Stereocontrolled Photocyclization of 1,2-Diketones Applied to Carbohydrate Models: A New Entry to *C*-Ketosides

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Received 16 March 2007

Abstract: Photolysis of 1-glycosyl-2,3-butanedione derivatives using visible light is a mild and selective procedure for the synthesis of chiral 1-hydroxy-1-methyl-5-oxaspiro[3.5]nonan-2-one carbohydrate derivatives. The results strongly suggest that stereocontrol of the cyclization is dependent on conformational and stereoelectronic factors which can be modulated efficiently by using photosensitizers in some cases. Further oxidative opening of the 1-hydroxy-1-methyl-2-cyclobutanone moiety affords new *C*-ketoside derivatives. This two-step process could be considered to be a stereocontrolled 1,3-transfer of an acetyl group.

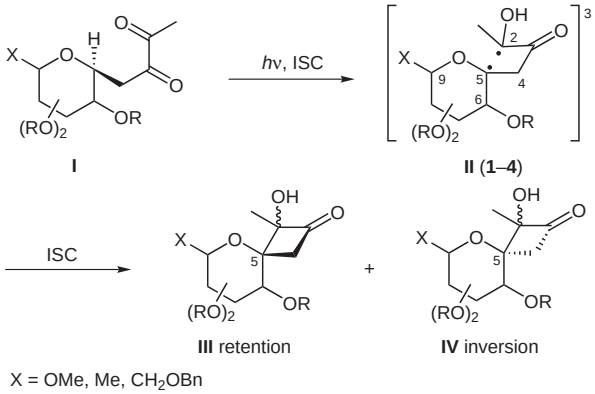
Key words: photochemistry, spiro compounds, memory effect, diastereoselectivity, glycosides

The Norrish–Yang photocyclization is an efficient method to generate regio- and stereocontrolled C–C bonds in mild conditions.[1] This reaction has been employed in organic synthesis, aliphatic and aromatic ketones, and α-keto esters being the most widely used reactants.[2] Although the photocyclization of 1,2-diketones to generate 2-hydroxy-cyclobutanones has been well studied since the early 1960s,[3] this methodology has seldom been applied[3a,4] and, as far as we know, only one case involved a chiral substrate.[5] Diastereoselective C–C bond formation, absence of additional reagents, high yields, and possible use of sunlight are the most attractive features of this methodology for the synthetic chemist and render the exploration of its scope and limitations highly interesting.

Herein, we report on the highly efficient use of a Norrish–Yang photocyclization to obtain new spirocyclic monosaccharide derivatives of types **III** and **IV** via a hydrogen-atom transfer (HAT) reaction promoted by a 1,2-diketone **I**, in its excited state, followed by C–C bond formation in a diastereoselective manner (Scheme 1). The conformational changes that the 1,4-diradical intermediate **II** suffers in its triplet state before the intersystem crossing (ISC) occurs, governs the reaction course.

We point to three main factors that are responsible for the behavior of transient intermediate **II**: lifetime of the 1,4-diradical species,[6] stereoelectronic interactions,[6b,7] and conformational restrictions.[8]

It has been reported that 1,2-diketones mainly undergo ISC to their triplet state and abstract hydrogen atoms with a very small rate constant related to alkyl and aryl ketones.[3] However, in our cases, the reactions were accomplished within relatively short times. It is noteworthy that a new factor has been introduced in these models. The hydrogen atom to be transferred is geminate to oxygen and may be specially activated. Furthermore, the 1,4-diradical intermediate **II** may be stabilized by a possible conjugative stabilizing interaction of the SOMO-C5 radical with the lone pair at the ring oxygen and the σ*-LUMO of the C6–O bond.[7] This C5-centered radical resembles the in-depth studied anomeric radical[9] where the C5–H bond has been replaced by a C5–alkyl, thus it will be named pseudo-anomeric radical. Such stabilization may affect the lifetime of intermediate **II**.



Scheme 1 Photocyclization of 1,2-diketones[10]

With the aim of rationalizing the role of the stereoelectronic and conformational factors in the stereocontrol of this process, we have synthesized a number of carbohydrate models shown in Table 1 and submitted to various photolysis conditions.[11]

Model **1** was selected due to its conformationally restricted $^4C_1$ pyranose ring.[12] 1,2-Diketone **1** was irradiated with outdoor sunlight in its crystalline form for 20 hours until the yellow color faded affording a mixture of compounds from which the main product **5a** was isolated in moderate yield after silica gel chromatography as a sole stereoisomer (entry 1). Side products of photooxidation and intermolecular reactions were formed, probably due to the presence of oxygen, long reaction time, and restricted mobility of the molecules in the crystalline net.[13] However, only one product **5a** was obtained in quantitative yield with $CHCl_3$ or C_6H_6 as solvent (entries 2 and 3). Slightly

SYNLETT 2007, No. 12, pp 1851–1856
Advanced online publication: 25.06.2007
DOI: 10.1055/s-2007-984523; Art ID: G08007ST

shorter reaction time was required with benzene. It is important to note that the deoxygenation of solvents was not necessary since no products of photooxidation were detected as long as the reaction time was not greatly extended. The reaction proceeded with total retention at C5. For this model, C5 presumably adopts a trigonal sp^2 hybridization at the 1,4-diradical intermediate **II-1** stage, and the ring moiety should not undergo dramatic conformational changes, which are especially restricted by the anomeric effect at C9. The existence of an intramolecular hydrogen bond probably enhanced the high stereocontrol at C2 and C5, since the introduction of a protic solvent led to a mixture of diastereoisomers (entry 4).[14]

Irradiation of model **2** with sunlight or a medium-pressure mercury lamp[15] gave the expected product **6** in excellent yields, as a mixture of three diastereoisomers (entries 5 and 6). The reaction proceeded predominantly with retention at C5 (**6a** and **6b**), although the inversion product **6c** was also isolated, showing a remarkably good memory effect[16]of 12 and 21, respectively [(**6a** + **6b**):**6c** = 12:1 and 21:1]. In this case, substrate **2** is in a $^4C_1$ conformation,[12] but the pyranosyl ring of the intermediate **II-2** is conformationally more flexible and distortions are more likely, and even more so when placing the OMe group in the axial position, because of the anomeric effect at C9.

The photoreaction of **2** in the presence of the triplet sensitizer benzophenone led almost to the same ratio of diastereoisomers of **6** (compare entries 6 and 7). The reaction was complete in half time, though the yield slightly decreased. In contrast, in the presence of pyrene, not only as a triplet quencher but also as a singlet sensitizer, product **6** was obtained with total diastereoselectivity and high yield, although longer reaction time was required (entry 8). Under these singlet conditions, the cyclization of the diradical **II-2** (S_1-spinisomer) intermediate is obviously so fast that rotations around the C4–C5 single bond do not take place and the C2–C5 bond is formed completely with retention, showing an excellent memory effect. The configuration of the asymmetric center C2 in this last experiment is probably controlled by the existence of an intramolecular hydrogen bond, steric factors, and restricted rotation of C2–C3 in the short-lived singlet diradical **II-2** intermediate.

The model **3** also adopts a $^4C_1$ conformation[12] with the transferring hydrogen atom in axial position. Irradiation of **3** either in chloroform or in benzene afforded the target compound **7** in good yields as a mixture of two diastereoisomers with complete retention (entries 9 and 10). The addition of pyrene significantly increased the reaction time but without altering the diastereoisomeric ratio at the C2 stereocenter (entry 11).

Photocyclization of the substrate **4** with sunlight in chloroform afforded the four possible stereoisomers of spiro compound **8** with good yield and a poor memory effect of 1.8 [(**8a** + **8b**)/(**8c** + **8d**) = 8:4.5] (entry 12). A ^{1}H NMR experiment indicated that starting compound **4** adopts a $^4C_1$ conformation with the transferring hydrogen atom in equatorial position.

Changes in the radiation source and solvents did not alter the outcome of the reaction considerably (entries 12–15). This reaction can be performed in a very efficient and environmentally friendly way as shown in entry 15.

Table 1 Photocyclization of 1,2-Diketones via HAT at a Pseudo-Anomeric Position[10]

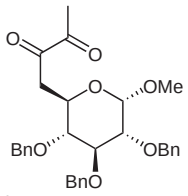
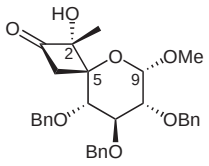
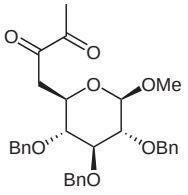
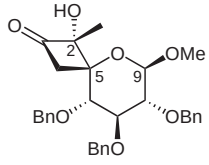
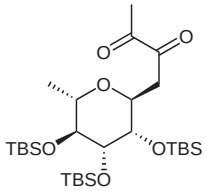
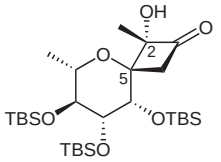
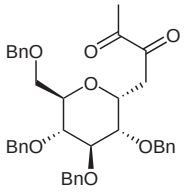
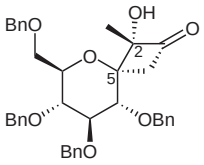
Entry	Substrate	Conditions[a]	Time (h)	Product ratio[b] **a**:**b**:**c**:**d**	Yield (%)
	 **1**			 **5**	
1		A	21	1:0:0:0	42
2		B	2	1:0:0:0	quant.
3		C	1.6	1:0:0:0	quant.
4		D	1.8	6:1:1:0	92
	 **2**			 **6**	

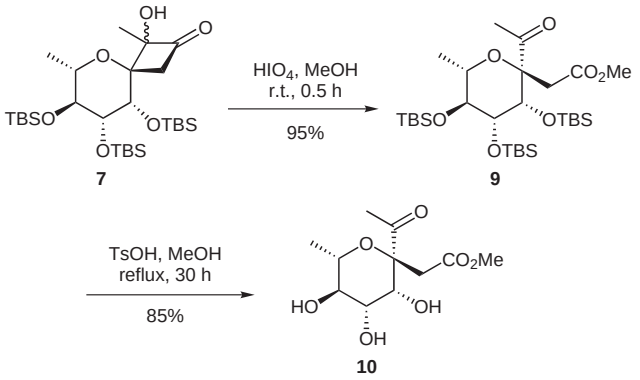
Table 1 Photocyclization of 1,2-Diketones via HAT at a Pseudo-Anomeric Position[10] (continued)

Entry	Substrate	Conditions[a]	Time (h)	Product ratio[b] **a**:**b**:**c**:**d**	Yield (%)
5		B	1	10:2:1:0	95
6		E	0.6	15:6:1:0	95
7		E[c]	0.3	11:3:1:0	88
8		E[d]	2.0	1:0:0:0	80
	 **3**			 **7**	
9		B	4	0:0:1:3	78
10		C	3	0:0:1:4	83
11		E[d]	13	0:0:1:4	87
	 **4**			 **8**	
12		B	4.5	1:7:2.5:2	92
13		E	1	1:7:2:2	90
14		F	2	1:3:1:1.5	80
15		A	2.5	1:6:2:2.5	85

[a] Conditions: A: sunlight, neat; B: sunlight, $CHCl_3$; C: sunlight, C_6H_6; D: sunlight, *t*-BuOH–$CHCl_3$ (3:1); E: UV lamp, $CHCl_3$; F: UV lamp, neat.
[b] For better understanding, the main diastereomer is depicted; **a** = 2*R*,5*R*; **b** = 2*S*,5*R*; **c** = 2*R*,5*S*; **d** = 2*S*,5*S*; diastereoisomer pairs **a**, **b** and **c**, **d** were formed with retention and inversion, respectively, in products **5**, **6**, and **8**; **c**, **d** were formed with retention in **7**. The ratios and stereochemistries were determined by ^{1}H NMR and NOE experiments, respectively.
[c] 0.5 M benzophenone, 38 mM substrate.
[d] 0.5 M pyrene, 38 mM substrate.

In addition to the cases commented in Table 1 (entries 8 and 11), pyrene has also been added to substrate **4** with the aim of modulating the stereoselectivity. Indeed, pyrene strongly inhibits the process, extending reaction times over beyond 48 hours and leading to the formation of contaminating side products, but scant influence on the stereoselectivity was observed. On the other hand, performing the photochemical reaction of substrates **2**–**4** in the presence of naphthalene did not affect either the reaction times or the diastereoisomeric ratios. The presence of added benzophenone as triplet sensitizer significantly reduced reaction times of models **1**, **3**, and **4** by approximately 30–50% but no changes were observed in the diastereoisomeric ratios.[17] These preliminary experiments suggest an excited triplet state but the high efficiency of pyrene in the stereocontrol of model **2** remains unclear at present. Basically, model **4** differs from model **1** in the nature of substituent X (OMe, CH_2OBn), which could provide a different feature for the 1,4-diradical intermediate **II**.

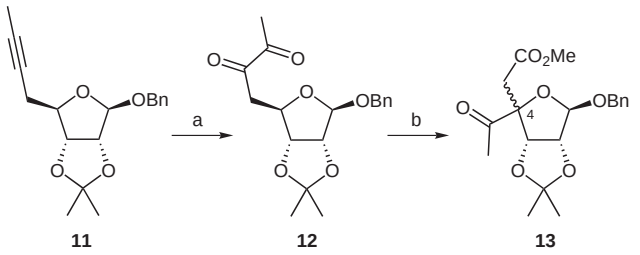
The 1-hydroxy-1-methyl-cyclobutan-2-one moiety could be opened with oxidative conditions in a preparative manner with excellent yield as depicted in Scheme 2.[3d] A diastereoisomeric mixture of compound **7** led to a single product, **9**, which after deprotection afforded a new *C*-ketoside **10**.



Scheme 2 Synthesis of *C*-ketosides

This procedure introduces a new entry into *C*-ketosides, which can only be accessed through chemical synthesis.[18] The two-step conversion of **3** into **9** can be considered to be a stereocontrolled 1,3-transfer of the acetyl group.

This methodology can be also extended to furanosyl derivatives. Ozonolysis of alkyne **11** followed by treatment with Me_2S[11a] afforded the 1,2-diketone **12** which was directly irradiated with sunlight to undergo the cyclization (Scheme 3). Due to the instability of the photocyclization products in silica gel, the oxidative opening was carried out without purification. This protocol of three consecutive steps protocol afforded the desired γ-ketoester **13** in moderate overall yield as an inseparable mixture of diastereoisomers (4*R*:4*S* = 5:1). This result indicates that the Norrish–Yang reaction proceeded predominantly with retention albeit with a small memory effect of 5. Steric hindrance at the β-face of the bicyclic compound **12** may be the reason to force the inversion on the pseudo-anomeric radical.



Scheme 3 *Reagents and conditions*: (a) O_3, CH_2Cl_2–MeOH (9:1), –78 °C, and then Me_2S, r.t., 0.5 h; (b) irradiation with sunlight, 40 min, and then HIO_4, MeOH, r.t., 1.5 h, 54% (over 3 steps).

C-Ketoside derivatives **10** and **13** are sugar-fused γ-ketoesters susceptible to be further modified to engineer versatile scaffolds and building blocks.

In summary, we have developed an efficient new strategy to synthesise *C*-ketosides using a diastereocontrolled Norrish–Yang photocyclization.[19] These preliminary results, regarding the memory effect observed, appear promising to expand the scope of this Norrish–Yang reaction with 1,2-diketones in asymmetric synthesis in the same way as arylketones or α-keto esters have already been used.[2] Further studies of the memory effect of this reaction, applied to other carbohydrate derivatives as well as noncyclic chiral compounds, are currently under way in our laboratory.

Acknowledgment

This work was supported by the Investigation programs No. CTQ2004-06381/BQU and CTQ2004-02367/BQU of the Ministerio de Educación y Ciencia, Spain, cofinanced with the Fondo Europeo de Desarrollo Regional (FEDER). A.J.H. and M.R. thank the Program I3P-CSIC and ULA-Venezuela, respectively, for research contracts. We thank Dr. C. C. González and A. González for fruitful discussions.

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(10) The numbering system used throughout the text is based on 1-methyl-2,3-alkanedione and corresponds to that depicted in structures of Table 1 and Schemes 1–3.
(11) The 1,2-diketones **1**–**4** shown in Table 1 were prepared from their corresponding alkynes via ozonolysis: (a) Favino, T. F.; Fronza, G.; Fuganti, C.; Fuganti, D.; Graselli, P.; Mele, A. *J. Org. Chem.* **1996**, *61*, 8975. (b) Or by oxidation with RuO_2/$NaIO_4$: Zibuck, R.; Seebach, D. *Helv. Chim. Acta* **1988**, *71*, 237.
(12) Conformation of substrates **1**–**4** were determined by ^{1}H NMR spectroscopic analysis.
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(14) Walther, K.; Kranz, U.; Henning, H.-G. *J. Prakt. Chem.* **1987**, *329*, 859.
(15) A 450 W ACE-Hanovia medium-pressure mercury lamp in an immersion well with 4.8 mm Pyrex walls.
(16) (a) The term of 'memory of chirality' is used here with the meaning that was proposed by Fuji: Fuji, K.; Kawabata, T. *Chem. Eur. J.* **1998**, *4*, 373. (b) For a discussion on the memory effect in photochemical reactions, see: Giese, B.; Wettstein, P.; Stähelin, C.; Barbosa, F.; Neuburger, M.; Zehnder, M.; Wessig, P. *Angew. Chem. Int. Ed.* **1999**, *38*, 2586; and references therein.
(17) Conditions: 1,2-diketone (40 mM), pyrene, naphthalene or benzophenone (0.5 M), $CHCl_3$, UV lamp (10 cm).
(18) To see a list of procedures to generate *C*-ketosides: Roberts, S. W.; Rainier, J. D. *Org. Lett.* **2005**, *7*, 1141.
(19) **General Procedure for the Photocyclization of 1,2-Diketones**
The corresponding 1,2-diketone placed in a Pyrex vessel with or without the indicated solvent (approx. 0.05 M) was irradiated with sunlight or a UV lamp, placed at 10 cm distance from the flask, until the reaction turned colorless. If it proceeded, the mixture was concentrated in vacuo. Column or Chromatotron® chromatography of the residue (hexanes–EtOAc mixtures) afforded the cyclic compounds.
General Procedure for the Photocyclization of 1,2-Diketones with Photosensitizers
The corresponding 1,2-diketone (0.038 mmol) and photosensitizer (benzophenone or pyrene; 0.5 mmol) was dissolved in $CDCl_3$ (1 mL) and placed in a NMR tube. The reaction mixture was irradiated with an UV lamp, placed at 10 cm distance from the flask, until complete conversion and the solvent was removed under vacuum. The reaction was monitored by ^{1}H NMR. Chromatotron® chromatography of the residue with hexanes to remove the photosensitizer followed by elution with hexanes–EtOAc mixtures afforded the cyclic compounds.
Data of some representative compounds are included; only the major compound from the mixtures is shown.
Compound **5a** (2*R*,5*R*): colorless oil; $[\alpha]_D$ +23.8 (*c* 0.3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.38 (3 H, s), 2.36 (1 H, d, *J* = 17.3 Hz), 2.91 (1 H, d, *J* = 17.3 Hz), 3.50 (1 H, dd, *J* = 3.7, 9.8 Hz), 3.53 (3 H, s), 3.76 (1 H, d, *J* = 9.8 Hz), 3.99 (1 H, br s), 4.34 (1 H, t, *J* = 9.8 Hz), 4.57 (1 H, d, *J* = 3.9 Hz), 4.66 (1 H, d, *J* = 11.9 Hz), 4.67 (1 H, d, *J* = 10.9 Hz), 4.75 (1 H, d, *J* = 10.9 Hz), 4.82 (1 H, d, *J* = 10.6 Hz), 4.83 (1 H, d, *J* = 12.0 Hz), 4.98 (1 H, d, *J* = 11.1 Hz), 7.15 (2 H, dd, *J* = 2.0, 7.6 Hz), 7.28–7.38 (13 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.6 (CH_3), 50.6 (CH_2), 59.7 (CH_3), 74.0 (CH_2), 76.0 (CH_2), 76.7 (CH_2), 77.8 (C), 78.2 (CH), 80.8 (CH), 83.3 (CH), 90.5 (C), 101.2 (CH), 128.2–129.3 (15 × CH), 136.5 (C), 138.5 (C), 138.7 (C), 208.2 (C). MS (EI): *m/z* (rel. int.) = 518 (<1) [M^+], 427 (<1), 412 (<1), 395 (<1), 91 (100). HRMS: *m/z* calcd for $C_{31}H_{34}O_7$: 518.2305; found: 518.2322. Anal. Calcd for $C_{31}H_{34}O_7$: C, 71.80; H, 6.61. Found: C, 71.90; H, 6.59.
Compound **6a** (2*R*,5*R*): colorless oil; $[\alpha]_D$ +1.4 (*c* 1.0). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.51 (3 H, s), 2.42 (1 H, d, *J* = 17.5 Hz), 3.03 (1 H, d, *J* = 17.5 Hz), 3.43 (1 H, dd, *J* = 8.1, 9.1 Hz), 3.61 (3 H, s), 3.86 (1 H, d, *J* = 9.5 Hz), 4.00 (1 H, br s), 4.15 (1 H, t, *J* = 9.4 Hz), 4.62 (1 H, d, *J* = 7.7 Hz), 4.68 (1 H, d, *J* = 10.9 Hz), 4.72 (1 H, d, *J* = 11.4 Hz), 4.75 (1 H, d, *J* = 11.7 Hz), 4.82 (1 H, d, *J* = 11.1 Hz), 4.93 (1 H, d, *J* = 11.1 Hz), 4.96 (1 H, d, *J* = 10.9 Hz), 7.15 (2 H, dd, *J* = 1.9, 7.1 Hz), 7.28–7.36 (13 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.7 (CH_3), 50.1 (CH_2), 57.7 (CH_3), 75.1 (CH_2), 75.6 (C), 76.1 (CH_2), 76.5 (CH_2), 81.6 (CH), 82.2 (CH), 82.8 (CH), 90.5 (C), 102.8 (CH), 128.1–129.2 (15 × CH), 136.5 (C), 138.6 (C), 138.7 (C), 206.6 (C). MS (EI): *m/z* (rel. int.) = 518 (<1) [M^+], 476 (1.1), 427 (<1), 395 (1), 91 (100). HRMS: *m/z* calcd for $C_{31}H_{34}O_7$: 518.2305; found: 518.2319.
Compound **7d** (2*S*,5*S*) [data taken from a (4:1) mixture of **7d**–**c**]: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.08 (3 H, s), 0.09 (3 H, s), 0.10 (3 H, s), 0.11 (6 H, s), 0.12 (3 H, s), 0.88 (18 H, s), 0.92 (9 H, s), 1.29 (3 H, d, *J* = 6.4 Hz), 1.34 (3 H, s), 2.75 (1 H, d, *J* = 17.5 Hz), 3.00 (1 H, d, *J* = 17.5 Hz), 3.42 (1 H, dq, *J* = 5.4, 6.4 Hz), 3.57 (1 H, dd, *J* = 2.0, 5.4 Hz), 3.76 (1 H, t, *J* = 2.0 Hz), 4.38 (1 H, d, *J* = 2.3 Hz), 4.71 (1 H, s, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = –5.2 (CH_3), –4.6 (CH_3), –4.3 (CH_3), –4.2 (CH_3), –3.9 (CH_3), –3.8 (CH_3), 17.8 (C), 17.9 (C), 18.0 (C), 18.9 (CH_3), 20.6 (CH_3), 25.6 (3 × CH_3), 25.8 (6 × CH_3), 51.4 (CH_2), 73.5 (CH), 75.7 (C), 76.1 (CH), 76.3 (CH), 77.4 (CH), 90.5 (C), 210.1 (C). MS (EI): *m/z* (rel. int.) = 574 (5) [M^+], 529 (17), 517 (22), 73 (100). HRMS: *m/z* calcd for $C_{28}H_{58}O_6Si_3$: 574.3541; found: 574.3534.
Compound **8b** (2*S*,5*R*) [data taken from a (3:1) mixture of **8b**–**c**]: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (3 H, s), 2.62 (1 H, d, *J* = 17.5 Hz), 3.31 (1 H, d, *J* = 17.5 Hz), 3.50 (1 H, m), 3.55 (1 H, m), 3.60 (1 H, t, *J* = 8.8 Hz), 3.70 (1 H, d, *J* = 8.6 Hz), 3.61–3.79 (2 H, m), 4.44 (1 H, d, *J* = 11.7 Hz), 4.46 (1 H, d, *J* = 11.8 Hz), 4.53 (1 H, d, *J* = 10.8 Hz), 4.58 (1 H, d, *J* = 10.8 Hz), 4.71 (1 H, d, *J* = 10.8 Hz), 3.74 (1 H, d, *J* = 10.8 Hz), 4.85 (1 H, d, *J* = 10.8 Hz), 5.04 (1 H, d, *J* = 11.4 Hz), 7.09–7.28 (20 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.6 (CH_3), 44.7 (CH_2), 68.3 (CH_2), 73.3 (CH_2), 73.7 (CH_2), 74.1 (CH_2), 75.1 (CH_2), 75.5 (CH), 76.2 (CH), 76.9 (C), 77.7 (CH), 86.4 (CH), 89.5 (C), 127.0–128.5 (20 × CH), 137.5 (C), 137.7 (C), 137.8 (C), 138.0 (C), 208.4 (C). MS (EI): *m/z* (rel. int.) = 608 (<1) [M^+] , 580 (1), 566 (<1), 517 (<1), 457 (1), 91 (100). HRMS: *m/z* calcd for $C_{38}H_{40}O_7$: 608.2777; found: 608.2770.
Compound **10**: colorless oil; $[\alpha]_D$ –81.2 (*c* 0.16). ^{1}H NMR (400 MHz, CD_3OD + D_2O): δ = 1.32 (3 H, d, *J* = 6.1 Hz), 2.28 (3 H, s), 3.01 (1 H, d, *J* = 15.4 Hz), 3.07 (1 H, d, *J* = 15.4 Hz), 3.43 (1 H, dd, *J* = 8.0, 10.3 Hz), 3.58 (1 H, dq, *J* = 10.4, 6.0 Hz), 3.66 (3 H, s), 3.67 (1 H, dd, *J* = 3.2, 5.0 Hz), 3.86 (1 H, d, *J* = 3.28 Hz). ^{13}C NMR (100 MHz, CD_3OD): δ = 19.1 (CH_3), 28.5 (CH_3), 38.2 (CH_2), 52.6 (CH_3), 72.9 (CH), 73.2 (CH), 74.2 (CH), 75.3 (CH), 86.6 (C), 171.7 (C), 213.9 (C). MS (EI): *m/z* (rel int.) = 263 (<1) [M^+ + H], 245 (<1), 231 (8), 201 (8). HRMS: *m/z* calcd for $C_{11}H_{19}O_7$: 263.1131; found: 263.1143. Anal. Calcd for $C_{11}H_{18}O_7$: C, 50.38; H, 6.92. Found: C, 50.28; H, 7.11.
Compound **13** (4*R*) [data taken from a (5:1) mixture]: white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (3 H, s), 1.45

(3 H, s), 2.38 (3 H, s), 2.87 (1 H, d, *J* = 15.9 Hz), 3.36 (1 H, d, *J* = 16.1 Hz), 3.63 (3 H, s), 4.42 (1 H, d, *J* = 11.7 Hz), 4.65 (1 H, d, *J* = 5.8 Hz), 4.67 (1 H, d, *J* = 11.4 Hz), 4.75 (1 H, d, *J* = 5.8 Hz), 5.33 (1 H, s), 7.27–7.37 (5 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.9 (CH_3), 25.7 (CH_3), 27.9 (CH_3), 41.9 (CH_2), 51.7 (CH_3), 69.8 (CH_2), 85.2 (CH), 85.6 (CH), 92.4 (C), 108.2 (CH), 112.9 (C), 127.6–128.5 (5 × CH), 136.9 (C), 170.0 (C), 208.9 (C). MS (EI): *m/z* (rel. int.) = 349 (1) [$M^+ - CH_3$], 321 (8), 91 (100). HRMS: *m/z* calcd for $C_{18}H_{21}O_7$: 349.1287; found: 349.1278. Anal. Calcd for $C_{19}H_{24}O_7$: C, 62.63; H, 6.64. Found: C, 62.88; H, 6.63.