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Synthesis of O-glycopyranosyl heterocyclic ketene aminals and their use as glycosyl donors

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Abstract

The synthesis and reactions of glycopyranosyl heterocyclic ketene aminals were investigated. Under mild conditions, the benzoyl-substituted heterocyclic ketene aminals **3** or **4** underwent O-glycosylation with tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**1**) using mercuric cyanide or silver trifluoromethanesulfonate as catalyst in acetonitrile to give O-glycopyranosyl heterocyclic ketene aminals **5–7** and **8–11**, respectively. The β-anomers were the sole products. By the O-glycosylation of heterocyclic ketene aminals with **1**, the O-attack of heterocyclic ketene aminals was carried out for the first time. Some of **5–11** in the synthesis of oligosaccharides **14** and **15** can provide a valuable leaving group at the anomeric position of the glycopyranosyl ring. Compounds **6c** or **10c** may be potentially useful as glycosyl donors in the synthesis of oligosaccharides. © 1996 Elsevier Science Ltd.

Keywords: Synthesis; Glycosylation; Heterocyclic ketene aminals

1. Introduction

Owing to the important roles that carbohydrates exhibit in biological recognition processes [1], the synthesis of these compounds is receiving increased attention. Many advances in the synthesis of carbohydrates have been made by the use of several methods [2], but there are no proven universal methods for glycosylation in this field. The search for highly stereoselective and high-yielding synthetic methods for oligosaccharide synthesis is still one of the important topics of carbohydrate chemistry.

Heterocyclic ketene aminals are a kind of ambident nucleophile [3] that show very intriguing structural characteristics. Due to the tautomerization (Scheme 1), they may

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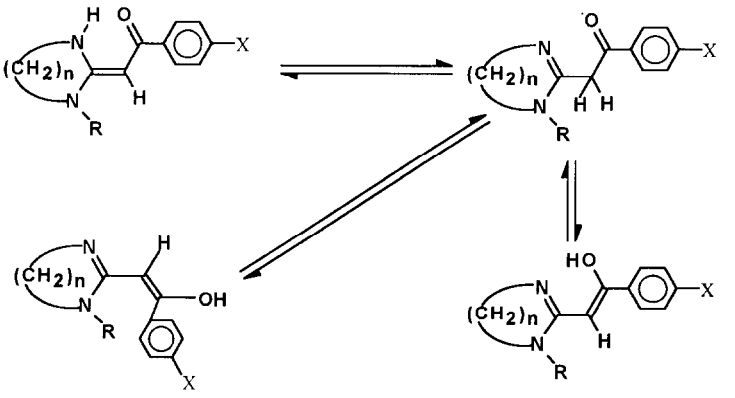


I (*E*-form) II (*Z*-form)

n = 2, 3 R = H, CH_3 X = H, CH_3O, CH_3, Cl, Br

Scheme 1.

exist in different tautomers (see Scheme 1), and the protected glycosyl donor may regioselectively attack them in three different ways, via C-, N- or O-attack, to give different products. The synthesis and reactions of heterocyclic ketene aminals have been extensively studied [4–18], but the glycosylation of heterocyclic ketene aminals has not been reported. Therefore, glycopyranosyl heterocyclic ketene aminals **5–11** were synthesized [1]. Additionally, **5–11** were further used as glycosyl donors in the synthesis of disaccharides **14** or **15**. We are delighted to report that some of compounds **5–11** demonstrate an activatable leaving group at the anomeric position of the glycosyl ring. Especially **6c** or **10c** can highly stereoselective react with acceptor **12** or **13** to give an α-glycosidic linkage in high yield and under mild conditions. Here we wish to report the results of synthesis of **5–11** and their use as glycosyl donors.

2. Results and discussion

Heterocyclic ketene aminals **2–4** were prepared from benzoyl-substituted ketene mercaptals by reaction with the corresponding diamines or methyl-substituted diamines by the literature method [20]. Either **3** or **4** reacted readily with tetra-*O*-acetyl-α-D-glucopyranosyl bromide [21] using mercuric cyanide or silver trifluoromethanesulfonate as catalyst in anhydrous acetonitrile to give the sole compounds **5–7** or **8–11** in good to excellent yields, respectively. But, 2-(benzoylmethylene)-1,3-dimethylimidazolidines (**2**) failed to react with **1** under similar conditions, with only starting material being recovered after a long reaction period. The reaction conditions, yields, and melting points of **5–7** and **8–11** are listed in Tables 1 and 2, respectively.

[1] The preliminary results of the glycosylation of heterocyclic ketene aminals with tetra-*O*-acetyl-α-D-glucopyranosyl bromide in the presence of mercuric cyanide have been published in a communication [19].

Table 1
Reaction conditions, yields, and melting points of products **5–7**

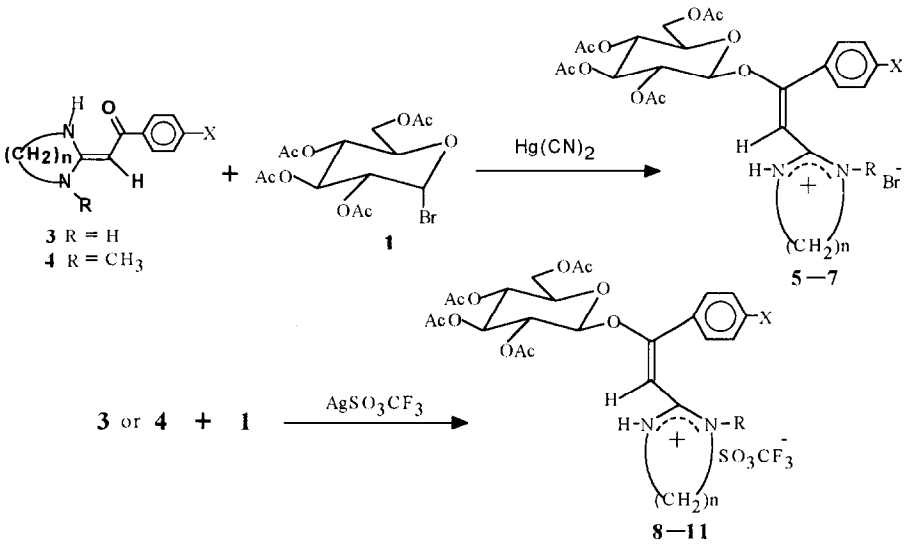
Product	Reaction conditions			Yield [b] (%)	mp (°C)
	method [a]	temp. (°C)	time (h)		
5a	A	RT	24	69	83–85
	B	RT	20	74	
5b	A	RT	30	68	91–93
	B	10	25	69	
5c	A	RT	30	82	95–97
	B	10	24	96	
5d	A	RT	30	83	88–90
	B	15	24	82	
6a	A	RT	38	70	101–103
	B	10	30	76	
6b	A	RT	30	66	82–84
	B	15	30	91	
6c	A	RT	24	79	97–99
	B	RT	24	75	
6d	A	RT	28	71	87–89
	B	10	24	89	
7c	A	RT	30	10	113–116
	B	RT	48	0	

[a] A: $Hg(CN)_2$–CaH_2 in CH_3CN; B: $Hg(CN)_2$–4AMS in CH_3CN.
[b] Isolated yield based on compound **3** or **4**.

Table 2
Reaction conditions, yields, and melting points of products **8–11**

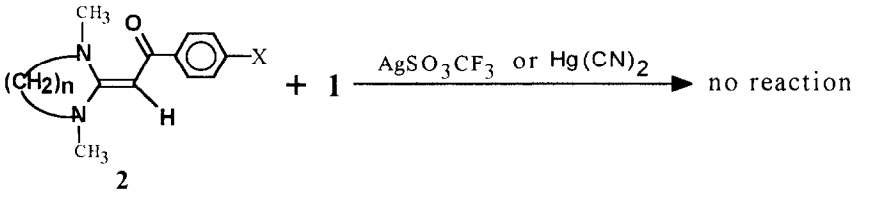
Product	Reaction conditions [a]		Yield [b] (%)	mp (°C)
	temp (°C)	time (h)		
8a	22	15	72	79–81
8b	12	18	71	86–88
8c	12	10	79	90–92
8d	10	12	81	94–95
9b	12	16	72	77–78
9c	10	12	83	102–104
9d	12	10	81	94–96
9e	10	18	54	118–120
10a	18	16	85	75–77
10b	15	18	81	108–110
10c	11	10	91	83–85
11b	10	16	79	70–72
11c	20	10	83	133–135
11e	12	10	81	130–131

[a] $AgSO_3CF_3$ as catalyst in CH_3CN.
[b] Isolated yield based on compound **3** or **4**.



5, 7, 8, 9 n = 2; 6, 10, 11 n = 3

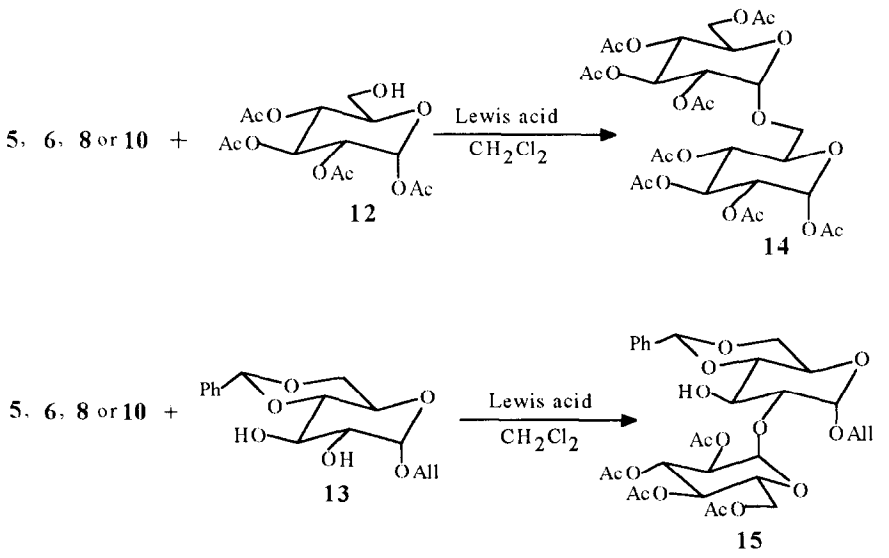
3-11	a	b	c	d	e
X	H	CH_3O	Cl	Br	CH_3



Scheme 2.

The reaction of **3** with **1** in the presence of mercuric cyanide–calcium hydride or mercuric cyanide–molecular sieve 4A (4AMS) gave **5–6** (66–96% yield). Strangely, **4** was found to be reluctant to undergo glycosylation under the same conditions, with only *E*-1-methyl-2-[1′-(2″,3″,4″,6″-tetra-*O*-acetyl-β-D-glucopyranosyl)]-*p*-chlorostyrenyl-tetrahydro imidazolium bromide (**7c**) being obtained in low yield (10%). However, reaction of either **3** or **4** with **1** in the presence of silver trifluoromethanesulfonate under milder conditions afforded the corresponding compounds **8**, **9**, **10**, and **11**, respectively, and neither C-glycosylation nor N-glycosylation was observed (see Scheme 2).

Structures for **5–11** were established on the basis of spectroscopic data and elemental analyses. Owing to the appearance of acetyl-protected glucopyranosyl group signals, as well as heterocyclic ketene aminal signals in ^{1}H NMR and ^{13}C NMR spectra, these facts were enough to prove that the glycosylation occurred between **3** or **4** with **1**. Further we observed that the IR spectra showed an NH stretching absorption band at ca. 3300 cm^{-1} and a strong carbonyl absorption for the acetyl group at ca. 1730 cm^{-1}, and that the



Scheme 3.

carbonyl absorption of the aroyl group of the heterocyclic ketene aminals at ca. 1600 cm^{-1} had disappeared. We also found the signals for two nitrogen protons (8.23–8.86 ppm) of **5**, **6**, **8** and **10** and one nitrogen proton (8.10–8.65 ppm) of **7**, **9**, and **11** and one ethylenic proton (5.65–6.15 ppm) of **5–11** in the ^1H NMR spectra. These data exclude either the N-glycosylation or C-glycosylation of **3** or **4**. The appearance of a new carbon signal (159.5–166.8 ppm) instead of the carbonyl carbon signal (ca. 180 ppm) in the ^{13}C NMR spectra unquestionably indicates that the monoglycosidated products of **3** or **4** resulted from O-glycosylation. From the NMR spectral data, the coupling constants between $H_{1''}$ and $H_{2''}$ (8.0–8.8 Hz) and chemical shifts of the $C_{1''}$ (97.1–97.7 ppm) of the glucopyranosyl ring also confirmed a β linkage of the protected glucopyranosyl group to the oxygen atom of heterocyclic ketene aminals in **5–11** [22,23]. This is the first example reported for of O-attack on heterocyclic ketene aminals by glycosyl donors.

In an attempt to use **5–11** as glycosyl donors, the reaction of **5–11** with partially protected sugar **12** or **13** for the synthesis of **14** or **15** was investigated. We found that, while **5**, **6**, **8** or **10** could react with **12** or **13** in CH_2Cl_2 using Lewis acids ($BF_3 \cdot Et_2O$ or TMSOTf) as catalyst to give **14** (36–95%) or **15** (29–90%) in different yields, respectively (see Scheme 3 and Table 3), **7**, **9** and **11** failed to react with the acceptor, apparently because of the decomposition of the *N*-methyl heterocyclic residue during the reaction. The results from Table 3 showed that glycopyranosyl *p*-chlorobenzoyl-substituted heterocyclic ketene aminals **6c** and **10c** with a very activatable, but stable, leaving group may be used as good donors to give **14** or **15** in excellent yields. From the spectroscopic data [22,24], an α-linkage for the two glycosyl rings in **14** and **15** is indicated. This may be due to the fact that they possess great steric hindrance and control the overall inversion of configuration at the anomeric center with the participa-

Table 3
Use of **5**, **6**, **8** and **10** in the synthesis of **14** and **15** [a]

Glycosyl donor	Method [b]	Reaction time (h) at RT for **14**	Yield (%) of **14** [c]	Reaction time (h) at RT for **15**	Yield (%) of **15** [c]
5a	A	4	36	3	41
	B	2	50	3	49
5b	A	3	51	2	39
	B	3	60	4	50
5c	A	3	69	1	60
	B	2	80	2	64
5d	A	2	51	3	60
	B	5	63	2	42
6a	A	2	43	3	62
	B	3	55	2	55
6b	B	4	59	1	61
6c	A	2	79	3	82
	B	2	87	3	90
6d	A	1	48	2	40
	B	4	45	5	48
8a	A	2	49	1	30
	B	3	63	2	51
8b	A	4	39	3	46
	B	1	45	2	32
8c	A	2	61	1	65
	B	1	91	2	89
8d	A	3	52	4	38
	B	5	47	2	60
10a	A	2	38	3	43
	B	1	49	2	37
10b	A	3	62	1	29
	B	2	49	2	34
10c	A	2	82	3	72
	B	2	95	1	85

[a] Only α-anomers isolated.
[b] A: $BF_3 \cdot Et_2O$ as catalyst in CH_2Cl_2; B: $AgSO_3CF_3$ as catalyst in CH_2Cl_2.
[c] Isolated yield based on compound **12** or **13**.

tion of a neighbouring group. From the above preliminary results, it is shown that some of glycopyranosyl heterocyclic ketene aminals may be good glycosyl donors that give high stereoselectivities in the synthesis of oligosaccharides. Further work is in progress on these aspects.

3. Experimental

General methods.—Melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra of $CDCl_3$ solutions were obtained on Varian Unity 200 and 300 MHz spectrometers. The chemical shifts are reported in ppm downfield from Me_4Si. J values are given in Hz. IR spectra were recorded with a Perkin–Elmer 782 spectrometer. Mass spectra were

recorded with a KYKY-ZHT-5 instrument. Elemental analyses were performed at the Analytical Laboratory of the Institute of Chemistry.

General procedure for the synthesis of compounds **5–7**.—*Method A*. To a mixture of benzoyl-substituted heterocyclic ketene aminals **3** or **4** (1 mmol) and calcium hydride (200 mg) was added 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**1**) (1.1 mmol) and mercuric cyanide (200 mg). The mixture was stirred at room temperature for 20–30 h. When TLC (10:1 $CHCl_3$–CH_3OH, silica gel) showed the absence of **3** or **4** and the presence of one new major spot. The mixture was filtered and washed with CH_2Cl_2 (10 mL). After removal of solvent, the fractionation of the residue on a column chromatography of silica gel (200–300 mesh) using the same eluant (100:1 ~ 25:1 $CHCl_3$–CH_3OH) gave pure compounds **5–7**.

Method B. The procedures are the same as method A except molecular sieve 4A (300 mg) was used instead of calcium hydride (200 mg).

*E-2-[1′-(2″,3″,4″,6″-Tetra-*O*-acetyl-β-*D*-glucopyranosyl)]-styrenyl-tetrahydroimidazolium bromide* (**5a**).—IR (KBr): 3319 (NH), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.38 (s, 2 H, NH), 7.60–7.25 (m, 5 H, Ar–H), 5.97 (s, 1 H, C=C–H), 5.21–5.00 (m, 3 H, Glu–$H_{2,3,4}$), 5.00 (d, 1 H, $J_{H1,H2}$ 8.2 Hz, Glu–H_1), 4.20–3.90 (m, 2 H, Glu–H_6), 4.09 (s, 4 H, N–CH_2CH_2–N), 3.42–3.34 (m, 1 H, Glu–H_5), 2.11, 2.08, 2.01, 1.98 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.8, 170.2, 169.6, 169.1, 166.2, 161.4, 131.6, 130.2, 129.0, 128.1, 97.2, 96.4, 72.5, 71.3, 70.6, 67.6, 61.1, 44.5, 20.9, 20.7, 20.4, 20.3; FABMS: 519 $(M–Br)^+$. Anal. Calcd for $C_{25}H_{31}BrN_2O_{10}$: C, 50.09; H, 5.21; N, 4.67. Found: C, 49.78; H, 5.60; N, 4.93.

*E-2-[1′-(2″,3″,4″,6″-Tetra-*O*-acetyl-β-*D*-glucopyranosyl)]-*p*-methoxystyrenyl-tetrahydroimidazolium bromide* (**5b**).—IR (KBr): 3322 (NH), 1730 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.69 (s, 2 H, NH), 7.44 (d, 2 H, Ar–H), 6.97 (d, 2 H, A–H), 6.02 (s, 1 H, C=C–H), 5.18–5.00 (m, 3 H, Glu–$H_{2,3,4}$), 4.90 (d, 1 H, $J_{H1,H2}$ 8.2 Hz, Glu–H_1), 4.22–3.92 (m, 2 H, Glu–H_6), 4.00 (s, 4 H, N–CH_2CH_2–N), 3.87 (s, 3 H, CH_3O), 3.48–3.38 (m, 1 H, Glu–H_5), 2.11, 2.08, 2.01, 1.99 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.8, 170.3, 169.7, 169.2, 166.7, 162.4, 162.2, 129.8, 122.0, 114.6, 97.5, 95.2, 72.8, 71.4, 71.0, 67.8, 61.2, 55.5, 44.1, 20.8, 20.6, 20.5, 20.4; FABMS: 549 $(M–Br)^+$. Anal. Calcd for $C_{26}H_{33}BrN_2O_{11}$: C, 49.61; H, 5.28; N, 4.45. Found: C, 49.16; H, 5.10; N, 4.94.

*E-2-[1′-(2″,3″,4″,6″-Tetra-*O*-acetyl-β-*D*-glucopyranosyl)]-*p*-chlorostyrenyl-tetrahydroimidazolium bromide* (**5c**).—IR (KBr): 3320 (NH), 1738 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.83 (s, 2 H, NH), 7.55–7.30 (m, 4 H, Ar–H), 6.09 (s, 1 H, C=C–H), 5.25–4.95 (m, 3 H, Glu–$H_{2,3,4}$), 4.90 (d, 1 H, $J_{H1,H2}$ 8.2 Hz, Glu–H_1), 4.18–3.95 (m, 2 H, Glu–H_6), 4.02 (s, 4 H, N–CH_2CH_2–N), 3.46–3.36 (m, 1 H, Glu–H_5), 2.19, 2.08, 2.03, 1.99 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.1, 170.2, 169.6, 169.2, 165.2, 161.7, 138.1, 129.3, 128.5, 97.3, 96.7, 72.8, 71.1, 71.0, 67.7, 61.2, 44.2, 20.8, 20.6, 20.4, 20.3; FABMS: 553 $(M–Br)^+$. Anal. Calcd for $C_{25}H_{30}BrClN_2O_{10}$: C, 47.37; H, 4.77; N, 4.42. Found: C, 46.94; H, 5.14; N, 4.16.

*E-2-[1′-(2″,3″,4″,6″-Tetra-*O*-acetyl-β-*D*-glucopyranosyl)]-*p*-bromostyrenyl-tetrahydroimidazolium bromide* (**5d**).—IR (KBr): 3325 (NH), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.86 (s, 2 H, NH), 7.63 (m, 2 H, Ar–H), 7.38 (m, 2 H, Ar–H), 6.11 (s, 1 H, C=C–H), 5.20–4.90 (m, 3 H, Glu–$H_{2,3,4}$), 4.85 (d, 1 H, $J_{H1,H2}$ 8.2 Hz, Glu–H_1),

4.18–3.92 (m, 2 H, Glu–H_6), 4.02 (s, 4 H, N–CH_2CH_2–N), 3.46–3.36 (m, 1 H, Glu–H_5), 2.20, 2.10, 2.05, 2.00 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.0, 170.2, 169.6, 169.2, 165.2, 161.7, 132.4, 129.5, 128.9, 126.6, 97.3, 96.8, 72.9, 71.1, 71.0, 67.6, 61.2, 44.2, 20.8, 20.6, 20.4, 20.3; FABMS: 597 $(M-Br)^+$. Anal. Calcd for $C_{25}H_{30}Br_2N_2O_{10}$: C, 44.26; H, 4.46; N, 4.13. Found: C, 43.72; H, 4.27; N, 3.80.

E-2-[1′-(2″,3″,4″,6″-Tetra-O-acetyl-β-D-glucopyranosyl)]-styrenyl-hexahydropyrimidinium bromide (**6a**).—IR (KBr): 3340 (NH), 1731 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.73 (s, 2 H, NH), 7.55–7.46 (m, 5 H, Ar–H), 6.15 (s, 1 H, C=C–H), 5.19–5.16 (m, 3 H, Glu–$H_{2,3,4}$), 4.88 (d, 1 H, $J_{H1,H2}$ 8.0 Hz, Glu–H_1), 4.23–3.96 (m, 2 H, Glu–H_6), 3.62 (t, 4 H, CH_2–N), 3.41–3.32 (m, 1 H, Glu–H_5), 2.20, 2.11, 2.04, 1.98 (s, 12 H, CH_3CO), 2.06 (qt, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 170.8, 170.2, 169.6, 169.3, 162.7, 155.5, 131.3, 130.6, 129.0, 128.3, 101.8, 97.2, 72.8, 71.5, 70.9, 67.9, 61.3, 39.1, 20.9, 20.7, 20.4, 20.3, 18.0; FABMS: 533 $(M-Br)^+$. Anal. Calcd for $C_{26}H_{33}BrN_2O_{10}$: C, 50.90; H, 5.42; N, 4.57. Found: C, 50.50; H, 5.88; N, 5.01.

E-2-[1′-(2″,3″,4″,6″-Tetra-O-acetyl-β-D-glucopyranosyl)]-p-methoxystyrenyl-hexahydropyrimidinium bromide (**6b**).—IR (KBr): 3328 (NH), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.25 (s, 2 H, NH), 7.48 (d, 2 H, Ar–H), 6.97 (d, 2 H, Ar–H), 5.89 (s, 1 H, C=C–H), 5.23–5.16 (m, 3 H, Glu–$H_{2,3,4}$), 4.90 (d, 1 H, $J_{H1,H2}$ 8.1 Hz, Glu–H_1), 4.27–3.96 (m, 2 H, Glu–H_6), 3.86 (s, 3 H, CH_3O), 3.64 (t, 4 H, CH_2–N), 3.48–3.39 (m, 1 H, Glu–H_5), 2.19, 2.10, 2.03, 1.98 (s, 12 H, CH_3CO), 2.07 (qt, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 170.5, 170.1, 169.5, 169.1, 163.1, 161.9, 155.7, 130.0, 122.7, 114.5, 100.7, 97.4, 72.7, 71.7, 70.8, 67.9, 61.2, 55.5, 39.3, 20.9, 20.7, 20.6, 20.4, 18.0; FABMS: 563 $(M-Br)^+$. Anal. Calcd for $C_{27}H_{35}BrN_2O_{11}$: C, 50.39; H, 5.48; N, 4.35. Found: C, 50.08; H, 4.91; N, 4.42.

E-2-[1′-(2″,3″,4″,6″-Tetra-O-acetyl-β-D-glucopyranosyl)]-p-chlorostyrenyl-hexahydropyrimidinium bromide (**6c**).—IR (KBr): 3328 (NH), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.23 (s, 2 H, NH), 7.52 (d, 2 H, Ar–H), 7.46 (d, 2 H, Ar–H), 5.97 (s, 1 H, C=C–H), 5.20–5.15 (m, 3 H, Glu–$H_{2,3,4}$), 4.82 (d, 1 H, $J_{H1,H2}$ 8.0 Hz, Glu–H_1), 4.25–3.98 (m, 2 H, Glu–H_6), 3.68 (t, 4 H, CH_2–N), 3.47–3.38 (m, 1 H, Glu–H_5), 2.12, 2.06, 2.03, 1.99 (s, 12 H, CH_3CO), 2.09 (qt, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.2, 169.6, 169.2, 161.6, 155.5, 137.5, 129.7, 129.3, 129.0, 102.2, 97.2, 72.7, 71.3, 70.7, 67.6, 61.2, 39.3, 20.9, 20.8, 20.4, 20.3, 17.8; FABMS: 567 $(M-Br)^+$. Anal. Calcd for $C_{26}H_{32}BrClN_2O_{10}$: C, 48.20; H, 4.98; N, 4.32. Found: C, 47.64; H, 5.05; N, 4.58.

E-2-[1′-(2″,3″,4″,6″-tetra-O-acetyl-β-D-glucopyranosyl)]-p-bromostyrenyl-hexahydropyrimidinium bromide (**6d**).—IR (KBr): 3319 (NH), 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.68 (s, 2 H, NH), 7.50–7.30 (m, 4 H, Ar–H), 5.92 (s, 1 H, C=C–H), 5.22–5.15 (m, 3 H, Glu–$H_{2,3,4}$), 4.83 (d, 1 H, $J_{H1,H2}$ 8.0 Hz, Glu–H_1), 4.22–3.92 (m, 2 H, Glu–H_6), 3.59 (t, 4 H, CH_2–N), 3.45–3.35 (m, 1 H, Glu–H_5), 2.19, 2.11, 2.02, 1.99 (s, 12 H, CH_3CO), 2.05 (qt, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 170.9, 170.2, 169.6, 169.3, 161.8, 155.4, 137.7, 129.3, 128.7, 101.9, 97.1, 72.9, 71.1, 70.9, 67.7, 61.2, 39.0, 20.9, 20.6, 20.4, 20.3, 17.9; FABMS: 611 $(M-Br)^+$. Anal. Calcd for $C_{26}H_{32}Br_2N_2O_{10}$: C, 45.10; H, 4.66; N, 4.05. Found: C, 45.38; H, 5.18; N, 4.04.

E-1-Methyl-2-[1′-(2″,3″,4″,6″-tetra-O-acetyl-β-D-glucopyranosyl)]-p-chlorostyrenyl-tetrahydroimidazolium bromide (**7c**).—IR (KBr): 3330 (NH), 1739 (C=O) cm^{-1}; ^1H

NMR ($CDCl_3$): δ 8.18 (s, 1 H, NH), 7.58 (d, 2 H, Ar–H), 7.45 (d, 2 H, Ar–H), 5.79 (s, 1 H, C=C–H), 5.25–5.00 (m, 3 H, Glu–$H_{2,3,4}$), 4.91 (d, 1 H, $J_{H1,H2}$ 8.2 Hz, Glu–H_1), 4.24–4.00 (m, 2 H, Glu–H_6), 4.02 (s, 4 H, N–CH_2CH_2–N), 3.54–3.45 (m, 1 H, Glu–H_5), 3.20 (s, 3 H, CH_3N), 2.19, 2.10, 2.06, 1.99 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.2, 169.6, 169.2, 165.6, 160.2, 137.9, 129.8, 129.2, 128.9, 97.5, 94.6, 72.5, 71.4, 70.7, 67.5, 61.2, 51.1, 42.8, 33.5, 20.6, 20.5, 20.4, 20.3; FABMS: 567 $(M–Br)^+$. Anal. Calcd for $C_{26}H_{32}BrClN_2O_{10}$: C, 48.20; H, 4.98; N, 4.32. Found: C, 48.21; H, 5.52; N, 4.95.

General procedure for the synthesis of compounds **8–11**.—A mixture of benzoyl-substituted heterocyclic ketene aminals **3** or **4** (1 mmol), 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**1**) (1.1 mmol) and silver trifluoromethanesulfonate (1 mmol) was stirred in acetonitrile (40 mL) in the dark for 10–18 h. When TLC (10:1 $CHCl_3$–CH_3OH) showed the presence of one new major spot, the mixture was filtered and washed with CH_2Cl_2 (15 mL). The solvent was evaporated, the residue was purified by silica gel column chromatography using the same eluant (100:1 ~ 50:1 $CHCl_3$–CH_3OH) to afford pure compounds **8–11**.

*E-2-[1′-(2″,3″,4″,6″-Tetra-*O*-acetyl-β-D-glucopyranosyl)]-styrenyl-tetrahydroimidazolium trifluoromethanesulfonate* (**8a**).—IR (KBr): 3340 (NH), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.82 (s, 2 H, NH), 7.58–7.38 (m, 5 H, Ar–H), 6.01 (s, 1 H, C=C–H), 5.23–5.05 (m, 3 H, Glu–$H_{2,3,4}$), 4.99 (d, 1 H, $J_{H1,H2}$ 8.2 Hz, Glu–H_1), 4.18–3.90 (m, 2 H, Glu–H_6), 3.97 (s, 4 H, N–CH_2CH_2–N), 3.38–3.30 (m, 1 H, Glu–H_5), 2.20, 2.11, 2.00, 1.98 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.0, 170.2, 169.6, 169.2, 166.7, 162.0, 131.8, 130.1, 129.1, 128.0, 97.4, 96.3, 72.9, 71.3, 71.1, 67.9, 61.3, 44.2, 20.8, 20.7, 20.5, 20.4; FABMS: 519 $(M–SO_3CF_3)^+$. Anal. Calcd for $C_{26}H_{31}F_3N_2O_{13}S$: C, 46.70; H, 4.67; N, 4.19. Found: C, 46.50; H, 5.25; N, 3.82.

*E-2-[1′-(2″,3″,4″,6″-Tetra-*O*-acetyl-β-D-glucopyranosyl)]-*p*-methoxystyrenyl-tetrahydroimidazolium trifluoromethanesulfonate* (**8b**).—IR (KBr): 3350 (NH), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.68 (s, 2 H, NH), 7.44 (d, 2 H, Ar–H), 6.97 (d, 2 H, Ar–H), 6.01 (s, 1 H, C=C–H), 5.25–5.08 (m, 3 H, Glu–$H_{2,3,4}$), 5.05 (d, 1 H, $J_{H1,H2}$ 8.8 Hz, Glu–H_1), 4.18–3.92 (m, 2 H, Glu–H_6), 3.99 (s, 4 H, N–CH_2CH_2–N), 3.87 (s, 3 H, CH_3O), 3.48–3.40 (m, 1 H, Glu–H_5), 2.19, 2.09, 2.03, 1.99 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.9, 170.3, 169.7, 169.3, 166.8, 162.4, 162.2, 129.8, 122.0, 114.6, 97.5, 95.2, 72.8, 71.4, 71.1, 67.8, 61.3, 55.5, 44.1, 20.8, 20.7, 20.5; FABMS: 549 $(M–SO_3CF_3)^+$. Anal. Calcd for $C_{27}H_{33}F_3N_2O_{14}S$: C, 46.42; H, 4.76; N, 4.01. Found: C, 46.75; H, 4.49; N, 3.89.

*E-2-[1′-(2″,3″,4″,6″-Tetra-*O*-acetyl-β-D-glucopyranosyl)]-*p*-chlorostyrenyl-tetrahydroimidazolium trifluoromethanesulfonate* (**8c**).—IR (KBr): 3358 (NH), 1738 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.77 (s, 2 H, NH), 7.46 (s, 4 H, Ar–H), 6.04 (s, 1 H, C=C–H), 5.23–5.05 (m, 3 H, Glu–$H_{2,3,4}$), 5.00 (d, 1 H, $J_{H1,H2}$ 8.2 Hz, Glu–H_1), 4.20–3.95 (m, 2 H, Glu–H_6), 4.01 (s, 4 H, N–CH_2CH_2–N), 3.46–3.38 (m, 1 H, Glu–H_5), 2.19, 2.14, 2.04, 1.99 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.0, 170.2, 169.6, 169.2, 165.3, 161.7, 138.1, 129.5, 129.4, 128.7, 97.5, 96.8, 72.8, 71.3, 71.1, 67.8, 61.3, 44.2, 20.7, 20.6, 20.4; FABMS: 553 $(M–SO_3CF_3)^+$. Anal. Calcd for $C_{26}H_{30}ClF_3N_2O_{13}S$: C, 44.22; H, 4.30; N, 3.99. Found: C, 43.72; H, 4.55; N, 4.21.

E-2-[1'-(2",3",4",6"-Tetra-O-*acetyl-β*-D-*glucopyranosyl)]*-p-*bromostyrenyl-tetrahydroimidazolium trifluoromethanesulfonate* (**8d**).—IR (KBr): 3335 (NH), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.82 (s, 2 H, NH), 7.62 (d, 2 H, Ar–H), 7.39 (d, 2 H, Ar–H), 6.08 (s, 1 H, C=C–H), 5.22–5.00 (m, 3 H, Glu–$H_{2,3,4}$), 4.90 (d, 1 H, $J_{H1,H2}$ 8.4 Hz, Glu–H_1), 4.20–3.95 (m, 2 H, Glu–H_6), 4.01 (s, 4 H, N–CH_2CH_2–N), 3.46–3.36 (m, 1 H, Glu–H_5), 2.19–1.99 (4s, 12H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.0, 170.1, 169.5, 169.1, 165.3, 161.8, 132.4, 129.6, 129.1, 126.5, 97.5, 96.8, 72.9, 71.3, 71.1, 67.8, 61.3, 44.2, 20.7, 20.6, 20.5, 20.4; FABMS: 597 $(M–SO_3CF_3)^+$. Anal. Calcd for $C_{26}H_{30}BrF_3N_2O_{13}S$: C, 41.77; H, 4.05; N, 3.75. Found: C, 42.36; H, 4.46; N, 4.13.

E-1-Methyl-2-[1'-(2",3",4",6"-tetra-O-*acetyl-β*-D-*glucopyranosyl)]*-p-*methoxystyrenyl-tetrahydroimidazolium trifluoromethanesulfonate* (**9b**).—IR (KBr): 3385 (NH), 1734 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.10 (s, 1 H, NH), 7.53 (d, 2 H, Ar–H), 6.99 (d, 2 H, Ar–H), 5.67 (s, 1 H, C=C–H), 5.25–5.02 (m, 3 H, Glu–$H_{2,3,4}$), 4.95 (d, 1 H, $J_{H1,H2}$ 8.2 Hz, Glu–H_1), 4.25–4.05 (m, 2 H, Glu–H_6), 4.01 (s, 4 H, N–CH_2CH_2–N), 3.88 (s, 3 H, CH_3O), 3.54–3.45 (m, 1 H, Glu–H_5), 3.19 (s, 3 H, CH_3N), 2.19, 2.10, 2.02, 1.99 (4s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.3, 169.7, 169.2, 167.2, 162.3, 160.6, 130.1, 122.3, 114.4, 97.6, 93.0, 72.1, 71.5, 70.7, 67.6, 61.2, 55.5, 51.1, 42.8, 33.5, 20.7, 20.6, 20.5, 20.4; FABMS: 563 $(M - SO_3CF_3)^+$. Anal. Calcd for $C_{28}H_{35}F_3N_2O_{14}S$: C, 47.19; H, 4.95; N, 3.93. Found: C, 47.10; H, 5.36; N, 3.80.

E-1-Methyl-2-[1'-(2",3",4",6"-tetra-O-*acetyl-β*-D-*glucopyranosyl)]*-p-*chlorostyrenyl-tetrahydroimidazolium trifluoromethanesulfonate* (**9c**).—IR (KBr): 3358 (NH), 1736 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.18 (s, 1 H, NH), 7.59 (d, 2 H, Ar–H), 7.47 (d, 2 H, Ar–H), 5.74 (s, 1 H, C=C–H), 5.22–5.01 (m, 3 H, Glu–$H_{2,3,4}$), 4.88 (d, 1 H, $J_{H1,H2}$ 8.2 Hz, Glu–H_1), 4.26–4.05 (m, 2 H, Glu–H_6), 4.02 (s, 4 H, N–CH_2CH_2–N), 3.53–4.43 (m, 1 H, Glu–H_5), 3.19 (s, 3 H, CH_3N), 2.19, 2.09, 2.04, 2.00 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.9, 170.3, 169.6, 169.3, 165.5, 160.5, 138.0, 130.1, 129.3, 129.0, 97.6, 94.7, 72.7, 71.5, 70.7, 67.6, 61.2, 51.2, 42.9, 33.7, 20.7, 20.6, 20.4; FABMS: 567 $(M–SO_3CF_3)^+$. Anal. Calcd for $C_{27}H_{32}ClF_3N_2O_{13}S$: C, 45.22; H, 4.50; N, 3.91. Found: C, 45.03; H, 4.60; N, 3.75.

E-1-Methyl-2-[1'-(2",3",4",6"-tetra-O-*acetyl-β*-D-*glucopyranosyl)]*-p-*bromostyrenyl-tetrahydroimidazolium trifluoromethanesulfonate* (**9d**).—IR (KBr): 3350 (NH), 1739 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.18 (s, 1 H, NH), 7.65 (d, 2 H, Ar–H), 7.48 (d, 2 H, Ar–H), 5.78 (s, 1 H, C=C–H), 5.22–5.00 (m, 3 H, Glu–$H_{2,3,4}$), 4.92 (d, 1 H, $J_{H1,H2}$ 8.2 Hz, Glu–H_1), 4.23–4.02 (m, 2 H, Glu–H_6), 4.03 (s, 4 H, N–CH_2CH_2–N), 3.55–3.43 (m, 1 H, Glu–H_5), 3.19 (s, 3 H, CH_3N), 2.20, 2.10, 2.04, 1.99 (4s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.9, 170.3, 169.6, 169.3, 165.7, 160.4, 132.3, 130.2, 130.0, 129.5, 97.6, 94.7, 72.6, 71.5, 70.8, 67.6, 61.3, 51.2, 42.9, 33.6, 20.7, 20.6, 20.5; FABMS: 611 $(M–SO_3CF_3)^+$. Anal. Calcd for $C_{27}H_{32}BrF_3N_2O_{13}S$: C, 42.58; H, 4.24; N, 3.68. Found: C, 42.49; H, 4.47; N, 3.87.

E-1-Methyl-2-[1'-(2",3",4",6"-tetra-O-*acetyl-β*-D-*glucopyranosyl)]*-p-*methylstyrenyl-tetrahydroimidazolium trifluoromethanesulfonate* (**9e**).—IR (KBr): 3362 (NH), 1733 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.18 (s, 1 H, NH), 7.45 (d, 2 H, Ar–H), 7.25 (d, 2 H, Ar–H), 5.65 (s, 1 H, C=C–H), 5.26–5.00 (m, 3 H, Glu–$H_{2,3,4}$), 4.90 (d, 1 H, $J_{H1,H2}$ 8.2 Hz, Glu–H_1), 4.26–4.01 (m, 2 H, Glu–H_6), 4.05 (s, 4 H, N–CH_2CH_2–N),

3.50–3.40 (m, 1 H, Glu–H_5), 3.19 (s, 3 H, CH_3N), 2.42 (s, 3 H, $PhCH_3$), 2.19, 2.11, 2.03, 2.00 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.9, 170.3, 169.7, 169.3, 167.4, 160.8, 142.5, 129.7, 128.4, 127.7, 97.7, 93.6, 72.7, 71.6, 70.8, 67.8, 61.3, 51.2, 42.9, 33.7, 21.5, 20.7, 20.6, 20.4; FABMS: 547 $(M-SO_3CF_3)^+$. Anal. Calcd for $C_{28}H_{35}F_3N_2O_{13}S$: C, 48.27; H, 5.06; N, 4.02. Found: C, 47.76; H, 5.49; N, 4.51.

*E-2-[1′-(2″,3″,4″,6″-Tetra-*O*-acetyl-β-*D*-glucopyranosyl)]-styrenyl-hexahydropyrimidinium trifluoromethanesulfonate* (**10a**).—IR (KBr): 3345 (NH), 1737 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.68 (s, 2 H, NH), 7.58–7.40 (m, 5 H, Ar–H), 5.80 (s, 1 H, C=C–H), 5.22–4.95 (m, 3 H, Glu–$H_{2,3,4}$), 4.87 (d, 1 H, $J_{H1,H2}$ 8.0 Hz, Glu–H_1), 4.18–3.92 (m, 2 H, Glu–H_6), 3.58 (t, 4 H, CH_2–N), 3.40–3.32 (m, 1 H, Glu–H_5), 2.19, 2.09, 2.02, 1.98 (s, 12 H, CH_3CO), 2.06 (qt, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 170.9, 170.2, 169.6, 169.3, 163.4, 155.7, 131.5, 130.3, 129.0, 128.1, 101.4, 97.2, 72.9, 71.3, 71.0, 67.9, 61.3, 39.1, 20.8, 20.7, 20.4, 18.0; FABMS: 533 $(M-SO_3CF_3)^+$. Anal. Calcd for $C_{27}H_{33}F_3N_2O_{13}S$: C, 47.50; H, 4.87; N, 4.10. Found: C, 47.73; H, 5.30; N, 4.65.

*E-2-[1′-(2″,3″,4″,6″-Tetra-*O*-acetyl-β-*D*-glucopyranosyl)]-*p*-methoxystyrenyl-hexahydropyrimidinium trifluoromethanesulfonate* (**10b**).—IR (KBr): 3342 (NH), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.59 (s, 2 H, NH), 7.42 (d, 2 H, Ar–H), 6.95 (d, 2 H, Ar–H), 5.78 (s, 1 H, C=C–H), 5.22–5.05 (m, 3 H, Glu–$H_{2,3,4}$), 4.95 (d, 1 H, $J_{H1,H2}$ 8.1 Hz, Glu–H_1), 4.22–3.90 (m, 2 H, Glu–H_6), 3.87 (s, 3 H, CH_3O), 3.58 (t, 4 H, CH_2–N), 3.40—-.32 (m, 1 H, Glu–H_5), 2.18, 2.10, 2.03, 1.99 (s, 12 H, CH_3CO), 2.00 (qt, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.3, 169.7, 169.3, 163.4, 162.0, 155.7, 129.7, 122.3, 114.4, 100.3, 97.2, 72.7, 71.3, 70.9, 67.8, 61.3, 55.5, 38.9, 20.7, 20.6, 20.4, 18.0; FABMS: 563 $(M-SO_3CF_3)^+$. Anal. Calcd for $C_{28}H_{35}F_3N_2O_{14}S$: C, 47.19; H, 4.95; N, 3.93. Found: C, 47.65; H, 4.99; N, 3.91.

*E-2-[1′-(2″,3″,4″,6″-Tetra-*O*-acetyl-β-*D*-glucopyranosyl)]-*p*-chlorostyrenyl-hexahydropyrimidinium trifluoromethanesulfonate* (**10c**).—IR (KBr): 3351 (NH), 1736 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.58 (s, 2 H, NH), 7.38 (s, 4 H, Ar–H), 5.79 (s, 1 H, C=C–H), 5.19–4.85 (m, 3 H, Glu–$H_{2,3,4}$), 4.82 (d, 1 H, $J_{H1,H2}$ 8.0 Hz, Glu–H_1), 4.18–3.85 (m, 2 H, Glu–H_6), 3.54 (t, 4 H, CH_2–N), 3.40–3.32 (m, 1 H, Glu–H_5), 2.15, 2.10, 2.04, 1.98 (s, 12 H, CH_3CO), 2.02 (qt, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 170.9, 170.2, 169.6, 169.3, 161.9, 155.5, 137.7, 129.5, 129.3, 129.0, 101.9, 97.3, 72.9, 71.3, 71.0, 67.9, 61.4, 39.1, 20.8, 20.6, 20.4, 17.9; FABMS: 567 $(M-SO_3CF_3)^+$. Anal. Calcd for $C_{27}H_{32}ClF_3N_2O_{13}S$: C, 45.22; H, 4.50; N, 3.91. Found: C, 45.23; H, 4.94; N, 3.45.

*E-1-Methyl-2-[1′-(2″,3″,4″,6″-tetra-*O*-acetyl-β-*D*-glucopyranosyl)]-*p*-methoxystyrenyl-hexahydropyrimidinium trifluoromethanesulfonate* (**11b**).—IR (KBr): 3360 (NH), 1738 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.49 (s, 1 H, NH), 7.53 (d, 2 H, Ar–H), 6.96 (d, 2 H, Ar–H), 5.80 (s, 1 H, C=C–H), 5.19–4.98 (m, 3 H, Glu–$H_{2,3,4}$), 4.86 (d, 1 H, $J_{H1,H2}$ 8.1 Hz, Glu–H_1), 4.42–4.02 (m, 2 H, Glu–H_6), 3.87 (s, 3 H, CH_3O), 3.54 (t, 4 H, CH_2–N), 3.58–3.50 (m, 1 H, Glu–H_5), 3.24 (s, 3 H, CH_3N), 2.15, 2.10, 2.00, 1.98 (4s, 12 H, CH_3CO), 2.04 (qt, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 170.2, 169.7, 169.6, 169.3, 161.9, 160.9, 156.6, 129.7, 122.6, 114.4, 100.0, 97.5, 72.5, 72.0, 70.7, 67.4, 61.0, 55.4, 48.1, 40.5, 38.5, 20.6, 20.5, 20.4, 18.7; FABMS: 577

$(M-SO_3CF_3)^+$. Anal. Calcd for $C_{29}H_{37}F_3N_2O_{14}S$: C, 47.93; H, 5.13; N, 3.86. Found: C, 47.45; H, 4.97; N, 3.95.

E-1-Methyl-2-[1'-(2'',3'',4'',6''-tetra-O-*acetyl-β*-D-*glucopyranosyl)]*-p-*chlorostyrenyl-hexahydropyrimidinium trifluoromethanesulfonate* (**11c**).—IR (KBr): 3245 (NH), 1734 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.65 (s, 1 H, NH), 7.58 (d, 2 H, Ar–H), 7.42 (d, 2 H, Ar–H), 5.86 (s, 1 H, C=C–H), 5.18–4.98 (m, 3 H, Glu–$H_{2,3,4}$), 4.79 (d, 1 H, $J_{H1,H2}$ 8.1 Hz, Glu–H_1), 4.39–4.01 (m, 2 H, Glu–H_6), 3.57 (t, 4 H, CH_2–N), 3.56–3.48 (m, 1 H, Glu–H_5), 3.22 (s, 3 H, CH_3N), 2.19, 2.08, 2.02, 1.98 (s, 12 H, CH_3CO), 2.10 (qt, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 170.2, 169.7, 169.6, 169.3, 159.5, 156.6, 137.5, 129.5, 129.3, 129.2, 102.0, 97.5, 72.6, 72.1, 70.8, 67.5, 61.1, 48.1, 40.5, 38.6, 20.6, 20.4, 18.7; FABMS: 581 $(M-SO_3CF_3)^+$. Anal. Calcd for $C_{28}H_{34}ClF_3N_2O_{13}S$: C, 45.99; H, 4.69; N, 3.83. Found: C, 45.65; H, 4.80; N, 3.65.

E-1-Methyl-2-[1'-(2'',3'',4'',6''-tetra-O-*acetyl-β*-D-*glucopyranosyl)]*-p-*methylstyrenyl-hexahydropyrimidinium trifluoromethanesulfonate* (**11e**).—IR (KBr): 3400 (NH), 1736 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.52 (s, 1 H, NH), 7.45 (d, 2 H, Ar–H), 7.25 (d, 2 H, Ar–H), 5.81 (s, 1 H, C=C–H), 5.18–4.99 (m, 3 H, Glu–$H_{2,3,4}$), 4.83 (d, 1 H, $J_{H1,H2}$ 8.1 Hz, Glu–H_1), 4.40–4.04 (m, 2 H, Glu–H_6), 3.56 (t, 4 H, CH_2–N), 3.40–3.30 (m, 1 H, Glu–H_5), 3.22 (s, 3 H, CH_3N), 2.42 (s, 3 H, $PhCH_3$), 2.18, 2.15, 2.04, 1.99 (s, 12 H, CH_3CO), 2.10 (qt, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 170.3, 169.9, 169.8, 169.4, 161.3, 156.7, 141.9, 129.8, 128.0, 127.7, 100.7, 97.5, 72.5, 72.1, 70.8, 67.5, 61.1, 48.2, 40.6, 38.6, 21.5, 20.7, 20.6, 20.5, 18.7; FABMS: 561 $(M-SO_3CF_3)^+$. Anal. Calcd for $C_{29}H_{37}F_3N_2O_{13}S$: C, 49.01; H, 5.25; N, 3.94. Found: C, 48.70; H, 4.81; N, 3.66.

6-O-(2'',3'',4'',6''-tetra-O-*acetyl-α*-D-*glucopyranosyl)-1,2,3,4-tetra*-O-*acetyl-α*-D-*glucopyranoside* (**14**).—To a mixture of **5**, **6**, **8** or **10** (1 mmol) and **12** (1 mmol) in CH_2Cl_2 (10 mL) was added Lewis acid (4 drops $BF_3 \cdot Et_2O$ or 2 drops TMSOTf). The mixture was stirred at room temperature for 1–5 h (see Table 3). When TLC (10:1 $CHCl_3$–CH_3OH) showed the presence of one new major spot, the solvent was evaporated, the residue was purified by silica gel column chromatography using the same eluant (75:1 $CHCl_3$–CH_3OH) to afford the pure compound **14** as colourless crystals, mp 95–97 °C; ^1H NMR ($CDCl_3$): δ 6.22 (d, 1 H, $J_{H1,H2}$ 3.4 Hz, Glu–H_1), 5.60–4.41 (m, 6 H, Glu–$H_{2,2'',3,3'',4,4''}$), 4.97 (d, 1 H, $J_{H1'',H2''}$ 3.4 Hz, Glu–$H_{1''}$), 4.37–3.90 (m, 6 H, Glu–$H_{5,5'',6,6''}$), 2.22–1.98 (8s, 24 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.5, 170.4, 169.9, 169.8, 169.7, 169.3, 168.8, 95.6 (C_1), 88.7 ($C_{1'}$), 72.1, 72.0, 70.0, 69.9, 69.6, 69.1, 68.5, 67.7, 62.3, 61.2, 20.9, 20.8, 20.7, 20.6, 20.5, 20.3; FABMS: 678 (M^+). Anal. Calcd for $C_{28}H_{38}O_{19}$: C, 49.56; H, 5.64. Found: C, 49.03; H, 5.68.

*Allyl 4,6-*O-*benzylidene-2-*O-*(2'',3'',4'',6''-tetra*-O-*acetyl-α*-D-*glucopyranosyl)-α*-D-*glucopyranoside* (**15**).—A mixture of **5**, **6**, **8** or **10** (1 mmol), **13** (1 mmol) and Lewis acid (2 drops $BF_3 \cdot Et_2O$ or 2 drops TMSOTf) in CH_2Cl_2 (10 mL) was stirred at room temperature for 1–5 h (see Table 3), at the end of which time TLC (10:1 $CHCl_3$–CH_3OH) showed the presence of one new major spot. The solvent was evaporated, the residue was purified by silica gel column chromatography using the same eluant (50:1 $CHCl_3$–CH_3OH) to afford pure compound **15** as colourless syrup; ^1H NMR ($CDCl_3$): δ 7.58–7.20 (m, 5 H, Ar–H), 5.95 (m, 1 H, CH_2=CC*H*CH_2O), 5.59 (d, 1 H, $J_{H1,H2}$ 3.2 Hz, Glu–H_1), 5.55–3.25 (m, 19 H, All–H, Ph–CH_2 and Glu–H, OH), 2.20–1.97 (4s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.3, 169.5, 169.3, 133.3, 128.9, 128.1, 126.2,

117.9, 101.6, 97.8 (C_1), 86.4$C_{1''}$), 80.8, 77.2, 72.5, 71.9, 71.1, 70.3, 69.9, 68.6, 68.5, 66.9, 62.4, 60.7, 20.4, 20.3; FABMS: 638 (M^+). Anal. Calcd for $C_{30}H_{38}O_{15}$: C, 56.42; H, 5.99. Found: C, 56.57; H, 5.82.

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