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

Dimitri Alvarez-Dorta,[a] Elisa I. León,*[a] Alan R. Kennedy,[b] Angeles Martín,[a] Inés Pérez-Martín,[a] Concepción Riesco-Fagundo,[a] and Ernesto Suárez*[a]

Abstract: The excitation of the innermost carbonyl of nono-2,3-diulose derivatives by irradiation with visible-light 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-(enol*exo*)-*exo-trig* 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 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 8C).

Keywords: carbohydrates · cyclopentitols · diketones · photochemistry · ring contraction

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 *a*-diketones.[1] 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.[2] Whereas photoelimination is usually the priority process with monoketones, *a*-diketones yield almost exclusively 2-hydroxycyclobutanones by photocyclization. Moreover, in *a*-diketones the 1,5-hydrogen abstraction apparently occurs only from the external carbonyl, such that the formation of acyl cyclobutanols has never been observed. The development of synthetic applications of this 1,5-hydrogen atom transfer reaction originated by *a*-diketones has been scant.[3] This is somewhat surprising since *a*-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 *a*-diketones.

The conversion of carbohydrate derivatives into enantiopure polyfunctionalized cyclopentanes has been extensively documented.[4] 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 ring-contraction methods represent a highly efficient biomimetic approach to the synthesis of cyclopentanols.[5] 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 ($[Cp_2ZrCl_2]/BF_3 \cdot OEt_2$)[6] or ($SmI_2/[Pd(PPh_3)_4]$),[7] oct-6-enopyranosiduronate (SmI_2),[8] hept-6-ynopyranosides ($SmI_2/[Pd(PPh_3)_4]$),[7] 6-deoxy-6-iodo-hexopyranoside (SmI_2)[9] and glucodialdo-1,5-hexopyranoside (SmI_2).[10]

In connection with our ongoing research programs on the reactivity of *a*-diketones[11] and intramolecular hydrogen

a. Dr. D. Alvarez-Dorta, Dr. E. I. León, Dr. A. Martín, Dr. I. Pérez-Martín, Dr. C. Riesco-Fagundo, Prof. Dr. E. Suárez
Instituto de Productos Naturales, y Agrobiología del C.S. I.C.
Carretera de la Esperanza 3, 38203 La Laguna, Tenerife (Spain)
Fax: (+34) 922-260-135
E-mail: eila@ipna.csic.es
esuarez@ipna.csic.es

b. Dr. A. R. Kennedy
WestCHEM Department of Pure and Applied Chemistry
University of Strathclyde
295 Cathedral Street, Glasgow G1 1XL (UK)

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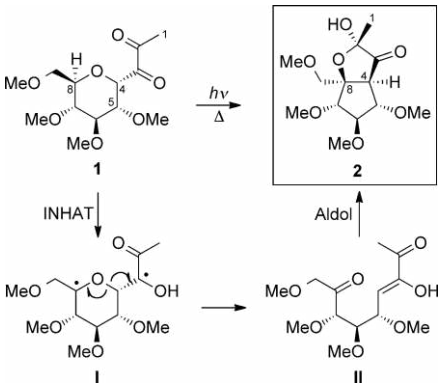


Scheme 1. Photochemistry of nono-2,3-diulose 1. INHAT = intramolecular hydrogen atom transfer.

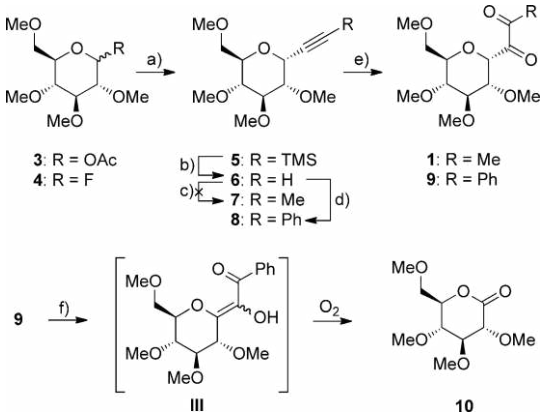
atom transfer (INHAT) promoted by alkoxyl radicals in carbohydrate chemistry,[12] we present herein our results on the photochemical reactivity of nono-2,3-diuloses (Scheme 1).[13] It is generally accepted that hydrogen atom abstraction by a photoexcited carbonyl closely resembles the hydrogen atom abstraction by alkoxyl radicals.[1a,b] 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[14] and 1-hydroxyethyl[15] tethers cyclized, with the $PhI(OAc)_2/I_2$ system, to give 6,8-dioxabicyclo[3.2.1]octane (1,5-HAT) and 2,9-dioxabicyclo[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-*b*-*syn* aldol cyclization. Finally, the regenerated α-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 α-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.

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 prepar- ing a variety of 2,3-diuloses belonging to carbohydrates in pyranose and furanose form.

Synthesis of a-*C*-propynyl glycosides: We based the preparation of these compounds on the α-ethynylation of sugars by C-glycosidation using nBu$_3$SnC÷CSiMe$_3$ in the presence of trimethylsilyl triflate (TMSOTf) followed by desilylation of the initial adducts, a methodology well established by the groups of Isobe[16] and Dondoni.[17] 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$_3$SnC÷CTMS (2 equiv), TMSOTf (2.5 equiv), CH_2Cl_2, 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$_3$SnC÷CMe (2 equiv), TMSOTf (2 equiv), CH_2Cl_2, MS 4 Å, room temperature, 2 h, 82%; for the synthesis of 7 from 4: n-Bu$_3$SnC÷CMe (2.5 equiv), $BF_3 \cdot OEt_2$ (2 equiv), CH_2Cl_2, MS 4 Å, room temperature, 1 h, 51%; b) NaOH (1.9 equiv), CH_2Cl_2/MeOH, 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_3 (excess), CH_2Cl_2, —78 °C, 2 h, then Me_2S (2.1 equiv), 6 h, dark; f) Daylight-lamp irradiation, C_6D_6, 30 °C, N_2, 9 h, then air, 48%, two steps. TMS = trimethylsilyl, OAc = acyl.

to accomplish the alkyne methylation by using several bases (nBuLi, 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.[18] A related attempt at C-glycosidation by treat-

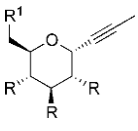
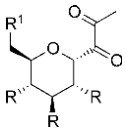
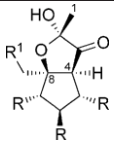
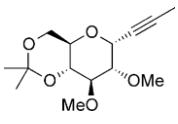
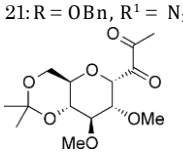
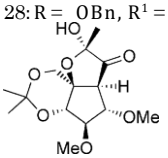
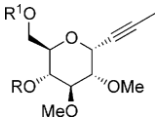
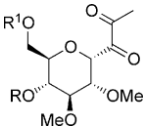
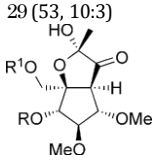
ment of acetate 3 and commercially available TMSC÷CMe was similarly unproductive. After extensive experimentation (see the Supporting Information) the *α*-*C*-propynyl glucoside 7 was obtained with good diastereoselectivity but in an unacceptable maximum yield of 33 %. Therefore, an alternative route was sought using nBu$_3$SnC÷CMe as glycosyl acceptor, which was prepared according to the procedure developed by Logue and Teng.[19] The reaction catalyzed by TMSOTf proceeded very smoothly to give 7 in good yield and diastereoselectivity (90 %, diastereomeric ratio (d.r.) *α*/ *β*, 10:1). Alternatively, by using glucopyranosyl fluoride 4 as glycosyl donor and $BF_3 \cdot OEt_2$ as catalyst the diastereoselectivity was improved since almost only the *α*-isomer of the product was detected. All the *α*-*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-d-*glycero*-l-*gulo*-oct-7-ynitol (9) was prepared by Sonogashira cross-coupling of alkyne 6 with iodobenzene.[20]

Diketones 1, 9 (Scheme 2), 18–24 (Table 1), 38–43 (Table 2), 58–61 (Table 3), and 70–72 (Table 4) were prepared from the corresponding non-2-ynitols by oxidation of the triple bond with ozone (Method A)[21] or $NaIO_4$/ $RuO_2 \cdot x\,H_2O$ (Method B).[22] *α*-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 *α*-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 *α*-diketones the conformation of the pyranose ring was carefully studied by analysis of its vicinal coupling constant values. A chair $^7C_4$ conformation (equivalent to $^4C_1$ 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 *α*-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 ^{1}H NMR spectroscopy of the crude reaction mixture (Table 1). With the aim of establishing the excitation behavior of the dicarbonyl system, a solution of 1 in [D$_6$]benzene containing 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.[23] In particular, the $^3J_{H4,H5}$ = 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 *b-syn* cyclization and the *S* stereochemistry of the hemiketal. Due to the flexibility of the cyclopentane, weighted average $^3J_{H,H}$ for the ring protons were calculated for the more popu-

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

α-*C*-Propynyl glucoside [%][a]	Method[b]	2,3-Diulose [%][a]	Product [%, d.r.][a,c]
			
7: R = R^1 = OMe (90)	A	1: R = R^1 = OMe[d]	2: R = R^1 = OMe (52)[e]
11: R = R^1 = OBn (86)	B	18: R = R^1 = OBn (62)	25: R = R^1 = OBn (58)
12: R = OBn, R^1 = ODPS	B	19: R = OBn, R^1 = ODPS (64)	26: R = OBn, R^1 = ODPS (65, 5:1)
13: R = OBn, R^1 = OAc	B	20: R = OBn, R^1 = OAc (47)	27: R = OBn, R^1 = OAc (67, 1:0.9)
14: R = OBn, R^1 = N$_3$	B	21: R = OBn, R^1 = N$_3$ (59)	28: R = OBn, R^1 = N$_3$ (55, 1.3:1)
			
15 (77)	A	22 (67)	29 (53, 10:3)
			
16: R = R^1 = TBS (68)	A	23: R = R^1 = TBS (75)	30: R = R^1 = TBS (63)
17: R = Ac, R^1 = TBS	A	24: R = Ac, R^1 = TBS (73)	31: 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.

lated conformers as determined by pseudorotational analysis.[24] 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°, 60 %) and $^6T_7/E_7$ (P_S = 189.1 °, 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: $^7T_6$ (P_N = 358.5 °). A small but significant $^4J_{H5,H7}$ coupling (ca. 1 Hz) can be detected, which is more consistent with the $^6T_7/E_7$ 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 ^{1}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 d = 5.56 ppm (J = 9 Hz) and a broad singlet exchangeable with D_2O at d = 6.73 ppm assignable to the transient photoenol could be observed.[25] 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 ^{1}H NMR spectroscopy (Scheme 2).[25, 26] 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 constants, which are undoubtedly consistent with a $^7C_4$ conformation.

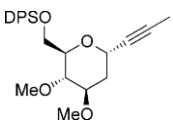
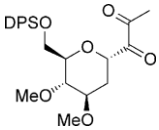
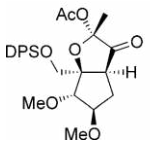
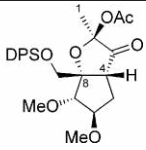
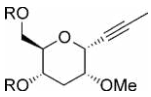
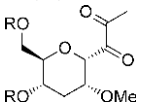
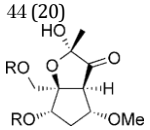
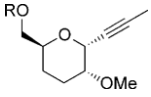
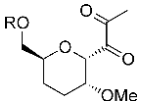
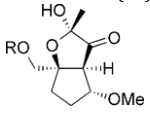
The other 2,3-diuloses belonging to d-glucopyranose series 18–24 (Table 1) with different substituents at C7 and C9, vicinal carbon atoms in the INHAT, were synthesized to determine the influence of steric and electronic effects in both the reactivity of the diradical intermediate I and the diastereoselectivity 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-*b-syn* aldol cyclization being observed. The somewhat lower yields obtained in the synthesis of 2 and 29 could be more related with the instability of the diulose itself.

The coupling constant $^3J_{H4,H5}$ proved to be diagnostic in distinguishing between the OH-*b-syn* and OH-*a-syn* aldol cyclization (see below, $^3J_{H4a,H5b}$ = 2–4 Hz is much smaller than $^3J_{H4b,H5b}$ = 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 ° ($^5E/^5T_6$ to E_6) were observed, whereas P values of 106–189 ° ($^4T_5$ to $^6T_7$) 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-*b-syn* 44 and OH-*a-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-*b-syn* cyclization structure was assigned to 44 by the $^3J_{H4a,H5b}$ = 4.4 Hz and substantiated by the observation of NOESY correlations between 1-Me and H7, and H4 and H6. Moreover, a larger $^3J_{H4,H5}$ = 9.8 Hz coupling constant

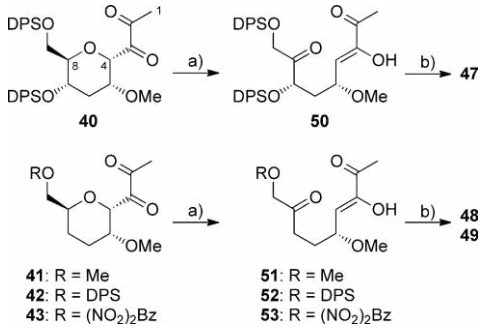
Table 2. Synthesis and photolysis of mono- and di-deoxy-2,3-diuloses in pyranose form.

a-C-Propynyl glycoside [%, d.r.][a]	Method[b]	2,3-Diulose [%][a]	Product [%, d.r.][a,c]	
				
32 (86)	B	38 (63)	44 (20)	45 (20)
				
33: R = Me (69, 22:1)	A	39: R = Me (65)	46: R = Me (57)	
34: R = DPS (87, 14:1)	A	40: R = DPS (77)	47: R = DPS (75)	
				
35: R = Me (91)	A	41: R = Me (69)	48: R = Me (52)	
36: R = DPS	B	42: R = DPS (71)	49: R = DPS (61, 10:1)	
37: R = $(NO_2)_2$Bz	B	43: R = $(NO_2)_2$Bz (71)[d]		

[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), 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] Thermolysis of 43 was never realized. Bz = benzyl.

and NOESY correlations between 1-Me and H6, and H4 and H7 were consistent with an OH-*α-syn* cyclization 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 thermally more stable, were cyclized in the dark at 60 °C to give carbocycles 48 and 49, respectively.

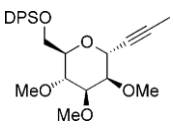
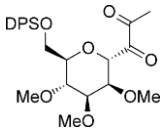
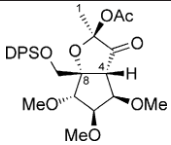
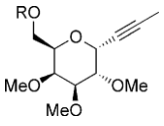
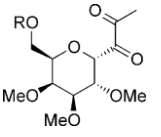
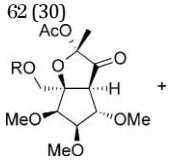
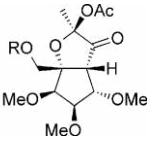
These thermal experiments, performed with strict exclusion of light, confirm that the aldol reaction proceeded with a high degree of diastereoselectivity, resulting in the exclusive formation of *syn*-aldols. We did not find any *anti*-aldol product that (having the *α*-diketone moiety unprotected) could 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 d-*galacto* 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 *α-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*α* proton by the external carbonyl under classical Norrish-Yang conditions is possible. Thus, competitive abstraction of H8*α* and H5*α* 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 ^{1}H NMR spectrum of the permethylated d-galactose model 59 exhibits ring coupling constants that strongly point to a $^4C_7$ chair conformation. It was therefore not very surprising that the photochemical reaction gave 2,3,4,6-tetra-*O*-methyl-*α*-d-galactono-1,5-lactone as the only detectable product in 80 % yield. Since in this geometric arrangement the *α*-diketone tether and the H8*α* 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*b* 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 $^7C_4$ chair.[27] Fortunately, the ring coupling constants ($^3J_{H4,H5}$ = 6.9, $^3J_{H5,H6}$ = 8.5, and $^3J_{H6,H7}$ =

Table 3. Synthesis and photolysis of 2,3-diuloses with *α*-d-*manno*- and *α*-d-*galacto*-pyranose stereochemistry.

α-C-Propynyl glycoside [%, d.r.][a]	Method[b]	2,3-Diulose [%][a]	Product [%][a]	
				
54	B	58 (53)	62 (30)	
				
55: R = Me (85, 1:1.1)	A	59: R = Me (58)[c]		
56: R = DPS	B	60: R = DPS (64)	63: R = DPS (23)	64: R = DPS (46)
57: R = Ac (87)	B	61: R = Ac (48)	65: R = Ac (19)	66: R = Ac (57)

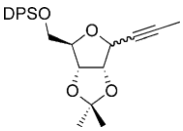
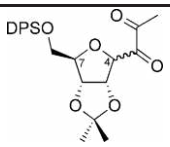
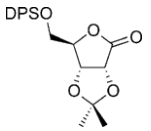
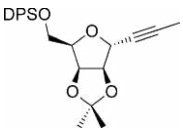
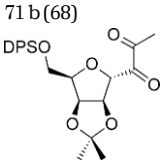
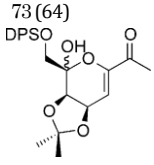
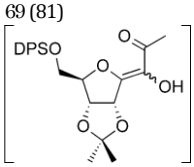
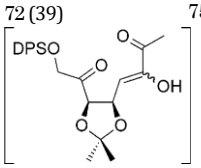
[a] Yield of the product isolated by using chromatography. [b] Method A: O_3 (excess), CH_2Cl_2, −78 °C, 2 h, then Me_2S (2.1 equiv), dark. Method B: $NaIO_4$ (4 equiv), $RuO_2 \cdot x\,H_2O$ (8.8 mg), $CCl_4/CH_3CN/H_2O$ (1:1:1.5), room temperature, dark. [c] Irradiation of 59 led to 2,3,4,6-tetra-*O*-methyl-d-galactono-1,5-lactone exclusively.

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 ^{1}H NMR spectroscopy and subsequent heating at 70 °C was necessary to accomplish the aldol cyclization.

The structure of 63 and 64 as *b-syn* and *a-syn* cyclization isomers, respectively, was assigned on the previously commented basis: The $^3J_{H4,H5}$ coupling constant, which is smaller for the *b-syn* isomer ($^3J_{H4a,H5b}$ = 2.9 Hz for 63 versus $^3J_{H4b,H5b}$ = 9.5 Hz for 64), and NOESY experiments. To calcu- late the ring coupling constants and NOE interaction the most populated conformer was determined to be $^7T_6$ 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 ob- tained in good overall yield (76 %), in which the *a-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 a and 71 b) 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 a led to the lactone 73 in moderate yield, presumably by oxidation of the photoenol intermediate 74 a, as previously observed in diketones 9 and 59 in which photoenolization competes with photoelimination.[26] The most populated conformer of 70 a has a phase angle of P = 256 °

Table 4. Synthesis and photolysis of 2,3-diuloses with *a*-d-*ribo*- and *a*-d-*lyxo*furanose stereochemistry.

a-C-Propynyl glycoside [%][a]	Method[b]	2,3-Diulose [%][a]	Product [%][a]
			
67 a (56)	B	70 a (69)	73 (65)
68 b (19)	B	71 b (68)	73 (64)
			
69 (81)	B	72 (39)	75[c]
			
74a		74b	

[a] Yield of the product isolated by using chromatography. [b] Meth- od 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] The product was chromatographically unsta- ble.

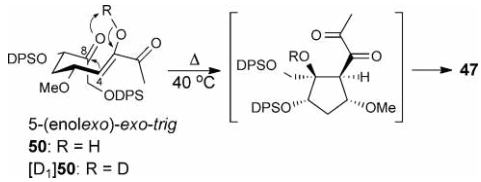
(^7T_o), wherein the *a*-diketone tether and the hydrogen at C7 lie in a *syn*-1,3-pseudo-diequatorial relationship. The distance between the oxygen at C3 and the extractable hydrogen at H7 on the minimum energy conformer was calculated as indicative of the 1,5-HAT feasibility. Since it is generally 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 $d_{C3=O\cdots H7}$ = 4.7 Å precludes any photochemical hydrogen abstraction.[28]

The abstraction at H7 is not geometrically feasible in the d-*ribo* isomer 71 b, 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 b gave the same lactone 73 in similar yield, demonstrating that in these sugar derivatives photoenolization also competes favorably with the Yang cyclization.[26] In contrast to d-*ribo* derivative 70 a, the furanose ring of the isomeric d- *lyxo* 72 adopts a conformation °E (P = 86 °) with the *a*-dike- tone 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 74 b. *a,b*-Unsaturated ketone 75 could not withstand chromatographic purification but the crude reaction residue was pure enough to allow complete analytical and spectroscopic characteriza- tion.

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 *a*-diketone that opens the pyranose ring leading to the acyclic photoenol II, which subsequently undergoes an intramolecular aldol cyclization reaction. The photoelimination implies an 1,5-HAT of the H8 by the excited innermost carbonyl of the *a*-diketone, followed by *b*-fragmentation of the 1,4-biradical intermediate I. The Norrish type II photoelimination, although very common in monoketones,[1a] is extremely rare in *a*-diketones, in which only a few synthetically irrelevant examples are documented.[29] 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.[30]

The distance between the carbonyl oxygen and the *g*-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.[31] It is not surprising, therefore, that the hydrogen abstraction is strongly dependent on the pyra- nose ring conformation of the *a-C*-glycoside: favored when a $^7C_4$ chair is adopted and highly disfavored in $^4C_7$ arrange- ments.

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.[32] According to Baldwin rules[33] 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



Scheme 4. Thermal kinetic studies with 50 and [D$_1$]50.

enophile and ene unit, respectively (Scheme 4).[34] 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.[36] 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.[37] Mechanistic studies of the ene-reaction have demonstrated that a large deuterium kinetic isotope effect (KIE; $k_H/k_D > 2$) indicates that the INHAT is the rate-limiting step and has often been taken as evidence of a concerted mechanism.[38] 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_H) and deuterated [D$_1$]50 (k_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_H/k_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).[10,39] 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 α-diketone moiety avoiding secondary photolysis.[40]

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 5α-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-*b*-*syn* cyclizations. The influence of this substituent is confirmed in the 5-deoxy-d-*gluco* derivative (38), in which an equimolecular mixture of OH-*b*-*syn* and OH-α-*syn* isomers was formed. Inversion of configuration at C5 in d-*manno* derivative (58) entails a more crowded *b*-face of the transition-state (TS) ring with exclusive formation of the OH-α-*syn* isomer. This effect is also observed in d-*galacto* derivatives (59–61), thus leading preferentially to a majority of OH-α-*syn* cyclization products.

Degradation of the masked α-diketones could be realized under oxidative conditions by using two different methodologies: With periodic acid in methanol (Method A)[41] or by *b*-fragmentation of the alkoxyl radical, generated from the hemiketal alcohol by reaction with the PhI(OAc)$_2$/I$_2$ system (Method B)[42] as depicted in Table 5. With method A the yields 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).

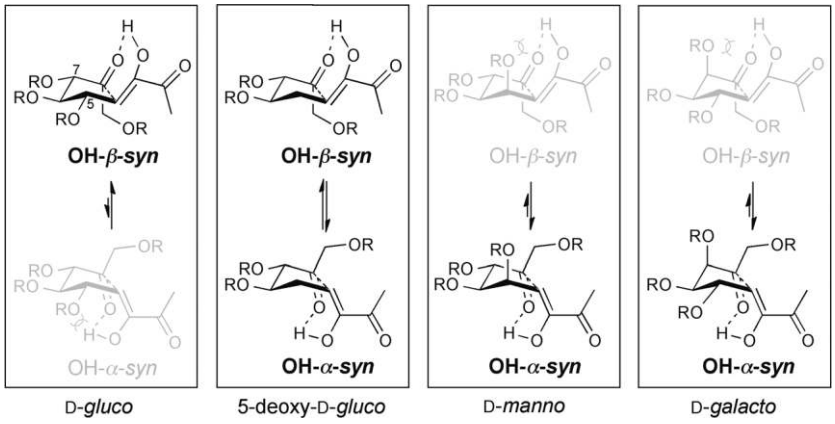
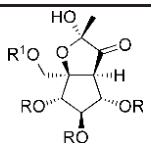
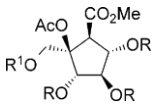
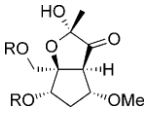
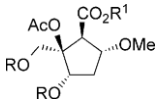
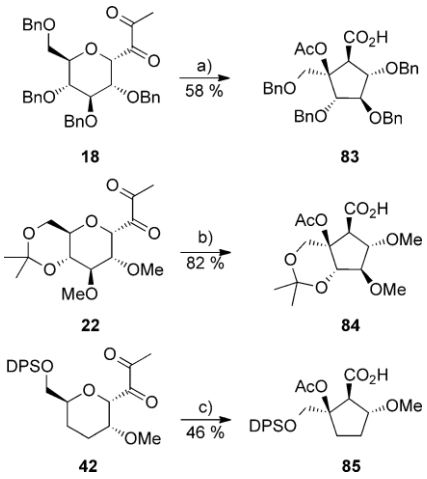


Figure 1. Proposed models for the stereochemical course of the aldol reaction. The transition state (TS) of the major isomer is highlighted.

Table 5. Synthesis of cyclopentitols.

Entry	Substrate	Method [%][a,b]	Product
			
1	2: R = R^1 = Me	A (85)[c]	76: R = R^1 = Me
2	25: R = R^1 = Bn	A (65)[c]	77: R = R^1 = Bn
3	26: R = Bn, R^1 = DPS	A (42)[c]	78: R = Bn, R^1 = DPS
			
4	46: R = Me	A (90)	79: R = Me, R^1 = H
5	46: R = Me	A (67),[c] B (69)[c]	80: R = Me, R^1 = Me
6	47: R = DPS	B (82)	81: R = DPS, R^1 = H
7	47: R = DPS	A (26),[c] B (60)[c]	82: R = DPS, R^1 = Me

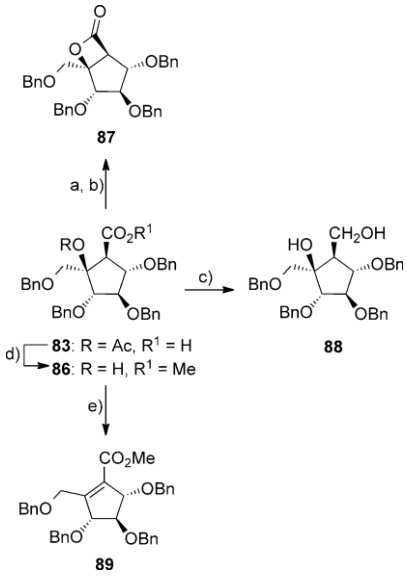
[a] Method A: $H_5IO_6 \cdot 2H_2O$, MeOH, room temperature; Method B: $PhI(OAc)_2$, I_2, *h*n, room temperature. [b] Yield of the product isolated by using chromatography. [c] Methylation with diazomethane.



Scheme 5. Synthesis of cyclopentitols from 2,3-diuloses in a one-pot, three-step sequence. a) Daylight-lamp irradiation, C_6D_6, 30 °C, 4 h, then $H_5IO_6 \cdot 2H_2O$, MeOH, room temperature, 3 h; b) daylight-lamp irradiation, C_6D_6, 36–40 °C, 2.5 h, then $PhI(OAc)_2$, I_2, *h*n, room temperature, 40 min; c) daylight-lamp irradiation, C_6D_6, 36–40 °C, 5 h, then $H_5IO_6 \cdot 2H_2O$, 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. *a*-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 *a*-hydroxyester 86 whose relative disposition was



Scheme 6. Some initial experiments on the reactivity of cyclopentitols. a) KOH, MeOH, room temperature, 24 h; b) $PhSO_2Cl$, Py, 0 °C, 14 h, 73 %, two-step; c) $LiAlH_4$, THF, 0 °C 4 h, 78 %; d) KOH, MeOH, room temperature, 24 h, then CH_2N_2, 99 %; e) Tf_2O, CH_2Cl_2, Py, 0 °C, 24 h, 93 %.

confirmed by dehydration to give the *a,b*-unsaturated ester 89. The *b*-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 $LiAlH_4$ afforded the diol 88 spectroscopically identical to the one synthesized by Chiara et al.[43]

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 one- pot 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 modifi- cations 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 syn- thetic application of the Norrish type II photoelimination in- itiated by the innermost carbonyl of a *a*-diketone. The im- portance of this reaction is that it uniquely generates an acy- clic keto–enol system, which is ideally suited for a subse- quent 5-(enol*exo*)-*exo-trig* intramolecular aldol cyclization. This thermal uncatalyzed aldol reaction in which a *Z* photo- enol 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-*b-syn* products, whereas an inverted OH-*a-syn* cyclization is observed for the d-*manno* series of carbohydrates.

Experimental Section

General procedure for the oxidation of *C*-propynyl glycosides to a-diketones: *Method A*: A solution of *C*-propynyl glycoside (1 equiv) in dry CH_2Cl_2 (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: $NaIO_4$ (3–4 equiv) and $RuO_2 \cdot x\,H_2O$ (3–12 mg) were added to a solution of *C*-propynyl glycoside (1 equiv) in CCl_4/CH_3CN/H_2O (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_2Cl_2, dried over anhydrous Na_2SO_4, 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_3SnCH_2CTMS (1.49 g, 3.86 mmol) was added to a solution of 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 mL, 4.83 mmol) was then added dropwise and the stirring continued for 3 h. The mixture was diluted with CH_2Cl_2 (32 mL), neutralized with Et_3N, 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 Na_2SO_4 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: $[\alpha]_D$ = + 130 $cm^3g^{-1}dm^{-1}$ (c = 3.53 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.18 (s, 9H), 3.16 (dd, J = 9.3, 9.8 Hz, 1H), 3.23 (dd, J = 5.6, 9.5 Hz, 1H), 3.39 (s, 3H), 3.43 (dd, J = 9.3, 9.3 Hz, 1H), 3.46 (s, 3H), 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, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = —0.1 (3 × CH_3), 58.5 (CH_3), 59.1 (CH_3), 60.4 (CH_3), 60.7 (CH_3), 66.5 (CH), 71.2 (CH_2), 73.1 (CH), 79.2 (CH), 80.7 (CH), 84.3 (CH), 94.8 (C), 99.7 ppm (C); IR (film): $\tilde{\nu}$ = 2931, 2190, 844 cm^{-1}; MS (EI): *m/z* (%): 316 (< 1) [M^+], 301 (< 1); HRMS (EI): *m/z*: calcd for $C_{15}H_{28}O_5Si$: 316.1706 [M^+]; found 316.1701; elemental analysis calcd (%) for $C_{15}H_{28}O_5Si$ (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 (1 n, 3.9 mL) was added to a solution of 5 (652 mg, 2.06 mmol) in CH_2Cl_2/MeOH (5:1, 72 mL). The mixture was stirred at room temperature for 2 h, neutralized with a solution of HCl 1 n and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, 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 $cm^3g^{-1}dm^{-1}$ (c = 1.64 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 58.4 (CH_3), 58.8 (CH_3), 60.1 (CH_3), 60.4 (CH_3), 65.6 (CH), 70.9 (CH), 73.1 (CH_2), 77.3 (CH), 77.8 (C), 78.8 (CH), 80.4 (CH), 84.1 ppm (CH); IR (film): $\tilde{\nu}$ = 3254, 2933, 2112 cm^{-1}; MS (EI): *m/z* (%): 244 (< 1) [M^+], 199 (7); HRMS (EI): *m/z* calcd for $C_{12}H_{20}O_5$: 244.1311 [M^+]; found: 244.1306; elemental analysis calcd (%) for $C_{12}H_{20}O_5$ (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 mL, 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_4Cl, 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 $cm^3g^{-1}dm^{-1}$ (c = 2.15 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.31 (dd, J = 9.8, 9.2 Hz, 1H), 3.33 (dd, J = 9.5, 5.6 Hz, 1H), 3.40 (s, 3H), 3.51 (s, 3H), 3.53 (dd, J = 9.3, 9.3 Hz, 1H), 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, 1H), 5.06 (d, J = 5.6 Hz, 1H), 7.30 (m, 3H), 7.46 ppm (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 59.0 (CH_3), 59.6 (CH_3), 60.8 (CH_3), 61.1 (CH_3), 67.0 (CH), 71.7 (CH_2), 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^{-1}; 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^+—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-2-ulose (9): Prepared from 8 (82 mg, 0.25 mmol) following the general procedure (Method A) using dimethyl sulfide (40 mL, 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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, 1H), 5.67 (d, J = 7.4 Hz, 1H), 6.96 (m, 2H), 7.07 (m, 1H), 7.98 ppm (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 58.5 (CH_3), 59.0 (CH_3), 59.9 (CH_3), 60.1 (CH_3), 71.8 (CH_2), 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 × CH), 190.8 (C), 203.7 ppm (C); IR (film): $\tilde{\nu}$ = 1716, 1672, 1450 cm^{-1}; MS (EI): *m/z* (%): 352 (2) [M^+], 247 (4), 219 (18); HRMS (EI): *m/z* calcd for $C_{18}H_{24}O_7$: 352.1522 [M^+]; 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 ^{1}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[45] (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 mmol) following the general procedure (Method A) using dimethyl sulfide (40 mL, 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. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 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); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 23.3 (CH_3), 59.1 (CH_3), 59.2 (CH_3), 59.8 (CH_3), 60.1 (CH_3), 71.5 (CH_2), 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^{-1}; MS (EI): *m/z* (%): 290 (< 1) [M^+], 247

(2); HRMS (EI): *m/z* calcd for $C_{13}H_{22}O_7$: 290.1366 [M^+]; 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*]furan-3(3a*H*)-one (2) (41 mg, 0.14 mmol, 52 % from 7) as a crystalline solid. M.p. 96.6–97.2 °C (*n*-hexane/EtOAc); $[\alpha]_D$ = + 138 cm^3 g^{-1} dm^{-1} (*c* = 1.22 in $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6; 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): δ = 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, 3 H), 3.25 (s, 6 H), 3.30 (d, *J* = 10.6 Hz, 1 H), 3.49 (d, *J* = 10.3 Hz, 1 H), 3.64 (complex signal, d, *J* = 8.2 Hz, 1 H), 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); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.41 (d, *J* = 0.9 Hz, 3 H), 3.08 (d, *J* = 4.1 Hz, 1 H), 3.42 (s, 3 H), 3.46 (s, 3 H), 3.48 (s, 3 H), 3.50 (s, 3 H), 3.58 (d, *J* = 10.4 Hz, 1 H), 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, 1 H), 3.71 (d, *J* = 10.4 Hz, 1 H), 5.05 ppm (br d, *J* = 0.9 Hz, 1 H, OH); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 21.1 (CH_3), 51.2 (CH), 57.5 (CH_3), 58.1 (CH_3), 58.7 (CH_3), 59.0 (CH_3), 74.2 (CH_2), 84.2 (CH), 87.6 (C), 88.4 (CH), 90.8 (CH), 99.7 (C), 208.1 ppm (C); IR (film): $\tilde{\nu}$ = 3337, 2949, 2836, 1760 cm^{-1}; MS (FAB): *m/z* (%): 290 (2) [M^+], 273 (100); HRMS (FAB): *m/z*: calcd for $C_{13}H_{22}O_7$: 290.1366 [M^+]; found: 290.1372; elemental analysis calcd (%) for $C_{13}H_{22}O_7$ (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_t = 290.31, orthorhombic, space group $P2_12_12_1$, a = 7.9261(6) Å, b = 9.2758(8) Å, c = 19.6176(17) Å, b = 90 °, V = 1442.3(2) Å^3, Z = 4, 1_{calcd} = 1.337 mg m^{-3}, $m(Mo_{K\alpha})$ = 0.71073 Å, $F(000)$ = 624, T = 123 (2) K, colorless crystal, 0.45 × 0.20 × 0.12 mm^3, collected reflections 12 479. 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_o| > 2s(|F_o|)) 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 ^{1}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 $NaIO_4$ (107 mg, 0.5 mmol) and $RuO_2 \cdot x\ H_2O$ (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: $[\alpha]_D$ = + 52 cm^3 g^{-1} dm^{-1} (*c* = 0.65 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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* = 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, 2 H), 5.56 (d, *J* = 7.4 Hz, 1 H), 7.09–7.30 ppm (m, 20 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 23.5 (CH_3), 68.9 (CH_2), 72.4 (CH), 73.4 (CH_2), 74.0 (CH_2), 74.5 (CH_2), 74.6 (CH), 74.9 (CH_2), 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^{-1}; 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 $C_{37}H_{38}O_7$ (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 gel column chromatography (hexanes/EtOAc 9:1), to give (2*S*,3a*S*,4*S*,5*R*,6*S*,6a*R*)-4,5,6-tris(benzyloxy)-6a-[(benzyloxy)methyl]-2-hydroxy-2-methyltetrahydro-2*H*-cyclopenta[*b*]furan-3(3a*H*)-one (25) (17 mg, 0.029 mmol, 58 %) as a colorless oil: $[\alpha]_D$ = + 31 cm^3 g^{-1} dm^{-1} (*c* = 0.9 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (s, 3 H), 3.21 (m, 1 H), 3.77 (d, *J* = 10.6 Hz, 1 H), 3.89 (d, *J* = 10.6 Hz, 1 H), 3.94 (m, 1 H), 4.00 (m, 2 H), 4.57–4.76 (m, 8 H), 5.09 (s, 1 H), 7.23–7.39 ppm (m, 20 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.6 (CH_3), 51.6 (CH), 71.8 (CH_2), 72.0 (CH_2), 72.6 (CH_2), 73.3 (CH_2), 74.3 (CH_2), 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 cm^{-1}; MS (EI): *m/z* (%): 594 (< 1) [M^+], 576 (< 1); HRMS (EI): *m/z* calcd for $C_{37}H_{38}O_7$: 594.2618 [M^+]; found: 594.2615; elemental analysis calcd (%) for $C_{37}H_{38}O_7$ (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 $NaIO_4$ (36 mg, 0.168 mmol) and $RuO_2 \cdot x\ H_2O$ (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: $[\alpha]_D$ = + 36 cm^3 g^{-1} dm^{-1} (*c* = 1.87 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07 (s, 9 H), 2.09 (s, 3 H), 3.81 (m, 2 H), 3.92 (dd, *J* = 11.7, 3.2 Hz, 1 H), 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); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.3 (C), 23.6 (CH_3), 26.5 (3 × CH_3), 62.9 (CH_2), 72.1 (CH), 74.2 (CH_2), 74.7 (CH_2), 75.2 (CH_2), 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^{-1}; 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 $C_{46}H_{50}O_7Si$ (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 $CDCl_3$ (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 (3a*S*,4*S*,5*R*,6*S*,6a*R*)-4,5,6-tris(benzyloxy)-6a-[(*tert*-butyldiphenylsilyl)oxy]-methyl-2-hydroxy-2-methyltetrahydro-2*H*-cyclopenta[*b*]furan-3(3a*H*)-one (26) as a mixture of isomers (26 mg, 0.035 mmol, d.r. 5:1, 65 %) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$; complex spectrum, only clearly distinguished signals are reported): δ = major isomer 1.08 (s, 9 H), 1.44 (s, 3 H), 3.29 (d, *J* = 4.5 Hz, 1 H), 5.09 ppm (s, 1 H); minor isomer 1.02 (s, 9 H), 1.49 (s, 3 H), 3.31 ppm (d, *J* = 3.7 Hz, 1 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) (complex spectrum, only clearly distinguished signals are reported): δ (major isomer) = 19.1 (C), 20.3 (CH_3), 26.8 (3 × CH_3), 50.9 (CH), 66.0 (CH_2), 88.8 (C), 99.1 (C), 207.8 ppm (C); δ (minor isomer) = 19.2 (C), 22.6 (CH_3), 26.8 (3 × CH_3), 53.4 (CH), 65.1 (CH_2), 88.8 (C), 100.1 (C), 210.7 ppm (C); IR (film): $\tilde{\nu}$ = 3374, 2928, 1765 cm^{-1}; MS (ESI$^+$): *m/z* (%): 765 (100) [M^++Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{46}H_{50}NaO_7Si$: 765.3224 [M^++Na]; found: 765.3226; elemental analysis calcd (%) for $C_{46}H_{50}O_7Si$ (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 $NaIO_4$ (116 mg, 0.542 mmol) and $RuO_2 \cdot x\ H_2O$ (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 cm^3 g^{-1} dm^{-1} (*c* = 0.62 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.05 (s, 3 H), 2.12 (s, 3 H), 3.49 (dd, *J* = 9.8, 7.2 Hz, 1 H), 3.80 (dd, *J* = 7.9, 7.2 Hz, 1 H), 4.07 (dd, *J* = 7.8, 7.2 Hz, 1 H), 4.21 (dd, *J* = 12.2, 4.8 Hz, 1 H), 4.33 (dd, *J* = 12.2, 2.1 Hz, 1 H), 4.45 (ddd, *J* = 9.8, 4.8, 2.1 Hz, 1 H), 4.503 (d, *J* = 10.6 Hz, 1 H), 4.506 (d, *J* = 11.1 Hz, 1 H), 4.59 (d, *J* = 10.6 Hz, 1 H), 4.74 (d, *J* = 10.9 Hz, 1 H), 4.76 (d, *J* = 11.4 Hz, 1 H), 4.81 (d, *J* = 11.3 Hz, 1 H), 5.57 (d, *J* = 7.2 Hz, 1 H), 7.10–7.35 ppm (m, 15 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.8

(CH_3), 23.5 (CH_3), 63.4 (CH_2), 72.6 (CH), 72.9 (CH), 73.9 (CH_2), 74.1 (CH_2), 74.6 (CH_2), 76.8 (CH), 78.1 (CH), 80.2 (CH), 127.8–128.5 (15× CH), 136.7 (C), 137.6 (C), 137.9 (C), 170.8 (C), 197.2 (C), 199.6 ppm (C); IR (film): $\tilde{\nu}$= 2928, 1735 cm^{-1}; MS (EI): *m/z* (%): 546 (2) [M^+], 475 (1); HRMS (EI): *m/z* calcd for $C_{32}H_{34}O_8$: 546.2254 [M^+]; found: 546.2236; elemental analysis calcd (%) for $C_{32}H_{34}O_8$ (546.61): C 70.31, H 6.27; found: C 70.34, H 6.27.

Photocyclization of 20: A deoxygenated solution of diketone 20 (35 mg, 0.064 mmol) in purified $CDCl_3$ (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 (3a*S*,4*S*,5*R*,6-*S*,6a*R*)-4,5,6-tris(benzyloxy)-6a-(acetyloxy)methyl-2-hydroxy-2-methyltetrahydro-2*H*-cyclopenta[*b*]furan-3(3a*H*)-one (27) a colorless oil as a mixture of isomers (23.5 mg, 0.043 mmol, d.r., 1:0.9, 67%): ^{1}H NMR (500 MHz, $CDCl_3$; complex spectrum, only clearly distinguished signals are reported): δ= 1.35 (s, 3H), 1.42 (s, 3H), 2.03 (s, 3H), 2.09 (s, 3H), 3.07 (d, *J*= 1.9 Hz, 1H), 3.11 (d, *J*= 3.2 Hz, 1H), 3.92 ppm (d, *J*= 5.4 Hz, 1H); ^{13}C NMR (100.6 MHz, C_6D_6; complex spectrum, only clearly distinguished signals are reported): δ= 20.8 (CH_3), 20.9 (CH_3), 21.5 (CH_3), 22.5 (CH_3), 52.7 (CH), 54.9 (CH), 65.8 (CH_2), 65.9 (CH_2), 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^{-1}; 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 $C_{32}H_{34}O_8$ (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 $NaIO_4$ (103 mg, 0.481 mmol) and $RuO_2 \cdot x\,H_2O$ (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 $cm^3g^{-1}dm^{-1}$ (*c* = 2.32 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 2.12 (s, 3H), 3.34 (dd, *J*= 13.3, 5.0 Hz, 1H), 3.51 (dd, *J*= 9.8, 7.2 Hz, 1H), 3.55 (dd, *J*= 13.3, 2.4 Hz, 1H), 3.77 (dd, *J*= 8.0, 7.4 Hz, 1H), 4.08 (dd, *J*= 8.2, 7.4 Hz, 1H), 4.43 (ddd, *J*= 9.7, 4.6, 2.1 Hz, 1H), 4.50–4.82 (m, 6H), 5.60 (d, *J*= 7.2 Hz, 1H), 7.18–7.37 ppm (m, 15H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ= 23.5 (CH_3), 51.7 (CH_2), 72.6 (CH), 74.0 (CH), 74.1 (CH_2), 74.3 (CH_2), 74.7 (CH_2), 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): $\tilde{\nu}$= 2925, 2099, 1731, 1715 cm^{-1}; MS (ESI$^+$): *m/z* (%): 584 (100) [M^++MeOH+Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{31}H_{35}N_3NaO_7$: 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 $CDCl_3$ (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_2O_3, hexanes/EtOAc 8:2) to give the isomeric mixture (3a*S*,4*S*,5*R*,6*S*,6a*R*)-6a-(azidomethyl)-4,5,6-tris(benzyloxy)-2-hydroxy-2-methyltetrahydro-2*H*-cyclopenta[b]furan-3(3a*H*)-one (28) (17 mg, 0.032 mmol, d.r. 1.3:1, 55 %) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ= 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, 1H), 3.78 (d, *J*= 10.6 Hz, 1H), 3.79 (d, *J*= 13.2 Hz, 1H), 3.89 (d, *J*= 4.4 Hz, 1H), 3.90 (d, *J*= 12.9 Hz, 1H), 3.97 (dd, *J*= 3.8, 3.5 Hz, 1H), 3.99 (dd, *J*= 5.4, 4.7 Hz, 1H), 4.07 (dd, *J*= 3.8, 3.8 Hz, 1H), 4.18 (ddd, *J*= 3.5, 2.4, 1.1 Hz, 1H), 4.20 (d, *J*= 4.1 Hz, 1H), 4.41–4.70 (m, 12H), 7.21–7.38 ppm (m, 30H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ= 21.3 (CH_3), 22.6 (CH_3), 52.8 (CH), 54.7 (CH_2), 54.7 (CH), 54.9 (CH_2), 71.6 (CH_2), 71.9 (CH_2), 72.3 (CH_2), 72.7 (CH_2), 73.2 (CH_2), 72.2 (CH_2), 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): $\tilde{\nu}$= 3414, 2105, 1767 cm^{-1}; MS (ESI$^+$): *m/z* (%): 552 (100) [M^++Na]; HRMS (ESI$^+$): *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*-**d**-*ido*-nono-2,3-diulose (22): Prepared from 15 (136.0 mg, 0.50 mmol) following the general procedure (Method A) using dimethyl sulfide (400 mL, 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: $[\alpha]_D$ = + 107 $cm^3g^{-1}dm^{-1}$ (*c* = 0.58 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ= 1.40 (s, 3H), 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, 1H), 5.51 ppm (d, *J*= 7.6 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ= 19.0 (CH_3), 23.4 (CH_3), 29.0 (CH_3), 60.0 (CH_3), 60.3 (CH_3), 62.5 (CH_2), 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 ($CHCl_3$, 0.2 mm): $\tilde{\nu}$= 2999, 1713 cm^{-1}; MS (ESI$^+$): *m/z* (%): 357 (100) [M^++MeOH+Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{15}H_{26}NaO_8$: 357.1525 [M^++MeOH+Na]; found: 357.1526; elemental analysis calcd (%) for $C_{14}H_{22}O_7$ (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 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 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: (2*S*,3a*S*,4*S*,5*R*,5a*S*,9a*R*)-2-hydroxy-4,5-dimethoxy-2,7,7-trimethyltetrahydrofuro[2',3':2,3]cyclopenta[1,2-*d*][1,3]dioxin-3(2*H*)-one) as a colorless oil: $[\alpha]_D$ = + 29 $cm^3g^{-1}dm^{-1}$ (*c* = 0.50, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$;): δ (major isomer) = 1.36 (s, 3H), 1.47 (s, 3H), 1.48 (s, 3H), 2.99 (d, *J*= 2.2 Hz, 1H), 3.30 (s, 3H), 3.42 (s, 3H), 3.76 (dd, *J*= 1.6, 1.3 Hz, 1H), 3.89 (d, *J*= 12.3 Hz, 1H), 3.92 (ddd, *J*= 2.2, 1.6, 1.3 Hz, 1H), 4.05 (d, *J*= 12.3 Hz, 1H), 4.11 ppm (dd, *J*= 1.3, 1.3 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (major isomer) = 22.3 (CH_3), 22.8 (CH_3), 25.5 (CH_3), 54.9 (CH), 56.0 (CH_3), 57.2 (CH_3), 66.4 (CH_2), 79.0 (CH), 87.9 (CH), 88.0 (C), 88.8 (CH), 99.7 (C), 99.8 (C), 210.8 ppm (C); IR ($CHCl_3$, 0.2 mm): $\tilde{\nu}$= 3581, 3016, 1770 cm^{-1}; MS (ESI$^+$): *m/z* (%): 325 (100) [M^++Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{14}H_{22}NaO_7$: 325.1263 [M^++Na]; found: 325.1252; elemental analysis calcd (%) for $C_{14}H_{22}O_7$ (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 mL, 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: $[\alpha]_D$ = + 74 $cm^3g^{-1}dm^{-1}$ (*c* = 0.82 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ= 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, 3H), 3.17 (dd, *J*= 8.5, 8.2 Hz, 1H), 3.38 (s, 3H), 3.51 (s, 3H), 3.55 (dd, *J*= 8.5, 7.3 Hz, 1H), 3.58 (dd, *J*= 9.1, 8.2 Hz, 1H), 3.75 (dd, *J*= 11.7, 3.5 Hz, 1H), 3.81 (dd, *J*= 11.7, 1.9 Hz, 1H), 4.02 (ddd, *J*= 9.2, 3.4, 1.9 Hz, 1H), 5.47 ppm (d, *J*= 7.2 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ= −5.4 (CH_3), −5.1 (CH_3), −5.0 (CH_3), −4.1 (CH_3), 18.1 (C), 18.4 (C), 23.5 (CH_3), 25.90 (3 × CH_3), 25.95 (3 × CH_3), 58.9 (CH_3), 60.6 (CH_3), 62.3 (CH_2), 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^{-1}; 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 $C_{23}H_{46}O_7Si_2$ (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 $CDCl_3$ (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_2O_3, 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: $[\alpha]_D$ = + 54 $cm^3g^{-1}dm^{-1}$ (*c* = 2.10 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ= 0.091 (s, 3H), 0.099 (s, 3H), 0.13 (s, 3H), 0.14 (s, 3H), 0.89 (s, 9H), 0.92

(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, 1 H), 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); ^{13}C NMR (100.6 MHz, $CDCl_3$): d = —5.7 (CH_3), —5.6 (CH_3), —5.1 (CH_3), —4.8 (CH_3), 18.0 (C), 18.4 (C), 20.3 (CH_3), 25.6 (3 × CH_3), 25.8 (3 × CH_3), 51.3 (CH), 57.6 (CH_3), 58.4 (CH_3), 65.9 (CH_2), 81.6 (CH), 72.1 (CH), 84.5 (CH), 89.4 (CH), 90.1 (CH), 98.7 (CH), 208.5 ppm (C); IR (film): $\tilde{\nu}$= 3368, 2931, 1765 cm^{-1}; MS (EI): *m/z* (%): 473 (2) [M^+ —OH], 433 (7); HRMS (EI): *m/z* calcd for $C_{23}H_{45}O_6Si_2$: 473.2755 [M^+ —OH]; found: 473.2761; elemental analysis calcd (%) for $C_{23}H_{46}O_7Si_2$ (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 *m*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: $[a]_D$ = + 76 cm^{3}g^{-1}dm^{-1} (c = 0.59 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): d = 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, 1H), 3.50 (s, 3H), 3.65 (dd, J= 11.4, 4.7 Hz, 1H), 3.74 (dd, J= 11.4, 3.2 Hz, 1H), 3.80 (dd, J= 6.8, 6.6 Hz, 1H), 4.16 (ddd, J= 8.8, 4.7, 3.2 Hz, 1H), 4.96 (dd, J= 8.8, 6.6 Hz, 1H), 5.47 ppm (d, J= 6.6 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): d=—5.5 (2 × CH_3), 18.3 (C), 21.0 (CH_3), 23.5 (CH_3), 25.8 (3 × CH_3), 58.9 (CH_3), 59.6 (CH_3), 63.0 (CH_2), 68.8 (CH), 72.9 (CH), 74.6 (CH), 79.6 (2 × CH), 169.7 (C), 197.1 (C), 198.5 ppm (C); IR ($CHCl_3$, 0.2 mm): $\tilde{\nu}$= 2933, 1738, 1715 cm^{-1}; MS (ESI$^+$): *m/z* (%): 473 (100) [M^++MeOH+Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{20}H_{38}NaO_9Si$: 473.2183 [M^++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: (2*S*,3a*S*,4*S*,5*R*,6*S*,6a*R*)-6a-[(*tert*-butyldimethylsilyl)oxy]- methyl-5-ethoxy-2-hydroxy-4-methoxy-2-methyl-3-oxohexahydro-2*H*-cyclopenta[*b*]furan-6-yl acetate) as a colorless oil: [a] = +56 cm^{3}g^{-1}dm^{-1} (c = 0.59 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): d (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, 1H), 3.34 (s, 3H), 3.38 (s, 3H), 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, 1H), 4.91 (d, J= 1.0 Hz, 1H), 5.21 ppm (dd, J= 2.5, 1.0 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): d (major isomer) =—5.64 (CH_3), —5.55 (CH_3), 18.4 (C), 20.0 (CH_3), 20.8 (CH_3), 25.8 (3 × CH_3), 52.7 (CH), 57.2 (CH_3), 57.3 (CH_3), 64.7 (CH_2), 80.5 (CH), 86.46 (CH), 86.58 (CH), 90.7 (C), 98.7 (C), 169.6 (C), 207.0 ppm (C); IR ($CHCl_3$, 0.2 mm): $\tilde{\nu}$= 2933, 1766, 1742 cm^{-1}; MS (ESI$^+$): *m/z* (%): 441 (100) [M^++Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{19}H_{34}NaO_8Si$: 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-**d**-*manno*-nono-2,3-diulose (38): Prepared from 32 (70 mg, 0.155 mmol) following the general procedure (Method B) using $NaIO_4$ (132 mg, 0.62 mmol) and $RuO_2 \cdot x\,H_2O$ (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 cm^{3}g^{-1}dm^{-1} (c = 0.94 in $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6): d = 1.18 (s, 9 H), 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 ppm (m, 10H); ^{13}C NMR (125.7 MHz, C_6D_6): d = 19.5 (C), 24.4 (CH_3), 27.0 (3 × CH_3), 28.6 (CH_2), 56.6 (CH_3), 59.7 (CH_3), 63.6 (CH_2), 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^{-1}; MS (ESI$^+$): *m/z* (%): 539 (100) [M^++MeOH+Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{28}H_{40}NaO_7Si$: 539.2441 [M^++MeOH+Na]; found: 539.2440; elemental analysis calcd (%) for $C_{27}H_{36}O_6Si$ (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 ^{1}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_2Cl_2 (0.82 mL) cooled to 0 °C and acetylated by adding Ac_2O (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*,5*R*,6*S*,6a*R*)-6a-[(*tert*-butyldiphenylsilyl)oxy]methyl-5,6-dimethoxy-2-methyl-3-oxohexahydro-2*H*-cyclopenta[*b*]furan-2-yl acetate (44) and (2*S*,3a*R*,5*R*,6*S*,6a*S*)-6a-[(*tert*-butyldiphenylsilyl)oxy]methyl-5,6-dimethoxy-2-methyl-3-oxohexahydro-2*H*-cyclopenta[*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: ^{1}H NMR (500 MHz, C_6D_6): d = 1.25 (s, 9H), 1.75 (s, 3H), 2.85 (s, 3H), 3.00 (s, 3H), 4.70 (d, J = 18.6 Hz, 1 H), 4.82 (d, J = 18.6 Hz, 1 H), 5.28 (dd, J = 7.5, 7.5 Hz, 1 H), 6.66 ppm (br s, 1 H, OH); ^{13}C NMR (125.7 MHz, C_6D_6): d = 19.6 (C), 22.3 (CH_3), 27.0 (3 × CH_3), 57.6 (CH_3), 59.3 (CH_3), 69.5 (CH_2), 111.6 (CH), 149.2 (C), 193.9 (C), 207.5 ppm (C).

Compound 44: colorless oil. $[a]_D$ =—2 cm^{3}g^{-1}dm^{-1} (c = 0.54 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): d = 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); ^{13}C NMR (100.6 MHz, $CDCl_3$): d = 19.3 (C), 20.7 (CH_3), 23.0 (CH_3), 26.9 (3 × CH_3), 31.7 (CH_2), 46.4 (CH), 56.4 (CH_3), 58.9 (CH_3), 64.4 (CH_2), 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): $\tilde{\nu}$= 2928, 1766, 1743 cm^{-1}; MS (ESI$^+$): *m/z* (%): 549 (100) [M^++Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{29}H_{38}NaO_7Si$: 549.2285 [M^++Na]; found: 549.2285; elemental analysis calcd (%) for $C_{29}H_{38}O_7Si$ (526.69): C 66.13, H 7.27; found: C 66.40, H 7.61.

Compound 45: colorless oil, $[a]_D$ =—15 cm^{3}g^{-1}dm^{-1} (c = 0.56 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): d = 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); ^{13}C NMR (100.6 MHz, $CDCl_3$): d = 19.3 (C), 20.5 (CH_3), 21.9 (CH_3), 26.9 (3 × CH_3), 30.4 (CH_2), 46.8 (CH), 57.5 (CH_3), 59.5 (CH_3), 65.4 (CH_2), 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^{-1}; MS (ESI$^+$): *m/z* (%): 549 (100) [M^++Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{29}H_{38}NaO_7Si$: 549.2285 [M^++Na]; found: 549.2288; elemental analysis calcd (%) for $C_{29}H_{38}O_7Si$ (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 *m*L, 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 to 6:4) to give 39 (83 mg, 0.315 mmol, 65 %) as a yellow oil: $[a]_D$ = + 126 cm^{3}g^{-1}dm^{-1} (c = 1.3 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): d = 1.72 (ddd, J = 13.2, 8.8, 7.6 Hz, 1 H), 2.19 (ddd, J = 13.2, 5.1, 3.8 Hz, 1 H), 2.26 (s, 3 H), 3.27 (s, 3 H), 3.35 (s, 3 H), 3.36 (m, 1 H), 3.40 (s, 3 H), 3.55 (dd, J = 10.7, 4.7 Hz, 1 H), 3.64 (dd, J = 10.7, 2.2 Hz, 1 H), 3.87 (ddd, J = 10.7, 6.6, 3.8 Hz, 1 H), 4.10 (ddd, J = 9.2, 4.7, 2.2 Hz, 1 H), 5.38 ppm (d, J = 6.9 Hz, 1 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): d = 23.4 (CH_3), 28.7 (CH_2), 56.8 (CH_3), 56.9 (CH_3),

59.2 (CH_3), 72.1 (CH_2), 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^{-1}; MS (EI): *m/z* (%): 260 (< 1) [M^+]; HRMS (EI): *m/z*: calcd for: 260.1260 [M^+]; found: 260.1261; elemental analysis calcd (%) for $C_{12}H_{20}O_6$ (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 ^{1}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_2O_3, hexanes/EtOAc 9:1!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 ^{1}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_2O_3, hexanes/EtOAc 9:1!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*]furan-3(3a*H*)-one (**46**) (20 mg, 0.077 mmol, 59 %) as a colorless oil. $[\alpha]_D$ = + 139 $cm^3g^{-1}dm^{-1}$(*c* = 1.01 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.35 (d, *J* = 0.95 Hz, 3H, 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, 1H), 3.35 (s, 3H), 3.37 (s, 3H), 3.48 (s, 3H), 3.75 (d, *J* = 10.1 Hz, 1H), 3.76 (dd, *J* = 5.0, 3.4 Hz, 1H), 3.78 (d, *J* = 10.4 Hz, 1H), 3.79 (ddd, *J* = 5.7, 2.5, 2.5 Hz, 1H), 5.35 ppm (d, *J* = 0.9 Hz, 1H, OH); ^{1}H NMR (500 MHz, C_6D_6): δ = 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, 1H), 2.70 (s, 3H), 2.98 (s, 3H), 3.13 (s, 3H), 3.18 (d, *J* = 2.8 Hz, 1H), 3.507 (dd, *J* = 5.0, 5.0 Hz, 1H), 3.513 (d, *J* = 10.4 Hz, 1H), 3.54 (d, *J* = 10.4 Hz, 1H), 3.66 (ddd, *J* = 6.3, 3.8, 2.8 Hz, 1H), 5.47 ppm (br s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.1 (CH_3), 35.4 (CH_2), 55.8 (CH), 57.3 (CH_3), 57.8 (CH_3), 59.5 (CH_3), 73.9 (CH_2), 84.5 (CH), 87.5 (CH), 91.2 (C), 98.7 (C), 210.1 ppm (C); ^{13}C NMR (125.7 MHz, C_6D_6): δ = 21.6 (CH_3), 35.8 (CH_2), 55.6 (CH), 56.8 (CH_3), 57.1 (CH_3), 58.7 (CH_3), 74.3 (CH_2), 83.4 (CH), 87.6 (CH), 91.6 (C), 99.6 (C), 209.6 ppm (C); IR (film): $\tilde{\nu}$ = 3348, 2936, 1760 cm^{-1}; MS (ESI$^+$): *m/z* (%): 283 (100) [M^++Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{12}H_{20}NaO_6$: 283.1158 [M^++Na]; found: 283.1147; elemental analysis calcd (%) for $C_{12}H_{20}O_6$ (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 *m*L, 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!9:1) to give **40** (81.4 mg, 0.11 mmol, 77 %) as a yellow oil: $[\alpha]_D$ = + 57.9 $cm^3g^{-1}dm^{-1}$(*c* = 0.95 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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, 1H), 2.25 (s, 3H), 3.10 (s, 3H), 3.44 (ddd, *J* = 10.4, 6.9, 4.6 Hz, 1H), 3.75 (dd, *J* = 11.2, 4.9 Hz, 1H), 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, 1H), 5.30 (d, *J* = 6.7 Hz, 1H), 7.27–7.42 (m, 12H), 7.61–7.64 ppm (m, 8H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 19.2 (C), 19.3 (C), 23.5 (CH_3), 26.8 (6 × CH_3), 34.0 (CH_2), 56.9 (CH_3), 63.9 (CH_2), 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 ($CHCl_3$, 0.2 mm): $\tilde{\nu}$ = 2933, 1714 cm^{-1}; MS (EI): *m/z* (%): 708 (< 1) [M^+], 651 (18), 135 (100); HRMS (EI): *m/z* calcd for $C_{42}H_{52}O_6Si_2$: 708.3302 [M^+]; found: 708.3286; elemental analysis calcd (%) for $C_{42}H_{52}O_6Si_2$ (709.03): C 71.15, H 7.39; found: C 71.48, H 7.00.

(3*Z*,5*R*,7*S*)-7,9-Bis[(*tert*-butyldiphenylsilyl)oxy]-3-hydroxy-5-methoxy-3-nonene-2,8-dione (**50**): A deoxygenated solution of diketone **40** (56 mg, 0.079 mmol) in purified $CDCl_3$ (0.6 mL), was placed in a resonance tube and irradiated with a daylight lamp at 15–20 °C. The reaction was monitored by ^{1}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. $[\alpha]_D$ = + 32.3 $cm^3g^{-1}dm^{-1}$ (*c* = 1.28 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ = 0.94 (s, 9H), 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, 1H), 2.24 (s, 3H), 3.03 (s, 3H), 4.20 (d, *J* = 17.7 Hz, 1H), 4.38 (dd, *J* = 6.3, 2.2 Hz, 1H), 4.52 (ddd, *J* = 10.8, 8.0, 2.7 Hz, 1H), 4.53 (d, *J* = 17.9 Hz, 1H), 5.34 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.49 (d, *J* = 1.3 Hz, 1H), 7.16–7.34 (m, 10H), 7.43–7.57 ppm (m, 10H); ^{13}C NMR (125.7 MHz, $CDCl_3$, 20 °C): δ = 19.18 (C), 19.21 (C), 23.1 (CH_3), 26.7 (3 × CH_3), 26.9 (3 × CH_3), 34.5 (CH_2), 56.7 (CH_3), 68.3 (CH_2), 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 ($CHCl_3$, 0.2 mm): $\tilde{\nu}$ = 3441, 2246, 1733, 1684, 1661 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 271 (sh) (3055), 264 (3841), 261 (3877), 255 (sh) (3441), 227 (5628 $mol^{-1}m^3cm^{-1}$); MS (EI): *m/z* (%): 665 (< 1) [M^+—Ac], 651 (4), 135 (100); HRMS (ESI$^+$): *m/z* calcd for $C_{42}H_{52}NaO_6Si_2$: 731.3200 [M^++Na]; found: 731.3198; elemental analysis calcd (%) for $C_{42}H_{52}O_6Si_2$ (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 [D_6]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 (1 H, 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_1]**50** (11.5 mg, 0.016 mmol) dissolved in [D_6]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_H/k_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_H = 5.42 × 10^{-5}, R^2 = 0.999) and [D_1]**50** (k_D = 1.48 × 10^{-5}, R^2 = 0.999).

Photocyclization of **40**: A deoxygenated solution of diketone **40** (19 mg, 0.027 mmol) in dry C_6D_6 (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 ^{1}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-2*H*-cyclopenta[*b*]furan-3(3a*H*)-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 $cm^3g^{-1}dm^{-1}$(*c* = 1.56 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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, 1H), 3.18 (dd, *J* = 2.6, 0.7 Hz, 1H), 3.26 (s, 3H), 3.63 (ddd, *J* = 5.9, 4.7, 2.9 Hz, 1H), 4.00 (d, *J* = 11.7 Hz, 1H), 4.05 (d, *J* = 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); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.1 (C), 19.2 (C), 20.7 (CH_3), 26.7 (3 × CH_3), 26.9 (3 × CH_3), 40.0 (CH_2), 54.8 (CH), 56.8 (CH_3), 66.8 (CH_2), 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 × CH), 209.9 ppm (C); IR ($CHCl_3$, 0.2 mm): $\tilde{\nu}$ = 3672, 3357, 2932, 1763 cm^{-1}; MS (EI): *m/z* (%): 651 (1) [M^+—*t*Bu], 633 (4), 135 (100); HRMS (ESI$^+$): *m/z* calcd for $C_{42}H_{52}NaO_6Si_2$: 731.3200 [M^++Na]; found:

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 *m*L, 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 $cm^3 g^{-1} dm^{-1}$ (*c* = 2.57 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): d = 1.48 (m, 1 H), 1.65 (m, 1 H), 1.75 (m, 1 H), 1.97 (m, 1 H), 2.27 (s, 3 H), 3.27 (s, 3 H), 3.38 (s, 3 H), 3.39–3.43 (m, 2 H), 3.74 (ddd, *J* = 9.2, 6.3, 4.0 Hz, 1 H), 4.44 (m, 1 H), 5.43 ppm (d, *J* = 6.3 Hz, 1 H); ^{13}C NMR (125.7 MHz, $CDCl_3$): d = 23.50 (CH_2), 23.54 (CH_2), 24.1 (CH_2), 56.9 (CH_3), 59.2 (CH_3), 70.6 (CH), 74.1 (CH), 75.0 (CH_2), 76.3 (CH), 197.8 (C), 200.8 ppm (C); IR ($CHCl_3$, 0.2 mm): $\tilde{n}$ = 2934, 1771, 1714, 1099 cm^{-1}; MS (ESI$^+$): *m/z* (%): 253 (100) [M^++Na], 229 (3); HRMS (ESI$^+$): *m/z* calcd for $C_{11}H_{18}NaO_5$: 253.1052 [M^++Na]; found: 253.1042; elemental analysis calcd (%) for $C_{11}H_{18}O_5$ (230.26): C 57.38, H 7.88; found: C 57.30, H 7.85.

(3*E*,5*R*)-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 $CDCl_3$ (0.3 mL), was placed in a resonance tube and irradiated with a daylight lamp at 30–33 °C. The reaction was monitored by ^{1}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 $cm^3 g^{-1} dm^{-1}$ (*c* = 0.32 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): d = 1.89 (m, 1 H), 1.96 (m, 1 H), 2.38 (s, 3 H), 2.50 (ddd, *J* = 17.4, 8.2, 6.1 Hz, 1 H), 2.59 (ddd, *J* = 17.4, 8.2, 6.6 Hz, 1 H), 3.30 (s, 3 H), 3.41 (s, 3 H), 4.01 (s, 2 H), 4.27 (ddd, *J* = 8.3, 7.4, 5.6 Hz, 1 H), 5.48 (dd, *J* = 8.3, 1.2 Hz, 1 H), 6.61 ppm (d, *J* = 1.2 Hz, 1 H); ^{13}C NMR (125.7 MHz, $CDCl_3$): d = 23.1 (CH_3), 28.2 (CH_2), 34.6 (CH_2), 56.9 (CH_3), 59.3 (CH_3), 75.1 (CH), 77.6 (CH_2), 115.5 (CH), 148.8 (C), 194.8 (C), 208.1 ppm (C); IR ($CHCl_3$, 0.2 mm): $\tilde{n}$ = 3435, 2935, 2252, 1731, 1682, 1663, 1350 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (e) = 260 nm (8003 $mol^{-1} m^3 cm^{-1}$); MS (EI): *m/z* (%): 230 (1) [M^+], 213 (1), 199 (1), 198 (12); HRMS (EI): *m/z*: calcd for $C_{11}H_{18}O_5$: 230.1154 [M^+]; found: 230.1153; elemental analysis calcd (%) for $C_{11}H_{18}O_5$ (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_6D_6 (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 ^{1}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_2O_3, hexanes/EtOAc 8:2) to give (2*S*,3a*S*,4*R*,6a*R*)-2-hydroxy-4-methoxy-6a-(methoxymethyl)-2-methyltetrahydro-2*H*-cyclopenta[*b*]furan-3(3a*H*)-one (48) (26.8 mg, 0.12 mmol, 52 %) as a colorless oil: $[a]_D$ = + 101 $cm^3 g^{-1} dm^{-1}$ (*c* = 0.34 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): d = 1.37 (br d, *J* = 1.4 Hz, 3 H), 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); ^{1}H NMR (500 MHz, C_6D_6): d = 1.26–1.35 (m, 1 H), 1.61 (d, *J* = 0.95 Hz, 3 H), 1.58–1.69 (m, 3 H), 2.68 (s, 3 H), 2.83 (d, *J* = 9.8 Hz, 1 H), 2.94 (s, 3 H), 3.04 (br s, 1 H), 3.24 (d, *J* = 9.5 Hz, 1 H), 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, $CDCl_3$): d = 20.4 (CH_3), 29.9 (CH_2), 33.9 (CH_2), 55.4 (CH), 56.4 (CH_3), 59.2 (CH_3), 77.1 (CH_2), 85.7 (CH), 90.1 (C), 98.8 (C), 209.5 ppm (C); IR ($CHCl_3$, 0.2 mm): $\tilde{n}$ = 3364, 2936, 1762, 1094 cm^{-1}; MS (ESI$^+$): *m/z* (%): 285 (28) [M^++MeOH+Na], 253 (100) [M^++Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{11}H_{18}NaO_5$: 253.1052 [M^++Na]; found: 253.1047; elemental analysis calcd (%) for $C_{11}H_{18}O_5$ (230.25): C 57.38, H 7.88; found: C 57.43, H 7.87.

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 $NaIO_4$ (56 mg, 0.26 mmol) and $RuO_2 \cdot x\,H_2O$ (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: $[a]_D$ = + 46 $cm^3 g^{-1} dm^{-1}$ (*c* = 1.53 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): d = 1.06 (s, 9 H), 1.51 (m, 1 H), 1.66 (m, 1 H), 1.88 (m, 1 H), 1.96 (m, 1 H), 2.29 (s, 3 H), 3.27 (s, 3 H), 3.66 (dd, *J* = 10.5, 5.7 Hz, 1 H), 3.72 (ddd, *J* = 5.8, 4.7, 4.1 Hz, 1 H), 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, 4 H); ^{13}C NMR (125.7 MHz, $CDCl_3$): d = 19.2 (C), 23.2 (CH_2), 23.6 (CH_2), 23.7 (CH_3), 26.8 (3 × CH_3), 56.8 (CH_3), 65.8 (CH_2), 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 ($CHCl_3$, 0.2 mm): $\tilde{n}$ = 2936, 1714 cm^{-1}; MS (EI): *m/z* (%): 397 (58) [M^+—*t*Bu], 199 (75); HRMS (EI): *m/z* calcd for $C_{22}H_{25}O_5Si$: 397.1471 [M^+—*t*Bu]; found: 397.1466; elemental analysis calcd (%) for $C_{26}H_{34}O_5Si$ (454.63): C 68.69, H 7.54; found: C 68.61, H 7.60.

(3*Z*,5*R*)-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 $CDCl_3$ (0.3 mL), was placed in a resonance tube and irradiated with a daylight-lamp at 30–35 °C for 3 h. The reaction was monitored by using ^{1}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. $[a]_D$ = + 4 $cm^3 g^{-1} dm^{-1}$ (*c* = 0.47 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): d = 1.10 (s, 9 H), 1.84 (m, 1 H), 1.96 (m, 1 H), 2.36 (s, 3 H), 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, 2 H), 4.26 (ddd, *J* = 8.2, 7.3, 6.0 Hz, 1 H), 5.47 (dd, *J* = 8.2, 1.1 Hz, 1 H), 6.60 (d, *J* = 1.1 Hz, 1 H), 7.37–7.44 (m, 6 H), 7.64–7.67 ppm (m, 4 H); ^{13}C NMR (125.7 MHz, $CDCl_3$): d = 19.2 (C), 23.1 (CH_3), 26.7 (3 × CH_3), 28.0 (CH_2), 34.3 (CH_2), 56.9 (CH_3), 69.7 (CH_2), 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 ($CHCl_3$, 0.2 mm): $\tilde{n}$ = 3435, 2933, 2249, 1714, 1681, 1662 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (e) = 272 (sh) (2914), 264 (3841), 261 (3877), 255 (sh) (3441), 227 nm (5628 $mol^{-1} m^3 cm^{-1}$); MS (EI): *m/z* (%): 437 (5) [M^+—OH], 365 (38), 199 (100); HRMS (EI): *m/z* calcd for $C_{26}H_{33}O_4Si$: 437.2148 [M^+—OH]; found: 437.2140; elemental analysis calcd (%) for $C_{26}H_{34}O_5Si$ (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_6D_6 (0.3 mL), was irradiated with a daylight lamp at 36–40 °C for 5 h. The reaction was monitored by ^{1}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_2O_3, hexanes/EtOAc 95:5) to give an inseparable mixture of hemiketal diastereomers (35.9 mg, 0.078 mmol, d.r. 10:1, 61 %) (major isomer: (2*S*,3a*S*,4*R*,6a*R*)-6a-[(*tert*-butyldiphenylsilyl)oxy]methyl-2-hydroxy-4-methoxy-2-methyltetrahydro-2*H*-cyclopenta[*b*]furan-3(3a*H*)-one (49)) as a colorless oil: $[a]_D$ = + 62 $cm^3 g^{-1} dm^{-1}$ (*c* = 0.98 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): d (major isomer) = 1.07 (s, 9 H), 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, 1 H), 3.10 (d, *J* = 1.9 Hz, 1 H), 3.22 (s, 3 H), 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); ^{13}C NMR (100.6 MHz, $CDCl_3$): d (major isomer) = 19.1 (C), 20.3 (CH_3), 26.8 (3 × CH_3), 30.3 (CH_2), 33.9 (CH_2), 55.5 (CH), 56.2 (CH_3), 69.0 (CH_2), 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 ($CHCl_3$, 0.2 mm): $\tilde{n}$ = 3356, 2935, 1762 cm^{-1}; MS (ESI$^+$): *m/z* (%): 477 (100) [M^++Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{26}H_{34}NaO_5Si$: 477.2073 [M^++Na]; found: 477.2076; elemental analysis calcd (%) for $C_{26}H_{34}O_5Si$ (454.63): C 68.69, H 7.54; found: C 68.64, H 7.76.

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 $NaIO_4$ (111.1mg, 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. $[a]_D$ = + 47 $cm^3g^{-1}dm^{-1}$ (c = 0.59 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): d = 1.52 (m, 1H), 1.79–1.88 (m, 2 H), 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); ^{13}C NMR (125.7 MHz, $CDCl_3$): d = 22.2 (CH_2), 23.1 (CH_2), 23.5 (CH_3), 56.9 (CH_3), 67.9 (CH_2), 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 ($CHCl_3$, 0.2 mm): $\tilde{\nu}$ = 2945, 1732 cm^{-1}; MS (EI): m/z (%): 410 (3) [M^+], 378 (4), 340 (14), 339 (85); HRMS (EI): m/z calcd for $C_{17}H_{18}N_2O_{10}$: 410.0961 [M^+]; found: 410.0957; elemental analysis calcd (%) for $C_{17}H_{18}N_2O_{10}$ (410.33): C 49.76, H 4.42, N 6.83; found: C 49.68, H 4.37, N 6.61.

(5*R*,6*Z*)-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 $CDCl_3$ (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 ^1H 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. $[a]_D$ = + 8 $cm^3g^{-1}dm^{-1}$ (c = 1.39, $CDCl_3$); ^1H NMR (400 MHz, $CDCl_3$): d = 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, 1H), 9.20 (d, J = 2.1 Hz, 2H), 9.25 ppm (dd, J = 2.1, 2.1, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): d = 23.1 (CH_3), 28.3 (CH_2), 34.7 (CH_2), 57.0 (CH_3), 69.3 (CH_2), 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 ($CHCl_3$, 0.2 mm): $\tilde{\nu}$ = 3103, 2934, 2258, 1736, 1682, 1664 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (e) = 255 (6229), 236 nm (6110 $mol^{-1}m^3cm^{-1}$); MS (EI): m/z (%): 410 (< 1) [M^+], 378 (2), 367 (1), 335 (17); HRMS (EI): m/z: calcd for $C_{17}H_{18}N_2O_{10}$: 410.0961 [M^+]; found: 410.0967; elemental analysis calcd (%) for $C_{17}H_{18}N_2O_{10}$ (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 $NaIO_4$ (88 mg, 0.412 mmol) and $RuO_2 \cdot x\ H_2O$ (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: $[a]_D$ = + 16 $cm^3g^{-1}dm^{-1}$ (c = 1.50 in $CHCl_3$); ^1H NMR (400 MHz, C_6D_6): d = 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, 1H), 3.81 (dd, J = 8.0, 8.0 Hz, 1H), 4.00 (dd, J = 3.4, 3.4 Hz, 1H), 4.02–4.06 (m, 3H), 5.28 (d, J = 3.4 Hz, 1H), 7.21–7.89 ppm (m, 10H); ^{13}C NMR (100.6 MHz, C_6D_6): d = 19.6 (C), 24.0 (CH_3), 27.1 (3 × CH_3), 57.5 (CH_3), 57.7 (CH_3), 59.8 (CH_3), 63.8 (CH_2), 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^{-1}; MS (ESI$^+$): m/z (%): 569 (100) [M^++MeOH+Na]; HRMS (ESI$^+$): m/z: calcd for $C_{29}H_{42}NaO_8Si$: 569.2547 [M^++MeOH+Na]; found: 569.2554; elemental analysis calcd (%) for $C_{28}H_{38}O_7Si$ (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_6D_6 (1 mL), was placed in a resonance tube and irradiated with a daylight lamp at 30 °C. The reaction was monitored by ^1H 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_2Cl_2 (0.7 mL) was acetylated at 0 °C with Ac_2O (30 *m*L, 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*,3a*R*,4*R*,5*R*,6*S*,6a*S*)-6a-[(*tert*-butyldiphenylsilyl)oxy]methyl-4,5,6-trimethoxy-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: ^1H NMR (400 MHz, C_6D_6): d = 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 (br d, J = 9.3 Hz, 1H), 6.73 ppm (br s, 1H, OH).

Compound 62: $[a]_D$ = –4 $cm^3g^{-1}dm^{-1}$ (c = 1.00 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): d = 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); ^{13}C NMR (125.7 MHz, $CDCl_3$): d = 19.3 (C), 20.4 (CH_3), 22.4 (CH_3), 26.8 (3 × CH_3), 51.8 (CH), 57.5 (CH_3), 58.0 (CH_3), 60.1 (CH_3), 64.8 (CH_2), 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^{-1}; MS (ESI$^+$): m/z (%): 579 (100) [M^++Na]; HRMS (ESI$^+$): m/z calcd for $C_{30}H_{40}NaO_8Si$: 579.2390 [M^++Na]; found: 579.2396; elemental analysis calcd (%) for $C_{30}H_{40}O_8Si$ (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-2,3-diulose (59): Prepared from 55 (150 mg, 0.581 mmol) following the general procedure (Method A) using dimethyl sulfide (85 *m*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 yellow 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). $[a]_D$ = –30 $cm^3g^{-1}dm^{-1}$ (c = 2.14 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): d = 2.35 (s, 3H), 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, 1H), 5.07 ppm (d, J = 2.2 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): d = 25.6 (CH_3), 58.3 (CH_3), 58.4 (CH_3), 59.8 (CH_3), 60.0 (CH_3), 73.0 (CH_2), 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^{-1}; 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 $C_{13}H_{22}O_7$ (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 ^1H 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[46] (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 $NaIO_4$ (89 mg, 0.416 mmol) and $RuO_2 \cdot x\ H_2O$ (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 $cm^3g^{-1}dm^{-1}$ (c = 0.25 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): d = 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); ^{13}C NMR (100.6 MHz, $CDCl_3$): d = 19.2 (CH_3), 23.5 (C), 26.9 (3 × CH_3), 57.8 (CH_3), 59.5 (CH_3), 60.7 (CH_3), 61.2 (CH_2), 71.9 (CH), 74.6 (CH), 75.4 (CH), 78.4 (CH), 81.2

(CH), 127.7–135.6 (10 × CH), 133.3 (C), 133.4 (C), 197.0 (C), 200.1 ppm (C); IR (film): $\tilde{\nu}$ = 2936, 1716 cm^{-1}; MS (ESI$^+$): *m/z* (%): 569 (100) [M^+ + MeOH + Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{29}H_{42}NaO_8Si$: 569.2547 [M^+ + MeOH + Na]; found: 569.2556; elemental analysis calcd (%) for $C_{28}H_{38}O_7Si$ (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_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 ^{1}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_2Cl_2 (0.6 mL), cooled at 0 °C, and acetylated with Ac_2O (20 mL, 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*,3a*R*,4*S*,5*R*,6*R*,6a*S*)-6a-[(*tert*-butyldiphenylsilyl)oxy]methyl-4,5,6-trimethoxy-2-methyl-3-oxohexahydro-2*H*-cyclopenta[*b*]furan-2-yl acetate (64) and (2*R*,3a*S*,4*S*,5*R*,6*R*,6a*R*)-6a-[(*tert*-butyldiphenylsilyl)oxy]methyl-4,5,6-trimethoxy-2-methyl-3-oxohexahydro-2*H*-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. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.25 (s, 9H), 1.85 (s, 3H), 2.89 (s, 3H), 3.13 (s, 3H), 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, 1H), 6.84 ppm (d, *J* = 1.3 Hz, OH); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 19.6 (C), 22.8 (CH_3), 27.0 (3 × CH_3), 57.0 (CH_3), 58.2 (CH_3), 59.9 (CH_3), 69.5 (CH_2), 111.7 (CH), 149.9 (C), 194.6 (C), 206.4 ppm (C).

Compound 63: colorless oil. $[\alpha]_D$ = + 14 cm^{3}g^{-1}dm^{-1} (*c* = 0.28 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.08 (s, 9H), 1.54 (s, 3H), 1.87 (s, 3H), 3.27 (d, *J* = 2.9 Hz, 1H), 3.36 (s, 3H), 3.45 (s, 3H), 3.48 (s, 3H), 3.70 (d, *J* = 10.3 Hz, 1H), 3.77 (dd, *J* = 4.2, 4.2 Hz, 1H), 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); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.3 (C), 20.7 (CH$_3$), 22.7 (CH_3), 26.8 (3 × CH_3), 53.3 (CH), 57.7 (CH_3), 57.8 (CH_3), 59.9 (CH_3), 65.4 (CH_2), 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^{-1}; MS (ESI$^+$): *m/z* (%): 579 (100) [M^+ + Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{30}H_{40}NaO_8Si$: 579.2390 [M^+ + 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; $[\alpha]_D$ = + 29 cm^{3}g^{-1}dm^{-1} (*c* = 0.38 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): 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); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 19.4 (C), 20.8 (CH_3), 22.0 (CH_3), 26.9 (3 × CH_3), 49.6 (CH), 58.9 (CH_3), 59.2 (CH_3), 60.9 (CH_3), 64.9 (CH_2), 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): $\tilde{\nu}$ = 2923, 1766, 1747 cm^{-1}; MS (ESI$^+$): *m/z* (%): 579 (100) [M^+ + Na]; HRMS (EI): *m/z* calcd for $C_{30}H_{40}NaO_8Si$: 579.2490 [M^+ + Na]; found: 579.2401; elemental analysis calcd (%) for $C_{30}H_{40}O_8Si$ (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 $NaIO_4$ (156 mg, 0.732 mmol) and $RuO_2 \cdot x\,H_2O$ (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 cm^{3}g^{-1}dm^{-1} (*c* = 0.71 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 20.8 (CH_3), 23.7 (CH_3), 58.4 (CH_3), 59.1 (CH_3), 59.6 (CH_3), 61.7 (CH_2), 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^{-1}; MS (ESI$^+$): *m/z* (%): 373 (100) [M^+ + MeOH + Na], 341 (21) [M^+ + Na]; HRMS (ESI$^+$): *m/z*: calcd for $C_{15}H_{26}NaO_9$: 373.1475 [M^+ + MeOH + Na]; found: 373.1465; elemental analysis calcd (%) for $C_{14}H_{22}O_8$ (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_6D_6 (0.5 mL), was placed in a resonance tube and irradiated with a daylight lamp at 30 °C. The reaction was monitored by ^{1}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_2Cl_2 (0.4 mL), cooled at 0 °C, and acetylated with Ac_2O (12 mL, 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: ^{1}H NMR (400 MHz, C_6D_6): δ = 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 (br s, 1H, OH); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 20.1 (CH_3), 22.7 (CH_3), 57.1 (CH_3), 58.7 (CH_3), 60.0 (CH_3), 67.7 (CH_2), 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 cm^{3}g^{-1}dm^{-1} (*c* = 0.56 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 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), 83.9 ppm (CH), (quaternary carbons not observed); IR (film): $\tilde{\nu}$ = 2922, 1766, 1742, 1731 cm^{-1}; MS (ESI$^+$): *m/z* (%): 383 (100) [M^+ + Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{16}H_{24}NaO_9$: 383.1318 [M^+ + Na]; found: 383.1322; elemental analysis calcd (%) for $C_{16}H_{24}O_9$ (360.36): C 53.33, H 6.71; found: C 53.43, H 6.46.

Compound 66: colorless oil. $[\alpha]_D$ = + 25 cm^{3}g^{-1}dm^{-1} (*c* = 0.56 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 20.8 (CH_3), 20.9 (CH_3), 21.7 (CH_3), 50.4 (CH), 58.8 (CH_3), 59.2 (CH_3), 60.6 (CH_3), 64.1 (CH_2), 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): $\tilde{\nu}$ = 2938, 1768, 1744 cm^{-1}; MS (ESI$^+$): *m/z* (%): 383 (100) [M^+ + Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{16}H_{24}NaO_9$: 383.1318 [M^+ + Na]; found: 383.1324; elemental analysis calcd (%) for $C_{16}H_{24}O_9$ (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 $NaIO_4$ (37 mg, 0.171 mmol) and $RuO_2 \cdot x\,H_2O$ (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[47] (2 mg, 0.005 mmol, 6%).

Compound 70: $[\alpha]_D$ = −4 cm^{3}g^{-1}dm^{-1} (*c* = 1.01 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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); ^{1}H NMR (500 MHz, C_6D_6): δ = 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,

J= 3.5, 2.8 Hz, 1H), 4.65 (d, J= 6.2, 1.1 Hz, 1H), 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); ^{13}C NMR (100.4 MHz, $CDCl_3$): d = 19.1 (C), 23.6 (CH_3), 24.8 (CH_3), 25.7 (CH_3), 26.9 (3 × CH_3), 65.9 (CH_2), 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}C NMR (100.4 MHz, C_6D_6): d = 19.2 (C), 23.1 (CH_3), 24.9 (CH_3), 26.0 (CH_3), 27.0 (3 × CH_3), 65.9 (CH_2), 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 ($CHCl_3$, 0.2 mm): $\tilde{\nu}$ = 2936, 1717 cm^{-1}; MS (ESI$^+$): *m/z* (%): 537 (100) [M^++MeOH+Na], 505 (72) [M^++Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{28}H_{38}O_7NaSi$: 537.2285 [M^++MeOH+Na]; found: 537.2288; calcd for $C_{27}H_{34}NaO_6Si$ [M^++Na]: 505.2022; found: 505.2025; elemental analysis calcd (%) for $C_{27}H_{34}O_6Si$ (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 ^{1}H NMR spectroscopy, leading to exclusive formation of the photoenol mixture 74 a (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 74 a: ^{1}H NMR (500 MHz, C_6D_6): d (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 (br s, 1H), 7.18–7.68 ppm (m, 10H); d (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, 1H), 3.41 (dd, J= 11.4, 2.5 Hz, 1H), 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, 10H); ^{13}C NMR (125.7 MHz, CDCl ;): d (major isomer) = 19.1 (C), 25.9 (CH_3), 26.1 (CH_3), 26.74 (3 × CH_3), 26.9 (CH_3), 65.0 (CH_2), 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); d (minor isomer) = 19.1 (C), 25.6 (CH), 25.7 (CH), 26.7 (3 × CH), 26.8 (CH), 65.1 (CH), 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-**d**-*allo*-octo-2,3-diulose (71): Prepared from 68 (47 mg, 0.102 mmol) following the general procedure (Method B) using $NaIO_4$ (73 mg, 0.340 mmol) and $RuO_2 \cdot x\ H_2O$ (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 mg, 0.069 mmol, 68%) and the known lactone 73 (3 mg, 0.007 mmol, 6%). $[\alpha]_D$ = —2 cm^{3}g^{-1}dm^{-1} (c = 1.88 in $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6, 30 °C; conformer A): d = 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: d = 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); ^{1}H NMR (500 MHz, C_6D_6, 70 °C): d = 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, 1H), 7.22–7.76 ppm (m, 10H); ^{13}C (100.6 MHz, C_6D_6, 30 °C): d (conformer A) = 19.4 (C), 24.0 (CH_3), 25.5 (CH_3), 27.03 (CH_3), 27.4 (3 × CH_3), 64.4 (CH_2), 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); d (conformer B) = 19.4 (C), 23.1 (CH_3), 25.4 (CH_3), 27.0 (CH_3), 27.6 (3 × CH_3), 64.7 (CH_2), 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_6D_6, 70 °C): d = 19.5 (C), 24.0 (CH_3), 25.6 (CH_3), 27.2 (CH_3), 27.4 (3 × CH_3), 64.6 (CH_2), 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 ($CHCl_3$, 0.2 mm): n< Ü = > = 2936, 1721 cm^{-1}; MS (ESI$^+$): *m/z* (%): 537 (100) [M^++MeOH+Na], 505 (38) [M^++Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{28}H_{38}O_7NaSi$: 537.2285 [M^++MeOH+Na]; found: 537.2293; calcd for $C_{27}H_{34}NaO_6Si$ [M^++Na]: 505.2022; found: 505.2033; elemental analysis calcd (%) for $C_{27}H_{34}O_6Si$ (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_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 ^{1}H NMR spectroscopy, leading to exclusive formation of the photoenol mixture 74 a (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-**d**-*talo*-octo-2,3-diulose (72): Prepared from 69 (70 mg, 0.160 mmol) following the general procedure (Method B) using $NaIO_4$ (116 mg, 0.540 mmol) and $RuO_2 \cdot x\ H_2O$ (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 cm^{3}g^{-1}dm^{-1} (c = 1.14 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): d = 1.05 (s, 9H), 1.32 (s, 3H), 1.42 (s, 3H), 2.37 (s, 3H), 3.93 (dd, J= 10.4, 6.3 Hz, 1H), 3.99 (dd, J= 10.4, 6.0 Hz, 1H), 4.08 (ddd, J= 6.0, 6.0, 3.5 Hz, 1H), 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); ^{13}C NMR (125.7 MHz, $CDCl_3$): d = 19.2 (C), 24.5 (CH_3), 25.3 (CH_3), 26.3 (CH_3), 26.8 (3 × CH_3), 61.8 (CH_2), 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); ^{1}H NMR (500 MHz, C_6D_6): d = 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); ^{13}C NMR (100.6 MHz, C_6D_6): d = 19.5 (C), 23.7 (CH_3), 25.2 (CH_3), 26.4 (CH_3), 27.0 (3 × CH_3), 62.5 (CH_2), 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 ($CHCl_3$, 0.2 mm): $\tilde{\nu}$ = 2933, 1719 cm^{-1}; MS (ESI$^+$): *m/z* (%): 537 (100) [M^++MeOH+Na]; 505 (39) [M^++Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{28}H_{38}NaO_7Si$ [M^++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 $C_{27}H_{34}O_6Si$ (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 $CDCl_3$ (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 ^{1}H NMR spectroscopy, leading to exclusive formation of 75 besides a small amount of photoenol intermediate 74 b. The mixture was kept at room temperature in the dark for 14 h for the complete transformation of 74 b 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 74 b: ^{1}H NMR (400 MHz, $CDCl_3$): d = 2.25 (s, 3H), 4.26 (d, J= 18.8 Hz, 1H), 4.39 (d, J= 18.5 Hz, 1H), 4.96 (d, J= 7.4 Hz, 1H), 5.37 (dd, J= 8.5, 1.3 Hz, 1H), 5.51 (dd, J= 8.7, 7.4 Hz, 1H), 6.71 (br d, J= 1.6 Hz, 1H).

Compound 75: ^{1}H (400 MHz, $CDCl_3$; major isomer): d = 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, 1H), 4.17 (dd, J= 5.8, 1.3 Hz, 1H), 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); d (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, 1H), 7.35–7.76 ppm (m, 10H); ^{13}C NMR (100.6 MHz, $CDCl_3$): d (major isomer) = 19.2 (C), 25.9 (CH_3), 26.5 (CH_3), 26.7 (CH_3), 26.80 (3 × CH_3), 66.8 (CH_2), 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); d (minor isomer) = 19.3 (C), 25.5 (CH_3), 26.78 (3 × CH_3), 65.7 (CH_2), 68.7

(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_2Cl_2): λ_{max} (ε) = 262 nm (sh) (2253 $mol^{-1}m^3cm^{-1}$), 259 nm (2374 $mol^{-1}m^3cm^{-1}$), 256 nm (sh) (2274 $mol^{-1}m^3cm^{-1}$), 228 nm (5844 $mol^{-1}m^3cm^{-1}$); IR ($CHCl_3$, 0.2 mm): $\tilde{\nu}$ = 3520, 2936, 1790, 1727, 1710 cm^{-1}; MS (ESI$^+$): *m/z* (%): 505 (100) [M^++Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{27}H_{34}NaO_6Si$: 505.2022 [M^++Na]; found: 505.2019; elemental analysis calcd (%) for $C_{27}H_{34}O_6Si$ (482.64): C 67.19, H 7.10; found: C 67.19, H 6.98.

Methyl (1*S*,2*R*,3*S*,4*R*,5*S*)-2-acetyloxy-3,4,5-trimethoxy-2-(methoxymethyl)cyclopentane-1-carboxylate (76): H_5IO_6 (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_2O 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: $[\alpha]_D$ = + 32 $cm^3g^{-1}dm^{-1}$ (*c* = 1.35 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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 (br d, *J* = 5.1 Hz, 1H), 3.94 (d, *J* = 9.8 Hz, 1H), 4.09 ppm (ddd, *J* = 8.8, 5.7, 0.6 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.7 (CH_3), 51.9 (CH), 52.2 (CH_3), 58.0 (CH_3), 58.3 (CH_3), 58.9 (CH_3), 59.3 (CH_3), 70.5 (CH_2), 84.7 (CH), 86.8 (CH), 86.9 (C), 88.6 (CH), 169.8 (C), 170.7 ppm (C); IR (film): $\tilde{\nu}$ = 3013, 2936, 1740 cm^{-1}; MS (EI): *m/z* (%): 321 (< 1) [M^++H], 260 (2); HRMS (EI): *m/z* calcd for $C_{14}H_{25}O_8$: 321.1549; found [M^++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 (1*S*,2*R*,3*S*,4*R*,5*S*)-2-acetyloxy-3,4,5-tris(benzyloxy)-2-(benzyloxymethyl)cyclopentane-1-carboxylate (77): H_5IO_6 (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_2O (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 $cm^3g^{-1}dm^{-1}$ (*c* = 0.52 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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, 1H), 4.29 (br d, *J* = 5.1 Hz, 1H), 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, 1H), 4.58 (d, *J* = 11.7 Hz, 1H), 4.61 (d, *J* = 11.7 Hz, 1H), 4.63 (d, *J* = 11.4 Hz, 1H), 4.65 (d, *J* = 11.4 Hz, 1H), 4.69 (d, *J* = 11.7 Hz, 1H), 7.23–7.31 ppm (m, 20H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 21.7 (CH_3), 51.9 (CH), 52.7 (CH), 68.7 (CH$_2$), 72.4 (CH$_2$), 72.8 (CH$_2$), 73.2 (CH$_2$), 73.4 (CH$_2$), 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^{-1}; MS (FAB): *m/z* (%): 647 (5) [M^++Na]; HRMS (FAB): *m/z*: calcd for $C_{38}H_{40}NaO_8$: 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 (1*S*,2*R*,3*S*,4*R*,5*S*)-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_2O (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 $cm^3g^{-1}dm^{-1}$ (*c* = 0.40 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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, 7.1 Hz, 1H), 4.23 (d, *J* = 9.8 Hz, 1H), 4.39 (d, *J* = 7.3 Hz, 1H), 4.52 (dd, *J* = 8.8, 6.9 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, 1H), 4.74 (d, *J* = 11.7 Hz, 1H), 7.19–7.4 (m, 21H), 7.65–7.69 ppm (m, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 19.3 (C), 21.6 (CH_3), 26.8 (3 × CH_3), 51.6 (CH), 51.8 (CH_3), 62.8 (CH_2), 72.7 (CH_2), 72.8 (CH_2), 73.7 (CH_2), 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), 128.2 (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 ($CHCl_3$, 0.2 mm): $\tilde{\nu}$ = 2929, 1745 cm^{-1}; MS (FAB): *m/z* (%): 795 (10) [M^++Na]; HRMS (FAB): *m/z* calcd for $C_{47}H_{52}NaO_8Si$, 795.3329 [M^++Na]; found: 795.3303; elemental analysis calcd for $C_{47}H_{52}O_8Si$ (772.99): C 73.03, H 6.78; found: C 73.16, H 6.99.

Methyl (1*S*,2*R*,3*S*,5*R*)-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_5IO_6 (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 $cm^3g^{-1}dm^{-1}$ (*c* = 0.55 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.80 (ddd, *J* = 14.2, 5.0, 5.0 Hz, 1H), 2.02 (s, 3H), 2.31 (ddd, *J* = 14.2, 7.3, 5.6 Hz, 1H), 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); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 21.7 (CH_3), 34.3 (CH_2), 57.6 (CH_3), 57.8 (CH_3), 59.6 (CH_3), 60.0 (CH), 73.4 (CH_2), 80.7 (CH), 84.1 (CH), 89.2 (C), 169.2 (C), 169.9 ppm (C); IR (film): $\tilde{\nu}$ = 3490, 2935, 1743 cm^{-1}; MS (ESI$^+$): *m/z* (%): 299 (100) [M^++Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{12}H_{20}O_7Na$: 299.1107 [M^++Na]; found: 299.1112; elemental analysis calcd (%) for $C_{12}H_{20}O_7$ (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 Et_2O 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: $[\alpha]_D$ = + 35 $cm^3g^{-1}dm^{-1}$ (*c* = 0.87 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.98 (s, 3H), 1.71 (ddd, *J* = 14.5, 3.8, 3.8 Hz, 1H), 2.40 (ddd, *J* = 14.2, 8.2, 6.0 Hz, 1H), 3.04 (d, *J* = 7.3 Hz, 1H), 3.29 (s, 3H), 3.33 (s, 3H), 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); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 21.8 (CH_3), 34.6 (CH_2), 52.0 (CH_3), 54.8 (CH), 57.4 (CH_3), 57.9 (CH_3), 59.1 (CH_3), 69.6 (CH_2), 81.2 (CH), 84.0 (CH), 91.0 (C), 169.7 (C), 171.4 ppm (C); IR (film): $\tilde{\nu}$ = 2935, 1737 cm^{-1}; MS (ESI$^+$): *m/z* (%): 313 (100) [M^++Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{13}H_{22}NaO_7$: 313.1263 [M^++Na]; found: 313.1261; elemental analysis calcd (%) for $C_{13}H_{22}O_7$ (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 %).

Methyl (1*S*,2*R*,3*S*,5*R*)-2-acetyloxy-3-[(*tert*-butyldiphenylsilyl)oxy]-2-[(*tert*-butyl diphenylsilyl)oxy]methyl-5-methoxycyclopentane-1-carboxylate (82): *Method B*: A solution of 47 (15.9 mg, 0.022 mmol) in dry CH_2Cl_2 (0.5 mL), containing (diacetoxyiodo)benzene (8.7 mg, 0.027 mmol) and iodine (5.7 mg, 0.022 mmol) was irradiated with a 80 W tungsten-filament lamp at room temperature under nitrogen for 2 h. Saturated aqueous sodium thiosulfate was then added until complete decol-

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 $cm^3 g^{-1} dm^{-1}$ (c = 0.75 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.75 (s, 9H), 1.07 (s, 9H), 1.47 (ddd, J = 12.9, 8.5, 8.5 Hz, 1H), 1.83 (s, 3H), 2.09 (ddd, J = 13.3, 6.9, 6.9 Hz, 1H), 3.23 (d, J = 7.9 Hz, 1H), 3.31 (s, 3H), 3.92 (d, J = 11.7 Hz, 1H), 4.29 (ddd, J = 8.2, 8.2, 6.9 Hz, 1H), 4.33 (d, J = 11.4 Hz, 1H), 4.65 (dd, J = 8.2, 6.6 Hz, 1H), 7.19–7.64 ppm (m, 20H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 18.9 (C), 19.2 (C), 21.4 (CH_3), 26.7 (3 × CH_3), 26.8 (3 × CH_3), 38.4 (CH_2), 57.8 (CH_3), 58.8 (CH), 69.2 (CH_2), 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^{-1}; MS (ESI$^+$): *m/z* (%): 747 (100) [M^++Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{42}H_{52}NaO_7Si_2$: 747.3149 [M^++Na]; found: 747.3171; elemental analysis calcd (%) for $C_{42}H_{52}O_7Si_2$ (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 CH_2Cl_2 (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: $[\alpha]_D$ = + 7.6 $cm^3 g^{-1} dm^{-1}$ (c = 1.51 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92 (s, 9H), 1.10 (s, 9H), 1.63 (ddd, J = 12.9, 8.2, 7.9 Hz, 1H), 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, 1H), 3.56 (s, 3H), 4.10 (ddd, J = 7.6, 7.6, 7.6 Hz, 1H), 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, 12H), 7.54–7.58 (m, 4H), 7.70–7.71 ppm (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.1 (C), 19.4 (C), 21.6 (CH_3), 26.9 (6 × CH_3), 37.8 (CH_2), 51.6 (CH_3), 54.0 (CH), 57.2 (CH_3), 65.0 (CH_2), 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^{-1}; MS (EI): *m/z* (%): 681 (19) [M^+—*t*Bu], 135 (100); HRMS (ESI$^+$): *m/z* calcd for $C_{43}H_{54}NaO_7Si_2$: 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_5IO_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_2O 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_2O at 0 °C afforded **82** (10.7 mg, 0.014 mmol, 60 %).

(1*S*,2*R*,3*S*,4*R*,5*S*)-2-Acetyloxy-3,4,5-tris(benzyloxy)-2-(benzyloxymethyl)-cyclopentanecarboxylic acid (**83**): A deoxygenated solution of **18** (80 mg, 0.135 mmol) in purified $CDCl_3$ (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 $cm^3 g^{-1} dm^{-1}$ (c = 1.87 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.98 (s, 3H), 3.26 (d, J = 9.1 Hz, 1H), 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, 1H), 4.61 (d, J = 11.7 Hz, 2H), 4.63 (dd, J = 9.1, 6.9 Hz, 1H), 4.66 (d, J = 10.7 Hz, 2H), 4.67 (d, J = 11.4 Hz, 1H), 4.68 (d, J = 11.9 Hz, 1H), 4.73 (d, J = 11.0 Hz, 1H), 4.87 (d, J = 11.0 Hz, 1H), 7.27–7.37 ppm (m, 20H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.6 (CH_3), 56.0 (CH), 71.6 (CH_2), 72.7 (CH_2), 73.6 (CH_2), 73.7 (CH_2), 74.3 (CH_2), 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^{-1}; MS (ESI$^+$): *m/z* (%): 633 (100) [M^++Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{37}H_{38}NaO_8$: 633.2464 [M^++Na]; found: 633.2463; elemental analysis calcd (%) for $C_{37}H_{38}O_8$ (610.69): C 72.77, H 6.27; found: C 72.68, H 6.27.

(4a*R*,5*S*,6*S*,7*R*,7a*S*)-4a-(Acetyloxy)-6,7-dimethoxy-2,2-dimethylhexahydrocyclopenta[*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 CH_2Cl_2 (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 $Na_2S_2O_3$ 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. $[\alpha]_D$ =—19 $cm^3 g^{-1} dm^{-1}$ (c = 0.44 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 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, 1H), 4.29 (ddd, J = 9.3, 3.2, 1.1 Hz, 1H), 4.53 (d, J = 11.9 Hz, 1H), 4.79 ppm (d, J = 1.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.8 (CH_3), 21.6 (CH_3), 28.2 (CH_3), 52.1 (CH), 57.7 (CH_3), 58.2 (CH_3), 59.5 (CH_2), 73.8 (CH), 83.3 (C), 86.8 (CH), 89.9 (CH), 99.1 (C), 170.2 (C), 173.2 ppm (C); IR ($CHCl_3$, 0.2 mm): $\tilde{\nu}$ = 3504, 3016, 1741, 1717 cm^{-1}; MS (ESI$^+$): *m/z* (%): 341 (100) [M^++Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{14}H_{22}NaO_8$: 341.1212 [M^++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.

(1*S*,2*R*,5*R*)-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 H_5IO_6 (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. $[\alpha]_D$ = + 1 $cm^3 g^{-1} dm^{-1}$ (c = 0.52 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 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, 1H), 4.386 (d, J = 10.4 Hz, 1H), 4.387 (ddd, J = 6.3, 6.3, 6.3 Hz, 1H), 7.38–7.48 (m, 6H), 7.63–7.67 ppm (m, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 19.2 (C), 21.8 (CH_3), 26.8 (3 × CH_3), 29.2 (CH_2), 32.1 (CH_2), 57.4 (CH_3), 59.0 (CH), 67.2 (CH_2), 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 ($CHCl_3$, 0.2 mm): $\tilde{\nu}$ = 2938, 1739 cm^{-1}; MS (ESI$^+$): *m/z* (%): 493 (100) [M^++Na]; HRMS (ESI$^+$): *m/z* calcd for $C_{26}H_{34}NaO_6Si$: 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 (1*S*,2*R*,3*S*,4*R*,5*S*)-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^+), filtered and concentrated under reduced pressure. A solution of the residue in Et_2O 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 $cm^3 g^{-1} dm^{-1}$ (c = 0.25 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 51.9 (CH_3), 54.0 (CH), 72.0 (CH_2), 72.30 (CH_2), 72.34 (CH_2), 72.8 (CH_2), 73.7

(CH_2), 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^{-1}; MS (ESI^+): *m/z* (%): 605 (100) [M^++Na]; HRMS (ESI^+): *m/z* calcd for $C_{36}H_{38}NaO_7$: 605.2515 [M^++Na]; found: 605.2513; elemental analysis calcd (%) for $C_{36}H_{38}O_7$ (582.68): C 74.21, H 6.57; found: C 74.42, H 6.60.

(1*S*,2*S*,3*R*,4*S*,5*R*)-2,3,4-Tris(benzyloxy)-5-(benzyloxy)methyl-6-oxabicyclo[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^+), filtered and concentrated under reduced pressure. Benzenesulfonyl chloride (16 *m*L, 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 Et_2O. 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. $[a]_D$ = + 2 $cm^3g^{-1}dm^{-1}$(*c* = 0.50 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): d = 3.97 (d, *J* = 12.0 Hz, 1H), 3.99 (d, *J* = 11.7 Hz, 1H), 4.00 (dd, *J* = 1.5 Hz, J_W = 1.4 Hz, 1H), 4.16 (ddd, *J* = 2.4, 2.0 Hz, J_W = 1.4 Hz, 1H), 4.19 (d, *J* = 4.7 Hz, 1H), 4.22 (dd, *J* = 1.9, 1.9 Hz, 1H), 4.47 (d, *J* = 12.0 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 11.7 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 12.3 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 12.3 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 7.22–7.36 ppm (m, 20H); ^{13}C NMR (100.6 MHz, $CDCl_3$): d = 60.5 (CH), 67.6 (CH_2), 71.1 (CH_2), 72.1 (CH_2), 73.0 (CH_2), 73.8 (CH_2), 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): $\tilde{\nu}$ = 2918, 1828, 1087 cm^{-1}; MS (ESI^+): *m/z* (%): 573 (100) [M^++Na]; HRMS (ESI^+): *m/z* calcd for $C_{35}H_{34}NaO_6$: 573.2253 [M^++Na]; found: 573.2249; elemental analysis (%) for $C_{35}H_{34}O_6$ (550.64): C 76.34, H 6.22; found: C 76.29, H 6.47.

(1*R*,2*S*,3*R*,4*S*,5*S*)-2,3,4-Tris(benzyloxy)-1-(benzyloxy)methyl-5-(hydroxymethyl)cyclopentanol (88): $LiAlH_4$ (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_2SO_4 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 to 4:6) to give 88 (18 mg, 0.032 mmol, 78 %) as a colorless oil: $[a]_D$ = −8.2 $cm^3g^{-1}dm^{-1}$(*c* = 0.11 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): d = 2.21 (ddd, *J* = 9.3, 6.0, 3.7 Hz, 1H), 3.61 (d, *J* = 9.5 Hz, 1H), 3.76 (d, *J* = 9.1 Hz, 1H), 3.79 (dd, *J* = 11.6, 6.0 Hz, 1H), 3.83 (d, *J* = 4.7 Hz, 1H), 3.87 (dd, *J* = 11.6, 3.5 Hz, 1H), 3.91 (dd, *J* = 5.4, 5.4 Hz, 1H), 4.09 (dd, *J* = 8.8, 5.4 Hz, 1H), 4.45–4.73 (m, 8H), 7.25–7.38 ppm (m, 20H); ^{1}H NMR (500 MHz, C_6D_6): d = 2.24 (br s, 1H), 2.31 (ddd, *J* = 4.7, 4.7, 9.5 Hz, 1H), 3.08 (br s, 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, 1H), 4.57 (d, *J* = 11.0 Hz, 1H), 4.62 (d, *J* = 11.7 Hz, 1H), 4.64 (d, *J* = 11.5 Hz, 1H), 4.67 (d, *J* = 11.7 Hz, 1H), 7.05–7.36 ppm (m, 20H); ^{13}C NMR (100.6 MHz, $CDCl_3$): d = 49.9 (CH), 60.5 (CH_2), 72.2 (CH_2), 72.6 (CH_2), 72.6 (CH_2), 73.1 (CH_2), 73.9 (CH_2), 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_6D_6): d = 50.0 (CH), 60.9 (CH_2), 72.2 (CH_2), 72.6 (CH_2), 72.8 (CH_2), 73.6 (CH_2), 73.7 (CH_2), 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^{-1}; MS (ESI): *m/z* (%): 577 (100) [M^++Na]; HRMS (ESI^+): *m/z* calcd for $C_{35}H_{38}NaO_6$: 577.2566 [M^++Na]; found: 577.2564; elemental analysis calcd (%) for $C_{35}H_{38}O_6$ (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_2O (14 *m*L, 0.081 mmol) was added dropwise to a solution of 86 (16 mg, 0.027 mmol) in dry CH_2Cl_2 containing dry pyridine (14 *m*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. $[a]_D$ = −16 $cm^3g^{-1}dm^{-1}$(*c* = 1.06 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): d = 3.72 (s, 3H), 4.05 (dd, *J* = 2.6, 2.4 Hz, 1H), 4.37 (d, *J* = 13.8 Hz, 1H), 4.45–4.71 (m, 8H), 4.63 (m, 1H), 4.69 (m, 1H), 4.83 (d, *J* = 13.8 Hz, 1H), 7.26–7.36 ppm (m, 20H); ^{13}C NMR (100.6 MHz, $CDCl_3$): d = 51.6 (CH_3), 64.6 (CH_2), 71.8 (CH_2), 72.2 (CH_2), 72.6 (CH_2), 72.9 (CH_2), 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^{-1}; MS (ESI^+): *m/z* (%): 587 (100) [M^++Na]; HRMS (ESI^+): *m/z* calcd for $C_{36}H_{36}NaO_6$: 587.2401 [M^++Na]; found: 587.2405; elemental analysis calcd (%) for $C_{36}H_{36}O_6$ (564.67): C 76.57, H 6.43; found: C 76.77, H 6.63.

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[24] $^3J_{H4,H5}$ = 4.7 Hz (calcd 4.1 Hz), $^3J_{H5,H6}$ = 5.0 Hz (calcd 4.7 Hz), $^3J_{H6,H7}$ = 6.1 Hz (calcd 5.9 Hz). Coupling constants were calculated with Maestro, Schrçdinger, LLC, New York, NY, 2009. Program PSEUROT as implemented in Matlab GUI (P. M. S. Hendrickx, J. C. Martins, *Chem. Cent. J.* 2008, *2*, 20) was used for the pseudorotational analysis. The $^3J_{H4,H5}$, $^3J_{H5,H6}$, and $^3J_{H6,H7}$ experimental constants were obtained by iterative simulation of the spectra using DAISY as implemented in TOPSPIN v. 2.1 for Bruker. For application of pseudorotational analysis to cyclopentane ring conformation, see: a) C. S. Callam, T. L. Lowary, *J. Org. Chem.* 2001, *66*, 8961 – 8972; b) C. Thibaudeau, A. Kumar, S. Bekiroglu, A. Matsuda, V. E. Marquez, J. Chattopadhyaya, *J. Org. Chem.* 1998, *63*, 5447 – 5462. For a description of the pseudorotation concept, see: c) C. Altona, M. Sundaralingam, *J. Am. Chem. Soc.* 1972, *94*, 8205 – 8212; d) J. B. Houseknecht, C. Altona, C. M. Hadad, T. L. Lowary, *J. Org. Chem.* 2002, *67*, 4647 – 4651.

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