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Highly stereoselective α-O-glucosylation of heterocyclic ketene aminals

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Abstract

A new series of α-glucosides of heterocyclic ketene aminals have been synthesized. The double bonds of the glucosides resulted in Z or E configuration by using CaH_2 or a Lewis acid as catalyst, respectively. A special complex of mercuric cyanide with glucopyranosides was the result when $Hg(CN)_2$ was used to catalyze the reaction.

Keywords: Synthesis; Glucosylation; Heterocyclic ketene aminal

1. Introduction

Recently, O-glucosylation of heterocyclic ketene aminals has been reported [1–3]. Due to neighboring group participation, the β configuration of the glucosides were obtained when acetyl was used as the protecting group of glucosyl donors. However, it is difficult to effect the α-O-glucosylation of heterocyclic ketene aminals because of the steric repulsion of the 1,2-cis configuration in the desired glucosides. In order to get the α-glucosides, we tried to use the benzyl as protecting group instead of acetyl. Fortunately, the desired α-glucosides of heterocyclic ketene aminals were obtained.

Herein we discuss the syntheses of α-glucosides from ketene aminals and the determination of their structure.

2. Result and discussion

Heterocyclic ketene aminals **1** or **2** were prepared by the literature method [4]. Either **1** or **2** was glucosylated with the *O*-benzyl-protected glucosyl chloride **3** in the presence of CaH_2 as promoter in anhydrous acetonitrile to furnish the compounds **4** or **5** in good yield. Structures of **4** and **5** were established on the basis of spectroscopic data and elemental analyses (Scheme 1).

The monoglucosylated derivatives of **1** or **2** were proved by the appearance of benzyl-protected glucopyranosyl group signals and heterocyclic ketene aminal signals in the ^1H and ^{13}C NMR spectra. The ^1H NMR spectra showed signals for two nitrogen protons (9.90–10.20 ppm in **4** or **5**, respectively) and one ethylenic proton (6.00–6.20 ppm), which indicated that glucosylation did not occur at either the N- or C-atoms. The appearance of a new carbon signal (160–166 ppm) instead of the carbonyl carbon signal (ca. 180–190 ppm) in the ^{13}C NMR spectra illustrated that O-at-

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tack products were obtained. The ^{1}H and ^{13}C NMR signals of **4** or **5** were assigned by $^{1}H-^{1}H$ COSY, $^{1}H-^{13}C$ COSY and DEPT spectra. The chemical shift of the hydrogen and carbon atoms of the glucopyranose ring could be given in order as follows: H-1 > H-5 > H-3 > H-6 > H-2 > H-4 and C-1 > C-3 > C-2 > C-4 > C-5 > C-6.

The α anomer of **4** or **5** was confirmed by the glucopyranosyl ring H-1–H-2 coupling constants ($J_{H-1,H-2}$ 3.40–3.70 Hz in **4** or **5**, respectively) [5,6]. Huang and coworkers have reported the β-O-glucosidation of benzoyl-substituted heterocyclic ketene aminals [2,3]. They used acetyl as protecting group of glycosyl donor. Owing to the neighboring group participation of acetyl, only β-glucosides were obtained. In this paper, benzyl was selected to use as the protecting group instead of either acetyl or benzoyl to avoid the neighboring-group participation. On the other hand, benzyl could promote the activity of the glycosyl donor by increasing the electron density on the glycosyl donor. Thus α-glucosides of heterocyclic ketene aminals were synthesized in good yields, probably resulting from repulsions of the lone electron pairs or from dipolar effects.

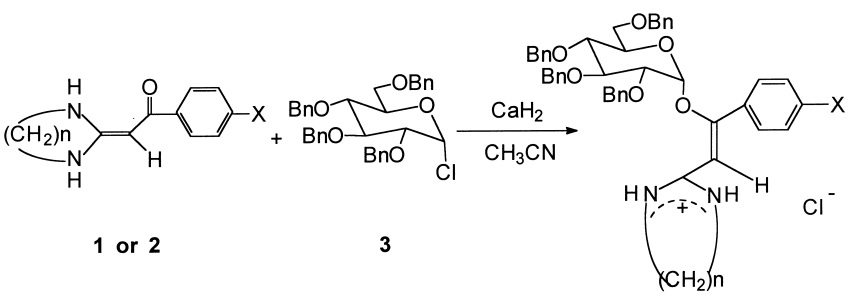
The configuration of the double bonds was determined by data in the literature [3] in which Z configuration of double bonds was formed when CaH_2 was used as catalyst.

Compound **2** was glucosylated with **3** to give compounds **6** when $AgSO_3CF_3$ was used as promoter. Compound **1** reacted with **3** to give mixed products, which were difficult to separate. The determination of structures of **6** was similar to that of **4** and **5**. The α and E configuration of **6** were confirmed according to data in the literature [3,5,6] (Scheme 2).

Then we tried to use mercuric cyanide to catalyze the reaction of heterocyclic ketene aminals **1** or **2** with glucosyl donor **3**. Mercuric heterocyclic ketene aminal *O*-glucoside complexes **7** or **8** resulted when excessive mercuric cyanide was used.

The structures and configurations of **7** or **8** have been determined mainly on the basis of their ^{1}H NMR, ^{13}C NMR, FABMS spectra, and the existence and existential state of mercuric cyanide were confirmed by electron spectroscopy (ES). The α and E configuration of **7** and **8** were established as the same as those of **6** (Scheme 3).

As described above, CaH_2 and $AgSO_3CF_3$ were used as promoters in the reaction of heterocyclic ketene aminals with the glucosyl donor, in which no complexes of heterocyclic ketene aminal *O*-glucosides with any promoter were obtained. Obviously, the differences that occurred in these similar reactions resulted from the special properties of mercuric cyanide. Ulbricht and Rogers have reported the rearrangement of *O*-glucosides to *N*-glucosides in the presence of mercuric bro-

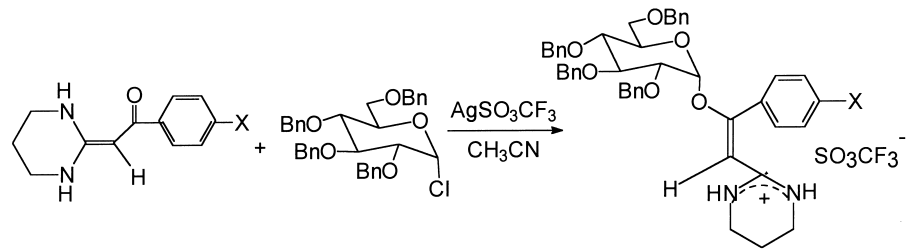


1 or 2 **3** **4 or 5**

1, 4 n = 2; **2, 5** n = 3

1, 2, 4, 5	a	b	c	d
X	H	CH_3	OCH_3	Cl

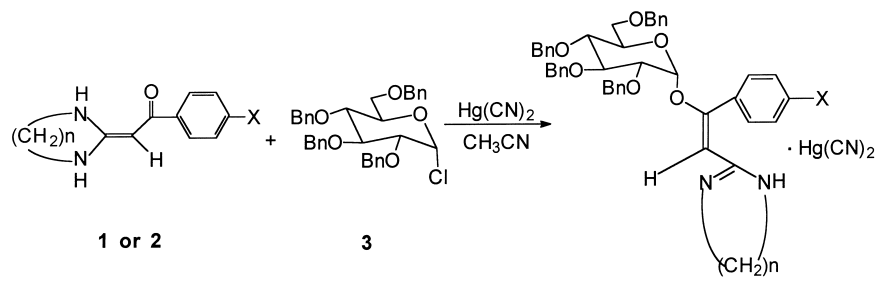
Scheme 1.



2 3 6

6	a	b	c	d
X	H	CH_3	OCH_3	Cl

Scheme 2.



1 or 2 3 7 or 8

7 n = 2; **8** n = 3

7, 8	a	b	c	d
X	H	CH_3	OCH_3	Cl

Scheme 3.

mide and suggested that the mechanism involved a mercuric complex [7,8]. The existence of mercuric cyanide in **7** or **8** was detected by ES, and the electron-binding energy of Hg^{2+} in **7** or **8** was about 0.6×10^{-4} eV lower than that in mercuric cyanide. A possible mechanism is suggested in Scheme 4.

At first, the chemical action of **1** or **2** with mercuric cyanide might form a four-coordination intermediate **I** or **II**, which might, in part, change to **II**. Because of the lesser steric hindrance in **II**, the glucosyl donor **3** might react with **II** to give the E configuration products **7** or **8**. An acetyl-protected glucosyl donor had been used to conduct the same reaction, but no mercuric cyanide glycoside complex was obtained. Therefore, this conclusion might result from the *O*-benzyl-protected glycosyl donor. Owing to the electron-donating effect of the benzyl-protected glycosyl donor, Hg could help to disperse the electrons on the glycosyl donor, and **7** or **8** might be formed. We had tried to separate the intermediates **I** or **II**, but failed.

3. Experimental

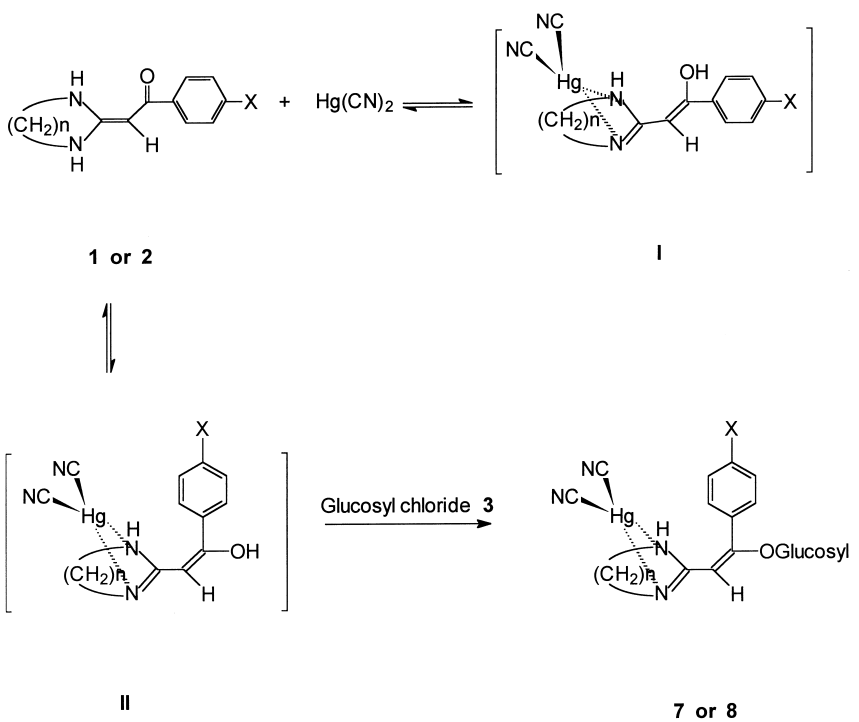
General methods.—Melting points are uncorrected. ^1H and ^{13}C NMR spectra of $CDCl_3$ solutions were obtained with a Varian Unity 200 MHz spectrometers. Chemical shifts are reported in ppm downfield from Me_4Si. *J* values are given in Hz. IR spectra were

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 **4** *or* **5**.—To a mixture of benzoyl-substituted heterocyclic ketene aminals (**1** or **2**) (1 mmol) and anhydrous acetonitrile (25 mL) were added 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl chloride [9] (1.1 mmol) and CaH_2 (1.0 g). The mixture was stirred at room temperature (rt) for 48 h. When TLC (10:1 $CHCl_3$–CH_3OH, silica gel) showed the absence of **1** or **2** and the appearance of one new major spot, the mixture was filtered and washed with CH_2Cl_2 (10 mL). After removal of solvent, purification 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 **4** or **5**.

*2-[(Z)-2-Phenyl-2-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyloxy)vinyl]imidazolidinium chloride* (**4a**). Foam, 63% yield; mp 44–46 °C; IR (KBr): 3248 (N–H), 1644, 1597, 1494, 1210 cm^{-1}; ^1H NMR ($CDCl_3$): δ 10.00 (s, 2 H, NH), 7.55–7.10 (m, 25 H, Ar–H), 6.08 (s, 1 H, C=C–H), 5.15 (d, 1 H, $J_{H\text{-}1,H\text{-}2}$ 3.66 Hz, Glc–H-1), 4.96–4.45 (m, 8 H, Ph–CH_2), 4.13–4.03 (m, 1 H, Glc–H-5), 3.98–3.88 (m, 1 H, Glc–H-3), 3.75–3.62 (m, 4 H, N–CH_2), 3.60–3.45 (m, 2 H, Glc–H-6), 3.38–3.17 (m, 2 H, Glc–H-2, H-4); ^{13}C NMR ($CDCl_3$): δ 169.78, 161.85, 137.46, 137.13, 137.05, 135.42, 131.38, 128.89, 128.59, 128.33, 128.19, 128.07, 127.58, 127.44, 127.32, 97.45, 94.45, 80.98, 78.47, 77.21, 75.24, 74.69, 74.29, 73.03, 71.55, 67.56, 43.17; FABMS: *m/z* 711 $[M-Cl]^+$. Anal. Calcd for $C_{45}H_{47}ClN_2O_6 \cdot 0.5H_2O$: C, 71.46; H, 6.40; N, 3.70. Found: C, 71.62; H, 6.63; N, 3.95.

*2-[(Z)-2-(*p*-Methylphenyl)-2-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyloxy)vinyl]-imidazolidinium chloride* (**4b**). Foam, 66% yield; mp 45–47 °C; IR (KBr): 3250 (N–H), 1644, 1603, 1510, 1209 cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.95 (s, 2 H, NH), 7.50–7.00 (m, 24 H, Ar–H), 6.05 (s, 1 H, C=C–H), 5.15 (d, 1 H, $J_{H\text{-}1,H\text{-}2}$ 3.66 Hz, Glc–H-1), 4.97–4.43 (m, 8 H, Ph–CH_2), 4.15–4.05 (m, 1 H, Glc–H-5), 4.00–3.90 (m, 1 H, Glc–H-3), 3.75–3.63 (m, 4 H, N–CH_2), 3.60–3.43 (m, 2 H, Glc–H-6), 3.30–3.15 (m, 2 H, Glc–H-2, H-4), 2.30 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$): δ 170.26, 162.03, 142.06, 137.51, 137.16, 135.42, 129.02, 128.73,



Scheme 4.

128.63, 128.38, 128.22, 128.12, 127.57, 127.44, 127.34, 97.36, 93.82, 81.06, 78.59, 77.20, 75.30, 74.75, 74.27, 73.12, 71.50, 67.78, 43.18, 21.14; FABMS: m/z 725 $[M-Cl]^+$. Anal. Calcd for $C_{46}H_{49}ClN_2O_6 \cdot 0.5H_2O$: C, 71.72; H, 6.54; N, 3.64. Found: C, 72.00; H, 6.55; N, 3.64.

*2-[(Z)-2-(*p*-Methoxyphenyl)-2-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyloxy)vinyl]-imidazolidinium chloride* (**4c**). Foam, 73% yield; mp 54–56 °C; IR (KBr): 3300 (N–H), 1660, 1620, 1580, 1200 cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.95 (s, 2 H, NH), 7.40 (d, 2 H, Ar–H), 7.33–7.07 (m, 20 H, Ar–H), 6.65 (d, 2 H, Ar–H), 6.00 (s, 1 H, C=C–H), 5.10 (d, 1 H, $J_{H\text{-}1,H\text{-}2}$ 3.60 Hz, Glc–H-1), 4.89–4.40 (m, 8 H, Ph–CH_2), 4.10–4.00 (m, 1 H, Glc–H-5), 3.95–3.84 (m, 1 H, Glc–H-3), 3.70 (s, 3 H, OCH_3), 3.60–3.72 (m, 4 H, N–CH_2), 3.55–3.40 (m, 2 H, Glc–H-6), 3.20–3.10 (m, 2 H, Glc–H-2, H-4); ^{13}C NMR ($CDCl_3$): δ 170.27, 162.35, 162.32, 137.64, 137.29, 135.50, 131.18, 128.88, 128.83, 128.54, 128.42, 128.32, 127.89, 127.85, 127.67, 127.61, 127.50, 123.54, 113.69, 97.41, 93.29, 81.30, 78.85, 77.15, 75.54, 74.97, 74.45, 73.32, 71.61, 68.08, 55.28, 43.31; FABMS: m/z 741 $[M-Cl]^+$. Anal. Calcd for $C_{46}H_{49}ClN_2O_7$: C, 71.07; H, 6.35; N, 3.60. Found: C, 71.04; H, 6.39; N, 3.57.

*2-[(Z)-2-(*p*-Chlorophenyl)-2-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyloxy)vinyl]-imidazolidinium chloride* (**4d**). Foam, 57% yield; mp 54–56 °C; IR (KBr): 3250 (N–H), 1646, 1593, 1493, 1210 cm^{-1}; ^1H NMR ($CDCl_3$): δ 10.14 (s, 2 H, NH), 7.44–7.14 (m, 24 H, Ar–H), 6.17 (s, 1 H, C=C–H), 5.08 (d, 1 H, $J_{H\text{-}1,H\text{-}2}$ 3.67 Hz, Glc–H-1), 5.00–4.45 (m, 8 H, Ph–CH_2), 4.15–4.04 (m, 1 H, Glc–H-5), 4.00–3.90 (m, 1 H, Glc–H-3), 3.75–3.63 (m, 4 H, N–CH_2), 3.62–3.52 (m, 2 H, Glc–H-6), 3.30–3.15 (m, 2 H, Glc–H-2, H-4); ^{13}C NMR ($CDCl_3$): δ 168.53, 161.81, 137.73, 137.51, 137.13, 137.05, 135.46, 130.52, 129.86, 128.76, 128.53, 128.41, 128.33, 128.26, 127.78, 127.72, 127.53, 127.42, 97.76, 95.05, 81.03, 78.58, 77.00, 75.40, 74.88, 74.61, 73.25, 71.67, 67.84, 43.30; FABMS: m/z 745 $[M-Cl]^+$. Anal. Calcd for $C_{45}H_{46}Cl_2N_2O_6$: C, 69.13; H, 5.93; N, 3.58. Found: C, 69.36; H, 5.76; N, 3.64.

*2-[(Z)-2-Phenyl-2-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyloxy)vinyl]hexahydropyrimidinium chloride* (**5a**). Foam, 80% yield; mp 55–57 °C; IR (KBr): 3277 (N–H), 1659, 1623, 1495, 1209 cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.95 (s, 2 H, NH), 7.55–7.10 (m, 25 H, Ar–H), 6.05 (s, 1 H, C=C–H), 5.17 (d, 1 H, $J_{H\text{-}1,H\text{-}2}$ 3.67 Hz, Glc–H-1), 4.95–4.46 (m, 8 H, Ph–CH_2), 4.15–4.05 (m, 1 H, Glc–H-5), 3.95–3.84 (m, 1 H, Glc–H-3), 3.80–3.65 (m, 4 H, Glc–H-2, H-4, H-6), 3.30–2.85 (m, 4 H, N–CH_2), 1.65 (quin, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 166.31, 154.93, 137.51, 137.19, 137.14, 135.58, 131.73, 131.03, 128.91, 128.55, 128.39, 128.30, 128.16, 127.71, 127.51, 127.36, 98.80, 97.09, 81.62, 78.86, 77.21, 75.57, 74.90, 74.37, 73.15, 71.53, 67.65, 37.88, 17.62; FABMS: m/z 725 $[M-Cl]^+$. Anal. Calcd for $C_{46}H_{49}ClN_2O_6 \cdot 0.5H_2O$: C, 71.72; H, 6.54; N, 3.64. Found: C, 71.91; H, 6.54; N, 3.78.

*2-[(Z)-2-(*p*-Methylphenyl)-2-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyloxy)vinyl]hexahydropyrimidinium chloride* (**5b**). Foam, 84% yield; mp 54–56 °C; IR (KBr): 3250 (N–H), 1658, 1623, 1210 cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.90 (s, 2 H, NH), 7.50–7.00 (m, 24 H, Ar–H), 6.01 (s, 1 H, C=C–H), 5.18 (d, 1 H, $J_{H\text{-}1,H\text{-}2}$ 3.42 Hz, Glc–H-1), 4.95–4.46 (m, 8 H, Ph–CH_2), 4.15–4.05 (m, 1 H, Glc–H-5), 3.95–3.85 (m, 1 H, Glc–H-3), 3.80–3.60 (m, 4 H, Glc–H-2, H-4, H-6), 3.30–2.85 (m, 4 H, N–CH_2), 2.34 (s, 3 H, CH_3), 1.65 (quin, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 166.73, 155.06, 141.56, 137.57, 137.24, 135.61, 128.99, 128.85, 128.76, 128.70, 128.46, 128.35, 128.25, 127.77, 127.66, 127.57, 127.40, 98.83, 97.04, 81.71, 78.98, 77.21, 75.65, 74.96, 74.36, 73.23, 71.49, 67.84, 38.00, 21.15, 17.80; FABMS: m/z 739 $[M-Cl]^+$. Anal. Calcd for $C_{47}H_{51}ClN_2O_6 \cdot 0.5H_2O$: C, 71.97; H, 6.68; N, 3.57. Found: C, 72.09; H, 6.74; N, 3.88.

*2-[(Z)-2-(*p*-Methoxyphenyl)-2-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyloxy)vinyl]hexahydropyrimidinium chloride* (**5c**). Foam, 88% yield; mp 60–62 °C; IR (KBr): 3285 (N–H), 1655, 1603, 1511, 1211 cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.85 (s, 2 H, NH), 7.45 (d, 2 H, Ar–H), 7.40–7.18 (m, 20 H, Ar–H), 6.75 (d, 2 H, Ar–H), 6.00 (s, 1 H, C=C–H), 5.18 (d, 1 H, $J_{H\text{-}1,H\text{-}2}$ 3.66 Hz, Glc–H-1), 4.98–4.45 (m, 8 H, Ph–CH_2), 4.18–4.05 (m, 1 H, Glc–H-5), 3.97–3.60 (m, 5 H, Glc–H-2, H-3, H-4, H-6), 3.75 (s, 3 H, OCH_3), 3.30–2.85 (m, 4 H,

N–CH_2), 1.66 (quin, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 166.50, 161.73, 155.04, 137.48, 137.19, 135.53, 130.74, 128.60, 128.38, 128.27, 128.17, 127.71, 127.50, 127.31, 123.79, 113.55, 98.04, 96.91, 81.65, 78.94, 77.21, 75.57, 74.89, 74.26, 73.13, 71.39, 67.94, 55.10, 37.83, 17.65; FABMS: m/z 755 $[M-Cl]^+$. Anal. Calcd for $C_{47}H_{51}ClN_2O_7$: C, 71.33; H, 6.50; N, 3.54. Found: C, 71.29; H, 6.68; N, 3.63.

*2-[(Z)-2-(*p*-Chlorophenyl)-2-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyloxy)vinyl]hexahydropyrimidinium chloride* (**5d**). Foam, 78% yield; mp 65–67 °C; IR (KBr): 3260 (N–H), 1660, 1624, 1493, 1208 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 9.90 (s, 2 H, NH), 7.55–7.10 (m, 24 H, Ar–H), 6.10 (s, 1 H, C=C–H), 5.10 (d, 1 H, $J_{H\text{-}1,H\text{-}2}$ 3.41 Hz, Glc–H-1), 4.97–4.40 (m, 8 H, Ph–CH_2), 4.15–4.05 (m, 1 H, Glc–H-5), 3.95–3.84 (m, 1 H, Glc–H-3), 3.80–3.60 (m, 4 H, Glc–H-2, H-4, H-6), 3.30–2.85 (m, 4 H, N–CH_2), 1.65 (quin, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 165.05, 154.88, 137.55, 137.27, 137.19, 137.14, 135.63, 130.39, 130.26, 128.81, 128.73, 128.49, 128.35, 128.27, 128.12, 128.01, 127.94, 127.79, 127.68, 127.57, 127.52, 127.38, 99.89, 97.45, 81.59, 78.93, 77.00, 75.61, 74.97, 74.63, 73.27, 71.69, 67.93, 37.95, 17.65; FABMS: m/z 759 $[M-Cl]^+$. Anal. Calcd for $C_{46}H_{48}Cl_2N_2O_6$: C, 69.42; H, 6.08; N, 3.52. Found: C, 69.61; H, 6.05; N, 3.53.

General procedure for the synthesis of compounds **6**.—The procedures were the same as those of **4** or **5**, except $AgSO_3CF_3$ was used instead of CaH_2.

2-[(E)-2-Phenyl-2-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyloxy)vinyl]hexahydropyrimidinium trifluoromethanesulfonate (**6a**). Foam, 62% yield; mp 44–46 °C; IR (KBr): 3266 (N–H), 1657, 1574, 1495, 1247 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.80 (s, 2 H, NH), 7.62–7.15 (m, 25 H, Ar–H), 6.20 (s, 1 H, C=C–H), 4.97–4.40 (m, 8 H, Ph–CH_2), 4.87 (d, 1 H, $J_{H\text{-}1,H\text{-}2}$ 3.18 Hz, Glc–H-1), 3.90–3.30 (m, 6 H, Glc–H-2, H-3, H-4, H-5, H-6), 3.30–3.05 (m, 4 H, N–CH_2), 1.68 (quin, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 162.77, 155.60, 137.75, 137.55, 137.34, 137.23, 131.61, 130.82, 129.01, 128.52, 128.28, 128.14, 127.97, 127.79, 103.12, 100.47, 83.87, 81.25, 76.36, 75.69, 75.31, 74.93, 74.38, 73.48, 67.30, 38.62, 17.85; FABMS: m/z 726 $[M+1-(CF_3SO_3)]^+$. Anal. Calcd for $C_{47}H_{49}F_3N_2O_9S$: C, 64.51; H, 5.64; N, 3.20. Found: C, 64.50; H, 5.62; N, 3.64.

*2-[(E)-2-(*p*-Methylphenyl)-2-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyloxy)vinyl]hexahydropyrimidinium trifluoromethanesulfonate* (**6b**). Foam, 65% yield; mp 47–49 °C; IR (KBr): 3287 (N–H), 1659, 1628, 1249 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.65 (s, 2 H, NH), 7.48 (d, 2 H, Ar–H), 7.40–7.14 (m, 20 H, Ar–H), 7.10 (d, 2 H, Ar–H), 6.05 (s, 1 H, C=C–H), 4.97–4.33 (m, 8 H, Ph–CH_2), 4.90 (d, 1 H, $J_{H\text{-}1,H\text{-}2}$ 3.09 Hz, Glc–H-1), 3.90–3.25 (m, 6 H, Glc–H-2, H-3, H-4, H-5, H-6), 3.23–3.05 (m, 4 H, N–CH_2), 2.30 (s, 3 H, CH_3), 1.68 (quin, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 163.26, 155.52, 141.85, 137.77, 137.57, 137.37, 129.51, 128.27, 128.23, 128.19, 128.12, 127.99, 127.92, 127.79, 127.68, 127.63, 127.54, 127.22, 101.76, 100.47, 83.76, 80.76, 76.37, 75.17, 74.90, 74.56, 74.44, 73.22, 67.41, 38.52, 21.18, 17.69; FABMS: m/z 740 $[M+1-(CF_3SO_3)]^+$. Anal. Calcd for $C_{48}H_{51}F_3N_2O_9S$: C, 64.85; H, 5.78; N, 3.15. Found: C, 64.46; H, 5.73; N, 3.30.

*2-[(E)-2-(*p*-Methoxyphenyl)-2-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyloxy)vinyl]hexahydropyrimidinium trifluoromethanesulfonate* (**6c**). Foam, 58% yield; mp 45–47 °C; IR (KBr): 3250 (N–H), 1660, 1600, 1515, 1250 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.71 (s, 2 H, NH), 7.55 (d, 2 H, Ar–H), 7.50–7.15 (m, 20 H, Ar–H), 6.80 (d, 2 H, Ar–H), 6.13 (s, 1 H, C=C–H), 5.00–4.30 (m, 8 H, Ph–CH_2), 4.90 (d, 1 H, $J_{H\text{-}1,H\text{-}2}$ 4.15 Hz, Glc–H-1), 3.95–3.30 (m, 6 H, Glc–H-2, H-3, H-4, H-5, H-6), 3.80 (s, 3 H, OCH_3), 3.40–3.05 (m, 4 H, N–CH_2), 1.71 (quin, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 162.80, 162.27, 155.74, 137.77, 137.52, 137.34, 137.21, 129.76, 128.50, 128.10, 127.98, 127.85, 127.77, 122.93, 114.42, 101.37, 100.66, 83.92, 81.45, 76.37, 75.70, 75.42, 74.96, 74.38, 73.49, 67.32, 55.39, 38.71, 17.99; FABMS: m/z 756 $[M+1-(CF_3SO_3)]^+$. Anal. Calcd for $C_{48}H_{51}F_3N_2O_{10}S\cdot0.5H_2O$: C, 63.08; H, 5.73; N, 3.06. Found: C, 62.90; H, 5.75; N, 2.96.

*2-[(E)-2-(*p*-Chlorophenyl)-2-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyloxy)vinyl]hexahydropyrimidinium trifluoromethanesulfonate* (**6d**). Foam, 60% yield; mp 45–47 °C; IR (KBr): 3280 (N–H), 1659, 1629, 1593, 1493,

1249 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.80 (s, 2 H, NH), 7.75–7.10 (m, 24 H, Ar–H), 6.18 (s, 1 H, C=C–H), 4.95–4.35 (m, 8 H, Ph–CH_2), 4.90 (d, 1 H, $J_{H\text{-}1,H\text{-}2}$ 3.66 Hz, Glc–H-1), 3.85–3.34 (m, 6 H, Glc–H-2, H-3, H-4, H-5, H-6), 3.25–3.10 (m, 4 H, N–CH_2), 1.65 (quin, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 161.47, 155.24, 137.64, 137.55, 129.47, 129.16, 129.12, 128.86, 128.74, 128.36, 128.22, 128.00, 127.73, 127.64, 127.29, 103.30, 100.56, 83.78, 80.90, 76.35, 75.53, 75.40, 74.74, 74.45, 73.33, 67.27, 38.57, 17.69; FABMS: m/z 760 $[M+1-(CF_3SO_3)]^+$. Anal. Calcd for $C_{47}H_{48}ClF_3N_2O_9S$: C, 62.07; H, 5.32; N, 3.08. Found: C, 62.23; H, 5.21; N, 3.50.

General procedure for the synthesis of compounds **7** *or* **8**. To a mixture of benzoyl-substituted heterocyclic ketene aminals **1** or **2** (1 mmol) and anhydrous acetonitrile (25 mL) were added 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl chloride [9] (1.1 mmol) and mercuric cyanide (1.0 g). The mixture was stirred at rt for 10–30 h. When TLC (10:1 $CHCl_3$–CH_3OH, silica gel) showed the absence of **1** or **2** and the appearance of one new major spot, the mixture was filtered and washed with CH_2Cl_2 (10 mL). After removal of solvent, fractionation of the residue by column chromatography on silica gel (200–300 mesh) using the same eluant (100:1 → 25:1 $CHCl_3$–CH_3OH) gave pure compounds **7** or **8**.

*2-[(*E*)-2-Phenyl-2-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyloxy)vinyl]imidazoline mercuric cyanide* (**7a**). Foam, 61% yield; mp 57–59 °C; IR (KBr): 3250 (N–H), 1637, 1595, 1492, 1070 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.70 (s, 1 H, NH), 7.70–7.10 (m, 25 H, Ar–H), 6.41 (s, 1 H, C=C–H), 4.97–4.35 (m, 8 H, Ph–CH_2), 4.86 (d, 1 H, $J_{H\text{-}1,H\text{-}2}$ 4.40 Hz, Glc–H-1), 3.98–3.60 (m, 5 H, Glc–H-2, H-3, H-5, H-6), 3.75–3.65 (m, 4 H, N–CH_2), 3.42–3.33 (m, 1 H, Glc–H-4); ^{13}C NMR ($CDCl_3$): δ 165.80, 162.35, 137.77, 137.62, 137.54, 137.25, 131.65, 131.18, 129.36, 129.02, 128.91, 128.46, 128.37, 128.06, 128.00, 127.78, 127.73, 126.80, 100.73, 96.04, 83.97, 81.03, 77.20, 75.42, 75.18, 74.85, 74.45, 73.26, 67.25, 44.63; FABMS: m/z 711 $[M+1-Hg(CN)_2]^+$. Anal. Calcd for $C_{47}H_{46}HgN_4O_6\cdot 1.5H_2O$: C, 56.99; H, 4.99; N, 5.66. Found: C, 57.01; H, 4.81; N, 5.90.

*2-[(*E*)-2-(p-Methylphenyl)-2-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyloxy)vinyl]imidazoline mercuric cyanide* (**7b**). Foam, 62% yield, mp 62–64 °C. IR (KBr): 3270 (N–H), 1640, 1592, 1492, 1070 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.80 (s, 1 H, NH), 7.56 (d, 2 H, Ar–H), 7.45–7.15 (m, 20 H, Ar–H), 7.11 (d, 2 H, Ar–H), 6.41 (s, 1 H, C=C–H), 4.97–4.35 (m, 8 H, Ph–CH_2), 4.87 (d, 1 H, $J_{H\text{-}1,H\text{-}2}$ 4.30 Hz, Glc–H-1), 3.95–3.60 (m, 5 H, Glc–H-2, H-3, H-5, H-6), 3.75–3.65 (m, 4 H, N–CH_2), 3.41–3.33 (m, 1 H, Glc–H-4), 2.35 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$): δ 166.19, 162.34, 142.72, 137.77, 137.59, 137.52, 137.19, 129.68, 129.06, 128.52, 128.47, 128.39, 128.17, 128.10, 128.00, 127.88, 127.81, 127.72, 100.82, 96.05, 83.96, 81.14, 77.15, 75.47, 75.25, 74.88, 74.40, 73.28, 67.20, 44.21, 21.49; FABMS: m/z 725 $[M+1-Hg(CN)_2]^+$. Anal. Calcd for $C_{48}H_{48}HgN_4O_6\cdot 0.5H_2O$: C, 58.44; H, 5.02; N, 5.68. Found: C, 58.40; H, 5.00; N, 5.48.

*2-[(*E*)-2-(p-Methoxyphenyl)-2-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyloxy)vinyl]imidazoline mercuric cyanide* (**7c**). Foam, 66% yield; mp 84–86 °C; IR (KBr): 3250 (N–H), 1635, 1590, 1504, 1065 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.70 (s, 1 H, NH), 7.65 (d, 2 H, Ar–H), 7.50–7.15 (m, 20 H, Ar–H), 6.80 (d, 2 H, Ar–H), 6.40 (s, 1 H, C=C–H), 5.00–4.35 (m, 8 H, Ph–CH_2), 4.93 (d, 1 H, $J_{H\text{-}1,H\text{-}2}$ 3.42 Hz, Glc–H-1), 3.85–3.58 (m, 5 H, Glc–H-2, H-3, H-5, H-6), 3.80 (s, 3 H, OCH_3), 3.77–3.65 (m, 4 H, N–CH_2), 3.42–3.33 (m, 1 H, Glc–H-4); ^{13}C NMR ($CDCl_3$): δ 166.31, 162.70, 162.61, 137.80, 137.55, 130.25, 129.07, 128.85, 128.52, 128.08, 127.87, 127.74, 114.45, 101.33, 96.88, 84.01, 81.39, 77.00, 75.62, 75.43, 74.99, 74.43, 73.31, 67.17, 55.44, 44.31; FABMS: m/z 741. $[M+1-Hg(CN)_2]^+$. Anal. Calcd for $C_{48}H_{48}HgN_4O_7$: C, 58.03; H, 4.87; N, 5.64. Found: C, 57.94; H, 5.11; N, 4.96.

*2-[(*E*)-2-(p-Chlorophenyl)-2-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyloxy)vinyl]imidazoline mercuric cyanide* (**7d**). Foam, 55% yield; mp 65–67 °C; IR (KBr): 3260 (N–H), 1640, 1588, 1490, 1070 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.70 (s, 1 H, NH), 7.60–7.10 (m, 24 H, Ar–H), 6.50 (s, 1 H, C=C–H), 5.00–4.35 (m, 8 H, Ph–CH_2), 4.93 (d, 1 H, $J_{H\text{-}1,H\text{-}2}$ 5.23 Hz, Glc–H-1), 4.10–3.55 (m, 5 H, Glc–H-2, H-3,

H-5, H-6), 3.75–3.64 (m, 4 H, N–CH_2), 3.45–3.35 (m, 1 H, Glc–H-4); ^{13}C NMR ($CDCl_3$): δ 164.50, 162.14, 138.04, 138.70, 137.54, 137.51, 137.10, 129.74, 129.25, 129.13, 128.98, 128.90, 128.65, 128.54, 128.47, 128.27, 128.01, 127.87, 127.80, 127.75, 100.92, 98.80, 83.99, 81.10, 77.24, 75.53, 75.37, 74.96, 74.48, 73.32, 67.17, 44.45; FABMS: m/z 745 $[M+1-Hg(CN)_2]^+$. Anal. Calcd for $C_{47}H_{45}ClHgN_4O_6 \cdot H_2O$: C, 55.56; H, 4.66; N, 5.52. Found: C, 55.75; H, 4.86; N, 4.75.

*2-[(*E*)-2-Phenyl-2-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyloxy)vinyl]tetrahydropyrimidine mercuric cyanide* (**8a**). Foam, 78% yield; mp 65–66 °C; IR (KBr): 3280 (N–H), 1650, 1618, 1490, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.65 (s, 1 H, NH), 7.75–7.10 (m, 25 H, Ar–H), 6.35 (s, 1 H, C=C–H), 4.97–4.20 (m, 8 H, Ph–CH_2), 4.90 (d, 1 H, $J_{H\text{-}1,H\text{-}2}$ 4.40 Hz, Glc–H-1), 3.93–3.80 (m, 1 H, Glc–H-5), 3.75–3.55 (m, 5 H, Glc–H-2, H-3, H-4, H-6), 3.48–3.15 (m, 4 H, N–CH_2), 1.85–1.70 (quin, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 161.98, 155.32, 137.74, 137.49, 137.28, 131.28, 131.00, 129.12, 128.90, 128.38, 127.86, 127.65, 127.04, 126.73, 103.64, 100.36, 83.81, 81.31, 77.20, 75.57, 75.25, 74.84, 74.31, 73.30, 67.10, 38.82, 17.67; FABMS: m/z 725 $[M+1-Hg(CN)_2]^+$. Anal. Calcd for $C_{48}H_{48}HgN_4O_6 \cdot H_2O$: C, 57.91; H, 5.06; N, 5.63. Found: C, 57.53; H, 4.94; N, 5.65.

*2-[(*E*)-2-(*p*-Methylphenyl)-2-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyloxy)vinyl]tetrahydropyrimidine mercuric cyanide* (**8b**). Foam, 60% yield; mp 67–69 °C; IR (KBr): 3280 (N–H), 1648, 1618, 1490, 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.65 (s, 1 H, NH), 7.52 (d, 2 H, Ar–H), 7.40–7.15 (m, 20 H, Ar–H), 7.10 (d, 2 H, Ar–H), 6.25 (s, 1 H, C=C–H), 4.97–4.38 (m, 8 H, Ph–CH_2), 4.90 (d, 1 H, $J_{H\text{-}1,H\text{-}2}$ 5.50 Hz, Glc–H-1), 3.92–3.80 (m, 1 H, Glc–H-5), 3.75–3.60 (m, 5 H, Glc–H-2, H-3, H-4, H-6), 3.40–3.15 (m, 4 H, N–CH_2), 2.35 (s, 3 H, CH_3), 1.85–1.73 (quin, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 162.43, 155.59,142.13, 137.87, 137.62, 137.41, 137.33, 129.82, 128.54, 128.49, 128.39, 128.20, 128.12, 128.07, 127.95, 127.82, 127.62, 103.00, 100.54, 83.98, 81.59, 77.22, 75.80, 75.49, 75.06, 74.42, 73.48, 67.20, 38.93, 21.48, 18.00; FABMS: m/z 739 $[M+1-Hg(CN)_2]^+$. Anal. Calcd for $C_{49}H_{50}HgN_4O_6$: C, 59.35; H, 5.08; N, 5.65. Found: C, 58.94; H, 5.19; N, 5.42.

*2-[(*E*)-2-(*p*-Methoxyphenyl)-2-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyloxy)vinyl]tetrahydropyrimidine mercuric cyanide* (**8c**). Foam, 85% yield; mp 67–69 °C; IR (KBr): 3270 (N–H), 1645, 1587, 1505, 1055 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.50 (s, 1 H, NH), 7.60 (d, 2 H, Ar–H), 7.50–7.10 (m, 20 H, Ar–H), 6.80 (d, 2 H, Ar–H), 6.20 (s, 1 H, C=C–H), 5.00–4.30 (m, 8 H, Ph–CH_2), 4.90 (d, 1 H, $J_{H\text{-}1,H\text{-}2}$ 4.90 Hz, Glc–H-1), 4.00–3.55 (m, 6 H, Glc–H-2, H-3, H-4, H-5, H-6), 3.75 (s, 3 H, OCH_3), 3.50–3.15 (m, 4 H, N–CH_2), 1.85–1.70 (quin, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 162.16, 162.05, 155.47, 143.76, 137.77, 137.49, 137.27, 129.68, 128.89, 128.74, 128.38, 127.93, 127.82, 127.67, 126.97, 126.71, 123.15, 114.38, 101.77, 100.54, 83.88, 81.45, 77.19, 75.61, 75.33, 74.88, 74.34, 73.30, 67.11, 55.29, 38.81, 17.78; FABMS: m/z 755 $[M+1-Hg(CN)_2]^+$. Anal. Calcd for $C_{49}H_{50}HgN_4O_7$: C, 58.41; H, 5.00; N, 5.56. Found: C, 57.94; H, 5.16; N, 5.78.

*2-[(*E*)-2-(*p*-Chlorophenyl)-2-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyloxy)vinyl]tetrahydropyrimidine mercuric cyanide* (**8d**). Foam, 63% yield; mp 70–72 °C; IR (KBr): 3280 (N–H), 1650, 1618, 1490, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.65 (s, 1 H, NH), 7.65–7.10 (m, 24 H, Ar–H), 6.38 (s, 1 H, C=C–H), 5.00–4.35 (m, 8 H, Ph–CH_2), 4.94 (d, 1 H, $J_{H\text{-}1,H\text{-}2}$ 3.17 Hz, Glc–H-1), 3.95–3.83 (m, 1 H, Glc–H-5), 3.77–3.55 (m, 5 H, Glc–H-2, H-3, H-4, H-6), 3.45–3.15 (m, 4 H, N–CH_2), 1.85–1.72 (quin, 2 H, C–CH_2–C); ^{13}C NMR ($CDCl_3$): δ 160.68, 155.20, 143.70, 137.73, 137.46, 137.27, 137.15, 128.49, 128.42, 128.35, 128.30, 128.24, 128.17, 128.07, 127.96, 127.93, 127.85, 127.71, 127.66, 104.28, 100.52, 83.87, 81.36, 77.20, 75.63, 75.39, 74.92, 74.42, 73.34, 67.10, 38.88, 17.67; FABMS: m/z 759 $[M+1-Hg(CN)_2]^+$. Anal. Calcd for $C_{48}H_{47}ClHgN_4O_6 \cdot H_2O$: C, 55.97; H, 4.80; N, 5.44. Found: C, 55.70; H, 4.69; N, 5.19.

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