (%): 577 (100) [ $M^+$ +Na]; HRMS (ESI<sup>+</sup>): m/zcalcd for  $C_{35}H_{38}NaO_6$ : 577.2566 [*M*<sup>+</sup>+Na]; found: 577.2564; elemental analysis calcd (%) for C<sub>35</sub>H<sub>38</sub>O<sub>6</sub> (554.67): C 73.79, H 6.91; found: C 73.39, H 7.31.

Methyl (3*R*,4*S*,5*S*)-3,4,5-tris(benzyloxy)-2-(benzyloxy)methyl-1-cyclopentene-1-carboxylate (89): Tf<sub>2</sub>O (14  $\mu$ L, 0.081 mmol) was added dropwise to a solution of 86 (16 mg, 0.027 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> containing dry pyridine (14  $\mu$ L) at 0 °C. The mixture was stirred at room temperature for 24 h, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexanes/EtOAc 8:2) to give 89 (14 mg, 0.025 mmol, 93 %) as a colorless oil. [a]<sub>D</sub> = -16 cm<sup>3</sup>g<sup>-1</sup>dm<sup>-1</sup> (c= 1.06 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.72 (s, 3H), 4.05 (dd,

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J=2.6, 2.4 Hz, 1 H), 4.37 (d, J=13.8 Hz, 1 H), 4.45–4.71 (m, 8 H), 4.63 (m, 1 H), 4.69 (m, 1 H), 4.83 (d, J=13.8 Hz, 1 H), 7.26–7.36 ppm (m, 20 H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$ =51.6 (CH<sub>3</sub>), 64.6 (CH<sub>2</sub>), 71.8 (CH<sub>2</sub>), 72.2 (CH<sub>2</sub>), 72.6 (CH<sub>2</sub>), 72.9 (CH<sub>2</sub>), 85.8 (CH), 85.9 (CH), 87.8 (CH), 127.6–128.4 (20×CH), 131.9 (C), 137.9 (C), 138.0 (C), 138.26 (C), 138.35 (C), 153.2 (C), 164.8 ppm (C); IR (film):  $\tilde{\nu}$ =2922, 1722, 1070 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): *m/z* (%): 587 (100) [*M*<sup>+</sup>+Na]; HRMS (ESI<sup>+</sup>): *m/z* calcd for C<sub>36</sub>H<sub>36</sub>NaO<sub>6</sub>: 587.2401 [*M*<sup>+</sup>+Na]; found: 587.2405; elemental analysis calcd (%) for C<sub>36</sub>H<sub>36</sub>O<sub>6</sub> (564.67): C 76.57, H 6.43; found: C 76.77, H 6.63.

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