Reductive Oxa Ring Opening of 7-Oxabicyclo[2.2.1]heptan-2-ones. Synthesis of C-α-Galactosides of Carbapentopyranoses

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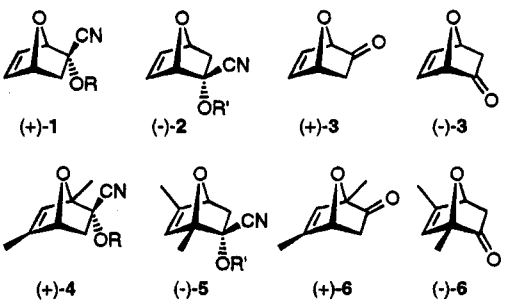
Photoinduced electron transfer from Et_3N to 7-oxabicyclo[2.2.1]heptan-2-ones can generate the corresponding 3-hydroxycyclohexanone derivatives. The method has been applied to the synthesis of C-α-D-galactopyranosides of carbapentopyranoses. Radical α-D-galactosidation of (±)-(1*RS*,4*RS*,5*RS*,6*RS*)-6-*endo*-methoxy-3-methylidene-5-*exo*-(phenylseleno)-7-oxabicyclo[2.2.1]hept-2-one ((±)-**51**) followed by seleno-Pummerer rearrangement and reduction with Bu_3SnH gave (+)-(1*R*,2*S*,3*S*,4*R*,6*R*)- ((+)-**58**) and (+)-(1*S*,2*R*,3*R*,4*S*,6*S*)-3-*endo*-methoxy-5-oxo-6-*endo*-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-galactopyranosyl)methyl]-7-oxabicyclo[2.2.1]hept-2-*endo*-yl acetate ((+)-**59**), which were separated by column chromatography. Irradiation (254 nm) in the presence of Et_3N gave (+)-(1*S*,2*R*,3*R*,6*R*)- ((+)-**60**) and (+)-(1*R*,2*S*,3*S*,6*S*)-2-hydroxy-6-methoxy-4-oxo-3-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-galactopyranosyl)methyl]cyclohexyl acetate (+)-**61**, respectively. $NaBH_4$ reduction and acetylation provided (+)-(1*S*,2*S*,3*R*,4*R*,5*R*)- ((+)-**62**) and (+)-(1*R*,2*R*,3*S*,4*S*,5*S*)-5-methoxy-2-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-galactopyranosyl)methyl]cyclohexa-1,3,4-triyl triacetate ((+)-**64**).

Introduction

Optically pure 7-oxabicyclo[2.2.1]hept-5-en-2-yl derivatives (+)-**1**, (−)-**2**, (+)-**3**, and (−)-**3** ("naked sugars" of the first generation)[1] and (+)-**4**, (−)-**5**, (+)-**6**, and (−)-**6** ("naked sugars" of the second generation)[2] have become useful chirons in the preparation of natural products and analogues[3] and of compounds of biological interest.[4] Introduction of substituents at their C(3), C(5), and C(6) centers can be carried out with high stereocontrol.[5] Except for 7-oxabicyclo[2.2.1]heptane derivatives bearing an electron-releasing substituent at C(1),[6] the opening of the oxa bridge requires relatively drastic conditions, which in some cases might lead to water elimination.[7] Derivatives having one carbanion-stabilizing substituent



at C(2) can be isomerized into the corresponding cyclohex-4-enols after deprotonation with an appropriate base[8] (E_{1cb}-like reactions). This type of isomerization can occur with a relatively weak base in the presence of an oxyphilic reagent.[9] Heterolytic cleavage of the ethereal bridge can be induced with a strong Brønstedt or Lewis acid with the participation of a neighboring group[10] or of an external nucleophile such as the bromide anion,[11] or through a Grob fragmentation.[12] Metal/halogen exchange of 2-halogeno-7-oxabicyclo[2.2.1]heptanes can also result in the 7-oxa ring opening.[13] 7-Oxabicyclo[2.2.1]-hept-2-ene derivatives have been reduced into cyclohexenols through S_N2 displacements by means of hydrides[14] or one-electron transfer processes.[15] Alternatively, simi-

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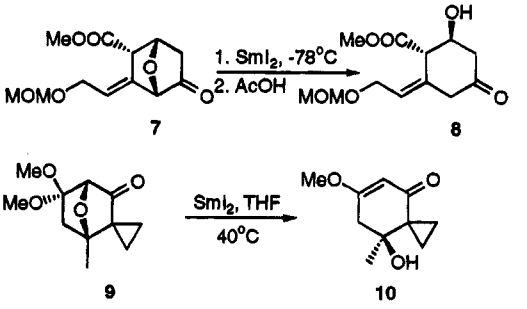
lar reductive ring opening can be carried out through S_N2' processes in which the external nucleophile is an alkylmetal[16] or a hydride reagent.[17] All these methods utilize relatively drastic conditions, and because of that they cannot be applied to all types of polysubstituted 7-oxabicyclo[2.2.1]heptane derivatives. In 1991, Cossy et al.[18] reported an alternative approach which relies on the intermediacy of ketyl radical anions derived from 7-oxabicyclo[2.2.1]heptan-2-ones that are generated under photochemical conditions (Scheme 1). In a study related to this method, De Schrijver and De Clercq[19] reported the reductive ethereal ring opening of **7** into **8** using SmI_2. A similar reaction (**9** → **10**) was presented recently by Padwa et al.[20]

Our photoreductive approach (Scheme 2) has now been

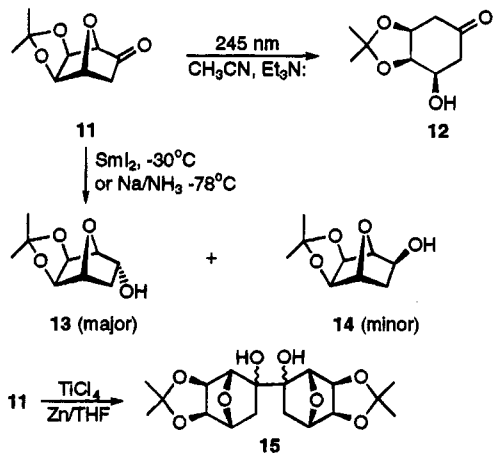
Scheme 1



tested with a variety of 7-oxabicyclo[2.2.1]heptan-2-one derivatives. In some cases, the 7-oxa ring opening can be carried out by our method where SmI_2 fails to induce it. In other cases, SmI_2 can be better than our photoinduced ethereal ring opening. The latter method has been applied to the synthesis of a new class of carbohydrate mimics that are C-glycosides of carbapentopyranoses.

Results and Discussion

Preliminary Results and Working Hypotheses. Irradiation of ketone **11**[5a] in CH_3CN (low-pressure Hg lamps, quartz vessel) in the presence of Et_3N gave the corresponding 3-hydroxycyclohexanone **12**. The best yield (80%, 75% of conversion) was obtained when a 1.5×10^{-2} M solution of **11** in acetonitrile was irradiated in the presence of 5 equiv of Et_3N. Because product **12** also absorbs the irradiation light (254 nm), the photoreaction had to be stopped before complete consumption of the starting material **11**.



Treatment of **11** with 3 mol equiv of SmI_2[21] in THF (−30 °C to +20 °C) led to the formation of the *endo* alcohol **13**[1b] (45% yield, 50% conversion). No trace of 7-oxa ring opened products were detected in the ^1H NMR spectrum of the crude reaction mixture. Similarly, treatment of **11** with Na in liquid NH_3 (−78 °C) gave a 10:1 mixture of the *endo* and *exo* alcohols **13** and **14**, respectively. Low-valent titanium salts are known to induce single electron transfer to ketones.[22] With the hope that such a process would induce the oxa ring opening, we treated **11** with a mixture of $TiCl_4$ and

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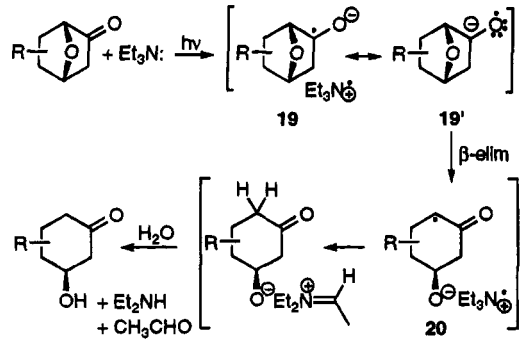
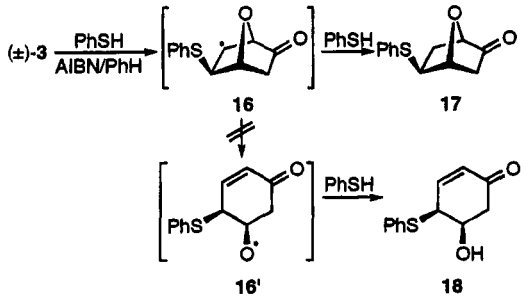
Scheme 2



activated zinc powder in THF.[23] This led to a 27% yield of a 11:2:1:7 mixture of the stereoisomeric pinacols **15**, with no trace of product **12** or products of its pinacolic coupling. **11** was found to be stable in the presence of $TiCl_3$. Although several examples of reactions involving 7-oxabicyclo[2.2.1]hept-2-yl radical intermediates were known not to undergo the ethereal ring opening,[24] we studied the radical addition of PhSH to 7-oxabicyclo-[2.2.1]hept-5-en-2-one ((±)-**3**) (PhH, AIBN) and found the exclusive formation of adduct **17** (90%).[25] This confirmed



that 7-oxabicyclo[2.2.1]hept-2-yl radical **16** is not capable of undergoing the 7-oxa ring opening to generate **18**. Although the process would liberate ca. 6 kcal/mol of ring strain,[26] the cyclohexoxy radical **16'** that results is expected to be less stable than the 7-oxabicyclo[2.2.1]-hept-2-yl radical ($DH°(Me_2CHO^•/H^•)$ = 104.5 kcal/mol, $DH°(Me_2CH^•/H^•)$ = 96.5 kcal/mol).[27] The ethereal ring opening (Scheme 2) is possible because it involves a ketyl radical-anion of type **19** ↔ **19'** that is not tightly bound to the positive counterion, the radical-cation $Et_3N^{•+}$, resulting from the one-electron transfer from Et_3N: to the excited state of the starting ketone.[28] In the cases of metallic and low valent metallic salt induced electron transfer, the counterion M^+ binds to the ketyl radical-anion and stabilizes it enough to make it to resemble a 2-alkoxy-7-oxabicyclo[2.2.1]hept-2-yl radical unable to undergo the C(1)−O(7) bond cleavage. The higher the electron density in the C(2)−O bond of **19**, the better it

Table 1. Photoreductive 7-Oxa Ring Openings[a]

ketone	conversion rate	products (yield)
(±)-**3**	100%	**21** (<5%) + (53%)
22[30] R=H	50%	**30** (50%)
23[5a] R=OH	35%	**31** (70%)
24[9a] R=OSi(*t*-Bu)Me_2	100%	**32** (0%)
25[31] R,R=*exo*-epoxy	100%	**33** (0%)
26[31] R=OMe, R'=OH	46%	**34** (35%)
27[32] R=OMe, R'=MeOCONH	60%	**35** (45%)
28	54%	**36** (30%)
29	100%	**37** (68%)

[a] 10^{-2} M solution in CH_3CN, quartz vessel, low-pressure Hg lamp, 5 mol equiv of Et_3N.

can transfer to the LUMO of the C(1)−O(7) bond and induce the 7-oxa ring opening. In the case of **19**·SmI_2, the corresponding intermediates undergo pinacolic couplings, and we propose that the 7-oxa ring openings are difficult because they are more like 7-oxanorbornyl-2-yl radicals than ketyl-anions. In the case of **11**, the solvent intervenes and reduces the intermediate. In other cases (e.g., **7**, **9**, see below) and depending on solvent and temperature,[20] it may isomerize into a α-ketocyclohexyl radical of type **20** (a relatively stable carbon-centered radical (α-keto substituent effect on radical stabilization is ca. 6−8 kcal/mol)[29] and then react with the medium.

Extension of the Method. In order to test the generality of our method, we have subjected 7-oxabicyclo-[2.2.1]hept-5-en-2-one ((±)-**3**) and 7-oxabicyclo[2.2.1]-heptan-2-ones **22**−**29** to the irradiation conditions optimized for reaction **11** → **12**. Our results are summarized in Table 1. The best yields were obtained with **11**, the corresponding diol **23**, and the tricyclic ketone **29** which were reduced into the corresponding 3-hydroxycyclohexanones **12** (80%), **31** (70%), and **37** (68%), respectively. With the bis-silyl ether **24**, no trace of the expected

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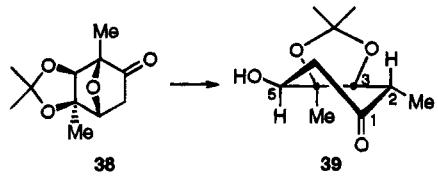
hydroxycyclohexanone **32** could be detected (^{1}H NMR) in the crude reaction mixture, although the starting ketone was consumed rapidly under our photochemical conditions. The same observation was made with the epoxy analogue **25**. Enone (±)-**3** produced 3-hydroxycyclohexanone **21** which was quickly converted into phenol through dehydration.

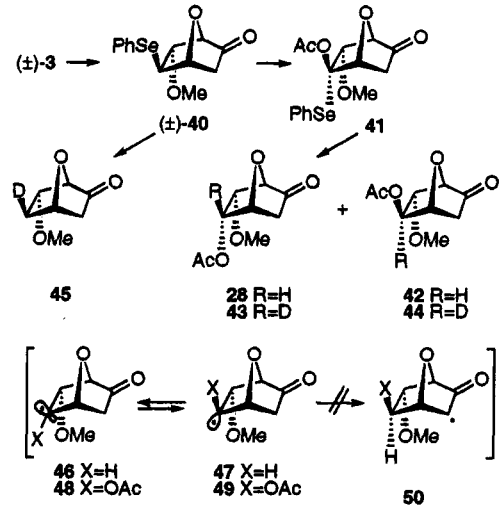
Under our photochemical conditions (254 nm, CH_3CN, 5 equiv of Et_3N, 20−25 °C), the ketoacetonide **38** derived from (±)-**6**[3a] was slowly transformed into a mixture of several compounds and polymeric material. After 50%



38 **39**

consumption of the starting material, the cyclohexanone **39** was isolated in 12% yield. The other products were not identified. They did not contain alcohols. Contrary to the nonmethylated analogue **11** that did not give any trace of the product of ethereal bridge cleavage **12** when treated with SmI_2, we found that **38** could be reduced slowly and selectively into **39** in the presence of 2 equiv of SmI_2 (0.04 M solution in THF). At 20 °C, 35% conversion was obtained after 2 days. This result suggests that the ketyl radical-anion intermediate of type **19**·SmI_2 undergoes the 7-oxa ring opening before hydrogen transfer from the solvent. Why this did not occur for the reaction **11** + SmI_2 remains difficult to explain. Tentatively, we propose that the methyl group at the bridgehead center C(1) in **38** makes the counterion SmI_2^+ not to be so tightly bound to the intermediate ketyl radical-anion, as in the case of **11**, and thus increases its nucleophilicity and the ease of 7-oxa ring opening. Interestingly, only one α-methylcyclohexanone (**39**) is formed in this reaction, probably for thermodynamic reasons, **39** being more stable than its 6-methyl epimer which would imply gauche interactions between the *cis* acetonide and 6-methyl groups. Cyclohexanone **39** adopts probably a half-chair conformation in which the 3-hydroxy and 6-methyl substituents occupy favorable pseudoequatorial positions. This hypothesis was consistent with the ^{1}H NMR characteristics of **39** and by NOE measured between signals assigned to Me-C(2) (1.23 ppm) and H-C(3) (4.18 ppm), H-C(3) and Me-C(4) (1.57 ppm), and Me-C(4) and H-C(5) (3.63 ppm).

Synthesis of New 7-Oxabicyclo[2.2.1]heptan-2-one Derivatives. Ketone **28** was prepared in the following way. Addition of PhSeCl to (±)-**3** in MeOH/$HC(OMe)_3$ gave (±)-**40**.[33] Oxidation with 1 equiv of *m*-chloroperbenzoic acid (*m*-CPBA) at −78 °C, followed by treatment with Ac_2O/AcONa-induced a seleno-Pummerer rearrangement[34] leading to **41** (77%), the treatment of which with Bu_3SnH and AIBN in benzene (80 °C) furnished a 3.8:1 mixture (93%) of **28** and **42**. No product of oxa ring opening could be seen in the ^{1}H-NMR spectrum of the crude reaction mixture. On using Bu_3SnD, a 3:1 mixture of the deuterated derivatives **43** and **44** was obtained. Under the same conditions, **40** afforded **45** as a sole product, with no incorporation of deuterium at the 5-*endo* position. These results show that the 7-oxabicyclo[2.2.1]heptyl radical arising from **41** is more prone than that issued from **40** to undergo quenching by Bu_3SnH(D) onto its *endo* face! Although we do not have direct evidence for it, we propose that this is due to the nonplanarity of the 7-oxabicyclo[2.2.1]hept-2-yl radical intermediates. In the case of **40**, the two radicals **46** and **47** have similar stability and equilibrate rapidly. Since the *endo* face is more hindered than the *exo* face of both bicyclic species **46** and **47**,[27] only **46** reacts and leads to **45** in the presence of Bu_3SnD. In the case of **41**, the equilibrium between the two radicals **48** and **49** might lie in favor of **49** in which the acetoxy and methoxy substituents avoid gauche interactions. This gives less chances for the tin hydride to react with **48** and makes possible it to attack the *endo* face of **49**, giving products **42** and **44**, together with **28** and **43**, respectively. Our results suggest that products **42** and **44** do not arise from a potential 1,3-hydrogen migration leading to the α-keto radical **50** since no deuterium was incorporated at the C(3) position of **44**.



Ketone **29** was derived from (±)-**3** by acetalization with propargyl alcohol, followed by bromination of the C(5)−C(6) double bond which led to 5-*exo*-bromo-6-*endo*-(prop-2-ynyloxy)-7-oxabicyclo[2.2.1]heptan-2-one.[35] Irradiation of this bromide (254 nm, CH_3CN, 0.05 M) in the presence of 10 equiv of Et_3N gave **29** (98% for 63% conversion). This photoreductive ring closure was at least 10 times as fast as the photoinduced 7-oxa ring opening of **29**.

Application to the Synthesis of α-C-Galactopyranosides of Carbapentopyranoses. Our photoreductive 7-oxa ring opening method has been applied to the synthesis of a new class of disaccharide mimics[36] that are α-C-galactopyranosides of carbapentopyranoses.[37] Several antibiotics and compounds of biological interest incorporate glycosides of cyclohexanepolyols.[38] Some cyclohexanepolyols have been called pseudo-sugars[39] or carba-sugars.[40] The replacement of the interglycosidic oxygen atom in a glycoside by a methylene group generate the corresponding deoxy(glycosylmethyl) analogue which may imitate the physical[41] and biological properties of the O-glycoside but should be inert toward acidic and enzymatic hydrolysis.

Treatment of the lithium enolate (LiHMDS, THF, −60 °C) of (±)-**40** with the Eschenmoser's salt (CH_2=NMe_2I)

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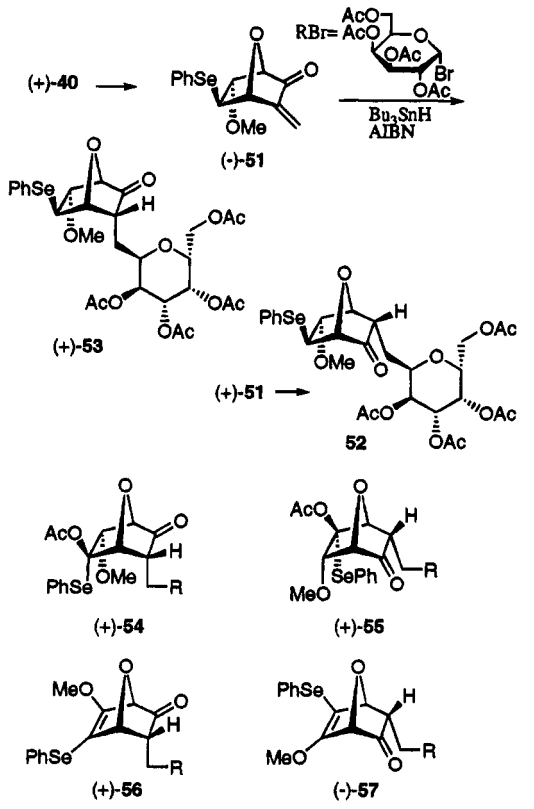
(35) Cossy, J.; Ranaivosata, J.-L.; Bellosta, V. *Tetrahedron Lett.* **1995**, *36*, 2067.



afforded enone (±)-**51** (75%). Radical glycosidation of (±)-**51** with acetobromogalactose[41b] gave a 1:1 mixture (73.5%) of the diastereomeric 3-*endo*-[(α-D-galactopyranosyl)-methyl]-7-oxabicyclo[2.2.1]heptan-2-ones **52** and (+)-**53**. Treatment of this mixture with 1 equiv of *m*-CPBA (THF, −78 °C) and then with Ac_2O/AcONa (−50 to 115 °C, 30 min) led to the seleno-Pummerer rearrangement that provided a mixture of (+)-**54**, (+)-**55**, (+)-**56**, and (−)-**57** from which a 1:1 mixture of (+)-**54** and (+)-**55** and a 1:1 mixture of (+)-**56** and (−)-**57** could be isolated in 82% and 12% yield, respectively, after flash chromatography on silica gel. These compounds could be separated by medium-pressure column chromatography (see Experimental Section) and were fully characterized by their spectral data and NOE measurements in their 400 MHz ^{1}H NMR spectra and COSY-DQF ^{1}H NMR spectra. Starting with optically pure "naked sugar" (+)-**3**, ketone (+)-**40**, enone (−)-**51** and α-galactosides (+)-**53**, (+)-**54**, and (+)-**56** were obtained. The *endo* relative configuration of C(3) in **52** and (+)-**53** was determined on the basis of the vicinal H-C(3)/H-C(4) coupling constants[42] of 6.1 and 6.0 Hz, respectively, observed in the ^{1}H NMR spectra of this compounds. The α configuration of the C-galactosides was confirmed by the ^3J(H-C(1′),H-C(2′)) = 3.3 Hz measured for **52** and (+)-**53**. The *endo* configuration of the PhSe substituent in (+)-**54** and (+)-**55** was confirmed by the observation of NOE's between the proton signals of the *o*-hydrogen atoms of the phenyl group and the methyl protons of the 5-*endo*-methoxy substituent, on one hand, and one of the CH_2−C(3) protons, on the other hand.

Radical reduction of a 1:1 mixture (+)-**54** and (+)-**55** with Bu_3SnH (AIBN, PhH, 80 °C) furnished a 1:1 mixture of (+)-**58** and (+)-**59** in 97% yield. No trace of the corresponding 5-*exo*-acetoxy derivative could be detected, suggesting that the 3-*endo*-[(tetra-*O*-acetyl)-α-D-galactopyranosyl)methyl group impedes Bu_3SnH to quench the 7-oxabicyclo[2.2.1]hept-2-yl radical intermediates onto their *endo* face, steric hindrance that was not present in the case of the reduction of **39**. Similarly, a 1:1 mixture of (+)-**58**/(+)-**59** was obtained in 67% overall yield when treated with Bu_3SnH/AIBN, the crude reaction mixture of the seleno-Pummerer rearrangement of the 1:1 mixture of **52** and (+)-**53**. Attempts to ring open the 7-oxa bridge in (+)-**58** and (+)-**59** with excess SmI_2 (0.1 M in THF, 20 °C) led to 40% conversion after 3 h and allowed one to isolate only 7% of the desired 3-hydroxycyclohexanones (+)-**60** and (+)-**61**, respectively. In the presence of 5% hexamethylphosphoric triamide, the SmI_2-induced ethereal bridge opening was completely inhibited! Irradiation of (+)-**58** and (+)-**59** in the presence of 5 equiv of Et_3N (quartz vessel 254 nm, 20 °C) in CH_3CN led to ca. 80% conversion after 3 h, and 5−15% of (+)-**60** and (+)-**61** were isolated together with polymeric material. Finally, we found that in 2-propanol (5 equiv of Et_3N, 0.064 molar solution, 20 °C) the photoinduced oxa ring opening was slower than in CH_3CN but furnished a better yield of the desired products (+)-**60** and (+)-**61** (60% conversion after 9 h, 35% yield).

The two-dimensional ^{1}H NMR COSY-DQF and NOESY spectra of (+)-**60** (^3J(H-C(1),H-C(2)) = 9.6 Hz, ^3J(H-C(1),H-C(6)) = 2 Hz, ^3J(H-C(5),H-C(6)) = 3.8 & 1.9 Hz:

(36) See, e.g.: Aebischer, B.; Bieri, J. H.; Prewo, R.; Vasella, A. *Helv. Chim. Acta* **1982**, *65*, 2251. Rouzaud, D.; Sinaÿ, P. *J. Chem. Soc., Chem. Commun.* **1983**, 1353. Beau, J.-M.; Sinaÿ, P. *Tetrahedron Lett.* **1985**, *26*, 6185, 6189, 6193. Danishefsky, S. J.; Pearson, W. H.; Harvey, F. D.; Maring, C. J.; Springer, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 1256. Giese, B.; Witzel, T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 450. Jarosz, S.; Mootoo, D.; Fraser-Reid, B. *Carbohydr. Res.* **1986**, *147*, 59. Babirad, S. A.; Wang, Y.; Kishi, Y. *J. Org. Chem.* **1987**, *52*, 1370. Babirad, S. A.; Wang, Y.; Kishi, Y.; Goekjian, P. G. *Ibid.* **1987**, *52*, 4825. Giese, B.; Dupuis, J.; Nix, M. *Org. Synth.* **1987**, *65*, 236. Giese, B. *Pure Appl. Chem.* **1988**, *60*, 1655. Carcano, M.; Nicotra, F.; Panza, L.; Russo, G. *J. Chem. Soc., Chem. Commun.* **1989**, 642. Boschetti, A.; Nicotra, F.; Panza, L.; Russo, G.; Zuchelli, L. *Ibid.* **1989**, 1085. Giese, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 969. Schmidt, R. R.; Preuss, R. *Tetrahedron Lett.* **1989**, *30*, 3409. Motherwell, W. B.; Ross, B. C.; Tozer, M. J. *Synlett* **1989**, 68. Martin, O. R.; Lai, W. *J. Org. Chem.* **1990**, *55*, 5188. Preuss, R.; Schmidt, R. R. *J. Carbohydr. Chem.* **1991**, *10*, 887. Haneda, T.; Goekjian, P. F.; Kim, S. H.; Kishi, Y. *J. Org. Chem.* **1992**, *57*, 490. Lay, L.; Nicotra, F., Panza, L.; Russo, G.; Caneva, E. *Ibid.* **1992**, *57*, 1304. Schmidt, R. R.; Beyerbaeh, A. *Liebigs Ann. Chem.* **1992**, 983. Preuss, R.; Jung, K. H.; Schmidt, R. R. *Ibid.* **1992**, 377. Bimwala, R. M.; Vogel, P. *J. Org. Chem.* **1992**, *57*, 2076. O'Leary, D. J.; Kishi, Y. *Ibid.* **1993**, *58*, 304. Martin, O. R.; Lai, W. *Ibid.* **1993**, *58*, 176. Martin, O. R.; Xie, F.; Kakarla, R.; Benhamza, R. *Synlett* **1993**, 165. Xin, Y. C.; Mallet, J.-M.; Sinaÿ, P. *J. Chem. Soc., Chem. Commun.* **1993**, 864. Vauzeilles, B.; Cravo, D.; Mallet, J.-M.; Sinaÿ, P. *Synlett* **1993**, 522. Wei, A.; Kishi, Y. *J. Org. Chem.* **1994**, *59*, 88. Nicotra, F.; Pangranzio, C.; Panza, L.; Russo, G. *J. Chem. Soc., Perkin Trans. I* **1994**, 333. Mazéas, D.; Skrydstrup, T.; Doumeix, O.; Beau, J.-M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1383. Paton, R. M.; Penman, K. J. *Tetrahedron Lett.* **1994**, *35*, 3163. Dietrich, H.; Schmidt, R. R. *Liebigs Ann. Chem.* **1994**, 975. Johnson, C. R.; Miller, M. W.; Golebiowski, A.; Sundrams, H.; Ksebati, M. B. *Tetrahedron Lett.* **1994**, *35*, 8991.

(37) For a preliminary communication, see: Ferritto, R.; Vogel, P. *Tetrahedron Lett.* **1995**, *36*, 3517.

(38) See, e.g.: Higton, A. A.; Roberts, A. D. *Dictionary of Antibiotics and Related Substances*; Bycroft, B. W., Ed.; Chapman & Hall: London, 1988. Suami, T. In *Carbohydrate Synthetic Methods and Applications in Medicinal Chemistry*; Ogura, H., Hasegawa, A., Suami, T., Eds.; Kodansha, Ltd., and VCH: Tokyo, 1992. Bach, G.; Breiding-Mack, S.; Grabley, S.; Hammann, P.; Hütter, K.; Thiericke, R.; Uhr, H.; Wink, J.; Zeeck, A. *Liebigs Ann. Chem.* **1993**, 241.

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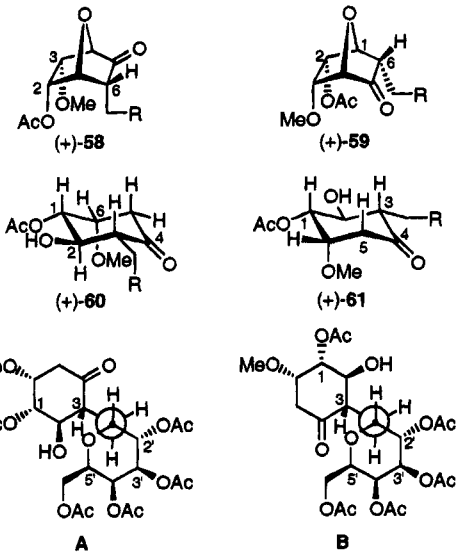
(40) Suami, T.; Ogawa, S. *Adv. Carbohydr. Chem. Biochem.* **1990**, *48*, 22.

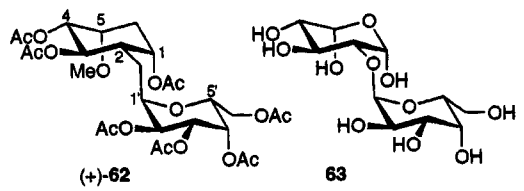
(41) See, e.g., the C-disaccharide conformations: (a) Kishi, Y. *Pure Appl. Chem.* **1993**, *65*, 771. Wei, A.; Kishi, Y. *J. Org. Chem.* **1994**, *59*, 88. (b) Martin, O. R.; Lai, W. *Ibid.* **1990**, *55*, 5188; **1993**, *58*, 176. López-Herrera, F. J.; Pino-González, M. S.; Planas-Ruiz, F. *Tetrahedron: Asymmetry* **1990**, *1*, 465. (d) Ferritto, R.; Vogel, P. *Ibid.* **1994**, *5*, 2077.

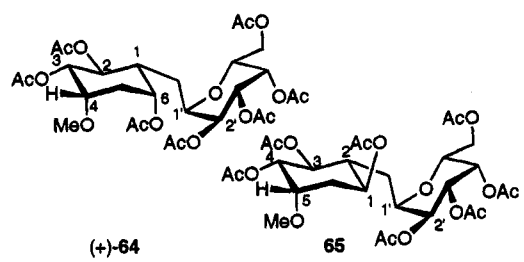
(42) Gagnaire, D.; Payo-Subiza, E. *Bull. Soc. Chim. Fr.* **1963**, 2627. Ramey, K. C.; Lini, D. C. *J. Magn. Reson.* **1970**, *3*, 94. Nelson, W. L.; Allen, D. R. *J. Heterocycl. Chem.* **1972**, *9*, 561. Kienzle, F. *Helv. Chim. Acta* **1975**, *58*, 1180. Mahaim, C.; Vogel, P. *Ibid.* **1982**, *65*, 866.



$^4C_1$ conformation) and (+)-**61** (^3J(H-C(1),H-C(2)) = 9.8 Hz, ^3J(H-C(1),H-C(6)) = 2.3 Hz, ^3J(H-C(5),H-C(6)) = 2.4 Hz: $^4C_1$ conformation) were consistent with chair conformations for both the cyclohexanone and α-D-C-galactoside moieties and with rotamers **A** and **B**, respectively, in which the σC(3)−CH_2 and σC(1′)−C(2′) bond are antiperiplanar as in other α-C-galactosides.[41d]

Reduction of (+)-**60** with $NaBH_4$ (MeOH, 0 °C) followed by acetylation (Ac_2O, pyridine, DMAP) gave (+)-**62** as a sole product, the structure of which was deduced from its spectral data (^3J(H-C(2),H-C(3)) = ^3J(H-C(3),H-C(4)) = 9.1 Hz, ^3J(H-C(4), H-C(5)) = 3.0 Hz, ^3J(H-C(1),H-C(6)) ≈ ^3J(H-C(1),H-C(2)) ≈ 2 Hz) and which can be seen as a protected form of the dicarba-analogue of 2-*O*-(α-D-galactopyranosyl)-D-xylopyranodialdehyde (**63**).





Reduction of (+)-**61** with $NaBH_4$ (MeOH, 0 °C) was less stereoselective and led to a 2.5:1 mixture of (+)-**64** and **65** after acetylation (Ac_2O, pyridine, DMAP), which were separated by flash chromatography on silica gel in 40% and 16% yield, respectively. Their structures were assigned by their 400 MHz ^1H NMR spectra through the use of double irradiation experiments (NOESY and COSY-DQF spectra). The conformations shown for (+)-**64** and **65** are consistent with their ^1H NMR data.

Conclusion

Photoinduced single electron transfer from Et_3N onto 7-oxabicyclo[2.2.1]heptan-2-ones can be an alternative method for the reductive 7-oxa ring opening of these systems into the corresponding 3-hydroxycyclohexanones. In some cases, it can be more successful than the procedure using SmI_2. In one case, we have found that the reductive ethereal ring opening occurs with SmI_2 but not under our photochemical conditions. The latter method has the advantage to be highly tolerant in terms of polyfuctionalities since it can be applied to 7-oxabicyclo-[2.2.1]heptan-2-ones bearing nonprotected hydroxyl groups. An application to the synthesis of 2-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-galactopyranosyl)methyl]-5-methoxycyclohexa-1,3,4-triyl triacetates has been presented. These compounds represent a new class of disaccharide mimics that can be considered as the α-C-galactopyranosides of carbapentopyranose derivatives.

Experimental Section

General. All reactions were run under a nitrogen or argon atmosphere. Reagents (Fluka, Aldrich) were used as received unless otherwise indicated. Tetrahydrofuran (THF) and ethyl ether (Et_2O) were distilled from blue sodium benzophenone ketyl solutions. Benzene, acetonitrile, and triethylamine were distilled from CaH_2. Flash chromatography (FC) was carried out on Kieselgel 60 (230−400 mesh, Merck) and preparative TLC on Merck Silica gel 60 GF_{254} plates. ^1H NMR J values are given in Hz. The 7-oxabicyclo[2.2.1]heptan-2-ones **11**,[5a] **22**,[30] **23**,[5a] **24**,[9a] **25**,[31] **26**,[31], **27**,[32] and **49**[3a] were prepared following known procedures.

(±)-(3*RS*,4*RS*,5*SR*)-3-Hydroxy-4,5-(isopropylidenedioxy)cyclohexanone (12). **11**[5a] (0.184 g, 1 mmol) and Et_3N (0.70 mL, 5 mmol) were dissolved in freshly distilled CH_3CN (67 mL), and the resulting solution was distributed in 10 mm ∅ quartz tubes of a merry-go-round irradiator mounted with eight low-pressure Philipps TUV 15 lamps (λ_{irr}: 254 nm). After 1 h of irradiation at 25 °C, the solutions were combined and the solvent was evaporated in vacuo. The residue was purified by flash chromatography (R_f(**12**) = 0.30, EtOAc/light petroleum 2:1) giving 25% of starting material and 110 mg (80% based on converted material) of **12** as colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ_H 4.65 (m, 1 H), 4.54 (m, 1 H), 3.99−4.08 (m, 1 H), 2.74 (dd, 1 H, ^2J = 16.9, ^3J = 3.8), 2.38−2.55 (m, 3 H), 1.73 (br s, 1 H), 1.48 (s, 3 H), 1.40 (s, 3 H).

(±)-(1*RS*,2*RS*,4*SR*,5*SR*,6*SR*)-5-*exo*,6-*exo*-(Isopropylidenedioxy)-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol (13). A solution of **11** (0.11 g, 0.6 mmol) in anhydrous THF (6 mL) was added to a stirred solution of SmI_2 (0.73 g, 1.8 mmol) in anhydrous THF (18 mL) at −30 °C. After the mixture was stirred at −30 °C for 15 h and at 20 °C for 1 h, saturated aqueous $NaHCO_3$ (0.2 mL) was added. The mixture was extracted with EtOAc (2 × 10 mL). The combined extracts were washed with brine (5 mL) and dried ($MgSO_4$). The solvent was evaporated and the residue purified by preparative TLC (EtOAc/light petroleum 1:1), giving 55 mg (50%) of **11** and 50 mg (45%) of **13** as colorless crystals. Data for **13**: mp 106 °C (lit.[43] 105−107 °C); ^1H NMR (300 MHz, $CDCl_3$) δ_H 4.92 (d, 1 H, ^3J = 5.7), 4.39−4.29 (m, 4 H), 2.37 (s, 1 H), 2.17 (ddd, 1 H, ^2J = 13.1, ^3J = 9.8, 6.3), 1.49, 1.32 (2s, 2 × 3 H), 1.04 (dd, 1 H, ^2J = 13.1, ^3J = 3).

(±)-(1*RS*,2*SR*,4*SR*,5*SR*,6*SR*)-5-*exo*,6-*exo*-(Isopropylidenedioxy)-7-oxabicyclo[2.2.1]heptan-2-*exo*-ol (14). A solution of **11** (0.24 g, 1.3 mmol) in anhydrous THF (10 mL) was added to a solution of Na (0.12 g, 5.2 mmol) in liquid NH_3 (50 mL) at -35 °C. After 30 min at −78 °C, NH_4Cl was added in small portions until decoloration occurred. The reaction mixture was gradually warmed to rt during which time NH_3 was allowed to evaporate. After addition of H_2O (4 mL), the mixture was extracted with Et_2O (3 × 50 mL). The combined extracts were washed successively with ice-cold 1 N HCl (2 mL) and brine (10 mL). After drying ($MgSO_4$), the solvent was evaporated in vacuo. The residue was purified by FC affording **11** (120

(43) Saf, R.; Faber, K.; Penn, G.; Griengl, H. *Tetrahedron* **1988**, *44*, 389.

mg, 50%), **13** (97 mg, 40%), and **14** (11 mg, 4.5%) as colorless crystals: mp 96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 4.47 (d, 1 H, ^3J = 6.1), 4.26 (br s, 1 H), 4.18 (d, 1 H, ^3J = 5.6), 4.14 (d, 1 H, ^3J = 5.6), 3.87 (br d, 1 H, ^3J = 6.7), 2.97 (s, 1 H), 1.74 (dd, 1 H, ^2J = 13.8, ^3J = 7.0), 1.52 (dddd, 1 H, ^2J = 13.8, ^3J = 6.1, J = 2.2, J = 1), 1.47, 1.27 (2 s, 2 × 3 H).

Mixture of (±)-2-(2′-hydroxy-5′-*exo*,6′-*exo*-(isopropylidenedioxy)-7′-oxabicyclo[2.2.1]hept-2′-yl)-5-*exo*,6-*exo*-(isopropylidenedioxy)-7-oxabicyclo[2.2.1]hept-2-ols (15). $TiCl_4$ (0.07 mL, 0.64 mmol) was added slowly (syringe) to a stirred suspension of activated Zn powder (65 mg, 1 mmol) in anhydrous THF (40 mL) cooled to 0 °C under a Ar atmosphere. After being stirred at 20 °C for 30 min, the mixture was cooled to 0 °C and **11** (60 mg, 0.32 mmol) was added. After the mixture was stirred at 0 °C for 1 h and at 20 °C for 17 h, 0.7 N aqueous HCl (15 mL) was added and the mixture extracted with EtOAc (10 mL, three times). The combined extracts were dried ($MgSO_4$), and the solvent was evaporated. FC (silica gel, EtOAc/light petroleum 1:1) gave 16 mg (27%) of a mixture of pinacols **15** as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.07, 5.02, 4.99, 4.92 (4d, ^3J = 5.6), 4.50–4.25 (m), 2.37–2.14 (m), 1.96–1.84 (s), 1.50, 1.47, 1.43 (3s), 1.35–1.02 (m).

(±)-(1*RS*,4*RS*,5*SR*)-5-*exo*-(Phenylthio)-7-oxabicyclo[2.2.1]-heptan-2-one (17). A mixture of **7** (0.60 g, 5.45 mmol), benzene (5.5 mL), thiophenol (1.12 mL, 10.90 mmol), and AIBN (50 mg) was stirred at 80 °C for 2 h and then at 20 °C for 2 days. 2 N aqueous NaOH (5 mL) was added, and the mixture was extracted with Et_2O (20 mL, three times). The combined extracts were washed with H_2O and dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue purified by FC affording 1.08 g (90%) of colorless crystals: mp 97 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.33 (m, 5 H), 4.74 (d, 1 H, ^3J = 6.0), 4.45 (d, 1 H, ^3J = 6.4), 3.55 (dd, ^{1}H, ^3J = 8.3, ^3J = 4.3), 2.54 (dddd, 1 H, ^2J = 17.5, ^3J = 6, ^4J = 1.1, 1.2), 2.27 (dd, 1 H, ^2J = 14, ^3J = 8.3), 2.05 (d, 1 H, ^2J = 17.5), 1.90 (dddt, 1 H, ^2J = 14, ^3J = 6.4, 4.3, ^4J = 1).

(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-3-*endo*-Methoxy-5-oxo-7-oxabicyclo[2.2.1]hept-2-*endo*-yl Acetate (28) and (±)-(1*RS*,2*SR*,3*SR*,4*RS*)-3-*endo*-Methoxy-5-oxo-7-oxabicyclo[2.2.1]hept-2-*exo*-yl Acetate (42). A mixture of **41** (80 mg, 0.224 mmol), anhydrous PhH (5 mL), AIBN (5 mg), and Bu_3SnH (0.12 mL, 0.448 mmol) was heated under reflux for 90 min. The solvent was evaporated, and CH_3CN (25 mL) was added. The solution was extracted with light petroleum (20 mL, three times). The CH_3CN solution was concentrated in vacuo and the residue purified by FC (EtOAc/light petroleum 1:1), giving 42 mg (93%) of a 3.8:1 mixture of **28** and **42** as a colorless oil. Characteristics of **28**: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.03 (ddd, 1 H, ^3J = 8.0, 5.1, ^4J = 1.1), 4.87 (t, 1 H, ^3J = 5.1), 4.43 (d, 1 H, ^3J = 5.4), 3.96 (dd, 1 H, ^3J = 8.0, 5.4), 3.32 (s, 3 H), 2.54 (d, 1 H, ^2J = 17.9), 2.43 (dd, ^2J = 17.9, ^3J = 5.1), 2.08 (s, 3 H). Characteristics of **42**: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 4.80 (s, 1 H), 4.75 (d, 1 H, ^3J = 6.0), 4.43 (d, 1 H, ^3J = 5.4), 3.90 (d, 1 H, ^3J = 5.4), 3.36 (s, 3 H), 2.54 (d, 1 H, ^2J = 17.9), 2.43 (dd, ^2J = 17.9, ^3J = 6.0), 2.11 (s, 3 H).

(±)-(1*RS*,2*SR*,6*SR*,7*RS*)-5-Methylidene-3,10-dioxatricyclo[5.2.1.0^{2,6}]decan-9-one (29). A mixture of (±)-5-*exo*-bromo-6-*endo*-(propargyloxy)-7-oxabicyclo[2.2.1]heptan-2-one[35] (0.245 g, 1 mmol), Et_3N (1.4 mL, 10 mmol), and anhydrous CH_3CN (20 mL) was irradiated (Rayonnet, Philipps TUV15 lamps (254 nm)) in quartz tubes for 30 min. The solvent was evaporated and the residue separated by FC (EtOAc/light petroleum), giving 37% of starting material and 102 mg (98%, based on converted material) of **29**, R_f = 0.70 (EtOAc/light petroleum 1:1), colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 5.08 (dt, 1 H, ^4J = 2.2, 2.1), 5.04 (td, 1 H, ^4J = 2.4, 1.9), 4.92 (dddd, 1 H, ^3J = 8.5, 5.4, ^4J = 1.1, ^5J = 0.6), 4.89 (ttd, 1 H, ^3J = 5.9, ^4J = 1.1, 1.0), 4.54 (m, 2 H), 4.37 (dddd, 1 H, ^3J = 5.4, ^4J = 0.6, 1 H, H(7)), 3.64 (m, 1 H), 2.46 (ddddd, ^2J = 17.9, ^3J = 5.9, ^4J = 1.0, 0.9, ^5J = 0.6), 2.35 (ddd, 1 H, ^2J = 17.9, J = 0.9, ^3J = 1.0, ^4J = 0.6).

(±)-3-Hydroxycyclohexanone (30). Prepared as **12** by irradiation of **22** (0.235 g, 2.1 mmol). Purification by preparative TLC, R_f = 0.30 (AcOEt/light petroleum 3:1), yielded 62 mg (50%, based on converted material) of a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 4.15 (m, 1 H), 3.10 (br s, 1 H), 2.61 (dd, 1 H, ^2J = 14.0, ^3J = 4.0), 2.38 (dd, 1 H, ^2J = 14.0, ^3J = 7.5), 2.28 (m, 2 H), 2.03 (m, 2 H), 1.73 (m, 2 H).

(±)-(3*SR*,4*RS*,5*SR*)-3,4,5-Trihydroxycyclohexanone (31). Same procedure as for the preparation of **12**, starting with **23** (0.087 g, 0.6 mmol).[5a] Purification by preparative TLC, R_f = 0.24 (EtOAc/MeOH 9:1), yielded 22 mg (70%, based on converted **23**) of a colorless oil: ^{1}H NMR (300 MHz, CD_3OD) δ_H 5.05 (s, 3 H), 4.37–4.24 (m, 2 H), 4.05 (dd, 1 H, ^3J = 6.2, ^3J = 2.6), 2.91 (ddd, 1 H, ^2J = 14.5, ^3J = 4.5, ^4J = 1.5), 2.80 (ddd, 1 H, ^2J = 14, ^3J = 8, ^4J = 1.5), 2.71 (ddd, 1 H, ^2J = 14, ^3J = 4.5, ^4J = 1.5), 2.51 (ddd, 1 H, ^2J = 14.5, ^3J = 6.4, ^4J = 1.5).

(±)-(3*SR*,4*RS*,5*RS*)-3,4-Dihydroxy-5-methoxycyclohexanone (34). Same procedure as for the preparation of **12**, starting with **26**[31] (0.142 g, 0.9 mmol). Purification by preparative TLC, R_f = 0.53 (EtOAc/MeOH 9:1), yielded 23 mg (35%, based on converted **26**) of a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 4.30 (ddd, 1 H, ^3J = 6, 4.3, 2.8), 3.96 (dd, 1 H, ^3J = 7.4, 2.8), 3.75 (ddd, 1 H, ^3J = 8.3, 7.4, 4.6), 3.38 (s, 3 H), 2.87 (ddd, 1 H, ^2J = 14.3, ^3J = 4.6, ^4J = 2), 2.66 (ddd, 1 H, ^2J = 14.8, ^3J = 6, ^4J = 2), 2.54 (ddd, 1 H, ^2J = 14.8, ^3J = 4.3, ^4J = 1), 2.36 (ddd, 1 H, ^2J = 14.3, ^3J = 8.3, ^4J = 1), 1.62 (br s, 2 H).

(±)-Ethyl (1′*RS*,2′*RS*,6′*RS*)-2′-Hydroxy-6′-methoxy-4-oxocyclohexyl Carbamate (35). Same procedure as for the preparation of **12**,, starting with **27**[32] (0.092 g, 0.4 mmol). Purification by preparative TLC, R_f = 0.20 (Et_2O), yielded 25 mg (45%, based on converted **27**) of a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 5.20 (br d, 1 H, J = 6.6), 4.47 (m, 1 H), 4.15 (q, 2 H, J = 7.1), 3.93 (ddd, 1 H, ^3J = 8.9, 6.6, 2.8), 3.78 (ddd, 1 H, ^3J = 9.3, 8.9, 4.8), 3.37 (s, 3 H), 2.88 (ddd, 1 H, ^2J = 14.3, ^3J = 4.8, ^4J = 2.0), 2.67 (ddd, 1 H, ^2J = 15.0, ^3J = 3.4, ^4J = 0.7), 2.55 (ddd, 1 H, ^2J = 15.0, ^3J = 4.8, ^4J = 2.0), 2.42 (ddd, 1 H, ^2J = 14.3, ^3J = 9.3, ^4J = 0.7), 1.66 (br s, 1 H), 1.27 (t, 3 H).

(±)-(1*RS*,2*SR*,6*SR*)-2-Hydroxy-6-methoxy-4-oxocyclohexyl Acetate (36). Same procedure as for the preparation of **12**, starting with **28** (65 mg, 0.35 mmol), Et_3N (0.22 mL, 1.625 mmol), and CH_3CN (6.5 mL). FC (EtOAc/light petroleum 2:1) gave 30 mg of **28** and 11 mg of **36** (30% based on converted **28**) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.19 (m, 1 H, ^3J = 7.6), 4.36 (m, 1 H), 3.94 (m, 1 H), 3.37 (s, 3 H), 2.82 (ddd, 1 H, ^2J = 14.9, ^3J = 5.1, ^4J = 1.9), 2.75 (ddd, 1 H, ^2J = 14.8, ^3J = 6.7, ^4J = 1.9), 2.60 (dd, 1 H, ^2J = 14.8, ^3J = 3.7), 2.46 (dd, 1 H, ^2J = 14.9, ^3J = 8.0), 2.25 (d, 1 H, ^3J = 4.0), 2.19 (s, 3 H).

(±)-(1*RS*,2*SR*,6*SR*)-2-Hydroxy-9-methylidene-7-oxabicyclo[4.3.0]decan-4-one (37). Same procedure as for the preparation of **12**, starting with **29** (0.051 g, 0.3 mmol), purification by FC, R_f = 0.36 (EtOAc/light petroleum 1:1), yielded 35 mg (68%) of a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 5.16 (m, 2 H), 4.48 (ddd, 1 H, ^3J = 6.6, 3.3, 2.9), 4.44 (dq, 1 H, ^2J = 13.6, ^4J = 1.8), 4.27 (dtd, 1 H, ^2J = 13.6, ^4J = 2.6, 1.5), 4.15 (dt, 1 H, ^3J = 5.2, 2.9), 2.97 (m, 1 H), 2.85 (dd, 1 H, ^2J = 17.3, ^3J = 3.3), 2.70 (dd, 1 H, ^2J = 17.3, ^3J = 2.9), 2.61 (dd, 1 H, ^2J = 16.5, ^3J = 2.9), 2.45 (ddd, 1 H, ^2J = 16.5, ^3J = 5.2, ^4J = 1.5), 2.00–2.30 (m, 1 H).

(±)-(2*RS*,3*RS*,4*SR*,5*SR*)-5-Hydroxy-3,4-(isopropylidenedioxy)-2,4-dimethylcyclohexanone (39). A mixture of **38**[3a,c] (20 mg, 0.09 mmol), anhydrous THF (0.5 mL), and 0.04 M SmI_2 in THF (4.7 mL) was stirred at 20 °C for 48 h. A saturated aqueous solution of $NaHCO_3$ (10 mL) was added, and the mixture was extracted with Et_2O (5 mL, three times). The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated. The residue was separated by FC (1 g of silica gel, EtOAc/light petroleum 1:1) to give 11 mg (55%) of **38** and 7 mg (35%) of **39** as a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ_H 4.18 (d, 1 H, ^3J = 2.0), 3.63 (ddd, 1 H, ^3J = 12.0, 11.0, 5.0), 2.59 (dd, 1 H, ^2J = 17.9, ^3J = 5.0), 2.36 (dd, 1 H, ^2J = 17.9, ^3J = 12.0), 2.36 (dq, 1 H, ^3J = 6.8, 2.0), 2.22 (d, 1 H, ^3J = 11.0), 1.57 (s, 3 H), 1.44, 1.42 (2 s, 2 × 3 H), 1.23 (d, 3 H, ^3J = 6.8).

(±)-(1*RS*,2*SR*,3*RS*,4*RS*)-3-*endo*-Methoxy-5-oxo-2-*endo*-(phenylseleno)-7-oxabicyclo[2.2.1]hept-2-*exo*-yl Acetate (41). A solution of *m*-CPBA (90%, 325 mg, 1.683 mmol) in anhydrous THF (2 mL) was added dropwise to a stirred solution of (±)-**40**[33] (0.5 g, 1.683 mmol) in anhydrous THF (10 mL) cooled to −78 °C. After the mixture was stirred at −78

°C for 15 min, Ac_2O (1 mL, 10.6 mmol) and AcONa (440 mg, 4.9 mmol) were added. The mixture was heated under reflux for 20 min. After the mixture was cooled to 20 °C, the solvent was evaporated and CH_2Cl_2 (40 mL) was added. The solution was washed with a saturated aqueous solution of $NaHCO_3$ (25 mL, twice), with a 5% aqueous solution of Na_2CO_3 (25 mL, twice), and finally with brine (25 mL). The combined aqueous layers were extracted with CH_2Cl_2 (25 mL). The combined organic phases were dried ($MgSO_4$), and the solvent was evaporated. FC (EtOAc/light petroleum 1:2) gave 0.46 g (77%) of a yellowish oil: ^1H NMR (400 MHz, $CDCl_3$) δ_H 7.55 (m, 2 H), 7.38 (m, 1 H), 7.31 (m, 2 H), 4.60 (d, 1 H, ^3J = 6.6), 4.46 (d, 1 H, ^3J = 5.6), 4.32 (dd, 1 H, ^3J = 5.6, 1.4), 3.60 (s, 3 H), 3.21 (d, 1 H, ^2J = 18), 2.53 (ddd, 1 H, ^2J = 18, ^3J = 6.6, ^4J = 1.0), 2.07 (s, 3 H).

(±)-(1*RS*,4*RS*,5*RS*,6*RS*)-5-*exo*-Deuterio-6-*endo*-methoxy-7-oxabicyclo[2.2.1]heptan-2-one (45). A mixture of (±)-**40**[33] (30 mg, 0.1 mmol), PhH (1 mL), AIBN (5 mg), and Bu_3SnD (0.042 mL, 0.15 mmol) was heated under reflux for 90 min. The solvent was evaporated, and CH_3CN (10 mL) was added. The solution was extracted with light petroleum (10 mL, three times). The CH_3CN solution was concentrated in vacuo giving 14 mg (98%), colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ_H 4.86 (d, 1 H, ^3J = 6.0), 4.43 (d, 1 H, ^3J = 5.2), 4.07 (br s, 1 H), 3.34 (s, 3 H), 2.52 (dd, 1 H, ^2J = 17.4, ^3J = 6.0), 2.17 (d, 1 H, ^2J = 17.4), 1.72 (s, 1 H).

(±)-(1*RS*,4*RS*,5*RS*,6*RS*)-6-*endo*-Methoxy-3-methylidene-5-*exo*-(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-one ((±)-51). A solution of BuLi (1.6 N in hexane, 20.2 mL, 32.3 mmol) was added dropwise to a stirred solution of $(Me_2Si)_2NH$ (7.9 mL, 37.7 mmol) in anhydrous THF (200 mL) cooled to 0 °C. After being stirred at 0 °C for 15 min, the mixture was cooled to −60 °C and a solution of (±)-**40**[33] (8 g, 26.9 mmol) in anhydrous THF (80 mL) was added slowly (automatic syringe) under stirring. The temperature must stay below −50 °C. After the mixture was stirred at −60 °C for 10 more min, Me_2NCH_2I (7.5 g, 40.3 mmol) was added portionwise under stirring. The mixture was allowed to warm to 20 °C in 14 h. Seven percent aqueous solution of HCl (200 mL) was added and the mixture extracted with light petroleum (100 mL, three times). The aqueous phase was neutralized to pH 8 with aqueous solution of Na_2CO_3 and extracted with CH_2Cl_2 (150 mL, three times). The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated. The residue was dissolved in anhydrous THF (100 mL), and MeI (20 mL) was added. After being stirred at 20 °C for 14 h, the solvent was evaporated. K_2CO_3 (9.7 g, 70 mmol) dissolved in H_2O (100 mL) and EtOAc (100 mL) were added. After vigourous stirring at 20 °C for 4 h, the aqueous phase was extracted with EtOAc (100 mL, twice). The combined organic phases were dried ($MgSO_4$), and the solvent was evaporated. FC (80 g of silica gel, EtOAc/light petroleum 1:2) gave 6.3 g (75%) of a yellow solid: mp 86−87 °C; ^1H NMR (400 MHz, $CDCl_3$) δ_H 7.62 (m, 2 H), 7.36 (m, 3 H), 5.96 (d, 1 H, ^4J = 1.3), 5.36 (s, 1 H), 4.97 (m, 1 H), 4.59 (dd, 1 H, ^3J = 5.4, ^4J = 1.1), 4.10 (m, 1 H), 3.42 (d, 1 H, ^3J = 2), 3.26 (s, 3 H).

(−)-(1*R*,4*R*,5*R*,6*R*)-6-*endo*-Methoxy-3-methylidene-5-*exo*-(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-one ((−)-51). Same procedure as for (±)-**51**, starting with (+)-**40**,[33] yellow oil: $[\alpha]^{25}_D$ = −0.9, $[\alpha]^{25}_{577}$ = +0.5, $[\alpha]^{25}_{546}$ = +9.8, $[\alpha]^{25}_{485}$ = +189, $[\alpha]^{25}_{405}$ = +278 (c = 2, $CHCl_3$).

1:1 Mixture of (1*R*,3*R*,4*S*,5*S*,6*S*)-6-*endo*-Methoxy-5-*exo*-(phenylseleno)-3-*endo*-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-galactopyranosyl)methyl]-7-oxabicyclo[2.2.1]hept-2-one (52) and (1*S*,3*S*,4*R*,5*R*,6*R*)-6-*endo*-Methoxy-5-*exo*-(phenylseleno)-3-*endo*-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-galactopyranosyl)methyl]-7-oxabicyclo[2.2.1]heptan-2-one ((+)-53). A solution of (±)-**51** (3 g, 9.7 mmol), Bu_3SnH (3.4 mL, 12.6 mmol), AIBN (150 mg), and PhH (12 mL) was added (automatic syringe) in 90 min to a solution of acetobromogalactose (5.185 g, 12.61 mmol) and AIBN (75 mg) in PhH (24 mL) heated under reflux. After being heated under reflux for 30 more min, the mixture was cooled to 20 °C and the solvent evaporated in vacuo (10^{-2} Torr). The residue was taken in CH_3CN (200 mL), and the solution was extracted with light petroleum (100 mL, three times). The CH_3CN solution was concentrated in vacuo and the residue purified by FC (300 g, silica gel, EtOAc/light petroleum 1:2), giving 0.9 g (21%) of 1-deoxyacetogalactose, 0.25 g (6%) of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-galactopyranose, and 4.56 g (73.4%) of a 1:1 mixture of **52**/(+)-**53** as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) of **52**: δ_H 7.60 (m, 2 H), 7.32 (m, 3 H), 5.38 (m, 1 H), 5.17 (m, 2 H), 4.77 (d, 1 H, ^3J = 6.0), 4.54 (d, 1 H, ^3J = 5.5), 4.15−4.00 (m, 4 H), 3.92 (m, 1 H), 3.18 (d, 1 H, ^3J = 2.1), 3.21 (s, 3 H), 2.74 (m, 1 H), 2.11, 2.09, 2.07, 2.01 (4 s, 4 × 3 H), 2.15, 1.35 (2 m, 2 H).

(1*S*,3*S*,4*R*,5*R*,6*R*)-6-*endo*-Methoxy-5-*exo*-(phenylseleno)-3-*endo*-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-galactopyranosyl)methyl]-7-oxabicyclo[2.2.1]heptan-2-one ((+)-53). Same procedure as above, starting with (−)-**51**, colorless crystals: mp 56−58 °C dec; $[\alpha]^{25}_D$ = +51.5, $[\alpha]^{25}_{577}$ = +54, $[\alpha]^{25}_{546}$ = +64, $[\alpha]^{25}_{435}$ = +123, $[\alpha]^{25}_{405}$ = +155 (c = 2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ_H 7.61 (m, 2 H), 7.33 (m, 3 H), 5.22 (dd, ^3J = 4.6, 3.1, 1 H), 5.12 (dd, 1 H, ^3J = 6.7, 3.1), 5.07 (dd, 1 H, ^3J = 6.7, 3.3), 4.82 (d, 1 H, ^3J = 6.1), 4.50 (d, 1 H, ^3J = 5.4), 4.42 (dd, 1 H, ^2J = 12.0, ^3J = 9.0), 4.24 (m, 1 H), 4.01 (d, 1 H, ^3J = 5.4), 3.97 (dd, 1 H, ^2J = 12.0, ^3J = 3.8), 3.65 (m, 1 H), 3.49 (d, 1 H, ^3J = 2.3), 3.23 (s, 3 H), 2.65 (m, 1 H), 2.09, 2.07 (2 s, 12 H), 1.82 (m, 1 H), 1.49 (m, 1 H).

(+)-(1*R*,2*S*,3*R*,4*R*,6*R*)-3-*endo*-Methoxy-5-oxo-2-*endo*-(phenylseleno)-6-*endo*-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-galactopyranosyl)methyl]-7-oxabicyclo[2.2.1]hept-2-*exo*-yl Acetate ((+)-54), (+)-(1*S*,2*R*,3*S*,4*S*,6*S*)-3-*endo*-methoxy-5-oxo-2-*endo*-(phenylseleno)-6-*endo*-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-galactopyranosyl)methyl]-7-oxabicyclo-[2.2.1]hept-2-*exo*-yl Acetate ((+)-55), (+)-(1*R*,4*R*,5*R*)-6-oxo-3-(phenylseleno)-5-*endo*-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-galactopyranosyl)methyl]-7-oxabicyclo[2.2.1]hept-2-en-2-yl Acetate ((+)-56), and (−)-(1*S*,4*S*,5*S*)-6-oxo-3-(phenylseleno)-5-*endo*-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-galactopyranosyl)methyl]-7-oxabicyclo[2.2.1]hept-2-en-2-yl Acetate ((−)-57). A solution of *m*-CPBA (55%, 161 mg, 0.467 mmol) in THF (5 mL) was added dropwise to a stirred solution of a 1:1 mixture of **52**/(+)-**53** (300 mg, 0.467 mmol) in anhydrous THF (10 mL) at −78 °C. After the mixture was stirred at −78 °C for 15 min (control of the end of the oxidation by TLC, EtOAc/light petroleum 1:1), Ac_2O (1 mL) and AcONa (0.4 g) were added, and the mixture was heated under reflux for 30 min. After the mixture was cooled to 20 °C, EtOAc (25 mL) was added and the solution washed with saturated aqueous solution of $NaHCO_3$ (25 mL, twice) and then with 5% aqueous solution of Na_2CO_3 (25 mL, twice). The aqueous phases were combined and extracted with EtOAc (25 mL). The combined organic extracts were dried ($MgSO_4$). The solvent was evaporated and the residue purified by FC, giving first 35 mg (12%) of a 1:1 mixture of (+)-**56** and (−)-**57** and then 269 mg (82%) of a 1:1 mixture of (+)-**54** and (+)-**55** as a colorless oil: (+)-**54** and (+)-**55** were separated by medium-pressure chromatography (Lobar) on LiChroprep Si 60 (15−25 μm, Merck) with EtOAc/light petroleum 1:1. Similarly, (+)-**56** and (−)-**57** were separated using EtOAc/light petroleum 1:2, same column.

Data for (+)-**54**: colorless crystals, mp 87−91 °C dec; $[\alpha]^{25}_D$ = +24, $[\alpha]^{25}_{577}$ = +24, $[\alpha]^{25}_{546}$ = +32, $[\alpha]^{25}_{435}$ = +68, $[\alpha]^{25}_{405}$ = +86 (c = 1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ_H 7.62 (m, 2 H), 7.37 (m, 3 H), 5.27 (t, 1 H, ^3J = 3.4), 5.23 (dd, 1 H, ^3J = 7.6, 4.1), 5.10 (dd, 1 H, ^3J = 3.4, 7.6), 5.03 (d, 1 H, ^3J = 6.2), 4.60 (d, 1 H, ^3J = 5.9), 4.43 (m, 2 H), 4.33 (dd, 1 H, ^2J = 12.0, ^3J = 8.5), 4.02 (dd, ^2J = 12.0, ^3J = 4.2), 3.71 (m, 1 H), 3.58 (s, 3 H), 2.94 (m, 1 H), 2.19 (m, 2 H), 2.11, 2.09, 2.06, 1.98 (4 s, 15 H).

Data for (+)-**55**: colorless crystals, mp 78−84 °C dec; $[\alpha]^{25}_D$ = +93, $[\alpha]^{25}_{577}$ = +98, $[\alpha]^{25}_{546}$ = +118, $[\alpha]^{25}_{435}$ = +225, $[\alpha]^{25}_{405}$ = +281 (c = 0.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ_H 7.51 (m, 2 H), 7.33 (m, 3 H), 5.44 (m, 1 H), 5.27 (m, 2 H), 5.17 (d, 1 H, ^3J = 6.0), 4.63 (d, 1 H, ^3J = 5.7), 4.48 (m, 2 H), 4.36 (dd, ^2J = 11.4, ^3J = 7.9), 4.19 (m, 1 H), 4.09 (dd, 1 H, ^2J = 11.4, ^3J = 4.7), 3.61 (s, 3 H), 2.99 (m, 1 H), 2.51 (m, 1 H), 2.26 (m, 1 H), 2.13, 2.07, 1.98, 1.95, 1.65 (5s, 15 H).

Data for (+)-**56**: colorless oil, $[\alpha]^{25}_D$ = +115, $[\alpha]^{25}_{577}$ = +120, $[\alpha]^{25}_{546}$ = +146, $[\alpha]^{25}_{546}$ = +338, $[\alpha]^{25}_{405}$ = +486 (c = 1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ_H 7.27−7.4 (m, 3 H), 7.5 (m, 2

H), 5.37 (t, 1 H, ^3J = 3.2), 5.25 (dd, 1 H, ^3J = 8.4, 4.4), 5.15 (dd, 1 H, ^3J = 8.4, 3.2), 5.09 (dd, 1 H, ^3J = 4.0, ^4J = 1.3), 4.65 (d, 1 H, ^4J = 1.3), 4.33 (m, 1 H), 4.19 (dd, 1 H, ^2J = 11.6, ^3J = 8.8), 4.09 (m, 1 H), 3.98 (s, 3 H), 3.81 (dd, 1 H, ^2J = 11.6, ^3J = 3.5), 2.49 (m, 1 H), 2.05, 1.85 (2 m, 2 H), 2.12, 2.10, 2.04, 1.86 (4 s, 12 H).

Data for (−)-**57**: colorless oil, $[\alpha]^{25}_D = -168$, $[\alpha]^{25}_{577} = -180$, $[\alpha]^{25}_{546} = -215$, $[\alpha]^{25}_{435} = -592$, $[\alpha]^{25}_{405} = -943$ (c = 1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ_H 7.27−7.40 (m, 3 H), 7.45 (m, 2 H), 5.40 (m, 1 H), 5.35 (dd, 1 H, ^3J = 10.1, 5.6), 5.23 (dd, 1 H, ^3J = 10.1, 3.3), 4.94 (dd, 1 H, ^3J = 3.9, ^4J = 1.2), 4.65 (d, 1 H, ^4J = 1.2), 4.25 (m, 1 H), 4.05 (m, 3 H), 3.97 (s, 3 H), 2.56 (m, 1 H), 2.28, 1.52 (2 m, 2 H), 2.12, 2.11, 2.01, 1.98 (4 s, 12 H).

(+)-(1*R*,2*S*,3*S*,4*R*,6*R*)-3-*endo*-Methoxy-5-oxo-6-*endo*-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-galactopyranosyl)methyl]-7-oxabicyclo[2.2.1]hept-2-*endo*-yl Acetate ((+)-58) and (+)-(1*S*,2*R*,3*R*,4*S*,6*S*)-3-*endo*-Methoxy-5-oxo-6-*endo*-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-galactopyranosyl)methyl]-7-oxabicyclo[2.2.1]hept-2-*endo*-yl Acetate ((+)-59). A 1:1 mixture of (+)-**54** and (+)-**55** (88 mg, 0.125 mmol), AIBN (5 mg), PhH (5 mL), and Bu_3SnH (0.066 mL, 0.25 mmol) was heated under reflux for 90 min. The solvent was evaporated in vacuo (10^{-2} Torr). The residue was taken with CH_3CN (25 mL) and the solution extracted with light petroleum (25 mL, 3 times). The CH_3CN solution was concentrated in vacuo and the residue purified by FC (EtOAc/light petroleum 1:1), giving 66.2 mg (97%) 1:1 mixture of (+)-**58** and (+)-**59** that were separated by medium-pressure column chromatography (Lobar, LiChroprep Si60, 15−25 μm, Merck, EtOAc/light petroleum 1:1).

Data for (+)-**58**: colorless crystals, mp 69−72 °C dec; $[\alpha]^{25}_D = +41$, $[\alpha]^{25}_{577} = +42$, $[\alpha]^{25}_{546} = +52$, $[\alpha]^{25}_{485} = +97$, $[\alpha]^{25}_{405} = +97$ (c = 1.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ_H 5.39 (t, 1 H, ^3J = 3.0), 5.23 (dd, 1 H, ^3J = 7.7, 3.8), 5.19 (dd, 1 H, ^3J = 7.7, 3.0), 5.10 (dd, 1 H, ^3J = 7.8, 4.9), 4.91 (t, 1 H, ^3J = 4.9), 4.60 (d, 1 H, ^3J = 5.6), 4.38 (m, 2 H), 4.20 (m, 1 H), 4.12 (dd, 1 H, ^2J = 11.7, ^3J = 4.3), 4.06 (dd, 1H, ^3J = 7.8, 5.6), 3.34 (s, 3 H), 2.80 (m, 1 H), 2.0−2.15 (2 m, 2 H), 2.12, 2.11, 2.10, 2.07, 2.06 (5 s, 15 H).

Data for (+)-**59**: colorless crystals, mp 76−79 °C dec; $[\alpha]^{25}_D = +117$, $[\alpha]^{25}_{577} = +122$, $[\alpha]^{25}_{546} = +142$, $[\alpha]^{25}_{435} = +243$, $[\alpha]^{25}_{405} = +284$ (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ_H 5.43 (t, ^3J = 3.2), 5.29 (dd, 1 H, ^3J = 9.2, 4.9), 5.26 (dd, 1 H, ^3J = 9.2, 3.2), 5.05 (dd, 1 H, ^3J = 7.9, 5.0), 4.93 (t, 1 H, ^3J = 5), 4.63 (d, 1 H, ^3J = 5.6), 4.30 (m, 2 H), 4.08 (m, 3 H), 3.30 (s, 3 H), 2.84 (m, 1 H), 2.20, 1.95 (2 m, 2 H), 2.11, 2.05, 2.03, 2.01, 1.98 (5 s, 15 H).

(+)-(1*S*,2*R*,3*R*,6*R*)-2-Hydroxy-6-methoxy-4-oxo-3-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-galactopyranosyl)methyl]-cyclohexyl Acetate ((+)-60). A solution of (+)-**58** (250 mg, 0.46 mmol) and Et_3N (0.33 mL, 2.3 mmol) in 2-propanol (11.5 mL) was placed in a quartz tube and irradiated in a Graentzel apparatus mounted with 12 low-pressure Hg lamps (λ_{irr} = 254 nm) for 9 h at 20 °C. The yellow solution was concentrated in vacuo and the residue purified by FC (EtOAc/light petroleum 2:1), yielding 167 mg (67%) of (+)-**58** and 23 mg (28% based on converted (+)-**58**) of (+)-**60** as colorless crystals: mp 74−78 °C dec; $[\alpha]^{25}_D = +46$, $[\alpha]^{25}_{577} = +47$, $[\alpha]^{25}_{546} = +58$, $[\alpha]^{25}_{435} = +104$, $[\alpha]^{25}_{405} = +100$ (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ_H 5.40 (m, 1 H), 5.32 (dd, 1 H, ^3J = 9.7, 5.3), 5.20 (dd, 1 H, ^3J = 9.7, 3.3), 5.06 (dd, 1 H, ^3J = 9.6, 2.5), 4.26 (m, 1 H), 4.24−4.03 (m, 3 H), 3.91 (m, 1 H), 3.87 (m, 1 H), 3.33 (s, 3 H), 2.80 (dd, 1 H, ^2J = 14.8, ^3J = 3.8), 2.60 (dd, 1 H, ^2J = 14.8, ^3J = 1.9), 2.54 (m, 2 H), 2.19, 2.12, 2.11, 2.07, 2.01 (5 s, 15 H), 1.99−2.2 (2 m, 2 H).

(+)-(1*R*,2*S*,3*S*,6*S*)-2-Hydroxy-6-methoxy-4-oxo-3-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-galactopyranosyl)methyl]-cyclohexyl Acetate ((+)-61). Same procedure as for the preparation of (+)-**60**, starting with (+)-**59** (177 mg, 0.323 mmol): yield 44 mg of (+)-**59** (29%) and 27.6 mg (20% based on reacted (+)-**59**) of (+)-**61** as colorless crystals; mp 81−84 °C dec; $[\alpha]^{25}_D = +67$, $[\alpha]^{25}_{577} = +69$, $[\alpha]^{25}_{546} = +82$, $[\alpha]^{25}_{435} = +147$, $[\alpha]^{25}_{405} = +176$ (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ_H 5.39 (t, 1 H, ^3J = 3.0), 5.25 (dd, 1 H, ^3J = 9.5, 5.0), 5.18 (dd, 1 H, ^3J = 9.5, 3.0), 5.07 (dd, 1 H, ^3J = 9.8, 2.3), 4.35 (m, 1 H), 4.28−4.15 (m, 3 H), 4.01 (dd, 1 H, ^2J = 10.3, ^3J = 2.6), 3.89 (d, 1 H, ^3J = 2.3), 3.31 (s, 3 H), 2.80 (dd, 1 H, ^2J = 14.9, ^3J = 3.7), 2.58 (m, 1 H), 2.53 (dd, 1 H, ^2J = 14.9, ^3J = 2.4), 2.15, 1.92 (2 m, 2 H), 2.15, 2.14, 2.10, 2.08, 2.02 (5 s, 15 H).

(+)-(1*S*,2*S*,3*R*,4*R*,5*R*)-5-Methoxy-2-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-galactopyranosyl)methyl]cyclohexa-1,3,4-triyl Triacetate ((+)-62). A mixture of (+)-**60** (19 mg, 0.034 mmol), MeOH (1 mL), and $NaBH_4$ (7 mg, 0.18 mmol) was stirred at 0 °C for 20 min. The solvent was evaporated in vacuo (10^{-2} Torr). Pyridine (1 mL), Ac_2O (0.1 mL), and DMAP (2 mg) were added, and the mixture was stirred at 20 °C for 14 h. The solvent was evaporated (10^{-2} Torr) and the residue purified by FC (EtOAc/light petroleum 1:1), yielding 10 mg (46%) of a colorless oil: $[\alpha]^{25}_D = +49$, $[\alpha]^{25}_{577} = +52$, $[\alpha]^{25}_{546} = +67$, $[\alpha]^{25}_{435} = +124$, $[\alpha]^{25}_{405} = +144$ (c = 0.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ_H 5.43 (t, 1 H, ^3J = 9.1), 5.40 (t, 1 H, ^3J = 3.0), 5.16 (dd, 1 H, ^3J = 8.9, 4.7), 5.17 (s, 1 H), 5.12 (dd, 1 H, ^3J = 8.9, 3.0,), 4.92 (dd, 1 H, ^3J = 9.1, 3.0), 4.27 (m, 1 H), 4.22 (dd, 1 H, ^2J = 11.6, ^3J = 7.4), 4.12 (dd, 1 H, ^2J = 11.6, ^3J = 4.8), 3.99 (m, 1 H), 3.75 (d, 1 H, ^3J = 3.0), 3.30 (s, 3 H), 2.49 (m, 1 H), 2.12, 2.10, 2.07, 2.06, 2.04, 2.03 (6 s, 21 H), 2.05 (m, 1 H), 1.71 (m, 1 H), 1.65 (m, 1 H), 1.48 (m, 1 H).

(+)-(1*R*,2*R*,3*S*,4*S*,5*S*)-5-Methoxy-2-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-galactopyranosyl)methyl)cyclohexa-1,3,4-triyl Triacetate ((+)-64) and (1*S*,2*R*,3*S*,4*S*,5*S*)-5-Methoxy-2-[(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-galactopyranosyl)-methyl]cyclohexa-1,3,4-triyl Triacetate (65). Same procedure as for the preparation of (+)-**62**, starting with (+)-**61** (33 mg, 0.06 mmol). FC (EtOAc/light petroleum 1:1) gave 6 mg (16%) of **65** and 15 mg (40%) of (+)-**64**.

Data of (+)-**64**: colorless oil, $[\alpha]^{25}_D = +34$, $[\alpha]^{25}_{577} = +37$, $[\alpha]^{25}_{546} = +49$, $[\alpha]^{25}_{435} = +88$, $[\alpha]^{25}_{405} = +98$ (c = 0.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ_H 5.49 (t, 1 H, ^3J = 9.4), 5.37 (t, 1 H, ^3J = 2.9), 5.17 (dd, 1 H, ^3J = 9.3, 5.0), 5.11 (dd, 1 H, ^3J = 9.3, 2.9), 5.0 (d, 1 H, ^3J = 3.3), 4.87 (dd, 1 H, ^3J = 9.4, 3.0), 4.27 (m, 1 H), 4.20 (dd, 1 H, ^2J = 11.5, ^3J = 7.1), 4.06 (dd, 1 H, ^2J = 11.5, ^3J = 5.3), 3.98 (m, 1 H), 3.74 (d, 1 H, ^3J = 3), 3.29 (s, 3 H), 2.55 (m, 1 H), 2.11, 2.07, 2.06, 2.03 (4s, 21 H), 2.12−2.0 (m, 2 H), 1.76, 1.56 (2 m, 2 H).

Data of **65**: colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ_H 5.46 (t, 1 H, ^3J = 10.6), 5.41 (m, 1 H), 5.22 (dd, 1 H, ^3J = 10.4, 5.5), 5.16 (dd, 1 H, ^3J = 10.4, 3.2), 4.83 (dd, 1 H, ^3J = 10.4, 2.9), 4.30 (m, 1 H), 4.12 (m, 3 H), 3.88 (m, 1 H), 3.49 (m, 1 H), 3.48 (s, 3 H), 2.36 (m, 1 H), 2.14 (m, 1 H), 1.78 (m, 1 H), 1.64 (m, 1 H), 1.50 (m, 1 H).

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Supporting Information Available: Spectral data and elemental analysis for various compounds (17 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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