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Stereoselective synthesis of O-galactosides of benzoyl-substituted heterocyclic ketene aminals

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Abstract

The stereoselective synthesis of O-galactosides of benzoyl-substituted heterocyclic ketene aminals was investigated. The benzoyl-substituted heterocyclic ketene aminals **1–4** reacted with 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**5**) in the presence of calcium hydride to give O-galactosides of benzoyl-substituted heterocyclic ketene aminals **6–9** with the Z-configuration. In comparison, **1–2** reacted with **5** in the presence of mercuric cyanide to give O-galactosides of benzoyl-substituted heterocyclic ketene aminals **10–11** with the E-configuration. Satisfactory results have been obtained in terms of both stereoselectivity and yield, and the β-anomers are the sole products.

Keywords: Synthesis; Galactosylation; Heterocyclic ketene aminals

1. Introduction

Heterocyclic ketene aminals are important intermediates for the synthesis of a wide variety of new heterocycles and fused heterocycles [1,2]. Some heterocyclic ketene aminals and their derivatives possess biological activities; therefore, the synthesis and reactions of heterocyclic ketene aminals have received much attention. Heterocyclic ketene aminals are a kind of ambident nucleophiles. Due to conjugation of the electron-donating amino groups and the electron-withdrawing substitutes, the double bond is highly polarized, which leads to enhanced nucleophilic reactivity of the α-carbon atom. Thus, the α-carbon usually attacks the electropositive site of electrophiles [3–10]. With the aid of strong base such as sodium hydride, the secondary amino group can also participate in the reaction to afford N-alkylation products [11–13].

Due to tautomerization, beazoyl-substituted heterocyclic ketene aminals may exist as different tautomers (Scheme 1), and the amidine-enols may also exist in two forms, the Z- and E-forms. Therefore, the electrophiles may attack in three ways: N-, C-, and O-attack to give different products and if the O-attack is taken place, the Z- and/or *E*- amidine-enol form may result. Recently, Z.-J. Li et al. have reported the O-glucosidation of benzoyl-substituted heterocyclic ketene aminals [14,15].

In the last 20 years, glycosidation has received much attention because a number of physiological activities of carbohydrates in biological systems have been gradually recognised. It has been proved that biological information in the living system is

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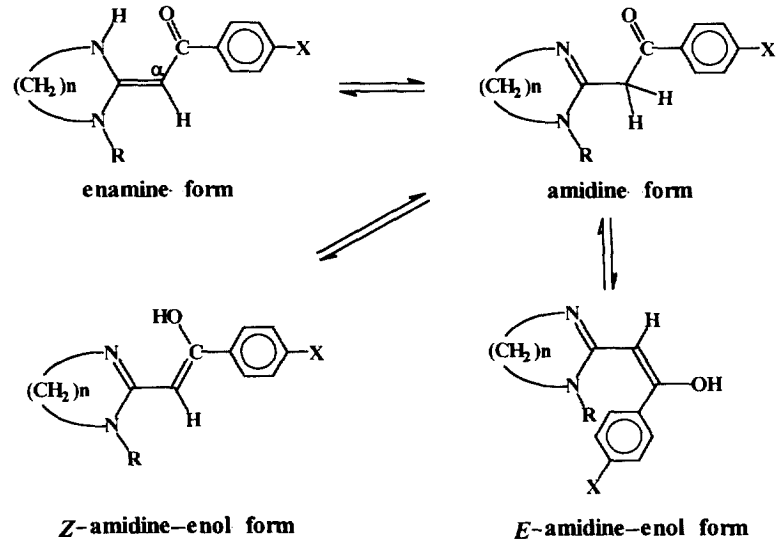


Scheme 1.

carried mainly by the carbohydrate part [16–18]. Galactosides and their derivatives also play important roles in living organisms [19–21]. Thus, galactosides of heterocyclic ketene aminals may change or enhance their biological activities. So the stereoselective synthesis of O-galactosides of benzoyl-substituted heterocyclic ketene aminals was investigated. Here we report the results of the reaction between the benzoyl-substituted heterocyclic ketene aminals **1–4** and 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**5**) in the presence of different catalysts (calcium hydride or mercuric cyanide) to afford the O-galactosidation products with different configurations (Z or E).

2. Results and discussion

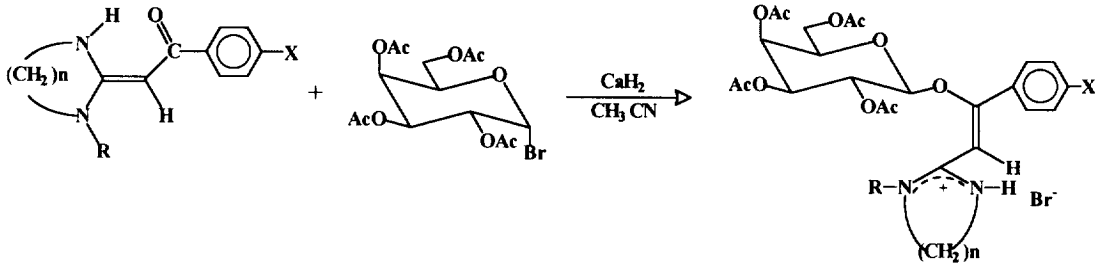
The benzoyl-substituted heterocyclic ketene aminals used were prepared from ketene dithioacetals with diamines by a literature method [22]. Under mild conditions, benzoyl-substituted heterocyclic ketene aminals **1–4** reacted readily with 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**5**) in the presence of calcium hydride in anhydrous acetonitrile to give the products **6–9** in moderate yields (Scheme 2). The reaction conditions, yields and melting points of **6–9** are listed in Table 1.

The structures of **6–9** were established by spectroscopic data, and the composition was confirmed by elemental analyses. It was proved by FABMS and elemental analyses that compounds **6–9** were monogalactosides of **1–4**. In their IR spectra, there was an NH stretching absorption band at ca. 3360 cm^{-1} and a very strong carbonyl absorption for the acetyl group at ca. 1730 cm^{-1}. Meanwhile, the carbonyl absorption of the aroyl group of the heterocyclic ketene aminals at ca. 1600 cm^{-1}

Table 1
Reaction conditions, yields, and melting points of products **6–9**

Product	Reaction conditions		Yield[a] (%)	mp (°C)
	Temperature (°C)	Time (days)		
6a	30	4	50	97–99
6b	30	4	35	101–103
6c	30	3	31	103–105
6d	30	4	37	105–107
6e	30	4	37	107–109
7a	30	4	43	114–116
7b	30	6.5	39	110–112
7c	30	3	38	113–115
7d	30	3.5	35	113–115
7e	30	4	57	105–107
8a	30	1.5	24	105–107
8b	30	1.5	27	86–88
8c	30	2	34	89–91
8d	30	2	25	91–93
9a	30	1.5	25	80–82
9b	30	1.5	29	89–91
9c	30	1.5	24	90–92
9d	30	1.5	35	99–101

[a] Isolated yield.



1, 2 R = H; 3, 4 R = CH_3 5 6, 7 R = H; 8, 9 R=CH_3

1, 3 n = 2; 2, 4 n = 3 6, 8 n = 2; 7, 9 n = 3

1-4, 6-9	a	b	c	d	e
X	H	CH_3	OCH_3	Cl	Br

Scheme 2.

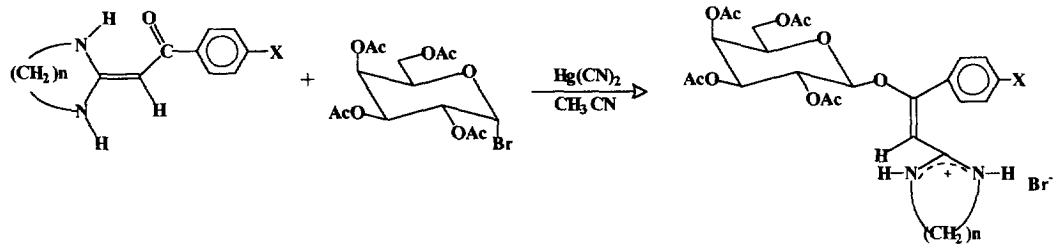
disappeared. In the ^1H NMR spectra, the signals of two nitrogen protons (9.24–9.50 ppm) of **6** and **7** and one nitrogen proton (8.43–9.99 ppm) of **8** and **9** were discovered. Furthermore, the signals of one ethylenic proton were shown to still exist at 6.26–6.49 ppm (**6** and **7**) and 5.61–5.98 ppm (**8** and **9**). These data exclude either the N-galactosidation or C-galactosidation of **1–4**. Moreover, the appearance of a new carbon signal (155.1–166.6 ppm) instead of a carbonyl carbon signal (ca. 180 ppm) in the ^{13}C NMR spectra indicates that the products **6–9** are O-galactosides of **1–4**. The β linkage of the protected galactopyranosyl group with the oxygen atom of heterocyclic ketene aminals in **6–9** was confirmed by the galactopyranosyl ring $H_{1'}$–$H_{2'}$ coupling constants ($J_{H1'\text{-}H2'}$ 7.7–8.2 Hz) in the ^1H NMR spectra. The β linkage formation is due to the participation of the neighboring acetyl group. The Z-configuration of the products **6–9** was determined by a demonstrated NOE between the benzene ring and the ethylenic proton.

Under mild conditions, benzoyl-substituted heterocyclic ketene aminals **1** and **2** reacted with 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**5**) using mercuric cyanide as catalyst in anhydrous acetonitrile to give products **10** and **11** (Scheme 3). Their elemental analyses and spectral data are similar with those of products **6** and **7**, and also proved that they are O-galactosides of **1** and **2**. The E-configuration of **10** and **11** was also determined by the NOE technique. This can also explain the shift to lower field of the ethylenic proton in **6** and **7** (6.26–6.49 ppm) with the Z-configuration due to the deshielding effect as compared with **10** and **11** (5.75–6.21 ppm) with the E-configuration. The galactopyranosyl ring $H_{1'}$-$H_{2'}$ coupling constants (7.8–8.2 Hz) in the ^1H NMR spectra indicated a β linkage between the protected galactopyranosyl group and the oxygen atom of heterocyclic ketene aminals. The reaction conditions, yields and melting points are listed in Table 2.

Table 2
Reaction conditions, yields, and melting points of products **10** and **11**

Product	Reaction conditions		Yield[a] (%)	mp (°C)
	Temperature (°C)	Time (h)		
10a	RT	50	46	94–96
10b	RT	30	44	91–93
10c	RT	50	33	96–98
10d	RT	30	44	96–98
10e	RT	35	50	97–99
11a	RT	30	34	111–113
11b	RT	30	35	88–90
11c	RT	30	35	115–117
11d	RT	20	53	102–105
11e	RT	50	47	86–88

[a] Isolated yield.

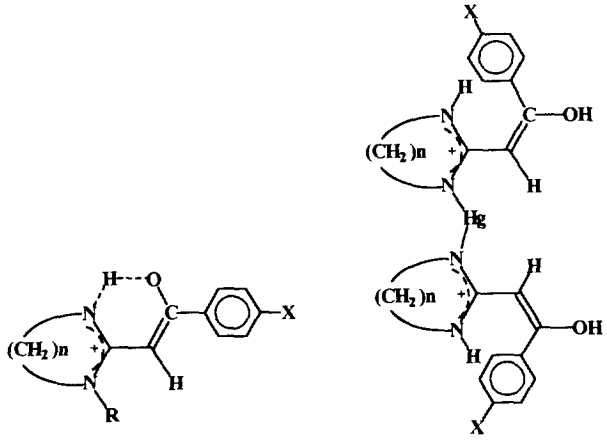


1, n = 2; **2**, n = 3 **5** **10**, n = 2; **11**, n = 3

1-2, 10-11	a	b	c	d	e
X	H	CH_3	OCH_3	Cl	Br

Scheme 3.

According to the results observed, the reaction mechanism may be proposed as follows (Scheme 4): In the presence of calcium hydride, the enol-amidine form with the Z-configuration (**A**) for the heterocyclic ketene aminal intermediate was formed at first, then galactosylation with **5** could be carried out with this intermediate to give the Z-configuration products **6–9**. When the galactosylation was carried out using mercuric cyanide as catalyst, the mercuric ion–ketene aminal complex may be formed at first. Due to steric effects, the complex with the E-configuration (**B**) may be more favorable; therefore, the galactosylation products **10** and **11** with the E-configuration resulted.



A (*Z*-form) B (*E*-form)

Scheme 4.

3. Experimental

General methods.—Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded with Varian 200 Unity and 300 MHz spectrometers in $CDCl_3$ solution with tetramethylsilane as the internal standard. IR spectra were recorded with a Perkin–Elmer 782 spectrometer. Mass spectra were recorded with a KYKY-ZHT-5 instrument. Elemental analyses were carried out by the Analytical Laboratory of the Institute of Chemistry.

General procedure for the synthesis of compounds (**6–9**).—A mixture of benzoyl-substituted heterocyclic ketene aminals **1–4** (1 mmol), 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**5**, 1 mmol) and calcium hydride (200 mg) in dried acetonitrile (25 mL) was stirred at 30 °C for 3–4 days. The mixture was filtered. After removal of solvent, the product was purified by column chromatography of silica gel (200–300 mesh) using 100:1 chloroform–methanol as eluant to give the pure compounds **6–9**.

*2-[(Z)-2-Phenyl-2-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyloxy)vinyl]imidazolidinium bromide* (**6a**).—IR (KBr): 3380 (NH), 1740 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 9.50 (s, 2 H, NH), 7.57–7.37 (m, 5 H, Ar-H), 6.40 (s, 1 H, C=C–H), 5.35–5.25 (m, 2 H, Gal-$H_{2,4}$), 5.01 (dd, 1 H, Gal-H_3), 4.92 (d, 1 H, $J_{H1,H2}$ 8.0 Hz, Gal-H_1), 4.12–3.94 (m, 2 H, Gal-H_6), 4.03 (s, 4 H, N–CH_2CH_2–N), 3.58–3.52 (m, 1 H, Gal-H_5), 2.21, 2.20, 2.03, 2.00 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.6, 170.2, 169.8,

169.5, 166.5, 161.8, 131.7, 130.1, 129.1, 128.1, 97.5, 96.1, 72.1, 69.3, 68.8, 66.6, 60.9, 44.0, 21.0, 20.6, 20.6, 20.4; 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, 50.13; H, 5.89; N, 4.72.

2-[(Z)-2-(p-Methylphenyl)-2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)vinyl]imidazolidinium bromide (**6b**).—IR (KBr): 3360 (NH), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.34 (s, 2 H, NH), 7.34 (d, 2 H, Ar–H), 7.25 (d, 2 H, Ar–H), 6.31 (s, 1 H, C=C–H), 5.34–5.25 (m, 2 H, Gal-$H_{2,4}$), 5.03 (dd, 1 H, Gal-H_3), 4.95 (d, 1 H, $J_{H1,H2}$ 8.0 Hz, Gal-H_1), 4.16–3.85 (m, 2 H, Gal-H_6), 4.04 (s, 4 H, N–CH_2CH_2–N), 3.63–3.57 (m, 1 H, Gal-H_5), 2.42 (s, 3 H, CH_3), 2.21, 2.21, 2.03, 2.02 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.0, 169.6, 169.4, 169.0, 166.4, 161.3, 141.7, 129.2, 127.6, 126.8, 97.1, 95.1, 71.5, 68.9, 68.4, 66.2, 60.6, 43.6, 21.1, 20.6, 20.3, 20.2, 20.0; 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, 50.36; H, 5.54; N, 4.13.

2-[(Z)-2-(p-Methoxyphenyl)-2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)vinyl]imidazolidinium bromide (**6c**).—IR (KBr): 3365 (NH), 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.36 (s, 2 H, NH), 7.42 (d, 2 H, Ar–H), 6.96 (d, 2 H, Ar–H), 6.39 (s, 1 H, C=C–H), 5.37–5.27 (m, 2 H, Gal-$H_{2,4}$), 5.02 (dd, 1 H, Gal-H_3), 4.96 (d, 1 H, $J_{H1,H2}$ 8.0 Hz, Gal-H_1), 4.10–3.96 (m, 2 H, Gal-H_6),4.02 (s, 4 H, N–CH_2CH_2–N), 3.87 (s, 3 H, CH_3O), 3.64–3.58 (m, 1 H, Gal-H_5), 2.21, 2.20, 2.04, 2.00 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.2, 170.1, 169.7, 169.5, 166.6, 162.1, 162.0, 129.8, 122.1, 114.5, 97.6, 95.2, 72.0, 69.4, 68.8, 66.5, 60.8, 55.5, 43.9, 20.9, 20.5, 20.5, 20.3; 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, 48.91; H, 5.22; N, 4.20.

2-[(Z)-2-(p-Chlorophenyl)-2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)vinyl]imidazolidinium bromide (**6d**).—IR (KBr): 3340 (NH), 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.46 (s, 2 H, NH), 7.45 (s, 4 H, Ar–H), 6.44 (s, 1 H, C=C–H), 5.37–5.22 (m, 2 H, Gal-$H_{2,4}$), 5.02 (dd, 1 H, Gal-H_3), 4.91 (d, 1 H, $J_{H1,H2}$ 7.8 Hz, Gal-H_1), 4.13–3.96 (m, 2 H, Gal-H_6), 4.03 (s, 4 H, N–CH_2CH_2–N), 3.64–3.57 (m, 1 H, Gal-H_5), 2.21, 2.20, 2.04, 2.00 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.4, 169.9, 169.6, 169.3, 164.9, 161.3, 137.6, 129.3, 129.2, 128.5, 97.4, 96.3, 72.0, 69.1, 68.7, 66.4, 60.9, 43.9, 20.9, 20.4, 20.4, 20.2; 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, 46.69; H, 5.45; N, 4.08.

2-[(Z)-2-(p-Bromophenyl)-2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)vinyl]imidazolidinium bromide (**6e**).—IR (KBr): 3360 (NH), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.48 (s, 2 H, NH), 7.61 (d, 2 H, Ar–H), 7.37 (d, 2 H, Ar–H), 6.49 (s, 1 H, C=C–H), 5.36–5.24 (m, 2 H, Gal-$H_{2,4}$), 5.03 (dd, 1 H, Gal-H_3), 4.91 (d, 1 H, $J_{H1,H2}$ 7.8 Hz, Gal-H_1), 4.15–3.95 (m, 2 H, Gal-H_6), 4.05 (s, 4 H, N–CH_2CH_2–N), 3.64–3.57 (m, 1 H, Gal-H_5), 2.22, 2.20, 2.03, 2.02 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.5, 169.9, 169.7, 169.3, 165.0, 161.5, 132.3, 129.6, 129.2, 126.1, 97.5, 96.5, 72.1, 69.3, 68.9, 66.6, 61.1, 44.1, 21.1, 20.7, 20.6, 20.4; 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, 44.18; H, 4.13; N, 4.68.

2-[(Z)-2-Phenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)vinyl]hexahydropyrimidinium bromide (**7a**).—IR (KBr): 3370 (NH), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.35 (s, 2 H, NH), 7.55–7.40 (m, 5 H, Ar–H), 6.33 (s, 1 H, C=C–H), 5.32–5.24 (m, 2 H, Gal-$H_{2,4}$), 4.96 (dd, 1 H, Gal-H_3), 4.84 (d, 1 H, $J_{H1,H2}$ 7.9 Hz, Gal-H_1), 4.06–4.00 (m, 2 H, Gal-H_6), 3.68–3.45 (m, 1 H, Gal-H_5), 3.57 (t, 4 H, CH_2–N), 2.05 (quin, 2 H, C–CH_2–C), 2.19, 2.18, 2.03, 1.98 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.0, 170.1, 169.6, 169.4, 163.1, 155.6, 131.3, 130.6, 129.0, 128.2, 101.2, 97.6, 72.2, 69.6, 68.9, 66.8, 60.9, 38.8, 20.9, 20.5, 20.4, 20.3, 18.1; 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, 50.81; H, 5.73; N, 4.74.

2-[(Z)-2-(p-Methylphenyl)-2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)vinyl]hexahydropyrimidinium bromide (**7b**).—IR (KBr): 3360 (NH), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.28 (s, 2 H, NH), 7.29 (d, 2 H, Ar–H), 7.19 (d, 2 H, Ar–H), 6.26 (s, 1 H, C=C–H), 5.30–5.22 (m, 2 H, Gal-$H_{2,4}$), 4.95 (dd, 1 H, Gal-H_3), 4.84 (d, 1 H, $J_{H1,H2}$ 8.0 Hz, Gal-H_1), 4.04–3.97 (m, 2 H, Gal-H_6), 3.64–3.43 (m, 1 H, Gal-H_5), 3.54 (t, 4 H, CH_2–N), 2.36 (s, 3 H, CH_3), 2.02 (quin, 2 H, C–CH_2–C), 2.19, 2.18, 2.03, 1.96 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.9, 170.1, 169.7, 169.4, 163.4, 155.7, 141.9, 129.7, 128.1, 127.7, 100.7, 97.7, 72.1, 69.7, 68.8, 66.8, 60.9, 3 8.8, 21.4, 20,9, 20.5, 20.5, 20.3, 18.2; FABMS: 547 $(M-Br)^+$. Anal. Calcd for $C_{27}H_{35}BrN_2O_{10}$: C, 51.68; H, 5.62; N, 4.47. Found: C, 50.97; H, 6.08; N, 4.35.

2-[(Z)-2-(p-Methoxyphenyl)-2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)vinyl]hexahydropyrimidinium bromide (**7c**).—IR (KBr): 3360 (NH),

1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.24 (s, 2 H, NH), 7.42 (d, 2 H, Ar–H), 6.95 (d, 2 H, Ar–H), 6.30 (s, 1 H, C=C–H), 5.36–5.26 (m, 2 H, Gal-$H_{2,4}$), 5.00 (dd, 1 H, Gal-H_3), 4.92 (d, 1 H, $J_{H1,H2}$ 8.1 Hz, Gal-H_1), 4.12–4.02 (m, 2 H, Gal-H_6), 3.86 (s, 3 H, CH_3O), 3.66–3.50 (m, 1 H, Gal-H_5), 3.57 (t, 4 H, CH_2–N), 2.01 (quin, 2 H, C–CH_2–C), 2.20, 2.19, 2.04, 2.00 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.6, 169.9, 169.5, 169.3, 163.0, 161.7, 155.4, 129.6, 122.4, 114.3, 100.0, 97.4, 71.9, 69.4, 68.5, 66.5, 60.7, 55.3, 38.5, 20.8, 20.4, 20.3, 20,1, 17.9; 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, 49.84; H, 5.33; N, 4.31.

*2-[(Z)-2-(*p*-Chlorophenyl)-2-(2,3,4,6-tetra-*O*-acetyl-*β*-*D*-galactopyranosyloxy)vinyl]hexahydropyrimidinium bromide* (**7d**).—IR (KBr): 3360 (NH), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.24 (s, 2 H, NH), 73.5 (s, 4 H, Ar–H), 6.31 (s, 1 H, C=C–H), 5.26–5.15 (m, 2 H, Gal-$H_{2,4}$), 4.94 (dd, 1 H, Gal-H_3), 4.79 (d, 1 H, $J_{H1,H2}$ 8.1 Hz, Gal-H_1), 4.02–3.88 (m, 2 H, Gal-H_6), 3.61–3.44 (m, 1 H, Gal-H_5), 3.53 (t, 4 H, CH_2–N), 1.95 (quin, 2 H, C–CH_2–C), 2.13, 2.12, 1.94, 1.90 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.9, 169.9, 169.5, 169.2, 161.3, 155.1, 137.2, 129.2, 129.1, 128.9, 101.4, 97.3, 71.9, 69.2, 68.5, 66.4, 60.8, 38.5, 20.8, 20.4, 20.3, 20.1, 17.7; 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, 47.51; H, 5.49; N, 4.44.

*2-[(Z)-2-(*p*-Bromophenyl)-2-(2,3,4,6-tetra-*O*-acetyl-*β*-*D*-galactopyranosyloxy)vinyl]hexahydropyrimidinium bromide* (**7e**).—IR (KBr): 3360 (NH), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.36 (s, 2 H, NH), 7.60 (d, 2 H, Ar–H), 7.38 (d, 2 H, Ar–H), 6.44 (s, 1 H, C=C–H), 5.35–5.23 (m, 2 H, Gal-$H_{2,4}$), 5.01 (dd, 1 H, Gal-H_3), 4.86 (d, 1 H, $J_{H1,H2}$ 8.2 Hz, Gal-H_1), 4.11–3.98 (m, 2 H, Gal-H_6), 3.63–3.52 (m, 1 H, Gal-H_5), 3.59 (t, 4 H, CH_2–N), 2.01 (quin, 2 H, C–CH_2–C), 2.20, 2.19, 2.05, 2.00 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.9, 169.8, 169.5, 169.2, 161.4, 155.0, 132.0, 130.0, 129.4, 125.6, 101.3, 97.3, 71.9, 69.2, 68.5, 66.5, 60.8, 38.6, 20.8, 20.4, 20.3, 20.1, 17.7; 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, 44.99; H, 4.82; N, 3.65.

*1-Methyl-2-[(Z)-2-phenyl-2-(2,3,4,6-tetra-*O*-acetyl-*β*-*D*-galactopyranosyloxy)vinyl]imidazolidinium bromide* (**8a**).—IR (KBr): 3370 (NH), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.84 (s, 1 H, NH), 7.60–7.45 (m, 5 H, Ar–H), 5.74 (s, 1 H, C=C–H), 5.33–5.20 (m, 2 H, Gal-$H_{2,4}$), 4.94 (dd, 1 H, Gal-H_3), 4.84 (d, 1 H, $J_{H1,H2}$ 8.0 Hz, Gal-H_1), 4.20–4.06 (m, 2 H, Gal-H_6), 4.04 (t, 2 H, N–CH_2), 4.02 (t, 2 H, N–CH_2), 3.62–3.57 (m, 1 H, Gal-H_5), 3.24 (s, 3 H, CH_3N), 2.17, 2.14, 2.00, 1.92 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.9, 170.0, 169.7, 169.4, 166.3, 160.9, 131.7, 130.6, 129.0, 128.4, 98.1, 93.9, 71.9, 69.7, 68.6, 66.6, 61.0, 51.7, 43.1, 34.6, 21.1, 20.5, 20.5, 20.3; 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, 50.84; H, 5.48; N, 4.58.

*1-Methyl-2-[(Z)-2-(*p*-methylphenyl)-2-(2,3,4,6-tetra-O-acetyl-*β*-*D*-galactopyranosyloxy)vinyl]imidazolidinium bromide* (**8b**).—IR (KBr): 3380 (NH), 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.60 (s, 1 H, NH), 7.41 (d, 2 H, Ar–H), 7.24 (d, 2 H, Ar–H), 5.66 (s, 1 H, C=C–H), 5.30–5.22 (m, 2 H, Gal-$H_{2,4}$), 4.93 (dd, 1 H, Gal-H_3), 4.85 (d, 1 H, $J_{H1,H2}$ 8.0 Hz, Gal-H_1), 4.23–3.96 (m, 2 H, Gal-H_6), 4.07 (t, 2 H, N–CH_2), 4.05 (t, 2 H, N–CH_2), 3.63–3.56 (m, 1 H, Gal-H_5), 3.23 (s, 3 H, CH_3N), 2.37 (s, 3 H, CH_3), 2.17, 2.15, 2.01, 1.93 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.0, 170.1, 169.8, 169.5, 166.6, 161.0, 142.5, 129.8, 128.5, 128.3, 98.1, 93.4, 72.0, 69.8, 68.7, 66.7, 61.0, 51.7, 43.1, 34.5, 21.5, 21.1, 20.5, 20.5, 20.3; FABMS: 547 $(M-Br)^+$. Anal. Calcd for $C_{27}H_{35}BrN_2O_{10}$: C, 51.68; H, 5.62; N, 4.47. Found: C, 50.50; H, 6.01; N, 4.20.

*1-Methyl-2-[(Z)-2-(*p*-methoxyphenyl)-2-(2,3,4,6-tetra-O-acetyl-*β*-*D*-galactopyranosyloxy)vinyl]imidazolidinium bromide* (**8c**).—IR (KBr): 3370 (NH), 1736 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.43 (s, 1 H, NH), 7.43 (d, 2 H, Ar–H), 6.88 (d, 2 H, Ar–H), 5.61 (s, 1 H, C=C–H), 5.23–5.14 (m, 2 H, Gal-$H_{2,4}$), 4.89 (dd, 1 H, Gal-H_3), 4.84 (d, 1 H, $J_{H1,H2}$ 8.2 Hz, Gal-H_1), 4.13–3.88 (m, 2 H, Gal-H_6), 4.00 (t, 2 H, N–CH_2), 3.97 (t, 2 H, N–CH_2), 3.75 (s, 3 H, OCH_3), 3.61–3.54 (m, 1 H, Gal-H_5), 3.18 (s, 3 H, CH_3N), 2.10, 2.08, 1.93, 1.85 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.7, 169.9, 169.6, 169.3, 166.6, 162.2, 160.8, 130.0, 122.4, 114.4, 98.0, 92.7, 71.8, 69.7, 68.6, 66.5, 60.9, 55.4, 51.5, 42.9, 34.4, 20.9, 20.5, 20,4, 20.2; 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, 50.64; H, 6.35; N, 4.43.

*1-Methyl-2-[(Z)-2-(*p*-chlorophenyl)-2-(2,3,4,6-tetra-O-acetyl-*β*-*D*-galactopyranosyloxy)vinyl]imidazolidinium bromide* (**8d**).—IR (KBr): 3380 (NH), 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.92 (s, 1 H, NH), 7.45–7.38 (m, 4 H, Ar–H), 5.88

(s, 1 H, C=C–H), 5.33–5.24 (m, 2 H, Gal-$H_{2,4}$), 4.96 (dd, 1 H, Gal-H_3), 4.84 (d, 1 H, $J_{H1,H2}$ 7.7 Hz, Gal-H_1), 4.20–3.95 (m, 2 H, Gal-H_6), 4.08 (t, 2 H, N–CH_2), 4.05 (t, 2 H, N–CH_2), 3.70–3.64 (m, 1 H, Gal-H_5), 3.26 (s, 3 H, CH_3N), 2.15, 2.12, 2.03, 1.99 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.9, 170.1, 169.7, 169.4, 164.6, 161.2, 138.1, 130.0, 129.4, 129.2, 98.3, 94.8, 72.1, 69.8, 68.7, 66.7, 61.1, 51.8, 43.2, 34.8, 21.2, 20.7, 20.6, 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, 48.06; H, 5.86; N, 4.35.

1-Methyl-2-[(Z)-2-phenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)vinyl]hexahydropyrimidinium bromide (**9a**).—IR (KBr): 3390 (NH), 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.57 (s, 1 H, NH), 7.52–7.20 (m, 5 H, Ar–H), 5.70 (s, 1 H, C=C–H), 5.13–5.05 (m, 2 H, Gal-$H_{2,4}$), 4.75 (dd, 1 H, Gal-H_3), 4.60 (d, 1 H, $J_{H1,H2}$ 8.0 Hz, Gal-H_1), 4.00–3.86 (m, 2 H, Gal-H_6), 3.52 (t, 2 H, N–CH_2), 3.48–3.40 (m, 1 H, Gal-H_5), 3.34 (t, 2 H, N–CH_2), 3.11 (s, 3 H, CH_3N), 2.02 (quin, 2 H, C–CH_2–C), 2.04, 1.99, 1.87, 1.76 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 169.7, 169.5, 169.3, 169.1, 160.2, 156.3, 130.7, 130.6, 128.4, 127.9, 100.1, 97.5, 71.2, 69.7, 68.1, 66.4, 60.6, 47.9, 40.5, 37.9, 20.7, 20.2, 20.1, 19.9, 18.5; FABMS: 547 $(M-Br)^+$. Anal. Calcd for $C_{27}H_{35}BrN_2O_{10}$: C, 51.68; H, 5.62; N, 4.47. Found: C, 50.95; H, 5.68; N, 4.72.

1-Methyl-2-[(Z)-2-(p-methylphenyl)-2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)vinyl]hexahydropyrimidinium bromide (**9b**).—IR (KBr): 3400 (NH), 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.65 (s, 1 H, NH), 7.47 (d, 2 H, Ar–H), 7.15 (d, 2 H, Ar–H), 5.78 (s, 1 H, C=C–H), 5.24–5.15 (m, 2 H, Gal-$H_{2,4}$), 4.84 (dd, 1 H, Gal-H_3), 4.69 (d, 1 H, $J_{H1,H2}$ 8.0 Hz, Gal-H_1), 4.11–3.98 (m, 2 H, Gal-H_6), 3.63 (t, 2 H, N–CH_2), 3.58–3.50 (m, 1 H, Gal-H_5), 3.45 (t, 2 H, N–CH_2), 3.19 (s, 3 H, CH_3N), 2.30 (s, 3 H, CH_3), 2,02 (quin, 2 H, C–CH_2–C), 2.13, 2.08, 1.97, 1.86 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.2, 170.0, 169.7, 169.5, 160.9, 156.9, 141.6, 129.6, 128.3, 128.1, 100.0, 97.9, 71.6, 70.2, 68.6, 66.8, 60.9, 48.3, 40.9, 38.3, 21.4, 21.1, 20.7, 20.3, 19.0; FABMS: 561 $(M-Br)^+$. Anal. Calcd for $C_{28}H_{37}BrN_2O_{10}$: C, 52.42; H, 5.81; N, 4.37. Found: C, 52.12; H, 6.04; N, 5.20.

1-Methyl-2-[(Z)-2-(p-methoxyphenyl)-2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)vinyl]hexahydropyrimidinium bromide (**9c**).—IR (KBr): 3380 (NH), 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.78 (s, 1 H, NH), 7.60 (d, 2 H, Ar–H), 6.89 (d, 2 H, Ar–H), 5.83 (s, 1 H, C=C–H), 5.28–5.19 (m, 2 H, Gal-$H_{2,4}$), 4.88 (dd, 1 H, Gal-H_3), 4.73 (d, 1 H, $J_{H1,H2}$ 8.0 Hz, Gal-H_1), 4.13–4.04 (m, 2 H, Gal-H_6), 3.79 (s, 3 H, OCH_3), 3.72–3.63 (m, 1 H, Gal-H_5), 3.50 (t, 2 H, N–CH_2), 3.46 (t, 2 H, N–CH_2), 3.22 (s, 3 H, CH_3N), 2.05 (quin, 2 H, C–CH_2–C), 2.17, 2.12, 2.01, 1.91 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.3, 170.1, 169.8, 169.6, 162.0, 160.7, 157.1, 130.2, 123.1, 114.5, 99.4, 98.1, 71.7, 70.3, 68.7, 66.9, 60.9, 55.5, 48.4, 41.0, 38.4, 21.2, 20.7, 20.6, 20.4, 19.0; FABMS: 577 $(M-Br)^+$. Anal. Calcd for $C_{28}H_{37}BrN_2O_{11}$: C, 51.14; H, 5.67; N, 4.26. Found: C, 51.96; H, 6.57; N, 5.00.

1-Methyl-2-[(Z)-2-(p-chlorophenyl)-2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)vinyl]hexahydropyrimidinium bromide (**9d**).—IR (KBr): 3390 (NH), 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.99 (s, 1 H, NH), 7.65 (d, 2 H, Ar–H), 7.34 (d, 2 H, Ar–H), 5.91 (s, 1 H, C=C–H), 5.27–5.17 (m, 2 H, Gal-$H_{2,4}$), 4.86 (dd, 1 H, Gal-H_3), 4.66 (d, 1 H, $J_{H1,H2}$ 8.0 Hz, Gal-H_1), 4.10–4.01 (m, 2 H, Gal-H_6), 3.70–3.62 (m, 1 H, Gal-H_5), 3.50 (t, 2 H, N–CH_2), 3.46 (t, 2 H, N–CH_2), 3.20 (s, 3 H, CH_3N), 2.05 (quin, 2 H, C–CH_2–C), 2.15, 2.10, 1.99, 1.88 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.2, 170.0, 169.7, 169.5, 159.0, 156.5, 137.3, 130.0, 129.9, 129.2, 101.3, 98.1, 71.7, 70.2, 68.6, 66.8, 61.0, 48.3, 40.9, 38.3, 21.2, 20.7, 20.6, 20.4, 18.9; FABMS: 581 $(M-Br)^+$. Anal. Calcd for $C_{27}H_{34}BrClN_2O_{10}$: C, 48.99; H, 5.18; N, 4.23. Found. C, 48.94; H, 5.88; N, 4.34.

General procedure for the synthesis of compounds (**10–11**).—A mixture of benzoyl-substituted heterocyclic ketene aminals **1–2** (1 mmol), 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**5**, 1 mmol) and mercuric cyanide (200 mg) in dried acetonitrile (25 mL) was stirred at room temperature for 1–2 days. The mixture was filtered. After removal of solvent, the product was purified by column chromatography of silica gel (200–300 mesh) using 100:1 chloroform-methanol as eluant to give the pure compounds **10–11**.

2-[(E)-2-Phenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)vinyl]imidazolidinium bromide (**10a**).—IR (KBr): 3340 (NH), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.35 (s, 2 H, NH), 7.55–7.43 (m, 5 H, Ar–H), 5.99 (s, 1 H, C=C–H), 5.35–5.28 (m, 2 H, Gal-$H_{2,4}$), 4.99 (dd, 1 H, Gal-H_3), 4.90 (d, 1 H, $J_{H1,H2}$ 8.1 Hz, Gal-H_1), 4.05–3.95 (m, 2 H, Gal-H_6), 4.05 (s, 4 H, N–CH_2CH_2–N), 3.60–3.51 (m, 1 H, Gal-H_5), 2.19, 2.17, 2.01, 1.97 (s, 12 H, CH_3CO); ^{13}C ($CDCl_3$): δ 171.6, 170.1, 169.9, 169.5,

166.8, 161.7, 131.8, 129.0, 128.4, 128.1, 97.8, 96.2, 72,1, 69.7, 68.9, 66.7, 61.1, 44.6, 21.2, 20.7, 20.6, 20.4; 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, 49.86; H, 5.39; N, 4.02.

2-[(E)-2-(p-Methylphenyl)-2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)vinyl]imidazolidinium bromide (**10b**).—IR (KBr): 3350 (NH), 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.60 (s, 2 H, NH), 7.40 (d, 2 H, Ar–H), 7.26 (d, 2 H, Ar–H), 6.12 (s, 1 H, C=C–H), 5.39–5.28 (m, 2 H, Gal-$H_{2,4}$), 4.99 (dd, 1 H, Gal-H_3), 4.91 (d, 1 H, $J_{H1,H2}$ 8.2 Hz, Gal-H_1), 4.08 (s, 4 H, N–CH_2CH_2–N), 4.00–3.90 (m, 2 H, Gal-H_6), 3.63–3.56 (m, 1 H, Gal-H_5), 2.41 (s, 3 H, CH_3), 2.21, 2.20, 2.05, 2.00 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.4, 170.0, 169.8, 169.4, 166.9, 161.6, 142.1, 129.6, 128.3, 127.5, 97.7, 96.1, 71.8, 69.7, 68.7, 66.6, 61.0, 44.5, 21.5, 21.1, 20.6, 20.6, 20.4; 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, 50.42; H, 6.32; N, 4.35.

2-[(E)-2-(p-Methoxyphenyl)-2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)vinyl]imidazolidinium bromide (**10c**).—IR (KBr): 3370 (NH), 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.15 (s, 2 H, NH), 7.51 (d, 2 H, Ar–H), 6.97 (d, 2 H, Ar–H), 5.98 (s, 1 H, C=C–H), 5.42–5.32 (m, 2 H, Gal-$H_{2,4}$), 5.01 (dd, 1 H, Gal-H_3), 4.94 (d, 1 H, $J_{H1,H2}$ 8.0 Hz, Gal-H_1), 4.12 (s, 4 H, N–CH_2CH_2–N), 4.10–4.02 (m, 2 H, Gal-H_6), 3.87 (s, 3 H, CH_3O), 3.68–3.58 (m, 1 H, Gal-H_5), 2.21, 2.20, 2.05, 2.00 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.4, 170.2, 169,9, 169.6, 167.0, 162.1, 161.7, 130.1, 122.3, 114.5, 97.7, 95.0, 71.9, 69.6, 68.6, 66.6, 61.0, 55.5, 44.5, 21.1, 20.7, 20.7, 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, 49.60; H, 5.28; N, 4.38.

2-[(E)-2-(p-Chlorophenyl)-2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)vinyl]imidazolidinium bromide (**10d**).—IR (KBr): 3370 (NH), 1740 (C=O) cm^{-1}; ^2H NMR ($CDCl_3$): δ 8.18 (s, 2 H, NH), 7.52 (d, 2 H, Ar–H), 7.47 (d, 2 H, Ar–H), 6.11 (s, 1 H, C=C–H), 5.39–5.30 (m, 2 H, Gal-$H_{2,4}$), 5.02 (dd, 1 H, Gal-H_3), 4.88 (d, 1 H, $J_{H1,H2}$ 7.9 Hz, Gal-H_1), 4.20–4.00 (m, 2 H, Gal-H_6), 4.13 (s, 4 H, N–CH_2CH_2–N), 3.68–3.58 (m, 1 H, Gal-H_5), 2.23, 2.21, 2.06, 2.00 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.9,170.1, 169.8, 169.5, 165.8, 161.4, 137.9, 130.0, 129.3, 128.6, 97.6, 96.1, 72.1, 69.4, 68.6, 66.6, 61.2, 44.5, 21.4, 20.7, 20.7, 20.4; 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, 47.27; H, 5.01; N, 4.46.

2-[(E)-2-(p-Bromophenyl)-2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)vinyl]imidazolidinium bromide (**10e**).—IR (KBr): 3360 (NH), 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.10 (s, 2 H, NH), 7.62 (d, 2 H, Ar–H), 7.47 (d, 2 H, Ar–H), 6.06 (s, 1 H, C=C–H), 5.40–5.28 (m, 2 H, Gal-$H_{2,4}$), 5.02 (dd, 1 H, Gal-H_3), 4.91 (d, 1 H, $J_{H1,H2}$ 8.1 Hz, Gal-H_1), 4.20–3.98 (m, 2 H, Gal-H_6), 4.13 (s, 4 H, N–CH_2CH_2–N), 3.64–3.59 (m, 1 H, Gal-H_5), 2.23, 2.20, 2.06, 1.99 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.8, 170.1, 169.8, 169.5, 165.8, 161.3, 132.2, 130.1, 129.1, 126.2, 97.6, 96.3, 72.0, 69.4, 68.6, 66.6, 61.2, 44.5, 21.3, 20.7, 20.6, 20.4; 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, 44.90; H, 4.70; N, 3.93.

2-[(E)-2-Phenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)vinyl]hexahydropyrimidinium bromide (**11a**).—IR (KBr): 3380 (NH), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.53 (s, 2 H, NH), 7.59–7.43 (m, 5 H, Ar–H), 6.02 (s, 1 H, C=C–H), 5.36–5.24 (m, 2 H, Gal-$H_{2,4}$), 4.98 (dd, 1 H, Gal-H_3), 4.86 (d, 1 H, $J_{H1,H2}$ 8.2 Hz, Gal-H_1), 4.14–4.00 (m, 2 H, Gal-H_6), 3.74–3.54 (m, 1 H, Gal-H_5), 3.64 (t, 4 H, CH_2–N), 2.02 (quin, 2 H, C–CH_2–C), 2.22, 2.20, 2.05, 1.98 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.3, 170.2, 169.8, 169.6, 163.2, 155.4, 131.3, 130.6, 129.0, 128.3, 101.2, 97.5, 72.0, 69.6, 68.6, 66.7, 61.0, 39.1, 21.1, 21.0, 20.7, 20.4, 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, 51.37; H, 5.60; N, 4.27.

2-[(E)-2-(p-Methylphenyl)-2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)vinyl]hexahydropyrimidinium bromide (**11b**).—IR (KBr): 3350 (NH), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.99 (s, 2 H, NH), 7.42 (d, 2 H, Ar–H), 7.26 (d, 2 H, Ar–H), 5.75 (s, 1 H, C=C–H), 5.40–5.28 (m, 2 H, Gal-$H_{2,4}$), 5.01 (dd, 1 H, Gal-H_3), 4.90 (d, 1 H, $J_{H1,H2}$ 8.0 Hz, Gal-H_1), 4.17–4.02 (m, 2 H, Gal-H_6), 3.74–3.55 (m, 1 H, Gal-H_5), 3.66 (t, 4H, CH_2–N), 2.41 (s, 3H, CH_3), 2.08 (quin, 2H, C–CH_2–C), 2.22, 2.21, 2.04, 2.00 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.3, 170.1, 169.8, 169.5, 164.1, 155.3, 141.7, 129.6, 128.3, 127.4, 100.4, 97.4, 71.7, 69.5, 68.4, 66.5, 60.9, 39.4, 21.5, 21.2, 20.7, 20.6, 20.4, 18.0; FABMS: 547 $(M-Br)^+$. Anal. Calcd for $C_{27}H_{35}BrN_2O_{10}$: C, 51.68; H, 5.62; N, 4.47. Found: C, 50.97; H, 5.36; N, 4.45.

2-[(E)-2-(p-Methoxyphenyl)-2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)vinyl]hexahydropyrimidinium bromide (**11c**).—IR (KBr): 3360 (NH), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.88 (s, 2 H, NH), 7.48 (d, 2 H, Ar–H), 6.95 (d, 2 H, Ar–H), 6.21 (s, 1 H, C=C–H), 5.42–5.27 (m, 2 H, Gal-$H_{2,4}$), 4.99 (dd, 1 H, Gal-H_3), 4.91 (d, 1 H, $J_{H1,H2}$ 8.0 Hz, Gal-H_1), 4.13–4.04 (m, 2 H, Gal-H_6), 3.85 (s, 3 H, CH_3O), 3.68–3.54 (m, 1 H, Gal-H_5), 3.60 (t, 4 H, CH_2–N), 2.02 (quin, 2 H, C–CH_2–C), 2.21, 2.20, 2.06, 2.00 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.0, 170.1, 169.7, 169.5, 163.2, 161.8, 155.5, 129.9, 122.6, 114.4,100.2, 97.6, 71.9, 69.6, 68.6, 66.6, 60.8, 55.5, 38.9, 20.8, 20.6, 20.5, 20.3, 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, 49.99; H, 5.41; N, 4.40.

2-[(E)-2-(p-Chlorophenyl)-2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)vinyl]hexahydropyrimidinium bromide (**11d**).—IR (KBr): 3360 (NH), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.74 (s, 2 H, NH), 7.52 (d, 2 H, Ar–H), 7.43 (d, 2 H, Ar–H), 6.14 (s, 1 H, C=C-H), 5.38–5.25 (m, 2 H, Gal-$H_{2,4}$), 5.01 (dd, 1 H, Gal-H_3), 4.86 (d, 1 H, $J_{H1,H2}$ 7.8 Hz, Gal-H_1), 4.14–3.98 (m, 2 H, Gal-H_6), 3.70–3.48 (m, 1 H, Gal-H_5), 3.62 (t, 4 H, CH_2–N), 2.01 (quin, 2 H, C–CH_2–C), 2.21, 2.20, 2.05, 1.98 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.2,170.1, 169.8, 169.4, 161.7, 155.2, 137.2, 129.8, 129.2, 128.2, 101.6, 97.6, 72.0, 69.6, 68.6, 66.7, 61.1, 39.1, 21.1, 20.7, 20.6, 20.4, 17.9; 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, 48.67; H, 5.61; N, 4.29.

2-[(E)-2-(p-Bromophenyl)-2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)vinyl]hexahydropyrimidinium bromide (**11e**).—IR (KBr): 3360 (NH), 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.11 (s, 2 H, NH), 7.62 (d, 2 H, Ar–H), 7.46 (d, 2 H, Ar–H), 5.87 (s, 1 H, C=C–H), 5.40–5.28 (m, 2 H, Gal-$H_{2,4}$), 5.01 (dd, 1 H, Gal-H_3), 4.85 (d, 1 H, $J_{H1,H2}$ 7.8 Hz, Gal-H_1), 4.20–4.00 (m, 2 H, Gal-H_6), 3.80–3.50 (m, 1 H, Gal-H_5), 3.66 (t, 4 H, CH_2–N), 2.04 (quin, 2 H, C–CH_2–C), 2.22, 2.20, 2.05, 2.02 (s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.1, 170.0, 169.6, 169.3, 161.5, 155.3, 132.2, 129.7, 129.6, 125.8, 101.7, 97.5, 72.1, 69.4, 68.7, 66.5, 61.0, 38.8, 21.1, 20.6, 20.6, 20.4, 18.0; 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, 45.04; H, 4.97; N, 3.80.

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