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Dioxane-type (2-naphthyl)methylene acetals of glycosides and their hydrogenolytic transformation into 6-*O*- and 4-*O*-(2-naphthyl)methyl (NAP) ethers

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Dedicated to Professor András Messmer on the occasion of his 80th birthday

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Abstract—α-, β-D-Gluco-, galacto-, 2-deoxy-2-phthalimido-β-D-glucopyranosides with different aglycons (methyl, allyl, *p*-methoxyphenyl, thioethyl) reacted with 2-naphthaldehyde dimethyl acetal to give rise to 4,6-*O*-(2-naphthyl)methylene acetals. The acetals were converted into fully protected compounds bearing benzoyl, benzyl, allyl, *p*-methoxybenzyl groups. The fully alkylated dioxane-type acetals were hydrogenolysed with AlH_3 ($3LiAlH_4$–$AlCl_3$) reagent to furnish 4-*O*-NAP/6-OH derivatives. All acetals were treated with $BH_3{\cdot}Me_3N$–$AlCl_3$ in THF and a reverse regioselectivity was observed, producing 6-*O*-NAP/4-OH derivatives. Similar regioselectivity was also observed by using $NaCNBH_3$–HCl reagent. In all reactions very mild reaction conditions were required, regioselectivity was better than 93:7, and the isolated yields were between 83–92%. All compounds were characterised by ^1H and ^{13}C NMR spectra. Solid-state and solution conformation of methyl 2,3-di-*O*-acetyl-4,6-*O*-(2-naphthyl)methylene-α-D-galactopyranoside were elucidated by X-ray and NMR measurements.

1. Introduction

The protecting group strategy plays an essential role not only in the design and syntheses of complex oligosaccharides[1] but also in the chemical transformation of sugars.[2] Acetals[2–4] and easily removable ether groups[5] belong to the most frequently applied protecting groups. The rules for the regio-,[6,7] stereo-[8] and chemoselective[9] transformations of the benzylidene acetals into hydroxy/benzyl ether derivatives are well-known. Although many reagents were used for hydrogenolysis of acetals, three of them are used in general: (i) $LiAlH_4$–$AlCl_3$;[6,7] (ii) $NaCNBH_3$–HCl[10,11] (or other strong protic acids); and (iii) $BH_3{\cdot}Me_3N$–$AlCl_3$.[12] Reagent (i) results in 4-*O*-alkyl/aryl/6-OH products, reagent (ii) induces opposite regioselectivity producing 4-OH/6-*O*-alkyl/aryl derivatives. The regioselectivity of the acetal cleavage using reagent (iii) is strongly solvent dependent, either of 4-OH/6-*O*-ether and 6-OH/4-*O*-ether can be prepared, with moderate yields, however, in some cases. The blocking group strategy based on benzylidene acetals/benzyl ethers is well supplemented by a *p*-methoxy counterpart,[13] but the higher acid sensitivity of these acetals and ethers diminish their preparative usefulness. Although (2-naphthyl)methyl (NAP) ethers have been previously described[14–16] their preparative usefulness was rediscovered[17,18] only very recently. Namely, it was shown that NAP ethers can be hydrogenolysed in the presence of benzyl ethers or esters[15] and they are less sensitive to acids than *p*-methoxybenzyl ethers. The most important observation, however, is that the NAP ethers can easily be removed by DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) under conditions when other usual protecting groups like acetyl, pivaloyl, phthalimido, benzyl and benzylidene survive.[17,18] On the basis of these observations the syntheses of some very complex oligosaccharides have also been accomplished.[19–22] In 2000 we have reported on the synthesis of (2-naphthyl)methylene acetals of hexapyranosides and converted them into (2-naphthyl)methyl (NAP) ethers.[23] To our knowledge, only the synthesis of *n*-pentenyl 2,3-di-*O*-benzoyl-4,6-*O*-(2-naphthyl)methylene-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-β-D-glucopyranoside[24] has been reported before. Last year hydrogenolysis of dioxane-type (2-naphtyl)methylene acetals of sugars were also published by Spencer et al.[25] For the hydrogenolysis of compound **7**[23] Spencer et al.[25] used DIBAL-H in toluene–dichloromethane and the

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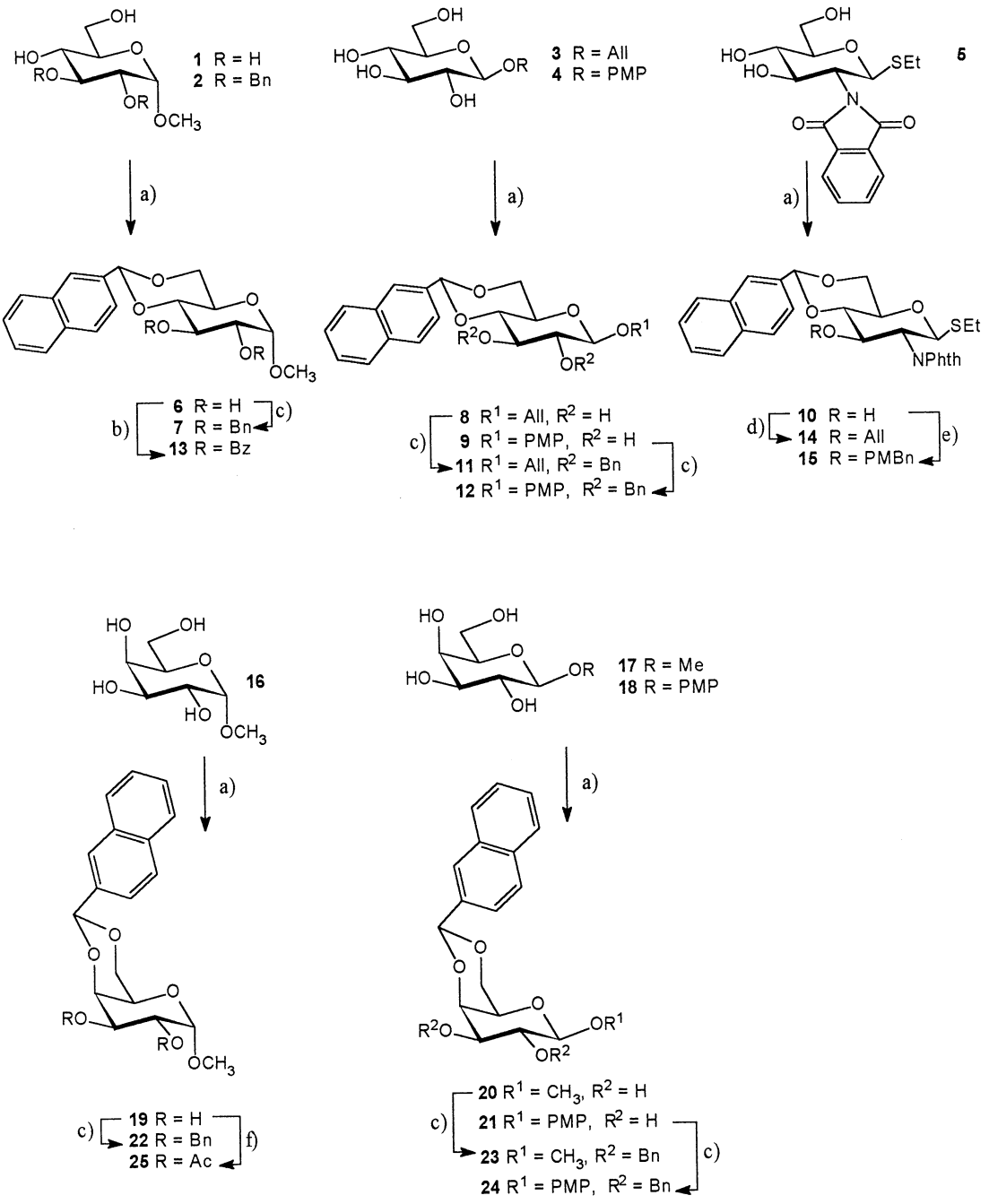

Figure 1. Reaction conditions: (a) 2-(dimethoxymethyl)naphthalene (1.2 equiv.), pTSA, DMF, rt, overnight (87–92%); (b) benzoyl chloride, pyridine (81.5%); (c) benzyl bromide, NaH, DMF (91–94%); (d) allyl bromide, NaH, DMF (88.3%); (e) *p*-methoxybenzyl chloride, NaH, DMF (83.5%); (f) acetic anhydride, pyridine (83%).

4-ONAP/6-OH derivative (**26**[23])was obtained in a yield of 60%. In the case of methyl 2,3-di-*O*-benzyl-4,6-*O*-(2-naphthyl)methylene-α-D-galactopyranoside (compound **22**) the authors assigned *R*-configuration to the acetal carbon in which the bulky naphthyl group must have an axial arrangement, but they did not gave any structural parameters to support this configuration. The hydrogenolysis of this poorly characterised compound with Et_3SiH–TfOH-4 Å Ms in dichloromethane resulted in 4-ONAP/6-OH derivative (84%), however, its hydrogenolysis with Et_3SiH–$PhBCl_2$ gave the 6-ONAP/4-OH compound (77%). These structures had not been verified by any data.

In this paper we wish to report on the extension of our previous work and to confirm the structure of all synthesized compounds giving full experimental details and spectroscopic parameters.

2. Results and discussions

2.1. Preparation of 4,6-*O*-(2-naphthyl)methylene acetals of hexopyranosides

In the glucopyranoside series methyl α-(**1**), methyl

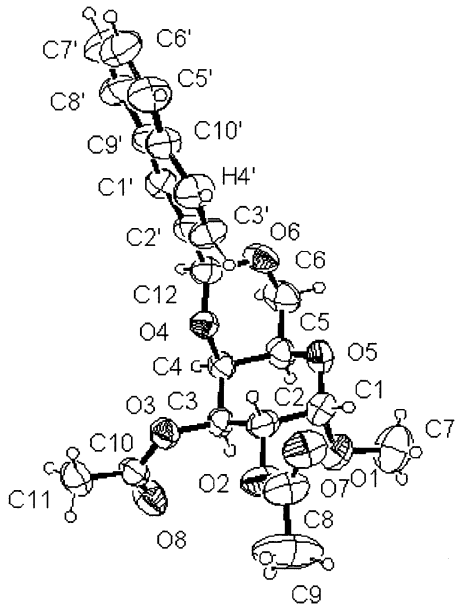

Figure 2. ORTEP view of **25** shown at 50% probability level. Only one of the molecules in the asymmetric unit is shown.

2,3-di-*O*-benzyl-α-(**2**), allyl β-(**3**), *p*-methoxyphenyl β-D-glucopyranoside (**4**) were reacted with 2-naphthaldehyde dimethyl acetal in DMF solution in the presence of *p*-toluenesulfonic acid (*p*-TSA) to give crystalline dioxane-type acetals (**6**–**9**). Compound **1** or **2** reacted with 2-naphthaldehyde too, but the acetal-formation was slow and the reaction did not go to completion overnight. Similar treatment of ethyl 2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**5**) with 2-naphthaldehyde dimethyl acetal yielded the desired acetal compound (**10**). Benzylation of compounds **6**, **8** and **9** gave the fully protected dioxane-type acetals **7**, **11** and **12**. Benzoylation of **6** resulted in compound **13**. Compound **10** was allylated or *p*-methoxybenzylated to obtain compounds **14** and **15** (Fig. 1).

The preparation of the (2-naphthyl)methylene acetals in the galactopyranoside series proceeded also very smoothly and, although the two six-membered rings are *cis*-fused, no steric hindrance was observed. Starting from methyl α-(**16**) methyl β-(**17**) and *p*-methoxyphenyl β-D-galactopyranoside (**18**) crystalline acetals (**19**–**21**) were isolated with good to excellent yields. Compounds **19**–**21** were benzylated to get the fully protected compounds **22**–**24**. For comparative X-ray crystallographic studies compound **19** was acetylated and the di-*O*-acetyl derivative (**25**) gave a single crystal suitable for X-ray structure determination. ORTEP view of **25** at 50% probability level with numbering scheme is shown at Fig. 2. These experiments unambiguously verified that the naphthyl group had an equatorial arrangement.

^{13}C and ^{1}H NMR spectra of all synthesised acetals were recorded and assigned (Tables 1–4). The characteristic spectral parameters were very similar to those observed for benzylidene and substituted benzylidene acetals,[26] namely, low field ^{13}C shift for C-6 and C-4 and extremely high field chemical shifts for C-5, especially in the case of the α-anomers. In the case of the β-anomers, the high field shifts of C-5 are less pronounced. These characteristic carbon chemical shift values are very similar in the gluco- and galacto series. The chemical shift values of the acetalic carbon show only small variations between 101 and 102 ppm. The typical aromatic (naphthyl) resonances are shown in Section 3.

2.2. Hydrogenolysis of 4,6-*O*-(2-naphthyl)methylene acetals of pyranosides

As mentioned before, in the field of carbohydrates three reagents ($LiAlH_4$–$AlCl_3$;[6,7] $NaCNBH_3$–HCl[10,11] and $BH_3{\cdot}Me_3N$–$AlCl_3$[12]) are generally applied for the transformation of benzylidene and *p*-methoxybenzylidene acetals into hydroxy/benzyl or hydroxy/*p*-methoxybenzyl ethers. Recently, additional reagents were proposed for preparative purposes, namely triethylsilane–trifluoroacetic acid,[27] $BH_3{\cdot}Me_2NH$–$BF_3{\cdot}OEt_2$ in CH_3CN,[28] triethylsilane–$TiCl_4$[29] and $BH_3{\cdot}THF$–Bu_2BOTf.[30]

All these reagents, except the $LiAlH_4$–$AlCl_3$, can be used in the presence of ethers, esters, amides and imides. The $LiAlH_4$–$AlCl_3$ is compatible only with ether substituents, providing excellent regioselectivity, the 4-OBn/6-OBn

Table 1. ^{13}C NMR data (δ) for compounds **6**–**25**

Compounds	C-1	C-2	C-3	C-4	C-5	C-6	C-ac	C-aglycon
6	99.9	72.6[a]	71.1[a]	81.1	62.3	68.9	101.8	55.3 (OCH_3)
7	99.2	79.1[a]	78.5[a]	82.1	62.3	69.1	101.3	55.3 (OCH_3)
8	102.1	74.5[a]	73.1[a]	80.6	66.4	68.7	101.9	70.6, 118.3, 133.7 (OAll)
9	102.2	73.9[a]	72.7[a]	80.4	65.8	68.0	101.0	55.0 (OCH_3)
10	82.2[a]	55.4	70.3	81.9a	69.4	68.6	101.9	14.8, 24.1 (SEt)
11	103.2	81.5[a]	80.9[a]	82.1[a]	66.0	68.8	101.3	70.7, 117.5, 133.7 (OAll)
12	103.2	81.3[a]	80.8[a]	81.9[a]	66.1	68.8	101.3	55.6 (OCH_3)
13	97.7	72.5[a]	69.5[a]	79.5	62.6	69.0	101.8	55.4 (OCH_3)
14	82.5[a]	54.5	75.8	81.7[a]	70.3	68.4	101.1	14.7, 23.8 (SEt)
15	81.5	54.6	82.9	74.8	70.4	68.5	101.4	14.8, 24.0 (SEt)
19	100.3	68.8[a]	68.6[a]	76.2	62.5	69.1	101.1	55.3 (OCH_3)
20	103.9	72.1[a]	70.0[a]	75.7	65.9	68.7	100.1	56.2 (OCH_3)
21	101.9	69.7	71.9	75.5	66.0	68.6	100.1	54.9 (OCH_3)
22	99.4	75.2	75.8	74.8	62.4	69.4	101.1	55.4 (OCH_3)
23	104.7	79.1[a]	78.3[a]	73.9	66.3	69.2	101.4	57.0 (OCH_3)
24	103.2	78.0	79.2	73.8	69.2	66.5	101.4	55.8 (OCH_3)
25	97.7	68.2	68.5	74.0	62.0	69.1	101.0	55.5 (OCH_3)

[a] Interchangeable assignments.

Table 2. ^{13}C NMR data (δ) for compounds **26–40**

Compounds	C-1	C-2	C-3	C-4	C-5	C-6	C-aglycon
26	98.1	81.9[a]	79.9[a]	77.6	70.6	61.8	55.1 (OCH_3)
27	102.8	84.5	82.3	77.6	75.0	62.1	70.6, 118.3, 133.7 (OAll)
28	102.5	84.4	82.0	77.3	75.1	62.0	55.6 (OCH_3)
29	98.1	79.5	81.4	69.9	70.6	69.2	55.1 (OCH_3)
30	102.7	81.6	83.9	71.3	74.0	70.1	70.3, 117.3, 133.9 (OAll)
31	102.7	81.5	84.0	71.1	74.4	69.9	55.5 (OCH_3)
32	81.1	54.5	78.0	79.8	73.2	70.5	14.8, 23.9 (SEt)
33	80.9	54.3	77.8	79.1	74.0	70.5	55.4 (OCH_3)
34	96.9	71.4	73.7	73.9	76.2	69.2	55.2 (OCH_3)
35	98.7	76.3	79.0	75.1	70.3	62.3	55.2 (OCH_3)
36	100.8	81.9[a]	79.4[a]	74.0	72.9	61.6	56.8 (OCH_3)
37	102.8	82.1[a]	79.3[a]	75.4	72.5	61.9	55.6 (OCH_3)
38	98.4	69.5	75.6	67.9	77.4	69.5	55.1 (OCH_3)
39	104.6	73.0	80.4	66.7	78.9	69.1	56.8 (OCH_3)
40	102.8	73.5	78.6	66.7	80.5	69.2	55.5 (OCH_3)

[a] Interchangeable assignments.

Table 3. ^1H NMR chemical shifts (δ in ppm) and coupling constants (J in Hz) for compounds **6–25**

Compounds	H-1, $J_{1,2}$	H-2, $J_{2,3}$	H-3, $J_{3,4}$	H-4, $J_{4,5}$	H-5, $J_{5,6a}$	H-6a, J_{gem}	H-6b, $J_{5,6b}$	H-ac	H-aglycon
6[a]	4.74d, 3.8	3.59dd, 9.3	3.92t, 9.3	3.48t, 9.3	3.81dt, 4.7	4.30dd, 10.2	3.74dd, 10.2	5.64s	3.0 (OCH_3)
7[a]	4.69d, 3.7	3.68dd, 9.3	4.19t, 9.3	3.75t, 9.3	3.97dt, 4.8	4.41dd, 10.2	3.84t, 10.2	5.76s	3.08 (OCH_3)
8[a]	4.44d, 7.9	3.54dd, 9.2	3.83t, 9.2	3.59t, 9.2	3.46dt, 10.5	4.36dd, 10.5	3.82t, 10.5	5.67s	5.93;5.23;5.33;4.13 (allyl)
9[b]	4.86d, 7.8	3.52[c]	3.75t, 9.8	3.53[c]	3.48dt, 4.7	4.27dd, 10.1	3.65dd, 4.5	5.66s	3.27 (OCH_3) 6.81;7.02 (arom)
10[a]	5.44d, 10.0	3.60–3.90m		4.30t, 9.8	4.70dt, 3.3	4.43dd, 10.0	3.6–3.9m	5.72s	1.20 t; 2.70 m (SEt)
11[a]	4.58d, 7.8	3.52t, 8.0	3.76t, 10.0	3.85t, 10.0	3.45m, 10.0	3.75dd, 10.0	3.40dd, 4.8	5.72s	5.95;5.38;5.27;4.42;4.17 (allyl)
12[a]	4.99d, 7.9	3.71t, 8.3	3.79–3.83m		3.50m	4.39dd, 10.5	3.86t, 10.0	5.70s	3.74 (OCH_3) 6.80;6.95 (arom)
13[a]	5.20d, 3.8	5.27dd, 9.8	6.10t, 9.8	3.92t, 9.8	4.13dt, 4.8	4.42dd, 10.3	3.96t, 9.6	5.72s	3.44 (OCH_3)
14[a]	5.45d, 10.6	4.39t, 10.4	4.50t, 10.2	3.80t, 9.0	3.76m, 4.7	4.45, 10.0	3.85, 10.0	5.72s	1.20t;2.70m (SEt)
15[a]	5.40d, 10.6	4.31t, 10.5	4.50[c]	3.90[c]	3.79dt, 4.8	4.50[c]	3.90[c]	5.81s	1.21t;2.70m (SEt)
19[d]	4.90d, 3.3	3.85–4.10				4.30dd, 12.2	4.12, 2.0	5.72s	3.45 (OCH_3)
20[b]	4.15[c]	3.56[c]	3.56[c]	4.14[c]	3.45	4.18, 12.2	4.07, 1.9	5.63s	3.47 (OCH_3)
21[b]	4.78d, 7.7	3.81, 9.7	3.66, 3.5	4.21, ~0	3.57, <1	4.18, 11.9	4.10, 1.2	5.67s	3.68 (OCH_3) 6.73;7.00 (arom)
22[a]	4.79d, 3.5	4.10dd, 10.0	4.00dd, 3.4	4.21d, ~0	3.60m	4.23	4.03	5.62s	3.38 (OCH_3)
23[a]	4.29d, 7.6	3.87dd, 9.5	3.56dd, 3.4	4.13d, ~0	3.29br	4.32dd, 12.3	4.03dd, 1.5	5.63s	3.61 (OCH_3)
24[a]	4.88d, 7.8	4.13dd, 9.8	3.65dd, 3.6	4.20d, 3.6	3.40dd, 1.0	4.36dd, 12.2	4.08dd, 1.6	5.65s	3.76 (OCH_3), 6.73; 7.00 (arom)
25[a]	5.16d, 3.2	5.42dd, 10.8	5.39dd, 10.9	4.56d, ~0	3.82br, <1	4.35d, 12.5	4.14dd, 1.5	5.69s	3.45 (OCH_3)

[a] Measured in $CDCl_3$.
[b] Measured in DMSO-d_6–$CDCl_3$.
[c] Overlap.
[d] Measured in MeOD–$CDCl_3$.

Table 4. ^1H NMR chemical shifts (δ in ppm) and coupling constants (J in Hz) for compounds **26–40**

	H-1, $J_{1,2}$	H-2, $J_{2,3}$	H-3, $J_{3,4}$	H-4, $J_{4,5}$	H-5, $J_{5,6a}$	H-6a, J_{gem}	H-6b, $J_{5,6b}$	H-aglycon
26	4.57d, 3.6	3.51dd, 9.7	4.04dd, 8.8	3.56–3.83m	3.56–3.83m	3.56–3.83m	3.56–3.83	3.38s (OCH_3)
27	4.47d, 7.8	3.44t, 8.2[a]	3.59t, 9.0[a]	3.67t, 9.0	3.36m, 2.5	3.86dd, 12.0	3.70dd, 4.6	5.91;5.31;5.18;4.36;4.12 (allyl)
28	4.92d, 7.5	3.67–3.88	3.67–3.88	3.67–3.88	3.55m	3.96dd, 11.8	~3.75	3.82 (OCH_3) 6.88;7.05 (arom)
29	4.63d, 3.1	3.53dd, 9.5	3.79t, 9.2	3.61t, 9.2	3.68–3.75m			3.30 (OCH_3)
30	4.53[b]	3.42–3.60			~3.65m, 3.5	3.87dd, 10.5	3.81dd, 5.0	5.90; 5.31; 5.20; 4.36; 4.17 (allyl)
31	4.81d, ~10	3.50–3.85				3.92dd, 10.5	~3.75	3.77 (OCH_3) 6.88;7.05 (arom)
32	5.32d, 9.8	3.65–4.33						2.65;1.20 (SEt)
33	5.30d, 9.8	3.65–4.33						2.63;1.17 (SEt)
34	5.15d, 3.6	5.27dd, 10.1	5.79t, 8.6	3.97[b]m	4.00[b]m, 4.0	3.88dd, 10.5	3.8dd, 3.1	3.41 (OCH_3)
35	4.72d, 4.2	4.07dd, 10.1	3.94dd, 3.0	3.89d, ~0	~3.7[b]m, 6.7	3.73dd, 10.3	3.47dd, 4.0	3.33 (OCH_3)
36	4.25d, 7.8	3.45–3.90			3.30brt	3.45–3.90		3.52 (OCH_3)
37	4.89d, 7.7	4.14dd, 9.7	3.62dd, 2.9	3.86d, ~0	3.83m, 6.7	4.87dd, 12.0	3.47m	3.75 (OCH_3) 6.80;7.00 (arom)
38	4.67d, 3.6	3.89dd, 8.0	3.86dd, 3.0	4.02d, ~0	3.83dd, 5.4	3.75dd, 10.2	3.70dd, 6.4	3.38 (OCH_3)
39	4.27d, 7.7	3.57t, 9.4	3.46dd, 3.4	4.00br, ~0	3.65m, 5.8	3.83dd, 10	3.77dd, 6.0	3.56 (OCH_3)
40	4.86d, 7.8	3.92t, 9.1	3.58dd, 3.3	4.07d, ~0	3.70t, 4.7	3.88dd, 10.1	3.82dd, 6.3	3.70 (OCH_3) 6.77;7.04 (arom)

Measured in $CDCl_3$.
[a] Interchangeable assignments.
[b] Overlap.

Table 5. The product distribution for the reductive ring-opening reactions

Starting compounds	$3LiAlH_4$–$AlCl_3$ (%)		$BH_3{\cdot}Me_3N$–$AlCl_3$ (%)	
	4-ONAP/6-OH	6-ONAP/4-OH	4-ONAP/6-OH	6-ONAP/4-OH
7	97	3	6.9	93.1
11	89.7	10.3	6.9	93.1
12	100	0	10.5	89.5
22	96.5	3.5	4.8	95.2
23	96.1	3.9	6.9	93.1
24	94.4	5.6	5.2	94.8

ratios being ≥9:1. The $Et_3SiH/TiCl_4$ and the $BH_3{\cdot}THF/Bu_2BOTf$ reagents gave rise to the formation of 4-OBn ethers, the latter one, however, provided mixtures, occasionally. All other reagents resulted in 6-*O*-benzyl ethers, but Et_3SiH–CF_3COOH[27] did not work in the galactopyranoside series.

The ether substituted 4,6-*O*-(2-naphthyl)methylene acetals (**7**, **11**, **12**, **22**–**24**) were cleaved by $LiAlH_4$–$AlCl_3$ reagent under very mild conditions, with only 3 equivalents of AlH_3 ($3LiAlH_4+AlCl_3$), at room temperature in dichloromethane/diethyl ether (1:1) solution. The reaction time varied between 20 min and 3 h. The regioselectivity was better than 94:6 (Table 5, determined by HPLC), favouring the 4-*O*-NAP ether (**26**, **28**, **35**–**37**, Fig. 3). The allyl glucoside **11** could be cleaved with slightly lower regioselectivity to **27** (~90%). These results demonstrated that the method is equally useful both in the gluco- and in the galacto series.

Fully substituted 4,6-*O*-(2-naphthyl)methylene acetals (**7**, **11**–**15** and **22**–**24**) in both series were treated with 6 equiv. of $BH_3{\cdot}Me_3N$–$AlCl_3$ reagent in abs. THF at room temperature to give rise to the 6-ONAP ethers (**29**–**34** and **38**–**40**), the regioselectivities being better than 93:7, except for **12** (~90%). Hydrogenolysis experiments on **11** and **12** indicated, that the aglycon has greater influence on the regioselectivity in the glucoside series, than in the galactoside series, using either $LiAlH_4$–$AlCl_3$ or $BH_3{\cdot}Me_3N$–$AlCl_3$ reagents. The regioselectivity of the ring cleavage reactions with $Me_3N{\cdot}BH_3$–$AlCl_3$ was somewhat higher for the galactopyranoside derivatives, than for the glucopyranosides.

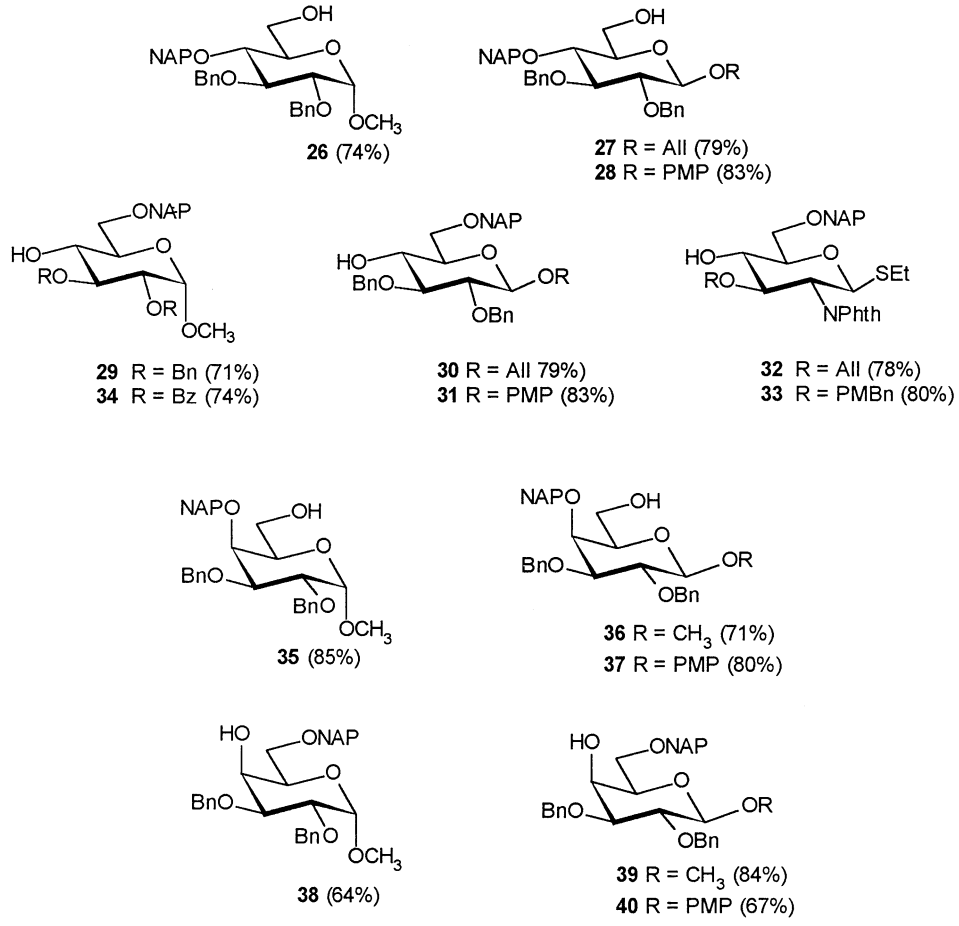

Figure 3. Hydrogenolytic products of the (2-naphthyl)methylene acetals of hexopyranosides.

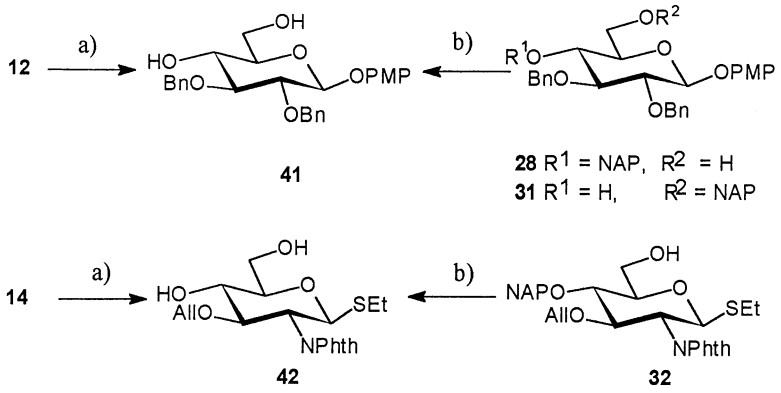

Figure 4. Reaction conditions: (a) DDQ (0.4 equiv.) in CH_3CN/H_2O (9:1), 2–3 h (79–83%); (b) DDQ (1.2 equiv.) in CH_2Cl_2/MeOH (4:1), 1 drop of water, 30–60 min (80–82%).

It is worth mentioning that the cleavage of **15** using $BH_3{\cdot}Me_3N-AlCl_3$ reagent gave ethyl 2-deoxy-6-*O*-(2-naphthyl)methyl-3-*O*-(*p*-methoxy)benzyl-2-phthalimido-1-thio-β-D-glucopyranoside (**33**) in a yield of 87%, without appreciable loss of the sensitive *p*-methoxybenzyl group.

Treatment of **7** and **13** with $NaCNBH_3$–HCl (12 equiv.) in THF, resulted in the formation of the 6-ONAP ethers **29** and **34** in a ratio of 91:9. The product distribution of the ring opening reaction was determined by HPLC and the data are presented in Table 5.

The structures of the ONAP ethers are evident from ^{13}C NMR data. Complete ^1H and ^{13}C NMR assignments were accomplished for all new compounds (Table 1–4). The ^{13}C α-shifts for the ONAP ethers are generally ~+7 ppm. It is noteworthy, that compound **32** and **33** showed unusual high field chemical shifts for C-4. We could not found completely assigned ^{13}C NMR data for related compounds in the literature. On the basis of the skeleton chemical shift values of ethyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside[31] and 3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide[32] ~79.5–77.4 ppm chemical shifts can be assigned as C-4, similarly to our observetion for **32** and **33**.

We also investigated the stability and the compatibility of the new acetals and the NAP ethers with other generally used protecting groups. Alkylation, acylation or silylation can be achieved in high yield in the presence of the (2-naphthyl)methylene acetals.[23]

2.3. Removal of the 2-(naphthyl)methylene acetals and NAP ethers

The removal of isopropylidene, benzylidene as well as dithioacetal protecting groups of sugars by DDQ has been reported.[33] The new acetal blocking group reported here can also be removed by using DDQ at room temperature, in a relatively short time (2–3 h); the yields are nearly quantitative (**12→41** and **14→42**). These reactions required 0.4 equiv. of freshly crystallized DDQ in acetonitrile/water (9:1) solution (Fig. 4).

The NAP ethers can also be cleaved in the presence of a variety of blocking groups (acetyl, pivaloyl, NPhth, benzyl and benzylidene).[17,18] We have found that DDQ smoothly removed the NAP group, while other protecting groups (benzoyl, TBDMS) survived.[23] Treatment of **28** or **31** with 1.2 equiv. of DDQ in CH_2Cl_2/MeOH (4:1) yielded **41**, respectively, in 30 min. Similarly, compound **32** resulted in the diol **42** (Fig. 4).

3. Experimental

3.1. General methods

Optical rotations were measured at room temperature with a Perkin–Elmer 241 automatic polarimeter. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. TLC was performed on Kieselgel 60 F_{254} (Merck) with detection by charring with 50% aqueous sulfuric acid. Column chromatography was performed on Silica Gel 60 (E. Merck 0.062–0.200 nm). The organic solutions were dried over $MgSO_4$, and concentrated in vacuum. The ^1H (200, 360 and 500 MHz) and ^{13}C NMR (50.3, 90.54, 125.76 MHz) spectra were recorded with Bruker WP-200SY, Bruker AM-360 and Bruker DRX-500 spectrometers for solutions in $CDCl_3$ or in D_2O. Internal references: TMS (0.00 ppm for ^1H), $CDCl_3$ (77.00 ppm for ^{13}C). Single crystal of **25**, suitable for X-ray diffraction measurement was obtained after recrystallization from EtOAc–*n*hexane. X-Ray diffraction data were collected at 293 (1) K, Enraf Nonius MACH3 diffractometer, Mo Kα radiation λ=0.71073 Å. Colourless block crystals (0.68×0.44×0.28 mm^3) of $C_{22}H_{24}O_8$, M=416.41, monoclinic, a=15.580 (8) Å, b=8.894 (6) Å, c=16.232 (6) Å, β=101.7 (1)°, V=2203 (2) $Å^3$, Z=4, space group: $P2_1$, ρ_{calc}=1.256 g cm^{-3}. $\omega-2\theta$ motion, θ_{max}=26°, 4586 measured, 3179 reflections were unique with $I>2\sigma(I)$, decay: 5%. The structure was solved using the SIR-92 software[34] and refined on F^2 using SHELX-97[35] program, publication material was prepared with the WINGX-97 suite,[36] $R(F)$= 0.0676 and $wR(F^2)$=0.2137 for 4586 reflections, 541 parameters.[37] Residual electron density: 0.502/−0.312 e $Å^{-3}$.

A Hewlett–Packard 1090 series II Liquid Chromatograph equipped with a diode array detector (DAD), an automatic samples and Chem Station were used for the separation experiments. The separation was performed using a LiChrospher Si-60 (250×4 mm^2) 5 mm column. Hexane/

ethyl acetate mixture was used as eluent. The effluent was monitored for UV active groups at 270 nm. The component ratio was given on the basis of the Area% of HPLC analysis.

3.2. General method A for the preparation of 4,6-*O*-(2-naphthyl)methylene acetals of hexopyranosides (6–10, 19–21)

To a solution of starting hexopyranoside in dry DMF (0.01 mol in 3–5 ml) 2-naphthaldehyde dimethyl acetal (1.2 equiv.) and catalytic amount of *p*-toluenesulfonic acid were added. The reaction mixture was stirred at room temperature for 24 h, then neutralized with triethylamine and evaporated in vacuo. The residue was dissolved in dichloromethane, washed with water (3×50 ml), dried and evaporated. The crude product was purified by crystallization.

In large scale (0.03 mol and above), the reaction mixture was poured into water, the precipitated product was filtered off and washed with water until neutral. The excess of the reagent was removed by successive washing with hexane, then the crude product was crystallized.

3.3. General method B for the alkylation of 4,6-*O*-(2-naphthyl)methylene acetals of hexopyranosides (7, 11, 12, 14, 15, 22–24)

To a solution of the starting acetal compound in dry DMF (0.01 mol in 10 ml) 80% NaH was added at 0°C (1.5 equiv./OH) and stirred for 30 min. Then alkyl bromide/chloride (1.2 equiv./OH) was added to the mixture and stirred until the t.l.c. showed complete conversion (1–2 h). After usual work-up procedure the residue was purified by crystallization or column chromatography.

3.4. General method C for the hydrogenolysis of 4,6-*O*-(2-naphthyl)methylene acetals of hexopyranosides with $LiAlH_4$–$AlCl_3$ (26–28, 35–37)

To a stirred solution of the starting acetal compound (0.01 mol) and $LiAlH_4$ (4.5 equiv.) in dry CH_2Cl_2/Et_2O (2:1, 15 ml), $AlCl_3$ in Et_2O (1.5 equiv. in 10 ml) was added dropwise at room temperature. After complete conversion (20 min–2 h) 2–3 ml of ethyl-acetate and 3–5 drops of water were added, the mixture was diluted with ethyl acetate, washed with water (3×50 ml), dried and concentrated. The residue was purified by crystallization or column chromatography.

3.5. General method D for the hydrogenolysis of 4,6-*O*-(2-naphthyl)methylene acetals of hexopyranosides with $Me_3N{\cdot}BH_3$–$AlCl_3$ (29–33, 38–40)

The mixture of the starting acetal compound (0.01 mol), 4 Å molecular sieves (2 g) and $Me_3N{\cdot}BH_3$ (6 equiv.) in dry THF (30 ml) was stirred for 30 min at room temperature, then $AlCl_3$ (6 equiv.) was added. After complete conversion (2–3 h) the mixture was filtered through a layer of Celite, diluted with CH_2Cl_2, washed with water, dried, concentrated and co-evaporated three times with MeOH.

3.6. General method E for the removal of 4,6-*O*-(2-naphthyl)methylene acetals of hexopyranosides

To a solution of starting acetal compound in acetonitrile/water 9:1 (10 ml/100 mg) was added freshly crystallized DDQ (0.4 equiv.). The reaction mixture was stirred at room temperature for several hours. After complete conversion the mixture was evaporated in vacuo, and the residue was purified by column chromatography.

3.7. General method F for the removal of (2-naphthyl)-methyl ether group of hexopyranosides

To a solution of starting NAP-ether in dichloromethane/methanol 4:1 (1–2 ml/100 mg) freshly crystallized DDQ (1.2 equiv.) and one drop of water were added, and the mixture was stirred at room temperature. After complete conversion (30–60 min) the mixture was evaporated in vacuo, and the residue was purified by column chromatography.

3.7.1. Methyl 4,6-*O*-(2-naphthyl)methylene-α-D-glucopyranoside (6). Compound **1** was converted by method A to give **6** (91.5%) as a white solid, mp 193–194°C (from EtOH), $[\alpha]_D$=+99.30 (*c* 0.50, chloroform); ν_{max} (KBr) 3464, 2956, 1344, 1128, 1072, 1056, 808, 756, 484 cm^{-1}; ^1H NMR δ (500 MHz, $CDCl_3$) 7.95–7.40 (7H, aromatic); ^{13}C NMR δ (125 MHz, $CDCl_3$) 134.4, 133.7, 132.8 (Cq, aromatic), 128.3, 128.1, 127.6, 126.4, 126.1, 125.8, 123.7 (CH, aromatic). Anal. calcd for $C_{18}H_{20}O_6$: C 65.05, H 6.07. Found: C 65.01, H 6.10.

3.7.2. Methyl 2,3-di-*O*-benzyl-4,6-*O*-(2-naphthyl)methylene-α-D-glucopyranoside (7). Compound **2**[38] was converted by method A to give **7** (94%) as white needles, mp 118–119°C (from EtOH), $[\alpha]_D$=−54.80 (*c* 0.33, chloroform).

Compound **7** was also prepared from **6** by method B using benzyl bromide, as the reagent. ν_{max} (KBr) 2970, 2914, 1454, 1386, 1088, 1052, 854, 792, 762, 474 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$) 8.05–7.20 (17H, m, aromatic); ^{13}C NMR δ (50 MHz, $CDCl_3$) 138.7, 138.1, 134.7 (2×), 133.5, 132.8 (C_q, aromatic), 128.4-123.6 (CH, aromatic). Anal. calcd for $C_{32}H_{32}O_6$: C 74.97, H 6.30. Found: C 75.02, H 6.22.

3.7.3. Allyl 4,6-*O*-(2-naphthyl)methylene-β-D-glucopyranoside (8). Compound **3**[39] was converted by method A to give **8** (87.2%) as white needles, mp 162–163°C (from EtOH), $[\alpha]_D$=−45.40 (*c* 0.61, chloroform). Anal. calcd for $C_{20}H_{22}O_6$: C 67.01, H 6.19. Found: C 67.11, H 6.13.

3.7.4. *p*-Methoxyphenyl 4,6-*O*-(2-naphthyl)methylene-β-D-glucopyranoside (9). Compound **4**[40] was converted by method A to give **9** (92%)as white crystals, mp 207–210°C (from EtOH), $[\alpha]_D$=−34.13 (*c* 0.15, chloroform); ν_{max} (KBr) 3404, 2888, 1508, 1402, 1366, 1220, 1176, 1082, 824, 760, 480 cm^{-1}; Anal. calcd for $C_{24}H_{24}O_7$: C 67.91, H 5.70. Found: C 67.71, H 5.66.

3.7.5. Ethyl 2-deoxy-4,6-*O*-(2-naphthyl)methylene-2-phthalimido-1-thio-β-D-glucopyranoside (10). Compound

5[41] was converted by method A to give **10** (91%) as white needles, mp 105–108°C (from EtOH), $[\alpha]_D=-11.78$ (*c* 0.24, chloroform); ν_{max} (KBr) 3442, 2970, 2872, 1774, 1714, 1626, 1388, 1092, 748, 480 cm^{-1}; Anal. calcd for $C_{27}H_{25}O_6NS$: C 65.97, H 5.13, N 2.85, S 6.52. Found: C 66.11, H 5.16, N 2.91, S 6.47.

3.7.6. Allyl 2,3-di-*O*-benzyl-4,6-*O*-(2-naphthyl)methylene-β-D-glucopyranoside (11). Compound **8** was converted by method B using benzyl bromide as the reagent to give the colourless syrupy **11** (91.4% after column chromatography in hexane/EtOAc, 8:2), $[\alpha]_D=-52.41$ (*c* 0.41, chloroform). Anal. calcd for $C_{34}H_{44}O_6$: C 74.42, H 8.08. Found: C 74.70, H 8.06.

3.7.7. *p*-Methoxyphenyl 2,3-di-*O*-benzyl-4,6-*O*-(2-naphthyl)methylene-β-D-glucopyranoside (12). Compound **9** was converted by method B using benzyl bromide as the reagent to give **12** (94%) as white needles, mp 180–183°C (from EtOH), $[\alpha]_D=-31.1$ (*c* 0.66, chloroform); ν_{max} (KBr) 3432, 2876, 1508, 1244, 1092, 1030, 798, 746, 472 cm^{-1}; Anal. calcd for $C_{38}H_{36}O_7$: C 75.48, H 6.00. Found: C 75.81, H 6.02.

3.7.8. Methyl 2,3-di-*O*-benzoyl-4,6-*O*-(2-naphthyl)-methylene-α-D-glucopyranoside (13). To a stirred solution of compound **6** (1.66 g, 5 mmol) in dry pyridine (5 ml) benzoyl chloride (1.74 ml, 15 mmol) was added at 0°C. After usual work-up procedure the residue was crystallized from EtOH to give **13** (81.5%) as white needles, mp 216–217°C, $[\alpha]_D=+35.61$ (*c* 0.40, chloroform). ^1H NMR δ (500 MHz, $CDCl_3$) 8.10–7.80 (17H, m, aromatic); ^{13}C NMR δ (125 MHz, $CDCl_3$) 134.3, 133.6 (C_q, aromatic), 133.3, 133.0 (CH, aromatic), 132.8 (C_q, aromatic), 130.0, 129.7, 129.0 (C_q, aromatic), 128.4, 128.3, 128.2, 128.0, 127.6, 126.3, 126.0, 125.7, 123.7 (CH, aromatic); ν_{max} (KBr) 2974, 2966, 2930, 1728, 1600, 1450, 1276, 1098, 1026, 806, 714, 486 cm^{-1}; MALDI-TOF measurment for $C_{32}H_{28}O_8$: 563.02 $[M+Na]^+$, calcd: 563.17.

3.7.9. Ethyl 3-*O*-allyl-2-deoxy-4,6-*O*-(2-naphthyl)methylene-2-phthalimido-1-thio-β-D-gluco-pyranoside (14). Compound **10** was converted by method B using allyl bromide as the reagent to give **14** (88.3% after column chromatography in hexane/EtOAc, 7:3) as a colourless syrup, $[\alpha]_D=-5.49$ (*c* 0.50, chloroform). Anal. calcd for $C_{30}H_{29}O_6NS$: C 67.78, H 5.50, N 2.63, S 6.03. Found: C 67.91, H 5.51, N 2.68, S: 6.05.

3.7.10. Ethyl 2-deoxy-3-*O*-(*p*-methoxybenzyl)-4,6-*O*-(2-naphthyl)methylene-2-phthalimido-1-thio-β-D-gluco-pyranoside (15). Compound **4** was converted by method B using *p*-methoxybenzyl chloride as the reagent to give **11** (86.5%) as white needles, mp 131–133°C (from EtOH), $[\alpha]_D=+49.09$ (*c* 0.40, chloroform); ν_{max} (KBr) 3456, 2926, 1714, 1388, 1066, 720, 484 cm^{-1}; MALDI-TOF measurment for $C_{35}H_{33}O_7NS$: 634.13 $[M+Na]^+$, calcd: 634.18.

3.7.11. Methyl 4,6-*O*-(2-naphthyl)methylene-α-D-galacto-pyranoside (19). Compound **16** was converted by method A to give **19** (91.5%) as white solid, mp 179–182°C (from EtOH), $[\alpha]_D=+99.46$ (*c* 0.48, chloroform); ν_{max} (KBr) 3422, 2362, 1344, 1092, 1044, 794, 778, 478 cm^{-1}; Anal. calcd for $C_{18}H_{20}O_6$: C 65.05, H 6.07. Found: C 64.84, H 6.01.

3.7.12. Methyl 4,6-*O*-(2-naphthyl)methylene-β-D-galactopyranoside (20). Compound **17** was converted by method A to give **20** (92.6%) as white solid, mp 223–224°C (from EtOH), $[\alpha]_D=-36.75$ (*c* 0.22, chloroform); ν_{max} (KBr) 3424, 2858, 1630, 1366, 1174, 1078, 1050, 1002, 822, 780, 480 cm^{-1}. Anal. calcd for $C_{18}H_{20}O_6$: C 65.05, H 6.07. Found: C 64.97, H 6.11.

3.7.13. *p*-Methoxyphenyl 4,6-*O*-(2-naphthyl)methylene-β-D-galactopyranoside (21). Compound **18**[42] was converted by method A to give **21** (91%) as white solid, mp 254–257°C (from EtOH), $[\alpha]_D=-85.38$ (*c* 0.22, DMSO); ν_{max} (KBr) 3428, 2862, 1508, 1402, 1366, 1220, 1176, 1082, 824, 760, 480 cm^{-1}. Anal. calcd for $C_{24}H_{24}O_7$: C 67.91, H 5.70. Found: C 68.24, H 5.80.

3.7.14. Methyl 2,3-di-*O*-benzyl-4,6-*O*-(2-naphthyl)-methylene-α-D-galactopyranoside (22). Compound **19** was converted by method B to give **22** (93.7%) as white needles, mp 122–124°C (from EtOH), $[\alpha]_D=+89.23$ (*c* 0.21, chloroform); ν_{max} (KBr) 3458, 2908, 1452, 1366, 1098, 1056, 1026, 820, 780, 474 cm^{-1}; Anal. calcd for $C_{32}H_{32}O_6$: C 74.98, H 6.29. Found: C 75.34, H 6.21.

3.7.15. Methyl 2,3-di-*O*-benzyl-4,6-*O*-(2-naphthyl)-methylene-β-D-galactopyranoside (23). Compound **20** was converted by method B to give **23** (94.2%) as white needles, mp 213–215°C (from EtOAc), $[\alpha]_D=+76.75$ (*c* 0.45, chloroform); ν_{max} (KBr) 3458, 2860, 1402, 1388, 1180, 1114, 1062, 822, 696, 476 cm^{-1}; Anal. calcd for $C_{32}H_{32}O_6$: C 74.98, H 6.29. Found: C 74.84, H 6.23.

3.7.16. *p*-Methoxyphenyl 2,3-di-*O*-benzyl-4,6-*O*-(2-naphthyl)methylene-β-D-galactopyranoside (24). Compound **21** was converted by method B to give **24** (90.6%) as white needles, mp 204–206°C (from EtOAc), $[\alpha]_D=-1.18$ (*c* 0.50, chloroform); ν_{max} (KBr) 3440, 3030, 1630, 1508, 1226, 1066, 1028, 824, 736, 478 cm^{-1}; MALDI-TOF measurment for $C_{38}H_{36}O_7$: 627.08, calcd: 627.24.

3.7.17. Methyl 2,3-di-*O*-acetyl-4,6-*O*-(2-naphthyl)methylene-α-D-galactopyranoside (25). To a stirred solution of compound **19** (500 mg) in dry pyridine (2 ml), acetic anhydride was added (1 ml). After usual work-up procedure the crystalline residue was recrystallized from EtOAc–*n*hexane to give **25** (83%) as white crystals, mp 184–186°C, $[\alpha]_D=+207.46$ (*c* 0.35, chloroform); ν_{max} (KBr) 3458, 2938, 1744, 1370, 1246, 1176, 1050, 990, 866, 826, 776, 482 cm^{-1}; MALDI-TOF measurment for $C_{22}H_{24}O_8$: 438.66 $[M+Na]^+$, calcd: 439.13.

3.7.18. Methyl 2,3-di-*O*-benzyl-4-*O*-(2-naphthyl)methylene-α-D-glucopyranoside (26). Compound **7** was converted by method C to give **26** (74%) as white needles, mp 68–73°C (from *c*-hexane), $[\alpha]_D=+1.07$ (*c* 0.37, chloroform). ^1H NMR δ (200 MHz, $CDCl_3$) 7.85–7.20 (17H, m, aromatic); ^{13}C NMR δ (50 MHz, $CDCl_3$) 138.7, 138.0, 135.5 (2×), 133.2, 132.9 (Cq, aromatic), 128.4–125.8 (CH, aromatic). Anal. calcd for $C_{32}H_{34}O_6$: C 74.69, H 6.66. Found: C 74.34, H 6.51.

3.7.19. Allyl 2,3-di-*O*-benzyl-4-*O*-(2-naphthyl)methyl-β-D-glucopyranoside (27). Compound **11** was converted by method C to give **27** (79%) as white needles, mp 105–108°C (from Et_2O), $[\alpha]_D=-20.58$ (*c* 0.19, chloroform). Anal. calcd for $C_{34}H_{36}O_6$: C 75.53, H 6.71. Found: C 75.14, H 6.67.

3.7.20. *p*-Methoxyphenyl 2,3-di-*O*-benzyl-4-*O*-(2-naphthyl)methyl-β-D-glucopyranoside (28). Compound **12** was converted by method C to give **28** (83%) as white needles, mp 154–155°C (from Et_2O), $[\alpha]_D=-19.23$ (*c* 0.33, chloroform); ν_{max} (KBr) 3438, 2912, 1632, 1508, 1232, 1068, 820, 750, 734, 476 cm^{-1}; MALDI-TOF measurment for $C_{38}H_{38}O_7$: 629.09 $[M+Na]^+$, calcd: 629.25.

3.7.21. Methyl 2,3-di-*O*-benzyl-6-*O*-(2-naphthyl)methyl-α-D-glucopyranoside (29). Compound **7** was converted by method D to give syrupy **29** (71%), $[\alpha]_D=+8.21$ (*c* 0.53, chloroform). ^1H NMR δ (500 MHz, $CDCl_3$) 7.85–7.20 (17H, m, aromatic); ^{13}C NMR δ (125 MHz, $CDCl_3$) 138.7, 138.0, 135.4 (2×), 133.1, 132.9 (C_q, aromatic), 128.5–125.5 (CH, aromatic). Anal. calcd for $C_{32}H_{34}O_6$: C 74.69, H 6.66. Found: C 74.93, H 6.57.

3.7.22. Allyl 2,3-di-*O*-benzyl-6-*O*-(2-naphthyl)methyl-β-D-glucopyranoside (30). Compound **11** was converted by method D to give **30** (79%) as white needles, mp 66–68°C (from EtOH), $[\alpha]_D=-27.99$ (*c* 0.18, chloroform). Anal. calcd for $C_{34}H_{36}O_6$: C 75.53, H 6.71. Found: C 75.97, H 6.68.

3.7.23. *p*-Methoxyphenyl 2,3-di-*O*-benzyl-6-*O*-(2-naphthyl)methyl-β-D-glucopyranoside (31). Compound **12** was converted by method D to give **31** (83%) as white needles, mp 119–120°C (from EtOH), $[\alpha]_D=-36.79$ (*c* 0.55, chloroform); ν_{max} (KBr) 3474, 3060, 3024, 1506, 0384, 1230, 1086, 822, 754, 744 cm^{-1}; MALDI-TOF measurment for $C_{38}H_{38}O_7$: 629.08 $[M+Na]^+$, calcd: 629.25.

3.7.24. Ethyl 3-*O*-allyl-2-deoxy-6-*O*-(2-naphthyl)methyl-2-phthalimido-1-thio-β-D-glucopyranoside (32). Compound **14** was converted by method D to give syrupy **32** (78%), $[\alpha]_D=+12.33$ (*c* 0.83, chloroform). Anal. calcd for $C_{30}H_{31}O_6NS$: C 67.52, H 5.86, N 2.62, S 6.01. Found: C 67.47, H 5.88, N 2.60, S 6.08.

3.7.25. Ethyl 2-deoxy-3-*O*-(*p*-methoxybenzyl)-6-*O*-(2-naphthyl)methyl-2-phthalimido-1-thio-β-D-glucopyranoside (33). Compound **15** was converted by method D to give syrupy **33** (80%), $[\alpha]_D=+41.33$ (*c* 0.21, chloroform); MALDI-TOF measurement for $C_{35}H_{35}O_7NS$: 636.11 $[M+Na]^+$, calcd: 636.23.

3.7.26. Methyl 2,3-di-*O*-benzoyl-6-*O*-(2-naphthyl)-methyl-α-D-glucopyranoside (34). Compound **13** was converted by method D to give syrupy **34** (74%), $[\alpha]_D=+109.95$ (*c* 0.67, chloroform); MALDI-TOF measurement for $C_{32}H_{30}O_8$: 567.03, $[M+Na]^+$, calcd: 567.19.

3.7.27. Methyl 2,3-di-*O*-benzyl-4-*O*-(2-naphthyl)methyl-α-D-galactopyranoside (35). Compound **22** was converted by method C to give syrupy **35** (85%), $[\alpha]_D=-3.95$ (*c* 0.50, chloroform). Anal. calcd for $C_{32}H_{34}O_6$: C 74.69, H 6.66. Found: C 74.98, H 6.69.

3.7.28. Methyl 2,3-di-*O*-benzyl-4-*O*-(2-naphthyl)methyl-β-D-galactopyranoside (36). Compound **23** was converted by method C to give syrupy **36** (71%), $[\alpha]_D=-20.05$ (*c* 0.37, chloroform). Anal. calcd for $C_{32}H_{34}O_6$: C 74.69, H 6.66. Found: C 75.14, H 6.61.

3.7.29. *p*-Methoxyphenyl 2,3-di-*O*-benzyl-4-*O*-(2-naphthyl)methyl-β-D-galactopyranoside (37). Compound **24** was converted by method C to give **37** (80%) as white needles, mp 153–155°C (from EtOAc–*n*hexane), $[\alpha]_D=-37.16$ (*c* 0.26, chloroform); ν_{max} (KBr) 3384, 2870, 1508, 1228, 1084, 1058, 820, 744, 698, 476 cm^{-1}; MALDI-TOF measurment for $C_{38}H_{38}O_7$: 629.11 $[M+Na]^+$, calcd: 629.25.

3.7.30. Methyl 2,3-di-*O*-benzyl-6-*O*-(2-naphthyl)methyl-α-D-galactopyranoside (38). Compound **22** was converted by method D to give syrupy **38** (64%), $[\alpha]_D=+24.11$ (*c* 0.81, chloroform). Anal. calcd for $C_{32}H_{34}O_6$: C 74.69, H 6.66. Found: C 75.23, H 6.68.

3.7.31. Methyl 2,3-di-*O*-benzyl-6-*O*-(2-naphthyl)methyl-β-D-galactopyranoside (39). Compound **23** was converted by method D to give syrupy **39** (84%), $[\alpha]_D=0$ (*c* 0.37, chloroform). Anal. calcd for $C_{32}H_{34}O_6$: C 74.69, H 6.66. Found: C 74.14, H 6.62.

3.7.32. *p*-Methoxyphenyl 2,3-di-*O*-benzyl-6-*O*-(2-naphthyl)methyl-β-D-galactopyranoside (40). Compound **24** was converted by method D to give **40** (67%) as white needles, mp 86–88°C (from EtOH), $[\alpha]_D=-6.39$ (*c* 0.31, chloroform); ν_{max} (KBr) 3446, 2910, 1506, 1364, 1216, 1096, 1062, 826, 740, 696, 474 cm^{-1}; MALDI-TOF measurment for $C_{38}H_{38}O_7$: 629.11 $[M+Na]^+$, calcd: 629.25.

3.7.33. *p*-Methoxyphenyl 2,3-di-*O*-benzyl-β-D-glucopyranoside (41). Compound **12** was converted by method E to give **41** (79%) as white needles, mp 96–98°C (from EtOH), $[\alpha]_D=-25.03$ (*c* 0.30, chloroform). Compound **41** was also prepared by method F, starting from **28** or **31**, respectively. Anal. calcd for $C_{27}H_{30}O_7$: C 69.51, H 6.48. Found: C 68.74, H 6.49.

3.7.34. Ethyl 3-*O*-allyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (42). Compound **14** was converted by method E to give syrupy **42** (83%), $[\alpha]_D=+21.97$ (*c* 3.54, chloroform). Compound **42** was also prepared by method F, starting from **32**. Anal. calcd for $C_{19}H_{23}O_6NS$: C 58.00, H 5.89, N 3.56, S 8.15. Found: C 57.74, H 5.94, N 3.66, S 8.19.

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