130. Glycosylidene Carbenes

Part 24[1])

Reactivity Modulation by Protecting Groups of the Addition of Glycosylidene Carbenes to Electron-Rich Alkenes

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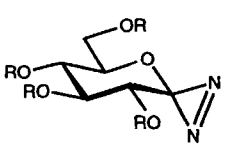
The reactivity of glycosylidene carbenes derived from pivaloylated *vs.* benzylated diazirines **1** and **2** towards enol ethers have been examined. The pivaloylated **1** led to higher yields of spirocyclopropanes than the benzylated **2**. Among the enol ethers tested, dihydrofuran **6** proved most reactive, yielding 71–72% of the spiro-linked tetrahydrofuran **7**, while the benzylated diazirine **2** afforded only 33% of the analogue **8** (*Scheme 1*). Other enol ethers proved much less reactive. The addition of **1** and **2** to the dihydropyran **10** and the 2,3-dihydro-5-methylfuran **15** gave low yields of single cyclopropanes (→ **12**, **14**, and**16**), and the glycals **17** and **18**, and (*E*)-1-methoxyoct-1-ene (**23**) did not react. The main products of these reactions were the azines (*Z*,*Z*)-**11** and (*Z*,*Z*)/(*E*,*E*)-**13**. Similarly, **1** and **2** reacted poorly with (*Z*)-1-methoxyoct-1-ene (**24**), leading to the cyclopropanes **25**/**26**/**27** and **28**/**29**/**30**/**31** (*Scheme 2*). Main products were again the azines (*Z*,*Z*)-**11** and (*Z*,*Z*)/(*E*,*E*)-**13**. The structure of **7** and **25** was established by X-ray analysis (*Figs. 1* and *2*). The mechanism of addition of glycosylidene carbenes to enol ethers is discussed. AM1 Calculations indicate that the $LUMO_{carbene}/HOMO_{alkoxyalkene}$ interaction is dominant at the beginning of the reaction, while the transition states are characterized by a dominant interaction of the doubly occupied, sp^2-hybridized orbital of the carbene with the LUMO of the enol ether. The relative reactivity of the carbenes towards either the enol ethers or the diazirines determine type and yields of the products.

1. Introduction. – The nucleophilic character of glycosylidene carbenes has been evidenced, among others, by their reaction with electron-poor alkenes (for reviews, see [2–4]). Thus, glycosylidene carbenes derived from the diazirines **1** [5], **2** [6], and **3** [7], and from the 4-toluenesulfonohydrazide sodium salts **4** [8] and **5** [9] add readily to electron-poor alkenes, leading to spirocyclopropanes. Yields of the products derived from the pivaloylated diazirine **1** were higher than those obtained from the benzylated diazirine **2**, showing that the nature of the protecting groups influences the (nucleophilic) reactivity



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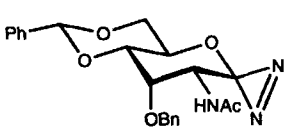
2 R = Bn



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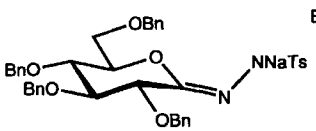

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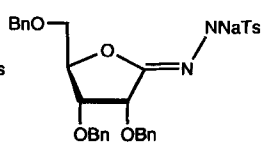

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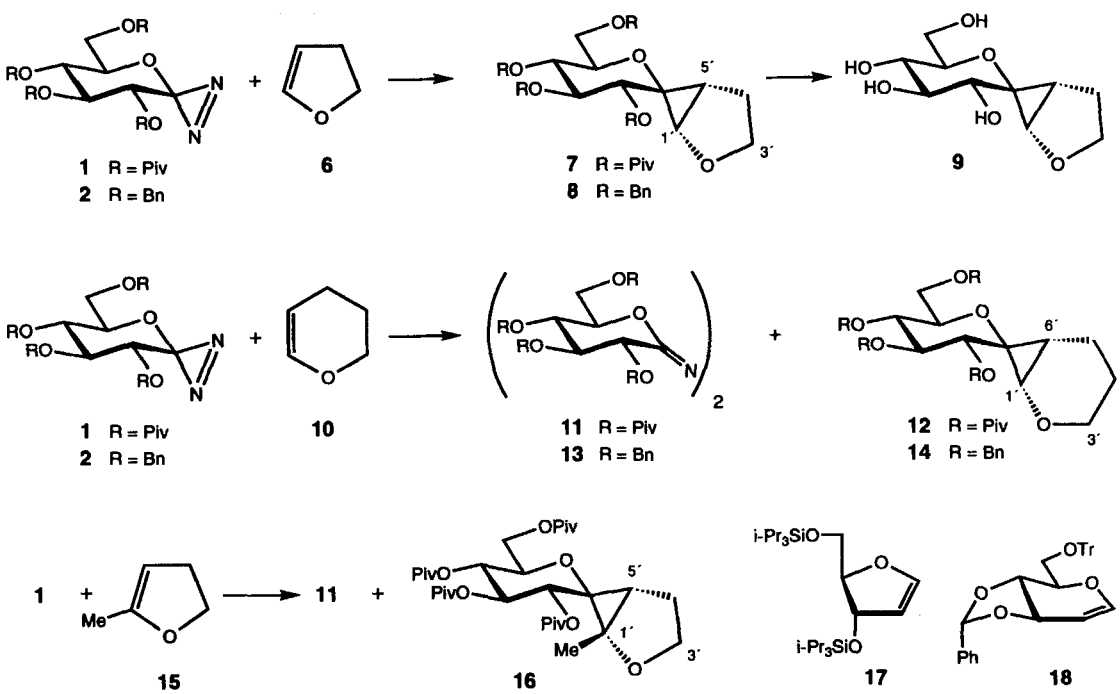
[1]) Part 23: [1].

of these alkoxycarbenes[2]). One expects the electrophilic properties of glycosylidene carbenes, evidenced by their reaction with phosphines [11], to be similarly influenced by the protecting groups. Only few examples for the addition of alkoxy carbenes (see [12] and refs. quoted therein), alkoxyalkyl carbenes [13], and alkoxyalkyl carbenoids [14] [15] to enol ethers are known, while the addition of mono- and dihalo carbenes to enol ethers, including glycals [16] [17], is amply documented.

To probe the influence of *O*-substituents on the reactivity of glycosylidene carbenes towards enol ethers, we chose the dihydrofurans **6** and **15** and the dihydropyran **10** as reaction partners. Alkyl substituents at the C=C bond usually raise the reactivity towards electrophilic carbenes [12] [18–20], and we expected dihydrofurans to be more reactive than dihydropyrans, by analogy to the reactivity difference between cyclopentenes and cyclohexenes [18] [21]. Addition to the (*E*)- and (*Z*)-1-methoxyoct-1-ene (**23** and **24**, resp.) should provide information about the diastereoselectivity of the cyclopropanation.

2. Results and Discussion. – Thermolysis at 45° or photolysis at −20 and −60° of the pivaloylated diazirine **1** in the presence of a 20–23-fold excess of the dihydrofuran **6** led diastereoselectively to the crystalline cyclopropane **7** (71–72%; *Scheme 1* and *Table 1*). Similarly, thermolysis of the benzylated diazirine **2** in the presence of the same excess of **6** at 23° gave selectively the analogous cyclopropane **8**, but only in 33% yield. Both **7** and **8** were deprotected in high yields to the same crystalline tetrol **9**.

Scheme 1



[2]) For a discussion of the ambiphilic character of (alkoxy)carbenes, see [10].

Table 1. *Products and Yields of the Reactions of the Diazirines* **1** *and* **2** *with Enol Ethers*

Diazirine	Enol ether (equiv.)	Solvent	Temp. [°]	Products (yields [%])	Ratio cyclopropanes/azines
1	**6** (20)	dioxane	45	**7** (72)	100: 0
1	**6** (22.7)	THF	−20	**7** (71)	100: 0
1	**6** (23.3)	THF	−60	**7** (72)	100: 0
2	**6** (22.5)	dioxane	23	**8** (33)	100: 0
1	**10** (32.2)	dioxane	45	(*Z,Z*)-**11** (55), **12** (14)	20: 80
1	**10** (29)	THF	−60	(*Z,Z*)-**11** (52), **12** (9)	15: 85
2	**10** (32.7)	dioxane	23	(*Z,Z*)-**13** (32), (*E,E*)-**13** (28), **14** (9)	13: 87
1	**15** (20.2)	dioxane	45	(*Z,Z*)-**11** (50), **16** (24)	32: 68
1	**17** (20)	dioxane	45	(*Z,Z*)-**11** (*ca.* 80)	0:100
1	**18** (20)	dioxane	45	(*Z,Z*)-**11** (*ca.* 80)	0:100
1	**23** (10.3)	dioxane	45	(*Z,Z*)-**11** (62)	0:100
2	**23** (10.1)	dioxane	23	(*Z,Z*)-**13** (43), (*E,E*)-**13** (17)	0:100
1	**24** (9.3)	dioxane	45	(*Z,Z*)-**11** (47), **25** (11), **26** (4), **27** (1.5)	26: 74
2	**24** (9.6)	dioxane	23	(*Z,Z*)-**13** (24), (*E,E*)-**13** (19), **28** (6), **29** (4.5), **31** (2), **30** (1.5)	25: 75

Thermolysis at 45° of **1** in the presence of a 30-fold excess of the dihydropyran **10** gave selectively the crystalline cyclopropane **12**, but only in a yield of 14%. The main product was the (*Z,Z*)-azine **11** (55%), the dominant product of the thermolysis of **1** in aprotic solvents [22]. Photolytic generation of the carbene at −60° led to a similar result (*Table 1*). The reaction at 23° between **2** and **10** proceeded similarly, but yielded only 9% of the cyclopropane **14**. Main products were the (*Z,Z*)- and (*E,E*)-azines **13** [22] (32 and 28%, resp.).

Surprisingly, thermolysis of **1** in the presence of the 2,3-dihydro-5-methylfuran **15** yielded only 24% of the crystalline cyclopropane **16**. Main product was again the (*Z,Z*)-azine **11** (55%). Attempts to prepare pseudodisaccharides by the reaction of glycosylidene carbenes with glycals failed; thermolysis of **1** and 20 equiv. of the D-ribal **17** [23] or the D-glucal **18** [24] led only to the formation of the (*Z,Z*)-azine **11**.

The cyclopropane moiety of **7**–**9**, **12**, and **14** is revealed by the upfield shift of the NMR signals of H–C(1′) (*d* at 3.88–4.24 ppm), H–C(5′) of **7**–**9** (1.41–2.07 ppm), H–C(6′) of **12** and **14** (0.81 and 1.16 ppm, resp.), C(1) (*s* at 64.4–68.4 ppm), C(1′) (**7**–**9**: *d* at 61.2–63.6 ppm; **12** and **14**: *d* at 51.3 and 52.15 ppm, resp.), C(5′) of **7**–**9** (*d* at 22.3–25.9 ppm), and C(6′) of **12** and **14** (*d* at 14.2 and 14.1 ppm resp.; *Exper. Part* and *Table 5*). Similar upfield shifts are observed for the corresponding signals of **16** (H–C(5′): *d* at 1.26; C(1) and C(1′): 2*s* at 67.5 and 68.4, C(5′): *d* at 27.8 ppm). *J*(1′,5′) of the tetrahydrofurans (6.3–6.6 Hz) is smaller than *J*(1′,6′) of the tetrahydropyrans (8.1 Hz).

The configuration of the glucopyranosylidene-derived spirocyclopropanes is readily assigned on the basis of nuclear *Overhauser* effects (*Table 2*) between the cyclopropyl H-atoms and either H–C(2), H–C(3), or H–C(5) [6] [7]. Thus, NOEs between the more strongly shielded cyclopropane H-atom and H–C(2), and between the less shielded cyclopropane H-atom, or the Me group of **16** and H–C(3) indicate the *exo*-position of C(2) in **7**, **12**, **14**, and **16** (*Table 2*).

These assignments are corroborated by an X-ray analysis of **7**[3]) (*Fig. 1*). The pyranose ring adopts a $^4C_1$ conformation and the tetrahydrofuran ring is nearly flat, as

[3]) Coordinates and thermal parameters have been deposited with the *Cambridge Crystallographic Data Center*, 12 Union Road, Cambridge CB2 1EZ, England.

Table 2. *Selected ^{1}H-NMR NOEs [%] for the Cyclopropanes* **7**, **12**, **14**, **16**, *and* **25–31**

Irradiated at	NOE at	**7**	**16**	**12**	**14**	**25**	**28**	**26**	**29**	**27**	**30**	**31**
HCOR[a])	HCR[b])	4.2	2.7	4.8		7.2	6.7		7.5	5.7		5.4
HCR[b])	HCOR[a])	6.9	2.6	7.0	6.5	8.1	8.3		5.8		6.8	
HCR[b])	H–C(2)	3.6	3.6	3.3	1.1	2.0	2.1					
H–C(2)	HCR[b])				1.3							
HCOR[a])	H–C(3)	4.4	2.8	4.0		4.3	2.5					
H–C(3)	HCOR[a])		8.1			2.9	3.6					
HCOR[a])	H–C(2)							2.9				
H–C(2)	HCOR[a])							2.5	1.4			
HCR[b])	H–C(3)								1.8			
H–C(5)	H–C(1″)								5.9			
H–C(2)	MeO									1.1		
H–C(3)	H–C(1″)									1.9, 2.2		
H–C(5)	HCR[b])									6.3		
H–COR[a])	H–C(5)											4.0
H–C(5)	H–COR[a])											4.0

[a]) Cyclopropane H-atom at lower field; Me group of **16**. [b]) Cyclopropane H-atom at higher field.

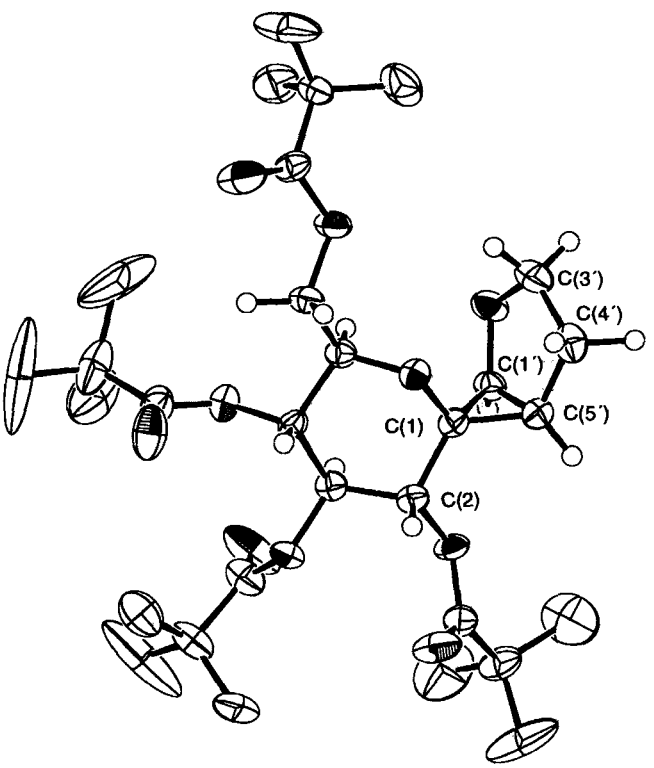
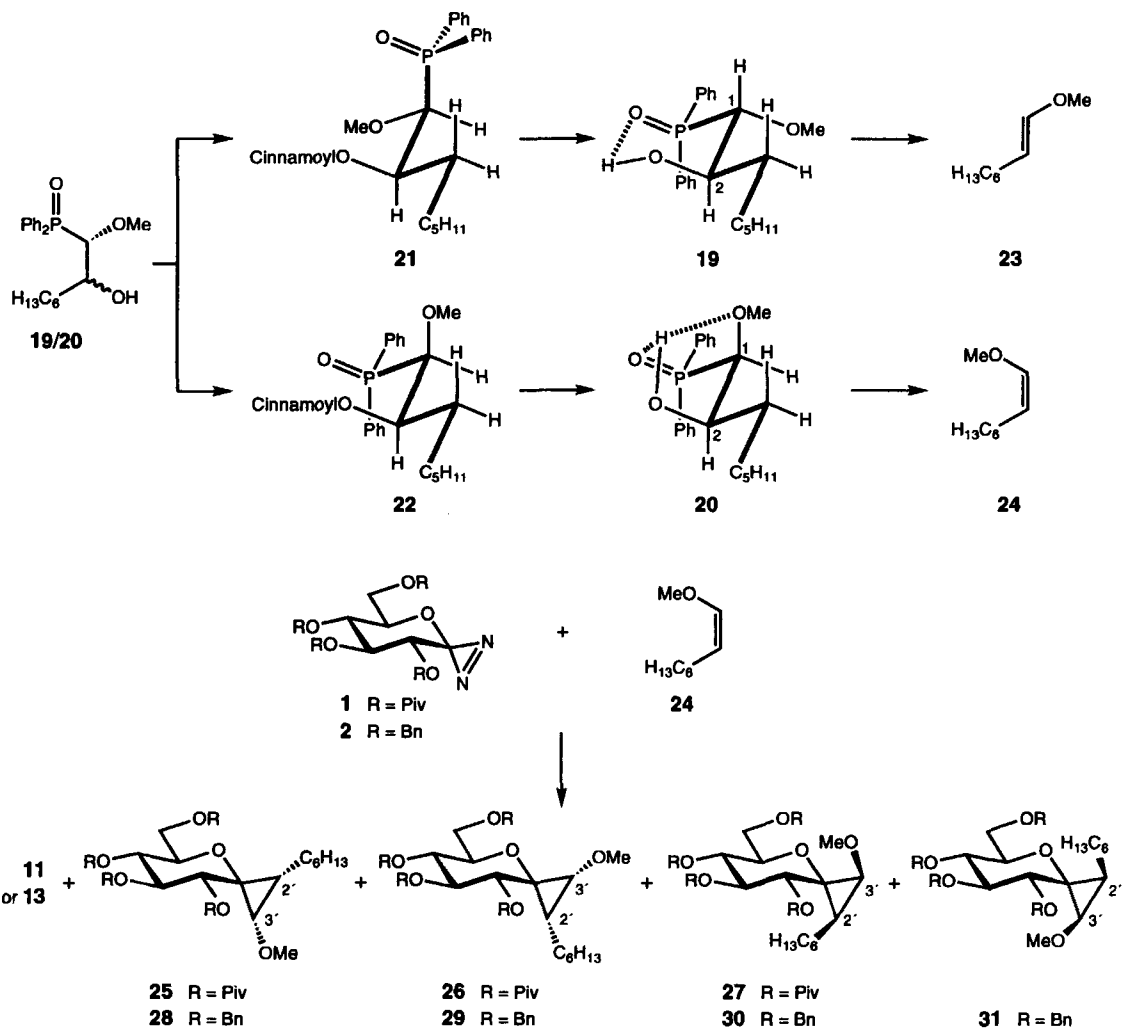


Fig. 1. *X-Ray structure of* **7**. Some disorder of *t*-Bu groups.

indicated by the dihedral angles C(1′)–O–C(3′)–C(4′) and O–C(3′)–C(4′)–C(5′) of 4.6 and −5.9°, respectively.

The diastereoselectivity of the cyclopropanation of **6**, **10**, and **15** – presumably reflecting the larger size of the BnO–C(2) group as compared to the ring O-atom – and the strongly differing reactivity of the cyclic enol ethers prompted us to examine the cyclopropanation of the aliphatic enol ethers **23** and **24** (*Scheme 2*). Several syntheses of these methoxyalkenes are known. They lead to mixtures **23**/**24** [25–27] or allowed the preparation of pure **23** [28] [29], but not of pure **24**. For this reason, we turned to the method of *Earnshaw et al.* [28] where a two step *Horner-Wittig* reaction [30] [31] allows the chromatographic separation of the intermediate diastereoisomeric 2-phosphinoyl-

Scheme 2



alkanol oxides (*cf.* [28] [32] [33]). Base-catalyzed reaction of diphenyl(methoxymethyl)phosphine oxide with heptanal [28] gave the 1-phosphinoyloctan-2-ol **19**/**20** in a ratio of 52:47. Crystallization from AcOEt yielded pure **19** [28]. The remaining mixture (**19**/**20** 43:57) could only be separated by prep. HPLC, whereas the cinnamates **21** and **22** were readily separated by flash chromatography on a 10-g scale. Saponification of **21** and **22** gave pure **19** and **20**, and, hence, by treatment with NaH [28], the diastereoisomerically pure (*E*)- and (*Z*)-enol ethers **23** [28] [29] and **24**, respectively.

The $J(1,2)$ value in the ^{1}H-NMR of **19** (8.8 Hz) deviates clearly from the $J(1,2)$ value of **21** (2.5 Hz), whereas the corresponding values of **20** and **22** (3.9 and 5.6 Hz, resp.) are similar, evidencing a strong conformational change induced by the acylation of **19**, but not of **20** (for convenience, the same numbering is used for **19**–**22**). The large $J(1,2)$ value of **19** together with $J(2,OH)$ of 1.2 Hz agree with an extended zig-zag conformation stabilized by an intramolecular H-bond OH···O=P, as depicted in *Scheme 2*. The small $J(1,2)$ value of **21**, evidences the depicted sickle conformation. Thus, the energy gain by the intramolecular H-bond of **19** overcompensates the unfavorable antiperiplanar arrangement of the MeO–C(1) and the HO–C(2) substituents and the 1,5-interaction of the HO–C(2) and the O=P substituents. Hence, destruction of the H-bond by acylation induces the observed conformational change. The rather small $J(1,2)$ value of **20** is in keeping with the expected zig-zag conformation. $J(2,OH)$ of 6.3 Hz of **20** indicates a dihedral angle of *ca.* 150° and suggests a bifurcated intramolecular H-bond to the P=O and MeO groups. The minor conformational change observed upon acylation of **20** is in keeping with the favorable *gauche*-arrangement of the MeO and OH groups. The assignment of an extended zig-zag conformation to **19**, **20**, and **22** and of a sickle conformation to **21** is corroborated by $^3J(P,C)$ long-range couplings in **19** (8.3 Hz), **20** (6.1 Hz), and **22** (3.8 Hz), but not in **21**.

Thermolysis of **1** or **2** in the presence of *ca.* 10 equiv. of the (*E*)-enol ether **23** led almost exclusively to azines: (*Z*,*Z*)-**11** and (*Z*,*Z*)- and (*E*,*E*)-**13** were isolated in 62, 43, and 17%, respectively (*Table 1*). No trace of cyclopropanes could be detected by ^{1}H-NMR spectroscopy. The (*Z*)-enol ether **24** proved more reactive than the (*E*)-isomer[4]), and thermolysis of **1** or **2** in the presence of *ca.* 10 equiv. of **24** gave mixtures of azines and cyclopropanes. The azine **11** (47%) and a 56:44 mixture of (*Z*,*Z*)/(*E*,*E*)-**13** (43%) were isolated by flash chromatography. Isolation of the cyclopropanes derived from **1** required repeated prep. HPLC and afforded crystalline **25** (11%), **26** (4%), and **27** (1.5%). Again, the yields of cyclopropanes derived from the benzyl-protected diazirine **2** were lower, and **28** (6%), an inseparable mixture **29**/**30** 3:1 (6%), and **31** (2%) were isolated by prep. HPLC.

Characteristic NMR chemical shifts are observed for H–C(2′) (0.62–1.44 ppm), H–C(3′) (2.79–3.43 ppm), and C(1) (*s* at 59.7–63.6 ppm) of the methoxycyclopropanes (*Exper. Part* and *Table 5*). $J(2',3')$ of 7.1–8.6 Hz indicates a *cis*-arrangement of the hexyl and the MeO substituent for all compounds (compare with $J(1',2')$ of 3–4 Hz in *trans*-1-alkoxy-2-alkylcyclopropanes [34–36]). Two different sets of products were detected by comparing the chemical-shift values for C(2′) and C(3′): on the one hand, **25**, **26**, **28**, and **29** (C(2′) at 21.8–22.4 ppm, C(3′) at 58.0–59.45 ppm) and, on the other hand, **27**, **30**, and **31** (C(2′) at 29.0–30.8 ppm, C(3′) at 65.1–66.1 ppm). As discussed above, NOEs between the cyclopropane H-atom and either H–C(2), H–C(3), or H–C(5) (*Table 2*) reveal the *cis*-arrangement of O(5), the alkyl, and the MeO groups, and the same configuration for the main cyclopropanes **25** and **28** as already observed for the addition products to the cyclic enol ethers. A *cis*-arrangement of C(2), the alkyl and the MeO groups is expected for **27**, **30**, and **31** and evidenced by NOEs between the MeO group and H–C(2), both H–C(1″) and H–C(3), and H–C(2′) and H–C(5) of **27** and between H–C(3′) and H–C(5) of **31** (*Table 2*). This shows that the chemical shift of C(2′) and C(3′) is strongly influenced by the relative position of the substituents on the cyclopropane ring rather than by the pseudoequatorial or pseudoaxial orientation of the anomeric *C*-substituents.

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[4]) *cis*-Olefins are usually more reactive in additions to carbene than *trans*-olefins, but the reactivity depends upon the nature and the generation of the carbene [19] [20].

The configurational assignment of the 1-hexyl-2-methoxyspirocyclopropanes is corroborated by the X-ray analysis of **25**[3]) (*Fig. 2*).

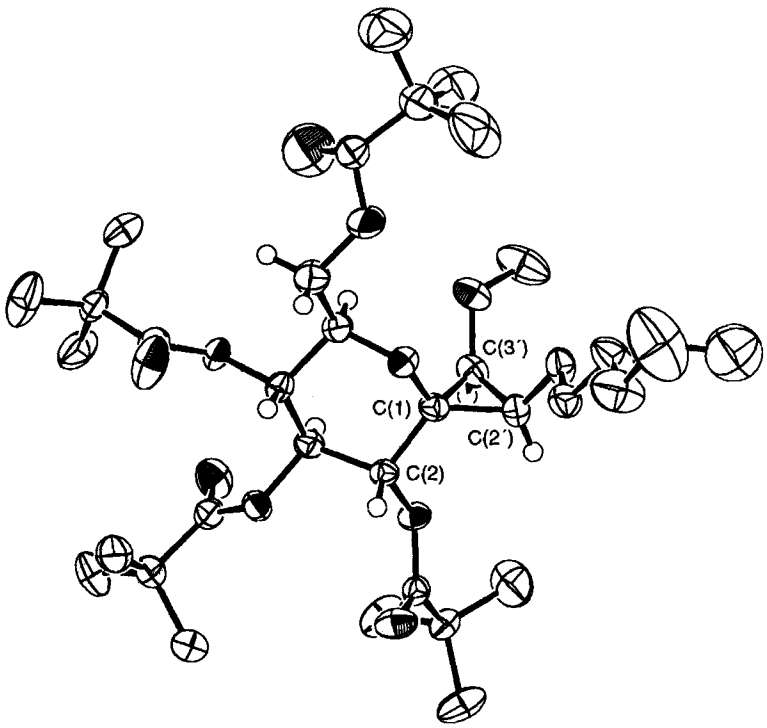

Fig. 2. *X-Ray structure of* **25**

The pyranose ring of the cyclopropanes with *cis*-oriented alkoxy substituents (**7**–**9**, **12**, **14**, **16**, **25**, **26**, **28**, and **29**) adopts a $^4C_1$ conformation in solution, as it has been observed for the solid state of **7** and **25**. In **27**, **30**, and **31**, the hexyl and the MeO groups are *cis* to C(2) and this may lead to unfavorable interactions with RO–C(2). Subtle factors determine the conformational equilibrium of these compounds. Thus, **27** in $CDCl_3$ ($J(2,3) = 8.8$, $J(3,4) = 9.1$, $J(4,5) = 9.9$ Hz) adopts a $^4C_1$, but **30** in C_6D_6 ($J(2,3) = 7.5$, $J(3,4) = 8.1$, $J(4,5) \approx 9.3$ Hz) and especially **31** in C_6D_6 ($J(2,3) = 4.8$, $J(3,4) = 7.5$, $J(4,5) = 9.8$ Hz) deviate increasingly from this conformation. Force-field calculations (Macromodel, MM3* force field, gas phase [37]) indicate that the most probable conformers are the two skew boats $^1S_5$ (calculated $J(2,3) = 0.5$, $J(3,4) = 7.6$, $J(4,5) = 9.2$ Hz) and $^0S_2$ (calculated $J(2,3) = 4.4$, $J(3,4) = 0.5$, $J(4,5) = 7.4$ Hz), equilibrating *via* the $B_{2,5}$. The J values suggest a *ca.* 4:1 $^4C_1/^1S_5$ equilibrium for **30** and a *ca.* 1:1 equilibrium for **31**.

In all these additions to enol ethers, the pivaloyl-protected carbene was clearly more reactive than the benzyl-protected analogue, in keeping with the stronger σ-acceptor properties of the pivaloyloxy group. The most reactive enol ether is the dihydrofuran **6**, leading in 71–72% to the pivaloylated cyclopropane **7**, but in only 33% to the benzylated analogue **7** (*Table 1*). The main products in all other reactions are the azines **11**

and **13**. The ratio of cyclopropanes to azines reflects the relative reactivity of the enol ethers and diazirines towards the carbene derived from either **1** or **2**. It decreases from dihydrofuran **6** *via* 2,3-dihydro-5-methylfuran **15**, (*Z*)-methoxyoctene **24**, and the dihydropyran **10** to (*E*)-methoxyoctene **23**. The addition of the glycosylidene carbenes derived from **1** and **2** to dimethyl maleate, an electron-poor alkene, was accompanied by partial isomerization to the fumarate [5] [6]. In contrast to this, the addition to **24** was stereospecific; no trace of **23** could be detected in the crude reaction mixtures. The addition is also highly stereoselective.

The *cis*-arrangement of O–C(1) and the substituents at other cyclopropane centers is expected on the basis of the different size of the two C(1) substituents. The dominant pseudoaxial orientation of the alkoxy substituted cyclopropane C-atom (C(1') in **7**, **8**, **12**, **14**, and **16**; C(3') in **25** and **28**) is more difficult to explain.

The configuration of the cyclopropanes is determined by the axial *vs.* equatorial approach of the enol ether, its face selectivity and orientation. An approach in the π-plane of the carbenes is assumed for electrophilic carbenes [12] [19] [20] [38]. AM1 Calculation of the frontier-orbital energies of the carbenes **C1** and **C2** derived from **1** and **2** and the model carbenes **C3**, **C4**, and **C5** (AMPAC 5.0 program [39]; *Fig. 3* and *Table 3*) shows that the acylated carbenes **C1** and **C4** possess a lower HOMO and a lower LUMO[5]) than the alkylated carbenes **C2**, **C3**, and **C5** (ΔE *ca.* 0.3 and 0.2 eV, resp.). RO–C(6) has a weak influence on the energy of the frontier orbitals. Calculation of the frontier-orbital energies of the enol ethers **15**, **6**, **10**, **24**, and **E** shows that the HOMO of the 2,3-dihydro-5-methylfuran **15** is lower in energy than the HOMO of the other enol ethers and that the LUMO of the dihydrofurans **15** and **6** is lower than the LUMO of **10**, **24**, and **E** (*ca.* 0.15–0.2 eV). The p_z coefficients of the enol ethers at C(α) and C(β) are not very different from each other, and somewhat larger at C(β) of the HOMO and at C(α) of the LUMO. The ΔE_E values [10] (*Table 3*) for these carbenes and enol ethers are smaller than the ΔE_N values (E, electrophilic interaction; N, nucleophilic interaction). This is in keeping with the assumption that the reaction is initiated by a dominant electrophilic interaction between the carbenes and the enol ethers. The ΔE_E values for the acylated carbenes **C1** and **C4** are somewhat smaller than the ΔE_E values for the alkylated carbenes **C2**, **C3**, and **C5** and indicate a higher electrophilic character of **C1** and **C4**[6]). The ΔE_N values for the interaction of the carbenes and the parent diazirines[5]) (**C1** and **1**, **C2** and **2**) show that azine formation is competitive with the addition to the enol ethers, and more so for the benzylated than for the pivaloylated carbene. This means that the lower yields of the cyclopropanes obtained from the *O*-benzylated carbene is the result of the higher reactivity of this carbene towards the starting diazirine **2** and not of the lowered electrophilicity relative to the pivaloylated carbene. This is corroborated by

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[5]) For **C2**, the lowest unoccupied orbital localized at the carbenic center corresponds to $LUMO^{+7}$. For **2**, the highest occupied orbital localized at the diazirine moiety corresponds to $HOMO^{-10}$. The electron density of the molecular orbitals LUMO to $LUMO^{+6}$ of **C2** and of HOMO to $HOMO^{-9}$ of **2** is mainly localized at the Ph groups.

[6]) The ΔE_E and ΔE_N values for the dihydrofuran **6** and the dihydropyran **10** are very similar and suggest a similar reactivity, in contradiction to the experimental observations, reflecting either the limitation of this factor and/or of the calculations.

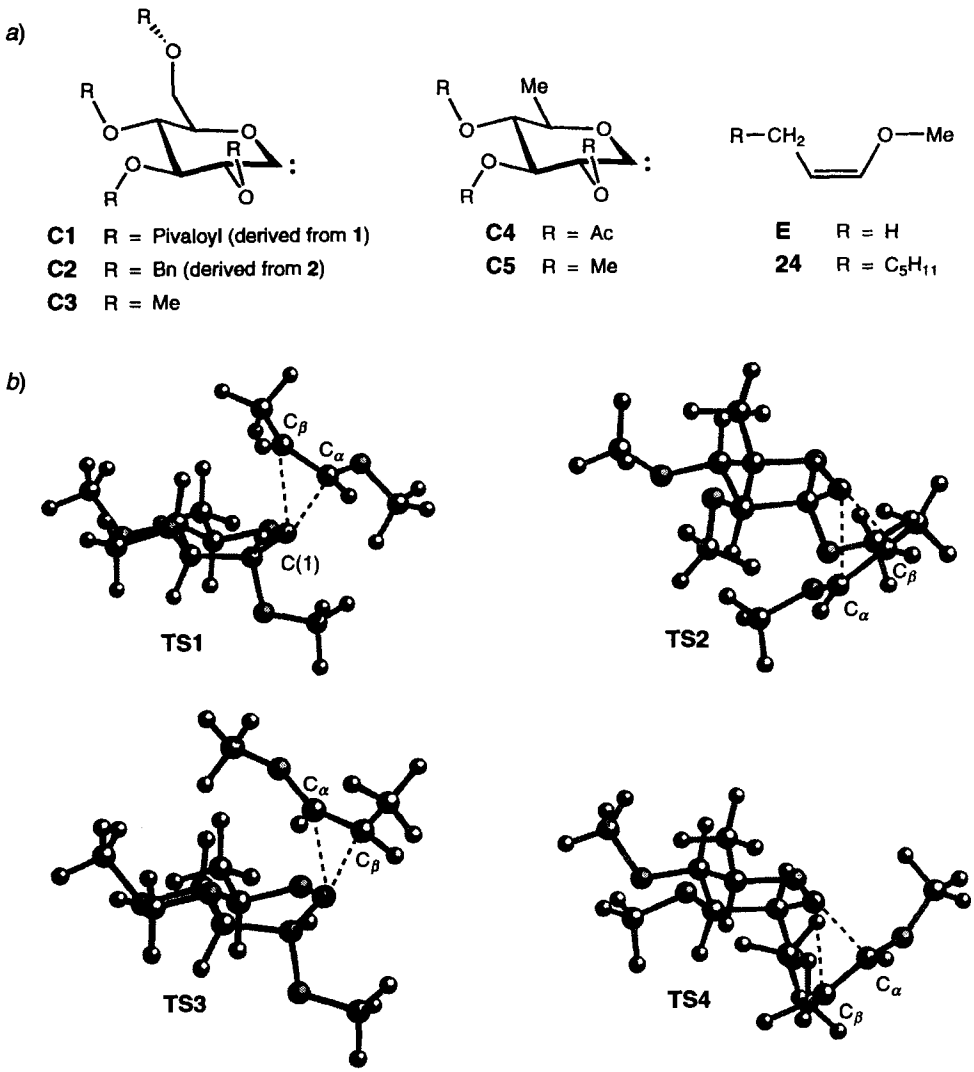

Fig. 3. a) *AM1 Calculation for carbenes and acyclic enol ethers* (starting geometries depicted); b) *AM1 calculated transition states for the addition of* **C5** *to* **E** *leading to* cis-*dialkoxycyclopropanes*

the calculations of the transition states for the addition of glycosylidene carbenes to enol ethers.

To evaluate the transition states, we calculated the ground-state structure of the products of the addition of 6-deoxy-2,3,4-tri-*O*-methyl-D-glucopyranosylidene (**C5**) to (*Z*)-1-methoxyprop-1-ene (**E**), *viz.* the two *cis*-dialkoxycyclopropanes corresponding to **28** and **29** and the energies associated with systematic lengthening of both the C(1)···C(α) and C(1)···C(β) bonds. Four transition states (**TS1**–**TS4** in *Fig. 3* and

Table 3. *AM1 Calculations* [39] *of the Frontier-Orbital Energies of the Carbenes* **C1**–**C5**[a]), *the Enol Ethers* **6**, **10**, **15**, **24**, *and* **E**[b]), *and the Diazirines* **1** *and* **2**: a) *Energies of HOMO and LUMO of Carbenes and Diazirines and Selected LUMO* p_z *Coefficients*; b) *Energies of HOMO and LUMO and Selected* p_z *Coefficients of Enol Ethers*; c) *Differential Frontier-Orbital Energies* ($\Delta E_E = LUMO_{carbene} - HOMO_{carbenophile}$; $\Delta E_N = LUMO_{carbenophile} - HOMO_{carbene}$) *for Carbene/Enol Ether or Carbene/Diazirine Additions*

a)

	HOMO [eV]	LUMO [eV]	p_z coefficients of LUMO at	
	C(1)	O(5)		
C1	– 9.356	0.408	0.79	– 0.37
C2	– 9.012	0.623[5])	0.78	– 0.37
C3	– 8.973	0.724	0.83	– 0.39
C4	– 9.344	0.411	0.79	– 0.37
C5	– 9.041	0.624	0.85	– 0.40
1	– 10.907	– 0.241		
2	– 10.888[5])	– 0.057		

b)

	HOMO [eV]	LUMO [eV]	p_z coefficients of HOMO at			p_z coefficients of LUMO at		
			C(β)	C(α)	O	C(β)	C(α)	O
15	– 8.924	1.150	– 0.65	– 0.46	0.43	0.63	– 0.69	0.19
6	– 9.120	1.193	– 0.63	– 0.47	0.47	0.63	– 0.71	0.21
10	– 9.139	1.319	– 0.69	– 0.49	0.46	0.62	– 0.69	0.20
24	– 9.060	1.385	– 0.62	– 0.52	0.45	0.66	– 0.69	0.18
E	– 9.042	1.389	– 0.63	– 0.52	0.46	0.66	– 0.69	0.19

c)

Carbene	Carbenophile	ΔE_E [eV]	ΔE_N [eV]	$\Delta E_N - \Delta E_E$ [eV]
C1	**15**	9.33	10.51	1.18
C1	**6**	9.53	10.55	1.02
C1	**10**	9.55	10.67	1.12
C2	**6**	9.74	10.21	0.47
C2	**10**	9.76	10.33	0.57
C1	**24**	9.47	10.74	1.27
C2	**24**	9.68	10.40	0.72
C3	**24**	9.78	10.36	0.58
C4	**24**	9.47	10.73	1.26
C5	**24**	9.68	10.53	0.75
C5	**E**	9.67	10.43	0.76
C1	**1**	11.32	9.12	– 2.20
C2	**2**	11.51	8.96	– 2.55

[a]) The starting geometry ($^4H_3$, *syn*-periplanar arrangement of the HCOR groups, *gg* conformation around C(5)–C(6) of **C1**–**C3** was optimized without systematic checking for local minima. [b]) *Anti*-periplanar arrangement of C(β)C(α)OMe in the starting geometry of **24** and **E**.

Table 4) were detected[7]). **TS1** and **TS2** lead to the major and **TS3** and **TS4** to the minor product. **TS1** and **TS3** result from an equatorial, and **TS2** and **TS4** from an axial attack of the enol ether. All transition states are characterized by two incipient C–C bonds of very unequal length, with a shorter pseudoequatorial C–C bond. **TS1** and **TS4** show a short C(1)–C(α) and **TS2** and **TS3** a short C(1)–C(β) bond. In so far as the incipient bond correlates with the energy of the orbital interaction, these bond lengths express a dominant interaction of the HOMO of the carbenes with the LUMO of the enol ethers, with a dominant interaction with C(α) (larger coefficient) in **TS1** and **TS4**, and with C(β) (smaller coefficient) in **TS2** and **TS3**. In agreement with this difference, the calculated $\Delta G^{\neq}$ values are smaller (and quite similar) for **TS1** and **TS4** than for **TS2** and **TS3**. The $^4H_3$ conformation of the isolated carbene was changed in the transition states to conformations close to ^4E; *i.e.*, a $^{4(3)}SB$ [40] (between ^4E and $^1S_5$) for an equatorial attack and a flat $^4C_1$ for an axial attack. This conformational difference is too weak to have a dominant influence upon the direction of the attack, but indicates that the pyranose ring of the cyclopropane obtained by equatorial attack adopts a boat conformation ($^1S_5$ from **TS1**) and the one obtained by axial attack a chair conformation ($^4C_1$ from **TS2**).

A similar calculation for the addition of the triacetoxycarbene **C4** to the enol ether **E** leads to the four transition states **TS5**–**TS8**, closely analogous to **TS1**–**TS4**, and the energies indicated in *Table 4*. The transition states **TS5** and **TS8** correspond to **TS1** and **TS4**, but possess a ^4E instead of $^{4(3)}SB$ conformation, and are clearly preferred, again indicating a dominant contribution of the $HOMO_{carbene}/LUMO_{enol\ ether}$ interaction. The

Table 4. *AM1 Calculations* [39] *of the Transition States for the Addition of* **C5** *or* **C4** *to* (Z)*-1-Methoxyprop-1-ene* (**E**) *Leading to* cis*-Dialkoxycyclopropanes*[a])

	Addition of **C5** to **E**				Addition of **C4** to **E**			
Transition state	**TS1**	**TS2**	**TS3**	**TS4**	**TS5**	**TS6**	**TS7**	**TS8**
Distance C(1)···C(β) [Å]	2.34	1.87	1.87	2.31	2.34	1.87	1.87	2.32
Distance C(1)···C(α) [Å]	1.87	2.38	2.41	1.87	1.87	2.38	2.39	1.87
Ring conformation	$^{4(3)}SB$ [40]	flat $^4C_1$	$^{4(3)}SB$	flat $^4C_1$	^4E	flat $^4C_1$	^4E	flat $^4C_1$
Direction of attack	eq.	ax.	eq.	ax.	eq.	ax.	eq.	ax.
Final energy [kcal/mol]	−140.9	−139.8	−138.4	−141.3	−266.8	−264.8	−264.9	−266.4
$\Delta G^{\neq}$ [kcal/mol][b])	14.2	15.3	16.7	13.8	12.4	14.4	14.3	12.8

[a]) Similar starting geometry as for **C5**, *anti*-periplanar arrangement of C(β)C(α)OMe. [b]) Referred to the sum (−155.1 and −279.2 kcal/mol, resp.) of the final energies of **C5** (−120.3 kcal/mol) or **C4** (−244.4 kcal/mol) and **E** (−34.8 kcal/mol).

[7]) Conformers near the transition states were obtained minimizing conformers with a fixed distance of 1.87 Å between C(1) and the 'pseudoequatorial' olefinic C-atom and a starting distance of > 2.2 Å between C(1) and the 'pseudoaxial' olefinic C-atom. For **TS1**–**TS4**, lengthening of this distance between C(1) and the 'pseudoequatorial' olefinic C-atom leads to decrease of the energy and increased distances between C(1) and the 'pseudoaxial' olefinic C-atom, whereas shortening of this distance to 1.82 Å leads to decrease of the energy accompanied by C–C bond formation between C(1) and the 'pseudoaxial' olefinic C-atom. In the transition states, the p and the sp^2 orbital of the carbene and the π orbital of the C=C bond are in the same plane. The doubly occupied sp^2 orbital of the carbene and the C–C bond of the enol ether deviate by *ca.* 45° from a parallel orientation.

lower $\Delta G^{\neq}$ values for **TS5** and **TS8** than for **TS1** and **TS4** are in keeping with the higher yields obtained in the addition of the pivaloylated **1** to the enol ethers.

The lower yields of the addition to the 2,3-dihydro-5-methylfuran **15** is not the result of an electronic, but of a steric factor: equatorial addition of **15** to the carbene derived from **1** and leading to **16** (*via* a transition state analogous to **TS5**) involves an unfavorable interaction between the methyl substituent of **15** and the PivO–C(2).

We thank Dr. *A. Linden*, University of Zürich, for the X-ray analyses, and the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for generous support.

Experimental Part

General. See [6]. HPLC: t_R in min.

(1R,1'S,5'R)-2,3,4,6-Tetra-O-pivaloylspiro[1,5-anhydro-D-glucitol-1,6'-[2]oxabicyclo[3.1.0]hexane] (**7**). a) A soln. of **6** (2.4 ml, 32.28 mmol) in 1,4-dioxane (5 ml) was heated under N_2 to 45°, treated dropwise with a cooled (0°) soln. of **1** [22] (850 mg, 1.61 mmol) in 1,4-dioxane (5 ml), and stirred for 2 h. Evaporation and prep. HPLC (hexane/Et_2O 4:1, 14 ml/min) of the residue (770 mg) gave **7** (661 mg, 72%; t_R 6.5) which afforded colorless needles from MeOH.

b) A soln. of **6** (13 ml, 17.25 mmol) in abs. THF (2 ml) was cooled under N_2 to −20°, treated dropwise with a cooled (0°) soln. of **1** (400 mg, 0.76 mmol) in abs. THF (2 ml), and irradiated (Hg lamp with *Solidex* filter) for 90 min. Evaporation and FC (hexane/AcOEt 2:1) gave **7** (305 mg, 71%).

c) As *b*), but at −60° with **1** (390 mg, 0.74 mmol) and **6** (1.3 ml, 17.25 mmol): **7** (304 mg, 72%). M.p. 167° (MeOH). R_f (hexane/Et_2O 1:2) 0.66. $[\alpha]_D^{25} = +70.8$ ($c = 1.11$, $CHCl_3$). IR (KBr): 2980*m*, 2940*m* (sh), 2900*w*, 2880*w*, 1740*s*, 1730*s* (sh), 1480*m*, 1460*w*, 1400*w*, 1365*w*, 1285*m*, 1180*s* (sh), 1150*s*, 1115*m* (sh), 1100*m*, 1090*m* (sh), 1035*m*, 890*w*, 760*w*. ^{1}H-NMR (400 MHz, C_6D_6): 5.59 (*d*, $J = 9.0$, H–C(2)); 5.55 (*t*, $J \approx 8.9$, H–C(3)); 5.44 (*dd*, $J = 8.7$, 10.1, H–C(4)); 4.35 (*dd*, $J = 1.3$, 12.6, H–C(6)); 4.02 (*dd*, $J = 5.0$, 12.6, H'–C(6)); 3.96–3.85 (*m*, 2 H–C(3')); 3.88 (*d*, $J = 6.3$, H–C(1')); 3.82 (*ddd*, $J = 1.4$, 5.0, 10.3, H–C(5)); 1.88 (br. *ddd*, $J = 5.4$, 8.2, 12.0, irrad. at 3.88 → *d*, $J = 12.0$, H–C(4')); 1.73–1.62 (*m*, irrad. at 3.88 → *dd*, $J = 6.8$, 12.0 H'–C(4')); 1.41 (*t*, $J \approx 6.5$, irrad. at 3.88 → *d*, $J = 6.9$, H–C(5')); 1.19, 1.16, 1.16, 0.99 (4*s*, 4 *t*-Bu). ^{1}H-NMR (400 MHz, $CDCl_3$): 5.37–5.29 (*AB*, irrad. at 4.02 → NOE (4.4%), irrad. at 1.60 → NOE (3.6%), H–C(2), H–C(3)); 5.23–5.14 (*m*, with virtual coupling, irrad. at 3.76 → change, H–C(4)); 4.21 (*dd*, $J = 1.6$, 12.6, irrad. at 3.76 → *d*, $J = 12.3$, H–C(6)); 4.15 (*ddd*, $J = 5.2$, 7.6, 9.2, irrad. at 2.18 → *d*, $J = 8.2$, H–C(3')); 4.02 (*d*, $J = 6.5$, irrad. at 1.60 → *s*, irrad. at 1.60 → NOE (6.9%), H–C(1')); 3.97 (*q*, $J = 7.9$, irrad. at 2.18 → *d*, $J \approx 7.5$, H'–C(3')); 3.94 (*dd*, $J = 5.3$, 12.5, irrad. at 3.76 → *d*, $J = 12.5$, H'–C(6)); 3.76 (*ddd*, $J = 1.6$, 5.3, 10.2, H–C(5)); 2.26–2.12 (*m*, irrad. at 1.60 → change, irrad. at 1.60 → NOE (2.3%), 2H–C(4')); 1.60 (*dt*, $J = 1.2$, 6.3, irrad. at 2.18 → *d*, $J = 6.4$, irrad. at 4.02 → NOE (4.2%), H–C(5')); 1.22, 1.15, 1.12, 1.11 (4*s*, 4 *t*-Bu). ^{13}C-NMR (50 MHz, C_6D_6): *Table 5*; additionally, 177.45, 176.88, 176.38, 176.04 (4*s*, 4C=O); 76.75 (*d*); 38.89, 38.85, 38.80, 38.69 (4*s*, 4 Me_3C); 27.36, 27.27, 27.19, 27.04 (4*q*, 4 Me_3C). CI-MS: 587 (32), 586 (100, $[M + NH_4]^+$), 366 (8), 367 (38), 346 (8), 323 (6), 263 (7). Anal. calc. for $C_{30}H_{48}O_{10}$ (568.71): C 63.36, H 8.51; found: C 63.59, H 8.39.

X-Ray Analysis of **7**. Crystals were obtained from MeOH. $C_{30}H_{48}O_{10}$ (568.7); orthorhombic $P2_12_12_1$; $a = 17.677(2)$, $b = 28.196(3)$, $c = 6.503(1)$ Å; $V = 3241.1(8)$ Å^3; $D_x = 1.165$ Mg/m^3; $Z = 4$. Intensities were measured in the ω-scan mode on an *Rigaku-AFC5R* diffractometer (graphite monochromator, MoK_α, $\lambda = 0.71069$ Å) at 173 K, $2\Theta_{(max)} = 55°$, scan speed of 4°/min in ω, scan width $(1.21 + 0.35 \tan\Theta)°$. Of the 5133 total collected reflections, 4971 unique reflections were observed. $R = 0.0526$, $R_w = 0.0438$. The structure was solved with the direct-methods routine of SHELXS-86 [41]. The non-H-atoms were refined anisotropically. All calculations were performed using the TEXSAN crystallographic software package of *Molecular Structure Corporation* [42].

(1R,1'S,5'R)-2,3,4,6-Tetra-O-benzylspiro[1,5-anhydro-D-glucitol-1,6'-[2]oxabicyclo[3.1.0]hexane] (**8**). A suspension of **6** (2 ml, 26.54 mmol) and 4 Å-molecular sieves (1.0 g) in abs. 1,4-dioxane (5 ml) was treated slowly at 23° with a cooled (0°) soln. of **2** [43] (650 mg, 1.18 mmol) in abs. 1,4-dioxane (5 ml), stirred for 2.5 h, and filtered through *Celite* (washing several times with CH_2Cl_2). Evaporation, FC (hexane/Et_2O 2:1), and prep. HPLC (hexane/AcOEt 2:1, 14 ml/min) gave **8** (233 mg, 33%; t_R 11.0). Colorless foam. R_f (hexane/AcOEt 1:1) 0.71. $[\alpha]_D^{25} = +55.4$ ($c = 1.15$, $CHCl_3$). IR ($CHCl_3$): 3050*w*, 3020*w* (br.), 3000*w*, 2950*w*, 2930*w*, 2920*w* (sh), 2900*w*, 2880*w*, 2860*w*, 1495*m*, 1450*m*, 1400*w* (br.), 1360*m*, 1315*w* (br.), 1240*m*, 1200*w*, 1150*m*, 1110*s*, 1090*s*, 1060*s* (sh), 1025*s*, 960*w*, 920*w* (br.), 810*w*, 790–700*w* (br.), 700*s*, 665*w*, 650*w*. ^{1}H-NMR (600 MHz, C_6D_6; assignment based

Table 5. *Selected ^{13}C-NMR Chemical Shifts* [ppm] *of* **7–9**, **12**, **14**, **16**, *and* **19–31**

Solvent	**7** C_6D_6	**8** C_6D_6	**9**[a]) D_2O	**9** (D_6)DMSO	**16** C_6D_6	**12** C_6D_6	**14** C_6D_6
C(1)	64.47	65.76	68.34	65.39	68.39[b])	60.35	61.21
C(2)	68.65[b])	79.70[b])	72.66	70.22[b])	69.22[c])	68.77[b])	79.43[b])
C(3)	76.75	87.62	79.65	77.73	77.55	75.84[c])	87.54
C(4)	69.04[b])	79.51[b])	72.93	70.67[b])	69.43[c])	68.92[b])	79.37[b])
C(5)	74.25	78.70[b])	82.33	80.28	73.71	74.41[c])	77.55[b])
C(6)	62.42	69.86	63.56	61.38	62.66	62.65	69.78
C(1′)	61.29	62.64	63.56	61.25	67.51[b])	51.33	52.15
C(3′)	73.27	73.36	75.86	71.52	72.21	64.62	64.69
C(4′)	25.24	25.77	27.09	24.87	26.49	14.46	15.06
C(5′)	24.11	24.43	25.91	22.38	27.80	22.69	23.09
C(6′)	–	–	–	–	–	14.17	14.10
Me	–	–	–	–	15.98	–	–

Solvent	**19**[e]) $CDCl_3$	**20**[e]) $CDCl_3$	**21**[e])[f]) $CDCl_3$	**22**[e])[f]) $CDCl_3$	**23** $CDCl_3$	**24** $CDCl_3$
C(1)	83.52 (85.7)	83.47 (85.3)	82.70 (87.3)	83.19 (86.2)	146.95	145.90
C(2)	71.24 (4.3)	70.83 (3.6)	73.21 (5.3)	72.58 (7.0)	103.35	107.20
C(3)	33.11 (8.3)	33.59 (6.1)	29.99	30.79 (3.8)	27.66	23.83
C(4)	25.05	25.50	25.49	24.98	30.76	29.76
C(5)	29.02	28.68	28.50	28.47	28.69	28.91
C(6)	31.48	31.34	31.26	31.16	31.73	31.70
C(7)	22.29	22.23	22.21	22.15	22.63	22.61
C(8)	13.80	13.75	13.74	13.69	14.06	14.02
MeO	61.60 (5.9)	61.20 (5.6)	60.62 (9.0)	62.14 (4.1)	55.89	59.38

Solvent	**25** $CDCl_3$	**26** $CDCl_3$	**27** $CDCl_3$	**28** C_6D_6	**29**[f])[g]) C_6D_6	**30**[g]) C_6D_6	**31** C_6D_6
C(1)	59.74	60.24	61.57	61.34	61.78	63.60	62.72
C(2)	68.56[b])	68.35[b])	67.61[b])	79.47[b])	79.37[b])	79.87[b])	78.36[b])
C(3)	75.22[c])	75.47[c])	73.65[c])	87.60	87.20	85.99	86.18
C(4)	68.91[b])	68.89[b])	69.00[b])	79.35[b])	79.38[b])	78.90[b])	78.00[b])
C(5)	73.61[c])	73.08[c])	73.29[c])	79.05[b])	79.24[b])	76.16[b])	75.94[b])
C(6)	62.42	62.57	62.11	69.39	69.46	69.95	69.93
C(2′)	22.08	21.80	29.07	22.39	21.85	29.84	30.81
C(3′)	58.07	58.18	65.15	59.45	58.71	66.09	65.32
C(1″)	19.53	20.15	21.21	20.58	21.19	22.26	22.18
C(2″)	29.22[d])	29.83[d])	30.35[d])	30.19[c])	30.56[c])	31.10[c])	30.14[c])
C(3″)	29.11[d])	29.42[d])	29.23[d])	29.89[c])	30.06[c])	30.14[c])	29.74[c])
C(4″)	31.59	31.72	31.73	32.23	32.19	32.09	32.12
C(5″)	22.56	22.58	22.60	23.07	23.03	[h])	23.01
C(6″)	14.00	13.96	14.02	14.29	14.25	[h])	14.25
MeO	59.08	58.94	59.19	58.95	59.57	[h])	58.85

[a]) Assignment based on a ^{1}H,^{13}C-COSY spectrum. [b]) [c]) [d]) Assignment may be interchanged. [e]) J(C,P) [Hz] in parenthesis. [f]) Same numbering as for **19**. [g]) Data from **29**/**30** 3:1. [h]) Hidden by other signals.

on a COSY-DQF spectrum): 7.31–7.23 (*m*, 4 arom. H); 7.23–7.05 (*m*, 16 arom. H); 4.90 (*d*, J = 11.4), 4.82 (*d*, J = 11.3), 4.77 (*d*, J = 11.3), 4.65 (*d*, J = 11.5), 4.64 (*d*, J = 11.3), 4.46 (*d*, J = 12.2), 4.34 (*d*, J = 12.8), 4.31 (*d*, J = 11.7, 8 PhC*H*); 4.24 (*d*, J = 6.5, H–C(1')); 4.11 (*t*, J = 8.2, H–C(3')); 4.08 (*dt*, $J \approx$ 4.8, 9.0, H'–C(3')); 3.87 (br. *dd*, $J \approx$ 4.0, 9.5, H–C(5)); 3.85 (*t*, J = 9.5, H–C(4)); 3.81 (*t*, $J \approx$ 8.8, H–C(3)); 3.73 (*d*, J = 8.7, H–C(2)); 3.71 (*dd*, J = 4.1, 10.9, H–C(6)); 3.66 (*dd*, J = 1.3, 10.7, H'–C(6)); 2.09 (*ddd*, J = 4.8, 8.5, 11.9, H–C(4')); 1.88 (*tdd*, $J \approx$ 7.1, 9.7, 11.9, H'–C(4')); 1.77 (*t*, J = 6.5, H–C(5')). ^{13}C-NMR (50 MHz, C_6D_6): *Table 5*; additionally, 139.69, 139.47, 139.14, 138.96 (4*s*); 128.86–127.76 (several *d*); 75.67, 75.19, 75.07, 73.49 (4*t*, 4 PhCH_2). CI-MS: 612 (11), 611 (47), 610 (100, $[M + NH_4]^+$). Anal. calc. for $C_{38}H_{40}O_6$ (592.74): C 77.00, H 6.80; found: C 77.17, H 6.65.

*(1*R*,1'*S*,5'*R*)-Spiro[1,5-anhydro*-D*-glucitol-1,6'-[2]oxabicyclo[3.1.0]hexane]* (**9**). *a*) From **7**: A suspension of **7** (250 mg, 1.07 mmol) in 1,4-dioxane/H_2O 1:1 (12 ml) was treated with 40% Bu_4NOH in H_2O (2 ml), stirred for 6 d at 23°, neutralized with *Dowex CCR-2* (H^+ form), and filtered. Evaporation of the filtrate, two FC (AcOEt/MeOH 3:1 and CH_2Cl_2/MeOH 4:1), and crystallization from MeOH/AcOEt gave **9** (84 mg, 82%) as colorless needles.

b) From **8**: A suspension of **8** (10 mg, 0.017 mmol) and $Pd(OH)_2$/C (18 mg) in MeOH (15 ml) was stirred under H_2 for 5 h and filtered through *Celite*. Evaporation and FC (CH_2Cl_2/MeOH 4:1) gave **9** (3.8 mg, 97%). M.p. 177° (MeOH/AcOEt). R_f (AcOEt/MeOH 1:1) 0.64, R_f (CH_2Cl_2/MeOH 4:1) 0.36. $[\alpha]_D^{25}$ = + 104.8 (c = 1.01, MeOH). IR (KBr): 3600–3160*s* (br.), 3070*m*, 2980*m*, 2960*m*, 2930*m* (sh), 2900*s* (br.), 1450*m*, 1420*s* (br.), 1380*w*, 1365*w*, 1345*w*, 1335*m* (sh), 1330*m* (sh), 1310*w*, 1260*m* (sh), 1250*s* (sh), 1240*s*, 1205*m*, 1170*w*, 1130*s* (sh), 1120*s*, 1100*s* (sh), 1090*s*, 1065*s*, 1030*s*, 1010*s*, 990*m*, 960*m*, 920*m*, 890*w*, 875*m*, 850*m*, 760*w*, 730*m*, 710–660*m* (br.), 645*m*, 615*m*. ^{1}H-NMR (600 MHz, D_2O): 4.17 (*ddd*, J = 4.5, 7.7, 9.9, H–C(3')); 4.05 (*d*, J = 6.6, H–C(1')); 3.96 (br. *q*, J = 8.1, H'–C(3')); 3.87 (*dd*, J = 2.2, 12.6, irrad. at 3.35 → *d*, J = 12.5, H–C(6)); 3.705 (*d*, J = 8.9, H–C(2)); 3.697 (*dd*, J = 5.9, 12.6, irrad. at 3.35 → *d*, J = 12.5, H'–C(6)); 3.51 (*t*, J = 9.0, H–C(3)); 3.45 (*t*, $J \approx$ 9.4, irrad. at 3.35 → br. *d*, $J \approx$ 9.5, H–C(4)); 3.35 (*ddd*, J = 2.3, 5.8, 9.7, H–C(5)); 2.30 (*tdd*, $J \approx$ 7.4, 9.8, 12.4, H–C(4')); 2.11 (*ddd*, J = 4.4, 8.8, 12.3, H'–C(4')); 2.07 (*t*, J = 6.6, H–C(5')). ^{1}H-NMR (400 MHz, (D_6)DMSO): 4.85 (*d*, J = 4.6, exchange with D_2O, OH); 4.83 (*d*, J = 5.3, exchange with D_2O, OH); 4.82 (*d*, J = 5.2, exchange with D_2O, OH); 4.38 (*t*, J = 5.8, exchange with D_2O, HO–C(6)); 3.93 (*dt*, J = 4.0, 7.2, H–C(3')); 3.88 (*t*, $J \approx$ 7.8, H'–C(3')); 3.76 (*d*, J = 6.3, H–C(1')); 3.62 (br. *dd*, J = 5.5, 11.1, addn. of D_2O → br. *d*, J = 11.5, H–C(6)); 3.40–3.27 (*m*, addn. of D_2O → 3.35, *dd*, J = 5.4, 11.5, H'–C(6), → 3.34, *d*, J = 8.8, H–C(2)); 3.15 (*m*, addn. of D_2O → *t*, $J \approx$ 8.5, irrad. at 3.34 → *d*, $J \approx$ 8.5, H–C(3)); 3.11–3.03 (*m*, addn. of D_2O → change, H–C(4), H–C(5)); 2.12–2.01 (*m*, H–C(4')); 1.93 (*ddd*, J = 3.9, 8.2, 11.7, H'–C(4')); 1.78 (*t*, J = 6.3, H–C(5')). ^{13}C-NMR (150 MHz, D_2O): *Table 5*. ^{13}C-NMR (50 MHz, (D_6)DMSO): *Table 5*. CI-MS: 251 (5), 250 (100, $[M + NH_4]^+$). Anal. calc. for $C_{10}H_{16}O_6$ (232.24): C 51.72, H 6.94; found: C 51.61, H 7.07.

*(1*R*,1'*S*,6'*R*)-2,3,4,6-Tetra*-O*-pivaloylspiro[1,5-anhydro*-D*-glucitol-1,7'-[2]oxabicyclo[4.1.0]heptane]* (**12**). *a*) A soln. of **10** (5 ml, 55.16 mmol) in 1,4-dioxane (5 ml) was heated under N_2 to 45°, treated dropwise with a cooled (0°) soln. of **1** (0.9 g, 1.71 mmol) in 1,4-dioxane (5 ml), and stirred for 3 h. Evaporation and prep. HPLC (hexane/Et_2O 3:1) of the residue (831 mg) gave (*Z*,*Z*)-**11** [22] (478 mg, 55%) and **12** (137 mg, 14%) which crystallized from MeOH.

b) A soln. of **10** (1.0 ml, 11.03 mmol) in abs. THF (2 ml) was cooled under N_2 to −60°, treated dropwise with a cooled (0°) soln. of **1** (200 mg, 0.38 mmol) in abs. THF (2 ml), and irradiated (Hg lamp with *Solidex* filter) for 2 h. Evaporation, FC (hexane/Et_2O 2:1), and prep. HPLC (hexane/Et_2O 3:1) gave (*Z*,*Z*)-**11** (101 mg, 52%) and **12** (20 mg, 9%). M.p. 200° (MeOH). R_f (hexane/Et_2O 1:2) 0.70. Prep. HPLC: t_R (hexane/Et_2O 3:1, 14 ml/min) 5.5 $[\alpha]_D^{25}$ = + 62.6 (c = 1.07, $CHCl_3$). IR (KBr): 3020*w* (sh), 2980*s*, 2940*m* (sh), 2910*m* (sh), 2880*m*, 1745*s*, 1480*s*, 1460*m*, 1440*m* (sh), 1400*m*, 1370*m*, 1275*s*, 1265*s* (sh), 1240*m*, 1230*m*, 1195*s* (sh), 1170*s* (sh), 1150*s* (sh), 1140*s*, 1120*s* (sh), 1100*s* (sh), 1090*s*, 1070*m*, 1040*s*, 980*m*, 945*m*, 895*m*, 870*m*, 760*m*, 640*m*. ^{1}H-NMR (400 MHz, C_6D_6): 5.67 (*d*, J = 9.1, irrad. at 0.81 → NOE (3.3%), H–C(2)); 5.62 (*t*, J = 9.0, irrad. at 3.65 → NOE (4.0%), H–C(3)); 5.49 (*t*, $J \approx$ 9.3, H–C(4)); 4.47 (*dd*, J = 1.1, 12.2, H–C(6)); 4.08 (*ddd*, J = 1.1, 5.0, 10.2, irrad. at 4.47 → *dd*, J = 4.9, 10.4, H–C(5)); 4.05 (*dd*, J = 5.1, 12.2, irrad. at 4.47 → *d*, J = 5.2, H'–C(6)); 3.65 (*d*, J = 8.1, irrad. at 0.81 → NOE (7.0%), H–C(1')); 3.57 (br. *td*, $J \approx$ 3.2, 10.5, irrad. at 1.72 → *dd*, J = 2.1, 10.4, H–C(3')); 3.05 (*dt*, $J \approx$ 2.0, 10.9, irrad. at 1.72 → *dd*, J = 1.7, 10.3, irrad. at 3.65 → NOE (2.8%), H'–C(3')); 1.79–1.66 (*m*, irrad. at 1.44 → change, H–C(4'), H–C(5')); 1.50–1.37 (*m*, irrad. at 0.81 → change, irrad. at 1.72 → change, irrad. at 0.81 → NOE (2.6%), H'–C(5')); 1.19, 1.17, 1.14 (3*s*, 3 *t*-Bu); 1.05–0.96 (*m*, irrad. at 0.81 → change, irrad. at 1.44 → change, irrad. at 1.72 → change, H'–C(4')); 0.99 (*s*, *t*-Bu); 0.81 (*t*, $J \approx$ 7.9, irrad. at 1.44 → *d*, J = 7.9, irrad. at 3.65 → NOE (4.8%), H–C(6')). ^{13}C-NMR (50 MHz, C_6D_6): *Table 5*; additionally, 177.53, 176.92, 176.43, 176.10 (4*s*, 4C=O); 38.91 (*s*, Me_3C); 38.82 (*s*, 2 Me_3C); 38.72 (*s*, Me_3C);

27.37 (*q*, Me_3C); 27.20 (*q*, 2 Me_3C); 27.07 (*q*, Me_3C). CI-MS: 601 (35), 600 (100, $[M + NH_4]^+$), 380 (18), 379 (82), 346 (26), 277 (27), 263 (7). Anal. calc. for $C_{31}H_{50}O_{10}$ (582.74): C 63.90, H 8.65; found: C 64.16, H 8.85.

*(1*R,*1'*S,*6'*R*)-2,3,4,6-Tetra-*O*-benzylspiro[1,5-anhydro-*D*-glucitol-1,7'-[2]oxabicyclo[4.1.0]heptane]* (**14**). *a*) A suspension of **10** (3.5 ml, 38.61 mmol) and 4 Å-molecular sieves (1.0 g) in 1,4-dioxane (5 ml) was treated slowly at 23° with a cooled (0°) soln. of **2** (650 mg, 1.18 mmol) in 1,4-dioxane (5 ml), stirred for 3 h, and filtered through *Celite* (washing several times with CH_2Cl_2). Evaporation and several crystallizations from AcOEt/hexane gave (*Z*,*Z*)-**13** [22] (150 mg) as colorless needles. FC (hexane/AcOEt 4:1) of the combined mother liquors gave (*Z*,*Z*)-**13** (50 mg; total 200 mg, 32%), (*E*,*E*)-**13** [22] (53 mg), and a mixture (*E*,*E*)-**13**/**14** (235 mg). Prep. HPLC (hexane/AcOEt 4:1) of this mixture afforded (*E*,*E*)-**13** (127 mg; total 180 mg, 28%) and **14** (65 mg, 9%). R_f (hexane/AcOEt 1:1) 0.72. Prep. HPLC: t_R (hexane/AcOEt 4:1, 15 ml/min) 4.9. $[\alpha]_D^{25} = +51.9$ (*c* = 1.4, $CHCl_3$). IR ($CHCl_3$): 3000*m*, 2950*m* (sh), 2920*m* (br.), 2860*m* (br.), 1495*m*, 1450*w*, 1400*w*, 1360*m*, 1305*w*, 1280*w*, 1260*m*, 1235*m*, 1185*w*, 1145*m*, 1125*s*, 1090*s*, 1070*s* (sh), 1025*s*, 1010*m* (br.), 910*w*, 870*w*, 695*s*, 645*w*. ^{1}H-NMR (400 MHz, C_6D_6): 7.36–7.22 (*m*, 4 arom. H); 7.20–7.02 (*m*, 16 arom. H); 4.93 (*d*, *J* = 11.4), 4.82 (*d*, *J* = 11.3), 4.76 (*d*, *J* = 11.4), 4.70 (*d*, *J* = 11.5), 4.68 (*d*, *J* = 11.4), 4.50 (*d*, *J* = 12.3), 4.38 (*d*, *J* = 12.2), 4.30 (*d*, *J* = 11.6, 8 PhC*H*); 4.10 (*ddd*, *J* = 1.9, 4.2, 9.5, H–C(5)); 3.93 (*t*, *J* ≈ 9.1, H–C(4)); 3.88 (*t*, *J* ≈ 8.7, H–C(3)); 3.88 (*d*, *J* = 8.1, irrad. at 1.15 → *s*, irrad. at 1.15 → NOE (6.5%), H–C(1')); 3.79 (*dd*, *J* = 4.0, 11.0, H–C(6)); 3.78 (*d*, *J* = 9.0, irrad. at 1.15 → NOE (1.1%), H–C(2)); 3.73 (*dd*, *J* = 1.9, 11.0, H'–C(6)); 3.66 (br. *td*, *J* = 3.3, 10.5, irrad. at 1.15 → *dd*, *J* = 3.5, 10.5, H–C(3')); 3.18 (*dt*, *J* = 2.0, 10.4, irrad. at 1.15 → *t*, *J* = 10.9, H'–C(3')); 1.96 (br. *dd*, *J* ≈ 6.0, 12.8, irrad. at 1.15 → *dd*, *J* ≈ 6.2, 13.0, H–C(5')); 1.92–1.82 (*m*, irrad. at 1.15 → change, irrad. at 1.15 → NOE (9.1%), H–C(4')); 1.67–1.55 (*m*, irrad. at 1.15 → br. *t*, *J* ≈ 11.5, irrad. at 1.15 → NOE (4.9%), H'–C(5')); 1.16 (*t*, *J* ≈ 7.9, irrad. at 3.78 → NOE (1.3%), H–C(6')); 1.20–1.09 (*m*, H'–C(4')). ^{13}C-NMR (50 MHz, C_6D_6): *Table 5*; additionally, 139.61, 139.44, 139.13, 138.93 (4*s*); 128.68–127.53 (several *d*); 75.50, 75.03, 74.83, 73.03 (4*t*, 4 $PhCH_2$). CI-MS: 626 (10), 625 (42), 624 (100, $[M + NH_4]^+$), 391 (6). Anal. calc. for $C_{39}H_{42}O_6$ (606.77): C 77.20, H 6.98; found: C 77.10, H 7.10.

*(1*S,*1'*S,*5'*R*)-1'-Methyl-2,3,4,6-tetra-*O*-pivaloylspiro[1,5-anhydro-*D*-glucitol-1,6'-[2]oxabicyclo[3.1.0]-hexane]* (**16**). A soln. of **15** (2.8 ml, 30.38 mmol) in 1,4-dioxane (5 ml) was heated under N_2 to 45°, treated dropwise with a cooled (0°) soln. of **1** (790 mg, 1.50 mmol) in 1,4-dioxane (5 ml), and stirred for 2 h. Evaporation and prep. HPLC (hexane/Et_2O 4:1) gave (*Z*,*Z*)-**11** (385 mg, 50%) and **16** (210 mg, 24%) which afforded colorless needles from MeOH. M.p. 175° (MeOH). R_f (hexane/Et_2O 1:2) 0.67. Prep. HPLC: t_R (hexane/Et_2O 4:1, 14 ml/min) 6.1. $[\alpha]_D^{25} = +60.3$ (*c* = 1.00, $CHCl_3$). IR (KBr): 2980*m*, 2940*m* (sh), 2910*w*, 2880*w*, 1740*s*, 1730*s* (sh), 1480*m*, 1460*w*, 1400*w*, 1370*w*, 1285*m*, 1210*w*, 1160*s*, 1150*s* (sh), 1100*m*, 1090*w*, 1050*w*, 1030*w*, 980*w*, 960*w*. ^{1}H-NMR (400 MHz, C_6D_6): 5.82 (*d*, *J* = 10.0, irrad. at 1.26 → NOE (3.6%), H–C(2)); 5.64 (*dd*, *J* = 8.9, 9.9, irrad. at 1.69 → NOE (2.8%), H–C(3)); 5.01 (*dd*, *J* = 8.8, 10.2, H–C(4)); 4.48–4.42 (*m*, with virtual coupling, H–C(6)); 4.03–3.87 (*m*, H–C(5), H'–C(6), 2 H–C(3')); 1.93 (*ddd*, *J* = 5.1, 8.6, 12.1, irrad. at 1.78 → change, H–C(4')); 1.82–1.72 (*m*, irrad. at 1.26 → NOE (5.1%), H'–C(4')); 1.69 (*s*, irrad. at 5.64 → NOE (8.1%), irrad. at 1.26 → NOE (2.6%), Me); 1.26 (*d*, *J* = 6.1, irrad. at 1.78 → *s*, irrad. at 1.69 → NOE (2.7%), H–C(5')); 1.20, 1.18, 1.17, 1.04 (4*s*, 4 *t*-Bu). ^{13}C-NMR (50 MHz, C_6D_6): *Table 5*; additionally, 177.47, 176.89, 176.48, 176.14 (4*s*, 4 C=O); 38.88 (*s*, Me_3C); 38.83 (*s*, 2 Me_3C); 38.69 (*s*, Me_3C); 27.41 (*q*, Me_3C); 27.26 (*q*, 2 Me_3C); 27.19 (*q*, Me_3C). CI-MS: 601 (35), 600 (100, $[M + NH_4]^+$), 481 (13), 380 (22), 379 (98), 279 (48), 277 (19), 179 (12), 177 (12). Anal. calc. for $C_{31}H_{50}O_{10}$ (582.74): C 63.90, H 8.65; found: C 64.11, H 8.77.

*(1*RS,*2*SR*)- and (1*RS,*2*RS*)-1-(Diphenylphosphinoyl)-1-methoxyoctan-2-ol* (**19** and **20**, resp.). Prepared according to [28]: **19**/**20** 52:48 (3.27 g, 79%). Crystallization (2×) from AcOEt gave pure **19** (0.51 g). A sample of the combined mother liquors (2.76 g, **19**/**20** 43:57) was separated by prep. HPLC (hexane/Et_2O/THF 4:3:3, 25 ml/min; t_R 23.2 (**20**) and 27.4 (**19**)).

Data of **19**: M.p. 111° ([28]: 111°). R_f (hexane/AcOEt 1:5) 0.44. IR ($CHCl_3$): 3450–3200*w* (br.), 3000*m*, 2960*s*, 2930*s*, 2880*m* (sh), 2860*m*, 2840*w* (sh), 1595*w*, 1490*w*, 1460*w*, 1440*s*, 1380*w*, 1315*w*, 1245*w* (br.), 1190*w* (sh), 1160*s*, 1120*s*, 1095*s*, 1070*s*, 1050*m*, 1030*m*, 1000*w*, 955*w*, 815*w*, 715*w*, 700*s*, 660*w*, 620*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.08–7.98 (*m*, 2 arom. H); 7.90–7.81 (*m*, 2 arom. H); 7.62–7.46 (*m*, 6 arom. H); 4.32 (br. *s*, exchange with D_2O, OH); 3.92 (*tq*, *J* ≈ 2.0, 9.0, addn. of D_2O → *dq*, *J* = 2.6, 9.2, H–C(2)); 3.72 (*dd*, ^2J(H,P) = 5.7, *J* = 8.8, irrad. at 3.92 → *dd*, *J* = 2.5, 5.5, H–C(1)); 3.26 (*s*, MeO); 1.76–1.68 (*m*, 1 H); 1.61–1.42 (*m*, 3 H); 1.39–1.20 (*m*, 6 H); 0.86 (*t*, *J* = 6.8, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): *Table 5*; additionally, 132.93–127.88 (*m*).

Data of **20**: Oil. R_f (hexane/AcOEt 1:5) 0.44. IR ($CHCl_3$): 3500–3200*w* (br.), 3000*m*, 2960*m*, 2930*m*, 2860*m*, 2840*w* (sh), 1595*w*, 1485*w*, 1460*w*, 1440*m*, 1380*w*, 1315*w*, 1250*w* (br.), 1200*m* (sh), 1165*s*, 1120*s*, 1095*s*, 1070*s*, 1050*s* (sh), 1030*s*, 1000*w*, 960*w*, 710*w* (sh), 700*m*, 660*w*, 625*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.05–7.97 (*m*, 2 arom. H); 7.89–7.82 (*m*, 2 arom. H); 7.59–7.45 (*m*, 6 arom. H); 4.05 (br. *dquint.*, *J* ≈ 11, 6.2, addn. of D_2O → *dq*, *J* ≈ 11, 6.2, H–C(2)); 3.93 (*dd*, *J* = 3.9, ^2J(H,P) = 6.0, H–C(1)); 3.30 (*s*, MeO); 3.27 (*d*, *J* = 6.3, exchange with D_2O,

HO–C(2)); 1.62–1.53 (*m*, 2H); 1.53–1.42 (*m*, 1H); 1.32–1.12 (*m*, 7H); 0.84 (*t*, *J* = 7.0, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): *Table 5*; additionally, 133.04–127.88 (*m*).

(1RS,1'SR)- and (1RS,1'SR)-1-[(Diphenylphosphinoyl)methoxymethyl]heptyl Cinnamate (**21** and **22**, resp.). A soln. of **19**/**20** 43:57 (22.8 g, 63 mmol) in pyridine (100 ml) and cinnamoyl chloride (21.0 g, 126 mmol) was stirred for 1.5 h at 23°. Evaporation, FC (CH_2Cl_2/AcOEt 3:1), and an additional FC (CH_2Cl_2/AcOEt 6:1 → 5:1 → 4:1 → 3:1) gave **21** (12.10 g, 39%), **22** (10.53 g, 34%), and **21**/**22** 8:92 (6.17 g, 20%).

Data of **21**: R_f (AcOEt/CH_2Cl_2 1:2) 0.64. IR ($CHCl_3$): 3060*w*, 2990*m* (sh), 2960*s*, 2930*s*, 2860*m*, 2830*w* (sh), 1710*s*, 1640*s*, 1595*w*, 1580*w*, 1500*w*, 1485*w*, 1470*m* (sh), 1450*m*, 1440*m*, 1380*w*, 1360*w*, 1330*m*, 1310*s*, 1280*m*, 1270*m* (br.), 1250*m*, 1160*s*, 1120*s*, 1100*s*, 1070*m*, 1050*m*, 1030*w*, 1000*m*, 990*m* (sh), 980*m*, 940*w* (br.), 870*w*, 710*m* (sh), 695*s*, 660*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.08–7.98 (*m*, 2 arom. H); 7.96–7.87 (*m*, 2 arom. H); 7.46 (*d*, *J* = 16.1, PhC*H*=CH); 7.57–7.34 (*m*, 11 arom. H); 5.96 (*d*, *J* = 16.0, PhCH=C*H*); 5.50 (*dddd*, *J* = 2.6, 3.6, 10.0, 12.2, H–C(1)); 4.21 (*dd*, *J* = 2.5, ^2J(H,P) = 9.6, irrad. at 5.50 → *d*, ^2J(H,P) = 9.5, H–C(1')); 3.36 (*s*, MeO); 2.11–2.00 (*m*, 1H); 1.92–1.83 (*m*, 1H); 1.40–1.14 (*m*, 8H); 0.84 (*t*, *J* = 7.0, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): *Table 5*; additionally, 165.95 (*s*, C=O); 144.55 (*d*, PhC*H*=CH); 133.93–127.76 (*m*); 117.23 (*d*, PhCH=C*H*). CI-MS: 492 (34), 491 (100, $[M + 1]^+$), 379 (29).

Data of **22**: R_f (AcOEt/CH_2Cl_2 1:2) 0.44. IR ($CHCl_3$): 3060*w*, 2990*s*, 2970*s* (sh), 2960*s*, 2930*s*, 2860*m*, 2830*w*, 1710*s*, 1640*s*, 1595*w*, 1580*w*, 1500*w*, 1465*m* (sh), 1450*s*, 1440*s*, 1380*w*, 1355*m* (sh), 1330*m*, 1310*s*, 1280*s*, 1270*m*, 1255*m*, 1170*s*, 1120*s*, 1100*s*, 1070*m*, 1045*m*, 1030*m*, 1020*m* (sh), 1000*m*, 990*m*, 980*m*, 940*w*, 885*w*, 865*w*, 845*w*, 815*w*, 710*m* (sh), 695*s*, 680*m* (sh), 660*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.14–8.06 (*m*, 2 arom. H); 7.91–7.82 (*m*, 2 arom. H); 7.48 (*d*, *J* = 15.9, PhC*H*=CH); 7.54–7.34 (*m*, 11 arom. H); 5.98 (*d*, *J* = 16.0, PhCH=C*H*); 5.53 (*qd*, *J* = 5.4, 10.3, H–C(1)); 3.96 (*dd*, *J* = 5.6, ^2J(H,P) = 10.0, irrad. at 5.53 → *d*, ^2J(H,P) = 9.9, H–C(1')); 3.19 (*s*, MeO); 1.98–1.87 (*m*, 1H); 1.87–1.76 (*m*, 1H); 1.40–1.14 (*m*, 8H); 0.83 (*t*, *J* = 6.9, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): *Table 5*; additionally, 165.55 (*s*, C=O); 144.35 (*d*, PhC*H*=CH); 133.93–127.67 (*m*); 117.08 (*d*, PhCH=C*H*). MS: 492 (34), 491 (100, $[M + 1]^+$).

Saponification of **21**. A soln. of **21** (12.1 g, 25 mmol) in 3% KOH in MeOH (250 ml, 0.134 mol) was stirred at 23° for 1.5 h and treated with Et_2O (1000 ml) and sat. $NaHCO_3$ soln. (500 ml). After separation and extraction of the aq. layer with Et_2O (300 ml), drying of the combined org. layers ($MgSO_4$), evaporation, and FC (AcOEt) gave **19** (7.73 g, 87%).

Saponification of **22**. Analogously to **21**, with **22** (10.5 g, 21 mmol): **20** (7.18 g, 93%).

(E)-1-Methoxyoct-1-ene (**23**) [28] [29]. Prepared according to [28]. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.28 (br. *d*, *J* = 12.6, H–C(1)); 4.73 (*td*, *J* = 7.3, 12.6, H–C(2)); 3.50 (*s*, MeO); 1.91 (br. *q*, *J* ≈ 6.9, 2H–C(3)); 1.38–1.22 (*m*, 8H); 0.89 (*t*, *J* = 6.9, Me). ^{13}C-NMR (100 MHz, $CDCl_3$): *Table 5*. EI-MS: 142 (11, M^+), 71 (100), 41 (24).

(Z)-1-Methoxyoct-1-ene (**24**). Similarly to **23**, with **20** (6.0 g, 17 mmol) and NaH (1.8 g, 0.075 mol) in THF (350 ml): **24** (2.05 g, 87%). IR ($CHCl_3$): 3030*w* (sh), 3000*m*, 2950*s* (sh), 2930*s*, 2860*s*, 2820*m* (sh), 1665*s*, 1460*s*, 1440*w* (sh), 1390*m*, 1380*w* (sh), 1260*s*, 1105*s*, 960*w*, 940*w*, 930*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.86 (*td*, *J* = 1.4, 6.2, H–C(1)); 4.34 (*dt*, *J* = 6.3, 7.3, H–C(2)); 3.58 (*s*, MeO); 2.05 (br. *q*, *J* ≈ 7.3, 2H–C(3)); 1.38–1.22 (*m*, 8H); 0.88 (*t*, *J* = 6.9, Me). ^{13}C-NMR (100 MHz, $CDCl_3$): *Table 5*. EI-MS: 142 (13, M^+), 71 (100), 41 (24).

Reaction of **1** *with* **24**. A soln. of **24** (2.0 g, 14.1 mmol) in abs. 1,4-dioxane (5 ml) was heated to 45° under N_2, slowly treated with a cooled (0°) soln. of **1** (800 mg, 1.519 mmol) in abs. 1,4-dioxane (5 ml), and stirred for 3 h. Evaporation (23°, 50 mbar) and FC (hexane/Et_2O 3:1) gave (*Z,Z*)-**11** (370 mg, 47%) and a mixture of the cyclopropanes **25**–**27** and **24** (^{1}H-NMR: no trace of **23**). The enol ether **24** was removed under high vacuum overnight. The fractions obtained at 4.5–5.8 min on prep. HPLC (hexane/AcOEt 4:1, 15 ml/min) of the residue (447 mg) were collected and evaporated. Prep. HPLC (hexane/CH_2Cl_2/ Et_2O 16:1:1, 15 ml/min) gave **25** (107 mg, 11%; t_R 11.8), **26** (41 mg, 4%; t_R 15.9), and **27** (15 mg, 1.5%; t_R 18.2).

*(1R,2'R,3'S)-2'-Hexyl-3'-methoxy-2,3,4,6-tetra-*O*-pivaloylspiro[1,5-anhydro-*D*-glucitol-1,1'-cyclopropane]* (**25**). Slow evaporation of a saturated soln. of **25** in hexane, gave colorless crystals. M.p. 103° (hexane). R_f (hexane/Et_2O 3:1) 0.61, R_f (hexane/CH_2Cl_2/Et_2O 16:1:1) 0.30. $[\alpha]_D^{25}$ = + 76.4 (*c* = 1.164, $CHCl_3$). IR ($CHCl_3$): 3030*w*, 2970*m*, 2930*m*, 2910*m* (sh), 2870*m*, 2860*w* (sh), 1740*s*, 1480*m*, 1460*m*, 1400*w*, 1370*w*, 1280*m*, 1235*w*, 1175*s* (sh), 1155*s* (sh), 1145*s*, 1095*m*, 1050*w*, 1035*m*, 1015*w*, 980*w*, 940*w*, 910*w*, 890*w*, 880*w* (sh). ^{1}H-NMR (400 MHz, $CDCl_3$): 5.35 (*t*, *J* ≈ 9.2, irrad. at 3.16 → NOE (4.3%), H–C(3)); 5.29 (*d*, *J* = 9.4, irrad. at 0.62 → NOE (2.0%), H–C(2)); 5.13 (*dd*, *J* = 8.9, 10.2, H–C(4)); 4.18 (*dd*, *J* = 1.8, 12.1, H–C(6)); 3.93 (*dd*, *J* = 6.5, 12.0, H'–C(6)); 3.84 (*ddd*, *J* = 1.8, 6.5, 10.2, irrad. at 5.35 → NOE (5.9%), H–C(5)); 3.40 (*s*, irrad. at 3.16 → NOE (5.8%), MeO); 3.16 (*d*, *J* = 7.2, irrad. at 0.63 → NOE (8.1%), irrad. at 5.35 → NOE (2.9%), H–C(3')); 1.51 (br. *dd*, *J* = 6.2, 13.2, H–C(1'')); 1.475 (*dt*, *J* ≈ 6.1, 13.3, H'–C(1'')); 1.39–1.24 (*m*, 8H); 1.22, 1.17 (*s*, 2 *t*-Bu); 1.12 (*s*, 2 *t*-Bu); 0.88 (*t*, *J* = 6.8, Me); 0.62 (*q*, *J* ≈ 7.1, irrad. at 3.17 → NOE (7.2%), H–C(2')). ^{13}C-NMR

(100 MHz, $CDCl_3$): *Table 5*; additionally, 177.99, 177.24, 176.66, 176.38 (4*s*, 4 C=O); 38.70 (*s*, 4 Me_3C); 27.18 (*q*, Me_3C); 27.07 (*q*, 3 Me_3C). CI-MS: 659 (40), 658 (100, $[M + NH_4]^+$), 539 (13), 438 (15), 437 (56). Anal. calc. for $C_{35}H_{60}O_{10}$ (640.86): C 65.60, H 9.44; found: C 65.87, H 9.66.

*(1S,2'S,3'R)-2'-Hexyl-3'-methoxy-2,3,4,6-tetra-*O*-pivaloylspiro[1,5-anhydro-*D*-glucitol-1,1'-cyclopropane]* (**26**). R_f (hexane/Et_2O 3:1) 0.61, R_f (hexane/CH_2Cl_2/Et_2O 16:1:1) 0.27. IR ($CHCl_3$): 3020*w*, 2970*s* (sh), 2960*s*, 2930*s*, 2910*m* (sh), 2870*m*, 2860*m* (sh), 1740*s*, 1480*s*, 1460*m*, 1425*w*, 1400*m*, 1370*m*, 1330*w*, 1280*s*, 1235*w*, 1170*s* (sh), 1155*s* (sh), 1145*s* (br.), 1095*m*, 1050*w*, 1035*m*, 1020*w* (sh), 985*w*, 940*w*, 920*w*(sh), 915*w*, 895*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.44 (*d*, J = 9.3, irrad. at 2.79 → NOE (2.9%), H–C(2)); 5.24 (*t*, J = 9.3, H–C(3)); 5.17 (*t*, $J \approx$ 9.6, irrad. at 5.44 → NOE (5.1%), H–C(4)); 4.09 (br. *d*, J = 4.1, 2H–C(6)); 3.67 (*td*, J = 4.4, 9.9, H–C(5)); 3.36 (*s*, irrad. at 2.79 → NOE (5.5%), MeO); 2.79 (*d*, J = 8.1, irrad. at 5.44 → NOE (2.5%), H–C(3')); 1.67–1.52 (*m*, 2H); 1.52–1.39 (*m*, 2H); 1.39–1.24 (*m*, 6H); 1.22, 1.17 (2*s*, 2 *t*-Bu); 1.12 (*s*, 2 *t*-Bu); 1.17–1.12 (*m*, H–C(2')); 0.90 (*t*, J = 6.7, Me). ^{13}C-NMR (100 MHz, $CDCl_3$): *Table 5*; additionally, 177.99, 177.24 (2*s*, 2 C=O); 176.52 (*s*, 2 C=O); 38.74 (*s*, 4 Me_3C); 27.18, 27.12, 27.05, 26.99 (4*q*, 4 Me_3C). CI-MS: 659 (40), 658 (100, $[M + NH_4]^+$), 438 (15), 437 (56).

*(1S,2'R,3'S)-2'-Hexyl-3'-methoxy-2,3,4,6-tetra-*O*-pivaloylspiro[1,5-anhydro-*D*-glucitol-1,1'-cyclopropane]* (**27**): R_f (hexane/Et_2O 3:1) 0.61, R_f (hexane/CH_2Cl_2/Et_2O 16:1:1) 0.25. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.76 (*d*, J = 8.8, H–C(2)); 5.33 (*t*, J = 8.8, irrad. at 3.64 → NOE (7.3%), H–C(3)); 5.17 (*t*, $J \approx$ 9.4, irrad. at 5.76 → NOE (4.3%), H–C(4)); 4.05 (*dd*, J = 2.3, 12.2, H–C(6)); 3.99 (*dd*, J = 5.8, 12.3, H'–C(6)); 3.64 (*ddd*, J = 2.3, 5.8, 9.9, H–C(5)); 3.33 (*s*, irrad. at 5.76 → NOE (1.1%), MeO); 3.30 (*d*, J = 8.6, H–C(3')); 1.83–1.72 (*m*, irrad. at 5.33 → NOE (1.9%), H–C(1'')); 1.72–1.62 (*m*, 1H); 1.55–1.42 (*m*, irrad. at 5.33 → NOE (2.2%), 2H); 1.42–1.26 (*m*, 6H); 1.21, 1.17 (*s*, 2 *t*-Bu); 1.14 (*s*, 2 *t*-Bu); 0.94 (*dt*, J = 5.7, 9.0, irrad. at 3.64 → NOE (6.3%), irrad. at 3.30 → NOE (5.7%), H–C(2')); 0.90 (*t*, J = 6.7, Me). ^{13}C-NMR (100 MHz, $CDCl_3$): *Table 5*; additionally, 177.95, 177.10, 176.63, 176.39 (4*s*, 4 C=O); 38.71 (*s*, 4 Me_3C); 27.21, 27.14, 27.10, 27.05 (4*q*, 4 Me_3C).

X-Ray Analysis of **25**. Crystals were obtained from hexane. $C_{35}H_{60}O_{10}$ (640.85); monoclinic $P2_1$; a = 13.048 (2), b = 10.833 (3), c = 14.505 (2) Å; β = 108.64 (1)°; V = 1942.7 (4) Å^3; D_x = 1.095 Mg/m^3; Z = 2. Intensities were measured in the ω-scan mode on an *Rigaku-AFC5R* diffractometer (graphite monochromator, MoK_α, λ = 0.71069 Å) at 173 K, $2\Theta_{(max)} \approx 55°$, scan speed of 16°/min in ω, scan width (1.37 + 0.35 tan Θ)°. Of the 4880 total collected reflections, 4679 unique reflections were observed. R = 0.0538, R_w = 0.0570. The structure was solved with the direct-methods routine of SHELXS-86 [41]. The non-H atoms were refined anisotropically, except for the disordered atoms which were refined isotropically. All calculations were performed using the TEXSAN crystallographic software package of *Molecular Structure Corporation* [42].

Reaction of **2** *with* **24**. A soln. of **24** (1 g, 7.0 mmol) in abs. 1,4-dioxane (5 ml) under N_2 was quickly treated with a cooled (0°) soln. of **2** (400 mg, 0.73 mmol) in abs. 1,4-dioxane (5 ml) and stirred for 3 h at 23°. Evaporation (23°/50 mbar) and FC (hexane/AcOEt 6:1) gave (*Z,Z*)-**13** (187 mg, 24%), (*E,E*)-**13** (148 mg, 19%), and a mixture of the cyclopropanes and **24** (^{1}H-NMR: no trace of **23**). The enol ether **24** was removed by drying under high vacuum overnight. Prep. HPLC (hexane/AcOEt 4:1, 16 ml/min) gave **28** (27 mg, 6%; t_R 3.7), an inseparable mixture **29**/**30** 3:1 (29 mg, 6%; t_R 4.0), and **31** (9 mg, 2%, t_R 4.3).

*(1R,2'R,3'S)-2,3,4,6-Tetra-*O*-benzyl-2'-hexyl-3'-methoxyspiro[1,5-anhydro-*D*-glucitol-1,1'-cyclopropane]* (**28**): R_f (hexane/AcOEt 4:1) 0.74. IR ($CHCl_3$): 3080*w* (sh), 3060*w*, 3030*w* (br.), 3000*m*, 2950*m* (sh), 2920*s*, 2860*s*, 2830*w* (sh), 2800*w* (sh), 1500*m*, 1465*m* (sh), 1455*s*, 1425*w*, 1400*w*, 1380*w* (sh), 1360*m*, 1310*w* (br.), 1260*m*, 1250*m*, 1200*w* (sh), 1155*s* (sh), 1140*s* (sh), 1130*s* (br.), 1090*s* (br.), 1070*s* (sh), 1030*s*, 1015*s* (sh), 955*w* (sh), 910*w*, 890*w* (sh), 700*s*, 660*w* (sh), 645*w*, 605*w*. ^{1}H-NMR (600 MHz, C_6D_6, assignment based on a ^{1}H,^{1}H-COSY spectrum): 7.36–7.31 (*m*, 4 arom. H); 7.27–7.24 (*m*, 2 arom. H); 7.21–7.04 (*m*, 14 arom. H); 4.95 (*d*, J = 11.3), 4.93 (*d*, J = 11.5), 4.89 (*d*, J = 11.4), 4.77 (*d*, J = 11.4), 4.74 (*d*, J = 11.3), 4.55 (*d*, J = 12.1), 4.47 (*d*, J = 11.2), 4.45 (*d*, J = 11.9, 8 PhC*H*); 4.02 (*dd*, J = 8.7, 9.9, H–C(4)); 3.97 (*td*, J = 2.6, 9.9, H–C(5)); 3.92 (*t*, J = 8.8, irrad. at 3.39 → NOE (2.5%), H–C(3)); 3.81 (*d*, J = 2.6, 2H–C(6)); 3.79 (*d*, J = 9.0, irrad. at 1.12 → NOE (2.1%), H–C(2)); 3.39 (*d*, J = 7.1, irrad. at 3.92 → NOE (3.6%), irrad. at 1.12 → NOE (8.3%), H–C(3')); 3.20 (*s*, irrad. at 3.39 → NOE (4.5%), MeO); 1.92 (*dddd*, J = 5.9, 7.5, 9.5, 13.7, irrad. at 1.12 → NOE (2%), H–C(1'')); 1.71 (*tdd*, J = 5.8, 9.4, 13.7, irrad. at 1.12 → NOE (4%), H'–C(1'')); 1.60–1.50 (*m*, 1H); 1.51–1.43 (*m*, 1H); 1.42–1.37 (*m*, 2H); 1.36–1.29 (*m*, 4H); 1.12 (*ddd*, J = 6.0, 7.1, 8.3, irrad. at 3.39 → NOE (6.7%), H–C(2')); 0.91 (*t*, J = 7.5, Me). ^{13}C-NMR (100 MHz, C_6D_6): *Table 5*; additionally, 139.69 (*s*); 139.48 (2*s*); 138.87 (*s*); 128.57–127.52 (several *d*); 75.46, 75.32, 74.93, 73.42 (4*t*, 4 PhCH_2). CI-MS: 684 (12), 683 (49), 682 (100, $[M + NH_4]^+$), 449 (25).

*(1S,2'S,3'R)- and (1S,2'R,3'S)-2,3,4,6-Tetra-*O*-benzyl-2'-hexyl-3'-methoxyspiro[1,5-anhydro-*D*-glucitol-1,1'-cyclopropane]* (**29**/**30**). R_f (hexane/AcOEt 4:1) 0.58. ^{1}H-NMR (600 MHz, C_6D_6; **29**/**30** 3:1; assignment based on

^{1}H,^{1}H-COSY): 7.37–7.25 (*m*, 6 arom. H); 7.20–7.05 (*m*, 14 arom. H); 4.94 (*d*, *J* = 11.2), 4.92 (*d*, *J* = 11.3), 4.88 (*d*, *J* = 11.3), 4.78 (*d*, *J* = 11.4), 4.69 (*d*, *J* = 11.2), 4.53 (*d*, *J* = 12.1), 4.47 (*d*, *J* = 11.5), 4.44 (*d*, *J* = 12.2, 8 PhC*H*); 3.90 (*t*, *J* ≈ 9.3, H–C(4)); 3.88 (*d*, *J* = 9.1, H–C(2)); 3.79 (*t*, *J* = 9.1, irrad. at 1.44 → NOE (1.8%), H–C(3)); 3.77 (*dd*, *J* = 1.8, 11.1, H–C(6)); 3.72 (*dd*, *J* = 4.2, 11.0, H′–C(6)); 3.65 (*ddd*, *J* = 1.9, 4.1, 9.8, H–C(5)); 3.34 (*s*, MeO); 3.22 (*d*, *J* = 8.1, irrad. at 1.44 → NOE (5.8%), irrad. at 3.88 → NOE (1.4%), H–C(3′)); 1.95 (br. *q*, *J* ≈ 9.3, H–C(1″)); 1.70–1.62 (*m*, irrad. at 3.65 → NOE (5.9%), H′–C(1′)); 1.58–1.47 (*m*, H–C(2′)); 1.44 (*dt*, *J* ≈ 4.6, 8.7, irrad. at 3.22 → NOE (7.5%), H–C(2′)); 1.41–1.30 (*m*, 3H); 1.30–1.23 (*m*, 4H); 0.87 (*t*, *J* ≈ 7.0, Me); **30**: 4.95 (*d*, *J* = 11.3), 4.92 (*d*, *J* = 11.3), 4.84 (*d*, *J* = 11.4), 4.75 (*d*, *J* = 10.8), 4.68 (*d*, *J* = 10.6), 4.64 (*d*, *J* = 11.3), 4.43 (*d*, *J* = 12.1), 4.36 (*d*, *J* = 12.1, 8 PhC*H*); 4.21 (*d*, *J* = 7.5, H–C(2)); 4.02 (*t*, *J* = 7.8, H–C(3)); 3.98 (*t*, *J* ≈ 8.7, H–C(4)); 3.74–371 (hidden by signals of **29**, H–C(5)); 3.69 (*dd*, *J* = 4.5, 10.4, H–C(6)); 3.60 (*dd*, *J* = 1.7, 10.4, H′–C(6)); 3.43 (*d*, *J* = 8.1, irrad. at 1.09 → NOE (6.8%), H–C(3′)); 3.19 (*s*, MeO); 1.93–1.83 (*m*, 2H–C(1″)); 1.56–1.25 (*m*, 8H); 1.09 (*dt*, *J* = 6.1, 8.3, H–C(2′)); 0.86 (*t*, *J* = 7.1, Me). ^{13}C-NMR (100 MHz, C_6D_6, **29**/**30** 3:1): *Table 5*; additionally, 139.6–138.7 (several *s*); 128.60–127.60 (several *d*); 75.47, 75.37, 75.08, 73.58 (4*t*, 4 PhCH_2 of **29**); 74.91, 74.69, 74.38 (3*t*, 3 PhCH_2 of **30**).

*(1*R*,2′*S*,3′*R*)-2,3,4,6-Tetra-*O*-benzyl-2′-hexyl-3′-methoxyspiro[1,5-anhydro*-D*-glucitol-1,1′-cyclopropane]* (**31**). R_f (hexane/AcOEt 4:1) 0.58. ^{1}H-NMR (600 MHz, C_6D_6, *ca.* 90% pure, assignment based on ^{1}H,^{1}H-COSY): 7.40 (br. *d*, *J* = 7.2, 2 arom. H); 7.31–7.26 (*m*, 6 arom. H); 7.19–7.12 (*m*, 10 arom. H); 7.11–7.05 (*m*, 2 arom. H); 4.92 (*d*, *J* = 11.4), 4.86 (*d*, *J* = 11.7, 2 PhC*H*); 4.69 (*d*, *J* = 11.3, 2 PhC*H*); 4.68 (*d*, *J* = 11.6), 4.63 (*d*, *J* = 11.4), 4.42 (*d*, *J* = 12.1), 4.34 (*d*, *J* = 12.1, 4 PhC*H*); 4.16 (*dd*, *J* = 7.6, 9.8, H–C(4)); 4.10 (*dd*, *J* = 4.8, 7.5, H–C(3)); 4.06 (*d*, *J* = 4.8, H–C(2)); 4.00 (*ddd*, *J* = 2.2, 3.6, 9.8, irrad. at 3.34 → NOE (4.0%), H–C(5)); 3.73 (*dd*, *J* = 3.7, 10.6, H–C(6)); 3.60 (*dd*, *J* = 2.1, 10.5, H′–C(6)); 3.34 (*d*, *J* = 8.1, irrad. at 4.00 → NOE (4.0%), H–C(3′)); 3.28 (*s*, MeO); 1.86 (*dddd*, *J* = 4.6, 6.2, 9.4, 13.8, H–C(1″)); 1.67 (*dtd*, *J* = 5.8, 9.4, 13.8, H′–C(1″)); 1.50–1.41 (*m*, 2H–C(2″)); 1.38 (*ddd*, *J* = 4.6, 8.2, 9.2, irrad. at 3.34 → NOE (5.4%), H–C(2′)); 1.32–1.17 (*m*, 6H); 0.86 (*t*, *J* = 7.1, Me). ^{13}C-NMR (100 MHz, C_6D_6): *Table 5*; additionally, 139.70, 139.20 (2*s*, 4 arom. C); 128.42–127.37 (several *d*); 74.41, 73.50, 73.41, 72.75 (4*t*, 4 PhCH_2).

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