# 197. Glycosylidene Carbenes

Part 5

## Synthesis of Glycono-1,5-lactone Tosylhydrazones as Precursors of Glycosylidene Carbenes[1])

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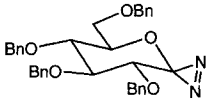
The benzyl- and the acyl-protected glyconolactone tosylhydrazones **6**, **9**, **12**, **16**, and **19** (*Scheme 1*) were prepared in good yields by treating the hemiacetals **4**, **7**, **10**, **14**, and **17** with *N*-tosylhydrazine, to give the *N*-glycosylhydrazines **5**, **8**, **11**, **15**, and **18**, and by oxidizing these hydrazines with *N*-bromosuccinimide (NBS) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), with $CrO_3$–dipyridine complex or with pyridinium dichromate. Photolysis of the sodium salt **20** of **6** (*Scheme 2*) in the presence of *N*-phenylmaleimide, dimethyl fumarate, or acrylonitrile gave the corresponding cyclopropanes **21–28** in satisfactory yields. Photolytic or thermolytic glycosidation of phenol and 4-methoxyphenol by **20** yielded the anomeric glycosides **29/30** and **31/32**, yields being marginally higher for the thermolytic process. Photolytic glycosidation of propan-2-ol gave the glycosides **33** and **34** in low yields only. Yields and ratios of products were compared to those obtained with the diazirine **1** as a source of glycosylidene carbenes. While the yields from **20** are lower, the ratios of products obtained in the photolytic reactions are in agreement with the formation of a common intermediate from both carbene precursors.

**Introduction.** – The sodium salts of lactone tosylhydrazones are well known precursors of alkoxy-alkyl carbenes [1–4], but have so far not been used for the generation of glycosylidene carbenes. We generated glycosylidene carbenes from diazirines, such as **1**, under very mild thermal or photochemical conditions and studied their insertion into O–H bonds [5–7] to prepare glycosides, their addition to acceptor-substituted alkenes to prepare spirocyclopropanes [8], and their reaction with diphenylphosphine, leading to glycosylphosphines [9]. The generation of glycosylidene carbenes from diazirines has several advantages, such as mildness of conditions, absence of interfering by-products, and compatibility with protecting groups of the alkoxy and the acyloxy type, but the

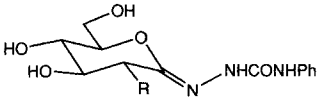
[1]) Presented, in part, at the '33rd IUPAC Congress', Budapest, 17–22th August 1991, Abstr. 405.

preparation of the diazirines requires several steps, and the diazirines can be stored for a limited time only. The geminal diazides, prepared by *Descotes* and coworkers [10] as precursors for glycosylidene carbenes in the synthesis of cyclopropanes [11] appear to be compatible only with protecting groups of the acyloxy type, and require photolysis.

Several glyconolactone hydrazones were prepared in the past by oxidation of the corresponding glycosylhydrazines [12][13]. *N*-Glycosyl-*N'*-tosylhydrazines (= *N'*-glycosyl-4-toluenesulfonohydrazides) are known [14] [15], but were not oxidized. We recently reported the preparation of the glyconolactone semicarbazones **2** and **3**, potent inhibitors of β-glycosidases, by oxidation of the corresponding glycosylhydrazines [16]. Glyconolactone sulfonylhydrazones can be prepared in good yields by treatment of glycosylidene-derived diaziridines with arylsulfonyl chlorides [17], but, with respect to the number of steps, this route offers no advantage over the preparation of diazirines. Oxidation of *N*-glycosyl-*N'*-tosylhydrazines to the corresponding hydrazones would constitute a short route to precursors of glycosylidene carbenes.




**1** Bn = $PhCH_2$




**2** R = OH
**3** R = NHAc

**Results.** – We studied the preparation of glycono-1,5-lactone tosylhydrazones derived from the known tetra-*O*-benzylated gluco-, manno-, and galactopyranoses **4**, **7**, and **10**, respectively, and from the acylated glucopyranoses **14** and **17** (*Scheme 1*). In each case, treatment of the hemiacetals with *N*-tosylhydrazine in MeCN or toluene under reflux gave the corresponding glycosylhydrazines **5**, **8**[2]), **11**, **15**, and **18** in high yields. The reaction of the benzylated hemiacetals, but not of the acylated analogues, was accelerated by catalytic amounts of AcOH. For the *gluco-* and *galacto*-isomers, we observed the exclusive formation of the β-D-anomers **5** and **11**, as evidenced by the large value for $J(1,2)$ (see *Table 1*). The *manno*-hydrazine **8** was obtained as a 10:1 mixture of α/β-D-anomers when the reaction was run in toluene, while the reaction in MeCN yielded only the α-D-anomer, as evidenced by the chemical shifts for C(1) (*cf. Table 2* and δ of C(1) for α- (92.8 ppm) and β-D-**7** (94.1 ppm) [18]). Oxidation of the hydrazines with *N*-bromosuccinimide (NBS) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gave the benzylated lactone tosylhydrazones in yields which were highest for the *gluco*-derivative **6** (81%), while the *galacto*-configurated lactone tosylhydrazone **12** was isolated in only 54% yield. The latter was easily hydrolysed to the hydroxyhydrazide **13**. The *manno*-derivative **8** was oxidized with the $CrO_3$–dipyridine complex [16] [19] yielding 70% of **9**. The acetylated hydrazine **15** was best oxidized with pyridinium dichromate [20] to give the hydrazone **16**[2]) in 90% yield, while oxidation of the analogous pivaloylated **18** with NBS and DBU led to 79% of **19**.

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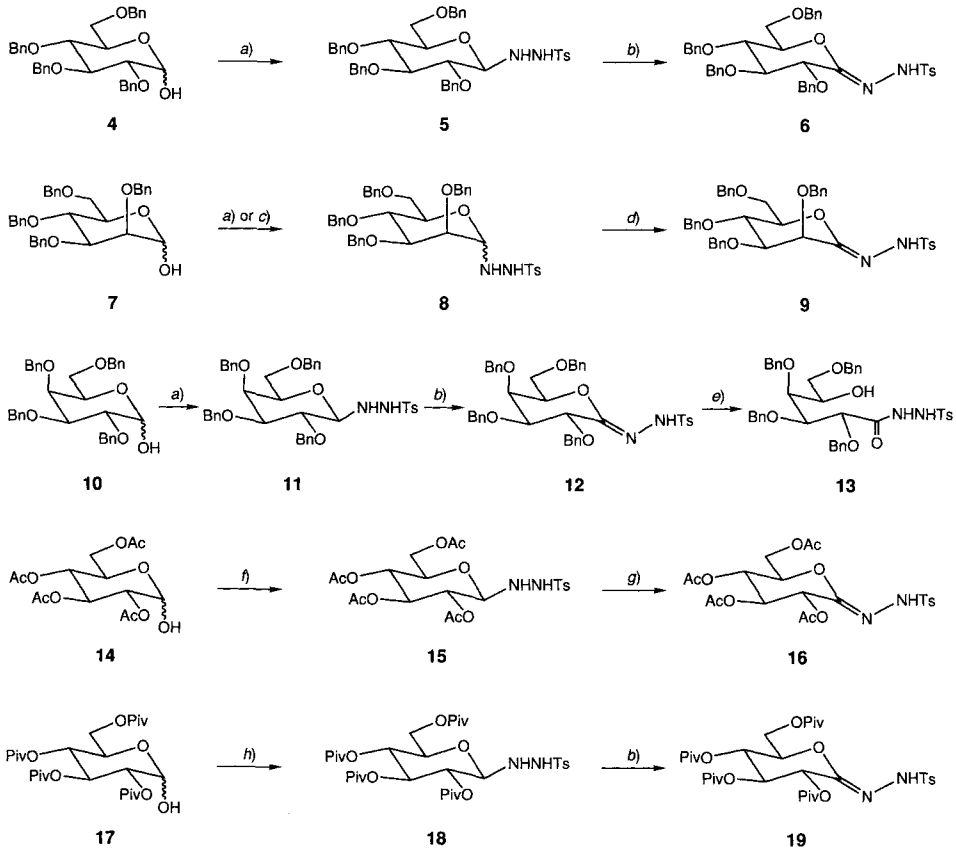
[2]) We thank Dr. *D. Wolk* for the first preparation of **8** and **9** and for the characterization of α-D-**8**, **9**, and **16**.

*Scheme 1*




Bn = $PhCH_2$, Ts = 4-$MeC_6H_4SO_2$, Piv = (*t*-Bu)CO

*a*) 1 Equiv. of $TsNHNH_2$, 0.05 equiv. of AcOH, toluene, reflux; 82 (**5**), 64 (**8**, α-D/β-D = 10:1) or 80% (**11**). *b*) 1.1 Equiv. of NBS, 1.2 equiv. of DBU, DMF, r.t.; 81 (**6**), 54 (**12**), or 79% (**20**). *c*) 1 Equiv. of $TsNHNH_2$, 0.05 equiv. of AcOH, MeCN, reflux, 62% of α-D-anomer. *d*) $CrO_3 \cdot 2C_5H_5N$, $CH_2Cl_2$, 0°, 70%. *e*) Wet solvents; 90%. *f*) 1 Equiv. of $TsNHNH_2$, MeCN, reflux; 73%. *g*) Pyridinium dichromate, $CH_2Cl_2$, r.t., 90%. *h*) 1 Equiv. of $TsNHNH_2$, toluene, reflux; 77%.

Although we did not rigorously determine the configuration at the newly formed C=N bond, the structural similarity with the (*Z*)-semicarbazone **2**, the structure of which was established by X-ray analysis [16], and with the glyconhydroximolactones, where the more stable isomers are (*Z*)-configurated [21], strongly suggests that the lactone tosylhydrazones **6**, **16**, and **19** are (*Z*)-configurated. The same appears to be true for the *manno*-isomer **9**[2]), while the configuration of the *galacto*-isomer **12** is presumably (*E*), as evidenced by the chemical shift of the C(1) signal, which differs by *ca.* 10 ppm from the one of the other benzylated glyconolactone tosylhydrazones. Similar $\Delta\delta$ values were found for (*E*)- and (*Z*)-isomers of ester tosylhydrazones [22] and for (*E*)- and (*Z*)-

Table 1. *Selected $^1$H-NMR Chemical Shifts*[ ppm] *and Coupling Constants* [Hz] *for 4-Toluenesulfonohydrazides* (400 MHz, $CDCl_3$)

| | **5** | **α-D-8** | **11** | **15** | **18** | **6** | **9** | **12** | **16** | **19** | **20** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| H–C(1) | 3.97[a]) | 3.98[a]) | 4.00[a]) | 4.22[a]) | 4.27[a]) | – | – | – | – | – | - |
| H–C(2) | 3.22[a]) | 3.90[a]) | 3.56-3.44 | 5.21 | 4.74 | 4.08 | 4.18 | 4.00 | 5.37 | 5.36 | 4.05 |
| H–C(3) | 3.58 | 3.48 | 3.56-3.44 | 4.74 | 5.32 | 3.83 | 3.67 | 3.91–3.88 | 5.37 | 5.26 | 3.73 |
| H–C(4) | 3.54 | 3.87[a]) | 3.87 | 4.95 | 5.02 | 3.61 | 4.18 | 3.70–3.67 | 5.05 | 5.18 | 3.49–3.40 |
| H–C(5) | 3.58[a]) | 3.31 | 3.56-3.44 | 3.63 | 3.66 | 4.46 | 3.97–3.93 | 4.41–4.08 | 4.45 | 4.28 | 4.25–4.21 |
| H–C(6) | 3.66–3.64 | 3.71 | 3.56-3.44 | 4.18[a]) | 4.13 | 3.72 | 3.72 | 3.65 | 4.28 | 4.33 | 3.49–3.40 |
| H'–C(6) | 3.66–3.64 | 3.68 | 3.56-3.44 | 4.08[a]) | 4.03[a]) | 3.66 | 3.68 | 3.45 | 4.28 | 4.15 | 3.49–3.40 |
| N*H*–C(1) | 4.06–3.97[b]) | 4.08 | 4.08 | 4.18–4.03[b]) | 4.01 | – | – | – | – | – | – |
| N*H*Ts | 6.59[c]) | 6.49[c]) | 6.36[c]) | 6.32[f]) | 6.30[c]) | 7.94 | 8.17 | 7.47–7.00[d]) | 7.89 | 8.06 | – |
| *J*(1,2) | 8.9[a]) | 2.2[a]) | 8.3[a]) | 9.5[a]) | 9.2[a]) | – | – | – | – | – | – |
| *J*(2,3) | 8.7[a]) | 2.7 | [d]) | 9.5 | 9.4 | 2.0 | 3.1 | 1.1 | 4.9 | 7.2 | 2.0 |
| *J*(3,4) | 9.3[a]) | 9.5 | 2.6 | 9.7 | 9.8 | 4.7 | 8.9 | [d]) | 5.7 | 7.5 | 5.4 |
| *J*(4,5) | 9.4[a]) | 9.8 | [d]) | 10.1 | 10.2 | 10.1 | 8.9 | [d]) | 9.9 | 9.8 | [d]) |
| *J*(5,6) | 2.1[a]) | 3.9 | [d]) | 4.6[a]) | 1.7 | 2.0 | 4.6 | [d]) | 3.5 | 1.9 | [d]) |
| *J*(5,6') | 4.1[a]) | 1.8 | [d]) | 2.2[a]) | 5.1 | 4.4 | 3.0 | 2.5 | 3.5 | 3.8 | [d]) |
| *J*(6,6') | [d]) | 10.5 | [d]) | 12.4[a]) | 12.4 | 11.1 | 11.2 | 10.1 | [d]) | 12.7 | [d]) |
| *J*(CH,NH)[d]) | | 10.3 | 10.3 | [d]) | 11.1 | – | – | – | – | – | – |

[a]) After $D_2O$ exchange. [b]) Hidden by other signals. [c]) Broad *s*, *J*(NH,N'H) < 2 Hz. [d]) Not determined. [e]) *J*(NH,N'H) = 2.5 Hz, [f]) *J*(NH,N'H) = 3.0 Hz.

Table 2. *Selected $^{13}$C-NMR Chemical Shifts* [ppm] *for 4-Toluenesulfonohydrazides* (50.6 MHz, $CDCl_3$)

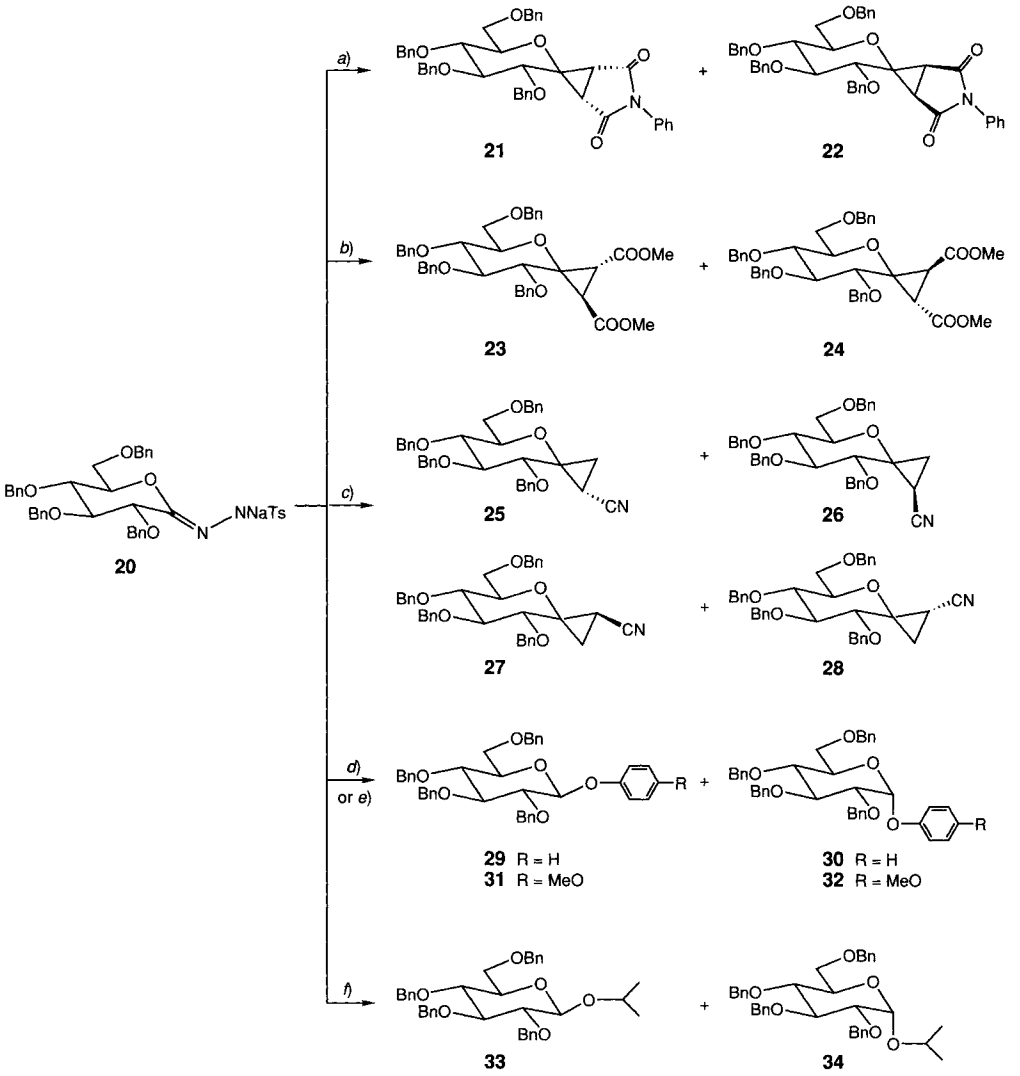
| | **5** | **α-D-8** | **β-D-8** | **11** | **15** | **18** | **6[a])** | **9** | **12** | **16** | **19[b])** | **20** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C(1) | 90.86 | 87.65 | 90.84 | 90.96 | 89.76 | 89.62 | 147.58 | 147.02 | 157.13 | 144.01 | 143.97 | 140.94[d]) |
| C(2) | 79.64[c]) | 76.42[c]) | 85.32[c]) | 74.04[c]) | 68.72[c]) | 68.95[c]) | 74.00 | 71.61[c]) | 70.25 | 67.93 | 67.68 | 73.46[c]) |
| C(3) | 85.23 | 83.95 | 85.46[c]) | 82.71 | 72.60[c]) | 72.12[c]) | 81.28 | 80.56[c]) | 85.94 | 71.31 | 71.06 | 83.06 |
| C(4) | 77.33[c]) | 74.73[c]) | 79.71[c]) | 73.69[c]) | 68.22[c]) | 67.62[c]) | 77.00 | 72.96[c]) | 78.89[c]) | 67.89 | 66.71 | 77.97 |
| C(5) | 75.63 | 74.98[c]) | 78.10[c]) | 76.88[c]) | 72.92[c]) | 73.30[c]) | 76.30 | 79.20[c]) | 78.51[c]) | 74.97 | 75.96 | 74.68[c]) |
| C(6) | 68.63 | 68.88 | 68.88 | 68.59 | 61.67 | 61.43 | 68.00 | 68.46 | 67.13 | 61.15 | 60.73 | 65.91 |

[a]) Assignments based upon a 2D C,H-correlated spectrum. [b]) Assignments based upon selective irradiations. [c]) Assignments may be interchanged. [d]) Assignments may be interchanged with the *s* at 140.74 and 140.18 ppm.

gluconhydroximolactone phosphates [21]. The chemical-shift values for H–C(2) of **6**, **9**, and **12** are, however, quite similar to each other, and leave some doubt about the configuration of **12**.

To establish that lactone tosylhydrazones are precursors of glycosylidene carbenes, we examined the reaction, under photolytic conditions, of the sodium salt **20** of **6** in THF as aprotic solvent [23] [24] with *N*-phenylmaleimide, dimethyl fumarate, and acrylonitrile on the one hand, and with phenol, 4-methoxyphenol, and propan-2-ol, on the other hand

*Scheme 2*




*a*) 10 Equiv. of *N*-phenylmaleimide, THF, *hv*; 49% (**21**/**22** 9:1). *b*) 1.1 Equiv. of dimethyl fumarate, THF, *hv*; 55% (**23**/**24** 1:1). *c*) 5.0 Equiv. of acrylonitrile, THF, *hv*; 69% (**25**/**26**/**27**/**28** 43:35:19:3). *d*) 2.8 Equiv. of phenol, THF, *hv*, 63% (**29**/**30** 7:1) or 3 equiv. of phenol, 2.5 equiv. of [15]crown-5, diethylene glycol dimethyl ether, 140°; 64% (**29**/**30** >98:2). *e*) 4.2 Equiv. of 4-methoxyphenol, THF, *hv*; 54% (**31**/**32** 50:1) or 4.0 equiv. of 4-methoxyphenol, 2.5 equiv. of [15]crown-5, diethylene glycol dimethyl ether, 140°; 55% (**31**/**32** 3:1). *f*) 18 Equiv. of i-PrOH, THF, *hv*; 22% (**33**/**34** 1:1).

(*Scheme 2*). The sodium salt **20** crystallizes as the sesquihydrate and was best prepared *in situ* by deprotonation of **6** with NaH. The reaction with *N*-phenylmaleimide gave the known cyclopropanes **21** and **22** [8] in the same ratio (9:1), but in lower yields (49 *vs.* 80%) as from the diazirine **1**. Reaction of **20** with 3 equiv. of dimethyl fumarate led in 55% to a 1:1 mixture of the known cyclopropanes **23** and **24** (72% and 3:2 from **1** [8]), while the reaction with acrylonitrile (5 equiv.) yielded 69% of the isomeric, known cyclopropanes **25–28** in a ratio of 43:35:19:3 (70% and 51:32:11:6 from **1** [8]). The similar ratios in which the cyclopropanes **23** and **24**, and **25–28** were obtained from either **20** or **1** strongly evidences that the reaction passes through a common intermediate, a carbene.

Glycosidation by photolysis of **20** in the presence of 3 equiv. of phenol or 4-methoxyphenol gave mixtures of the anomeric glycosides **29/30** and **31/32** in yields of 63 and 54% and in $\alpha$-D/$\beta$-D ratios of 1:5 and 1:7, respectively. The same glycosides were obtained from **1** in the presence of 1 equiv. of phenol or 4-methoxyphenol in yields of 70 and 69% and in ratios of 1:3 and 1:4, respectively [6]. *C*-Glycosides were obtained as by-products (13 and 16%) in the reaction of phenol and 4-methoxyphenol with **1**, but not with **20**. Photolytic glycosidation of propan-2-ol (18 equiv.) by **20** gave a 1:1 mixture of the glycosides **33** and **34** [5] in a low yield (22%), while photolytic glycosidation of propan-2-ol (1 equiv.) by **1** at –65° yielded 71% of **33** and **34** [25]. Thermolysis of **20** and phenol or 4-methoxyphenol at 140° in diglyme and in the presence of excess [15]crown-5 also led to **29/30** (2:98) and **31/32** (1:3), respectively, in slightly higher yields than by photolysis, while attempts to obtain cyclopropanes by thermolysis of **20** failed.

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## Experimental Part

*General.* Solvents and liquid reagents were distilled, solid reagents were recrystallized, and THF was distilled over Na and kept under $N_2$. Irradiations were performed with a high-pressure Hg-lamp (HPK 125 *Philips*) equipped with a fused quartz filter. Qual. TLC: 0.25 mm precoated silica-gel plates (*Merck*, Kieselgel *60 F254*) with the solvent system indicated; detection by spraying the plates with a soln. of 5% vanillin in conc. $H_2SO_4$ soln. followed by heating at *ca.* 200°. Flash chromatography (FC): silica gel *Merck 60* (0.040–0.063 mm). M.p. uncorrected. IR spectra: KBr or 3% $CHCl_3$ soln.

N'-*(2,3,4,6-Tetra*-O-*benzyl*-$\beta$-D-*glucopyranosyl)*-*4-toluenesulfonohydrazide* (**5**). A soln. of **4** (20.10 g, 37.2 mmol) [26] and AcOH (0.1 ml, 1.85 mmol) in toluene (200 ml) was treated portionwise with solid 4-toluenesulfonohydrazide (6.93 g, 37.2 mmol) and heated to reflux for 1.5 h. The cold mixture was washed with $H_2O$ and twice with brine, dried ($MgSO_4$), and evaporated. Crystallization from EtOH gave **5** (21.46 g, 82%). Fine needles. $R_f$ (toluene/MeOH 9:1) 0.49. M.p. 152°. $[\alpha]_D^{25} = -7.0$ ($c = 0.91$, $CHCl_3$). IR (KBr): 3280*m*, 3090*m*, 3065*m*, 3035*m*, 2910*m*, 2870*m*, 1600*w*, 1560*w*, 1540*w*, 1495*m*, 1455*m*, 1400*m*, 1360*m*, 1330*s*, 1210*m*, 1160*s*, 1070*s*, 1030*s*, 990*m*, 910*w*, 815*m*, 750*s*, 695*s*, 665*m*. $^1$H-NMR (400 MHz, $CDCl_3$): 7.78 (*d*, $J = 8.3$, 2 arom. H); 7.36–7.10 (*m*, 20 arom. H); 7.19 (*d*, $J = 8.1$, 2 arom. H); 6.59 (*s*, exchange with $D_2O$, NH); 4.87 (*d*, $J = 10.9$, 1 H, PhC$H_2$); 4.85 (*d*, $J = 10.8$, 1 H, PhC$H_2$); 4.78 (*d*, $J = 10.8$, 1 H, PhC$H_2$); 4.76 (*d*, $J = 10.9$, 1 H, PhC$H_2$); 4.59 (*d*, $J = 10.8$, 1 H, PhC$H_2$); 4.56 (*d*, $J = 12.1$, 1 H, PhC$H_2$); 4.49 (*d*, $J = 12.1$, 1 H, PhC$H_2$); 4.48 (*d*, $J = 10.9$, 1 H, PhC$H_2$); 4.06–3.97 (*m*, 2 H, NH exchange with $D_2O$; addn. of $D_2O \rightarrow$ 3.97, *d*, $J = 8.9$, H–C(1)); 3.66–3.64 (*m*, 2 H–C(6)); 3.58 (*t*, $J \approx 8.4$; addn. of $D_2O \rightarrow$ *t*, $J = 8.7$, H–C(3)); 3.54 (*t*, $J \approx 8.8$, addn. of $D_2O \rightarrow$ 3.51, *t*, $J \approx 9.3$, H–C(4)); 3.35–3.31 (*m*, addn. of $D_2O \rightarrow$ 3.58, *ddd*, $J = 2.1, 4.1, 9.4$, H–C(5)); 3.22 (*t*, $J \approx 8.3$, addn. of $D_2O \rightarrow$ *t*,

$J$ = 8.7, H–C(2)); 2.39 (*s*, Me). $^{13}$C-NMR (50.6 MHz, $CDCl_3$): 143.81 (*s*); 138.40 (*s*); 138.20 (*s*); 137.91 (*s*); 137.52 (*s*); 135.15 (*s*); 129.47–127.40 (several *d*); 90.86 (*d*); 85.23 (*d*); 79.64 (*d*); 77.33 (*d*); 75.63 (*d*); 75.36 (*t*); 74.85 (*t*); 74.31 (*t*); 73.47 (*t*); 68.63 (*t*); 21.50 (*q*, Me). CI-MS: 644 (10), 539 (13), 526 (20), 525 (12), 524 (30), 435 (22), 434 (11), 433 (37), 431 (22), 430 (50), 429 (12), 428 (12), 427 (24), 426 (12), 425 (32), 417 (15), 415 (11), 413 (11), 412 (28), 397 (14), 396 (29), 369 (29), 343 (21), 338 (21), 337 (80), 325 (13), 324 (18), 323 (29), 322 (100), 321 (26), 319 (20), 309 (44), 307 (39), 306 (100), 271 (14), 269 (11), 263 (16), 253 (19), 247 (23), 246 (12), 245 (50), 219 (22), 217 (42), 216 (11), 203 (14), 201 (26), 197 (13), 181 (40), 179 (26), 157 (27), 155 (17), 139 (39), 91 (55). Anal. calc. for $C_{41}H_{44}N_2O_7S$ (708.87): C 69.47, H 6.26, N 3.96; found: C 69.60, H 6.34, N 4.11.

N'-*(2,3,4,6-Tetra*-O-*benzyl-α/β*-D-*mannopyranosyl)-4-toluenesulfonohydrazide* (**8**)[2] [14]. *a*) A soln. of **7** (200 mg, 0.37 mmol) [27] and AcOH (1.06 µl, 0.019 mmol) in MeCN (15 ml) was treated with solid 4-toluenesulfonohydrazide (103 mg, 0.55 mmol) and heated to reflux for 24 h. MeCN was distilled off at 40° *i.v.* and the residue was dissolved in $Et_2O$. The org. layer was washed with $H_2O$ and twice with brine, dried ($MgSO_4$) and evaporated. FC ($CH_2Cl_2$/MeOH 99.4:0.6) gave pure α-D-**8** (164 mg, 62%).

*b*) A soln. of **7** (17.51 g, 32.4 mmol) and AcOH (80 µl, 1.4 mmol) in toluene (150 ml) was treated with solid 4-toluenesulfonohydrazide (5.33 g, 28.6 mmol) and heated to reflux for 3 h. The org. layer was washed with cold $H_2O$ and twice with brine, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 4:1 → 2:1) gave **8** (14.75 g, 64%; α-D/β-D 10:1).

*Data of* α-D-**8**: Colourless oil. $R_f$ (toluene/MeOH 96:4) 0.44. $[\alpha]_D^{25}$ = –43.7 (*c* = 1.02, $CHCl_3$). IR (KBr): 3420*w* (br.), 3300(sh), 3230*m* (br.), 3060*m*, 3030*m*, 2920*m*, 2880*m*, 1740*w* (br.), 1650(sh), 1595*m*, 1495*m*, 1455*s*, 1395(sh), 1365*m*, 1330*s*, 1305(sh), 1255*m*, 1210*m*, 1165*s*, 1090*s* (br.), 1060*s*, 1025*s*, 900*m* (br.), 815*m*, 735*s*, 695*s*, 660(sh), 605*m*. $^1$H-NMR (400 MHz, $CDCl_3$): 7.75 (*d*, *J* = 8.3, 2 arom. H); 7.35–7.12 (*m*, 22 arom. H); 6.49 (br. *s*, exchange with $D_2O$, NH); 4.90 (*d*, *J* = 11.0, 1 H, PhC$H_2$); 4.83 (*d*, *J* = 11.0, 1 H, PhC$H_2$); 4.73 (*d*, *J* = 11.7, 1 H, PhC$H_2$); 4.69 (*d*, *J* = 11.7, 1 H, PhC$H_2$); 4.62 (*d*, *J* = 12.1, 1 H, PhC$H_2$); 4.54 (*d*, *J* = 11.0, 1 H, PhC$H_2$); 4.50 (*d*, *J* = 11.0, 1 H, PhC$H_2$); 4.48 (*d*, *J* = 12.1, 1 H, PhC$H_2$); 4.40 (br. *d*, *J* = 11.4, exchange with $D_2O$, NH); 3.99 (*dd*, *J* = 1.0, 10.3, addn. of $D_2O$ → 3.98, *d*, *J* = 1.0, H–C(1)); 3.90 (br. *s* and *t* (*J* = 9.6), irrad. at 3.31 → 3.90 (*d*, *J* = 2.2) and 3.90 (*d*, *J* = 9.6), addn. of $D_2O$ → 3.90, *d*, *J* = 2.2, H–C(2) and 3.87, *t*, *J* = 9.6, H–C(4)); 3.71 (*dd*, *J* = 3.9, 10.5), 3.68 (*dd*, *J* = 1.8, 10.5, irrad. at 3.31 → *AB*, $J_{AB}$ = 10.5, addn. of $D_2O$ → 3.69, *d*, *J* = 3.4, 2 H–C(6)); 3.48 (*dd*, *J* = 2.7, 9.5, H–C(3)); 3.31 (*td*, *J* = 3.2, 9.8, H–C(5)); 2.45 (*s*, Me). $^{13}$C-NMR (50.6 MHz, $CDCl_3$): 143.78 (*s*); 138.13 (*s*); 137.99 (*s*, 2 C); 137.91 (*s*); 135.40 (*s*); 129.46–127.53 (several *d*); 87.65 (*d*); 83.95 (*d*); 76.42 (*d*); 75.13 (*t*); 74.98 (*d*); 74.73 (*d*); 74.59 (*t*); 73.48 (*t*); 72.71 (*t*); 68.88 (*t*); 21.57 (*q*, Me). CI-MS: 534 (30), 524 (25), 369 (30), 337 (75), 322 (37), 307 (31), 306 (100), 249 (25), 247 (30), 201 (26), 157 (29). Anal. calc. for $C_{41}H_{44}N_2O_7S$ (708.87): C 69.47, H 6.26, N 3.96, S 4.53; found: C 69.24, H 6.50, N 3.73, S 4.45.

*Data of* β-D-**8** (obtained from a mixture α-D/β-D *ca.* 2:1): $^1$H-NMR (400 MHz, $CDCl_3$): 6.49 (br. *s*, exchange with $D_2O$, NH); 2.39 (*s*, Me). $^{13}$C-NMR (50.6 MHz, $CDCl_3$): 144.04 (*s*); 135.36(s); 90.84 (d); 85.46 (d); 79.71 (d).

N'-*(2,3,4,6-Tetra*-O-*benzyl-β*-D-*galactopyranosyl)-4-toluenesulfonohydrazide* (**11**). A soln. of **10** (19.71 g, 36.5 mmol) [27] and AcOH (85 µl) in toluene (200 ml) was treated portionwise with solid 4-toluenesulfonohydrazide (6.79 g, 36.4 mmol) and heated to reflux for 1 h. The cold mixture was washed with $H_2O$ and twice with brine, dried ($MgSO_4$), and concentrated. FC (hexane/AcOEt 3:1) gave **11** (20.79 g, 80%). Yellow solid. $R_f$ ($CH_2Cl_2$/MeOH 98:2) 0.58. M.p. 50–53°. $[\alpha]_D^{25}$ = –10.7 (*c* = 1.13, $CHCl_3$). IR (KBr): 3450*s* (br.), 3300(sh), 3060*w*, 3025*w*, 2920*w*, 2860*w*, 1600*m* (br.), 1595*m*, 1560*m*, 1540*m*, 1495*m*, 1455*s*, 1395*w*, 1360*m*, 1330*m*, 1210*w*, 1165*s*, 1090*s*, 1030*m*, 910*w*, 815*w*, 735*m*, 695*m*, 660*w*. $^1$H-NMR (400 MHz, $CDCl_3$): 7.77 (*d*, *J* = 8.3, 2 arom. H); 7.73–7.19 (*m*, 20 arom. H); 7.17 (*d*, *J* = 8.0, 2 arom. H); 6.36 (*s*, exchange with $D_2O$, NH); 4.89 (*d*, *J* = 11.5, 1 H, PhC$H_2$); 4.79 (*d*, *J* = 10.8, 1 H, PhC$H_2$); 4.72 (*d*, *J* = 11.8, 1 H, PhC$H_2$); 4.68 (*d*, *J* = 11.8, 1 H, PhC$H_2$); 4.63 (*d*, *J* = 10.8, 1 H, PhC$H_2$); 4.56 (*d*, *J* = 11.5, 1 H, PhC$H_2$); 4.45 (*d*, *J* = 11.8, 1 H, PhC$H_2$); 4.40 (*d*, *J* = 11.8, 1 H, PhC$H_2$); 4.08 (*d*, *J* = 10.3, exchange with $D_2O$, NH); 4.01 (*dd*, *J* = 8.0, 10.2, addn. of $D_2O$ → 4.00, *d*, *J* = 8.3, H–C(1)); 3.87 (*d*, *J* = 2.6, H–C(4)); 3.56–3.44 (*m*, H–C(2), H–C(3), H–C(5), 2 H–C(6)); 2.38 (*s*, Me). $^{13}$C-NMR (50.6 MHz, $CDCl_3$): 143.68 (*s*); 138.45 (*s*); 138.38 (*s*); 138.28 (*s*); 137.66 (*s*); 135.21 (*s*); 129.54–127.32 (several *d*); 90.96 (*d*); 82.71 (*d*); 76.88 (*d*); 74.62 (*t*); 74.04 (*d*); 73.69 (*d*); 73.46 (*t*); 72.97 (*t*); 68.59 (*t*); 21.45 (*q*, Me). CI-MS: 710 (19), 709 (39, $[M+1]^+$), 708 (84), 671 (11), 622 (11), 554 (18), 540 (11), 539 (21), 526 (15), 448 (12), 433 (12), 431 (20), 324 (11), 322 (18), 307 (12), 306 (27), 295 (11), 294 (17), 216 (11), 201 (11), 181 (36), 179 (12), 157 (66), 147 (15), 139 (26), 108 (13), 107 (31), 92 (15), 91 (100). Anal. calc. for $C_{41}H_{44}N_2O_7S$ (708.87): C 69.47, H 6.26, N 3.96, S 4.53; found: C 69.49, H 6.49, N 4.02, S 4.46.

N'-*(2,3,4,6-Tetra*-O-*acetyl-β*-D-*glucopyranosyl)-4-toluenesulfonohydrazide* (**15**) [14]. A soln. of **14** (30.6 g, 87.9 mmol) in MeCN (200 ml) was treated portionwise with solid 4-toluenesulfonohydrazide (17.6 g, 87.9 mmol) and heated to reflux for 8 h. MeCN was distilled off at 40° *i.v.* and the residue dissolved in $Et_2O$. The org. layer was washed with $H_2O$ and twice with brine, dried ($MgSO_4$), and concentrated. Crystallization from EtOH

gave **15** (31.28 g, 73%; [14]: 86%). Fine needles. $R_f$ (toluene/MeOH 9:1) 0.29. M.p. 141° ( [14]: 141°). IR (KBr): 3330*w*, 3220*w*, 2950*w*, 1750*s*, 1600*w*, 1430*w*, 1370*m*, 1320*m*, 1250*s*, 1230*s*, 1160*s*, 1090*m*, 1035*s*, 910*w*, 815*m*, 685*w*. $^1$H-NMR (400 MHz, $CDCl_3$): 7.72 (*d*, *J* = 8.2, 2 arom. H); 7.32 (*d*, *J* = 8.2, 2 arom. H); 6.32 (*d*, *J* = 3.0, exchange with $D_2O$, NH); 5.21 (*t*, *J* = 9.5, H–C(2)); 4.95 (*t*, *J* ≈ 9.7, H–C(4)); 4.74 (*t*, *J* ≈ 9.5, H–C(3)); 4.25–4.20 (*m*, 2 H, addn. of $D_2O$ → 4.22, *d*, *J* = 9.5, H–C(1) and 4.18, *dd*, *J* = 4.6, 13.0, H–C(6)); 4.18–4.03 (*m*, 2 H; NH exchange with $D_2O$, addn. of $D_2O$ → 4.08, *dd*, *J* = 2.2, 12.4, H–C(6)); 3.63 (*ddd*, *J* = 2.2, 4.5, 10.1, H–C(5)); 2.45 (*s*, Me); 2.09 (*s*, Ac); 2.08 (*s*, Ac); 2.02 (*s*, Ac); 2.00 (*s*, Ac). $^{13}$C-NMR (50.6 MHz, $CDCl_3$): 170.54 (*s*, Ac); 169.88 (*s*, 2 Ac); 169.40 (*s*, Ac); 144.22 (*s*); 134.69 (*s*); 129.46 (*d*, 2 arom. C); 128.01 (*d*, 2 arom. C); 89.76 (*d*); 72.92 (*d*); 72.60 (*d*); 68.72 (*d*); 68.22 (*d*); 61.67 (*t*); 21.50 (*q*, Me); 20.60 (*q*, Me); 20.56 (*q*, 2 Me); 20.40 (*q*, Me). CI-MS: 517 (3, $[M + 1]^+$), 457 (14), 430 (11), 429 (54), 369 (10), 291 (13), 273 (35), 255 (67), 231 (12), 213 (70), 157 (78), 154 (10), 153 (100), 139 (47).

N'-*(2,3,4,6-Tetra*-O-*pivaloyl*-β-D-*glucopyranosyl)*-*4-toluenesulfonohydrazide* (**18**). A soln. of **17** (10.81 g, 20.9 mmol) [28] in toluene (100 ml) was treated portionwise with solid 4-toluenesulfonohydrazide (3.82 g, 20.5 mmol) and heated to reflux for 10 h. The cold mixture was washed with $H_2O$ and twice with brine, dried ($MgSO_4$), and concentrated. FC ($CH_2Cl_2$/MeOH 98:2) gave **18** (11.03 g, 77%). A sample was crystallized from $Et_2O$/hexane. Fine needles. $R_f$ ($CH_2Cl_2$/MeOH 98:2) 0.70. M.p. 144–145°. $[\alpha]_D^{25}$ = –24.1 (*c* = 1.03, $CHCl_3$). IR (KBr): 3310*m*, 2970*s*, 2935(sh), 2905(sh), 2875*m*, 1740*s*, 1595*w*, 1480*s*, 1460*m*, 1395*m*, 1365*m*, 1330*m*, 1280*s*, 1230*m*, 1165*s* (br.), 1140*s* (br.), 1095(sh), 1035*s*, 1015(sh), 980*m*, 940*w*, 895*m*, 875*w*, 815*m*, 765*m*, 705*w*, 660*m*. $^1$H-NMR (400 MHz, $CDCl_3$): 7.72 (*d*, *J* = 8.2, 2 arom. H); 7.30 (*d*, *J* = 8.1, 2 arom. H); 6.30 (br. *s*, exchange with $D_2O$, NH); 5.32 (*t*, *J* = 9.5, irrad. at 5.02 → *d*, *J* = 9.4, H–C(3)); 5.02 (*t*, *J* = 9.8, irrad. at 3.66 → *d*, *J* = 9.0, H–C(4)); 4.74 (*t*, *J* = 9.4, H–C(2)); 4.28 (*dd*, *J* = 9.4, 10.9, addn. of $D_2O$ → *d*, *J* = 9.2, H–C(1)); 4.13 (*dd*, *J* =1.7, 12.4, irrad. at 3.66 → *d*, *J* = 12.2, H–C(6)); 4.06–4.01 (*m*, addn. of $D_2O$ → 4.03, *dd*, *J* = 5.1, 12.5, H–C(6)); 4.01 (*d*, *J* = 11.1, exchange with $D_2O$, NH); 3.66 (*ddd*, *J* = 1.7, 5.1, 10.2, H–C(5)); 2.44 (*s*, Me); 1.24 (*s*, *t*-Bu); 1.16 (*s*, *t*-Bu); 1.14 (*s*, *t*-Bu); 1.09 (*s*, *t*-Bu). $^{13}$C-NMR: (50.6 MHz, $CDCl_3$): 177.95 (*s*); 177.26 (*s*); 176.71 (*s*); 176.22 (*s*); 143.91 (*s*); 135.11 (*s*); 129.38 (*d*, 2 arom. C); 127.80 (*d*, 2 arom. C); 89.62 (*d*); 73.30 (*d*); 72.12 (*d*); 68.95 (*d*); 67.62 (*d*); 61.43 (*t*); 38.72 (*s*); 38.55 (*s*); 38.50 (*s*); 38.42 (*s*); 26.96 (*q*, 2 $Me_3C$); 26.91 (*q*, $Me_3C$); 26.86 (*q*, $Me_3C$); 21.39 (*q*, Me). CI-MS: 685 (1, $[M + 1]^+$), 583 (10), 555 (10), 529 (22), 499 (23), 399 (29), 382 (16), 381 (72), 298 (17), 297 (100), 196 (10), 195 (89), 157 (37), 139 (30), 103 (31). Anal. calc. for $C_{33}H_{52}N_2O_{11}S$ (684.84): C 57.88, H 7.65, N 4.09, S 4.68; found: C 58.05, H 7.63, N 3.93, S 4.91.

N'-*(2,3,4,6-Tetra*-O-*benzyl*-D-*glucopyranosylidene)*-*4-toluenesulfonohydrazide* (**6**). A soln. of **5** (1.00 g, 1.41 mmol) in DMF (10 ml) was treated with DBU (250 µl, 1.7 mmol) and portionwise with NBS (280 mg, 1.50 mmol) and stirred for 45 min at r.t. [29]. After the addition of $H_2O$, the mixture was extracted with $Et_2O$ (6×), the org. layer washed with $H_2O$ and brine, dried ($MgSO_4$), and concentrated. The residue was crystallized from AcOEt/hexane and the mother liquor purified by FC (hexane/AcOEt 2:1). Drying at r.t. *i.v.* gave **6** (0.81 g, 81%). $R_f$ (hexane/AcOEt 2:1) 0.24. M.p. 132–132.5°. $[\alpha]_D^{25}$ = +2.3 (*c* = 0.51, $CHCl_3$). UV (EtOH): 215 (3113). UV (THF): 236 (3177). IR (KBr): 3440*m* (br.), 3240*m*, 3080*w*, 3060*w*, 3030*w*, 2920*w*, 2870*w*, 1645*m*, 1600*w*, 1495*w*, 1455*m*, 1415*w*, 1390*s*, 1365*w*, 1330*s*, 1310*w*, 1290*m*, 1250*w*, 1215*w*, 1185*w*, 1165*s*, 1150*w*, 1120*m*, 1110*m*, 1095*s*, 1065*s*, 1028*m*, 1010*w*, 980*w*, 935*w*, 925*w*, 895*w*, 855*w*, 820*w*, 800*w*, 760*w*, 730*s*, 695*s*, 630*w*, 620*w*. IR ($CHCl_3$): 3290*w* (br.), 3070*w*, 3020*w*, 2920*w*, 2870*w*, 1660*w*, 1600*w*, 1495*w*, 1455*m*, 1390*m*, 1365*m*, 1345*m*, 1290*m*, 1170*s*, 1090*s*, 1070*s*, 1030*s*, 910*w*, 815*w*, 700*s*, 660*m*. $^1$H-NMR (400 MHz, $CDCl_3$): 7.94 (*s*, exchange with $D_2O$, NH); 7.82 (*d*, *J* = 8.2, 2 arom. H); 7.40–7.11 (*m*, 22 arom. H); 4.55 (*d*, *J* = 12.0, 1 H, PhC$H_2$); 4.53 (*d*, *J* = 11.3, 1 H, PhC$H_2$); 4.51 (*d*, *J* = 12.3, 1 H, PhC$H_2$); 4.48 (*d*, *J* = 11.7, 1 H, PhC$H_2$); 4.46 (*ddd*, *J* = 2.0, 4.4, 10.1, H–C(5)); 4.39 (*d*, *J* = 11.3, 1 H, PhC$H_2$); 4.30 (*d*, *J* = 11.9, 1 H, PhC$H_2$); 4.28 (*d*, *J* = 11.6, 1 H, PhC$H_2$); 4.21 (*d*, *J* = 11.9, 1 H, PhC$H_2$); 4.08 (*d*, *J* = 2.0, H–C(2)); 3.83 (*dd*, *J* = 2.0, 4.7, H–C(3)); 3.72 (*dd*, *J* = 2.0, 11.1, H–C(6)); 3.66 (*dd*, *J* = 4.4, 11.1, H–C(6)); 3.61(*dd*, *J* = 4.7, 10.1, H–C(4)); 2.30 (*s*, Me). $^{13}$C-NMR (50.6 MHz, $CDCl_3$): 147.58 (*s*); 143.78 (*s*); 137.55 (*s*); 137.45 (*s*); 137.01 (*s*); 136.82 (*s*); 135.34 (*s*); 129.95–127.52 (several *d*); 81.28 (*d*); 77.00 (*d*); 76.30 (*d*); 74.00 (*d*); 73.35 (*t*); 72.98 (*t*); 71.50 (*t*); 70.34 (*t*); 68.00 (*t*); 21.43 (*q*, Me). CI-MS: 709 (11), 708 (45), 707 (100, $[M + 1]^+$), 580 (10), 579 (25), 553 (20), 430 (12), 157 (11). Anal. calc. for $C_{41}H_{42}N_2O_7S$ (706.86): C 69.67, H 6.00, N 3.97; found: C 69.77, H 5.99, N 3.77.

N'-*(2,3,4,6-Tetra*-O-*benzyl*-D-*mannopyranosylidene)*-*4-toluenesulfonohydrazide* (**9**)[2]. Under $N_2$, a soln. of pyridine (1.84 ml, 22.8 mmol) in $CH_2Cl_2$ (25 ml) was treated with $CrO_3$ (1.14 g, 11.4 mmol) [19], stirred for 15 min, and cooled to 0°. After the addition of **8** (981 mg, 1.90 mmol), stirring of the black mixture was continued for 1 h at 0°. The mixture was filtered and the residue washed with $CH_2Cl_2$ (3×). After the addition of $Et_2O$ (40 ml) and $H_2O$ (40 ml), the emulsion was filtered again. The org. layer was separated and washed with 0.4M $NaHCO_3$ (3×), dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 4:1), and drying *i.v.* gave **9** (508 mg, 52%). Colourless foam. $R_f$ (toluene/MeOH 96:4) 0.51. M.p. 40°. $[\alpha]_D^{25}$ = +17.4 (*c* = 1.06, $CHCl_3$). IR ($CHCl_3$): 3300*w*,

3020*w*, 2920*w*, 2870*w*, 1645*m*, 1600*m*, 1495*w*, 1455*m*, 1380*m*, 1340*m*, 1290*m*, 1165*s*, 1090*s*, 1030*s*, 910*w*, 690*m*. $^1$H-NMR (400 MHz, $CDCl_3$): 8.17 (*s*, exchange with $D_2O$, NH); 7.85 (*d*, *J* = 8.3, 2 arom. H); 7.35–7.16 (*m*, 22 arom. H); 4.86 (*d*, *J* = 10.6, 1 H, PhC*H*$_2$); 4.56 (*d*, *J* = 11.9, 1 H, PhC*H*$_2$); 4.50 (*d*, *J* = 10.6, 1 H, PhC*H*$_2$); 4.49 (*d*, *J* = 11.9, 1 H, PhC*H*$_2$); 4.48 (*d*, *J* = 11.9, 1 H, PhC*H*$_2$); 4.43 (*d*, *J* = 11.9, 1 H, PhC*H*$_2$); 4.32 (*d*, *J* = 12.2, 1 H, PhC*H*$_2$); 4.18 (*t*, *J* = 8.9, H–C(4)); 4.18 (*d*, *J* = 3.1, H–C(2)); 4.12 (*d*, *J* = 12.2, 1 H, PhC*H*$_2$); 3.97–3.93 (*m*, H–C(5)); 3.72 (*dd*, *J* = 4.6, 11.2, H–C(6)); 3.68 (*dd*, *J* = 3.0, 11.3, H–C(6)); 3.67 (*dd*, *J* = 3.2, 9.0, H–C(3)); 2.33 (*s*, Me). $^{13}$C-NMR (50.6 MHz, $CDCl_3$): 147.02 (*s*); 144.02 (*s*); 137.72 (*s*); 137.54 (*s*); 137.45 (*s*); 137.00 (*s*); 135.17 (*s*); 129.46–127.60 (several *d*); 80.56 (*d*); 79.20 (*d*); 74.80 (*t*); 73.25 (*t*); 72.96 (*d*); 71.61 (*d*); 71.42 (*t*); 70.00 (*t*); 68.46 (*t*); 21.43 (*q*, Me). CI-MS : 707 (100, $[M + 1]^+$), 553 (18), 542 (21), 447 (15), 339 (16), 296 (29). Anal. calc. for $C_{41}H_{42}N_2O_7S$ (706.86): C 69.67, H 6.00, N 3.97, S 4.54; found: C 69.50, H 6.21, N 3.76, S 4.30.

N'-*(2,3,4,6-Tetra*-O-*benzyl*-D-*galactopyranosylidene)-4-toluenesulfonohydrazide* (**12**) *and* N'-*(2,3,4,6-Tetra*-O-*benzyl*-D-*galactonoyl)-4-toluenesulfonohydrazide* (**13**). A soln. of **11** (16.36 g, 23.1 mmol) in DMF (200 ml) was treated with DBU (4.0 ml, 25.4 mmol) and portionwise with NBS (4.53 g, 25.4 mmol) and stirred for 45 min at r.t. (TLC: complete conversion of **11**). Workup as described for **6** and FC (hexane/AcOEt 4:1) gave pure fractions of **12** which mostly decomposed upon standing at r.t. overnight. An additional FC gave **12** (0.75 g, 5%) and **13** (8.00 g, 49%). In the absence of moisture, **12** was stable for several months.

*Data of* **12**: Yellowish foam. $R_f$ (hexane/AcOEt 2:1) 0.33. M.p. 50–54°. $[\alpha]_D^{25} = -20.0$ (*c* = 0.07, $CHCl_3$). IR ($CHCl_3$): 3290*w* (br.), 3060*m*, 3010*m*, 2930*m*, 2870*m*, 1660*m*, 1560*w*, 1495*m*, 1455*m*, 1365*s*, 1305*m*, 1295*m*, 1255*m*, 1170*s*, 1090*s* (br.), 1060*s*, 1030*s*, 935*w*, 910*w*, 885*w*, 815*m*, 700*s*, 665*m*. IR (KBr): 3450*m* (br.), 3090(sh), 3060*m*, 3030*m*, 2920*m*, 2870*m*, 1660*w* (br.), 1595*w*, 1560*w*, 1540*w*, 1495*m*, 1455*m*, 1365*s*, 1305*m*, 1295*m*, 1255*m*, 1210*m*, 1170*s*, 1090*s* (br.), 1060*s*, 1030*m*, 815*m*, 740*s*, 700*s*, 665*m*. $^1$H-NMR (400 MHz, $CDCl_3$): 7.66 (*d*, *J* = 8.3, 2 arom. H); 7.47–7.00 (*m*, 22 arom. H, NH); 4.84 (*d*, *J* = 11.1, 1 H, PhC*H*$_2$); 4.62 (*d*, *J* = 10.1, 1 H, PhC*H*$_2$); 4.54 (*s*, PhC*H*$_2$); 4.55–4.35 (*m*, 2 PhC*H*$_2$, H–C(5)); 4.00 (*d*, *J* = 1.1, H–C(2)); 3.91–3.88 (*m*, H–C(3)); 3.70–3.67 (*m*, H–C(4)); 3.65 (*m*, H–C(6)); 3.45 (*dd*, *J* = 2.5, 10.1, H–C(6)); 2.40 (*s*, Me). $^{13}$C-NMR (50.6 MHz, $CDCl_3$): 157.13 (*s*); 144.13 (*s*); 137.76 (*s*); 137.39 (*s*); 137.34 (*s*); 136.15 (*s*); 133.78 (*s*); 129.73–126.91 (several *d*); 85.94 (*d*); 78.89 (*d*); 78.51 (*d*); 75.15 (*t*); 73.62 (*t*); 73.56 (*t*); 72.45 (*t*); 70.25 (*d*); 67.13 (*t*); 21.52 (*q*, Me). CI-MS : 708 (12), 707 (34, $[M + 1]^+$), 706 (47), 705 (100), 551 (14), 549 (12), 441 (12), 296 (11), 275 (37), 261 (12), 260 (75), 241 (17), 239 (27), 174 (42), 156 (20), 139 (41), 108 (33), 106 (15), 91 (17). Anal. calc. for $C_{41}H_{42}N_2O_7S$ (706.86): C 69.67, H 6.00, N 3.97, S 4.5; found: C 69.90, H 6.00, N 3.79, S 4.42.

*Data of* **13**: Colourless foam. $R_f$ (hexane/AcOEt 2:1) 0.12. M.p. 46–48°. $pK_{HA}$ (EtOH/$H_2O$ 1:1) 8.55. $[\alpha]_D^{25}$ = +17.2 (*c* = 0.92, $CHCl_3$). IR ($CHCl_3$): 3560*w*, 3390*w*, 3270*w*, 3070*w*, 3020*m* (br.), 2920*w*, 2870*m*, 1695*m*, 1600*m*, 1495*m*, 1455*m*, 1400*m*, 1350*s*, 1310*m*, 1290*m*, 1170*s*, 1090*s*, 1070*s*, 1030*m*, 910*w*, 860*w*, 815*m*, 700*s*, 670*m*. IR (KBr): 3400*m* (br.), 3220*m*, 3060*m*, 3030*m*, 2920(sh), 2870*m*, 1695*m*, 1600*m*, 1495*m*, 1455*m*, 1400*m*, 1345*s*, 1250*w* (br.), 1210*m*, 1170*s*, 1090*s*, 1070*s*, 1030*m*, 905*w*, 815*m*, 740*m*, 700*s*, 670(sh), 605*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 8.29 (*d*, *J* = 4.2, exchange with $D_2O$, NH); 7.74 (*d*, *J* = 8.4, 2 arom. H); 7.39–7.09 (*m*, 22 arom. H); 6.86 (*d*, *J* = 4.4, exchange with $D_2O$, NH); 4.61 (*d*, *J* = 11.1, 1 H, PhC*H*$_2$); 4.53 (*d*, *J* = 11.9, 1 H, PhC*H*$_2$); 4.45 (*d*, *J* = 11.9, 1 H, PhC*H*$_2$); 4.44 (*d*, *J* = 11.1, 1 H, PhC*H*$_2$); 4.37 (*d*, *J* = 10.7, 1 H, PhC*H*$_2$); 4.33 (*d*, *J* = 10.8, 1 H, PhC*H*$_2$); 4.24 (*d*, *J* = 11.5, 1 H, PhC*H*$_2$); 4.13 (*d*, *J* = 11.1, 1 H, PhC*H*$_2$); 4.09–4.01 (*m*, H–C(5)); 4.06 (*d*, *J* = 2.3, H–C(2)); 3.94 (*dd*, *J* = 2.3, 8.1, H–C(3)); 3.78 (*dd*, *J* = 1.5, 8.1, H–C(4)); 3.55 (*dd*, *J* = 6.5, 9.4, H–C(6)); 3.46 ( *dd*, *J* = 6.5, 9.4, H–C(6)); 2.40 (*s*, Me); 2.38 (*d*, *J* = 9.3, exchange with $D_2O$, OH). $^1$H-NMR (400 MHz, $C_6D_6$): 8.56 (br. *s*, exchange with $D_2O$, NH); 7.86 (*d*, *J* = 8.3, 2 arom. H); 7.55 (br. *s*, exchange with $D_2O$, NH); 7.31–7.03 (*m*, 20 arom. H); 6.70 (*d*, *J* = 8.1, 2 arom. H); 4.67 (*d*, *J* = 11.1, 1 H, PhC*H*$_2$); 4.54 (*d*, *J* = 11.1, 1 H, PhC*H*$_2$); 4.45 (*d*, *J* = 11.2, 1 H, PhC*H*$_2$); 4.35 (*s*, PhC*H*$_2$); 4.28 (*d*, *J* = 2.8, H–C(2)); 4.24 (*dd*, *J* = 2.9, 7.8, H–C(3)); 4.22–4.17 (*m*, H–C(5)); 4.16 (*d*, *J* = 12.0, 1 H, PhC*H*$_2$); 4.10 (*d*, *J* = 11.2, 1 H, PhC*H*$_2$); 3.94 (*dd*, *J* = 1.4, 7.5, H–C(4)); 3.48 (*dd*, *J* = 6.2, 9.4, H–C(6)); 3.37 ( *dd*, *J* = 6.8, 9.4, H–C(6)); 2.60 (*d*, *J* = 7.6, exchange with $D_2O$, OH); 1.78 (*s*, Me). $^{13}$C-NMR (50.6 MHz, $CDCl_3$): 170.15 (*s*); 144.80 (*s*); 137.77 (*s*); 137.70 (*s*); 137.21 (*s*); 136.05 (*s*); 133.70 (*s*); 129.52–127.26 (several *d*); 79.16 (*d*); 78.90 (*d*); 77.00 (*d*); 74.93 (*t*); 73.60 (*t*); 73.20 (*t*, 2 C); 71.13 (*t*); 69.03 (*d*); 21.55 (*q*, Me). CI-MS: 707 (7, $[M - OH]^+$), 647 (17), 646 (35), 557 (35), 556 (100), 204 (15), 198 (13), 181 (22), 139 (14), 108 (13), 91 (16). Anal. calc. for $C_{41}H_{44}N_2O_8S \cdot 0.5H_2O$ (732.85): C 67.20, H 6.19, N 3.82, S 4.37; found: C 67.43, H 6.53, N 3.68, S 4.47.

N'-*(2,3,4,6-Tetra*-O-*acetyl*-D-*glucopyranosylidene)-4-toluenesulfonohydrazide* (**16**)[2]. A cooled (0°) suspension of pyridinium dichromate (21.50 g, 57 mmol) in $CH_2Cl_2$ (150 ml) was treated dropwise with a soln. of **15** (5.00 g, 9.5 mmol) in $CH_2Cl_2$ (50 ml) [20] and stirred at r.t. for 5 h. The mixture was filtered through a pad of silica gel ($CH_2Cl_2$). Concentration of the filtrate, FC (hexane/AcOEt 2:1→1:1), and drying *i.v.* gave **16** (4.40 g, 90%). $R_f$ ($CH_2Cl_2$/MeOH 98:2) 0.46. M.p. 54–56°. $[\alpha]_D^{25}$ = +60.6 (*c* = 1.04, $CHCl_3$). IR (KBr): 3470*m* (br.), 3220(sh), 2960*w*, 1750*s*, 1670*w*, 1595*w*, 1430*m*, 1370*m*, 1340*m*, 1230*s* (br.), 1170*s*, 1090(sh), 1040*s*, 900*w*

(br.), 815*w*, 665*w*. $^1$H-NMR (400 MHz, $CDCl_3$): 7.89 (*s*, exchange with $D_2O$, NH); 7.81 (*d*, *J* = 8.3, 2 arom. H); 7.32 (*d*, *J* = 8.1, 2 arom. H); 5.37 (*d*, *J* = 4.9, H–C(2)); 5.18 (*t*, *J* ≈ 5.3, H–C(3)); 5.05 (*dd*, *J* = 5.7, 9.9, H–C(4)); 4.45 (*td*, *J* ≈ 3.5, 9.9, H–C(5)); 4.28 (*d*, *J* = 3.5, 2 H–C(6)); 2.43 (*s*, Me); 2.11 (*s*, Me); 2.10 (*s*, Me); 2.06 (*s*, Me); 2.00 (*s*, Me).$^{13}$C-NMR (50.6 MHz, $CDCl_3$): 170.37 (*s*); 168.98 (*s*); 168.95 (*s*); 168.27 (*s*); 144.01 (*s*); 143.48 (*s*); 135.07 (*s*); 129.41 (*d*, 2 C); 127.85 (*d*, 2 C); 74.97 (*d*); 71.31 (*d*); 67.93 (*d*); 67.89 (*d*); 61.15 (*t*); 21.46 (*q*, Me); 20.53 (*q*, Me); 20.49 (*q*, Me); 20.40 (*q*, Me). CI-MS : 332 (15), 331 (100, $[M - Ts]^+$), 271 (25), 229 (15), 169 (54), 109 (23), 99 (26), 73 (24). Anal. calc. for $C_{21}H_{26}N_2O_{11}S$ (514.50): C 49.02, H 5.09, N 5.44, S 6.23; found: C 49.26, H 5.34, N 5.29, S 6.02.

N'-*(2,3,4,6-Tetra*-O-*pivaloyl*-D-*glucopyranosylidene)-4-toluenesulfonohydrazide* (**19**). A soln. of **18** (200 mg, 0.29 mmol) in DMF (5 ml) was treated with DBU (45 µl, 0.29 mmol) and NBS (68 mg, 0.38 mmol) and stirred for 90 min at r.t. Workup as described for **6**, FC (hexane/AcOEt 2:1), and crystallization from $Et_2O$/hexane gave **19** (157 mg, 79%). Colourless needles. $R_f$ (hexane/AcOEt 2:1) 0.47. M.p. 149–151°. $[\alpha]_D^{25}$ = +37.9 (*c* = 0.66, $CHCl_3$). IR (KBr): 3310(sh), 2980*m*, 2930(sh), 2850*m*, 1745*s*, 1670*m*, 1610*m*, 1595*w*, 1480*m*, 1460*m*, 1395*m*, 1375*m*, 1345*m*, 1280*m*, 1250(sh), 1165*s*, 1135*s*, 1055*m*, 1035*m*, 1000*w*, 920*w*, 895*w*, 810*w*, 760*w*, 720*w*, 675*w* . $^1$H-NMR (400 MHz, $CDCl_3$): 8.06 (*s*, exchange with $D_2O$, NH); 7.73 (*d*, *J* = 8.3, 2 arom. H); 7.27 (*d*, *J* = 8.0, 2 arom. H); 5.36 (*d*, *J* = 7.2, H–C(2)); 5.26 (*t*, *J* = 7.3, H–C(3)); 5.18 (*dd*, *J* = 7.5, 9.8, H–C(4)); 4.33 (*dd*, *J* = 1.9, 12.7, H–C(6)); 4.28 (*ddd*, *J* = 1.8, 3.8, 9.8, H–C(5)); 4.15 (*dd*, *J* = 3.8, 12.7, H–C(6)); 2.40 (*s*, Me); 1.19 (*s*, *t*-Bu); 1.17 (*s*, *t*-Bu); 1.13 (*s*, *t*-Bu); 1.07 (*s*, *t*-Bu). $^{13}$C-NMR (50.6 MHz, $CDCl_3$): 177.71 (*s*); 176.33 (*s*); 176.03 (*s*); 176.00 (*s*); 143.97 (*s*); 143.61 (*s*); 135.26 (*s*); 129.46 (*d*, 2 C); 127.85 (*d*, 2 C); 75.96 (*d*); 71.06 (*d*); 67.68 (*d*); 66.71 (*d*); 60.73 (*t*); 38.87 (*s*, 2 C); 38.67 (*s*); 38.57 (*s*); 27.01 (*q*, 2 $Me_3$C); 26.90 (*q*, $Me_3$C); 26.86 (*q*, $Me_3$C); 21.46 (*q*, Me). CI-MS: 685 (11), 684 (33), 683 (79, $[M + 1]^+$), 581 (14), 532 (24), 516 (12), 515 (37), 499 (11), 481 (27), 413 (11), 392 (17), 391 (62), 317 (30), 313 (10), 297 (40), 279 (12), 277 (10), 211 (14), 210 (12), 197 (16), 195 (51), 189 (16), 174 (11), 172 (18), 157 (39), 141 (12), 140 (11), 139 (31), 120 (14), 111 (15), 103 (100), 95 (13). Anal. calc. for $C_{33}H_{50}N_2O_{11}S \cdot 0.5H_2O$ (691.82): C 57.29, H 7.43, N 4.05, S 4.63; found: C 57.00, H 7.44, N 3.91, S 4.87.

N-*Sodio*-N'-*(2,3,4,6-tetra*-O-*benzyl*-D-*glucopyranosylidene)-4-toluenesulfonohydrazidate–Water (1/1.5)* (**20** · 1.5 $H_2O$). A suspension of **6** (4.02 g, 5.7 mmol) in MeOH (25 ml) was treated with 4.35M NaOMe (4 ml, 17.4 mmol) in MeOH [2c] and stirred for 15 min at r.t. The clear soln. was concentrated to *ca.* 20% of the volume and treated with wet $Et_2O$ (*ca.* 20 ml). After 20 min, the formed precipitate was filtered off, washed with wet $Et_2O$ (3×), and dried at 0.05 Torr for 24 h affording **20** · 1.5 $H_2O$ (4.01 g, 97%). Fine colourless plates. M.p. 193.5°. $[\alpha]_D^{25}$ = +4.9 (*c* = 0.98, $CHCl_3$). UV (EtOH): *ca.* 290 (sh, 400), 218 (2534). UV (THF): 240 (br., 1201). IR (KBr): 3450*m* (br.), 3060*w*, 3020*w*, 2920*w*, 2870*w*, 1635*w* , 1600(sh), 1495*w*, 1455*m*, 1370*w*, 1235*m*, 1135*s*, 1090*s*, 1065*s*, 1030*s*, 915*w*, 815*w*, 735*m*, 700*m*, 660*m*, 610*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 7.98 (*d*, *J* = 8.1, 2 arom. H); 7.26–6.78 (*m*, 22 arom. H); 4.58 (*d*, *J* = 12.6, 1 H, PhC$H_2$); 4.48 (*d*, *J* = 11.4, 1 H, PhC$H_2$); 4.47 (*d*, *J* = 12.7, 1 H, PhC$H_2$); 4.34 (*d*, *J* = 12.1, 1 H, PhC$H_2$); 4.33 (*d*, *J* = 11.1, 1 H, PhC$H_2$); 4.25–4.21 (*m*, H–C(5)); 4.23 (*d*, *J* = 11.6, 1 H, PhC$H_2$); 4.20 (*d*, *J* = 12.1, 1 H, PhC$H_2$); 4.05 (*d*, *J* = 2.0, H–C(2)); 3.98 (*d*, *J* = 11.2, 1 H, PhC$H_2$); 3.73 (*dd*, *J* = 2.0, 5.4, H–C(3)); 3.49–3.40 (*m*, H–C(4), 2 H–C(6)); 2.15 (*s*, Me). $^{13}$C-NMR (50.6 MHz, $CDCl_3$): 140.94 (*s*); 140.74 (*s*); 140.18 (*s*); 137.85 (*s*); 137.81 (*s*); 137.57 (*s*); 137.12 (*s*); 129.12–127.32 (several *d*); 83.06 (*d*); 77.97 (*d*); 74.68 (*d*); 73.46 (*d*); 72.78 (*t*, 2 C); 71.30 (*t*); 69.43 (*t*); 65.91 (*t*); 21.04 (*q*, Me) CI-MS: 505 (12), 464 (30), 463 (94), 416 (13), 415 (45), 399 (28), 397 (12), 371 (21), 337 (23), 325 (14), 323 (11), 308 (23), 307 (100), 253 (14), 247 (23), 217 (16), 181 (29), 139 (33), 91 (89). Anal. calc. for $C_{41}H_{42}N_2NaO_7S \cdot 1.5$ $H_2O$ (756.87): C 65.06, H 5.99, N 3.70, S 4.24; found: C 65.47, H 5.68, N 3.76, S 4.45.

*Reaction of* **6** *or* **20** · 1.5 $H_2O$ *with* N-*Phenylmaleimide. a*) In a quartz vessel, a soln. of **20** · 1.5 $H_2O$ (280 mg, 0.38 mmol) and *N*-phenylmaleimide (500 mg, 2.88 mmol) in THF (25 ml) under $N_2$ was irradiated for 5 h. At the end, the temp. within the reaction vessel was 60–62°. After evaporation, the residue was dissolved in AcOEt, washed with $H_2O$ (3×) and brine, dried ($MgSO_4$), concentrated at 30°/*i.v.*, and filtered through silica gel (hexane/AcOEt 2:1). FC (hexane/AcOEt 4:1) of the concentrated filtrate gave **21** (114 mg, 44%) and **22** [8] (14 mg, 5%).

*b*) In a quartz vessel, a suspension of NaH (80% NaH in white oil washed with dry hexane and dried, 24 mg, 1.0 mmol) and **6** (501 mg, 0.71 mmol) in THF (25 ml) was stirred under $N_2$ for 10 min. The clear soln. was treated with *N*-phenylmaleimide (1.036 g, 5.98 mmol) and irradiated at r.t. for 3.5 h. At the end, the temp. within the vessel was 60–62°. Workup as described in *Procedure a* and FC gave **6** (250 mg, 50%) and **21/22** (61 mg, 12%, ratio not determined).

*c*) A suspension of NaH (24 mg, 1.0 mmol) and **6** (501 mg, 0.71 mmol) in diethylene glycol dimethyl ether (20 ml) was stirred under $N_2$ for 10 min. The yellowish soln. was treated with [15]crown-5 (350 µl, 1.77 mmol) and *N*-phenylmaleimide (1.016 g, 5.87 mmol) and heated at 140° for 3.5 h. TLC showed the absence of **6**, **21**, and **22** and the presence of decomposition products.

*Reaction of* **6** *with Dimethyl Fumarate.* According to the reaction of **6** with *N*-phenylmaleimide, *Procedure b*, the photolysis of **6** (501 mg, 0.71 mmol) and dimethyl fumarate (128 mg, 0.89 mmol) gave **23/24** [8] (261 mg, 55%; HPLC: **23/24** 1:1).

*Reaction of* **6** *or* **20** · 1.5 $H_2O$ *with Acrylonitrile. a*) In a quartz vessel, a soln. of **20** · 1.5 $H_2O$ (500 mg, 0.66 mmol) and acrylonitrile (0.25 ml, 3.77 mmol) in THF (25 ml) under $N_2$ was irradiated for 5 h at r.t. Workup as described for **21/22** and FC (hexane/$Et_2O$ 10:1→ 4:1) gave **25/26/27/28** [8] (235 mg, 62%; HPLC: **25/26/27/28** 40:39:18:3).

*b*) According to the reaction of **6** with *N*-phenylmaleimide, *Procedure b*, the photolysis of **6** (501 mg, 0.71 mmol) and acrylonitrile (0.25 ml, 3.54 mmol) gave **6** (11 mg, 2%) and **25/26/27/28** (282 mg, 69%; HPLC: **25/26/27/28** 43:35:19:3).

*c*) According to the reaction of **6** with *N*-phenylmaleimide, *Procedure c*, the thermolysis of **6** (204 mg, 0.29 mmol) and acrylonitrile (150 mg, 1.21 mmol) gave only decomposition products.

*Reaction of* **6** *or* **20** · 1.5 $H_2O$ *with Phenol. a*) In a quartz vessel, a soln. of **20** · 1.5 $H_2O$ (500 mg, 0.66 mmol) and phenol (186 mg, 1.98 mmol) in THF (25 ml) under $N_2$ was irradiated for 5 h. After concentration, the residue was dissolved in AcOEt, washed with 2M NaOH (3×) and brine, dried ($MgSO_4$), concentrated at 30°/*i.v.*, and filtered through silica gel (hexane/AcOEt 2:1). FC (hexane/$Et_2O$ 4:1) of the concentrated filtrate gave **29/30** [6] (237 mg, 58%; HPLC: **29/30** 4:1) and **4** (41 mg, 12%).

*b*) In a quartz vessel, a suspension of NaH (24 mg, 1.0 mmol) and **6** (501 mg, 0.71 mmol) in THF (25 ml) was stirred under $N_2$ for 10 min. The clear soln. was treated with phenol (186 mg, 1.98 mmol) and irradiated at r.t. for 3.5 h. Workup as described in *Procedure a* and FC gave **29/30** (276 mg, 63%; HPLC: **29/30** 7:1).

*c*) A suspension of NaH (24 mg, 1.0 mmol) and **6** (501 mg, 0.71 mmol) in diethylene glycol dimethyl ether (20 ml) was stirred under $N_2$ for 10 min. The yellowish soln. was treated with [15]crown-5 (350 µl, 1.77 mmol) and phenol (198 mg, 2.10 mmol) and heated at 140° for 3.5 h. After concentration at 95°/14 Torr, the residue was treated as described in *Procedure a*: **29/30** (282 mg, 64%; HPLC: **29/30** >98:2).

*Reaction of* **6** *or* **20** · 1.5 $H_2O$ *with 4-Methoxyphenol. a*) In a quartz vessel, a soln. of **20** · 1.5 $H_2O$ (428 mg, 0.57 mmol) and 4-methoxyphenol (800 mg, 6.44 mmol) in THF (25 ml) under $N_2$ was irradiated for 5 h at r.t. Workup as described for **29/30** and FC (hexane/$Et_2O$ 4:1) gave **31/32** [6] (183 mg, 48%; HPLC: **31/32** 6:1), **6** (34 mg, 8%), and **4** (24 mg, 8%).

*b*) According to the reaction with phenol, *Procedure b*, the photolysis of **6** (496 mg, 0.70 mmol) and 4-methoxyphenol (370 mg, 2.98 mmol) gave **6** (35 mg, 7%) and **31/32** (246 mg, 54%; HPLC: **31/32** 50:1).

*c*) According to the reaction with phenol, *Procedure c*, the thermolysis of **6** (204 mg, 0.29 mmol) and 4-methoxyphenol (150 mg, 1.21 mmol) gave **6** (5 mg, 2%) and **31/32** (103 mg, 55%; HPLC: **31/32** 3:1).

*Reaction of* **6** *with Propan-2-ol.* According to the reaction with *N*-phenylmaleimide, *Procedure b*, the photolysis of **6** (501 mg, 0.71 mmol) and i-PrOH (1.0 ml, 18 mmol) gave **33/34** [5] (89 mg, 22%; HPLC: **33/34** 1:2).

## REFERENCES


[1] a) R. J. Crawford, R. Raap, *Proc. Chem. Soc.* **1963**, 370; b) R. J. Crawford, R. Raap, *Can. J. Chem.* **1965**, *43*, 126; c) *ibid.* **1965**, *43*, 356.

[2] a) W. C. Agosta, A. M. Foster, *J. Chem. Soc., Chem. Commun.* **1971**, *49*, 433; b) A. B. Smith, A. M. Foster, W. C. Agosta, *J. Am. Chem. Soc.* **1972**, *94*, 5100; c) A. M. Foster, W. C. Agosta, *ibid.* **1972**, *94*, 5777; d) *ibid.* **1973**, *95*, 608; e) S. Ayral-Kaloustian, W. C. Agosta, *J. Org. Chem.* **1982**, *47*, 284.

[3] P. Yates, R. O. Loutfy, *Acc. Chem. Res.* **1975**, *8*, 209.

[4] M. A. Kesselmayer, R. S. Sheridan, *J. Am. Chem. Soc.* **1986**, *108*, 99.

[5] K. Briner, A. Vasella, *Helv. Chim. Acta* **1989**, *72*, 1371.

[6] K. Briner, A. Vasella, *Helv. Chim. Acta* **1990**, *73*, 1764.

[7] A. Vasella, *Pure Appl. Chem.* **1991**, *63*, 507.

[8] A. Vasella, C. A. A. Waldraff, *Helv. Chim. Acta* **1991**, *74*, 585.

[9] A. Vasella, G. Baudin, L. Panza, *Heteroatom Chem.* **1991**, *2*, 151.

[10] J.-P. Praly, Z. El Kharraf, G. Descotes, *J. Chem. Soc., Chem. Commun.* **1990**, 431.

[11] J.-P. Praly, Z. El Kharraf, G. Descotes, *Tetrahedron Lett.* **1990**, *31*, 4441.

[12] F. Ruff, I. Schuster, A. Gérécs, *Acta Chim. Acad. Sci. Hung.* **1968**, *57*, 111.

[13] A. Gérécs, *Acta Chim. Acad. Sci. Hung.* **1975**, *84*, 467.

[14] B. Helferich, H. Schirp, *Chem. Ber.* **1953**, 547.
[15] D. G. Easterby, L. Hough, J. K. N. Jones, *J. Chem. Soc.* **1951**, 3416.
[16] D. R. Wolk, A. Vasella, F. Schweikart, M. G. Peter, *Helv. Chim. Acta,* in press.
[17] S. E. Mangholz, A. Vasella, unpublished results.
[18] E. Decoster, J.-M. Lacombe, J.-L. Strebler, B. Ferrari, A. A. Pavia, *J. Carbohydr. Chem.* **1983**, *2*, 329.
[19] P. J. Garegg, B. Samuelsson, *Carbohydr. Res.* **1978**, *67*, 267.
[20] R. D'Ascoli, M. D'Auria, L. Nucciarelli, G. Piancatelli, A. Scettri, *Tetrahedron Lett.* **1980**, *21*, 4521.
[21] D. Beer, A. Vasella, *Helv. Chim. Acta* **1985**, *68*, 2254.
[22] P. G. Williard, L. A. Grab, J. P. Springer, *Tetrahedron Lett.* **1981**, *22*, 2731.
[23] W. Kirmse, 'Carbene Chemistry', Academic Press, New York–London, 1971, p. 30.
[24] R. H. Shapiro, *Org. React.* **1976**, *23*, 405.
[25] K. Briner, A. Vasella, in preparation.
[26] C. P. J. Glaudemans, H. G. Fletcher, Jr., in 'Methods in Carbohydrate Chemistry', Eds. R. L. Whistler and J. N. BeMiller, Academic Press, New York–London, 1972, Vol. 6, p. 373.
[27] S. Koto, N. Morishima, Y. Miyata, S. Zen, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2639.
[28] P. Zimmermann, R. Bommer, T. Bär, R. R. Schmidt, *J. Carbohydr. Chem.* **1988**, *7*, 435.
[29] S. Hanessian, D. H. Wong, M. Therien, *Synthesis* **1981**, 394.